

# Supplementary Material (ESI) for Chemical Communications  
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**Electronic Supporting Information:**

**Electrocatalytic Hydrogen Evolution by Cobalt Difluoroboryl-  
diglyoximate Complexes**

Xile Hu, Brandi M. Cossairt, Bruce S. Brunschwig, Nathan S. Lewis, and Jonas C.  
Peters\*

*Division of Chemistry and Chemical Engineering, Arnold and Mabel Beckman  
Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena,  
California 91125, USA. Fax: +1 626 5774088; Tel: +1 626 3954036; Email:  
[jpeters@caltech.edu](mailto:jpeters@caltech.edu).*

## Experimental Section

All manipulations were carried out under an inert atmosphere using standard Schlenk techniques or a nitrogen-filled glovebox. Unless otherwise noted, all solvents were deoxygenated and dried by sparging with N<sub>2</sub> gas and passage through an activated alumina column. HBF<sub>4</sub>·Et<sub>2</sub>O and CF<sub>3</sub>COOH were degassed by standard freeze-pump-thaw procedures prior to use. All other reagents were purchased from commercial sources and used without further purification. Complexes **1**<sup>1</sup> and **2**<sup>2</sup> were synthesized according to literature methods.

**Physical methods.** IR spectra were recorded on a Bio-Red Excalibur FTS 3000 spectrometer controlled by WinIR Pro software. UV-Vis measurements were carried out using a Varian Cary 50 Bio Spectrophotometer controlled by Cary WinUV software. NMR spectra were recorded using a Varian Mercury 300 spectrometer. <sup>1</sup>H NMR chemical shifts were referenced to residual solvent as determined relative to Me<sub>4</sub>Si (δ = 0 ppm). <sup>19</sup>F{<sup>1</sup>H} chemical shifts were referenced to an external standard (neat BF<sub>3</sub>·Et<sub>2</sub>O, δ = 0 ppm). MS data were obtained by injection of a acetonitrile solution onto a Hewlett-Packard 1100MSD mass spectrometer. Cyclic voltammetric measurements were recorded using a CHI 600B electrochemical analyzer using either a glassy carbon working electrode (BAS, surface area = 0.07 cm<sup>2</sup>) or a platinum electrode (BAS, surface area = 0.02 cm<sup>2</sup>), a platinum wire auxiliary electrode, and an Ag/AgNO<sub>3</sub> (0.01 M) reference electrode filled with acetonitrile and [<sup>n</sup>Bu<sub>4</sub>][ClO<sub>4</sub>] (0.1 M). All potentials were referenced to Fc/Fc<sup>+</sup> as an internal standard and converted to SCE by adding 0.38 V to the measured potentials.<sup>3</sup> The concentration of [HBF<sub>4</sub>·Et<sub>2</sub>O] and [HCl·Et<sub>2</sub>O] were calibrated by measuring the pH of aqueous solutions of known volume of the acids using

a Beckman 32 PH meter. Bulk electrolysis experiments were done in a custom-made gas-tight H-type cell using a reticulated vitreous carbon working electrode (BAS), an Ag/AgNO<sub>3</sub> reference electrode, and a coiled platinum counter electrode. The counter electrode was separated from the working electrode by a glassy frit. The amount of H<sub>2</sub> gas evolved was quantified by analyzing the gas mixture in the headspace using a Thermo Finnigan DeltaplusXP system equipped with Finnigan trace GC and an Isotope Ratio Mass Spectrometer. The total amount of H<sub>2</sub> produced was calculated as the sum of H<sub>2</sub> in the headspace and H<sub>2</sub> dissolved in the solvent (calculated using Henry's Law).

**Acid stability of 1 and 2.** In acetonitrile, complex **1** has a characteristic absorption band centered at 424 cm<sup>-1</sup>, which decays with time in the presence of acids. The reaction rates of **1** towards acids were measured by monitoring the decay of this absorption band using UV-Vis spectroscopy. Measurements were carried out under pseudo first-order conditions (acid/complex ratio > 10 : 1) at room temperature. At least two trials were carried out for each measurement. It is found that **1** reacts with HCl·Et<sub>2</sub>O with a rate constant of 0.053(1) M<sup>-1</sup> s<sup>-1</sup>, first order with respect to the concentration of **1** and first order with respect to the concentration of HCl·Et<sub>2</sub>O. The reaction of **1** with HBF<sub>4</sub>·Et<sub>2</sub>O is faster, with a rate constant of 8(1) x 10<sup>2</sup> M<sup>-2</sup> s<sup>-1</sup>, first order with respect to the concentration of **1** and second order with respect to the concentration of HBF<sub>4</sub>·Et<sub>2</sub>O. Complex **1** does not undergo appreciable reaction with CF<sub>3</sub>COOH.

Similarly, the reaction rates of **2** with acids were measured by monitoring the decay of its characteristic absorption band at 465 cm<sup>-1</sup> in acetonitrile. Measurements were carried out under pseudo first-order conditions (acid/complex ratio > 10 : 1) at room temperature. At least two trials were carried out for each measurement. The reaction of

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**2** with HCl·Et<sub>2</sub>O has a rate constant of  $2.4(2) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ , first order with respect to the concentration of **2** and first order with respect to the concentration of HCl·Et<sub>2</sub>O. The reaction of **2** with HBF<sub>4</sub>·Et<sub>2</sub>O has a rate constant of  $35(1) \text{ M}^{-2} \text{ s}^{-1}$ , first order with respect to the concentration of **2** and second order with respect to the concentration of HBF<sub>4</sub>·Et<sub>2</sub>O.

**Cl<sup>-</sup> binding for 1 and 2.** The binding of Cl<sup>-</sup> to **1** and **2** does not change their UV-Vis spectra significantly enough to allow for a determination of the binding constants. The binding constants are estimated by comparing the peak heights of the cathodic waves for **1** and **1**·Cl<sup>-</sup> (ca.  $700 \text{ M}^{-2}$ ), and **2** and **2**·Cl<sup>-</sup> (ca.  $2600 \text{ M}^{-2}$ ).

**Synthesis of [Co(dm<sup>g</sup>BF<sub>2</sub>)<sub>2</sub>(CO)]CoCp<sub>2</sub>.** A solution of CoCp<sub>2</sub> (32 mg, 0.17 mmol) in acetonitrile was added to a solution of **1** (83 mg, 0.18 mmol) in acetonitrile at room temperature. The resulting solution was sparged with CO gas and the reaction mixture was stirred for 2 h before evaporated to dryness. The resulting purple solid was collected on a filter frit, washed with THF and diethyl ether, and dried in vacuum. Yield: 82 mg (76 %). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN): δ = 2.53 (s, 12 H), 5.63 (s, 10 H) ppm. <sup>19</sup>F{<sup>1</sup>H} NMR (282 MHz, CD<sub>3</sub>CN) : δ = 152.2 (m, 2F), 154.4 (m, 2F) ppm. IR (KBr): ν(CO) = 2015 cm<sup>-1</sup>. ESI-MS: 385.1 (Co(dm<sup>g</sup>BF<sub>2</sub>)<sub>2</sub><sup>-</sup>).

**Synthesis of [Co(dp<sup>g</sup>BF<sub>2</sub>)<sub>2</sub>(CO)]CoCp<sub>2</sub>.** Similar to the synthesis of [Co(dm<sup>g</sup>BF<sub>2</sub>)<sub>2</sub>(CO)]CoCp<sub>2</sub>. Yield: 53 mg (81 %). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN): δ = 5.63 (s, 10 H), 7.10 (br, 20 H) ppm. <sup>19</sup>F{<sup>1</sup>H} NMR (282 MHz, CD<sub>3</sub>CN) : δ = 154.5 (m, 2F), 155.2 (m, 2F) ppm. IR (KBr): ν(CO) = 2026 cm<sup>-1</sup>. ESI-MS: 633 (Co(dp<sup>g</sup>BF<sub>2</sub>)<sub>2</sub><sup>-</sup>).

**Electrochemistry of **1** and **2** in the presence of  $[\text{nBu}_4][\text{Cl}]$ .**

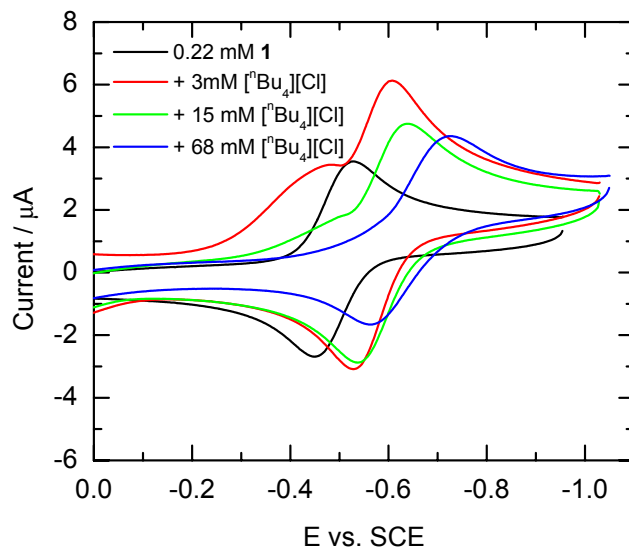


Figure S1. Cyclic voltammogram of **1** in the presence of  $[\text{nBu}_4][\text{Cl}]$  recorded in an acetonitrile solution containing 0.1 M  $[\text{nBu}_4][\text{ClO}_4]$ . Scan rate: 100 mV/s; Glassy carbon working electrode.

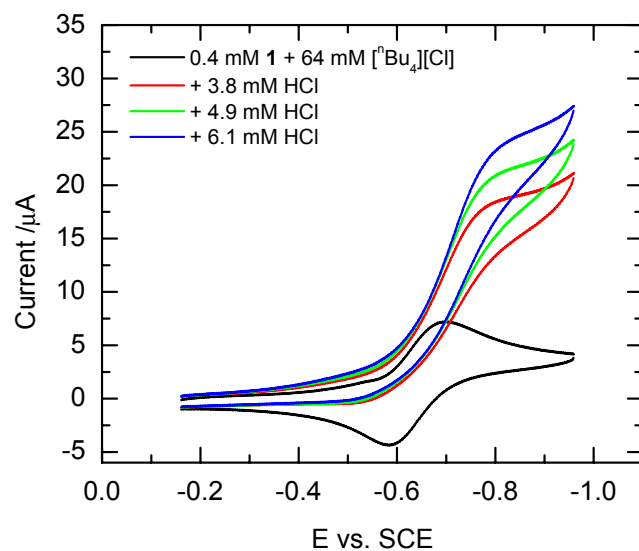


Figure S2. Cyclic voltammogram of **1** in the presence of HCl recorded in an acetonitrile solution containing 0.1 M  $[\text{nBu}_4][\text{ClO}_4]$  and large excess of  $[\text{nBu}_4][\text{Cl}]$ . Scan rate: 100 mV/s; Glassy carbon working electrode.

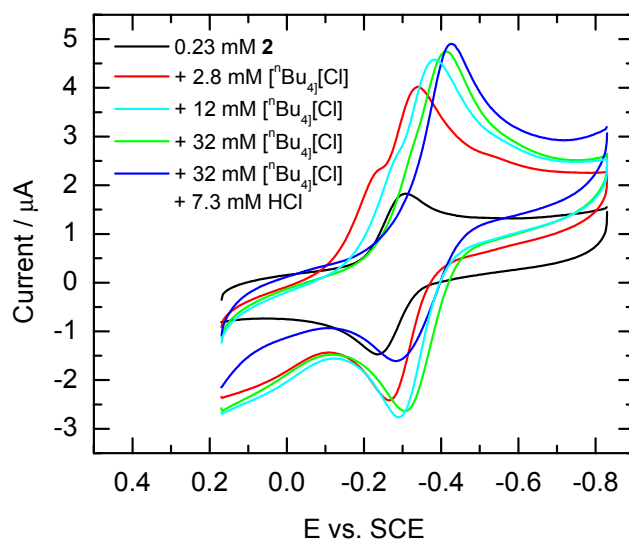


Figure S3. Cyclic voltammogram of **2** in the presence of  $[n\text{Bu}_4][\text{Cl}]$  recorded in an acetonitrile solution containing 0.1 M  $[n\text{Bu}_4][\text{ClO}_4]$ . Scan rate: 100 mV/s; Glassy carbon working electrode.

**Electrochemistry of 1 in the presence of HBF<sub>4</sub>.**

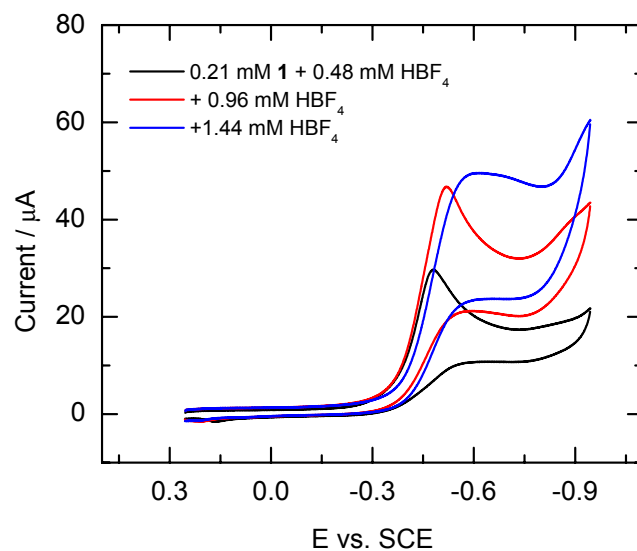


Figure S4. Cyclic voltammogram of **1** in the presence of HBF<sub>4</sub> recorded in an acetonitrile solution containing 0.1 M [<sup>n</sup>Bu<sub>4</sub>][ClO<sub>4</sub>]. Scan rate: 100 mV/s; Glassy carbon working electrode.



**Electrochemistry of 1 and 2 in the presence of CO.**

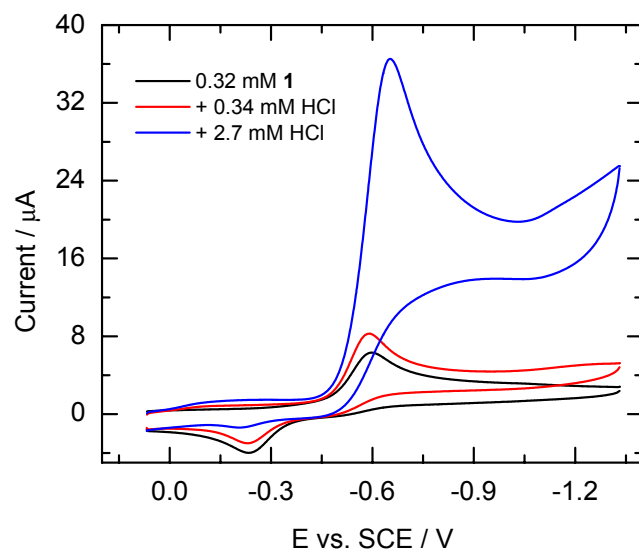


Figure S5. Cyclic voltammogram of **1** in the presence of HCl recorded in an CO saturated acetonitrile solution containing 0.1 M [ $n\text{Bu}_4$ ][ $\text{ClO}_4$ ]. Scan rate: 100 mV/s; Glassy carbon working electrode.

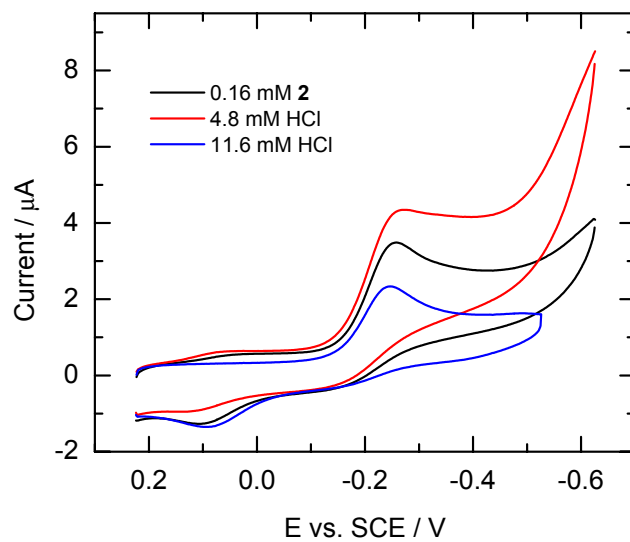


Figure S6. Cyclic voltammogram of **2** in the presence of HCl recorded in an CO saturated acetonitrile solution containing 0.1 M [ $n\text{Bu}_4$ ][ $\text{ClO}_4$ ]. Scan rate: 100 mV/s; Glassy carbon working electrode.

**Electrochemistry of HCl, HBF<sub>4</sub>, and CF<sub>3</sub>COOH without the catalyst.**

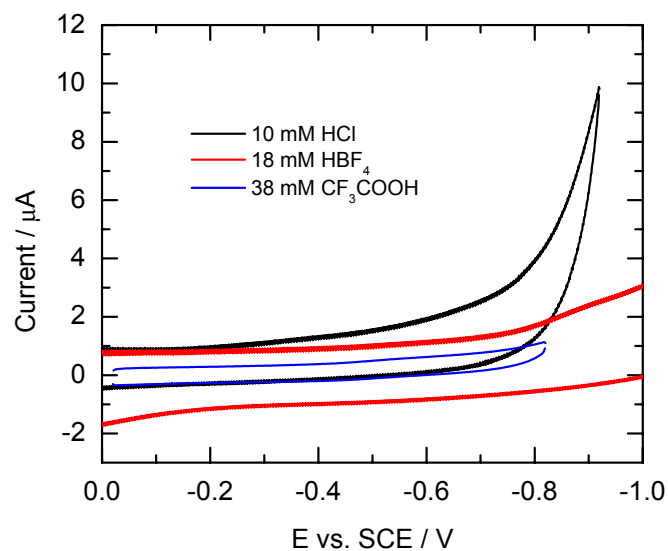


Figure S7. Cyclic voltammogram of HCl, HBF<sub>4</sub>, and CF<sub>3</sub>COOH recorded in an acetonitrile solution containing 0.1 M [<sup>n</sup>Bu<sub>4</sub>][ClO<sub>4</sub>]. Scan rate: 100 mV/s; Glassy carbon working electrode.

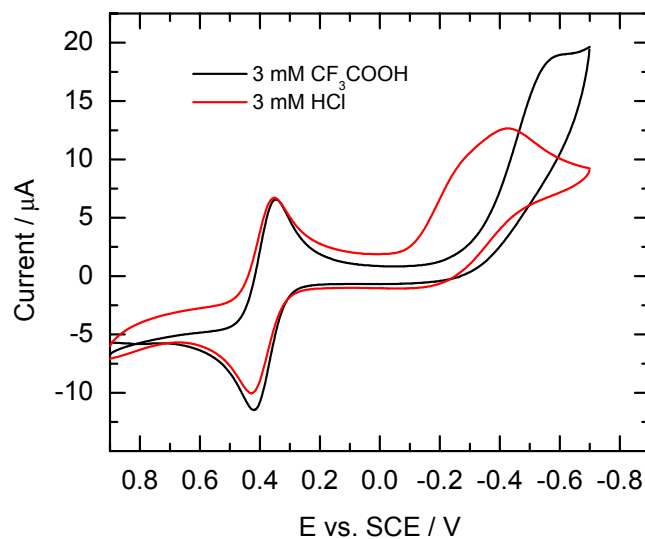


Figure S8. Cyclic voltammogram of HCl and  $\text{CF}_3\text{COOH}$  on a platinum electrode recorded in an acetonitrile solution containing 0.1 M  $[\text{nBu}_4][\text{ClO}_4]$ ; Ferrocene was added as the internal potential reference ( $E^{\circ'} = -0.38$  V). Scan rate: 100 mV/s; Platinum working electrode (BAS PTE, area =  $0.02$   $\text{cm}^2$ ).

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