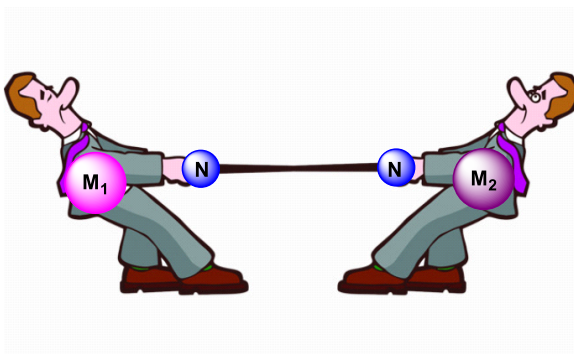




Seminar

Multimetallic Complexes Applied in Dinitrogen Fixation



Reporter: Yifei Huang

Major: Organic Chemistry

Tutor: Professor Zhangjie Shi



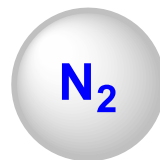
Content

- **Background**
- **Dinitrogen Fixation Through Multimetallic Complexes Supported by Bridged Ligand**
- **Summary and Outlook**

Background—Significance of N₂ Fixation

'N' Element Presents in:

- Organic: R-NH₂, R-NO₂...
- Inorganic: NH₃, HNO₃...
- Life: Protein, Nucleic Acid...



Abundant in Air

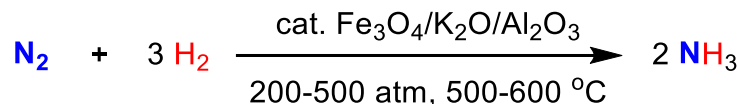
Difficulties in N₂ Fixation:

- Nonpolar Molecular
- Bond Dissociation Energy: 944 kJ/mol
- Ionization Potential: 15.6 eV
- HOMO-LUMO Gap: 10.82 eV

Most Organisms Lack the Ability to Metabolize N₂

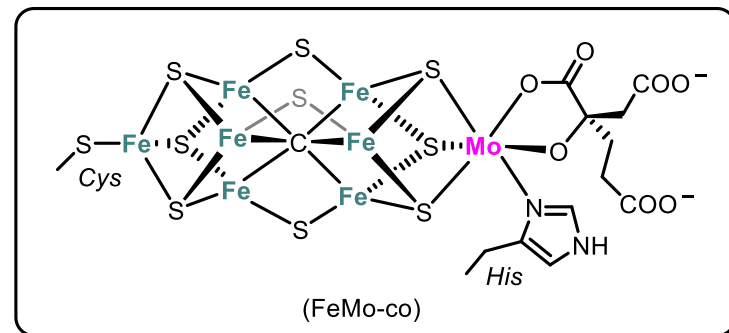
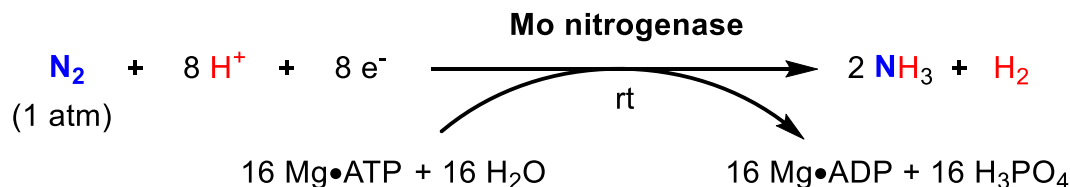
Haber-Bosch Process

The greatest invention of the 20th century



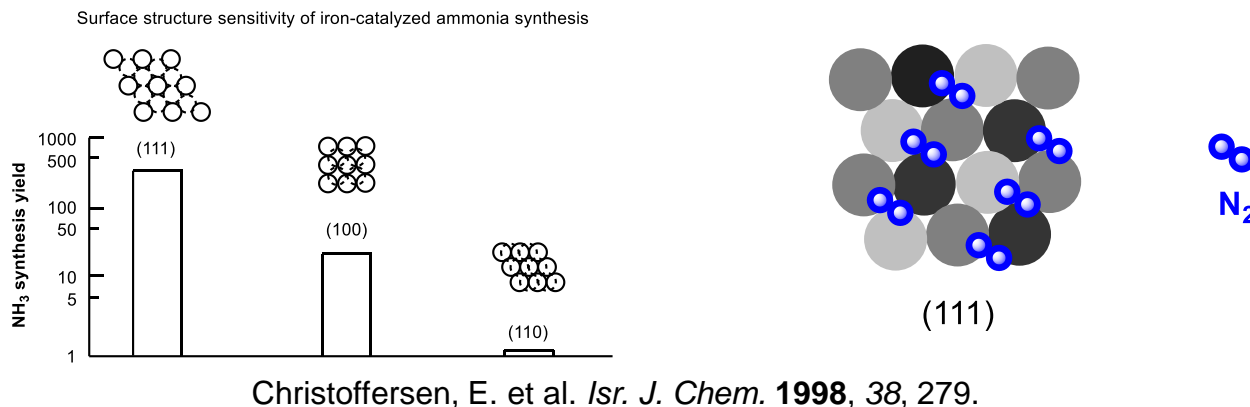
von Laue, M. *Naturwissenschaften*, **1934**, 22, 97; Boudart, M. *Top. Catal.* **1994**, 1, 405.

Biological Nitrogen Fixation

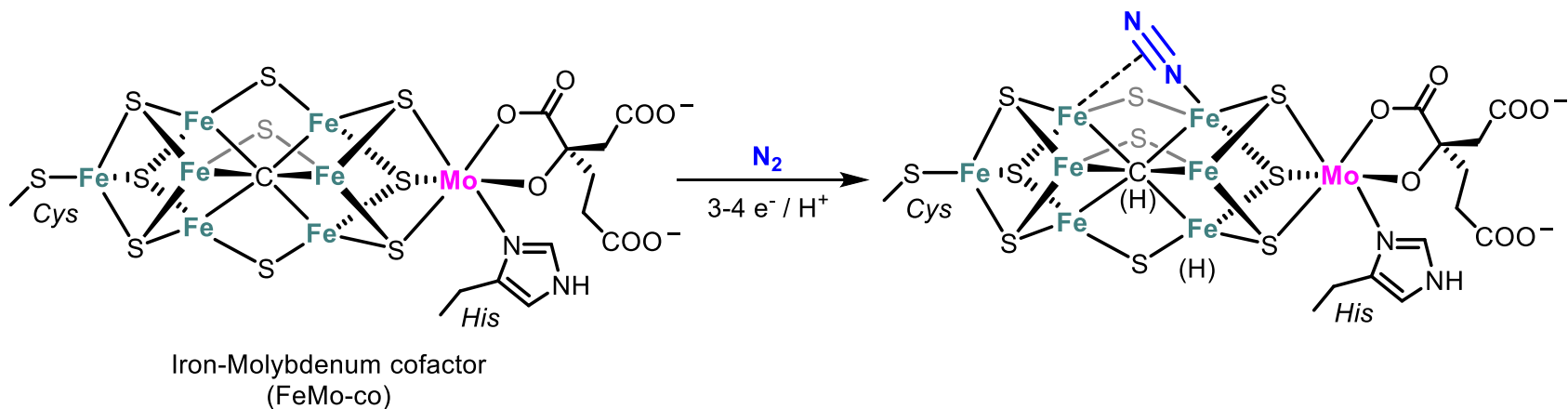


Background—Significance of Multimetallic Cooperation

Coordination Mode of N₂ in Haber-Bosch Process



Coordination Mode of N₂ in FeMo-co

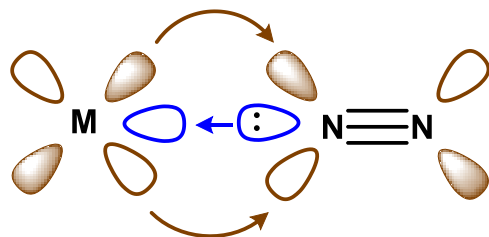


Spatzal, T. et al. *Science* **2014**, 345, 1620.

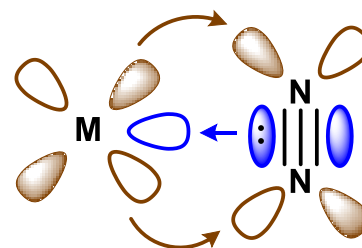
Background—General Dinitrogen Coordination Mode

Activation Modes of N₂ fixation through Transition Metals

end-on activation mode

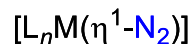


side-on activation mode

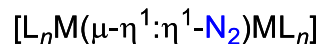
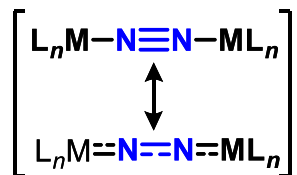


Coordination Modes of N₂ with Metals

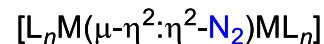
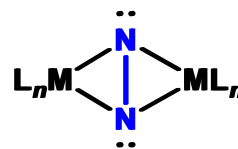
Terminal end-on



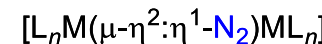
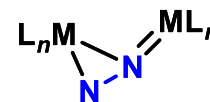
End-on bridging



Side-on bridging

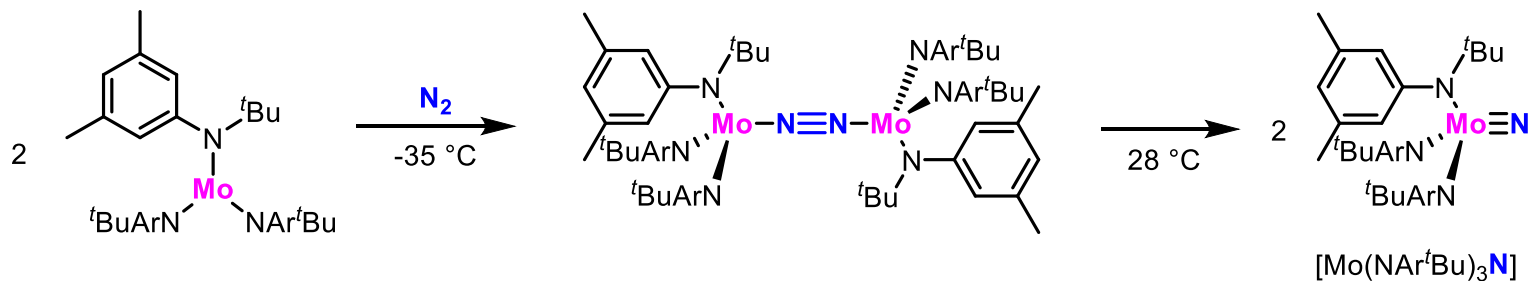


Side-on/end-on bridging



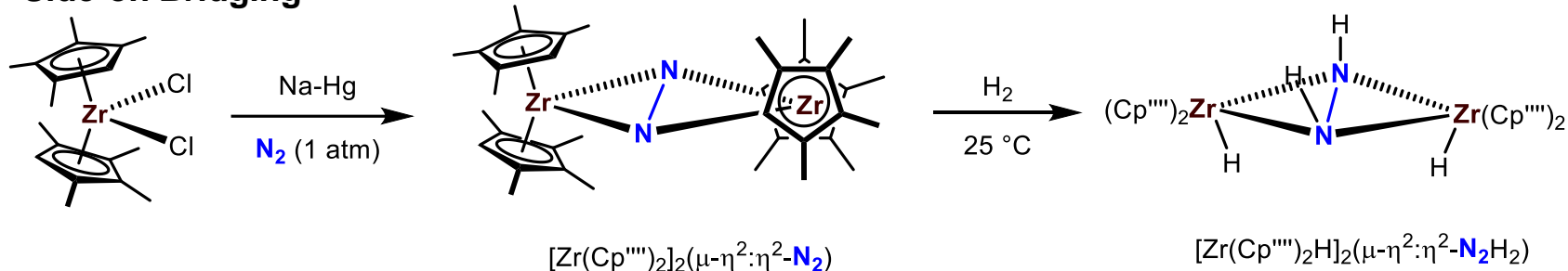
Background—Multimetallic Cooperation in Dinitrogen Fixation

End-on Bridging



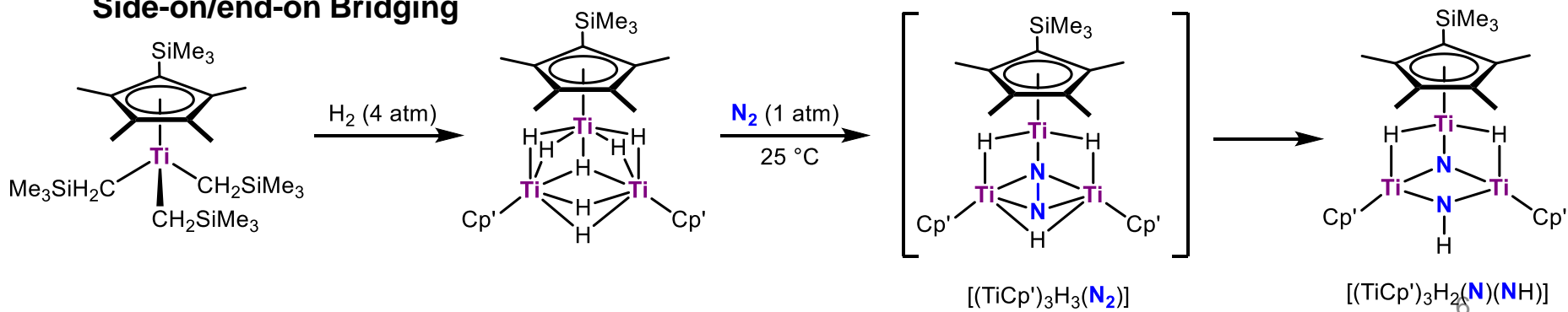
Cummins, C. C. et al. *Science* **1995**, 268, 861.

Side-on Bridging



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

Side-on/end-on Bridging



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

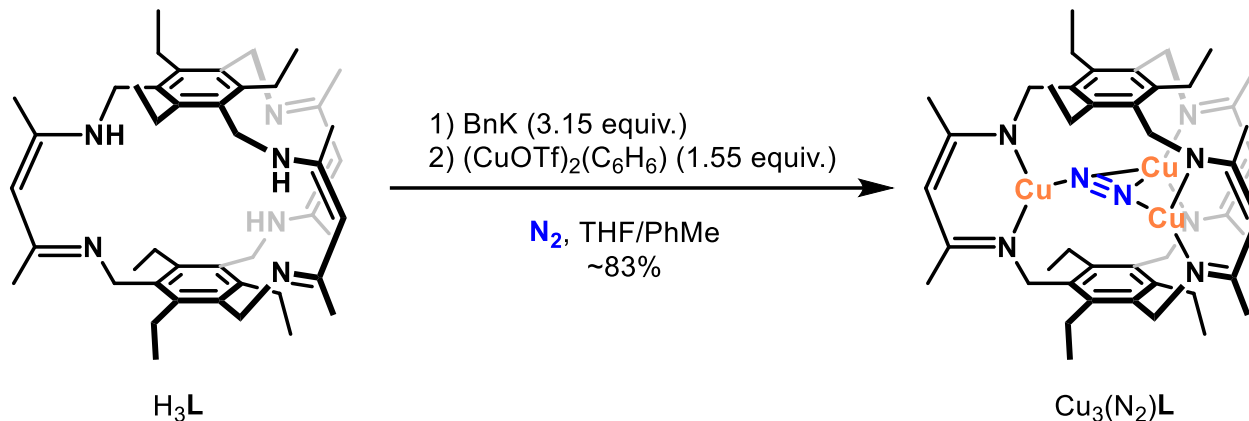


Content

- Background
- **Dinitrogen Fixation Through Multimetallic Complexes Supported by Bridged Ligand**
- Summary and Outlook

Triscopper Complexes Supported by Tris(β -diketimine) Cyclophane Ligand

Murray's Work:



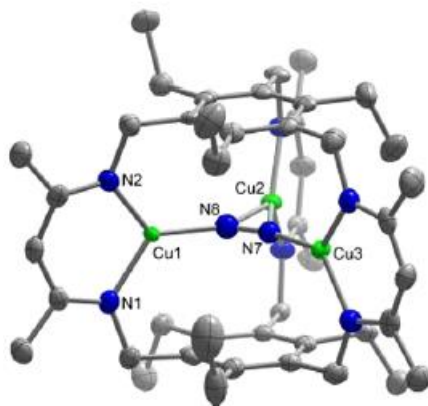
N₂ coordination mode:

μ - η^1 : η^2 : η^1

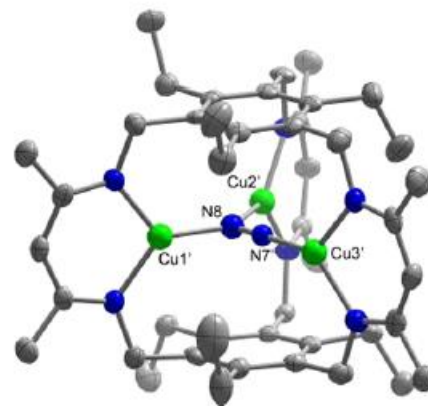
Length of N-N bond:

1.0956(1) Å

(Free N₂: 1.0976 Å)



higher (left, 75%) lower (right, 25%) occupancy positions of N7



N₂ coordination mode:

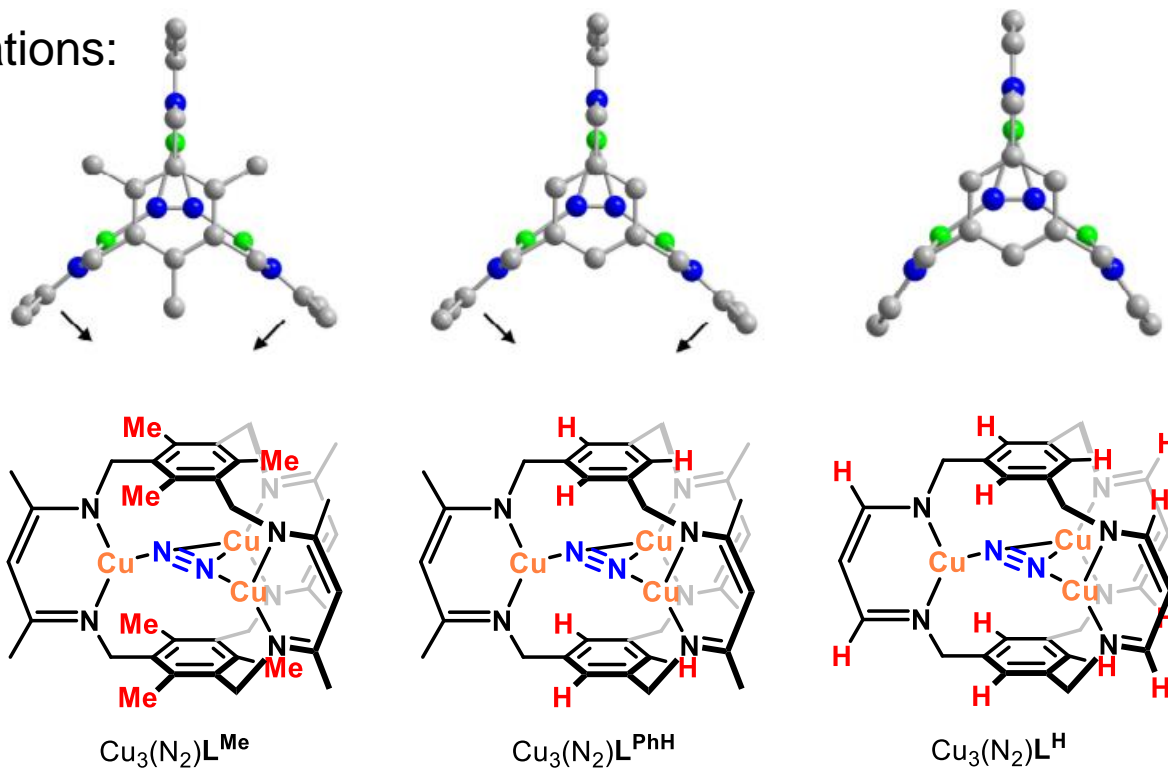
μ - η^1 : η^1 : η^1

Length of N-N bond:

1.0854(1) Å

Triscopper Complexes Supported by Tris(β -diketimine) Cyclophane Ligand

DFT Calculations:

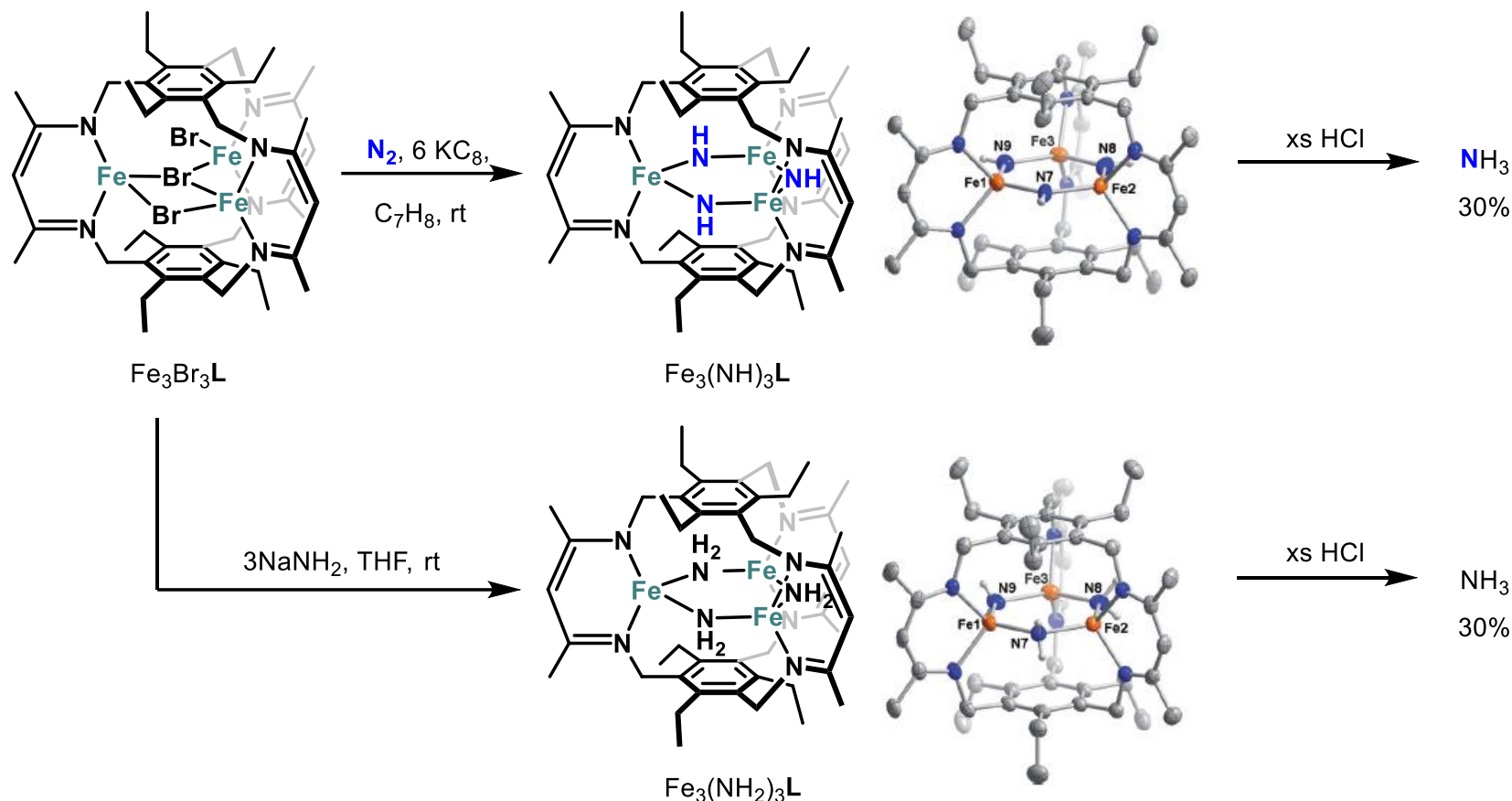


N-N Length	1.125 Å	1.167 Å	1.168 Å
N_2 Stretching frequencies	2094.3 cm^{-1}	1951.5 cm^{-1}	1937.2 cm^{-1}

The solution structure likely adopts more activated configuration(s) than the solid-state one.

Trisiron Complexes Supported by Tris(β -diketimine) Cyclophane Ligand

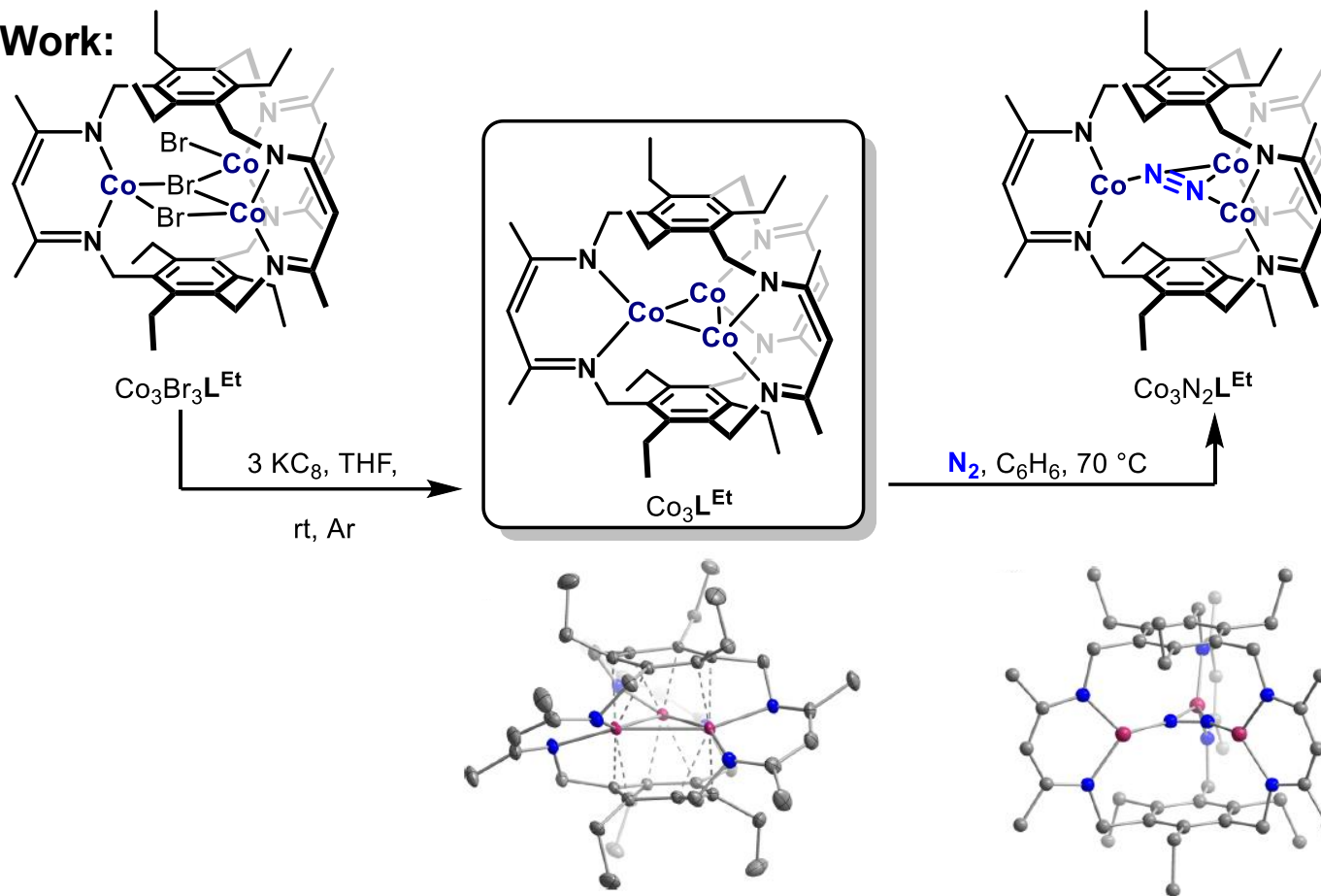
Murray's Work:



The presence of NH group but not OH group is demonstrated by ^{15}N labeled experiment and elemental analysis.

Triscobalt Complexes Supported by Tris(β -diketimine) Cyclophane Ligand

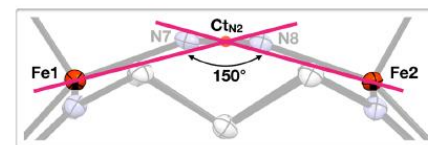
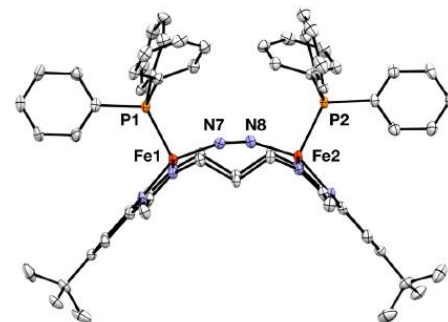
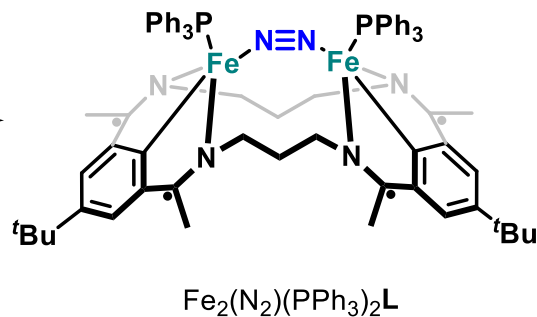
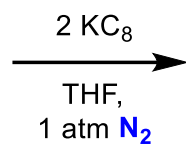
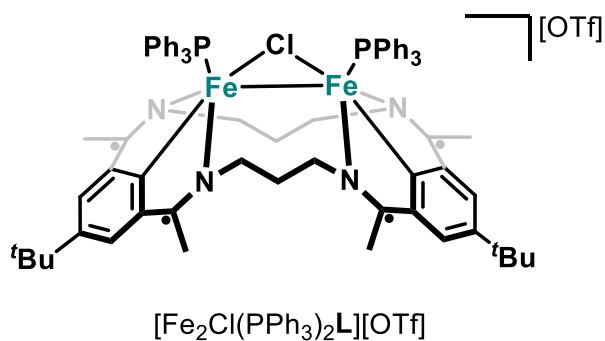
Murray's Work:



N_2 Stretching frequency of $\text{Co}_3\text{N}_2\text{L}^{\text{Et}}$: 1717 cm^{-1} (vs 2094.3 cm^{-1} of $\text{Cu}_3\text{N}_2\text{L}^{\text{Me}}$)
Unlike $\text{Cu}_3\text{N}_2\text{L}^{\text{Et}}$, $\text{Co}_3\text{N}_2\text{L}^{\text{Et}}$ is stable under vacuum or Ar without N_2 dissociation.

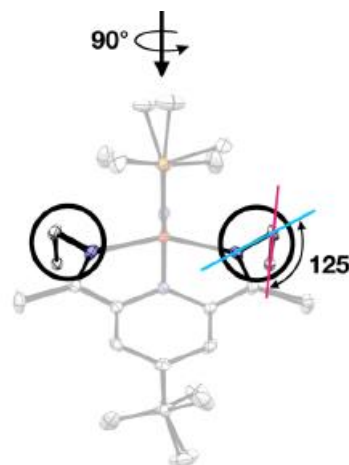
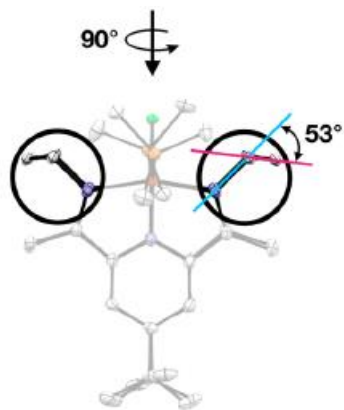
Diiron Complexes Supported by ${}^3\text{PDI}_2$ Ligand

Tomson's Work:



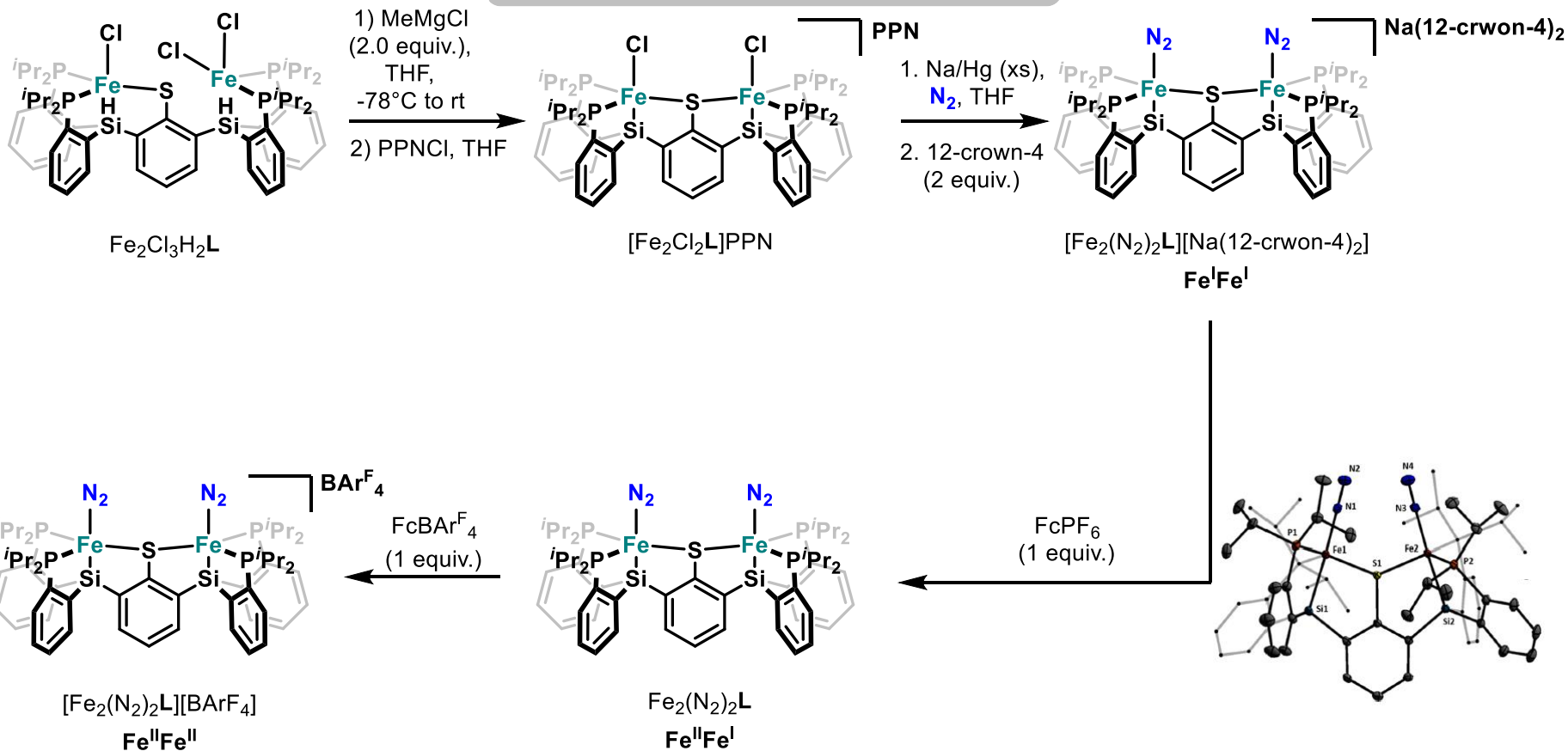
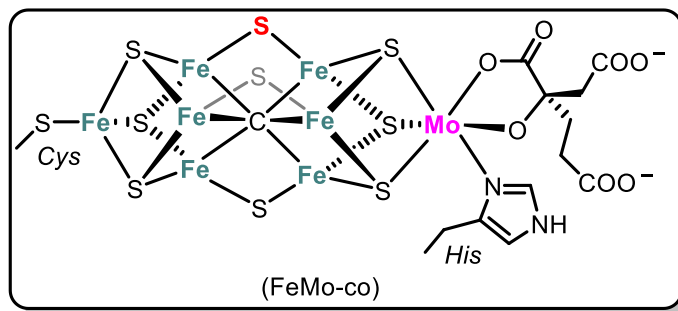
N-N Length:
1.139(4) Å

N_2 Stretching frequency:
1959 cm^{-1}

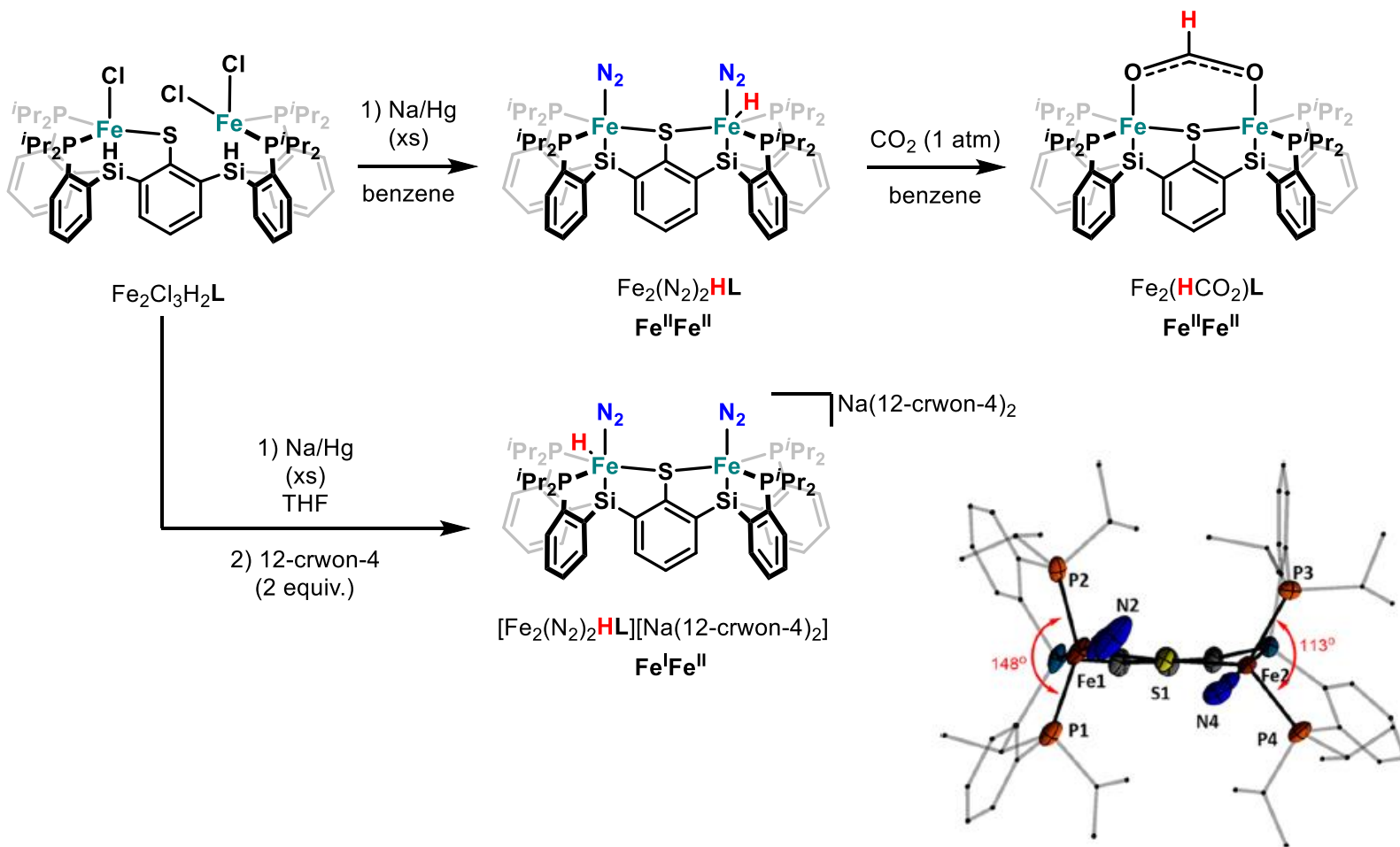


Diiron Complexes Supported by Sulfur Bridged Ligand

Peters' Work:

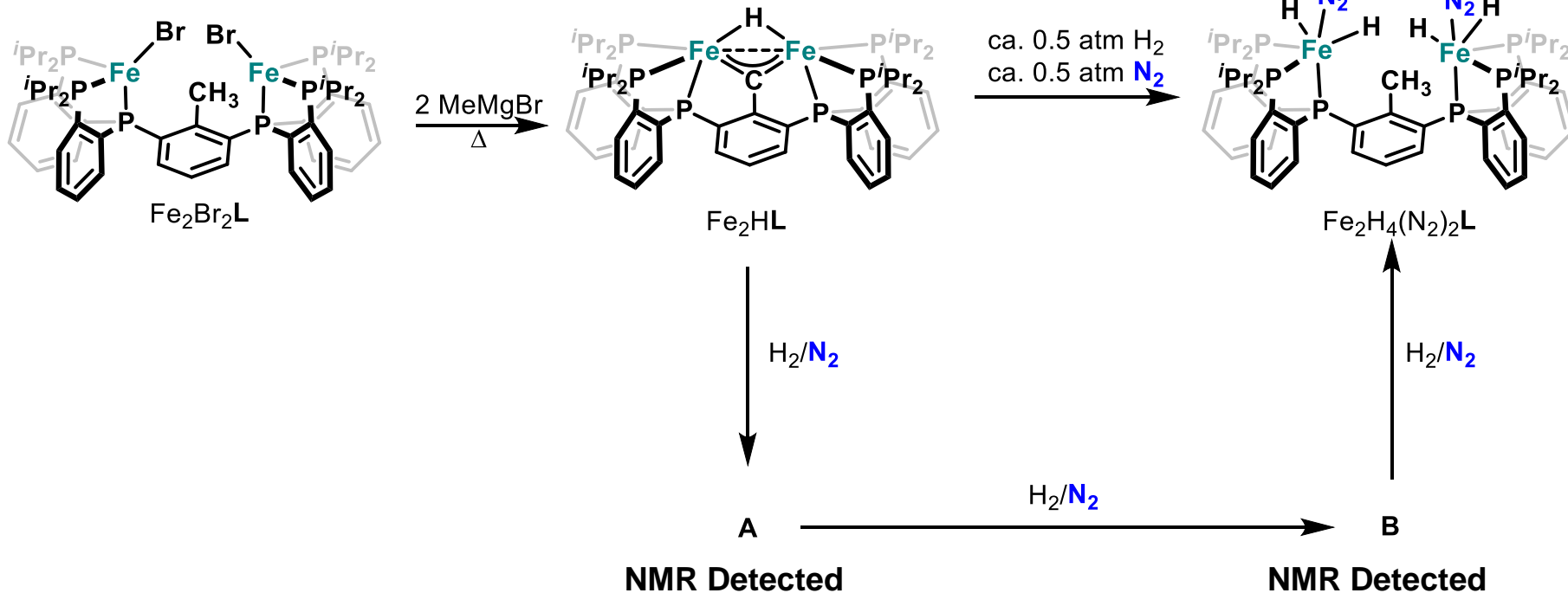
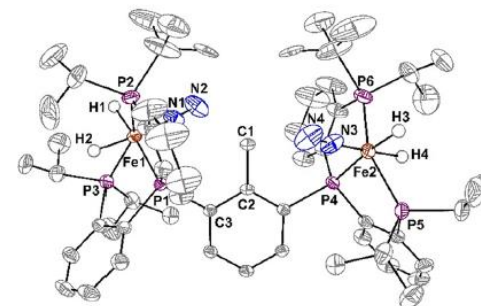
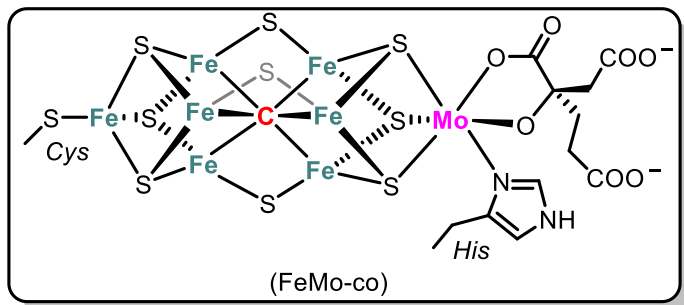


Diiron Complexes Supported by Sulfur Bridged Ligand

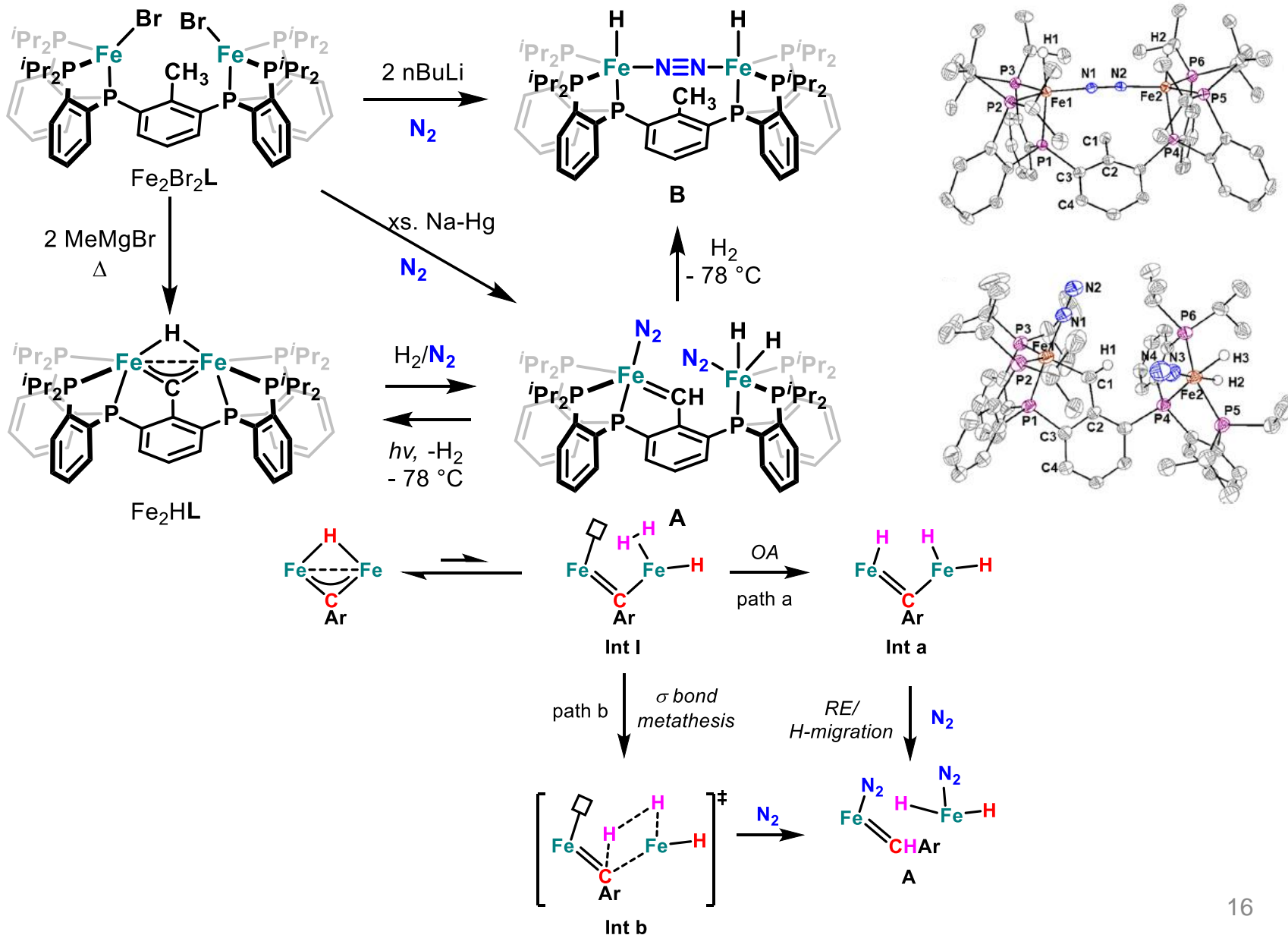


Diiron Complexes Supported by Carbon Bridged Ligand

Agapie's Work:

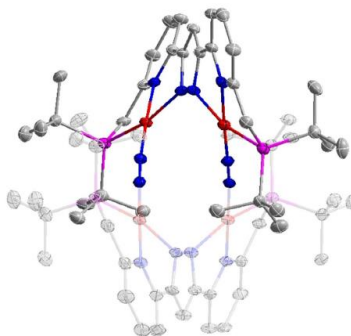
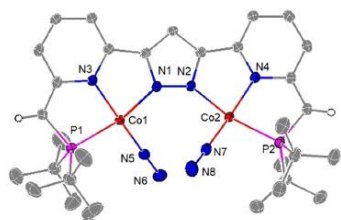
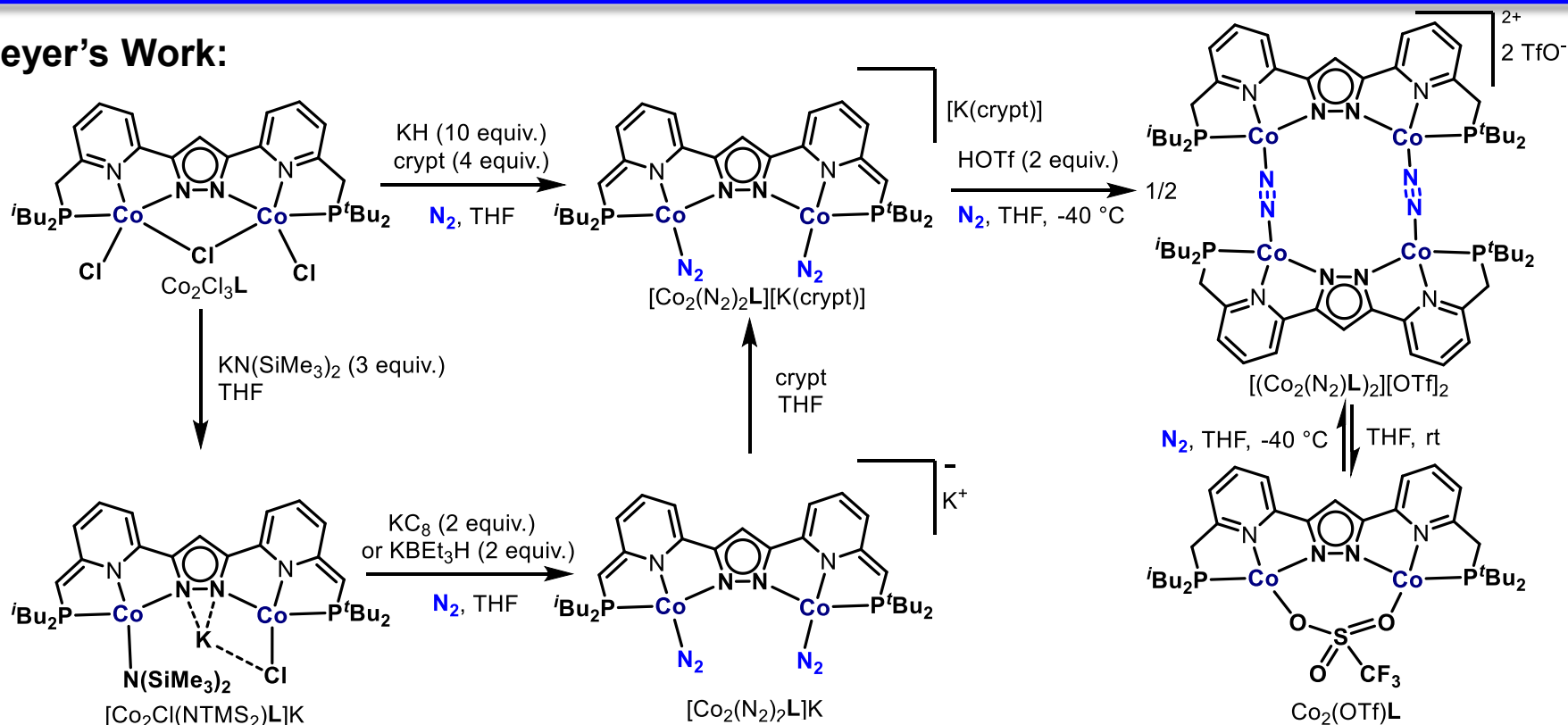


Diiron Complexes Supported by Carbon Bridged Ligand

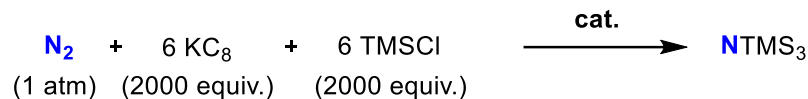


Dicobalt Complexes Supported by Two-in-One Pincer Ligand

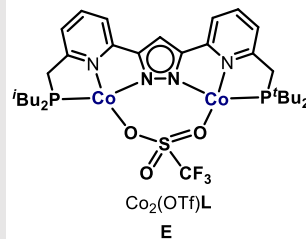
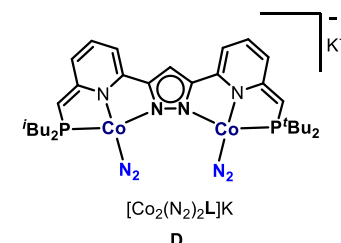
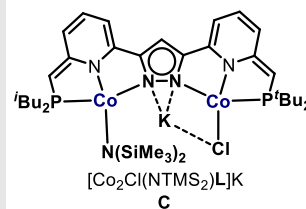
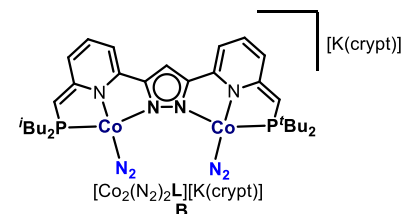
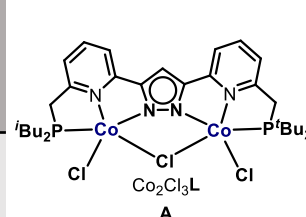
Meyer's Work:



Dicobalt Complexes Supported by Two-in-One Pincer Ligand

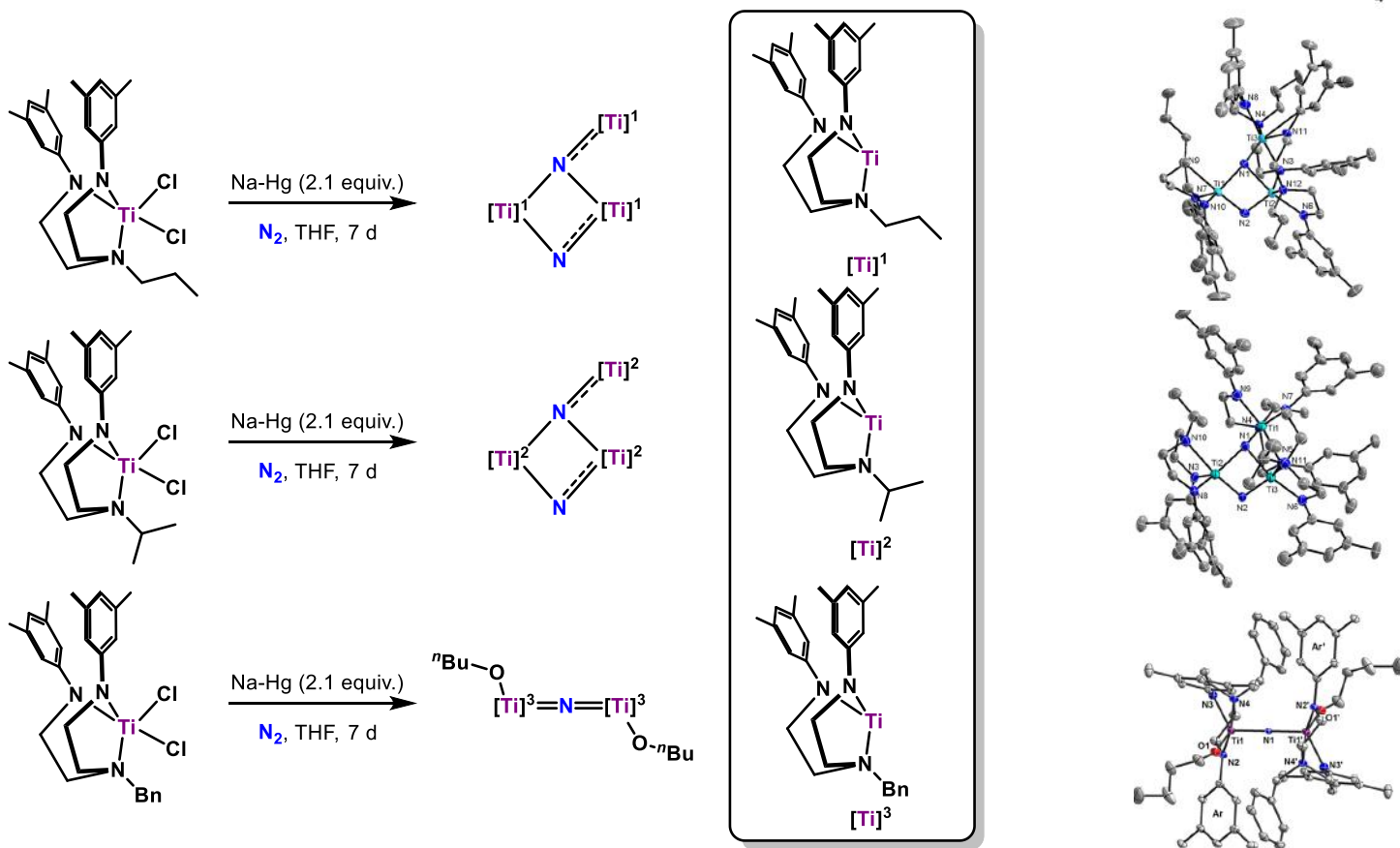
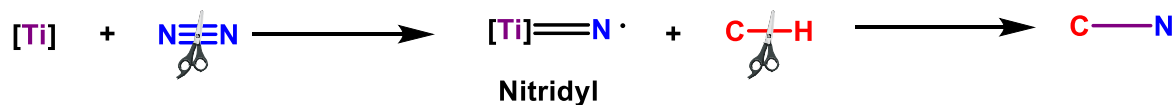


Entry	Catalyst	Conditions	N(TMS) ₃ (mmol)	N(TMS) ₃ / Catalyst (N(TMS) ₃ / Co atom)	Yield
1	E	- 40 °C 2 h; rt 22 h	1.04	208 (104)	31.2
2	D	- 40 °C 2 h; rt 22 h	1.17	234 (117)	35.1
3	C	- 40 °C 2 h; rt 22 h	1.14	228 (114)	34.2
4	B	- 40 °C 2 h; rt 22 h	1.20	240 (120)	36.0
5	B	- 90 °C 2 h; rt 22 h	1.10	219 (109.5)	32.9
6	B	rt 24 h	0.75	150 (75)	22.4
7	A	- 40 °C 2 h; rt 22 h	0.95	190 (95)	28.5
8	2.0 equiv. CoCl ₂	- 40 °C 2 h; rt 22 h	0.58	58 (58)	17.4
9	2.0 equiv. CoCl ₂	rt 24 h	0.1	10 (10)	3.0
10	none	- 40 °C 2 h; rt 22 h	0	0 (0)	0

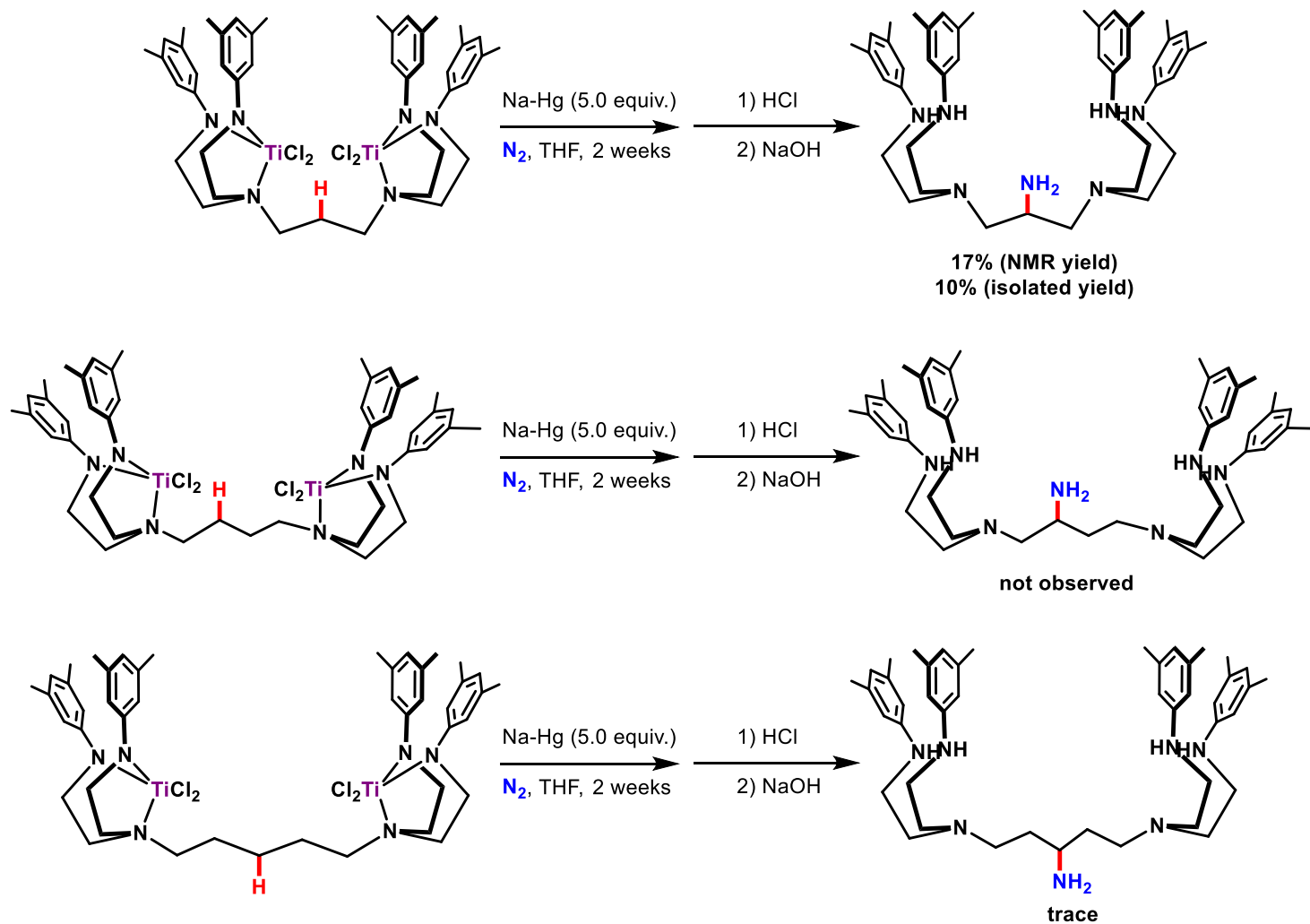


Dititanium Complexes Supported by 3C-Bridged Ligand

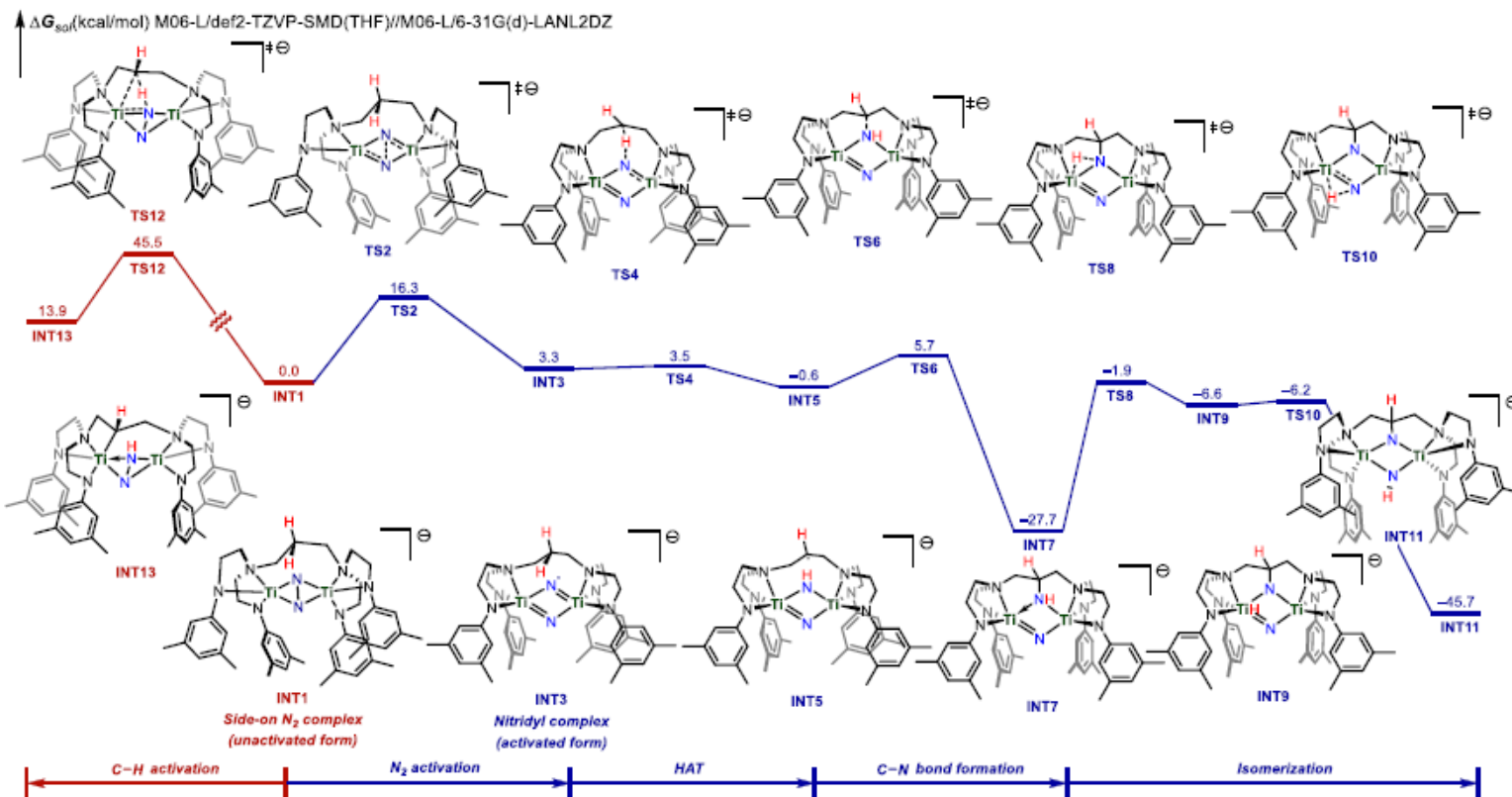
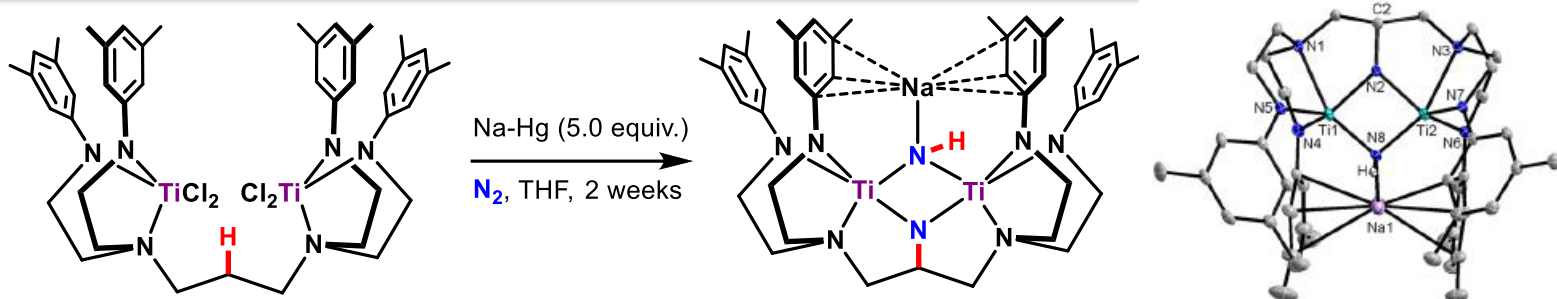
Shi's Work:



Dititanium Complexes Supported by 3C-Bridged Ligand



Dititanium Complexes Supported by 3C-Bridged Ligand

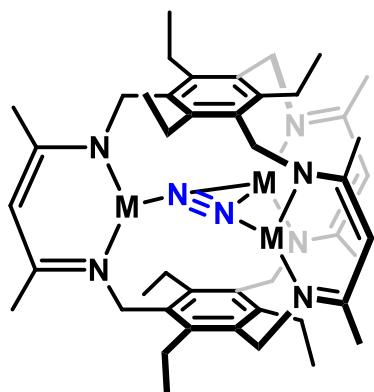




Content

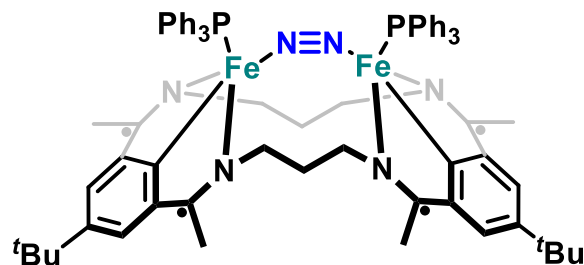
- Background
- Dinitrogen Fixation Through Multimetallic Complexes Supported by Bridged Ligand
- Summary and Outlook

Summary

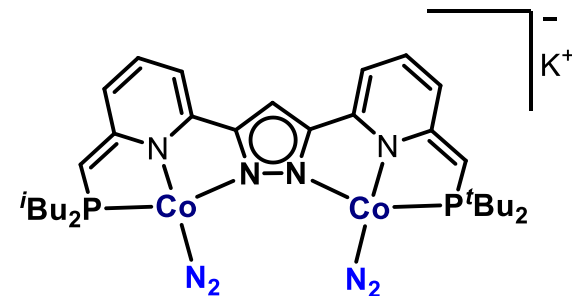


M = Cu, Co

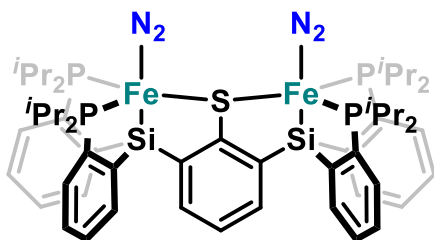
Murray, L. J. et al. *J. Am. Chem. Soc.*
2014, 136, 13502;
J. Am. Chem. Soc. **2021**, 143, 5649.



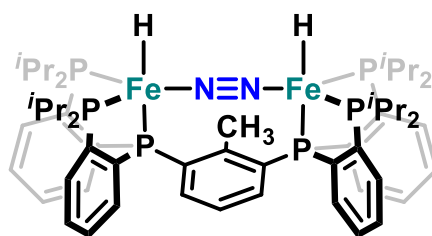
Tomson, N. C. et al. *J. Am. Chem. Soc.*
2020, 142, 8142.



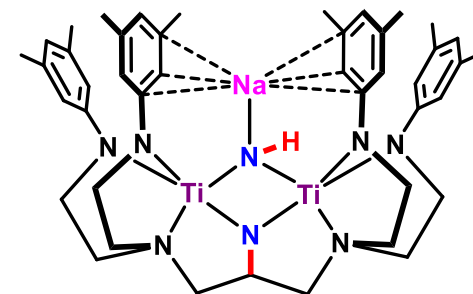
Meyer, F. et al. *Angew. Chem. Int. Ed.*
2021, 60, 14480.



Peters, J. C. et al. *J. Am. Chem. Soc.*
2015, 137, 23, 7310.



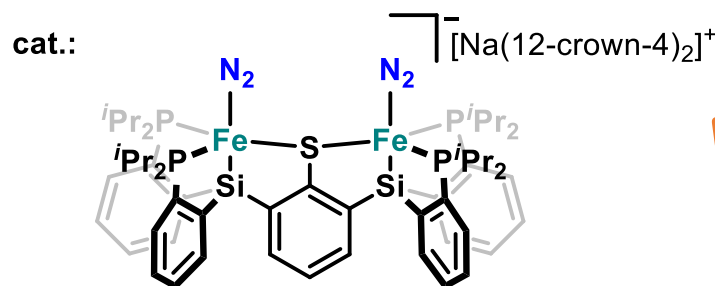
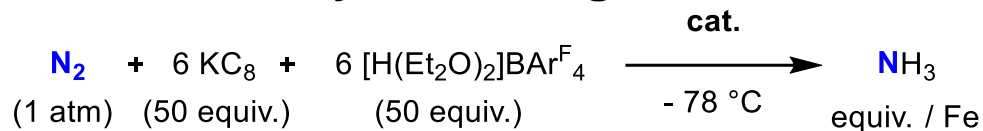
Agapie, T. et al. *J. Am. Chem. Soc.*
2020, 142, 10059.



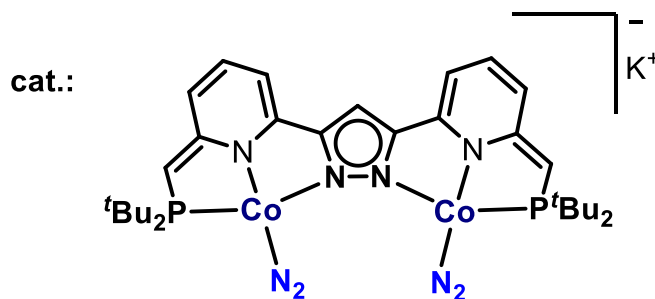
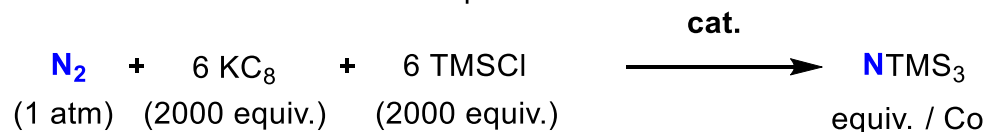
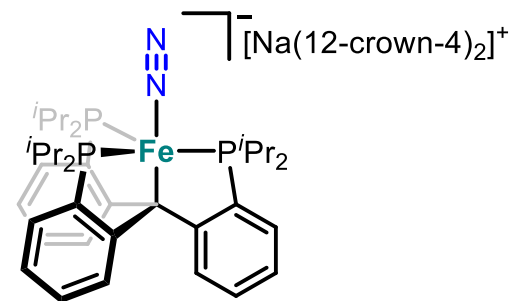
Xie, S.-J. et al. *J. Am. Chem. Soc.*
2023, 145, 6773.

Summary

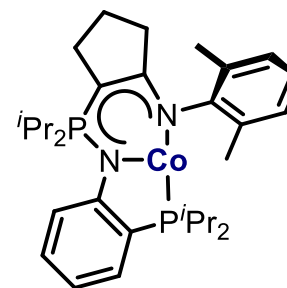
Catalytic Dinitrogen Transformation Performance



VS



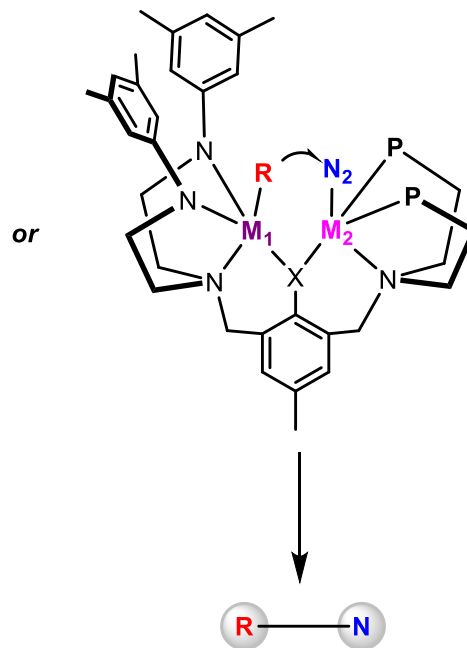
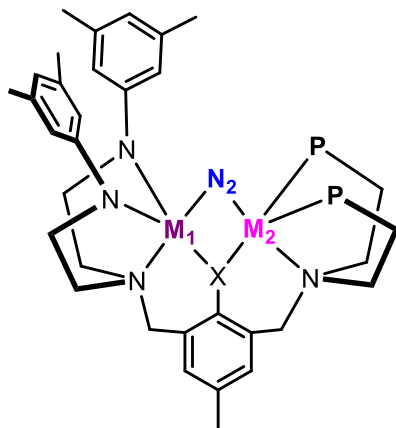
VS



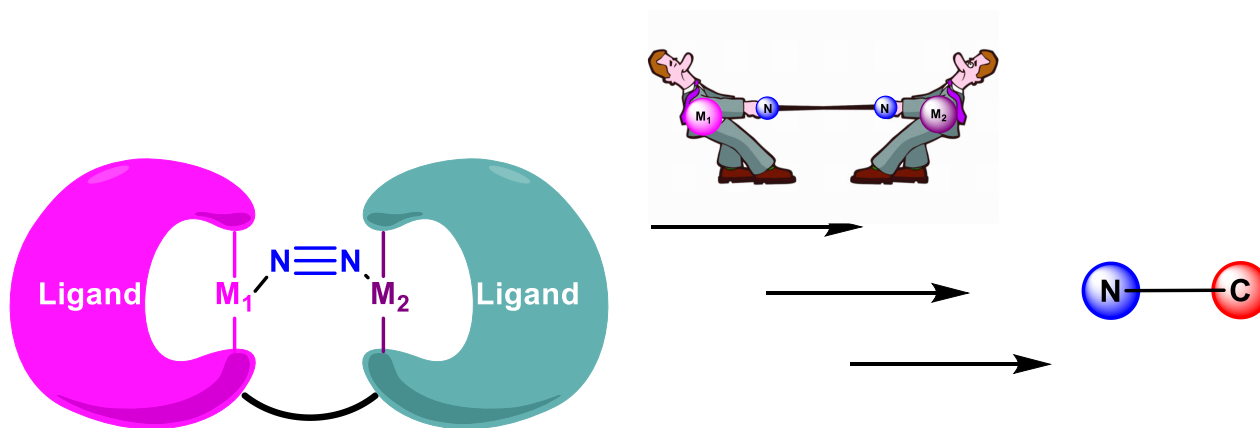
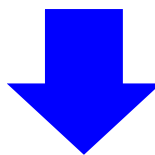
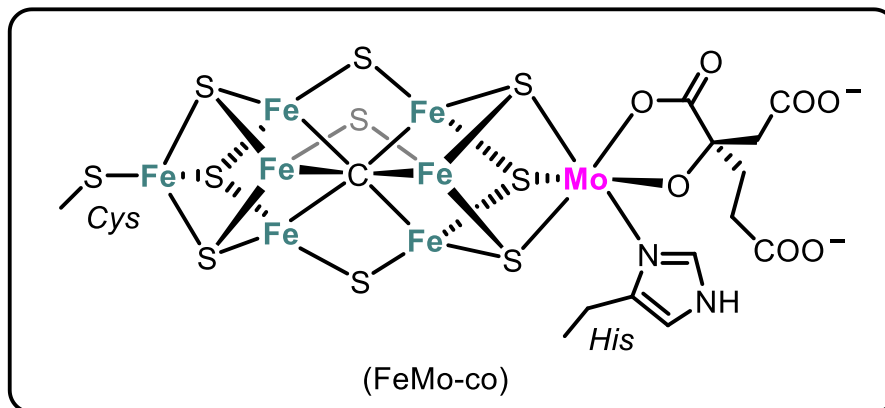
Outlook

- **Hard to Transform**
- **Low Yield**
- **Low Catalytic Performance**

- **New Ligands**
- **New Metal Centers**
- **Heterometallic Complexes**

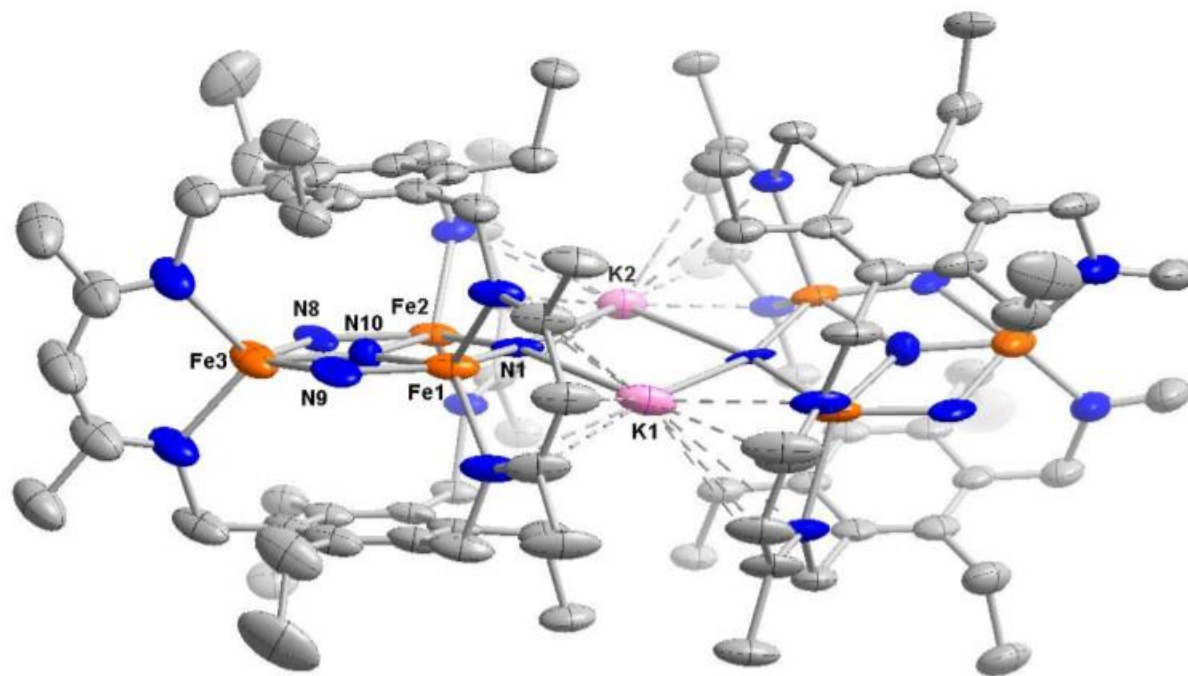


Outlook

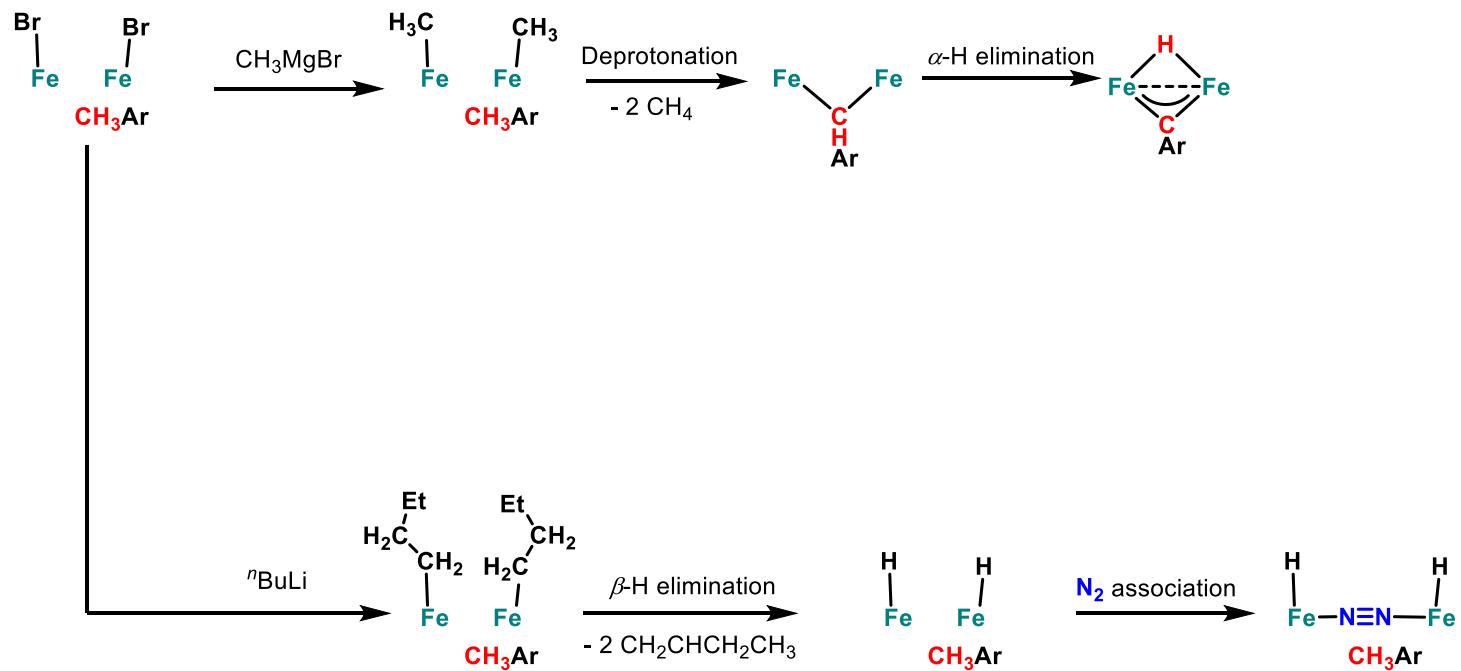




Thank You for Listening!



Murray, L. J. et al. *Angew. Chem. Int. Ed.* **2015**, *54*, 1499.



Agapie, T. et al. *J. Am. Chem. Soc.* **2020**, *142*, 10059.