



Electrocatalytic Transformation of N₂ Using Molecular Catalysts

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PART

I

Background



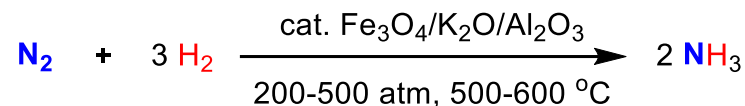
Accounts for 78.3 %
in the atmosphere

“Life element”

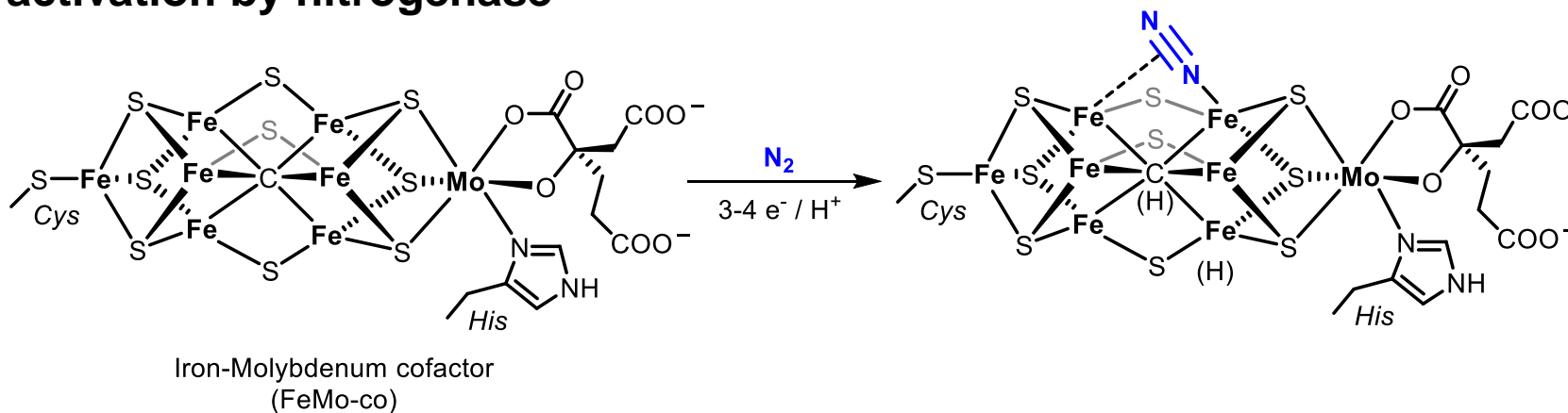
- ◆ Organic compound: R-NH₂, R-NO₂...
- ◆ Inorganic compound: NH₃, HNO₃...
- ◆ Biomatter: protein, Nucleic acid...

- Nonpolar molecule
- Bond dissociation energy: 944 kJ/mol
- HOMO-LUMO energy gap: 10.82 eV
- Ionization potential: 15.6 eV

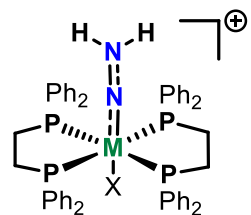
Haber-Bosch process



Dinitrogen activation by nitrogenase

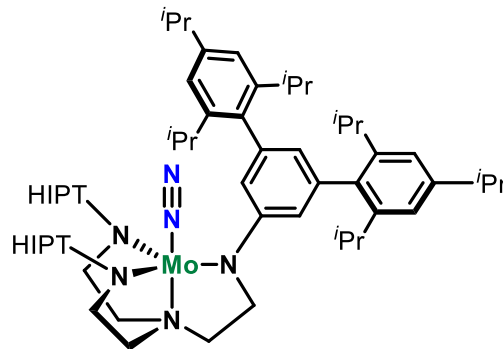


Well-studied N₂R catalysts

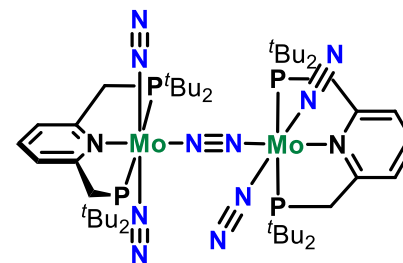


M = Mo, W; X = Cl, Br

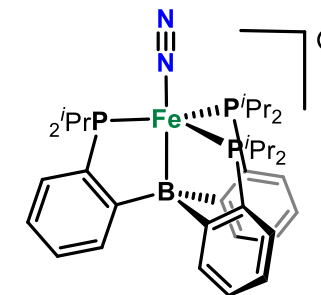
Chatt, 1972
Protonation of N₂ ligand



Schrock, 2003
Mo-based
N₂-to-NH₃ catalyst

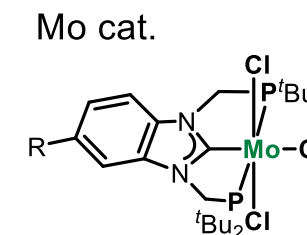
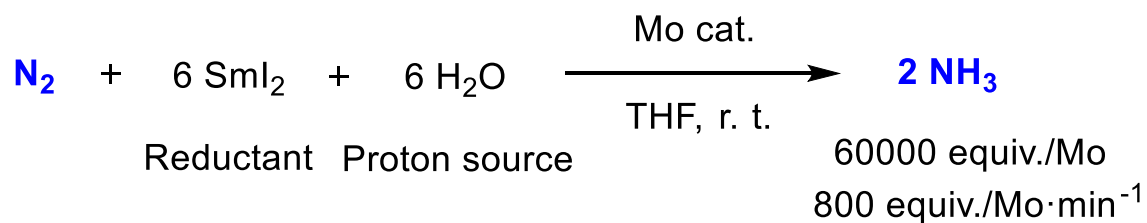


Nishibayashi, 2010
Mo-based
N₂-to-NH₃ catalyst



Peters, 2013
Fe-based
N₂-to-NH₃ catalyst

Nishibayashi, 2019, 2023

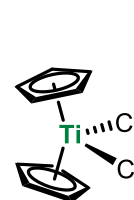
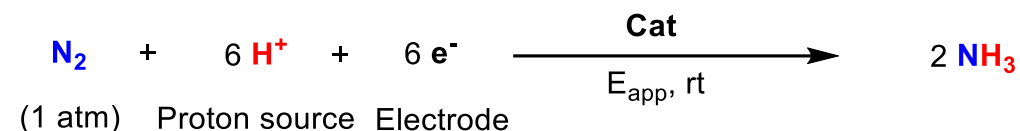
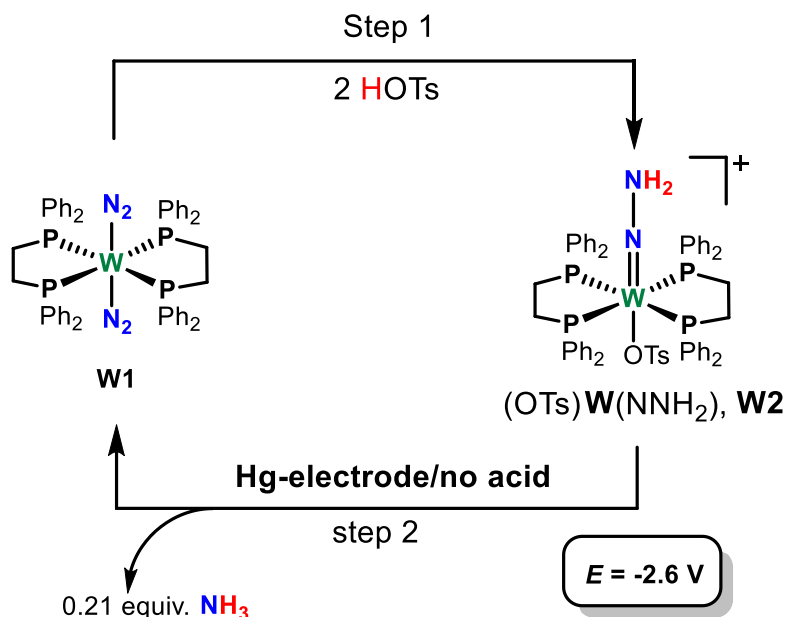


- In-depth mechanism research
- Excellent chemical selectivity
- High catalytic efficiency

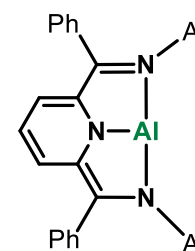
➤ Expensive reducing agents and proton sources

Early progress towards electrochemical transformation of N₂ to NH₃

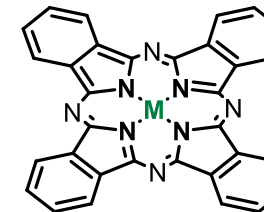
Pickett, 1985



Ti1



Al1



M = Fe, Co, Sn

MPc

Entry	Catalyst	Proton source	FE _{NH₃}	TON
1	Ti1	H ₂ O	1.44 %	0.34
2	Al1	DMAPH ⁺	<1 %	0.21
3	FePc	HCl	9.73 %	12.56

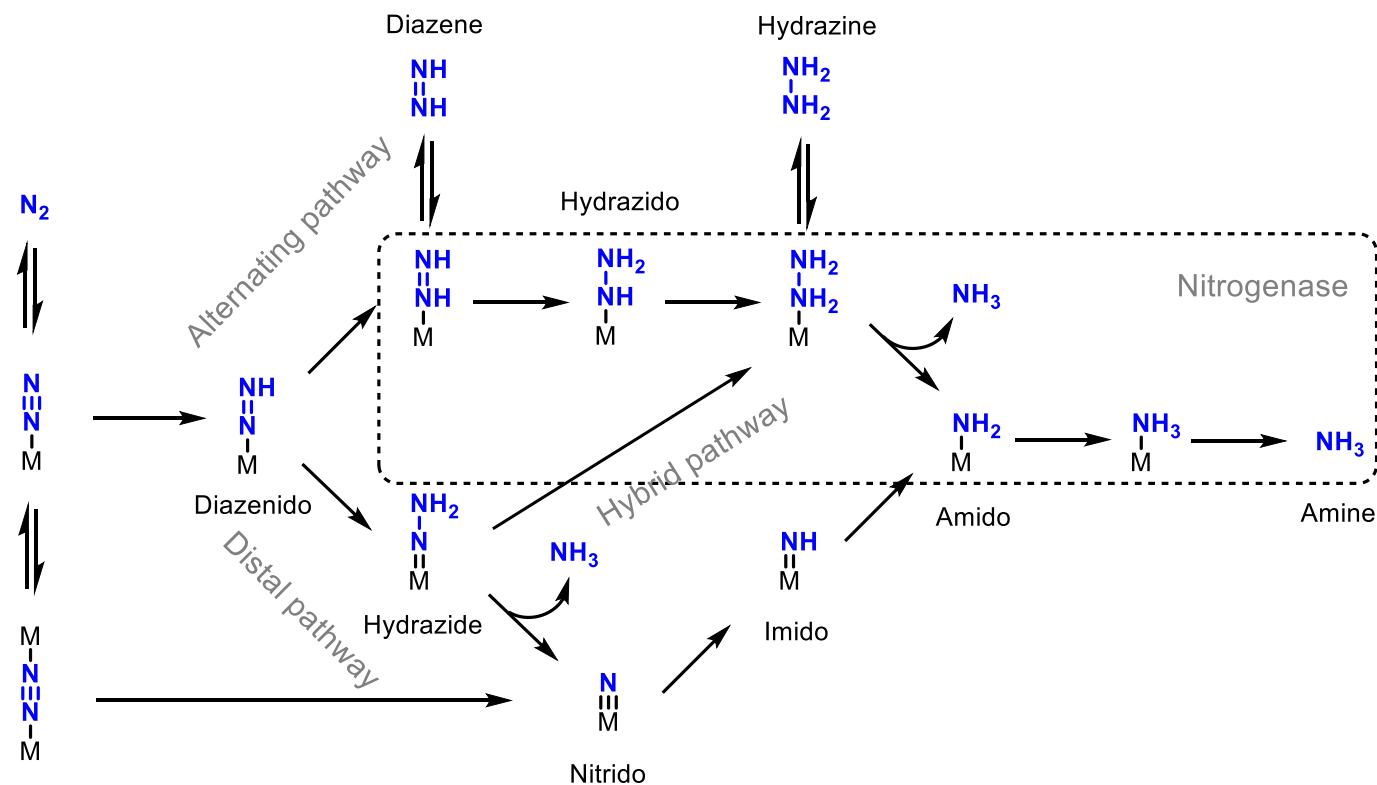
- Strong HER side reaction
- Low turnover number
- Inefficient N₂RR molecular catalysts

PART

II

**Electrocatalytic
transformation of N_2 to NH_3**

Possible pathways of dinitrogen reduction to ammonia



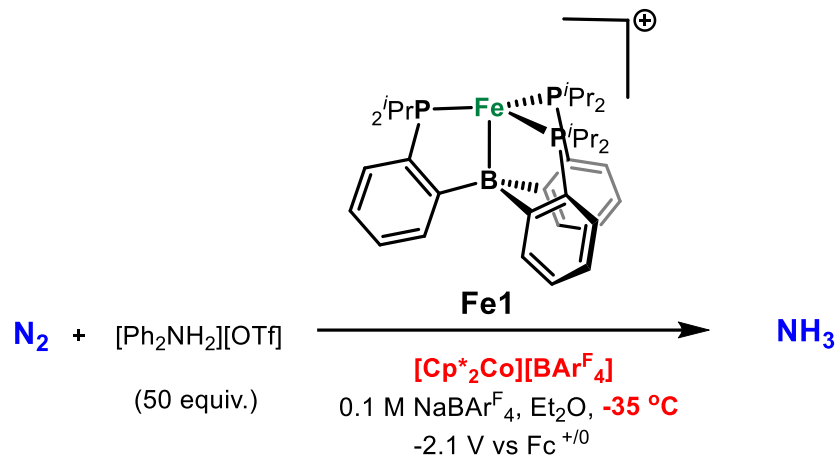
➤ How to fix and activate nitrogen

- Different metals and dinitrogen coordination modes

➤ How to provide electrons and protons

- Reduction potential and pKa
- Stepwise or PCET

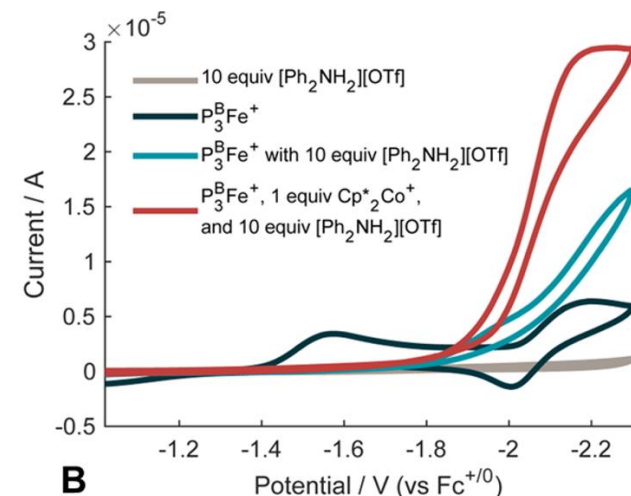
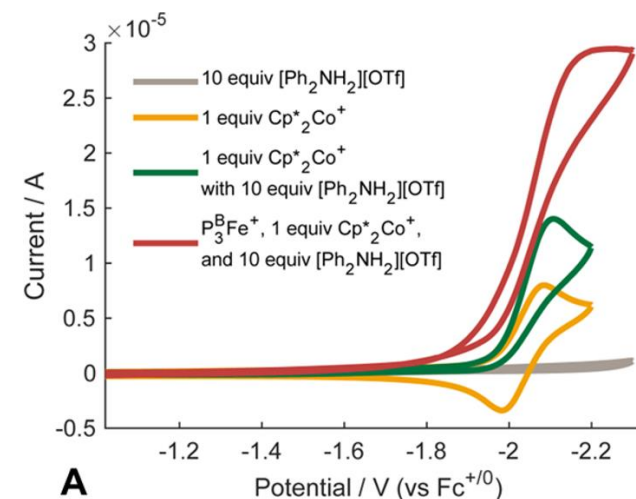
Peters, 2018



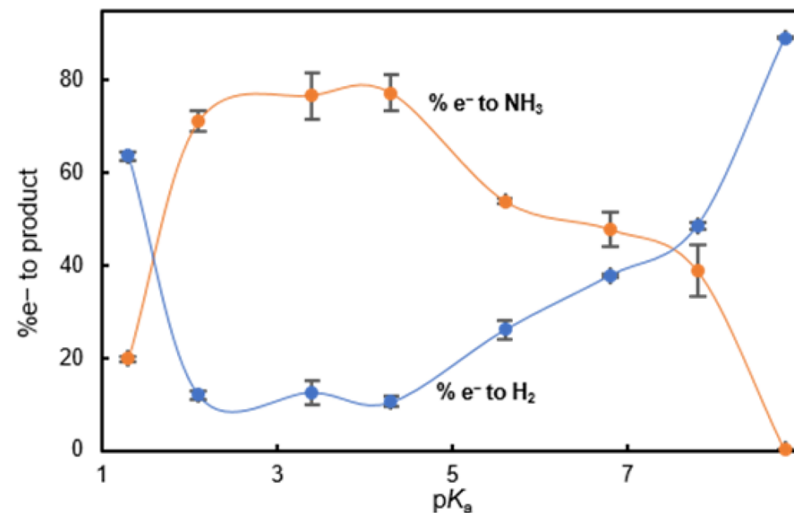
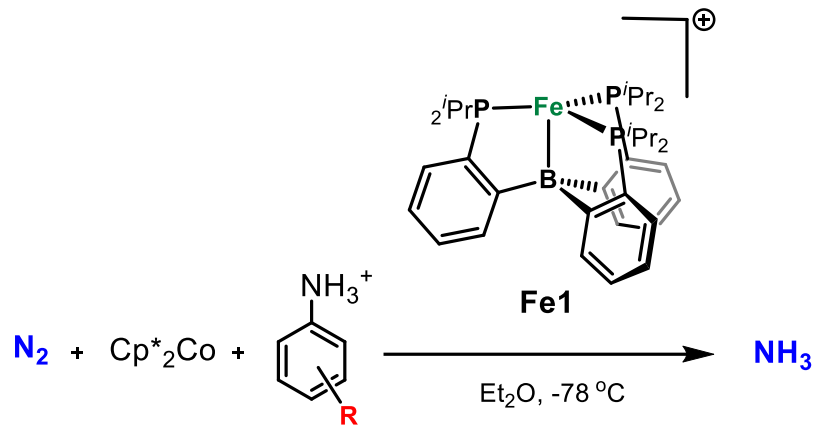
entry	equiv Cp* ₂ Co ⁺	equiv NH ₃ (per Fe)	equiv NH ₃ (per Co)	NH ₃ FE (%)
1	0	2.6 ± 0.3		24 ± 5
2	0	2.6 ± 0.6		18 ± 1
3	1	4.0 ± 0.6	4.0 ± 0.6	28 ± 5
4	5	4.0 ± 0.6	0.8 ± 0.1	25 ± 3
6	10	4 ± 1	0.4 ± 0.1	24 ± 7

All CPE experiments were conducted by a glassy carbon plate working electrode, Ag⁺⁰ reference couple isolated by a CoralPor frit, and a solid sodium auxiliary electrode. Working and auxiliary chambers were separated by a sintered glass frit.

➤ Relevant cyclic voltammograms under N₂



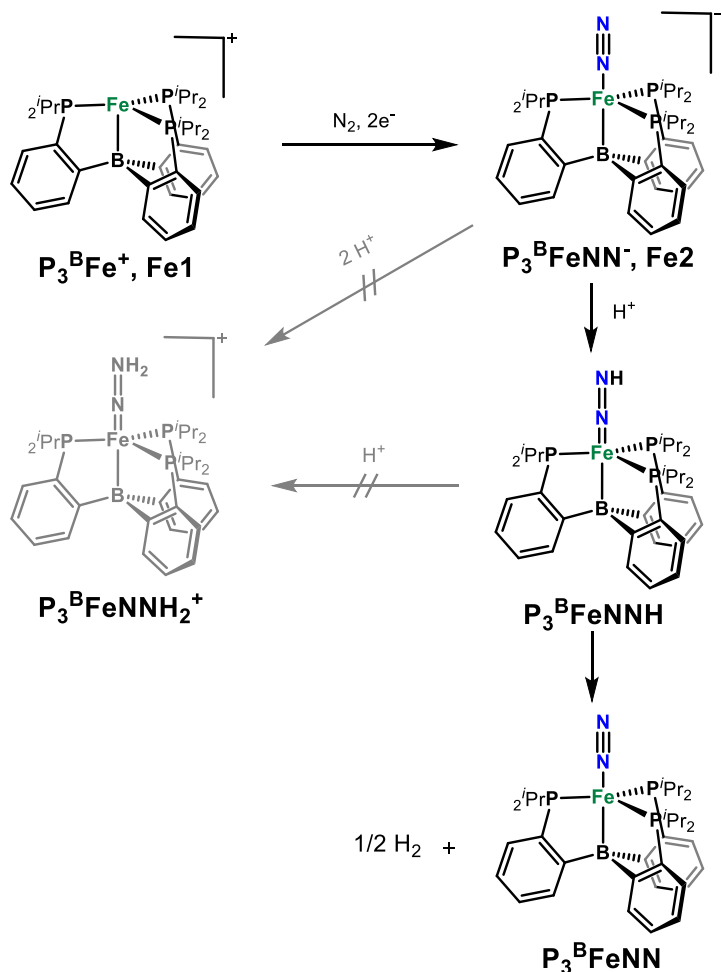
Exploring pK_a effects



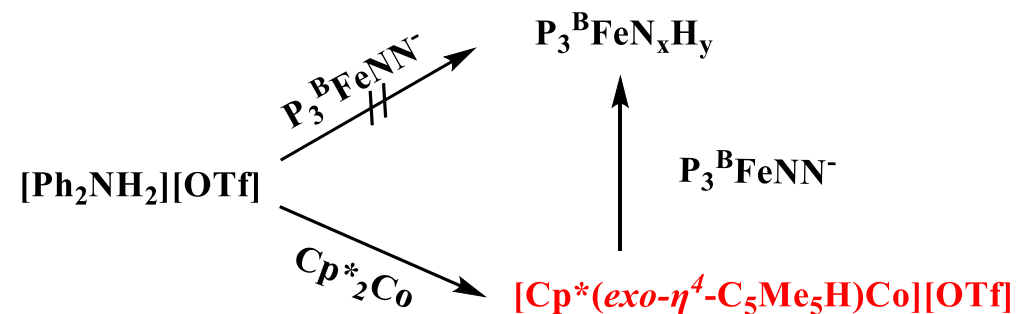
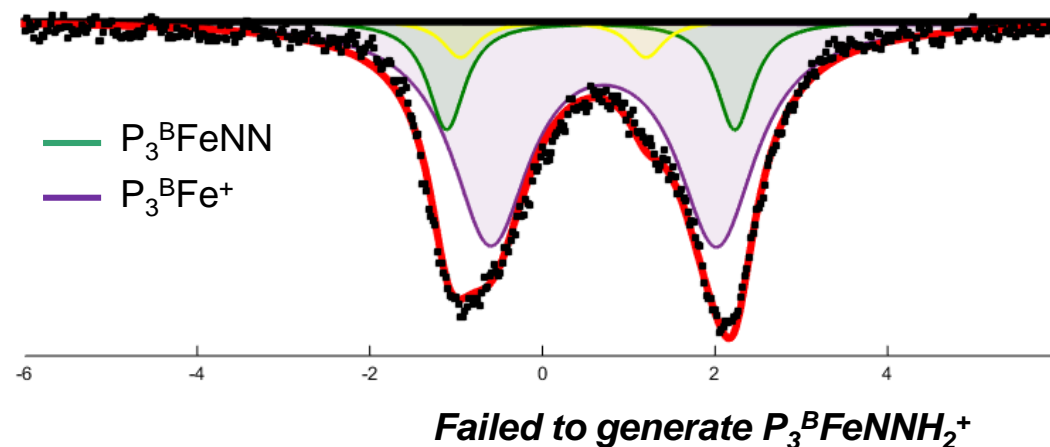
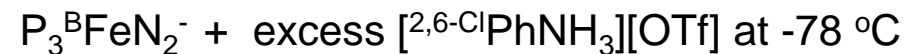
	pK _a ^{exp} (THF)	pK _a ^{calc} (298 K)	pK _d ^{calc} (195 K)	equiv of NH ₃ /Fe	% yield of NH ₃ /e ⁻	% yield of H ₂ /e ⁻	total yield/e ⁻
[4-OMePhNH ₃][OTf]	8.8	9.6	15.7	0.04 ± 0.01	0.2 ± 0.1	89.1 ± 0.2	89.3
[PhNH ₃][OTf]	7.8	7.7	13.8	7.3 ± 0.1	40.4 ± 0.5	48.6 ± 0.7	87.5
[2,6-MePhNH ₃][OTf]	6.8	7.3	13.2	8.6 ± 0.7	47.5 ± 4.0	37.8 ± 0.2	85.6
[Cp*(<i>exo</i> -η ⁴ -C ₅ Me ₅ H)Co][OTf]	N/A	9.2	11.8				
[2-ClPhNH ₃][OTf]	5.6	5.6	6.0	10.7 ± 0.1	53.9 ± 0.4	26.1 ± 1.9	80.0
[2,5-ClPhNH ₃][OTf]	4.3	4.0	5.0	13.9 ± 0.7	77.5 ± 3.8	10.5 ± 1.1	87.7
[2,6-ClPhNH ₃][OTf]	3.4	3.4	3.4	13.8 ± 0.9	76.7 ± 4.9	12.6 ± 2.5	89.3
[2,4,6-ClPhNH ₃][OTf]	2.1	2.7	1.8	12.8 ± 0.4	70.9 ± 2.2	12.0 ± 0.8	83.1
[<i>per</i> -ClPhNH ₃][OTf]	1.3	0.8	0.4	3.6 ± 0.1	19.9 ± 0.5	63.5 ± 1.1	83.5

Exploring pKa effects

- Anilinium triflate acids are unable to generate the N-H bonds of early stage N₂RR intermediates

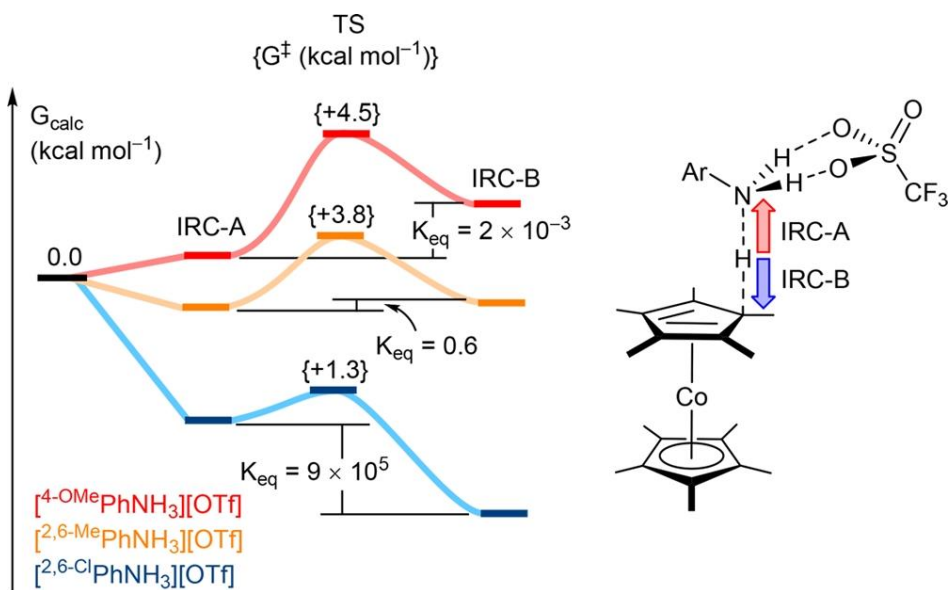


- Stoichiometric studies

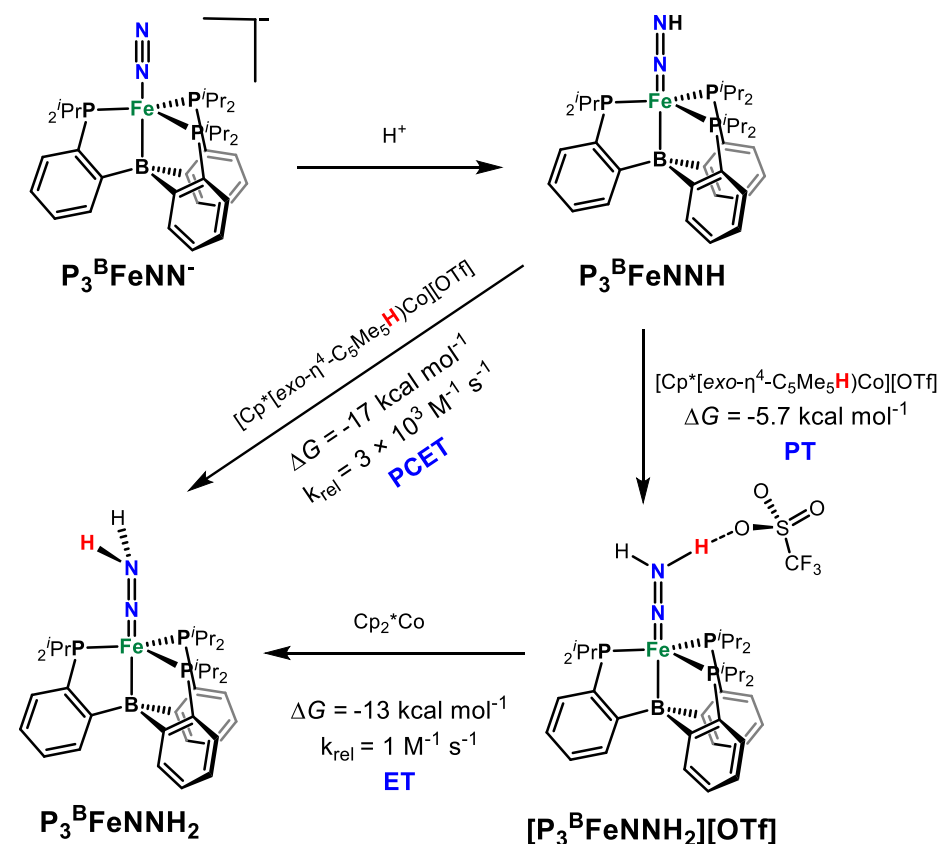


Cp*₂Co protonation and PCET to P₃^BFeN_xH_y

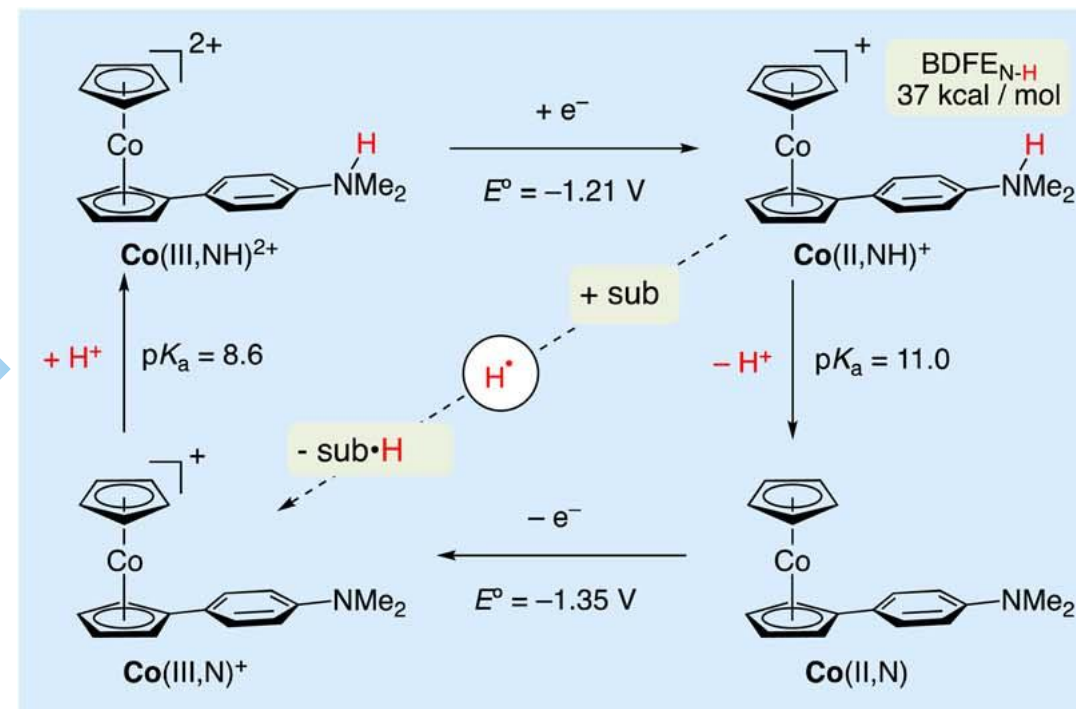
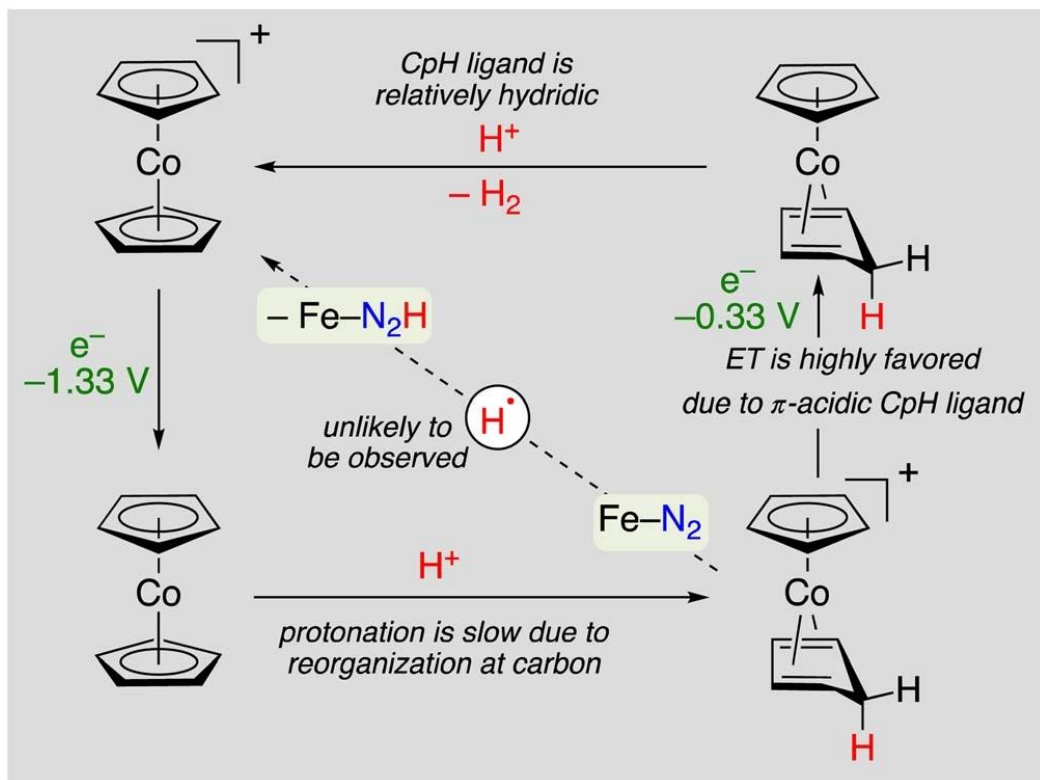
- Kinetics and thermodynamics of protonation of Cp*₂Co



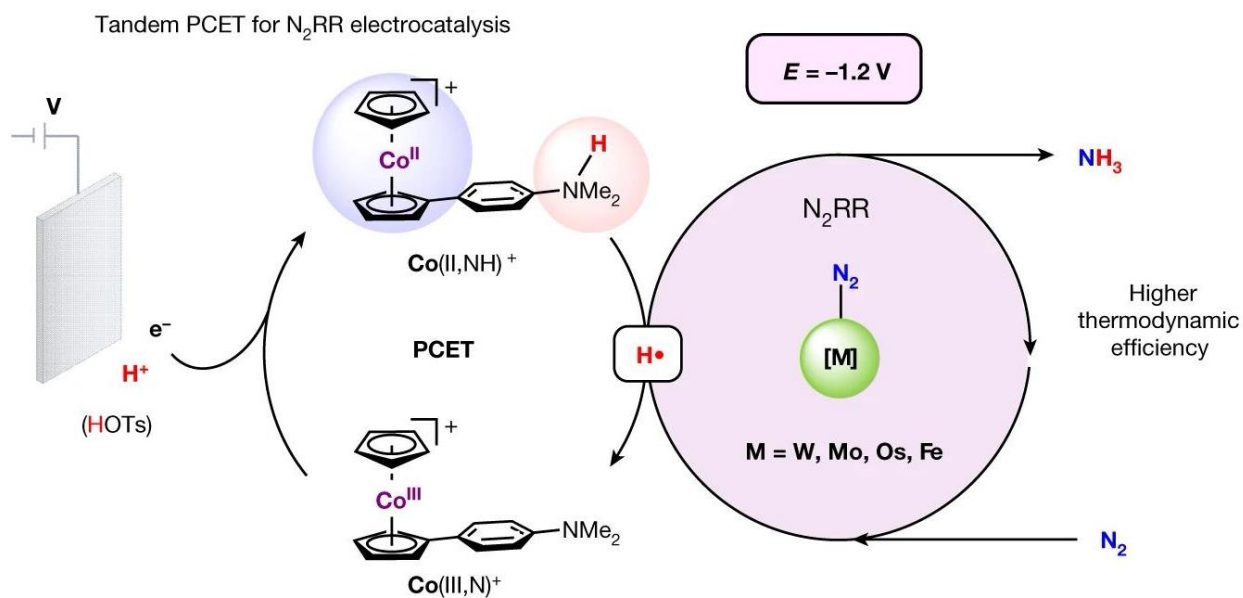
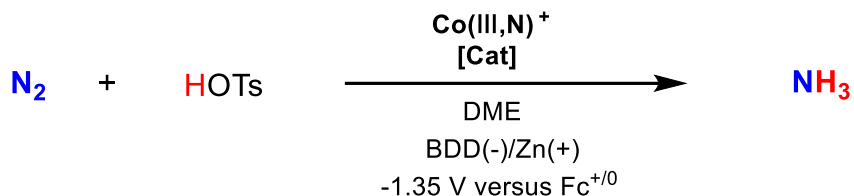
- Calculated thermodynamics and kinetics of synchronous PCET and asynchronous PCET progress



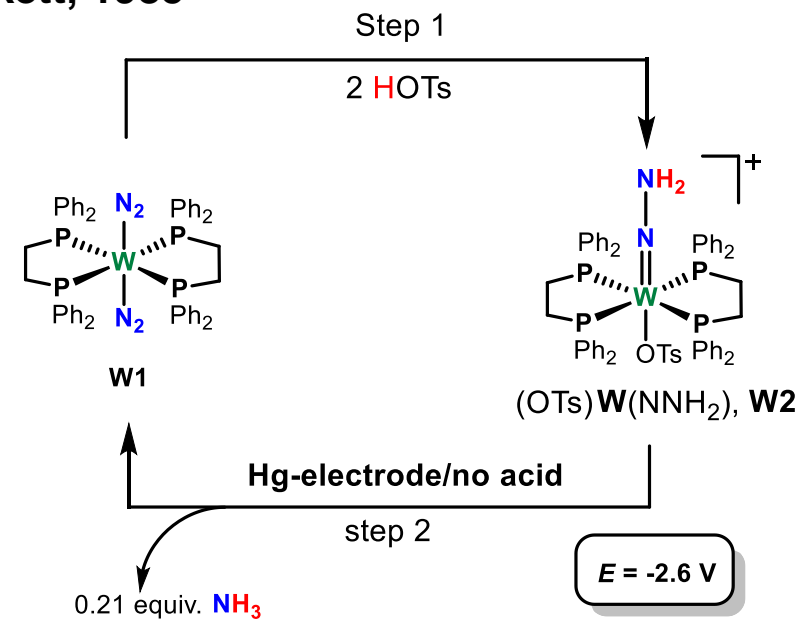
Design of the PCET mediator: decouple the protonation and reduction



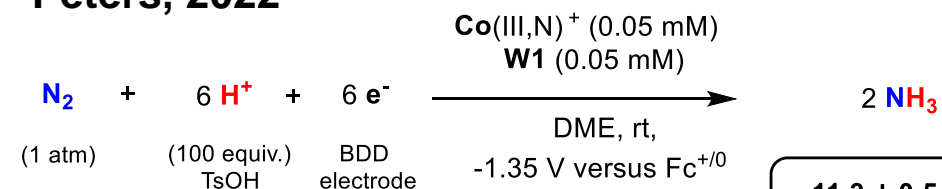
Peters, 2022



Pickett, 1985

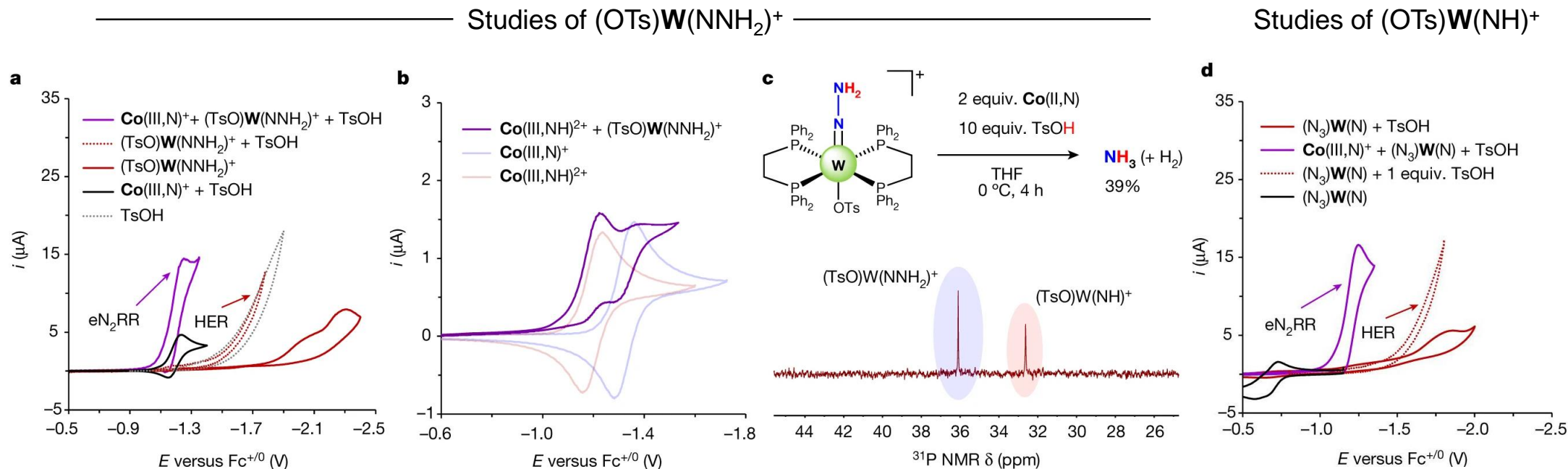


Peters, 2022

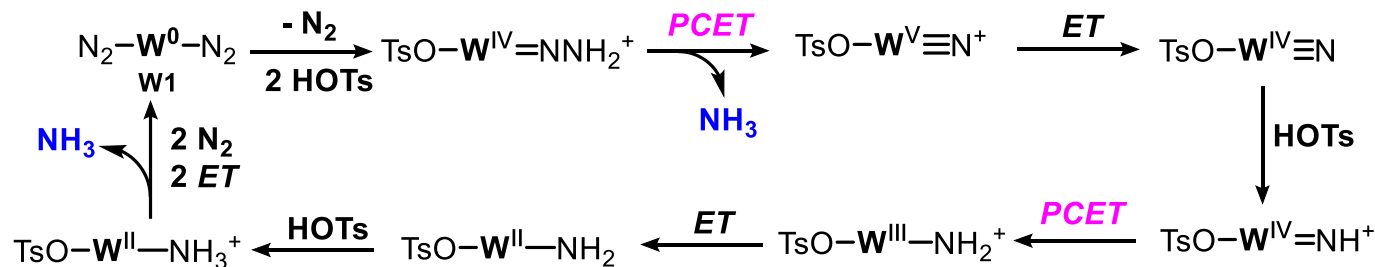


$11.3 \pm 0.5 \text{ equiv.}$
 $44.5 \pm 1.9 \% \text{ FE}$

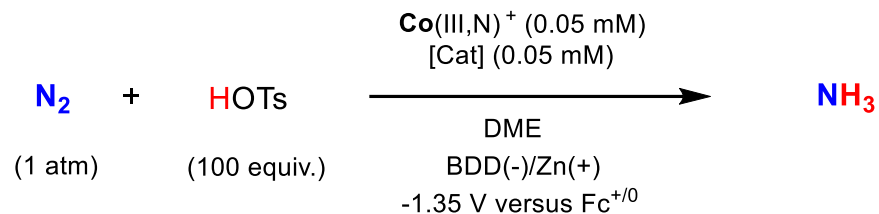
Mechanistic insights into tandem PCET N₂RR



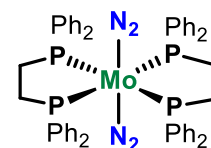
Distal pathway:



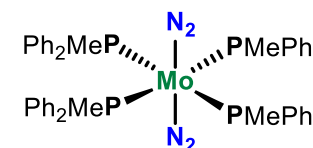
Electrocatalytic N₂RR using reported molecular catalysts



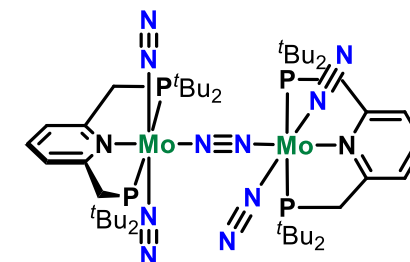
catalyst	equiv NH ₃ /Cat	NH ₃ FE (%)
W1	11.3 ± 0.5	44.5 ± 1.9
Mo1	13	51
Mo2	14	55
Mo3	8.7	34
Mo4	<0.1	<1.0
Os1	5.6	22
Fe3	4.5	18
Fe4	1.5	4.5



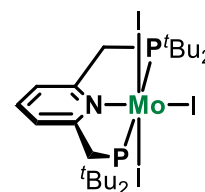
Mo1



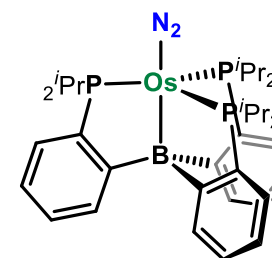
Mo2



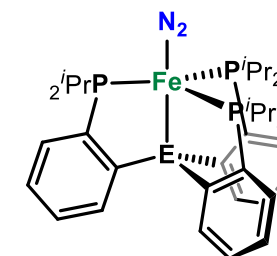
Mo3



Mo4

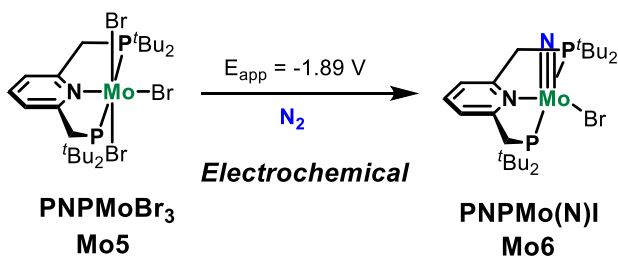
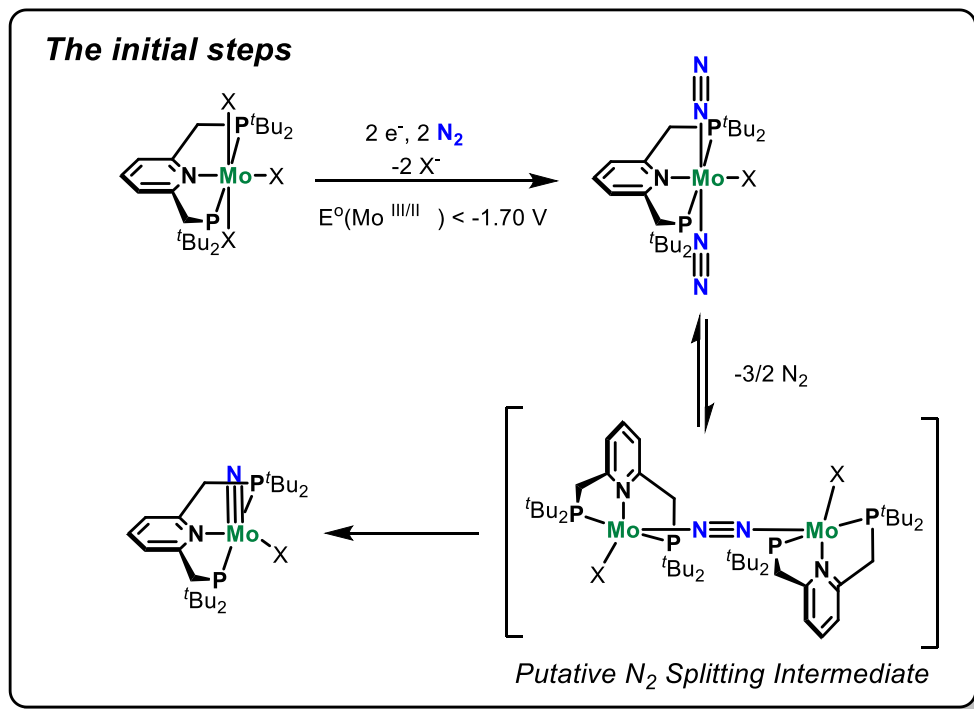


Os1



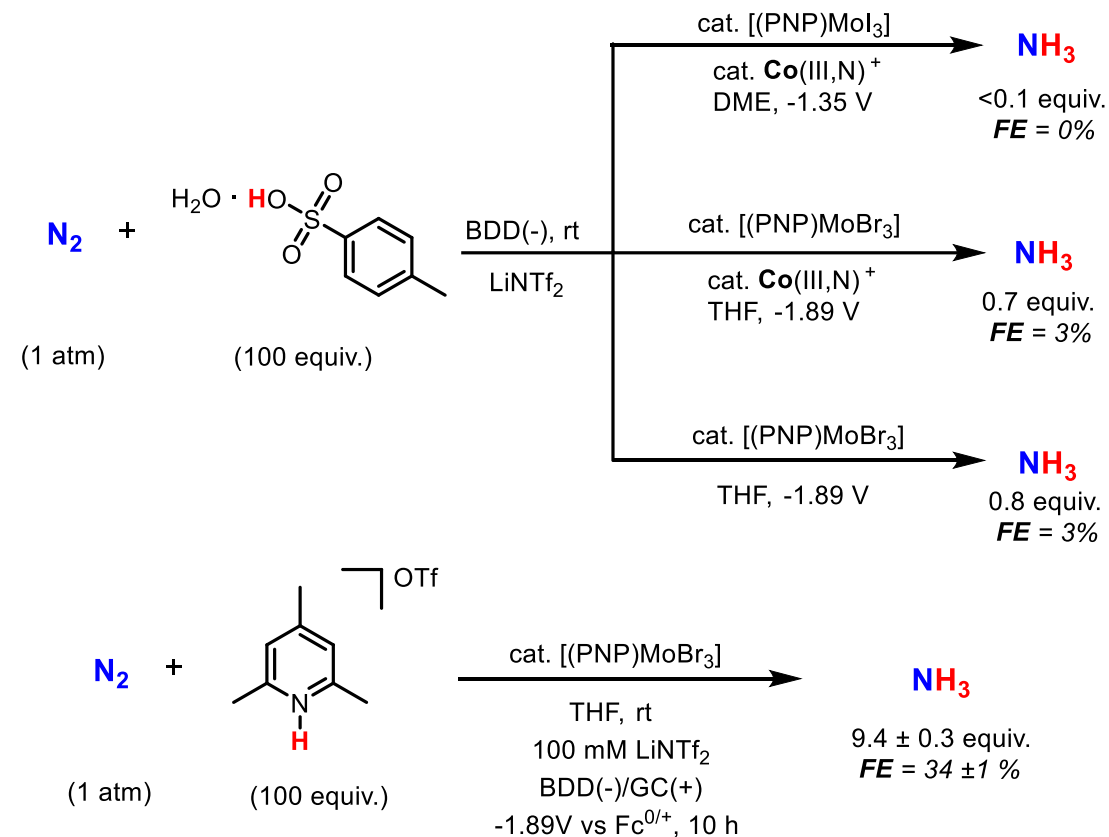
Fe3 (E = B)
Fe4 (E = Si)

Peters, 2023



Cannot be promoted by Cobalt mediator

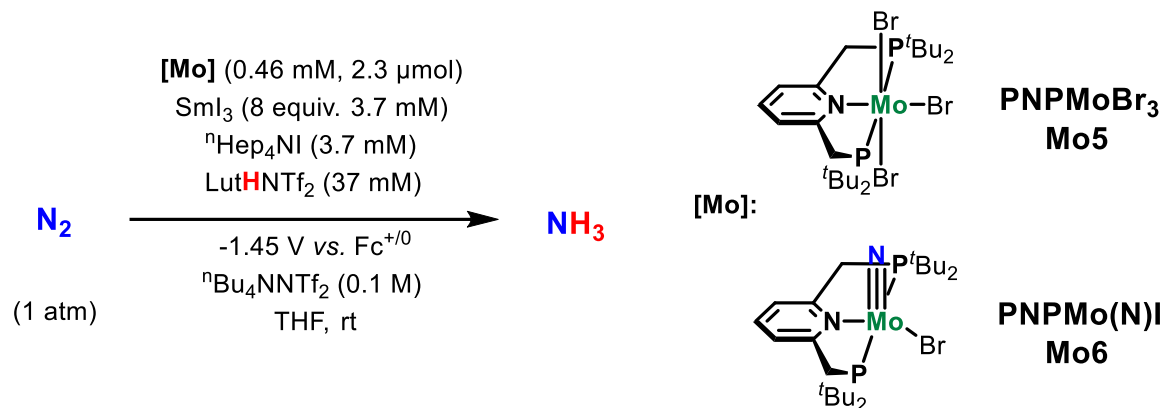
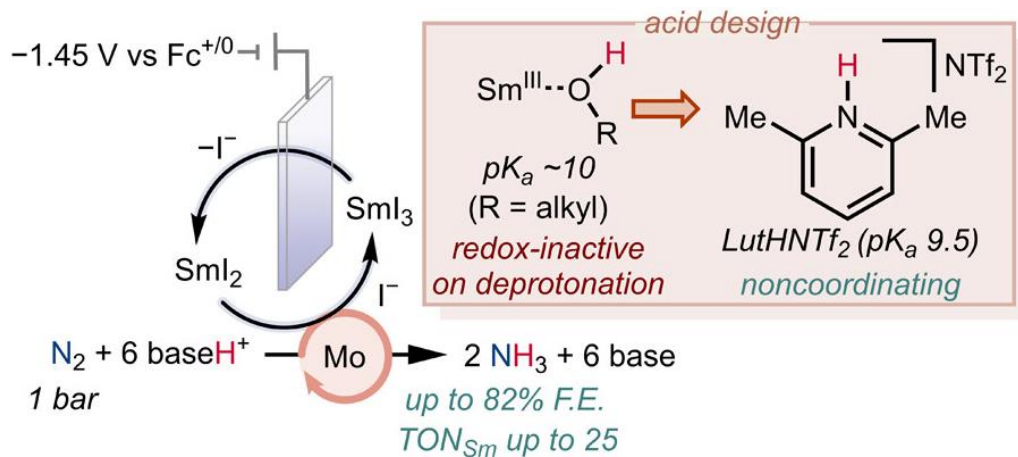
➤ Replacing the proton source to enable electrocatalytic NH₃ generation



Electrocatalytic transformation of N₂ to NH₃

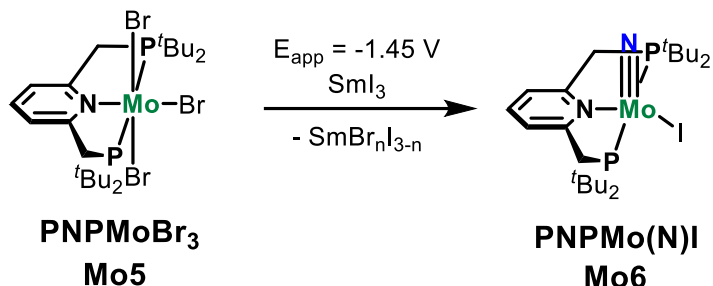
Peters, 2025

Nishibayashi, 2019

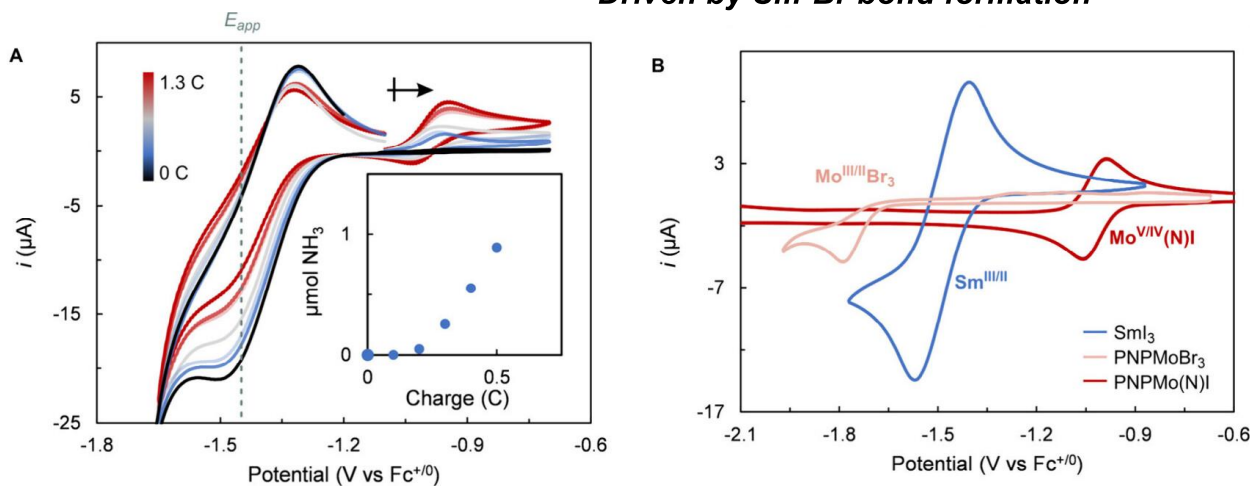


entry	variation	equiv NH ₃ (per Mo)	NH ₃ FE (%)	e ⁻ /Sm
[Mo] = PNPMoBr ₃				
1	None	16.9 ± 0.3	82 ± 2	6.3 ± 0.1
2	No Sm	0.5	20	
3	GdI ₃ instead of SmI ₃	2.0	27	
4	+ 1 equiv. H ₂ O per Sm	2.4	42	0.8
5	ColNTf ₂ (pK _a = 10.4)	2.8	35	1.0
[Mo] = PNPMo(N)I				
6	None	16.7	82	6.3
7	No Sm	1.3	33	
8	2 equiv. Sm	12.5	75	19

- CVs under the standard conditions with PNPMoBr₃ recorded after passage of 0.1–1.3 C



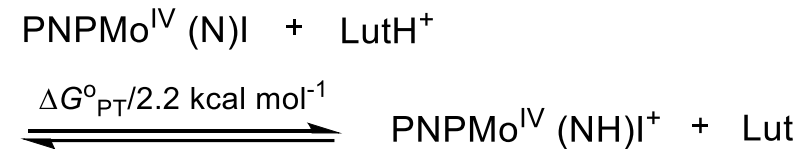
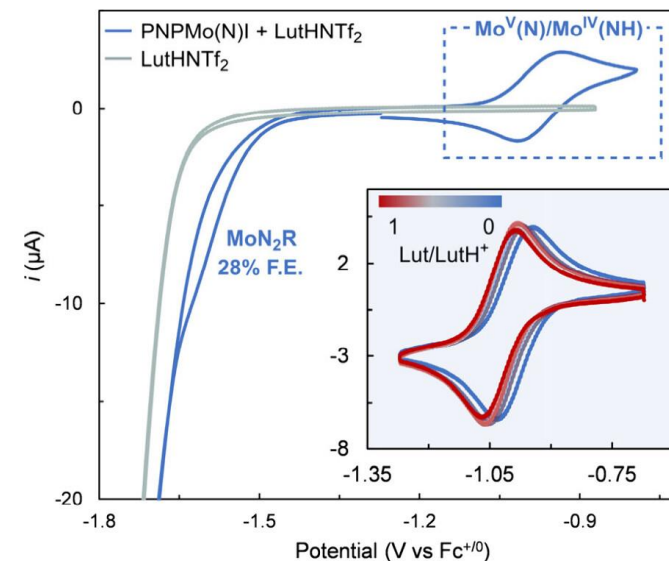
Driven by Sm-Br bond formation



Induction period corresponds to Sm-mediated reduction of the PNPMoBr₃ to form PNPMo(N)I

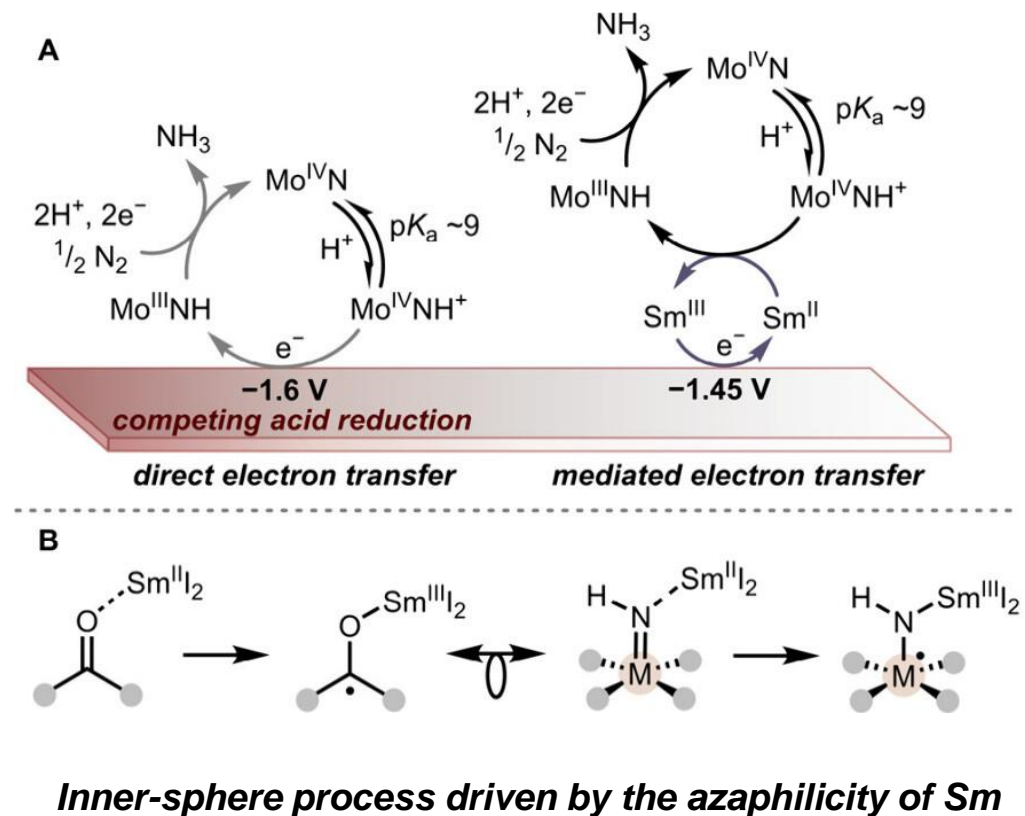
a) J. C. Peters, et al. *J. Am. Chem. Soc.* **2025**, *147*, 4695.

- CV of PNPMo(N)I in the presence of LutHNTf₂

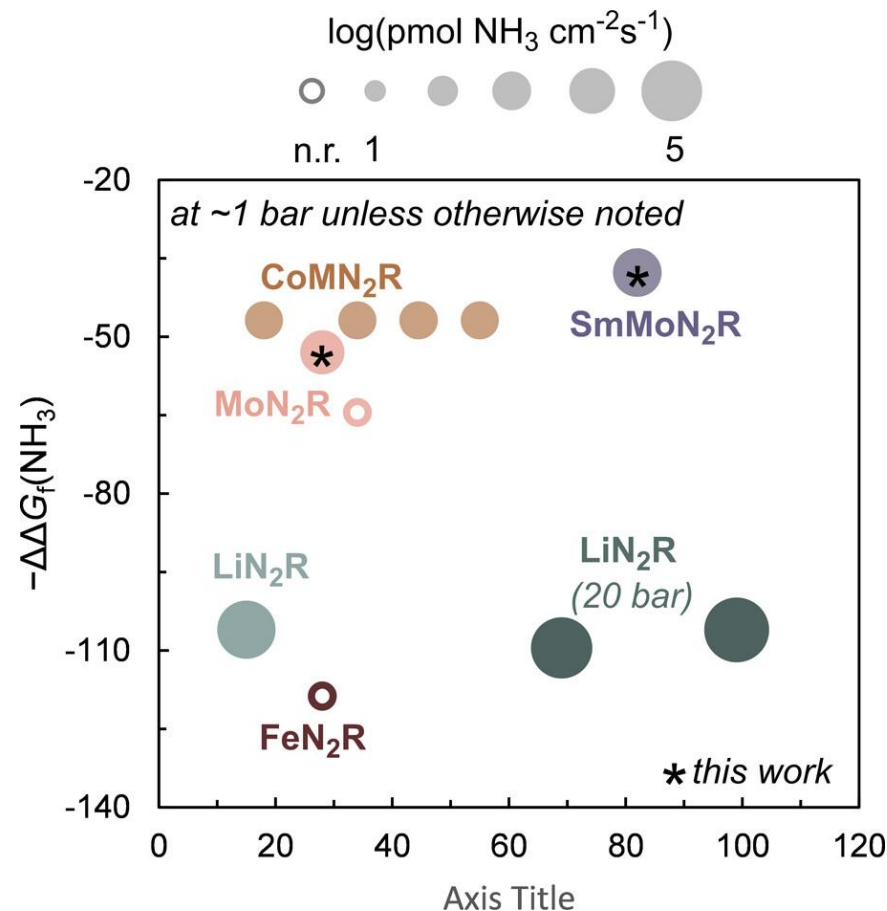


Electrocatalytic transformation of N₂ to NH₃

- Proposed role of Sm^{III/II} redox in the mediation of selective Mo-catalyzed N₂R



- Comparison of the overpotential, FE, and yield rate of representative eN₂Rs from the literature

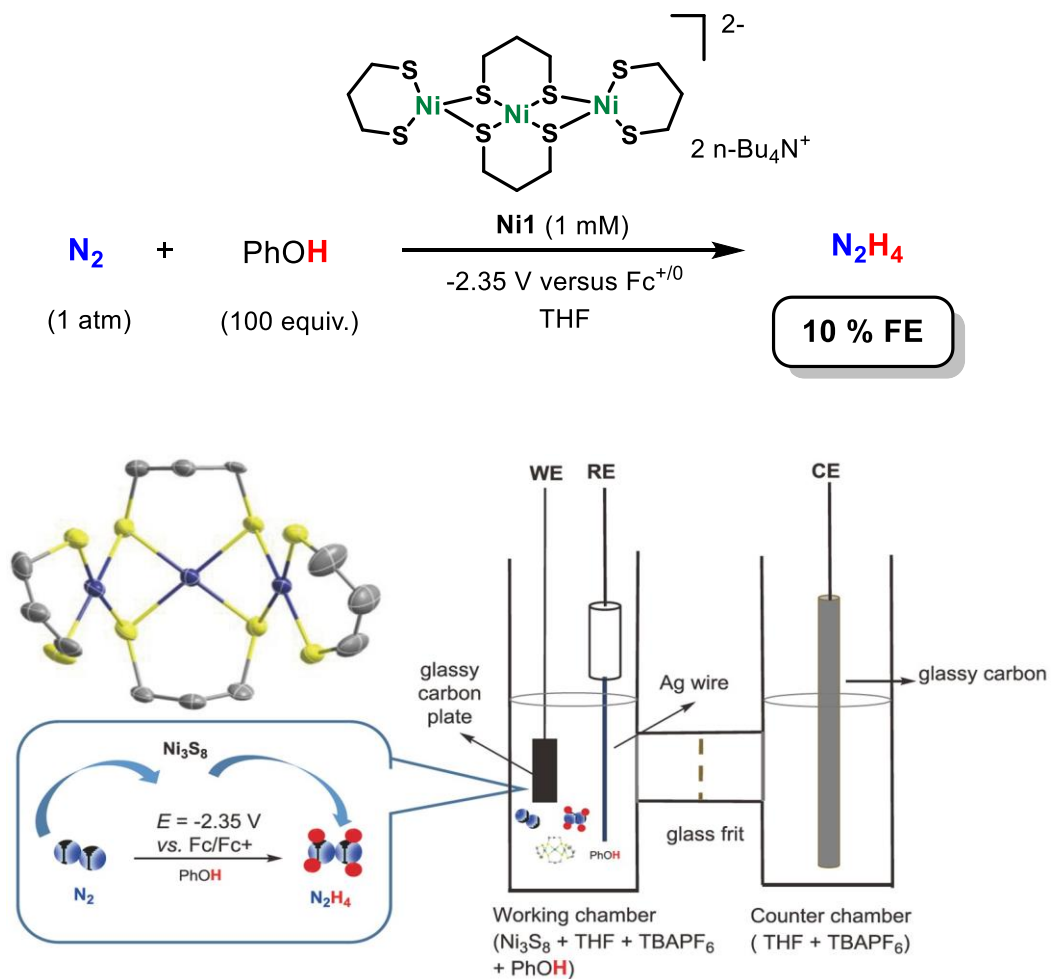


PART

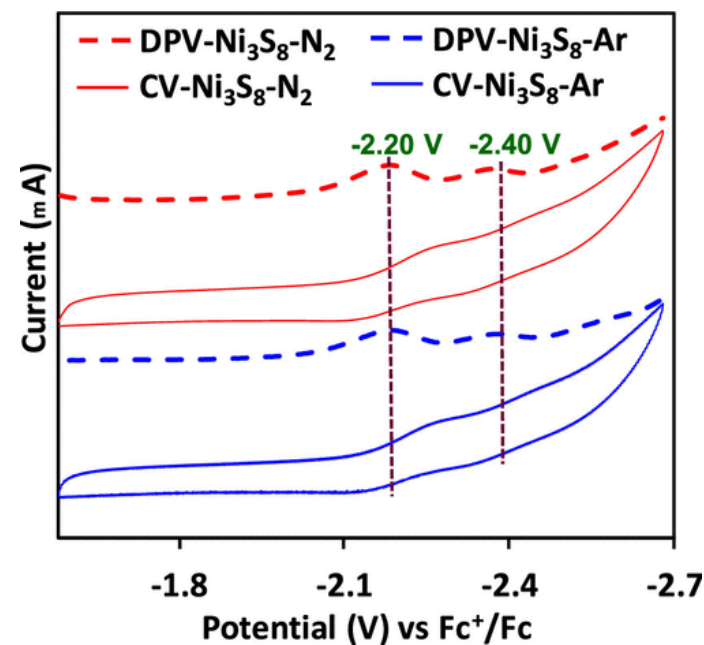
III

**Electrocatalytic
transformation of N_2 to N_2H_4**

Dey, 2020



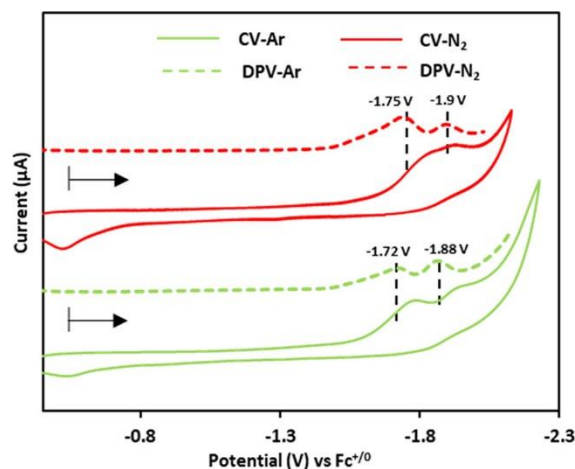
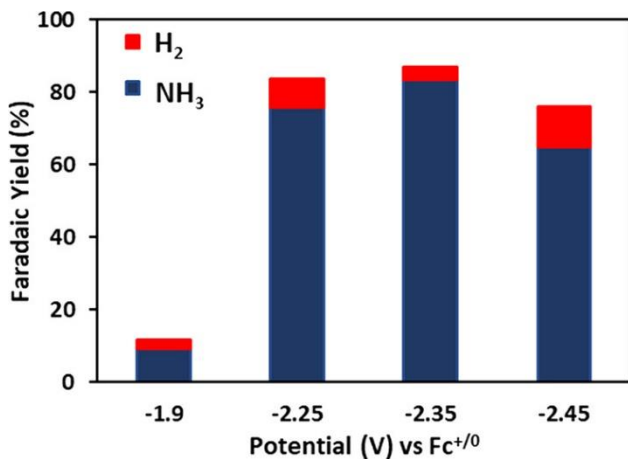
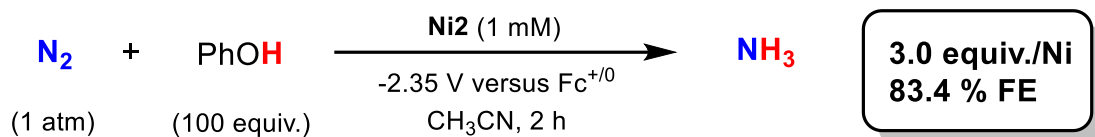
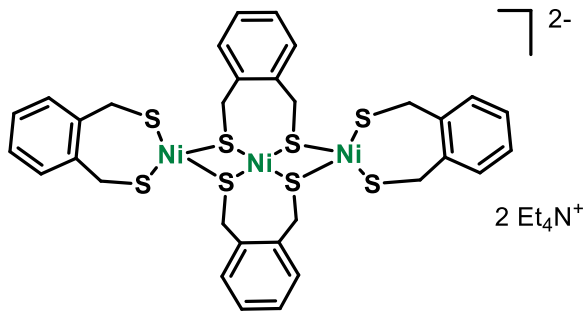
➤ DPV and CV of Ni1 in THF solution



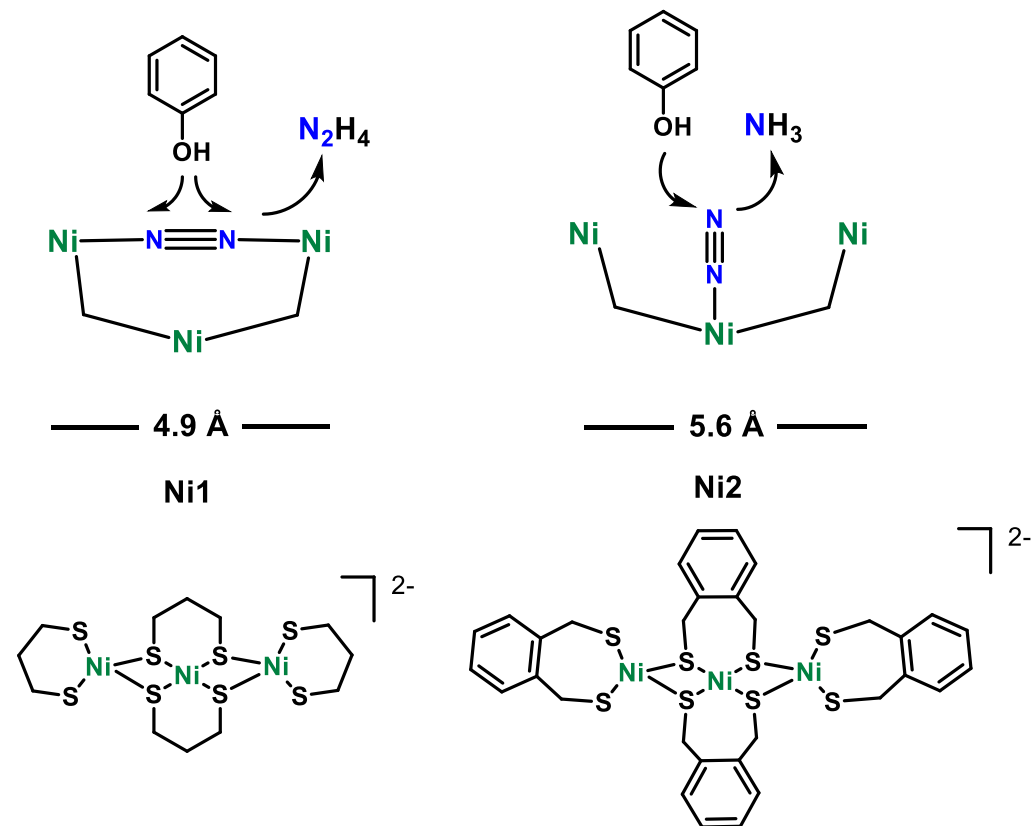
N_2RR requires the all Ni(I) state

Electrocatalytic transformation of N₂ to N₂H₄

Dey, 2025



➤ Possible N₂ binding modes to Ni1 and Ni2 which offer different access of the proton source to proximal and distal nitrogen atoms



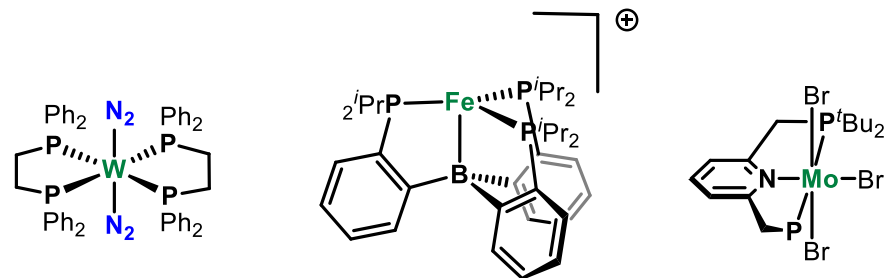
- **Highly selective ammonia-producing catalyst**
- **N₂RR requires further reduction below the all Ni(I) state**

**PART
IV**

**Summary and
Outlook**

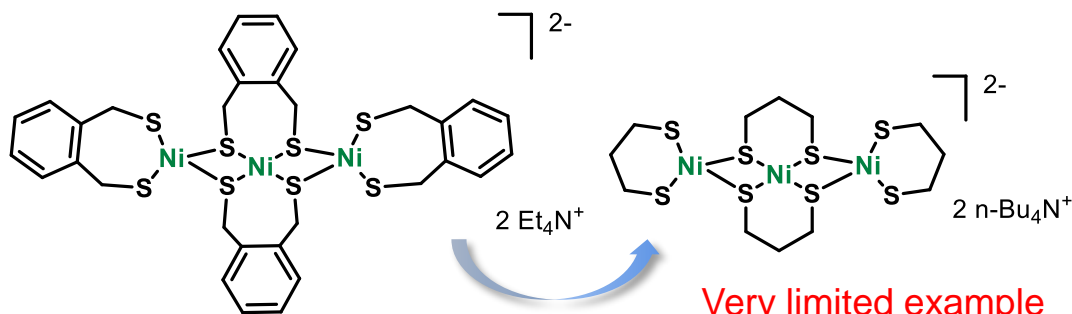
Summary: Electrochemical transformation of N₂ using molecular catalysts

N₂ to NH₃

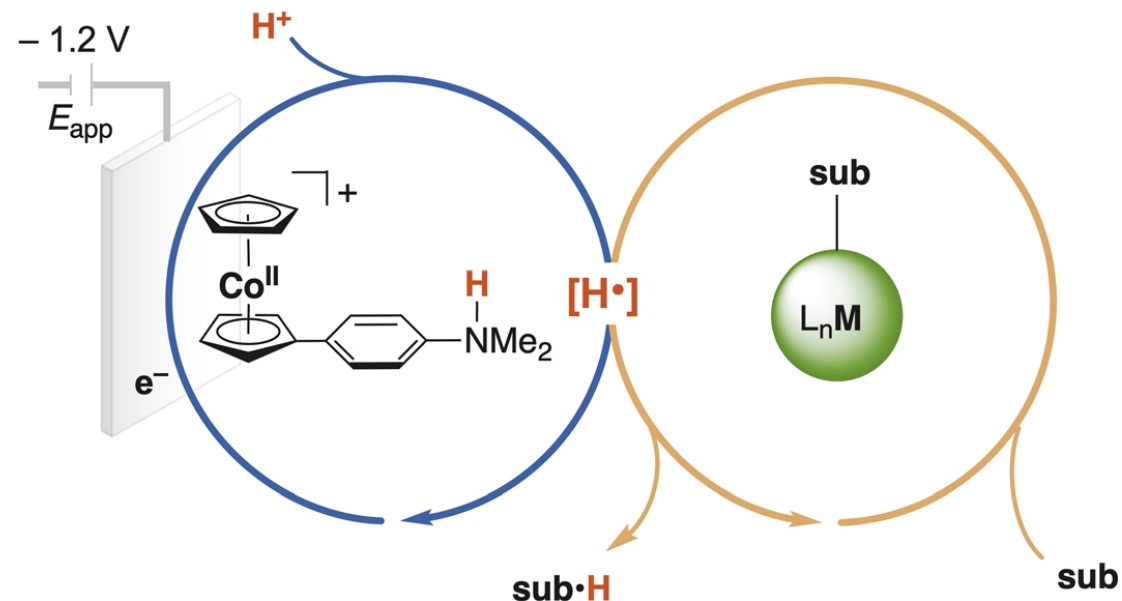


- High Faradaic efficiency
- Low overpotential
- Low NH₃ production rate
- Expensive proton sources

N₂ to N₂H₄

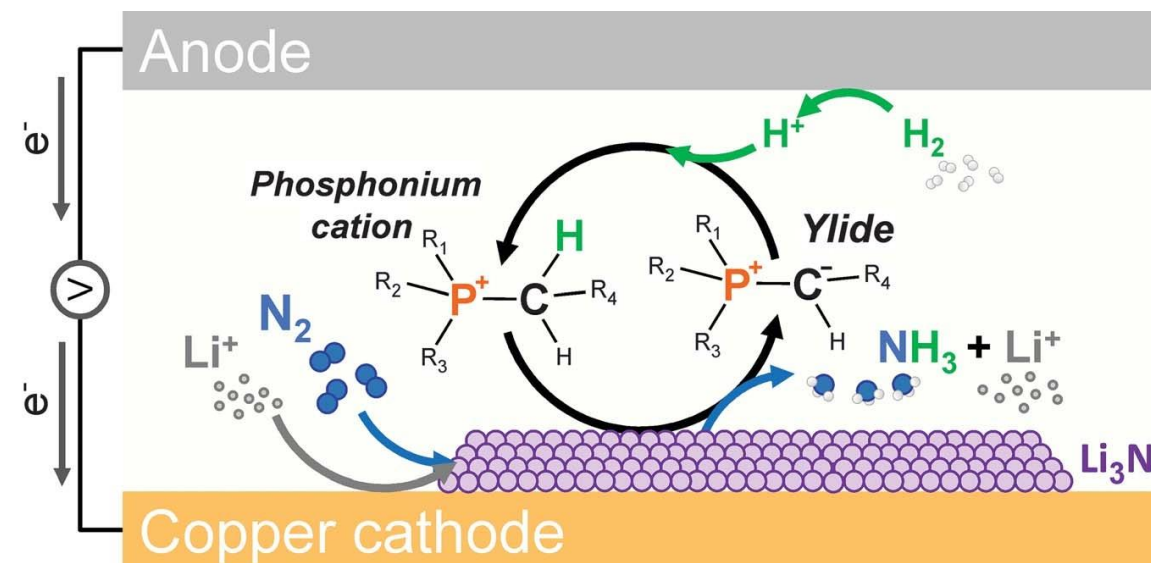


Tandem catalysis via electrocatalytic PCET (ePCET)



Outlook

- Ammonia synthesis using hydrogen or water as the sustainable proton source

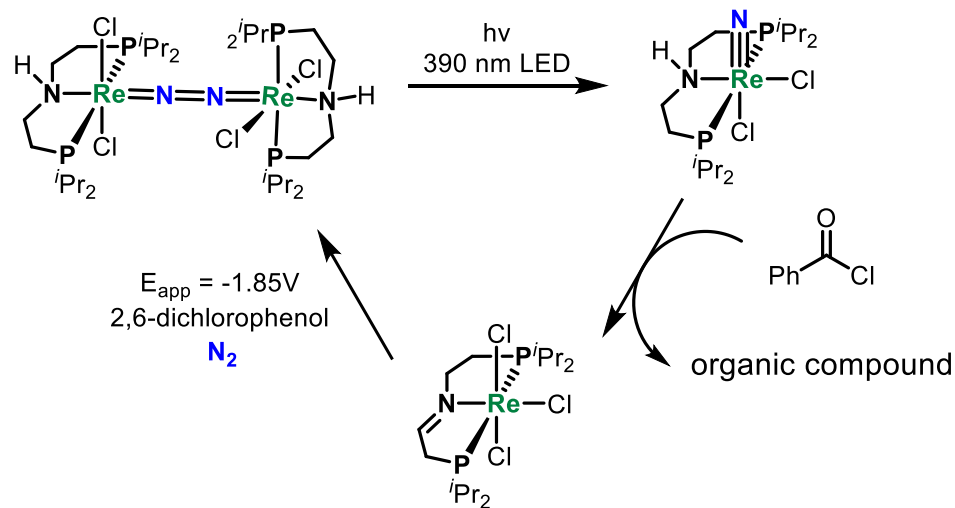


- Develop new catalysts and PCET reagents
- Coupling with hydrogen oxidation, and using proton shuttles to transport protons

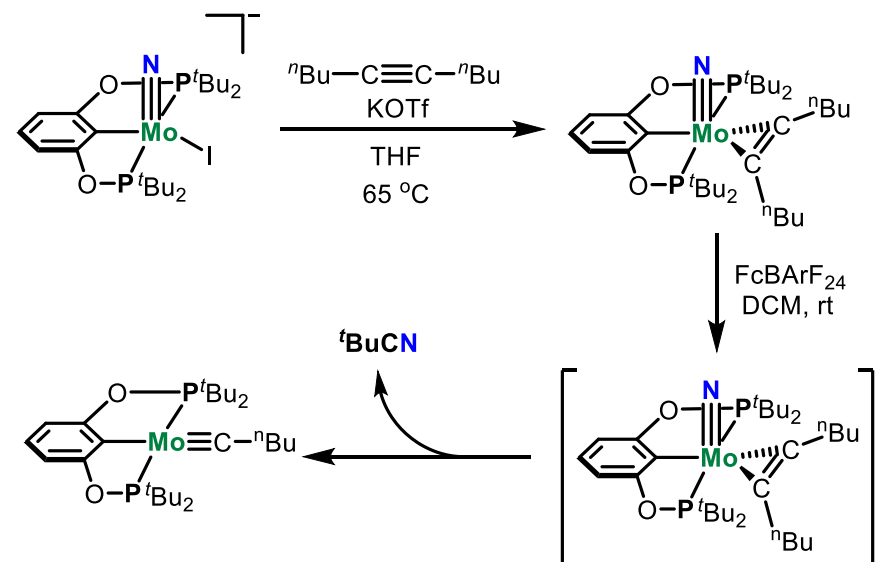
Outlook

- Electrocatalytic conversion from dinitrogen to high-value nitrogen-containing organic compounds

Schneider, 2019



Mézailles, 2021



- Develop new carbon-installing reagents that are compatible with acidic and reductive conditions
- Design of systems using hemilabile ligands capable of mild N₂ activation pathways

Thanks for listening