1. Introduction

The development of robust hydrogen evolution catalysts that are made of inexpensive and earth abundant materials is of considerable current interest.1 Fe–Ni and Fe–Fe hydrogenases produce dihydrogen in water at close to the thermodynamic potential of −0.41 V vs the normal hydrogen electrode (NHE) at pH = 7.2 However, most known molecular H2 evolution catalysts, based either on the structure of the active site of hydrogenases3 or on metal complexes having simple macrocyclic ligands,4–6 catalyze H2 evolution in organic solvents at fairly negative potentials, from −1.1 to −2 V vs a saturated calomel electrode (SCE).7

A select number of molecular systems reported to date show promise for H2 evolution at more positive potentials. DuBois et al. have shown that a Cp2Mo2S2 system catalyzes electrochemical H2 evolution at −0.26 V vs SCE in CH3CN using p-cyanonilinium as the acid source, and a [Ni(PPh3)2(CH3CN)]2+...
CN)\textsuperscript{2+} system catalyzes H\textsubscript{2} evolution at \(-0.46\) V vs SCE using triflic acid as the acid source.\textsuperscript{8,9} We and others have shown that Co(diglyoxime) complexes evolve H\textsubscript{2} at relatively positive potentials either catalytically or electrocatalytically.\textsuperscript{10–12} For example, Co(dmgBF\textsubscript{2})\textsubscript{2}(CH\textsubscript{3}CN)\textsubscript{2} (1, dmgBF\textsubscript{2} = difluoroboryl-dimethylglyoxime)\textsuperscript{11} catalyzes H\textsubscript{2} evolution in acidic CH\textsubscript{3}CN at \(-0.55\) V vs SCE using CF\textsubscript{3}COOH or HCl as the acid source, whereas Co(dpgBF\textsubscript{2})\textsubscript{2}(CH\textsubscript{3}CN)\textsubscript{2} (2, dpgBF\textsubscript{2} = difluoroboryl-diphenylglyoxime)\textsuperscript{13} produces H\textsubscript{2} at even higher potentials (\(-0.28\) V vs SCE) in acidic CH\textsubscript{3}CN using HCl or HBF\textsubscript{4} or Et\textsubscript{3}O as the acid source (Scheme 1). Similarly, Artero et al. have shown that [Co(dmgH)\textsubscript{2}PyCl][dmgH = dimethylglyoxime] catalyzes H\textsubscript{2} evolution at \(-1.03\) V vs SCE in acidic DMF solutions using Et\textsubscript{3}NHCl as the acid source.\textsuperscript{12}

In this work, we report the electrochemical and electrocatalytic behavior of a series of cobalt complexes having BF\textsubscript{2}-bridged diglyoxime or propane-bridged macrocyclic tetrainime ligands. The behavior of this series of complexes has allowed for the formulation of a correlation between the activity of H\textsubscript{2} evolution and the Co\textsuperscript{II/III} reduction potentials of the various complexes. Electrochemical evidence for Co(III) hydride intermediates is presented, and a plausible mechanism of the H\textsubscript{2} evolution reaction is discussed. Furthermore, complex 1, Co(dmgBF\textsubscript{2})\textsubscript{2}(CH\textsubscript{3}CN)\textsubscript{2}, is shown to be a molecular catalyst able to mediate both H\textsubscript{2} evolution and oxidation, confirming its low overpotential for H\textsubscript{2} evolution. To the best of our knowledge, this is the first such demonstration to be reported for a synthetic catalyst.

2. Results

2.1. Electrocatalytic H\textsubscript{2} Evolution by Cobalt Difluoroboryl-Diglyoximate Complexes 1 and 2. Figure 1 shows the cyclic voltammogram (CV) of 1 (0.3 mM, 0.1 M \([\text{Bu}_4\text{N}]\text{ClO}_4\), CH\textsubscript{3}CN) at a glassy carbon electrode. The reversible redox process shown at \(-0.55\) V vs SCE in the absence of acid was assigned to the Co\textsuperscript{II/III} couple. Upon addition of the monohydrate of toluenesulfonic acid (tosic acid, TsOH)\textsubscript{H}, dpgBF\textsubscript{2} produces H\textsubscript{2} at even higher potentials (0.55 V vs SCE in the absence of acid was observed at a potential close to the formal reduction potential, \(E^\text{\textsuperscript{0}}(\text{Co II/I})\), for Co(III) hydride in solution at potentials more negative than \(-1.0\) V vs SCE, and the background current was found to be negligible at the potentials where catalysis occurred using catalyst 1 or 2. The rise in the catalytic current at \(-0.6\) V vs SCE in Figure 2 is due to the H\textsubscript{2} evolution. The solid-state molecular structure of the Co(III)–H intermediate (vide infra).

2.2. Structural Characterization of Complexes 2 and 3. The solid-state molecular structure of the Co(II) form of catalyst 2 was determined by X-ray crystallography (Figure 3). The refined structure reveals a six-coordinate cobalt(II) ion that is ligated by a planar difluoroboryl-diglyoxime ligand and two trans-oriented acetomimite molecules. The cobalt ion is located on a crystallographically defined inversion center. The observed axial Co–N\textsubscript{nitrite} distance of 2.241(3) Å is much longer than the 1.886(5) Å averaged Co–N\textsubscript{imine} distance in the glyoxime plane. The Co(I) form of the complexes can be conveniently synthesized by chemical methods. For instance, [Co(dpgBF\textsubscript{2})\textsubscript{2}(CH\textsubscript{3}CN)]\textsuperscript{2+} (3) was synthesized by reducing 2 with 1 equiv of Na/Hg or Co(Cp\textsubscript{2})\textsubscript{2} in CH\textsubscript{3}CN. The refined solid-state molecular structure of 3 (Figure 4) contains a five-coordinate cobalt(I) center in a distorted square-pyramidal ligand environment. The Co–N\textsubscript{nitrite} distance is 1.973(2) Å for 3, 0.268 Å shorter than that in 2. Because of this strong Co–N\textsubscript{nitrite} interaction, the cobalt ion is displaced 0.27 Å toward the nitrite ligand from the plane defined by the macroyclic imine ligand. The average Co–N\textsubscript{nitrite} distance of 1.851(6) Å for 3 is slightly shorter (0.035 Å) than that in 2, consistent with expectations for a higher degree of metal to ligand \(\pi\)-backbonding.

2.3. Electrocatalytic H\textsubscript{2} Evolution by Cobalt Macrocyclic Tetrainime Complexes 4a–6b. Complexes 4a–6b\textsuperscript{17–20} (Scheme 1).

2) each exhibited reversible cyclic voltammetric behavior for the CoII/III redox couple, with $E^\circ$ values vs SCE in CH$_3$CN of −0.38 V for 4a, −0.35 V for 4b, −0.25 V for 5a, −0.20 V for 5b, −0.15 V for 6a, and −0.08 V for 6b. The value of $E^\circ$ shifted by ~60 mV as a result of each substitution of a methyl group on the Tim ligand by the more electron-withdrawing phenyl group. This potential shift is comparable to the 65 mV potential shift that results from the substitution of phenyl for methyl in the cobalt difluoroboryl-diglyoxime complexes, 1 vs 2. Substitution of two anionic bromide ligands by two neutral acetonitrile ligands shifted the potential by 20, 50, and 70 mV for 4a to 4b, 5a to 5b, and 6a to 6b, respectively. The axial bromide ligands in 4a, 5a, and 6a were not replaced by acetonitrile upon dissolution in acetonitrile, as such solutions remained green, indicative of the bromide complexes, rather than turning pale-yellow indicative of the acetonitrile adduct complexes. All bromide complexes exhibited reversible CoIII/II behavior.

showed that the catalysis by 4b (21) Assuming etherated HBF$_4$ completely dissociates into etherated proton and no redox waves for their Co III/II couples between 0.3 V to couples (Table 2), while all acetonitrile complexes exhibited no redox waves for their Co II/I form on the time scale of the CV measurements.

Figure 5 shows the CV of 4a. In CH$_3$CN with 0.1 M [Bu$_4$N][ClO$_4$], reversible reductions were observed for the Co III/I couple at ~0.06 V vs SCE and for the Co II/I couple at ~0.38 V vs SCE. Addition of TsOH-H$_2$O to an unstirred solution of 0.15 mM 4a (0.1 M [Bu$_4$N][ClO$_4$] in CH$_3$CN) produced a catalytic wave at a potential close to the position of $E^{\circ'}$(Co III/I) for 4a. At low acid concentrations, the catalytic wave had a peak-like shape, but for higher acid concentrations the current approached a plateau at potentials more negative than $E^{\circ'}$(Co III/I). The potential at which catalysis took place remained nearly constant with increasing acid concentration. No catalytic waves were observed at potentials near the $E^{\circ'}$(Co III/I), consistent with the fact that this potential was significantly more positive than the thermodynamic potential for hydrogen evolution using tosic acid as the proton source (vide infra). Similar behavior was observed when HBF$_4$-Et$_2$O was used as the proton source (Figure S1, Supporting Information). Hence, complex 4a is a catalyst for electrochemical H$_2$ evolution in acidic CH$_3$CN solutions, and the catalysis is associated with reduction of the Co(II) complex to its Co(I) state.

Complex 4b was also found to catalyze electrochemical H$_2$ evolution in acidic CH$_3$CN solutions, when either TsOH-H$_2$O or HBF$_4$-Et$_2$O was the acid. As for 4a, the CV (Figure S2) showed that the catalysis by 4b occurred at the Co II/I potential.

The CV of 5a and 5b in CH$_3$CN solutions did not vary upon addition of TsOH-H$_2$O. However, catalytic proton reduction was observed when HBF$_4$-Et$_2$O (pK$_a$ = 0.1)\(^{21,22}\) was used as the proton source (Figure S3). This behavior suggests that the proton activity obtained with TsOH-H$_2$O (pK$_a$ = 8.0)\(^{22,23}\) is not high enough to produce dihydrogen from the Co(I) forms of complexes 5a and 5b. Complexes 6a and 6b were also probed for electrochemical hydrogen evolution, but no catalysis was observed using either TsOH-H$_2$O or HBF$_4$-Et$_2$O as the acid source. In addition, no catalysis was observed for complexes 4a–6b when the weak acid CF$_3$COOH (pK$_a$ = 12.7)\(^{22,23}\) was used as the acid source.

2.4. Stability of Co Macrocyclic Tetraimine Complexes in the Presence of Acid. The stability of 4a–5b in the presence of excess acid was evaluated by electronic absorption spectroscopy (monitored at ~400 nm for 4a and 5a, and ~270 nm for 4b and 5b). These complexes showed negligible degradation over a period of several days in the presence of a 25-fold excess of TsOH-H$_2$O (10 mM), suggesting that these complexes are more acid tolerant than 1 and 2. Under the same conditions, 1 degraded ~10% in 1 h and 2 degraded ~10% in 4 h. Complexes 4a–5b degraded in the presence of excess HBF$_4$-Et$_2$O but more slowly than 1 and 2. For example, 4a and 4b degraded only 5% in 2 h in the presence of a 30-fold excess of HBF$_4$-Et$_2$O (3 mM), while under the same conditions 1 and 2 degraded completely within minutes.\(^{10}\) The Co(II) complexes [Co$_4$ (Tim$_{Me/Ph}$)](CH$_3$CN)$_2$\(^2+\) (4c) and [Co$_4$ (Tim$_{Me/Ph}$) (CH$_3$CN)$_2$\(^2+\) (5c) had stabilities that were similar to those for 4b and 5b, respectively.

2.5. Catalytic Efficiency of Co Tetraimine Complexes for H$_2$ Evolution as Determined by Bulk Electrolysis. Previous bulk electrolysis experiments indicated that the catalytic currents observed by cyclic voltammetry for complexes 1 and 2 were associated with electrocatalytic evolution of H$_2$, with approximately quantitative faradaic yields for H$_2$ production. Turnover numbers (TNs) were >5 (TN = moles of hydrogen produced divided by moles of catalyst used) were observed, without appreciable decomposition of the catalysts.\(^{10}\) To evaluate the behavior of the Co tetracyclical complexes, analogous bulk electrolysis experiments were performed with solutions of 4a–5b (Table 1). During bulk electrolysis potentials were applied at ~0.58 V (for 4a–b) or ~0.48 V (for 5a–b) vs SCE. Solutions that contained an excess of acid and catalysts 4a–5b turned from green to red-purple upon electrolysis. This behavior suggested that under such conditions the catalyst was reduced to Co(II) form, [Co$_4$ (Tim$_{Me/Ph}$)](CH$_3$CN)$_2$\(^2+\) (4c) or [Co$_4$ (Tim$_{Me/Ph}$) (CH$_3$CN)$_2$\(^2+\) (5c).\(^{19}\) The CV of 4c and 5c was identical to that of 4b and 5b.

When a cobalt complex having a Tim$_{Me}$ ligand (4a–4c) was used in bulk electrolysis experiments, H$_2$ was produced (as determined by GC–MS) in quantitative faradaic yields (Table 1). After five turnovers, no deactivation of the catalyst was observed. However, when a cobalt complex having the Tim$_{Me/Ph}$ ligand (5a–5c) was used as the catalyst, the faradaic yield for H$_2$ production was only 20–25%. After two turnovers, appreciable deactivation of the catalyst was observed. The lower faradaic yields observed for 5a–5c most likely reflect the decomposition of intermediate species during the course of electrolysis, rather than the acid sensitivity of the precatalysts, since 5a–5c are in fact somewhat more stable in the presence of an excess of acid than are 4a–4c.

2.6. Kinetic and Mechanistic Analysis. CV data for complexes 1, 2, 4a, and 4b were obtained as a function of acid and catalyst concentrations.\(^{24}\) The CV of the catalysts, with no added acid, had well-defined reversible Co IV reductions (peak separations of 80 ± 10 mV). The potentials for all the complexes are shown in Table 2. The diffusion coefficient for each catalyst, 4a–6b when the weak acid CF$_3$COOH (pK$_a$ = 12.7)\(^{22,23}\) was used as the acid source.
determined by simulation of its CV in the absence of acid, is shown in Table 2.

The overall rate constant for H$_2$ evolution may be estimated from the height of the catalytic plateau current at high overpotentials.$^{14,15}$ A plateau shape is only observed when the rate of the reduction of the catalytic species at the electrode is equal to the rate of its reoxidation by the acid. Additionally, the acid concentration in the reaction region must not be depleted.$^{14,15}$ Under these conditions, for a reaction that is first order in both catalyst and acid, the value of the current in the plateau region is given by

$$i_c = nFE^{°}C_p(\frac{D}{S})^{1/2}$$  

(1)

where $n$ is the number of electrons, $i_c$ is the plateau current (mA), $F$ is Faraday’s constant (96 485 C mol$^{-1}$), $S$ is the area of the electrode surface (cm$^2$), $C_p$ is the bulk concentration of redox active species (M), $D$ is the diffusion coefficient (cm$^2$ s$^{-1}$), $i$ is the reaction rate constant (M$^{-1}$ s$^{-1}$), and $C_i$ is the bulk concentration of acid (M).$^{14,15}$

The dependence of $i_c$ on the concentrations of catalyst and acid was measured for the complexes. For H$_2$ evolution catalyzed by 1 or 4a using TsOH$\cdot$H$_2$O as the acid, the catalytic waves did not exhibit, but approached, a plateau shape under certain conditions. The peak values of such catalytic currents were taken as approximations for the values of the plateau currents. As shown in Figure 6, for catalysis by 1, the catalytic rate was found to be first order in the concentration of acid and less than first order in the concentration of catalyst. For catalysis by 4a, the catalytic rate was found to be first order in the concentrations of both acid and catalyst (Figure S4).

The catalytic waves reached a plateau shape using 2 or 4b as the H$_2$ evolution catalyst when the concentration of TsOH$\cdot$H$_2$O was much larger than that of the catalyst. In these cases, the catalytic rate followed a first-order dependence on the concentration of both acid and catalyst (Figures S5–S6). Approximate catalytic rate constants, $k_{app}$, with TsOH$\cdot$H$_2$O were obtained using eq 1 (Table 2).

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**Table 1. Summary of Bulk Electrolysis Results**

<table>
<thead>
<tr>
<th>complex</th>
<th>proton source</th>
<th>concn of catalyst (mM)</th>
<th>concn of acid (mM)</th>
<th>volume (mL)</th>
<th>potential (V vs SCE)</th>
<th>duration (min)</th>
<th>charge (coulomb)</th>
<th>faradaic yield for H$_2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>TsOH$\cdot$H$_2$O</td>
<td>0.9</td>
<td>21</td>
<td>100</td>
<td>−0.58</td>
<td>30</td>
<td>49</td>
<td>~90</td>
</tr>
<tr>
<td>4b/4c</td>
<td>TsOH$\cdot$H$_2$O</td>
<td>0.8</td>
<td>22</td>
<td>100</td>
<td>−0.58</td>
<td>30</td>
<td>54</td>
<td>~100</td>
</tr>
<tr>
<td>5a</td>
<td>HBF$_4$$\cdot$Et$_2$O</td>
<td>0.9</td>
<td>20</td>
<td>100</td>
<td>−0.48</td>
<td>30</td>
<td>15</td>
<td>~20</td>
</tr>
<tr>
<td>5b/5c</td>
<td>HBF$_4$$\cdot$Et$_2$O</td>
<td>0.7</td>
<td>20</td>
<td>100</td>
<td>−0.48</td>
<td>30</td>
<td>16</td>
<td>~25</td>
</tr>
</tbody>
</table>

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**Figure 6.** Dependence of the catalytic plateau current, $i_c$, on the concentrations of catalyst (top) and acid (bottom) for complex 1; TsOH$\cdot$H$_2$O was used as the acid, with a scan rate of 100 mV/s and $S = 0.07$ cm$^2$. In the plots the plateau current was set to zero in the absence of acid, as predicted by eq 1, even though the catalyst has a nonzero peak current under such conditions.

---

Digital simulations of the cyclic voltammetric data were performed to study the mechanism of electrocatalytic H$_2$ evolution for complexes 1, 2, 4a, and 4b. The CV was simulated assuming either a monometallic or a bimetallic mechanism (Scheme 3) for H$_2$ formation.

For catalysis by 1, when a monometallic mechanism (eqs 2–6) was assumed, it was not possible to use a common set of parameters to simulate the CV for a given concentration of catalyst in the presence of incremental amounts of TsOH$\cdot$H$_2$O. The simulated currents increased with acid (TsOH$\cdot$H$_2$O) much more rapidly than observed experimentally. In addition, the simulated CV maintained its peak-type shape at all concentrations of acid used experimentally, while the experimental CV approached a plateau shape as the acid concentration increased. Hence, electrocatalytic H$_2$ evolution by 1 is not dominated by a simple monometallic mechanism.

Simulation of the CV for catalyst 1 assuming a bimetallic mechanism (eqs 2–4 and 7) gave rise to a more satisfactory simulation of the experimental data for a given concentration.
of catalyst in the presence of incremental amounts of TsOH-H₂O (Figures S7 and S8). However, for different concentrations of catalysts, the rate constants obtained were different. At lower catalyst concentration larger rate constants were obtained ([I] = 0.22 mM; k₄ = 1.5 × 10⁶ M⁻¹ s⁻¹, k₅ = 1.5 × 10⁸ M⁻¹ s⁻¹) than at higher catalyst concentration ([I] = 1.0 mM; k₄ = 7 × 10⁷ M⁻¹ s⁻¹, k₅ = 9 × 10⁶ M⁻¹ s⁻¹) (Figures S7 and S8).

The changes in calculated rate constants with catalyst concentration are consistent with Figure 6, which suggests that the catalysis by 1 is less than first order in catalyst. Therefore the CV data indicate that the production of H₂ is most likely to proceed by a bimetallic pathway; however, direct kinetic evidence to support this conclusion is needed.

For catalysis by 4a, a monometallic mechanism was also ruled out because simulations indicated that a monometallic pathway would give rise to catalytic waves for the oxidation of H₂ by Co(III) (step 5) at the Co(III) potential. These oxidative catalytic currents were not observed in our experiments. On the other hand, a bimetallic mechanism with the same set of rate constants can be used to simulate the catalytic waves from two different concentrations of catalyst in the presence of incremental amounts of acid (Figures S9 and S10).

For catalysis by 2 and 4b, the catalytic waves can be crudely simulated using either a monometallic or a bimetallic mechanism. Simulation itself therefore does not distinguish between these two mechanisms without prior knowledge of the equilibrium constants and/or reaction rates of the key chemical steps (Figures S11–S14).

2.7. Evidence for a Cobalt(III) Hydride Intermediate. In the presence of TsOH-H₂O, a quasi-reversible redox wave for complex 1 was observed when the potential was scanned negative of E°°(Co(II)) (Figure 7); however, no catalytic wave was observed at this reduction potential. In the absence of acid, no such wave was observed. We tentatively assign this wave to the “Co(III)=H”/“Co(II)=H” redox couple produced by the putative [HCo(CH₂CN)(dmgbF₂)₂] intermediate formed in situ upon reduction of 1 in the presence of acid (see discussion). The electrochemistry of course cannot distinguish between a cobalt or ligand centered reduction of the Co(III)=H.

No reversible redox wave for a Co(III)=H/Co(II)=H couple was observed for 2. Instead, a catalytic wave was observed at a potential of −0.85 V vs SCE, i.e., 570 mV more negative than the value of E°°(Co(II)) for 2 (Figure S15).

Redox waves for the Co(III)=H/Co(II)=H couple were also observed for 4a → b (Figure S16). In contrast, for complexes 5a → b in the absence of acid, at potentials close to those expected for the Co(III)=H/Co(II)=H couples, redox waves were observed. This reduction of a Co(I) species is likely a ligand-centered redox process. The intermediacy of a Co(III)=H could therefore not be ascertained from the cyclic voltammetric data for these two complexes.

2.8. Hydrogen Oxidation. We have studied the cobalt complexes 1 and 2 to determine their ability to electrocatalytically oxidize hydrogen under 1 atm of H₂ in CH₂CN solutions buffered with either [Bu₄N][CF₃CO₂] (for 1) or [Bu₄N][TsO] (for 2). No oxidation activity could be detected at scan rates between 100 and 1000 mV per second near the Co(II/I) potential; however, we observed that H₂ was oxidized by 1 in the presence of [Bu₄N][CF₃CO₂] in CH₂CN over a period of several days, reaching an equilibrium mixture represented by eq 8 (Figure 8).

\[
[\text{Co}^{II}(\text{dmgbF}_2)_2(\text{CH}_2\text{CN})] + \frac{1}{2}\text{H}_2 + \quad [\text{NBu}_4][\text{CF}_3\text{CO}_2] \leftrightarrow \text{CF}_3\text{COOH} + \\
[\text{Co}^{I}(\text{dmgbF}_2)_2(\text{CH}_2\text{CN})][\text{NBu}_4] + \text{CH}_2\text{CN}
\]

As shown in Figure 8, when 1 atm of H₂ was initially added to a solution of 1.6 mM 1 in the presence of 66 mM [NBu₄][CF₃CO₂], the solution maintained its yellow color, indicative of the [Co⁸(dmgbF₂)₂(CH₂CN)₂] species in solution. With time, the solution gradually turned dark blue, indicative of the formation of [Co⁹(dmgbF₂)₂(CH₂CN)₂⁺] in the reaction medium. After 34 h, the reaction reached equilibrium, and the concentrations of [Co⁸(dmgbF₂)₂(CH₂CN)₂] (0.55 mM) and [Co⁹(dmgbF₂)₂(CH₂CN)₂⁺] (1.05 mM) were determined using their extinction coefficients at 630 nm (for Co(I)) and 440 (for Co(II)). The absence of isosbestic points in Figure 8 suggests the possibility that some degradation occurs over prolonged periods of time under these conditions, perhaps due to side reactions that reduce the...
unsaturated ligand backbone. The equilibrium constant for eq 8 is approximated to be 0.03 atm−1/2, corresponding to an overpotential of approximately 90 mV for H2 evolution by catalyst 1. We were not able to observe similar H2 oxidation by 2 in the presence of [nBu4N][TsO] in CH3CN over a few weeks, indicating that H2 oxidation by 2 was appreciably slower.

3. Discussion

3.1. Structural Aspects of Co Diglyoxime Complexes. Complex 2 is the only crystallographically characterized cobalt(I) complex with the (dpgBF2)2 ligand. The salient features of its structure are similar to those of Co(dmgBF2)2(CH3OH)2, which has an average Co−N(imine) distance of 1.876(4) Å and a Co−O(CH3OH) distance of 2.264(4) Å.25

Complex 3 is the only crystallographically characterized cobalt(I) complex of the (dpgBF2)2 ligand. In general, structurally characterized cobalt(I) complexes with macrocyclic imine ligands are rare. Espenson and co-workers reported the structurally related complex [Co(dmgBF2)(py)][nBu4N], in which the Co(I)−N(imine) bond has an average distance of 1.839(3) Å, also shorter than the corresponding bond (1.878(4) Å) in its Co(II) analogue.26 The bond contraction was also attributed to a higher degree of π-back-bonding in the cobalt(I) complex.26 The cobalt(I) center is displaced 0.26 Å toward the pyridine ligand above the macrocyclic plane of the (dmgBF2)2 ligand.

3.2. Mechanistic Aspects of Electrocatalytic H2 Evolution from the Cyclic Voltammetric Behavior of Co Macrocycles. The electrochemistry of 1 and 2 (Scheme 1) had been previously investigated in the presence of CF3COOH (pKa = 12.7 in CH3CN), HCl−Et2O (pKa = 8.9), and HBF4−Et2O (pKa = 0.1).21−23 Catalytic waves were observed corresponding to hydrogen evolution near the value of E′′(CoII/CoI)(−0.55 V for 1 and −0.28 V for 2 in CH3CN vs SCE), using HBF4−Et2O, HCl−Et2O, and CF3COOH as the acids for 1, and HBF4−Et2O and HCl−Et2O as the acids for 2.10 The presence of a large excess of coordinated chloride anion had a profound influence on the shape and position of the observed catalytic waves when HCl−Et2O was used as the acid. Thus we have used p-toluenesulfonic acid (TsOH-H2O, pKa = 8.0) in this study.22,23 which is similar in acid strength to HCl−Et2O, but features a much more weakly coordinating counterion.

A clear correlation was observed between the activity toward H2 evolution and the CoII/CoI potentials of the catalysts, with those complexes having more negative CoII/CoI potentials being more active. For the cobalt catalysts investigated here, the complex with the most negative CoII/CoI reduction potential, 1, mediated H2 evolution using the weakest acid CF3COOH (pKa = 12.7),21 while the complexes with more positive potentials, 2, 4a, and 4b, required stronger acids, such as TsOH-H2O (pKa = 8.0). The complexes with the most positive potentials, 5a and 5b, required an even stronger acid, such as HBF4−Et2O (pKa = 0.1). For complexes that are more readily reduced than 5b, such as 6a and 6b, no catalysis was observed even with HBF4−Et2O as the acid. When using the same acid, the more negative the CoII/CoI potential, the faster the catalysis (Table 2). These observations reflect that the basicity of the active Co(I) species is related to its CoII/CoI redox potential. A similar trend has been observed by Collman and co-workers for cofacial bis(alkyl) diporphyrin complexes that also catalyze H2 evolution, but at much more negative potentials (−1.2 to −1.8 V vs SCE) than those for the Co macrocycles investigated here.5 The more easily reduced diporphyrin complexes produced H2 at more positive potentials but required stronger acids to achieve reasonable reaction rates.5

For the electrocatalysts examined here, H2 evolution occurred at potentials just negative of the E′′(CoII/CoI) values for the complexes. Thus H2 production required prior generation of the Co(I) species. This conclusion is in accord with that of Espenson and co-workers, who studied the evolution of H2 using Co-(dmgBF2)2(H2O)2 as the catalyst, CrCl3 as the electron donor, and HCl(aq) as the proton source.11 Stopped-flow kinetics experiments in that system allowed identification of a chloride-bridged complex [(H2O)CrCl−Co(dmgBF2)2]+ as an intermediate. This intermediate was suggested to decompose to a cobalt(I) species [LCo(dmgBF2)2]+, which thereafter reacted with a proton to form a cobalt(III) hydride, [H−Co(L)(dmgBF2)2]+.11 The Co(III) hydride was presumed to react further to produce H2. Two mechanisms were considered: one that involved the protonation of the hydride ligand to produce H2, and the other involving a bimetallic reaction of two Co(III) hydrides.11

Similar mechanisms can be envisioned for electrocatalytic H2 evolution by the catalysts 1−2 and 4a−5b, except that the active Co(I) species is generated electrochemically (Scheme 3). The CV of the CoII/CoI couples, with no added acid, was electrochemically reversible. Thus the rates of interfacial electron transfer from the electrode to the Co(II) catalysts are faster than
the rate of diffusion of the Co(II) species to the electrode surface.\textsuperscript{14} The electrocatalysis differs from the chemical catalysis because the reduction of the Co(II) by chromous ion is slow ($k \approx 0.25$ s$^{-1}$ for generation of [Co(dmgBF$_2$)$_2$]$^{2+}$ from [H$_2$O]-Cr$^{-}$(Co(dmgBF$_2$)$_2$)$^{3+}$) and rate limiting for H$_2$ evolution. The electrochemical H$_2$ evolution studied here in CH$_3$CN is much more rapid.

The presumed Co(III)$\rightarrow$H complexes that are formed upon protonation of the Co(I) can in principle be further reduced to form Co(II)$\rightarrow$H species, which could go on to produce H$_2$. We have not been able to synthesize a genuine Co(III)$\rightarrow$H complex with (dmgBF$_2$)$_2$, (dpqBF$_2$)$_2$, or Tim$_8$ ($R = M_{e}, M_{e}/P_{h}$, and Ph) as the supporting ligand. Protonation of the Co(I) species with toxic acid, CF$_3$COOH, or anisidinium (pK$_a$ = 11.8)\textsuperscript{22} gave Co(II) complexes with the corresponding ligands, with no evidence for the formation of a long-lived cobalt(III)$\rightarrow$H species. Likewise, reduction of the Co(III) halide complexes with NaBH$_4$ or NaEt$_3$BH gave similar Co(II) products. This would be consistent with a Co(III)$\rightarrow$H species that can bimolecularly release H$_2$ at a rate that precludes its isolation (eq 7 in Scheme 3). The potentials for reported Co(III) complexes of cobalt(III) alkyl complexes RCo(dmgBF$_2$)$_2$(H$_2$O) ($R = C_{3}H_{7}, C_{6}H_{5}, n-C_{3}H_{7}$) are $-1$ V vs SCE.\textsuperscript{27} We expect that the potential for the Co(III) couple of cobalt(III) hydride complexes, HCo(dmgBF$_2$)$_2$(L), should be similar to that of RCo(dmgBF$_2$)$_2$(L) and be significantly more negative than $E^\circ$(Co(II)) for the parent Co(dmgBF$_2$)$_2$(L)$_2$. Because electrocatalysis occurs near the measured value of $E^\circ$(Co(II)) for all of the catalysts studied here, the intermediacy of a Co(II)$\rightarrow$H species seems highly unlikely. More negative potentials, however, could facilitate a pathway for H$_2$ evolution that is mediated by a Co(II)$\rightarrow$H species.

Scheme 3 shows two limiting reaction pathways for the formation of H$_2$ from a cobalt(III) hydride. The measured potentials for the reductions of the Co(III) and Co(II) couples (eqs 2 and 3) along with the H$_2$ evolution potential\textsuperscript{22,28--30}:

\[
HA + e^- \rightarrow H_2 + A^- \quad E^\circ(\text{HA})
\]

yield the equilibrium constant for the following monometallic reaction:

\[
\text{Co(I)} + 2 HA \rightarrow \text{Co(III)} + H_2 + 2A^- \quad K_{\text{mono}}
\]

We obtain

\[
eq 2 \times eq(9) - eq(2) - eq(3)
\]

and

\[
K_{\text{mono}} = \exp \left\{ \frac{e(2E^\circ(\text{HA}) - E^\circ(\text{Co}^{\text{III}}) - E^\circ(\text{Co}^{\text{II}}))}{k_B T} \right\}
\]

or

\[
K_{\text{mono}} = \exp \left\{ \frac{[e(E^\circ(\text{HA}) - E^\circ(\text{Co}^{\text{III}})) + (E^\circ(\text{HA}) - E^\circ(\text{Co}^{\text{II}}))]}{k_B T} \right\}
\]

where $e$ is the charge on the electron, $k_B$ is the Boltzmann constant, and $T$ is the temperature. The values of $E^\circ(\text{HA})$ have been estimated as $-0.51$, $-0.23$ and $+0.23$ V vs SCE for

| Table 3. Equilibrium Constants for the Reduction of an Acid by the Co(I) Complexes |
|----------------------------------|---|---|
| acid                             | pK$_{\text{mono}}$ | pK$_{\text{bi}}$ |
| CF$_3$COOH                       | 1  | -1.13 |
| TsOH$\cdot$H$_2$O                | 1  | -1.9  |
| HBF$_3$$\cdot$Et$_3$O            | 1  | 13.7  |
| CF$_3$COOH                       | 2  | -17.6 |
| TsOH$\cdot$H$_2$O                | 2  | -8.1  |
| HBF$_3$$\cdot$Et$_3$O            | 2  | 7.4   |
| CF$_3$COOH                       | 4a | -9.9  |
| TsOH$\cdot$H$_2$O                | 4a | -0.34 |
| HBF$_3$$\cdot$Et$_3$O            | 4a | 15.2  |

CF$_3$COOH, TsOH$\cdot$H$_2$O, and HBF$_3$$\cdot$Et$_3$O, respectively (vide infra).\textsuperscript{28,29}

The equilibrium constant for the bimetallic pathway can also be estimated in a similar manner with

\[
2\text{Co(I) + 2 HA} \rightarrow 2\text{Co(II) + H}_2 + 2\text{A}^- \quad K_{\text{bi}}
\]

and

\[
K_{\text{bi}} = \exp \left\{ 2(2E^\circ(\text{HA}) - E^\circ(\text{Co}^{\text{III}}))/k_BT \right\}
\]

Calculations for the mono and bimetallic equilibrium constants are shown in Table 3 for CF$_3$COOH, TsOH$\cdot$H$_2$O, and HBF$_3$$\cdot$Et$_3$O. For complex 1 and 2 the monometallic reduction of acid, K$_{\text{mono}}$ is very unfavorable, except in the presence of the strongest acid HBF$_3$$\cdot$Et$_3$O. However, K$_{\text{bi}}$ is generally favorable except for complexes 2 and 4a with the weakest acid, CF$_3$COOH.

The complete reaction for the reduction of acid by the Co(I) complex for either pathway is given by eq 13. For the monometallic pathway, the reduction of the acid by Co(I), eq 10, must be driven by the comproportionation reaction of Co(III) produced in eq 10 with Co(I). It seems unlikely that a very unfavorable equilibrium constant of less than $1 \times 10^{-10}$ can be compensated by the reduction of Co(III). The monometallic pathway is only likely to be important for very strong acids and/or complexes with a relatively negative Co(III)/II potential. A similar argument has been made by Spiro et al. to rule out a monometallic mechanism in a cobalt catalyzed hydrogen evolution system.\textsuperscript{31}

The kinetics of the bimetallic pathway can be derived using a steady state approach (see Supporting Information for details). Two limiting rate laws result. One applies when the protonation step (eq 4) is fast:


\textsuperscript{(29) We chose a potential of $-0.14$ V vs Fc/Fc$^+$ (i.e., $0.24$ V vs SCE using [Bu$_4$]ClO$_4$ as the electrolyte, see ref 30) as the thermodynamic potential for H$^+/\text{H}_2$ in acetonitrile. This potential was determined by Daniele, S., et al. using platinumized platinum as the working electrode. A reversible H$^+/\text{H}_2$ couple was observed in acetonitrile, and the potential for this couple corresponds to the true thermodynamic potential for this reaction. It is noted, however, that Parker, V. D., et al. (J. Am. Chem. Soc. 2004, 126, 2738--2743) estimated values of $-0.05$ V and $-0.07$ V vs Fc/Fc$^+$, respectively, for H$^+/\text{H}_2$ in acetonitrile, based on the junction potential between aqueous and acetonitrile solutions.}


\textsuperscript{(31) Kellett, R. M.; Spiro, T. G. Inorg. Chem. 1985, 24, 2373--2377.}
This rate law requires a second-order dependence on the concentrations of Co(I) and acid and an inverse second-order dependence on the concentration of the conjugate base of the acid. The square of the equilibrium constant appears as would be expected for a rapid pre-equilibrium. Our electrochemical data do not support this rate law since a first-order dependence on cobalt and acid is observed, except for complex 1 where the dependence on cobalt was less than first order. The second limiting scenario occurs when the formation of Co(III)−H is rate limiting (eq 4) and the subsequent reactions are fast. For this case we obtain

\[
Rate = k_2 [\text{Co(I)}][\text{HA}] [A^-]^{-1}
\]

The rate is first order in both acid and cobalt, and only the kinetics of the formation of the hydride are important. This case is consistent with most of the observations.

Digital simulation of the cyclic voltammetric data was used to study the mechanism of the H2 evolution catalysis. The simulations suggest that catalysis by I and 4a proceeds, at least predominantly, through a bimetallic mechanism. This is consistent with the previous study by Espenson and co-workers on the mechanism of stoichiometric H2 formation from a kinetically stabilized Co(III)−H species, \( \text{HCo(P}^\text{Bu}_3)\text{(dmgH}) \). Espenson’s study suggested that H2 was formed predominantly by the bimetallic mechanism (eq 7) with a rate constant of \( 1.7 \times 10^4 \) M\(^{-1}\) s\(^{-1}\); however, H2 was also formed by protonation of \( \text{HCo(P}^\text{Bu}_3)\text{(dmgH}} \) (eqs 5 and 6), albeit with a much lower rate constant of \( 0.42 \) M\(^{-1}\) s\(^{-1}\). Simulations were not able to distinguish the bimetallic and monometallic pathways for catalysis by 2 and 4b.

After submission of this manuscript, a related study by Artero et al. on the electrocatalytic H2 evolution by I appeared. Their simulation studies led them to conclude that H2 evolution proceeded via a monometallic mechanism at the Co(III) potential when the p-cyanoanilinium cation \( (pK_a = 7.6 \text{ in CH}_3\text{CN}) \) was used as the proton source. The bimetallic mechanism was ruled out by the authors based on the fact that it could not be simulated to fit the data obtained using different acids (\( \text{CF}_3\text{COOH}, \text{p-cyanoanilinium, and Et}_3\text{NH})\)). Surprised by the discrepancy between our electrochemical conclusions using tosic acid and those of Artero and co-workers using p-cyanoanilinium, we undertook an independent evaluation of H2 evolution catalysis by I using p-cyanoanilinium as the acid in our lab. When collected under the same conditions as those reported by Artero et al., our experimental data were consistent. Additionally, we examined the electrocatalysis with an acid/catalyst ratio larger than 10, which was not presented in Artero’s paper (Figures S17–18). We found that both the monometallic and bimetallic mechanisms can be used to satisfactorily simulate the experimental data when the acid/catalyst ratio is ca. 10 or less. However, only by assuming a bimetallic mechanism can the simulated catalytic waves match the experimental waves collected over the entire range of acid/catalyst ratios (1/1–40/1).

### 3.3. Observation of Co(III)−H Intermediates in H2 Evolution

Evidence for a cobalt(III)−hydride intermediate was obtained by the observation of a nearly reversible Co(III)−H/Co(II)−H couple \( (E^{\text{pr}} \approx -1.0 \text{ V vs SCE}) \) for the \( \text{[HCoCH}_2\text{CN(dmgBF}}_2\text{)]} \) intermediate species formed in situ upon reduction of the Co(II) species in the presence of acid (Figure 7). As mentioned above the \( E^{\text{pr}} \) value for this redox wave is close to the \( E^{\text{pr}} \) of -1.1 V vs SCE that has been observed for various \( \text{RCo(dmgBF}}_2\text{)} \) (R = \( \text{CH}_3, \text{C}_2\text{H}_5, \text{n-C}_3\text{H}_7 \)) complexes.

When the catalysis at the Co(III) potential of the original complex is rapid and the concentration of acid is not too large, the concentrations of acid and Co(III)−H in the reaction layer near the electrode at the Co(III)−H/Co(II)−H potential will be low. Therefore, only small amounts of Co(II)−H are formed at steady state. The Co(II)−H would then react only slowly due to the low concentrations of Co(II)−H and acid. This would enable a reoxidation wave for what is presumably an even more reactive Co(II)−H species to be observed, as shown in Figure 7. Similar observations have been made by Artero et al. on H2 evolution catalysis by I using a p-cyanoanilinium salt as the acid.

No reversible redox wave for a Co(III)−H/Co(II)−H couple could be observed for 2. Rather, a catalytic wave was observed at a potential ~570 mV more negative than those for the Co(III) potential. This catalytic wave can be attributed to electrocatalytic H2 evolution by a Co(II)−H species \( \text{[HCo(CH}_3\text{CN(dpgBF}}_2\text{)]} \), which can be alternatively formulated as a cobalt(III) hydride species with a ligand radical anion. Because the catalysis for 2 is slow at the \( E^{\text{pr}} \) of the Co(III) potential, the concentrations of the \( \text{[HCo(CH}_3\text{CN(dpgBF}}_2\text{)]} \) intermediate and acid in the reaction layer are presumably large enough to trigger a catalytic wave at the Co(III)−H/Co(II)−H potential. Thus no reoxidation wave for \( \text{[HCo(CH}_3\text{CN(dpgBF}}_2\text{)]} \) was observed. Artero et al. observed a similar catalytic wave at the Co(III)−H/Co(II) potential for I using a very weak acid, \( \text{Et}_3\text{NHCl} \) as the acid in \( \text{CH}_3\text{CN} \) (\( pK_a = 18.7 \)).

Quasi-reversible redox waves for the Co(III)−H/Co(II)−H couple could be observed for 4a−b because the catalysis at Co(III) potentials for 4a−b is efficient and hence the concentrations of \( \text{[HCo(Br)(TMMe)}_2\text{]+} \) intermediates and of acid are small in the reaction layer at the Co(III)−H/Co(II)−H potential. The cyclic voltammetric scan is again fast enough to reoxidize Co(II)−H prior to its reaction with either the acid or itself.

These observations of redox/catalytic waves associated with Co(III)−H/Co(II)−H couples in the H2 evolution catalysis by complexes 1−2 and 4a−b provide evidence for the intermediacy of Co(III) hydride species in the electrocatalysis and help to validate eq 4 in Scheme 3. This study can also be compared to that of Saveant and co-workers on H2 evolution catalyzed by an iron porphyrin complex (tetraphenylporphyrin)FeCl. The intermediacy of an Fe(II) hydride species was proposed in their
study due to the appearance of a nearly reversible redox wave at −1.88 V vs SCE, 280 mV more negative than the $E^\circ$ value for the catalytically active Fe$^{III}$ couple. Similar to the present system, the $E^\circ$ potential for the Fe(II)−H/Fe(III)−H couple was close to those of −1.95 V vs SCE found for the Fe(II)−R/Fe(III)−R couples, where R is a methyl or an ethyl group.

3.4. Overpotential for Hydrogen Evolution. Hydrogen Oxidation Activity, and Comparison between Low Overpotential Catalysts. The reduction potential for H$_2$ evolution, $E^\circ_{\text{H}_2}$ (HA/H$_2$A), from a solution of an acid HA, $A^- + \text{H}_2 \rightleftharpoons \frac{1}{2}\text{H}_2 + \text{HA}$, varies with acid strength. The potential is related to the proton reduction potential, $E^\circ_{\text{H}_2/OH}$ (H$^+$ + e$^-$ = $\frac{1}{2}$H$_2$), by

$$E^\circ_{\text{HA}/\text{H}_2A} = E^\circ_{\text{H}_2/OH} - 0.059 \, pK_a(\text{HA})$$

$E^\circ_{\text{H}_2/OH}$ is 0.24 V vs SCE in CH$_3$CN using [Bu$_4$N][ClO$_4$] as the electrolyte.$^{29,30}$ Thus, in CH$_3$CN, the value of $E^\circ_{\text{HA}/\text{H}_2A}$ has been estimated to be −0.51, −0.23, and 0.23 V vs SCE for CF$_3$COOH, TsOH⋅H$_2$O, and HF$_2$Et$_2$O, respectively.$^{22,28,29,35}$ The complexes studied herein appear to catalyze H$_2$ evolution at measurable rates close to the reversible HA/H$_2A$ potential, for a given acid in CH$_3$CN. The overpotential determined by electrochemistry is 40 mV using 1 as the catalyst and CF$_3$COOH as the acid and is 50 mV using 2 as the catalyst and TsOH⋅H$_2$O as the acid. We have studied the cobalt complexes 1 and 2 to determine their ability to electrocatalytically oxidize hydrogen under 1 atm of H$_2$ in CH$_3$CN solutions buffered with either [Bu$_4$N][CF$_3$CO$_2$] (for 1) or [Bu$_4$N][TsO] (for 2). No oxidation activity could be detected at scan rates between 100 and 1000 mV per second near the Co$^{II}$/I potential. We attributed this to the slow reaction rates for H$_2$ oxidation catalyzed by 1 and 2. In support of this view, H$_2$ was oxidized by 1 in the presence of [Bu$_4$N][CF$_3$CO$_2$] in CH$_3$CN over a period of several days, reaching an equilibrium mixture (Figure 8). The equilibrium constant for eq 8 is calculated to be −0.03 atm$^{1/2}$, corresponding to an overpotential of ∼90 mV for H$_2$ evolution by catalyst 1. We did not observe similar H$_2$ oxidation by 2 in the presence of [Bu$_4$N][TsO] in CH$_3$CN over a few weeks, indicating that H$_2$ oxidation by 2 was appreciably slower.$^{36}$

The overpotentials for H$_2$ evolution catalyzed by complexes 1 and 2 are among the smallest established for any synthetic complex. Considering the thermodynamic potentials of the acid used in each case,$^{28-30,35}$ the Cp$_2$MnO$_2$S$_2$ and [Ni(P$_{Ph_2}$NC$_6$H$_5$)](CH$_3$CN)$_2^+$ systems by DuBois et al. have estimated overpotentials of 120 mV and 570 mV, respectively, and the [Co(dmglH)$_2$PyCl] system by Artero et al. has an overpotential of 180 mV. To the best of our knowledge, 1 is the first synthetic complex to be established to mediate both H$_2$ evolution and oxidation, enabling the direct measurement of its modest overpotential for H$_2$ evolution.

4. Conclusions

Cobalt complexes supported by macrocyclic glyoxime and tetraimine ligands catalyzed electrochemical H$_2$ evolution at potentials between −0.55 V and −0.20 V vs SCE in CH$_3$CN. The overpotentials for the electrocatalysis, relative to the thermodynamic potentials for H$_2$ evolution in acidic CH$_3$CN, are estimated to be small. Compared to literature values for the thermodynamic potential in CH$_3$CN, overpotentials are estimated to be ∼40 mV for 1 and ∼50 mV for 2. Most significantly, we have shown experimentally that 1 can mediate both H$_2$ evolution and oxidation. We estimate from our equilibrium measurements of a solution containing both H$_2$ and acid that the overpotential is 90 mV for 1.

The potential at which H$_2$ evolution occurs can be controlled by modulating the electronic properties of the ligand, with less electron donating ligands giving rise to a more easily reduced complex that catalyzes H$_2$ evolution at a more positive potential. However, for the series of Co complexes described here, the positive shift of the catalytic wave correlates with a decreased activity for electrocatalysis. Evidence for the existence of a Co(III)−H intermediate has been obtained from the cyclic voltammetric data. Digital simulations of the voltammetry of the electrocatalysis suggest that H$_2$ evolution catalyzed by 1 and 4a in the presence of moderately weak acids in acetonitrile proceeds predominantly via a bimetallic mechanism. Ongoing work will attempt to more directly probe the mechanism of these H$_2$ evolving systems using stopped-flow methods.

5. Experimental Section

5.1. Chemicals and Reagents. All manipulations were carried out under an inert N$_2$(g) atmosphere using standard Schlenk or glovebox techniques. Unless otherwise noted, all solvents were deoxygenated by sparging with N$_2$(g) and were dried by passing through an activated alumina column. Prior to use, HF$_2$Et$_2$O and CF$_3$COOH were degassed by standard freeze–pump–thaw procedures. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., and were degassed and stored over activated 3 Å molecular sieves prior to use. All other reagents were purchased from commercial sources and used without further purification. p-Cyanoanilinium tetrafluoroborate and anisidinium tetrafluoroborate were synthesized following the method reported by DuBois et al.$^9$ with the exception that fluoroboric acid in ether was used as the acid source. Complexes 1, 2, 4a, 4b, 5a, 5b, 5c, 6a, 18, and 6b were synthesized according to literature methods; complex Co(dmglBF$_2$)$_2$(CH$_3$CN)CoCp$_2$ was prepared as described before.$^{10}$

5.2. Physical Methods. 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. 'H NMR chemical shifts were referenced to solvent as determined relative to Me$_4$Si (δ = 0 ppm). $^{19}$F('H) chemical shifts were referenced to an external standard (neat CF$_3$CO$_2$Et, δ = 0 ppm). X-ray diffraction studies were carried out in the Beckman Institute Crystallographic Facility on a Bruker Smart 1000 CCD Diffractometer. Cyclic voltammetric measurements were recorded by a CHI 600B electrochemical analyzer that was connected to a glassy carbon working electrode (surface area = 0.07 cm$^2$), a platinum wire auxiliary electrode, and a Ag/AgNO$_3$ (0.01 M) reference electrode filled with acetonitrile and [Bu$_4$N][ClO$_4$] (0.1 M). All potentials were referenced to Fc/Fc$^+$ as an internal standard and were calibrated to SCE by adding 0.38 V to the measured potentials.$^{36}$ The concentrations of HF$_2$Et$_2$O, TsOH⋅H$_2$O, and CF$_3$COOH were calibrated by measuring the pH of aqueous solutions of known volume/quantity of the acids using a Beckman 32 pH meter.

Simulation of the cyclic voltammetry was performed using the DigiElch program by M. Rudolph.$^{37}$ The standard potentials for

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(36) One reviewer suggested that the pK$_a$ for TsOH⋅H$_2$O should be about 7 in acetonitrile due to a large self-association constant upon deprotonation. If this is true, the overpotential for 2 will be 109 mV, probably too large for H$_2$ oxidation by 2 to be observed.
electron-transfer reactions (1) and (3) were taken from cyclic voltammetric measurements. The rate of charge transfer was set as 10⁷ cm/s (a = 0.5). A diffusion coefficient of 10⁻⁵ cm² s⁻¹ was assumed for all acid present in the reaction mixture, and a semi-infinite 1-D diffusion model was used in the simulation. The geometry of the electrode was assumed to be planar. See Supporting Information for detailed parameters.

 Bulk electrolysis experiments were done in a custom-made, gastight, H-type cell that was equipped with a reticulated vitreous working electrode (BAS), a Ag/AgNO₃ reference electrode, and a coiled Pt counter electrode. The counter electrode was separated from the working electrode by a glass frit. The amount of H₂ gas evolved was quantified by analyzing the gas mixture in the headspace using a Thermo Finnigan DELTAPLUS+XP system equipped with Finnigan trace GC and an Isotope Ratio Mass spectrometer. The total amount of H₂ produced was calculated as the sum of the H₂ in the headspace plus H₂ dissolved in the solvent (calculated using Henry’s Law, with a constant of 275 atm⁻¹).

5.3. Synthesis of \([\text{Co}(d\text{pgBF}_2)\text{Cl}]\text{CoCp}_2\) \((3-\text{CoCp}_2)\). A solution of \(\text{CoCp}_2\) (32 mg, 0.17 mmol) in CH₃CN was added to a solution of 2 (113 mg, 0.17 mmol) in CH₃CN at room temperature. The reaction mixture was stirred for 2 h before being evaporated to dryness. The resulting purple solid was collected on a filter frit, washed with diethyl ether, and dried in a vacuum. Yield: 110 mg (75%).

\[ \text{C}_{40}\text{H}_{33}\text{F}_4\text{N}_5\text{B}_2\text{O}_4\text{Co}_2: \text{C}, 55.66\%; \text{H}, 3.85\%; \text{N}, 8.11\%. \text{Found}: \text{C}, 55.24\%; \text{H}, 3.71\%; \text{N}, 8.09\%. \]

5.4. Crystallographic Details for \([\text{Co}(d\text{pgBF}_2)\text{Cl}]\text{CoCp}_2\) \((3-\text{Na})\). Single crystals suitable for X-ray diffraction studies were grown by diffusion of diethyl ether into a solution of 3 in CH₃CN in the presence of 2 equiv of 12-crown-4. A crystal of dimensions 0.15 mm × 0.08 mm × 0.05 mm was obtained and was mounted onto a glass fiber. A total of 79 724 reflections (−16 ≤ h ≤ 16, −19 ≤ l ≤ 19, −39 ≤ k ≤ 38) were collected at \(T = 100(2) \text{K}\) in the range of 1.37° to 28.55° of which 12 962 were unique (\(R_{int} = 0.0830\%\)); Mo Kα radiation (\(λ = 0.71073 \text{Å}\)). The structure was solved by the Direct method. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated idealized positions. One acetonitrile solvent molecule and one diethyl ether solvent molecule were found in each asymmetric unit. These solvent molecules were severely disordered and could not be refined accurately. The residual peak and hole electron densities were 1.374 and −0.980 eÅ⁻³, respectively. The absorption coefficient was 0.402 mm⁻¹. The least-squares refinement converged normally with residuals of \(R(F) = 0.0554, wR(F^2) = 0.1016\) and a GOF = 1.042 (\(I > 2σ(I)\)).

\[ \text{C}_{202.18}\text{H}_{236.64}\text{B}_{8}\text{C}_{12}\text{F}_{19}\text{N}_{23.01}\text{O}_{51.04}\text{Na}_{4}\text{Co}_{4}; \text{space group P2(1)}/\text{n}, \text{monoclinic, a} = 12.444(2), \text{b} = 14.709(3), \text{c} = 29.884(6), \text{α} = 90°, \text{β} = 93.319°, \gamma = 90°, V = 5461.0(19) \text{Å}^3, Z = 5, \rho_{calc} = 1.376 \text{Mg/m}^3. \]

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Supporting Information Available: Steady state analysis for the rate law of electrocatalysis; electrocatalysis of \(4a\) in HBF₄·Et₂O, of \(4b\) in TsOH·H₂O and HBF₄·Et₂O, and of \(5a-5b\) in HBF₄·Et₂O; variations of catalytic currents \(i_c\) on the concentration of catalyst and acid for \(2, 4a, \) and \(4b\); simulation of catalytic waves for \(1, 2, 4a, \) and \(4b\); catalytic waves of \(2\) and \(4a\) showing evidence of cobalt(III) hydrides; and crystallographic data for \(2\) and \(3\). This information is available free of charge via the Internet at http://pubs.acs.org.

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