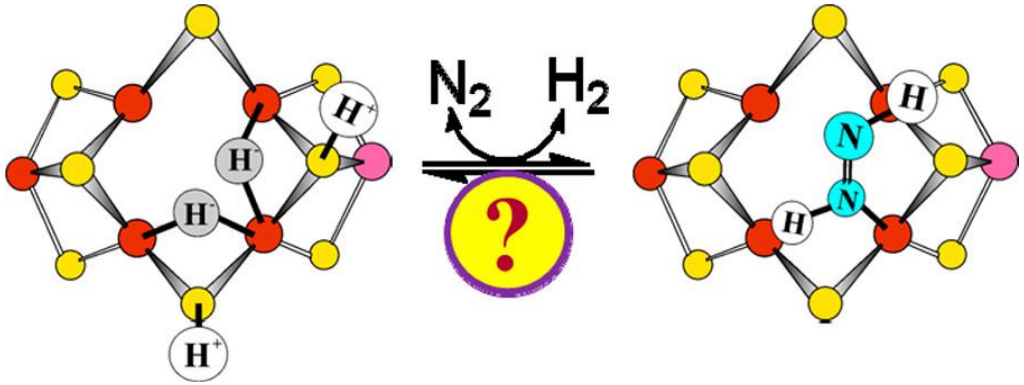
Seminar

Transition Metal Hydride-Mediated Activation and Functionalization of Dinitrogen



Speaker： Yu-Sheng Lu (逯誉生)

Supervisors： Prof. Zhang-Jie Shi

Dr. Dan-Dan Zhai

2026.5.8

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    2.1 Mononuclear Transition Metal Hydride Complexes

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1.1 Introduction-Nature and Industry's Common Approach to N_2 Fixation

78% of Earth's atmosphere

Vital element

- Organic : R-NH_2,R-NO_2…
- Inorganic : NH_3, HNO_3…
- Biogenic : Protein, Nucleoside…

N_2

Inert molecule

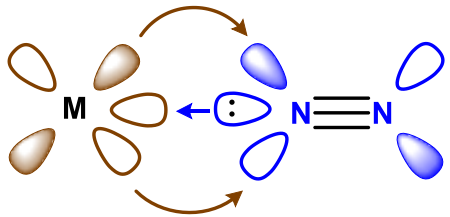
- Nonpolarity
- Strong N-N bond : 944 kJ/mol
- HOMO-LUMO Gap : 10.82 eV

Activation of Dinitrogen by Transition Metals

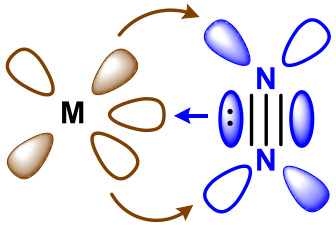
$$N_2 + 10\,H^+ + 8\,e^- + 16\,ATP \xrightarrow{\text{FeMo-co}} 2\,NH_4^+ + H_2 + 16\,ADP + 16\,P_i$$

$$N_2 + 3\,H_2 \xrightarrow[200\text{-}500\ atm,\ 500\text{-}600\ ^oC]{\text{cat. } Fe_3O_4/K_2O/Al_2O_3} 2\,NH_3$$

end-on activation mode



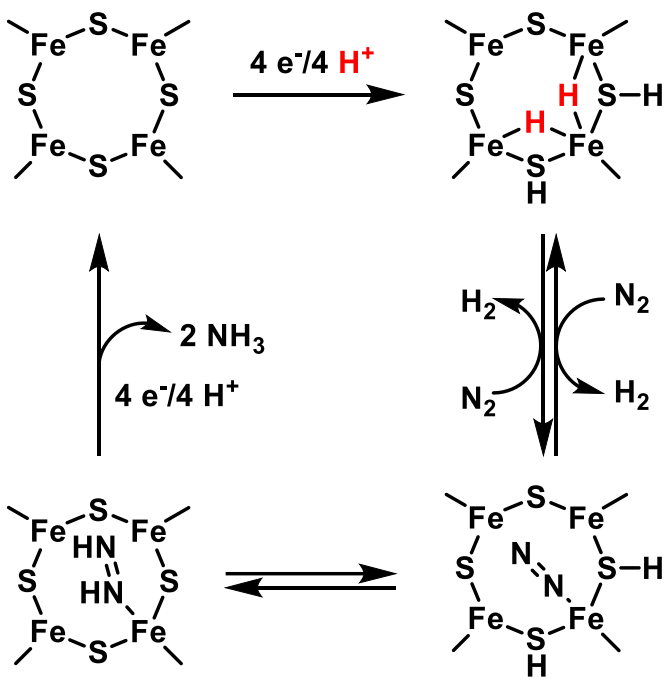
side-on activation mode



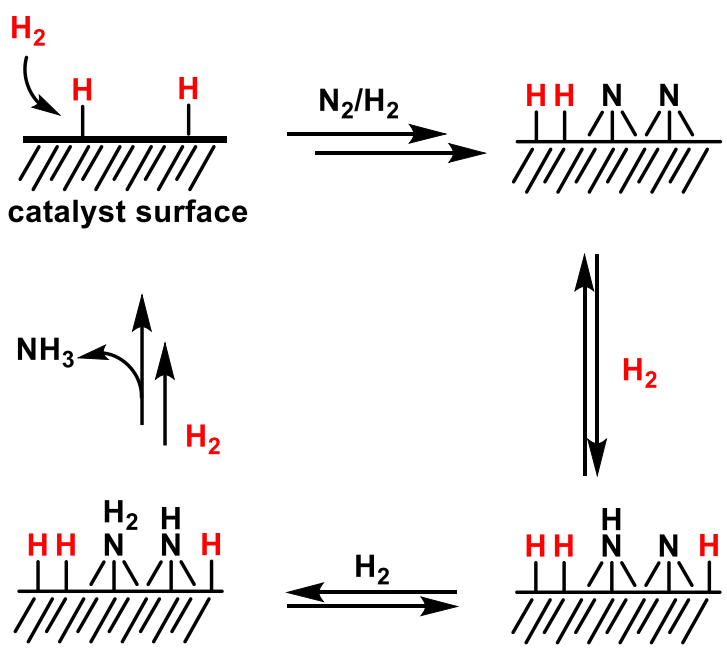
a) M. von Laue, et al. *Naturwissenschaften.* **1934**, *22*, 97; b) M. Boudart, et al. *Top. Catal.* **1994**, *1*, 405

1.1 Introduction-Nature and Industry's Common Approach to N_2 Fixation

Proposed pathways for ammonia formation by nitrogenase enzyme and the Haber–Bosch process



(A) Nitrogenase enzyme



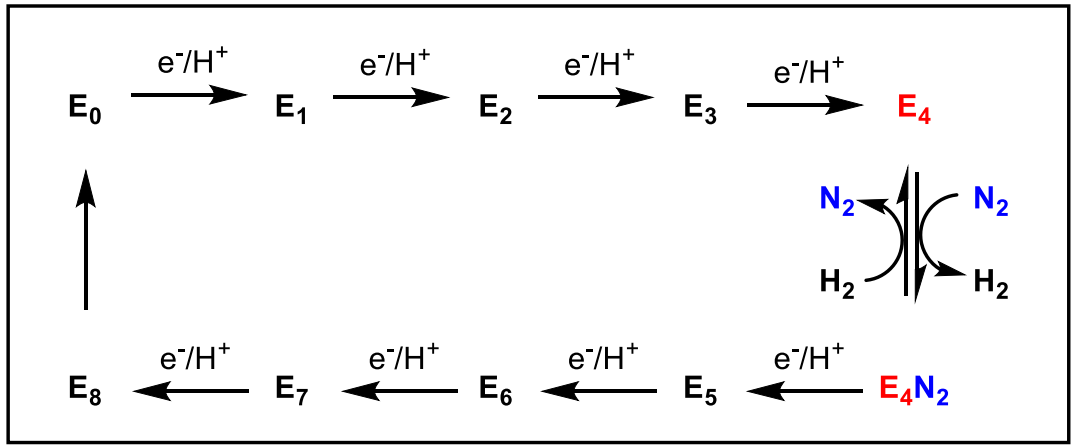
(B) the Haber–Bosch process

a) B. M. Hoffman, et al. *Chem. Rev.* **2014**, *114*, 4041–4062; b) G. Ertl, et al. *Catal. Rev. Sci. Eng.* **1980**, *21*, 201–223

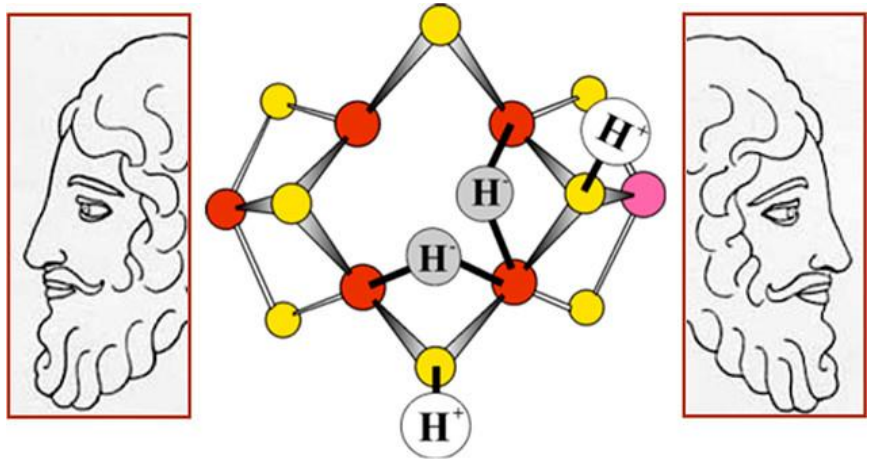
1.2 Mechanism of Nitrogen Fixation by Nitrogenase

$$N_2 + 6\,H^+ + 6\,e^- \xrightarrow{\text{In theory}} 2\,NH_3$$

$$N_2 + 8\,H^+ + 8\,e^- + 16\,ATP \xrightarrow{\text{FeMo-co}} 2\,NH_3 + H_2 + 16\,ADP + 16\,P_i$$



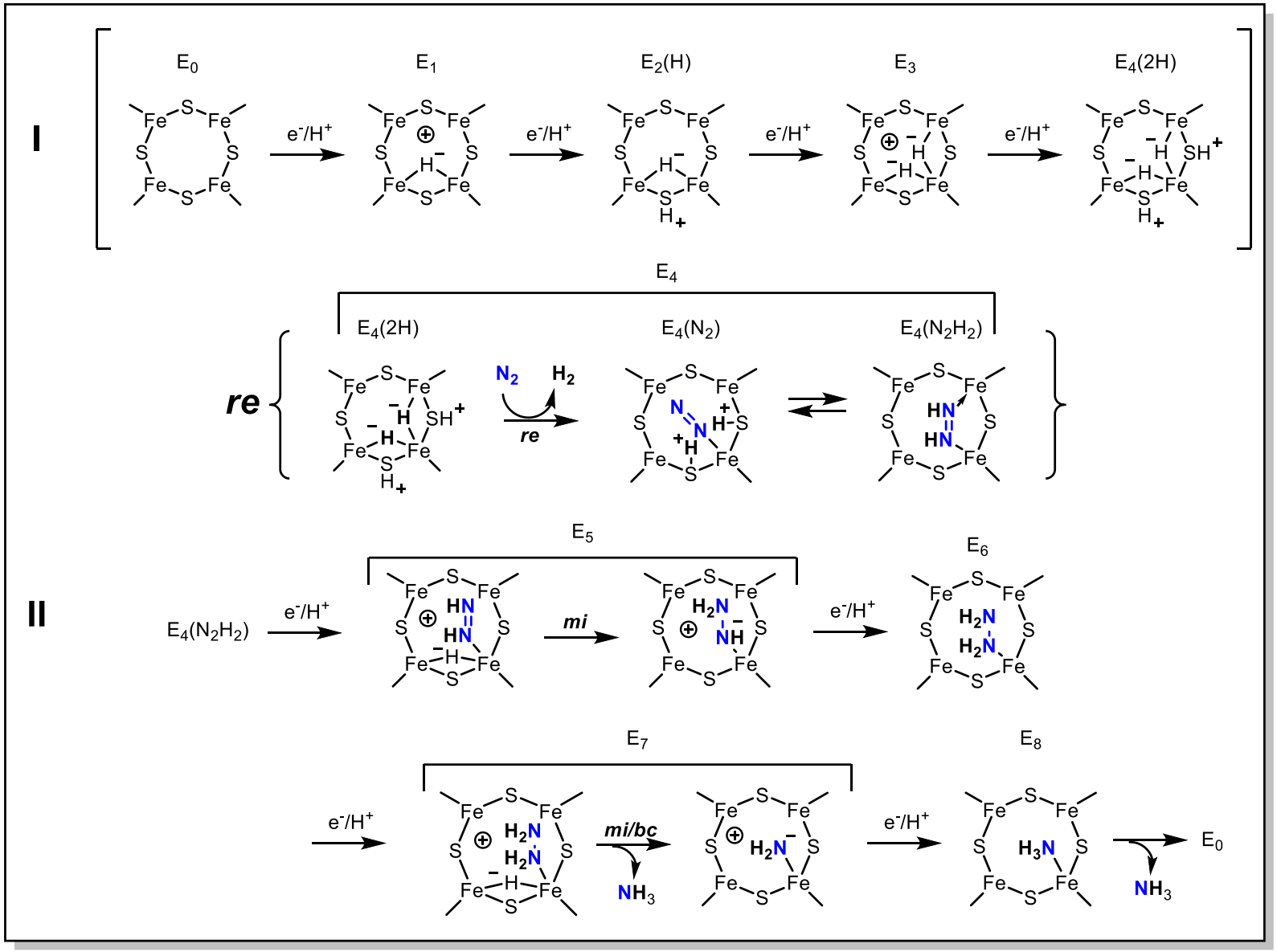
Highly simplified LT kinetic scheme



Proposed E4: The "Janus Intermediate"

a) B. M. Hoffman, et al. *Acc. Chem. Res.* **2013**, *46*, 587–595

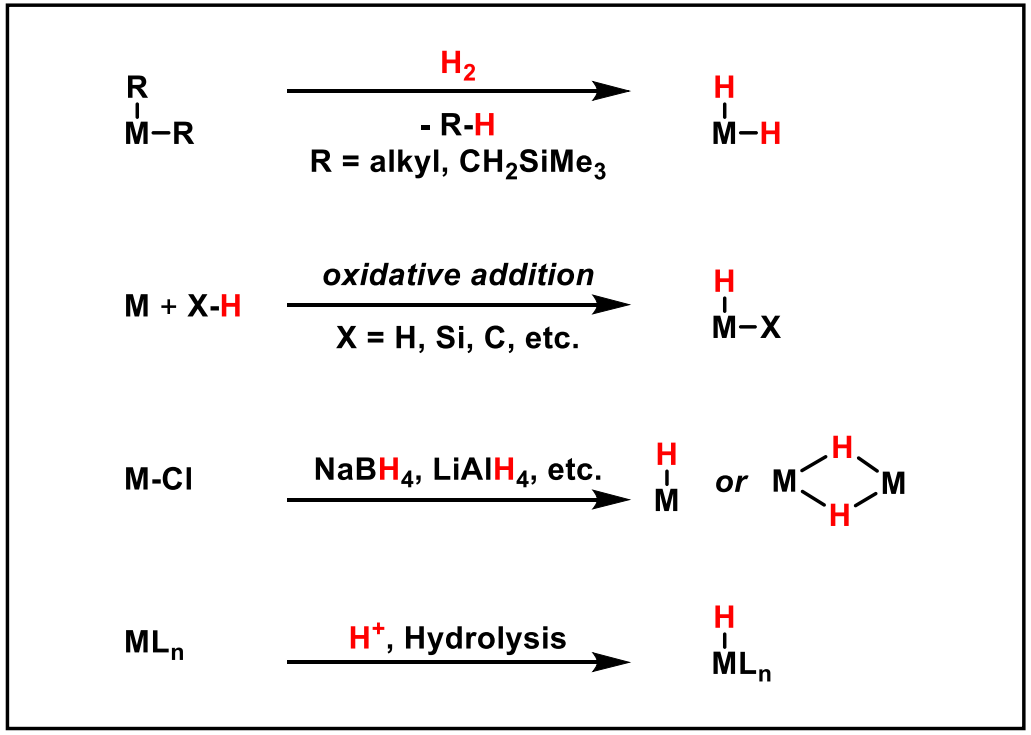
1.2 Mechanism of Nitrogen Fixation by Nitrogenase



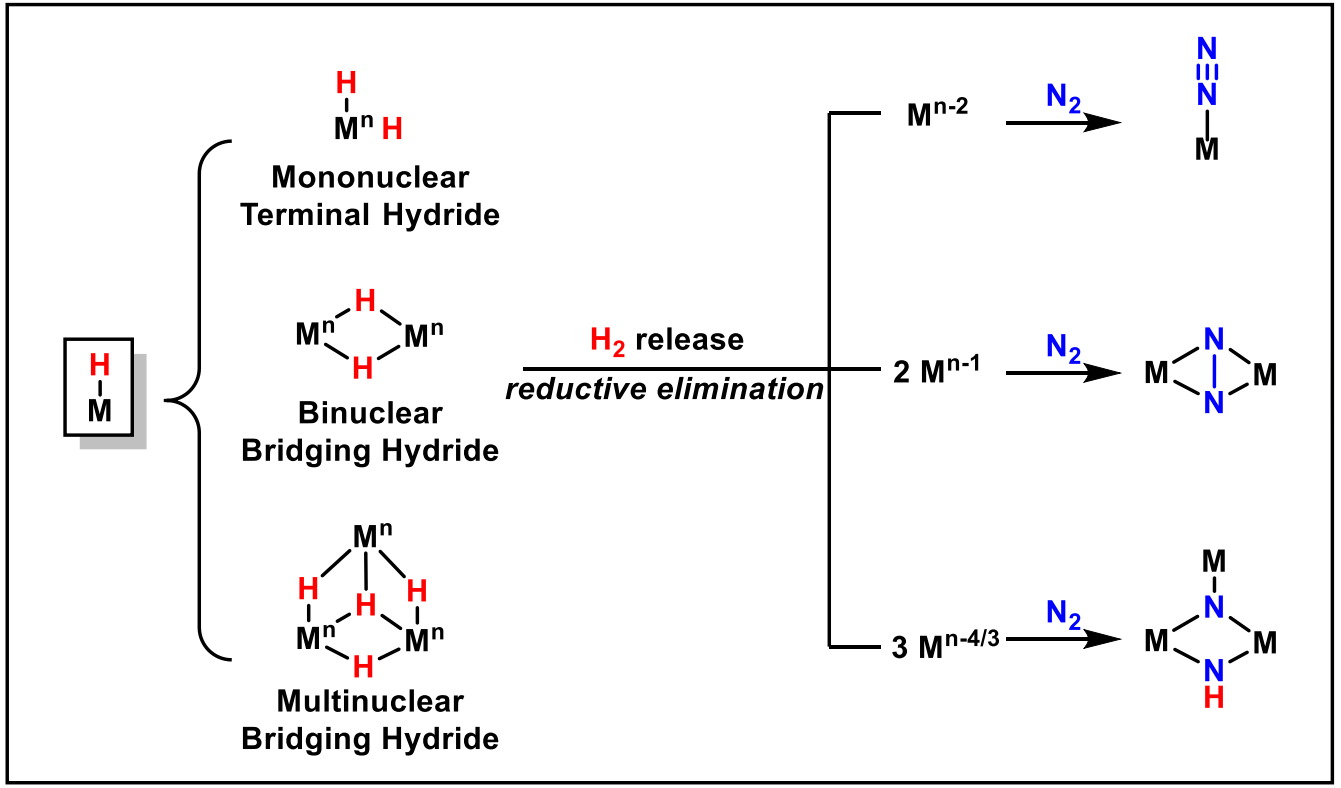
a) B. M. Hoffman, et al. *Chem. Rev.* **2014**, *114*, 4041–4062; b) B. M. Hoffman, et al. *J. Am. Chem. Soc.* **2015**, *137*, 3610–3615

1.3 Activation of N_2 by Mono- and Multimetallic Hydrides

Diverse Synthesis of Transition Metal Hydrides



N_2 Fixation by Transition Metal Hydrides: Accumulation of Electrons and Protons



a) R. B. Saillant, et al. *Chem. Rev.* **1972**, *72*, 231–281

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2.3 Trinuclear Transition Metal Hydride Complexes

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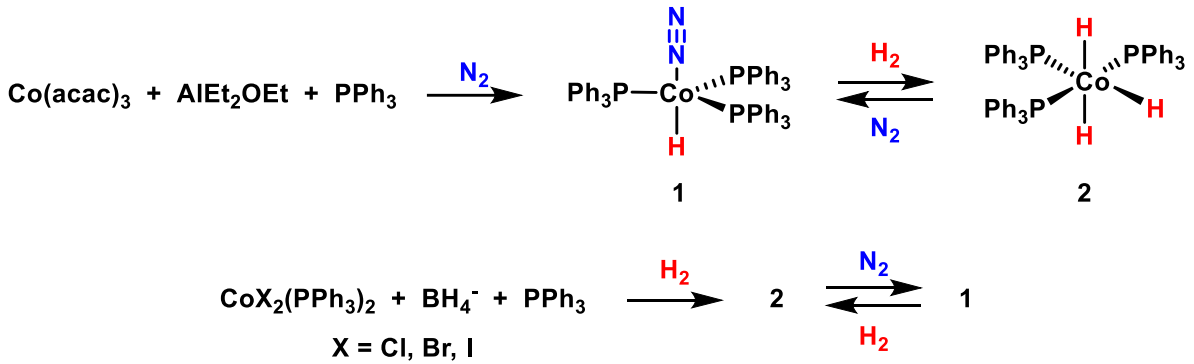
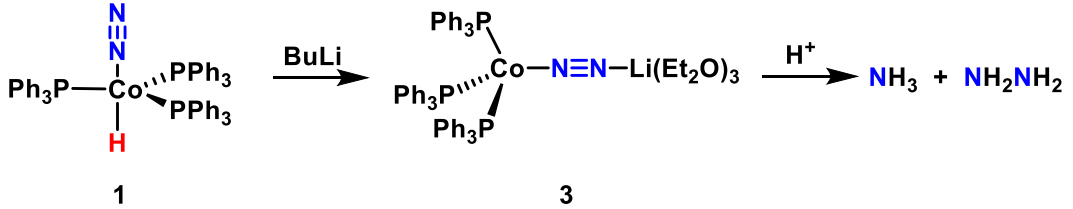
2.1 Mononuclear Transition Metal Hydride Complexes

2.1.1 Group 9 Transition Metal Hydrides

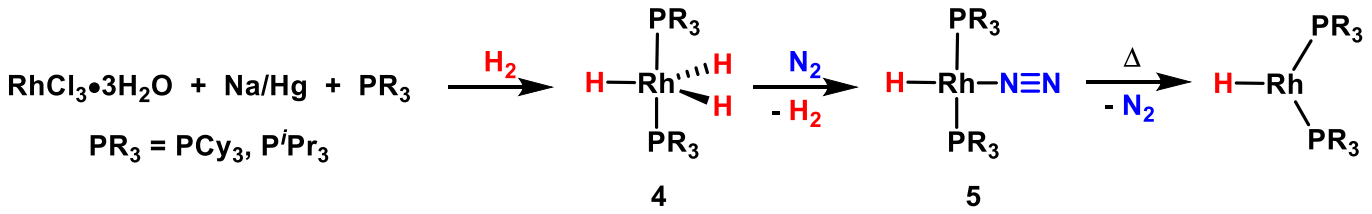
Reversible hydrogenation of 1



Protonation of 3



Reaction of trihydride 4 with N_2



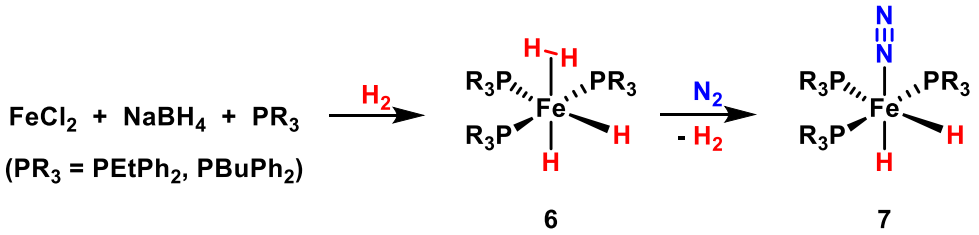
a) A. Yamamoto, et al. *J. Am. Chem. Soc.* **1967**, *89*, 3071; b) M. Rossi , et al. *Chem. Commun.* **1967**, *109*, 316

c) A. Yamamoto, et al. *Organometallics.* **1983**, *2*, 1429–1436; d) T. Yoshida, et al. *J. Organomet. Chem.* **1979**, *181*, 183–201

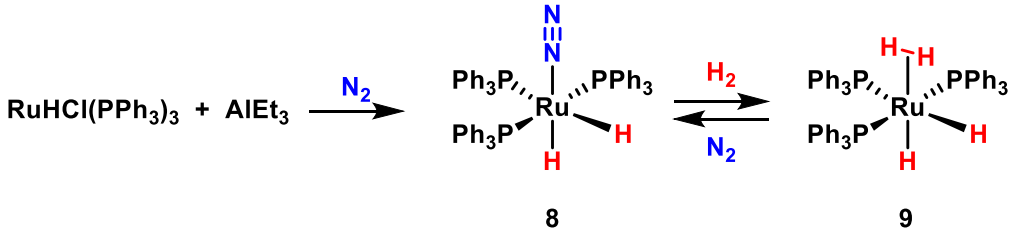
2.1 Mononuclear Transition Metal Hydride Complexes

2.1.2 Group 8 Transition Metal Hydrides

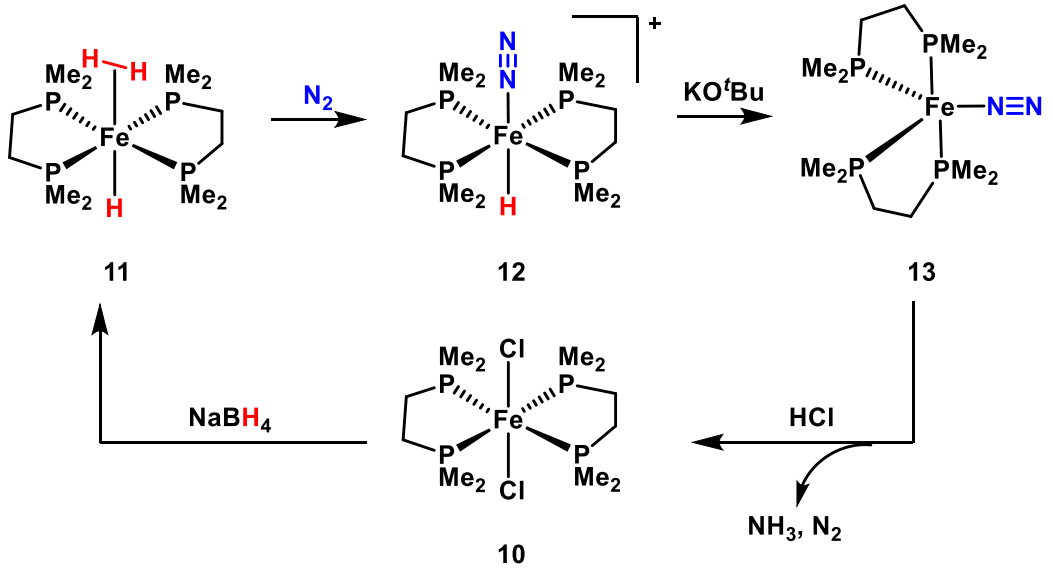
Synthesis and N_2 coordination of 6



Synthesis and hydrogenation of 8



A synthetic cycle for transformation of N_2 to NH_3 by the iron complexes 10~13

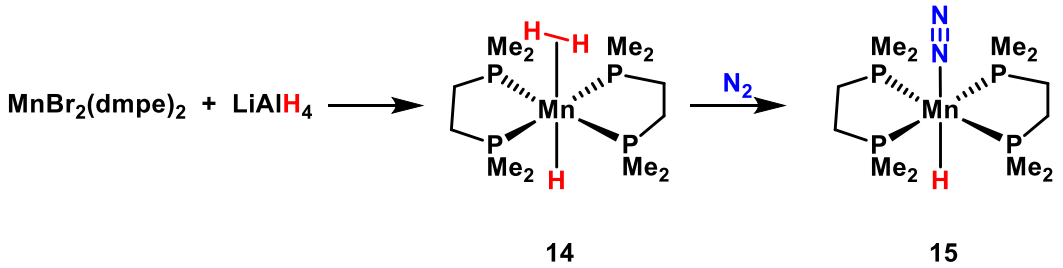


a) L. S. Van Der Sluys, et al. *J. Am. Chem. Soc.* **1990**, *112*, 4831–4841; b) W. H. Knoth, et al. *J. Am. Chem. Soc.* **1972**, *94*, 104–109
c) G. J. Leigh, et al. *J. Am. Chem. Soc.* **1991**, *113*, 5862–5863

2.1 Mononuclear Transition Metal Hydride Complexes

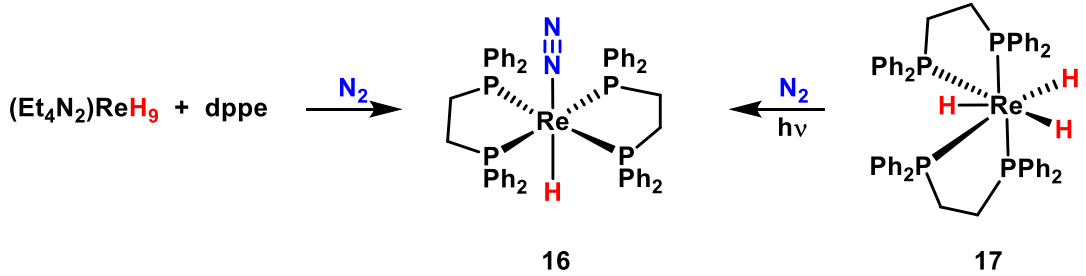
2.1.3 Group 7 Transition Metal Hydrides

Synthesis of 14 and its reaction with N_2



14 15

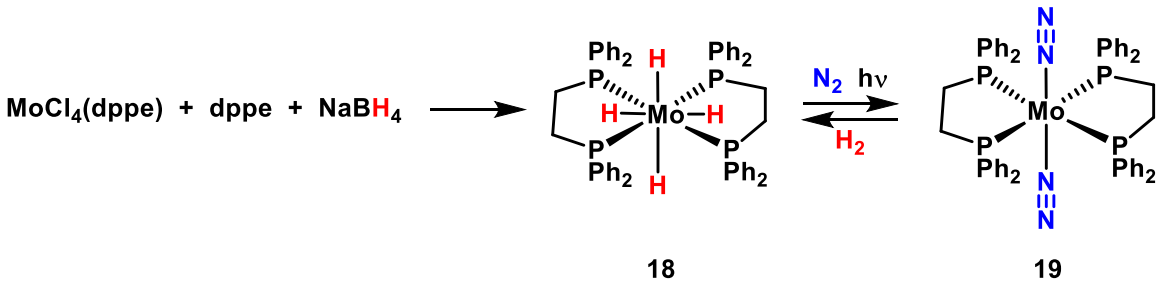
Synthesis of 16 from 17 with light



16 17

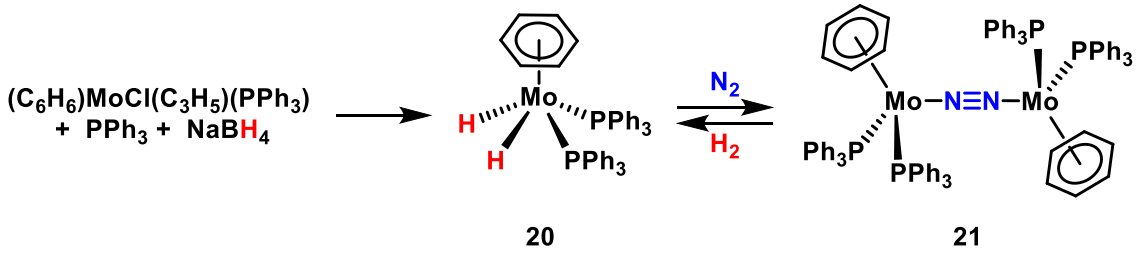
2.1.4 Group 6 Transition Metal Hydrides

The reaction of 18 with N_2 under UV irradiation



18 19

Formation of 21 from 20



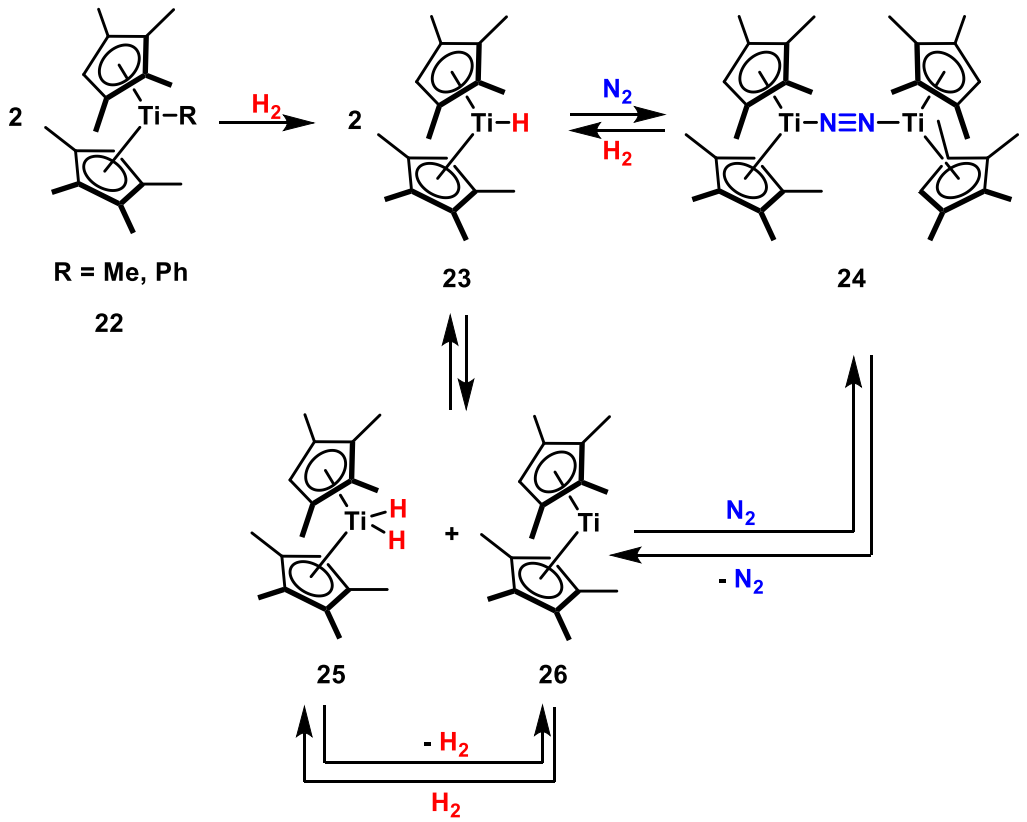
20 21

a) G. S. Girolami, et al. *J. Chem. Soc. Dalton. Trans.* **1985**, 921–929; b) G. L. Geoffrey, et al. *J. Am. Chem. Soc.* **1981**, *103*, 379–384
c) G. L. Geoffrey, et al. *Inorg. Chem.* **1980**, *19*, 1821–1822; d) W. E. Silverthorn, et al. *Chem. Commun.* **1971**, 557–558

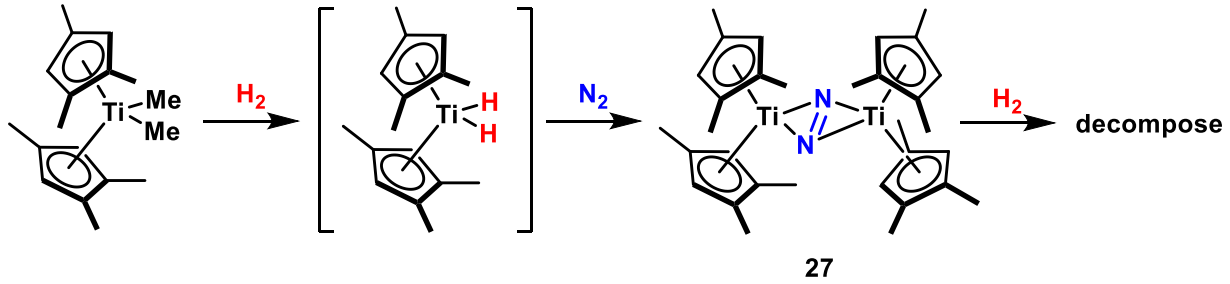
2.1 Mononuclear Transition Metal Hydride Complexes

2.1.5 Group 4 Transition Metal Hydrides

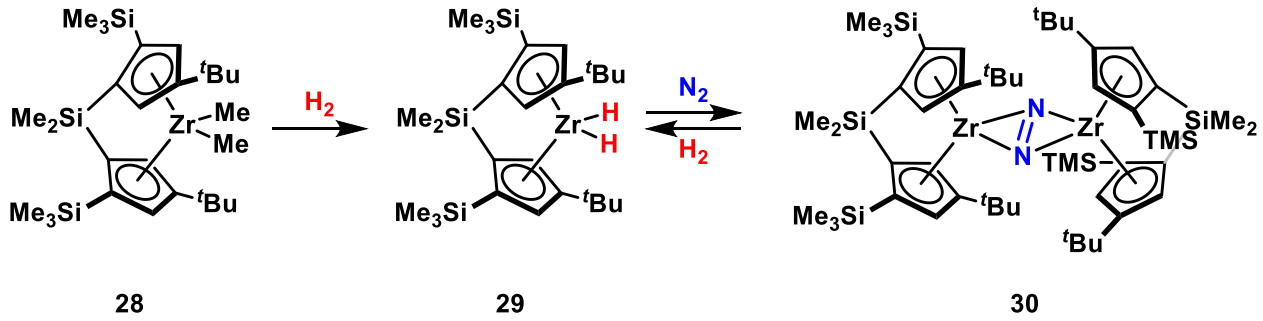
Synthesis of 24 through hydride 23



Formation of side-on bound dinitrogen complex 27



Reversible formation of 30 from 29 with N_2



a) J. M. de Wolf , et al. *Organometallics.* **2006**, *25*, 1530–1543; b) T. E. Hanna, et al. *Organometallics.* **2007**, *26*, 2431–2438
c) P. J. Chirik, et al. *Organometallics.* **2001**, *20*, 534–544

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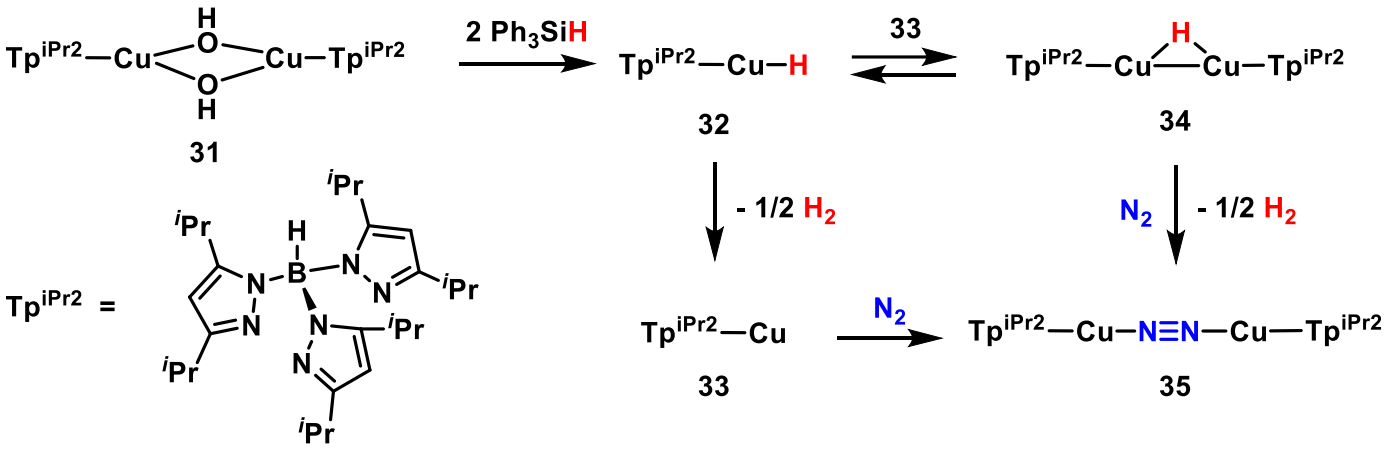
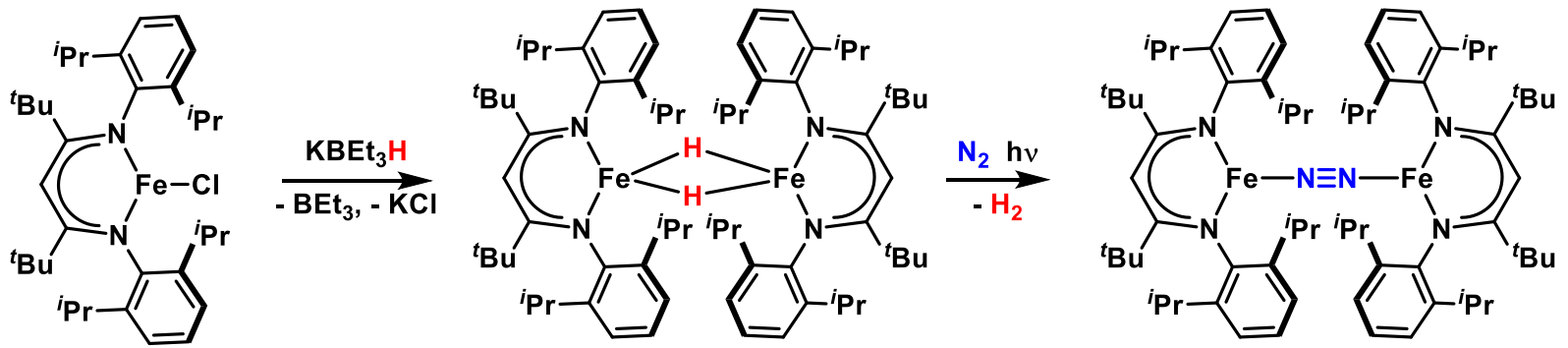
2.2 Binuclear Transition Metal Hydride Complexes

Reaction of the Mixed-Valence Dicopper Hydride 34 with N_2



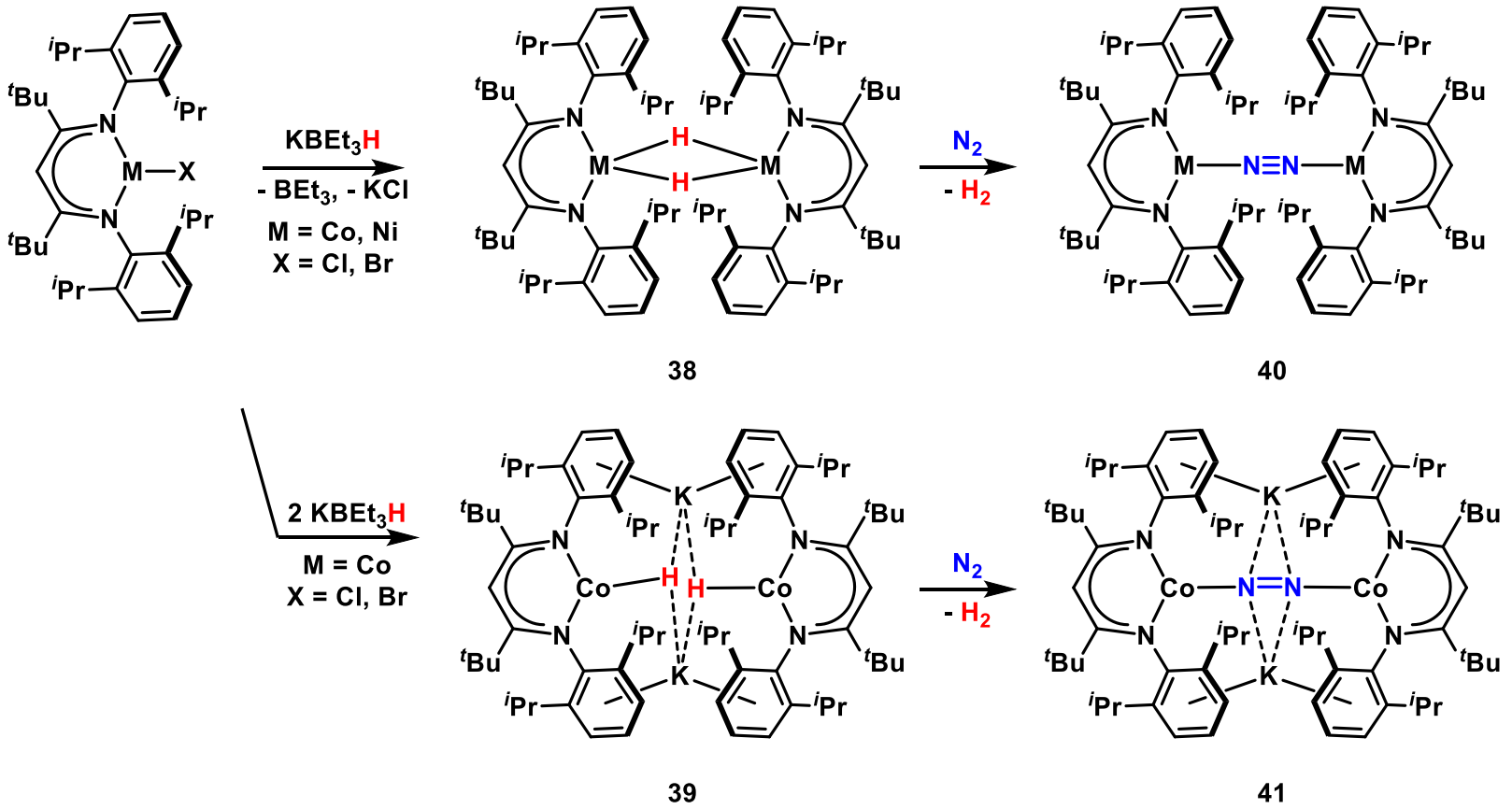
Reactions of the Low-Coordinate Fe Hydride Complex 36 with N_2



a) T. H. Warren, et al. *Angew. Chem. Int. Ed.* **2016**, 55, 9927–9931; b) P. L. Holland, et al. *J. Am. Chem. Soc.* **2006**, *128*, 756–769

2.2 Binuclear Transition Metal Hydride Complexes

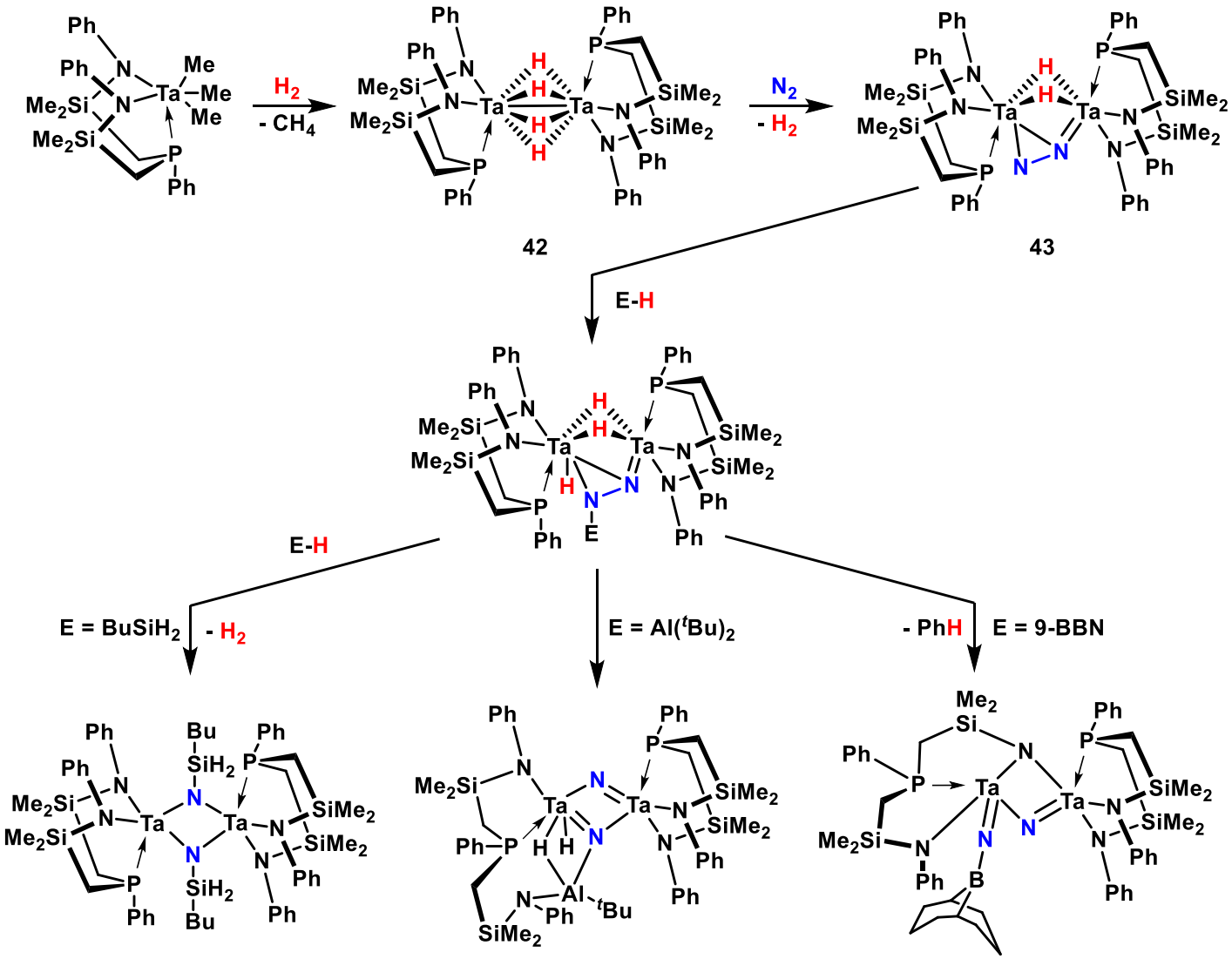
Reactions of the Low-Coordinate Co/Ni Hydride Complexes 38-39 with N_2



a) P. L. Holland, et al. *J. Am. Chem. Soc.* **2009**, *131*, 10804–10805; b) C. Limberg, et al. *Angew. Chem. Int. Ed.* **2009**, *48*, 3357–3361

2.2 Binuclear Transition Metal Hydride Complexes

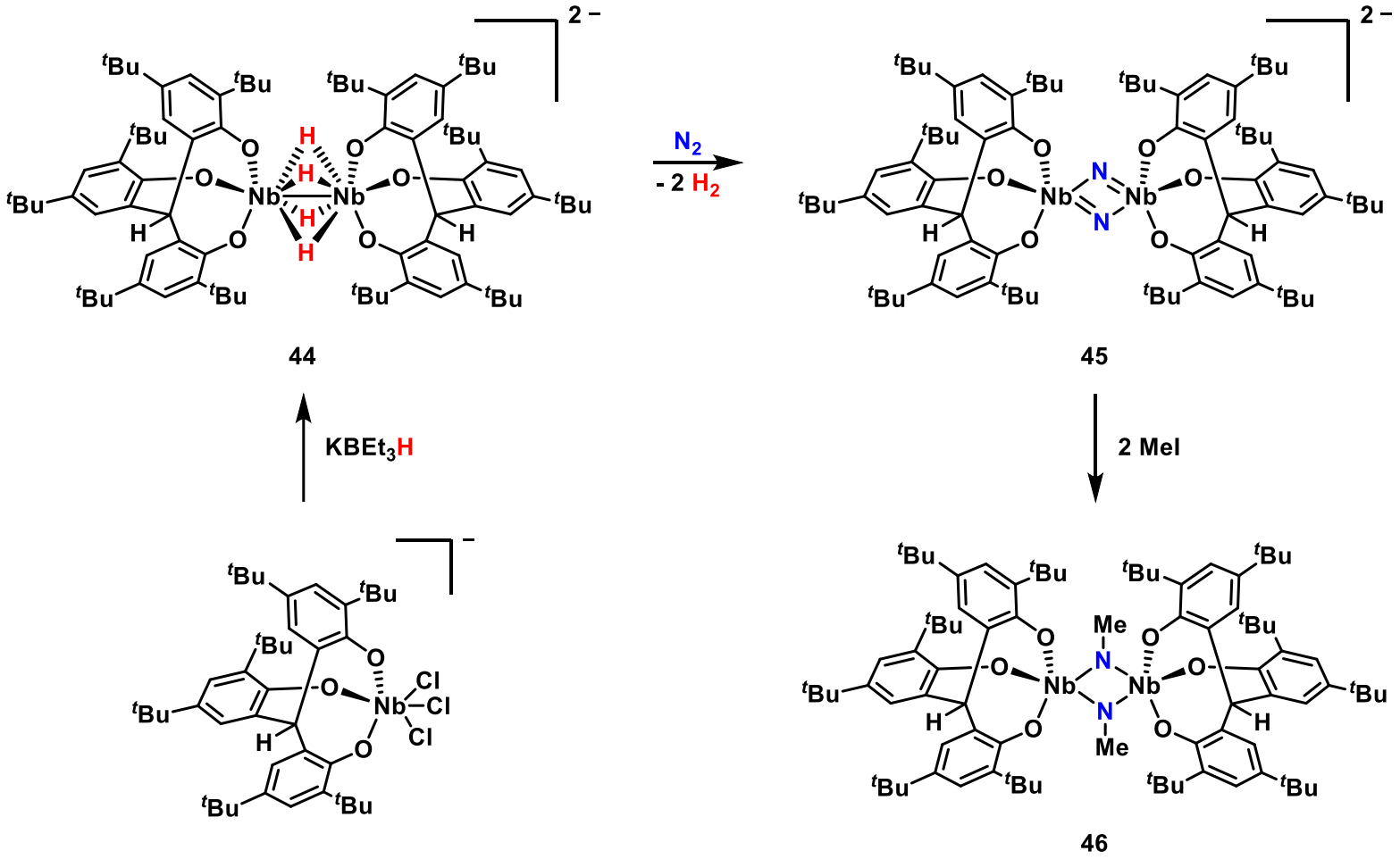
Functionalization of N_2 using Binuclear Tantalum Hydride Complex 42



a) M. D. Fryzuk, et al. *J. Am. Chem. Soc.* **1998**, *120*, 11024–11025; b) M. D. Fryzuk, et al. *J. Am. Chem. Soc.* **2003**, *125*, 3234–3235

2.2 Binuclear Transition Metal Hydride Complexes

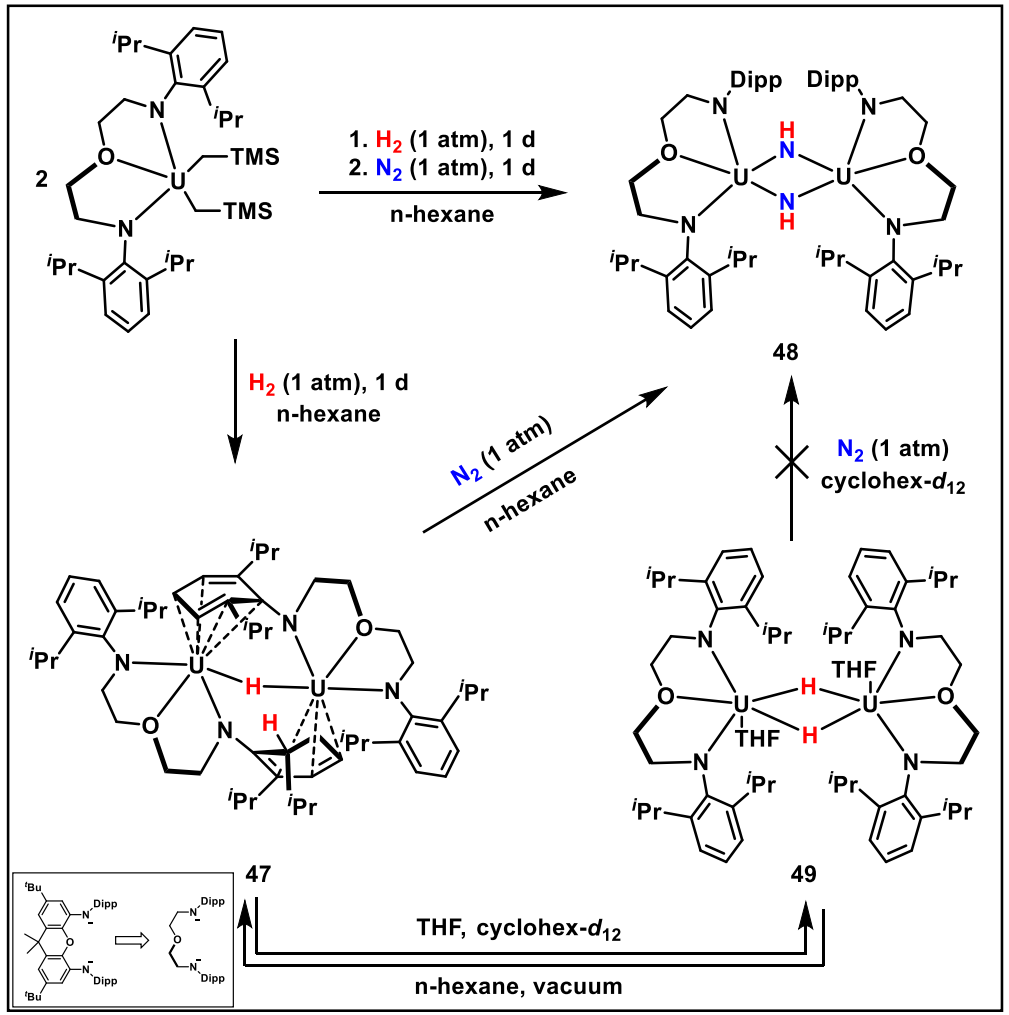
Cleavage of N_2 by a Diniobium Tetrahydride Complex 42

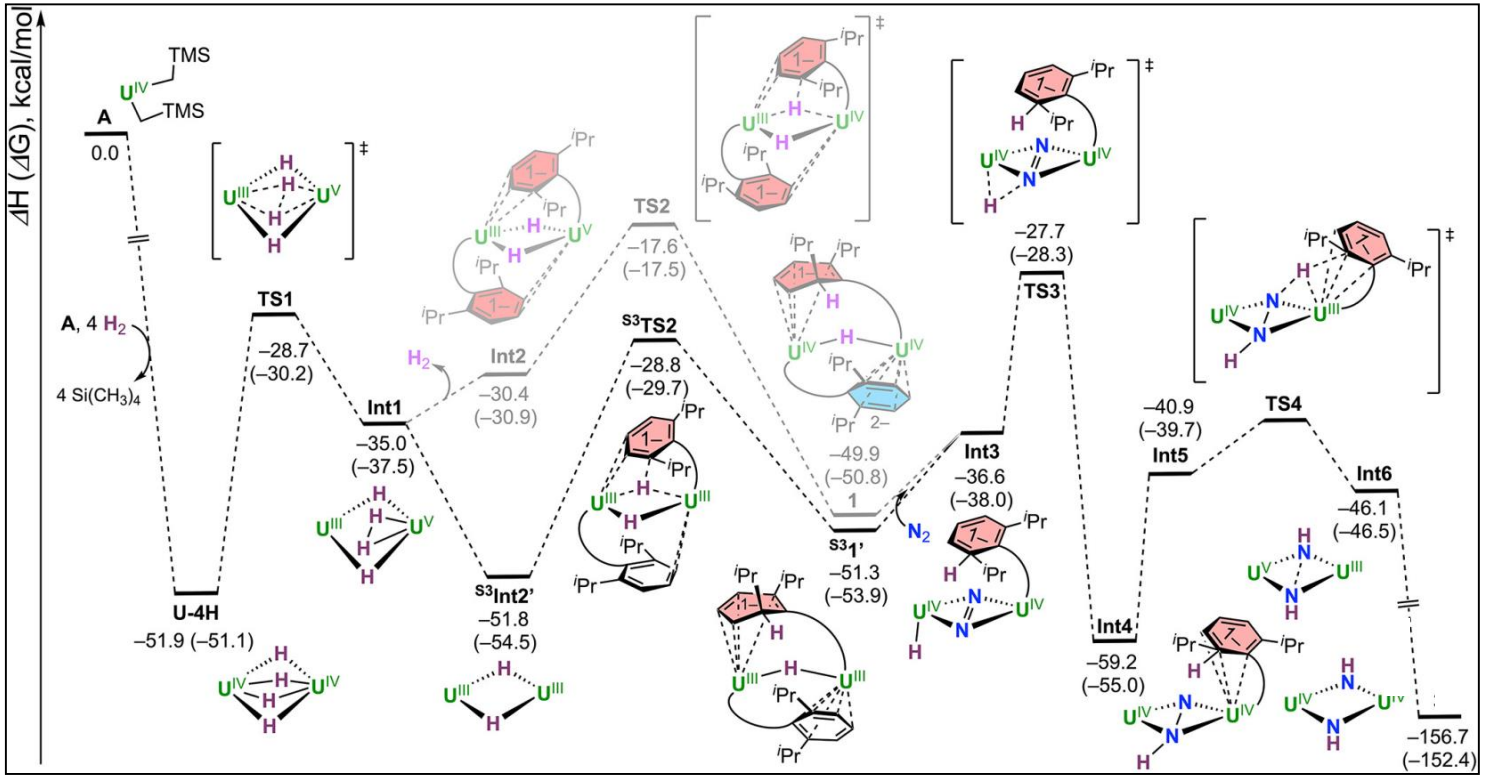


a) H. Kawaguchi, et al. *Angew. Chem. Int. Ed.* **2007**, *46*, 8778–8781

2.2 Binuclear Transition Metal Hydride Complexes

Cleavage and Hydrogenation of N_2 by a Diuranium Hydride Complex 47

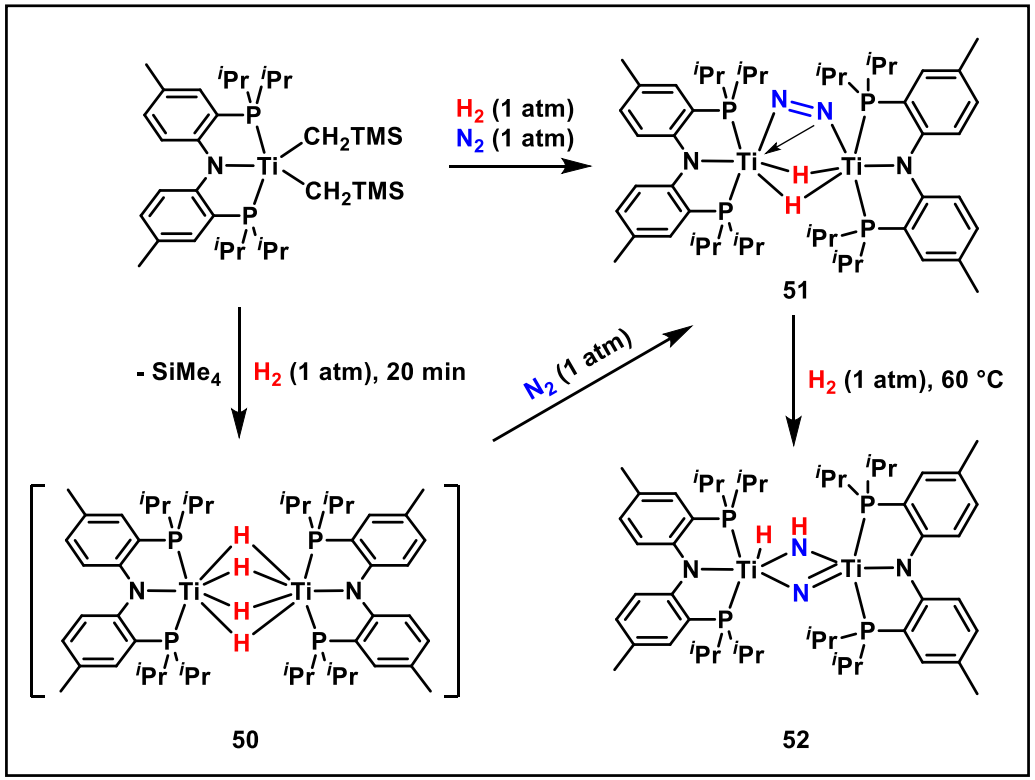


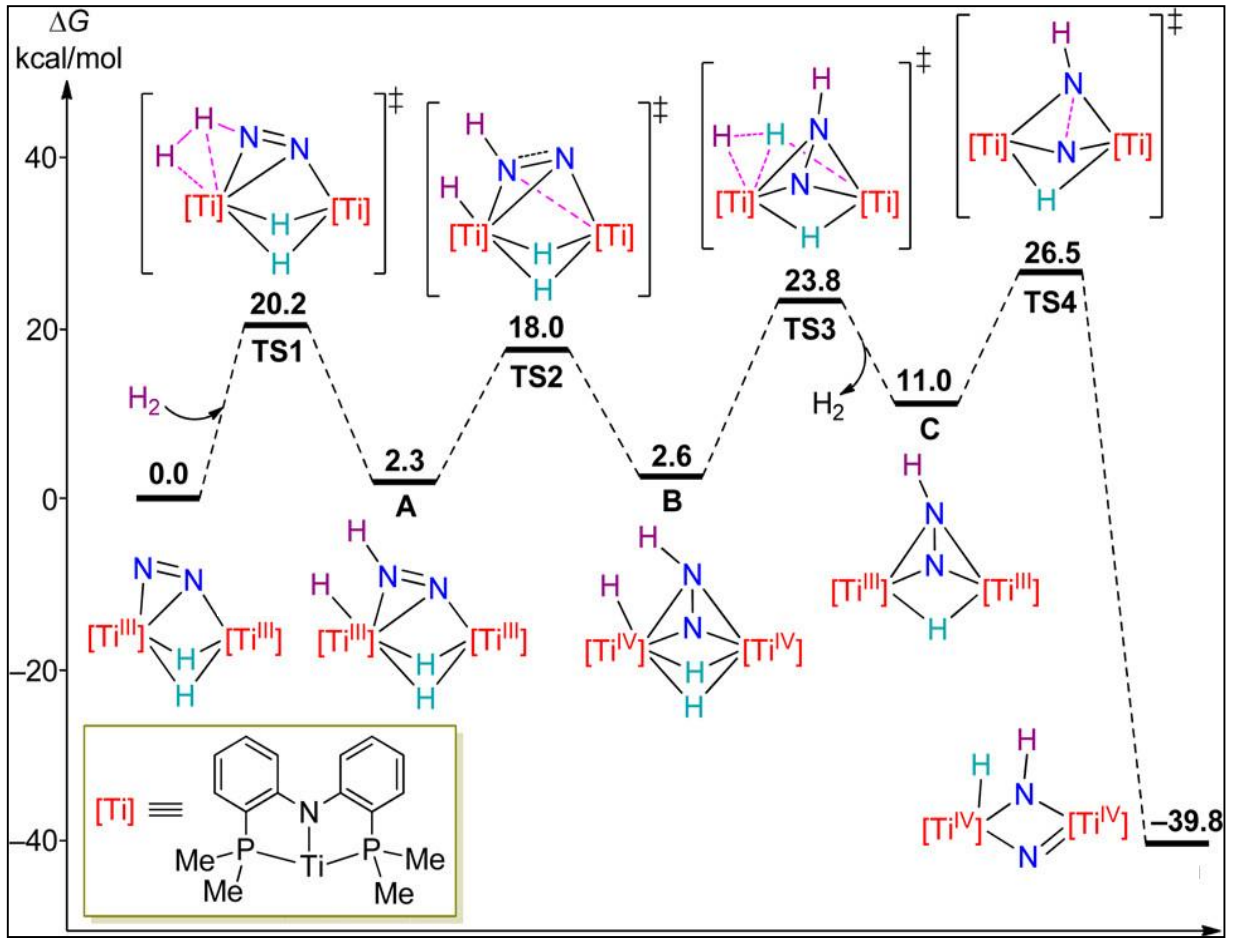


a) M. Mazzanti, et al. *J. Am. Chem. Soc.* **2026**, *148*, 9231–9237

2.2 Binuclear Transition Metal Hydride Complexes

Reaction of PNP-Ligated Titanium Complex 50 with N_2

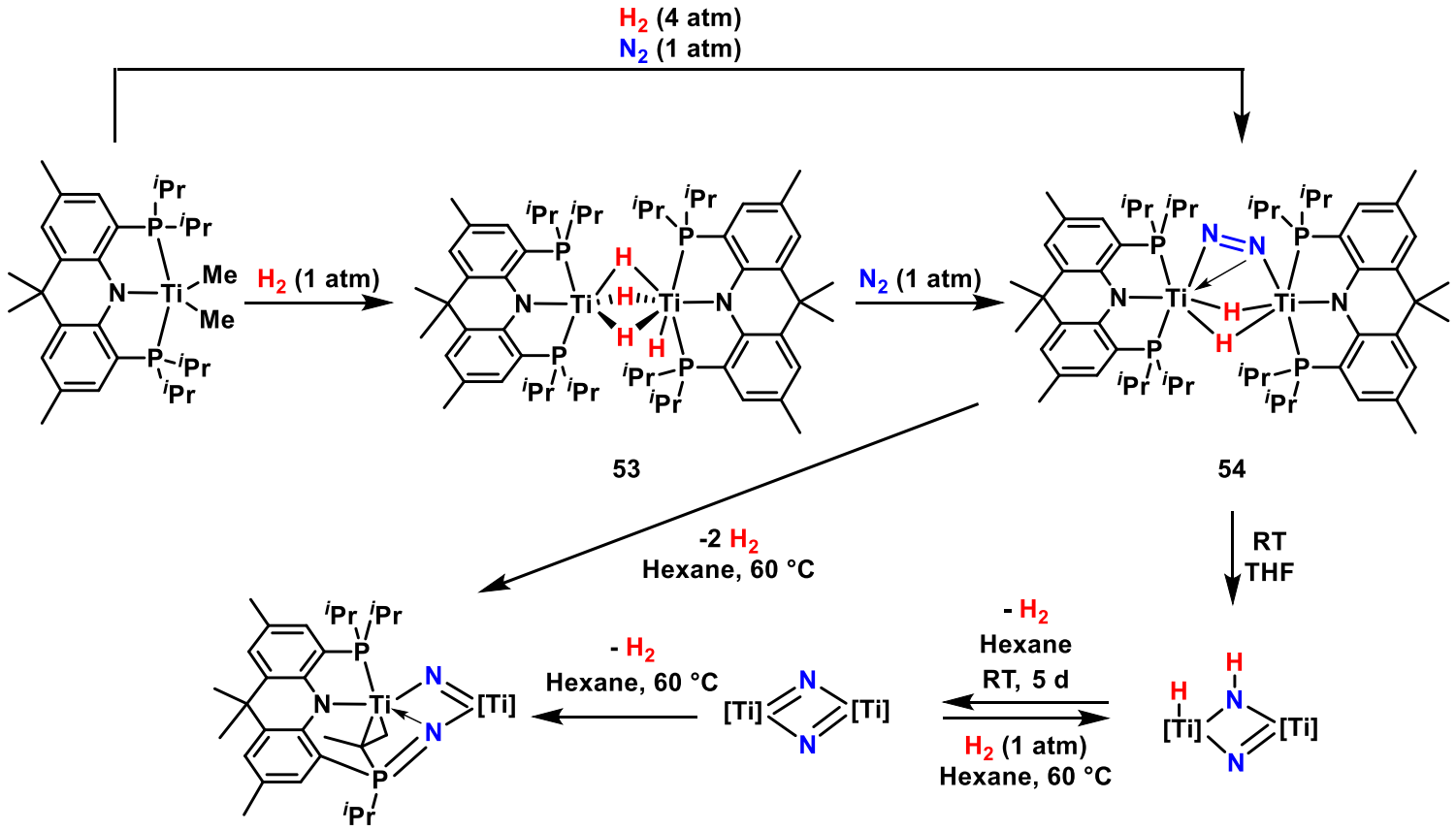




a) Z. Hou, et al. *J. Am. Chem. Soc.* **2017**, *139*, 1818−1821

2.2 Binuclear Transition Metal Hydride Complexes

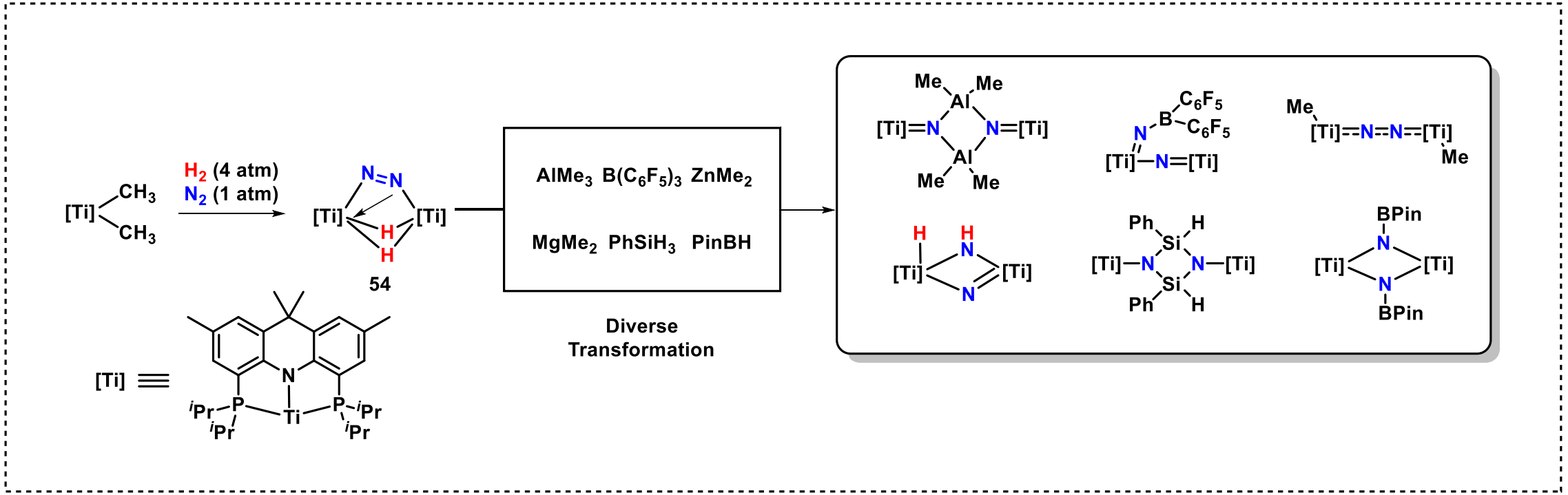
Reaction of Pincer-PNP-Ligated Titanium Hydride Complex 53 with N_2



a) Z. Hou, et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 8635–8644

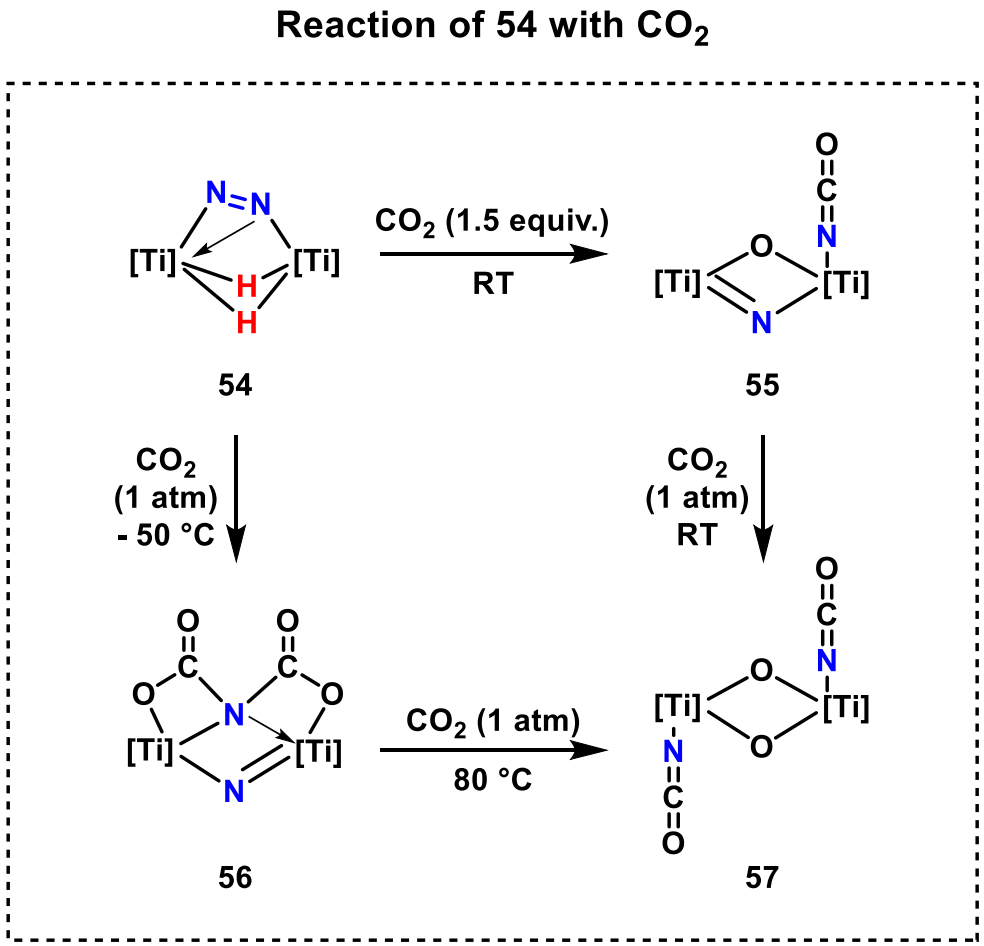
2.2 Binuclear Transition Metal Hydride Complexes

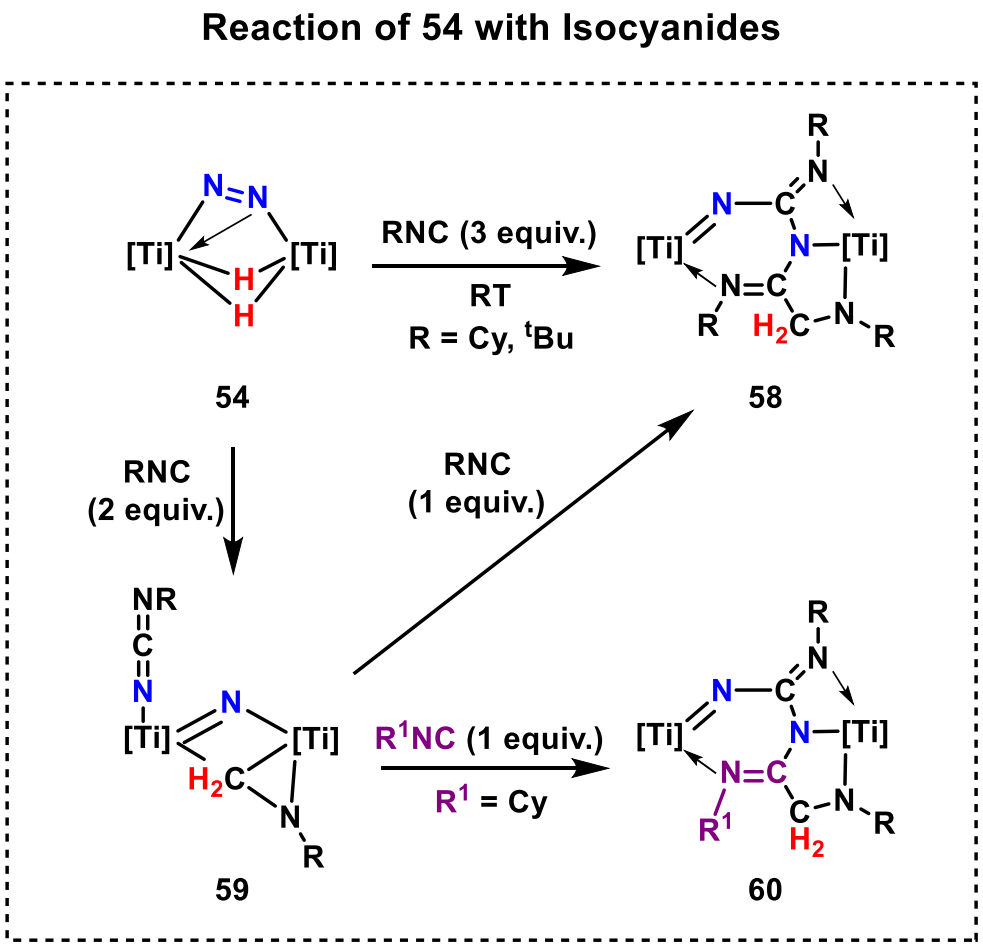
Reaction of 54 with Electrophiles



a) Z. Hou, et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 8635–8644

2.2 Binuclear Transition Metal Hydride Complexes

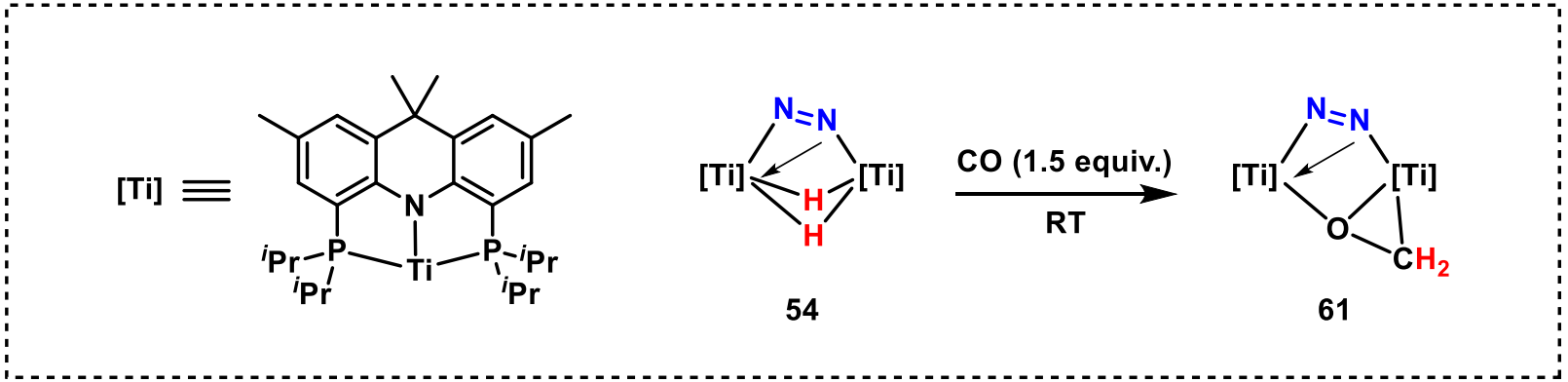




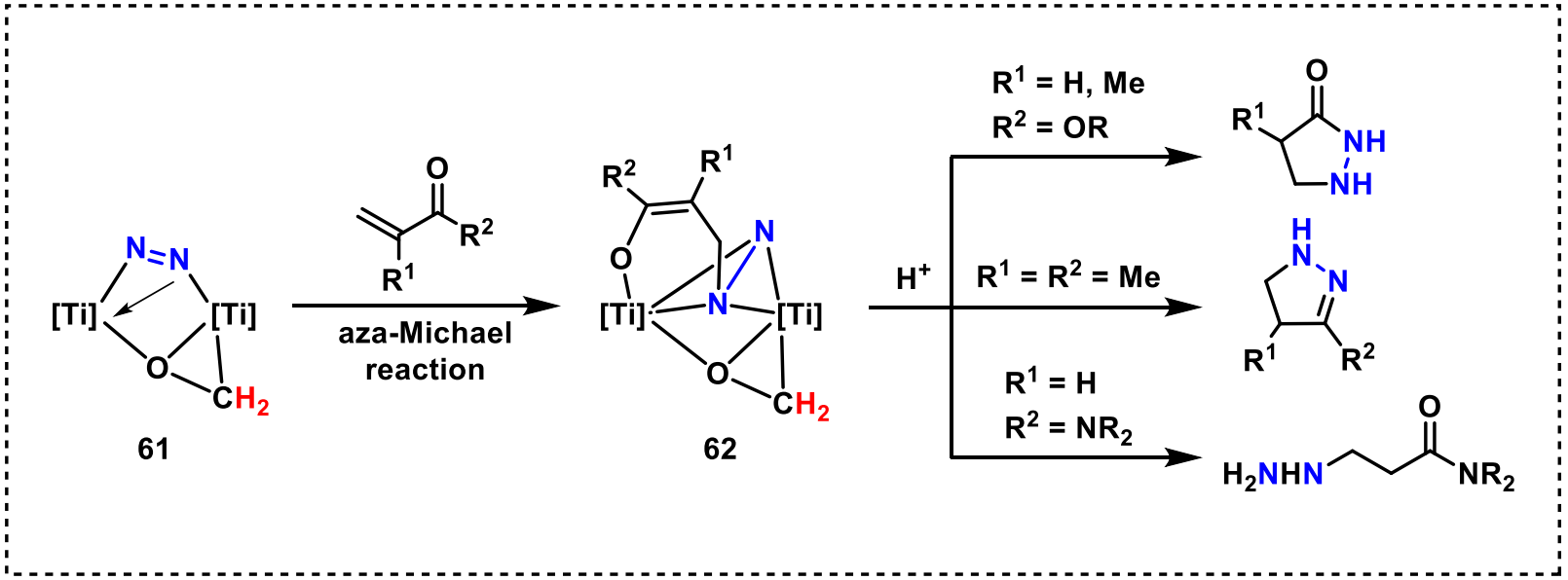
a) Z. Hou, et al. *J. Am. Chem. Soc.* **2022**, *144*, 6972−6980; b) Z. Hou, et al. *J. Am. Chem. Soc.* **2024**, *146*, 10984−10992

2.2 Binuclear Transition Metal Hydride Complexes

Reaction of 54 with CO



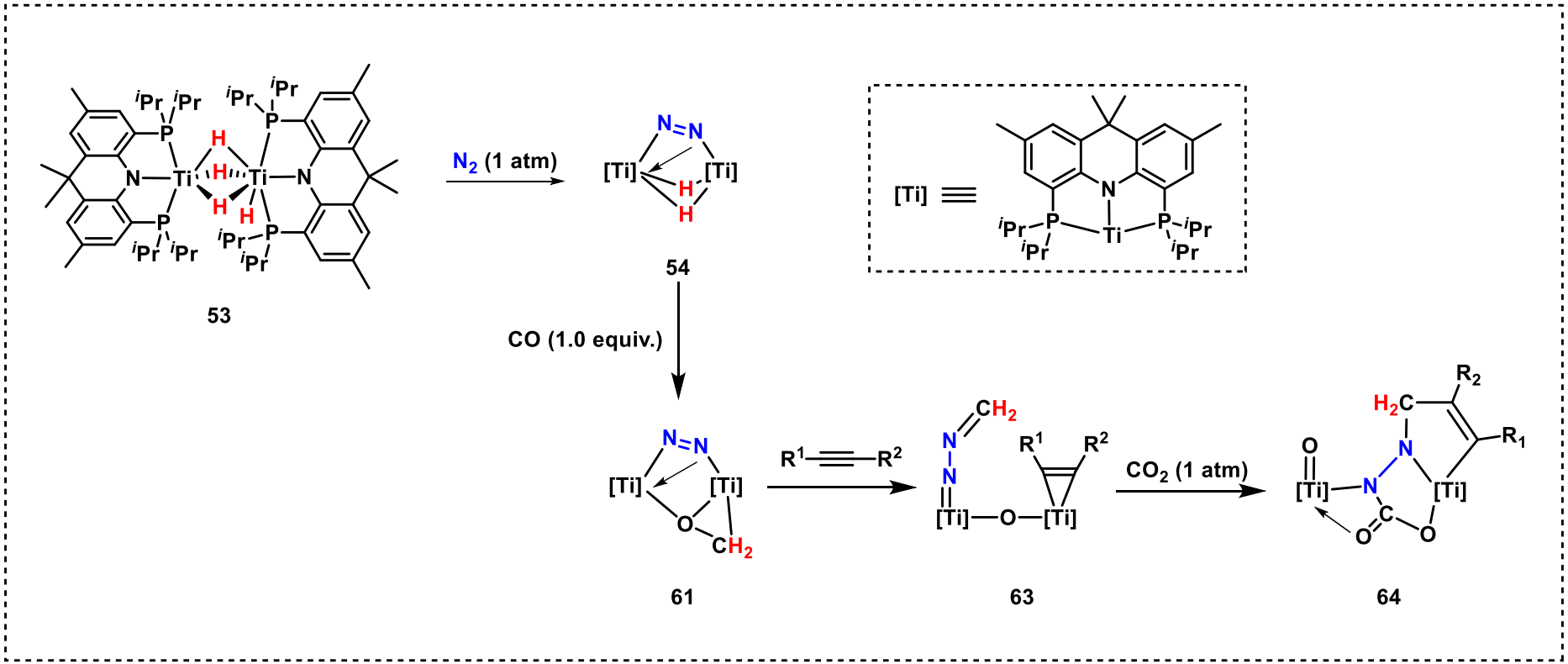
Reaction of 61 with α,β-unsaturated Carbonyl Compounds



a) Z. Hou, et al. *J. Am. Chem. Soc.* **2023**, *145*, 22803−22813

2.2 Binuclear Transition Metal Hydride Complexes

Cascade Coupling of N_2, CO, Alkynes, and CO_2 Mediated by 53



a) Z. Hou, et al. *J. Am. Chem. Soc.* **2026**, *148*, 14435−14442

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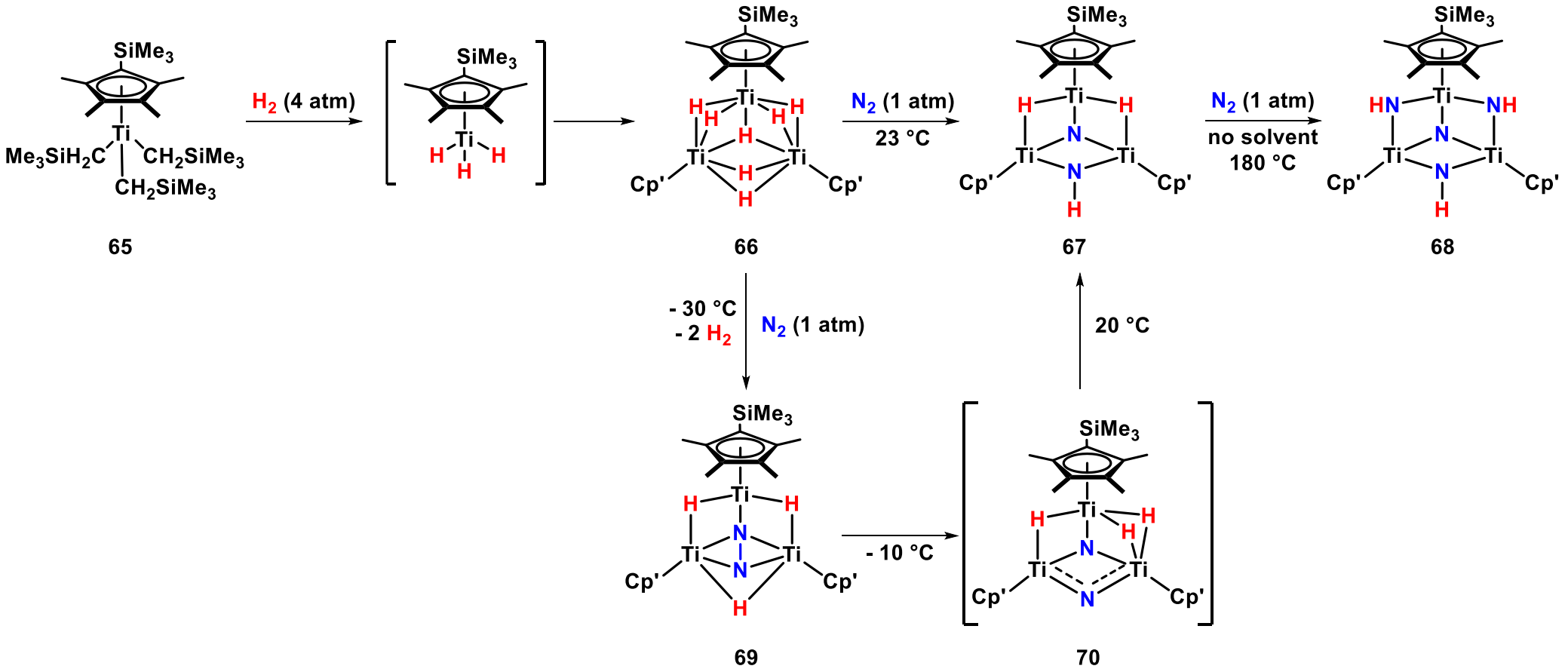
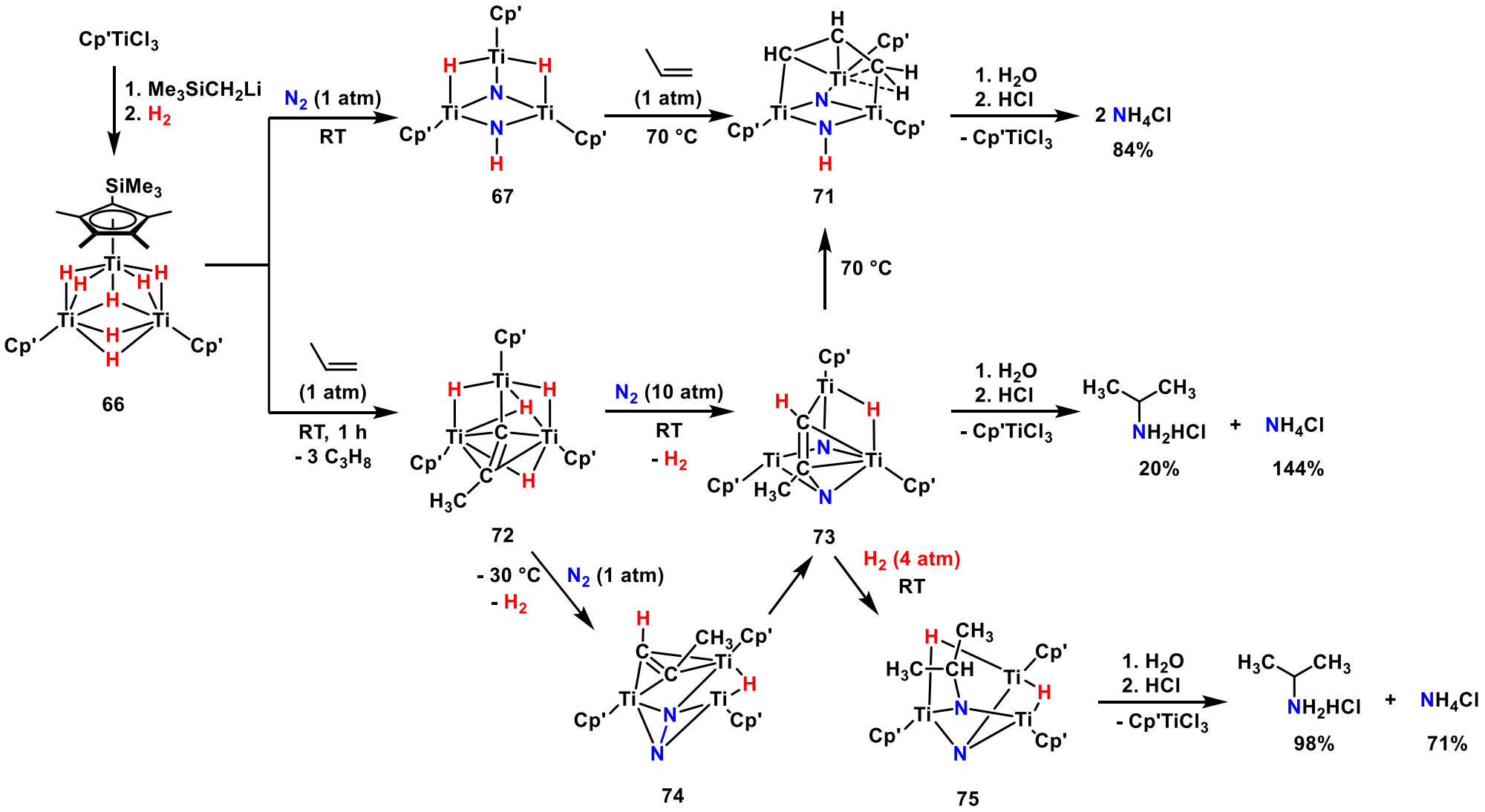
N_2 Cleavage and Hydrogenation by Polyhydride 66



a) Z. Hou, et al. *Science.* **2013**, *340*, 1549−1551

2.3 Trinuclear Transition Metal Hydride Complexes

Activation and Transformation of Propylene and N_2 in a Trititanium Hydride Framework 66



a) Z. Hou, et al. *Nature*. **2024**, *632*, 307−312

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2. Metal Hydride-Mediated Activation of N_2

    2.1 Mononuclear Transition Metal Hydride Complexes

    2.2 Binuclear Transition Metal Hydride Complexes

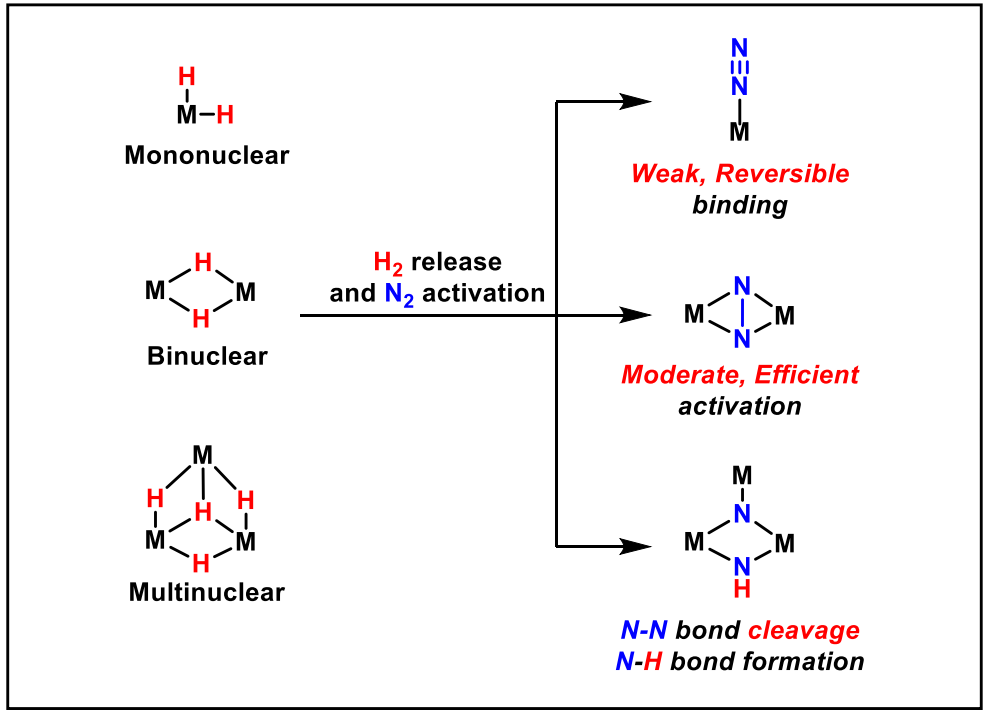
    2.3 Trinuclear Transition Metal Hydride Complexes

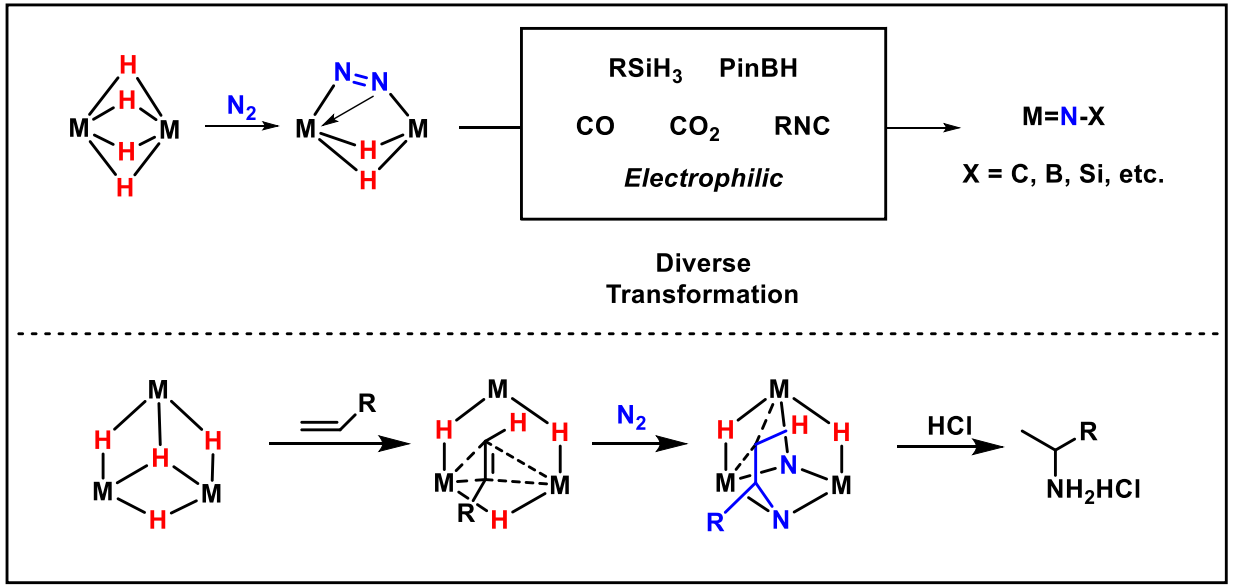
3. Summary and Outlook

3. Summary and Outlook

Summary

- Hydride ligands can serve as both electron and proton sources
- Reactivity toward N_2 increases from mono- to multinuclear hydrides
- Hydride-mediated N_2 activation broadens the derivatization pathways

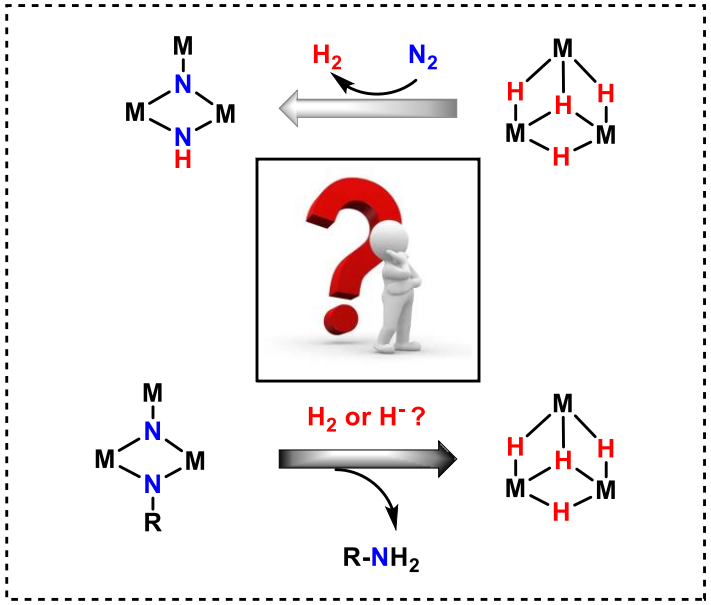


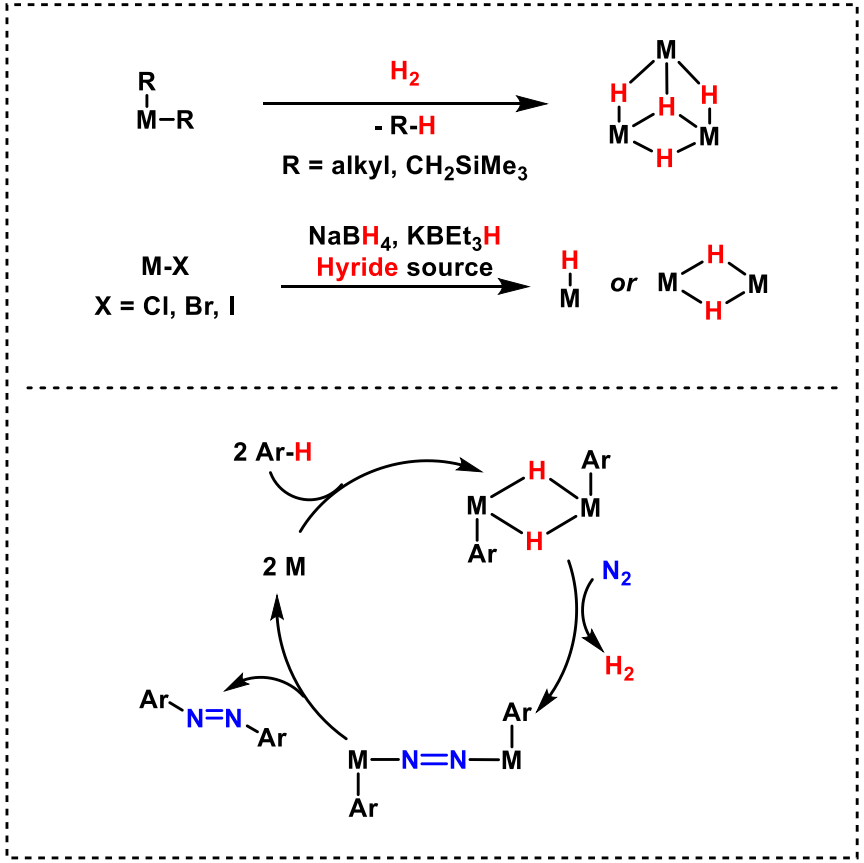


3. Summary and Outlook

Outlook

- Understanding cooperative effects and catalytic cycles
- Expanding functionalization





Thank you for your attention