Supplementary Material (ESI) for Chemical Communications

Electrocatalytic Reduction of Protons to Hydrogen by a Water-Compatible Cobalt Polypyridyl Platform

Julian P. Bigi,[a,c] Tamara E. Hanna,[a,c] W. Hill Harman,[a,c] Alicia Chang,[a] and Christopher J. Chang*[a,b,c]

[a]Department of Chemistry and the [b]Howard Hughes Medical Institute, University of California, Berkeley, California 94720, USA, and [c]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA.

General Synthetic Methods. Unless noted otherwise, all manipulations were carried out at room temperature under a dinitrogen atmosphere in a VAC glovebox or using high-vacuum Schlenk techniques. Methylene chloride, diethyl ether, tetrahydrofuran, and pentane were dried over activated 4 Å molecular sieves, passed through a column of activated alumina, and sparged with nitrogen prior to use. Acetonitrile, acetonitrile-d_3, propionitrile and butyronitrile were refluxed over CaH_2, distilled, and sparged with nitrogen. All other reagents and solvents were purchased from commercial sources and used without further purification.

Physical Methods. NMR spectra were recorded on Bruker spectrometers operating at 300 or 400 MHz as noted. Chemical shifts are reported in ppm relative to residual protiated solvent; coupling constants are reported in Hz. Magnetic susceptibility measurements were made using Evans' method: an NMR tube containing the paramagnetic compound in CD_3CN was fitted with an insert containing only CD_3CN. The paramagnetic shift of the CHD_2CN signal was used to calculate the room temperature solution magnetic moment.T[1] Mass spectra were determined at the University of California, Berkeley Mass Spectrometry Facility. UV/Vis experiments were conducted on a Varian Cary 50 BIO UV-Visible Spectrophotometer. Non-aqueous electrochemical experiments were conducted under an inert atmosphere in 0.1 M Bu_4NPF_6 in CH_3CN. Cyclic voltammetry experiments were carried out using BASI's Epsilon potentiostat and C-3 cell stand. The working electrode was a glassy carbon disk (3.0 mm diameter) and the counter electrode was a platinum wire. A silver wire in a glass tube with a porous Vycor tip filled with 0.01 $AgNO_3$ in 0.1 M Bu_4NPF_6 in CH_3CN was used as a reference electrode. The scan rate for all cyclic voltammograms was 100 mV/sec. All potentials were referenced against Fc/Fc^+ as an internal standard and converted to SCE by adding 0.40 V to the measured potentials.[2] Electrochemical experiments conducted in 1:1 H_2O:CH_3CN were performed under a blanket of dinitrogen in 0.1 M KNO_3 and referenced with an aqueous Ag/AgCl electrode (BASI) and converted to SCE.

General Methods for X-ray Crystallography. Crystals were mounted on Kaptan loops in Paratone-N hydrocarbon oil. All data collection was performed on a Bruker (formerly Siemens) SMART diffractometer/CCD area detector equipped with a low temperature apparatus. Data integration was performed using SAINT. Preliminary data analysis and

absorption correction were performed using XPREP and SADABS[3]. Structure solution by direct methods and refinement were performed using the SHELX software package[4]. Hydrogen atoms were included in calculated positions, but not refined. In the case of chiral space groups, the correct enantiomer was determined by comparison of calculated and observed Friedel pairs.

2-(Bis(2-pyridyl)(hydroxy)methyl-6-bromopyridine (1). 2,6-Dibromopyridine (14.5 g, 61.4 mmol) was dissolved in 250 mL of ether and cooled to -78 ºC. 1.6 M *n*-Butyllithium in hexanes (42.2 mL, 67.6 mmol) was then added slowly over 25 minutes to produce a dark orange solution which was stirred an additional 20 minutes. Dipyridyl ketone (10.4 g, 56.6 mmol) was added as a 100 mL solution in THF over the course of 20 minutes to produce a dark brown mixture. After two hours of stirring at -78 ºC, the mixture was warmed to 0 ºC, acidified to pH 3.5 with 150 mL of 5% HCl, basified with 20 mL of saturated aqueous Na_2CO_3, and extracted into $CHCl_3$ (3 × 50 mL). The organics were combined, dried over Na_2SO_4, and removed under reduced pressure to afford a red oil. This oil was purified by passage through a plug of silica gel followed by hexanes and ether washes to provide **1** as an orange solid (9.68 g, 28.3 mmol, 50%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.01 (br s, 1H), 7.20 (ddd, 6.0 Hz, 4.8 Hz, 2.4 Hz, 2H), 7.36 (dd, 8.0 Hz, 0.8 Hz, 1H), 7.53 (t, 7.6 Hz, 1H), 7.69 (m, 4H), 7.73 (dd, 7.6 Hz, 0.8 Hz, 1H), 8.53 (dt, 4.8 Hz, 1.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 81.1, 121.9, 122.7, 123.3, 126.9, 136.7, 138.9, 140.4, 148.0, 162.3, 164.7.

2-(Bis(2-pyridyl)(methoxy)methyl-6-bromopyridine (2). Compound **1** (4.50 g, 13.2 mmol) was dissolved in 100 mL of THF to form an orange solution. Addition of NaH (1.58 g, 65.8 mmol) produced immediate bubbling and the formation of a peach mixture. Methyl iodide (9.33 g, 65.8 mmol) was then added slowly after which the reaction was heated to 40 ºC overnight. During this time the reaction became orange with precipitation of a colorless solid. The reaction was then acidified with 25 mL 5% HCl to a pH of 4 to produce a bright red solution. The solution was basified with 9 mL of saturated aqueous Na_2CO_3 to pH 9 with the precipitation of a white solid from the red solution. The mixture was extracted 3 × 30 mL with $CHCl_3$ and the organics were combined and dried over Na_2SO_4. Removal of solvent under reduced pressure followed by recrystallization from ether afforded **2** as a white solid (2.43 g, 6.83 mmol, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.28 (s, 3H), 7.17 (m, 2H), 7.33 (d, 8.0 Hz, 1H), 7.51 (t, 7.8 Hz, 1H), 7.68 (m, 5H), 8.57 (d, 4.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.06, 88.02, 122.24, 122.98, 124.14, 126.56, 136.09, 138.20, 140.49, 148.39, 160.81, 162.69.

2-(Bis(2-pyridyl)(methoxy)methyl-6-pyridylpyridine (PY4; 3). A 350-mL heavy-walled flask was charged with **2** (1.01 g, 2.84 mmol), 2-trimethylstannylpyridine[5] (687 mg, 2.87 mmol), $Pd(PPh_3)_4$ (35 mg, 0.030 mmol), CuI (12 mg, 0.063 mmol), and 60 mL of DMF. The reaction was heated to 100 ºC for 24 hr. The reaction was then cooled to room temperature and the DMF was removed under reduced pressure to give a dark brown oil. Silica gel chromatography (10% MeOH in CH_2Cl_2), followed by recrystallization from ether afforded **3** as a white solid (643 mg, 1.81 mmol, 64%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.34 (s, 3H), 7.18 (m, 3H), 7.70 (m, 7H), 8.08 (d, 8.1 Hz, 1H), 8.30 (d, 7.8 Hz, 1H), 8.61 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.37, 88.78,

119.45, 121.42, 122.19, 123.69, 124.23, 124.62, 136.01, 136.94, 137.30, 148.48, 149.07, 154.56, 156.45, 160.88, 161.72. HRESIMS (MH^+) *m/z* calcd for $C_{22}H_{19}N_4O$ 355.1553, found 355.1557.

[(PY4)Co(NCCH$_3$)$_2$](PF$_6$)$_2$.THF (4). To a stirring, colorless slurry of PY4 (158 mg, 0.446 mmol) in CH_3CN was added $CoCl_2$ (57.9 mg, 0.446 mmol). Within five minutes, the reaction mixture turned grey colored. After two hours, $TlPF_6$ (312 mg, 0.892 mmol) was added with immediate precipitation of TlCl and the formation of a red solution. The reaction mixture was filtered through celite to remove TlCl and the volatiles were removed under reduced pressure. Red-orange crystals of **4**, suitable for X-ray diffraction, were isolated by recrystallization from CH_3CN/THF/pentane (247 mg, 0.288 mmol, 65%). Anal. Calc. for $C_{30}H_{32}CoF_{12}N_6O_2P_2$: C, 42.02; H, 3.76; N, 9.80. Found: C, 41.87; H, 3.56; N, 9.98%. ^{1}H NMR (300 MHz, CD_3CN): δ 5.60, 14.02, 18.31, 31.50, 39.12, 61.74, 62.57, 78.32, 83.83, 87.57. Magnetic susceptibility[6] (CD_3CN): μ_{eff} = 4.3 μ_{BM}. HRESIMS (M^{2+}) *m/z* calcd for $C_{22}H_{18}CoN_4O$ 206.5401, found 206.5405.

[(PY4)Zn(NCCH$_3$)](PF$_6$)$_2$ (5). To a slurry of PY4 (154 mg, 0.435 mmol) in CH_3CN was added $ZnCl_2$ (59.1 mg, 0.434 mmol) to produce a turbid, colorless mixture. Following overnight stirring, $TlPF_6$ was added to the mixture with immediate TlCl precipitation. The resulting mixture was stirred for eight hours, filtered through celite to remove the TlCl, and concentrated under reduced pressure. Colorless crystals of **5**, suitable for X-ray diffraction, were obtained by recrystallization from CH_3CN layered beneath ether (157 mg, 0.209 mmol, 48%). Anal. Calc. for $C_{24}H_{21}F_{12}N_5OP_2Zn$: C, 38.39; H, 2.82; N, 9.33. Found: C, 38.20; H, 2.56; N, 9.16%. ^{1}H NMR (300 MHz, CD_3CN): δ 4.03 (s, 3H), 7.62 (m, 2H), 7.95 (t, 6.5 Hz, 1H), 8.19 (m, 5H), 8.33 (m, 3H), 8.50 (d, 8.1 Hz, 1H), 8.85 (d, 5.4 Hz, 2H), 9.15 (d, 4.8 Hz, 1H). ^{13}C NMR (75 MHz, CD_3CN): 56.64, 81.95, 120.21, 121.98, 122.28, 122.53, 124.05, 126.54, 140.82, 141.62, 142.31, 146.98, 147.35, 148.64, 154.85, 155.23. HRESIMS (M^{2+}) *m/z* calcd for $C_{22}H_{18}N_4OZn$ 209.0381, found 209.0385.

Controlled-Potential Electrolysis. A solution with a trifluoroacetic acid concentration of 65 mM in 100 mM Bu_4NPF_6 in CH_3CN was electrolyzed in the presence of **4** for 30 minutes at -1.0 V vs SCE in a custom-built, gas-tight electrochemical cell. Aliquots of the head-space gas were removed with a gas-tight syringe following electrolysis and the production of H_2 with a Faraday yield of 99% was confirmed by GC analysis with a thermal conductivity detector.

Spectroelectrochemistry. Electronic spectra were recorded using a Cary 5000 UV/Vis/NIR spectrophotometer interfaced to Varian WinUV software. The absorption spectra of the electrogenerated species were obtained *in situ*, by the use of a cryostatted Optically Semi-Transparent Thin-Layer Electrosynthetic (OSTTLE) cell (path length 1.0 mm) mounted in the light-path of the spectrophotometer.

The OSTTLE cell, which was secured in the beam of the spectrophotometer, was of quartz construction. A platinum gauze working electrode (70% transmittance) was located centrally in the optical beam in the lower section of the cell. To ensure electrolysis occurred only at the platinum gauze, the section of wire passing to the top of the cell was sheathed by poly(tetrafluoroethylene) {PTFE} tubing. A platinum wire auxiliary electrode and Ag/Ag^+ reference electrode were positioned in the upper section

of the cell and were separated from the solution by salt bridges containing electrolyte solution. A matching section of platinum gauze was placed in the reference beam.

All solutions were prepared under an N_2 atmosphere in a glovebox. Appropriate potentials were applied using a Bioanalytical Systems BAS 100A Electrochemical Analyzer. Both the current and potential were monitored during the electrolysis. By this method, the electrogenerated species were obtained *in situ*, and their absorption spectra recorded at regular intervals throughout the electrolysis. The attainment of a steady-state spectrum and the decay of the current to a constant minimum at a potential appropriately beyond $E_{1/2}$ (for the redox process in question) are indicative of the complete conversion of the starting material. The reversibility of the spectral data was confirmed by the regeneration of the starting spectrum following the attainment of the steady-state spectrum for the reduced species.

Proton Reduction: Kinetics Studies. Cyclic voltammetry was used to investigate the kinetics of the electrocatalysis. All kinetics studies were conducted in electrochemical cells with 5 mL solutions of 100 mM Bu_4NPF_6 in CH_3CN. The working electrode was a glassy carbon disk (3.0 mm diameter) and the counter electrode was a platinum wire. A silver wire in a glass tube with a porous Vycor tip filled with 0.1 M Bu_4NPF_6 in CH_3CN was used as a pseudo-reference electrode. Where the electrocatalytic current did not reach a plateau, the current at the top of the catalytic peak in the cyclic voltammogram was taken as equivalent to the plateau current.

Order with Respect to Catalyst. Trifluoroacetic acid was added to a solution of 100 mM Bu_4NPF_6 in CH_3CN in an electrochemistry cell to afford an acid concentration of 65 mM. Aliquots of a 22.6 mM stock solution of **4** were then added to the cell and cyclic voltammograms were taken. The order of the proton reduction in catalyst was determined by plotting the plateau current vs. catalyst concentration (Figure S2).

Order with Respect to Acid. Aliquots of neat trifluoroacetic acid were added to a 1.0 mM solution of **4** in 100 mM Bu_4NPF_6 and cyclic voltammograms were recorded. The order of the proton reduction electrocatalysis in acid was determined by plotting the plateau current vs the concentration of acid (Figure S3).

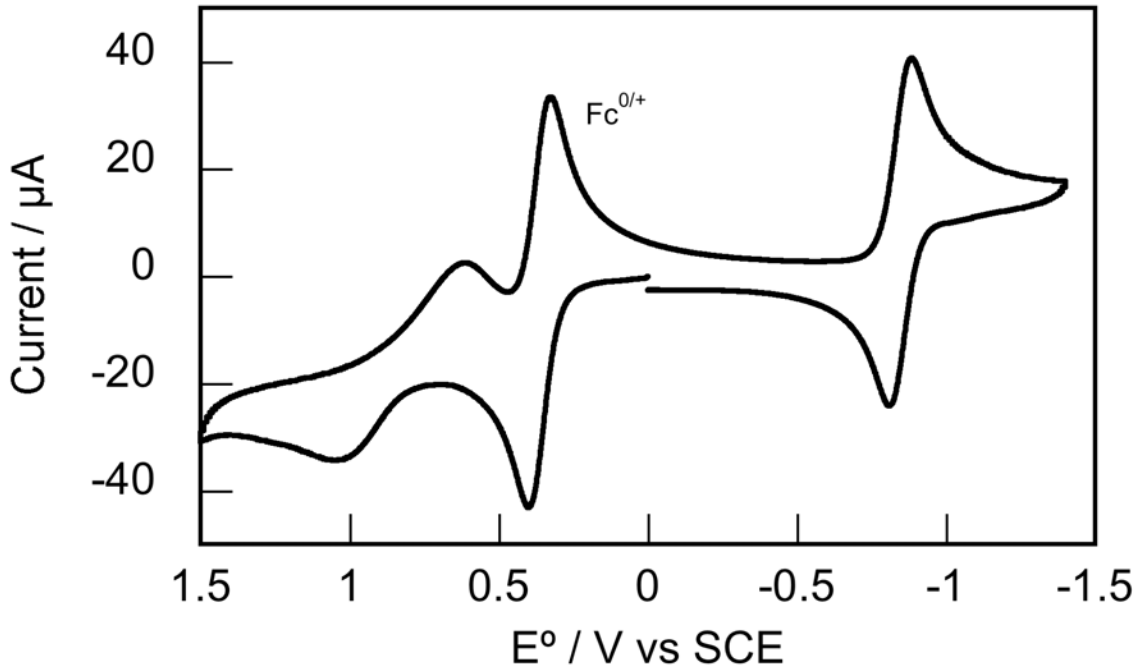

Fig S1. Cyclic voltammogram of complex **4** in 0.1 M Bu_4NPF_6 in acetonitrile with ferrocene as an internal standard. Scan rate: 100 mV/sec; glassy carbon electrode.

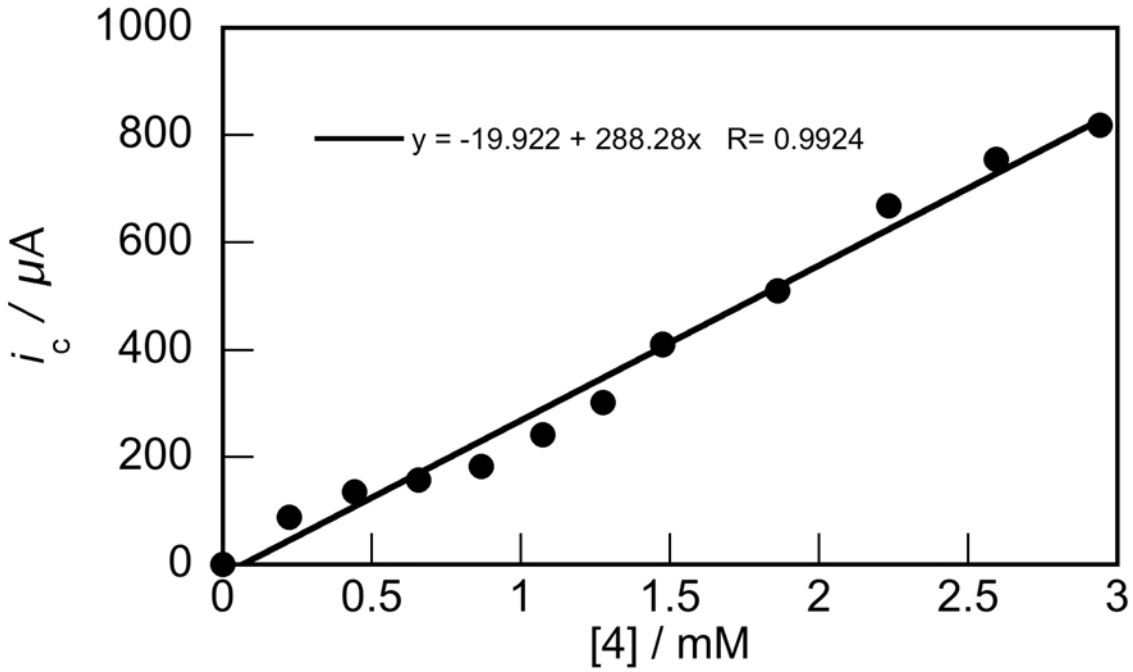

Fig. S2. Electrocatalytic current for complex **4** in the presence of 65 mM TFA as a function of [**4**] in 0.1 M Bu_4NPF_6 in acetonitrile. Scan rate: 100 mV/sec; glassy carbon electrode.

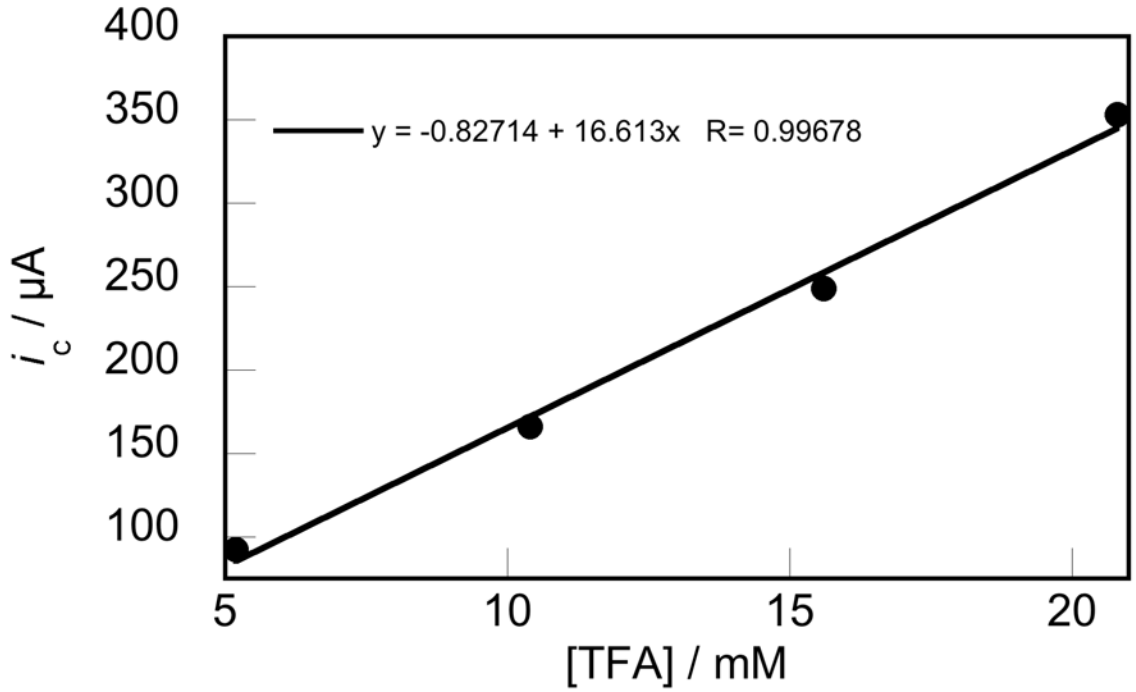

Fig. S3. Electrocatalytic current for 1.0 mM of **4** as a function of [TFA] in 0.1 M Bu_4NPF_6 in acetonitrile. Scan rate: 100 mV/sec; glassy carbon electrode.

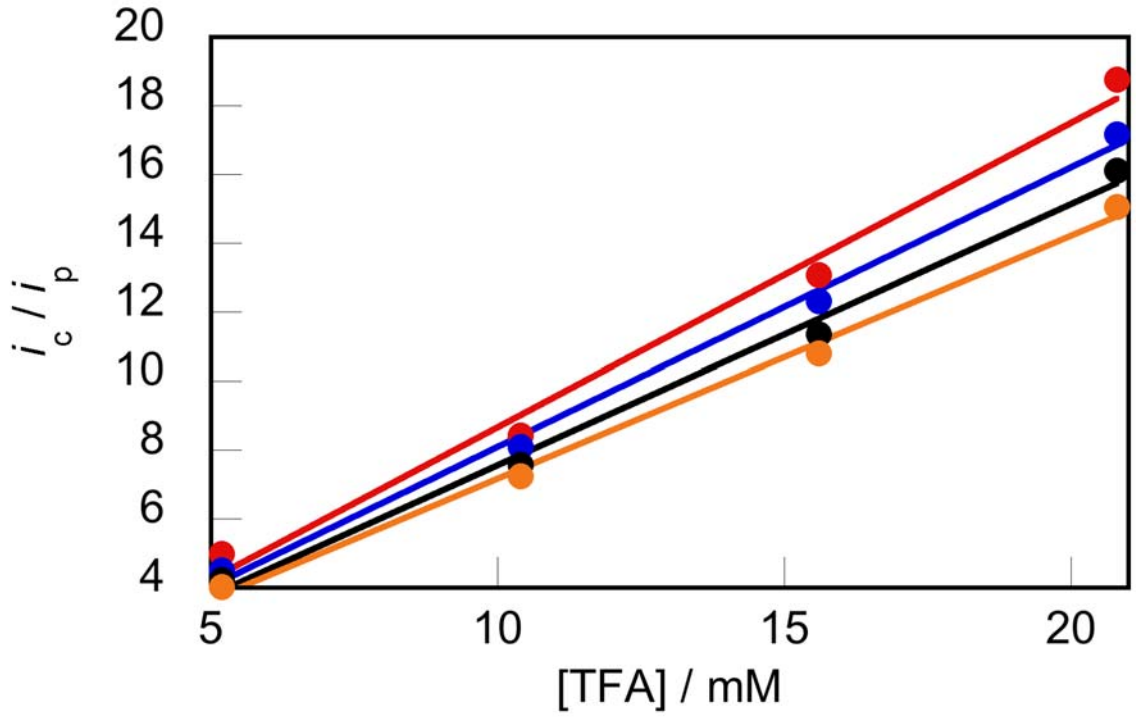

Fig. S4. Plot of i_c/i_p as a function of [TFA] for 1.0 mM of **4** in 0.1 M Bu_4NPF_6 in acetonitrile; glassy carbon electrode. 250 mV/sec (orange), 0.705x+0.114; 100 mV/sec (black), 0.759x-0.0378; 50 mV/sec (blue), 0.812x-0.0303; 25 mV/sec (red), 0.883x-0.167. The slopes of these lines are plotted vs $\nu^{-1/2}$ in Fig. 3 in the text.

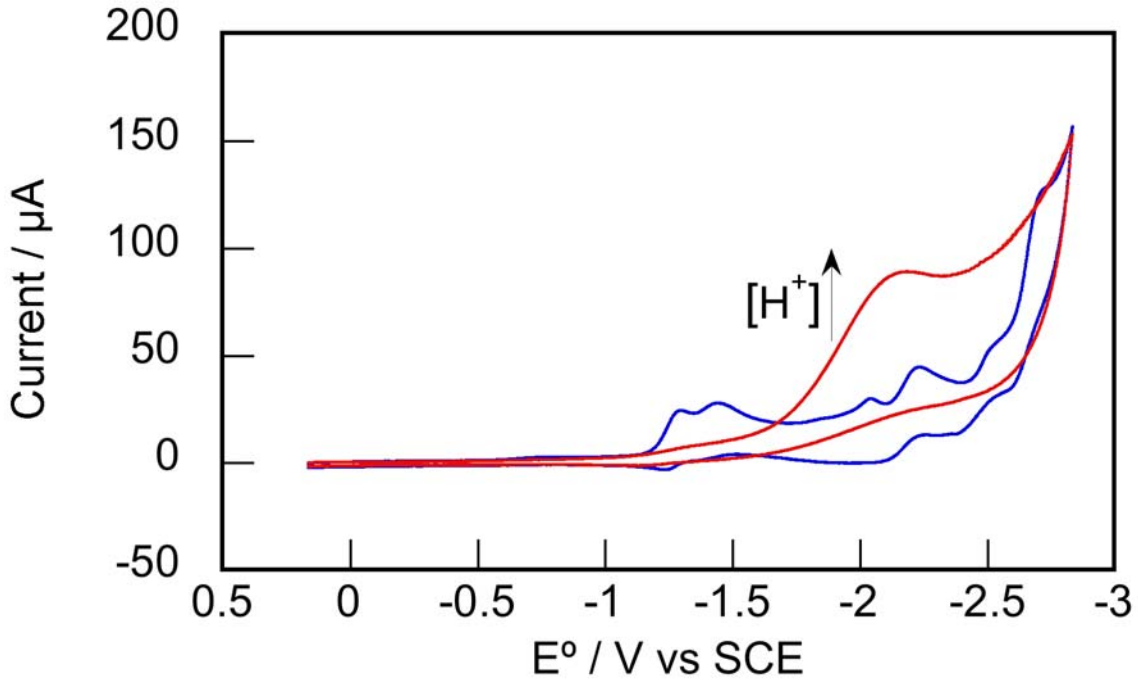

Fig. S5. Cyclic voltammogram of complex **5** in 0.1 M Bu_4NPF_6 in acetonitrile in the presence of TFA: (bottom to top) 1.0 mM of **5** with no acid, 1.0 mM of **5** with 10 mM TFA. Scan rate: 100 mV/sec; glassy carbon electrode.

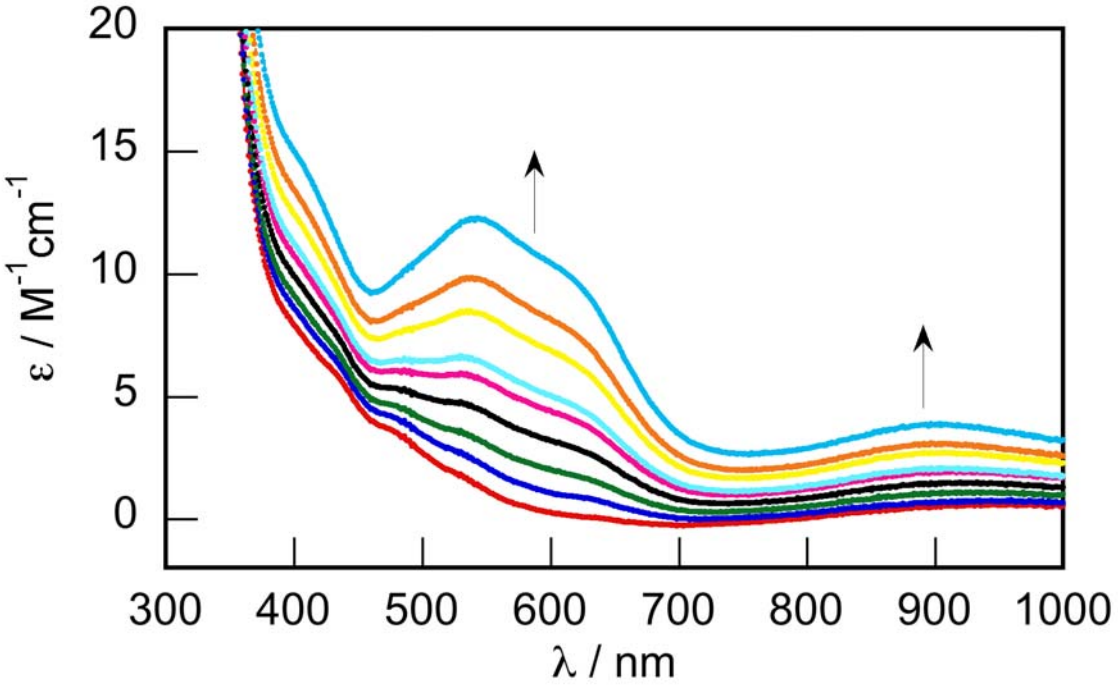

Fig. S6. Electronic absorption spectrum of 23.5 mM of **4** in 0.1 Bu_4NPF_6 in acetonitrile upon electrochemical reduction at a platinum gauze electrode.

Table S1. Crystallographic Details for Complexes **4** and **5**.

	4	**5**
Empirical Formula	$C_{30}H_{32}CoF_{12}N_6O_2P_2$	$C_{24}H_{21}F_{12}N_5OP_2Zn$
Formula Weight	857.49	750.77
T (K)	136	143
λ (Å)	0.71073	0.71073
Crystal System	Monoclinic	Monoclinic
Space Group	$P2_1/c$	$P2_1/n$
a (Å)	11.9665(12)	14.0273(77)
b (Å)	11.8487(12)	13.6709(75)
c (Å)	25.024(2)	16.2887(89)
α (°)	90	90
β (°)	90.723(2)	110.767(6)
γ (°)	90	90
V	3547.8(6)	2921(3)
Z	4	4
ρ_{calc} (g/cm^3)	1.605	1.707
μ (mm^{-1})	0.676	1.057
reflctns collected	19864	11717
T_{min}/T_{max}	0.91	0.81
data/restr/params	7232/0/480	4635/0/410
$2\theta_{max}$ (°)	52.8	48.9
R, R_w (%; I>2σ)	5.2, 13.3	6.4, 18.5
GOF	1.05	1.08
max shift/error	0.004	0.004

Table S2. Co electrocatalysts for proton reduction. * = $Co^{2+/1+}$; # = $Co^{3+/2+}$; $ = $Co^{1+/0}$; E_{cpe} = potential of controlled potential electrolysis. HDME = hanging drop mercury electrode. Entries are left blank when the data are not reported.

Complex	E° (SCE)	E_{cpe} (SCE)	Medium	% H_2 yield	Electrode	TOF (hr^{-1})	Reference
CoTMAP	-0.66*	-0.95	Aqueous, 0.1 M TFA	>90	Hg pool	2	6
CoTMPyP	-0.75*	-0.95	Aqueous, 0.1 M TFA	>90	Hg pool	2	6
CoTPyP		-0.95	Aqueous, 0.1 M TFA	>90	Hg pool	2	6
$Co(C_5H_5CO_2H)_2]^+$	-0.87#	-0.9	0.1 M KCl, phosphate buffer, pH 6.5	42	Hg pool	1.1	7
Co(sepulchrate)]$^{3+}$	-0.54#	-0.7	0.1 M KCl, phthalate buffer, pH 4.0	55	Hg pool	0.85	7
Co(6,13-dimethyl-4,11-diene-N_4)]$^{2+}$	ca -1.5*	-1.5	0.1 M KNO_3	90	Hg pool	9	8
Co(4,11-diene-N_4)]$^{2+}$	ca -1.6*	-1.6	0.1 M KNO_3	93	Hg pool	7.8	8
Co(trans-diammac)]$^{3+}$	-0.8#	-1.05	Phosphate pH 7		Hg pool/HDME	<1	9
Co(cis-diammac)]$^{3+}$	-0.67#	-1.05	Phosphate pH 7		Hg pool/HDME	<1	9
$CpCo(P(OMe)_3)_2$	-0.32$	-1.15	Aqueous pH 5	100	Hg pool	1.1	10
Cobis(triazacyclodecane)]$^{3+}$	ca. -0.7#, -1.55*		Britton-Robinson buffer, pH 2.7-10.3		HDME		11
$Co(dmgBF_2)_2$	-0.55*	-0.72	CH_3CN/TFA	ca 100	Carbon	20	12
$Co(dpgBF_2)_2$	-0.29*	-0.37	CH_3CN/HCl	ca 90	Carbon	11	12
$Co(dmgH)_2(py)Cl$[14]	-0.98*	-0.9	DCE/Et_3NHBF_4	85-100	Carbon	40	13
4	-0.9*, +0.87 #	-1.0	CH_3CN/TFA	99	Carbon	ca. 40	this work

References

1. D. F. Evans, *J. Chem. Soc* 1959, 2003-2005.
2. N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877-910.
3. G. M. Sheldrick, *SHELXTL*, Bruker AXS Inc.: Madison, WI (USA), 2005.
4. (a) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, 467-473; (b) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112-122; (c) G. M. Sheldrick, *SHELXL-97: Program for crystal structure determination*, University of Göttingen: Göttingen, Germany, 1997.
5. R. Dorta, L. Konstantinovski, L. J. W. Shimon, Y. Ben-David and D. Milstein *Eur. J. Inorg. Chem.* 2003, 70-76.
6. R. M. Kellett and T. G. Spiro, *Inorg. Chem.*, 1985, **24**, 2373-2377.
7. V. Houlding, T. Geiger, U. Koelle and M. Graetzel, *J. Chem. Soc., Chem. Commun.*, 1982, 681-683.
8. B. J. Fisher and R. Eisenberg, *J. Am. Chem. Soc.*, 1980, **102**, 7361-7363.
9. P. V. Bernhardt and L. A. Jones, *Inorg. Chem.*, 1999, **38**, 5086-5090.
10. U. Koelle and S. Paul (Ohst), *Inorg. Chem.*, 1986, **25**, 2689-2694.
11. R. Abdel-Hamid, H. M. El-Sagher, A. M. Abdel-Mawgoud and A. Nafady, *Polyhedron*, 1998, **17**, 4535-4541.
12. X. Hu, B. M. Cossairt, B. S. Brunschwig, N. S. Lewis and J. C. Peters, *Chem. Commun.*, 2005, 4723-4725.
13. M. Razavet, V. Artero and M. Fontecave, *Inorg. Chem.*, 2005, **44**, 4786-4795.
14. These potentials are referenced against Ag/AgCl.