Supporting Information for:

Hydrogen Evolution by Cobalt Tetraimine Catalysts Adsorbed on Electrode Surfaces

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Experimental

**X-ray Structure determinations.** X-ray diffraction studies were carried out on a Bruker Circle 3 diffractometer equipped with a CCD detector. Measurements were carried out at -175 °C using Mo Kα (λ = 0.71073 Å). Crystals were mounted on a Kaptan loop with Paratone-N oil. Initial lattice parameters were obtained from a least-squares analysis of more than 100 centered reflections; these parameters were later refined against all data. Data were integrated and corrected for Lorentz polarization effects using SAINT and were corrected for absorption effects using SADABS2.3.

Space group assignments were based upon systematic absences, $E$ statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps and were refined against all data using the SHELXTL 5.0 software package. Thermal parameters for all non-hydrogen atoms were refined anisotropically and hydrogen atoms were assigned to ideal positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogens).

**Other Physical Measurements.** Elemental analyses were performed by Columbia Analytical Services. $^1$H and $^{19}$F NMR spectra were recorded at ambient temperature using a Varian 300 MHz spectrometer, proton chemical shifts were referenced to residual solvent, and fluorine chemical shifts were referenced to $C_6F_6$. IR measurements were obtained on samples prepared as KBr pellets using a Bio-Rad Excalibur FTS 3000 spectrometer. Mass Spectra were collected using a Bruker Daltonics APEXIV 4.7 Tesla Fourier Transform Ion Cyclotron Resonance Mass Spectrometer equipped with an Electrospray Ionization Source. Electrochemical measurements were recorded in a glovebox under a dinitrogen atmosphere using a CH Instruments Electrochemical Analyzer, a glassy carbon working electrode, a platinum wire auxiliary-electrode, and an Ag/AgNO$_3$ nonaqueous reference electrode. Reported potentials are all referenced to the SCE couple, and were determined using ferrocene as an internal standard. Unless otherwise noted, solvents used for electrochemical measurements were deoxygenated and dried by thorough sparging with N$_2$ gas followed by passage through an activated alumina column. Faradaic yield measurements were performed in a gas tight H-cell. Non-aqueous measurements were performed on 10 mg of catalyst in acetonitrile solutions of 53 mM tosic acid and 0.1 M Bu$_4$NClO$_4$. Aqueous experiments were performed using 0.1 M phosphate solutions buffered at the appropriate pH. Headspace samples were analysed using an Agilent 7890A GC-TCD to determine the percentage of H$_2$ gas in the headspace. The total amount of H$_2$ produced was
calculated as the sum of the H\textsubscript{2} in the headspace plus H\textsubscript{2} dissolved in the solvent (calculated using Henry’s Law, with a constant of 275 atm\textsuperscript{-1}).

**Preparation of Compounds.** Deuterated solvents were purchased from Cambridge Isotopes Laboratories, Inc. and were degassed and stored over activated 3 Å molecular sieves prior to use. Ether and MeCN were deoxygenated and dried by thorough sparging with N\textsubscript{2} gas followed by passage through an activated alumina column. A literature procedure was used to prepare Co(dmgBF\textsubscript{2})\textsubscript{2}(MeCN)\textsubscript{2} (1).\textsuperscript{1} All other reagents were purchased from commercial vendors and used without further purification.

\textbf{[(Ph-Me\textsubscript{2}diimineO)\textsubscript{2}H]CoBr\textsubscript{2} (2).} Solid 2,4-butanedionemonooxime (5.9 g, 59 mmol) was added to a 50 mL EtOH solution of aniline (5.5 g, 59 mmol) and the reaction mixture was stirred and heated at 60 °C for 1 h. After the solution had cooled to room temperature solid CoBr\textsubscript{2}⋅2H\textsubscript{2}O (7.5 g, 29 mmol) was added. Within 30 min a brown precipitate had formed and the reaction was stirred for a further 16 h. The product was collected by filtration, washed with 50 mL of EtOH and 50 mL of ether, and dried under vacuum to yield 8.6 g (52 %) of 2 as a brown solid. \textsuperscript{1}H NMR (300 MHz, CD\textsubscript{3}CN, ppm): 7.40 (s, 1H, O-H-O), 7.15 (t, 2H, J = 7.8 Hz Ar), 6.94 (t, 4H, J = 8.1 Hz, Ar), 6.80 (d, 4H, J = 6.9 Hz, Ar), 2.59 (s, 6H, CH\textsubscript{3}), 2.05 (s, 6H, CH\textsubscript{3}). Anal. Calcd. for C\textsubscript{20}H\textsubscript{23}Br\textsubscript{2}CoN\textsubscript{4}O\textsubscript{2}⋅1/2CH\textsubscript{3}CH\textsubscript{2}OH: C, 42.52; H, 4.42; N, 9.44. Found: C, 42.60; H, 4.52; N, 9.68. An ES-MS analysis for this compound could not be obtained.

\textbf{[(Ph-Me\textsubscript{2}diimineO)\textsubscript{2}BF\textsubscript{2}]CoBr\textsubscript{2} (3).} Ether (5 mL), compound 2 (2.5 g, 4.4 mmol), and NaCH\textsubscript{2}COO (0.44 g, 5.3 mmol) were stirred together under a dinitrogen atmosphere. To the resulting suspension, BF\textsubscript{3}⋅Et\textsubscript{2}O was added (10 mL) and the green suspension was stirred at room temperature for 16 h. The pale green powder was collected by filtration and washed with ether (3 × 20 mL). The resulting powder was suspended in water (10 mL) and stirred for 6 h to remove any remaining NaOAc and then collected by filtration, washed with ether (3 × 20 mL) dried under vacuum to give 1.2 g (44 %) of 3. In some cases the reaction was found by \textsuperscript{1}H-NMR spectroscopy (or cyclic voltammetry, which is more sensitive) to be incomplete; then the partially converted material was subjected again to the reaction conditions described above. Upon dissolution in MeCN the color changed to brown which is possibly indicative of axial ligand exchange, as is the broadened NMR spectrum. \textsuperscript{1}H NMR (300 MHz, DMSO-\textsubscript{d}\textsubscript{6}, ppm): 7.30 (td, 2H, Ar), 7.05 (t, 4H, Ar), 6.30 (d, 4H, Ar), 2.08 (s, 6H, CH\textsubscript{3}), 1.72 (s, 6H, CH\textsubscript{3}). \textsuperscript{19}F NMR (300 MHz, CD\textsubscript{2}Cl\textsubscript{2}, ppm): -147.
(BF$_2$). Anal. Calcd. for C$_{20}$H$_{22}$BBr$_2$CoF$_2$N$_4$O$_2$·2H$_2$O: C, 36.73; H, 4.01; N, 8.57. Found: C, 37.22; H, 3.69; N, 8.05. ES$^+$-MS $m/z$: 585 [3 – Br + MeCN + 3H]$^+$. 

[(MeOPh-Me$_2$diimineO)$_2$H]CoBr$_2$ (4). Compound 4 was prepared in an analogous manner to 2 using 2,4-butanedionemonooxime (2.9 g, 28 mmol), 4-methoxyaniline (3.4 g, 28 mmol), CoBr$_2$·2H$_2$O (3.6 g, 14 mmol) and EtOH (50 mL) to give 5.2 g (30%) of product as a yellow-brown solid. $^1$H NMR (300 MHz, CD$_2$Cl$_2$, ppm): 6.77 (d, 4H, $J = 6.9$ Hz, Ar), 6.47 (d, 4H, $J = 6.9$ Hz, Ar), 3.80 (s, 6H, OMe), 2.63 (s, 6H, CH$_3$), 2.11 (s, 6H, CH$_3$). Anal. Calcd. for C$_{22}$H$_{27}$Br$_2$CoN$_4$O$_4$: C, 41.93; H, 4.32; N, 8.89. Found: C, 41.84; H, 4.17; N, 8.67. ES$^+$-MS $m/z$: 633 [4 – 2H]$^+$. 

[(MeOPh-Me$_2$diimineO)$_2$BF$_2$]CoBr$_2$ (5). Ether (5 mL), compound 4 (2.0 g, 3.18 mmol), and Bu$_4$NCH$_3$COO (1.2 g, 3.8 mmol) were stirred together under a dinitrogen atmosphere. To the resulting suspension, BF$_3$·Et$_2$O was added (10 mL) and the green suspension was stirred at room temperature for 16 h. The light brown powder was collected by filtration and washed with ether (3 × 20 mL) to give 1.2 g (72%) of 5. In some cases the reaction was found by $^1$H-NMR spectroscopy (or cyclic voltammetry, which is more sensitive) to be incomplete; then the partially converted material was subjected again to the reaction conditions described above. $^1$H NMR (300 MHz, CD$_2$Cl$_2$, ppm): 6.85 (d, 4H, $J = 6.6$ Hz, Ar), 6.48 (d, 4H, $J = 6.6$ Hz, Ar), 3.80 (s, 6H, OMe), 2.72 (s, 6H, CH$_3$), 2.18 (s, 6H, CH$_3$). $^{19}$F NMR (300 MHz, CD$_2$Cl$_2$, ppm): -145 (BF$_2$). Anal. Calcd. for C$_{22}$H$_{26}$BBr$_2$CoF$_2$N$_4$O$_4$·1.5Et$_2$O: C, 42.61; H, 5.14; N, 7.10. Found: C, 42.82; H, 4.72; N, 7.45. ES$^+$-MS $m/z$: 640 [5 – Br - 2H + MeCN]$^+$. 

[(HOOCCH$_2$Ph-Me$_2$diimineO)$_2$H]CoBr$_2$ (6). Compound 6 was prepared in an analogous manner to 2 using 2,4-butanedionemonooxime (4.1 g, 41 mmol), 4-aminophenylacetic acid (6.1 g, 41 mmol), and CoBr$_2$·2H$_2$O (5.1 g, 21 mmol) to give 7.2 g (26%) of product as a green solid. $^1$H NMR (300 MHz, DMSO-$d_6$, ppm): 12.2 (br, 1H, O-H-O), 6.85 (d, 4H, $J = 8.1$ Hz, Ar), 6.62 (d, 4H, $J = 8.1$ Hz, Ar), 3.55 (s, 6H, CH$_2$), 2.58 (s, 6H, CH$_3$), 2.10 (s, 6H, CH$_3$). Anal. Calcd. for C$_{24}$H$_{27}$Br$_2$CoN$_4$O$_6$·CH$_3$CH$_2$OH: C, 42.64; H, 4.54; N, 8.05. Found: C, 42.82; H, 4.72; N, 7.80. ES$^-$-MS $m/z$: 685 [6 – H]$^-$. 

[(HOOCCH$_2$Ph-Me$_2$diimineO)$_2$BF$_2$]CoBr$_2$ (7). Compound 7 was prepared in an analogous manner to 5, using 6 (2.5 g, 3.6 mmol), Bu$_4$CH$_3$COO (1.5 g, 4.8 mmol), BF$_3$·Et$_2$O (10 mL) and ether (5 mL) to give 1.6 g (62%) of product as a light green solid. $^1$H NMR (300 MHz, DMSO-$d_6$, ppm): 6.84 (d, 4H, $J = 8.4$ Hz, Ar), 6.67 (d, 4H, $J = 8.1$ Hz, Ar), 3.53 (s, 4H, CH$_2$), 2.65 (s, 6H, CH$_3$), 2.18 (s, 6H, CH$_3$). $^{19}$F NMR (300 MHz, DMSO-$d_6$, ppm): -145 (BF$_2$). Anal. Calcd. for
C_{24}H_{26}BBr_2CoF_2N_4O_6: C, 39.27; H, 3.57; N, 7.63. Found: C, 39.33; H, 3.53; N, 7.53. ES^-MS m/z: 733 [\text{7} - \text{H}].

[(\text{PhPh-Me_2diimineO})_2\text{H}]\text{CoBr}_2 (8). Compound 8 was prepared in an analogous manner to 2 using 2,4-butanedionemonooxime (6.0 g, 60 mmol), 2-aminobiphenyl (9.6 g, 60 mmol), CoBr_2\cdot2\text{H}_2\text{O} (7.5 g, 29 mmol) and EtOH (150 mL) to give 7.2 g (17%) of product as a brown solid. ^1H NMR (300 MHz, CD_2Cl_2, ppm): 8.0 (d, 2H, J = 7.8 Hz, Ar), 7.92 (d, 4H, J = 6.3 Hz, Ar), 7.36 (m, 6H, Ar), 7.25 (d, 2H, J = 6.9 Hz, Ar), 7.10 (t, 2H, J = 7.2 Hz, Ar), 6.61 (t, 2H, J = 7.2 Hz, Ar), 2.42 (s, 6H, CH_3), 1.74 (s, 6H, CH_3). Anal. Calcd. for C_{32}H_{31}Br_2CoN_4O_2\cdot\text{CH}_3\text{OH}: C, 52.54; H, 4.68; N, 7.43. Found: C, 52.55; H, 4.52; N, 7.45. ES^-MS m/z: 723 [8 + \text{H}].

[(\text{PhPh-Me_2diimineO})_2\text{BF}_2]\text{CoBr}_2 (9). Compound 9 was prepared in an analogous manner to 3, using 8 (2.0 g, 2.7 mmol), Bu_4\text{CH}_3\text{COO} (1.2 g, 3.8 mmol), BF_3\cdot\text{Et}_2\text{O} (10 mL) and ether (5 mL) to give 1.3 g (61%) of product as a light green solid. ^1H NMR (300 MHz, CD_2Cl_2, ppm): 8.04 (d, 2H, J = 8.1 Hz, Ar), 7.89 (d, 4H, J = 7.8 Hz, Ar), 7.39 (m, 6H, Ar), 7.29 (d, 2H, J = 7.8 Hz, Ar), 7.18 (t, 2H, J = 7.8 Hz, Ar), 6.61 (t, 2H, J = 8.0 Hz, Ar), 2.49 (s, 6H, CH_3), 1.84 (s, 6H, CH_3). ^19F NMR (300 MHz, CD_2Cl_2, ppm): -146 (BF_2). Anal. Calcd. for C_{32}H_{30}BBr_2CoF_2N_4O_2: C, 49.9; H, 3.93; N, 7.27. Found: C, 49.52; H, 3.66; N, 7.11. ES^+MS m/z: 610 [7 – 2\text{Br} - 3\text{H}]^+.

References
Table S1. Electrochemical data for complexes 2 – 9. TsOH.2H₂O is used as the acid.

<table>
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<tr>
<th>Compound</th>
<th>$E_{1/2}$ Co$^{III/II}$</th>
<th>$E_{1/2}$ Co$^{II/III}$</th>
<th>$E_{cat}$ (V)</th>
<th>$\eta$ (V)</th>
<th>q (C)</th>
<th>Farad. Yield (%)</th>
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<td>-0.08</td>
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<tr>
<td>3</td>
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<tr>
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<td>-0.75</td>
<td>0.52</td>
<td>52</td>
<td>~10</td>
</tr>
<tr>
<td>5</td>
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<td>-0.70</td>
<td>0.47</td>
<td>78</td>
<td>~55</td>
</tr>
<tr>
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<td>100</td>
<td>~20</td>
</tr>
<tr>
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<td>0.45</td>
<td>50</td>
<td>~70</td>
</tr>
<tr>
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<td>-0.66</td>
<td>0.43</td>
<td>60</td>
<td>~20</td>
</tr>
<tr>
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<td>-0.58</td>
<td>0.35</td>
<td>50</td>
<td>~75</td>
</tr>
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</table>

$a$: Irreversible reduction wave. Value quoted refers to the Co$^{III} \rightarrow$ Co$^{II}$ peak position.
Figure S1. (a) Structure of (a) [(Ph-Me2diimineO)2BF2]CoBr2 (3); (b) [(CH3OPh-Me2diimineO)2H]CoBr2 (4); (c) [(CH3OPh-Me2diimineO)2BF2]CoBr2 (5); (d) [(PhPh-Me2diimineO)2H]CoBr2 (8); and (e) [(HOOCCH2Ph-Me2diimineO)2H]CoBr2 (6). Purple, blue, white, red, and green ellipsoids represent Co, N, C, O, and Br atoms respectively; ellipsoids are shown at the 50% probability level. Calculated H atoms have been omitted for clarity.
**Figure S2.** Cyclic voltammograms for complexes 2 - 9 with tosic acid as the proton source in 0.1M Bu₄NCIO₄ MeCN solution
Figure S3. Cyclic voltammograms of 4 (left) and 5 (right) recorded in 0.1 M Bu₄NClO₄ MeCN solution in the presence of Et₄NOTs.

Figure S4. Cyclic voltamogram for 7 recorded using ITO-coated glass as the working electrode in a 0.1 M Bu₄NClO₄ MeCN solution. $E_{1/2} = -0.41$ V vs. SCE and $E_p = 100$ mV.

Figure S4a. Cyclic voltamogram recorded using ITO-coated glass as the working electrode in a 0.1 M Bu₄NClO₄ MeCN solution (black); and with added tosic acid (red). Reduction of the ITO occurs at approximately 400 mV more negative than reduction of protons by the catalyst 7.
**Figure S5.** Reduction Peak current vs. scan rate for 7 adsorbed at an ITO electrode recorded in 0.1 M TBAClO₄.

**Experimental and Theoretical Determination of Surface Coverage of 7 on ITO**

F = Faraday’s constant = 96485, n = number of electrons = 1, \(i_p\) = peak current (A), R = ideal gas constant = 8.314 JK⁻¹mol⁻¹, T = temperature = 298 K, ν = scan rate (V/s), A = electrode surface area = 0.5 cm², \(\Gamma_0^*\) = surface concentration (mol/cm²).

Experimentally determined surface concentration:

\[
\text{Slope} = \frac{n^2F^2}{4RT} \cdot \frac{A\Gamma_0^*}{4RT} = 0.0058
\]

\[
\Gamma_0^* = \frac{(6e-5*4*8.314*298)(1*96485^2*0.5)}{1*96485^2*0.5} = 1.3 \times 10^{-10} \text{ mol/cm}^2
\]

Theoretical monolayer concentration estimated from crystal structure

Theoretical \(\Gamma_0^* = 2.0 \times 10^{-10} \text{ mol/cm}^2\)

\[i_p = \frac{_____}{4RT}\]
Figure S6. Experiment performed using a GC working electrode modified with 1. (a) CV recorded in 0.1M Bu₄NClO₄, 10 mM Bu₄NOTs MeCN solution. (b) CV recorded in 0.1M Bu₄NClO₄ MeCN and shows catalyst stripped from the electrode surface after one scan. Plots: Current (µA) vs. Potential vs. SCE (V)

Figure S7. Control experiments performed as described in the text for plating of 1 onto a GC working electrode. Following electroplating, the above CV’s were collected in 0.63 mM TsOH, 0.1 M Bu₄NClO₄ MeCN solution. (a) using CoBr₂ (b) no added cobalt source. Plots: Current (µA) vs. Potential vs. SCE (V)

Figure S8. Experiment performed using a GC working electrode after electrolysis at -0.30 V vs. SCE in 53 mM TsOH, 0.1M Bu₄NClO₄ MeCN solution in the presence of (a) 3 and (b) 10. The Cyclic voltammogram was recorded in 0.1M Bu₄NClO₄ MeCN and shows catalyst stripped from the electrode surface after one scan. Plots: Current (µA) vs. Potential vs. SCE (V)
**Figure S9.** CV using a GC working electrode after electrolysis at -0.30 V vs. SCE in 53 mM TsOH, 0.1M Bu₄NClO₄ MeCN with 10. CV recorded in pH 2 aqueous phosphate buffer and shows the catalyst stripped from the electrode surface after one scan.

**Figure S10.** Cyclic voltammograms recorded for compound 1 in phosphate buffered solutions of pH 7, 4, 3, and 2. Plots: Current (µA) vs. Potential vs. SCE (V)

**Figure S11.** Control experiment performed for adsorbing onto GC. 1 was not included in the solution. CV was collected in aqueous 0.1 M phosphate buffer solution (pH noted in the figure).

**Figure S12.** CV recorded with 1 in 0.1 M NaClO₄, 20 mM NaOAc, 20mM HOAc solution at pH 4.5 & 7. Plots: Current (µA) vs. Potential vs. SCE (V)