

Catalytic N₂ Fixation

Literature seminar #3

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2020/9/2

Contents

1. Introduction

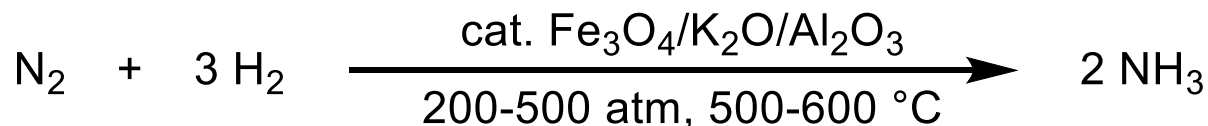
2. Developement of Mo catalysts

3. Developement of Fe catalysts

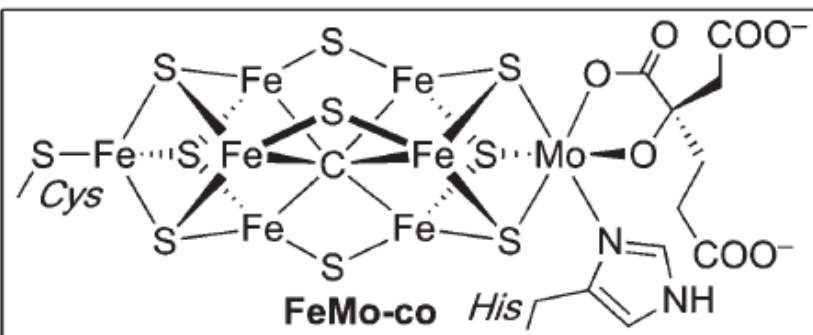
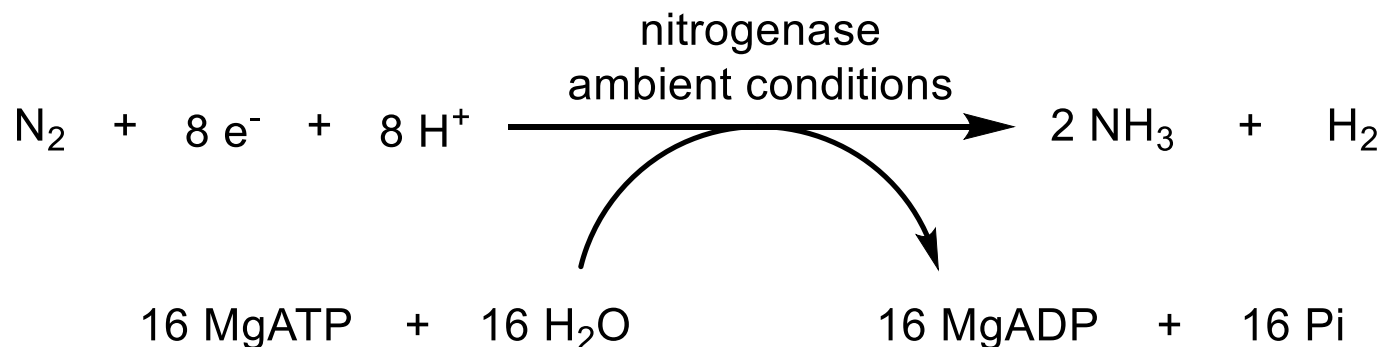
4. Summary

Introduction

- Conventional catalytic N₂ fixation
 - Haber-Bosch process



- Nitrogenase



- Three types of nitrogenase have been found.
 - FeMo-nitrogenase
 - FeV-nitrogenase
 - FeFe-nitrogenase

Nishibayashi, Y. *Dalton Trans.*, **2018**, 47, 11290.

Chalkley, M. J., Drover, M. W., Peters, J. C. *Chem. Rev.* **2020**, 120, 5582.

Introduction

- History of development of N₂ fixation catalysts

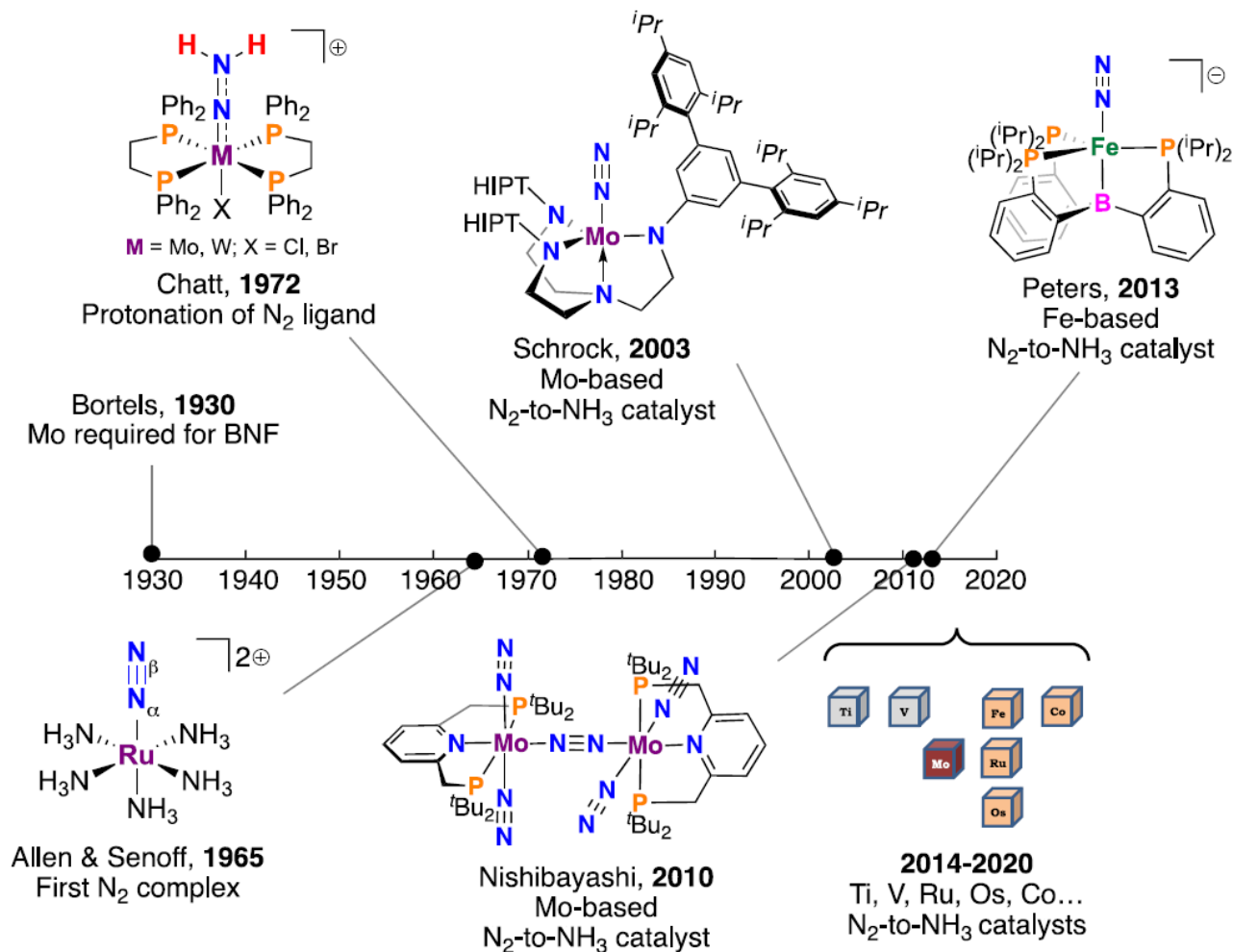
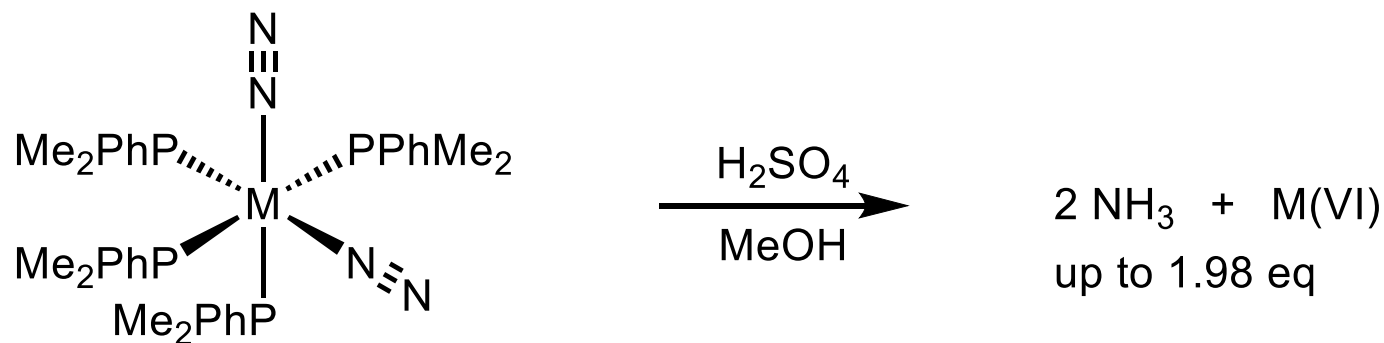


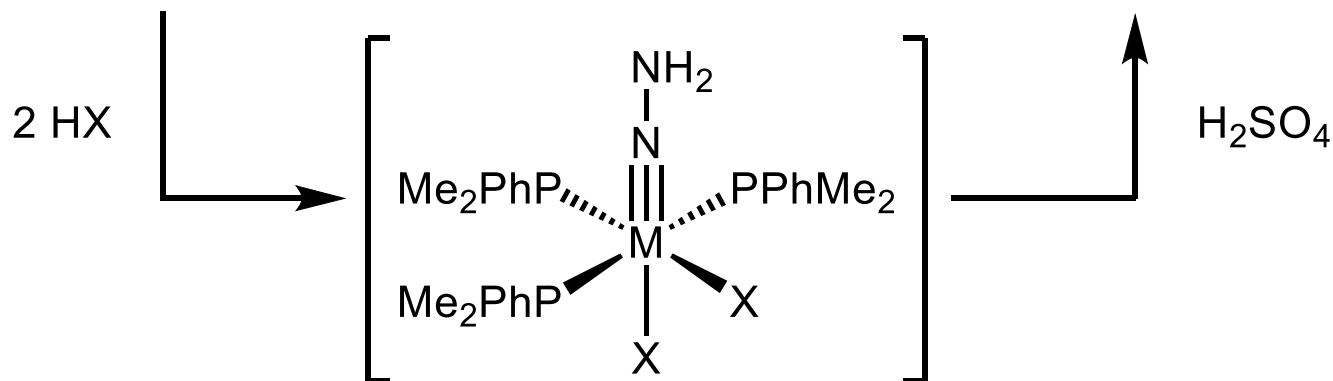
Figure 2. Timeline (1930 to present) of selected advances in nitrogen fixation catalysis by synthetically well-defined complexes.^{18,37,48–56}

Introduction

- Protonation of Mo- and W-N₂ complexes



M = Mo, W



Chatt, J., Pearman, A. J., Richards, R. L. *Nature* **1975**, 253, 39.

Chatt, J., Dilworth, J. R., Richards, R. L. *Chem. Rev.* **1978**, 78, 589.

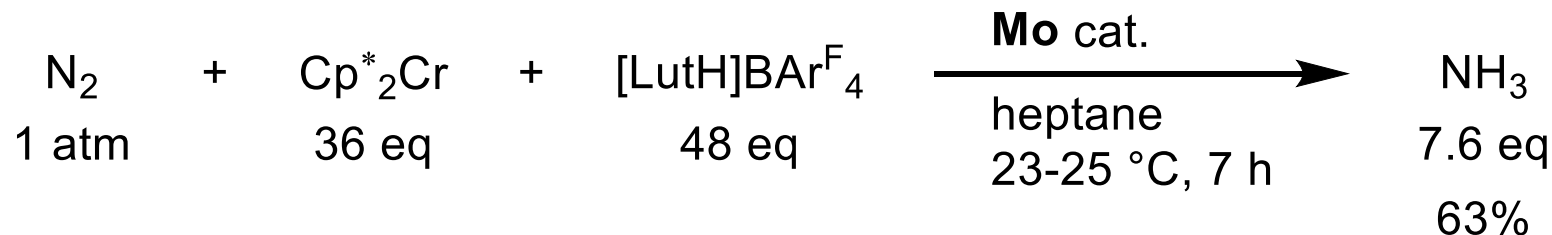
Nishibayashi, Y. *Dalton Trans.*, **2018**, 47, 11290.

Chalkley, M. J., Drover, M. W., Peters, J. C. *Chem. Rev.* **2020**, 120, 5582.

Development of Mo Catalysts

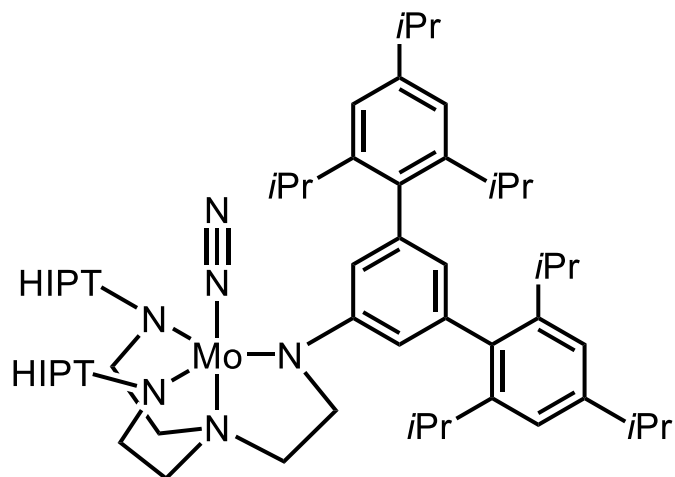
Mo Catalysts

- In 2003 Schrock group reported a Mo catalyst for N₂ reduction to ammonia.



[LutH]⁺ = 2,6-lutidinium

Ar^F = 3,5-(CF₃)₂C₆H₃

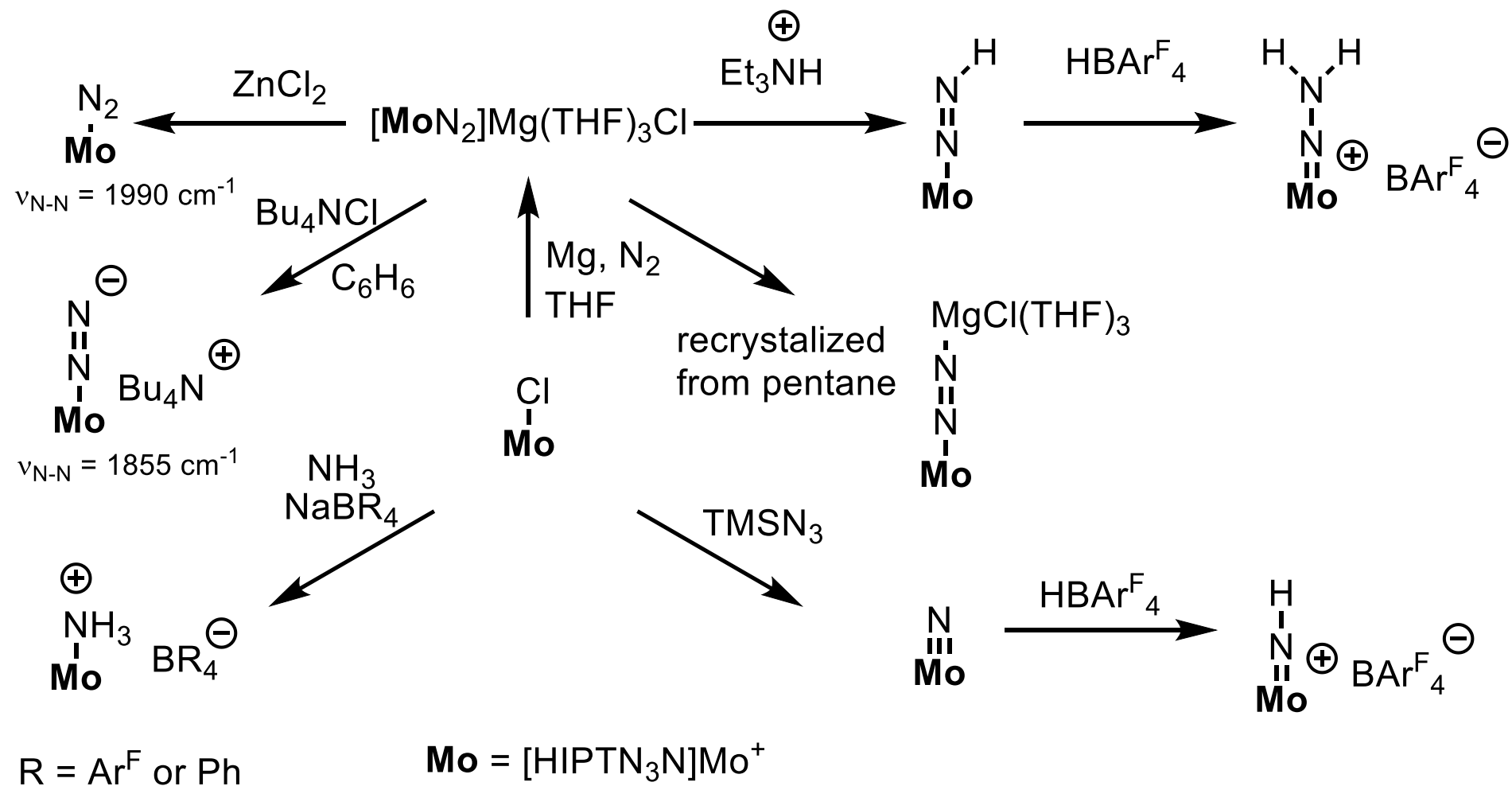


Mo cat. [HITPN₃N]MoN₂

- Slow addition of reductant and proton source is critical for high efficiency.
- Cp^{*}₂Cr was added over 6 h. (added over 25 s → 24% yield)
- Concentration of [LutH]BAr^F₄ would be low due to low solubility.
- Triamidoamine ligand [HITPN₃N]₃⁻
 - prevents formation of undesirable bimetallic species [ArN₃N]Mo-N=N-Mo[ArN₃N]
 - protects coordination site of intermediates
 - increases solubility

Mo Catalysts

- Synthesis of Mo complexes



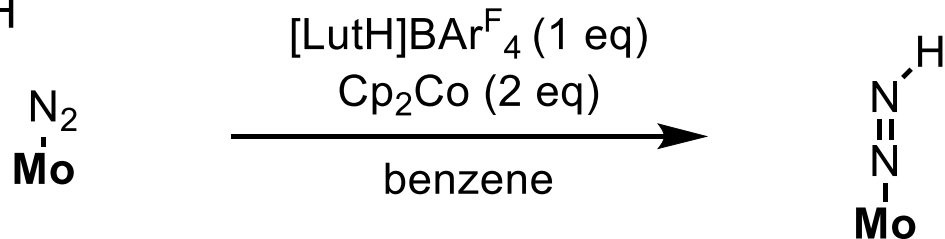
Yandulov, D. V., Schrock, R. R. *J. Am. Chem. Soc.* **2002**, *124*, 6252.

Yandulov, D. V., Schrock, R. R., Rheingold, A. L., Ceccarelli, C., Davis, W. M. *Inorg. Chem.* **2003**, *42*, 796₈

Yandulov, D. V., Schrock, R. R. *Inorg. Chem.* **2005**, *44*, 1103.

Mo Catalysts

• MoN₂ to MoN=NH



quantitative

Yandulov, D. V., Schrock, R. R. *J. Am. Chem. Soc.* **2002**, *124*, 6252.

Scheme 1. Three Possible Mechanisms for Addition of a Proton and an Electron to MoN₂ To Yield Mo–N=NH

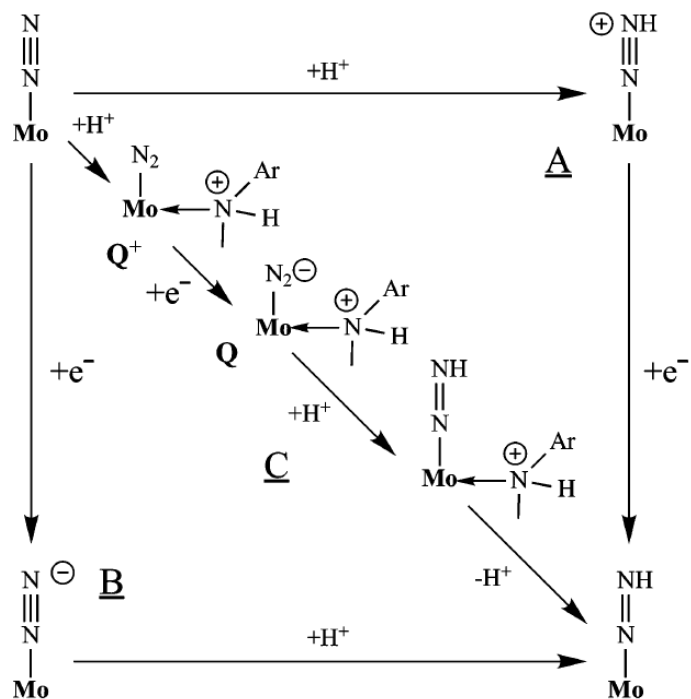


Table 3. Electrochemical Properties of Catalytic Mo Intermediates and Metallocene Reductants^a

couple	E° (THF)	E° (PhF)
MoN ₂ ⁺⁰	-0.42 (I_{pa}) ^b	-0.66
MoN ₂ ^{0/-}	-1.81	-2.01
MoN=NH ⁺⁰		~0 ^c
Mo=NNH ₂ ⁺⁰	1.47 (I_{pc}) ^d	-1.56 qr ^e
Mo=NH ⁺⁰	-1.25 qr	-1.38 qr
Mo(NH ₃) ⁺⁰	-1.51	-1.63
CoCp ₂ ⁺⁰	-1.33	-1.33
CrCp ₂ ⁺⁰	-1.47	-1.63
CoCp ₂ ^{*+0}	-1.84	-2.01

^a Formal potentials (E° , V) measured by cyclic voltammetry in 0.4 M [Bu₄N][PF₆] in THF at 1.6 mm Pt disk, or 0.1 M [Bu₄N][BAr'₄] in PhF at 3.0 mm glassy carbon disk at 22 °C and referenced to FeCp₂⁺⁰. ^b Anodic peak potential of irreversible oxidation at scan rate of 500 mV/s. ^c Onset of multiple irreversible oxidation waves. ^d Cathodic peak potential of irreversible reduction at scan rate of 50 mV/s. ^e qr = quasireversible.

- Path A is unlikely.
 - MoN₂ + [LutH]⁺ → No evidence of N_β protonation
 - failure of electrochemical oxidation of MoN=NH
- The authors proposed path B is the most likely.

Mo Catalysts

- Reduction of $\text{Mo}=\text{NNH}_2^+$

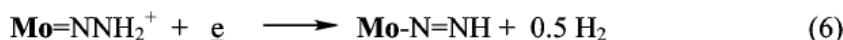
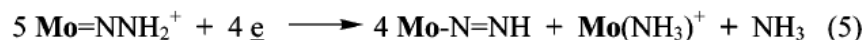
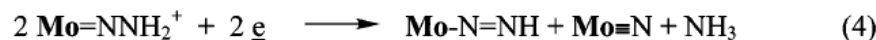
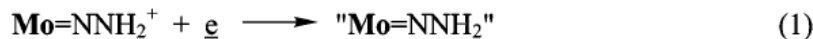
Table 4. The Results of Chemical Reductions of $\text{Mo}=\text{NNH}_2^+$ ^a

entry	reductant	$\text{MoN}=\text{NH}$	$\text{Mo}\equiv\text{N}$	$\text{Mo}(\text{NH}_3)^+$	$\text{Mo}(\text{NH}_3)$	efficiency, % ^b
1	2 CoCp ₂	0.83	0	0.17		85
2	1.2 CrCp* ₂	0.88	0.06		0.06	42
3	2 CrCp* ₂	0.78	0.14		0.08	68
4	4 CrCp* ₂ ^c	0.63	0.37		0	74
5	2 CoCp* ₂ ^d	0.55	0.45		0	90

^a Determined by integration of ¹H NMR spectra in C₆D₆ after 10–30 min of mixing the reagents. These spectra also showed complete conversion of $\text{Mo}=\text{NNH}_2^+$. ^b $\text{Mo}=\text{NNH}_2^+$ consumed in reactions 4 and 5 (Scheme 2) out of the total amount. ^c Carried out in the presence of 4 equiv of BPh₃.

^d This reaction also yields ~7% of MoN_2 and 0.39 equiv of NH₃.

Scheme 2. Sequence of Reactions Proposed To Take Place upon Reduction of $[\text{Mo}=\text{NNH}_2][\text{BAr}'_4]^a$

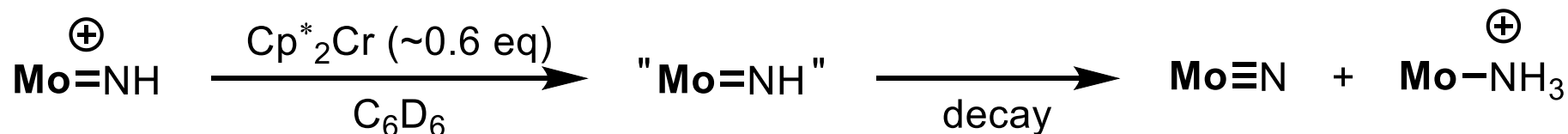


^a e = redundant.

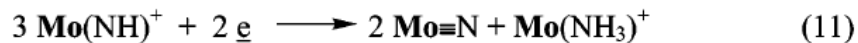
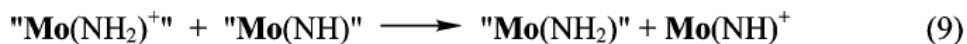
- The result can be attributed to disproportionation and reduction (eq1-3) and competing reduction of acidic proton (eq 6).

Mo Catalysts

- Reduction of $\text{Mo}=\text{NH}^{\oplus}$



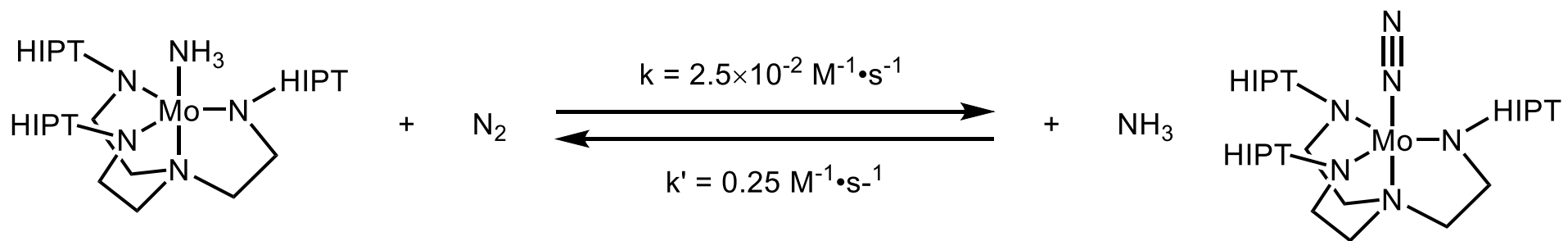
Scheme 3. Sequence of Reactions Proposed To Take Place upon Reduction of $[\text{Mo}=\text{NH}][\text{BAR}'_4]$



- Stoichiometry of resulting mixture was eq 11.
- The eq 11 is thought to be sum of eq 7-10.

Mo Catalysts

- Ligand exchange of NH_3 to N_2

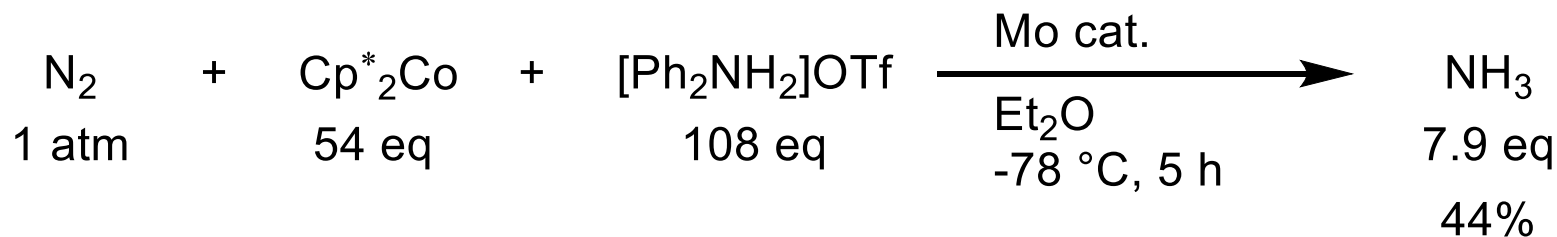


$$K_{\text{eq}} = \frac{[\text{MoN}_2][\text{NH}_3]}{[\text{MoNH}_3][\text{N}_2]} \sim 0.1$$

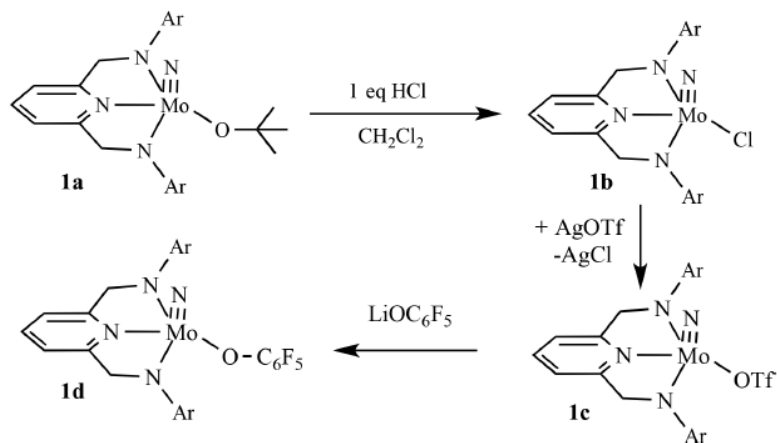
- Displacement of NH_3 by N_2 can occur relatively quickly.
- But the conversion rate is slowed by the reverse reaction if NH_3 isn't efficiently removed.

Mo Catalysts

- In 2017 Schrock group reported Mo pyridine-based diamido ligand complex catalysts.



Scheme 1. Syntheses of $[\text{Ar}_2\text{N}_3]\text{Mo}(\text{N})(\text{X})$ Complexes

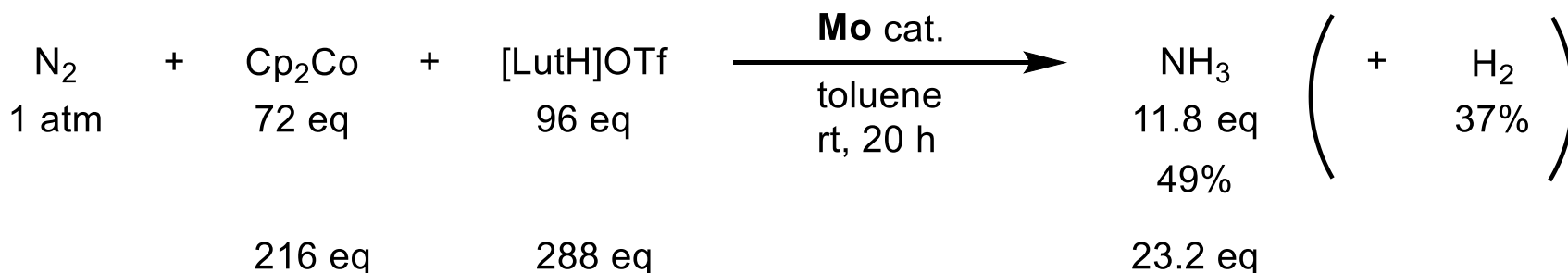


Mo cat. = 1a

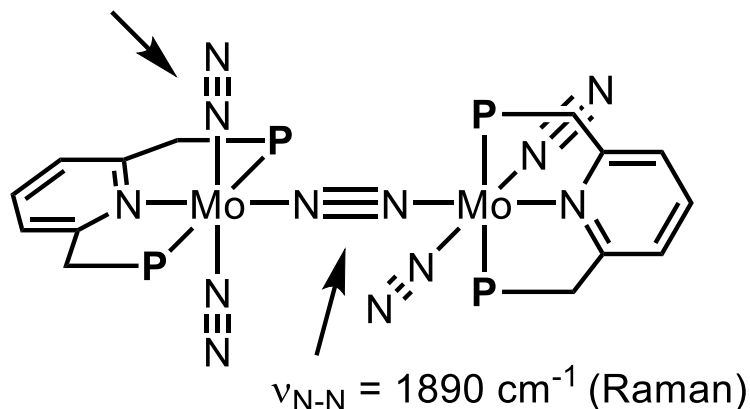
- Only 1a has catalyst activity
complex 1b : No NH_3
1c, 1d : 1.3 eq NH_3 was obtained.
- The reaction mechanism is unknown.

Mo Catalysts

- In 2011 Nishibayashi group reported a Mo PNP-pincer complex catalyst.



$\nu_{\text{N-N}} = 1936 \text{ cm}^{-1}$ (IR)



Mo cat.

P = PtBu_2

- Compared to Schrock's report, the yield was low, but TON improved.
- Only free PNP ligand was observed from the mixture after the reaction.

Mo Catalysts

- Reductant and proton source effect

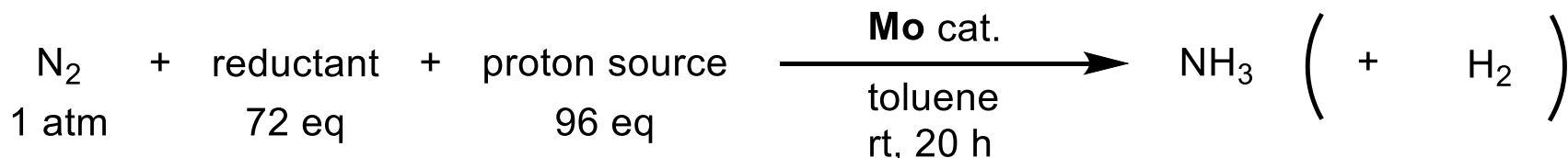


Table 3 | Reduction of dinitrogen with reductant and [LutH]OTf in the presence of 2a.

Run	Reductant	$E_{1/2}$ (V)*	NH ₃ (mol. equiv./2a) [†]	H ₂ (mol. equiv./2a) [†]
1	CoCp ₂	-1.15	11.8	13.4
2	— [‡]		1.0	0.2
3	CrCp* ₂	-1.35	12.2	4.2
4	CrCp ₂	-0.88	0	0

To a suspension of **2a** and [LutH]OTf (0.96 mmol) in toluene (2.5 ml) was added a solution of reductant (0.72 mmol) in toluene (2.5 ml) via a syringe pump at room temperature over a period of 5 h, followed by stirring at room temperature for another 15 h under 1 atm dinitrogen. *Electrochemical data ($E_{1/2}$) of reductant in MeCN vs. Ag/Ag⁺ in 0.1 M AgNO₃ (ref. 37). [†]Mol. equiv. based on **2a**. [‡]In the absence of reductant.

Table 4 | Reduction of dinitrogen with CoCp₂ and proton source in the presence of 2a.

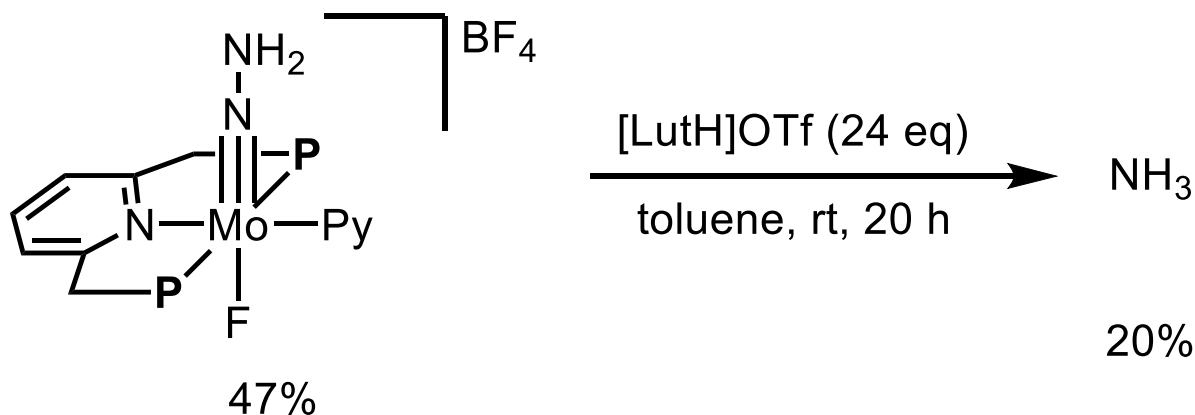
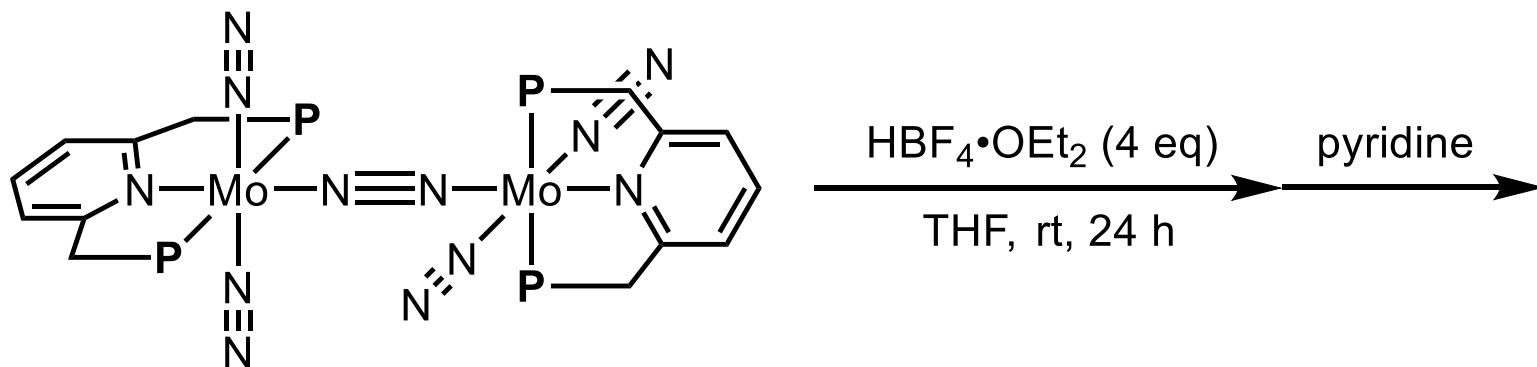
Run	HX (proton source)	pK _a *	NH ₃ (mol. equiv./2a) [†]	H ₂ (mol. equiv./2a) [†]
1	[LutH]OTf	14.4	11.8	13.4
2	— [‡]		0	0
3	[LutH]BAR' ₄	14.4	2.7	19.0
4	[LutH]Cl	14.4	0.7	0.1
5	[2-PicH]OTf	13.9	9.1	16.6
6	[PyH]OTf	12.6	3.9	20.4
7	HOTf	2.6	1.7	1.1

To a suspension of **2a** and proton source (0.96 mmol) in toluene (2.5 ml) was added a solution of CoCp₂ (0.72 mmol) in toluene (2.5 ml) via a syringe pump at room temperature over a period of 5 h, followed by stirring at room temperature for another 15 h under 1 atm dinitrogen. *pK_a values of proton source in MeCN (see refs 38 and 39). [†]Mol. equiv. based on **2a**. [‡]In the absence of proton source.

- Counter anion of lutidinium salt is important.

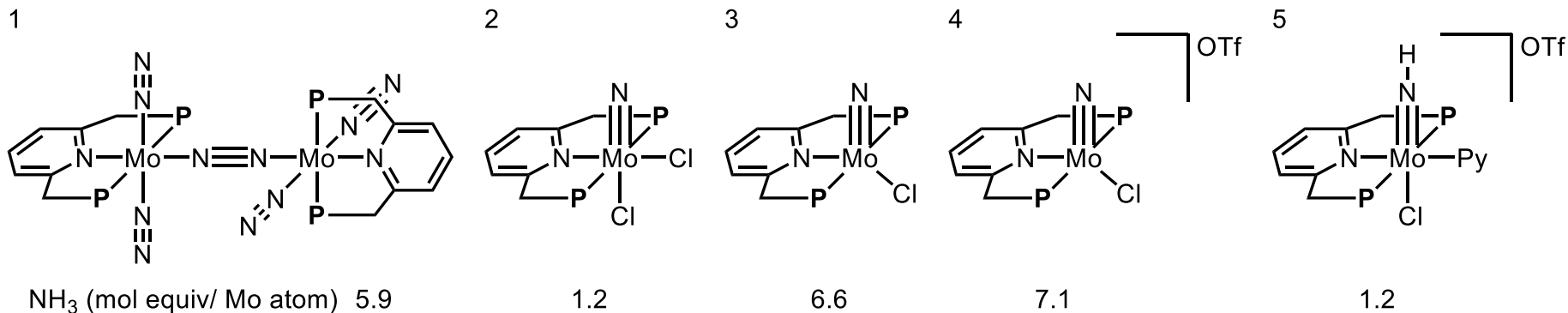
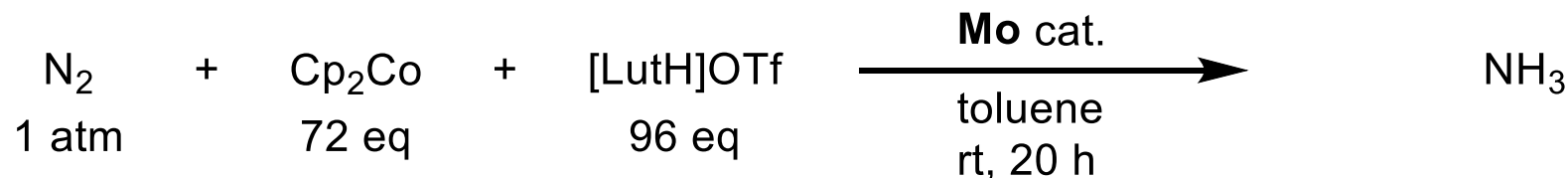
Mo Catalysts

- Protonation of the Mo complex



Mo Catalysts

- Reactivity of Mo complexes

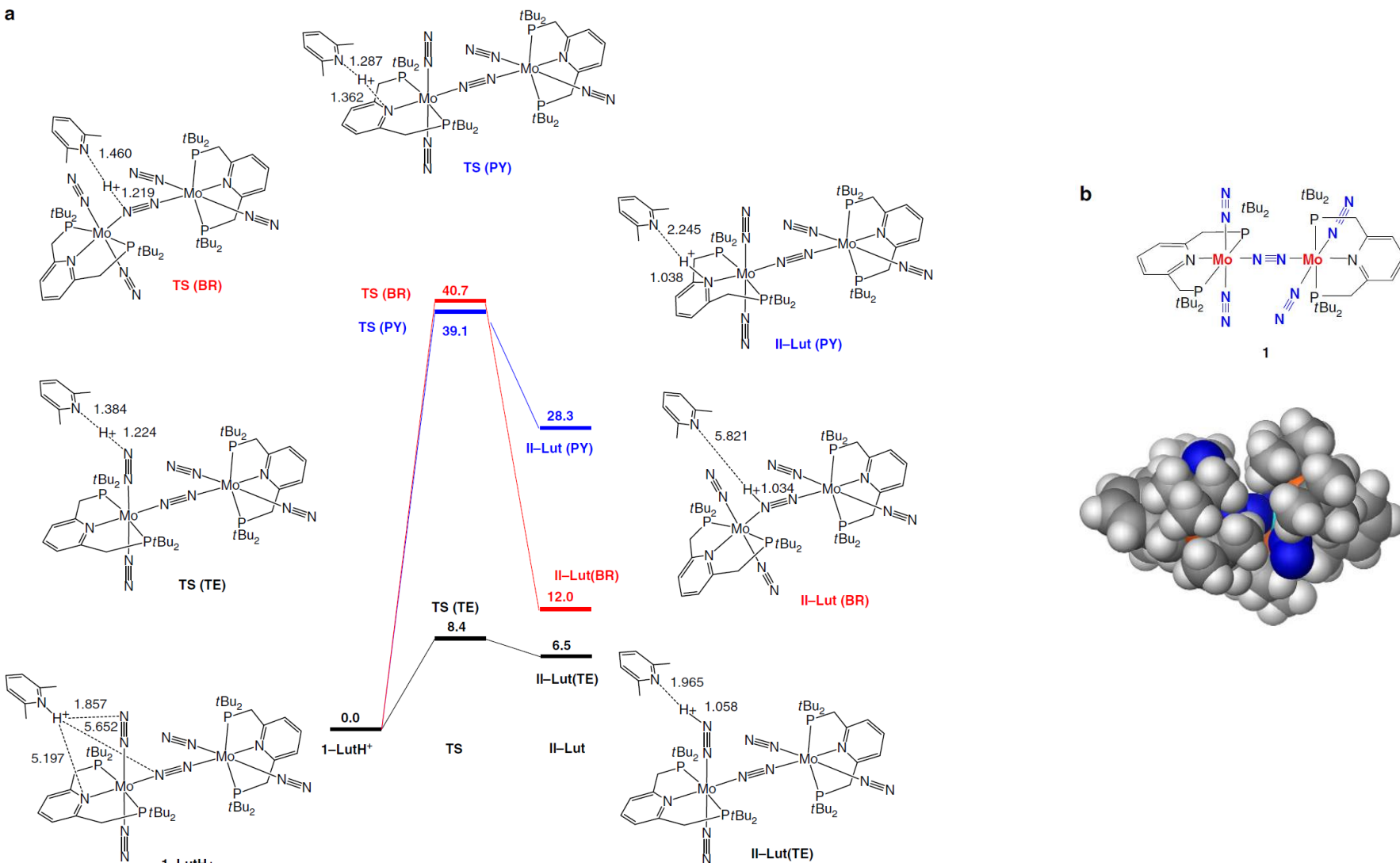


catalyst 1, 3, 4: catalytic activity

catalyst 2, 5: inhibition by second Cl and Py coordination

Mo Catalysts

- DFT study for the first protonation step

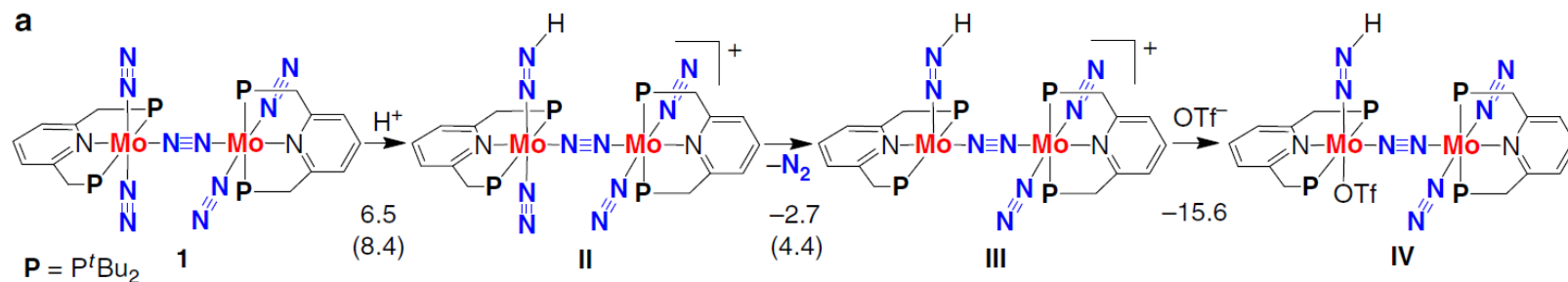


Tanaka, H., Arashiba, K., Kuriyama, S., Sasada, A., Nakajima, K., Yoshizawa, K., Nishibayashi, Y. *Nat. Commun.* **2014**, *5*, 3737.

Mo Catalysts

- DFT study for the first protonation step

- Protonation at terminal N₂



- Ligand exchange to OTf group is important for the first protonation.

Mo Catalysts

• Separation of dinuclear Mo complexes

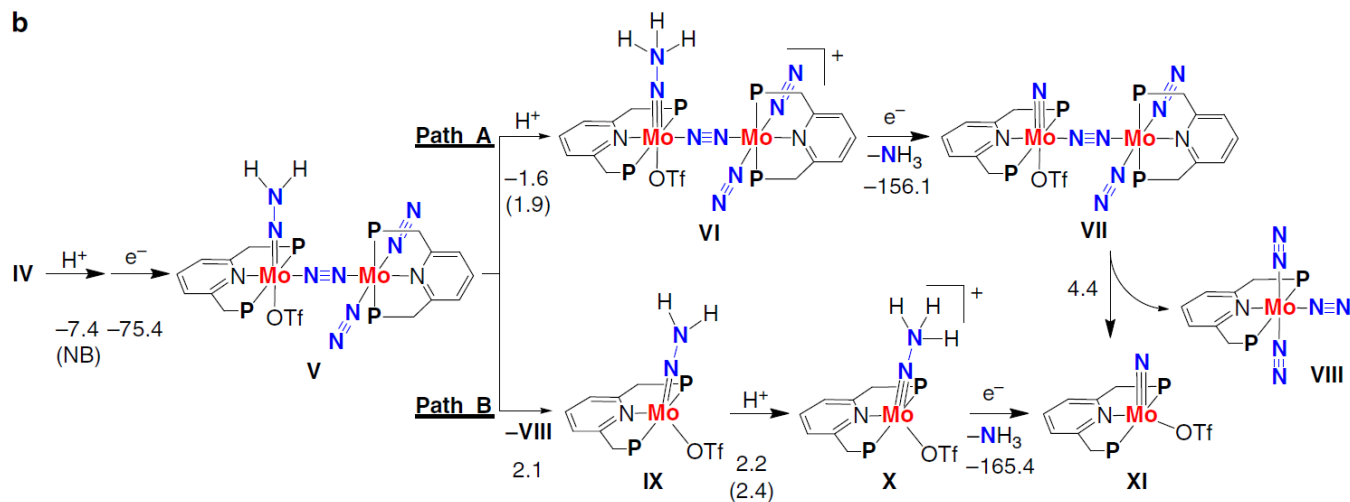


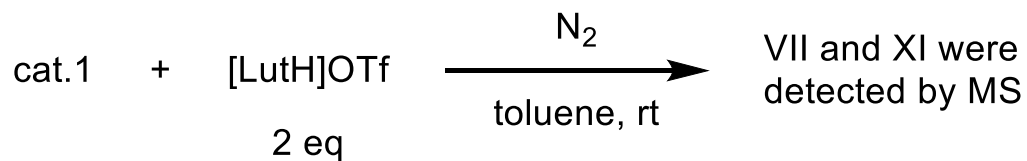
Table 2 | Bond dissociation energies.

Bond	BDE (Kcal mol ⁻¹)*				
	1	IV	V	VI [†]	VII
Mo-N _α	24.9	19.2	2.1	13.7	4.4
Mo-N _β	24.9	30.0	26.9	– [‡]	36.4

*Bond dissociation energies between an Mo atom and the bridging N₂ ligand in **1**, **IV**, **V**, **VI** and **VII**.

[†]Optimization of reduced **VI** results in formation of **VII** and NH₃.

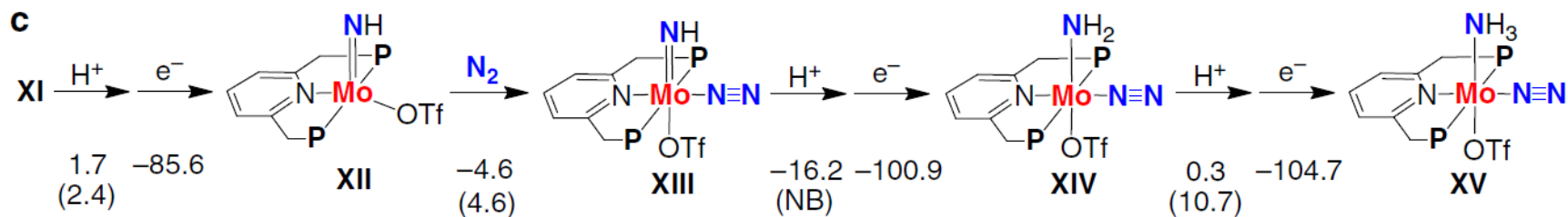
[‡]The N-NH₃ bond in [Mo(OTf)(N₂)(NNH₃)] is spontaneously cleaved.



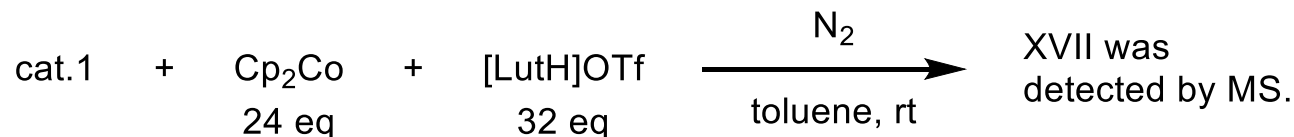
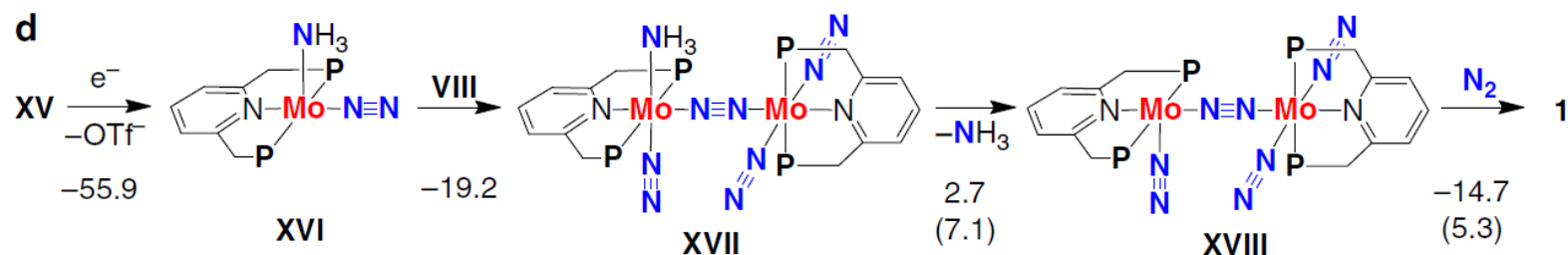
Tanaka, H., Arashiba, K., Kuriyama, S., Sasada, A., Nakajima, K., Yoshizawa, K., Nishibayashi, Y. *Nat. Commun.* **2014**, *5*, 3737.

Mo Catalysts

- Protonation and reduction of XI via XIII



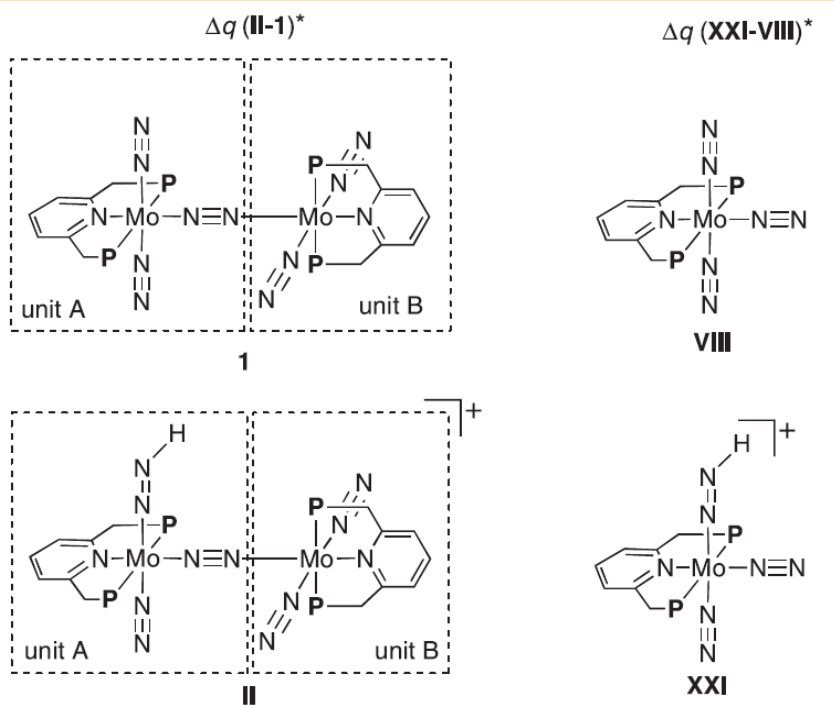
- Ligand exchange of NH_3 to N_2 and regeneration of the dinuclear complex



Mo Catalysts

- Synergy of two Mo cores

Table 3 | Differences in the NPA atomic charge (Δq).

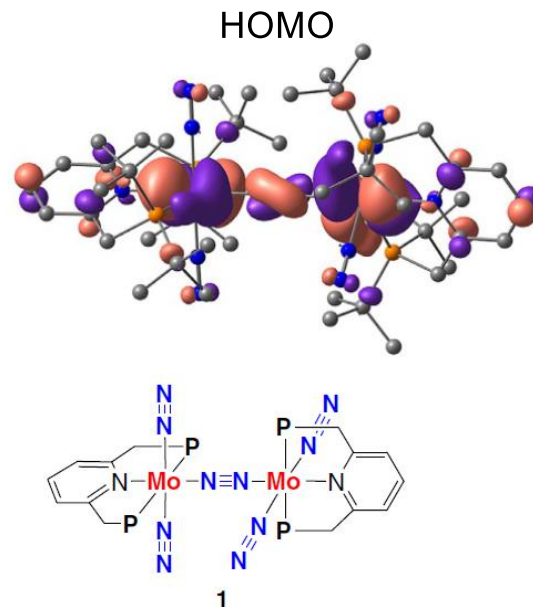


	unit A	unit B		
Mo	+0.33	+0.11	Mo	+0.38
NNH	-0.03	-	NNH	+0.07
NN _{terminal}	+0.17	+0.03	NN _{axial}	+0.17
NN _{bridging}	-0.06	-	NN _{equatorial}	+0.09
Pincer	+0.24	+0.17	Pincer	+0.29
Total	+0.66	+0.34	Total	+1.00

NPA, natural population analysis.

*Differences in the NPA atomic charge (Δq) between dinitrogen and protonated complexes obtained for dinuclear (**I** and **II**) and mononuclear (**VIII** and **XXI**) molybdenum complexes.

b



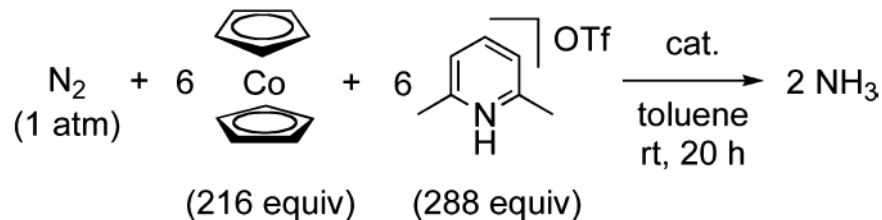
- Unit B supports the protonation step by donating 0.34 e⁻ electron to unit A after protonation.

Tanaka, H., Arashiba, K., Kuriyama, S., Sasada, A., Nakajima, K., Yoshizawa, K., Nishibayashi, Y. *Nat. Commun.* **2014**, *5*, 3737.

Mo Catalysts

- 4-substituted PNP-pincer ligands

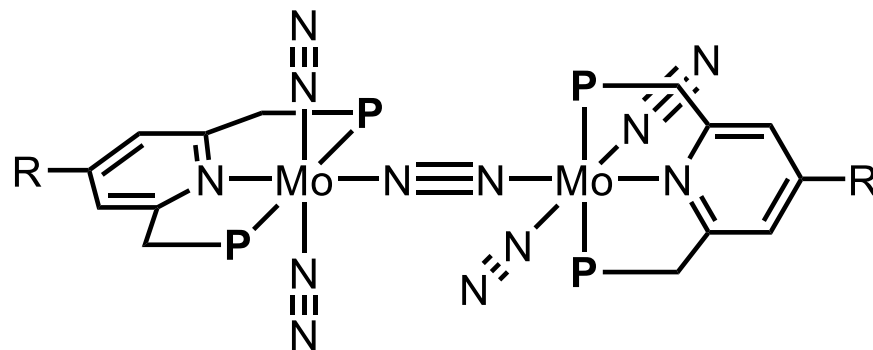
Table 2. Molybdenum-Catalyzed Reduction of Molecular Dinitrogen into Ammonia under Ambient Conditions^a



run	cat.	R	NH_3^b (equiv)	NH_3^c (%)	H_2 (equiv)	H_2^c (%)
1	1a	H	23	31	46	43
2	1b	Ph	21	30	46	43
3	1c	Me_3Si	23	32	44	40
4	1d	^tBu	28	39	45	41
5	1e	Me	31	44	36	33
6	1f	MeO	34	47	36	33

^aTo a mixture of the catalyst (1: 0.010 mmol) and $[\text{LutH}]\text{OTf}$ (288 equiv to the catalyst) as proton source in toluene (1.0 mL) was added a solution of CoCp_2 (216 equiv to the catalyst) as a reductant in toluene (4.0 mL) at room temperature over a period of 1 h, followed by stirring at room temperature for another 19 h under an atmospheric pressure of dinitrogen. ^bMol equiv to the catalyst. ^cYield based on CoCp_2 .

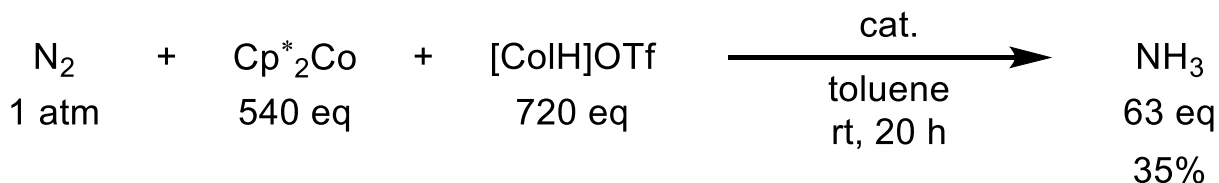
cat.



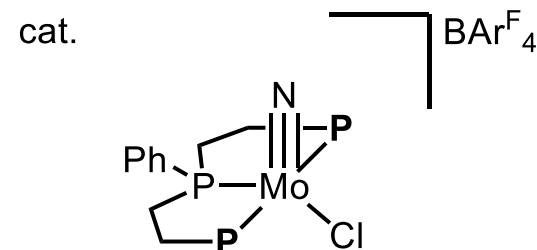
- Electron-donating group increases catalyst activity by acceleration of the first protonation step.

Mo Catalysts

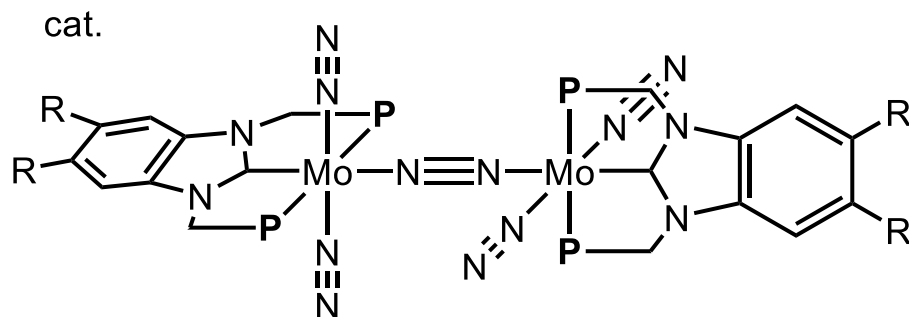
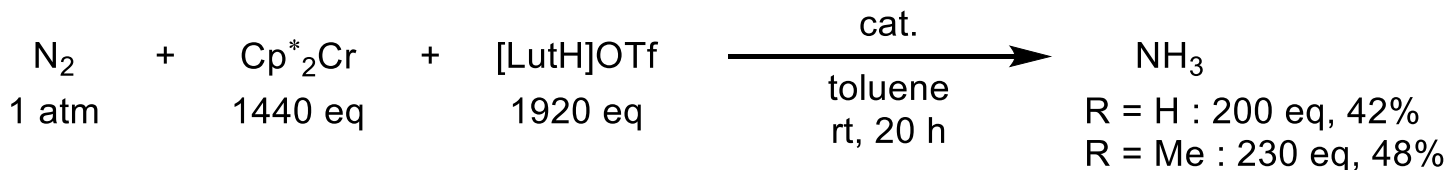
- PPP and PCP pincer complexes are more effective N₂ fixation catalysts.



[CoH]⁺ = 2,4,6-trimethylpyridinium



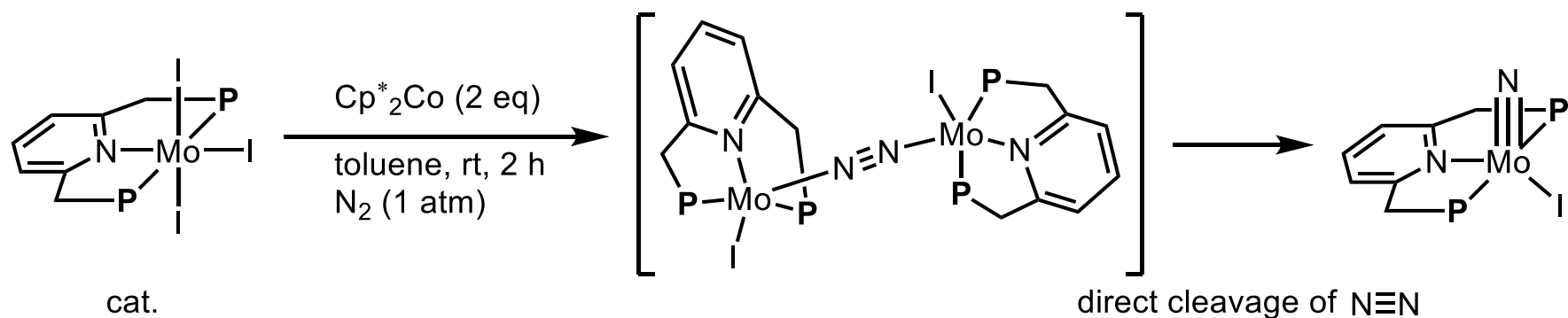
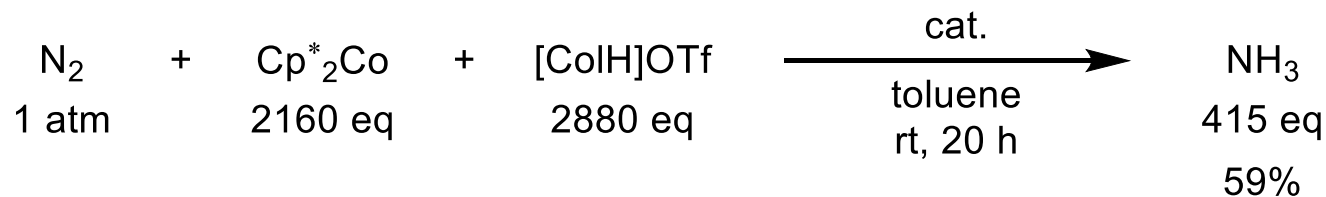
Arashiba, K., Kinoshita, E., Kuriyama, S., Eizawa, A., Nakajima, K., Tanaka, H., Yoshizawa, K., Nishibayashi, Y. *J. Am. Chem. Soc.* **2015**, *137*, 5666.



Eizawa, A., Arashiba, K., Tanaka, H., Kuriyama, S., Matsuo, Y., Nakajima, K., Yoshizawa, K., Nishibayashi, Y. *Nat. Commun.* **2017**, *8*, 14874. 25

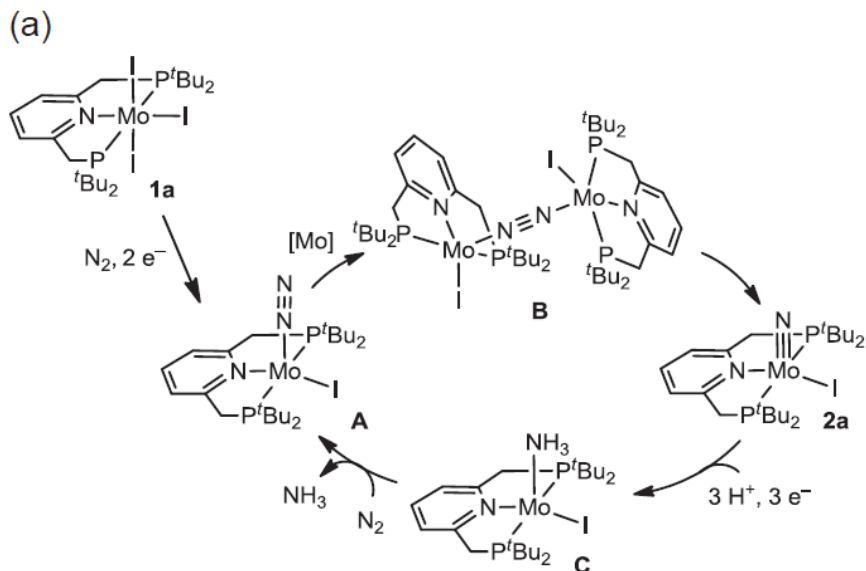
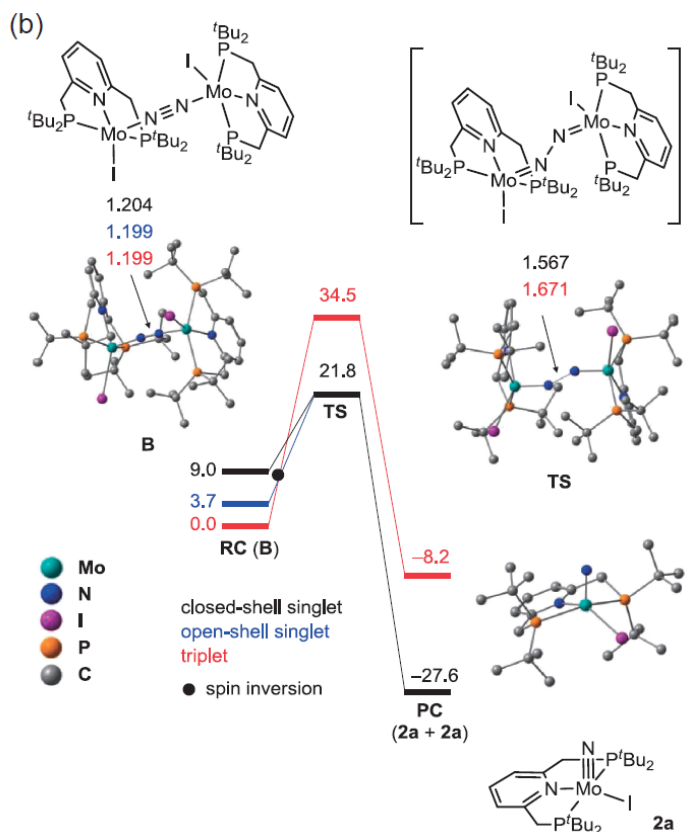
Mo Catalysts

- Nishibayashi reported another reaction pathway by a Mo-iodine PNP-pincer complex catalyst.



Mo Catalysts

• Proposed mechanism

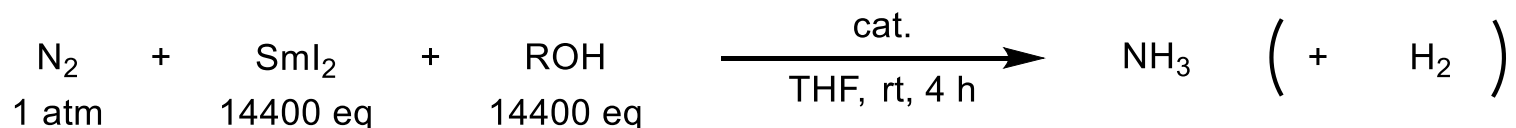


- Mo(I)—N≡N—Mo(I) would promote direct N≡N cleavage with spin inversion.

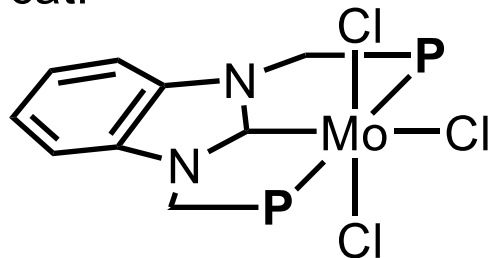
Figure 6. (a) A plausible reaction pathway. (b) Free energy profile calculated at 298.15 K (ΔG_{298} , kcal/mol) for direct cleavage of nitrogen–nitrogen triple bond of the bridging dinitrogen ligand in **B** yielding two molecules of **2a**, together with optimized structures of **B** (reactant complex, **RC**), transition state (**TS**), and **2a**. Energies and bond distances are given in kcal/mol and Å.

Mo Catalysts

- In 2019 highly efficient SmI_2/ROH condition was reported.



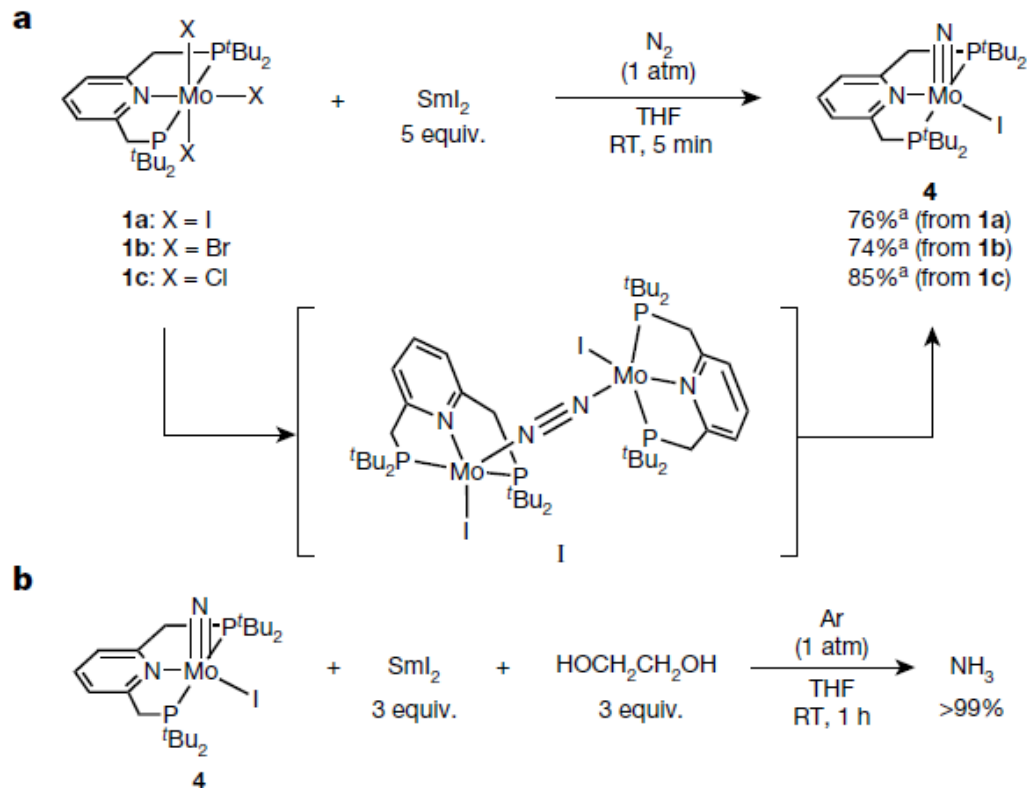
cat.



ROH	NH ₃	H ₂
	3650 ± 250 eq/Mo 76 ± 6%	1600 ± 150 eq/Mo 22 ± 2%
H ₂ O	4350 ± 150 eq/Mo 91 ± 4%	150 ± 100 eq/Mo 2 ± 1%

Mo Catalysts

- Stoichiometric reactions



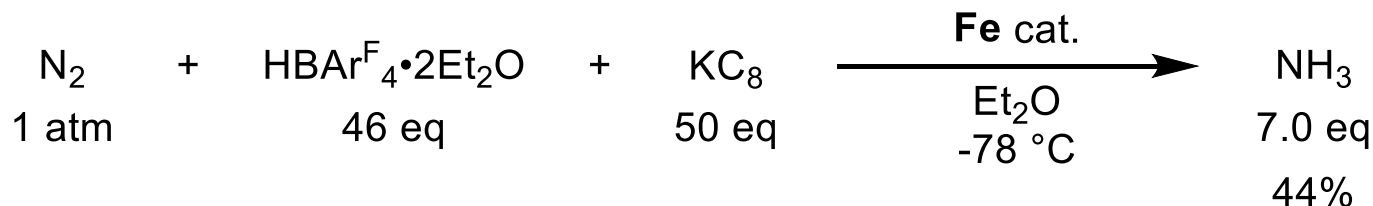
- The authors proposed that the reaction proceeds via direct $\text{N}\equiv\text{N}$ cleavage pathway.

Fig. 2 | Stoichiometric reactions of ammonia formation in reaction system B. a, Stoichiometric reduction of molybdenum trihalide complexes (**1a–c**) to a molybdenum nitride complex (**4**) under 1 atm of N_2 . b, Stoichiometric formation of ammonia from **4**. ^aYield based on NMR. $\text{SmI}_2(\text{THF})_2$ was used as the source of SmI_2 .

Developement of Fe Catalysts

Fe Catalysts

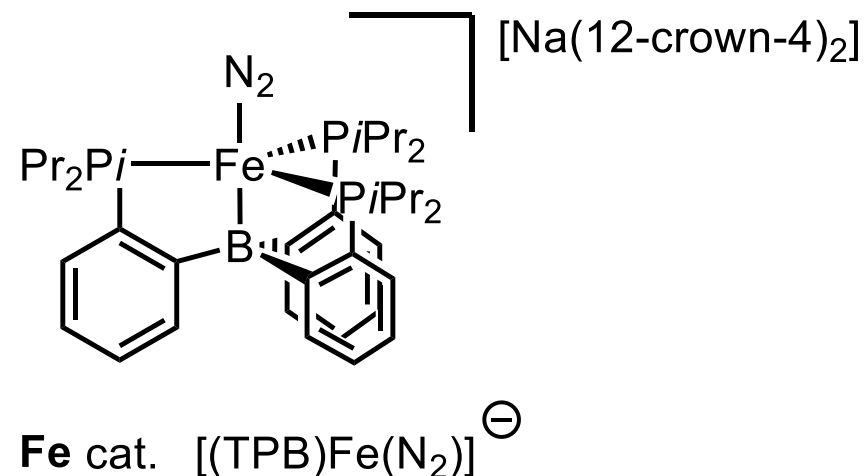
- In 2013 Peters group reported the first Fe complex catalyst for N₂ fixation.



Variations on standard conditions using [(TPB)FeN₂][Na(12-crown-4)₂]

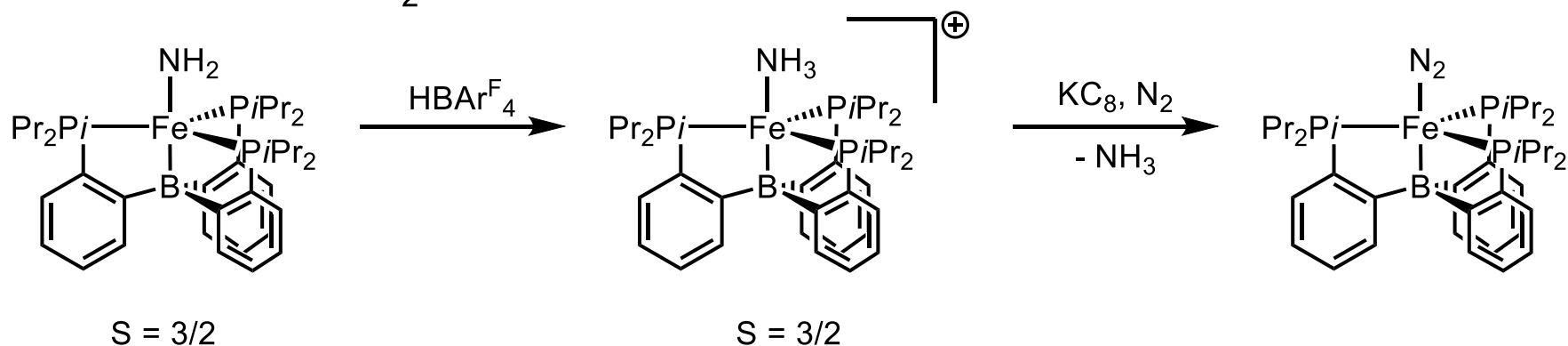
Entry	Variation	NH ₃ equiv./Fe†
10	HOTf as acid	0.4
11	[Lutidinium][BAR ^F ₄] as acid	<0.1
12	HCl as acid	<0.1
13	Cp* ₂ Co as reductant	0.6
14	Cp* ₂ Cr as reductant	<0.2
15	K metal as reductant	0.4

- 78 °C reaction condition
- N₂H₄ was not observed.
- Combination of HBAr^F₄•2Et₂O and KC₈ was effective.



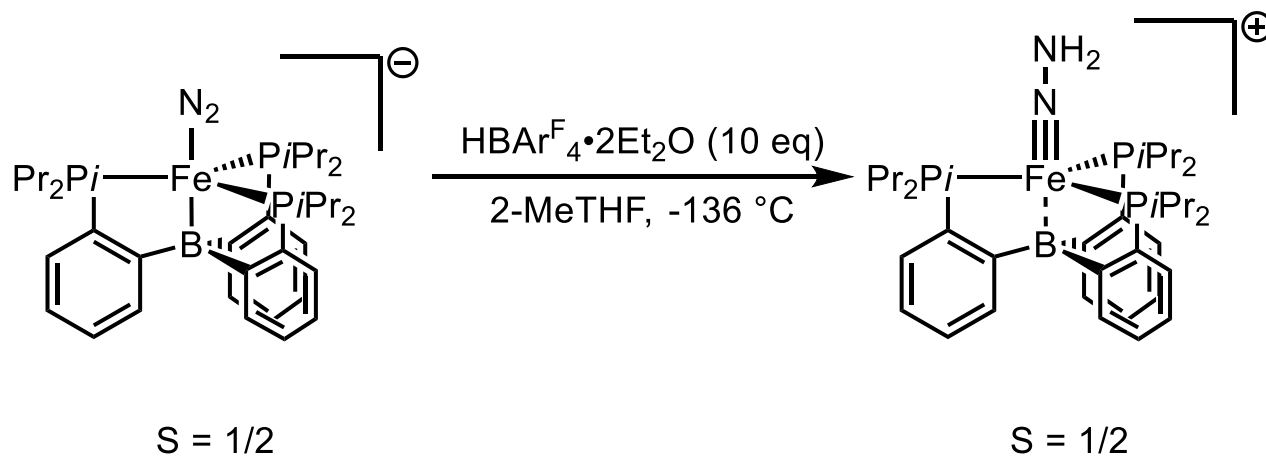
Fe Catalysts

- Conversion of Fe-NH₂ intermediate



Anderson, J. S., Moret, M.-E., Peters, J. C. *J. Am. Chem. Soc.* **2013**, 135, 534.

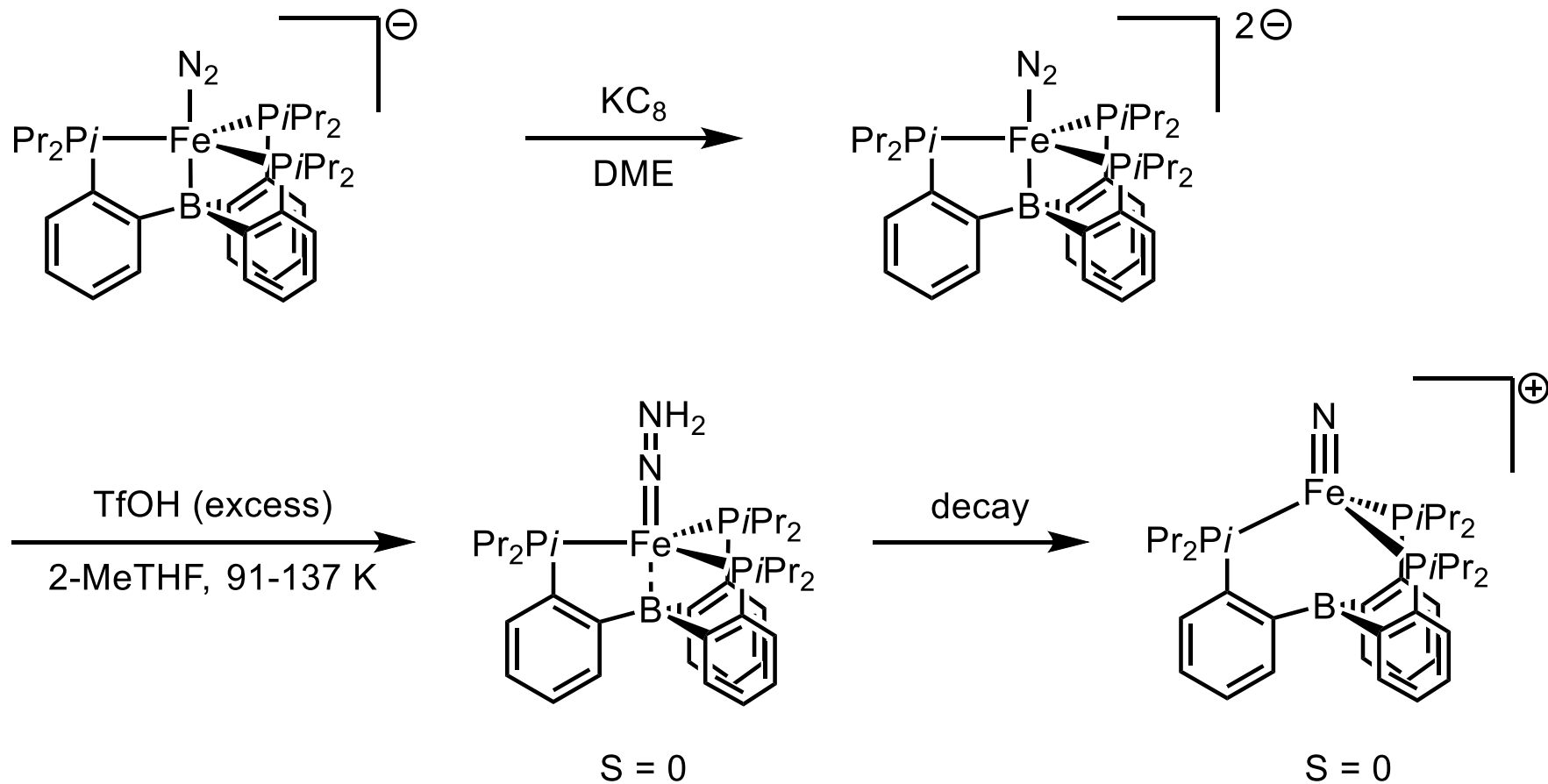
- Protonation of Fe-N₂⁻ complex



Anderson, J. S., Cutsail III, G. E., Rittle, J., Connor, B. A., Gunderson, W. A., Zhang, L., Hoffman, B. M., Peters, J. C. *J. Am. Chem. Soc.* **2015**, 137, 7803.

Fe Catalysts

- Generation of Fe(IV) nitride complex



Fe Catalysts

- Proposed cycle

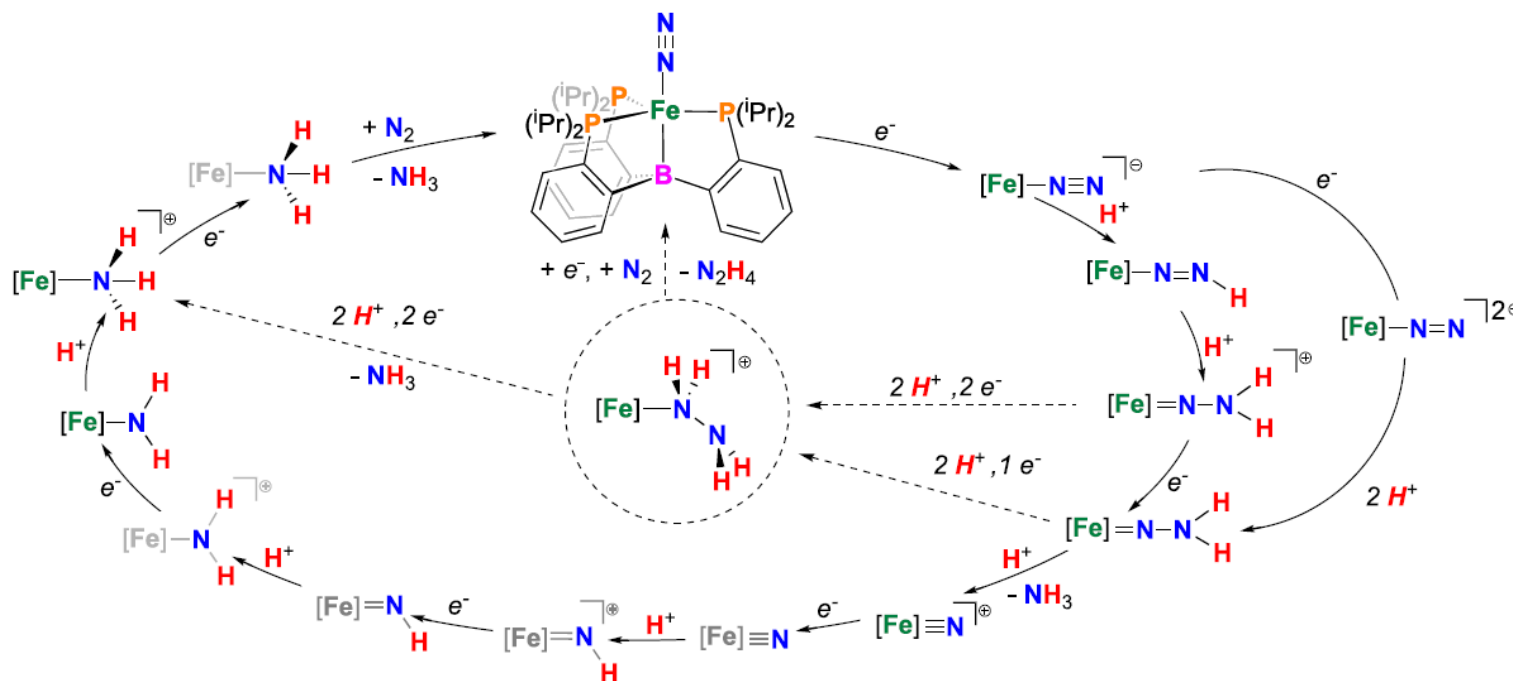


Figure 45. A proposed N₂RR cycle for Peters' (P₃^B)Fe platform. Characterized compounds are shown in green and unobserved complexes in gray. Solid arrows indicate a distal mechanism of nitrogen fixation, while dashed arrows indicate hybrid mechanisms of nitrogen fixation.^{109,112–114,176,182} Note that steps are shown as discrete e⁻ and H⁺ transfer steps, though concerted PCET steps may also be operative.

Castillo, T. J. D., Thompson, N. B., Peters, J. C. *J. Am. Chem. Soc.* **2016**, *138*, 5341.

Chalkley, M. J., Drover, M. W., Peters, J. C. *Chem. Rev.* **2020**, *120*, 5582.³⁴

Fe Catalysts

- Peters group reported another reaction condition via PCET mechanism.

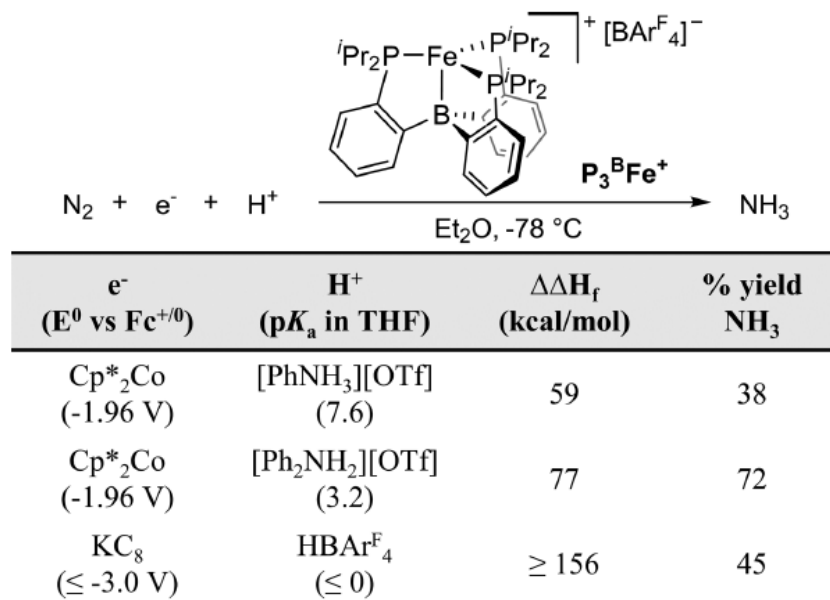


Figure 1. Summary of conditions used for catalytic N_2 -to- NH_3 conversion by $\text{P}_3^{\text{B}}\text{Fe}^+$ highlighting the estimated enthalpic driving force ($\Delta\Delta H_f$).^{14–19}

- Combination of milder reductant and acid efficiently promoted N_2 reduction.
- Mössbauer spectrum at 5 min under this condition showed
(TPB) FeN_2 (53%), (TPB)Fe (18%), and unknown Fe(II) species (22%).
- Off-path state borohydrido-hydrido species was not observed.

Fe Catalysts

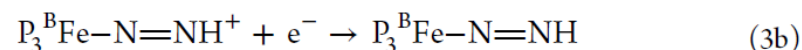
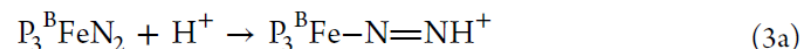
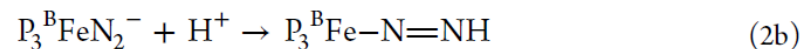
- Based on pK_a, protonation of (TPB)Fe-N=N is difficult.

Table 2. Calculated pK_a Values and BDEs of Selected Species^a

species	pK _a	BDE ^b
Ph ₂ NH ₂ ⁺	1.4 ^c	
PhNH ₃ ⁺	6.8	
lutidinium	14.5	
<i>endo</i> -Cp*Co(η ⁴ -C ₅ Me ₅ H) ⁺	16.8	31
<i>exo</i> -Cp*Co(η ⁴ -C ₅ Me ₅ H) ⁺	16.8	31
<i>endo</i> -Cp*Cr(η ⁴ -C ₅ Me ₅ H) ⁺	17.3	37
<i>exo</i> -Cp*Cr(η ⁴ -C ₅ Me ₅ H) ⁺	12.1	30
P ₃ ^B Fe-N=NH ⁺	-3.7	
P ₃ ^B Fe-N=NH	38.7	35
P ₃ ^B Fe=N-NH ₂ ⁺	14.4	51
P ₃ ^B Fe=N-NH ₂		47
[HIPTN ₃ N]Mo-N=NH		51

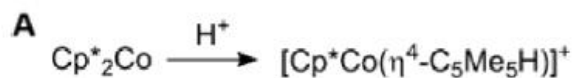
^aCalculations were performed using the M06-L³⁴ functional with a def2-TZVP basis set on Fe and Mo and a def2-SVP basis set on all other atoms³⁵ (see the Supporting Information). ^bIn kcal/mol. ^cpK_a values were calculated in Et₂O and reported relative to (Et₂O)₇H⁺.

• ET-PT or PT-ET pathway

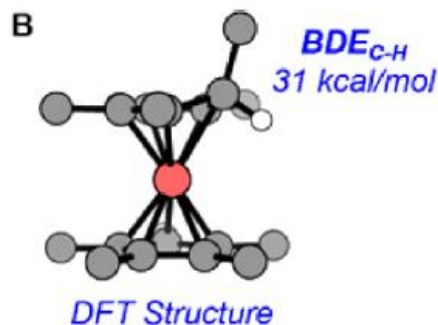


Fe Catalysts

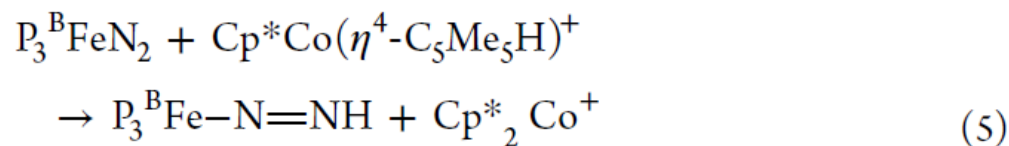
- The authors suggest metallocene-mediated PCET pathway.
- Protonation of Cp^*_2Co by Ph_2NH_2^+ and PhNH_3^+ is possible.



Acid	ΔG_{calc}
Ph_2NH_2^+	-21 kcal/mol
PhNH_3^+	-13 kcal/mol



- PCET process is thermodynamically favored.

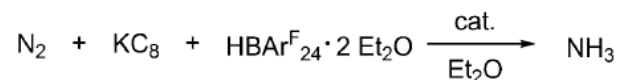


- $(\text{TPB})\text{Fe}=\text{N}=\text{NH}$: $BDE(\text{N-H}) = 35 \text{ kcal/mol}$
- $\text{Cp}^*\text{Co}(\eta^4\text{-C}_5\text{Me}_5\text{H})^+$: $BDE(\text{C-H}) = 31 \text{ kcal/mol}$

Fe Catalysts

- Peters group reported catalytic N₂ reduction by (CAAC)₂Fe complex.

Table 1: Catalytic reduction of N₂ to NH₃.^[a]

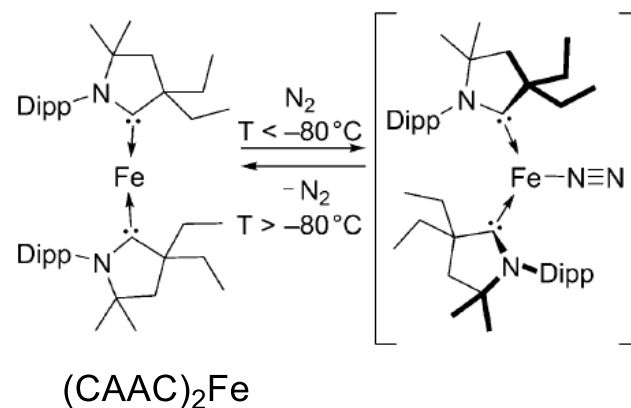
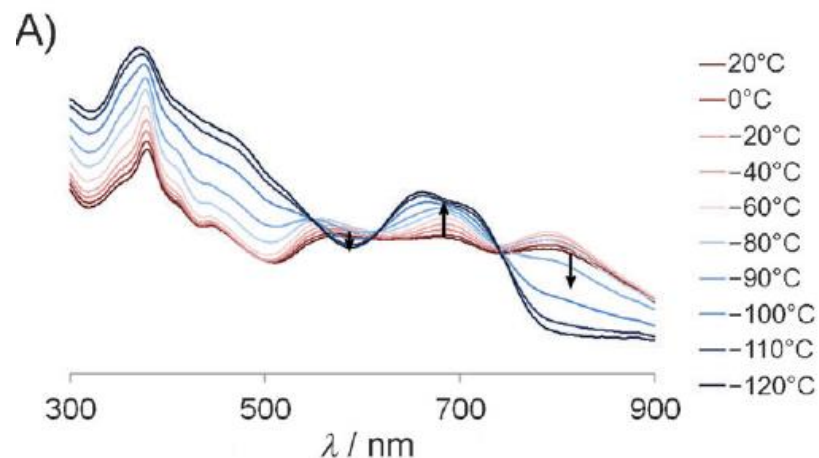


Run	Catalyst	T [°C]	Equiv NH ₃ per Fe
1	[(CAAC) ₂ Fe]	-113	3.0 ± 0.7
2	[(CAAC) ₂ Fe]	-95	3.3 ± 1.1
3	[(CAAC) ₂ Fe]	-78	0.9 ± 0.3 ^[b]
4	[(CAAC) ₂ Fe]	-50	0.3 ± 0.2 ^[b]
5	[(CAAC) ₂ Fe]	23	0.4 ± 0.2 ^[b]
6	[(CAAC) ₂ Fe][BAr ^F ₄]	-95	3.4 ± 1.0
7	[(CAAC) ₂ FeN ₂][K(18-c-6)]	-95	2.6 ± 0.6
8	CAAC ^[c]	-95	< 0.1
9	none	-95	< 0.1

[a] Catalytic conditions: catalyst (0.002 mmol), KC₈ (0.1 mmol), HBAr^F₄·2 Et₂O (0.1 mmol), Et₂O, 45 min. Yields are an average of 8 independent runs and were determined by the indophenol method (See the Supporting Information). [b] Average of 4 runs. [c] 0.004 mmol of CAAC used.

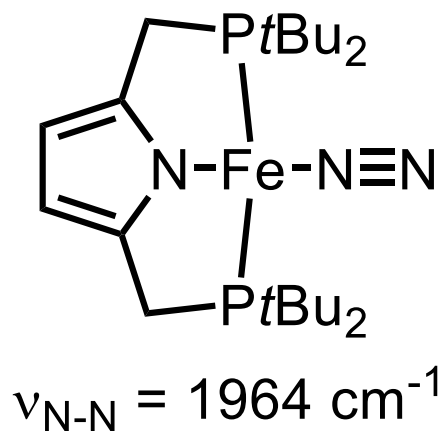
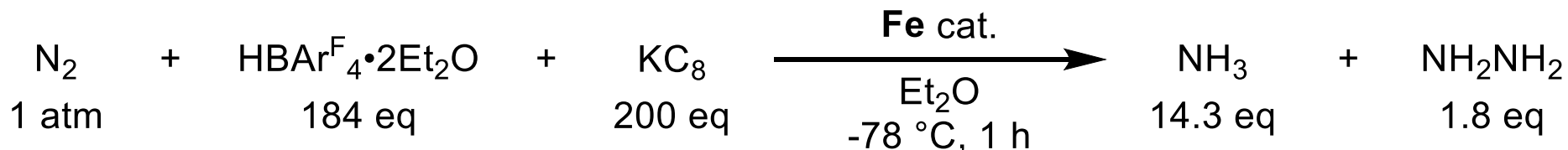
- Temperature dependence was observed.

- UV/Vis spectra of (CAAC)₂Fe under N₂



Fe Catalysts

- Nishibayashi group reported a Fe PNP-pincer complex for N₂ fixation catalyst.



Fe cat.

- KC₈/HBAr^F₄ at -78 °C reaction condition was employed that Peters reported.
- NH₂NH₂ was observed as a minor product.

Fe Catalysts

- Protonation of Fe(I) complex occurred at pyrrole ring.

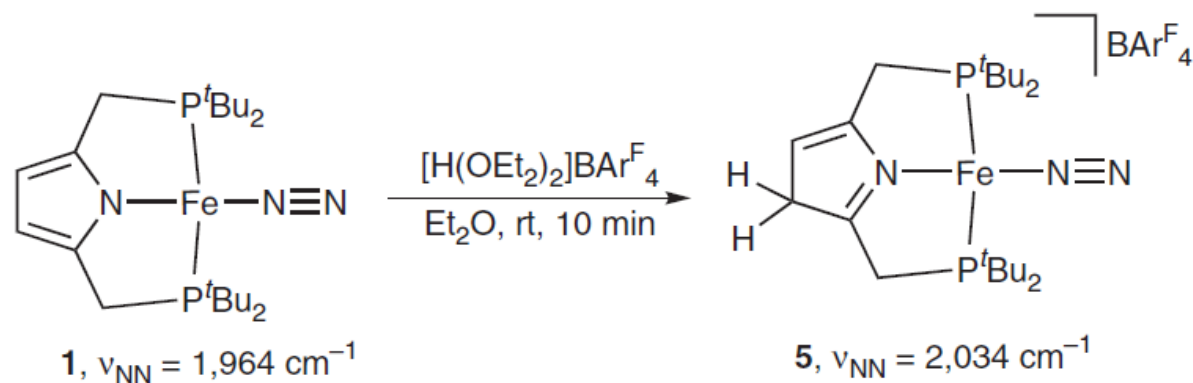
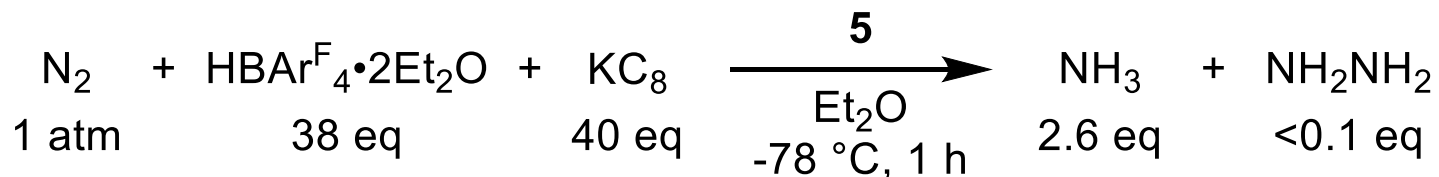


Figure 6 | Reactivity of iron-dinitrogen complex 1. Protonation of **1** with $[\text{H}(\text{OEt}_2)_2]\text{BARF}_4$ occurred at the pyrrole ring to give **5**.

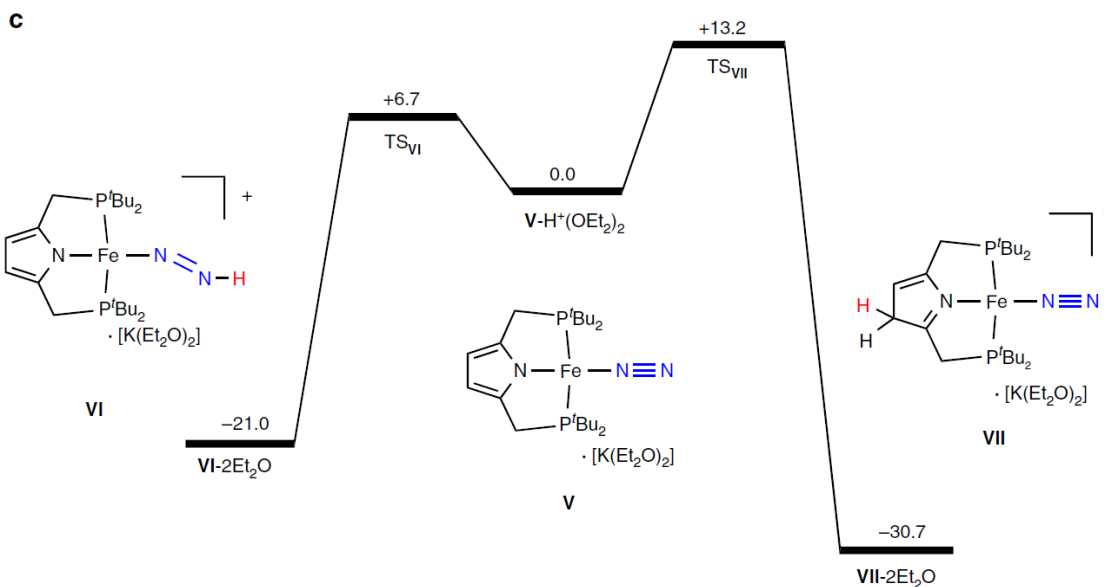
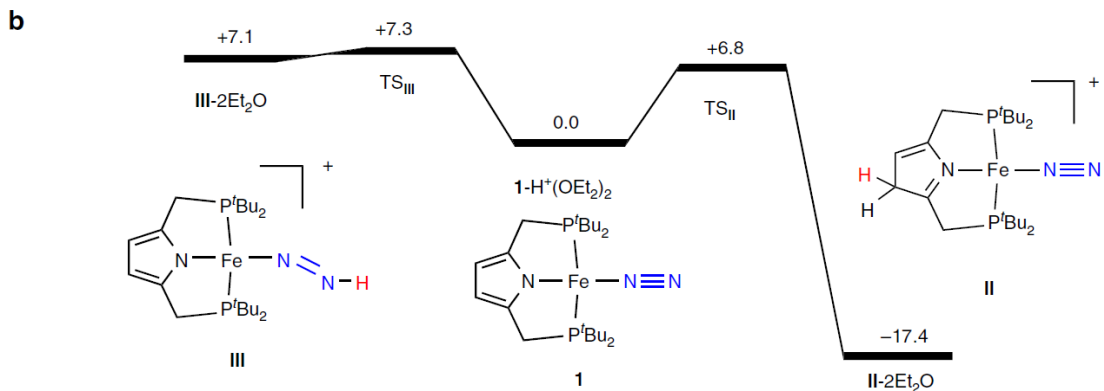
- The complex 5 showed lower reactivity.



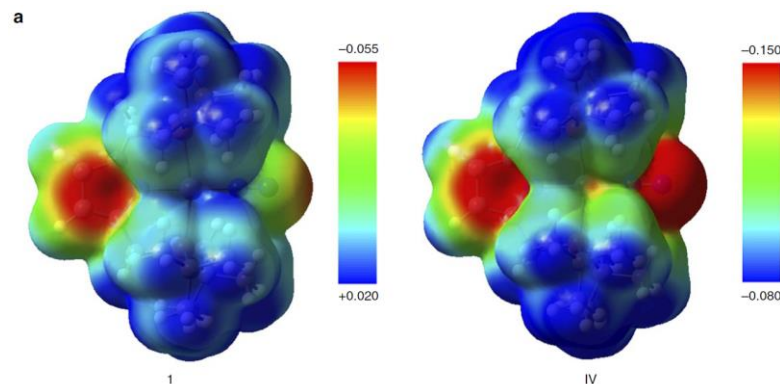
- Maybe this process is one of deactivation pathways.

Fe Catalysts

• DFT study



• Electrostatic potential map

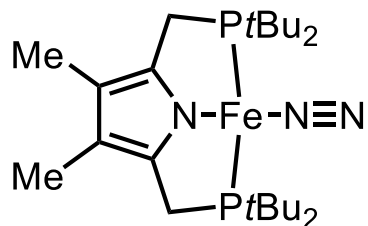
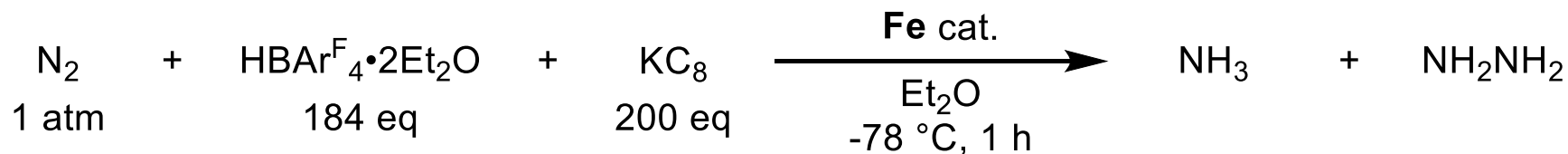


1 : Protonation of pyrrole ring is highly exergonic.

V : Protonation of N₂ can proceed with low activation energy, and this process is highly exergonic.

Fe Catalysts

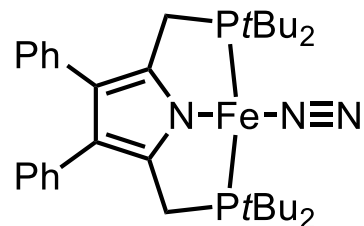
- Methyl substituent at pyrrole ring increases catalyst activity.



$$\nu_{\text{N-N}} = 1959 \text{ cm}^{-1}$$

$$\text{NH}_3 \quad 22.7 \text{ eq}$$

$$\text{NH}_2\text{NH}_2 \quad 1.7 \text{ eq}$$



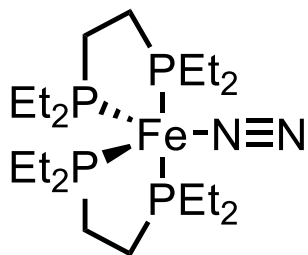
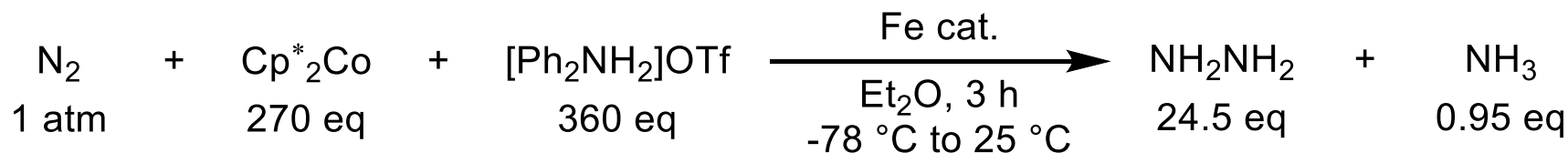
$$\nu_{\text{N-N}} = 1969 \text{ cm}^{-1}$$

$$\text{NH}_3 \quad 4.7 \text{ eq}$$

$$\text{NH}_2\text{NH}_2 \quad 1.2 \text{ eq}$$

Fe Catalysts

- Ashley reported catalytic N₂ reduction by simple Fe(depe)₂(N₂) complex.



Fe cat. Fe(depe)₂(N₂)

- The catalytic reduction afforded N₂H₄ in high selectivity.
- The reaction mechanism is unknown.

Summary

- Catalytic N₂ fixation has been studied due to both industrial and biological interests.
- Mo and Fe catalysts have been mainly studied, and recently some other metal catalysts also have been reported.
- Reaction mechanism of catalytic N₂ reduction has been extensively investigated. But uncertainties of the mechanism still remain in some catalysts.