

*Appendix 4*

SUPPLEMENTARY INFORMATION FOR CHAPTER 5: FE-MEDIATED  
NITROGEN FIXATION WITH A METALLOCENE MEDIATOR:  
EXPLORING  $P_{K_A}$  EFFECTS AND DEMONSTRATING  
ELECTROCATALYSIS

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### A4.1 Experimental Details

#### General Considerations

All manipulations were carried out using standard Schlenk or glovebox techniques under an N<sub>2</sub> atmosphere. Solvents were deoxygenated and dried by thoroughly sparging with N<sub>2</sub> followed by passage through an activated alumina column in a solvent purification system by SG Water, USA LLC. Non-halogenated solvents were tested with sodium benzophenone ketyl in tetrahydrofuran (THF) in order to confirm the absence of oxygen and water. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., degassed, and dried over activated 3-Å molecular sieves prior to use.

$Cp^*_2Co$ ,<sup>1</sup>  $[P_3^BFe][BAr^F_4]$ ,<sup>2</sup>  $[P_3^BFeN_2][Na(Et_2O)_3]$ ,<sup>3</sup>  $[P_3^BFeN_2][Na(12-crown-4)_2]$ ,<sup>3</sup>  $[H(OEt_2)][BAr^F_4]$  ( $HBAr^F_4$ ;  $BAr^F_4$  = tetrakis- (3,5-bis(trifluoromethyl)phenyl)borate)<sup>4</sup>,

sodium  $\text{BAr}^{\text{F}_4}$  ( $\text{NaBAr}^{\text{F}_4}$ )<sup>4</sup>, and  $^{15}\text{N}$ -diphenylammonium triflate ( $[\text{Ph}_2^{15}\text{NH}_2][\text{OTf}]$ )<sup>5,6</sup> were prepared according to literature procedures. All other reagents were purchased from commercial vendors and used without further purification unless otherwise stated. Diethyl ether ( $\text{Et}_2\text{O}$ ) used in the experiments herein was stirred over  $\text{Na/K}$  ( $\geq 2$  hours) and filtered through celite before use.

### **Gas Chromatography**

$\text{H}_2$  was quantified on an Agilent 7890A gas chromatograph (HP-PLOT U, 30 m, 0.32 mm ID; 30 °C isothermal; nitrogen carrier gas) using a thermal conductivity detector. A 10 mL manual injection was used and integration area was converted to percent  $\text{H}_2$  composition by use of a calibration obtained from injection of  $\text{H}_2$  solutions in  $\text{N}_2$  of known concentration.

### **Mössbauer Spectroscopy**

Mössbauer spectra were recorded on a spectrometer from SEE Co. (Edina, MN) operating in the constant acceleration mode in a transmission geometry. The sample was kept in an SVT-400 cryostat from Janis (Wilmington, MA). The quoted isomer shifts are relative to the centroid of the spectrum of a metallic foil of  $\alpha$ -Fe at room temperature (RT). Solution samples were transferred to a sample cup and freeze-quenched with liquid nitrogen inside of the glovebox and then immersed in liquid  $\text{N}_2$  until mounted in the cryostat. Data analysis was performed using version 4 of the program WMOSS ([www.wmoss.org](http://www.wmoss.org)) and quadrupole doublets were fit to Lorentzian lineshapes. See discussion below for detailed notes on the fitting procedure.

### **Ammonia Quantification**

Reaction mixtures are cooled to 77 K and allowed to freeze. The reaction vessel is then opened to atmosphere and to the frozen solution is slowly added a twofold excess (with respect to acid) solution of a NaO<sup>t</sup>Bu solution in MeOH (0.25 mM) over 1-2 minutes. This solution is allowed to freeze and a Schlenk tube adapter is added and the headspace of the tube is evacuated. After sealing the tube is then allowed to warm to RT and stirred at RT for at least 10 minutes. An additional Schlenk tube is charged with HCl (3 mL of a 2.0 M solution in Et<sub>2</sub>O, 6 mmol) to serve as a collection flask. The volatiles of the reaction mixture are vacuum transferred at RT into this collection flask. After completion of the vacuum transfer, the collection flask is sealed and warmed to RT and stirred vigorously for 10 minutes. Solvent is removed in vacuo, and the remaining residue is dissolved in DMSO-*d*<sub>6</sub> containing 20 mM 1,3,5-trimethoxybenzene as an internal standard. The ammonium chloride is quantified by integration relative to the 1,3,5-trimethoxybenzene internal standard.

### Computational Methods

All stationary point geometries were calculated using DFT-D<sub>3</sub> (Grimmes D<sub>3</sub> dispersion correction<sup>7</sup>) with an TPSS functional,<sup>8</sup> a def2-TZVP<sup>9</sup> basis set on transition metals and a def2-SVP<sup>7</sup> basis set on all other atoms. Calculations were performed, in part, using Xtreme Science and Engineering Discovery Environment (XSEDE) resources.<sup>10</sup> Calculations were performed on the full P<sub>3</sub><sup>B</sup>Fe scaffold. Geometries were optimized using the NWChem 6.5 package.<sup>11</sup> All single point energy, frequency and solvation energy calculations were performed with the ORCA package.<sup>12</sup> Frequency calculations were used to confirm true minima and to determine gas phase free energy values ( $G_{\text{gas}}$ ). Single point solvation calculations were done using an SMD solvation

model<sup>13, 14</sup> with diethyl ether solvent and were used to determine solvated internal energy ( $E_{\text{soln}}$ ). Free energies of solvation were approximated using the difference in gas phase internal energy ( $E_{\text{gas}}$ ) and solvated internal energy ( $\Delta G_{\text{solv}} \approx E_{\text{soln}} - E_{\text{gas}}$ ) and the free energy of a species in solution was then calculated using the gas phase free energy ( $G_{\text{gas}}$ ) and the free energy of solvation ( $G_{\text{soln}} = G_{\text{gas}} + \Delta G_{\text{solv}}$ ).<sup>15,16</sup> All reduction potentials were calculated referenced to  $\text{Fc}^{+/0}$  and using the standard Nernst relation  $\Delta G = -nFE^0$ .

## A4.2 Synthetic Details:

### General Procedure for the Synthesis of the Anilinium Triflates

Prior to use the amine was purified (aniline and 2,6-dimethylaniline by distillation and the remaining substituted anilines by sublimation). To a 100 mL round bottom flask in the glovebox was added the desired aniline which was subsequently dissolved in 50 mL of  $\text{Et}_2\text{O}$  (no additional drying with NaK). To this was added dropwise (1 equiv) of HOTf with stirring over five minutes. Immediate precipitation of white solid was observed and the reaction mixture was allowed to stir for thirty minutes. The reaction mixture was then filtered and the resulting white powder was washed with  $\text{Et}_2\text{O}$  (50 mL) and pentane (50 mL). The resulting white microcrystalline material was then dried under vacuum. Yields of greater than 90% of microcrystalline material was obtained in this manner in all cases.

4-methoxyanilinium triflate ( $[\text{}^4\text{-OMePhNH}_3][\text{OTf}]$ ):  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 400 MHz): 7.52 (m, 2 H), 7.28 (m, 2H), 4.30 (br, 3H).

anilinium triflate ([PhNH<sub>3</sub>][OTf]): <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): 7.50 (m, 2 H), 7.41 (m, 1H), 7.34 (m, 2H).

2,6-dimethylanilinium triflate ([<sup>2,6</sup>-MePhNH<sub>3</sub>][OTf]): <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): 7.14 (m, 3H), 2.32 (br, 6H).

2-chloroanilinium triflate ([<sup>2</sup>-ClPhNH<sub>3</sub>][OTf]): <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): 7.32 (m, 1H), 7.15 (m, 1H), 7.02 (m, 1H), 6.82 (m, 1H).

2,5-chloroanilinium triflate ([<sup>2,5</sup>-ClPhNH<sub>3</sub>][OTf]): <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): 7.19 (apparent d, 1H, <sup>3</sup>J(H-H) = 8.5 Hz), 6.83 (apparent dd, 1H, <sup>3</sup>J(H-H) = 2.5 Hz, 0.9 Hz), 6.56 (m, 1H).

2,6-chloroanilinium triflate ([<sup>2,6</sup>-ClPhNH<sub>3</sub>][OTf]): <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): 7.22 (d, 2H, <sup>3</sup>J(H-H) = 8.0 Hz), 6.57 (t, 1H, <sup>3</sup>J(H-H) = 8.0 Hz).

2,4,6-chloroanilinium triflate ([<sup>2,4,6</sup>-ClPhNH<sub>3</sub>][OTf]): <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): 7.37 (s, 2H).

**Preparation of decamethylcobaltocenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate), [Cp\*<sub>2</sub>Co][BAr<sup>F</sup><sub>4</sub>]**

A RT solution of HBar<sup>F</sup><sub>4</sub> (96.1 mg, 0.095 mmol) in Et<sub>2</sub>O (6 mL) is added dropwise to a stirred, RT solution of Cp\*<sub>2</sub>Co (32.9 mg, 0.1 mmol) in Et<sub>2</sub>O (6 mL). This mixture is allowed to stir 30 min and then reduced to dryness in vacuo. The resulting solid residue is washed with pentane (3 x 2 mL) to yield [Cp\*<sub>2</sub>Co][BAr<sup>F</sup><sub>4</sub>] as a bright yellow solid (104 mg isolated, 92% yield).

$^1\text{H}$  NMR (THF-*d*8, 300 MHz):  $\delta$  7.79 (8H, s,  $\text{BAr}^{\text{F}_4}$ ),  $\delta$  7.58 (4H, s,  $\text{BAr}^{\text{F}_4}$ ),  $\delta$  1.75 (30H, s,  $\text{Cp}^*_2\text{Co}$ ).

### A4.3 Ammonia Generation Details

#### Standard $\text{NH}_3$ Generation Reaction Procedure

All solvents are stirred with Na/K for  $\geq 2$  hours and filtered prior to use. In a nitrogen-filled glovebox, the precatalyst (2.3  $\mu\text{mol}$ ) was weighed into a vial. The precatalyst was then transferred quantitatively into a long tube with a female 24-40 joint at the top using THF. The THF was then evaporated to provide a thin film of precatalyst at the bottom of tube. The tube is then charged with a stir bar, the acid (108 equiv), and  $\text{Cp}^*_2\text{Co}$  (41.2 mg, 54 equiv) as solids. The tube is then sealed at RT with a septum that is secured with copper wire (this ensures a known volume of  $\text{N}_2$  in the reaction vessel, which is important for  $\text{H}_2$  detection). The tube is then chilled to 77 K and allowed to equilibrate for 10 minutes. To the chilled tube is added 1 mL of  $\text{Et}_2\text{O}$ . The temperature of the system is allowed to equilibrate for 5 minutes. This tube is passed out of the box into a liquid  $\text{N}_2$  bath and transported to a fume hood. The tube is then transferred to a dry ice/acetone bath where it thaws and is allowed to stir at  $-78$  °C for four hours. At this point the headspace of the tube is sampled with a 10 mL sealable gas syringe which is used to analyze for  $\text{H}_2$  by GC. The tube is then allowed to warm to RT with stirring and then stirred at RT for a further ten minutes. At this point the previously described procedure for quantifying ammonia was employed. To ensure reproducibility, all experiments were conducted in 395 mL tubes (51 mm OD) using 25 mm stir bars and stirring was conducted at  $\sim 650$  rpm.

**Table A4.1:** NMR quantification results for standard NH<sub>3</sub> generation experiments with [P<sub>3</sub><sup>B</sup>Fe][BAr<sup>F</sup><sub>4</sub>]

Entry	Acid	Integration Relative to Internal Standard	% Yield NH <sub>3</sub> (error)	% Yield H <sub>2</sub> (error)
1	[ <sup>4-OMe</sup> PhNH <sub>3</sub> ][OTf]	0.01, 0.02	0.2 ± 0.1	89.1 ± 0.2
2	[PhNH <sub>3</sub> ][OTf]	3.42, 3.33	40.4 ± 0.5	48.6 ± 0.7
3	[ <sup>2,6-Me</sup> PhNH <sub>3</sub> ][OTf]	4.30, 3.63	47.5 ± 4.0	37.8 ± 0.2
4	[ <sup>2-Cl</sup> PhNH <sub>3</sub> ][OTf]	4.98, 4.92	59.3 ± 0.4	26.1 ± 1.9
5	[ <sup>2,5-Cl</sup> PhNH <sub>3</sub> ][OTf]	6.78, 6.15	77.5 ± 3.8	10.5 ± 1.1
6	[ <sup>2,6-Cl</sup> PhNH <sub>3</sub> ][OTf]	6.81, 6.00	76.7 ± 4.9	12.6 ± 2.5
7	[ <sup>2,6-Cl</sup> PhNH <sub>3</sub> ][OTf]*	6.60, 5.81	74.4 ± 4.7	14.2 ± 3.4
8	[ <sup>2,6-Cl</sup> PhNH <sub>3</sub> ][BAr <sup>F</sup> <sub>4</sub> ]	4.12, 3.0	42.7 ± 6.7	18.8 ± 0.8
9	[ <sup>2,4,6-Cl</sup> PhNH <sub>3</sub> ][OTf]	5.73, 6.10	70.9 ± 2.2	12.0 ± 0.8
10	pentachloroaniliniu m triflate ([ <sup>per-Cl</sup> PhNH <sub>3</sub> ][OTf])	1.62, 1.70	19.9 ± 0.5	63.5 ± 1.1

\*Run performed with [P<sub>3</sub><sup>B</sup>FeN<sub>2</sub>][Na(Et<sub>2</sub>O)<sub>3</sub>] as the precatalyst.

#### A4.4 H<sub>2</sub> Monitoring Details

##### Standard Background Generation Reaction Procedure

All solvents are stirred with Na/K for  $\geq 2$  hours and filtered prior to use. In a nitrogen-filled glovebox, a long tube with a female 24-40 joint is charged with a stir bar, the acid (108 equiv) and Cp\*<sub>2</sub>Co (41.2 mg, 54 equiv). The tube is then sealed at RT with a septum that is secured with copper wire. The tube is then chilled to 77 K and allowed to equilibrate for 10 minutes. To the chilled tube is added 1 mL of Et<sub>2</sub>O. The temperature of the system is allowed to equilibrate for 5 minutes. This tube is passed out of the box into a liquid N<sub>2</sub> bath and transported to a fume hood. The tube is then transferred to a dry ice/acetone bath where it thaws and is allowed to stir at  $-78$  °C for four hours. At this point the headspace of the tube is sampled with a 10 mL sealable gas syringe which is used to analyze for H<sub>2</sub>.

**Table A4.2:** Data for Background H<sub>2</sub> Quantification Experiments

Acid	GC Integration for H <sub>2</sub>	% Yield H <sub>2</sub>
[ <sup>4</sup> -OMePhNH <sub>3</sub> ][OTf]	49.8	31.5
[PhNH <sub>3</sub> ][OTf]	24.0	15.2
[ <sup>2,6</sup> -MePhNH <sub>3</sub> ][OTf]	8.2	5.2
[ <sup>2</sup> -ClPhNH <sub>3</sub> ][OTf]	47.2	29.9
[ <sup>2,5</sup> -ClPhNH <sub>3</sub> ][OTf]	37.1	23.5



$[\text{}^{2,6}\text{-ClPhNH}_3][\text{OTf}]$	77.8	49.2
$[\text{}^{2,4,6}\text{-ClPhNH}_3][\text{OTf}]$	34.8	22.0
$[\text{}^{\text{per-Cl}}\text{PhNH}_3][\text{OTf}]$	98.3	62.3

### H<sub>2</sub> Evolution Kinetics

All solvents are stirred with Na/K for  $\geq 2$  hours and filtered prior to use. For the catalyzed run, the precatalyst was then transferred quantitatively into a Schlenk tube using THF. The THF was then evaporated to provide a thin film of precatalyst at the bottom of the long tube with a female 24-40 joint. The tube is then charged with a stir bar and the  $[\text{}^{2,6}\text{-ClPhNH}_3][\text{OTf}]$  (77.9 mg, 108 equiv) and  $\text{Cp}^*\text{}_2\text{Co}$  (41.2 mg, 54 equiv) are added as solids. The tube is then sealed at RT with a septum that is secured with copper wire. The tube is then chilled to 77 K and allowed to equilibrate for 10 minutes. To the chilled tube is added 1 mL of Et<sub>2</sub>O. The temperature of the system is allowed to equilibrate for 5 minutes. This tube is passed out of the box into a liquid N<sub>2</sub> bath and transported to a fume hood. The tube is then transferred to a dry ice/acetone bath where it thaws and is allowed to stir at  $-78$  °C. As soon as the stir bar is freed from the frozen solution and stirring begins the timing is started. At the time points noted below the headspace was sampled for H<sub>2</sub> with a 10 mL sealable gas syringe.

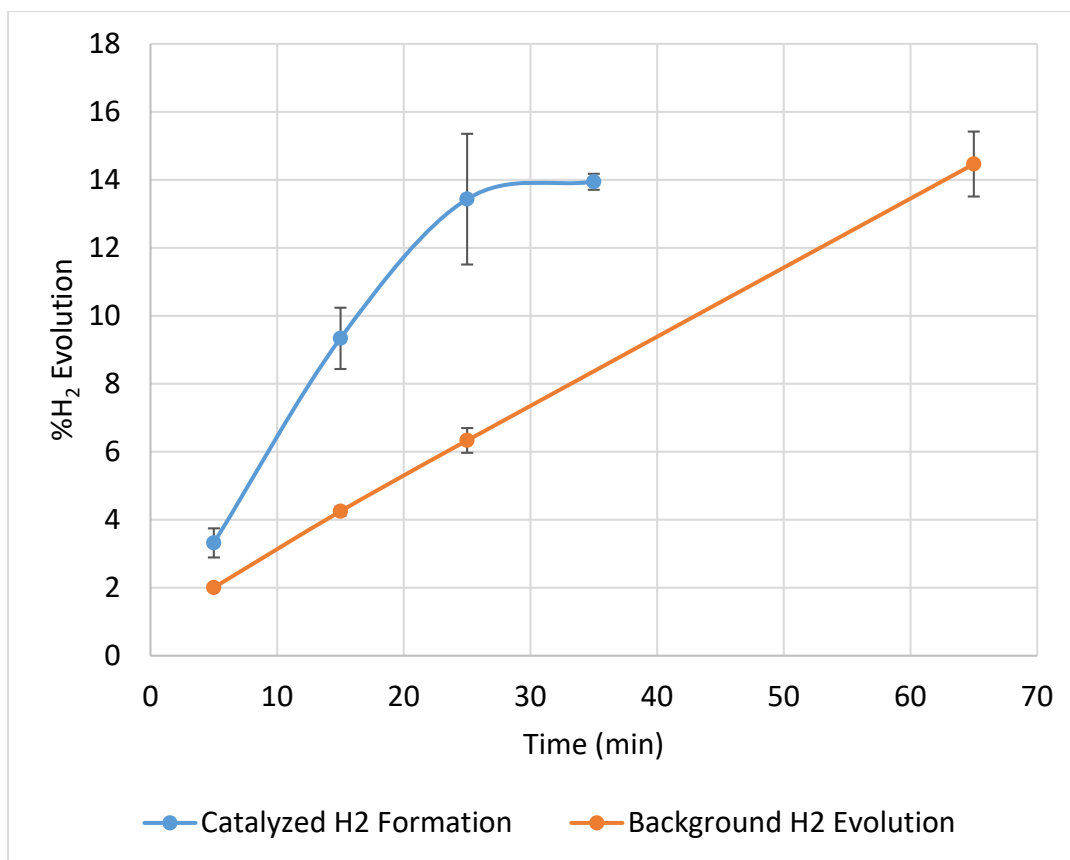
**Table A4.3:** Time points for catalyzed H<sub>2</sub> evolution from 2,6-dichloroanilinium triflate and  $\text{Cp}^*\text{}_2\text{Co}$

Time (min)	GC Integration for H <sub>2</sub>	% Yield H <sub>2</sub> (error)

5	3.8, 6.4	3.3 ± 0.9
15	11.6, 16.9	9.3 ± 1.8
25	14.7, 26.2	13.4 ± 3.8
35	22.5, 20.8	13.9 ± 0.5

**Table A4.4.** Time points for uncatalyzed H<sub>2</sub> evolution from 2,6-dichloroanilinium triflate and Cp\*<sub>2</sub>Co

Time (min)	GC Integration for H <sub>2</sub>	% Yield H <sub>2</sub> (error)
5	3.3, 2.9	2.0 ± 0.1
15	7.0, 6.2	4.3 ± 0.3
25	8.8, 11.1	6.3 ± 0.8
65	20.7, 27.0	14.5 ± 1.7



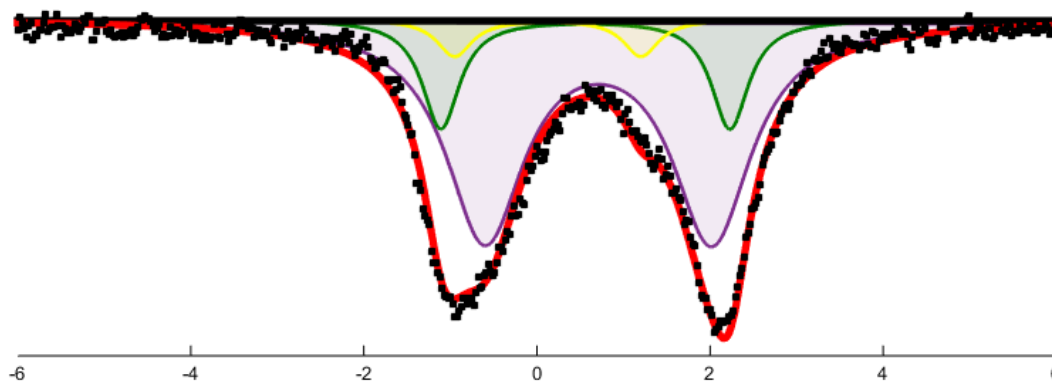
**Figure A4.1.** Comparison of catalyzed and uncatalyzed H<sub>2</sub> evolution from 2,6-dichloroanilinium triflate and Cp\*<sub>2</sub>Co at early time points.

#### A4.5 Mössbauer Spectroscopy

##### General Procedure for Freeze-Quench Mössbauer Spectroscopy

All solvents are stirred with Na/K for  $\geq 2$  hours and filtered prior to use. In a nitrogen-filled glovebox, the desired <sup>57</sup>Fe species (0.0023 mmol) is quantitatively transferred using THF to a vial and then evaporated to yield a thin film. That vial is charged with a small stir bar and the other reagents as solids. The vial is then chilled to 77 K in a liquid nitrogen bath and allowed to equilibrate for five minutes. To the chilled tube is added 1 mL of Et<sub>2</sub>O and this allowed to equilibrate for another five minutes. The

vial is then transferred to a cold well that has been pre-cooled for at least fifteen minutes to  $-78\text{ }^{\circ}\text{C}$  with a dry ice/acetone bath. When the stir bar is freed from the frozen solvent and begins to stir the time is started. At the time noted the stirring is stopped and using a prechilled pipette the reaction mixture is transferred in one portion to a pre-chilled Mössbauer cup sitting in a vial. The vial is then placed in a liquid nitrogen bath causing the reaction mixture to freeze in approximately twenty seconds. The Mössbauer cup is then submerged in the liquid nitrogen and then removed from the glovebox and standard procedure is used to mount the sample on the Mössbauer spectrometer.



**Figure A4.2.** Mössbauer spectrum collected from a reaction freeze quenched after stirring for 5 minutes at  $-78\text{ }^{\circ}\text{C}$  in 1 mL of  $\text{Et}_2\text{O}$  between  $[\text{P}_3^{\text{B}}(^{57}\text{Fe})\text{N}_2][\text{Na}(\text{Et}_2\text{O})_3]$  and excess  $2,6\text{-}[^{2,6}\text{-Cl}]\text{PhNH}_3[\text{OTf}]$  (50 equiv). Raw data shown as black points, simulation as a solid red line, with components in green, purple, and yellow (see Table A4.3 for parameters). The spectrum was collected at 80 K with a parallel applied magnetic field of 50 mT in  $\text{Et}_2\text{O}$ .

*Fitting details for Figure A4.2:* Three quadrupole doublets were found to be necessary to obtain an adequate simulation. Although a variety of parameters could potentially simulate the relatively broad absorptions observed here, previous reactivity of  $\text{P}_3^{\text{B}}\text{FeN}_2^-$

with acid<sup>19</sup> suggested that  $P_3^BFeN_2$  and  $P_3^BFe^+$  were likely products. Satisfyingly if the known isomer shift and quadrupole splitting for one of those species was fixed during the fitting process and the other components were allowed to refine freely the other major component was found to be the complementary species.<sup>19</sup> The third species was always unchanged in these simulations and represents an unknown species. Its presence in the fit is demanded by the inflection point on the more negative side of the right-hand absorbance. Modeling this feature also helps to capture the asymmetry of the left-hand absorbance while using the symmetric line-shapes we expect for  $P_3^BFeN_2$  (green) and  $P_3^BFe^+$  (purple). The broad linewidths for  $P_3^BFe^+$  have been observed previously and may be explained by the existence of unbound and bound varieties of the species with the reaction mixture providing potential ligands such as  $OTf^-$ ,  $^{2,6-Cl}PhNH_2$ , and  $N_2$ .

**Table A4.5:** Simulation parameters for Mossbauer spectrum in Figure A4.2.

Component	$\delta$ (mm s <sup>-1</sup> )	$\Delta E_Q$ (mm s <sup>-1</sup> )	Linewidths, $\Gamma_L/\Gamma_R$ (mm s <sup>-1</sup> )	Relative area
A (green)	$0.58 \pm 0.02$	$3.28 \pm 0.07$	0.52/0.52	0.26
B (purple)	$0.76 \pm 0.02$	$2.57 \pm 0.05$	1.10/1.10	0.63
C (yellow)	$0.13 \pm 0.02$	$2.24 \pm 0.04$	0.50/0.50	0.11

## A4.6 EPR Spectroscopy

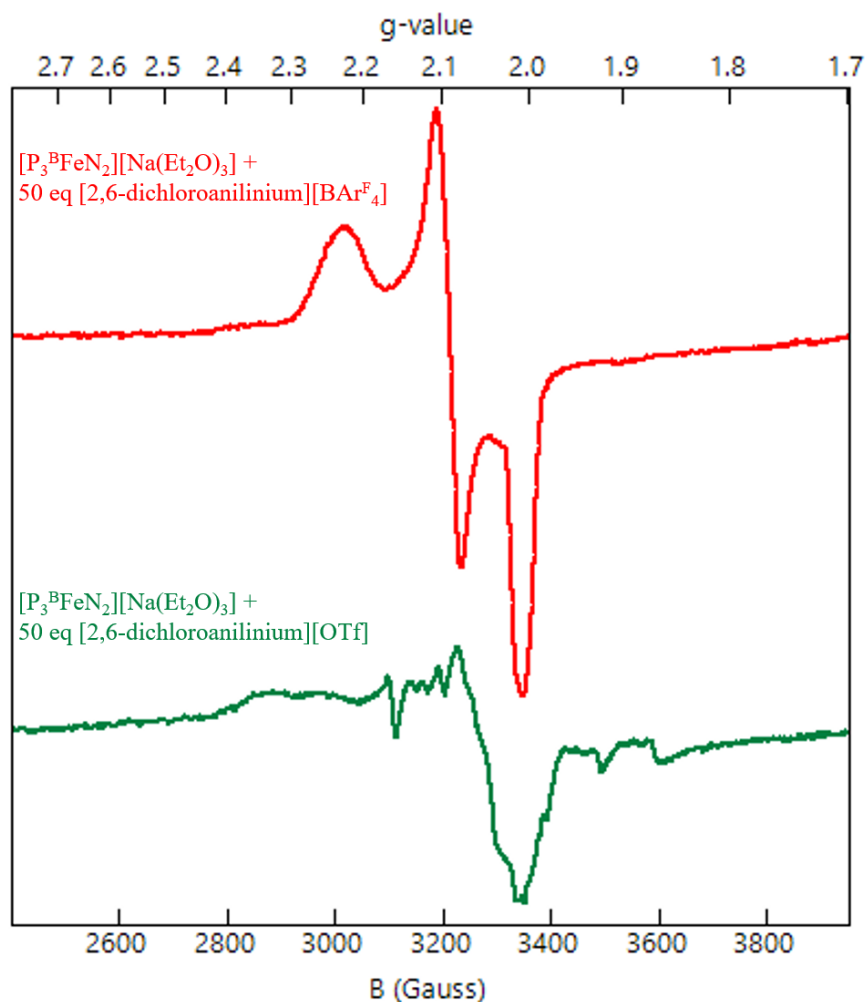
### General Procedure for EPR Spectroscopy

All solvents are stirred with Na/K for  $\geq 2$  hours and filtered prior to use. In a nitrogen-filled glovebox, the desired Fe species (0.0023 mmol) is quantitatively transferred using THF to a vial and then evaporated to yield a thin film. That vial is charged with a small stir bar and the acid (0.116 mmol, 50 equiv) as solids ( $[\text{}^{2,6}\text{-Cl}^{\text{PhNH}_3}][\text{OTf}]$  or  $[\text{}^{2,6}\text{-Cl}^{\text{PhNH}_3}][\text{BAr}^{\text{F}_4}]$ ). The vial is then chilled to 77 K in a liquid nitrogen bath and allowed to equilibrate for five minutes. To the chilled tube is added 1 mL of Et<sub>2</sub>O (for HOTf 50 equiv have been dissolved in this 1 mL of Et<sub>2</sub>O at RT) and this allowed to equilibrate for another five minutes. The vial is then transferred to a cold well that has been pre-cooled for at least fifteen minutes to  $-78$  °C with a dry ice/acetone bath. When the stir bar is freed from the frozen solvent and begins to stir the time is started. The reaction mixture is stirred for five minutes and then stirring is stopped. Using a pre-chilled pipette approximately 0.5 mL of the reaction mixture is rapidly transferred to a pre-chilled X-band EPR tube. The X-band EPR tube is then placed in a liquid nitrogen bath causing the reaction mixture to freeze in approximately twenty seconds. The EPR tube is then sealed and removed from the glovebox in liquid nitrogen.

### Comment on Stoichiometric Reactivity

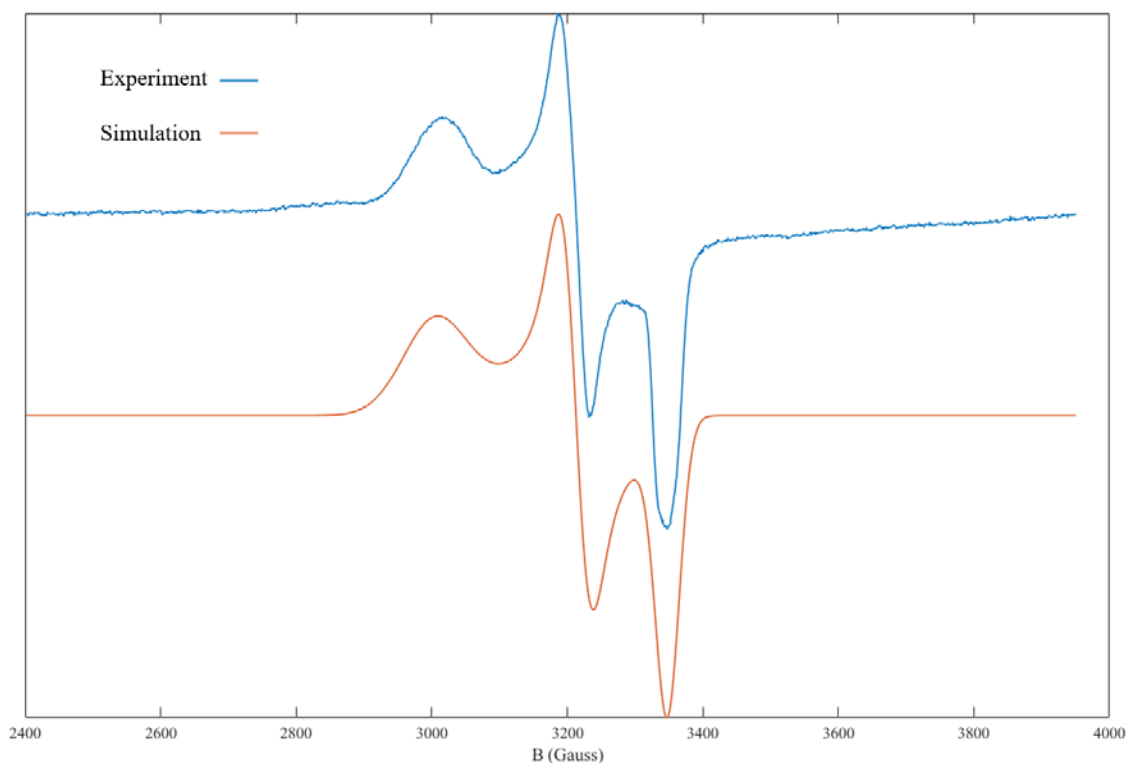
In our attempt to model the catalytic reaction mixture we were interested in the reactivity of  $\text{P}_3^{\text{B}}\text{FeN}_2^-$  (observed previously both from mixing  $[\text{P}_3^{\text{B}}\text{Fe}][\text{BAr}^{\text{F}_4}]$  with excess  $\text{Cp}^*\text{Co}$  and under the catalytic reaction conditions) with acid. In order to achieve

this we wanted to prepare independently known  $P_3^BFeN_2^-$  species to model the proposed catalytic intermediate  $[P_3^BFeN_2][Cp^*_2Co]$ . We chose  $[P_3^BFeN_2][Na(Et_2O)_3]$  because we believed that its solubility in  $Et_2O$  likely modeled that of  $[P_3^BFeN_2][Cp^*_2Co]$ .



**Figure A4.3.** The continuous wave, X-band EPR at 77K in  $Et_2O$  of reaction mixtures freeze-quenched after five minutes. In red is the reaction of  $[P_3^BFeN_2][Na(Et_2O)_3]$  with 50 equiv of  $[2,6\text{-Cl}_2\text{PhNH}_3][BAR^F_4]$  clearly demonstrating the formation of  $[P_3^BFeNNH_2][BAR^F_4]$ . In green is reaction of  $[P_3^BFeN_2][Na(Et_2O)_3]$  with 50 equiv of  $[2,6\text{-Cl}_2\text{PhNH}_3][OTf]$ .

$^{2,6}\text{-ClPhNH}_3][\text{OTf}]$  in which the small residual species is neither the starting material ( $[\text{P}_3^{\text{B}}\text{FeN}_2][\text{Na}(\text{Et}_2\text{O})_3]$ ) or the desired product ( $[\text{P}_3^{\text{B}}\text{FeNNH}_2][\text{OTf}]$ ). Although we do not know the chemical identity of this species we note that it is very similar to the EPR observed in the reaction of  $[\text{P}_3^{\text{B}}\text{FeN}_2][\text{Na}(12\text{-crown-}4)_2]$  with 1 equiv of  $\text{HBAr}^{\text{F}_4}$ .<sup>19</sup> We hypothesize therefore that it may represent a Fe–H side product.



**Figure A4.4.** In blue is the continuous wave, X-band EPR spectrum at 77K of a reaction mixture of 50 equiv  $[\text{}^{2,6}\text{-ClPhNH}_3][\text{BAr}^{\text{F}_4}]$  with  $[\text{P}_3^{\text{B}}\text{FeN}_2][\text{Na}(12\text{-crown-}4)_2]$  quenched with liquid nitrogen after 5 minutes. In orange is the simulation of this spectrum (fitting details below)

*Fitting details for Figure A4.4:* The parameters used to fit the spectrum were obtained using the esfit application in the easyspin program.<sup>20</sup> The fitting program obtains the best fit by minimizing the root mean square deviation from the data.



The data was fit with the following parameters:  $g_1 = 2.23899$ ,  $g_2 = 2.09189$ ,  $g_3 = 2.00664$ , and a line broadening of 323.8530, 71.2309, and 38.7902 MHz respectively. These parameters represent only a very small perturbation from those used previously to model  $[\text{P}_3^{\text{B}}\text{FeNNH}_2][\text{BAr}^{\text{F}}_4]$ :  $g_1 = 2.222$ ,  $g_2 = 2.091$ ,  $g_3 = 2.006$  and a line broadening of 256, 113, and 41 MHz respectively.<sup>19</sup> The slightly broader spectrum observed here precludes resolution of the small phosphorus coupling on  $g_3$ . We believe that this broadening arises from either the use of a non-glassing solvent (Et<sub>2</sub>O vs 2-MeTHF) or via small differences in hydrogen-bonding that arise from the presence of 2,6-dichloroaniline.

#### A4.7 Acid Quench of $\text{P}_3^{\text{B}}\text{FeN}_2^-$

##### Standard Acid Quench Procedure

All solvents are stirred with Na/K for  $\geq 2$  hours and filtered prior to use. In a nitrogen-filled glovebox, the desired Fe species (2.3  $\mu\text{mol}$ ) was weighed into a vial. The Fe species was then transferred quantitatively into a Schlenk tube using THF. The THF was then evaporated to provide a thin film of Fe species at the bottom of the Schlenk tube. The tube is then charged with a stir bar and acid (0.116 mmol, 50 equiv) as solids  $9[{}^{2,6}\text{-ClPhNH}_3][\text{OTf}]$  or  $[{}^{2,6}\text{-ClPhNH}_3][\text{BAr}^{\text{F}}_4]$  is added as a solid. The tube is then sealed at RT with a septum and a Konte's valve that is left partially open. The tube is then chilled to 77 K and allowed to equilibrate for 10 minutes. To the chilled tube is added 1 mL of Et<sub>2</sub>O through the septum. The temperature of the system is allowed to equilibrate for 5 minutes and then the Konte's valve is sealed. This tube is passed out of the box into a liquid N<sub>2</sub> bath and transported to a fume hood. The tube is then transferred to a dry ice/acetone bath where it thaws and is allowed to stir at  $-78$  °C for three hours. At the

end of the reaction the Konte's valve is opened and the reaction headspace is allowed to equilibrate. At this point the headspace of the tube is sampled with a 10 mL sealable gas syringe which is used to analyze for H<sub>2</sub>. The tube is then allowed to warm to RT with stirring and then stirred at RT for a further ten minutes. At this point the previously described procedure for quantifying ammonia was employed.

**Table A4.6. Comparative NH<sub>3</sub> and H<sub>2</sub> Yields for [2,6-ClPhNH<sub>3</sub>][OTf] and [2,6-ClPhNH<sub>3</sub>][BAr<sup>F</sup><sub>4</sub>]**

Acid	Yield of NH <sub>3</sub> (equiv)	% Yield H <sub>2</sub>
[2,6-ClPhNH <sub>3</sub> ][OTf]	0.0 ± 0.0	43.7 ± 4.6
[2,6-ClPhNH <sub>3</sub> ][BAr <sup>F</sup> <sub>4</sub> ]	0.20 ± 0.03	37.8 ± 7.6

#### A4.8 Solubility Measurement

##### Procedure for Measuring Solubility of Cp\*<sub>2</sub>Co:

All solvents are stirred with Na/K for ≥ 2 hours and filtered prior to use. In a nitrogen-filled glovebox, a Schlenk tube is charged with a stir bar and the Cp\*<sub>2</sub>Co (41.2 mg, 0.125 mmol) is added to the tube. The tube is then chilled to 77 K in a liquid nitrogen bath and allowed to equilibrate for 5 minutes. To the chilled tube is added 1 mL of Et<sub>2</sub>O. The temperature of the system is allowed to equilibrate for 5 minutes and then the Schlenk tube is transferred to the cold well which has been prechilled to -78 °C for fifteen minutes. After five minutes of stirring at ~ 620 rpm, the stirring is stopped. With a prechilled pipette the entirety of the reaction mixture is transferred to a similarly prechilled celite pad for filtration. Filtration yielded a pale green solution that was then

warmed to RT and the solvent was removed under reduced pressure. The vial was then extracted with a 20 mM solution of 1,3,5-trimethoxybenzene in  $C_6D_6$ . The NMR was then measured and the  $Cp^*_2Co$  signal was integrated relative to the 1,3,5-trimethoxybenzene standard. The accuracy of this integration procedure was confirmed by performing this procedure on a sample of  $Cp^*_2Co$  that had simply been weighed into a vial. Repetition of this experiment resulted in  $Cp^*_2Co$  concentrations between 5-6 mM.

**Procedure for Measuring Solubility of  $[^{2,6-Cl}PhNH_3][OTf]$ :**

All solvents are stirred with Na/K for  $\geq 2$  hours and filtered prior to use. In a nitrogen-filled glovebox, a Schlenk tube is charged with a stir bar and the  $[^{2,6-Cl}PhNH_3][OTf]$  (77.9 mg, 0.250 mmol) is added to the tube. The tube is then chilled to 77 K in a liquid nitrogen bath and allowed to equilibrate for 5 minutes. To the chilled tube is added 1 mL of  $Et_2O$ . The temperature of the system is allowed to equilibrate for 5 minutes and then the Schlenk tube is transferred to the cold well which has been prechilled to  $-78$  °C for fifteen minutes. After five minutes of stirring at  $\sim 620$  rpm, the stirring is stopped. With a prechilled pipette the entirety of the reaction mixture is transferred to a similarly prechilled celite pad for filtration. Filtration yielded a colorless solution that was then warmed to RT and the solvent was removed under reduced pressure. The vial was then extracted with a 20 mM solution of 1,3,5-trimethoxybenzene in  $THF-d_8$ . The NMR was then measured and the two signals for  $[^{2,6-Cl}PhNH_3][OTf]$  were integrated relative to the 1,3,5-trimethoxybenzene standard. The result was a  $[^{2,6-Cl}PhNH_3][OTf]$  concentration of 0.4 mM.

## A4.9 Controlled Potential Electrolysis (CPE) and Cyclic Voltammetry (CV) Details

### General considerations:

All manipulations are carried out in an N<sub>2</sub>-filled glove box. For CPE experiments a sealable H-cell consisting of two compartments separated by a fine porosity sintered glass frit is cooled to  $-35\text{ }^{\circ}\text{C}$  in a cold well and charged with 4 mL (working chamber) and 4 mL (auxiliary chamber) of 0.1 M NaBAR<sup>F</sup><sub>4</sub> solution in Et<sub>2</sub>O, the solutions are also cooled to  $-35\text{ }^{\circ}\text{C}$  and the solution for the working chamber may contain additional chemical components as described below. The working chamber is outfitted with a glassy carbon working electrode, rectangular prismatic in shape with dimensions of 10 mm  $\times$  2 mm and submerged in the working chamber solution to a depth of  $\sim$  10 mm. The working chamber is also equipped with a Ag/AgPF<sub>6</sub> in 0.1 M NaBAR<sup>F</sup><sub>4</sub> Et<sub>2</sub>O reference electrode isolated by a CoralPor<sup>TM</sup> frit (obtained from BASi) and referenced externally to Fc<sup>+0</sup>. The auxiliary chamber is outfitted with a solid sodium auxiliary electrode ( $\sim$  5 mm  $\times$   $\sim$  1 mm rectangular prism, submerged to  $\sim$  5 mm). The cell is sealed before electrolysis. The cell is connected to a CH Instruments 600B electrochemical analyzer and controlled potential bulk electrolysis experiments were performed at  $-35\text{ }^{\circ}\text{C}$  with stirring, cold well external bath temperature maintained by a SP Scientific FTS Systems FC100 immersion cooler.

CV experiments are conducted in a single compartment cell cooled to  $-35\text{ }^{\circ}\text{C}$  in a cold well in 0.1 M NaBAR<sup>F</sup><sub>4</sub> Et<sub>2</sub>O solution, again cold well external bath temperature maintained by a SP Scientific FTS Systems FC100 immersion cooler. The working electrode is a glassy carbon disk, the reference electrode is a Ag/AgPF<sub>6</sub> in 0.1 M NaBAR<sup>F</sup><sub>4</sub> Et<sub>2</sub>O reference electrode isolated by a CoralPor<sup>TM</sup> frit (obtained from BASi)

and referenced externally to  $\text{Fc}^{+/0}$ , the auxiliary electrode is a platinum wire. Measurements conducted with a CH Instruments 600B electrochemical analyzer

### **General methodology for controlled potential electrolysis experiments:**

To the working chamber is added 3 mg of  $[\text{P}_3^{\text{B}}\text{Fe}][\text{BAr}^{\text{F}_4}]$  (2  $\mu\text{mol}$ ), 100  $\mu\text{mol}$  of acid (e.g.  $[\text{Ph}_2\text{NH}_2][\text{OTf}]$ ), 0-23.8 mg of  $[\text{Cp}^*\text{Co}][\text{BAr}^{\text{F}_4}]$  (0-20  $\mu\text{mol}$ ), and a magnetic stir bar. The cell is held at a working potential of  $-2.1$  V vs  $\text{Fc}^{+/0}$  until the current passed in the cell falls to 1% of the initial current pass or until 21.5 hours have passed. After that time the potential bias is removed, the headspace of the cell is sampled with a sealable gas syringe (10 mL), which is immediately analyzed by GC for the presence of  $\text{H}_2$ . Then an additional 100  $\mu\text{mol}$  of acid in 2 mL 0.1 M  $\text{NaBAr}^{\text{F}_4}$  solution in  $\text{Et}_2\text{O}$  is injected through rubber septa into both chambers to sequester  $\text{NH}_3$  as  $[\text{NH}_4][\text{OTf}]$ . The cell is allowed to stir at  $-35$  °C for 10 minutes and then warmed to RT. The contents of both chambers are then transferred to a Schlenk tube (cell washed with additional  $\text{Et}_2\text{O}$ ) and this material is analyzed for  $\text{NH}_3$  by base digestion, vacuum transfer of volatiles, and NMR integration as described in section S1.4

### **Methodology for controlled potential electrolysis experiments with reloading of substrate:**

To the working chamber is added 3 mg of  $[\text{P}_3^{\text{B}}\text{Fe}][\text{BAr}^{\text{F}_4}]$  (2  $\mu\text{mol}$ ), 100  $\mu\text{mol}$  of acid (e.g.  $[\text{Ph}_2\text{NH}_2][\text{OTf}]$ ), 0-23.8 mg of  $[\text{Cp}^*\text{Co}][\text{BAr}^{\text{F}_4}]$  (0-20  $\mu\text{mol}$ ), and a magnetic stir bar. The cell is held at a working potential of  $-2.1$  V vs  $\text{Fc}^{+/0}$  until the current passed in the cell falls to 1% of the initial current pass or until 21.5 hours have passed. After that

time the potential bias is removed. An additional 100  $\mu\text{mol}$  of acid in 2 mL 0.1 M  $\text{NaBAR}^{\text{F}_4}$  solution in  $\text{Et}_2\text{O}$  is then added to the working chamber of the cell via injection through a rubber septum. The cell is then held at a working potential of  $-2.1$  V vs  $\text{Fc}^{+/0}$  until the current passed in the cell falls to 1% of the initial current pass or until 21.5 hours have passed. After that time the potential bias is removed, the headspace of the cell is sampled with a sealable gas syringe (10 mL), which is immediately analyzed by GC for the presence of  $\text{H}_2$ . Then an additional 100  $\mu\text{mol}$  of acid in 2 mL 0.1 M  $\text{NaBAR}^{\text{F}_4}$  solution in  $\text{Et}_2\text{O}$  is injected through rubber septa into both chambers of the cell to sequester  $\text{NH}_3$  as  $[\text{NH}_4][\text{OTf}]$ . The cell is allowed to stir at  $-35$   $^\circ\text{C}$  for 10 minutes and then warmed to RT. The contents of both chambers are then transferred to a Schlenk tube (cell washed with additional  $\text{Et}_2\text{O}$ ) and this material is analyzed for  $\text{NH}_3$  by base digestion, vacuum transfer of volatiles, and NMR integration as described in section S1.4

**Table A4.7. Controlled Potential Electrolysis Data.**

Entry	Acid	Equiv [Cp* <sub>2</sub> Co] [BAR <sup>F</sup> <sub>4</sub> ]	Time (h)	Charge Passed (C)	Yield of NH <sub>3</sub> (equiv per Fe)	FE NH <sub>3</sub> (%)	FE H <sub>2</sub> <sup>a</sup> (%)
1	[Ph <sub>2</sub> NH <sub>2</sub> ] [OTf]	0	42	7.5	2.3	18	80
2	[Ph <sub>2</sub> NH <sub>2</sub> ] [OTf]	0	63	6.2	2.8	26	25
3	[Ph <sub>2</sub> NH <sub>2</sub> ]	0	43	5.4	2.6	28	53

	[OTf]						
Avg					$2.6 \pm 0.3$	$24 \pm 5$	
$4^b$	[Ph <sub>2</sub> NH <sub>2</sub> ] [OTf]	0	43	7.5	2.2	17	67
$5^b$	[Ph <sub>2</sub> NH <sub>2</sub> ] [OTf]	0	43	9.0	3.0	19	22
Avg					$2.6 \pm 0.6$	$18 \pm 1$	
6	[Ph <sub>2</sub> NH <sub>2</sub> ] [OTf]	1	17	8.1	4.4	31	56
7	[Ph <sub>2</sub> NH <sub>2</sub> ] [OTf]	1	22	8.3	3.5	24	47
Avg					$4.0 \pm 0.6$	$28 \pm 5$	
8	[Ph <sub>2</sub> NH <sub>2</sub> ] [OTf]	5	17	8.5	3.9	26	61
9	[Ph <sub>2</sub> NH <sub>2</sub> ] [OTf]	5	21	9.1	3.5	22	57
10	[Ph <sub>2</sub> NH <sub>2</sub> ] [OTf]	5	22	9.5	4.6	28	27

Avg					$4.0 \pm 0.6$	$25 \pm 3$	
11	[Ph <sub>2</sub> NH <sub>2</sub> ] [OTf]	10	21	9.4	3.0	19	64
12	[Ph <sub>2</sub> NH <sub>2</sub> ] [OTf]	10	10	10.2	5.1	29	47
Avg					$4 \pm 1$	$24 \pm 7$	
13	[PhNH <sub>3</sub> ] [OTf]	5	15	9.0	1.2	8	48
14	[PhNH <sub>3</sub> ] [OTf]	5	22	7.8	0.6	4	35
Avg					$0.9 \pm 0.4$	$6 \pm 3$	
15	[ <sup>2,6</sup> - ClPhNH <sub>3</sub> ] [OTf]	5	17	10.6	2.0	11	44
16	[ <sup>2,6</sup> - ClPhNH <sub>3</sub> ] [OTf]	5	17	10.7	1.7	9	41
Avg					$1.9 \pm 0.2$	$10 \pm 1$	
17 <sup>b</sup>	[Ph <sub>2</sub> NH <sub>2</sub> ]	5	32	17.3	6.1	20	43



	[OTf]						
18 <sup>b</sup>	[Ph <sub>2</sub> NH <sub>2</sub> ] [OTf]	5	22	18.7	6.7	21	32
19 <sup>b</sup>	[Ph <sub>2</sub> NH <sub>2</sub> ] [OTf]	5	37	13.7	4.7	20	38
20 <sup>b</sup>	[Ph <sub>2</sub> NH <sub>2</sub> ] [OTf]	5	41	15.3	4.8	18	52
21 <sup>b</sup>	[Ph <sub>2</sub> NH <sub>2</sub> ] [OTf]	5	43	17.8	5.4	18	31
Avg					5.5 ± 0.9	19 ± 1	
22A <sup>c</sup>	[Ph <sub>2</sub> NH <sub>2</sub> ] [OTf]	5	21.5	9.5	4.6	28	27
22B <sup>c</sup>	[Ph <sub>2</sub> NH <sub>2</sub> ] [OTf]	5	11.5	9.2	0.0	0	88
23 <sup>d</sup>	[Ph <sub>2</sub> NH <sub>2</sub> ] [OTf]	5	16	9.2	0.0	0	75
24 <sup>e</sup>	[Ph <sub>2</sub> NH <sub>2</sub> ] [OTf]	5	43	0.0	0.3	N/A	N/A
25 <sup>f</sup>	[Ph <sub>2</sub> NH <sub>2</sub> ]	Chemical	21.5	N/A	1.3	7.8 e <sup>-</sup>	50 e <sup>-</sup>

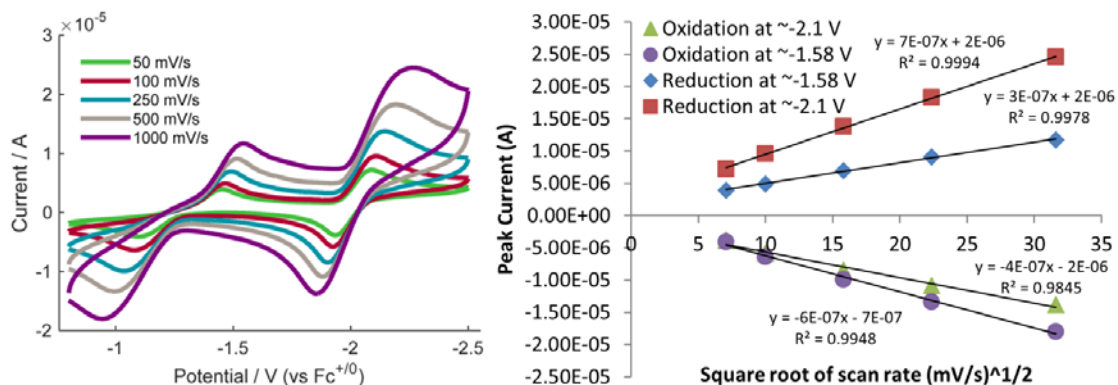
	[OTf]	runs					
26 <sup>f</sup>	[Ph <sub>2</sub> NH <sub>2</sub> ]	Chemical	21.5	N/A	2.3	13.8 e <sup>-</sup>	31 e <sup>-</sup>
	[OTf]	runs					
Avg					1.8 ± 0.7	11 ± 4	

<sup>a</sup>Some ports of the cell are sealed with septa and one of these is pierced before the electrolysis begins to pressure equilibrate the cell as it cools to -35 °C, we note therefore that H<sub>2</sub> gas may escape from the cell particular during long experiments, indeed a test of H<sub>2</sub> retention in the cell under equivalent conditions revealed leakage of H<sub>2</sub> (60% recovery), thus the detected % yield of H<sub>2</sub> reported here should be considered a lower limit. <sup>b</sup>These experiments were conducted using the reloading protocol as described above. <sup>c</sup>Electrode rinse test as described in main text. <sup>d</sup>Control experiment with no [P<sub>3</sub><sup>B</sup>Fe][BAr<sup>F</sup><sub>4</sub>] included but including a typical loading of 11.9 mg (10 μmol) of [Cp\*<sub>2</sub>Co][BAr<sup>F</sup><sub>4</sub>]. <sup>e</sup>Control experiment in which the cell with all components, including the sodium auxiliary electrode, was assembled and stirred at -35 °C for 43 hours but neither a potential bias was applied, nor were the working and auxiliary electrodes externally connected. This experiment thus interrogates the ability of the sodium electrode to function as a chemical reductant for N<sub>2</sub>RR under the CPE conditions. <sup>f</sup>Chemical catalysis runs at -35 °C in 0.1 M NaBAr<sup>F</sup><sub>4</sub> Et<sub>2</sub>O solution with 50 equiv (100 μmol) of Cp\*<sub>2</sub>Co included as a chemical reductant as well as [P<sub>3</sub><sup>B</sup>Fe][BAr<sup>F</sup><sub>4</sub>] (2 μmol) and 100 μmol of acid ([Ph<sub>2</sub>NH<sub>2</sub>][OTf]).

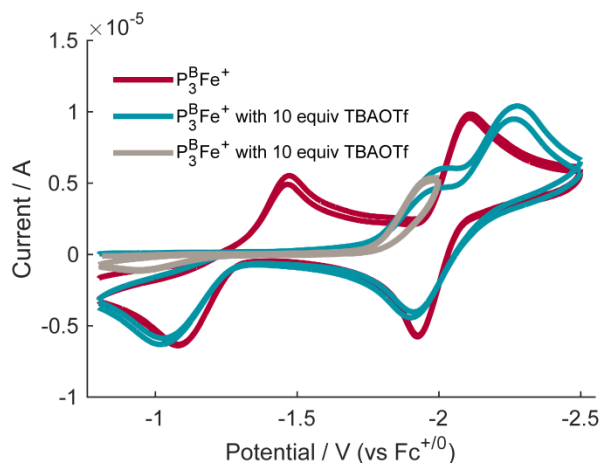
**Control experiment for the possibility of NH<sub>3</sub> being generated in a chemical rather than electrochemical process during acidic workup:**

As per the general CPE methodologies described in S9.2 and S9.3, after electrolysis additional acid is added to the cell to sequester generated  $\text{NH}_3$  as an ammonium salt to facilitate transfer of these materials to a Schlenk tube, ultimately allowing  $\text{NH}_3$  quantitation via base digestion and vacuum transfer as described in S1.4. This presents the possibility that electrochemically reduced species formed during electrolysis (e.g.,  $\text{P}_3^{\text{B}}\text{FeN}_2^-$  and  $\text{Cp}^*_2\text{Co}$ ) could react with this additional acid after the electrolysis was complete to generate  $\text{NH}_3$  in a chemical reaction. A control experiment to determine the extent to which this type of reactivity might contribute to the total  $\text{NH}_3$  yield observed from the CPE experiments was conducted. The H-cell is assembled via the standard methodology and charged with a typical loading of  $[\text{P}_3^{\text{B}}\text{Fe}][\text{BAr}^{\text{F}}_4]$  (2  $\mu\text{mol}$ ) and  $[\text{Cp}^*_2\text{Co}][\text{BAr}^{\text{F}}_4]$  (10  $\mu\text{mol}$ , 5 equiv) but without initial acid (i.e., no  $[\text{Ph}_2\text{NH}_2][\text{OTf}]$ ). Electrolysis is then carried out at  $-2.1$  V vs  $\text{Fc}^{+/0}$  until the current pass in the cell falls to 1% of the initial current passed (in this case 1.12 C of charge were passed, corresponding to 11.6  $\mu\text{mol}$  of reducing equivalents stored in the system, which approaches the theoretical limit of reducing equivalents that the loading of  $[\text{P}_3^{\text{B}}\text{Fe}][\text{BAr}^{\text{F}}_4]$  (2  $\mu\text{mol}$ ) and  $[\text{Cp}^*_2\text{Co}][\text{BAr}^{\text{F}}_4]$  (10  $\mu\text{mol}$ ) could store) at this potential. This post electrolysis mixture is then treated with acid and analyzed for  $\text{NH}_3$  via the standard methodology. This experiment yielded 0.2 equiv  $\text{NH}_3$  (relative to Fe) indicating that chemical  $\text{N}_2\text{RR}$  between electrochemically reduced species during the acidic workup is very minor.

### Additional CV data:



**Figure A4.5.** Cyclic voltammograms of 0.5 mM  $[P_3^B Fe][BAr^F_4]$  at varied scan rates (left) and plot of peak current versus square root of scan rate for each feature (right) showing linear dependence in all cases. All spectra are collected in 0.1 M  $NaBAr^F_4$  solution in  $Et_2O$  at  $-35$  °C using a glassy carbon working electrode, and externally referenced to the  $Fc^{+/0}$  couple.



**Figure A4.6.** Cyclic voltammograms of 0.5 mM  $[P_3^B Fe][BAr^F_4]$  (red trace) and  $[P_3^B Fe][BAr^F_4]$  with 10 equiv of tetrabutylammonium trifluoromethanesulfonate

([TBA][OTf]) (blue and gray traces). The traces with [TBA][OTf] show disappearance of a wave corresponding to the  $P_3^BFe^{+/0}$  couple at  $\sim -1.58$  V (present in the red trace). This phenomenon, as in the case with acidic triflate sources as described in the main text, is likely due to triflate binding (to generate  $P_3^BFeOTf$ , thereby attenuating the wave associated with the reduction of  $P_3^BFe^+$  and  $P_3^BFeN_2^+$ ). If the scan is stopped and reversed at  $-2.0$  (before the  $P_3^BFeN_2^{0/-}$  couple) no reversibility is observed, consistent with a chemical step (dissociation of triflate) being coupled with this redox event. We note that in the presence of  $OTf^-$  it appears that the second reductive feature is also slightly anodically shifted. We believe this to be due to slow  $N_2$  binding kinetics and thus this wave would represent a convolution of the  $0/1-$  reduction processes for both a vacant and an  $N_2$  bound  $P_3^BFe$ . All spectra are collected in  $0.1$  M  $NaBARF_4$  solution in  $Et_2O$  at  $-35$  °C using a glassy carbon working electrode, and externally referenced to the  $Fc^{+/0}$  couple.

#### **A4.10 Computational Details**

##### **Calculation of Acid Dissociation Constants**

Acid dissociation constants ( $pK_a$  and  $pK_d$ ) were performed were optimized and solvated as discussed in the general methods section. For  $pK_a$  values, the  $\Delta G$  for the exchange of a proton ( $H^+$ ) between the acid of interest and  $^{2,6-Cl}PhNH_2/^{2,6-Cl}PhNH_3^+$ . For  $pK_d$  values, the same approach was used except that the net exchange of a HOTf unit was calculated. In all cases the dissociation constant was reference to the literature value for the  $pK_a$  of  $^{2,6-Cl}PhNH_3^+$  in THF.

##### **Determination of PT, ET and PCET Kinetics**

Kinetic barriers for reported for PT, ET and PCET were performed in one of two ways. Internal consistency between the methods was determined where possible. Values are summarized in Table A4.8.

*Method A. Marcus Theory.* Standard Marcus theory expressions<sup>21</sup> were used in method A. Inner sphere reorganization energies for PT or PCET were calculated using the method developed by the group of Hammes-Schiffer (Eq. S1) utilizing the force constants for the reactant ( $f_j^r$ ) and product ( $f_j^p$ ) species and the change in equilibrium bond length ( $\Delta q_j$ ).<sup>22</sup>

$$\lambda_{is,PT/PCET} = \sum_j \frac{f_j^r f_j^p}{f_j^r + f_j^p} \Delta q_j^2 \quad (\text{Eq. S1})$$

Outer sphere reorganization energies were calculated using a continuum solvation model for the solvation of a point charge ( $\lambda_{os,ET}$ )<sup>21</sup> or a dipole ( $\lambda_{os,PT}$ ).<sup>22-24</sup> The  $\lambda_{os,PCET}$  was approximated using Eq. S2, where  $\theta$  is the angle between the ET and PT vectors.<sup>22</sup> It was determined via analysis of the structure of a constrained optimization (in which the Fe–H–Co distance was kept constant) that  $\theta$  is between 0 and 45°, a range which corresponds to an insignificant variation (less than 0.2 kcal mol<sup>-1</sup>) in  $\lambda_{os,PCET}$ .

$$\lambda_{os,PCET} = \lambda_{os,PT} + \lambda_{os,ET} - (\lambda_{os,PT} * \lambda_{os,ET}) \cos(\theta) \quad (\text{Eq. S2})$$

Relative rates for a bimolecular PT/ET vs PCET ( $k_{bi}$ ) pathway for reaction shown in Table A4.8, Equation 6 were determined via the method outline by the group of Hammes-Schiffer in which the bimolecular rate constant for PT, ET or PCET is approximated by Eq. S3.

$$k_{\text{bi}} = K_{\text{A}} * k_{\text{uni}} \quad (\text{Eq. S3})$$

$K_{\text{A}}$  represents the pre-arrangement equilibrium constant and  $k_{\text{uni}}$  represents the unimolecular rate constant for PCET or ET.<sup>25</sup> Along an PT/ET pathway, the barriers calculated suggest that  $k^{\text{PT}} > k^{\text{ET}}$ . In approximating  $k_{\text{uni}}$  for PCET and ET, we made extensive use of the webPCET portal.<sup>26</sup> The electronic coupling for PCET and ET was assumed to be equal. In order to approximate a lower bound for  $k^{\text{PCET}}/k^{\text{ET}}$ , the pre-arrangement equilibrium ( $K_{\text{A}}$ ) was also assumed to be equal for PCET and ET. We believe this represents a lower bound as the approximation for  $K_{\text{A}}$  does not include any hydrogen bonding interactions for a PCET pathway.

*Method B. Optimization of a 1<sup>st</sup> Order Saddle Point.* PT barriers for the protonation of Cp\*<sub>2</sub>Co were also found by optimization of a 1<sup>st</sup> order saddle point. That the optimized structure represented a 1<sup>st</sup> order saddle point was confirmed with a frequency calculation, which showed only one imaginary frequency.

**Table A4.8. Overview of Parameters Used to Calculate Kinetic Barriers**

1. $[\text{}^{2,6\text{-Cl}}\text{PhNH}_3][\text{OTf}] + \text{Cp}^*\text{}_2\text{Co} \rightarrow \text{Cp}^*\text{Co}(\textit{exo}\text{-}\eta^4\text{-C}_5\text{Me}_5\text{H})\text{-OTf} + \text{}^{2,6\text{-Cl}}\text{PhNH}_2$
2. $[\text{}^{2,6\text{-Me}}\text{PhNH}_3][\text{OTf}] + \text{Cp}^*\text{}_2\text{Co} \rightarrow \text{Cp}^*\text{Co}(\textit{exo}\text{-}\eta^4\text{-C}_5\text{Me}_5\text{H})\text{-OTf} + \text{}^{2,6\text{-Me}}\text{PhNH}_2$
3. $[\text{}^{4\text{-OMe}}\text{PhNH}_3][\text{OTf}] + \text{Cp}^*\text{}_2\text{Co} \rightarrow \text{Cp}^*\text{Co}(\textit{exo}\text{-}\eta^4\text{-C}_5\text{Me}_5\text{H})\text{-OTf} + \text{}^{4\text{-OMe}}\text{PhNH}_2$
4. $\text{P}_3^{\text{B}}\text{FeNNH} + [\text{Cp}^*\text{Co}(\textit{exo}\text{-}\eta^4\text{-C}_5\text{Me}_5\text{H})][\text{OTf}] \rightarrow [\text{P}_3^{\text{B}}\text{FeNNH}_2][\text{OTf}] + \text{Cp}^*\text{}_2\text{Co}$
5. $[\text{P}_3^{\text{B}}\text{FeNNH}_2][\text{OTf}] + \text{Cp}^*\text{}_2\text{Co} \rightarrow \text{P}_3^{\text{B}}\text{FeNNH}_2 + [\text{Cp}^*\text{}_2\text{Co}][\text{OTf}]$

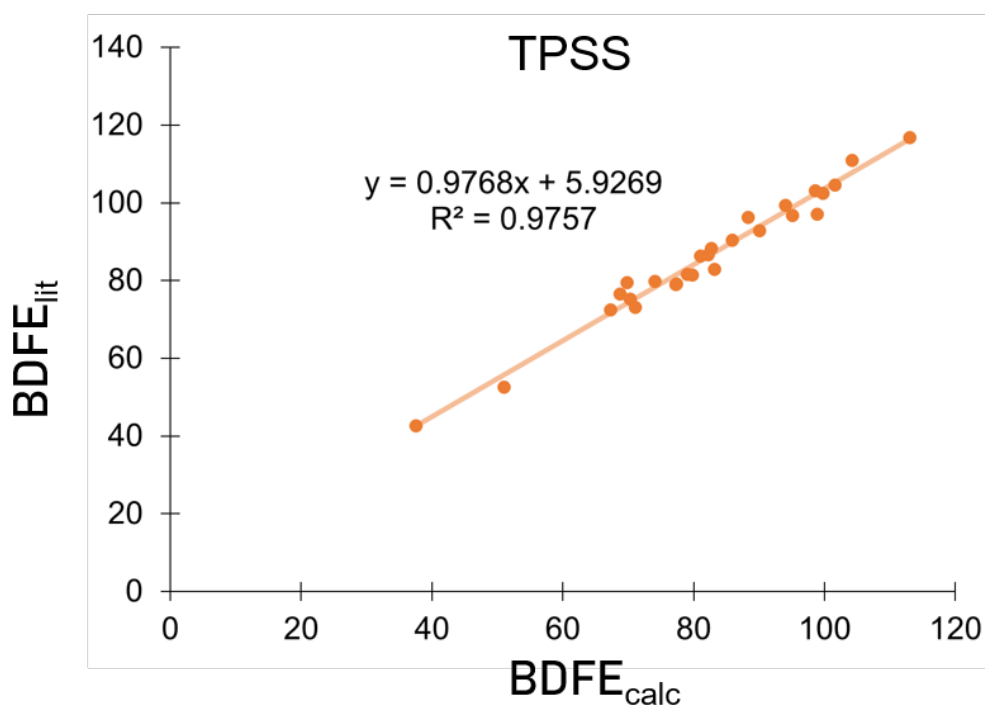
6. $P_3^BFeNNH + [Cp^*Co(exo-\eta^4-C_5Me_5H)][OTf] \rightarrow P_3^BFeNNH_2 + [Cp^*_2Co][OTf]$				
Reaction	$\lambda_{is}$	$\lambda_{os}$	Barrier  { $k_{rel}$ }	Method
1	N/A	N/A	1.3 kcal mol <sup>-1</sup>	A
1	7.5 kcal mol <sup>-1</sup>	6.3 kcal mol <sup>-1</sup>	1.3 kcal mol <sup>-1</sup>	B
2	N/A	N/A	3.8 kcal mol <sup>-1</sup>	A
2	7.5 kcal mol <sup>-1</sup>	6.3 kcal mol <sup>-1</sup>	3.6 kcal mol <sup>-1</sup>	B
3	N/A	N/A	4.5 kcal mol <sup>-1</sup>	A
3	7.5 kcal mol <sup>-1</sup>	6.3 kcal mol <sup>-1</sup>	4.8 kcal mol <sup>-1</sup>	B
4	8.9 kcal mol <sup>-1</sup>	6.3 kcal mol <sup>-1</sup>	1.5 kcal mol <sup>-1</sup>	A
5	8.9 kcal mol <sup>-1</sup>	25.0 kcal mol <sup>-1</sup>	4.1 kcal mol <sup>-1</sup>	A <sup>a</sup>
			{ $k_{rel} \equiv 1$ }	
6	13.7 kcal mol <sup>-1</sup>	0-10 kcal mol <sup>-1</sup>	0.2 – 0.6 kcal mol <sup>-1</sup>	A
			{2000 – 4500}	

<sup>a</sup> The barrier for  $[P_3^BFeNNH_2][OTf]$  reduction was calculated assuming that rate-determining reduction to  $[P_3^BFeNNH_2][OTf]^-$  precedes  $OTf^-$  release.

### BDFE Calculations



Bond dissociation free energies (BDFE) of X–H bonds were calculated in the gas-phase using a series of known reference compounds.<sup>27</sup> The free-energy difference between the H-atom donor/acceptor pair was calculated based on the thermochemical information provided by frequency calculations after structure optimizations using the procedure described in the general computational section. A linear plot of  $\Delta G$  vs  $BDFE_{lit}$  was generated to form a calibration curve (Figure A4.7). BDFE predictions were generated by application of the line of best fit to the calculated  $\Delta G$  of the unknown species.



**Figure A4.7.**  $BDFE_{calc}$  and  $BDFE_{lit}$  plotted for species of known  $BDFE_{E-H}$ . Line of best fit is shown.

**Table A4.9. Data used to generate the plot and line of best fit shown in Figure A4.5.**

Species	$\Delta G$ (E-H) (kcal mol <sup>-1</sup> )	$\Delta G$ (E <sup>•</sup> ) (kcal mol <sup>-1</sup> )	$\Delta G_{\text{calc}}$ (kcal mol <sup>-1</sup> )	BDFE <sub>E-H</sub> (kcal mol <sup>-1</sup> )
HOOH	-151.4	-150.8	69.8	79.7
MeOH	-115.6	-115.0	88.3	96.4
EtOOH	-230.0	-229.4	68.7	76.6
H <sub>2</sub> O	-76.4	-75.7	104.2	111.0
NH <sub>3</sub>	-56.5	-55.8	94.0	99.4
Me <sub>3</sub> CH	-158.3	-157.6	82.7	88.3
PhOH	-307.2	-306.6	74.0	79.8
Et <sub>2</sub> NH	-213.6	-212.9	81.0	86.4
NH <sub>2</sub> NH <sub>2</sub>	-111.8	-111.1	67.3	72.6
OH <sup>-</sup>	-75.7	-75.0	98.6	103.1
PhSH	-630.2	-629.5	70.3	75.3
NH <sub>4</sub> <sup>+</sup>	-56.8	-56.1	113.0	116.9
Me <sub>2</sub> CH <sub>2</sub>	-119.0	-118.4	85.9	90.4

HC(O)OOH	-264.7	-264.1	82.2	86.8
OOH	-150.8	-150.2	37.5	42.7
C <sub>6</sub> H <sub>6</sub>	-232.1	-231.4	101.6	104.7
C <sub>2</sub> H <sub>4</sub>	-78.5	-77.8	99.7	102.5
C <sub>2</sub> H <sub>6</sub>	-79.7	-79.1	90.0	92.9
PhCH <sub>3</sub>	-271.3	-270.7	79.0	81.6
CH <sub>4</sub>	-40.5	-39.8	95.1	96.8
CpH	-193.9	-193.3	71.0	73.2
EtSH	-477.8	-477.2	77.2	79.1
MeSH	-438.6	-437.9	77.3	79.2
PhNH <sub>2</sub>	-287.4	-286.7	79.8	81.5
NHNH	-110.6	-110.0	51.0	52.6
H <sub>2</sub> S	-399.3	-398.7	83.1	83.0
H <sub>2</sub>	-1.2	-0.5	98.8	97.2

**Calculated Reduction Potentials for Selected [Ar<sub>n</sub>NH<sub>(4-n)</sub>][OTf] and Ar<sub>n</sub>NH<sub>(3-n)</sub>**

**Table A4.10. Calculated Reduction Potentials of Selected Species**

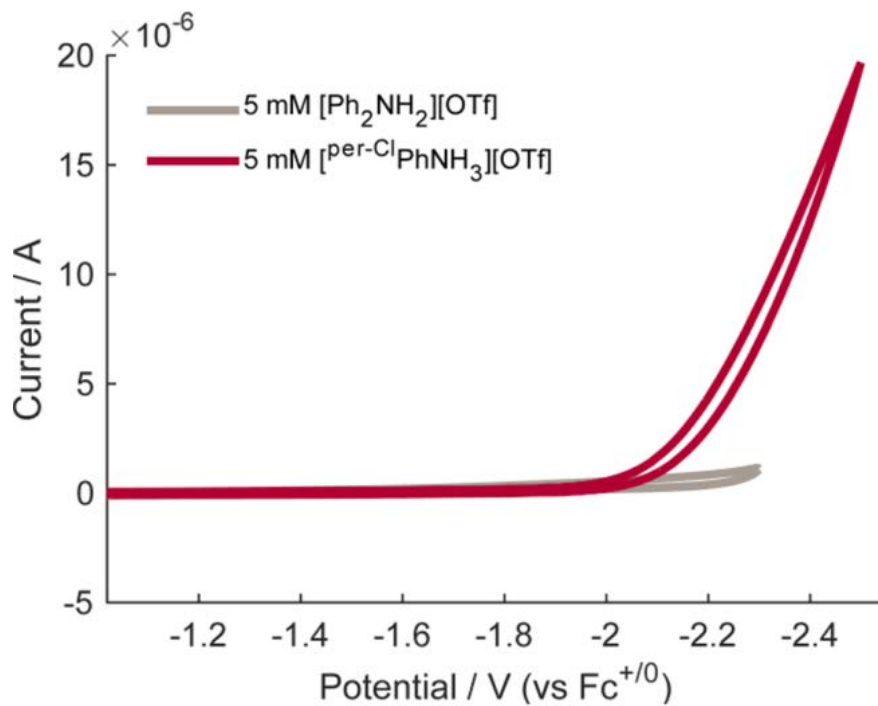
Species	$E^{\circ}$ (V vs $\text{Fc}^{+/0}$ )
$[\text{}^4\text{-OMePhNH}_3][\text{OTf}]$	-3.8 V
$\text{}^4\text{-OMePhNH}_2$	-3.4 V
$[\text{}^{2,6}\text{-MePhNH}_3][\text{OTf}]$	-3.8 V
$[\text{}^{2,6}\text{-ClPhNH}_3][\text{OTf}]$	-2.4 V
$[\text{}^{2,6}\text{-ClPhNH}_3]^+$	-2.0 V
$[\text{Ph}_2\text{NH}_2]^+$	$< -2.5 \text{ V}^a$
$\text{Ph}_2\text{NH}$	-3.1 V
$[\text{}^{\text{per-Cl}}\text{PhNH}_3][\text{OTf}]$	-2.0 V
$\text{Cp}^*\text{}_2\text{Co}$	-2.2 V

<sup>a</sup> Potential for the formation of  $\text{Ph}_2\text{NH}^{\bullet} + \text{H}^{\bullet}$  is reported. No ‘reversible’ minima was found.

### Discussion of the Anomalous Behavior of $[\text{}^{\text{per-Cl}}\text{PhNH}_3][\text{OTf}]$

Determining the reduction potential of the acids using electrochemical techniques is challenging due to the significant, electrode catalyzed HER observed upon scanning anodically (see Figure A4.8). However, as expected due to the lower  $pK_a$  of  $[\text{}^{\text{per-Cl}}\text{PhNH}_3][\text{OTf}]$  compared to  $[\text{Ph}_2\text{NH}_2][\text{OTf}]$  we see an earlier onset of the reduction potential and a higher current density. These processes are likely electrode-mediated and

thus do not reflect a pure reduction potential, so to better estimate the outer-sphere reduction potential of the acids employed we have used DFT (Table A4.10). In many cases, attempts to optimize the one electron reduced species results in a chemical step (*i.e.*, loss of  $\text{Cl}^-$  or  $\text{H}\bullet$ ) precluding determination of the reversible redox potential for the system. We are, however, able to find (*in silico*) a well-behaved reduction for  $[\text{per-Cl}^-\text{PhNH}_3][\text{OTf}]$  of  $-2.0$  V. As a comparison, the high efficiency acid,  $[\text{2,6-Cl}^-\text{PhNH}_3][\text{OTf}]$ , has a reduction potential of  $-2.4$  V. This leads us to believe for  $[\text{per-Cl}^-\text{PhNH}_3][\text{OTf}]$  rather than engaging in an inner-sphere proton transfer with  $\text{Cp}^*\text{Co}$  ( $E_{\text{calc}}^0(\text{Cp}^*\text{Co}^{0/+}) = -2.18$  V) it is likely that an outer sphere electron transfer occurs first. This change in mechanism would explain the increased  $\text{H}_2$  yields and the decreased  $\text{N}_2\text{RR}$  efficiency. In contrast,  $[\text{2,6-Cl}^-\text{PhNH}_3][\text{OTf}]$  should be resistant to reduction and thus able to protonate the metallocene and engage in the mechanism discussed in the main text.



**Figure A4.8.** Cyclic voltammograms of 5 mM  $[\text{Ph}_2\text{NH}_2][\text{OTf}]$  (gray trace) and 5 mM  $[\text{per-ClPhNH}_3][\text{OTf}]$  (red trace). All spectra are collected in 0.1 M  $\text{NaBAR}_4^{\text{F}_4}$  solution in  $\text{Et}_2\text{O}$  at  $-35^\circ\text{C}$  using a glassy carbon working electrode and externally referenced to the  $\text{Fc}^{+/0}$  couple. Scan rate is 100 mV/s.

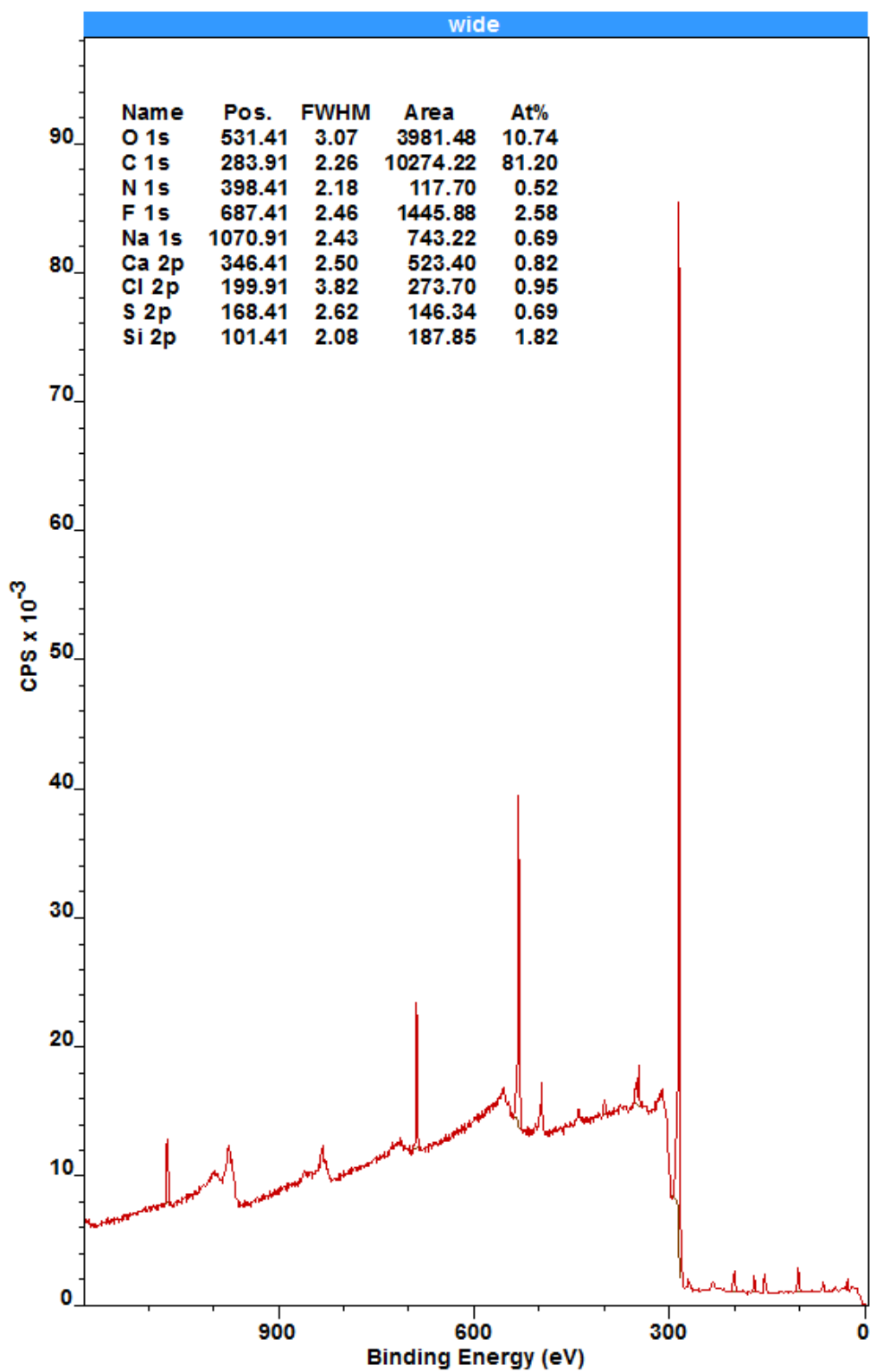
#### A4.11 X-ray Photoelectron Spectroscopy (XPS) details

The surface composition of the carbon electrode surface after a 15 hour bulk electrolysis in the presence of  $[P_3^BFe][BAr^F_4]$ ,  $[Cp^*_2Co][BAr^F_4]$ ,  $[Ph_2NH_2][OTf]$  and  $N_2$  was determined via XPS on a Kratos Axis Nova spectrometer with DLD (Kratos Analytical; Manchester, UK). The excitation source for all analysis was monochromatic Al  $K\alpha_{1,2}$  ( $h\nu = 1486.6$  eV) operating at 10 mA and 15 kV. The X-ray source was directed at  $54^\circ$  with respect to the sample normal. A base pressure of  $1 \times 10^{-9}$  Torr is maintained in the analytical chamber, which rises to  $5 \times 10^{-9}$  Torr during spectral acquisition. All spectra were acquired using the hybrid lens magnification mode and slot aperture, resulting in an analyzed area of  $700 \mu m \times 400 \mu m$ . Survey scans were collected using 160 eV pass energy, while narrow region scans used 10 eV; charge compensation via the attached  $e^-$ -flood source was not necessary in this study.

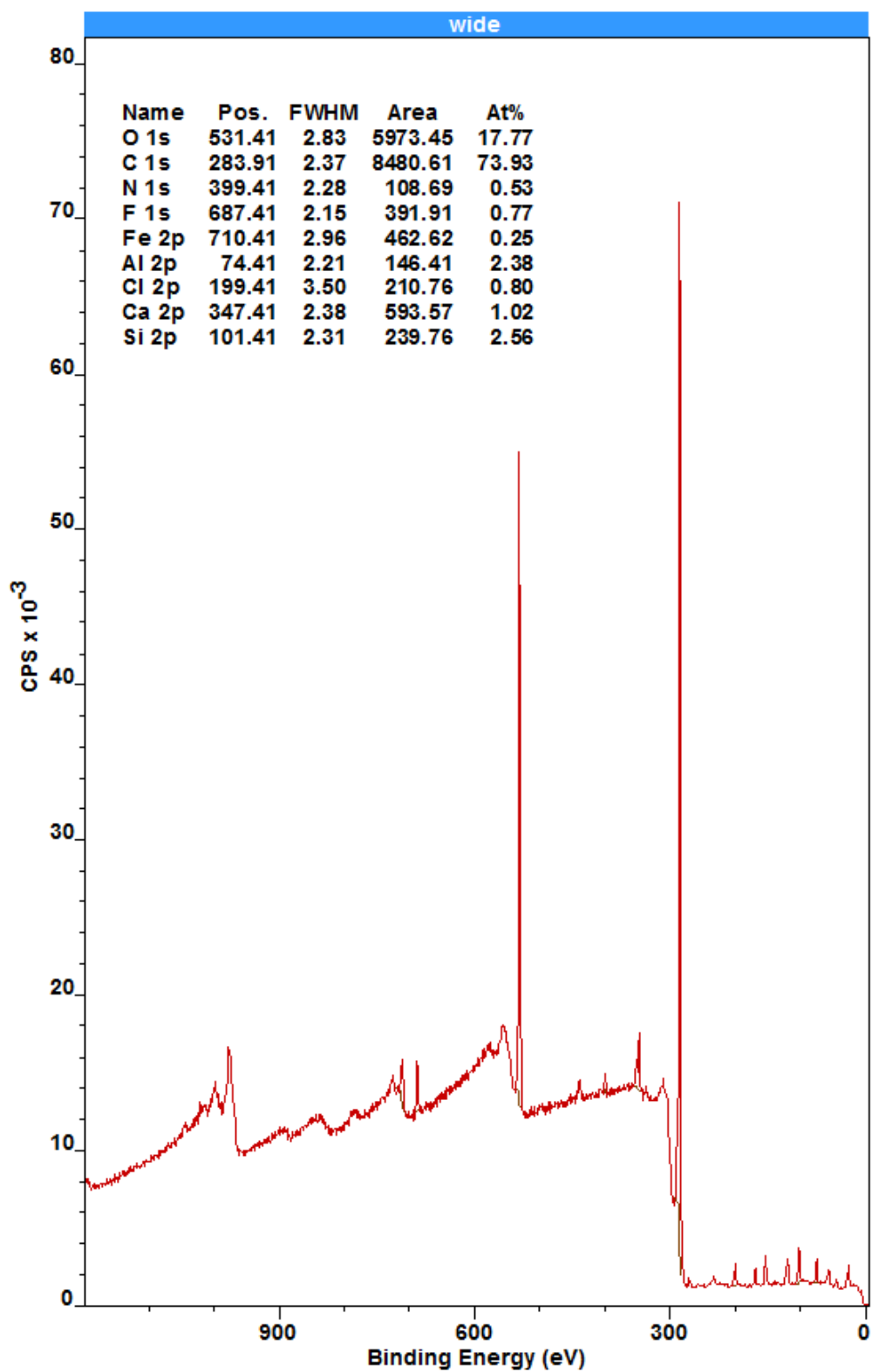
Subsequent peak fitting and composition analysis was performed using CasaXPS version 2.3.16 (Casa Software Ltd.; Teignmouth, UK). Energy scale correction for the survey and narrow energy regions was accomplished by setting the large component in the C 1s spectrum, corresponding to a C 1s C(=C) transition, to 284.8 eV. All components were fit using a Gaussian 30% Lorentzian convolution function. For quantification, Shirley baselines were employed where there was a noticeable change in CPS before and after the peak in the survey spectrum; otherwise, linear was chosen. Atomic percentages were calculated using the CasaXPS packages for regions and/or components and are reported herein. Calculations were performed using region or

component areas normalized to relative sensitivity factors specific to the instrument conditions with deconvolution from the spectrometer transmission function.





**Figure A4.9.** XPS survey scan of a section of a glassy carbon plate which was not exposed to the working chamber solution during a 15 hour bulk electrolysis in the presence of  $[\text{P}_3^{\text{B}}\text{Fe}][\text{BAr}^{\text{F}_4}]$ ,  $[\text{Cp}^*\text{Co}][\text{BAr}^{\text{F}_4}]$ ,  $[\text{Ph}_2\text{NH}_2][\text{OTf}]$  and  $\text{N}_2$  at  $-2.1$  V (vs  $\text{Fc}^{+/0}$ ). XPS and Auger peaks are assigned as labeled in the legend, which also includes atomic percentages calculated from component fits from scans of individual XPS regions. This material represents a baseline of the electrode surface composition resulting from cleaning, polishing, and handling prior to CPE experiments and is provided for comparison to a XPS survey scan of a section of the same glassy carbon plate which was exposed to the working chamber solution during a 15 hour bulk electrolysis in the presence of  $[\text{P}_3^{\text{B}}\text{Fe}][\text{BAr}^{\text{F}_4}]$ ,  $[\text{Cp}^*\text{Co}][\text{BAr}^{\text{F}_4}]$ ,  $[\text{Ph}_2\text{NH}_2][\text{OTf}]$  and  $\text{N}_2$  at  $-2.1$  V (vs  $\text{Fc}^{+/0}$ ) presented in figure A4.10.



**Figure A4.10.** XPS survey scan of a section of a glassy carbon plate which was exposed to the working chamber solution during a 15 hour bulk electrolysis in the presence of  $[P_3^BFe][BAr^F_4]$ ,  $[Cp^*Co][BAr^F_4]$ ,  $[Ph_2NH_2][OTf]$  and  $N_2$  at  $-2.1$  V (vs  $Fc^{+/0}$ ). XPS and Auger peaks are assigned as labeled in the legend, which also includes atomic percentages calculated from component fits from scans of individual XPS regions. This material represents a post-electrolysis state of the electrode surface composition for comparison to a XPS survey scan of a section of the same glassy carbon plate which was not exposed to the working chamber solution during a 15 hour bulk electrolysis in the presence of  $[P_3^BFe][BAr^F_4]$ ,  $[Cp^*Co][BAr^F_4]$ ,  $[Ph_2NH_2][OTf]$  and  $N_2$  at  $-2.1$  V (vs  $Fc^{+/0}$ ) presented in figure A4.9. Notably this active surface scan reveals a small Fe signal, likely resulting from some degree of decomposition of the  $[P_3^BFe][BAr^F_4]$  catalyst over the course of the 15 hour electrolysis; however it is also possible that this small Fe signal is the result of contamination during the handling of the sample. This Fe 2p signal occurs at 710.4 eV, but due to the weak signal intensity it is not possible to confidently assign its oxidation state. Although, the signal does not appear consistent with Fe(0) whose signal is typically around 707 eV; we would also note though that the handling process involves transferring the electrode quickly in air which could result in oxidation of Fe(0) that was present. Also notable is that no new Co signal is observed in the post-electrolysis scan suggesting that  $[Cp^*Co][BAr^F_4]$  does not decompose to a surface bound Co species in detectable amounts during the electrolysis. Phosphorus is not detectable in the survey scan.

#### A4.12 p*K*<sub>a</sub> Determination Strategy

Bosch et al. published a procedure for converting a p*K*<sub>a</sub> in THF into the equivalent p*K*<sub>a</sub> in different solvents.<sup>28</sup> Although not all of the p*K*<sub>a</sub> values have been experimentally determined in THF the values obtained from converting from MeCN or H<sub>2</sub>O into a THF value is quite accurate. So we have used these converted values in the text. Where available a number measured in THF has been used, if not the MeCN derived value is used. If neither is available then the H<sub>2</sub>O derived value is used.

Solvent conversion equations:

$$\text{p}K_{\text{a}}(\text{THF}) = 0.78 \times \text{p}K_{\text{a}}(\text{MeCN}) - 0.52$$

$$\text{p}K_{\text{a}}(\text{THF}) = 1.19 \times \text{p}K_{\text{a}}(\text{H}_2\text{O}) + 2.13$$

Acid	p <i>K</i> <sub>a</sub> in MeCN	p <i>K</i> <sub>a</sub> in H <sub>2</sub> O	Converted p <i>K</i> <sub>a</sub> <sup>a</sup>	Experimental p <i>K</i> <sub>a</sub> in THF
[ <sup>4</sup> -OMePhNH <sub>3</sub> ][OTf]	11.86 <sup>29</sup>	5.29 <sup>31</sup>	8.8 (8.4)	8.8 <sup>28</sup>
[PhNH <sub>3</sub> ][OTf]	10.62 <sup>29</sup>	4.58 <sup>31</sup>	7.8 (7.6)	8.0 <sup>28</sup>
[ <sup>2,6</sup> -MePhNH <sub>3</sub> ][OTf]	--	3.89 <sup>31</sup>	-- (6.8)	
[ <sup>2</sup> -ClPhNH <sub>3</sub> ][OTf]	7.86 <sup>29</sup>	2.64 <sup>31</sup>	5.6 (5.3)	6.0 <sup>28</sup>

[ <sup>2,5</sup> -ClPhNH <sub>3</sub> ][OTf]	6.21 <sup>30</sup>	1.53 <sup>29</sup>	4.3 (4.0)	4.5 <sup>28</sup>
[ <sup>2,6</sup> -ClPhNH <sub>3</sub> ][OTf]	5.06 <sup>29</sup>	0.42 <sup>32</sup>	3.4 (2.6)	
[ <sup>2,4,6</sup> -ClPhNH <sub>3</sub> ][OTf]	--	-0.03 <sup>32</sup>	-- (2.1)	
[ <sup>per</sup> -ClPhNH <sub>3</sub> ][OTf]	2.35 <sup>30</sup>	--	1.3 (--)	
collidinium triflate	14.98 <sup>29</sup>	--	11.2 (--)	
benzylammonium triflate	--	9.34 <sup>33</sup>	-- (13.2)	

<sup>a</sup>First is listed the value converted from THF and then in parentheses is the value converted from H<sub>2</sub>O.

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