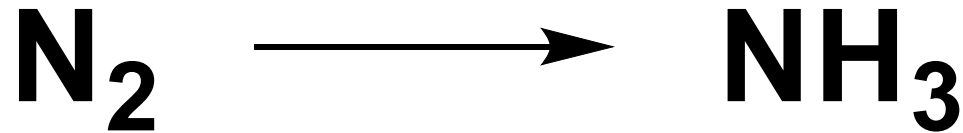


# New Methods of Nitrogen Fixation System



Today' topic

1. General feature and history of  $\text{N}_2$  fixation system

1.1 Haber-Bosch process

1.2 Nitrogenase

1.3 Dinitrogen-complex

2. Approach of  $\text{N}_2$  activation under normal temperature and pressure

2.1.  $\text{N}_2$  fixation using  $\text{H}_2$

2.2.  $\text{N}_2$  fixation using proton source

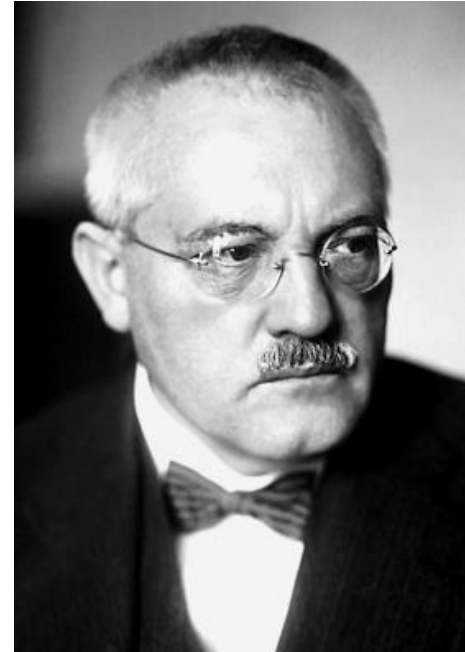
2.3  $\text{N}_2$  fixation using polyhydride complex

3. Application of  $\text{NH}_3$  in the future

## 1.1 Haber-Bosch process



**Fritz Haber (1868-1934)**  
Nobel prizes, in 1918



**Carl Bosch (1874-1940)**  
Nobel prizes, in 1931

**Sir William Crookes predicted scarcity of food by population increase in 1898 and called scientists's attention to new nitrogen fixation system for human life**



**Haber process was invented in 1909 and developed to industrialization by Bosch in 1913**



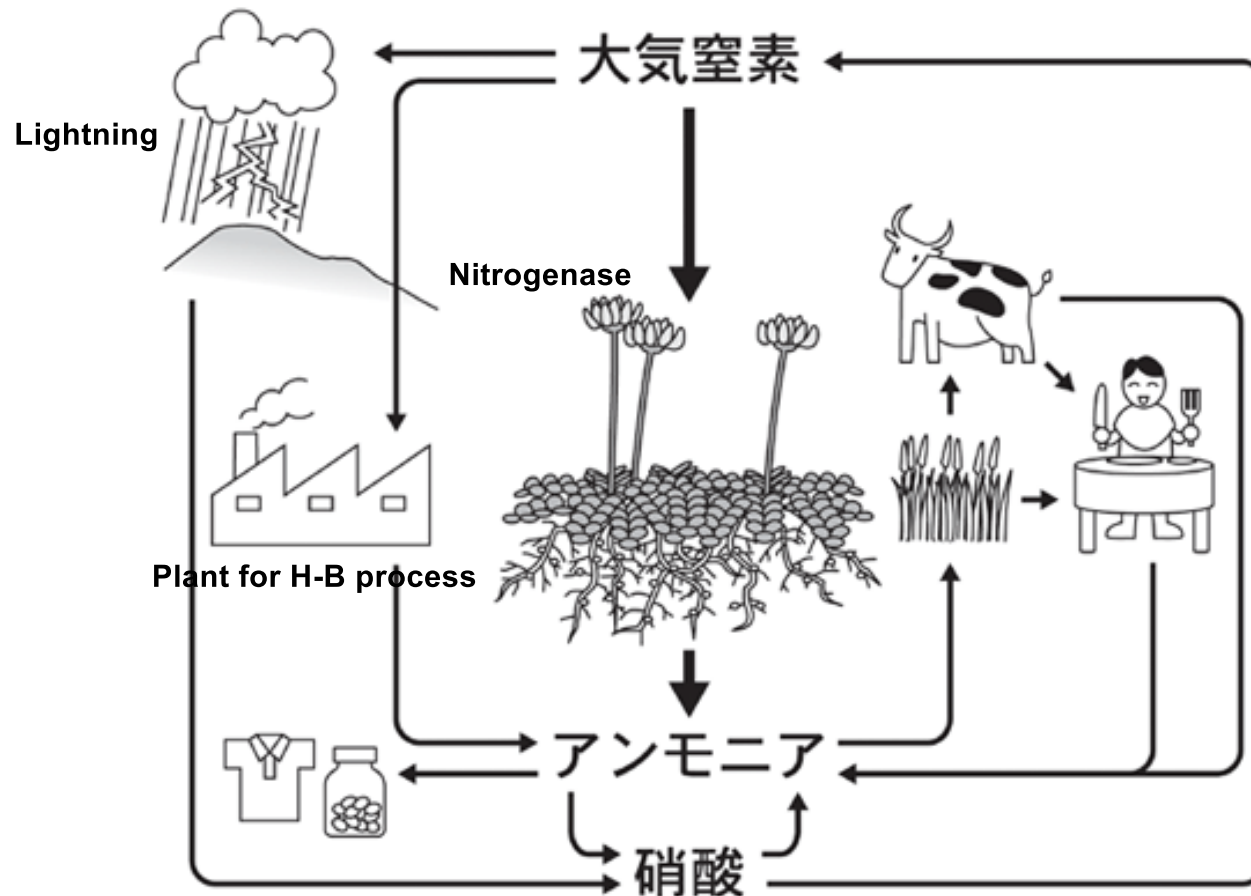
**It has been the main industrial route to synthesis ammonia until now**

# 1.1 Haber-Bosch process

## Nitrogen Cycle

the process by which nitrogen is converted between its various chemical forms.

Animal and plants in the world couldn't incorporate  $N_2$  as N element in their body.  
For introducing N element in their body,  $N_2$  need to be converted to  $NH_3$

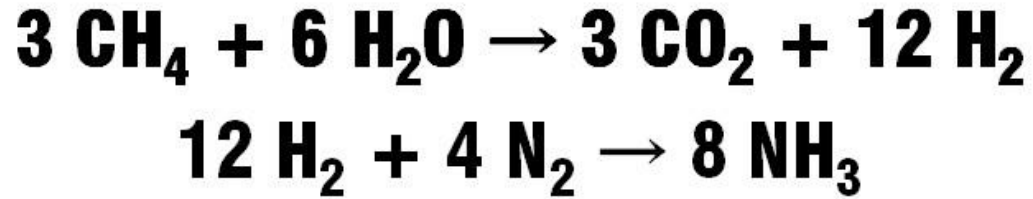


cited by homepage in Nishibayashi's laboratory

## 1.1 Haber-Bosch process

First industrial Haber-Bosch process operated at the BASF

General scheme

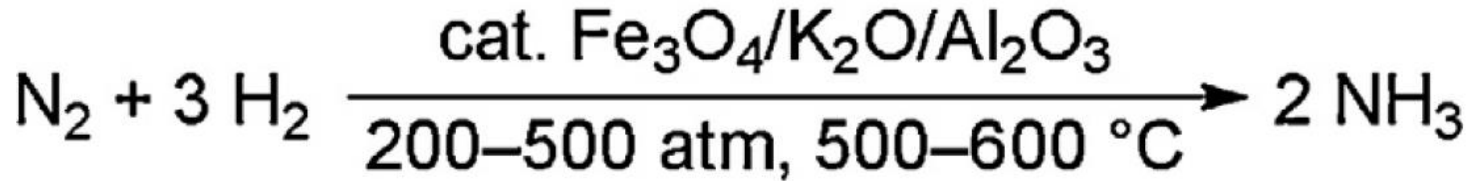


Habor process has been called **the method for "making breads from coal and air" !!**

**About the half amount of food in the world is produced by Harbor-Bosch process nowadays !!**

## 1.1 Haber-Bosch process

N<sub>2</sub> fixation by Haber-Bosch process



cat. role: 1. Fe<sub>3</sub>O<sub>4</sub> is reduced to Fe in the condition, Fe provide  $\pi$  back donation to N<sub>2</sub>.  
2. K<sub>2</sub>O support  $\pi$  back donation of Fe  
3. Al<sub>2</sub>O<sub>3</sub> inhibit aggregation of Fe

$\Delta G^\circ = -7.7 \text{ kcal/mol}$  at 298 K, 1atm in the overall reaction



an equilibrium composition with 96% ammonia from a 1:3 of N<sub>2</sub> and H<sub>2</sub>.

the thermodynamics of nitrogen fixation can be favorable, but.....

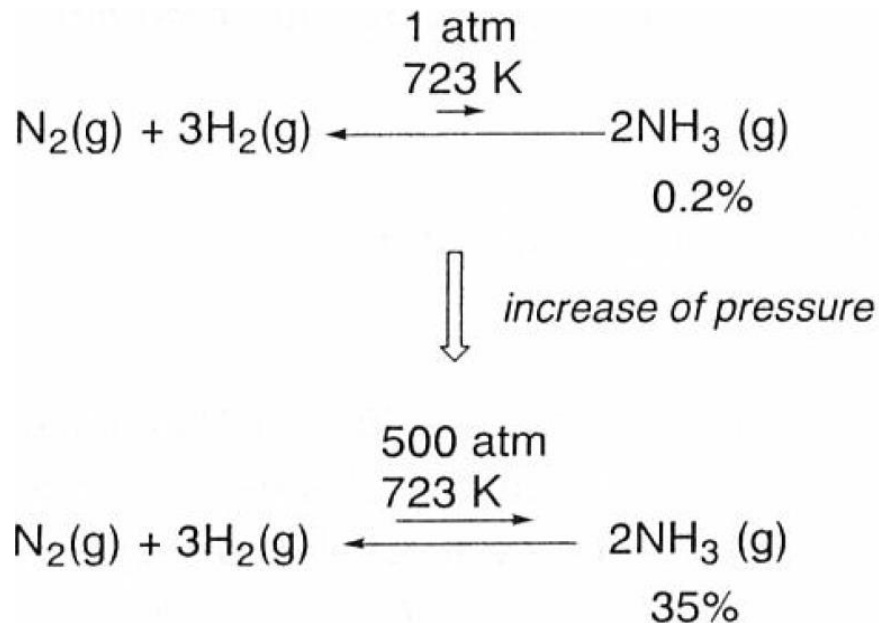
J. B.Howard *et al*, *Chem. Rev.* **1996**, 96, 2965.



the kinetic stability of the N<sub>2</sub> triple bond complicated realization of ammonia synthesis

## 1.1 Haber-Bosch process

Equilibrium shifts toward the reactants

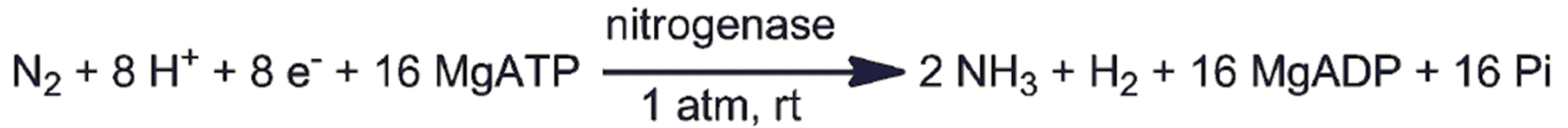


High temperatures are required for N<sub>2</sub> triple bond dissociation, which is the rate-determining step. But the equilibrium shifts toward the reactants with increasing temperature, so the reaction pressure is needed.

**If N<sub>2</sub> bond dissociation is realized in low temperature, reaction pressure isn't needed**

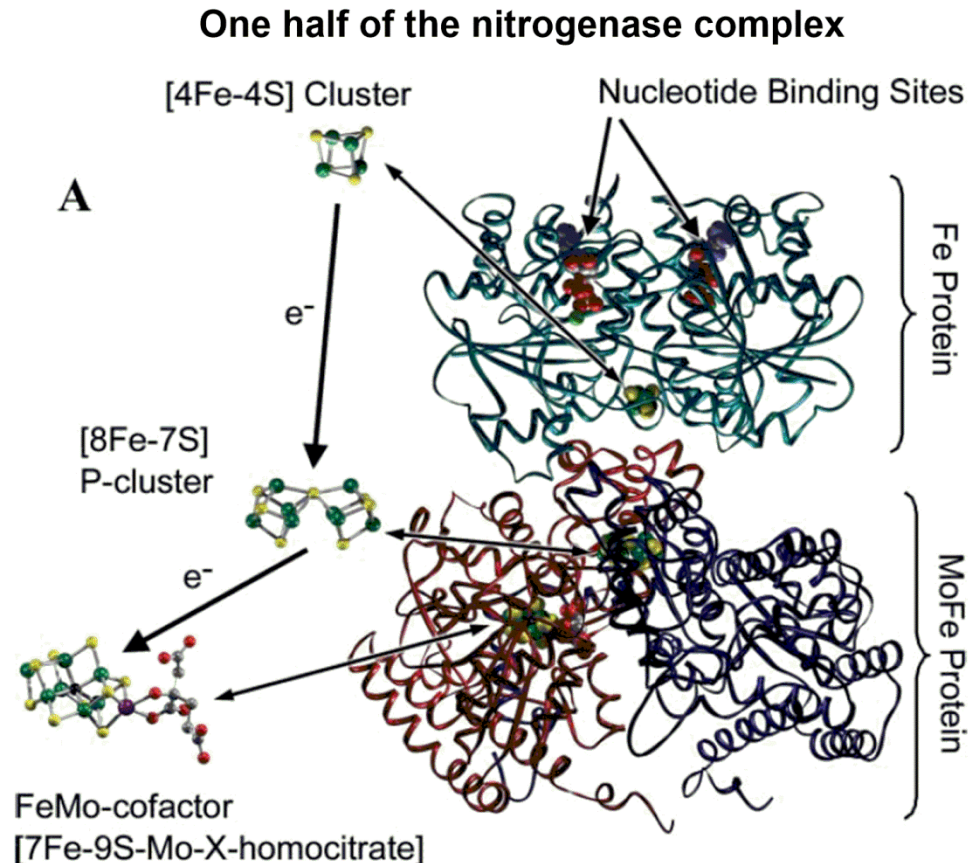
## 1.2 Nitrogenase

Nitrogenases are enzymes used by prokaryotic organisms to fix atmospheric nitrogen gas, and composed of two proteins, Fe protein and MoFe protein



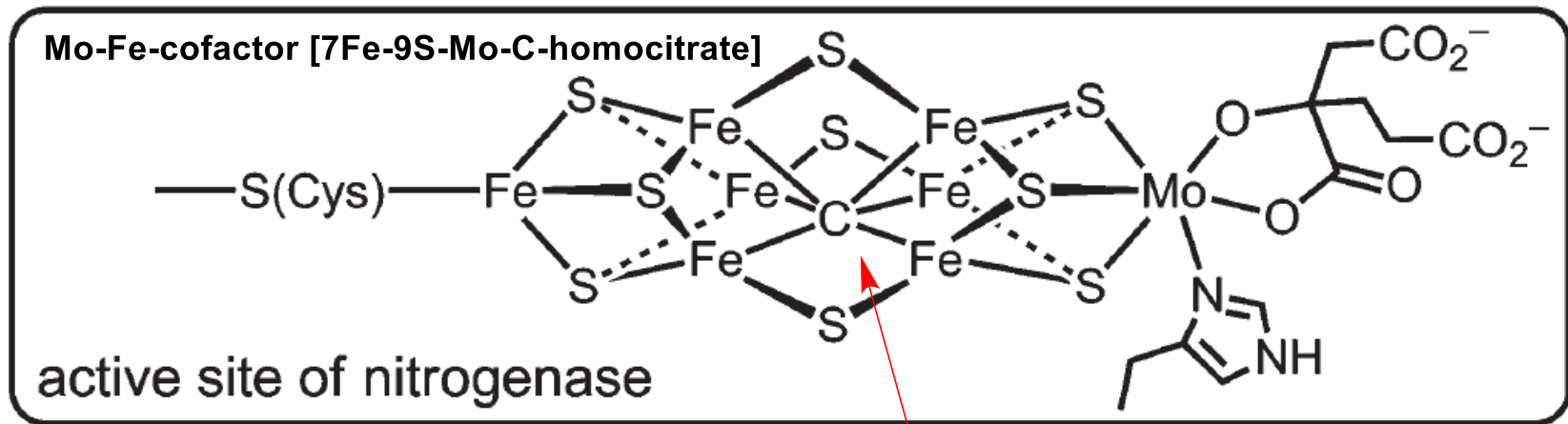
under mild reaction conditions

The yield of  $\text{NH}_3 = 75\%$



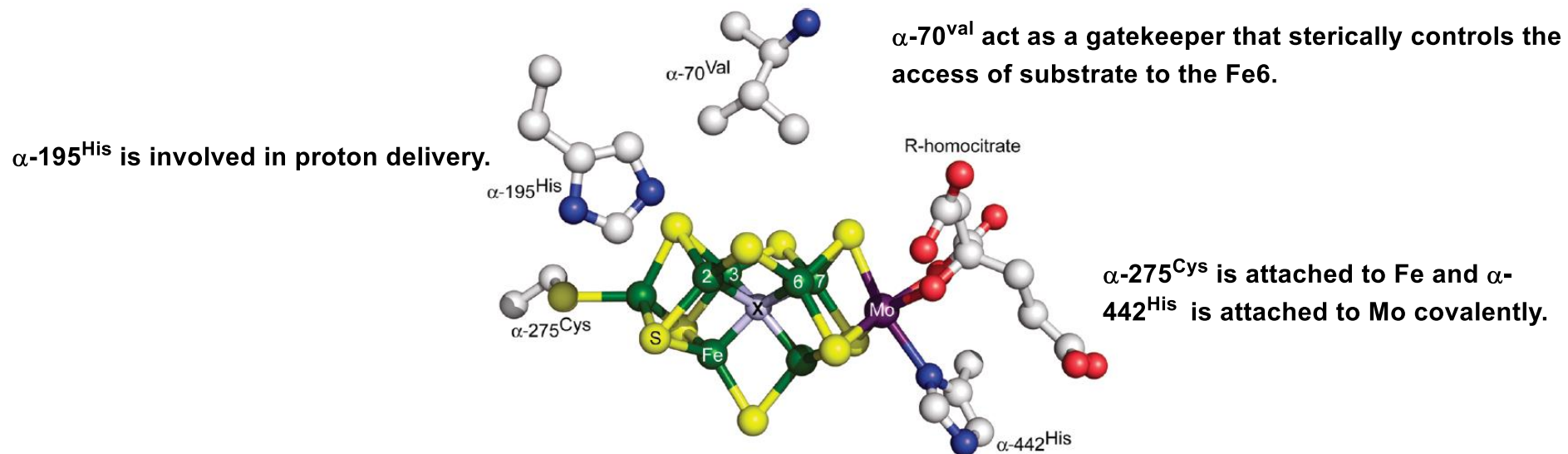
## 1.2 Nitrogenase

B. M. Hoffman *et al*, *Acc. Chem. Res.* **2005**, 42, 609.



recently identified as carbon O, Einsle *et al*, *Science* **2011**, 334, 940.  
S, Debeer *et al*, *Science*, **2011**, 334, 974.

The mechanisms for nitrogen fixation divided in two main groups (conversion at Mo and conversion at Fe) has been unclear...





## 1.2 Nitrogenase

### Elucidation of the mechanism

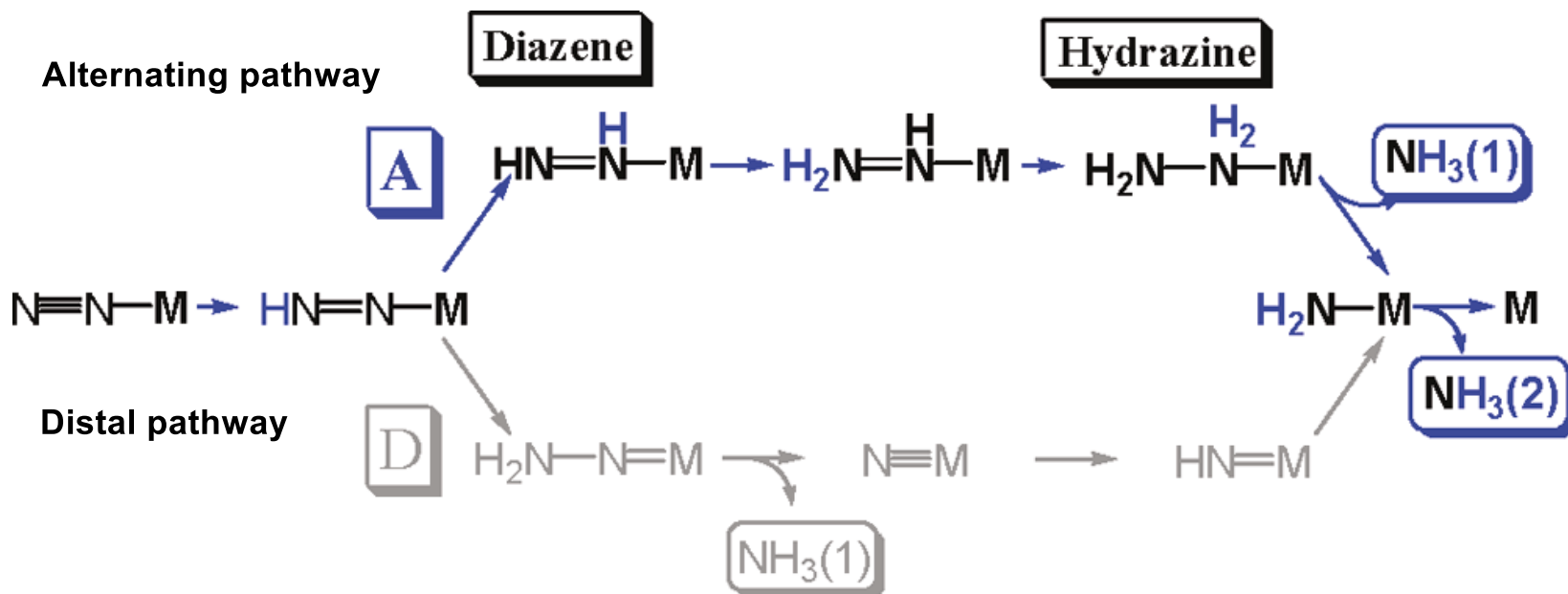
L. C. Seefeldt *et al*, *Dalton Trans.*, **2006**, 2277.

Mutation of the amino acid residue such as  $\alpha$ -195<sup>His</sup>,  $\alpha$ -70<sup>val</sup>, and Freezing the MoFe protein



These two changes successfully sought to trap states during reduction of N<sub>2</sub>, a diazene, and hydrazine

Nitrogenase has been thought to conduct N<sub>2</sub> fixation by Alternating pathway



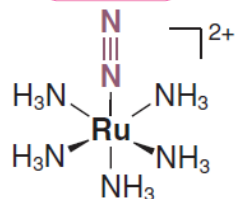
Imitating nitrogenase, N<sub>2</sub> fixation under mild condition in artificial reaction system would be realized ?

# 1.3 Dinitrogen-complex

## Various dinitrogen-complex

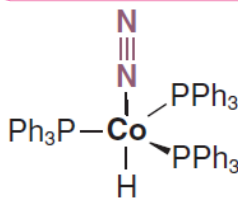
Kagakudojin, *Chemistry*, 2013, 6, 37.

世界初の窒素錯体



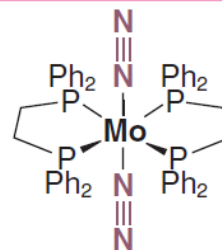
A. D. Allen  
(1965年)

世界初の窒素分子由来の窒素錯体



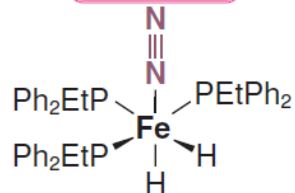
A. Yamamotoら  
(1967年)

世界初のモリブデン窒素錯体



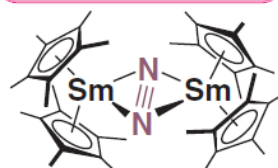
M. Hidaiら (1968年)

世界初の鉄窒素錯体



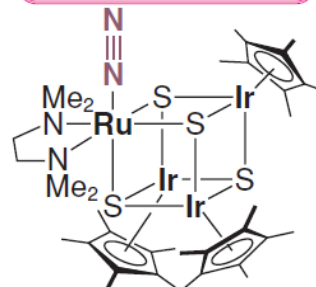
A. Saccoら  
(1968年)

世界初のf族金属 side-on型窒素錯体



W. J. Evansら  
(1988年)

世界初のキュバン型窒素錯体



Y. Mizobeら (2007年)

## Character of Dinitrogen-ligand and complex

1. N<sub>2</sub> ligand is isoelectronic to CO, but weaker  $\sigma$ -donor and  $\pi$ -acceptor.
2. usual binding mode is end-on.
3. strong  $\pi$ -back donation can stabilize N<sub>2</sub> complex.
4. distance of N<sub>2</sub> bond of complex is longer than N<sub>2</sub> molecule
5. Redox mode of N<sub>2</sub> complexes are generally [N<sub>2</sub>]<sup>0</sup>, [N<sub>2</sub>]<sup>2-</sup>, [N<sub>2</sub>]<sup>4-</sup>.

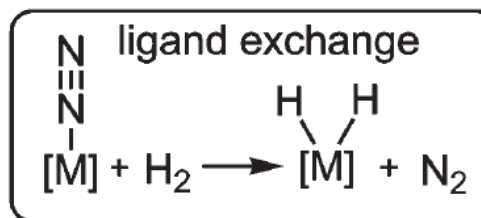
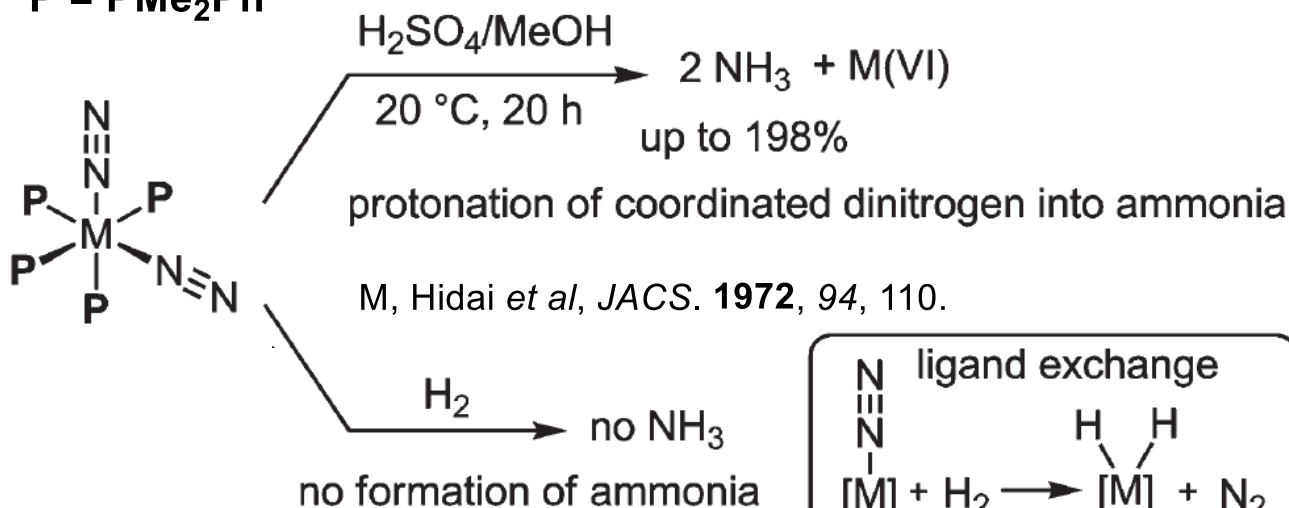
## 1.3 Dinitrogen-complex

### The breakthrough of stoichiometric N<sub>2</sub> fixation

Conversion from N<sub>2</sub> to NH<sub>3</sub> needs 6 electron.

M = Mo and W J. Chatt *et al*, *Nature* 1975, 253, 39.

P = PMe<sub>2</sub>Ph



M = Mo

P = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> (DPPE)

#### 2.1. N<sub>2</sub> fixation using H<sub>2</sub>

Hidai group discovered the formation of MoP<sub>2</sub>H<sub>2</sub> (Mo with trans dihydrides by IR)

⇒ It is difficult for nitrogen complex to react with H<sub>2</sub> directly to produce NH<sub>3</sub>

#### 2.2. N<sub>2</sub> fixation using proton source

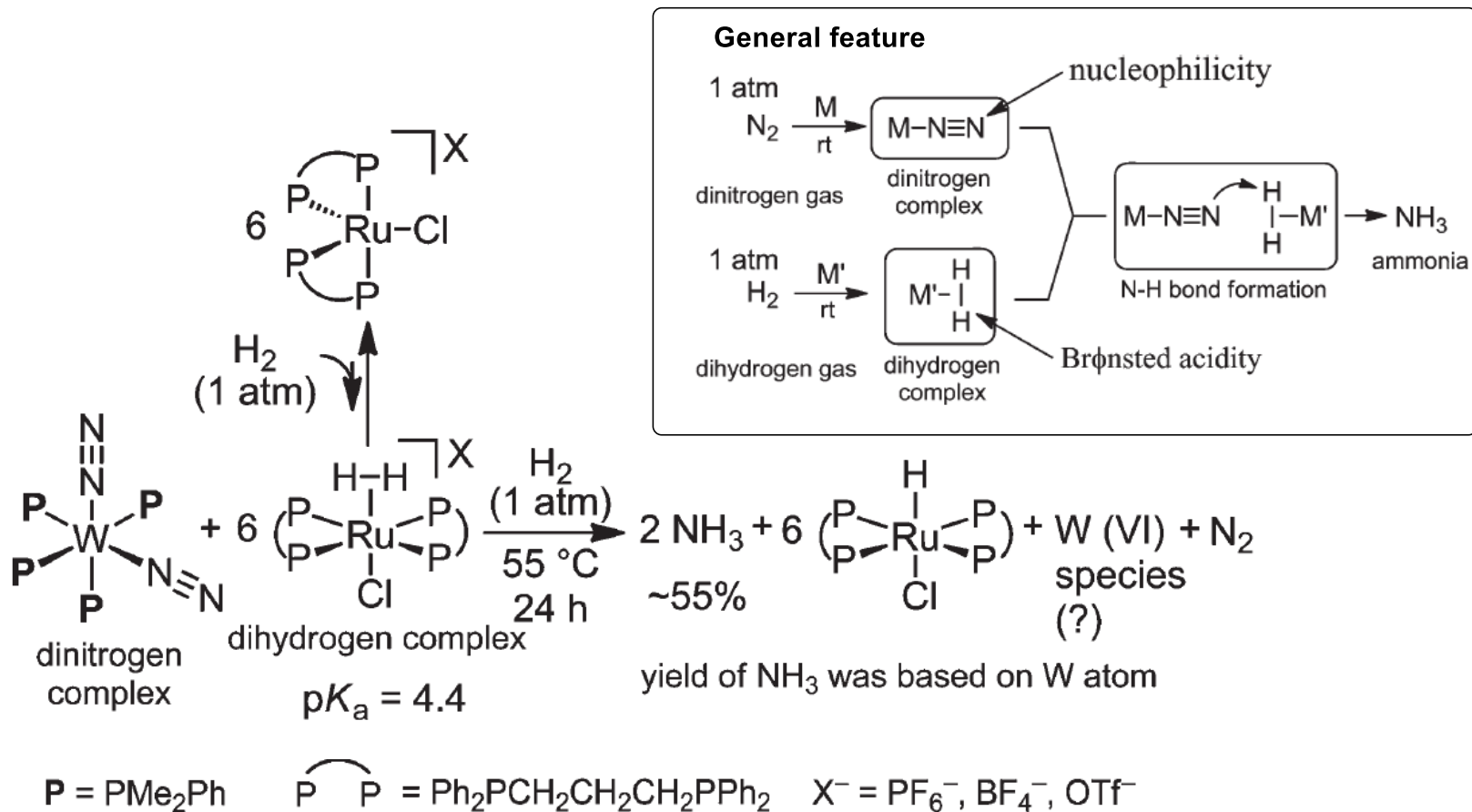
Chatt group succeeded stoichiometric N<sub>2</sub> fixation under a protic condition.

⇒ If nitrogen complex is regenerated by reduction of M (VI), cat. cycle is enabled

## 2.1. N<sub>2</sub> fixation using H<sub>2</sub>

### The first example of N<sub>2</sub> fixation using hydrogen under mild condition

Y. Nishibayashi, S. Iwai and M. Hidai, *Science*, **1998**, 279, 540.

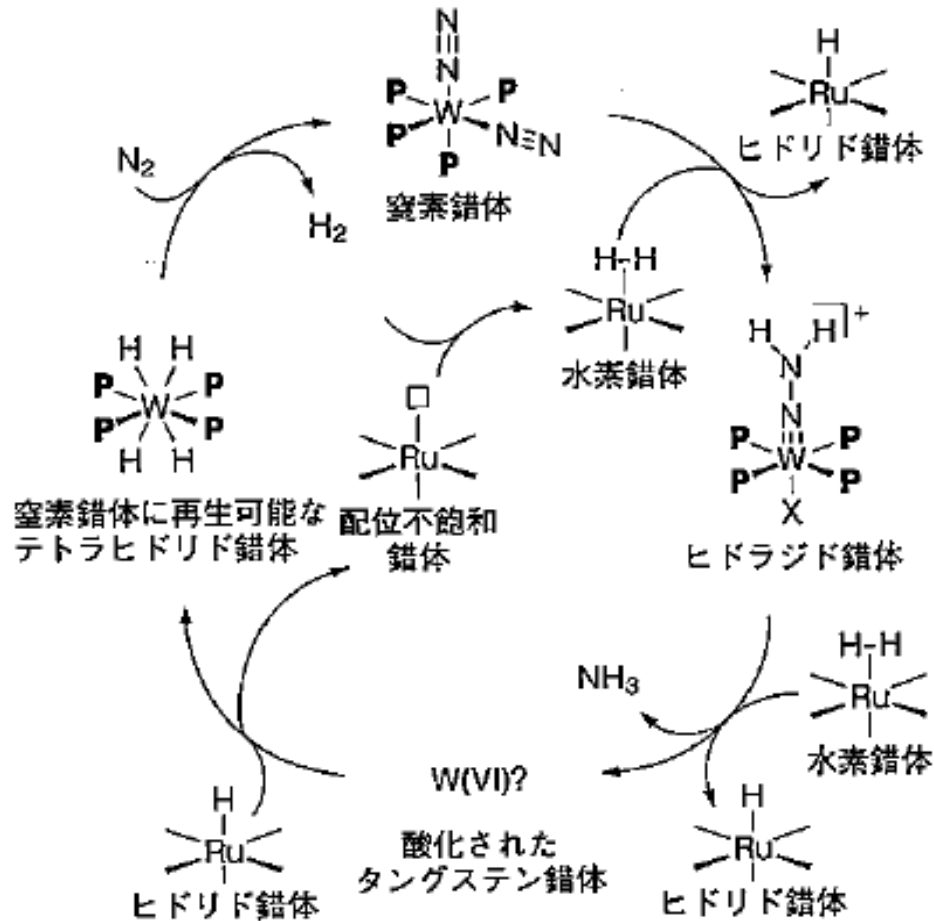


Direct treatment of W complex with 10 eq. of Ru complex under above condition afforded NH<sub>3</sub> in 22% yield the condition using Fe-H and Co-H instead of Ru-H afforded N.R. (M, Hidai *et al*, *JACS*. 1972, 94, 110.)

## 2.1. N<sub>2</sub> fixation using H<sub>2</sub>

### Reaction mechanism

Kagaku Dojin, bond activation and molecular activation, published in 2011



Because W complex acted as reductant, catalytic cycle wasn't achieved.



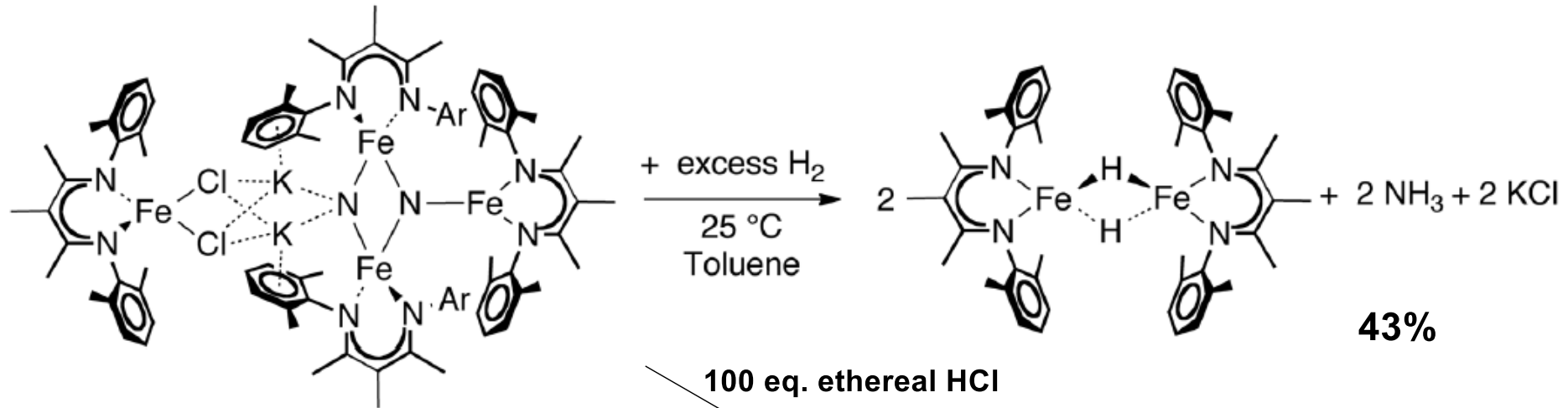
If the remaining Ru-H act as the reduction of the W(VI) to regenerate, catalytic cycle will be realized

## 2.1. N<sub>2</sub> fixation using H<sub>2</sub>

### Recent development of N<sub>2</sub> fixation using H<sub>2</sub>

#### N<sub>2</sub> Reduction and Hydrogenation to Ammonia by a Iron-Potassium Complex

P.L. Holland *et al*, *Science* **2011**, 334, 780.



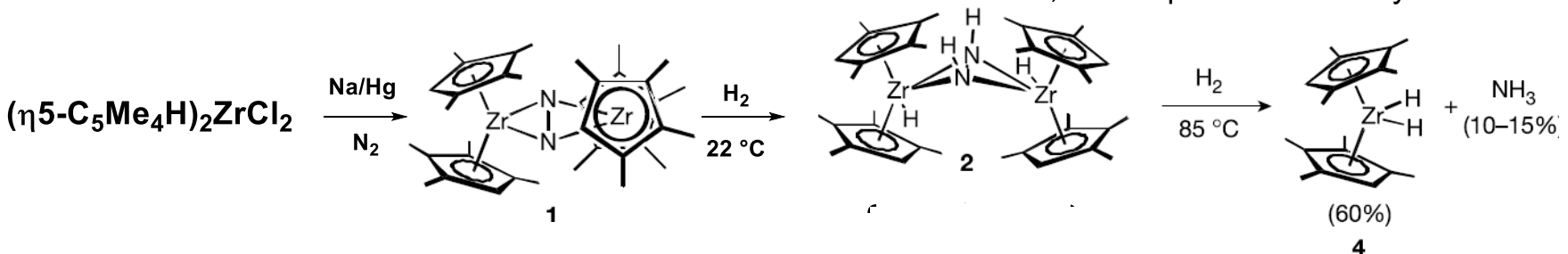
a high yield of ammonia with acid demonstrates that the N-N bond is completely cleaved and that the nitrides are nucleophilic.

NH<sub>4</sub>Cl **82%**

#### First report Incorporating two H of H<sub>2</sub> to N<sub>2</sub> complex

J. Chirik *et al*, *Nature* **2004**, 427, 527.

Hf, Ti complex was also synthesized by Chirik.



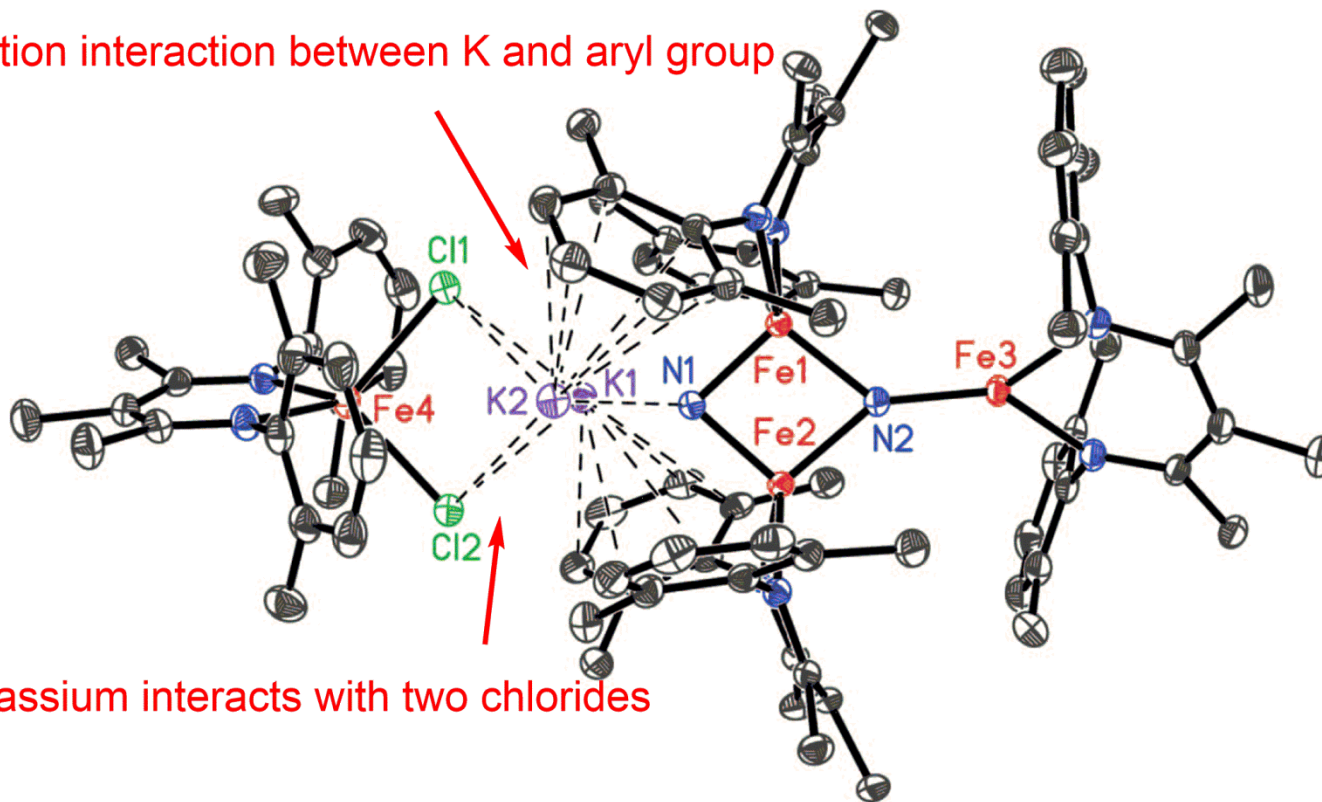
If Cp\* as ligand was used, H<sub>2</sub> wasn't activated (Bercaw, 1976)

## 2.1. N<sub>2</sub> fixation using H<sub>2</sub>

X-ray crystallography shows the molecular structure

Fe1-N1, 1.812(2) Å; Fe1-N2, 1.906(2) Å; Fe2-N1, 1.809(2) Å; Fe2-N2, 1.918(2) Å; Fe3-N2, 1.832(2) Å; N1-N2, 2.799(2) Å

$\pi$ -cation interaction between K and aryl group



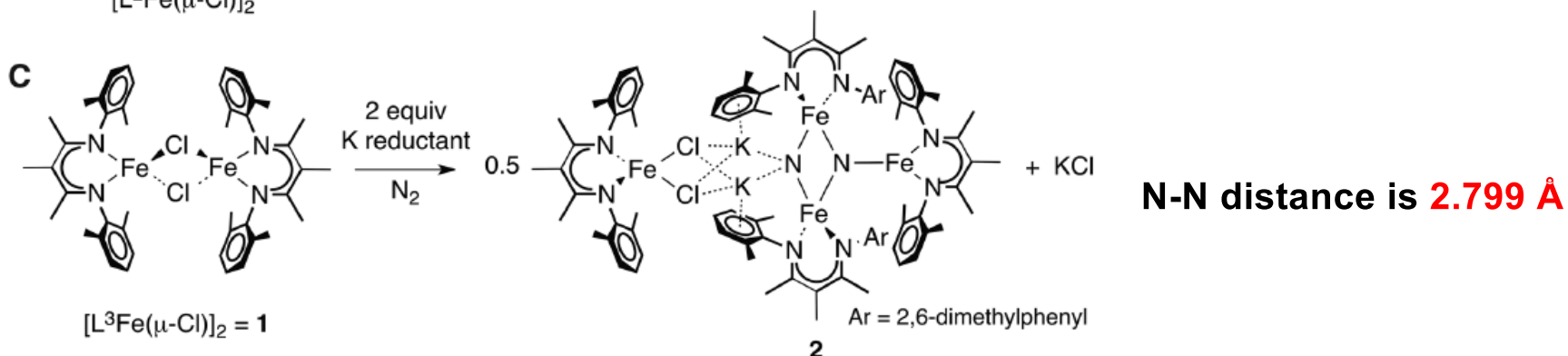
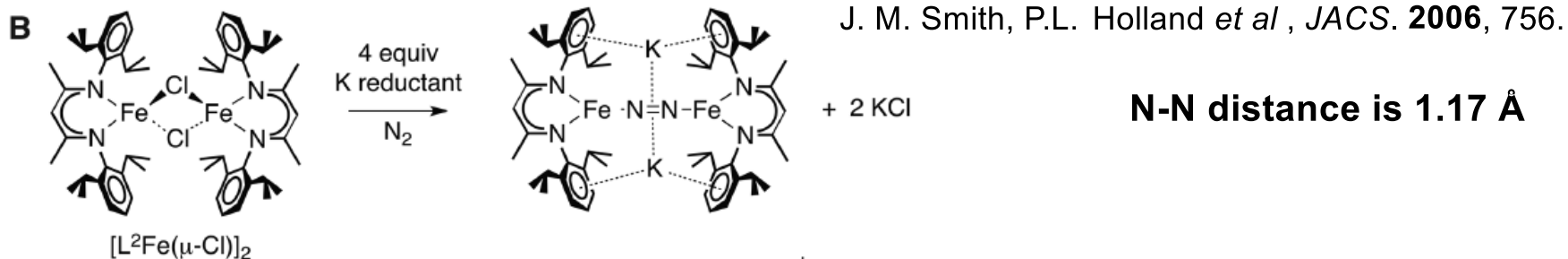
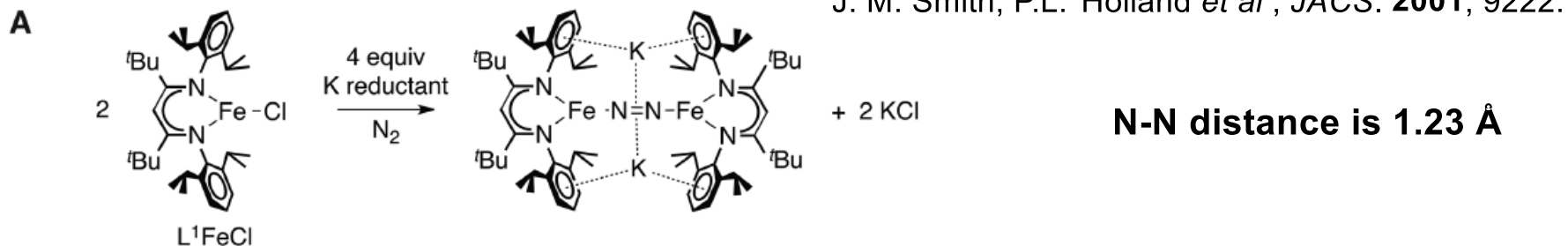
Each potassium interacts with two chlorides

♠ High spin Fe 1,2 (III), Fe 3,4 (II) was assigned by Mössbauer and magnetic properties

## 2.1. N<sub>2</sub> fixation using H<sub>2</sub>

### Iron-Potassium Complex Analogue

N-N distance is 1.10 Å (free N<sub>2</sub>), 1.14 Å (general mono,di-Fe complex), 1.25 Å (diazene), 1.45 Å (hydrazine)



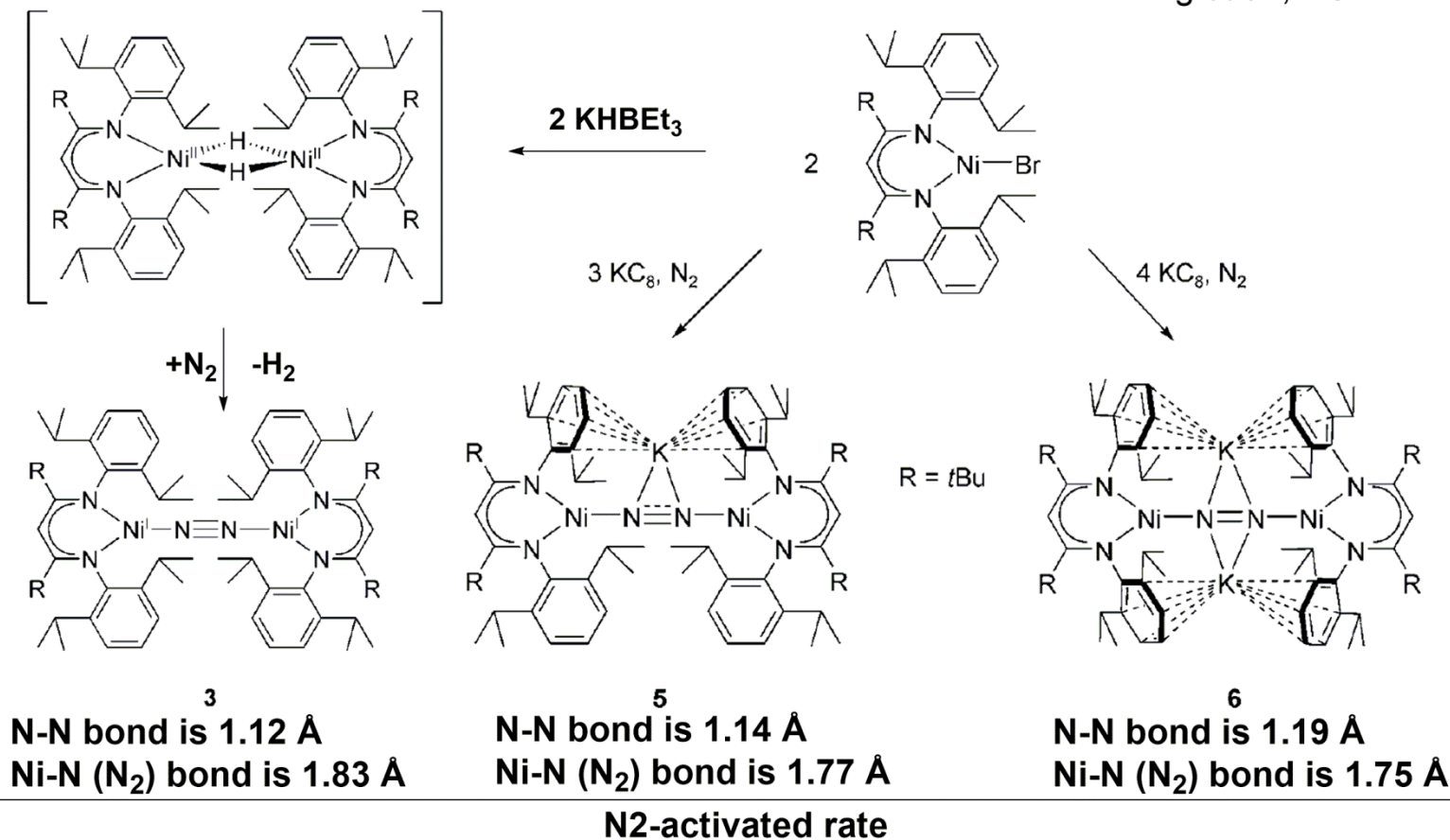
**C: there is no N-N bond; six-electron reduction of N<sub>2</sub> ; [N<sub>2</sub>]<sup>6-</sup>**



## 2.1. N<sub>2</sub> fixation using H<sub>2</sub>

### Ni(I)-Potassium Complex

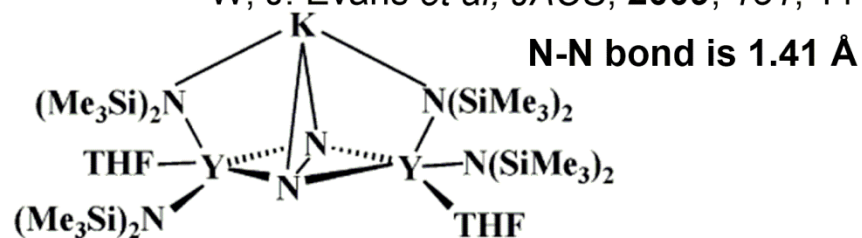
S. Limberg *et al.*, *ACIE* 2009, 48, 3357.



### Y-(N<sub>2</sub>)<sup>3-</sup> Radical Complexes

W, J. Evans *et al.*, *JACS*, 2009, 131, 11195.

◆ [N<sub>2</sub>]<sup>3-</sup> redox mode was only reported



## 2.1. N<sub>2</sub> fixation using H<sub>2</sub>

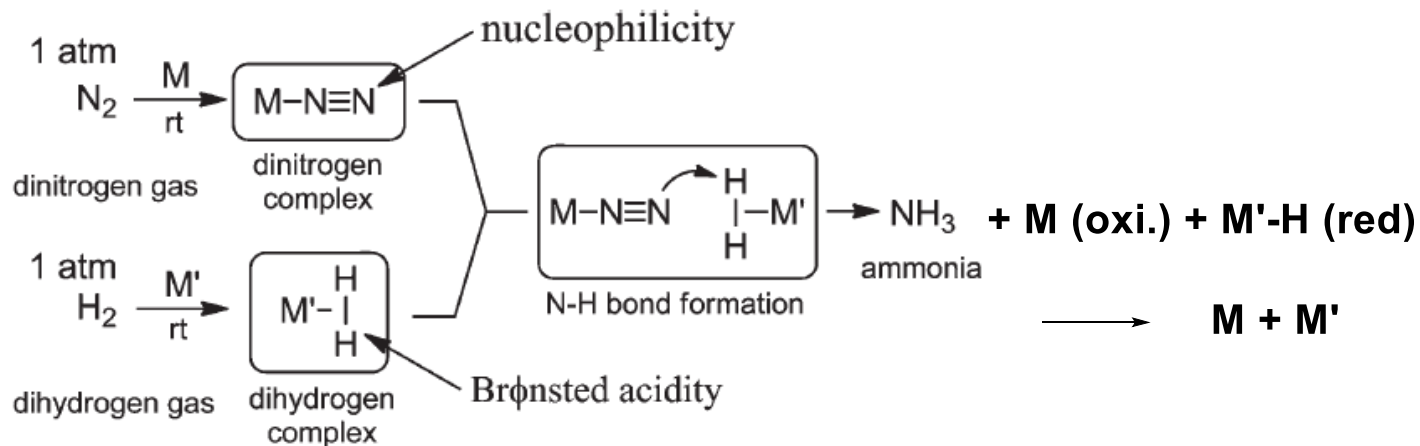
### Short Summary 2.1.

Under mild reaction condition, catalytic N<sub>2</sub> fixation using H<sub>2</sub> hasn't been reported...

**Problematic point : How H<sub>2</sub> is utilized as reductant (H<sup>-</sup>), instead of metal reductant**

I think most possible reaction system to realize catalytic reaction using H<sub>2</sub>

Y. Nishibayashi, S. Iwai and M. Hidai., *Science*, **1998**, 279, 540.



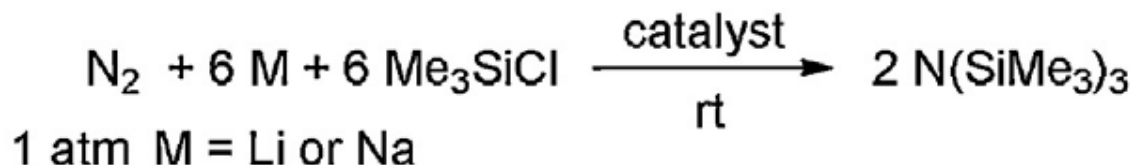
**corporated use of two complex is desirable  
(one can activate H<sub>2</sub>, while the other can activate N<sub>2</sub>)**

## 2.2. N<sub>2</sub> fixation using proton source

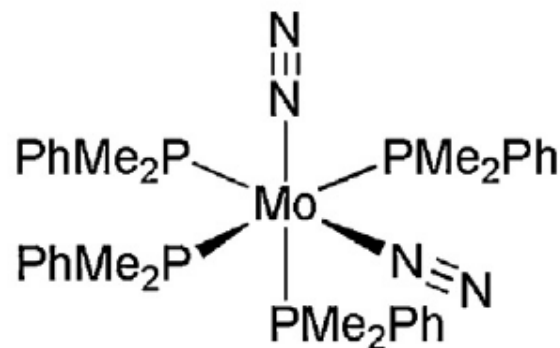
### First catalytic synthesis of NH<sub>3</sub> equivalent

K. Shiina *et al*, *JACS*, **1972**, *94*, 9266.

M. Hidai *et al*, *JACS*, **1989**, *111*, 1939.



catalyst: CrCl<sub>3</sub>



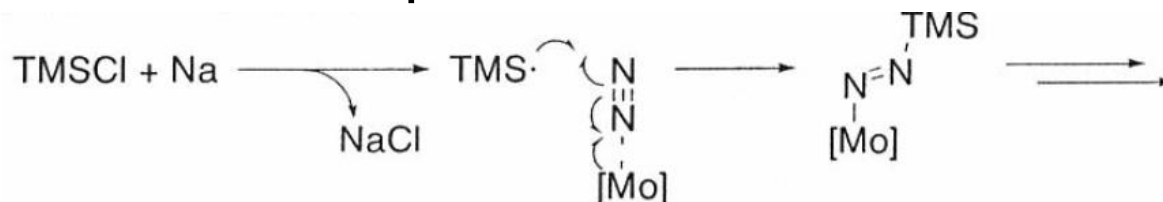
reducing reagent: M = Li

M = Na

amount of silylamine: 5 equiv (6.3%)      24 equiv (36.6%)

Byproduct (TMS<sub>2</sub>)      **25.1%**      **39.0%**

### Proposed mechanism

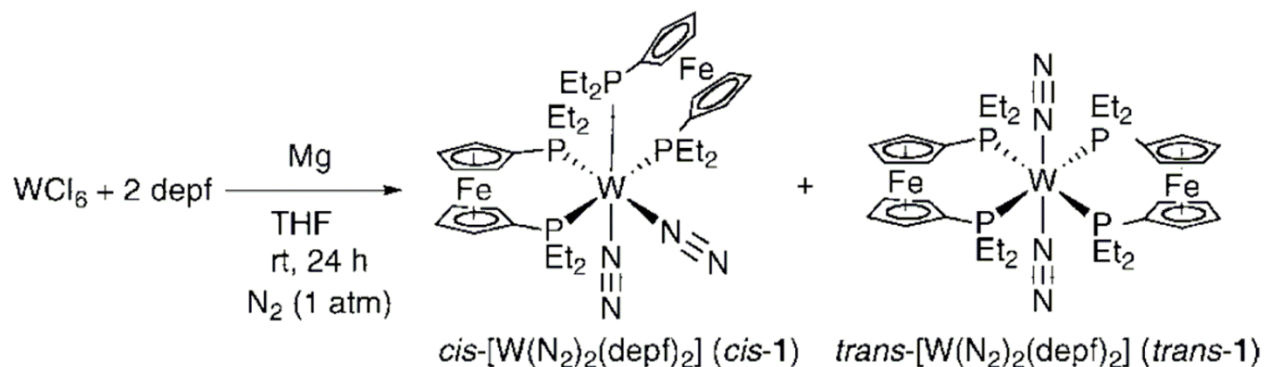


## 2.2. N<sub>2</sub> fixation using proton source

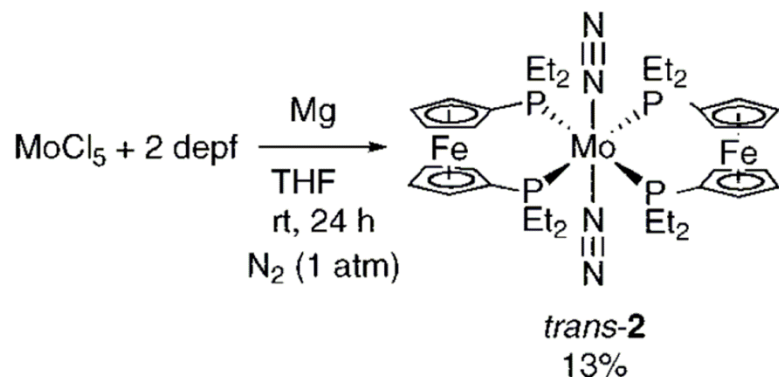
### Development of synthesis of NH<sub>3</sub> equivalent

Y. Nishibayashi *et al*, *organometalics*, **2008**, *27*, 3947.

Background: Nishibayashi's group reported chiral ferrocene complex (*ACIE*, **2006**, *45*, 3819).  
As an extension of their study, They have now envisaged the preparation of W and Mo-dinitrogen complexes bearing ferrocenyldiphosphines as auxiliary ligands.



The ratio of *cis*:*trans* = 6:1, *cis*-isomer was isolated in 19% by recrystallization



complex <sup>a</sup>	$\nu_{NN}/\text{cm}^{-1b}$	$E_{1/2}/V^c$
<i>cis</i> -W(N <sub>2</sub> ) <sub>2</sub> (depfp) <sub>2</sub> ( <i>cis</i> -1)	1972, 1906	-0.88qr
<i>cis</i> -W(N <sub>2</sub> ) <sub>2</sub> (PPhMe <sub>2</sub> ) <sub>4</sub>	1991, 1913	-0.83qr
<i>trans</i> -W(N <sub>2</sub> ) <sub>2</sub> (depfp) <sub>2</sub> ( <i>trans</i> -1)	1883	-0.95
<i>trans</i> -W(N <sub>2</sub> ) <sub>2</sub> (depe) <sub>2</sub>	1904	-0.96
<i>trans</i> -Mo(N <sub>2</sub> ) <sub>2</sub> (depfp) <sub>2</sub> ( <i>trans</i> -2)	1907	-0.97
<i>trans</i> -Mo(N <sub>2</sub> ) <sub>2</sub> (depe) <sub>2</sub>	1928	-0.97

the electron donation from each depf ligand proved to be as strong as trialkylphosphine ligands

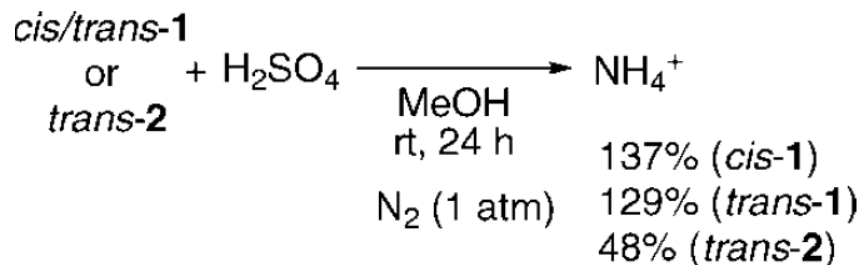
No *cis* isomer was observed at all due to fast *cis*-*trans* isomerization of molybdenum analogues.

the depf ligand has the ability of strong  $\pi$ -back-donation from the metal center to the N<sub>2</sub> ligands.

## 2.2. N<sub>2</sub> fixation using proton source

### Reactivity of new catalyst

Y. Nishibayashi *et al*, *organometalics*, **2008**, 27, 3947.

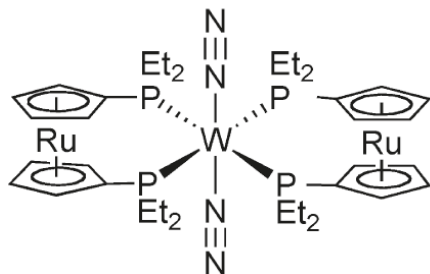


**W,Mo-dinitrogen complexes bearing conventional diphosphines such as 1,2-bis(diphenylphosphino) ethane does not produce ammonia.**

**trans-isomer is only obtained in below cases and ammonia also was generated.**

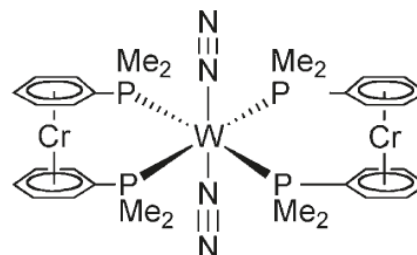
Y. Nishibayashi *et al*, *organometalics*, **2009**, 28, 4741.

Ruthenoceneyldiphosphine



Y. Nishibayashi *et al*, *organometalics*, **2009**, 28, 5821.

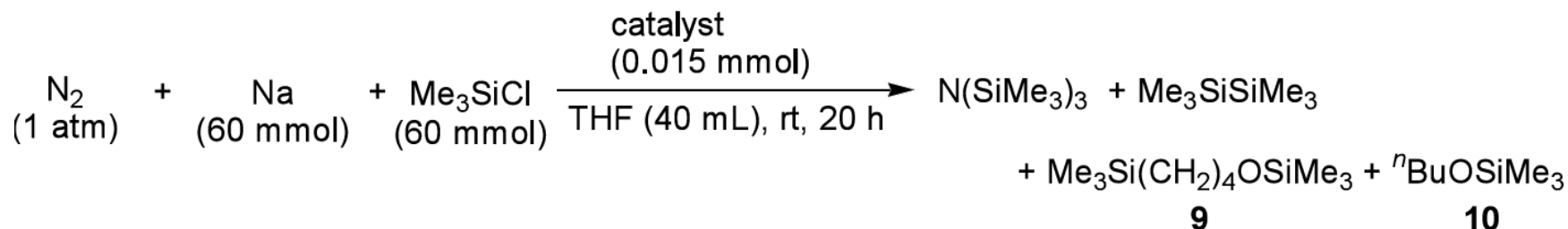
Bis(dialkylphosphinobenzene)chromiums



## 2.2. N<sub>2</sub> fixation using proton source

### Catalytic formation of silylamine from molecular dinitrogen

Y. Nishibayashi *et al*, *JACS*, **2011**, *133*, 3498.



run	catalyst	TON <sup>b</sup>	recovery of Me <sub>3</sub> SiCl (mmol) <sup>c</sup>	amount (mmol) <sup>c</sup>			
				N(SiMe <sub>3</sub> ) <sub>3</sub>	Me <sub>3</sub> SiSiMe <sub>3</sub>	<b>9</b>	<b>10</b>
1	<b>1a</b>	90	43.4	1.35	0.73	5.97	1.19
<b>10<sup>d</sup></b>	<b>1a</b>	<b>2</b>	<b>47.6</b>	<b>0.03</b>	<b>4.01</b>	<b>2.71</b>	<b>0.13</b>
11	none	0	56.1	not detected	0.62	0.18	not detected

d: the reaction was carried out under Ar

Byproducts **9**, **10** weren't seen, in using CrCl<sub>3</sub>, Mo(PMe<sub>2</sub>Ph)<sub>3</sub> in Shiina and Hidai's reports or in run **11**

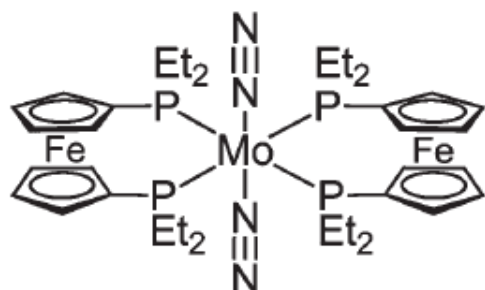
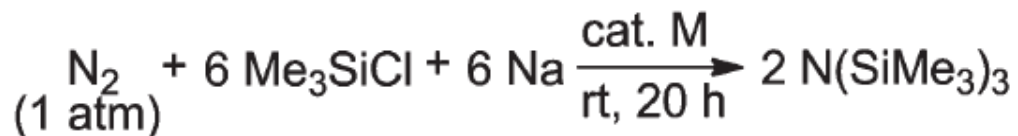
⇒ Ferrocene is key part to produce byproducts **9**, **10** derived from THF

N(SiMe<sub>3</sub>)<sub>3</sub> was formed under Ar in run **10**, but N(SiMe<sub>3</sub>)<sub>3</sub> wasn't observed under dry air

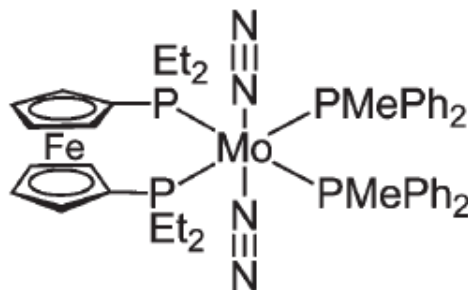
⇒ O<sub>2</sub> in the air inhibited the generation of radical species such as SiMe<sub>3</sub> radical

## 2.2. N<sub>2</sub> fixation using proton source

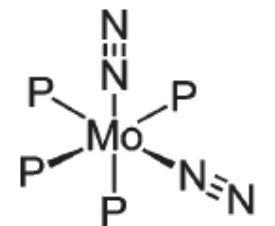
The activities of various Mo or W catalyst



90 equiv / cat.

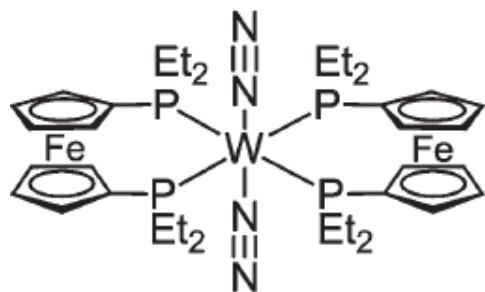


54 equiv / cat.

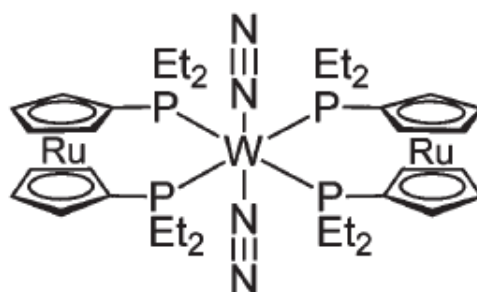


P = PMe<sub>2</sub>Ph

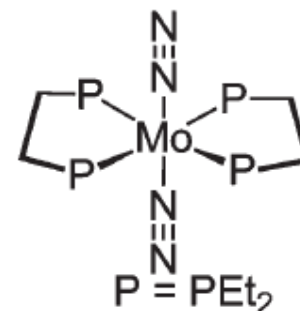
32 equiv / cat.



53 equiv / cat.



3 equiv / cat.



P = PEt<sub>2</sub>

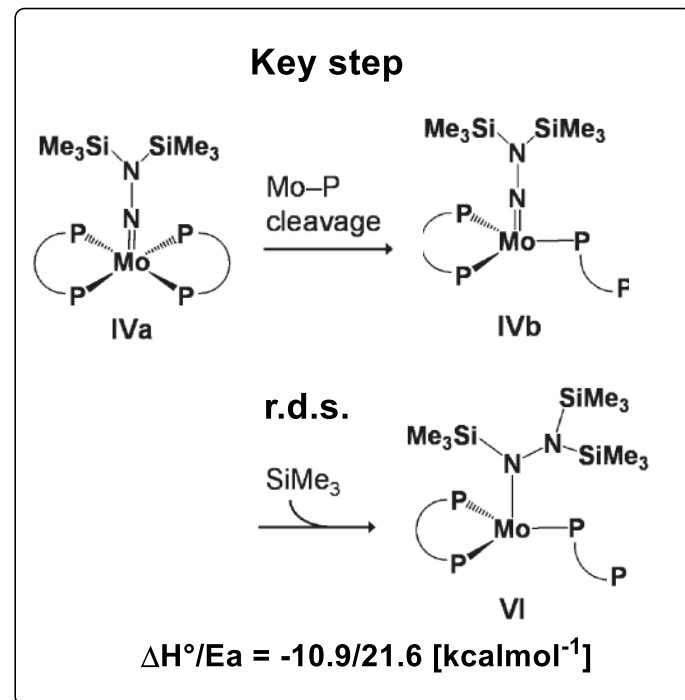
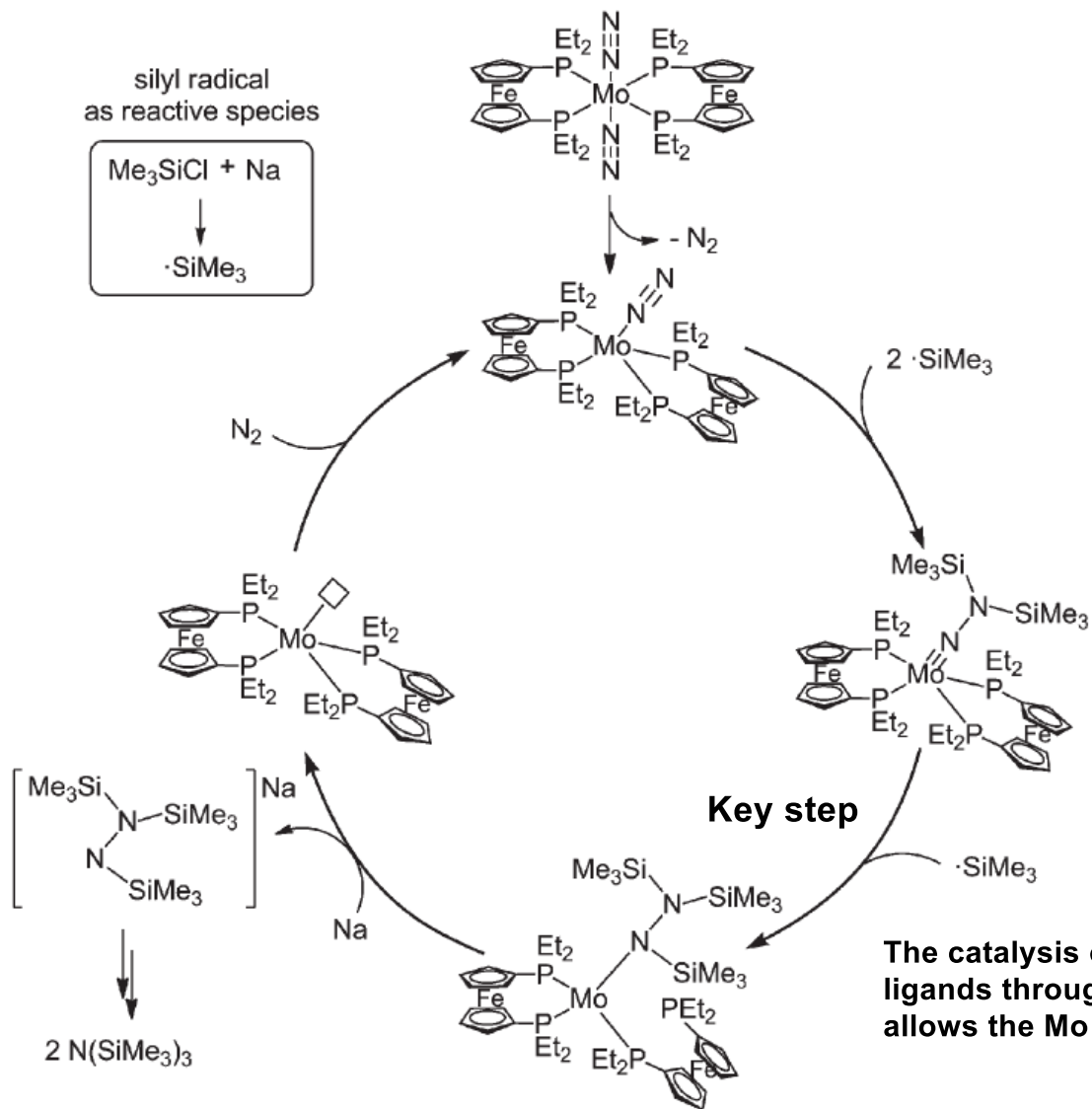
12 equiv / cat.

## 2.2. N<sub>2</sub> fixation using proton source

### Reaction mechanism

The mechanism was elucidated by DFT calculation in Fe(II) and Mo(0)

Almost all of the reaction steps proceed in an exergonic way with reasonably low activation barriers



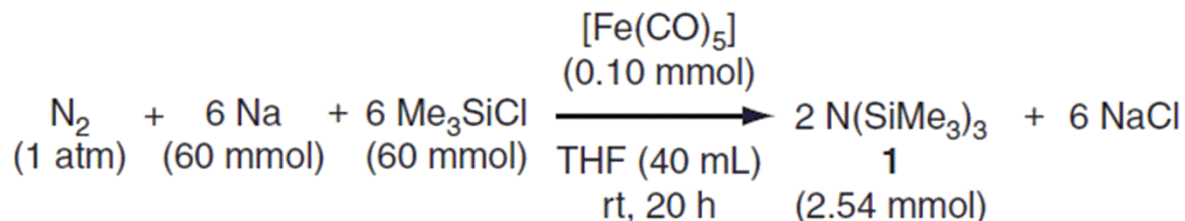
The catalysis of 1a would be sterically controlled by the depf ligands through its bulkiness and the flexible Mo-P bond that allows the Mo center to adopt various coordination numbers.



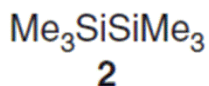
## 2.2. N<sub>2</sub> fixation using proton source

only ferrocenyl diphosphine as assistant ligand afforded a little amount of silylamine !!

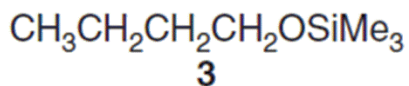
Y. Nishibayashi *et al*, Nat. commun, **2012**, 3, 1254.



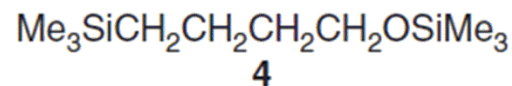
25 equiv. based on the Fe atom  
(13% yield based on Na and Me<sub>3</sub>SiCl)



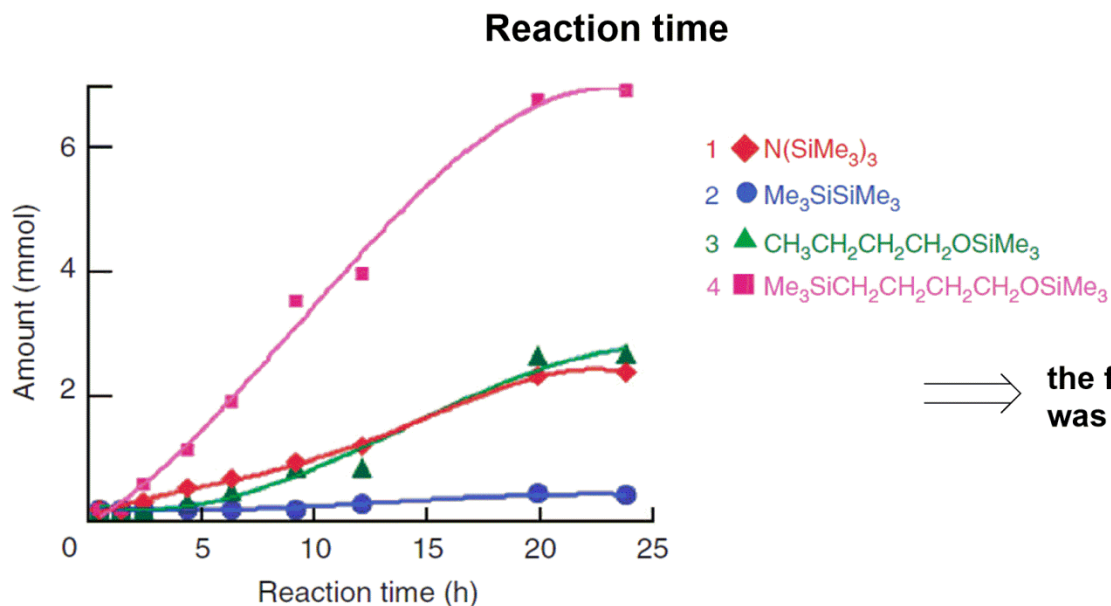
0.50 mmol



5.09 mmol



8.98 mmol



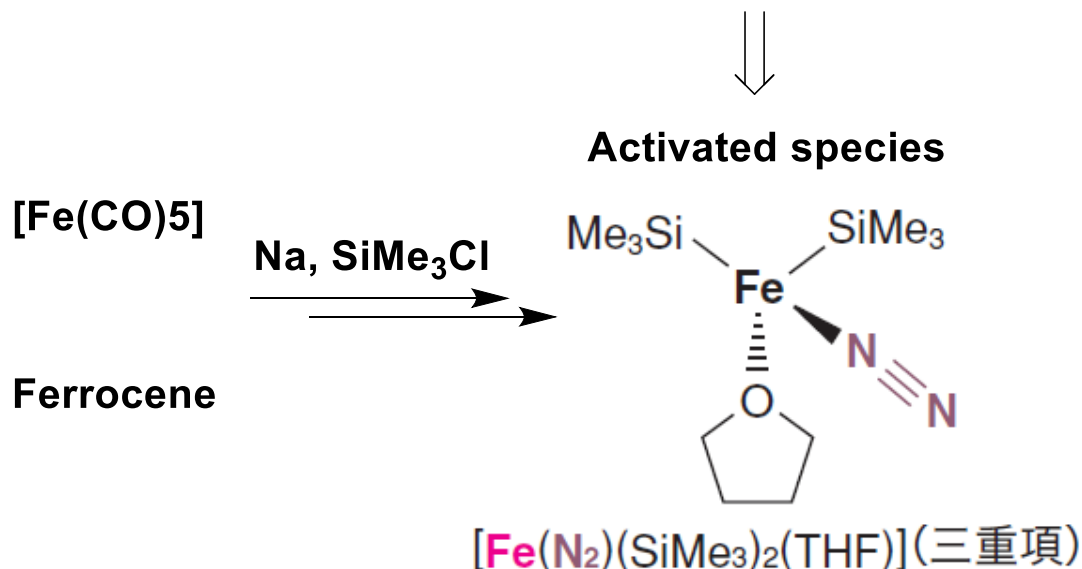
⇒ the formation of byproducts was also catalyzed by Fe cat.

## 2.2. N<sub>2</sub> fixation using proton source

### Catalytic formation of silylamine from molecular dinitrogen

1. [Fe(CO)<sub>5</sub>] and ferrocenes have almost the same catalytic activity.
2. [Fe(SiMe<sub>3</sub>)<sub>2</sub>(CO)<sub>4</sub>] worked as one of the most effective catalysts.
3. The reaction of [Na<sub>2</sub>Fe(CO)<sub>4</sub>], prepared from [Fe(CO)<sub>5</sub>] and Na, with Me<sub>3</sub>SiCl has been known to give [Fe(SiMe<sub>3</sub>)<sub>2</sub>(CO)<sub>4</sub>],
4. ferrocene with reducing agents afforded the corresponding low-valent Fe(0 or -II) complexes which may be easily converted into the Fe(II)(SiMe<sub>3</sub>)<sub>2</sub> species by treatment with Me<sub>3</sub>SiCl and/or Me<sub>3</sub>Si radical.

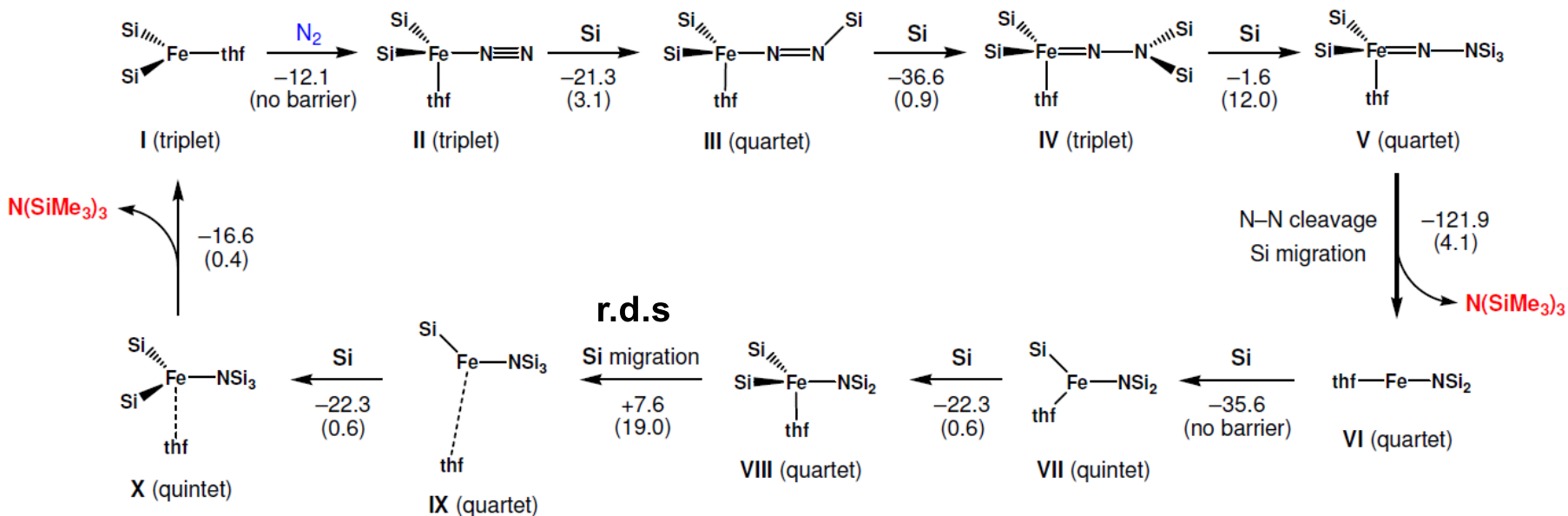
These results indicate that two Me<sub>3</sub>Si groups can readily be introduced to the Fe atom of the Fe complexes under the catalytic conditions



## 2.2. N<sub>2</sub> fixation using proton source

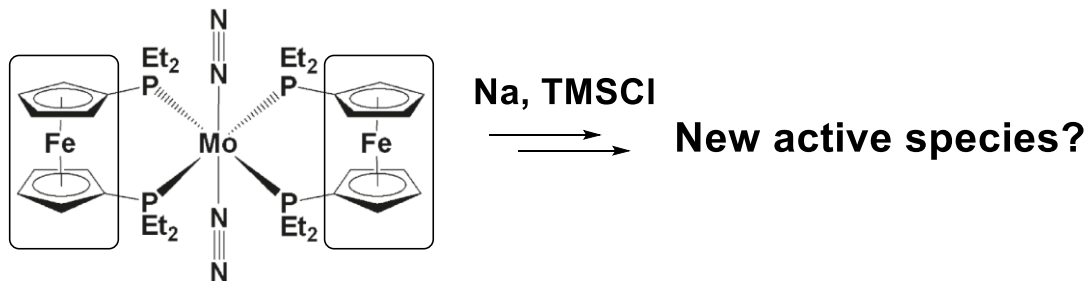
### Reaction mechanism

End on N was attacked by Si radical



It remains unclear as to why the mechanism is changed...

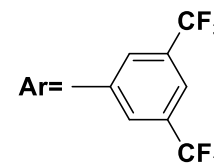
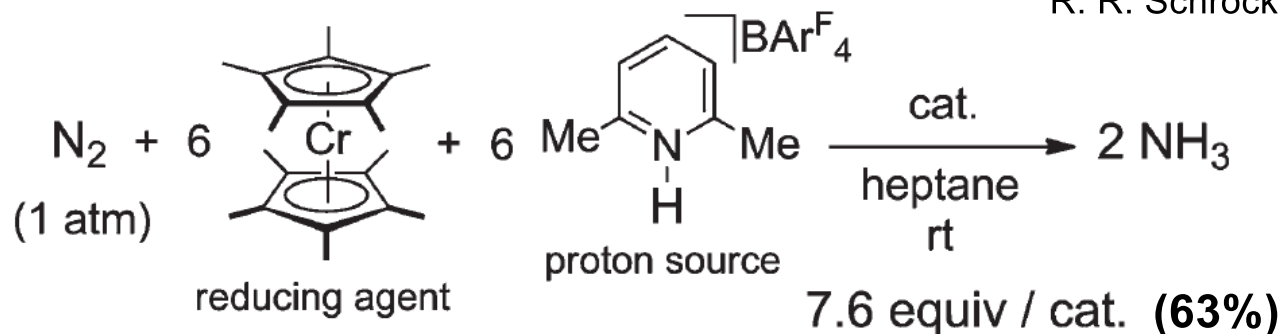
Possibly Mo-ferrocene complex also was changed to another active species ?



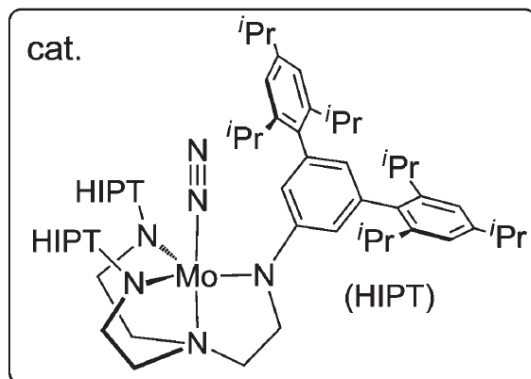
## 2.2. N<sub>2</sub> fixation using proton source

### Catalytic Reduction of Dinitrogen to Ammonia at a Single Molybdenum Center

R. R. Schrock *et al*, *Science* **2003**, 301, 76.



Until now, development of TON or yield haven't seen.....



Character of ligand :

to prevent any bimetallic reactions (aside from electron transfer).

to maximize steric protection of a metal coordination site in a monometallic species.

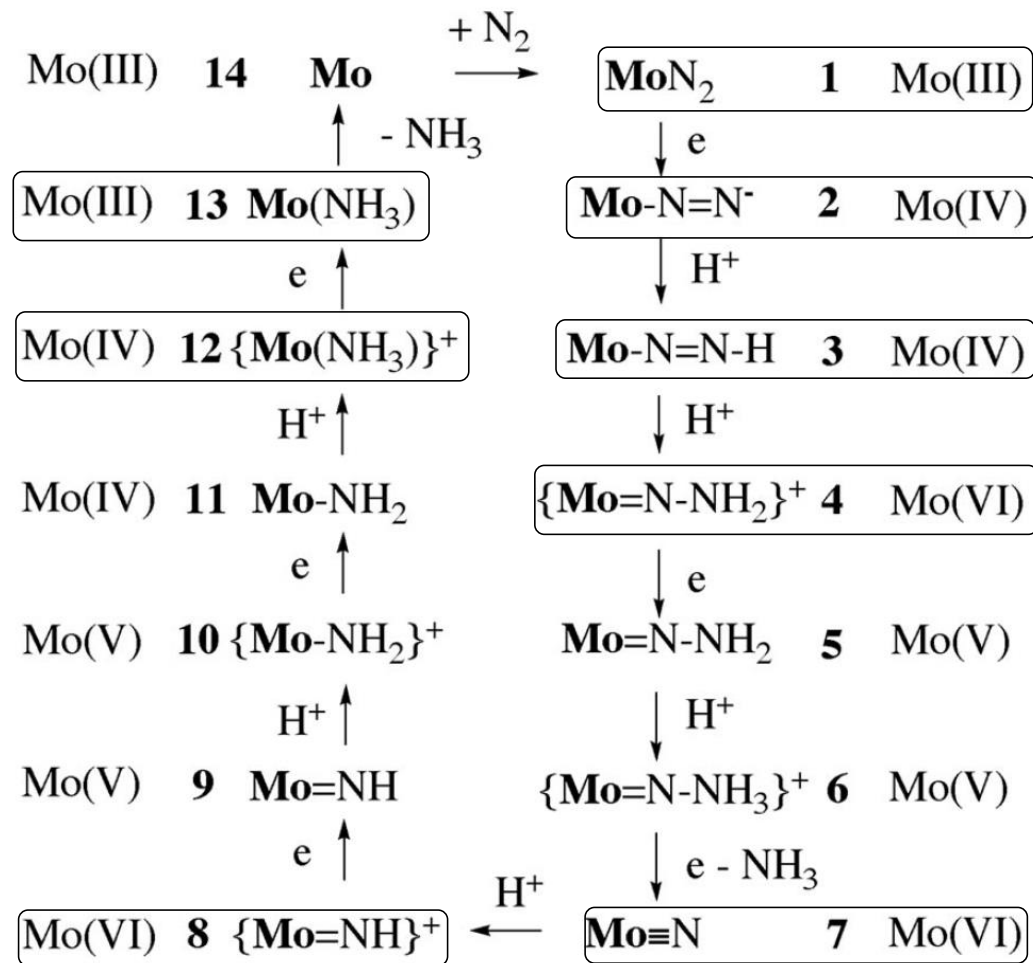
to provide increased solubility of intermediates in nonpolar solvents.

Problem : CrCp\*<sub>2</sub> was oxidized rapidly by {LutH}{BAR<sub>4</sub>} in C<sub>6</sub>D<sub>6</sub>

Solution : The choice of heptane as the solvent ensured that the concentration of sparingly soluble [LutH][BAR<sub>4</sub>] in solution would be low.

The suspension was with cat. then stirred vigorously as a solution of CrCp\*<sub>2</sub> was added with a syringe pump over a period of 6 hours.

## 2.2. N<sub>2</sub> fixation using proton source

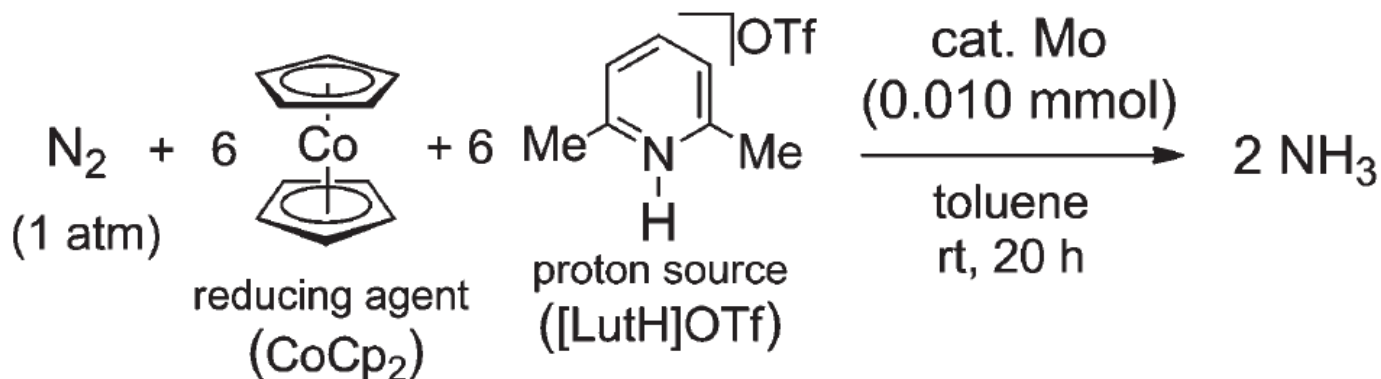


Eight of the proposed intermediates (**1**, **2**, **3**, **4**, **7**, **8**, **12**, **13**) have been isolated, with the exception of **7**, all are extremely sensitive to oxygen.  
 counter anion of **4**, **8**, **12** were  $\text{BAr}_4^-$  ( $\text{Ar} = 3,5\text{-(CF}_3\text{)}_2\text{C}_6\text{H}_3$ )

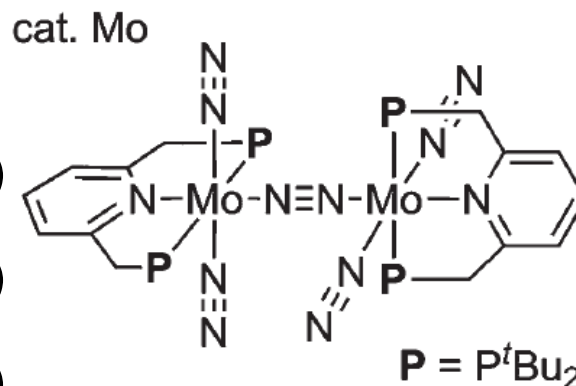
## 2.2. N<sub>2</sub> fixation using proton source

PNP-type pincer ligands leads to the catalytic reduction of dinitrogen into ammonia

Y. Nishibayashi, Nat. Chem., 2011, 3, 120



CoCp <sub>2</sub> (mmol)	[LutH]OTf (mmol)	NH <sub>3</sub> (equiv / cat.)
0.72	0.96	12 (50%)
1.44	1.92	20 (42%)
2.16	2.88	23 (32%)



Compared to Schrock's system, TON was better but yield was worse.

## 2.2. N<sub>2</sub> fixation using proton source

In the case of using another reductant and H<sup>+</sup> source

### Reductant

$\text{N}_2 \text{ (1 atm)} + 6 \text{ reductant (0.72 mmol)} + 6 \text{ [LutH]OTf (0.96 mmol)} \xrightarrow[\text{Toluene rt, 20 h}]{\text{2a (0.010 mmol)}} 2 \text{ NH}_3$				
Run	Reductant	$E_{1/2}$ (V) <sup>*</sup>	NH <sub>3</sub> (mol. equiv./2a) <sup>†</sup>	H <sub>2</sub> (mol. equiv./2a) <sup>†</sup>
1	CoCp <sub>2</sub>	-1.15	11.8	13.4
2	— <sup>‡</sup>		1.0	0.2
3	CrCp <sup>*</sup> <sub>2</sub>	-1.35	12.2	4.2
4	CrCp <sub>2</sub>	-0.88	0	0

⇒ In schrock system, CoCp is less effective reductant.

### H<sup>+</sup> source

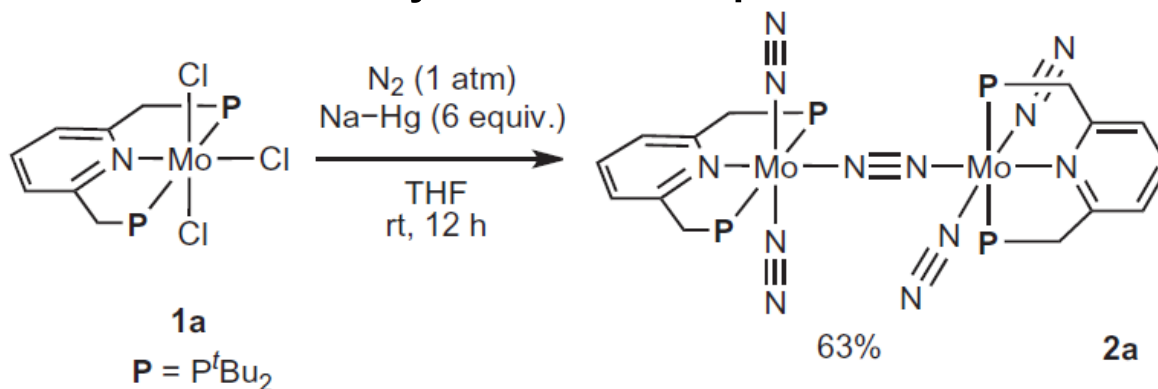
$\text{N}_2 \text{ (1 atm)} + 6 \text{ CoCp}_2 \text{ (0.72 mmol)} + 6 \text{ HX (0.96 mmol)} \xrightarrow[\text{Toluene, rt, 20 h}]{\text{2a (0.010 mmol)}} 2 \text{ NH}_3$				
Run	HX (proton source)	$pK_a$ <sup>*</sup>	NH <sub>3</sub> (mol. equiv./2a) <sup>†</sup>	H <sub>2</sub> (mol. equiv./2a) <sup>†</sup>
1	[LutH]OTf	14.4	11.8	13.4
2	— <sup>‡</sup>		0	0
3	[LutH]BAr' <sub>4</sub>	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

⇒

OTf anion in the proton source promotes the reaction, proton source with high acidity worked as less effective proton sources.

## 2.2. N<sub>2</sub> fixation using proton source

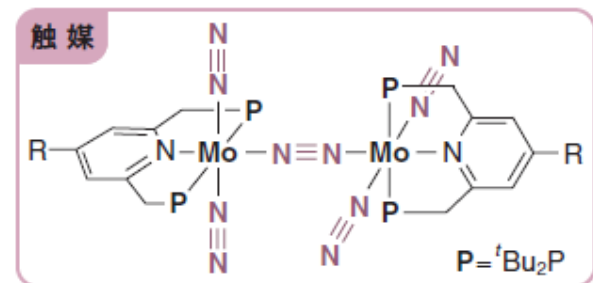
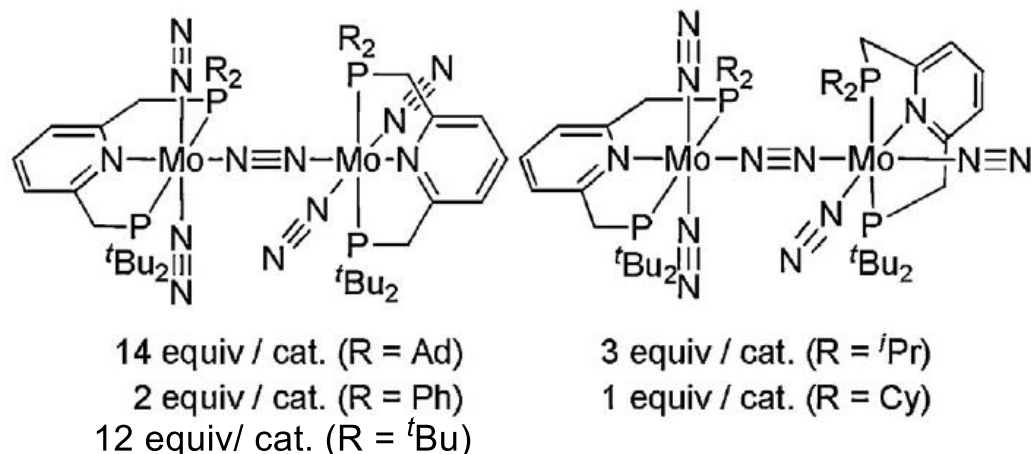
### Synthesis of complex



In the case of P = P<sup>i</sup>Pr<sub>2</sub>, P = 1-adamantyl<sub>2</sub>P, the complex wasn't formed

### Complexes bearing unsymmetric PNP-type pincer ligands

Y. Nishibayashi *et al*, *Organometallics*, **2012**, 31, 8437.



触媒当たり23当量のアノモニアが生成 (R=H)  
触媒当たり52当量のアノモニアが生成 (R=OMe)

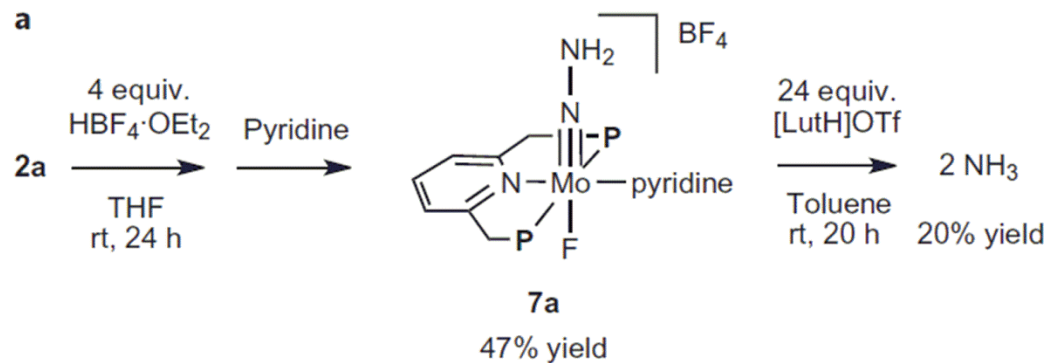
Kagakudojin, *Chemistry*, **2013**, 6, 37.

- ♣ Unsymmetric Ad ligand contributed to increasing of TON.
- ♣ 4-substituent in pyridine play critical role to increase TON.

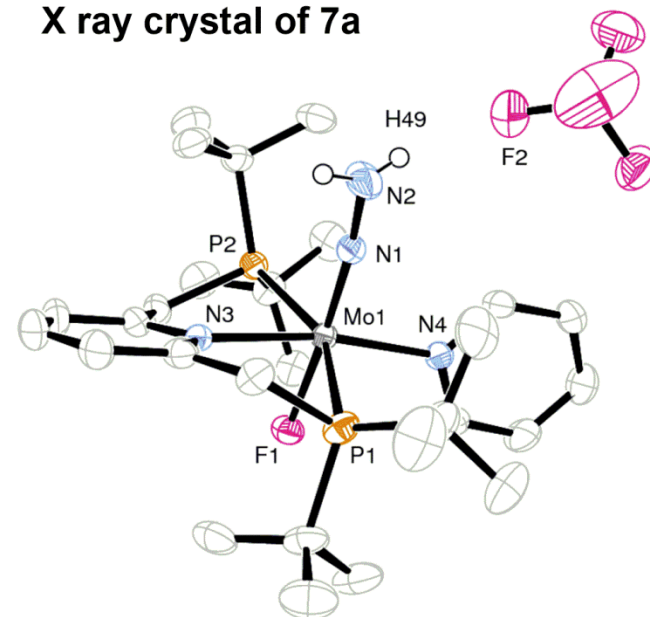


## 2.2. N<sub>2</sub> fixation using proton source

Stoichiometric reaction to obtain information on the reaction pathway



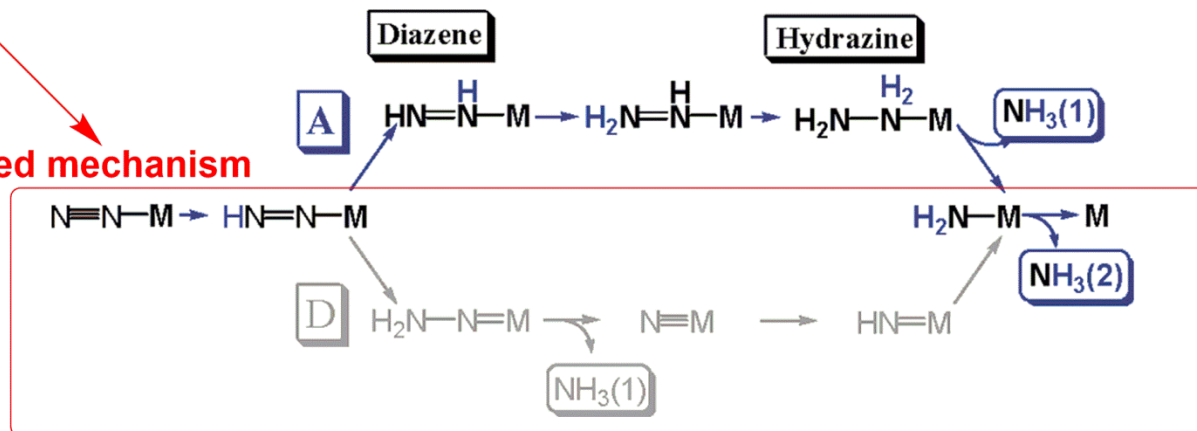
X ray crystal of 7a



Hydrazido complex 7a was obtained in proton only. NH<sub>3</sub> was generated from 2a via formation of 7a

→ In the catalytic cycle, hydrazide complex was also formed as intermediate

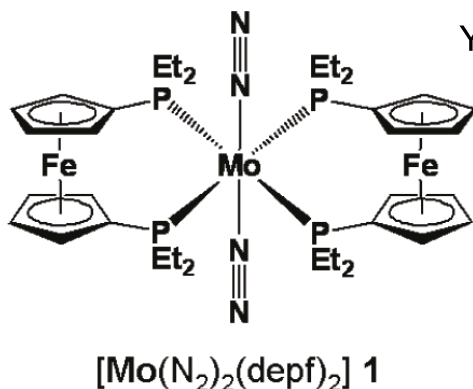
Proposed mechanism



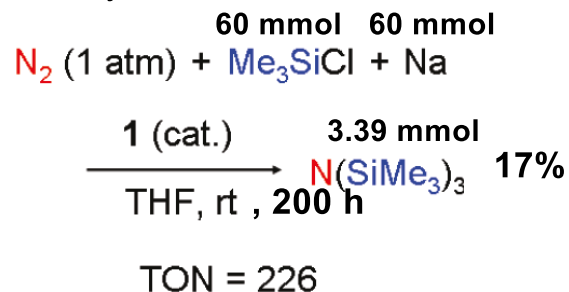
## 2.2. N<sub>2</sub> fixation using proton source

### Short Summary 2.2.

Compared to N<sub>2</sub> fixation using H<sub>2</sub>, catalytic reaction has been developed. Shown below scheme is highest performance of TON in synthesis of NH<sub>3</sub> equivalent



Y. Nishibayashi *et al*, *JACS*, **2011**, 133, 3498.



on the other hand....

Schrock, Nishibayashi's groups has been reported catalytic N<sub>2</sub> fixation using metallocene as reductant, organic acid as proton source recently.



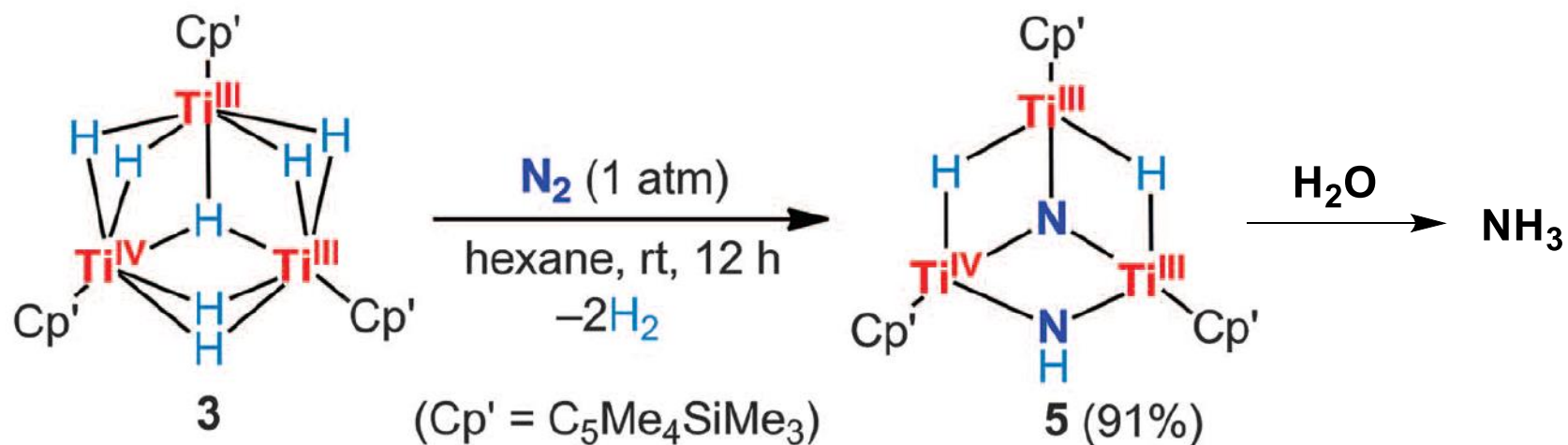
To industrialize.....

The ideal system is to use H<sub>2</sub>O as proton source, electron from electricity as reductant !

## 2.3 N<sub>2</sub> fixation using polyhydride complex

### Dinitrogen Cleavage and Hydrogenation by a Trinuclear Titanium Polyhydride Complex

Z. Hou *et al*, *Science* **2013**, *340*, 1549.



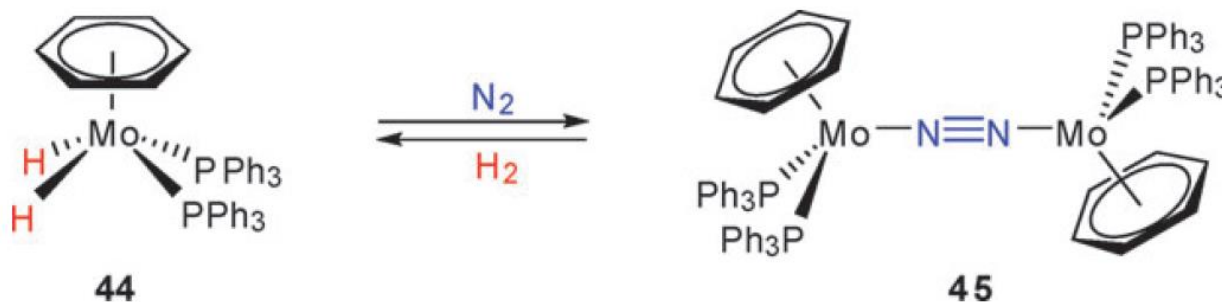
**Metal hydrides cleave N<sub>2</sub> triple bond !!**

## 2.3 N<sub>2</sub> fixation using polyhydride complex

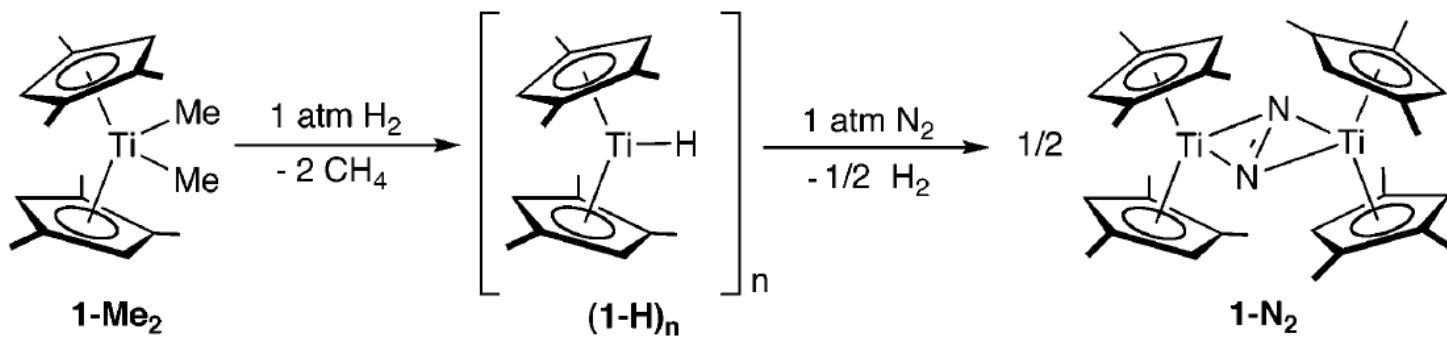
### Precedents of reactivity of metal hydride complexes toward N<sub>2</sub>

D. Fryzuk *et al*, *Chem. Commun.* **2010**, 46, 1013.

Reversible equilibrium between MoH<sub>2</sub> complex and dinuclear N<sub>2</sub> derivative - W. E. Silverthorn (1971)



Formation of diazene complex via Ti hydride complex - P. J. Chirik (2007)

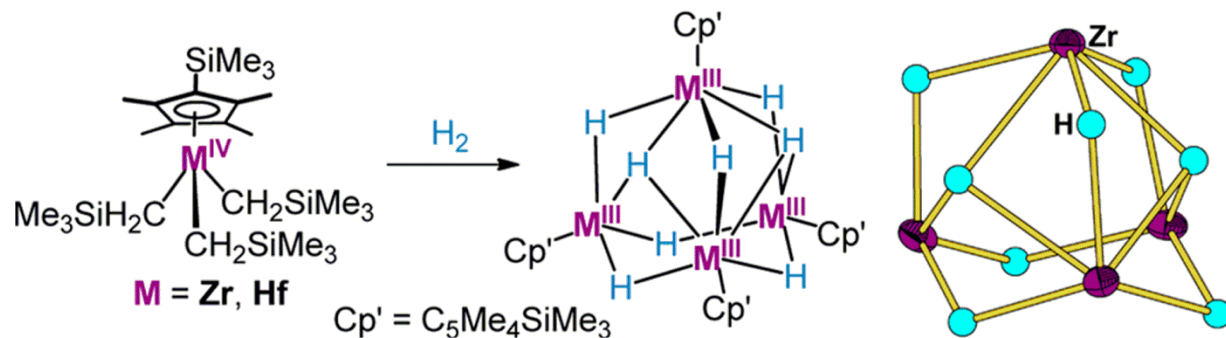


The hydride of M-H complex hasn't been incorporated to N<sub>2</sub>.

## 2.3 N<sub>2</sub> fixation using polyhydride complex

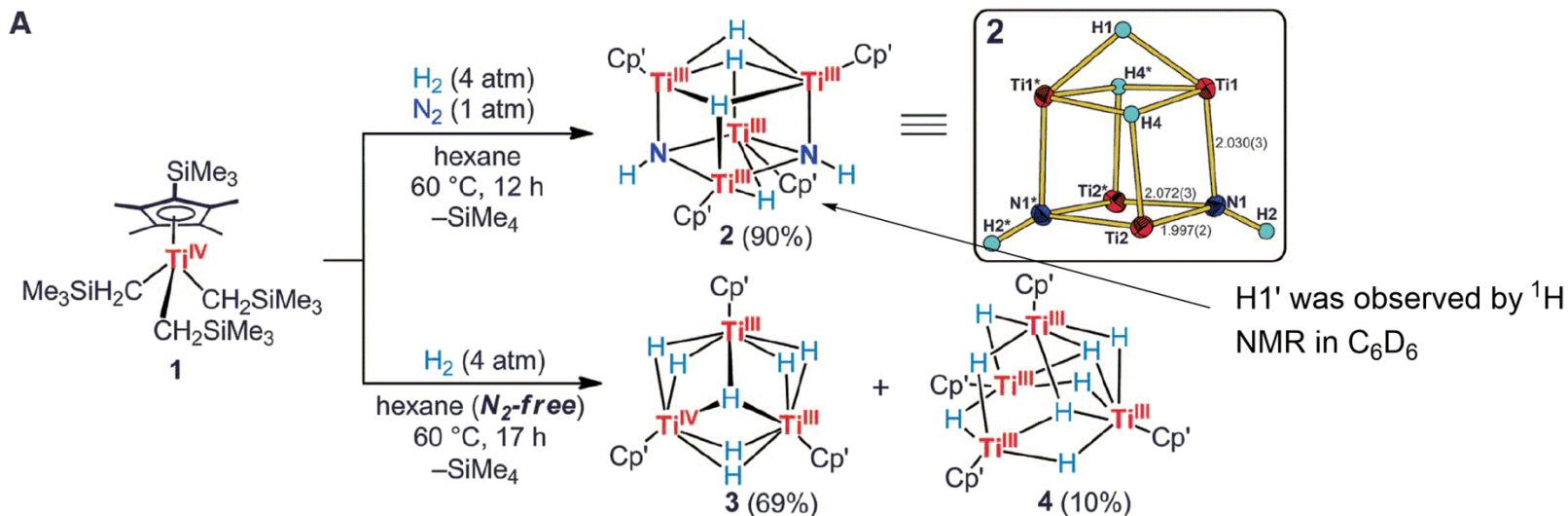
### Tetranuclear Zirconium and Hafnium polyhydride complexes

Z. Hou *et al*, *Organometallics*, 2013, 32, 2145.



Motivation: [Cp<sub>2</sub>MH<sub>n</sub>] (n=1, 2) complex in group 4 transition metal have been extensively reported. On the other hand, half-sandwich type [CpMH<sub>n</sub>] have hardly been studied.

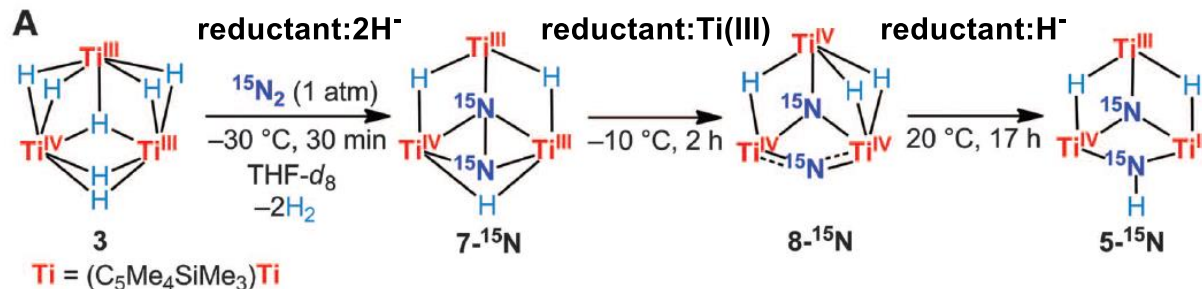
In an attempt to synthesize a titanium analog, Ti complex with N<sub>2</sub> (in glove box) was formed.



tetranuclear Ti, Zr, Hf complex didn't react with N<sub>2</sub>.

## 2.3 N<sub>2</sub> fixation using polyhydride complex

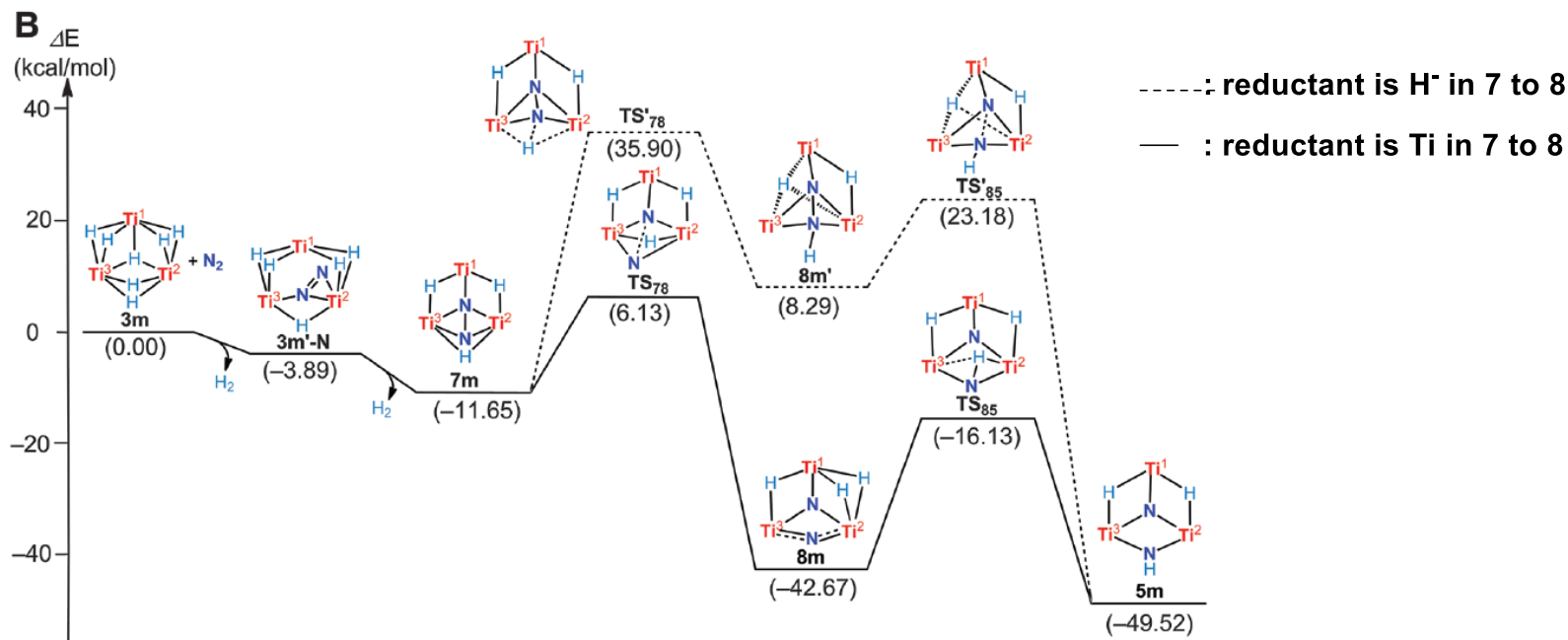
Observed intermediates with <sup>15</sup>N<sub>2</sub> by <sup>1</sup>H and <sup>15</sup>N NMR spectroscopy



the difference of valence in Ti(IV) and Ti(III) play a critical role to reduce N<sub>2</sub>

1. LUMO orbital of Ti(IV) activate HOMO orbital of N<sub>2</sub>
2. H<sup>-</sup> between Ti(IV) and Ti(III) have high reductive potential for polarization

DFT calculated energy profile for the reaction of 3m with N<sub>2</sub>

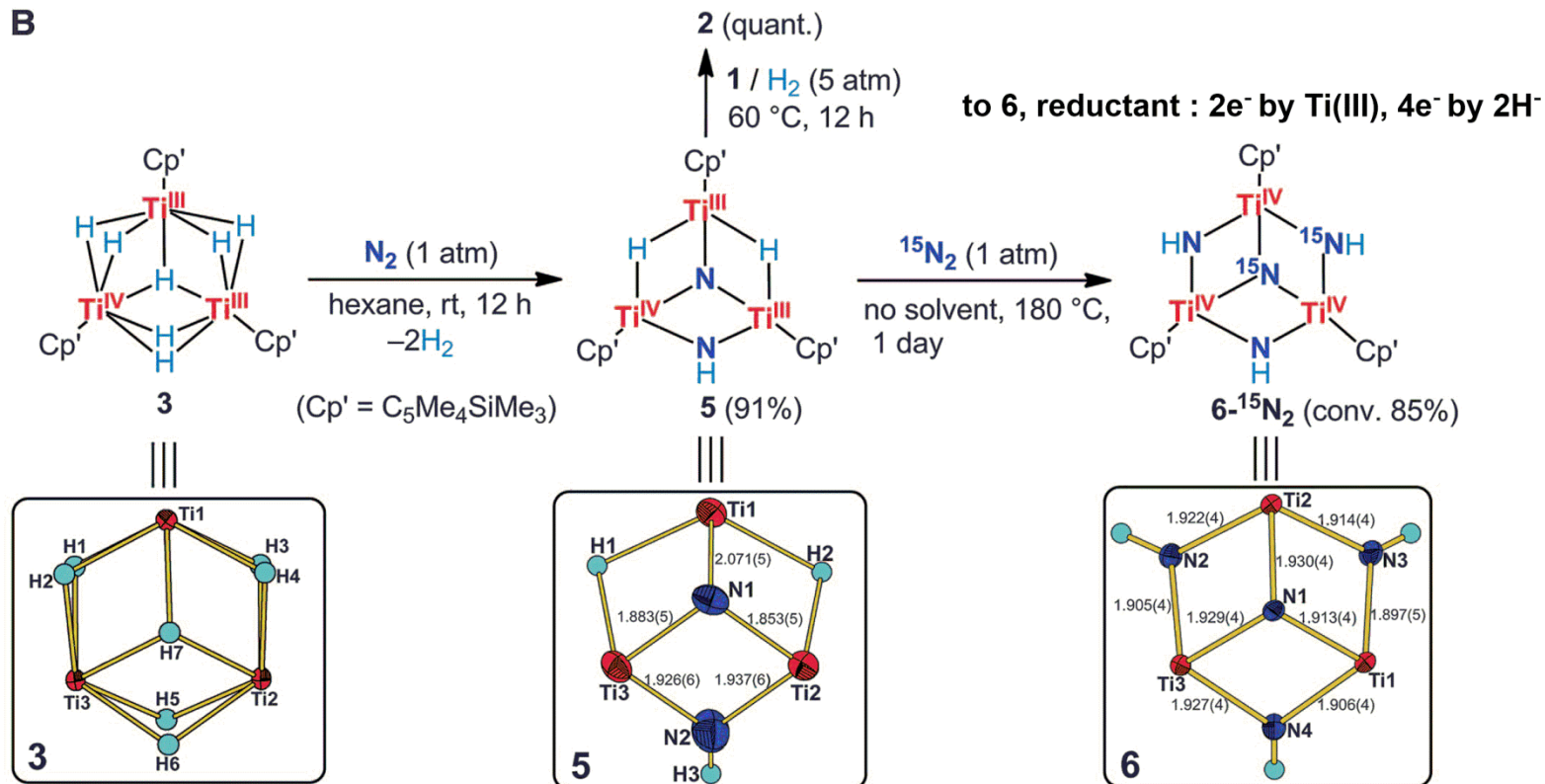


the cleavage of N-N bond and formation of N-H bond have higher energy barriers than other steps.

## 2.3 N<sub>2</sub> fixation using polyhydride complex

### Reactivity of Ti complex

B



- ♣ No apparent reaction between 5 or 6 and H<sub>2</sub> (up to 8 atm) was observed at room or higher temperatures (up to 150 °C).
- ♣ when the hydrogenolysis of 1 with H<sub>2</sub> was carried out in the presence of 1 equiv of 5, 2 was formed quantitatively through generating Ti hydride species such as Cp'TiH<sub>3</sub> formed in situ by hydrogenolysis of 1



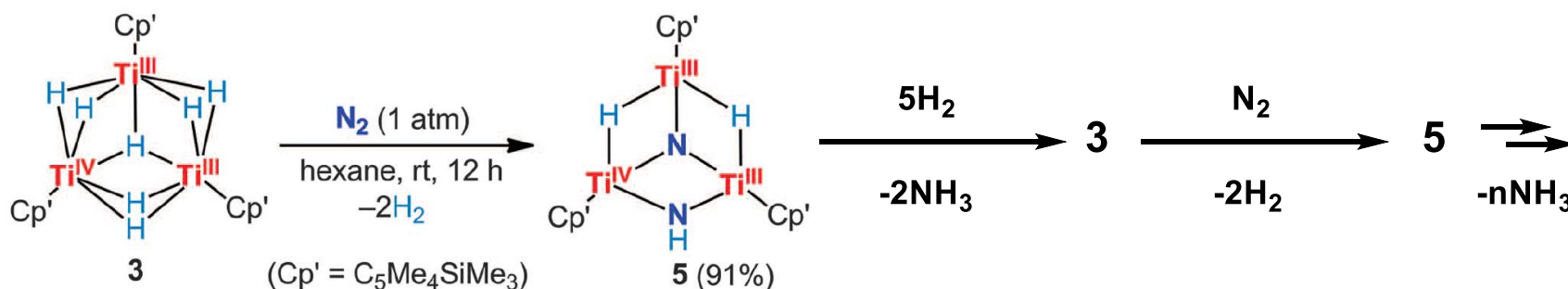
## 2.3 N<sub>2</sub> fixation using polyhydride complex

### Short Summary 2.3.

Hou's report is maybe breakthrough to conduct catalytic N<sub>2</sub> fixation using H<sub>2</sub> under mild condition.

Until now, H-H bond has been cleaved by metal complex which activated N<sub>2</sub> to generate NH<sub>3</sub>. On the other hand, this report is the reversed strategy.

Desirable cycle will work if Ti-N bond of 5 is cleaved by H<sub>2</sub>.....

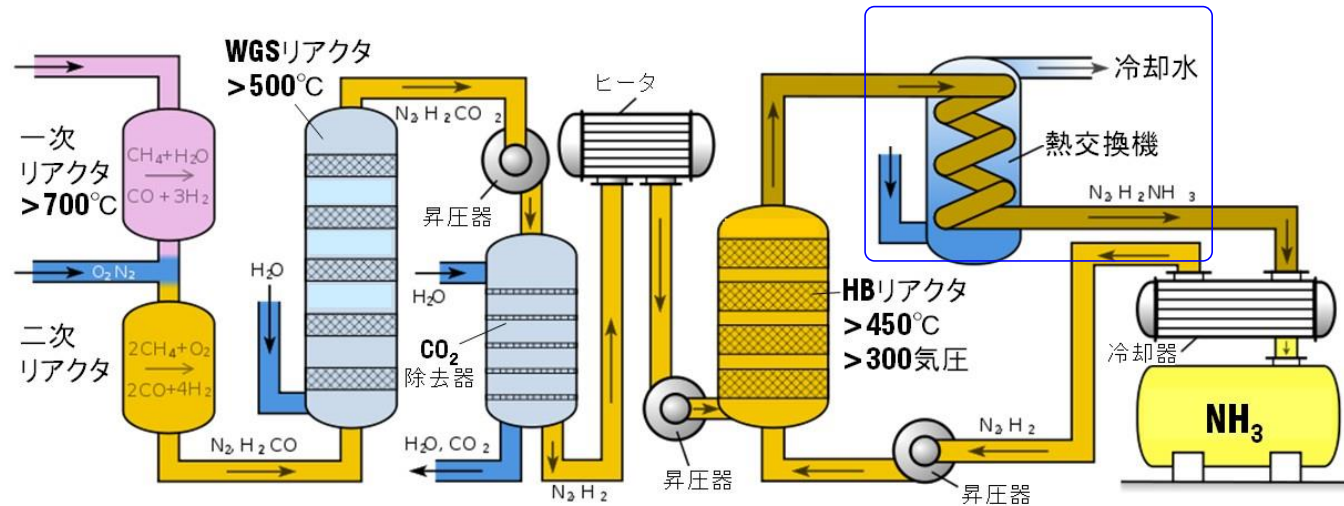




### 3. Application of NH<sub>3</sub> in the future

If these reserchs are developed, low temperture and pressure process would replace industrial Harbor-Bosh process immediately ??

#### Industrial process



**New problem: Under low pressure, freezing system is needed for liquefaction of NH<sub>3</sub> in the plant**



N<sub>2</sub> fixation under mild condition don't need large-scale plant

**Low temperature and pressure process would be suitable in nitrogen fixation in small-scale and distributed type**



### 3. Application of NH<sub>3</sub> in the future

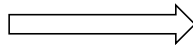
#### Toward Realization of Clean Energy Industry

R.G.Compton et al, *Energ. Environ. Sci.* **2011**, 4, 1255.

S. Tao et al, *Int. J. Hydrogen Energ.* **2012**, 37, 1482.

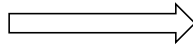
#### Desirable energy

Primary Energy



**Renewable sources**

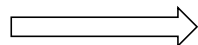
Secondary Energy  
(Energy Carrier)



**Carbon free energy**  
**Hydrogen, NH<sub>3</sub> (L. Green Jr. in 1982)**

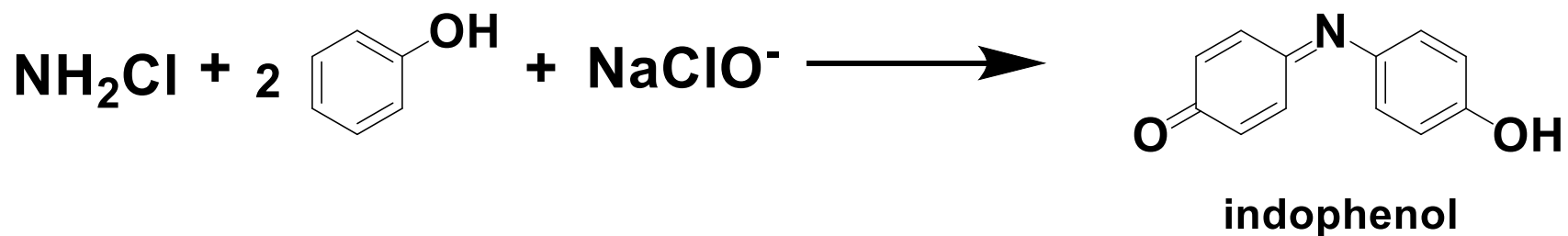
*J Hydrog Energy*, **1982**, 7, 355

While the introduction of a hydrogen economy has its merits (**stockale**, **clean**), the associated problems with on-board **hydrogen storage** are still a barrier to implementation.....



**NH<sub>3</sub> is good storage of H<sub>2</sub> because of easy storage, containing 17.6 wt% H<sub>2</sub>, prepared infrastructure !!!**

indophenol blue method to measure the yield of  $\text{NH}_3$



By measuring absorbance of indophenol, the yield is determined