

Supporting Information for

# Molecular Mechanisms of Cobalt Catalyzed Hydrogen Evolution

by

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**Bulk electrolysis experiments.** Bulk electrolysis experiments were conducted in a sealed 2-chamber cell, where the first chamber held the working and reference electrodes in 65 mL of 0.1 M  $[n\text{Bu}_4\text{N}][\text{PF}_6]$  in acetonitrile with 0.3 mM catalyst and 6.0 mM  $\text{TsOH}\cdot\text{H}_2\text{O}$ , and the second held the auxiliary electrode in 25 mL 0.1 M  $[n\text{Bu}_4\text{N}][\text{PF}_6]$  in acetonitrile. The two chambers were separated by a fine glass frit. 12 cm  $\times$  3 cm  $\times$  1 cm glassy carbon plates were used as the working and the auxiliary electrodes. The reference electrode was a silver wire immersed in 0.1 M  $[n\text{Bu}_4\text{N}][\text{PF}_6]$  acetonitrile solution, which was separated from the solution by a Vycor frit. Each bulk electrolysis experiment lasted two hours at the specified potential under vigorous stirring, and the amount of  $\text{H}_2$  evolved was quantified from an analysis of the headspace (78 mL) with an Agilent 7890A gas chromatograph using a thermal conductivity detector. The total amount of hydrogen produced was determined as the sum of  $\text{H}_2$  in the headspace plus the hydrogen dissolved in the solution calculated using Henry's Law, with a constant of  $5.4 \times 10^3$  atm. Faradaic efficiencies were determined by dividing the measured hydrogen produced by the amount of hydrogen expected based on the charge passed during the bulk electrolysis experiment.

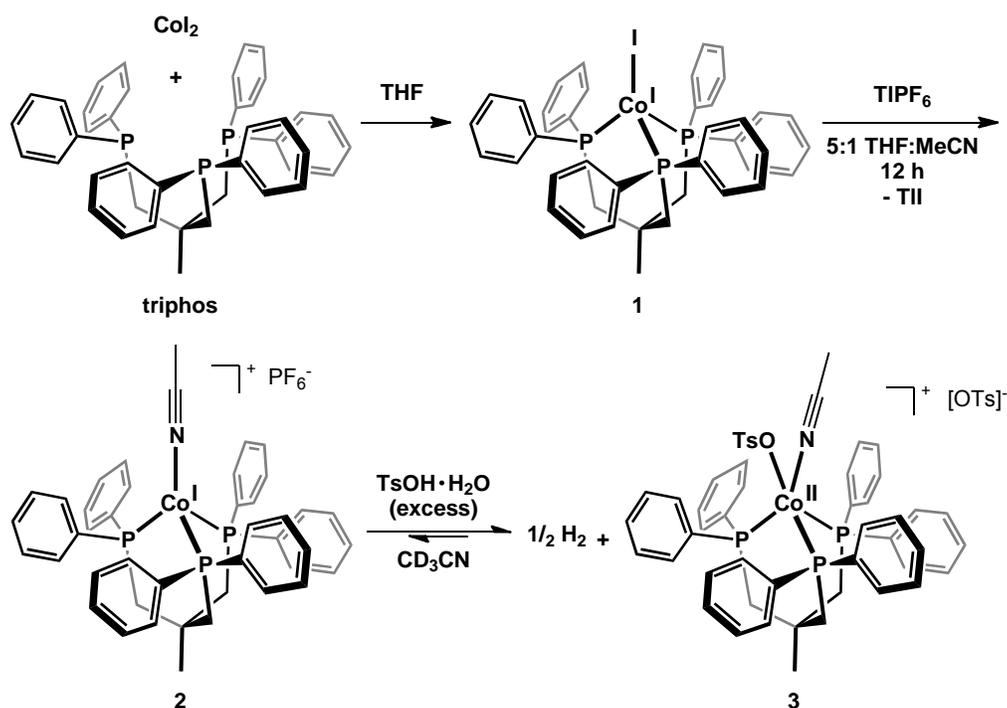
**General Information for the reaction between **3** and H<sub>2</sub> (1 atm).** A 0.7 mL MeCN stock solution of **3** (16.4 mM) and dihydroanthracene (4.1 mM) was transfer to a J. Young tube. The reaction mixture was degassed (3×), using the freeze-pump-thaw technique. The reaction mixture was allowed to warm up to room temperature and then exposed to 1 atmosphere of hydrogen. Reaction progress was monitored by <sup>1</sup>H NMR spectroscopy at 25 °C.

**General Information for the simulated kinetics.** Simulated electrochemical studies were performed using the DigiElch 6.F program. All the reduction potentials were referenced to ferrocene/ferrocenium couple. Simulated kinetics studies were performed using the Matlab program.

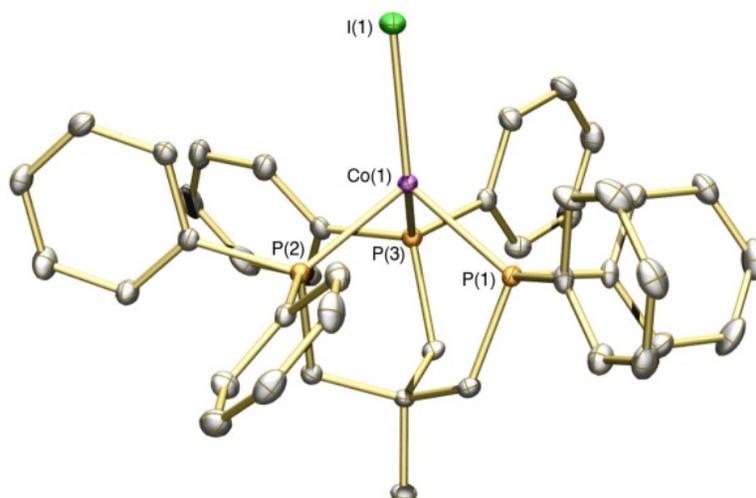
**Co(triphos)(I) (**1**).** A THF (1 mL) suspension of anhydrous cobalt iodide (II) (151 mg, 0.4819 mmole) was added to a THF solution (2 mL) of triphos ligand (301 mg, 0.4819 mmole) in a 20 mL vial equipped with a magnetic stir bar. The reaction mixture was stirred at room temperature for 3 days. The pink precipitate generated was collected on a fine porosity frit and washed with THF (294 mg, yield = 75%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz): δ 15.47 (s), 14.00 (br), 0.60 (br), –0.93 (s), –2.09 (br). UV/Vis, λ in nm (ε in M<sup>-1</sup>cm<sup>-1</sup>): 320 (13 650), 850 (120). Anal. Calcd for C<sub>41</sub>H<sub>39</sub>CoIP<sub>3</sub>: C, 60.76; H, 4.85. Found: C, 61.08; H, 4.83. X-ray quality crystals were obtained by vapor diffusion of Et<sub>2</sub>O over a THF solution of **1** at room temperature.

**[Co(triphos)(MeCN)][PF<sub>6</sub>] (**2**).** A THF (5 mL) solution of TlPF<sub>6</sub> (91 mg, 0.2616 mmole) was added to a MeCN (1 mL) suspension of Co(triphos)(I) (212 mg, 0.2616 mmole) in a 20 mL vial equipped with a magnetic stir bar. The reaction mixture was stirred at room temperature for 20 minutes. The generated yellow precipitate is filtered through Celite and the blue solution is recrystallized by vapor diffusion of Et<sub>2</sub>O at room temperature to generate blue crystals (165 mg, yield = 73%). <sup>1</sup>H NMR (CD<sub>3</sub>CN, 300 MHz): δ 15.40 (br), –0.77 (s), –1.45 (s); <sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 300 MHz): δ –11.17 (d, J<sub>PF</sub> = 706 Hz). UV/Vis, λ in nm (ε in M<sup>-1</sup>cm<sup>-1</sup>): 305 (17 050), 570 (82), 900 (261). Anal. Calcd for C<sub>43</sub>H<sub>42</sub>CoF<sub>6</sub>NP<sub>4</sub>: C, 59.39; H, 4.87; N, 1.61. Found: C, 59.16; H, 4.91; N, 1.52. X-ray quality crystals were obtained by vapor diffusion of Et<sub>2</sub>O over an acetonitrile solution of **2** at room temperature.

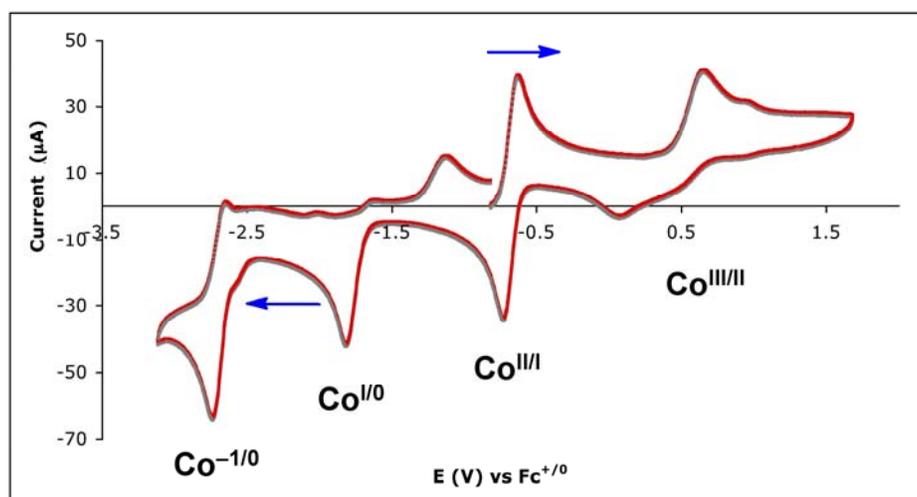
**[Co(triphos)(OTs)(MeCN)][OTs]·TsOH (3).** An acetonitrile solution (0.3 mL) of TsOH·H<sub>2</sub>O (52 mg, 0.2725 mmole) was added to an acetonitrile solution (0.3 mL) of [Co(triphos)(MeCN)][PF<sub>6</sub>] (79 mg, 0.0908 mmole) in a 1 dram vial equipped with a magnetic stir bar. The reaction mixture was stirred at room temperature for 10 hours. The green solution is recrystallized by vapor diffusion of Et<sub>2</sub>O at room temperature to generate yellow/green crystals (70 mg, yield = 60%). <sup>1</sup>H NMR (CD<sub>3</sub>CN, 300 MHz): δ 10.36 (br), 7.62 (br), 7.22 (s), 2.48 (s), 0.29 (br). UV/Vis, λ in nm (ε in M<sup>-1</sup>cm<sup>-1</sup>): 285 (6 300), 820 (400). Anal. Calcd for C<sub>64</sub>H<sub>64</sub>CoNO<sub>9</sub>P<sub>3</sub>S<sub>3</sub>: C, 62.03; H, 5.21; N, 1.13. Found: C, 61.76; H, 4.86; N, 1.23. X-ray quality crystals were obtained by vapor diffusion of Et<sub>2</sub>O over an acetonitrile solution of **3** at room temperature.



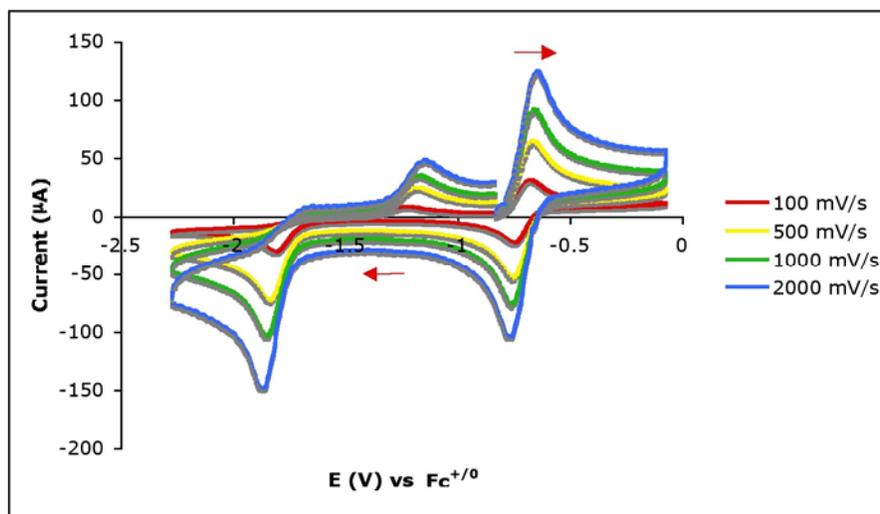
**Figure S1.** Synthesis of cobalt species.



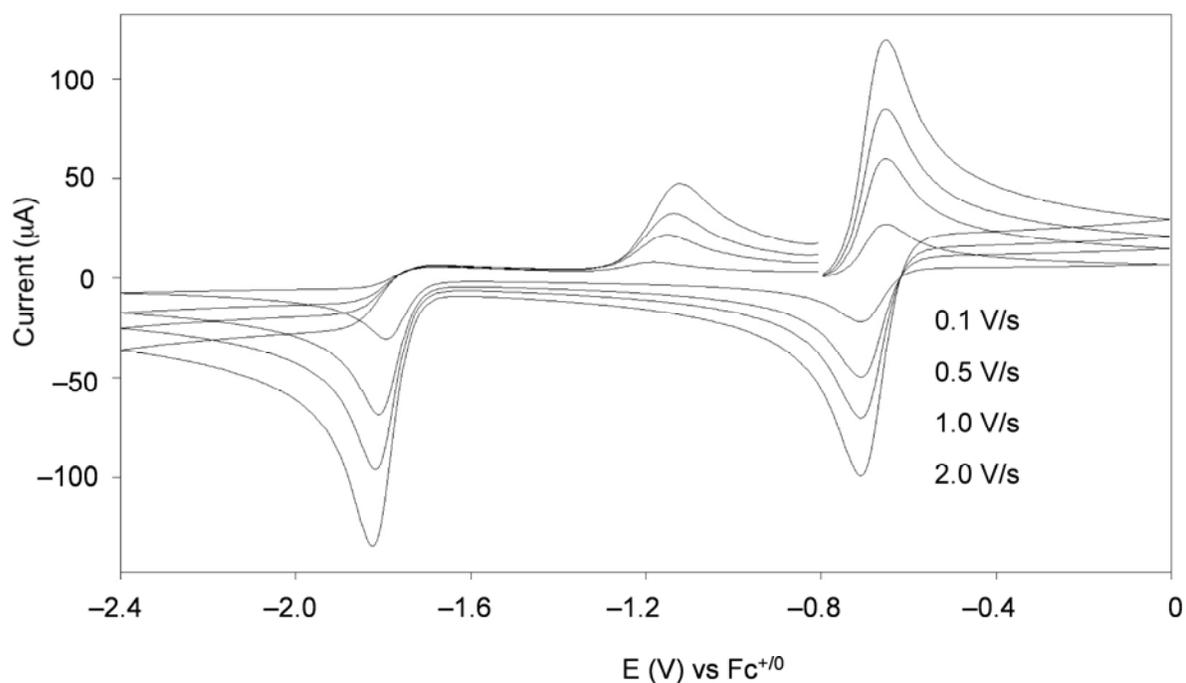
**Figure S2.** Structure of **1**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Co(1)–I(1) = 2.5437(4), Co(1)–P(1) = 2.2320(7), Co(1)–P(2) = 2.2282(8), Co(1)–P(3) = 2.2363(6), I(1)–Co(1)–P(1) = 127.14(2), I(1)–Co(1)–P(2) = 117.31(2), I(1)–Co(1)–P(3) = 127.16(2).



**Figure S3.** Cyclic voltammogram of **2** (2.5 mM) in acetonitrile solution containing 0.1 M  $[n\text{Bu}_4\text{N}][\text{PF}_6]$ . Scan rate:  $100 \text{ mV s}^{-1}$ ; glassy carbon electrode.



**Figure S4A.** Cyclic voltammogram of **2** (1.0 mM) in acetonitrile containing 0.1 M  $[n\text{Bu}_4\text{N}][\text{PF}_6]$ . Varying scan rate; glassy carbon electrode.

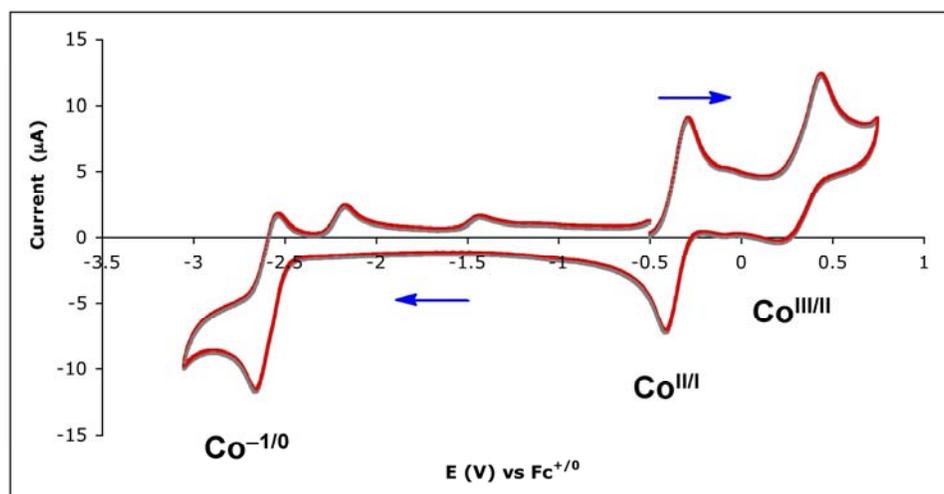


**B)** \_

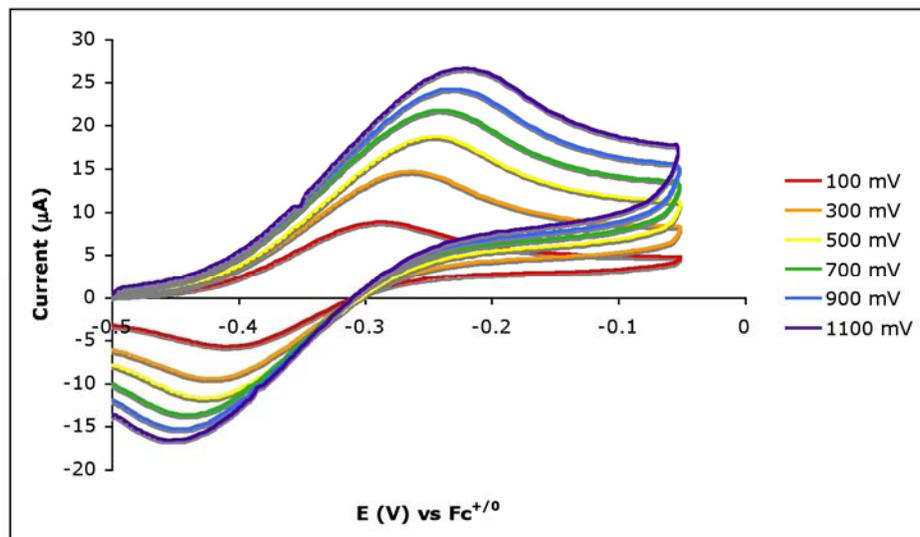
**Figure S4B.** Numerical simulations of cyclic voltammogram of **2** (1.0 mM) in acetonitrile containing 0.1 M  $[n\text{Bu}_4\text{N}][\text{PF}_6]$  as a function of scan rate (2, 1, 0.5, 0.1  $\text{V s}^{-1}$ ); simulation parameters in the following table. Simulations studies performed using the DigiElch 6.F program;  $k_s$  = rate constant of the electrode;  $k_f$  = rate constant of the forward reaction;  $k_b$  = rate constant of the backward (reverse) reaction.

Electrode Reaction	$E^\circ$ vs. $\text{Fc}^{+/0}$	$k_s$ , $\text{cm s}^{-1}$		
$\text{Co}^{\text{II}} + \text{e}^- \leftrightarrow \text{Co}^{\text{I}}$	-0.68	$10^4$		
$\text{Co}^{\text{I}} + \text{e}^- \leftrightarrow \text{Co}^0$	-1.81	$10^4$		
$\text{Co}_A^{\text{I}} + \text{e}^- \leftrightarrow \text{Co}_A^0$	-1.0	0.5		
	$K_{\text{eq}}$	$k_f$ , $\text{s}^{-1}$	$k_b$ , $\text{s}^{-1}$	
$\text{Co}^0 \leftrightarrow \text{Co}_A^0$	25	100	4	
$\text{Co}^{\text{I}} \leftrightarrow \text{Co}_A^{\text{I}}$	$5 \times 10^{-13}$	$1 \times 10^{-3}$	$2 \times 10^9$	

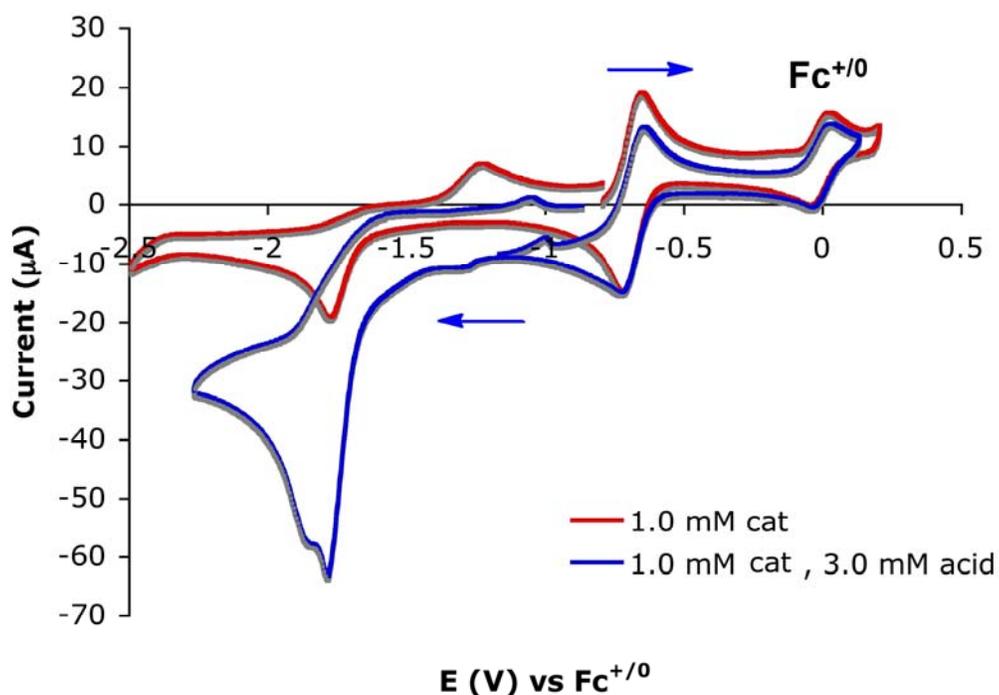
A second  $\text{Co}^0$  species ( $\text{Co}_A^0$ ) is introduced in the simulation to account for the irreversibility of the  $\text{Co}^{\text{I}/0}$  cathodic wave at  $-1.81$  V and the appearance of an anodic wave at  $\sim -1.15$  V. The formation of  $\text{Co}_A^{\text{I}}$  from  $\text{Co}^{\text{I}}$  is energetically unfavorable and kinetically slow. The  $\text{Co}_A^{\text{I}}$  species is unlikely to be involved in catalysis of HA ( $\text{TsOH} \cdot \text{H}_2\text{O}$ ) reduction. We do not have enough information to evaluate the role of  $\text{Co}_A^0$  in catalysis of HA ( $\text{TsOH} \cdot \text{H}_2\text{O}$ ) reduction, and it is neglected in subsequent simulations.



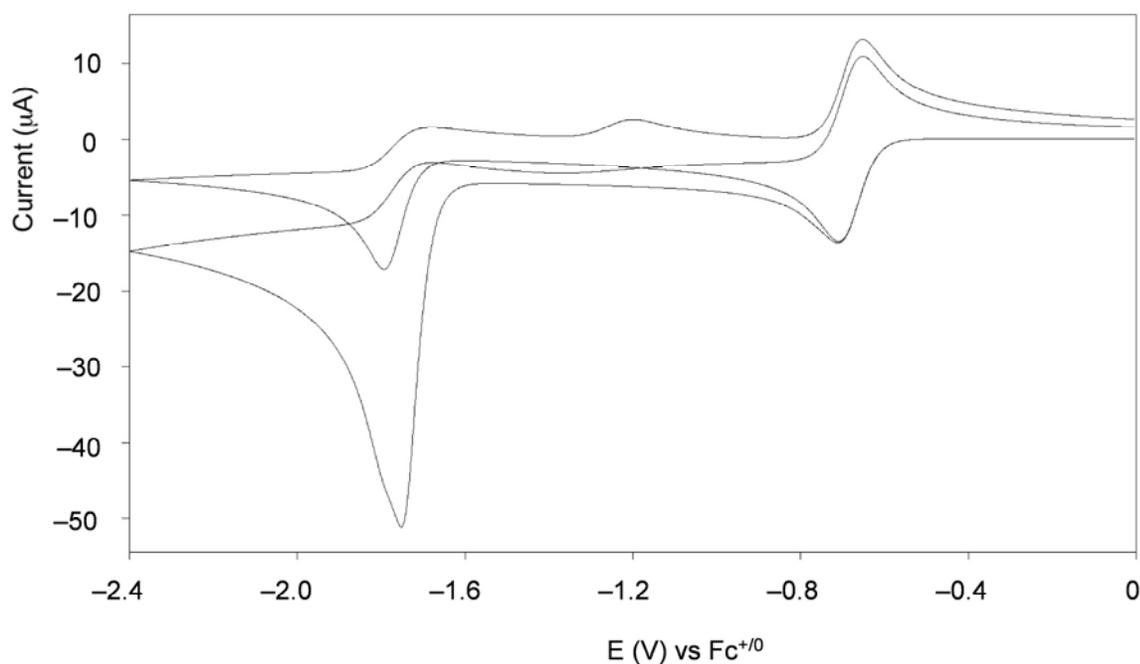
**Figure S5.** Cyclic voltammogram of **1** (0.7 mM) in THF containing 0.1 M  $[\text{nBu}_4\text{N}][\text{PF}_6]$ . Scan rate:  $100 \text{ mV s}^{-1}$ ; glassy carbon electrode.



**Figure S6.** Cyclic voltammogram of **1** (0.7 mM) in THF containing 0.1 M  $[n\text{Bu}_4\text{N}][\text{PF}_6]$ . Varying scan rate; glassy carbon electrode.

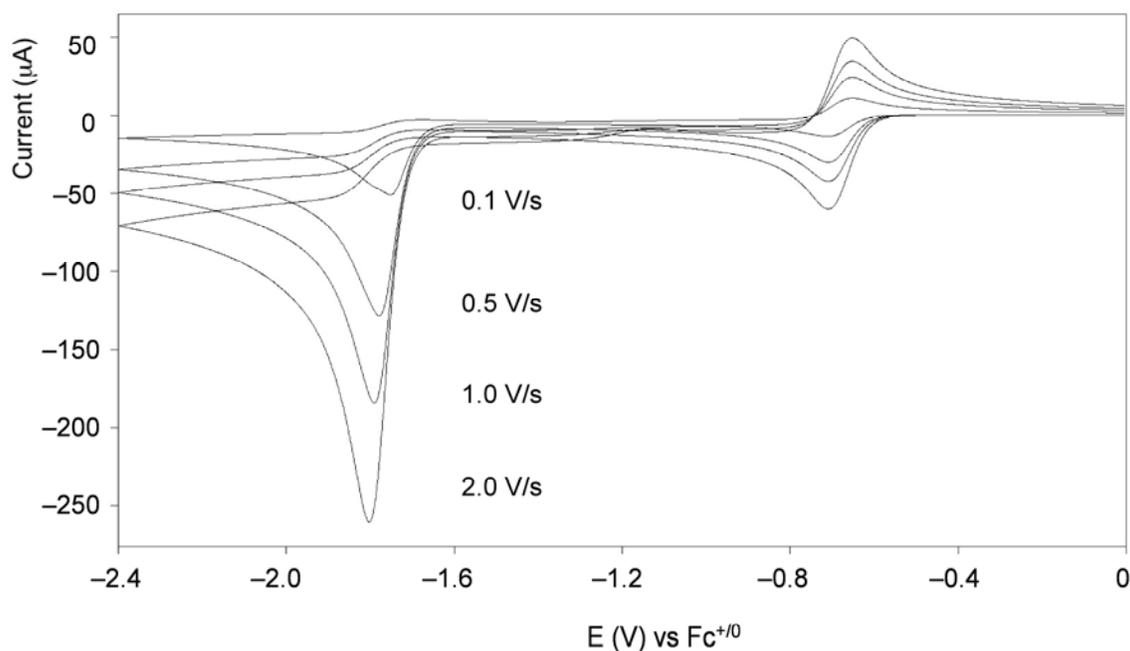
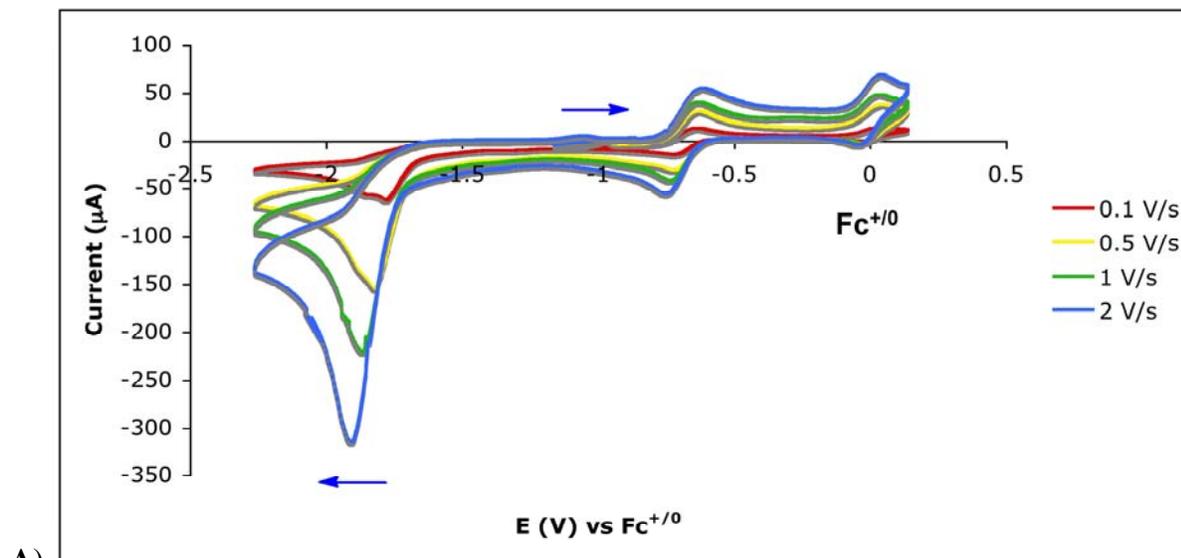


**Figure S7A.** Cyclic voltammograms of **2** (1.0 mM) in 0.1 M  $[n\text{Bu}_4\text{N}][\text{PF}_6]$  acetonitrile solution in the absence and presence of  $\text{TsOH}\cdot\text{H}_2\text{O}$  (3.0 mM) and ferrocene. Scan rate:  $100 \text{ mV s}^{-1}$ ; glassy carbon electrode.

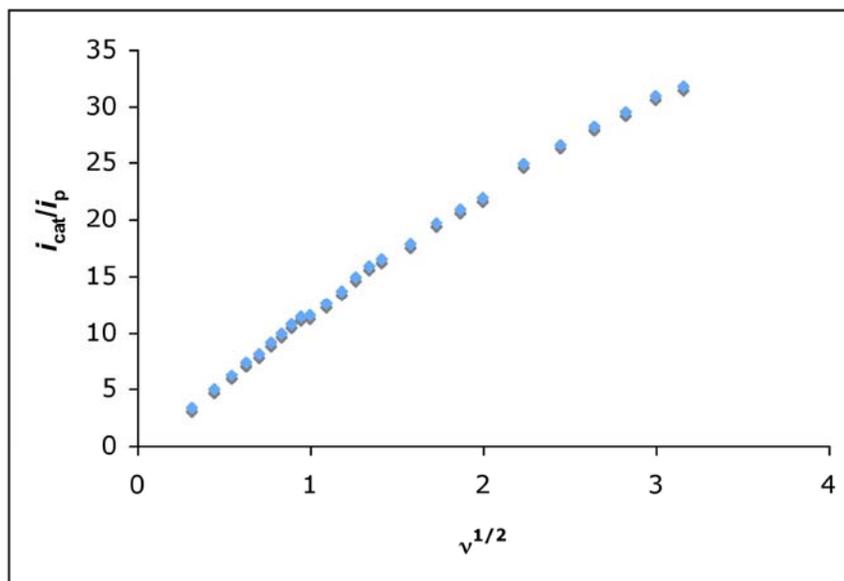


Electrode Reaction	$E^\circ$ vs. $\text{Fc}^{+/0}$	$k_s$ , $\text{cm s}^{-1}$	
$\text{Co}^{\text{II}} + \text{e}^- \leftrightarrow \text{Co}^{\text{I}}$	-0.68	$10^4$	
$\text{Co}^{\text{I}} + \text{e}^- \leftrightarrow \text{Co}^0$	-1.81	$10^4$	
$\text{Co}_A^{\text{I}} + \text{e}^- \leftrightarrow \text{Co}_A^0$	-1.0	0.5	
$\text{Co}^{\text{III}}\text{-H} + \text{e}^- \leftrightarrow \text{Co}^{\text{II}}\text{-H}$	-0.857	$10^4$	
	$K_{\text{eq}}$	$k_f$	$k_b$
$\text{Co}^{\text{I}} + \text{HA} \leftrightarrow \text{Co}^{\text{III}}\text{-H} + \text{A}^-$	0.2	$25 \text{ M}^{-1}\text{s}^{-1}$	$125 \text{ M}^{-1}\text{s}^{-1}$
$\text{Co}^0 + \text{HA} \leftrightarrow \text{Co}^{\text{II}}\text{-H} + \text{A}^-$	$2.5 \times 10^{15}$	$10^6 \text{ M}^{-1}\text{s}^{-1}$	$3.9 \times 10^{-10} \text{ M}^{-1}\text{s}^{-1}$
$\text{Co}^{\text{II}}\text{-H} + \text{HA} \leftrightarrow \text{H}_2\text{Co}^{\text{II}} + \text{A}^-$	37	$10^7 \text{ M}^{-1}\text{s}^{-1}$	$2.7 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$
$\text{Co}^{\text{I}} + \text{Co}^{\text{III}}\text{-H} \leftrightarrow \text{Co}^{\text{II}} + \text{Co}^{\text{II}}\text{-H}$	$10^{-3}$	$6 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}$	$58 \text{ M}^{-1}\text{s}^{-1}$
$\text{H}_2\text{Co}^{\text{II}} \leftrightarrow \text{Co}^{\text{II}} + \text{H}_{2(\text{s})}$	1M	$10^9 \text{ s}^{-1}$	$10^9 \text{ M}^{-1}\text{s}^{-1}$
$\text{Co}^0 \leftrightarrow \text{Co}_A^0$	25	$10^2 \text{ s}^{-1}$	$4 \text{ s}^{-1}$
$\text{Co}^{\text{I}} \leftrightarrow \text{Co}_A^{\text{I}}$	$5 \times 10^{-13}$	$10^{-3} \text{ s}^{-1}$	$2 \times 10^9 \text{ s}^{-1}$

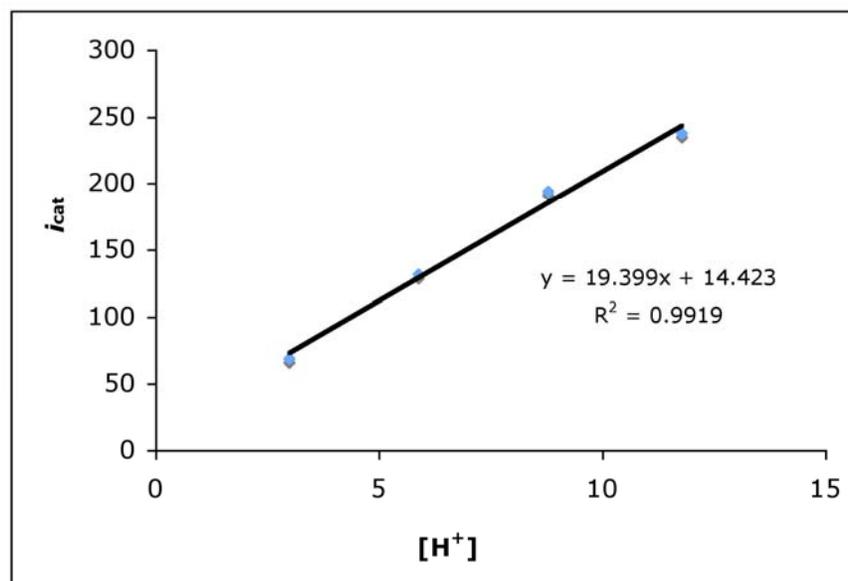
**Figure S7B.** Simulations of cyclic voltammograms of **2** (1.0 mM) in 0.1 M  $[\text{nBu}_4\text{N}][\text{PF}_6]$  acetonitrile solution in the absence and presence of  $\text{TsOH}\cdot\text{H}_2\text{O}$  (3.0 mM) and ferrocene. Scan rate:  $100 \text{ mV s}^{-1}$ ; simulation parameters in the foregoing table. Simulations studies performed using the DigiElch 6.F program;  $k_s$  = rate constant of the electrode;  $k_f$  = rate constant of the forward reaction;  $k_b$  = rate constant of the backward (reverse) reaction.



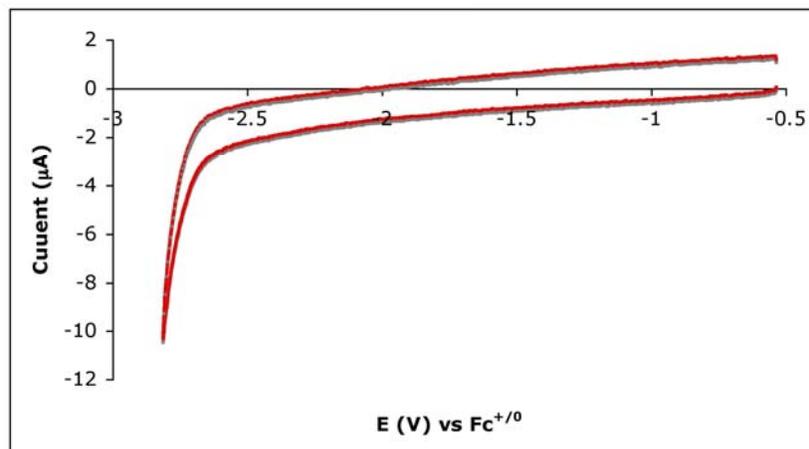
**Figure S8.** Scan rate dependence of a 0.1 M  $[\text{nBu}_4\text{N}][\text{PF}_6]$  acetonitrile solution of **2** (1.0 mM) in the presence of  $\text{TsOH}\cdot\text{H}_2\text{O}$  (3.0 mM). **A)** Experimental; Glassy carbon electrode; **B)** Simulated; Scan rates: 0.1, 0.5, 1.0, and 2.0 V/s; simulation parameters are the same as those used in Figure S7B. Simulations studies performed using the DigiElch 6.F program;  $k_s$  = rate constant of the electrode;  $k_f$  = rate constant of the forward reaction;  $k_b$  = rate constant of the backward (reverse) reaction.



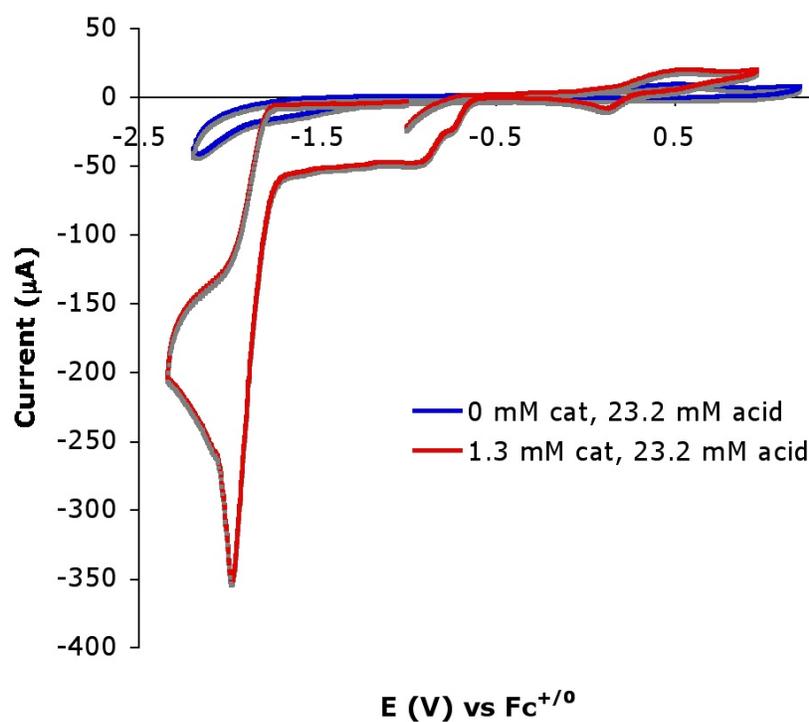
**Figure S9.** Plot of the square root of the scan rate ( $v$ ) vs  $i_{cat}/i_p$  for **2** (1.0 mM) in the presence of TsOH•H<sub>2</sub>O (3.0 mM) at  $-1.81$  V vs Fc<sup>+0</sup>. Glassy carbon electrode.



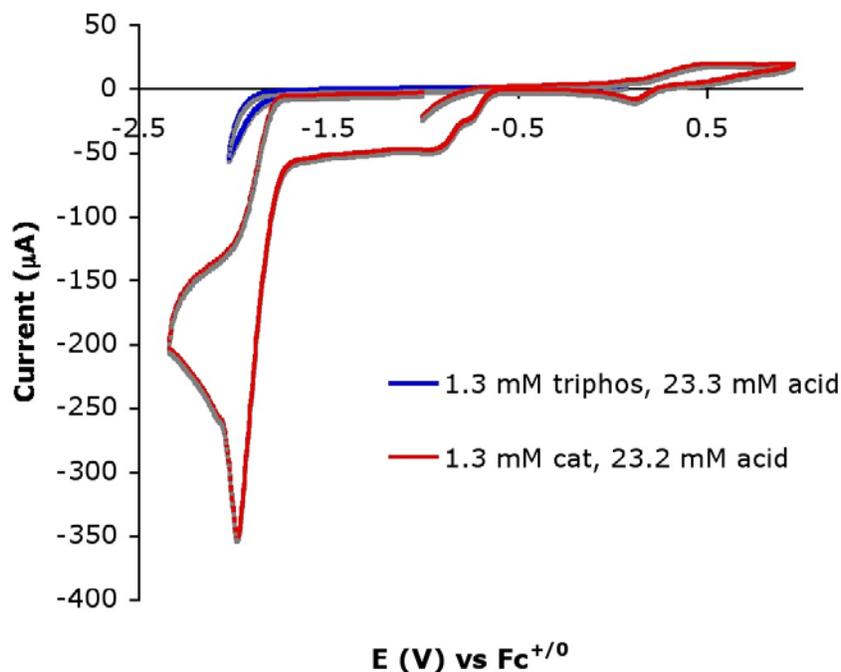
**Figure S10.** Electrochemical current for **2** (1.0 mM) as a function of [TsOH•H<sub>2</sub>O] in 0.1 M [nBu<sub>4</sub>N][PF<sub>6</sub>] acetonitrile solution at  $-1.81$  V vs Fc<sup>+0</sup>. Scan rate: 100 mV/s; glassy carbon electrode.



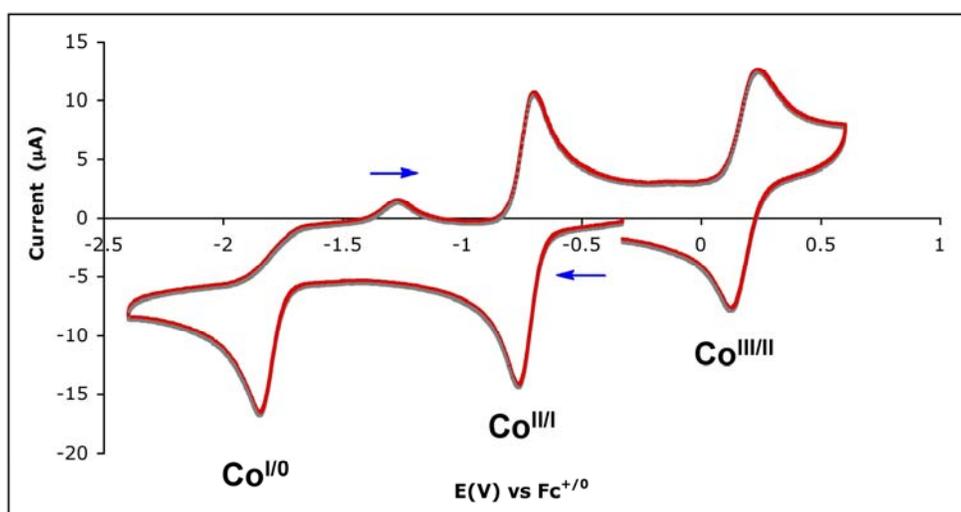
**Figure S11.** Cyclic voltammogram of triphos ligand (2.5 mM) in acetonitrile containing 0.1 M  $[n\text{Bu}_4\text{N}][\text{PF}_6]$ . Scan rate:  $100 \text{ mV s}^{-1}$ ; glassy carbon electrode.



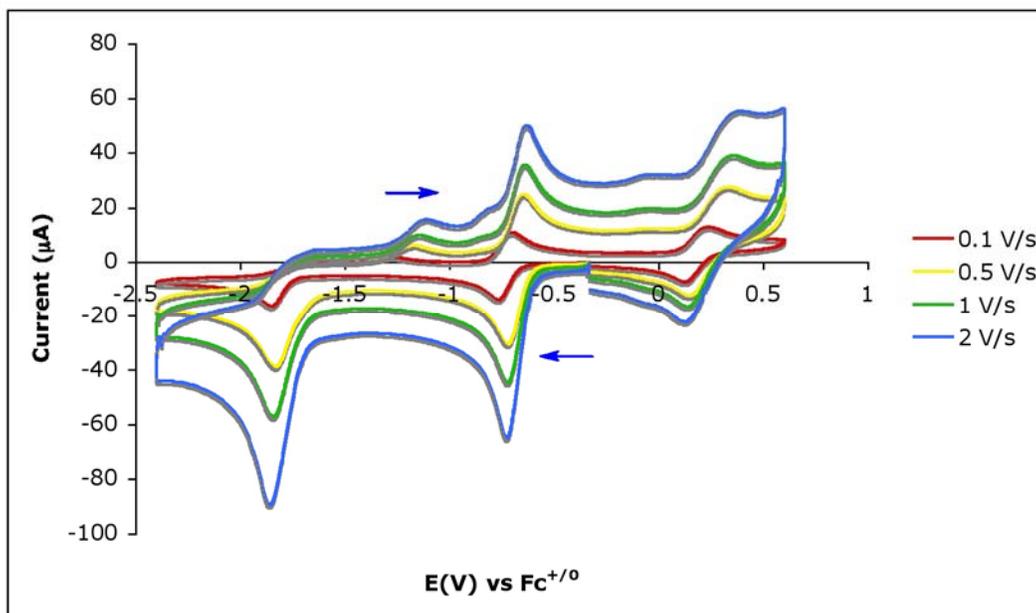
**Figure S12.** Cyclic voltammograms of  $\text{TsOH}\cdot\text{H}_2\text{O}$  (23.2 mM) in acetonitrile containing 0.1 M  $[n\text{Bu}_4\text{N}][\text{PF}_6]$  in the presence and absence of **2**. Scan rate:  $100 \text{ mV s}^{-1}$ ; glassy carbon electrode.



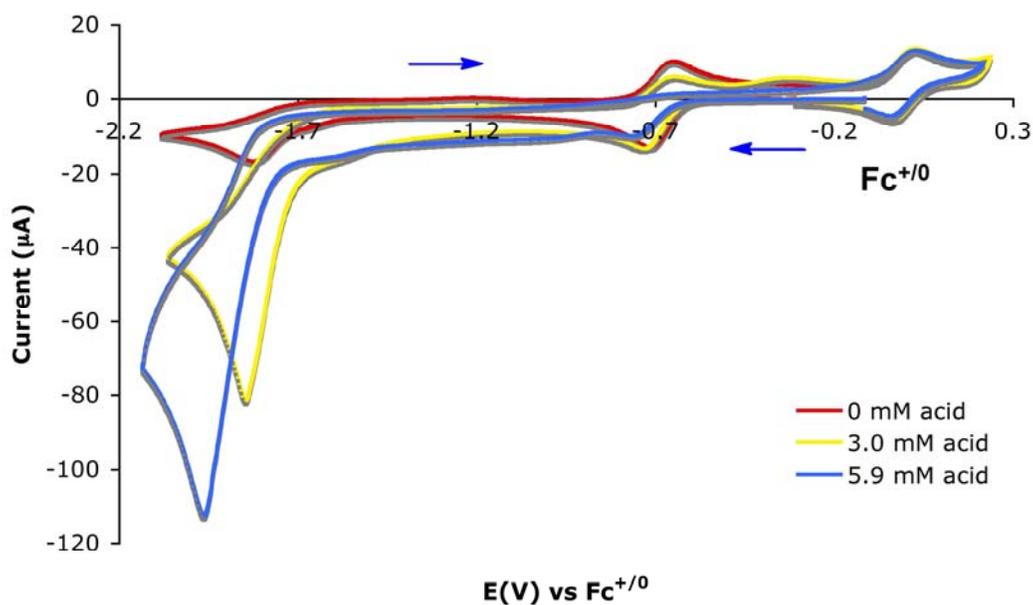
**Figure S13.** Cyclic voltammograms of TsOH•H<sub>2</sub>O (23.2 mM) in acetonitrile containing 0.1 M [nBu<sub>4</sub>N][PF<sub>6</sub>] in the presence of free ligand, triphos (1.3 mM), and **2** (1.3 mM). Scan rate: 100 mV s<sup>-1</sup>; glassy carbon electrode.



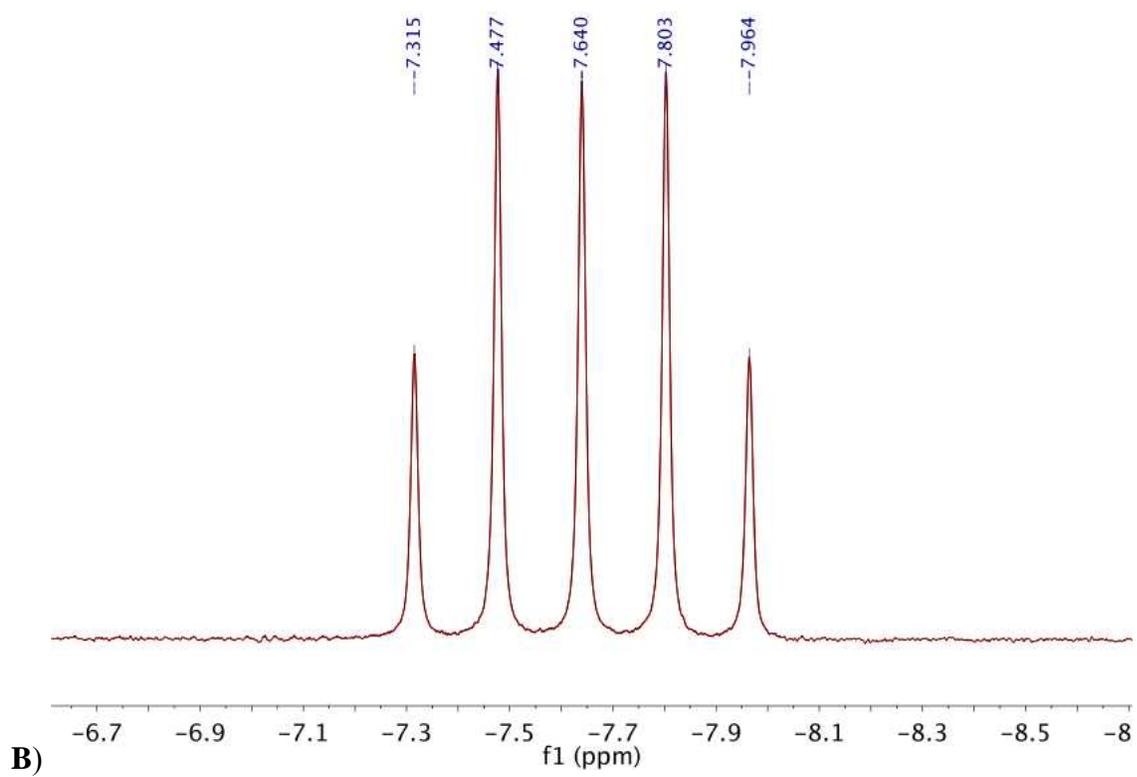
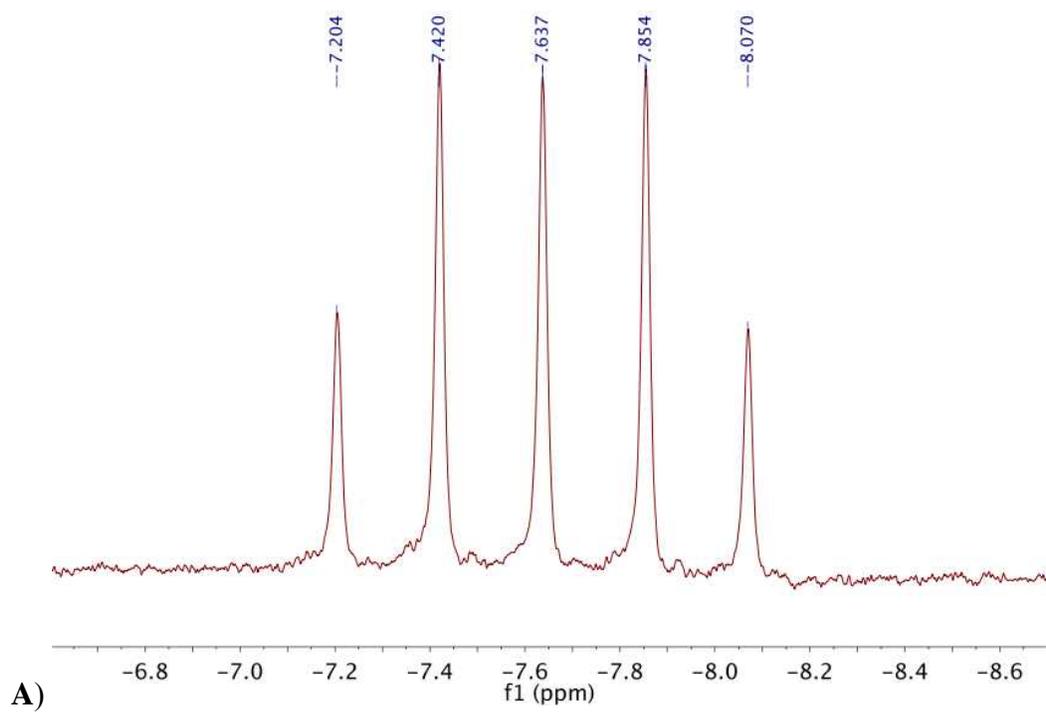
**Figure S14.** Cyclic voltammogram of **3** (0.7 mM) in acetonitrile solution containing 0.1 M [nBu<sub>4</sub>N][PF<sub>6</sub>]. Scan rate: 100 mV s<sup>-1</sup>; glassy carbon electrode.

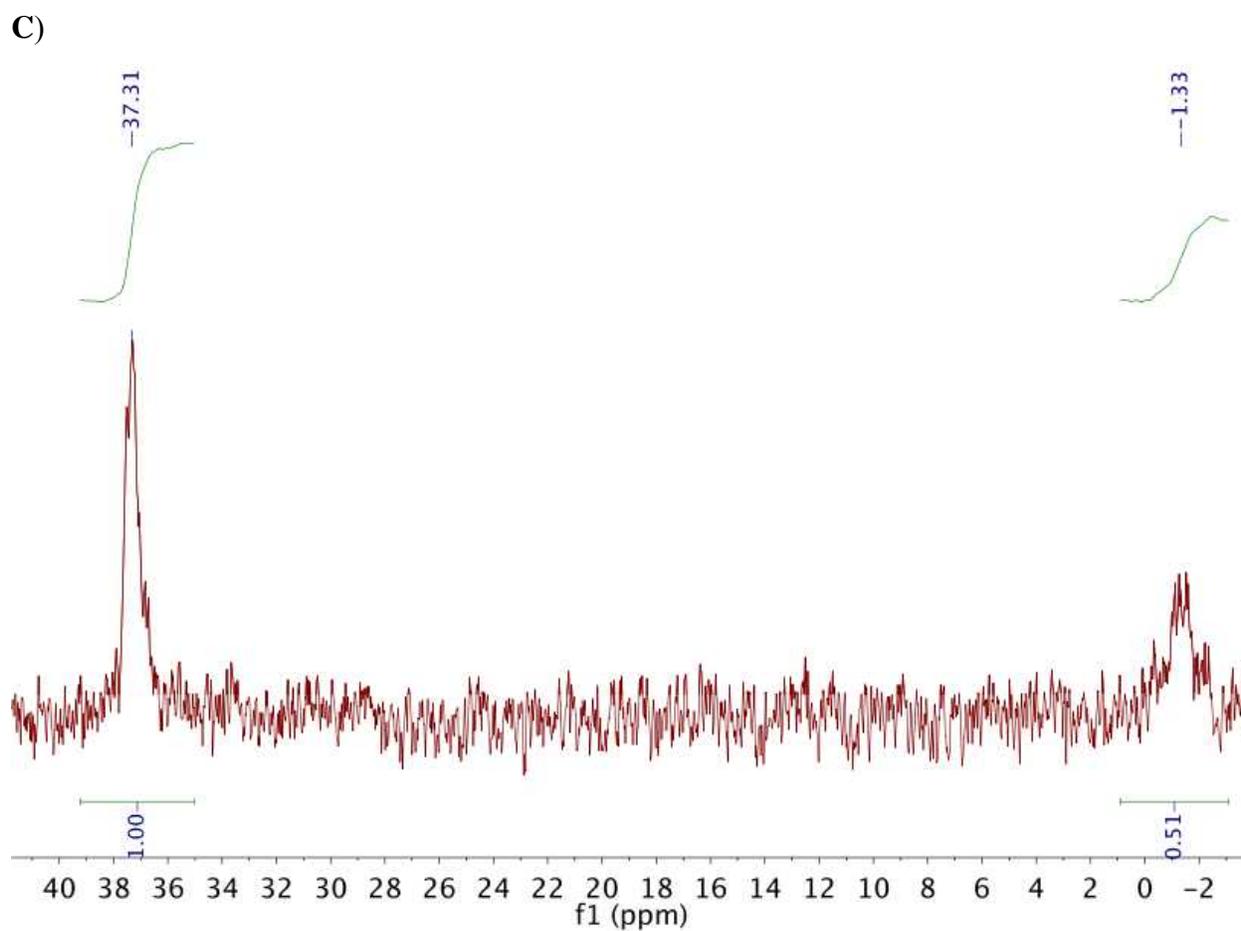


**Figure S15.** Cyclic voltammogram of **3** (0.7 mM) in acetonitrile solution containing 0.1 M  $[n\text{Bu}_4\text{N}][\text{PF}_6]$ . Varying scan rate; glassy carbon electrode.

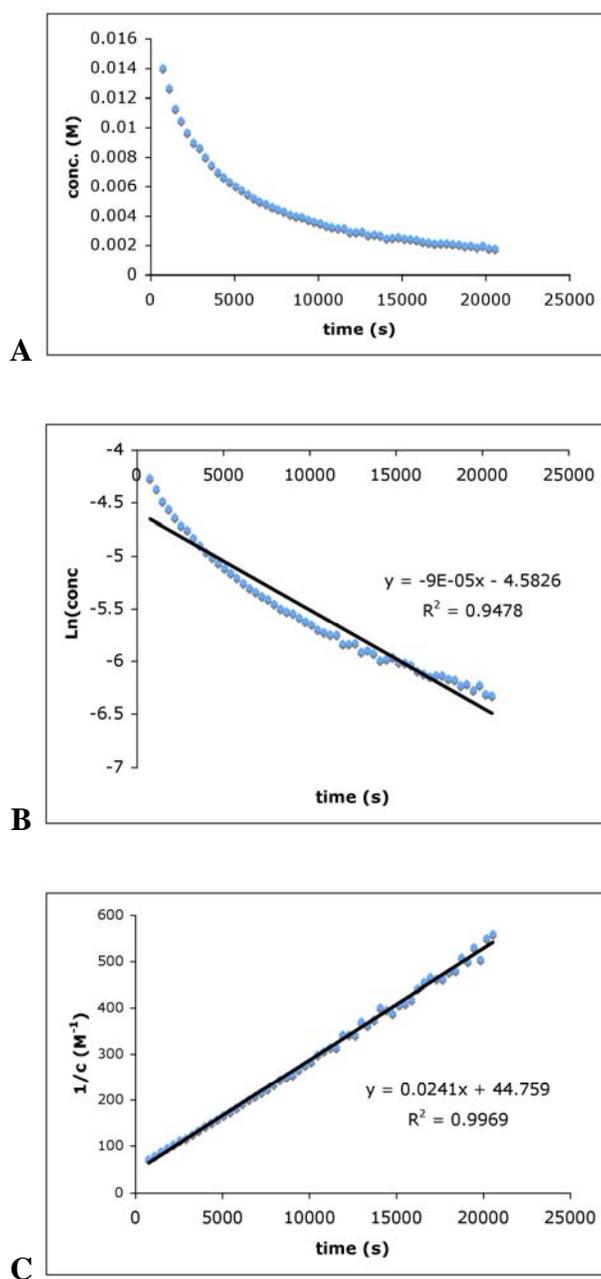


**Figure S16.** Cyclic voltammograms of **3** (0.7 mM) in acetonitrile containing 0.1 M  $[n\text{Bu}_4\text{N}][\text{PF}_6]$  in the presence of  $\text{TsOH}\cdot\text{H}_2\text{O}$  and ferrocene. Scan rate:  $100\text{ mV s}^{-1}$ ; glassy carbon electrode.





**Figure S17.** **A)** 300 MHz  $^1\text{H}$  NMR spectrum of the *in situ* generated  $\text{Co}^{\text{III}}\text{-H}$ ; **B)** 400 MHz  $^1\text{H}$  NMR spectrum of the *in situ* generated  $\text{Co}^{\text{III}}\text{-H}$ ; **C)** 121 MHz  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the *in situ* generated  $\text{Co}^{\text{III}}\text{-H}$ .

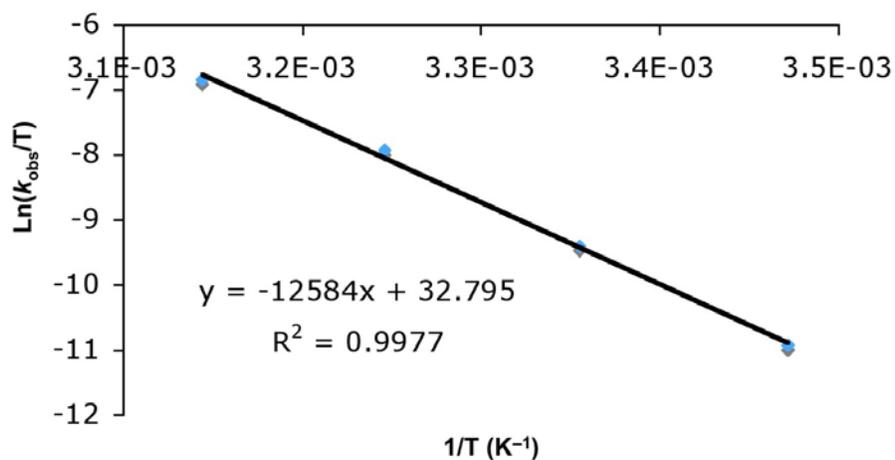


**Figure S18.** Kinetics studies following the decay of the  $\text{Co}^{\text{III}}\text{-H}$  by  $^1\text{H}$  NMR spectroscopy.  $[\text{Co}]_0 = 16.4 \text{ mM}$ ;  $[\text{acid}] = 0.164 \text{ M}$ ;  $0.7 \text{ mL MeCN-}d_3$ . **A)** Plot of the concentration of  $\text{Co}^{\text{III}}\text{-H}$  versus time; **B)** Plot of the natural logarithm of the concentration of  $\text{Co}^{\text{III}}\text{-H}$  versus time – fit to a first order reaction; **C)** Plot of  $1/\text{concentration}$  of  $\text{Co}^{\text{III}}\text{-H}$  versus time – fit to a second order reaction.

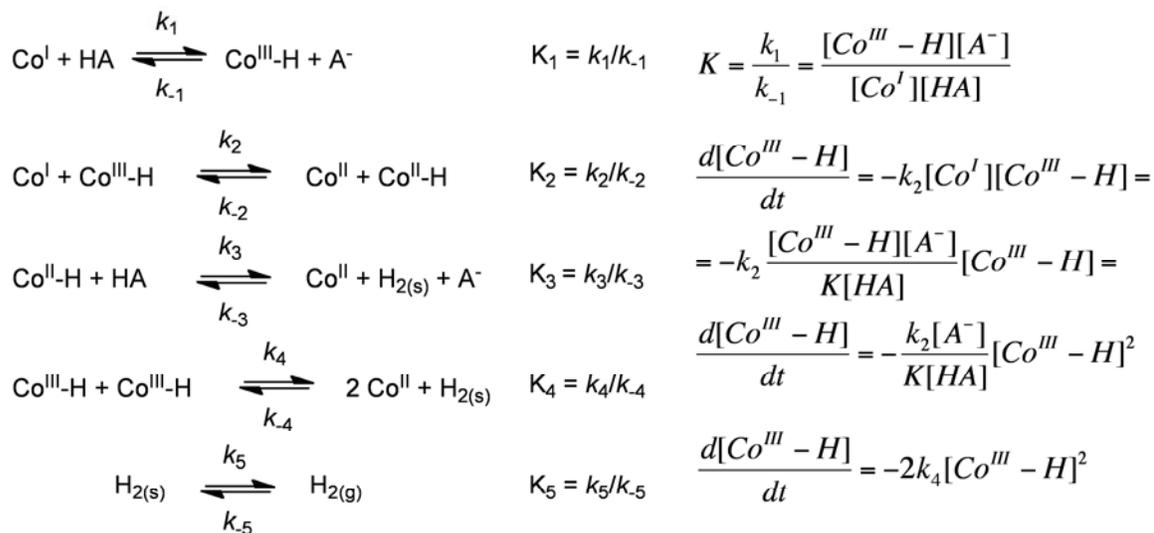
Entry	Temp. (°C) <sup>a</sup>	$k_{\text{obs}}$ (M <sup>-1</sup> s <sup>-1</sup> )
1	15	0.005
2	25	0.024
3	35	0.109
4	45	0.333

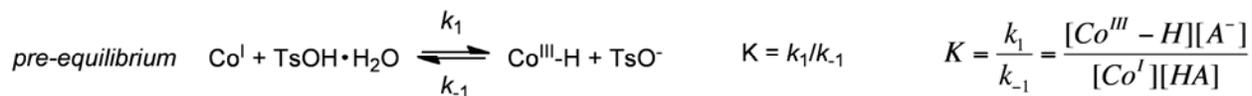
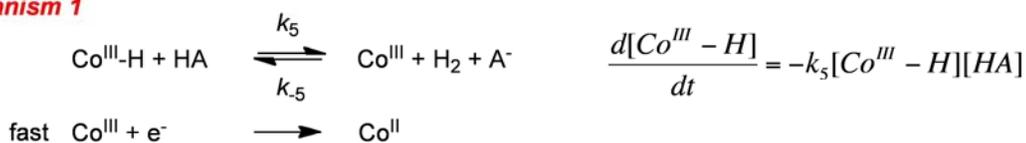
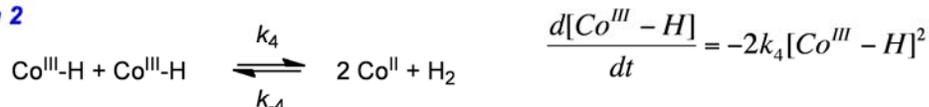
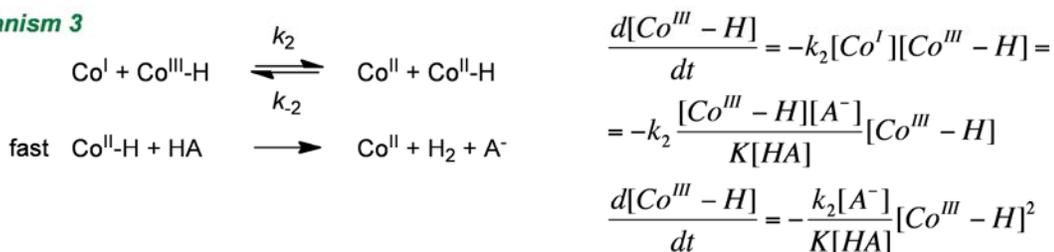
<sup>a</sup>[Co]<sub>0</sub> = 16.4 mM; [acid] = 0.164 M; 0.7 mL MeCN-*d*<sub>3</sub>.

**Table S1.** Table for  $k_{\text{obs}}$  at 15, 25, 35, and 45 °C.



**Figure S19.** Eyring plot.

**Heterolytic/Homolytic****Scheme S1.** Mechanisms employed for the simulated kinetics.

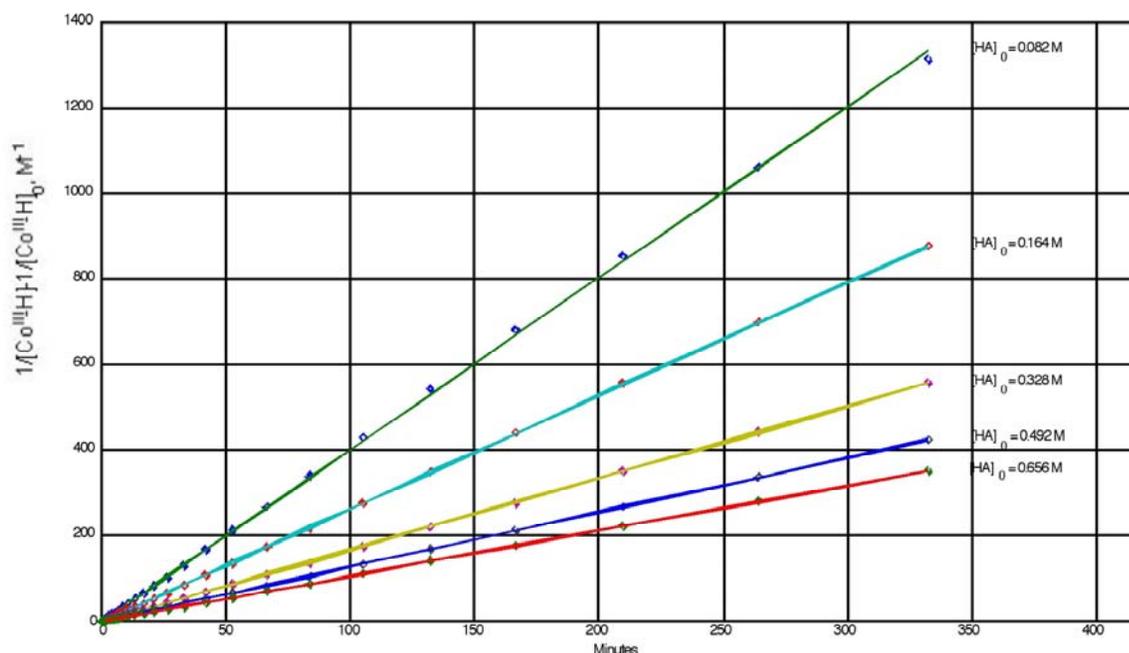
**Mechanism 1****Mechanism 2****Mechanism 3**

**Mechanisms 2 and 3**  $\frac{d[\text{Co}^{\text{III}}\text{-H}]}{dt} = -2k_4[\text{Co}^{\text{III}}\text{-H}] - \frac{k_2k_{-1}[\text{A}^-]}{k_1[\text{HA}]}[\text{Co}^{\text{III}}\text{-H}]^2$

$$k_{\text{obs}} = 2k_4 + \frac{k_2k_{-1}[\text{A}^-]}{k_1[\text{HA}]}$$

**Scheme S2.** The proposed mechanisms and the rate laws associated with them.

The back reactions ( $k_{-5}$ ,  $k_{-4}$ ,  $k_{-2}$ ) are neglected. The protonation of the  $\text{Co}^{\text{II}}\text{-H}$  is assumed to be fast, and therefore,  $k_3$  is not rate determining.



**Figure S20.** Simulated kinetics at an initial  $[\text{Co}]_0 = 16.4 \text{ mM}$  and varying amounts of acids.

		$k_2 \text{ M}^{-1} \text{ s}^{-1}$			
		$6.0 \times 10^{-2}$	$6.0 \times 10^{-2}$	$5.0 \times 10^{-2}$	$5.0 \times 10^{-2}$
		$k_4, \text{ M}^{-1} \text{ s}^{-1}$			
		$2.5 \times 10^{-3}$	$2.5 \times 10^{-4}$	$2.5 \times 10^{-3}$	$2.5 \times 10^{-4}$
$[\text{HA}]_0, \text{ M}$	$k_{\text{obsd}}, \text{ M}^{-1} \text{ s}^{-1}$	$k_{\text{obsd}}(\text{sim}), \text{ M}^{-1} \text{ s}^{-1}$			
0.082	0.0642(2)	0.067	0.065	0.057	0.054
0.164	0.0238(3)	0.044	0.041	0.037	0.034
0.328	0.0137(2)	0.028	0.024	0.024	0.020
0.492	0.0115(2)	0.021	0.017	0.018	0.014
0.656	0.0097(2)	0.018	0.013	0.015	0.011

$$K_{\text{eq}} = 2.2 \text{ atm}$$

$$K_1 = 2.0 \times 10^{-1}$$

$$K_2 = 1.0 \times 10^{-3}$$

$$K_3 = 37 \text{ M}$$

$$K_4 = 1.85 \times 10^{-1} \text{ M}$$

$$K_5 = 2.9 \times 10^2 \text{ atm M}^{-1}$$

$$k_1 = 2.5 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_3 = 1.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_5 = 1.0 \times 10^2 \text{ s}^{-1}$$

**Table S2.** Kinetics simulation parameters using an initial  $[\text{Co}]_0 = 16.4 \text{ mM}$  and varying amounts of acid.

**Table S3.** Crystal data and structure refinement for Co(triphos)(I) (**1**) (CCDC 838815).

Empirical formula	C <sub>41</sub> H <sub>39</sub> P <sub>3</sub> ICo	
Formula weight	810.46	
Crystallization Solvent	THF, diethyl ether	
Crystal Habit	needle	
Crystal size	0.30 × 0.09 × 0.03 mm <sup>3</sup>	
Crystal color	purple/pink	
Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoK $\alpha$	
Temperature	100(2) K	
$\theta$ range for 9925 reflections used in lattice determination	2.31 to 27.63°	
Unit cell dimensions	a = 20.3591(6) Å	$\alpha = 90^\circ$
	b = 10.2917(3) Å	$\beta = 90^\circ$
	c = 17.0536(6) Å	$\gamma = 90^\circ$
Volume	3573.24(19) Å <sup>3</sup>	
Z	4	
Crystal system	Orthorhombic	
Space group	Pna2 <sub>1</sub>	
Density (calculated)	1.507 g/cm <sup>3</sup>	
F(000)	1640	
Data collection program	Bruker APEX2 v2009.7-0	
$\theta$ range for data collection	2.22 to 32.65°	
Completeness to $\theta_{\max}$	99.9 %	
Index ranges	$-30 \leq h \leq 30, -15 \leq k \leq 15, -25 \leq l \leq 25$	
Data collection scan type	$\omega$ scans; 8 settings	
Data reduction program	Bruker SAINT-Plus v7.68A	
Reflections collected	81474	
Independent reflections	13000 [ $R_{\text{int}} = 0.0723$ ]	
Absorption coefficient	1.507 mm <sup>-1</sup>	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7464 and 0.6228
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on $F^2$
Data / restraints / parameters	13000 / 1 / 416
Treatment of hydrogen atoms	Riding
Goodness-of-fit on $F^2$	1.382
Final R indices [ $I > 2\sigma(I)$ , 10945 reflections]	$R_1 = 0.0374$ , $wR_2 = 0.0571$
R indices (all data)	$R_1 = 0.0521$ , $wR_2 = 0.0592$
Type of weighting scheme used	Sigma
Weighting scheme used	$w = 1/\sigma^2(F_o^2)$
Max shift/error	0.004
Average shift/error	0.000
Absolute structure determination	Anomalous differences
Absolute structure parameter	-0.005(9)
Largest diff. peak and hole	1.803 and -0.858 e $\text{\AA}^{-3}$

### Special Refinement Details for Co(triphos)(I) (1) (CCDC 838815).

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor ( $wR$ ) and goodness of fit ( $S$ ) are based on  $F^2$ , conventional  $R$ -factors ( $R$ ) are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating  $R$ -factors(gt) etc. and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Table S4.** Crystal data and structure refinement for [Co(triphos)(MeCN)][PF<sub>6</sub>] (**2**) (CCDC 844598).

Empirical formula	[C <sub>43</sub> H <sub>42</sub> NP <sub>3</sub> Co][PF <sub>6</sub> ]
Formula weight	869.59
Crystallization Solvent	Acetonitrile/THF/diethyl ether
Crystal Habit	blade
Crystal size	0.38 × 0.28 × 0.07 mm <sup>3</sup>
Crystal color	Dichroic purple blue/ light blue
Type of diffractometer	Bruker KAPPA APEX II
Wavelength	0.71073 Å MoKa
Temperature	100(2) K
θ range for 9546 reflections used in lattice determination	3.13 to 29.72°
Unit cell dimensions	a = 20.6085(17) Å      α = 90° b = 14.1669(12) Å      β = 90° c = 27.202(2) Å      γ = 90°
Volume	7942.0(11) Å <sup>3</sup>
Z	8
Crystal system	Orthorhombic
Space group	Pca2 <sub>1</sub>
Density (calculated)	1.455 g/cm <sup>3</sup>
F(000)	3584
θ range for data collection	2.87 to 29.79°
Completeness to θ <sub>max</sub>	99.8 %
Index ranges	-28 ≤ h ≤ 28, -19 ≤ k ≤ 18, -38 ≤ l ≤ 37
Data collection scan type	ω scans; 8 settings
Reflections collected	172385
Independent reflections	22657 [R <sub>int</sub> = 0.0524]
Absorption coefficient	0.655 mm <sup>-1</sup>
Absorption correction	None
Max. and min. transmission	0.9556 and 0.7890

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on $F^2$
Data / restraints / parameters	22657 / 1 / 1046
Treatment of hydrogen atoms	Riding
Goodness-of-fit on $F^2$	2.580
Final R indices [ $I > 2\sigma(I)$ , 18897 reflections]	$R_1 = 0.0449$ , $wR_2 = 0.0661$
R indices (all data)	$R_1 = 0.0582$ , $wR_2 = 0.0668$
Type of weighting scheme used	Sigma
Weighting scheme used	$w = 1/\sigma^2(Fo^2)$
Max shift/error	0.003
Average shift/error	0.000
Absolute structure parameter	0.382(10)
Largest diff. peak and hole	1.837 and $-0.625 \text{ e } \text{\AA}^{-3}$

### Special Refinement Details for [Co(triphos)(MeCN)][PF<sub>6</sub>] (2) (CCDC 844598).

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

The crystal contains disordered hexafluorophosphate which was modeled with the minor component fluorine as isotropic atoms. Additionally, the crystal is a racemic twin with the refined twin ratio of 0.618:0.382.

Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor ( $wR$ ) and goodness of fit ( $S$ ) are based on  $F^2$ , conventional  $R$ -factors ( $R$ ) are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating  $R$ -factors(gt) etc. and is

not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Table S5.** Crystal data and structure refinement for [Co(triphos)(OTs)(MeCN)][OTs]•TsOH (**3**). (CCDC 846384).

Empirical formula	[C <sub>50</sub> H <sub>49</sub> NO <sub>3</sub> P <sub>3</sub> SCo] <sup>+</sup> [C <sub>7</sub> H <sub>7</sub> O <sub>3</sub> S] <sup>-</sup> • C <sub>7</sub> H <sub>8</sub> O <sub>3</sub> S • 0.5(C <sub>4</sub> H <sub>10</sub> O) • 0.45(O)	
Formula weight	1284.24	
Crystallization Solvent	Diethyl ether/acetonitrile/water	
Crystal Habit	plate	
Crystal size	0.34 × 0.29 × 0.02 mm <sup>3</sup>	
Crystal color	yellow	
Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 9816 reflections used in lattice determination	2.29 to 30.48°	
Unit cell dimensions	a = 10.3448(11) Å	α = 82.782(7)°
	b = 12.0949(14) Å	β = 79.521(6)°
	c = 25.564(3) Å	γ = 84.207(7)°
Volume	3110.3(6) Å <sup>3</sup>	
Z	2	
Crystal system	Triclinic	
Space group	P $\bar{1}$	
Density (calculated)	1.371 g/cm <sup>3</sup>	
F(000)	1344	
θ range for data collection	1.81 to 30.62°	
Completeness to θ <sub>max</sub>	99.3 %	
Index ranges	-14 ≤ h ≤ 13, -17 ≤ k ≤ 17, -36 ≤ l ≤ 36	
Data collection scan type	ω scans; 16 settings	
Reflections collected	129130	
Independent reflections	19063 [R <sub>int</sub> = 0.0719]	
Absorption coefficient	0.513 mm <sup>-1</sup>	
Absorption correction	None	

Max. and min. transmission	0.9898 and 0.8448
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on $F^2$
Data / restraints / parameters	19063 / 0 / 742
Treatment of hydrogen atoms	Riding
Goodness-of-fit on $F^2$	2.385
Final R indices [ $I > 2\sigma(I)$ , 13238 reflections]	$R_1 = 0.0552$ , $wR_2 = 0.0918$
R indices (all data)	$R_1 = 0.0847$ , $wR_2 = 0.0931$
Type of weighting scheme used	Sigma
Weighting scheme used	$w = 1/\sigma^2(F_o^2)$
Max shift/error	0.017
Average shift/error	0.000
Largest diff. peak and hole	1.032 and $-5.459 \text{ e } \text{\AA}^{-3}$

**Special Refinement Details for [Co(triphos)(OTs)(MeCN)][OTs]•TsOH (3). (CCDC 846384).**

Crystals were mounted on a loop then placed on the diffractometer under a nitrogen stream at 100K.

The asymmetric unit contains both tosylate (as a counterion) and tosylic acid (the second figure illustrates their orientation). The solvent region is occupied by a molecule of diethyl ether situated across a center of symmetry (occupancy set at 0.5) such that two atoms overlap with the symmetry related moiety. Additionally, there appears to be three molecules of water (total occupancy set at 0.5) modeled as oxygen atoms.

Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor ( $wR$ ) and goodness of fit ( $S$ ) are based on  $F^2$ , conventional  $R$ -factors ( $R$ ) are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating  $R$ -factors(gt) etc. and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.