Supplementary Material:

Evaluating Electrocatalytic Activity for Hydrogen Evolving Cobalt and Nickel Complexes in Solution

Charles C. L. McCrory, Nathaniel K. Szymczak, and Jonas C. Peters
Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA. E-mail: cmccrory@umich.edu, jpeters@caltech.edu

Table of Contents

Figure S1. Controlled-Potential Electrolysis Charge-Time Plots S2

Figure S2. Attempted H2-oxidation by 6 S3
Section S1. Bulk Electrolysis Charge-Time Plots

![Graphs showing bulk electrolysis charge-time plots](image)

**Figure S1.** Bulk electrolysis measurements in a stirred solution of 0.3 mM of 1 (a, c) and 2 (b, d) in the presence of 5.2 mM TsOH (a, b) and 2,6-dichloroanalinium (c, d) measured at -1.01 V vs. Fc/Fc⁺. The solid line is the measured charge as a function of time. The dashed lines are extrapolated from the first 360 s of each plot, and represent the theoretical charge-time curves for a well-stirred system under steady-state control. The numbers in the bottom right corner of each plot are the percentage difference between the measured and theoretical charge at 60 mins. This analysis suggests a much larger deviation from linearity for 2 in TsOH than for 1 in TsOH or either 1 or 2 in 2,6-DCA, consistent with electrochemically-mediated degradation of 2 in TsOH. Note that the Faradaic efficiency averaged over 3-5 experiments for the reduction of 2,6-dichloroanalinium by 1 is ε = 99 ± 3%, and by 2 is ε = 98 ± 4%.
Section S2. Attempted \( \text{H}_2 \text{ Oxidation with 6.} \)

**Figure S2.** Cyclic voltammogram of 0.3 mM 5 with 0.25 mM Et\(_3\)N under Ar (black) and 523 psia H\(_2\) (red). The blue line is in the presence of 240 mM Et\(_3\)N and under 531 psia H\(_2\), but in the absence of 5. (Supporting electrolyte is 0.1 M \((n\text{Bu}_4\text{N})\text{ClO}_4\) in CH\(_3\)CN, scan rate = 0.05 V/s)