Electronic Supporting Information for

Electrode initiated proton-coupled electron transfer to promote degradation of a nickel(II) coordination complex

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General experimental details including synthesis of 1

General Considerations. Syntheses were performed in a nitrogen filled glovebox. Acetonitrile (Fisher Scientific, HPLC grade, >99.9%) and diethyl ether (Fisher Scientific, >99%) were dried and degassed with argon using a Pure Process Technology solvent system. 1,3propanedithiol (Aldrich, 99%), bis(diphenylphosphino)propane (dppp; Aldrich, 97%), and triethylammonium chloride (Aldrich, 98%) were used as received. Tetrabutylammonium hexafluorophosphate (Acros Organics, 98%) was recrystallized from hot ethanol (Decon Labs, Inc., 200 proof), filtered, washed with cold ethanol, and dried at room temperature under vacuum for 19 hours. Amberlyst® A21 ion exchange resin (Aldrich) was dried between 80-90 °C for about 10 hours. [Ni(CH₃CN)₆][BF₄]₂ was prepared by literature methods.¹ [Et₃NH][BF₄] was prepared as reported before,² however, note that no reprecipitation from CH₃CN by Et₂O was performed and that the originally reported synthesis was incorrect in stating that reprecipitation was performed. Water (Milli-Q system) for kinetic isotope experiments was degassed with three freeze-pump-thaw cycles. Deuterium oxide (Cambridge Isotopes Laboratories, Inc., 99.9%) was degassed with nitrogen. CD₃CN (Cambridge Isotopes Laboratories, Inc., 99.8%) was degassed with three freeze-pump-thaw cycles, passed through activated alumina to remove water, and stored over activated 3 Å molecular sieves. Elemental analysis was performed by Atlantic Microlabs, Inc. NMR spectra were recorded on a Bruker 400 MHz spectrometer with ¹H spectra referenced to proteo solvent impurities³ and ³¹P spectra referenced against an external 85% D₃PO₄ standard. UV-vis spectra were recorded in a nitrogen filled glovebox using fiber optic cables connected to an Agilent Cary 60 UV-vis spectrophotometer. Gas chromatography was performed using a Varian 450-GC instrument and a calibration curve used to quantify the amount of hydrogen present in the headspace of bulk electrolysis cells (see SI for full details). X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra DLD X-ray Photoelectron Spectrometer. Spectra were obtained with a monochromatic AI Ka X-ray source, and survey and high resolution scans were obtained with pass energies of 80 and 20 eV, respectively. Samples for XPS analysis were loaded into an airtight container and transferred to the instrument using a N₂ glovebag. All spectra were corrected to the C 1s peak at 284.6 eV. SEM images were obtained with a Hitachi S-4700 SEM operated with an accelerating voltage of 20 kV.

Synthesis of 1. Attempts to synthesize **1** in the same manner as the previously reported analogous compound with a N-Me at the bridgehead of the phosphine⁴ were unsuccessful due to difficultly removing the $[Et_3NH][BF_4]$ byproduct. Consequently, solid beads of ion exchange resin with amine functionalities were used instead of Et_3N . In a nitrogen-filled glovebox, 0.4 g (0.84 mmols, 1 eq) of $[Ni(CH_3CN)_6](BF_4)_2$ and 15 mL of CH_3CN were added to a 100 mL ovendried Schlenk flask equipped with a stir bar. While stirring, 0.3275 g (0.79 mmols, 0.95 eq) of bis(diphenylphosphino)propane dissolved in 10 mL of CH_3CN were added quickly dropwise, turning the solution red. Resin base (3.19 g) suspended in 25 mL of CH_3CN was added followed by 0.1085 g (1.00 mmols, 1.2 eq) of 1,3-propanedithiol dissolved in 5 mL of CH_3CN . After stirring for two days at room temperature, solvent was removed under vacuum and the remaining sludge extracted with 20 mL of CH_3CN and filtered. To the filtrate was added ca. 22 mL Et_2O and the solution cooled at -35 °C for six days to yield dark red crystals. After decanting the supernatant the solids were washed three times with ca. 2 mL of Et_2O . Additional crystals were

obtained by drying the supernatant under vacuum, adding ca. 4 mL CH₃CN and 1 mL Et₂O, cooling for seven days at -35 °C, decanting, and washing the crystallized solids three times with ca. 2 mL Et₂O. The solids from both recrystallizations were combined and dried under vacuum for 6.5 hours. Yield 0.069 g, 15%. ¹H NMR (CD₃CN, ppm): 7.74 (multiplet, 8H), 7.44-7.34 (b. multiplet, 12H), 2.36 (multiplet, 4H), 2.21 (multiplet, 4H), and 1.80 (multiplet, 4H). ³¹P{¹H} NMR (CD₃CN, ppm): 12.40. Full ¹H and ³¹P{¹H} assignments are given below. Anal. Calcd.: C, 62.41; H, 5.59. Found: C, 62.45; H, 5.64.

Electrochemical Methods. Electrochemistry was performed in a nitrogen filled glovebox with either a Pine Instruments WaveNow or WaveDriver potentiostat using glassy carbon working electrodes, a glassy carbon counter electrode, and a silver wire pseudoreference. The WaveNow potentiostat was pumped into the glovebox and connected to an external computer via a custom USB feedthrough while the WaveDriver potentiostat was kept external to the glovebox and the electrode leads were connected with a custom shielded electrode cable feedthrough. All scans were absolutely referenced to ferrocene either added at the end of each measurement set (e.g., for measurements where electrodes were prepared for surface analysis) or present for each scan. Ohmic drop errors were approximately corrected as before.² Glassy carbon disk electrodes (CH Instruments, 3 mm diameter) or glassy carbon plate electrodes for bulk electrolysis (ALS Co., Ltd., Japan, 10 x 10 x 1 mm) were polished with 0.05 micron alumina powder (CH Instruments, contained no agglomerating agents) Milli-Q water slurries, rinsed, and ultrasonicated briefly in HPLC grade water to remove residual polishing powder. The pseudoreference silver wire electrode was submerged in a glass tube fitted with a porous glass Vycor tip containing either 100 or 250 mM $[Bu_4N][PF_6]$ in acetonitrile depending on the electrolyte concentration of the solution. Bulk electrolysis was performed using a custom threecompartment cell (Allen Scientific Glass Inc., see Supporting Information for photo and engineering draft) equipped with a septum for removing gas aliquots for GC analysis.

Each working electrode was pretreated with two cyclical scans from approximately 0.7 V to -2.8 V (the exact value varied in accordance with the silver wire pseudoreference) at 200 mV/s in 0.1 or 0.25 M [Bu₄N][PF₆]. For all experiments, background voltammograms at the respective scan rate were taken. Following pretreatment and background scans, each electrode was rinsed with CH₃CN and air dried. The solution was stirred between scans. Fresh electrodes were used for every single scan, except for analysis of the reversible **1** Ni^{II/I} couple which was found to be identical on repeated scans, for rinse test experiments, and for preparation of electrodes for bulk electrolysis.

NMR Spectra and Structural Assignment of 1

Compound **1** was characterized by ¹H, ³¹P{¹H}, ¹H-¹H gradient enhanced COSY, and ¹H-³¹P HMQC. This data, along with elemental analysis and comparison to the NMR spectrum of a reported analog of **1** where the phosphine bridgehead methylene is replaced with an N-Me,⁴ support the structural assignment of **1** as depicted in Scheme S1.



Scheme S1. Compound **1** with expected unique ¹H peaks.



Figure S1. ¹H NMR of **1** in CD₃CN (400 MHz) with proton assignments per Scheme S1.





Figure S4. Upfield region of ¹H-¹H gradient enhanced COSY NMR of **1** in CD₃CN (400 MHz). This spectrum reveals that the broad multiplet at 1.8 ppm is actually two overlapping signals, as evidenced by the off-diagonal peaks with both the **e** and **f** sets of protons. The two overlapping peaks are consequently assigned as the bridgehead methylenes of both the phosphine and dithiolate ligands, while **e** is assigned as the four methylene protons next to phosphorus on the phosphine and **f** the four methylene protons next to sulfur on the dithiolate.



Figure S5. ¹H-³¹P HMQC NMR spectrum (CD₃CN, 400 MHz) of **1**. The interaction of the phosphorus signal with the aromatic protons **c** and the methylene protons **e** is visible, supporting assignment of **e** as the methylene protons on the phosphine.

Bulk Electrolysis and Hydrogen Detection

Glassy carbon plates (1 x 1 x 0.1 cm,) were treated for 10 minutes in a solution of 0.4 mM 1 and 10 mM [Et₃NH][BF₄] at a potential of -1.7 V vs. Fc/Fc⁺. After thorough rinsing of the electrode, the plate was held at -1.7 V vs. Fc/Fc⁺ in a bulk electrolysis cell containing 25 mM [Et₃NH][BF₄] for 15 minutes. A 1 mL Vici Pressure-Lok Precision Analytical Syringe was used to sample 1 mL of the gas headspace and used to inject three ca. 0.3 mL samples into a Varian 450-GC with a pulsed discharge helium ionization detector and the average integrated hydrogen peak area calculated. A calibration curve made from samples of 0.5, 1.0, 3.0, and 5.0 v/v % H₂ in air for this specific instrument⁵ was used to determine the volume fraction of hydrogen. Consequently, the number of moles of hydrogen produced was determined using the known headspace volume of the central compartment. Henry's Law was used to estimate the number of moles of dissolved hydrogen in the working compartment solution and added to the moles of headspace hydrogen to find the total amount of hydrogen produced. The Henry's Law constant for hydrogen in acetonitrile was estimated to be 5700 atm from literature values for the mole fraction solubility of hydrogen measured at different partial pressures of hydrogen at 298 K.⁶ The Faradaic efficiency was then found by the ratio of the moles of hydrogen produced divided by the theoretical amount of hydrogen produced from integration of the total current passed. The experimental Faradaic efficiency was approximately 100%.



Figure S6. Photo of three-compartment bulk electrolysis cell used to produce hydrogen for detection by bulk electrolysis. Cell was custom made by Allen Scientific Glass, Inc. The Pt coil counter electrode was purchased from BioLogic Science Instruments.



Figure S7. Technical drawing of bulk electrolysis cell (by Allen Scientific Glass, Inc).

CVs of 1 and estimation of diffusion coefficient and heterogeneous rate constant



Figure S8. Ohmic-drop corrected CVs of 1.1 mM **1** in CH_3CN , 0.1 M $[Bu_4N][PF_6]$ at 0.05, 0.075, 0.1, 0.25, 0.5, 0.75, 1, 2.5, 5, 7.5, and 10 V/s.



Figure S9. Background subtracted cathodic peak currents for **1** plotted versus the square root of the scan rate.

The diffusion coefficient D_0 was estimated for **1** using the Randles-Sevcik equation⁷

$$i_{\text{peak}} = (2.69 \cdot 10^5) n^{3/2} \text{AD}_0^{1/2} C_0^* v^{1/2}$$

Using the slope found in Figure S9 a D₀ of $1 \cdot 10^{-5}$ cm²s⁻¹ was found for **1**.

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(V/s)	ΔE _p (mV)	ψ	k ⁰ (cm ² s ⁻¹)
0.05	63	7.18	0.06
0.075	63	8.51	0.08
0.1	62	9.68	0.11
0.25	66	4.19	0.07
0.5	64	6.82	0.17
0.75	67	3.59	0.11
1	65	5.21	0.18
2.5	77	1.39	0.08
5	92	0.70	0.06
7.5	105	0.47	0.05
10	114	0.38	0.04

Table S1. Measured peak-to-peak separation as a function of scan rate, and calculated psi and k^0 values, as described in text.

It is challenging to precisely determine the heterogeneous electron transfer rate constant k^0 , as uncompensated solution resistance leads to increases in peak-to-peak broadening indistinguishable from that caused by a slow k^0 at higher scan rates.⁸ Here, we estimated the solution resistance as before² and corrected our cyclic voltammograms prior to analysis. The resulting corrected ΔE_p values for the peak-to-peak separation of the cathodic and anodic peaks of the Ni^{II}/Ni^I couple of **1** are recorded in Table S1 as a function of scan rate. The method of Nicholson⁸ was then utilized to estimate k^0 , where first a dimensionless charge transfer parameter ψ was estimated using the following expression:⁸

$$\ln(\psi) = 3.69 - 1.16 \ln(\Delta E_{\rm p} - 59)$$

 k^0 can then be estimated from

$$\mathbf{k}^{0} = \psi \left(\frac{\pi \mathbf{D}_{0} F \upsilon}{RT}\right)^{1/2} (\mathbf{D}_{\mathrm{R}}/\mathbf{D}_{\mathrm{O}})^{\alpha/2}$$

Where D_R and D_O are the diffusion coefficients of the reduced and oxidized forms of **1**, respectively (here assumed to be equal) and α is the transfer coefficient, here assumed to be 0.5. The resulting values of k^0 (Table S1) span approximately 0.05 to 0.2 with an average of 0.09. We consequently *approximate* k^0 for **1** as 0.1 cm² s⁻¹.

Scanning electron micrographs of electrode treated with 1 and [Et₃NH][BF₄]



Figure 10. Scanning electron micrograph of a cross section of a glassy carbon plate electrolyzed with 0.3 mM **1** and 10 mM [Et₃NH][BF₄] for 30 minutes at -1.74 V vs. Fc⁺/Fc.



Figure S11. Scanning electron micrograph of a top-down view of a glassy carbon plate electrolyzed with 0.3 mM **1** and 10 mM $[Et_3NH^+][BF_4^-]$ for 30 minutes at -1.74 V vs. Fc⁺/Fc.

X-ray photoelectron spectroscopy data

Table S2. XPS peak positions and atomicconcentrations for a bare glassy carbonelectrode.peakatomic concentration (%)

•		•
S 2p	0.14	
Р 2р	0.00	
O 1s	3.11	
C 1s	95.33	
F 1s	0.78	
N 1s	0.63	



Figure S12. XPS spectrum of [Bu₄N][PF₆] dropcast onto a gold-plated silicon wafer.

Table S3. XP	S peak pos	sitions and	atomic	concentratior	۱S
for dropcast	[Bu ₄ N][PF ₆]	on a gold-	plated si	licon wafer.	

peak	atomic concentration (%)
S 2p	0.35
Р 2р	3.50
O 1s	2.29
C 1s	65.17
F 1s	24.36
N 1s	4.33



Figure S13. XPS spectrum of 1,3-bis(diphenylphosphino)propane (dppp) dropcast onto a gold-plated silicon wafer.

Table S4. XPS peak positions and atomicconcentrations for dropcast dppp on a gold-plated silicon wafer.

peak	atomic concentration (%)
Р 2р	4.8
O 1s	4.7
Si 2p	3.4
C 1s	87.1



Figure S14. XPS spectrum of 1 dropcast onto a gold-plated silicon wafer.

Table S5. XPS peak positions and atomicconcentrations for dropcast 1 on a gold-platedsilicon wafer

peak	atomic concentration (%)
Ni 2p	2.31
S 2p	4.18
Р 2р	4.70
O 1s	0.87
C 1s	86.39
F 1s	1.56



Figure S15. XPS spectrum of [Et₃NH][BF₄] dropcast onto a gold-plated silicon wafer.

Table	S6.	XPS	pea	ık	position	s and	atomic
concer	ntration Nyzer	ons 1 with	for 1 a	a hd	glassy [Ft_NH][F	carbon	plate
peak	nyzec	at	omi		oncentral	ion (%)	
O 1s					0.76	. ,	
C 1s					48.22		
F 1s					34.13		

B 1s	8.70
N 1s	8.19



Figure S16. High resolution XPS spectra of the Ni 2p region for both dropcast 1 and a plate electrolyzed with 1 and $[Et_3NH][BF_4]$.



Figure S17. High resolution XPS spectra of the S 2p region for both dropcast 1 and a plate electrolyzed with 1 and $[Et_3NH][BF_4]$.



Figure S18. Scan rate dependence of cathodic peak current of prewave for a solution of 0.6 mM **1** and 0.5 eq. of $[Et_3NH][BF_4]$ in acetonitrile.

<u>UV-vis spectroscopy of **1** titrated with $[Et_3NH^+][BF_4]$ </u>



Figure S19. UV-vis spectra of 0.4 mM **1** in CH3CN with and without 50 mM [Et₃NH][BF₄]. Addition of [Et₃NH][BF₄] to a solution of only 0.25 M [Bu₄N][PF₆] was found to shift the baseline upwards, so the 50 mM spectrum above was background subtracted with a spectrum of only 50 mM [Et₃NH][BF₄].

¹<u>H NMR spectroscopy of **1** titrated with [Et₃NH][BF₄]</u>



Figure S20. ¹H NMR of 1.4 mM **1** without (bottom) and with 199 molar equivalents of $[Et_3NH][BF_4]$ in CD₃CN. Solvent impurities are denoted. No peak shift of any of **1**'s peaks was observed.





Figure S21. ³¹P{¹H} NMR spectrum of a solution of 1.8 mM 1, 50 mM [Et₃NH][BF₄], and 0.25 M [Bu₄N][PF₆] after electrolysis at -1.97 V using a 1 x 2 x 0.2 cm glassy carbon plate electrode (about 1 x 1 cm was actually immersed). Free dppp phosphine ligand is observed (-16 ppm), as well as unreacted **1** at 12.97 ppm. Use of CH₃CN instead of CD₃CN explains why both the free **1** peak (12.40 ppm in CD₃CN) and the free dppp ligand (-16.65 in CD₃CN) show up approximately 0.65 ppm further downfield than expected.

Estimation of diffusion limited rate of reaction of 1⁻ and [Et₃NH][BF₄]

The diffusion limited bimolecular rate of reaction of $\mathbf{1}^{-}$ and $[Et_3NH][BF_4]$ was estimated using the Debye-Smoluchowski relation⁹

$$k_{diff} = 4\pi N_{\rm A} (D_1 + D_2)\beta$$

where N_A is Avogadro's number, D_1 and D_2 are the diffusion coefficients of the two reacting species (here **1** and Et₃NH⁺) and β is the effective reaction radius, taken as the sum of the radii for **1** and Et₃NH⁺ and estimated to be 8.5 Å. The diffusion coefficient of **1**⁻ was assumed to be equal to that of **1** which was obtained electrochemically to be 1 x 10⁻⁵ cm² s⁻¹ (see above) while the diffusion coefficient of Et₃NH⁺ was estimated by ¹H DOSY NMR to be 2.2 x 10⁻⁵ cm² s⁻¹. As both reactants **1**⁻ and Et₃NH⁺ are charged, β was further modified to reflect electrostatic interactions via¹⁰

$$\beta = \frac{R_c}{(\exp(R_c/R) - 1)} \exp(R_c \kappa)$$

where the Onsager radius R_c is given by

$$R_c = (z_1 z_2 e^2 / 4\pi \varepsilon_r \varepsilon_0 k_B T)$$

where *R* is the reactant radius (as above, approximated for $\mathbf{1}^{-}$ and Et_3NH^{+} as 8.5 Å) z_1 and z_2 are the respective charges of the two species (here -1 and +1 for $\mathbf{1}^{-}$ and Et_3NH^{+}), e is the elementary charge, ε_r is the relative permittivity of the solvent, ε_0 the permittivity of vacuum, k_B the Boltzmann constant, and T temperature. The relative permittivity of CH₃CN at room temperature is approximately 36.1.¹¹ The Debye length κ is given by

$$\kappa = \sqrt{\frac{2\mathrm{e}^2 N_a 1000}{\varepsilon_\mathrm{r} \varepsilon_0 \mathrm{k_B} \mathrm{T}}} I_c$$

where I_c is the ionic concentration, e.g., the electrolyte concentration (mols/L).

Consequently, the diffusion limited rate was estimated as $4.5 \times 1010 \text{ L mols}^{-1} \text{ s}^{-1}$.

Simulation details for ErCiEi mechanism

The simulated $E_rC_iE_i$ peak shift data depicted in Figure 6 of the manuscript was simulated using *DigiElch*. The following parameters were used:

Parameter	Experimental value	Estimated value	Rationale for estimated values
α (1 st Ε)		0.3, 0.5, or 0.7	normal range for α values ⁷
α (2 nd E)		0.5	assumed to be close to the average $lpha$ value 7
k^{0} (1 st E)	0.1 cm s ⁻¹	0 1 1	
<i>K</i> ° (2 [™] E) Da	$1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	0.1 cm s ⁻	assumed to be similar to k° for the first E
Dp D₄	$2.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$		
[P] = [A]	0.005 M		
A	0.071 cm ²		
E ₁ (1 ³⁴ E)	-1.92 V		The value of the 3 nd E was not found to
E ₂ (2 nd E)		-1.42 V	significantly affect the peak position (see Figure
2 ()			S22 and discussion below)
	0.25	$-E_{2} = 0$	V
	0 20 ع ²	$\int E_2^2 = 0$.5 V
	A/cr	$E_2 = 1$	V
	Ĕ 0.15	-	
	tis 0 10	1	
	Der		
	0.05 eut	-	
	0.00 Cri	1	
	5.00	+	
		0.8 0.6 0.	4 0.2 0.0 -0.2 -0.4 -0.6

Table S7. Parameters used to simulate the data show in Figure 6.

Figure S22. Simulated CVs for the $E_rC_iE_i$ mechanism using the parameters in Table S7 (except E_1 was set as 0 V instead of -1.92 V). The value of E_2 , which from experimental data is likely more positive than E_1 , was varied from 0 V to 1 V. Very little difference in the peak shift was observed; consequently, E_2 was set as -1.42 V for the simulation of the data shown in Figure 6.

Notes on ¹H DOSY NMR of [Et₃NH][BF₄]



Figure S23. ¹H DOSY NMR spectrum of a 9 mM CD₃CN solution of [Et₃NH][BF₄].

The diffusion coefficient of $[Et_3NH][BF_4]$ was estimated using ¹H DOSY NMR on a 500 MHz Bruker spectrometer. The pulse width was calibrated by varying the pulse width until null peaks were observed for both triethylammonium peaks, with the calibrated 90° pulse found to be 8.55 µs. T_1 and T_2 relaxation times for both triethylammonium peaks were estimated using inversion recovery experiments. These relaxation times were utilized to check that the ¹H DOSY experiment was run with sufficient delay times to allow for proton relaxation. The proton peak for CHD₂CN was found to relax very slowly; in order to decrease the measurement time the relaxation delays used were only long enough for the triethylammonium peak; hence the value found for CHD₂CN is not accurate. The DOSY data were processed in MestReNova version 8.1.0-11315 using the built-in Bayesian DOSY Transform method.

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