Supplementary Information for

A Mechanistic Study of Proton Reduction by a Pentapyridine Cobalt Complex: Evidence for the Involvement of an Anation-Based Pathway

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Materials

The ligands PY5Me₂, CF₃PY5Me₂, and NMe₂PY5Me₂ were synthesized as previously described, as were $[Co(PY5Me_2)(MeCN)](OTf)_2$, $[Co(CF_3PY5Me_2)(MeCN)](OTf)_2$ (5) and $[Co(NMe_2PY5Me_2)(MeCN)](OTf)_2$ (6) were also synthesized as previously described. All other compounds purchased from chemical vendors were used as received. Acetonitrile, toluene, and tetrahydrofuran were dried over activated 4 Å molecular sieves, passed over a column of activated alumina, and stored over 3 Å molecular sieves under an N₂ atmosphere. Unless otherwise noted, all manipulations were performed at room temperature under an N₂ atmosphere using either Schlenk or glove box techniques.

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. UV-visible spectra were recorded on a Hewlet-Packard 8452A photodiode array spectrometer. Spectroelectrochemical experiments were obtained using a reticulated vitreous carbon working electrode and platinum electrodes as the reference and auxiliary electrodes. Contact to the vitreous carbon electrode was achieved using a Pt wire. The auxiliary electrode was separated from the solution using a Vycor tip.An Agilent 490-GC micro-gas chromatograph with a mol sieve column and heated syringe injector was used for H₂ quantification. Carbon, hydrogen, and nitrogen analyses were obtained from the Microanalytical Laboratory of the University of California, Berkeley. Mass spectra were determined at the University of California, Berkeley Mass Spectrometry Facility. Cyclic voltammetry experiments were carried out using BASI's Epsilon potentiostat. A glassy carbon working electrode and silver (reference) and platinum (auxiliary) wires were used for cyclic voltammetry experiments in CH₃CN with Bu₄NPF₆ as a supporting electrolyte. Ferrocene ($E_{Fc+/0} = 0.64$ V vs SHE) was added during each experiment as an internal reference. Single-crystal X-Ray diffraction was conducted at University of California, Berkeley, College of Chemistry, X-Ray Crystallography Facility. Crystals were mounted on nylon loops in Paratone-N hydrocarbon oil. Air-sensitive samples were transferred from the glove box to Paratone-N and mounted quickly to avoid decomposition. All data collections were performed on either a Bruker SMART, or Bruker APEX diffractometer equipped with a CCD area detector and a low temperature apparatus. Data integration was performed using SAINT. Preliminary data analysis and absorption correction were performed using XPREP and SADABS. Structure solution and refinement was performed using SHELX software package. All DFT calculations on 4 were carried out using the Gaussian09 program suite at the unrestricted B3LYP/6-31G(d) level of theory. Starting geometries were derived from the crystal structure of 4, where C-H bond distances were first normalized to 1.083 Å. The geometries were first run for ca. 200 cycles using default settings, and then the integration grid (Ultrafine) and maximum step size were each made smaller to finish the minimization on the apparently very flat potential energy surface. Final structures each contained no imaginary frequencies. Molecular orbitals were orthogonalized for maximal α/β overlap prior to visualization.

Crystallographic Structure Determinations

The X-ray crystallographic data collection was carried out on a Bruker three-circle diffractometer mounted with an SMART 1000 detector using monochromated Mo Kα radiation (0.71073 Å) outfitted with a low-temperature, nitrogen-stream aperture, an APEXII CCD detector, and equipped with an Oxford Cryostream 700. The structure was solved using direct methods in conjunction with standard difference Fourier techniques and refined by full-matrix least-squares procedures.⁴ A semi-empirical absorption correction (SADABS) was applied to the diffraction data for all structures. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were treated as idealized contributions and refined isotropically. A summary of crystallographic data is given in Table S1. All software used for diffraction data processing and crystal-structure solution and refinement are contained in the APEX2 program suite (Bruker AXS, Madison, WI).

Syntheses

Synthesis of $[Co(PY5Me_2)(MeCN)](PF_6)_2$ (1·(PF₆)). 1 equivalent of CoCl₂ (29.3 mg, 225 µmol) was added to 1 equivalent of PY5Me₂ (100.0 mg, 225 µmol) in 10 mL of acetonitrile. After 20 minutes, 2 equivalents of AgPF₆ (56.9 mg, 450 µmol) were added to the blue-green slurry. The addition of AgPF₆ resulted in the immediate precipitation of silver chloride and the formation of a light orange solution. The reaction was allowed to stir for an additional 2 hours before being filtered and concentrated to 1 mL. Xray quality crystals were obtained by slow diffusion of diethyl ether into a concentrated acetonitrile solution of $3 \cdot (PF_6)_2$. Yield: 150.0 mg, 84% yield. Anal. Calcd. for $C_{31}H_{28}CoF_{12}P_2N_6$: C, 44.67%; H, 3.39%; N, 10.08%. Found: C, 44.20%; H, 3.50%; N, 9.91%.

Synthesis of $[Co(PY5Me_2)](BPh_4)(3\cdot BPh_4)$. 1 equivalent of Co(PPh₃)₃Cl (197.8 mg, 225 µmol) was added to 1 equivalent of PY5Me₂ (100.0 mg, 225 µmol) in 10 mL of toluene; after stirring overnight the reaction color had changed from lime-green to dark blue. The reaction was filtered, and the remaining blue solid was washed with 20 mL of toluene and 20 mL of diethyl ether to remove residual PPh₃ and dried under vacuum. The solid was suspended in THF, and 1 equivalent of NaBPh₄ (77.0 mg, 225 µmol) was added; the resulting dark blue solution was allowed to stir overnight. Removal of the resulting NaCl via filtration, removal of the bulk THF solvent, and subsequent recrystallization via slow diffusion of diethyl ether into a difluorobenzene solution produced X-ray quality crystals. Yield: 65.0 mg, 79% yield. Anal. Calcd. for C₆₃H₅₇CoBN₅OF₂: C, 75.07%; H, 5.70%; N, 6.95%. Found: C, 74.31%; H, 5.54%; N, 6.91%.

Synthesis of $[Co(PY5Me_2)(MeCN)](OTf)_2(BF_4)$ (2·(OTf)_2(BF_4)). 1 equivalent of NOBF₄ (13.9 µmol) was added to 1 equivalent of 3·(OTf)_2 (100.0 mg, 119 µmol) in 10 mL of acetonitrile. The light orange solution intensified in color. The reaction was allowed to stir for an additional 2 hours before being filtered and concentrated to 1 mL. X-ray quality crystals were obtained by slow diffusion of diethyl ether into a concentrated acetonitrile solution of 3·(OTf)_2. Yield: 80.0 mg, 72% yield. Anal. Calcd. for C₃₁H₂₅BCoF₁₀N₅O₅S₂: C, 41.96%; H, 2.84%; N, 7.89%. Found: C, 41.44%; H, 2.86%; N, 8.72%.

Synthesis of $[Co(PY5Me_2)(OAc)](MeCN)(OTf)_2$ (4). 1 equivalent of NaBH(OAc)_3 (22.8 mg, 108 µmol) was added to 1 equivalent of 2·(OTf)_2(BF_4) (100.0 mg, 108 µmol) in 10 mL of acetonitrile. The light orange solution became pink in color after 1 hour. The reaction was allowed to stir for an additional 2 hours before being filtered and concentrated to 1 mL. X-ray quality crystals were obtained by slow diffusion of diethyl ether into a concentrated acetonitrile solution of 6. Yield: 70 mg, 79% yield. Anal. Calcd. for C₃₅H₃₁CoF₆N₆O₇S₂: C, 46.11%; H, 3.47%; N, 9.33%. Found: C, 46.67%; H, 2.90%; N, 9.41%.

Experimental Procedures

Kinetic experiments with catalytic amounts of $1 \cdot (OTf)_2$ *and acetic acid.* A typical kinetic experiment was conducted as follows. A flask was charged with 5 mL of a stock solution of Bu₄NPF₆ and $3 \cdot (OTf)_2$ in acetonitrile (100 mM and 1 mM, respectively) and subsequently purged with N₂. Cyclic voltammograms were recorded at 50, 100, 250, and 500 mV/s. Glacial acetic acid was then added in known increments; cyclic voltammograms were recorded at 50, 100, 250, and 500 mV/s. after each increment. Dependencies on both [AcOH] and [1] were determined.

Kinetic experiments with stoichiometric amounts of $1 \cdot (OTf)_2$ *and acetic acid.* A typical kinetic experiment was conducted as follows. A flask was charged with 5 mL of a stock solution of Bu₄NPF₆ and $3 \cdot (OTf)_2$ in acetonitrile (500 mM and 10 mM, respectively) and subsequently purged with N₂. Cyclic voltammograms were recorded at 50, 100, 250, and 500 mV/s. Glacial acetic acid was then added in known increments; cyclic voltammograms were recorded at 50, 100, 250, and 500 mV/s. after each increment. Dependencies on both [AcOH] and [1] were determined.

Titration of $1 \cdot (OTf)_2$ *with tetrabutylammonium acetate.* A flask was charged with 5 mL of a stock solution of Bu₄NPF₆ and $3 \cdot (OTf)_2$ in acetonitrile (500 mM and 10 mM, respectively) and subsequently purged with N₂. Cyclic voltammograms were recorded at 50, 100, 250, and 500 mV/s. Tetrabutylammonium acetate was added to give final concentrations of 5 and 10 mM; cyclic voltammograms were recorded at 50, 100, 250, and 500 mV/s after each addition.

Kinetic experiments with catalytic amounts of $1 \cdot (OTf)_2$ and 1:1 tetrabutylammonium acetate:acetic acid mixture. A typical kinetic experiment was conducted as follows. A flask was charged with 5 mL of a stock solution of Bu₄NPF₆ and $3 \cdot (OTf)_2$ in acetonitrile (100 mM and 1 mM, respectively) and subsequently purged with N₂. Cyclic voltammograms were recorded at 50, 100, 250, and 500 mV/s. A 1:1 tetrabutylammonium acetate:acetic acid solution in acetonitrile (500 mM concentration in each component) was then added in known increments; cyclic voltammograms were recorded at 50, 100, 250, and 500 mV/s after each increment. Dependencies on both [Bu₄NOAc:AcOH] and [1] were determined.

Faradaic efficiency determination with 1:1 tetrabutylammonium acetate:acetic acid mixture. Controlled-potential electrolysis was conducted using a custom-made air-tight glass double compartment cell separated by a glass frit. The working compartment was fitted with a glassy carbon rod working electrode (2.5 mm diameter, 2 cm length) and a Ag/AgNO₃ reference electrode. The auxiliary compartment was fitted with a Pt gauze electrode. The working compartment was filled with 10 mL of 35 mM acetic acid in a 0.1 M Bu₄NPF₆ acetonitrile solution, while the auxiliary compartment was filled with 5 mL of 0.1 M Bu₄NPF₆ acetonitrile solution, resulting in equal solution levels in both compartments. Solution diffusion across the glass frit was slow under static pressure. Both compartments were sparged for 15 min with N₂ and cyclic voltammograms were recorded as controls. Catalyst $1(CF_3SO_3)_2$ (0.1 mM) was then added and a cyclic voltammogram was recorded. Electrolysis was conducted for 2 h and the headspace was subjected to gas chromatographic analysis. An Agilent 490-GC Micro-Gas Chromatograph with a molecular sieve column and heated syringe injector was used for product detection. The column was heated to 80 °C under Ar gas flow and an average sample volume of 200 nL was injected onto the column.

Calibration. Using the double-compartment cell described above, the working compartment was filled with 50 mL of 35 mM acetic acid in a 0.1 M Bu_4NPF_6 acetonitrile solution, while the auxiliary compartment was filled with 70 mL of a 0.1 M Bu_4NPF_6 acetonitrile solution. Both compartments were sparged thoroughly with N₂ and sealed. A 3 mL aliquot of the headspace was removed and replaced with 3 mL of CH₄. Aliquots of 0.5, 1, 2, and 3 mL of H₂ were introduced to the headspace and the solution was allowed to stir for at least 30 min. A sample of the headspace was injected into the gas chromatograph and the ratio of CH₄ and H₂ was taken as points on a calibration curve

Titration of different acids into solutions of $[Co(X-PY5Me_2)(MeCN)]^{2^+}$. The follow procedure was repeated for compounds 5 and 6. A flask was charged with 3 mL of a stock solution of Bu₄NPF₆ and 1·(OTf)₂ in acetonitrile (100 mM and 1 mM, respectively) and subsequently purged with N₂. Cyclic voltammograms were recorded at 50, 100, 250, and 500 mV/s. 50 µL of a 600 mM acid solution was added to the flask (final [acid] = 10 mM), and cyclic voltammograms were recorded at 50, 100, 250, and 500 mV/s. The potential at which the observed current equaled 8 µA was plotted versus acid pKa.

Spectroelectrochemical experiments with $1 \cdot (OTf)_2$. 4 mL of a solution containing Bu₄NPF₆ and $1 \cdot (OTf)_2$ in acetonitrile (100 mM and 1 mM, respectively) was added to a 1-cm cuvette equipped with a reticulated vitreous carbon working electrode. A starting spectrum was recorded as a baseline. A potential of -900 mV vs SHE was applied, and the current and potential were monitored during electrolysis.

UV-visible spectroscopic experiments examining protonation of 4. 4 mL of a 168 mM solution of p-toluenesulfonic acid was added to a 1-cm pathlength UV-Vis cuvette equipped with a Schlenk valve. 50 μ L of a 64 mM solution of **3**·BPh₄ was added (0.8 mM final concentration) was added via syringe, and spectra recorded at known intervals. Dead time between mixing and the attainment of the first spectrum was approximately 30 seconds.

Empirical formula	$C_{31}H_{28}CoF_{12}N_6P_2$	
Formula weight	833.46	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
	$a = 11.4618(13) \text{ Å}, \alpha = 109.795(2)^{\circ}$	
Unit cell dimensions	$b = 12.5008(14) \text{ Å}, \beta = 108.383(2)^{\circ}$	
	$c = 13.1640(15)$ Å, $\gamma = 90.824(2)^{\circ}$	
Volume	1668.6 Å ³	
Z	2	
Density (calculated)	1.659	
Absorption coefficient	0.712	
F(000)	842	
Crystal size	$0.14 \ge 0.14 \ge 0.12 \text{ mm}^3$	
Theta range for collection	1.75° to 25.38°	
Index ranges	-12<=h<=13, -15<=k<=13, -15<=l<=15	
Reflections collected	9548	
Independent reflections	5362	
Completeness to max	88.6 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least squares on F ²	
Data/restrains/parameters	5362 / 0 / 472	
Goodness-of-fit ^a	1.020	
Final R indices ^{b} [I > 2d(I)]	$R_1 = 0.0399, wR_2 = 0.0975$	
R indices ^{b} (all data)	$R_1 = 0.0523, wR_2 = 0.1069$	
Largest diff. peak and hole	0.476 and -0.431 e Å ⁻³	

Table S1. Crystallographic data for [Co(PY5Me₂)(MeCN)](PF₆)₂ (1·(PF₆)₂).

^a GooF =
$$\left[\sum \left[w(F_o^2 - F_c^2)^2\right]/(n-p)\right]^{1/2}$$

^b $R_1 = \sum \left\|F_o\right| - \left|F_c\right\|/\sum |F_o|, \ wR_2 = \left\{\sum \left[w(F_c^2 - F_o^2)^2\right]/\sum \left[w(F_o^2)^2\right]\right\}^{1/2}$

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Empirical formula	$C_{144}H_{130}B_4Co_4F_{40}N_{30}O_{24}S_8$
Formula weight	3960.22
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	Cc
	$a = 17.791 \text{ Å}, \alpha = 90^{\circ}$
Unit cell dimensions	$b = 16.341 \text{ Å}, \beta = 97.47^{\circ}$
	$c = 27.415 \text{ Å}, \gamma = 90^{\circ}$
Volume	7902.4 Å ³
Z	2
Density (calculated)	1.664
Absorption coefficient	0.645
F(000)	4024
Crystal size	$0.20 \ge 0.16 \ge 0.12 \text{ mm}^3$
Theta range for collection	1.50° to 25.37°
Index ranges	-21<=h<=21, -19<=k<=19, -33<=l<=32
Reflections collected	55077
Independent reflections	13504
Completeness to max	99.7 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least squares on F^2
Data/restrains/parameters	13504 / 8 / 1153
Goodness-of-fit ^a	1.044
Final R indices ^{b} [I > 2d(I)]	$R_1 = 0.0707, wR_2 = 0.1913$
R indices ^{b} (all data)	$R_1 = 0.0776, wR_2 = 0.2010$
Largest diff. peak and hole	1.575 and -1.025 e Å ⁻³

Table S2. Crystallographic data for [Co(PY5Me₂)(MeCN)](OTf)₂BF₄ (2·(OTf)₂BF₄).

^{*a*} GooF =
$$\left[\sum \left[w(F_o^2 - F_c^2)^2\right]/(n-p)\right]^{1/2}$$

^{*b*} $R_1 = \sum \left\|F_o\right| - \left|F_c\right\| / \sum \left|F_o\right|, \ wR_2 = \left\{\sum \left[w(F_c^2 - F_o^2)^2\right] / \sum \left[w(F_o^2)^2\right]\right\}^{1/2}$

Table S3.	Crystallographic	data for [[Co(P]	$Y5Me_2$]BPh ₄	$(3 \cdot BPh_4)$
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Empirical formula	C ₅₃ H ₄₅ BCoN ₅	
Formula weight	821.70	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
	$a = 10.9829(8)$ Å, $\alpha = 102.458(5)^{\circ}$	
Unit cell dimensions	$b = 13.7142(9)$ Å, $\beta = 107.971(5)^{\circ}$	
	$c = 17.0064(13)$ Å, $\gamma = 101.250(5)^{\circ}$	
Volume	2282.8(3) Å ³	
Z	4	
Density (calculated)	1.195	
Absorption coefficient	3.250	
F(000)	842	
Crystal size	0.10 x 0.06 x 0.02 mm ³	
Theta range for collection	2.86° to 63.68°	
Index ranges	-12<=h<=12, -14<=k<=15, -19<=l<=19	
Reflections collected	20067	
Independent reflections	7242	
Completeness to max	96.5 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least squares on F ²	
Data/restrains/parameters	7242 / 0 / 542	
Goodness-of-fit ^a	0.997	
Final R indices ^{b} [I > 2d(I)]	$R_1 = 0.0625, wR_2 = 0.1524$	
R indices ^{b} (all data)	$R_1 = 0.0957, wR_2 = 0.1685$	
Largest diff neak and hole	0.408 and -0.402 e Å ⁻³	

^{*a*} GooF =
$$\left[\sum \left[w(F_o^2 - F_c^2)^2\right]/(n - p)\right]^{1/2}$$

^{*b*} $R_1 = \sum \left\|F_o\right| - \left|F_c\right\| / \sum \left|F_o\right|, \ wR_2 = \left\{\sum \left[w(F_c^2 - F_o^2)^2\right] / \sum \left[w(F_o^2)^2\right]\right\}^{1/2}$

Empirical formula	$C_{33}H_{25}CoF_6N_5O_8S_2$
Formula weight	856.63
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
	$a = 11.9400(3)$ Å, $\alpha = 65.6960(10)^{\circ}$
Unit cell dimensions	$b = 12.8220(3)$ Å, $\beta = 78.9150(10)^{\circ}$
	$c = 15.3280(3)$ Å, $\gamma = 66.5570(10)^{\circ}$
Volume	1960.99(8) Å ³
Z	2
Density (calculated)	1.273
Absorption coefficient	0.612
F(000)	764
Crystal size	$0.16 \ge 0.10 \ge 0.07 \text{ mm}^3$
Theta range for collection	1.46° to 25.39°
Index ranges	-14<=h<=14, -15<=k<=15, -18<=l<=18
Reflections collected	33375
Independent reflections	7167
Completeness to max	99.5 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least squares on F ²
Data/restrains/parameters	7167 / 0 / 499
Goodness-of-fit ^a	1.076
Final R indices ^{<i>b</i>} $[I > 2d(I)]$	$R_1 = 0.0362, wR_2 = 0.0922$
R indices ^{b} (all data)	$R_1 = 0.0412, wR_2 = 0.0946$
Largest diff. peak and hole	0.628 and -0.644 e Å ⁻³

Table S4. Crystallographic data for [Co(PY5Me₂)(OAc)](OTf)₂ (4·(OTf)₂).

^a GooF =
$$\left[\sum \left[w(F_o^2 - F_c^2)^2\right]/(n - p)\right]^{1/2}$$

^b $R_1 = \sum \left\|F_o\right| - \left|F_c\right\| / \sum \left|F_o\right|, \ wR_2 = \left\{\sum \left[w(F_c^2 - F_o^2)^2\right] / \sum \left[w(F_o^2)^2\right]\right]^{1/2}$



Fig. S1: UV-visible spectrum of 2 in acetonitrile (top) and ¹H-NMR spectrum in CD₃CN (bottom).



Fig. S2. Depictions of the two SOMOs calculated for the triplet 3, shown at an isosurface value of 0.03.



Fig. S3: UV-visible spectrum of 3 in acetonitrile.



Fig. S4: Difference electronic absorption spectrum 1 mM of **1** in 0.1 Bu_4NPF_6 in acetonitrile upon electrochemical reduction at a vitreous carbon electrode.



Fig. S5: Full cyclic voltammetry under catalytic conditions. Conditions: $[Bu_4NPF_6] = 100 \text{ mM}$. Working/auxiliary/reference electrodes = glassy carbon disk/Pt wire/silver wire. Scan rate of 100 mV/s, [1] = 1 mM, [AcOH] = 0 - 28 mM.



Fig. S6: Cyclic voltammetry of **1** with acetic acid examining behavior when the potential is scan to -1300 mV (black) and -950 mV (red). Conditions: $[Bu_4NPF_6] = 100$ mM. Working/auxiliary/reference electrodes = glassy carbon disk/Pt wire/silver wire. Scan rate of 100 mV/s, [1] = 1 mM, [AcOH] = 28 mM.



Fig. S7: Peak current vs square root scan rate for 1:1 acetate/acid at high acid/acetate concentrations. Conditions: [1] = 1 mM, [AcOH: Bu₄NOAc] = 12 mM.



Fig. S8: Cyclic voltammetry of **1** with 1 equivalent of phenol (black) and 0.5 equivalents of phenoxide (red) in acetonitrile. Conditions: $[Bu_4NPF_6] = 200 \text{ mM}$. Working/auxiliary/reference electrodes = glassy carbon disk/Pt wire/silver wire. Scan rate of 100 mV/s, [1] = 10 mM, [PhOH] = 10 mM, [NaOPh] = 5 mM.



Fig. S9: UV-Vis protonation studies of 3. Conditions: [5] = 0.8 mM, [TsOH] = 168 mM.