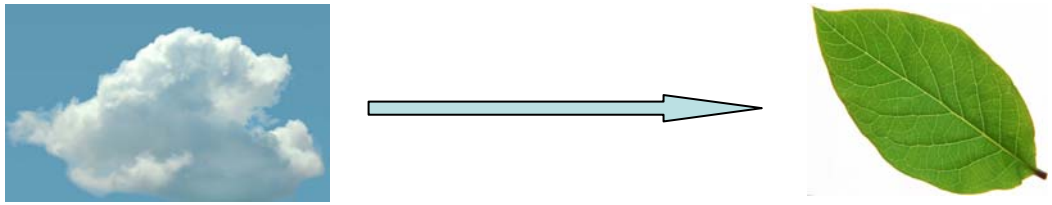
Developments in the Reduction of Dinitrogen



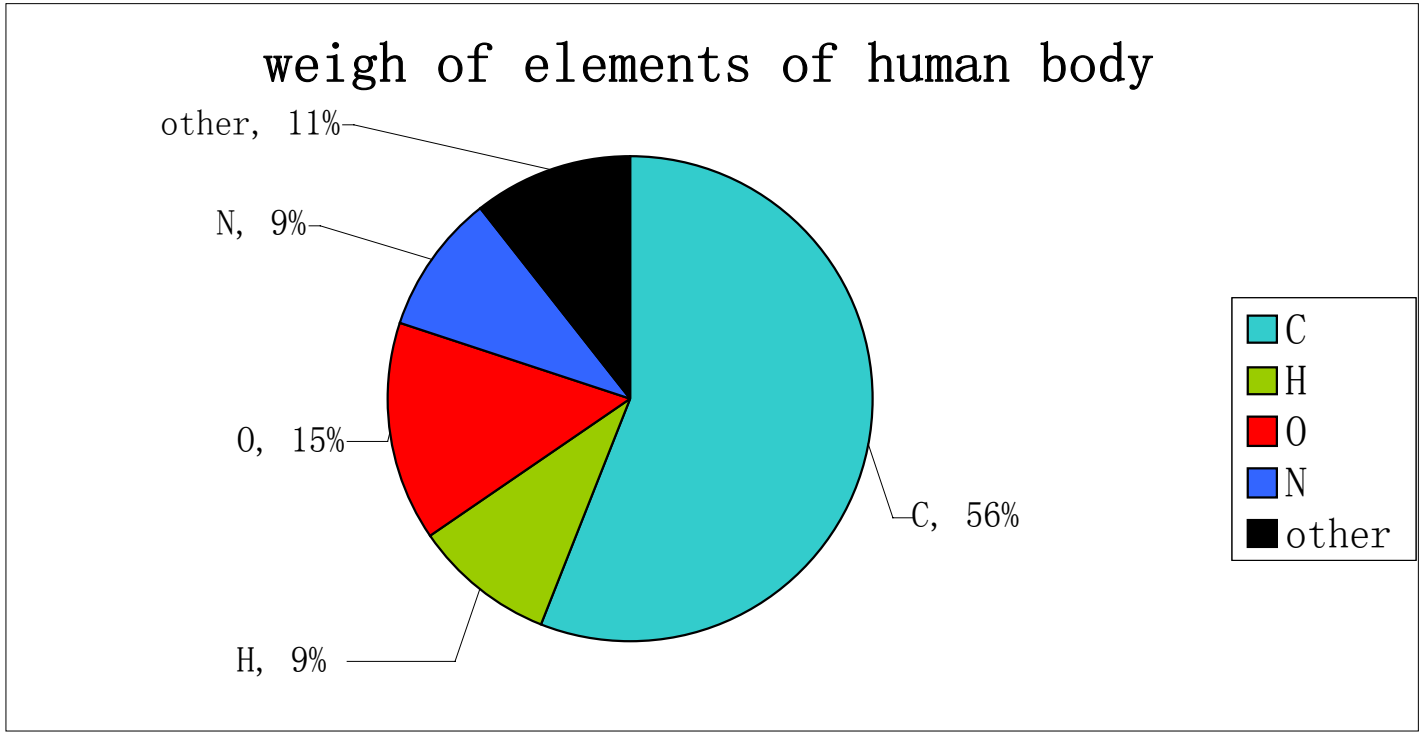
N_2 in air

N in life

Pan Hu
2014.12.8.

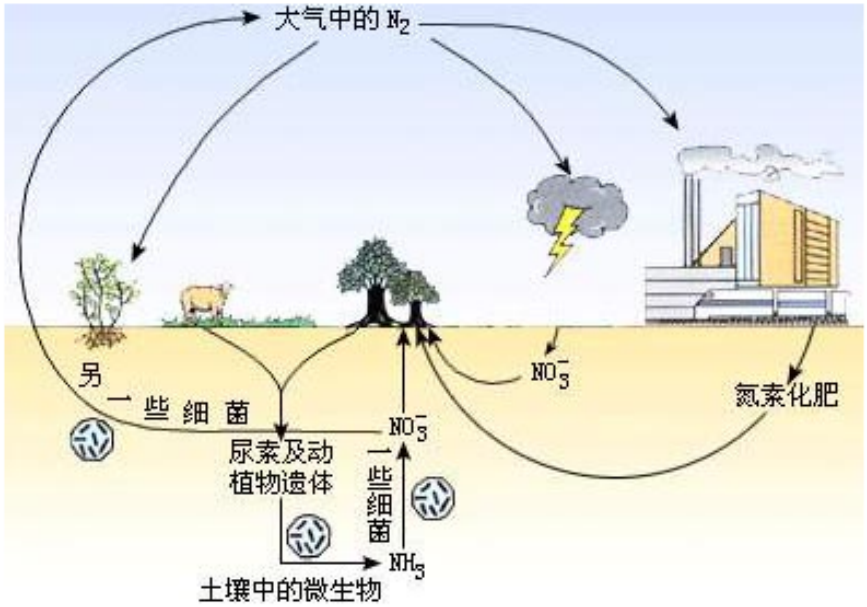
- Background Information
- Brief Introduction of Synthetic Ammonia Industry
- the Homogeneous Reduction of Dinitrogen
- Summary

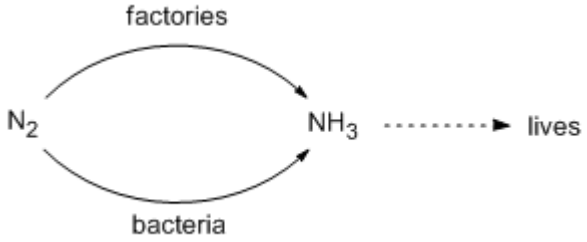
Background Information



Background Information

图2-14氮循环示意图





Human pruduce 200M tons ammonia annual

Synthetic Ammonia Industry

1895:

calcium acetylide

$$Ca^{2+}(C{\equiv}C)^{2-} + N_2 \longrightarrow CaCN_2$$

$$CaCN_2 + H_2O \longrightarrow NH_3 + CaCO_3$$

high energy cost

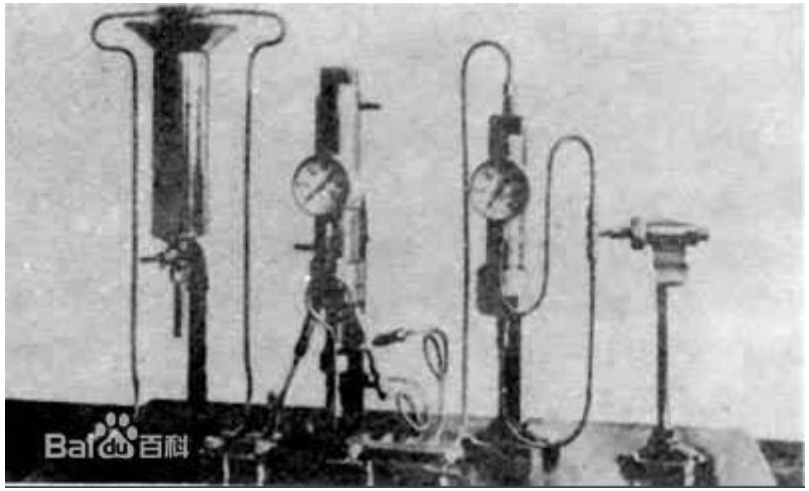
Synthetic Ammonia Industry

1909: **Haber-Bosh Process**

Fritz Haber

$$2N_2 + 3H_2 \rightleftharpoons 2NH_3$$

catalyst: **iron** oxidant



Most important discovery in the 20th.

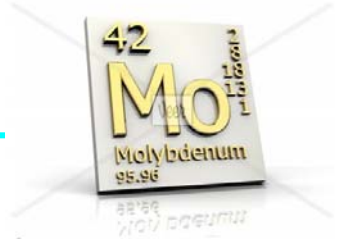
300~500°C, **20~50MPa**

- Higher Conversion but Lower Pressure?

catalyst optimization

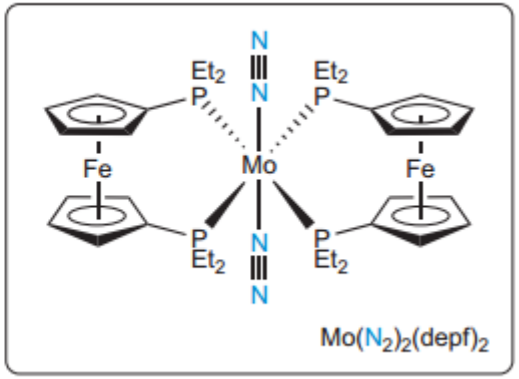
new dinitrogen reduction reaction

the Homogeneous Reduction of Dinitrogen



$$N_2\ (1\ atm) + Me_3SiCl + Na \xrightarrow[THF]{Mo(N_2)_2(depf)_2\ (cat.)} N(SiMe_3)_3$$

226 equiv. per Mo



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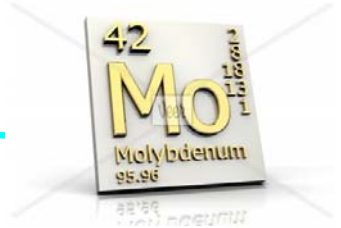

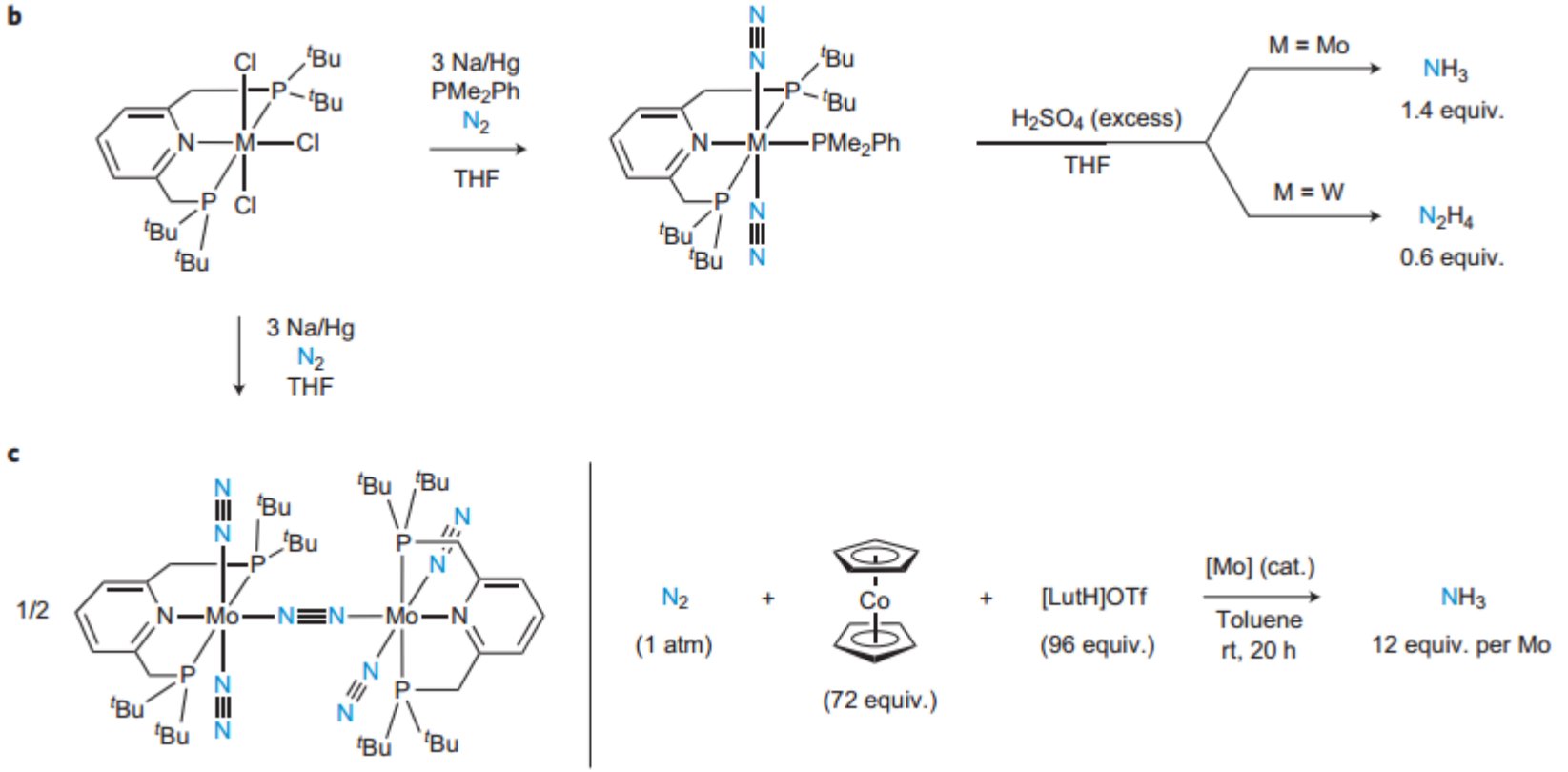

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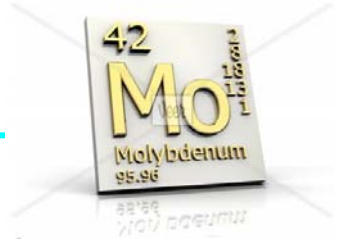

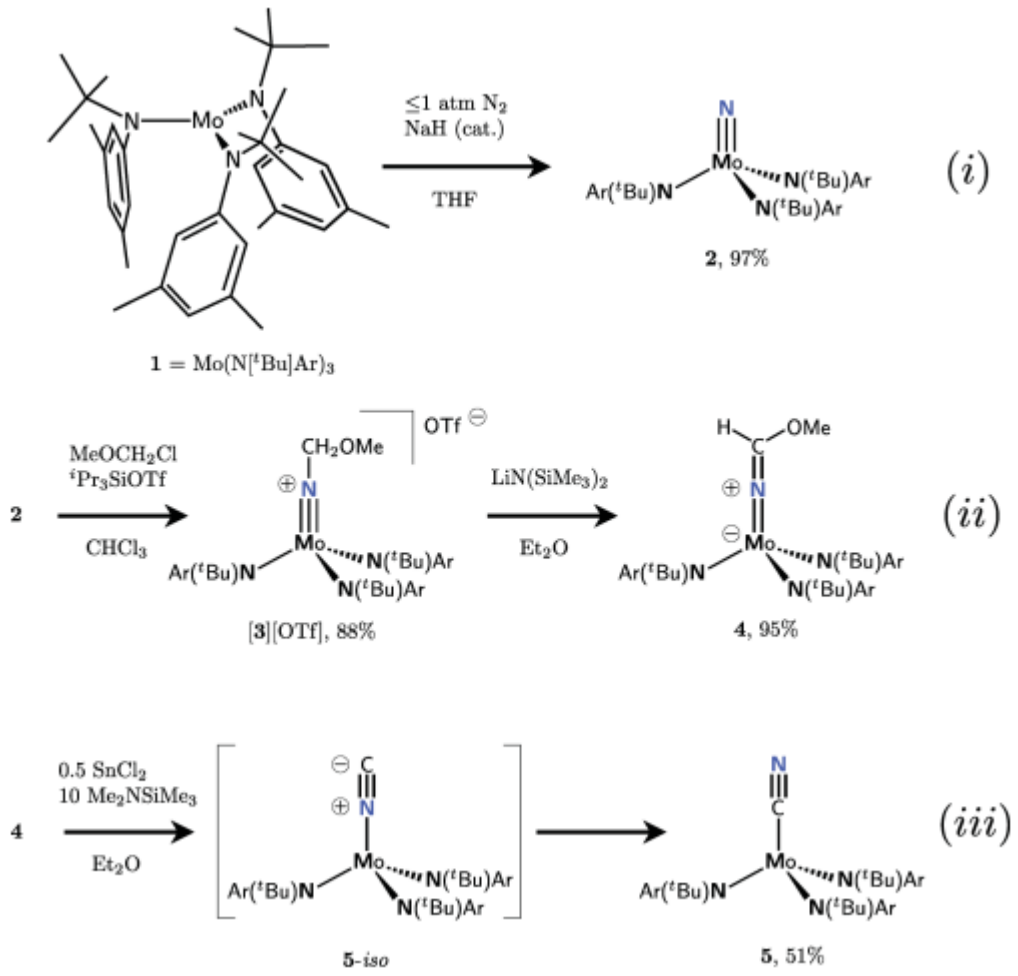

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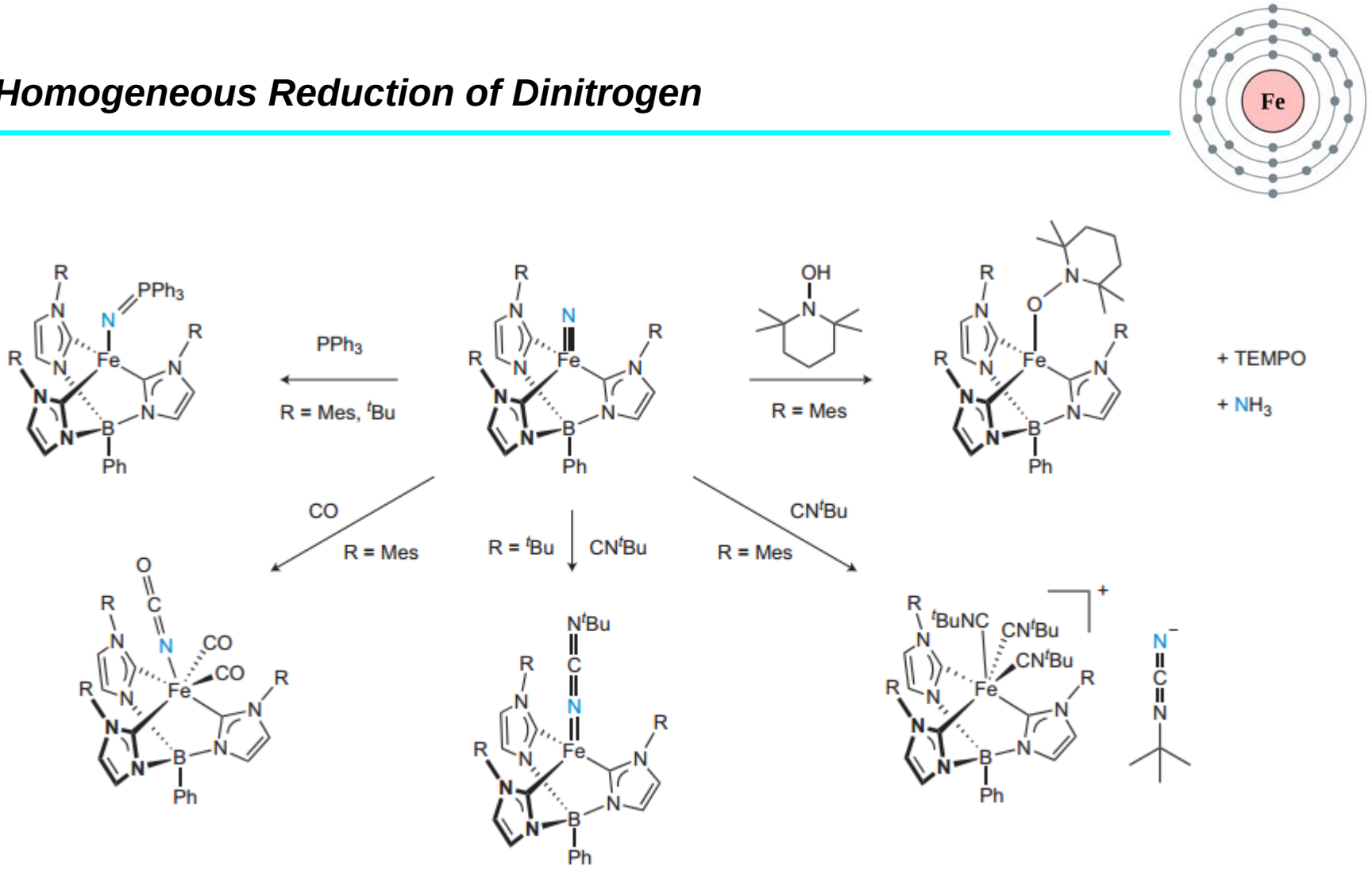

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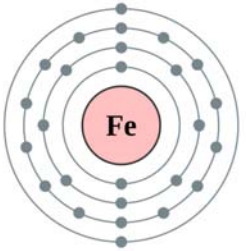
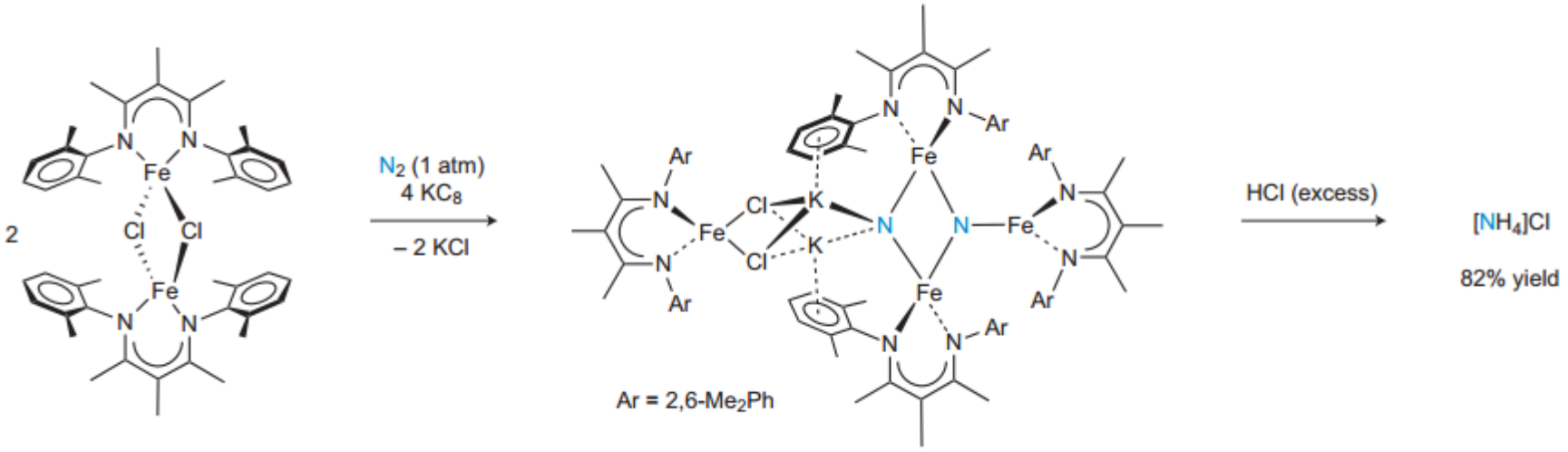


First example of high-yielding N_2 conversion to NH_3 with an Fe-based system.



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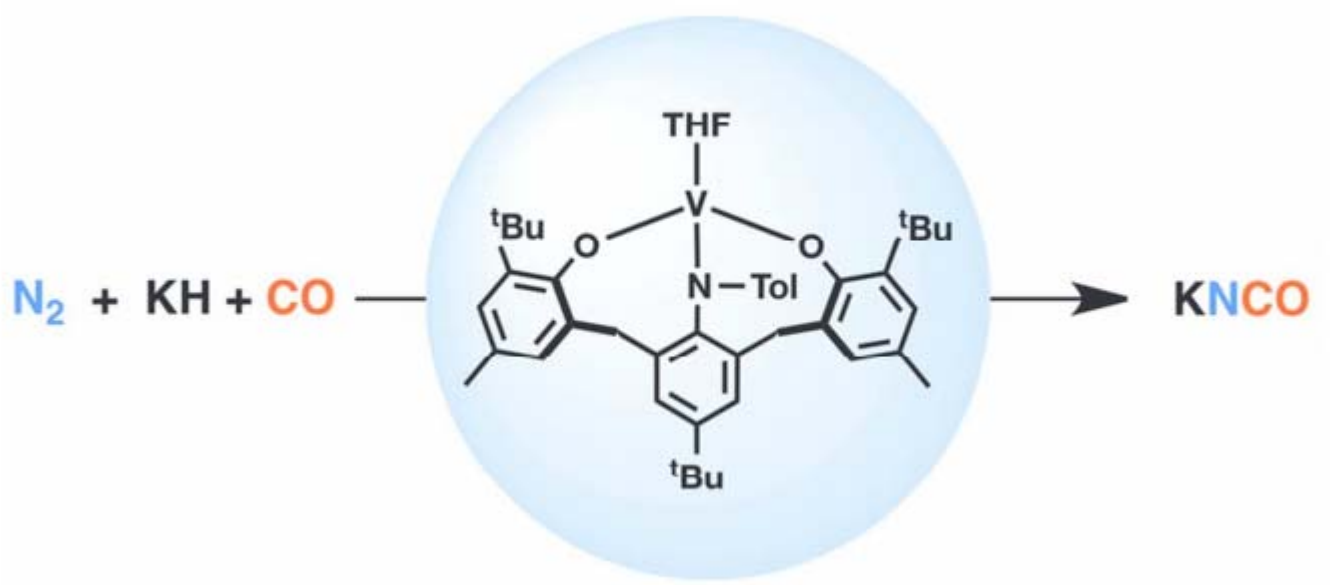
the Homogeneous Reduction of Dinitrogen

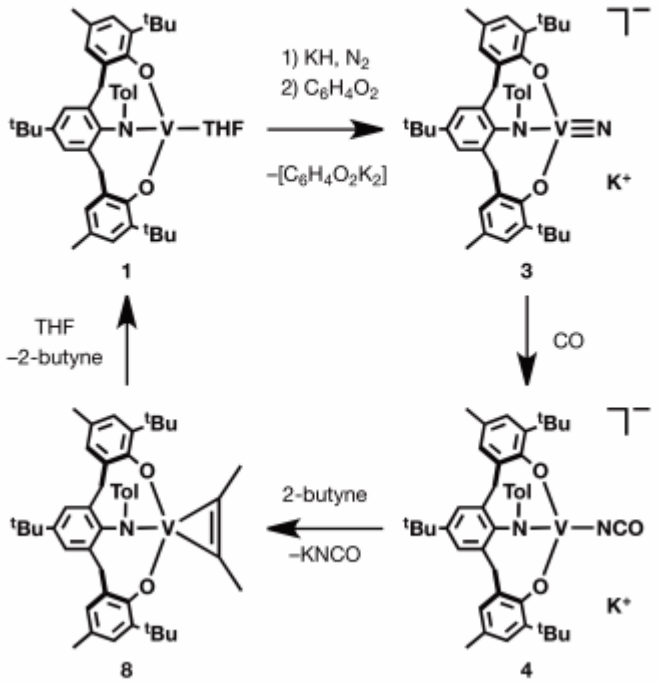
Nitrogen Atom Transfer from a Dinitrogen-Derived Vanadium Ni-tride Complex to Carbon Monoxide and Isocyanide

Yutaka Ishida, and Hiroyuki Kawaguchi

J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/ja510317h • Publication Date (Web): 20 Nov 2014

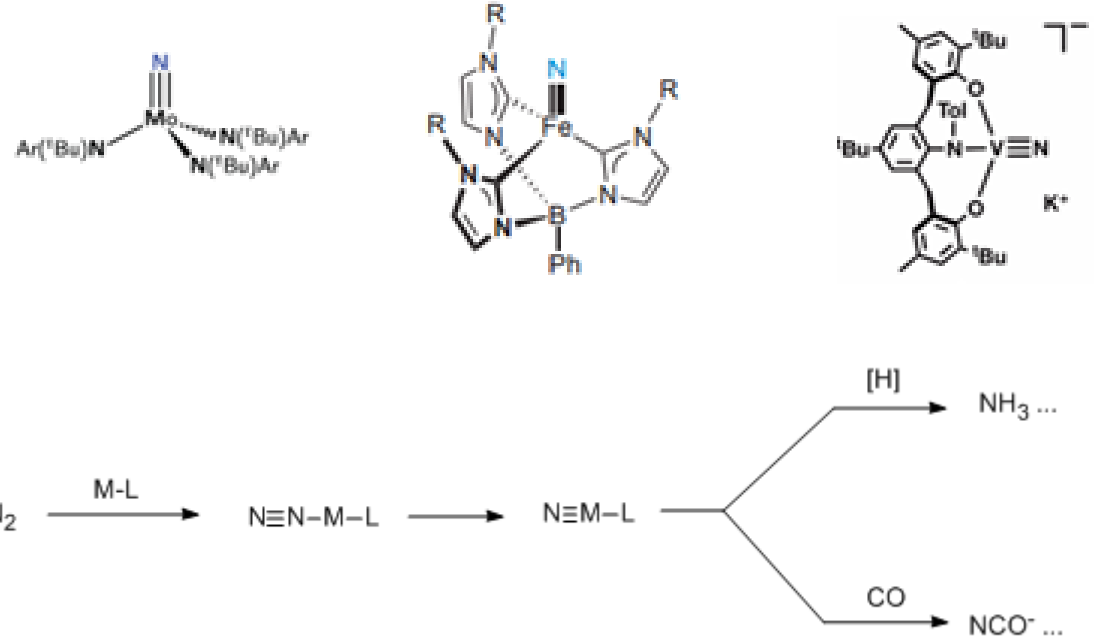


Scheme 2. Synthetic Cycle for the Conversion of N_2 and CO into $[NCO]^-$



Summary

- High oxidant-level transition metal plays a very important role



- One emerging theme is the importance of the supporting ligand.

THANK YOU