Supplemental Information for:

Distinguishing between homogeneous and heterogeneous hydrogen-evolution catalysis with molecular cobalt complexes

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Experimental Details

All manipulations were carried out in dry N₂-filled gloveboxes (Vacuum Atmospheres Co., Hawthorne, CA) or under N₂ atmosphere using standard Schlenk techniques unless otherwise noted. All solvents were of commercial grade and dried over activated alumina using a PPT Glass Contour (Nashua, NH) solvent purification system prior to use, and were stored over molecular sieves. All chemicals were from major commercial suppliers and used after extensive drying. NOBF₄ was dried *in vacuo* overnight. Deuterated NMR solvent was purchased from Cambridge Isotope Laboratories; CD₃CN was dried over CaH₂. ¹H, ¹¹B, and ¹⁹F NMR spectra were collected on a 400 MHz Bruker spectrometer and referenced to the residual protio-solvent signal in the case of ¹H, and to the deuterium lock signal in the case of ¹¹B and ¹⁹F unless otherwise noted.

Protonated dimethylformamide ($[DMFH]^+[OTf]^-$) and anilinium triflate ($[C_6H_5NH_3]^+[OTf]^-$) were synthesized by the methods of Favier and Duñach¹. [Co(NCMe)₆][BF₄]₂², [Co^{II}(dmgH)₂]³ and [Co^{II}(dmgBF₂)₂]⁴ were prepared according to previously developed procedures in the literature.

Infrared spectra were recorded on a PerkinElmer Spectrum 100 FTIR spectrometer at room temperature; solution samples were prepared inside a dry N₂-atmosphere glovebox and sealed in 0.1 mm NaCl cells. All measurements were collected in tetrahydrofuran (THF) solution in order to access the spectral regions of interest.

Electrochemical experiments were carried out in a N₂-filled glovebox in dry, degassed MeCN. 0.10 M tetra(n-butylammonium) hexafluorophosphate ($[^{n}Bu_{4}N]^{+}[PF_{6}]^{-}$; Sigma-Aldrich, electrochemical grade) served as the supporting electrolyte. Measurements were made with a Gamry Reference 600+ Potentiostat/Galvanostat using a standard three-electrode configuration. The working electrode was the basal plane of highly oriented pyrolytic graphite (HOPG) (GraphiteStore.com, Buffalo Grove, Ill.; surface area: 0.09 cm²), the counter electrode was a platinum wire (Kurt J. Lesker, Jefferson Hills, PA; 99.99%, 0.5 mm diameter), and a silver wire immersed in electrolyte served as a pseudo-reference electrode (CH Instruments). The reference was separated from the working solution by a Vycor frit (Bioanalytical Systems, Inc.). Ferrocene (Sigma Aldrich; twice-sublimed) was added to an electrolyte solution prior to the beginning of each experiment; the midpoint potential of the ferrocenium/ferrocene couple (denoted as Fc^{+/0}) served as an external standard for comparison of the recorded potentials. Concentrations of analyte for cyclic voltammetry were 2 mM unless otherwise stated.

Electrochemical quartz crystal microbalance (EQCM) experiments were likewise carried out in a N₂-filled glovebox. 0.10 M tetra(n-butylammonium) hexafluorophosphate (Sigma-Aldrich; electrochemical grade) in acetonitrile again served as the supporting electrolyte. Measurements were conducted with a Gamry eQCM 10M quartz crystal microbalance. Solutions were prepared in a static Teflon cell. An AT-cut quartz disc sputtered with gold and having a nominal resonant frequency of 10 MHz was used as the working electrode (Gamry Instruments; electroactive area ca. 0.205 cm²). The counter electrode was a platinum wire (Kurt J. Lesker, Jefferson Hills, PA; 99.99%, 0.5 mm diameter), and a silver wire immersed in electrolyte served as a pseudoreference electrode (CH Instruments). The reference was separated from the working solution by a Vycor frit (Bioanalytical Systems, Inc.). X-ray photoelectron spectra were collected using a Physical Electronics (Phi) VersaProbe II system. The sample chamber was kept at $<5 \times 10^{-9}$ torr and ejected electrons were collected at an angle of 45° from the surface normal. Survey scans were performed to identify the elements on the surface of carbon electrodes, while additional high-resolution spectra were obtained for details on specific elements.

The XPS data were analyzed using the program Computer Aided Surface Analysis for X-ray Photoelectron Spectroscopy (CasaXPS; from Casa Software Ltd., Teignmouth, UK). All XPS signals reported here are binding energies and are reported in eV. Backgrounds were fit with standard Shirley or linear backgrounds. Element peaks were fit with a standard Gaussian-Lorentzian line shape. For the Co high-resolution spectra, the data were best fit with a single contribution in every case, and fits were constrained based only on peak area.

Gas analysis for determination of gas evolution was performed with a Shimadzu GC-2014 Custom-GC gas chromatograph with a thermal conductivity detector and dual flame-ionization detectors. A custom set of 8 columns and timed valves enable quantitative analysis of the following gases: hydrogen, nitrogen, oxygen, carbon dioxide, carbon monoxide, methane, ethane, ethylene, and ethyne. Argon serves as the carrier gas. The instrument was calibrated prior to experimental runs with a standard checkout gas mixture (Agilent 5190-0519) to obtain qualitative data for H_2 and other gases. Calibration curves over a range of 100–10,000 ppm were constructed with prepared mixtures of H_2 in N_2 to enable H_2 quantification.

Synthesis of [Co(NCMe)₆][BF₄]₂

Under inert atmosphere, a dry Schlenk flask was loaded with 874 mg of cobalt metal powder (14.8 mmol) and 347 mg (2.97 mmol) of NO⁺BF₄⁻; 40 mL of dry, degassed MeCN was added to this mixture by cannula transfer. The reaction vessel was exposed to vacuum until bubbling, then backfilled with N₂ gas over three cycles. The reaction was allowed to proceed under static vacuum conditions for 12 hours. The solution was then concentrated and cannula transferred to a fresh flask, where the product was crashed out by addition of diethyl ether of equal volume, filtered, and washed with additional ether. The solid, light pink material was then dried *in vacuo* overnight at 80°C. Yield: 45% (410 mg). Spectroscopic characterization and magnetic susceptibility measurements were in agreement with reported literature.²

Synthesis of Co(dmgH)₂

To a dry Schlenk flask under inert atmosphere, 2 g (8.0 mmol) $Co(OAc)_2 \cdot 4H_2O$ and 2.04 g dimethylglyoxime (17.5 mmol) were solubilized in 80 mL of dry, degassed MeCN added via cannula transfer. The reaction was stirred for two hours under positive N₂ pressure and solvent removed by vacuum. The red solid was then washed with 20 mL of degassed water and dried under reduced pressure overnight at 80°C. Yield: 1.77 g (76%). Spectroscopic characterization of the complex agreed with the reported literature.³

Synthesis of Co(dmgBF₂)₂

The preparation of **1** was based on synthetic procedures developed previously in the literature. A dry Schlenk flask was charged with 136 mg (0.470 mmol) $Co(dmgH)_2$, 30 mL dry, degassed Et₂O and 0.82 mL of BF₃·Et₂O (6.58 mmol) was delivered via syringe. The reaction vessel was first sonicated, then evacuated (5 times) until the solution bubbled vigorously, once every 20 minutes over the first 2 hour time course of the reaction. The reaction was allowed to proceed for 24 hours, then solvent was removed via cannula and the solid product washed twice with 5 mL

of ether. The yellow-brown powder product was then dried overnight at 80 °C *in vacuo*. Yield: 64% (115 mg). Spectroscopic characterization of the complex agreed with reported literature.⁴

Infrared Spectroscopy



Figure S1. Infrared spectra of **2** in THF: reaction of **2** with acid. (a): Direct comparison of free dimethylglyoxime vibration observed in sample of free ligand versus a solution of **2** treated with 2 equiv. of $[DMFH]^+[OTf]^-$. (b): Low frequency region lacking free-base N-H vibration.



Figure S2. Infrared spectra of 1 in THF: reaction of 1 with acid. (a): High frequency region where vibration could be expected for free dimethylglyoxime. (b): Low frequency region where new signal is observed which is consistent with the out-of-plane N-H stretch in free-base porphyrins.⁵

NMR Spectra



Figure S3. ¹⁹F NMR spectra (376 MHz, CD_3CN) of 1: reaction of 1 with acid. A sharp diamagnetic signal at -152 ppm appears when 1 is treated with 3 equiv. $[DMFH]^+[OTf]^-$ (spectrum 3). The response at ca. -80 ppm in spectrum 3 is assigned as the broadened triflate signal, in agreement with spectrum 1 and 2.



Figure S4. ¹¹B NMR spectra (128 MHz, CD_3CN) of 1: reaction of 1 with acid. Growth of a sharp diamagnetic signal occurs at 0 ppm upon addition of 3 equiv. [DMFH]⁺[OTf]⁻ (spectrum 2). No decomposition is observed by NMR when 1 is treated with 3 equiv. $[C_6H_5NH_3]^+[OTf]^-$ (spectrum 1).

Electrochemistry



Figure S5. Electrochemical reversibility and scan rate dependence of **1**. (a) Cyclic voltammetry of **1** at various scan rates. 2 mM of **1** in MeCN $(0.1 \text{ M} [^{n}\text{Bu}_4\text{N}]^{+}[\text{PF}_6]^{-}$ supporting electrolyte). (b) Linear dependence of peak current on the square root of scan rate, as expected for a diffusional process. Data collected on a HOPG working electrode.



Figure S6. Cyclic voltammetry data of **1** in the presence of acid. **Blue:** 2 mM solution of **1** in MeCN (0.1 M $[^{n}Bu_{4}N]^{+}[PF_{6}]^{-}$ supporting electrolyte) treated with 3 equiv. $[DMFH]^{+}[OTf]^{-}$. **Black:** 6 mM solution of $[DMFH]^{+}[OTf]^{-}$ (acid-only blank). Data collected on a HOPG working electrode; the scan rate was 100 mV/s.



Figure S7. Cyclic voltammetry data of **5** both with and without acid. Full width scans of 2 mM **5** independently run with and without 3 equiv. of $[DMFH]^+[OTf]^-$. Note the presence of previously described stripping wave at ca. +0.3 V. Conducted in MeCN (0.1 M $[^nBu_4N]^+[PF_6]^-$ supporting electrolyte). Data collected on a HOPG working electrode; the scan rate was 100 mV/s.



Figure S8. Diffusional behavior of **5**. (a): Cyclic voltammograms of a 2 mM **5** at varying scan rates. (b): Linear dependence of the cathodic peak current on the square root of scan rate, as expected for a diffusional process. Conducted in MeCN (0.1 M $[^{n}Bu_{4}N]^{+}[PF_{6}]^{-}$ supporting electrolyte). Data collected on a HOPG working electrode.

EQCM



Figure S9. EQCM of **1** versus electrolyte-only 'blank' solution. (a): *Black:* Cyclic voltammogram of 2 mM solution of **1**. *Blue:* Mass change response measured by EQCM during the cycle. (b): *Black:* Cyclic voltammogram of electrolyte solution without **1**. *Blue:* Mass change response measured by EQCM during the cycle. Conducted in MeCN (0.1 M $[^{n}Bu_{4}N]^{+}[PF_{6}]^{-}$ supporting electrolyte). Experimental conditions: Au working electrode, 100 mV/s scan rate.



Figure S10. EQCM of 1 treated with acid versus electrolyte-only blank. (a): *Black:* Cyclic voltammogram of 2 mM solution of 1 and 6 mM $[DMFH]^+[OTf]^-$. *Blue:* Mass change response measured by EQCM during the cycle. (b): *Black:* Cyclic voltammogram of electrolyte solution without 1. *Blue:* Mass change response measured by EQCM during the cycle. Conducted in MeCN (0.1 M $[^nBu_4N]^+[PF_6]^-$ supporting electrolyte). Experimental conditions: Au working electrode, 100 mV/s scan rate.



Figure S11. Mass response of **1** with acid vs. response of Au electrode with acid. Offset are the mass responses observed by EQCM during cyclic voltammetry. **Blue line:** 2 mM **1** with 3 equiv. $[DMFH]^+[OTf]^-$. **Gray line:** 6 mM $[DMFH]^+[OTf]^-$. Similar mass response ($\Delta m \approx 0$ ng) is observed for a cobalt-free solution of 6 mM $[C_6H_5NH_3]^+[OTf]^-$. Conducted in MeCN (0.1 M $[^nBu_4N][PF_6]$ supporting electrolyte). Experimental conditions: Au working electrode, 100 mV/s scan rate.



Figure S12. EQCM response of **1** treated with 3 equiv. anilinium triflate. **Black:** Cyclic voltammogram of 2 mM solution of **1** with 3 equiv. of $[C_6H_5NH_3]^+[OTf]^-$. **Blue:** Mass response recorded by EQCM during the voltammogram. The mass change observed is virtually indistinguishable from response of blank electrolyte solution. Conducted in MeCN (0.1 M $[^nBu_4N]^+[PF_6]^-$ supporting electrolyte). Experimental conditions: Au working electrode, 100 mV/s scan rate.



Figure S13. Linear sweep voltammetry demonstrating cobalt corrosion by acid. (a): The potential was swept from 0 V vs. $Fc^{+/0}$ to -1.35 V at 100 mV/s scan rate; immediately upon reaching -1.35 V, polarization ceased. (b): The EQCM monitored mass change on the electrode surface before, during, and after polarization. All mass deposited is corroded from the surface within 10 seconds. Experimental conditions: carried out in MeCN, 0.1 M [ⁿBu₄N]⁺[PF₆]⁻; 2 mM 1; 6 mM [DMFH]⁺[OTf]⁻; Au working electrode.



Figure S14. Overlay of EQCM measurements on **5** without acid and **5** in the presence of $[DMFH]^+[OTf]^-$. (a): *Black:* Cyclic voltammogram of a 2 mM solution of **5**. *Blue:* EQCM-recorded mass response. (b): *Black:* Cyclic voltammogram of a 2 mM solution of **5** and 6 mM solution of $[DMFH]^+[OTf]^-$. *Blue:* EQCM-recorded mass response. Both experiments give similar mass depositions on the electrode surface. Conducted in MeCN (0.1 M [ⁿBu₄N]⁺[PF₆]⁻ supporting electrolyte). Experimental conditions: Au working electrode, 100 mV/s scan rate.



Figure S15. Scan rate dependence of mass deposition from **5**. EQCM data of a 2 mM solution of **5** in MeCN (0.1 M $[^{n}Bu_{4}N]^{+}[PF_{6}]^{-}$ supporting electrolyte). (a): Cyclic voltammograms of **5** at varying scan rates on Au working electrode. (b): EQCM mass response corresponding to voltammograms in (a). At slower scan rates, more time is spent at sufficiently negative potentials to drive cobalt deposition, resulting in larger observed mass increases.



Figure S16. Scan rate dependence of mass deposition from **5** treated with acid. EQCM data of a 2 mM solution of **5** in MeCN (0.1 M [${}^{n}Bu_{4}N$] ${}^{+}[PF_{6}]^{-}$ supporting electrolyte) with 6 mM [DMFH] ${}^{+}[OTf]^{-}$. (a): Cyclic voltammograms of **5** at varying scan rates on Au working electrode. (b): EQCM mass response corresponding to voltammograms in (a). It is observed that the response is similar to the case of **5** without acid addition.



Figure S17. Reproducibility of EQCM measurements of deposition of cobalt from **5**. EQCM data in the time domain representing five cyclic voltammogram cycles (scanning from 0.68 V to -1.46 V vs Fc^{+/0} at 100 mV/s). Conducted in MeCN (0.1 M [ⁿBu₄N]⁺[PF₆]⁻ supporting electrolyte) on Au working electrode. We conclude that mass deposition and stripping is reproducible and complete on each individual cycle.

X-ray photoelectron spectroscopy



Figure S18. Survey scans of blank carbon electrode. The only signals observed are those from the carbon electrode material (C 1s, C KLL Auger), a small adventitious oxygen signal (O 1s and O KLL), and a very small adventitious fluorine signal (F 1s, F KLL).



Figure S19. Cobalt 2p region of a blank carbon electrode. There is no detectable cobalt.



Figure S20. Survey spectrum of a carbon electrode with electrodeposited cobalt arising from reduction of **5**. Electrode was polarized at -1.5 V for 5 min. in a 2 mM solution of **5**, then rinsed with MeCN and transferred to the XPS instrument. Exposure to air upon transfer to the XPS instrument results in oxidation of cobalt metal to cobalt oxide. All expected signals for cobalt are detected: Co 3p, Co 3s, Co LMM Auger, Co 2p, and Co 2s. Nitrogen (N 1s, N KLL) and phosphorous (P 2p), along with an enhanced fluorine content (F 1s, F KLL) suggest electrolyte salt ([ⁿBu₄N]⁺[PF₆]⁻) remain on the surface despite rinsing with blank MeCN.



Figure S21. Cobalt 2p region of cobalt electrode prepared as described in Figure S20. Transparent gray points are measured spectral data. Black lines are Shirley backgrounds and overall fit in the analysis window. Blue line is Co $2p_{3/2}$ peak, and red line is Co $2p_{1/2}$ peak. Predicted area ratio of 2:1 agrees with measured data. Green lines are paramagnetic satellites arising from Co²⁺ content on the surface.



Figure S22. Survey scans of a carbon electrode after polarization in a solution containing 1 and acid. **Blue:** The electrode was polarized at -0.34 V for 5 min. in a 2 mM solution of 1 treated with 3 equiv. [DMFH]⁺[OTf]⁻. **Red:** The electrode was polarized at -1.35 V for 5 min. in a 2 mM solution of 1 treated with 3 equiv. [DMFH]⁺[OTf]⁻. Each sample was then rinsed with MeCN and transferred to the XPS instrument.

Carbon and oxygen are present as in untreated blank electrodes (C 1s, C KLL, O 1s, O KLL). New peaks are present corresponding to phosphorous (P 2p and P 2s) and nitrogen (N 1s), and enhanced signals are present corresponding to fluorine (F 1s and F KLL). These signals arise from electrolyte ($[^{n}Bu_{4}N]^{+}[PF_{6}]^{-}$) adsorbed on the surface due to incomplete rinsing.

Notably, no cobalt is apparent on the surface in either case. Even after polarization at -1.35 V (red line), a voltage known from EQCM to drive electrodeposition, no signal for cobalt on the surface is detected, suggesting rapid corrosion of any deposited material before the electrode could be transferred out of the acid-containing electrolyte solution. As expected, the control spectrum (blue line) contains no cobalt on the surface.



Figure S23. Cobalt 2p region of XP spectra collected on a carbon electrode after polarization in a solution containing **1** and acid. **Blue:** Electrode was polarized at -0.34 V for 5 min. from a 2 mM solution of **1** with 3 equiv. [DMFH]⁺[OTf]⁻, then rinsed with MeCN and transferred to the XPS instrument. **Red:** Electrode was polarized at -1.5 V for 5 min. from a 2 mM solution of **1** with 3 equiv. [DMFH]⁺[OTf]⁻, then rinsed with MeCN and transferred to the XPS instrument. **Red:** Electrode was polarized at -1.5 V for 5 min. from a 2 mM solution of **1** with 3 equiv. [DMFH]⁺[OTf]⁻, then rinsed with MeCN and transferred to the XPS instrument. There are no signals for cobalt.

Gas Chromatography

Samples for GC analysis were prepared by exposure of electrodeposited cobalt to strong acid $[DMFH]^+[OTf]^-)$ under inert atmosphere conditions in a glovebox. A 1 cm² HOPG carbon electrode was used as the working electrode in a typical three-electrode configuration (Pt counter electrode, silver pseudo-reference referenced externally to the ferrocenium/ferrocene couple). In a 2 mM solution of **5**, the electrode was polarized to -1.46 V vs. Fc^{+/0} for 40 min. in a chronoamperometric mode. The charge passed was determined from integration of this curve and mass of cobalt estimated from conversion of charge to expected cobalt mass deposited, assuming a two-electron process. This electrode, as well as a blank control electrode, were transferred to sealed flasks containing 40 mL of MeCN with 80 mL of free headspace.

 $[DMFH]^+[OTf]^-$ in a minimal volume of MeCN was syringed into the flasks to generate a solution concentration of 6 mM acid. The flasks were then stirred, sealed, for thirty minutes before headspace was analyzed with a 10 mL airtight syringe. H₂ was not observed in the sample taken with the blank electrode. The headspace from the vessel containing the carbon electrode bearing electrodeposited cobalt gave rise to a response on the GC instrument which, when compared to calibration curves previously generated, corresponded to 257 ppm of H₂. From this value, with given headspace, the overall amount of H₂ gas formed during Co corrosion was calculated (Yield: 67% H₂ per Co).

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