

Supporting Information:

**Electrocatalytic Hydrogen Evolution at Low Overpotentials by
Cobalt Macroyclic Glyoxime and Tetra-Imine Complexes**

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General Parameters for Simulation

Scan Rate	Cycles	R _u (Ohm)	CdI(F)	Temp.(K)	Geometry	Area(cm ²)
0.1 V/s	1	0	0	298.2	Planar	0.07

Diffusion	Potential Steps (V)	Gauss-Newton Iteration	Noise Level (A)
Semi-Infinite 1D	0.005	2	0

Space perpendicular to electrode:

Grid Expansion Factor	Rel. Truncation Error	Xmas/SQRT(Dt)
0.5	0.0001	6

Local FEM error level: 0.05

Steady State analysis of the bimetallic pathway

We have written the kinetic equations for the bimetallic pathway as:



$$\frac{d[\text{Co(III)-H}]}{dt} = k_4[\text{Co(I)}][\text{HA}] - k_{-4}[\text{Co(III)-H}][\text{A}] - 2k_7[\text{Co(III)-H}]^2$$

$$\frac{d[\text{Co(II)}]}{dt} = 2k_7[\text{Co(III)-H}]^2 = 2 \frac{d[\text{H}_2]}{dt}$$

Assuming a steady state for Co(III)-H

$$2k_7[\text{Co(III)-H}]^2 + k_{-4}[\text{Co(III)-H}][\text{HA}] - k_4[\text{Co(I)}][\text{HA}] = 0$$

solving we obtain,

$$[\text{Co(III)-H}] = \frac{-k_{-4}[\text{A}] \pm \sqrt{(k_{-4}[\text{A}])^2 + 8k_7k_4[\text{Co(I)}][\text{HA}]}}{2k_7}$$

If the first term in the square root is larger then second, $(k_{-4}[\text{A}])^2 >> 8k_7k_4[\text{Co(I)}][\text{HA}]$, then,

$$\begin{aligned} [\text{Co(III)-H}] &= \frac{-k_{-4}[\text{A}] + k_{-4}[\text{A}] \sqrt{1 + \frac{8k_7k_4[\text{Co(I)}][\text{HA}]}{(k_{-4}[\text{A}])^2}}}{4k_7} \\ &\approx \frac{-k_{-4}[\text{A}] + k_{-4}[\text{A}] + \frac{1}{2} \frac{8k_{-4}k_7k_4[\text{Co(I)}][\text{HA}]}{(k_{-4}[\text{A}])^2}}{4k_7} \\ [\text{Co(III)-H}] &\approx \frac{1}{2} \frac{8k_7k_4[\text{Co(I)}][\text{HA}]}{4k_7k_{-4}[\text{A}]} \\ &= \frac{k_4[\text{Co(I)}][\text{HA}]}{k_{-4}[\text{A}]} \\ &= K_4 \frac{[\text{Co(I)}][\text{HA}]}{[\text{A}]} \\ \frac{d[\text{H}_2]}{dt} &= k_7K_4^2 \frac{[\text{CoI}]^2[\text{HA}]^2}{[\text{A}]^2} \end{aligned}$$

The rate is second order in $[\text{Co(I)}]$ and $[\text{HA}]$ and inverse in $[\text{A}]^2$ with a rate constant as the product of the equilibrium constant for the rapid formation of the precursor hydride and the rate constant of the slow hydrogen formation reaction.

If second term is larger, $(k_{-4}[\text{A}])^2 << 8k_7k_4[\text{Co(I)}][\text{HA}]$, then:

$$[\text{Co(III)-H}] = \frac{-k_{-4}[\text{A}] + \sqrt{8k_7k_4[\text{Co(I)}][\text{HA}]}}{4k_7} \sqrt{1 + \frac{(k_{-4}[\text{A}])^2}{4k_7k_4[\text{Co(I)}][\text{HA}]}}$$

$$\begin{aligned}
&\approx \frac{\sqrt{8k_7 k_4 [\text{Co(I)}][\text{HA}]} - k_4 [\text{A}]}{4k_7} \\
&= \sqrt{\frac{k_4 [\text{Co(I)}][\text{HA}]}{2k_7}} \\
\frac{d[\text{H}_2]}{dt} &= k_7 \left(\sqrt{\frac{k_4 [\text{Co(I)}][\text{HA}]}{2k_7}} \right)^2 \\
&= k_4 [\text{Co(I)}][\text{HA}]
\end{aligned}$$

The rate is first order in $[\text{Co(I)}]$ and $[\text{HA}]$ with a rate constant of the show hydride formation reaction.

Electrocatalysis of **4a in the presence of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$.**

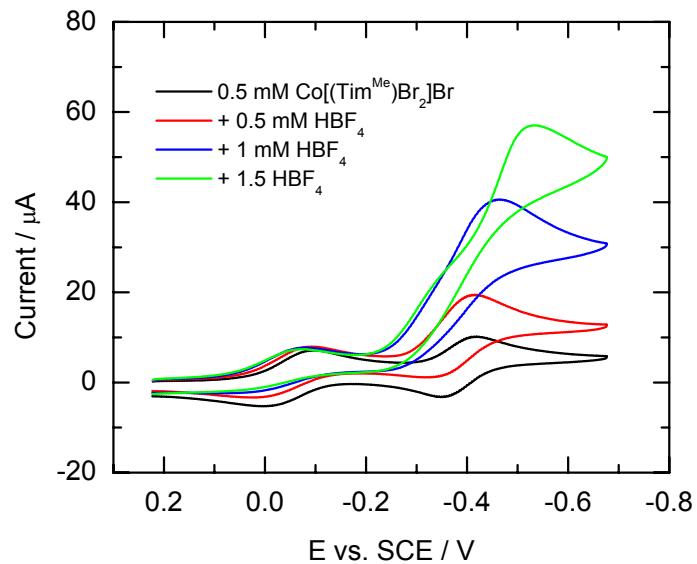


Figure S1. Cyclic voltammogram of **4a** in the presence of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ recorded in an acetonitrile solution containing $0.1 \text{ M [}^n\text{Bu}_4\text{][ClO}_4]$. Scan rate: 100 mV/s .

Electrocatalysis of **4b in the presence of $\text{TsOH}\cdot\text{H}_2\text{O}$ or $\text{HBF}_4\cdot\text{Et}_2\text{O}$.**

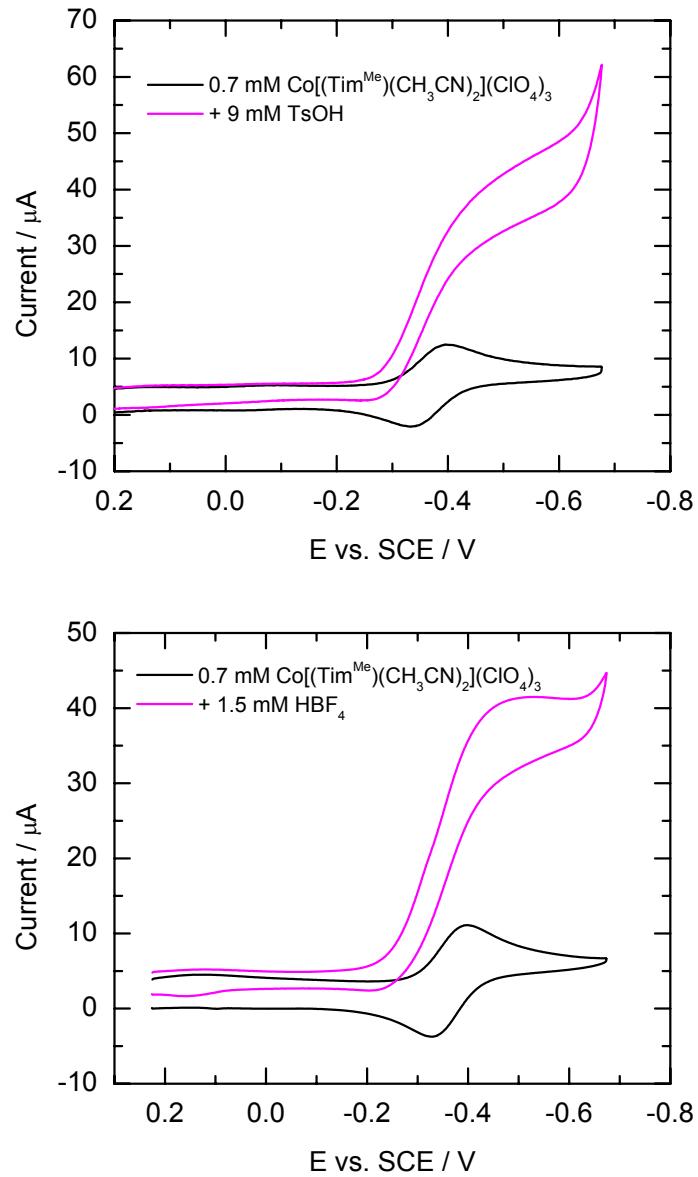


Figure S2. Cyclic voltammogram of **4b** in the presence of $\text{TsOH}\cdot\text{H}_2\text{O}$ (top) or $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (bottom) recorded in an acetonitrile solution containing 0.1 M [ⁿBu₄][ClO₄]. Scan rate: 100 mV/s.

Electrocatalysis of **5a–b in the presence of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$.**

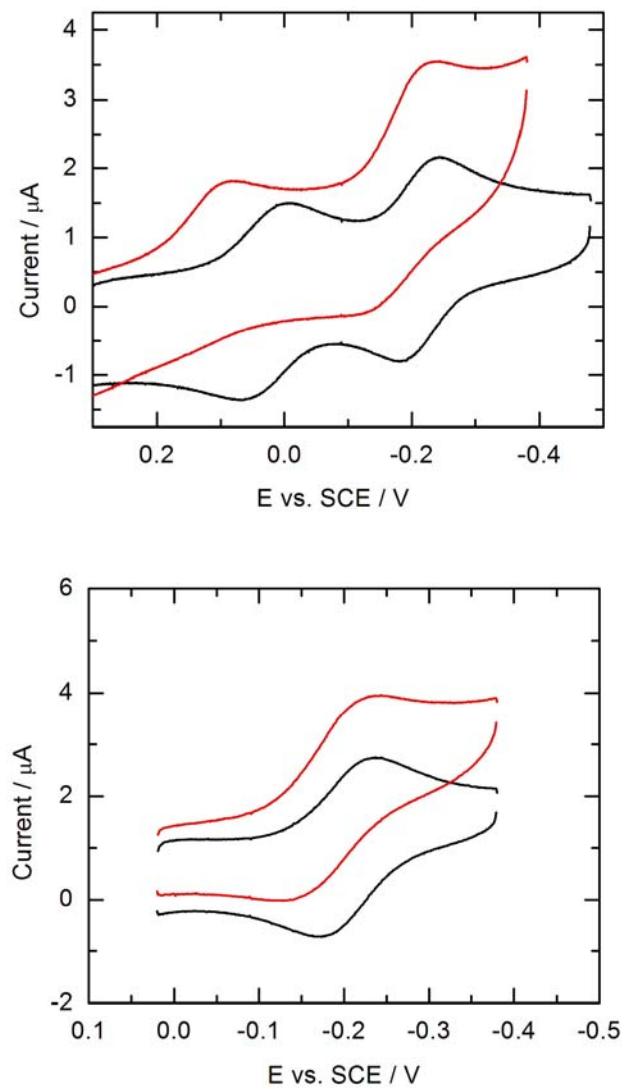


Figure S3. (Top): Cyclic voltammogram of 0.1 mM **5a** in CH_3CN solution containing 0.1 M [$^n\text{Bu}_4\text{N}\right]\text{ClO}_4]$ in the absence (black) and presence (red) of 1.5 mM $\text{HBF}_4 \cdot \text{Et}_2\text{O}$. (Bottom): Cyclic voltammogram of 0.15 mM **5b** in CH_3CN solution containing 0.1 M [$^n\text{Bu}_4\text{N}\right]\text{ClO}_4]$ in the absence (black) and presence (red) of 1.5 mM $\text{HBF}_4 \cdot \text{Et}_2\text{O}$. Scan rate: 100 mV /s⁻¹; Glassy carbon electrode. The reaction for the shift in the Co^{III/II} potential upon addition of acid is not clear at this point.

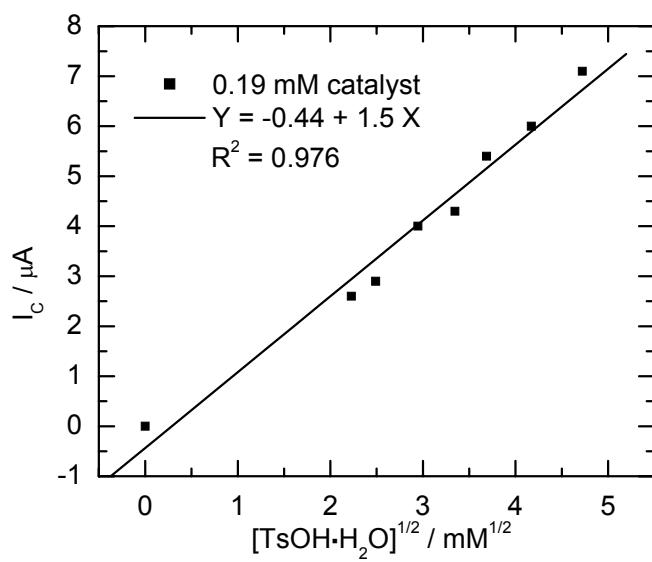
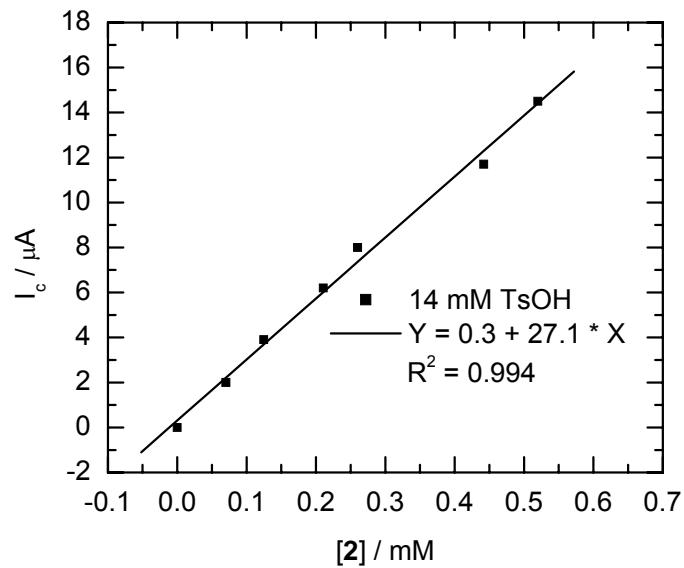


Figure S4. Dependence of the catalytic current i_c on the concentrations of catalyst and acid for complex **2**; $\text{TsOH}\cdot\text{H}_2\text{O}$ was used as the acid, with a scan rate of 100 mV/s.

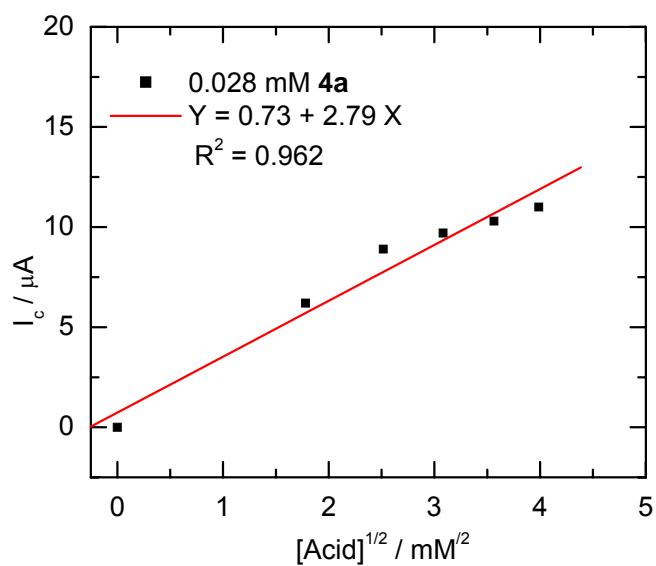
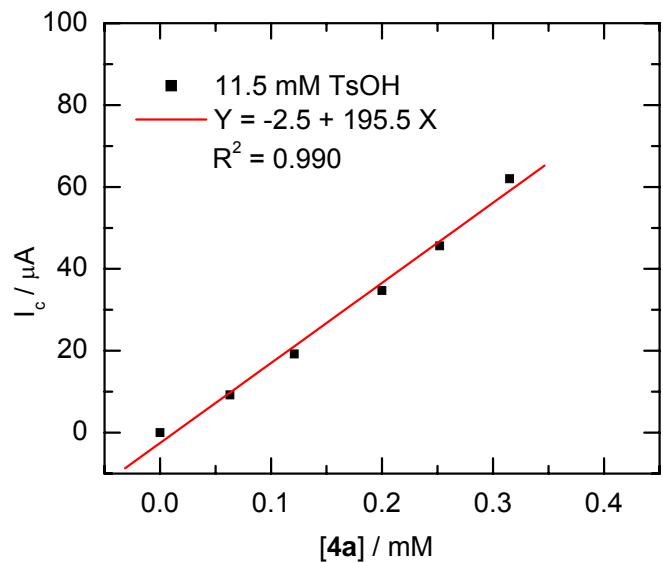


Figure S5. Dependence of the catalytic current i_c on the concentrations of catalyst and acid for complex **4a**; $\text{TsOH}\cdot\text{H}_2\text{O}$ was used as the acid.

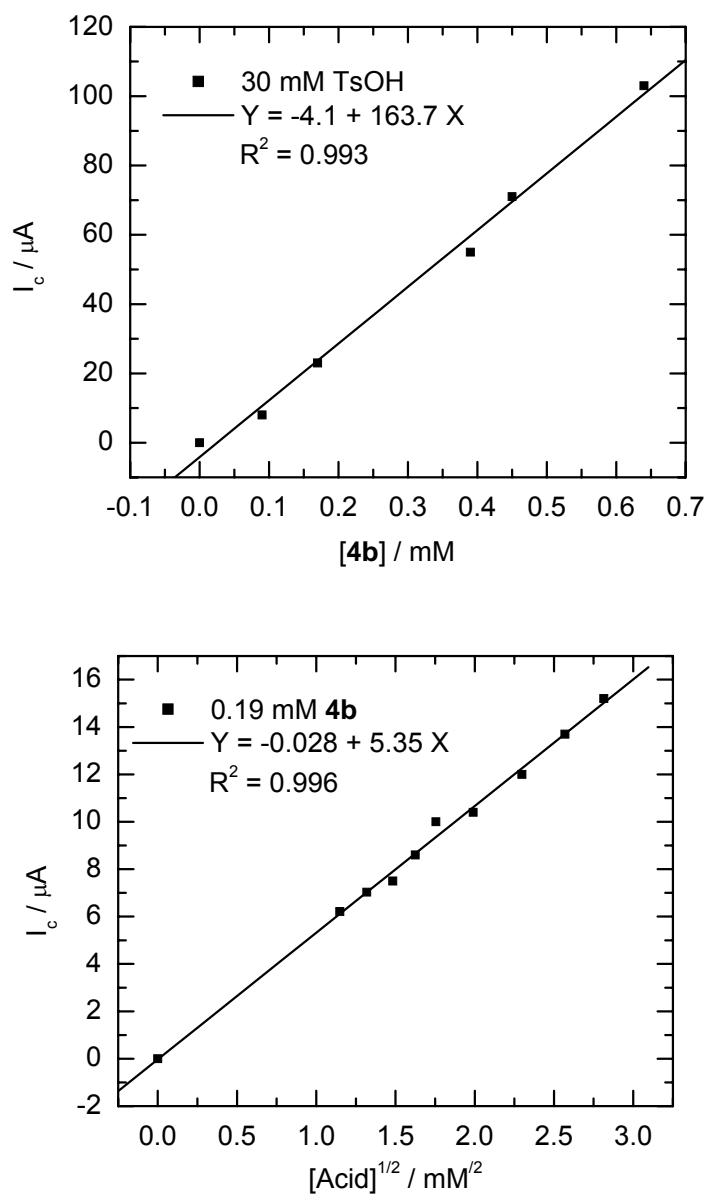


Figure S6. Dependence of the catalytic current i_c on the concentrations of catalyst and acid for complex **4b**; $\text{TsOH}\cdot\text{H}_2\text{O}$ was used as the acid.

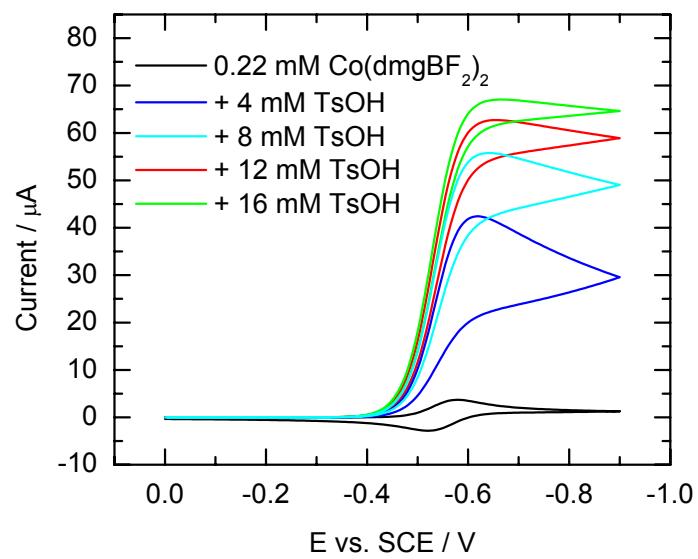
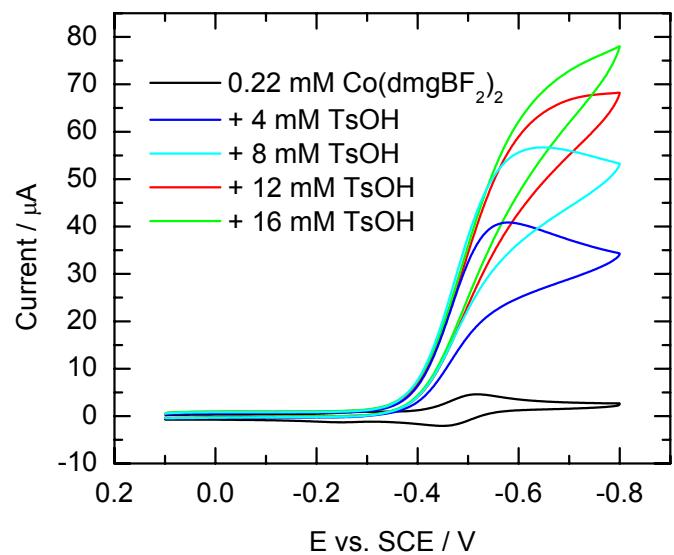


Figure S7. Experimental and simulated spectra of the catalytic waves for H₂ evolution catalysis using 0.22 mM of **1** as the catalyst; top: experimental data; bottom: simulation using a bimetallic mechanism.

Specific Parameters for Simulation in Figure S7:

Estart (V)	Erev (V)	Eend (V)
0	-0.9	0

Charge Transfer reactions:

Rxn	E (V)	α	K _s (cm/s)
Co(III) + e ⁻ → Co(II)	0.2	0.5	10000
Co(II) + e ⁻ → Co(II)	-0.55	0.5	10000
H ⁺ + e ⁻ → s	-0.23	0.5	0

Chemical reactions:

Rxn	K _{eq}	k _f	k _b *
Co(I) + H ⁺ → Co-H	1e5	1.5e5	1.5
s + s → H ₂	1	1e10	1e10
Co-H + Co-H → A + H ₂	1	1.5e6	1.5e6
A → Co(II) + Co(II)	6.55*	1e10	1.53e9

* These constants are automatically calculated by the program

Species:

	D (cm ² /s)	C (M)		D (cm ² /s)	C (M)		D (cm ² /s)	C (M)
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Co(III)	8e-6	0	Co-H	8e-6	0	A	8e-6	0
Co(II)	8e-6	2.2e-4	H ₂	1e-5	0			
Co(I)	8e-6	0	s	1e-5	0			

Acid concentrations, H⁺ represents TsOH

	D (cm ² /s)	C (M)				
H ⁺	1e-5	0	4e-3	8e-3	12e-3	16e-3

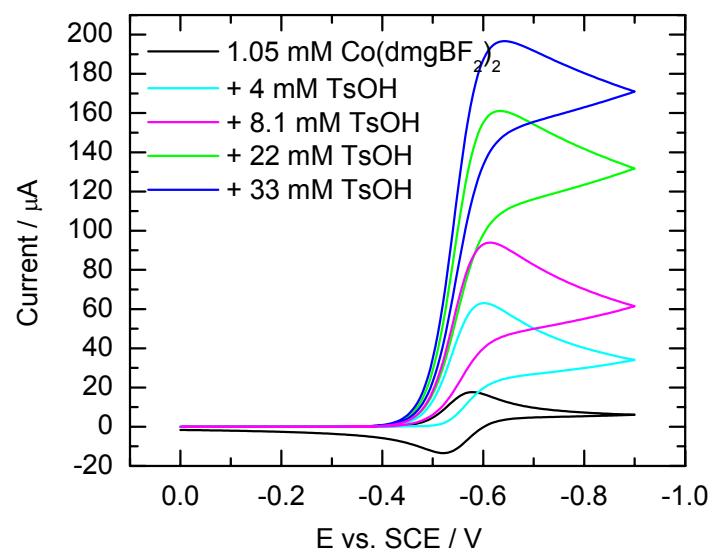
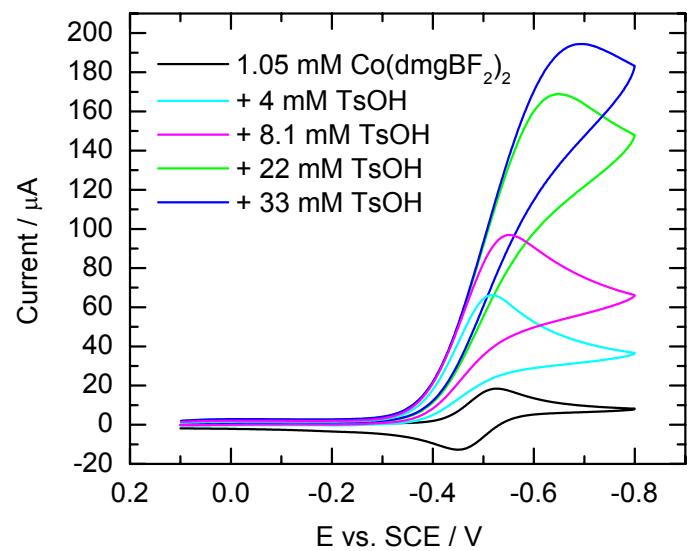


Figure S8. Experimental and simulated spectra of the catalytic waves for H₂ evolution catalysis using 1.05 mM of **1** as the catalyst; top: experimental data; bottom: simulation using a bimetallic mechanism.

Specific Parameters for Simulation in Figure S8:

Estart (V)	Erev (V)	Eend (V)
0	-0.9	0

Charge Transfer reactions:

Rxn	E (V)	α	Ks (cm/s)
Co(III) + e ⁻ → Co(II)	0.2	0.5	10000
Co(II) + e ⁻ → Co(II)	-0.55	0.5	10000
H ⁺ + e ⁻ → s	-0.23	0.5	0

Chemical reactions:

Rxn	K _{eq}	k _f	k _b *
Co(I) + H ⁺ → Co-H	1e5	7000	0.07
s + s → H ₂	1	1e10	1e10
Co-H + Co-H → A + H ₂	1	9e5	9e5
A → Co(II) + Co(II)	6.55*	1e10	1.53e9

* These constants are automatically calculated by the program

Species:

	D (cm ² /s)	C (M)		D (cm ² /s)	C (M)		D (cm ² /s)	C (M)
Co(III)	8e-6	0	Co-H	8e-6	0	A	8e-6	0
Co(II)	8e-6	1.05e-3	H ₂	1e-5	0			
Co(I)	8e-6	0	s	1e-5	0			

Acid concentrations, H⁺ represents TsOH

	D (cm ² /s)	C (M)	C (M)	C (M)	C (M)	C (M)
H ⁺	1e-5	0	4e-3	8.1e-3	22e-3	33e-3

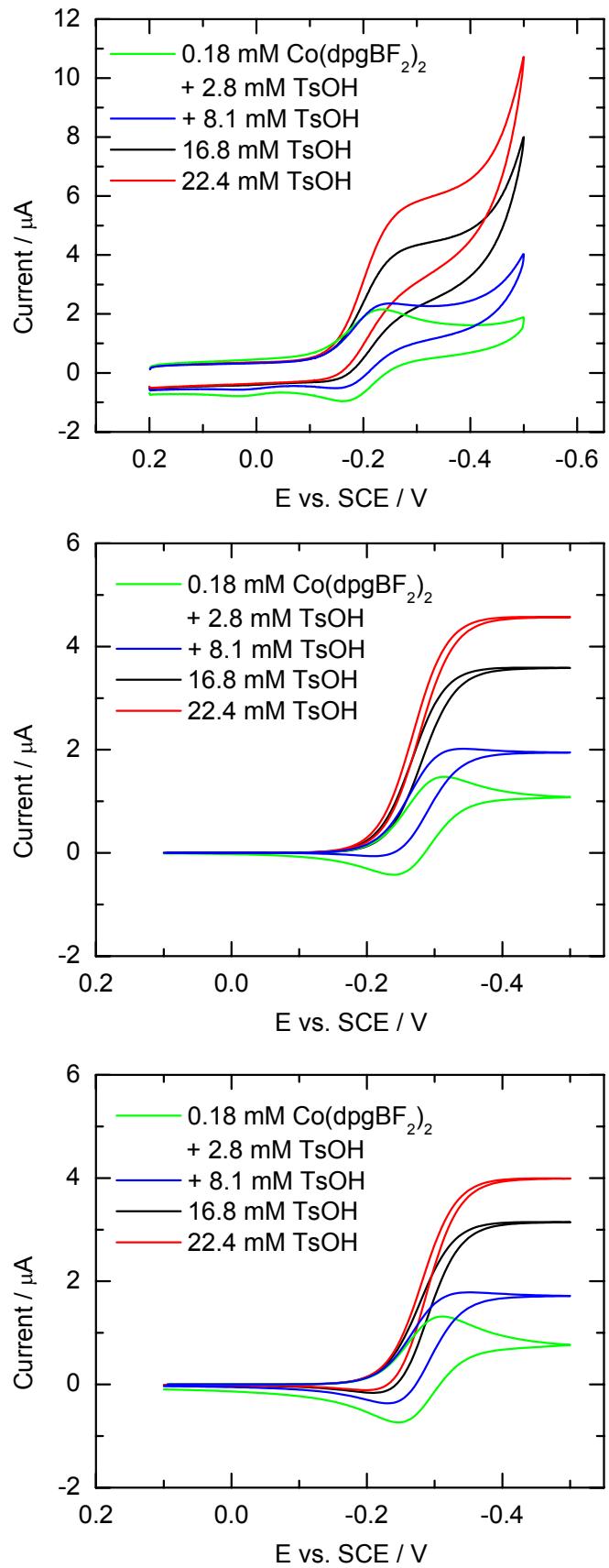


Figure S9. Experimental and simulated spectra of the catalytic waves for H₂ evolution catalysis using 0.18 mM of **2** as the catalyst; top: experimental data (the increase of current near E = -0.6 V is due to catalytic current at the Co(III)-H/Co(II)-H couple, see main text); middle: simulation using a monometallic mechanism; bottom: simulation using a bimetallic mechanism. As shown in the figure, the simulations can not distinguish a monometallic mechanism from a bimetallic mechanism.

Specific Parameters for Simulation in Figure S9:

Estart (V)	Erev (V)	Eend (V)
0.1	-0.5	0.1

Charge Transfer reactions:

Rxn	E (V)	α	K _s (cm/s)
Co(III) + e ⁻ → Co(II)	0.3	0.5	10000
Co(II) + e ⁻ → Co(II)	-0.28	0.5	10000
H ⁺ + e ⁻ → s	-0.23	0.5	0

Chemical reactions for monometallic mechanism:

Rxn	K _{eq}	k _f	k _{b*}
Co(I) + H ⁺ → Co-H	50	5000	100
s + s → H ₂	1	1e10	1e10
Co-H + H ⁺ → Co(III) + H ₂	1.54	800	518
Co(III) + Co(I) → Co(II) + Co(II)	6e9*	1e10	1.53

Chemical reactions for bimetallic mechanism:

Rxn	Keq	kf	kb*
$\text{Co(I)} + \text{H}^+ \rightarrow \text{Co-H}$	10	4e4	4e3
$\text{s} + \text{s} \rightarrow \text{H}_2$	1	1e10	1e10
$\text{Co-H} + \text{Co-H} \rightarrow \text{A} + \text{H}_2$	4900*	1e6	204
$\text{A} \rightarrow \text{Co(II)} + \text{Co(II)}$	1e6	1e10	1e4

* These constants are automatically calculated by the program

Species:

	D (cm ² /s)	C (M)		D (cm ² /s)	C (M)		D (cm ² /s)	C (M)
Co(III)	1.4e-6	0	Co-H	1.4e-6	0	A	1.4e-6	0
Co(II)	1.4e-6	1.8e-4	H ₂	1e-5	0			
Co(I)	1.4e-6	0	s	1e-5	0			

Acid concentrations, H⁺ represents TsOH

	D (cm ² /s)	C (M)	C (M)	C (M)	C (M)	C (M)
H ⁺	1e-5	0	2.8e-3	8.4e-3	16.8e-3	22.4e-3

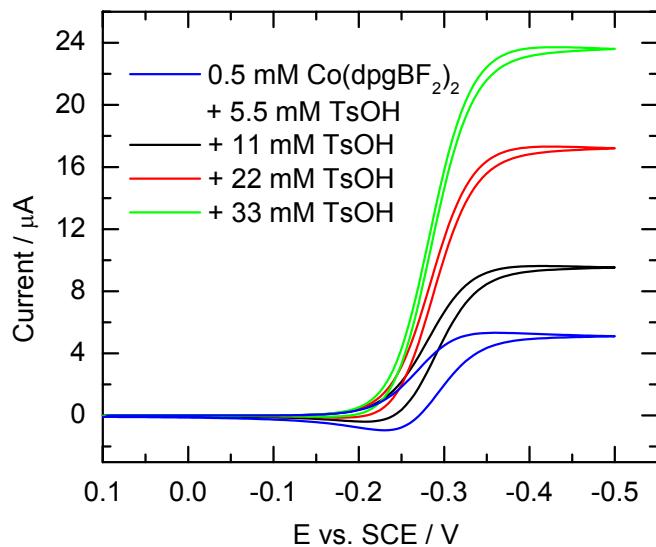
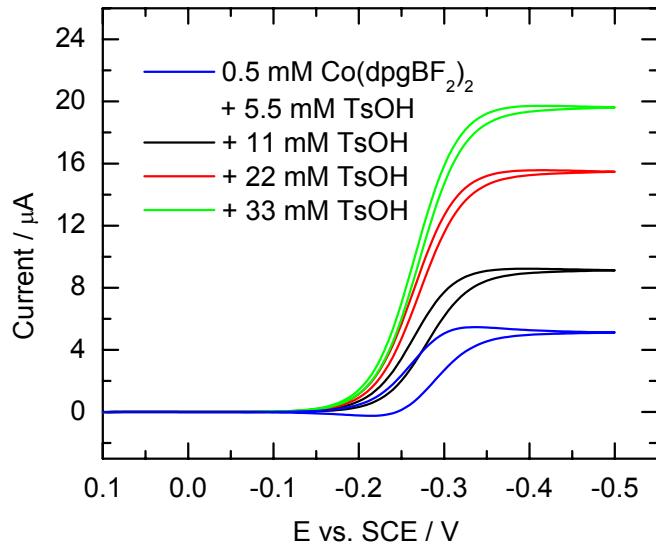
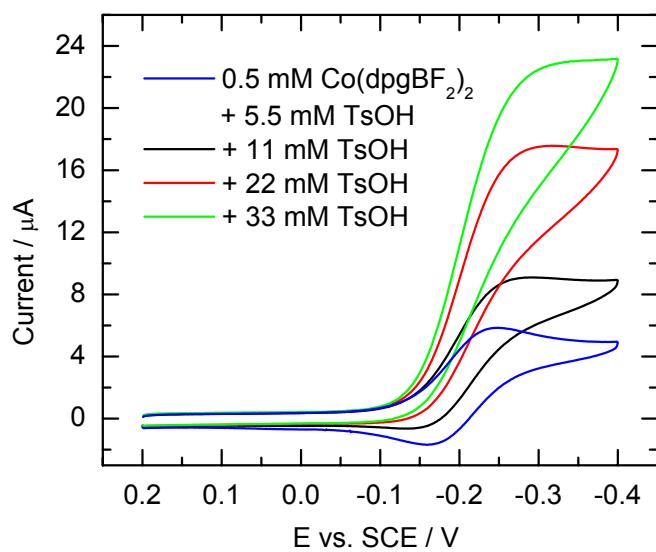


Figure S10. Experimental and simulated spectra of the catalytic waves for H₂ evolution catalysis using 0.5 mM of **2** as the catalyst; top: experimental data; middle: simulation using a monometallic mechanism; bottom: simulation using a bimetallic mechanism. As shown in the figure, the simulations can not distinguish a monometallic mechanism from a bimetallic mechanism.

Specific Parameters for Simulation in Figure S10:

Estart (V)	Erev (V)	Eend (V)
0.1	-0.5	0.1

Charge Transfer reactions:

Rxn	E (V)	α	K _s (cm/s)
Co(III) + e ⁻ → Co(II)	0.3	0.5	10000
Co(II) + e ⁻ → Co(II)	-0.28	0.5	10000
H ⁺ + e ⁻ → s	-0.23	0.5	0

Chemical reactions for monometallic mechanism:

Rxn	K _{eq}	k _f	k _{b*}
Co(I) + H ⁺ → Co-H	50	5000	100
s + s → H ₂	1	1e10	1e10
Co-H + H ⁺ → Co(III) + H ₂	1.54	800	518
Co(III) + Co(I) → Co(II) + Co(II)	6e9*	1e10	1.53

Chemical reactions for bimetallic mechanism:

Rxn	Keq	kf	kb*
Co(I) + H ⁺ → Co-H	10	4e4	4e3
s + s → H ₂	1	1e10	1e10
Co-H + Co-H → A + H ₂	4900*	1e6	204
A → Co(II) + Co(II)	1e6	1e10	1e4

* These constants are automatically calculated by the program

Species:

	D (cm ² /s)	C (M)		D (cm ² /s)	C (M)		D (cm ² /s)	C (M)
Co(III)	1.4e-6	0	Co-H	1.4e-6	0	A	1.4e-6	0
Co(II)	1.4e-6	5e-4	H ₂	1e-5	0			
Co(I)	1.4e-6	0	s	1e-5	0			

Acid concentrations, H⁺ represents TsOH

	D (cm ² /s)	C (M)	C (M)	C (M)	C (M)	C (M)
H ⁺	1e-5	0	5.5e-3	11e-3	22e-3	33e-3

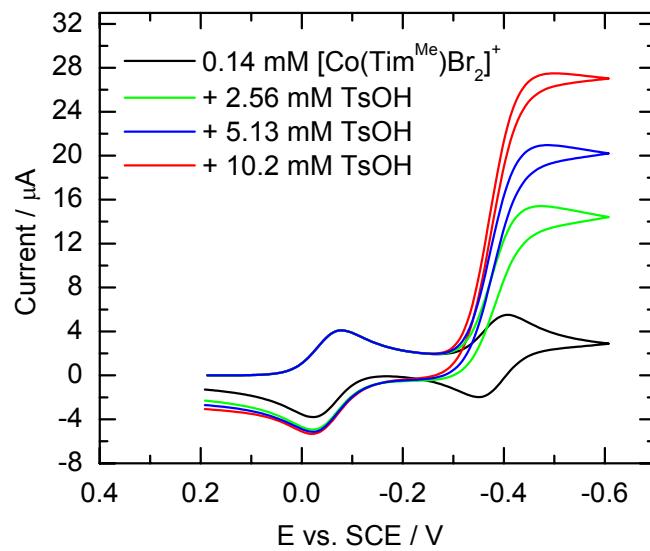
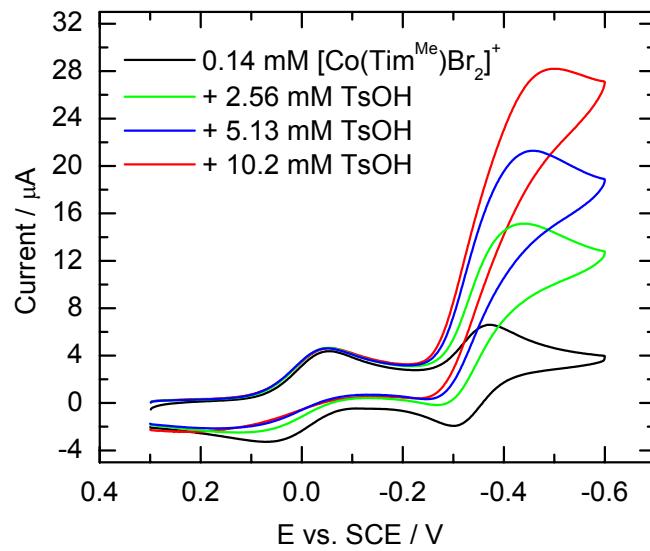


Figure S11. Experimental and simulated spectra of the catalytic waves for H₂ evolution catalysis using 0.14 mM of **4a** as the catalyst; top: experimental data; bottom: simulation using a bimetallic mechanism.

Specific Parameters for Simulation in Figure S11:

Estart (V)	Erev (V)	Eend (V)
0.2	-0.6	0.2

Charge Transfer reactions:

Rxn	E (V)	α	Ks (cm/s)
Co(III) + $e^- \rightarrow$ Co(II)	-0.05	0.5	10000
Co(II) + $e^- \rightarrow$ Co(II)	-0.38	0.5	10000
$H^+ + e^- \rightarrow s$	-0.23	0.5	0

Chemical reactions:

Rxn	Keq	kf	kb*
Co(I) + $H^+ \rightarrow$ Co-H	1e3	1e4	10
$s + s \rightarrow H_2$	1	1e10	1e10
Co-H + Co-H $\rightarrow A + H_2$	0.001	1e6	1e9
$A \rightarrow Co(II) + Co(II)$	117.5*	1e10	8.5e7

* These constants are automatically calculated by the program

Species:

	D (cm ² /s)	C (M)		D (cm ² /s)	C (M)		D (cm ² /s)	C (M)
Co(III)	2.5e-5	0	Co-H	2.5e-5	0	A	2.5e-5	0
Co(II)	2.5e-5	1.38e-4	H_2	1e-5	0			
Co(I)	2.5e-5	0	s	1e-5	0			

Acid concentrations, H^+ represents TsOH

	D (cm ² /s)	C (M)	C (M)	C (M)	C (M)
H^+	1e-5	0	2.56e-3	5.13e-3	10.2e-3

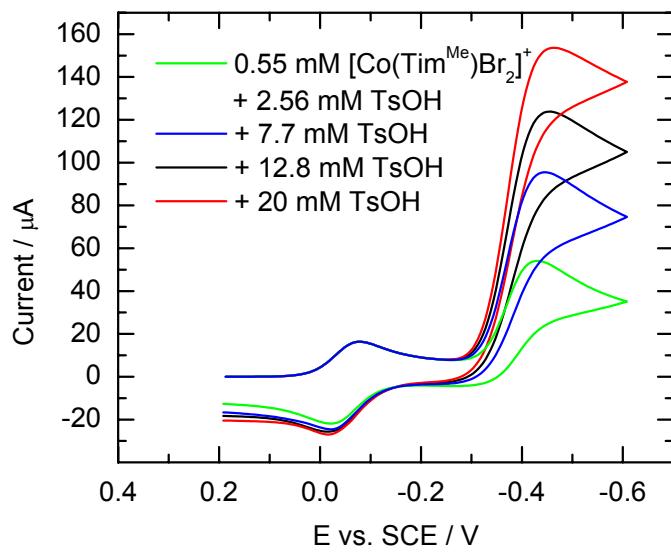
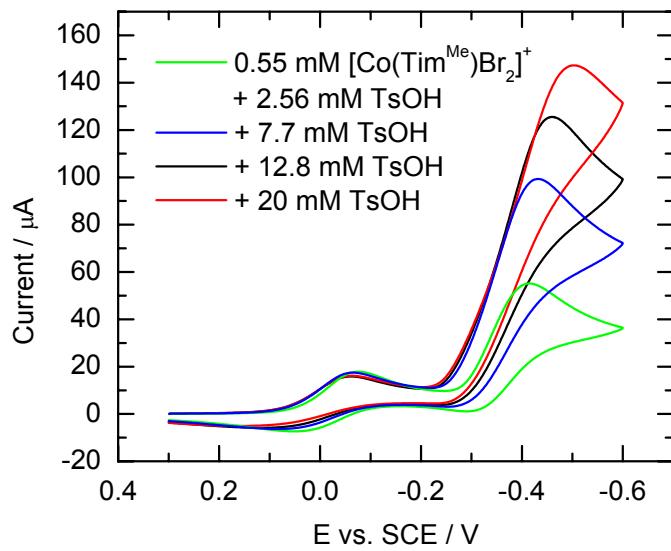


Figure S12. Experimental and simulated spectra of the catalytic waves for H₂ evolution catalysis using 0.55 mM of **4a** as the catalyst; top: experimental data; bottom: simulation using a bimetallic mechanism.

Specific Parameters for Simulation in Figure S12:

Estart (V)	Erev (V)	Eend (V)
0.2	-0.6	0.2

Charge Transfer reactions:

Rxn	E (V)	α	Ks (cm/s)
$\text{Co(III)} + \text{e}^- \rightarrow \text{Co(II)}$	-0.05	0.5	10000
$\text{Co(II)} + \text{e}^- \rightarrow \text{Co(II)}$	-0.38	0.5	10000
$\text{H}^+ + \text{e}^- \rightarrow \text{s}$	-0.23	0.5	0

Chemical reactions:

Rxn	Keq	kf	kb*
$\text{Co(I)} + \text{H}^+ \rightarrow \text{Co-H}$	1e3	1e4	10
$\text{s} + \text{s} \rightarrow \text{H}_2$	1	1e10	1e10
$\text{Co-H} + \text{Co-H} \rightarrow \text{A} + \text{H}_2$	0.001	1e6	1e9
$\text{A} \rightarrow \text{Co(II)} + \text{Co(II)}$	117.5*	1e10	8.5e7

* These constants are automatically calculated by the program

Species:

	D (cm ² /s)	C (M)		D (cm ² /s)	C (M)		D (cm ² /s)	C (M)
Co(III)	2.5e-5	0	Co-H	2.5e-5	0	A	2.5e-5	0
Co(II)	2.5e-5	5.5e-4	H ₂	1e-5	0			

Co(I)	2.5e-5	0	s	1e-5	0
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Acid concentrations, H^+ represents TsOH

	D (cm ² /s)	C (M)	C (M)	C (M)	C (M)
H^+	1e-5	2.56e-3	7.7e-3	12.8e-3	20e-3

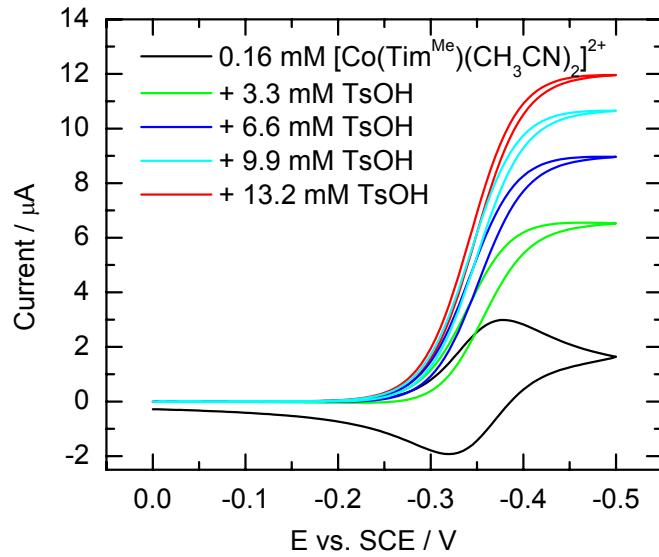
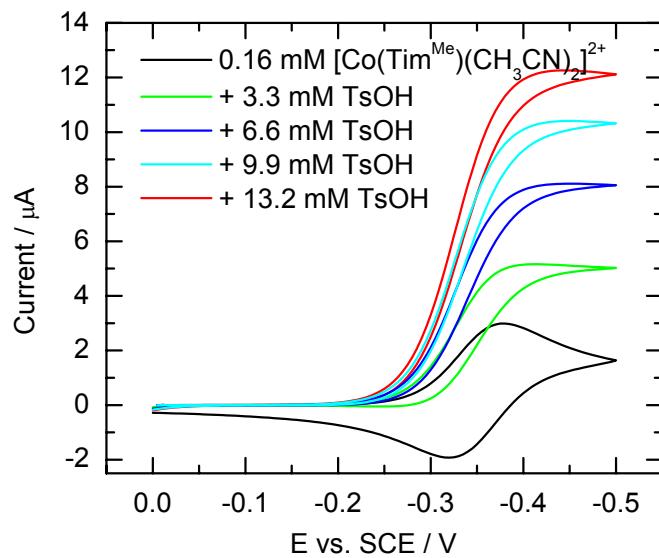
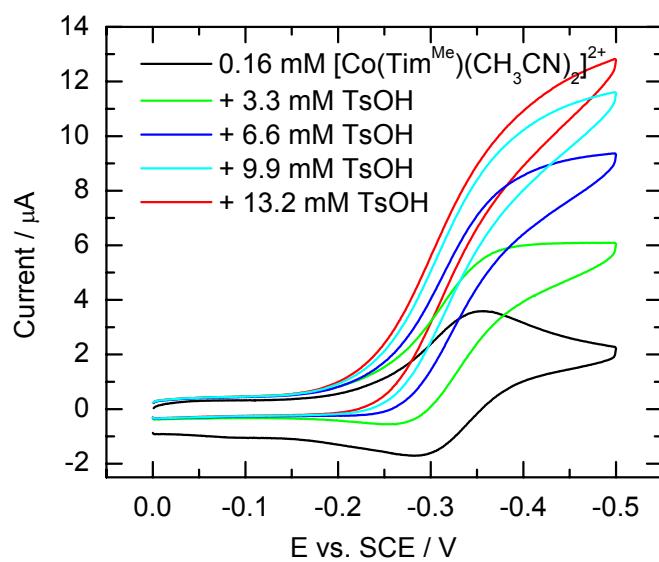


Figure S13. Experimental and simulated spectra of the catalytic waves for H₂ evolution catalysis using 0.16 mM of **4b** as the catalyst; top: experimental data; middle: simulation using a monometallic mechanism; bottom: simulation using a bimetallic mechanism. As shown in the figure, the simulations can not distinguish a monometallic mechanism from a bimetallic mechanism.

Specific Parameters for Simulation in Figure S13:

Estart (V)	Erev (V)	Eend (V)
0	-0.5	0

Charge Transfer reactions:

Rxn	E (V)	α	K _s (cm/s)
Co(III) + e ⁻ → Co(II)	0.2	0.5	10000
Co(II) + e ⁻ → Co(II)	-0.35	0.5	10000
H ⁺ + e ⁻ → s	-0.23	0.5	0

Chemical reactions for monometallic mechanism:

Rxn	K _{eq}	k _f	k _{b*}
Co(I) + H ⁺ → Co-H	300	8000	26.6
s + s → H ₂	1	1e10	1e10
Co-H + H ⁺ → Co(III) + H ₂	1.9e-8	650	4e10
Co(III) + Co(I) → Co(II) + Co(II)	1.9e9*	1e10	5

Chemical reactions for bimetallic mechanism:

Rxn	Keq	kf	kb*
$\text{Co(I)} + \text{H}^+ \rightarrow \text{Co-H}$	500	2e3	4
$\text{s} + \text{s} \rightarrow \text{H}_2$	1	1e10	1e10
$\text{Co-H} + \text{Co-H} \rightarrow \text{A} + \text{H}_2$	1000	3e5	300
$\text{A} \rightarrow \text{Co(II)} + \text{Co(II)}$	4.5e5*	1e10	2.2e4

* These constants are automatically calculated by the program

Species:

	D (cm ² /s)	C (M)		D (cm ² /s)	C (M)		D (cm ² /s)	C (M)
Co(III)	1.2e-5	0	Co-H	1.2e-5	0	A	1.2e-5	0
Co(II)	1.2e-5	1.59e-4	H ₂	1e-5	0			
Co(I)	1.2e-5	0	s	1e-5	0			

Acid concentrations, H⁺ represents TsOH

	D (cm ² /s)	C (M)	C (M)	C (M)	C (M)	C (M)
H ⁺	1e-5	0	2.8e-3	8.4e-3	16.8e-3	22.4e-3

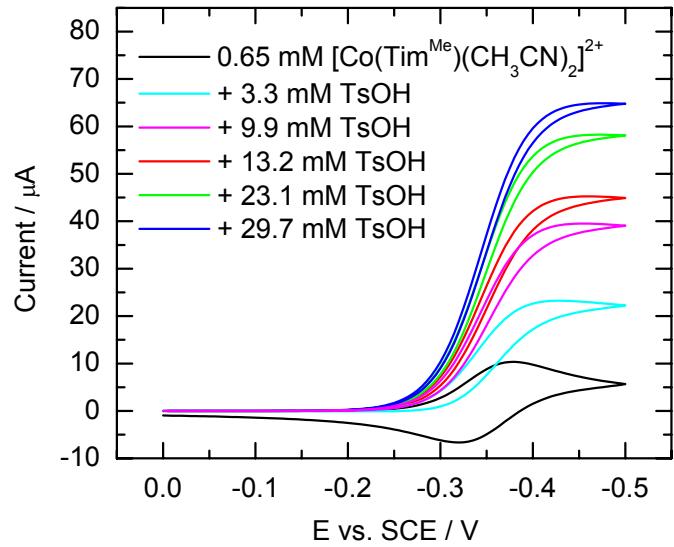
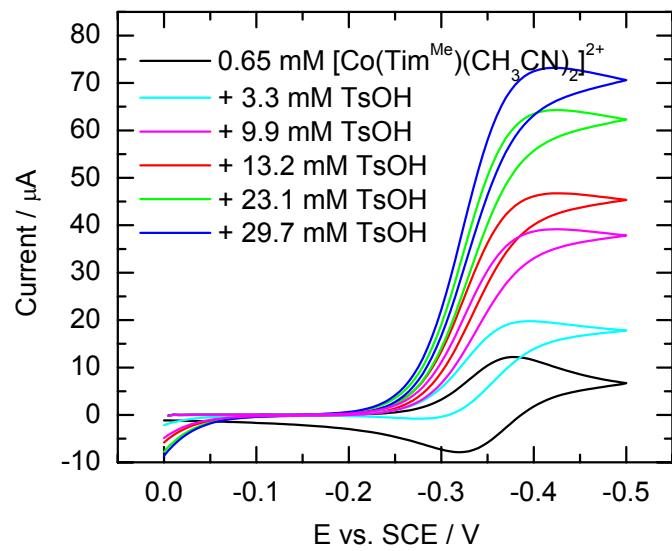
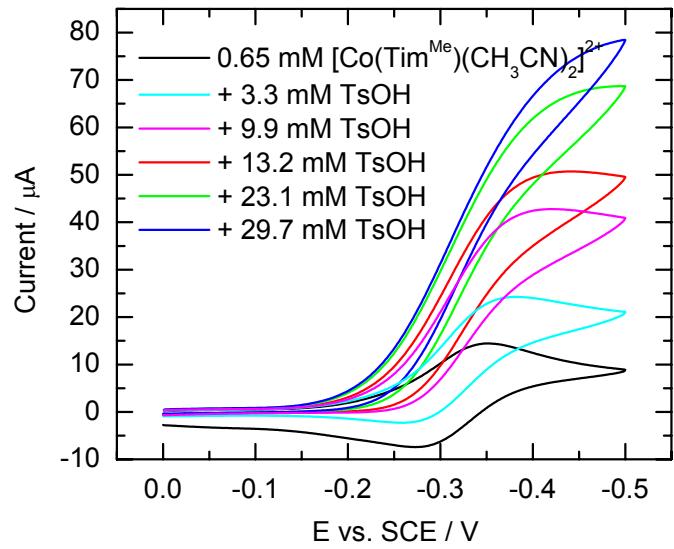


Figure S14. Experimental and simulated spectra of the catalytic waves for H₂ evolution catalysis using 0.65 mM of **4b** as the catalyst; top: experimental data; middle: simulation using a monometallic mechanism; bottom: simulation using a bimetallic mechanism. As shown in the figure, the simulations can not distinguish a monometallic mechanism from a bimetallic mechanism.

Specific Parameters for Simulation in Figure S14:

Estart (V)	Erev (V)	Eend (V)
0	-0.5	0

Charge Transfer reactions:

Rxn	E (V)	α	K _s (cm/s)
Co(III) + e ⁻ → Co(II)	0.2	0.5	10000
Co(II) + e ⁻ → Co(II)	-0.35	0.5	10000
H ⁺ + e ⁻ → s	-0.23	0.5	0

Chemical reactions for monometallic mechanism:

Rxn	K _{eq}	k _f	k _{b*}
Co(I) + H ⁺ → Co-H	300	8000	26.6
s + s → H ₂	1	1e10	1e10
Co-H + H ⁺ → Co(III) + H ₂	1.9e-8	650	4e10
Co(III) + Co(I) → Co(II) + Co(II)	1.9e9*	1e10	5

Chemical reactions for bimetallic mechanism:

Rxn	Keq	kf	kb*
Co(I) + H ⁺ → Co-H	500	2e3	4
s + s → H ₂	1	1e10	1e10
Co-H + Co-H → A + H ₂	1000	3e5	300
A → Co(II) + Co(II)	4.5e5*	1e10	2.2e4

* These constants are automatically calculated by the program

Species:

	D (cm ² /s)	C (M)		D (cm ² /s)	C (M)		D (cm ² /s)	C (M)
Co(III)	1.2e-5	0	Co-H	1.2e-5	0	A	1.2e-5	0
Co(II)	1.2e-5	1.59e-4	H ₂	1e-5	0			
Co(I)	1.2e-5	0	s	1e-5	0			

Acid concentrations, H⁺ represents TsOH

	D (cm ² /s)	C (M)	C (M)	C (M)	C (M)	C (M)	C (M)
H ⁺	1e-5	0	3.3e-3	9.9e-3	13.2e-3	23.1e-3	29.7e-3

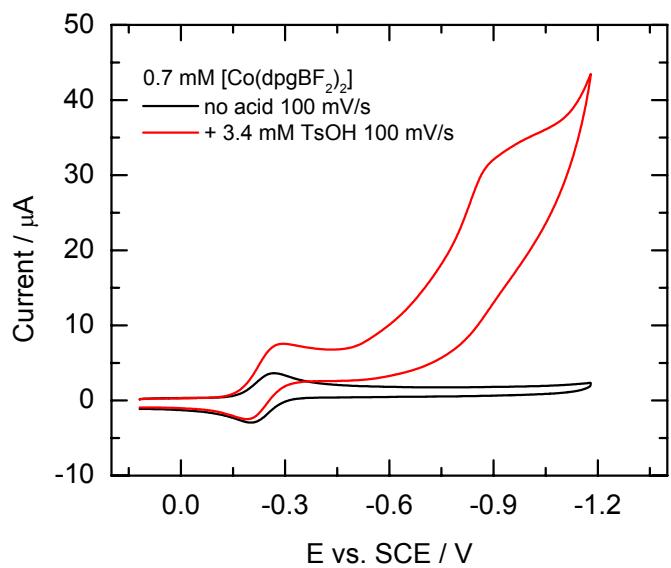


Figure S15. Cyclic voltammogram of 0.7 mM **2** in CH_3CN solution containing 0.1 M $[^n\text{Bu}_4\text{N}][\text{ClO}_4]$ in the absence (black) and presence (red) of 3.4 mM $\text{TsOH}\cdot\text{H}_2\text{O}$ showing a catalytic wave negative of the $\text{Co}^{II/I}$ potential. Scan rate: 100 mV /s⁻¹; Glassy carbon electrode.

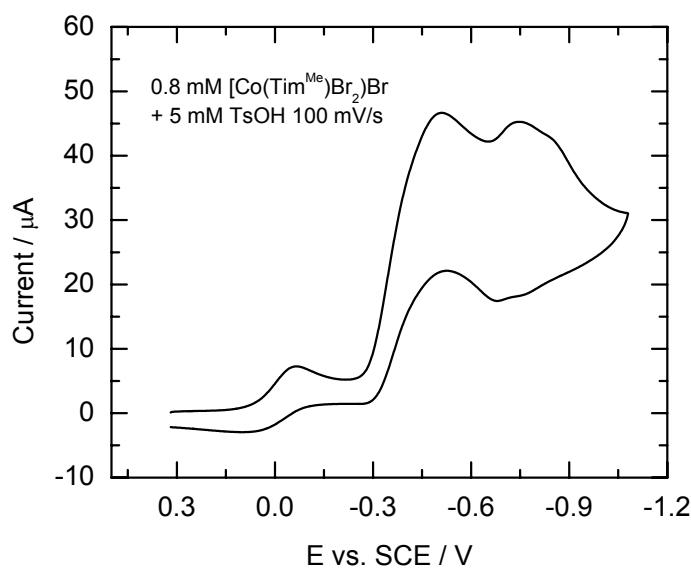


Figure S16. Cyclic voltammogram of 0.8 mM **4a** in CH₃CN solution containing 0.1 M [ⁿBu₄N][ClO₄] in presence of 5 mM TsOH•H₂O showing a redox wave negative of the Co^{II/I} potential. Scan rate: 100 mV / s⁻¹; Glassy carbon electrode.

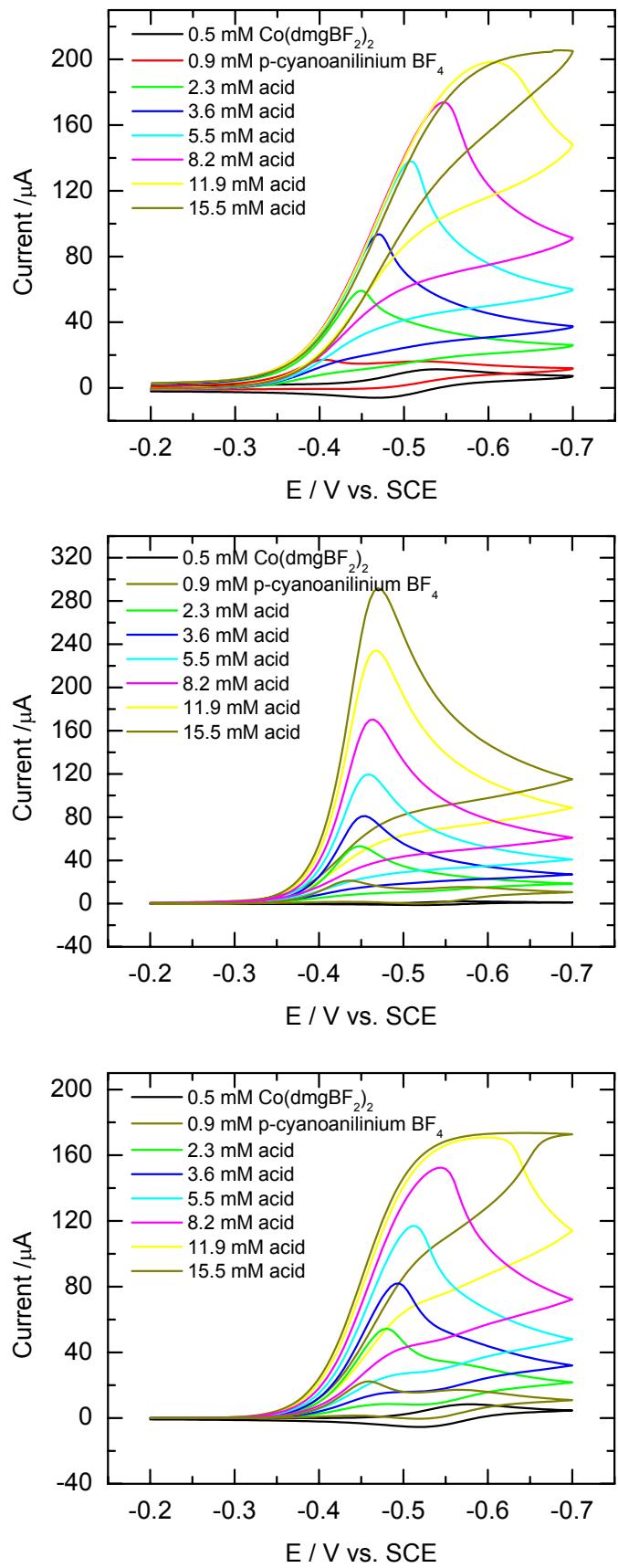


Figure S17. Experimental and simulated spectra of the catalytic waves for H₂ evolution catalysis using 0.5 mM of **1** as the catalyst and p-cyanoanilinium BF₄ as the acid; top: experimental data; middle: simulation using a monometallic mechanism; bottom: simulation using a bimetallic mechanism. As shown in the figure, only simulations assuming a bimetallic mechanism could give rise to satisfactory fits to the experimental data collected under all conditions.

Specific Parameters for Simulation in Figure S17:

Estart (V)	Erev (V)	Eend (V)
0	-0.5	0

Charge Transfer reactions:

Rxn	E (V)	α	K _s (cm/s)
Co(III) + e ⁻ → Co(II)	0.2	0.5	10000
Co(II) + e ⁻ → Co(II)	-0.35	0.5	10000
H ⁺ + e ⁻ → s	-0.20	0.5	0

Chemical reactions for monometallic mechanism:

Rxn	K _{eq}	k _f	k _{b*}
Co(I) + H ⁺ → Co-H	3e5	7e7	233
s + s → H ₂	1	1e10	1e10
Co-H + H ⁺ → Co(III) + H ₂	4.7e-7	1e10	2e16
Co(III) + Co(I) → Co(II) + Co(II)	4.7e12*	1e10	0.002

Chemical reactions for bimetallic mechanism:

Rxn	Keq	kf	kb*
Co(I) + H ⁺ → Co-H	3e5	1e8	333
s + s → H ₂	1	1e10	1e10
Co-H + Co-H → A + H ₂	1	5e5	5e5
A → Co(II) + Co(II)	7.5*	1e10	1.3e9

* These constants are automatically calculated by the program

Species:

	D (cm ² /s)	C (M)		D (cm ² /s)	C (M)		D (cm ² /s)	C (M)
Co(III)	1.2e-5	0	Co-H	1.2e-5	0	A	1.2e-5	0
Co(II)	1.2e-5	5e-4	H ₂	1e-5	0			
Co(I)	1.2e-5	0	s	1e-5	0			

Acid concentrations, H⁺ represents p-cyanoanilinium.

	D (cm ² /s)	C (M)	C (M)	C (M)	C (M)	C (M)	C (M)	C (M)	C (M)
H ⁺	1e-5	0	0.9e-3	2.3e-3	3.6e-3	5.5e-3	8.2e-3	11.9e-3	15.5e-3

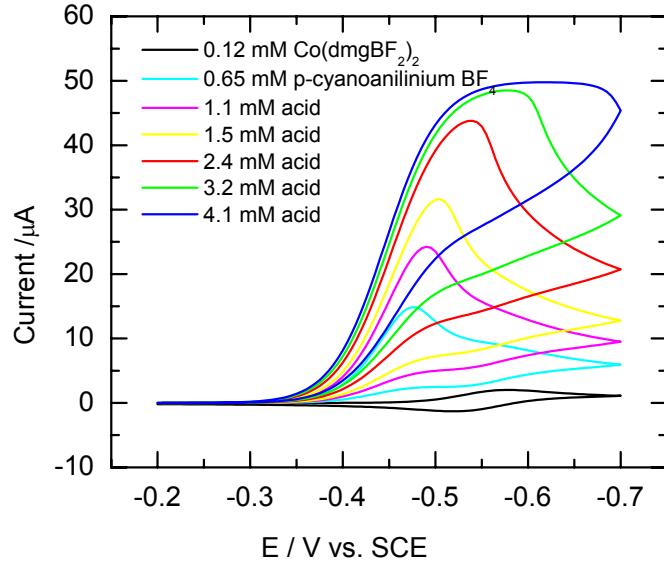
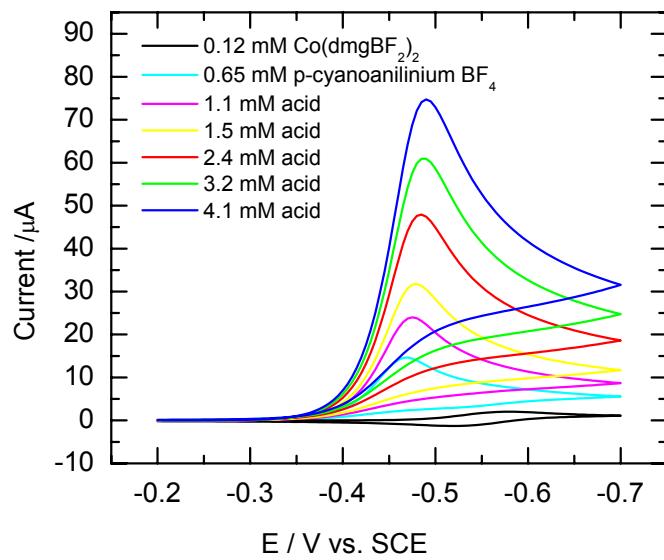
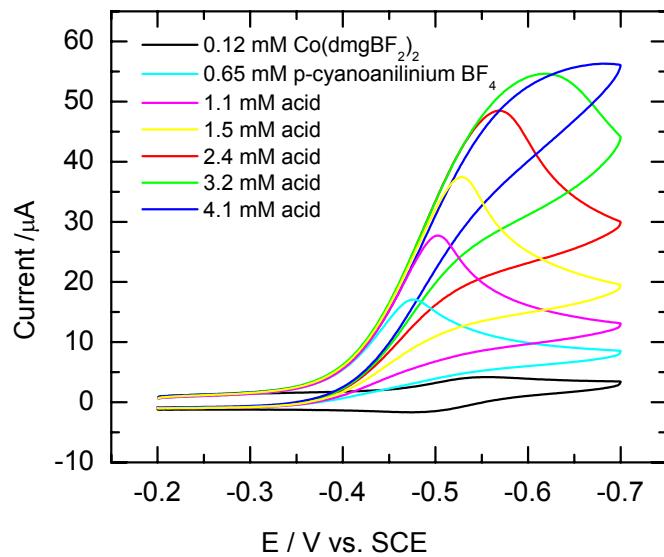


Figure S18. Experimental and simulated spectra of the catalytic waves for H₂ evolution catalysis using 0.12 mM of **1** as the catalyst and p-cyanoanilinium BF₄ as the acid; top: experimental data; middle: simulation using a monometallic mechanism; bottom: simulation using a bimetallic mechanism. As shown in the figure, only simulations assuming a bimetallic mechanism could give rise to satisfactory fits to the experimental data collected under all conditions.

Specific Parameters for Simulation in Figure S18:

Estart (V)	Erev (V)	Eend (V)
0	-0.5	0

Charge Transfer reactions:

Rxn	E (V)	α	K _s (cm/s)
Co(III) + e ⁻ → Co(II)	0.2	0.5	10000
Co(II) + e ⁻ → Co(II)	-0.35	0.5	10000
H ⁺ + e ⁻ → s	-0.20	0.5	0

Chemical reactions for monometallic mechanism:

Rxn	K _{eq}	k _f	k _{b*}
Co(I) + H ⁺ → Co-H	3e5	7e7	233
s + s → H ₂	1	1e10	1e10
Co-H + H ⁺ → Co(III) + H ₂	4.7e-7	1e10	2e16
Co(III) + Co(I) → Co(II) + Co(II)	4.7e12*	1e10	0.002

Chemical reactions for bimetallic mechanism:

Rxn	Keq	kf	kb*
Co(I) + H ⁺ → Co-H	3e5	1e9	3333
s + s → H ₂	1	1e10	1e10
Co-H + Co-H → A + H ₂	1	3e6	5e5
A → Co(II) + Co(II)	7.5*	1e10	1.3e9

* These constants are automatically calculated by the program

Species:

	D (cm ² /s)	C (M)		D (cm ² /s)	C (M)		D (cm ² /s)	C (M)
Co(III)	1.2e-5	0	Co-H	1.2e-5	0	A	1.2e-5	0
Co(II)	1.2e-5	1.2e-4	H ₂	1e-5	0			
Co(I)	1.2e-5	0	s	1e-5	0			

Acid concentrations, H⁺ represents p-cyanoanilinium.

	D (cm ² /s)	C (M)	C (M)	C (M)	C (M)	C (M)	C (M)	C (M)
H ⁺	1e-5	0	0.65e-3	1.1e-3	1.5e-3	2.4e-3	3.2e-3	4.1e-3