

Reaction of Cobaloxime with Hydrogen Evolution

Literature Seminar

B4 Yuki Nishioka

2019/01/31(Thu)

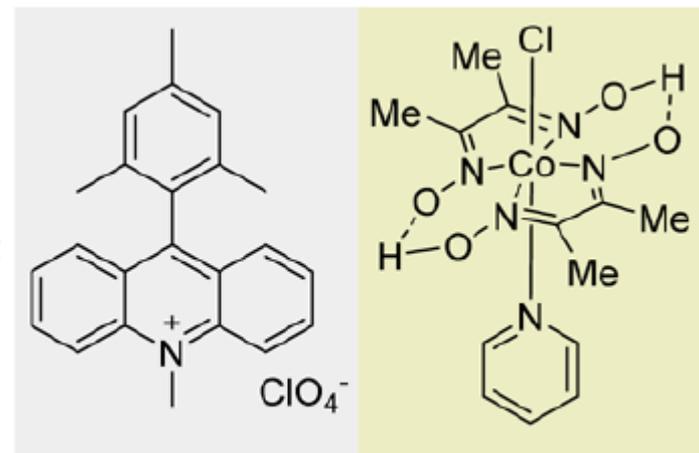
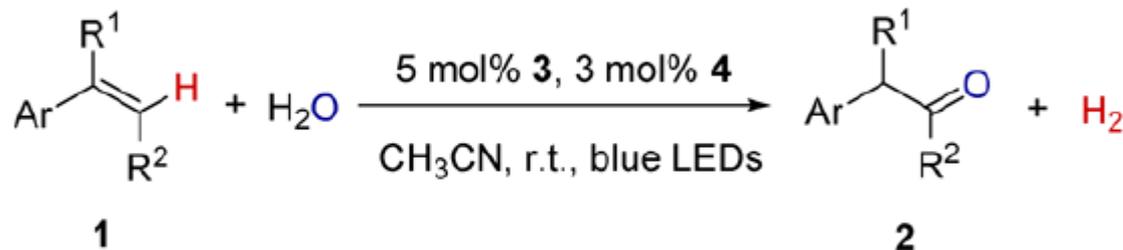
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- Electrochemical System
- Thermodynamic Analysis
- Synthesis using cobaloxime
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Introduction

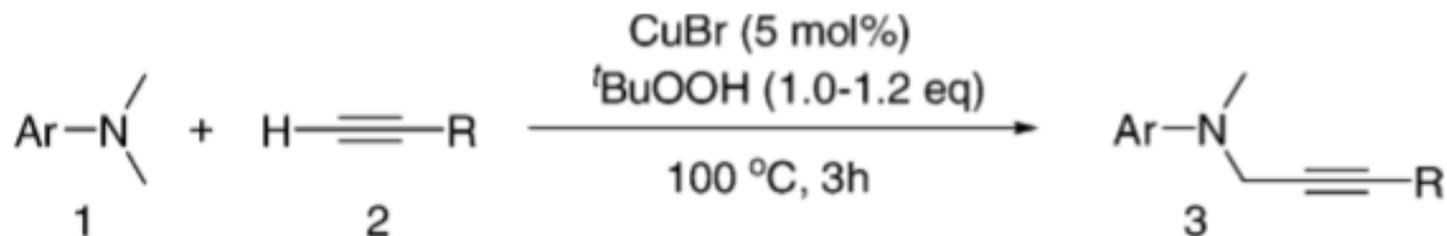


3: $\text{Acr}^+ \text{-Mes ClO}_4^-$ 4: $\text{Co}(\text{dmgH})_2\text{pyCl}$

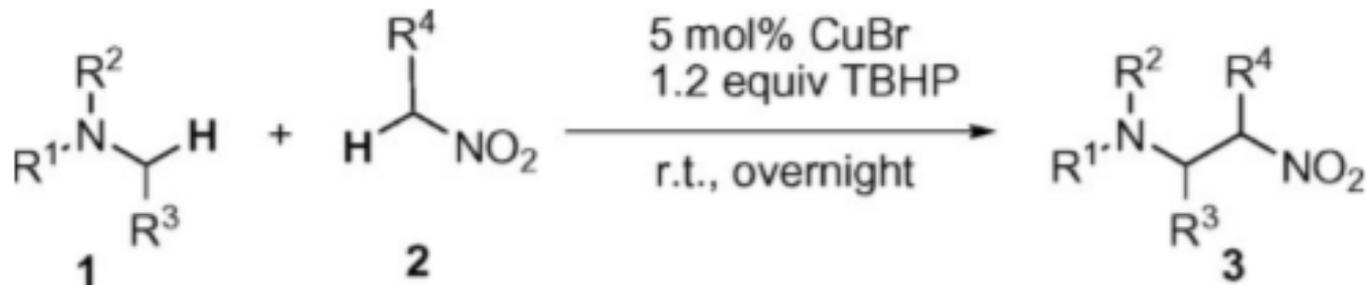
Aiwen Lei *et al.* *J. Am. Chem. Soc.* **2016**, *138*, 12037

- Anti-Markovnikov regioselectivity oxygenation of alkenes
- Reaction without hydrogen acceptor

Introduction



Zhiping Li and Chao-Jun Li, *J. Am. Chem. Soc.* **2004**, *126*, 11810

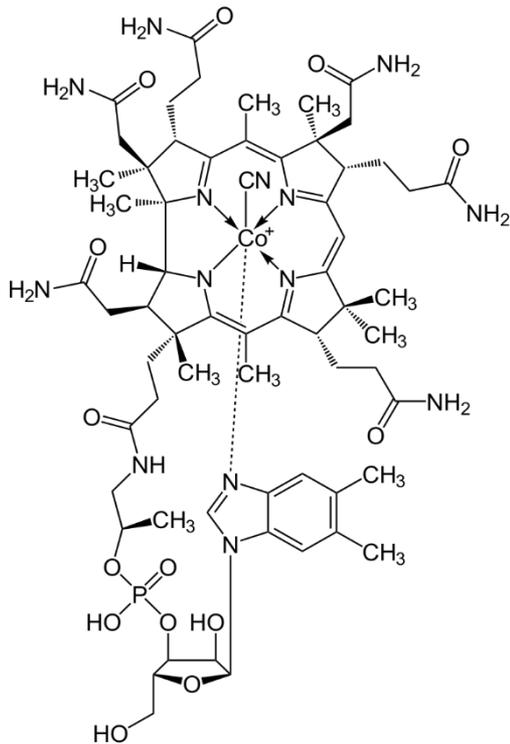


Chao-Jun Li *et al.* *Proc. Natl. Acad. Sci. USA*, **2006**, *103*, 8928.

**In the conventional dehydrogenative cross coupling reaction,
hydrogen acceptor is required.**

→Not clean reaction

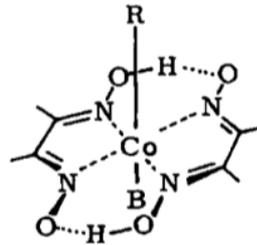
Introduction



Cyanocobalamin,
<https://ja.wikipedia.org/wiki/シアノコバラミン>

Tab. 1. Durch Grignard-Reaktion aus $\text{CoX}(\text{D}_2\text{H}_2)\text{B}$ dargestellte Organyle des Cobaloxims

R (Organylrest)	B (Base)	Schmp.
C_6H_5-	Pyridin	276° (Zers.)
	$\text{N}(\text{CH}_3)_3$	206° (Zers.)
	$\text{P}(\text{C}_6\text{H}_5)_3$	211°
	$\text{P}(\text{n-C}_4\text{H}_9)_3$	235° (Zers.)
$(p)\text{CH}_3\text{O}-\text{C}_6\text{H}_4-$	Pyridin	238° (Zers.)
$\text{C}_6\text{H}_5\text{CH}_2-$	Pyridin	200° (Zers.)
	$\text{P}(\text{C}_6\text{H}_5)_3$	149°
$\text{C}_6\text{H}_5\text{C}\equiv\text{C}-$	Pyridin	206° (Zers.)
CH_3-	$\text{P}(\text{C}_6\text{H}_5)_3$	190°
C_2H_5-	$\text{P}(\text{C}_6\text{H}_5)_3$	174°

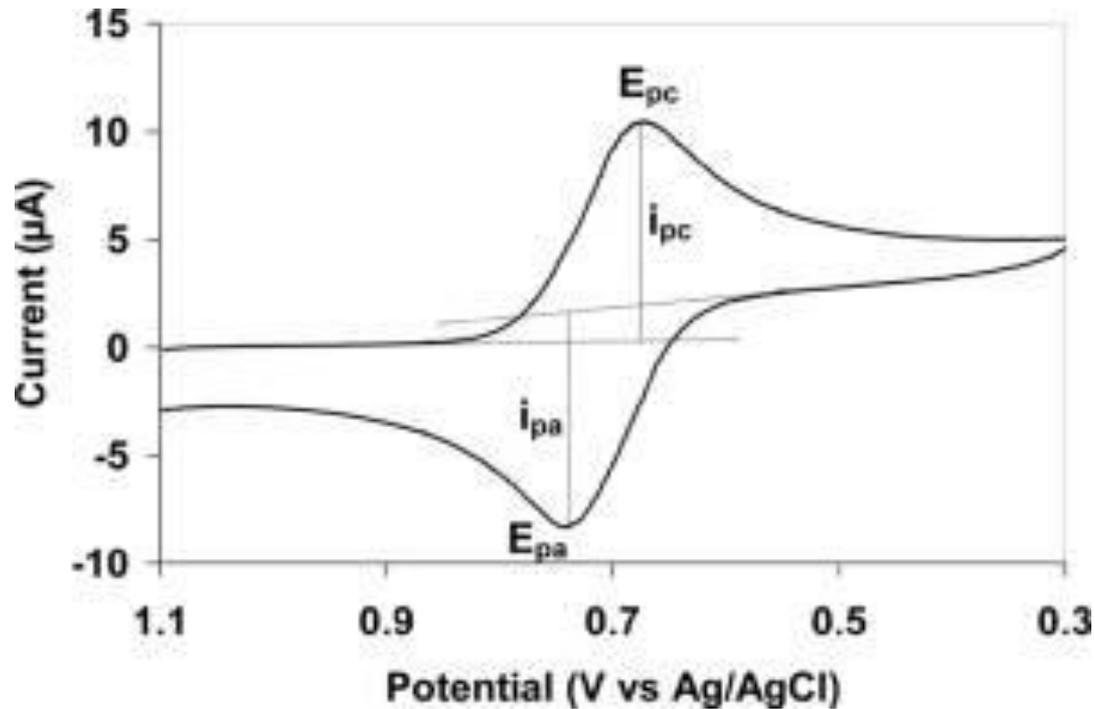


G.N. Schrauzer, K. Kohle, *Chem. Ber.*, **1964**, 97, 3056

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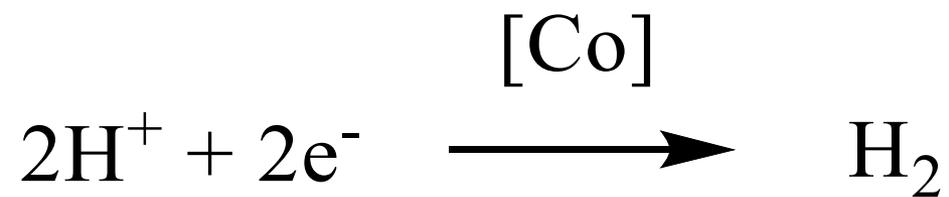
Cyclic Voltammetry



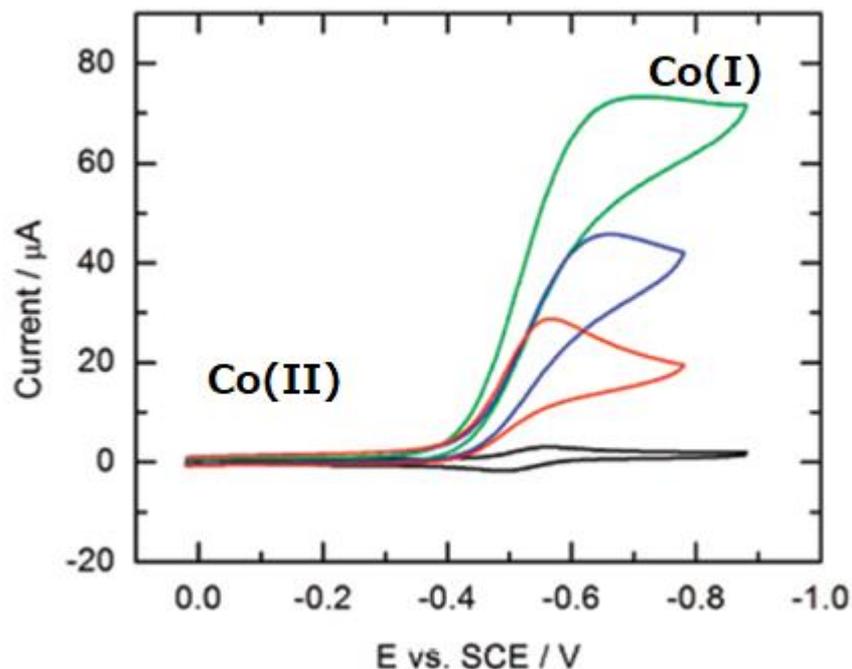
<https://ja.wikipedia.org/wiki/サイクリックボルタンメトリー>

$$E_0 = (E_{pc} + E_{pa})/2 \quad \leftarrow \text{酸化還元電位}$$

Hydrogen Evolution by Cobaloxime



Cyclic Voltammogram of 1



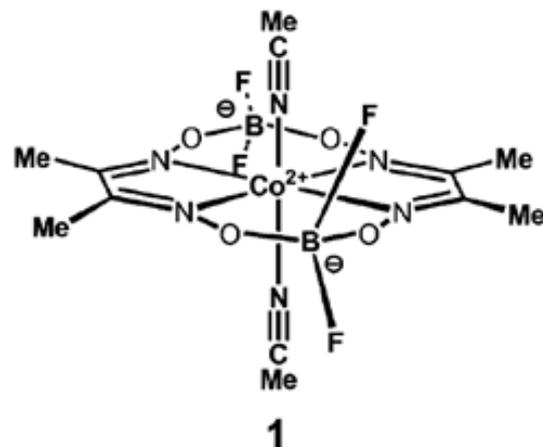
CV of **1** (0.3 mM) in CH_3CN containing 0.1 M $[\text{nBu}_4\text{N}][\text{ClO}_4]$ in the presence of tosic acid:

Black; no acid

Red; 1.5 mM $\text{TsOH} \cdot \text{H}_2\text{O}$

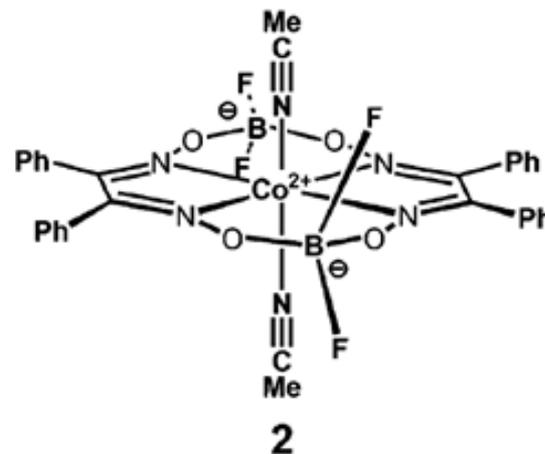
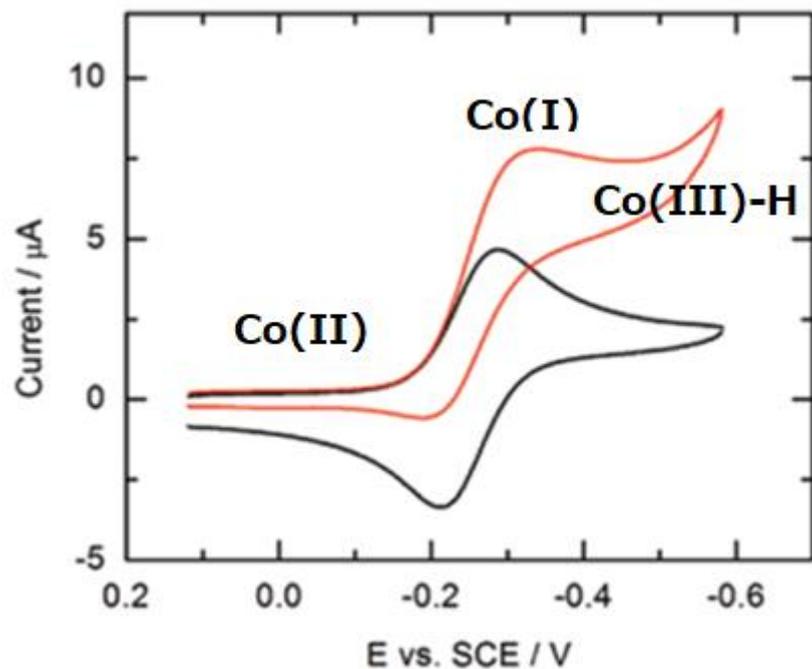
Blue; 4.5 mM $\text{TsOH} \cdot \text{H}_2\text{O}$

Green; 9 mM $\text{TsOH} \cdot \text{H}_2\text{O}$



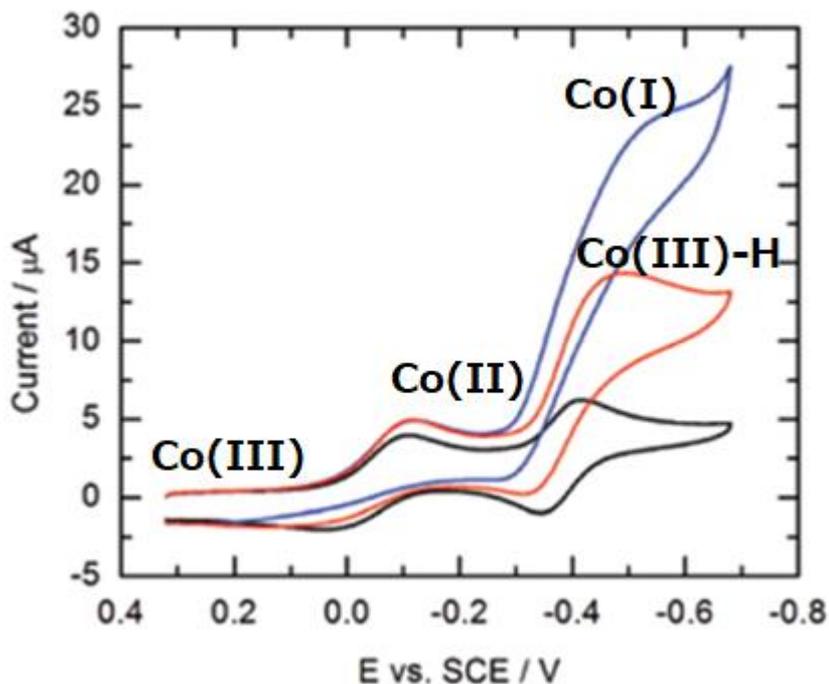
- **-0.55 V vs SCE in the absence of acid was assigned to the $\text{Co}^{\text{II/I}}$.**
- **The potential ($\text{Co}^{\text{II/I}}$) did not change as the acid concentration was varied.**

Cyclic Voltammogram of 2



- CV of 2 was similar to that of 1.
- The current at -0.6 V vs SCE is due to the existence of Co(III)-H intermediate.
- The direct reduction of acid containing tosic acid took place at -1.0 V vs SCE.

Cyclic Voltammogram of 4a (TsOH)

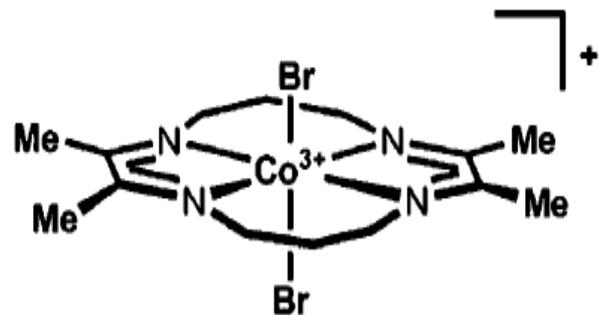


CV of **4a** (0.15 mM) in CH₃CN containing 0.1 M [nBu₄N][ClO₄] in the presence of tosic acid:

Black; no acid

Red; 1.5 mM TsOH·H₂O

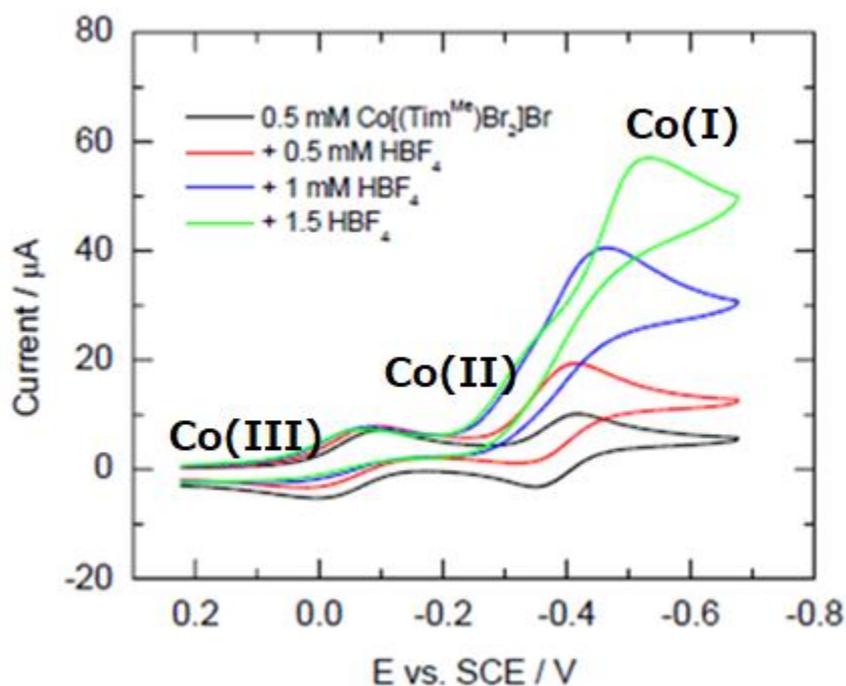
Blue; 9 mM TsOH·H₂O



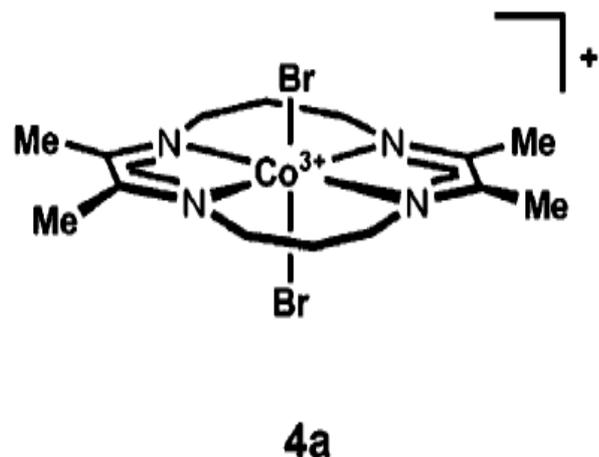
4a

- Reversible reductions were observed for the Co^{III/II} at -0.06 V vs SCE and for the Co^{II/I} at -0.38 V vs SCE.
- No catalytic waves were observed at potentials near the $E(\text{Co}^{\text{III/II}})$.

Cyclic Voltammogram of 4a (HBF₄)

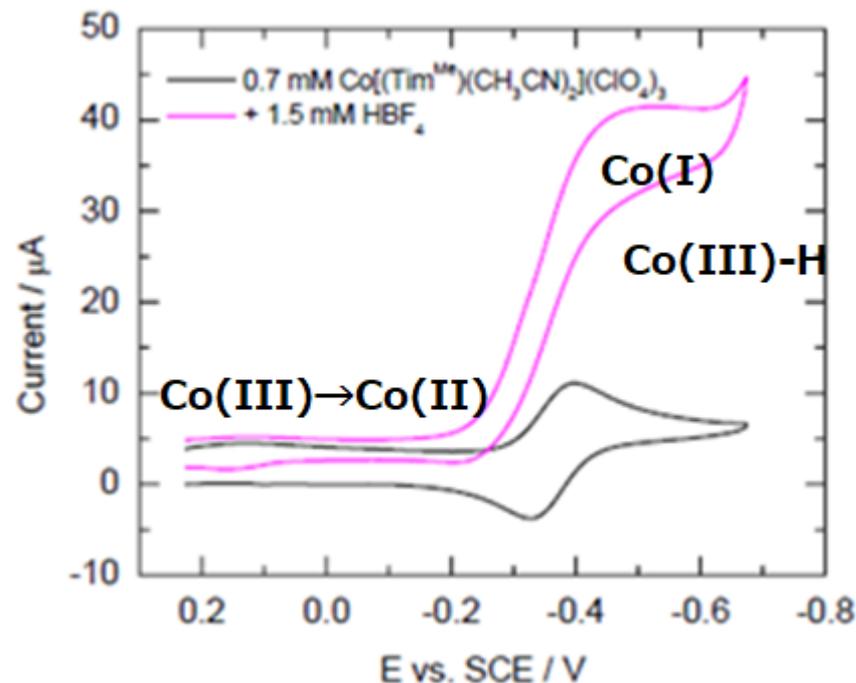
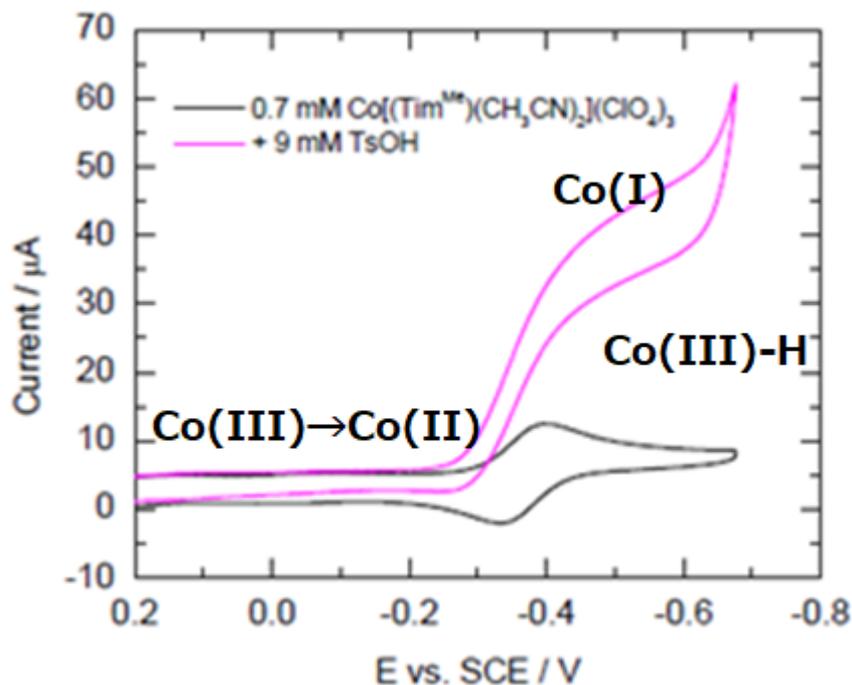


CV of **4a** (0.5 mM) in CH₃CN containing 0.1 M [nBu₄N][ClO₄] in the presence of HBF₄·Et₂O:



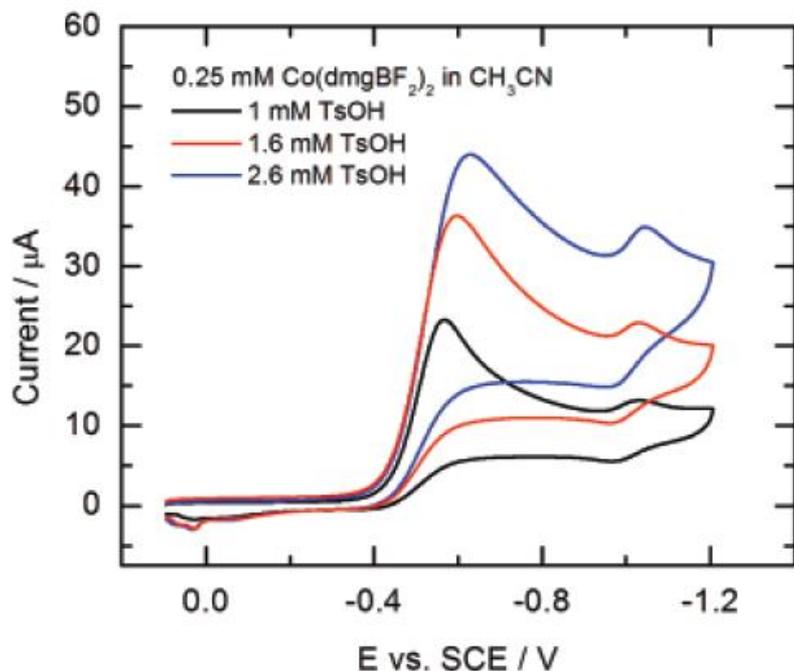
▪ CV of **4a** in the presence of HBF₄·Et₂O was similar to that of **4a** in the presence of tosic acid.

Cyclic Voltammogram of 4b



• Reversible reductions were observed for the $\text{Co}^{\text{II/I}}$ at -0.35 V vs SCE.

Quasi-reversible Redox Wave for 1

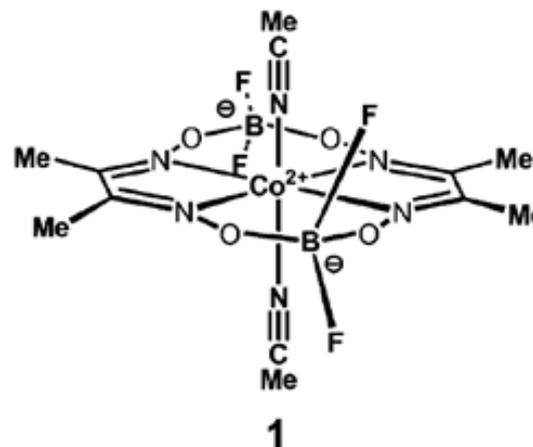


CV of **1** (0.25 mM) in CH_3CN in the presence of tosic acid:

Black; 1 mM TsOH

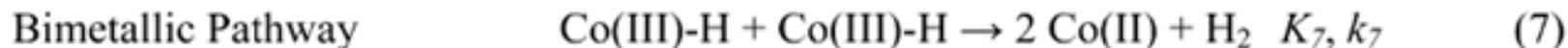
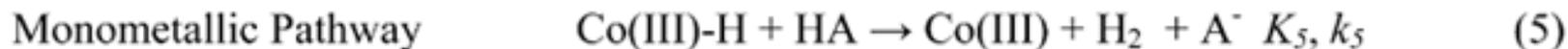
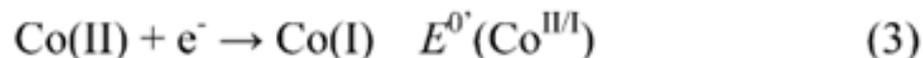
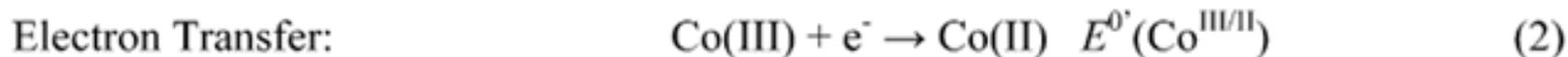
Red; 1.6 mM TsOH

Blue; 2.6 mM TsOH



- In the absence of acid, no this wave was observed.
- Authors tentatively assign this wave to the “Co(III)-H”/“Co(II)-H” redox couple.

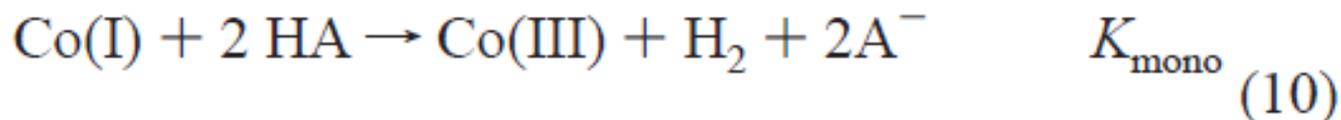
Reaction Mechanism of H₂ Evolution



Jonas C. Peters *et al.* *J. Am. Chem. Soc.* **2007**, *129*, 8988

Is hydrogen evolution due to monometallic pathway or bimetallic pathway?

Equilibrium Constant of Monometallic Pathway

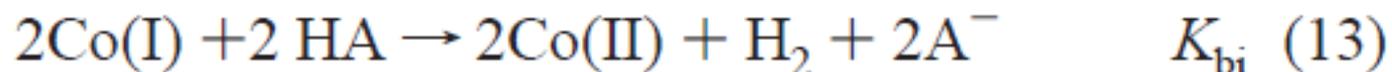


$$\text{eq}(10) = 2 \times \text{eq}(9) - \text{eq}(2) - \text{eq}(3) \quad (11)$$

$$\begin{aligned} K_{\text{mono}} &= \exp \left\{ \frac{e(2E^{\circ'}(\text{HA}) - E^{\circ'}(\text{Co}^{\text{III/II}}) - E^{\circ'}(\text{Co}^{\text{II/I}}))}{k_{\text{B}}T} \right\} \\ &= \exp \left\{ \frac{e[(E^{\circ'}(\text{HA}) - E^{\circ'}(\text{Co}^{\text{III/II}})) + (E^{\circ'}(\text{HA}) - E^{\circ'}(\text{Co}^{\text{II/I}}))]}{k_{\text{B}}T} \right\} \end{aligned} \quad (12)$$

$$\left(\begin{array}{l} \Delta G = -RT \ln K \\ \Delta G = -nFE \end{array} \right)$$

Equilibrium Constant of Bimetallic Pathway



$$\text{eq(13)} = 2 \times \text{eq(9)} - 2 \times \text{eq(3)} \quad (14)$$

$$K_{\text{bi}} = \exp\{2e(E^{\circ'}(\text{HA}) - E^{\circ'}(\text{Co}^{\text{II/I}}))/k_{\text{B}}T\} \quad (15)$$

Calculation Result of pK_{mono} and pK_{bi}

Table 3. Equilibrium Constants for the Reduction of an Acid by the Co(I) Complexes

acid		pK_{mono}	pK_{bi}
CF ₃ COOH	1	-11.3	1.4
TsOH·H ₂ O	1	-1.9	10.8
HBF ₄ ·Et ₂ O	1	13.7	26.4
CF ₃ COOH	2	-17.6	-7.8
TsOH·H ₂ O	2	-8.1	1.7
HBF ₄ ·Et ₂ O	2	7.4	17.2
CF ₃ COOH	4a	-9.9	-4.4
TsOH·H ₂ O	4a	-0.34	5.1
HBF ₄ ·Et ₂ O	4a	15.2	20.6

Jonas C. Peters *et al.* *J. Am. Chem. Soc.* **2007**, *129*, 8988

For complex 1 and 2 the monometallic reduction of acid, K_{mono} is very unfavorable, except in the presence of the strongest acid HBF₄·Et₂O.

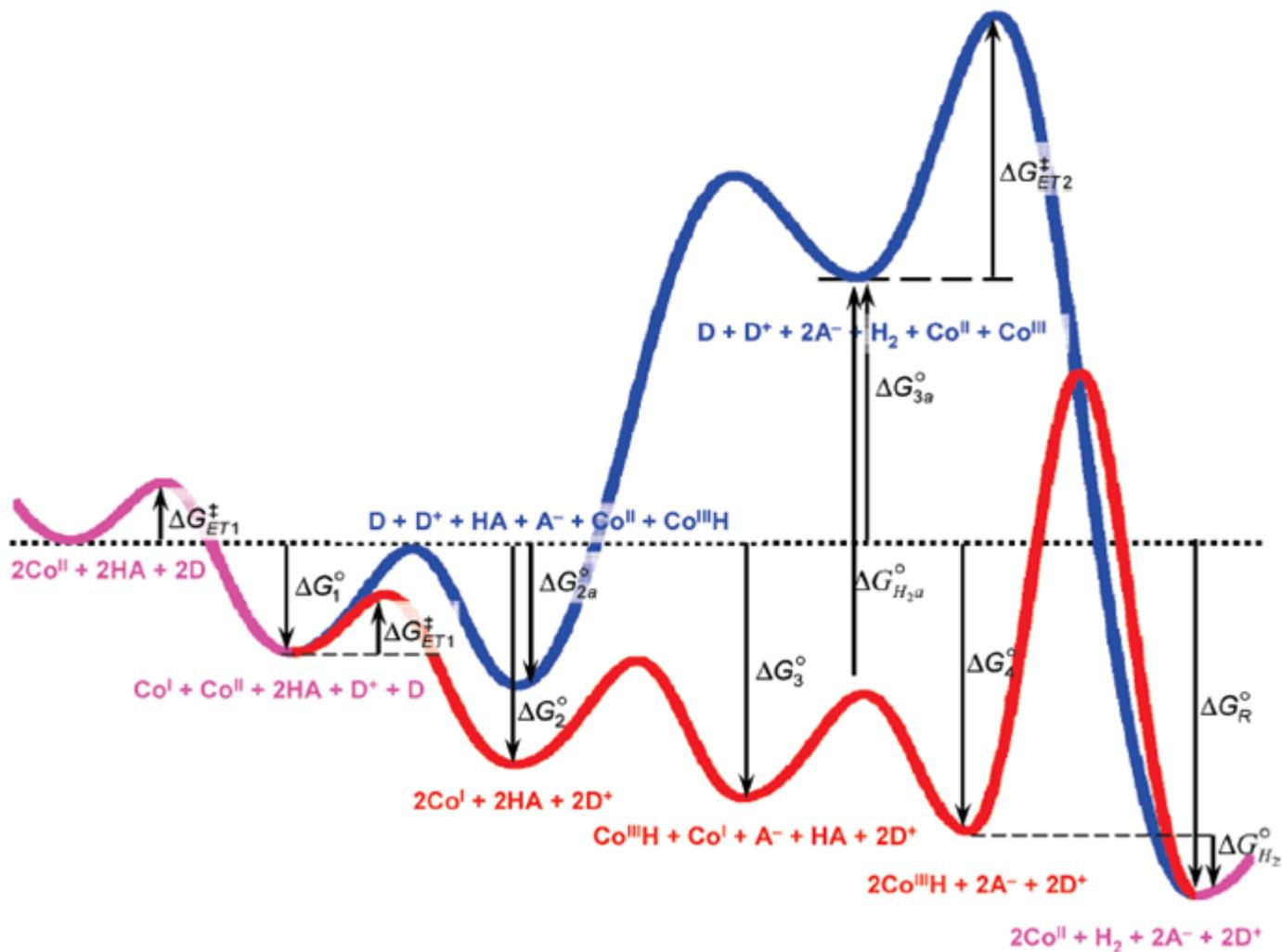
Short Summary

- **By using cobaloxime, hydrogen can be evolved with energy saving.**
- **Reagents with high reducing power become unnecessary.**
- **For complex 1 and 2 the monometallic reduction of acid, K_{mono} is very unfavorable, except in the presence of the strongest acid $\text{HBF}_4 \cdot \text{Et}_2\text{O}$.**

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Thermodynamic Analysis of Reaction Mechanism



Harry B. Gray *et al.* *J. Am. Chem. Soc.* **2010**, *132*, 1060

Thermodynamic Analysis of Reaction Mechanism

ΔG_1°	$3 \left[E_{\text{D}^\circ/\text{D}}^\circ - E_{\text{Co}^\text{II}/\text{Co}^\text{I}}^\circ \right]$
ΔG_2°	$\Delta G_1^\circ + 3 \left[E_{\text{D}^\circ/\text{D}}^\circ - E_{\text{Co}^\text{II}/\text{Co}^\text{I}}^\circ \right]$
ΔG_3°	$\Delta G_2^\circ + 2.303RT \left[pK_a(\text{HA}) - pK_a(\text{Co}^\text{III}\text{H}) \right]$
ΔG_4°	$\Delta G_3^\circ + 2.303RT \left[pK_a(\text{HA}) - pK_a(\text{Co}^\text{III}\text{H}) \right]$
ΔG_R°	$23 \left[E_{\text{D}^\circ/\text{D}}^\circ - E_{\text{HA}/\text{H}_2}^\circ \right]$
$\Delta G_{\text{H}_2}^\circ$	$23 \left[E_{\text{Co}^\text{II}/\text{Co}^\text{I}}^\circ - E_{\text{HA}/\text{H}_2}^\circ \right] - 2(2.303RT) \left[pK_a(\text{HA}) - pK_a(\text{Co}^\text{III}\text{H}) \right]$ $\Delta G_R^\circ - \Delta G_4^\circ$
ΔG_{2a}°	$\Delta G_1^\circ + 2.303RT \left[pK_a(\text{HA}) - pK_a(\text{Co}^\text{III}\text{H}) \right]$
ΔG_{3a}°	$3 \left[E_{\text{D}^\circ/\text{D}}^\circ + E_{\text{Co}^\text{III}/\text{Co}^\text{II}}^\circ - 2E_{\text{HA}/\text{H}_2}^\circ \right]$
$\Delta G_{\text{H}_2a}^\circ$	$3 \left[E_{\text{Co}^\text{II}/\text{Co}^\text{I}}^\circ + E_{\text{Co}^\text{III}/\text{Co}^\text{II}}^\circ - 2E_{\text{HA}/\text{H}_2}^\circ \right] - 2.303RT \left[pK_a(\text{HA}) - pK_a(\text{Co}^\text{III}\text{H}) \right]$ $\Delta G_{3a}^\circ - \Delta G_{2a}^\circ$

Harry B. Gray *et al.* *J. Am. Chem. Soc.* **2010**, *132*, 1060

Thermodynamic Analysis of Reaction Mechanism

$$\Delta G^\circ = -nF\Delta E^\circ$$

n number of electrons

F Faraday's constant, 96485.31 C mol⁻¹

R 8.31441 J K⁻¹ mol⁻¹

T 293.15 K

Harry B. Gray *et al.* *J. Am. Chem. Soc.* **2010**, 132, 1060

$$\Delta G = -RT \ln K$$

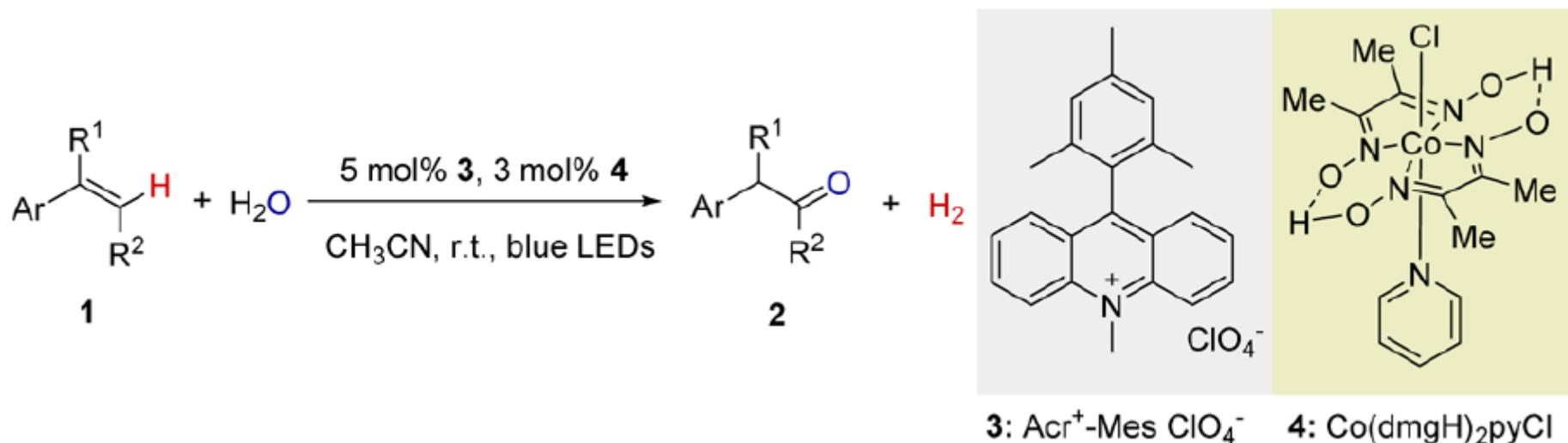
$$\Delta G = -2.302RT \log K$$

$$\Delta G = 2.302RT pK_a$$

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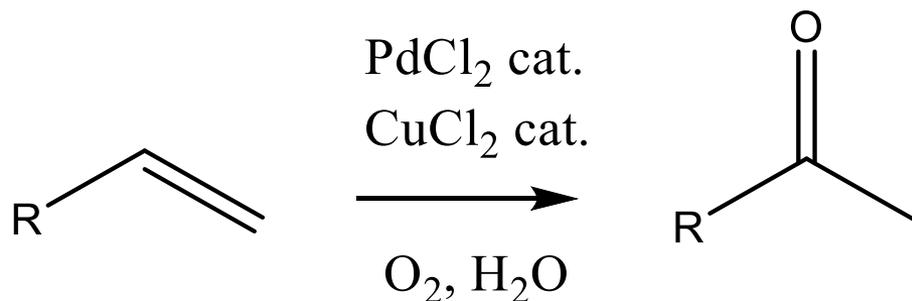
Reaction Accompanied by Hydrogen Evolution



Aiwen Lei *et al.* *J. Am. Chem. Soc.* **2016**, *138*, 12037

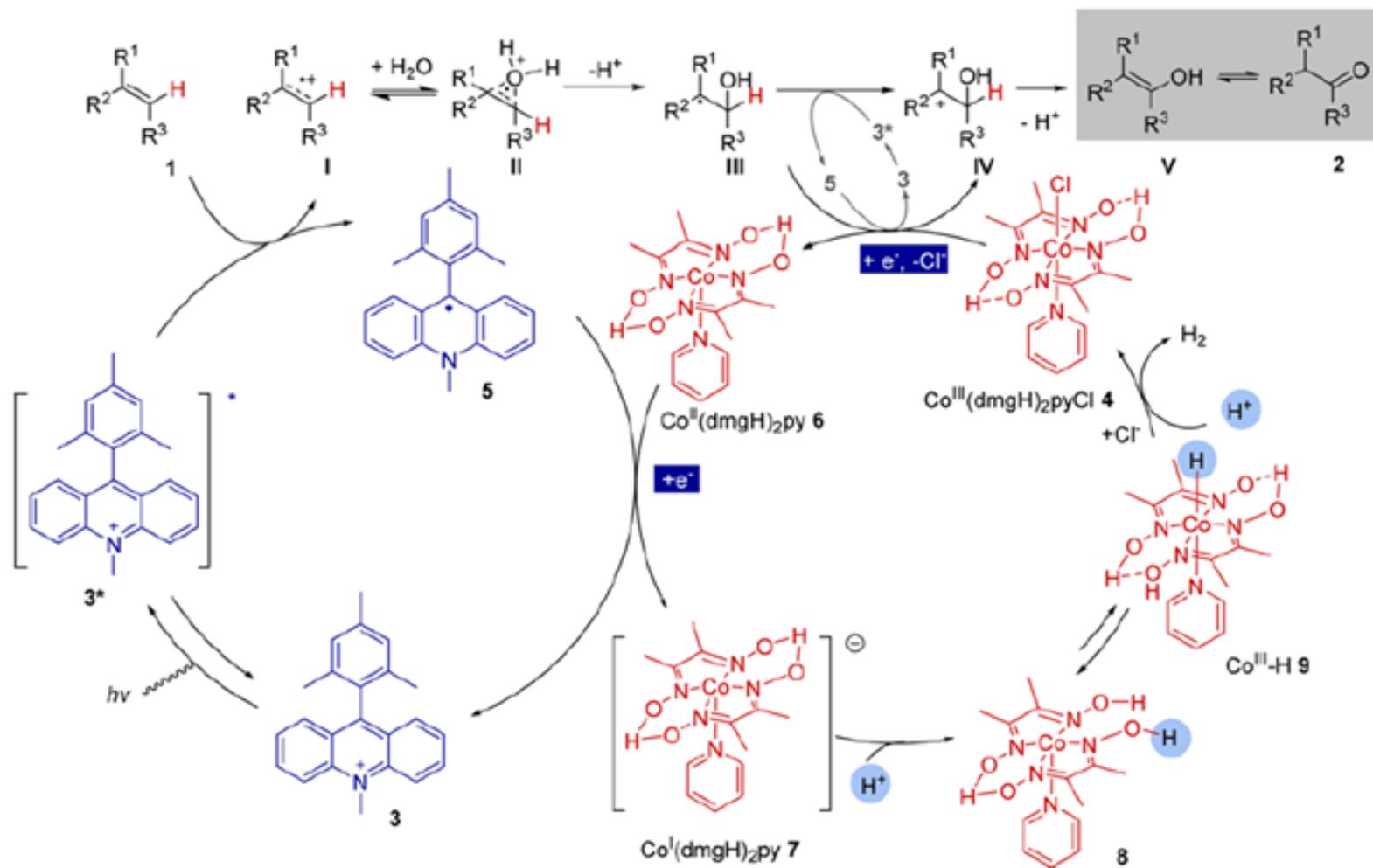
- Anti-Markovnikov regioselectivity oxygenation of alkenes
- Reaction without hydrogen acceptor

Conventional Wacker Oxidation

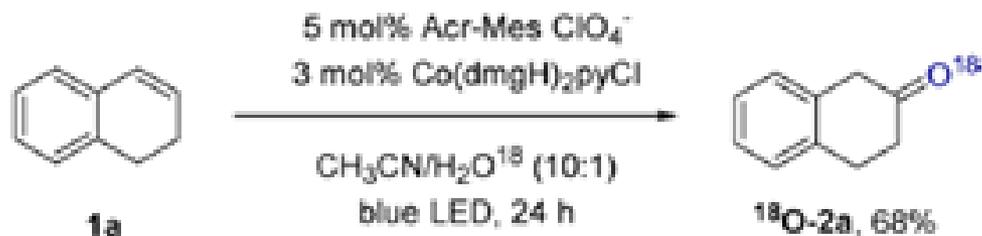
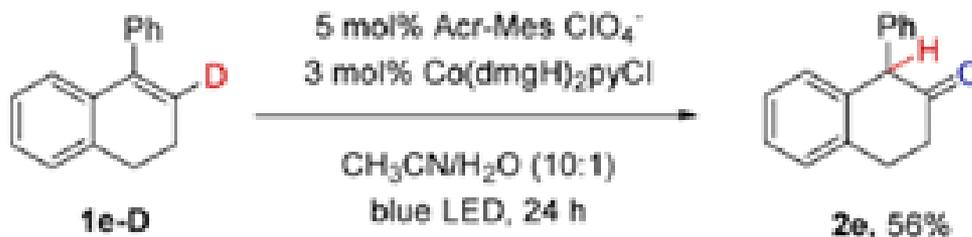
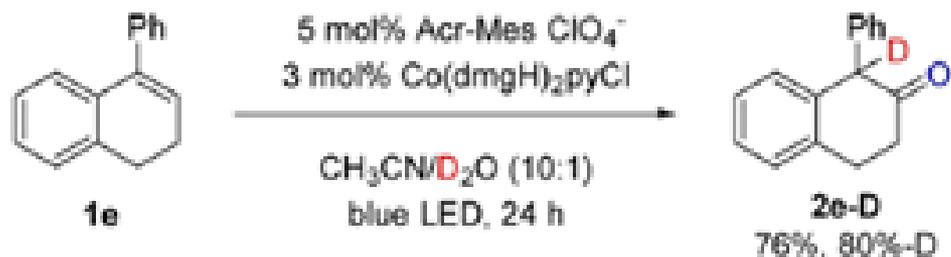


- It can only oxidize terminal alkene.
- Anti-Markovnikov regioselectivity oxygenation of alkenes

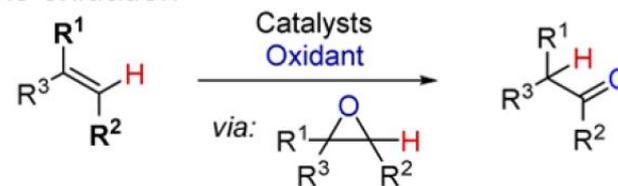
Reaction Mechanism



Isotope Labelling Experiments



B. Epoxidation-Isomerization (E-I) Wacker-like oxidation



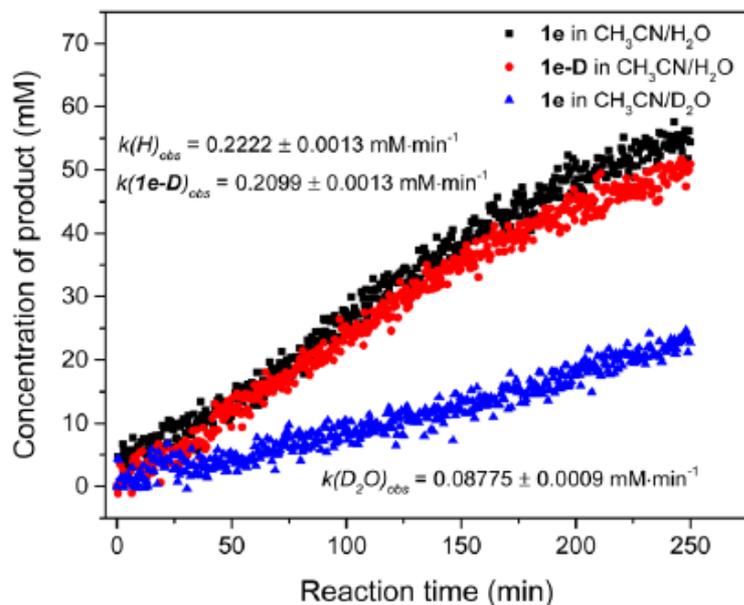
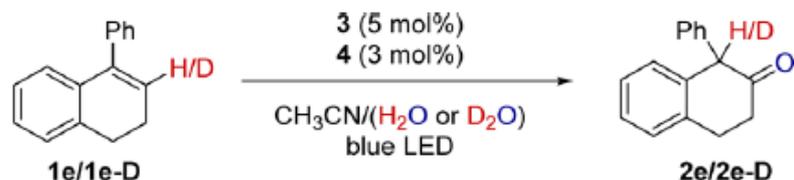
▪ The epoxidation–isomerization pathway can be ruled out.

▪ O atom of carbonyl compounds originates from water

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Kinetic Isotope Effect Experiments

Scheme 5. Kinetic Isotope Effect Experiments^a

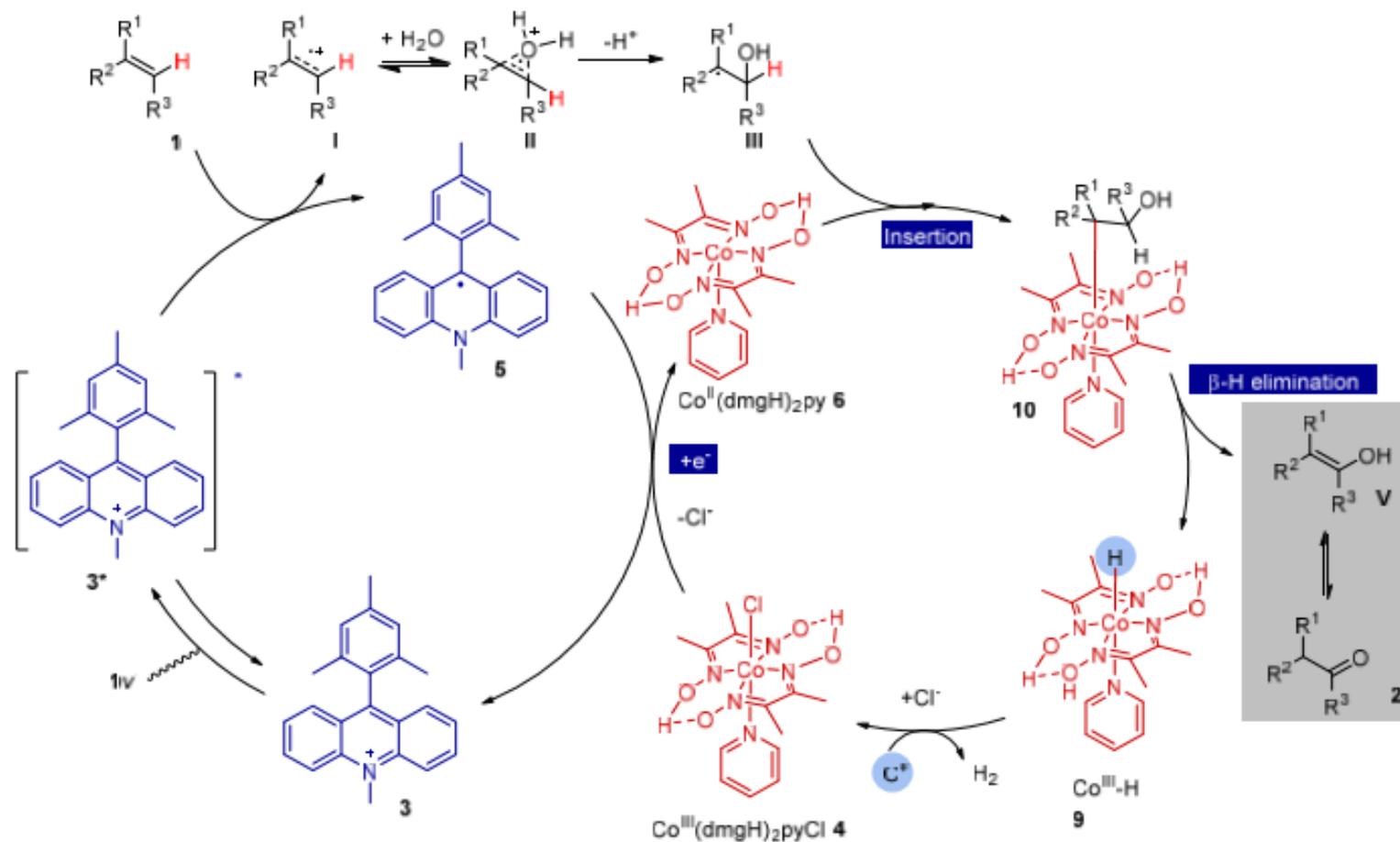


▪ C–H bond breaking of the olefin is not involved in the rate-determining step of the reaction.

▪ The rate-determining step of the transformation might involve the O–H bond cleavage of water.

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Alternative Reaction Mechanism



Aiwen Lei *et al.* *J. Am. Chem. Soc.* **2016**, *138*, 12037

Proposal of Reaction Mechanism

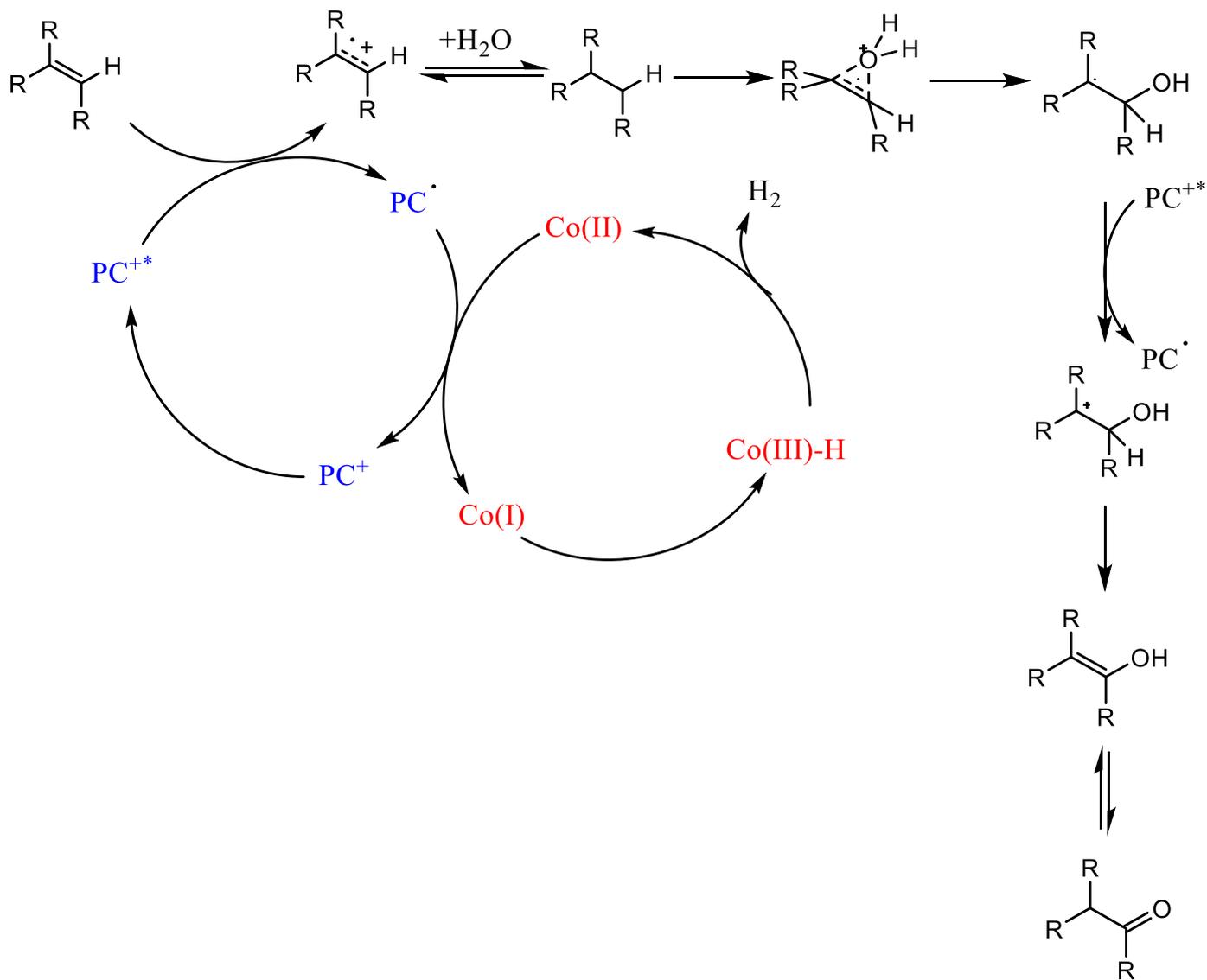


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Summary

- **Cobaloxime can achieve reaction without hydrogen acceptor**
- **The reaction catalyzed by cobaloxime proceed with bimetallic pathway**