# PCET mediators for electrocatalytic reduction of small molecules

M2, Takeshi Inoue, 2024/7/26

### Contents

#### Basics of

- 1. Electrochemistry
- 2. Proton-coupled electron transfer

#### Main

#### 1. Cobaltocene-Brønsted base

- Development of PCET mediator
- N<sub>2</sub> fixation

#### 2. Ferrocene-Brønsted base-Anthracene

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Summary

# 1. Basics of electrochemical reaction



Frit or permeable membrane

Baran, P. S. et al. Acc. Chem. Res. 2020, 53, 72. 4

### 1. Redox potential

Redox potential( $E^0$ ) = The potential required to induce electron transfer



#### [Redox potential of representative functional groups]



# 1. Cyclic voltammetry



#### [Redox potential(E<sup>0</sup>)]

$$\frac{E_{pa}+E_{pc}}{2}=E_{1/2}^r\approx E^0$$

Analysis of ET in the reaction



 When the oxidized form is lost by a chemical reaction, the CV shows irreversible peak.

\* Throughout this presentation, all redox potentials are reported versus Fc<sup>+/0</sup>.

Baran, P. S. *et al. Acc. Chem. Res.* **2020**, *53*, 72. Stahl, S. S. *et al. J. Org. Chem.* **2021**, *86*, 15875.

### 2. Proton-coupled electron transfer



- ET/PT, PT/ET; The stepwise transfer of H<sup>+</sup> and e<sup>-</sup>.
- Concerted PCET; Synergistic transfer of H<sup>+</sup> and e<sup>-</sup> in single kinetic step.
   (This concerted pathway called PCET in this presentation).
- PCET is common mechanism not only in synthetic chemistry, but also in biological system. (e.g., hydrogenases)

Knowles, R. R. *et al. Chem. Rev.* **2022**, *122*, 2017. Happe, T. *et al. Proc. Natl. Acad. Sci. U. S. A.* **2020**, *117*, 20520.



# **Winsties of PCET (Concerted PCET)**

Potential energy surface



- The PCET pathway has lower activation energy by the movement of protons(positive charge) in a direction that counteracts that of electrons (negative charge).
- → Advantages in efficiency and selectivity(directionality) of hydrogen atom transfer.

For detailed physical explanation, please refer to the followings;

Schiffer, A. H. *Acc. Chem. Res.* **2001**, *34*, 273. Hammarström, L. et al. J. *Am. Chem. Soc.* **2021**, *143*, 560

### 2. Bond dissociation free energy

Relationship between BDFE and pKa & redox potential.



**BDFE** (kcal/mol) =  $1.37 \cdot \mathbf{pKa}(M-H) + 23.06 \cdot \mathbf{E}^{0}(M-M) + \frac{23.06 \cdot \mathbf{E}^{0}(H+/H)}{= C_{G}}$  (Constant)

$$X-H + Y \xrightarrow{\Delta G^0} X + Y-H; \quad \Delta G^0 = BDFE(XH) - BDFE(YH)$$

C<sub>G</sub>; Solvent-dependent thermodynamic constant to account for the energy required to form **H**<sup>+</sup> from **H**<sup>+</sup> and **e**<sup>−</sup>

Harrelson, J. A. *et al. J. Am. Chem. Soc.* **1988**, *110*, 1229. Nicholas, A. P., Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2165.

### **Abbreviations**

- **PCET**; (Concerted) **P**roton-**C**oupled **E**lectron **T**ransfer
- **BDFE**; Bond Dissociation Free Energy
- **BDE**; **Bond Dissociation Enthalpy**
- HER; Hydrogen Evolution Rection
- N<sub>2</sub>RR; N<sub>2</sub>(Dinitrogen) Reduction Reaction
- CO<sub>2</sub>RR; CO<sub>2</sub> Reduction Reaction
- **CSS**; Charge Separation State
- **CR**; Charge Recombination
- **SET**; Single Electron Transfer

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# Hydrofunctionalization of unsaturated bond



1. Conventional H• generation



BDFE<sub>O-H</sub> = 27~35 kcal/mol
 X Stoichiometric reductant

2. Electrochemical reduction



× Competing HER× Electrode passivation

### **Development of PCET mediator**



- Facilitate the colocalization of H<sup>+</sup> and e<sup>-</sup> at relatively anodic potential.
- Prevent electrode passivation by avoiding the formation of reactive radical intermediates at the electrode surface.



# **Cp<sub>2</sub>Co mediator**

Hydrogen atom transfer to acetophenone

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# Trials with Cp<sub>2</sub>Co mediator



[1] Slow due to the high reorganization energy;  $sp^2 \rightarrow sp^3$ .

[2] Fast due to *CpH* ligand; *anodic shift of E*<sup>0</sup> *of* [3] *by π-accepting diene ligand*.

[3] Inefficient hydrogen atom transfer[4] due to low concentration of H• donor[3].

### **Development of novel PCET mediator**

Aniline appended cobaltocene



- 1. Rigid aniline-Brønsted base motif accelerates the rate of protonation by minimized reorganization.
- 2. Insulate the Co<sup>III/II</sup> redox couple; the immediate coordination sphere at cobalt remains unchanged.

### **Development of novel PCET mediator**

BDFE was dramatically decreased by reduction. (redox-induced bond weakening).



# Model reaction using acetophenone



Entry	Mediator	TM (%)	TM (FE %)	rSM (%)	HER (FE %)	TONs
1	Cp <sub>2</sub> Co	5	3	0	66	3
2	-	10	47	0	-	-
3	[CpCoCp <sup>ℕ</sup> ]⁺	83	39	11	45	~40

[Entry 3]

- PCET mediator kinetically attenuates the thermally favorable HER reaction.
- HER reaction likely begins to dominate at low ketone concentrations.

$$FE = N_{product} (mol) \div \frac{Q(C)}{Faraday \ Constant \ (C/mol)}$$

### Thermodynamical and kinetical characteristics

DFT calculation



DFT calculation supports the thermodynamic preference of PCET pathway.
 (Circumvent high energy intermediates in PT/ET and ET/PT.)

Dependence of PCET kinetics



#### PCET med., Substrate

= 1<sup>st</sup> order dependence

#### **Proton source**

= 0<sup>th</sup> order

### Thermodynamical and kinetical characteristics

Kinetic isotope effect





• Large KIE; 4.9 ± 0.7 was observed.

 $\rightarrow$  Rate-determining PCET process

Modest negative slope
 More electron rich substrate ⇔ faster PCET
 More electron deficient substrate ⇔ slower PCET

This PCET process(TS) involves more proton transfer than electron transfer character.

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# Introduction of N<sub>2</sub> fixation

**Carl Bosch** The Novel Prize in Chemistry 1931

#### Haber-Bosch process

 $N_2 + 3H_2 \xrightarrow{\text{cat. Fe}_3O_2/K_2O/Al_2O_3} 2NH_3$ 



**Fritz Haber** The Novel Prize in Chemistry 1918

- This reaction enables continuous population growth through the production of fertilizers.
- Very high temperatures and pressures are required. (2 % of global energy consumption)
- Alternative methods have been reported using transition metal catalysts.

e.g.)  

$$N_2 + 6Sml_2 + 6ROH \xrightarrow{Mo cat.} 2NH_3 + 6Sml_2(OR) + H_2$$
  
(1 atom)  
 $Peters, J. C. et al. Chem. Rev. 2020, 120, 5582.$   
Nishibayashi, Y. et al. Nature. 2019, 568, 536.  
Hetterscheid, D. G. H. et al. Chem. Soc. Rev. 2014, 43, 5183 22

### **Electrocatalytic N<sub>2</sub> fixation (N<sub>2</sub>RR)**



× Electrocatalytic reduction in acidic conditions suffers from  $N_2$ -selectivity over hydrogen evolution reaction(HER).

; HER is thermodynamically and often kinetically dominant. (BDFA<sub>H-H</sub>=104 kcal/mol)

### **Electrochemical N<sub>2</sub> reduction reaction**



Co(II,NH) + Higher thermodynamic PCET efficiency [M] H• H<sup>+</sup> (HOTs) M = W, Mo, Os, Fe Coll Peters, J. C. et al. Nature, 2022, 609, 71. NMe<sub>2</sub> <sup>1)</sup>; Peters, J. C. et al. J. Am. Chem. Soc. **2018**, 140, 6122. Co(III,N) <sup>2)</sup>; Pickett, C. J. & Talarmin, J. *Nature*. **1985**, 317, 652.

### **Result of N<sub>2</sub>RR with PCET mediator**



#### Current profile



- Both catalysts are required.
- No current was observed in the absence of mediator.
   → Uncoupled ET/PT is not facile at this potential.

### **Mechanistic insights**



# **Mechanistic insights**

Intermediate (TsO)W(NH)+



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### **Other metal catalysts**

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Results of N <sub>2</sub> RR							
	N <sub>a</sub> + HOTs	[Co] (0.05 [Cat] (0.05	mM) 5 mM) ────────────────────────────────────				
1 ;	tm) (100 equi	iv.) DME BDD(–)/Z –1.35 V vers	'n(+) us Fc <sup>+/0</sup>				
	Catalyst	Equiv. NH <sub>3</sub> /Cat	FE (%)				
	<b>W</b> (N <sub>2</sub> ) <sub>2</sub>	11.3 ± 0.5	44.5 ± 1.9				
	<b>W</b> (N <sub>2</sub> ) <sub>2</sub> *	40	43				
	1	13	51				
	2	14	55				
	3	8.7	34				
	4	<0.1	<1.0				
	5	5.6	22				
	6	4.5	18				
	7	1.5	4.5				

• Broad applicability.

# **Short summary**



- First example of electrocatalytic N<sub>2</sub> fixation by a tandem approach.
- High FE of N<sub>2</sub> fixation in mild conditions; room temperature & atmospheric pressure.
- Reducing competing hydrogen evolution reaction (but, still 39% FE of HER).
- Higher reactivity is required for more extensive applications.

Peters, J. C. *et al. Science*, **2020**, 369, 850. Peters, J. C. *et al. Nature*, **2022**, 609, 71. Walker, A., Mougel, V. *Chimia*. **2024**, 78, 251.

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### **Phtotoelectrochemical PCET mediator**

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- More powerful H-atom donating capacity by photoexcitation. (BDFE ~ 17 kcal/mol)
- Even lower cathodic potential. (Higher substrate-selectivity over HER)
- Sufficiently long-lived excited state for the intermolecular reactivity utilizing Marcus inverted effect.

# **Potential energy surfaces**



• When the vibrational levels can be approximated as a harmonic oscillator, it is represented by a quadratic function.



• The chemical reaction proceeds through the intersection of the energy surfaces of the reactants and products

#### Arrhenius equation

$$k = A \cdot exp\left(-\frac{E_a}{k_B T}\right)$$



- $\Delta E > 4$  kJ/mol
- Adiabatic process; κ = 1 (e.g., EDA complex ...)

- $\Delta E \leq 4 \text{ kJ/mol}$
- Non-adiabatic process; κ <1 (e.g., *Ir photocatalyst* ...)

Marcus theory was developed to explain the outer-sphere process.

# **Reorganization energy in SET**

#### Franck–Condon principle;

There is no change in the arrangement of the nuclei of reactants and surrounding solvent molecules at the moment of electron transfer. (ET rate >> motion of nuclei)

Self-exchange reaction;  $[Fe^{II}(H_2O)_6]^{2+} + [Fe^{III}(H_2O)_6]^{3+}$ 



Total reorganization energy of SET( $\lambda$ );

[<mark>Fe<sup>III</sup>(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup></mark>

 $\lambda = \lambda_{inner}(\text{structure}) + \lambda_{outer}(\text{solvent})$ 



**(2) Effect of solvent molecules** 



 $[Fe^{II}(H_2O)_6]^{2+}$ 

+

■ Normal region ( $\Delta G^0 < \lambda$ )





Rudolph A. Marcus The Novel Prize in Chemistry 1992

**Reaction coordinate** 

**Decrease of**  $\Delta G^0$ ; More exergonic  $\Leftrightarrow$  **Decrease of**  $\Delta G^{\ddagger}$ ; Faster SET

Barrierless region ( $\Delta G^0 = \lambda$ )



 $\Delta G^0 = \lambda \Leftrightarrow \Delta G^{\ddagger} = 0$ ; Electron transfer proceeds rapidly without an energy barrier.

Inverted region ( $\Delta G^0 > \lambda$ )



Decrease of  $\triangle G^0$ ; More exergonic  $\Leftrightarrow$  Increase of  $\triangle G^{\ddagger}$ ; Slower SET (Counterintuitive)

**Reaction coordinate** 



- Small reorganization energy;  $\lambda_1 \Leftrightarrow$  **Inverted region** at  $\Delta G_1$
- Large reorganization energy;  $\lambda_2 \Leftrightarrow$  Normal region at  $\Delta G_1$
- Minimizing the reorganization energy (rigid structure...) is important for slowing down the SET rate by utilizing the inverted region.

### **Incorporation of photosensitizer**

#### Catalyst design



- Generation of highly reductive H· donor by photoinduced intramolecular SET.
- Regeneration of mediator at substantially anodic potential.





Peters, J. C. et al. J. Am. Chem. Soc. 2024, 146, 12750. 39

# Working model

Catalytic cycle

Jablonski diagram



[Hypothesis]

- Appended mild reductant(ferrocene) enables efficient quenching of <sup>1</sup>anthracene<sup>\*</sup>.
- CSS might be extended by Marcus inverted effect.

### **Spectroscopic analysis**



- <sup>1</sup>anthracene\* (400~475nm fluorescence) is heavily quenched by intramolecular SET from ferrocene.
- Fast SET (k<sub>cs</sub> > 5 × 10<sup>10</sup>) at low driving force (0.6 eV) implies a modest reorganization barrier.

 Absorption of produced species is consistent with the spectrum of spectroelectrochemically prepared anthracene radical anion.

{Fc-N-an}  $\frac{E_{app} = -2.4 \text{ V vs. Fc}^{+/0}}{\text{THF, 0.7 M TBAPF}_{6}}$  {Fc-N-an<sup>•-</sup>}

### **Spectroscopic analysis**



- This mediator has long-lived CSS;τ = 0.9 ~1.3 μs ([lr(ppy)<sub>2</sub>dtbbpy]PF<sub>6</sub>; τ = 0.54 μs)\*
- Back electron transfer has high driving force(2.5 eV) and closed shell product.
   → BET is likely to be in Marcus inverted region.

#### [PicH][OTf]; H<sup>+</sup> source



\*Ochola, J. R., Wolf, M. O. *Org. Biomol. Chem.* **2016**, *14*, 9088. Peters, J. C. *et al. J. Am. Chem. Soc.* **2024**, *146*, 12750.

### **Control experiment**



4  $Cp_2Fe + {N-an}^{(2)}$  instead of {Fc-N-an} 0

<sup>(1)</sup>; Weak acid incapable of protonating the amine group.

<sup>(2)</sup>; Inefficient intermolecular reduction due to the short lifetime of <sup>1</sup>anthracene\*.

#### **Stoichiometric photochemical reaction**



• No HER was observed.

#### **Photoelectrocatalytic reaction**





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# Summary

PCET mediator for electrocatalytic activation of small molecules



- Novel molecular design & comprehensive mechanistic analysis.
- High reactivity in mild conditions.
- Minimized hydrogen evolution reaction.
- (?) Applicability to more synthetically valuable transformation; Generality of this strategy.

(e.g., Hydrogen atom transfer to unactivated alkene  $\cdots$ )

### Thank you for your kind attention.

### Appendix

【参考資料】

- Walker, A., Mougel, V. Chimia. 2024, 78, 251.
- 分子光化学の原理(著者; Nicholas, J. T. 他 訳者; 井上 晴夫 他)
- 大学院講義有機化学 第2版 I (著者;野依 良治 他)
- 量子化学 基礎からのアプローチ(著者;真船 文隆)
- 金属錯体の電子移動と電気化学 錯体化学選書 9 (著者;西原 寛)
- http://mol-chem.com/photoinduced\_electron\_transfer/index.html

#### Another example of PCET mediator ~ Fe-S cluster for Electrocatalytic CO<sub>2</sub>RR ~



#### Challenges in Selectivity



### **PCET mediator for efficient M-H formation**



- Biomimetic iron-sulfur cluster was utilized as a hydrogen atom transfer mediator.
- Multiple site nature of PCET on Fe-S cluster, in which protonation occurs at a sulfur base, whereas reduction occurs at a Fe centre, constitute a kinetic advantage by the lower reorganization energy.

### Catalytic activity and spectroscopic characterization

☆

CV chart



 New redox process at –1.85V resulting from the synergistic combination of Fe-S and Mn<sup>I</sup>-cat





#### Thermodynamic and kinetic considerations





### **Synthesis of PCET mediator**



The reduction of catalyst can also be performed electrochemically.

#### **Reaction set-up**

Peters, J. C. et al. Nature, 2022, 609, 71.

Controlled potential electrolyses (CPEs) were carried out in a gas-tight, two-compartment or H-cell equipped with a frit to separate anodic from cathodic chambers (Fig. S1). This cell also features two necks, one in each compartment, sealed using a septum that allows for bubbling of different gasses other than the <sup>14</sup>N<sub>2</sub>, such as Argon and <sup>15</sup>N<sub>2</sub>, needed in control experiments. Either a BDD plate (dimensions 1x1 cm) or a high surface area reticulated vitreous carbon foam was employed as the working electrode, a Ag/AgOTf (5 mM) as the reference electrode, and a Zn plate as the sacrificial counter electrode. In a typical experiment, 6 mL of solvent containing 0.2-0.1 M of the specified electrolyte and the tosic acid was added to the electrochemical cell, 3 mL per compartment. For experiments including the catalysts, the cathodic chamber was also charged with the corresponding amount of **Co**(III,N)<sup>+</sup> mediator and **W**(N<sub>2</sub>)<sub>2</sub> (or other N<sub>2</sub>RR catalyst), or both were taken from concentrated stock solutions (1 mg/mL). The electrochemical cell was assembled inside an N<sub>2</sub> glove box in which the CPC experiment was also performed. The potential applied during the CPC experiment was set to -1.35 V vs Fc<sup>+/0</sup> according to the peak current observed for the catalytic wave from previous CVs. The solution was stirred throughout the CPC experiment.

### **Reaction set-up**

Peters, J. C. *et al. J. Am. Chem. Soc.* **2024**, *146*, 12750.

#### 1. Stoichiometric photochemical reaction

General set up for a typical photochemical experiment: in a  $N_2$  filled glove box, the corresponding mass of the {**Fc–N–an**} mediator, the [PicH][OTf] acid and the substrate was weighed and placed in a vial with a magnetic stir bar. Subsequently, 1 ml of dried and degassed THF was added and the vial was closed with a septum to ensure inert atmosphere. The vial was brought out of the glove box and irradiated with a 390 nm LED lamp during 1 h. Stirring and refrigeration with a fan was maintained throughout the experiment.

General work up methodology: after the reaction, the reaction vessel was open to air and 1 ml of HCl in diethyl ether was delivered. After stirring for 5 min, the mixture was evaporated to dryness. The remaining solids were extracted with 5 ml of diethyl ether, which was subsequently filtered, washed with concentrated solution of saturated NH<sub>4</sub>Cl and water, dried over sodium sulfate and evaporated to dryness. Subsequently, 1 ml of CDCl<sub>3</sub> and 5  $\mu$ L of CH<sub>2</sub>Br<sub>2</sub> as internal standard were added and <sup>1</sup>H NMR was performed to analyze for product formation.

### **Reaction set-up**

Peters, J. C. *et al. J. Am. Chem. Soc.* **2024**, *146*, 12750.

#### 2. Photoelectrocatalytic reaction

General Controlled Potential Coulometry (CPC) Procedure: Carbon cloth electrodes were cut to 5  $cm^2$  and used as obtained from the supplier. Controlled potential coulometry (CPC) experiments were carried out in a gas-tight two compartment cell using a carbon cloth (dimensions 1 x 2 cm) working electrode, a Pt wire pseudo-reference electrode, and a carbon cloth (5 cm<sup>2</sup>) or Zn foil (10 cm<sup>2</sup>) counter electrode. The solution was stirred throughout the CPC. In a typical experiment with an organic substrate, a 6 mL solution of 0.15 M [TBA][PF<sub>6</sub>] with two equivalents of acid (based on desired number of H-atom equivalents delivered to substrate) in DME was added to the solution which was added to the electrochemical cell distributing evenly between both compartments. Then, an appropriate amount of substrate (50 mM in 3 mL) and {Fc-N-an} (1 mM in 3 mL) was added to the working compartment. After the appropriate reaction time, the solution was quenched with 2 M HCl in ether (1 mL) except for the acid sensitive N-phenylbenzaldimine. After 5 min of stirring, the solvent was evaporated under reduced pressure until dryness. The resulting solids were dissolved in diethyl ether (20 mL). For the diphenylfumarate reaction, ethyl acetate (10 mL) was first added to the carbon cloth working electrode, then sonicated to extract the remaining starting material (sparingly soluble in diethyl ether) before 100 mL of diethyl ether was added. The solution was subsequently washed with either 1 M HCl (aq, acetophenone), sat. NaHCO<sub>3</sub> (aq, *N*-phenylbenzaldimine), or 0.1 M Na<sub>2</sub>CO<sub>3</sub> (aq, diphenylfumarate) solution (20 mL) and extracted with ether (5 x 20 mL). The organic layers were combined, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. A crude <sup>1</sup>H-NMR was taken with CH<sub>2</sub>Br<sub>2</sub> as internal standard. In reactions where ferrocene oxidation was used as the anodic reaction, an amount of ferrocene equivalent to that of the acid in the working compartment was dissolved in the counter compartment. Upon completion of the CPC, the counter compartment is a deep blue color, indicating the formation of  $Fc^+$ .



### **Other applications of PCET mediator**

- 1. Stahl S. S. et al. Cooperative electrocatalytic alcohol oxidation with electron-proton-transfer mediators. *Nature*. **2016**, *535*, 406.
- Peters, J. C. et al. Electrocatalytic Reduction of C-C π-Bonds via a Cobaltocene- Derived Concerted Proton-Electron Transfer Mediator: Fumarate Hydrogenation as a Model Study. *J. Am. Chem. Soc.* 2021, 143, 9303
- 3. Waymouth, R. M. et al. Electron-Rich Phenoxyl Mediators Improve Thermodynamic Performance of Electrocatalytic Alcohol Oxidation with an Iridium Pincer Complex. *J. Am. Chem. Soc.* **2020**, *142*, 19368.
- 4. Peters, J. C. et al. Electrocatalytic Ketyl-Olefin Cyclization at a Favorable Applied Bias Enabled by a Concerted Proton–Electron Transfer Mediator. *Inorg. Chem.* **2022**, *61*, 6672
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- 6. Meyer, G. J. et al. Direct Evidence for a Sequential Electron Transfer–Proton Transfer Mechanism in the PCET Reduction of a Metal Hydroxide Catalyst. J. Am. Chem. Soc. **2024**, 146, 1742.
- 7. *Peters, J. C. et al.* Catalytic Reduction of Cyanide to Ammonia and Methane at a Mononuclear Fe Site. *J. Am. Chem. Soc.* **2024**, *146*, 5343
- 8. Waymouth, R. M. et al. Cobaltocene-Mediated Catalytic Hydride Transfer: Strategies for Electrocatalytic Hydrogenation. *J. Am. Chem. Soc.* **2024**, *146*, 17075.