

Rapid Water Reduction to H₂ Catalyzed by a Cobalt Bis(iminopyridine) Complex

Bryan D. Stubbert, Jonas C. Peters, and Harry B. Gray

Supporting Information

General Considerations	S-2
Electrochemistry	S-2
Synthesis of 1 (PF ₆) ₂	S-3
Figure S1	S-4
Figure S2	S-9
Figure S3	S-10
Figure S4	S-10
Figure S5	S-11
Table S1	S-12
Complete Ref. 2	S-12
References	S-12

General considerations. All manipulations were carried out in an MBraun glovebox or using standard Schlenk techniques under an atmosphere of N₂ or Ar. Solvents were degassed and dried by thoroughly sparging with N₂ gas followed by passage through an activated alumina column. Unless otherwise noted, all reagents were purchased from commercial vendors and used without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., degassed, and stored over 3A molecular sieves prior to use. Milli-Q water was used in the preparation of all aqueous solutions, which were rigorously degassed (3 × freeze-pump-thaw cycles) or extensively sparged (≥ 30 min) with Ar prior to contact with catalyst. NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer and referenced according to the solvent residual peak.^{S1} Absorbance spectra were recorded on a Varian Cary Bio50 UV-Visible Spectrophotometer using degassed solutions in Teflon valve sealed quartz cells. Gas chromatograms for headspace analyses were recorded on an Agilent Technologies 7890A GC System, with peak areas calibrated for % H₂ by volume. Volumetric Faradaic yields were measured by displacement of water, mineral oil, or Hg in a graduated buret secured in a horizontal position. High resolution mass spectra (ESI-MS) were obtained using a JEOL JMS-600H magnetic sector mass spectrometer at the California Institute of Technology Mass Spectral Facility. Elemental analyses are reported as the average of duplicate runs carried out by Columbia Analytical Services, Tucson, AZ. [Co(CH₃CN)₆](PF₆)₂ was prepared in 82% yield according to the literature procedure for [Co(CH₃CN)₆](BF₄)₂,^{S2} substituting NO(PF₆) for NO(BF₄). 2-Acetylpyridine and 1,3-diaminopropane were dried by passage through a plug of neutral alumina and degassed (3 × freeze-pump-thaw cycles) prior to use and storage in the glovebox.

Electrochemistry. Solutions for electrochemical analysis were prepared from **1**(PF₆)₂ stored and weighed in the glovebox under an N₂ atmosphere. A CH Instruments 660D or 600B Electrochemical Analyzer was used for aqueous and acetonitrile solutions, respectively. Aqueous measurements were obtained using a Bioanalytical Systems Controlled Growth Mercury Drop Electrode (BAS CGME) working electrode run in static mode with an average drop surface area of 0.013 ± 0.002 cm² (calculated by determining the average weight of a single drop collected in each buffer medium)^{S3} and a commercially available saturated calomel reference electrode (SCE). Data is reported as the average of three runs obtained at a given set of experimental parameters using a fresh Hg drop for each run. In acetonitrile, a glassy carbon disk served as the working electrode (area = 0.07 cm²). A platinum wire was used as the auxiliary electrode in cyclic and linear sweep voltammograms, each performed in a single compartment cell in the glovebox (N₂ atmosphere) or in aqueous solutions on the benchtop (sparged ≥ 30 min with Ar prior to and between runs, and blanketed with Ar during runs). The nonaqueous reference electrode

was Ag⁺/Ag, exhibiting a reversible Fc⁺/Fc couple centered at +0.14 V in CH₃CN when added as an internal standard. Bulk controlled potential electrolysis experiments were performed in an N₂ atmosphere using a mercury pool working electrode (area = 0.8 or 1.8 cm²), aqueous AgCl/Ag reference electrode stored in a 3 M NaCl solution, and either a silver or platinum mesh auxiliary electrode in rapidly stirred solutions sealed in gastight dual compartment cells bearing Teflon valves and ground glass stopcocks amenable to GC analysis and/or volumetric displacement of headspace gases. Concentrations of **1**²⁺ in all media ranged from 0.1 to 1 mM, with 0.05 or 0.1 M aqueous buffer or 0.1 M tetra(*n*-butyl)ammonium hexafluorophosphate (TBAH). Unless otherwise noted, electrodes were purchased from CH Instruments. The diffusion coefficient for **1**²⁺ was estimated to be 4 × 10⁻⁵ cm²s⁻¹, determined from the slope of the *j*_{max} vs *v*^{1/2} plot measured for a CH₃CN solution containing 0.51 mM **1**²⁺ and 0.1 M TBAH (Figure S4) according to the Randles-Sevcik equation (eq S1).^{S3,S4}

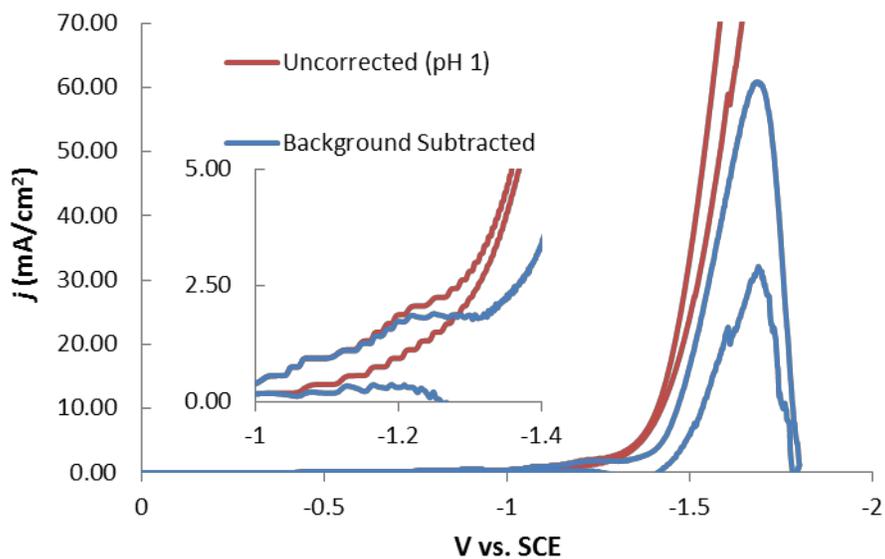
$$j = n^{3/2}FC_0^*D_0v^{1/2} \quad (\text{S1})$$

Background voltammograms obtained prior to dissolution of **1**²⁺ were subtracted from all data with little effect (≤ 5% change) on data collected in CH₃CN or from aqueous solutions of pH ≥ 4. A significant overcorrection results at -1.3 V vs SCE for solutions with pH ≤ 3, though this data is omitted from CV analyses given the apparent complex decomposition under these conditions.

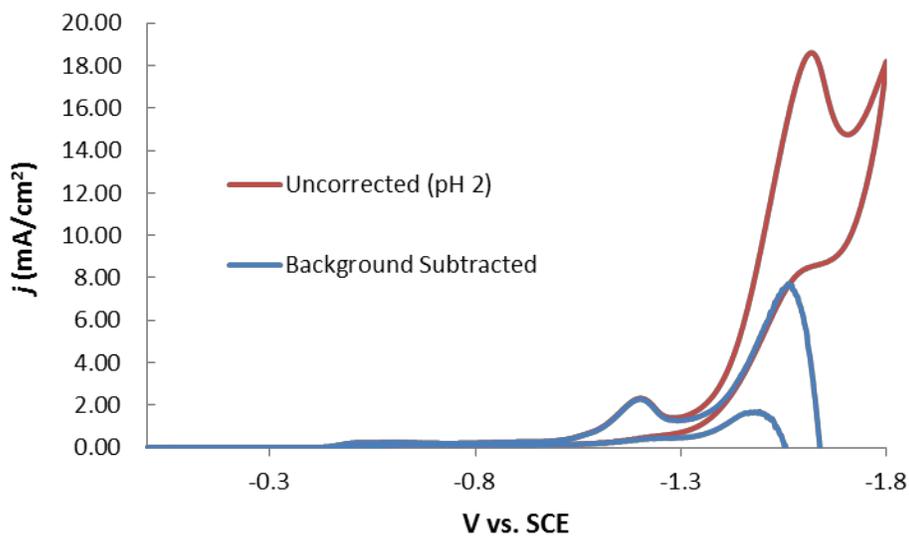
Synthesis of [Co(MePyN)₂^{pn}(H₂O)₂](PF₆)₂ (1**(PF₆)₂).** A 100 mL sidearm flask in the glovebox was charged with a stir bar and a solution of 2-acetylpyridine (0.245 g, 2.02 mmol) in acetonitrile (7 mL). To this colorless solution was added an acetonitrile solution (7 mL) of 1,3-diaminopropane (74.7 mg, 1.01 mmol). After stirring for 15 minutes at room temperature, a pink solution of [Co(CH₃CN)₆](PF₆)₂ (0.600 g, 1.01 mmol) in acetonitrile (10 mL) was added dropwise over 5 minutes while stirring rapidly. The red-orange solution was allowed to stir overnight at ambient temperature before evacuating to dryness. The red-orange residue that remained was covered with Et₂O (3 × 10 mL) and ground into a powder with a spatula before removing volatiles in vacuo. An orange powder was obtained in 93% yield (0.626 g, 0.94 mmol). ¹H NMR (300 MHz, 20 °C, CD₃CN, δ) 90.2 (sharp), 86.5, 55.5, 44.6, 18.6, -8.2 (sharp), -56.1, -83.6 ppm, all broad singlets except where noted. ¹⁹F NMR (282 MHz) -71.76 ppm (d, *J* = 706.8 Hz). ESI-MS (*M*⁺) Calc. for C₁₇H₂₀N₄Co: 339.1020. Found: 339.1016. Anal. Calcd. for C₁₉H₂₇N₅CoF₁₂O₂P₂: C, 32.31; H, 3.85; N, 9.92. Found: C, 32.48; H, 3.47; N, 9.46.

Figure S1. Representative cyclic voltammograms of aqueous solutions of 1^{2+} obtained at room temperature with a scan rate of 100 mV/s. Concentrations of 1^{2+} and aqueous buffer are indicated for each pH. Current densities calculated for an average mercury drop area of 0.013 cm^2 .

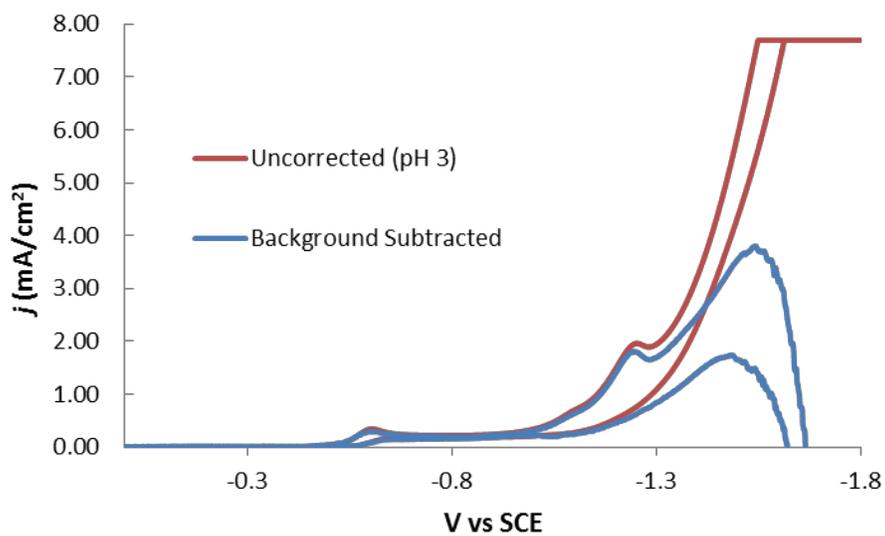
(a) pH 1.0, 0.34 mM 1^{2+} , 0.1 M KCl/HCl



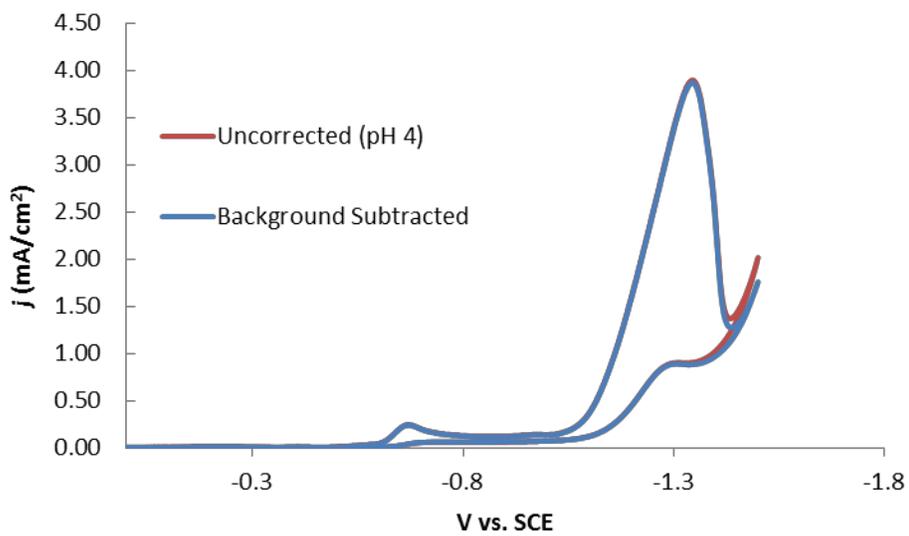
(b) pH 2.0, 0.33 mM 1^{2+} , 0.05 M NaP_i



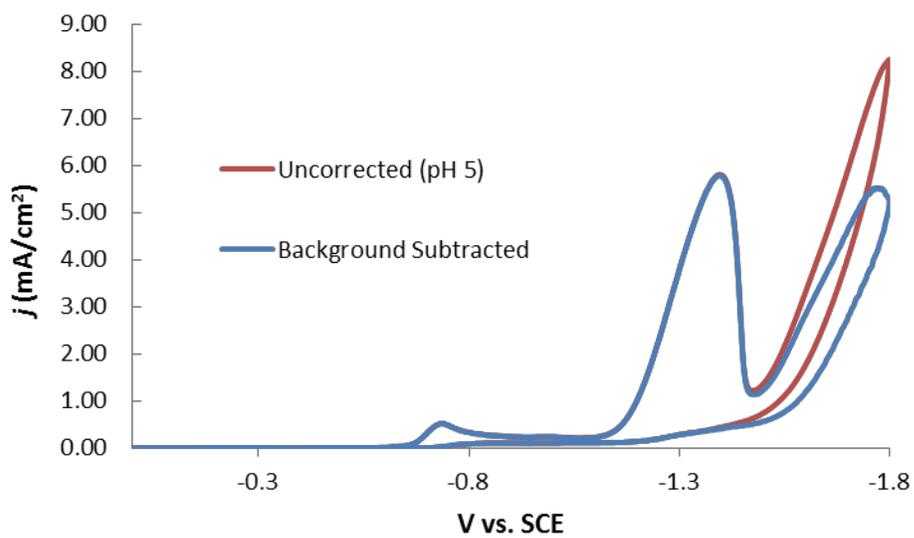
(c) pH 3.0, 0.32 mM $\mathbf{1}^{2+}$, 0.05 M sodium citrate



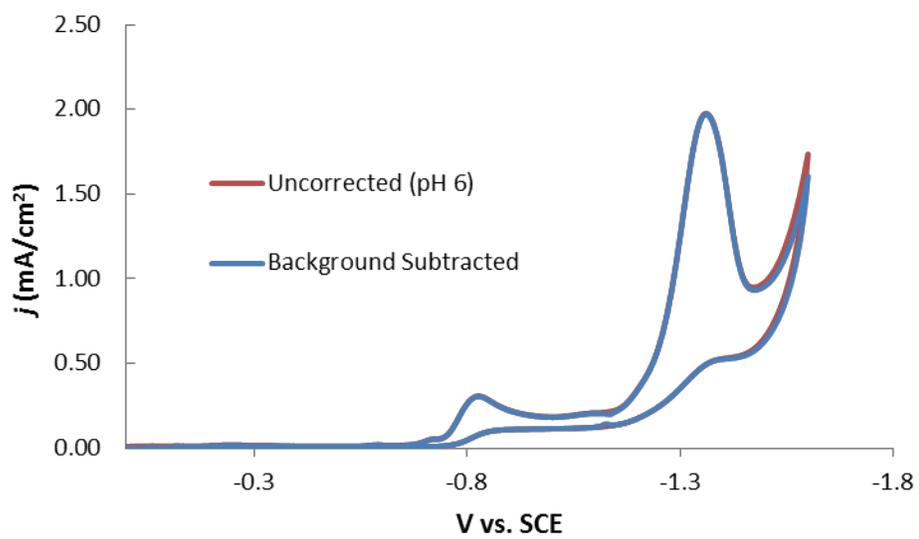
(d) pH 4.1, 0.12 mM $\mathbf{1}^{2+}$, 0.05 M sodium citrate



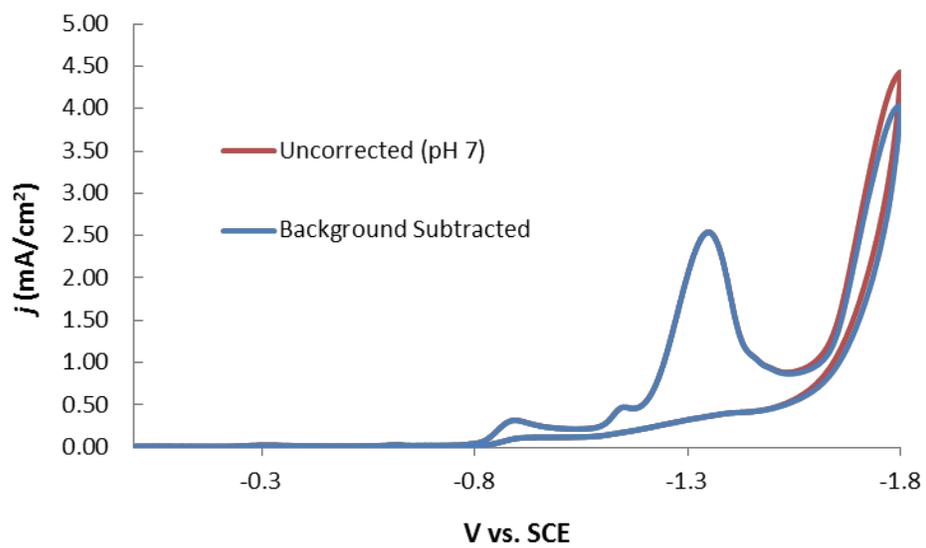
(e) pH 5.0, 0.35 mM 1^{2+} , 0.05 M sodium citrate



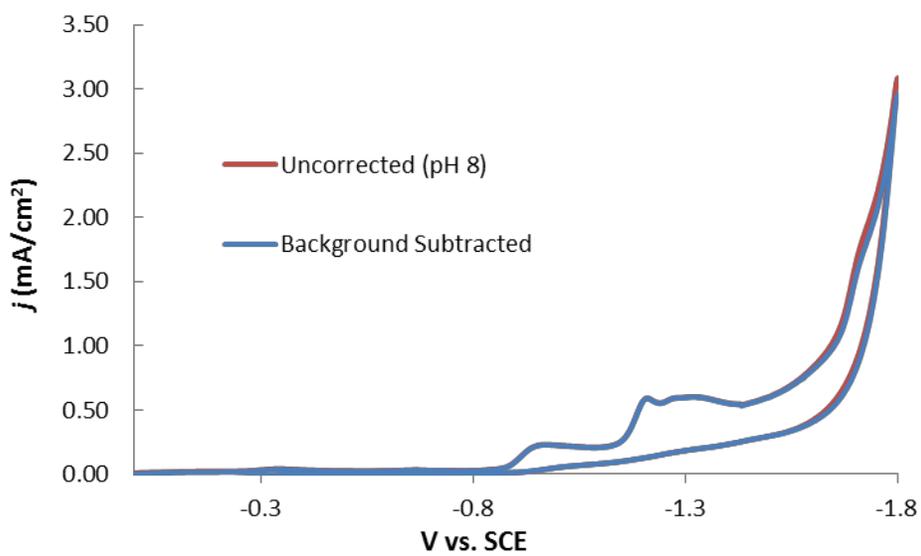
(f) pH 6.1, 0.32 mM 1^{2+} , 0.05 M sodium citrate



(g) pH 7.0, 0.30 mM 1^{2+} , 0.05 M NaP_i



(h) pH 8.0, 0.33 mM 1^{2+} , 0.05 M NaP_i



(i) pH 9.0, 0.33 mM $\mathbf{1}^{2+}$, 0.05 M sodium borax

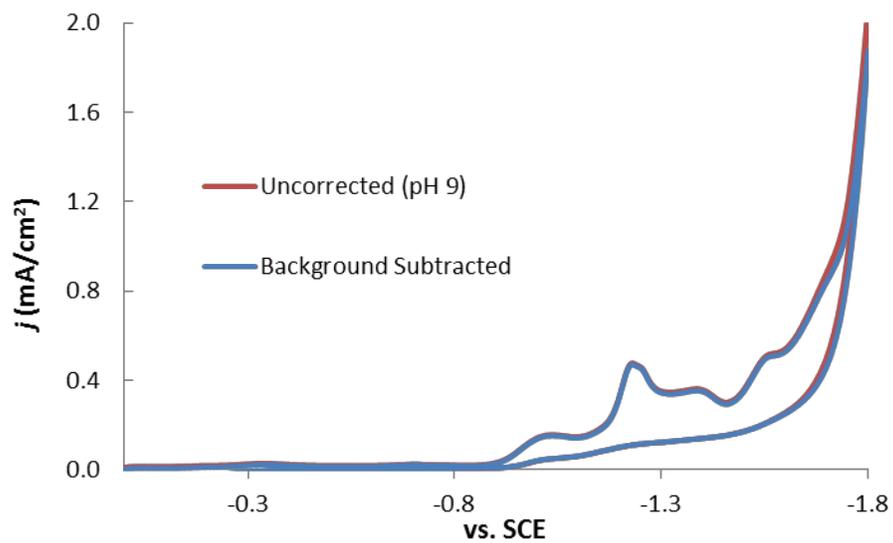
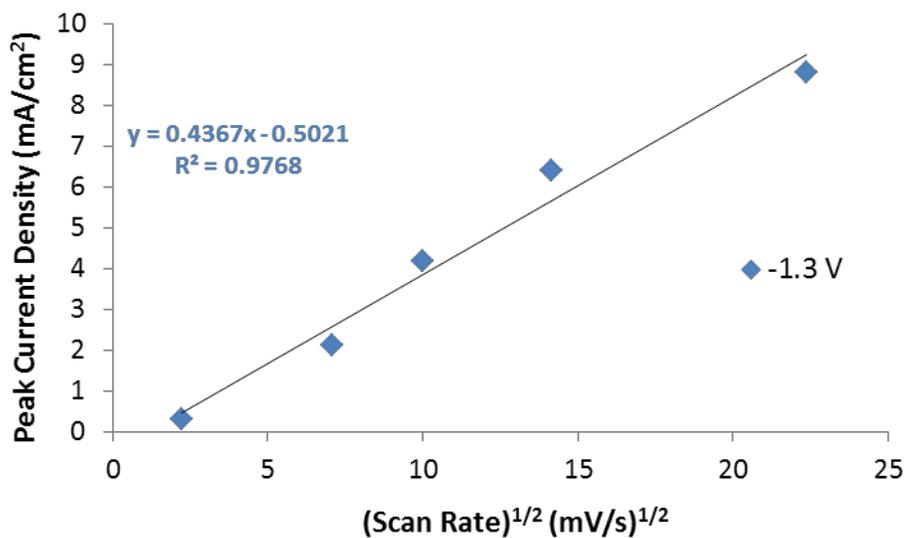


Figure S2. Overlaid plots of current density vs (scan rate)^{1/2} for selected reductions relevant to electrocatalysis at pH 4.1 and 7.0. CV data obtained in buffered aqueous media (0.05 M citrate or phosphate; Hg drop area = 0.013 cm²).

(a) pH 4.1, 0.12 mM $\mathbf{1}^{2+}$, 0.05 M sodium citrate



(b) pH 7.0, 0.30 mM $\mathbf{1}^{2+}$, 0.05 M sodium phosphate

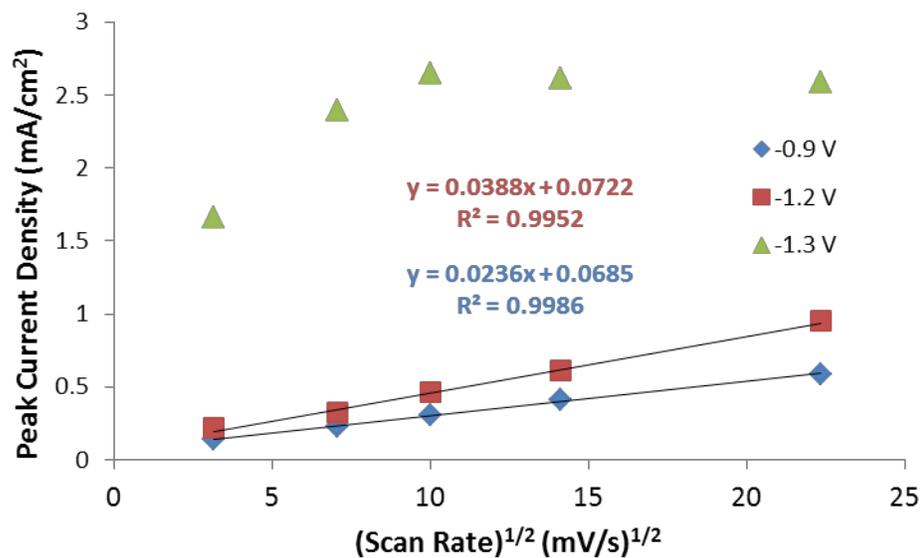


Figure S3. Dependence of current density (mA/cm^2) on the concentration of 1^{2+} over the range 0.1 to 1 mM in aqueous 0.05 M citrate buffer at pH 4.5. Additional data for 5 and 10 mM [Co] are shown but not included in the line fit.

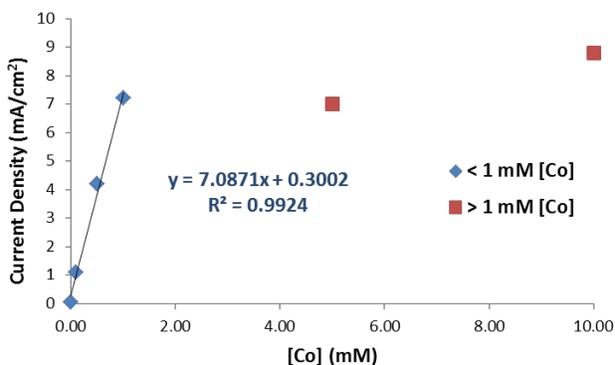


Figure S4. Overlaid plots of maximum current density vs $(\text{scan rate})^{1/2}$ for reductions relevant to electrocatalysis. CV data obtained in CH_3CN solution with 0.51 mM 1^{2+} and 0.1 M TBAH (Fc^+/Fc observed at +0.14 V vs Ag^+/Ag ; GCE area = 0.07 cm^2).

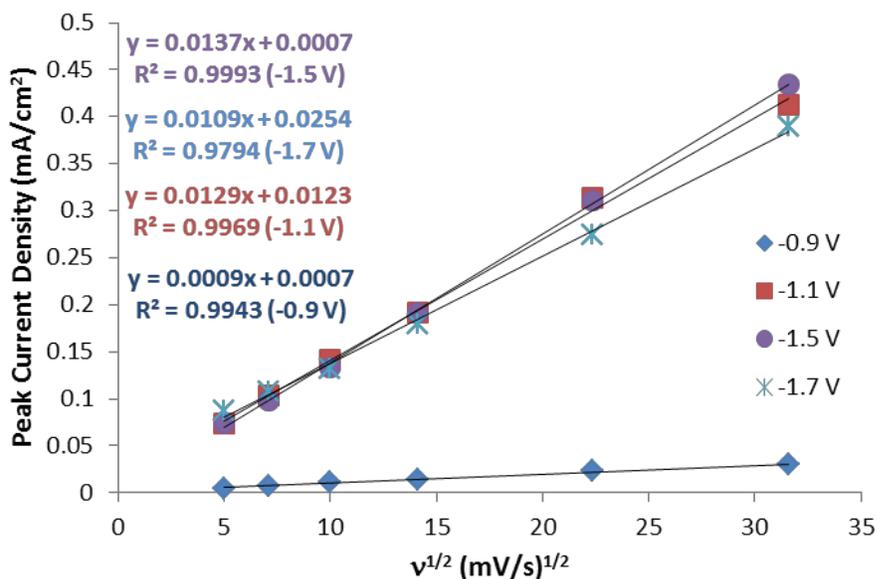
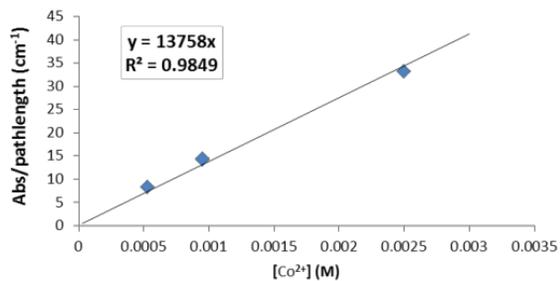
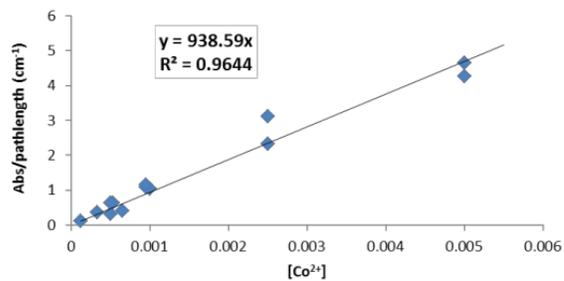


Figure S5. Aggregation plots of UV-visible absorbance spectra obtained for 0.1 to 5 mM solutions of 1^{2+} in neutral H_2O at room temperature in Teflon valve sealed quartz cells with pathlength 0.1 to 7.5 cm.

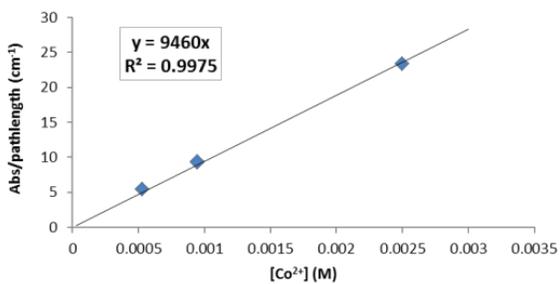
(a) 230 nm



(c) 310 nm



(b) 275 nm



(d) 450 nm

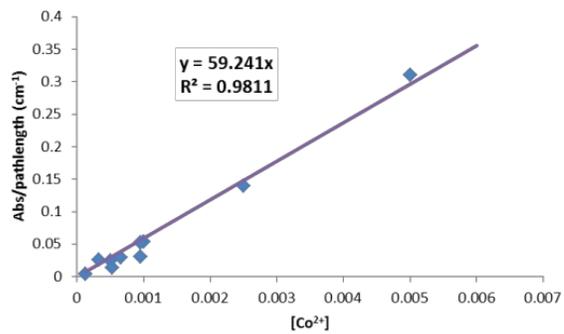


Table S1. Summary of potentials corresponding to the observed reduction waves shown in Figures 2 and 4.

Electrolyte Medium	Co ^{3+/2+}	Co ^{2+/1+}	Catalysis/ligand j_{\max}
Acetonitrile (vs Ag ⁺ /Ag)	-0.34 V	-0.86 V	-1.15 V
pH 4.1 (vs SCE)	-0.67 V	Not Observed	-1.34 V
pH 7.0 (vs SCE)	-0.90 V	-1.05 V	-1.34 V

Experimental conditions: acetonitrile (0.5 mM [Co²⁺], 0.1 M TBAH, N₂ atmosphere), pH 4.1 (0.1 mM [Co²⁺], 0.05 M sodium citrate, Ar sparge/blanket), pH 7.0 (0.3 mM [Co²⁺], 0.05 M sodium phosphate, Ar sparge/blanket). Nonaqueous Ag⁺/Ag pseudoreference electrode shows Fc⁺/Fc E^{o'} = +0.14 V. Aqueous experiments show pH dependent behavior for the irreversible wave assigned as Co^{3+/2+} (extrapolates to -0.38 V vs SCE at pH 0). The potentials shown here correspond to the local j_{\max} for processes scanned cathodically and are not reversible reduction potentials.

Complete text for reference 2:

Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; DuBois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R.; Tumas, W. *Chem. Rev.* **2001**, *101*, 953.

References

-
- (S1) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176.
- (S2) Heintz, R. A.; Smith, J. A.; Szalay, P. S.; Weisgerber, A.; Dunbar, K. R.; Beck, K.; Coucouvanis, D. *Inorg. Synth.* **2002**, *33*, 75
- (S3) *Laboratory Techniques in Electroanalytical Chemistry* 2nd ed.; Kissinger, P. T.; Heineman, W. R., Ed.; Marcel Dekker, Inc: New York, 1996.
- (S4) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; 2nd ed.; John Wiley: New York, 2000.