ACTIVATION OF MOLECULAR NITROGEN WITH TRANSITION METAL COMPLEXES

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NH_3 Fuel Conference

Portland, OR
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HABER-BOSCH PROCESS

150 million tons of ammonia/year from nitrogen and hydrogen

- **Catalytic steam reforming**

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

- **Water gas shift reaction**

$$CO + H_2O \rightarrow CO_2 + H_2$$

- **Catalytic NH_3 formation**

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

300-550^{0}C, up to 250 atm

Fe or Ru oxide cat

KINETICS VS THERMODYNAMICS

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

- *Yields of ammonia are lower at high temperatures*
- *125 bar of H_2/N_2 (3:1 molar ratio)*

  125℃, yield is 91%.

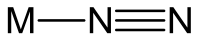
  500℃, yield is 12%
- *Must increase pressure to counteract temperature effect*

NEED CATALYST

TO LOWER KINETIC BARRIER

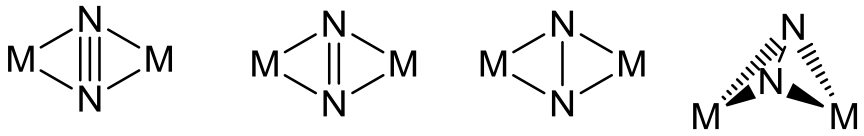
ACTIVATION OF N_2 BY BINDING TO COMPLEXES

End-on Monometallic

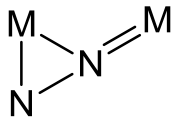


End-on Bimetallic

Side-on Bimetallic



Side-on End-on Bimetallic

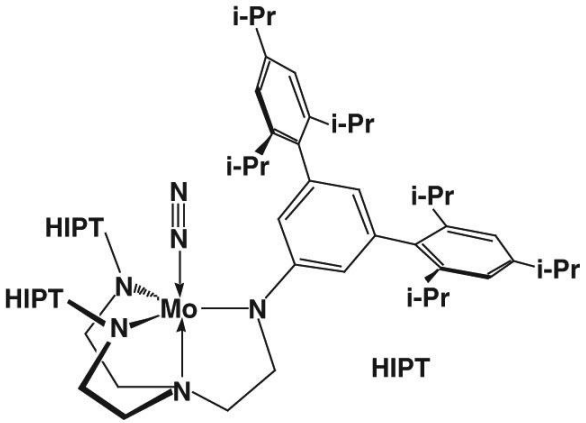


Binding to metals often leads to weakening of N-N triple bond

Free N_2:	**PhN ═ NPh**	**NH_2 — NH_2**
N-N 1.0975 Å	**1.255**	**1.460**
ν_{NN} 2331 cm^{-1}	**1442**	**1111**

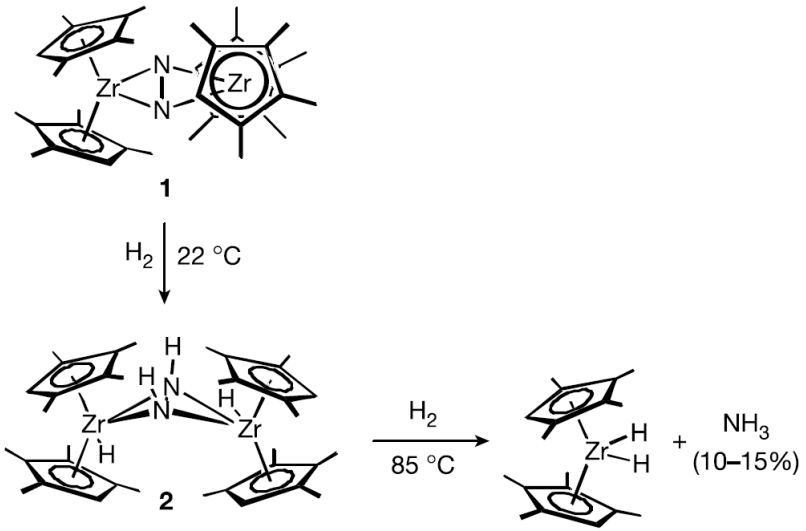
M. D. Fryzuk, *Chem. Rev.* 2004, 104, 385; *Acc. Chem. Res.* 2009, 42, 127

ACTIVATION AND CLEAVAGE OF N_2

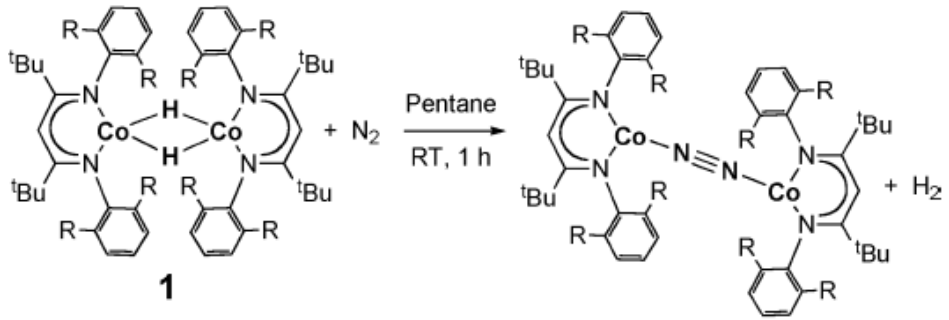


Cat for N_2 to NH_3 - 4 cycles

Yandulov, Schrock *Science* 2003, 301, 76

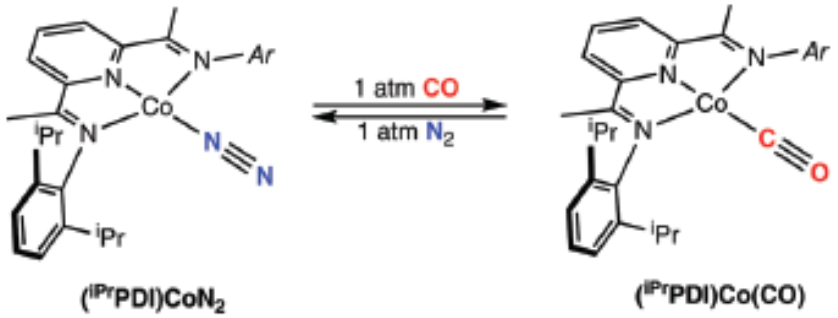


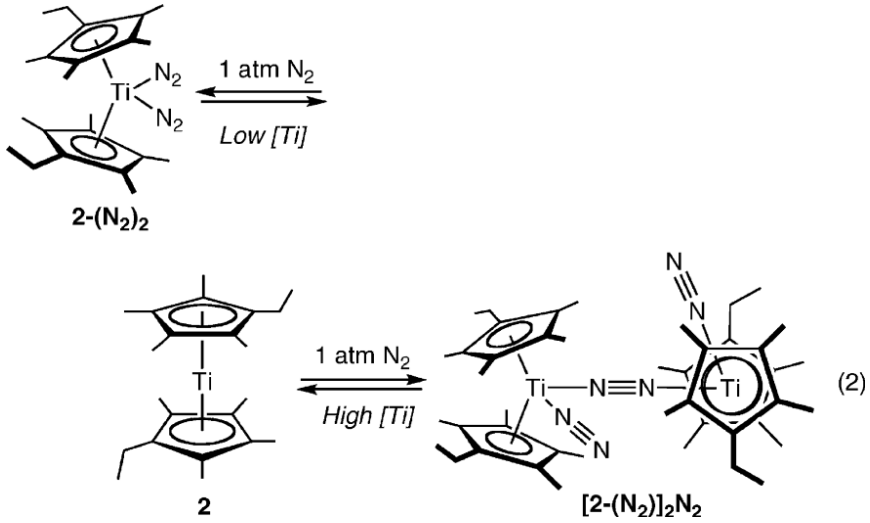
Chirik et al, Nature 2004, 427, 527



Holland et al, JACS 2009, 10804

MORE EXAMPLES





N_2-COMPLEXES ARE KNOWN FOR MANY METALS, BUT BOUND NITROGEN IS NOT VERY REACTIVE

Chirik et al, J. Am. Chem. Soc. 2010, Organometallics 2011

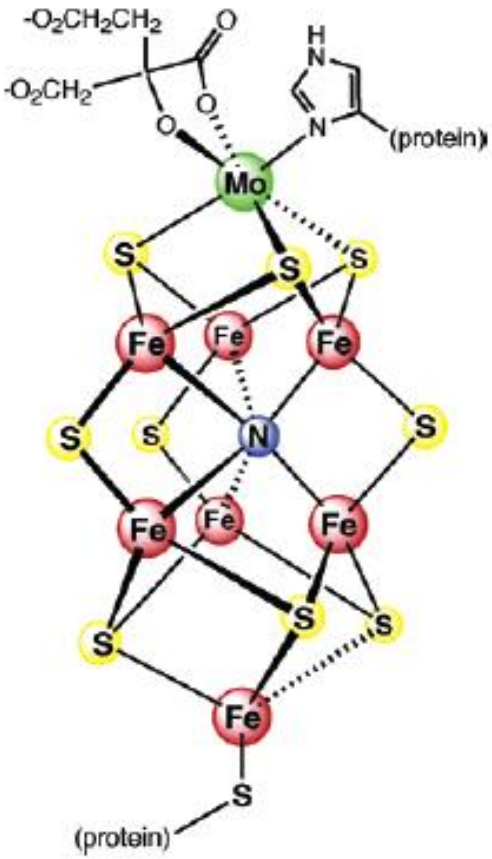
BIOLOGICAL NITROGEN FIXATION

Plants (at ambient temperature & pressure):

N_2 from air

↓ Enzyme (= catalyst)
+ protons + electrons

$NH_3 + H_2$



NITROGENASE ENZYMES (Fe, Mo, V)

Three kinds characterized to date:

- *Molybdenum + Iron*
- *Vanadium + Iron*
- *Iron only*

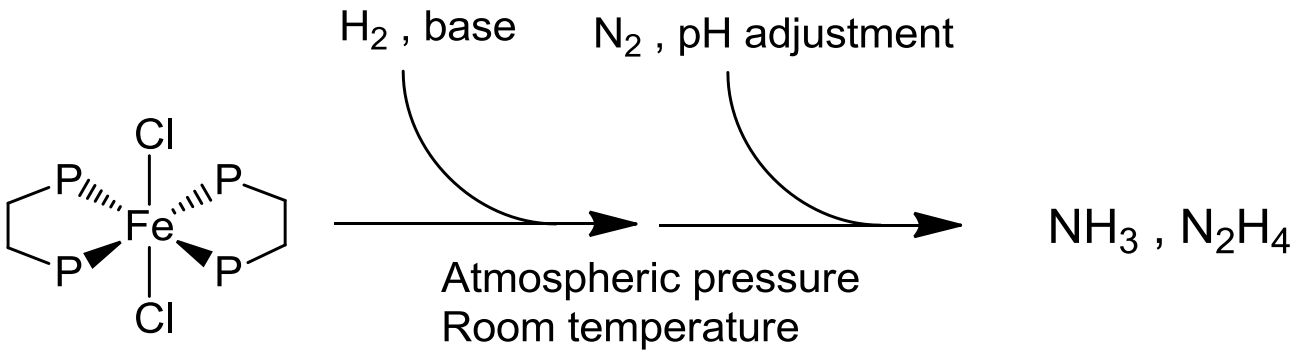
IRON SEEMS ESSENTIAL FOR BIOLOGICAL N_2 REDUCTION

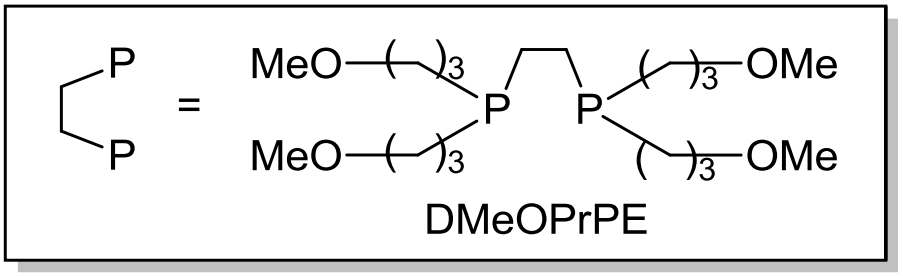
M. D. Fryzuk, *Chem. Rev.* 2004, 104, 385; Hazari, Chem. Soc. Rev. 2010, 4044

OUR PLAN

PREPARE NOVEL IRON COMPLEXES AS CANDIDATES FOR NITROGEN ACTIVATION

KNOWN REDUCTION OF N_2 TO NH_3 AT IRON

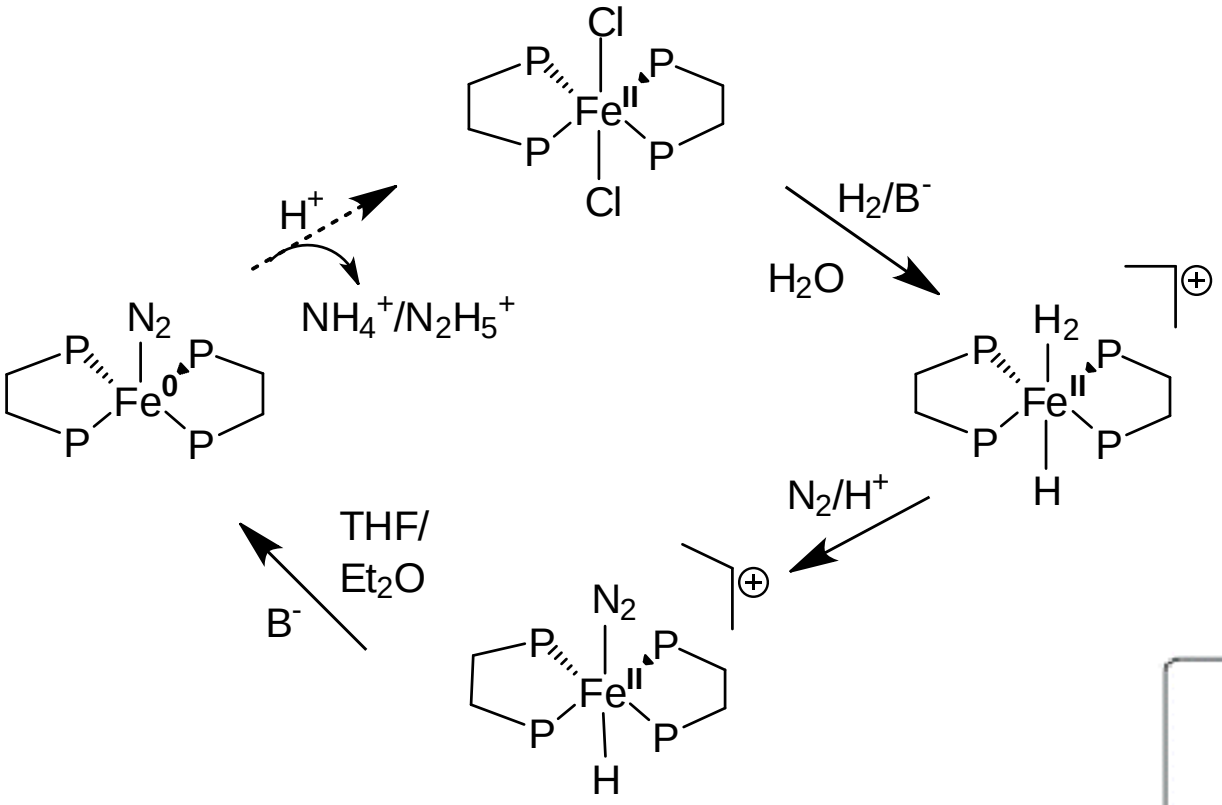


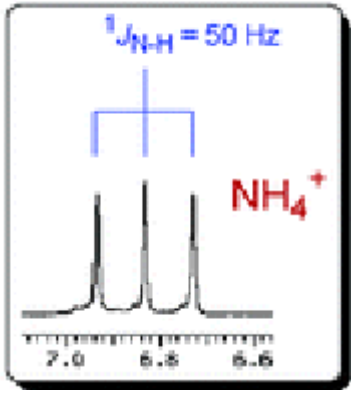


1,2-bis(bis(methoxypropyl)phosphino)ethane)

Gilbertson, J. D.; Szymczak, N. K.; Tyler, D. R. *J. Am. Chem. Soc.* **2005**, *127*, 10184.

$Fe(P_2)_2Cl_2 + H_2 / N_2$





Gilbertson, J. D.; Szymczak, N. K.; Tyler, D. R. *J. Am. Chem. Soc.* **2005**, *127*, 10184.
Leigh, G. J.; Jimenez-Tenorio, M. *J. Am. Chem. Soc.* **1991**, *113*, 5862.

PROBLEMS

- *Starting complex $(P_2)_2Fe^{II}Cl_2$ not stable in water*

  (hydrolyzes in 24 hours, H^+-catalyzed)

- *Protonation of $(P_2)_2Fe^0N_2$ causes hydrolytic destruction of complex*

  (free protonated ligand observed)

- *Every step carried out independently (protonation/deprotonation)*

- *Need a "single pot" catalytic process*

OUR STRATEGY

Use ligands that:

•Bind more strongly (polydentate, binuclear), but

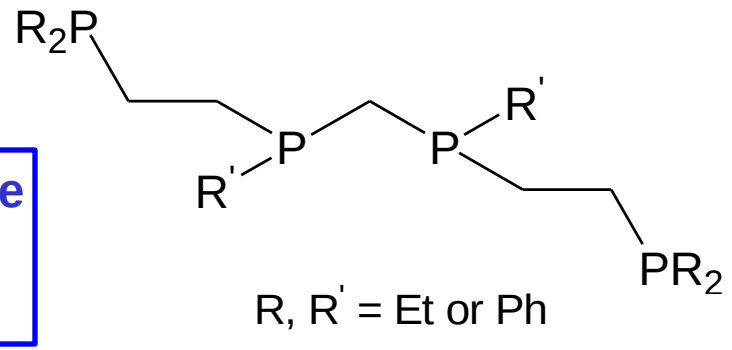
do not significantly perturb electronic structure

•Bind in a folded configuration to provide “reaction pocket” and strain in ligand back-bone

•Encourage temporary dissociation of one coordinating atom to allow binding of reactants (nitrogen, hydrogen)

•Keep remaining three atoms firmly bound to preserve integrity of complex

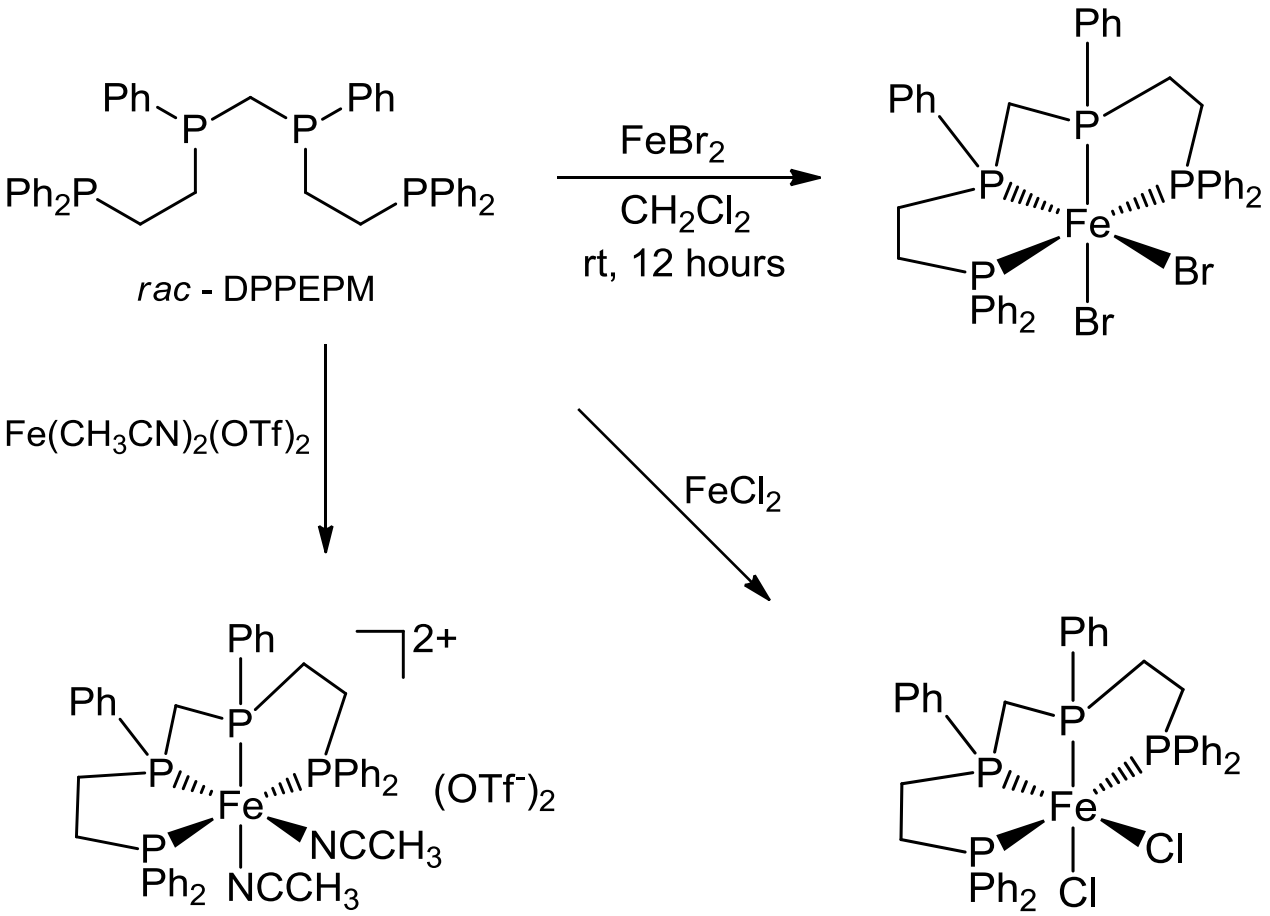
4 Phosphorus atoms – tetradentate
Similar electronic structure as P2
Short bridge – *cis*-structure ?



R, R' = Et or Ph

DPPEPM, DPPEPE

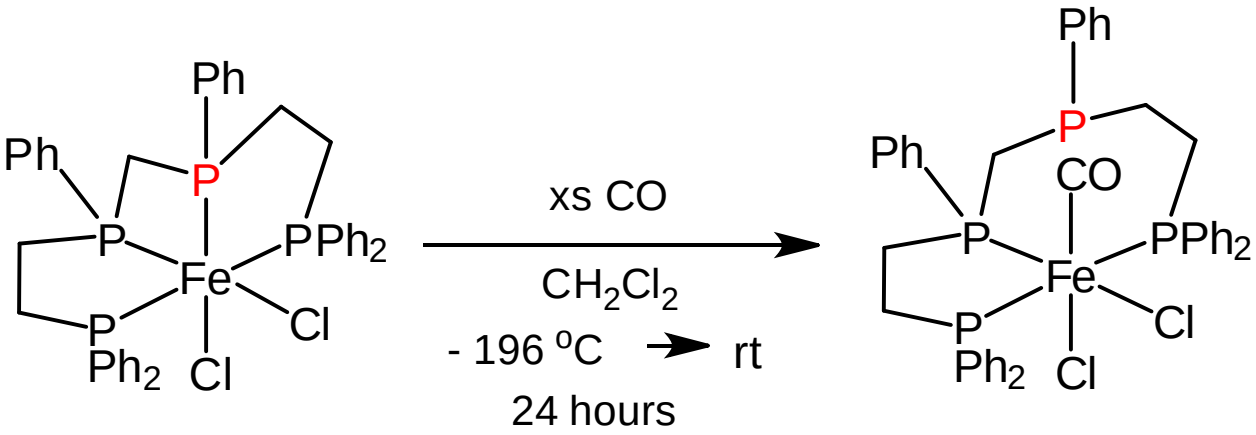
SYNTHESIS OF IRON COMPLEXES



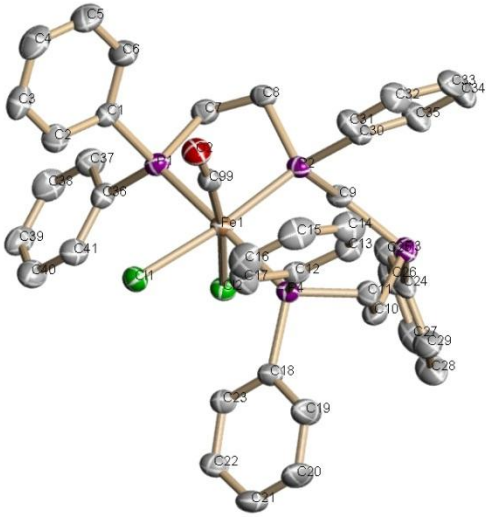
Cis-geometry is common for this ligand!

Jana, Ellern, Pestovsky, Sadow, Bakac Inorg. Chem. **2011,** 50, 3010

WEAK COORDINATION POSITION

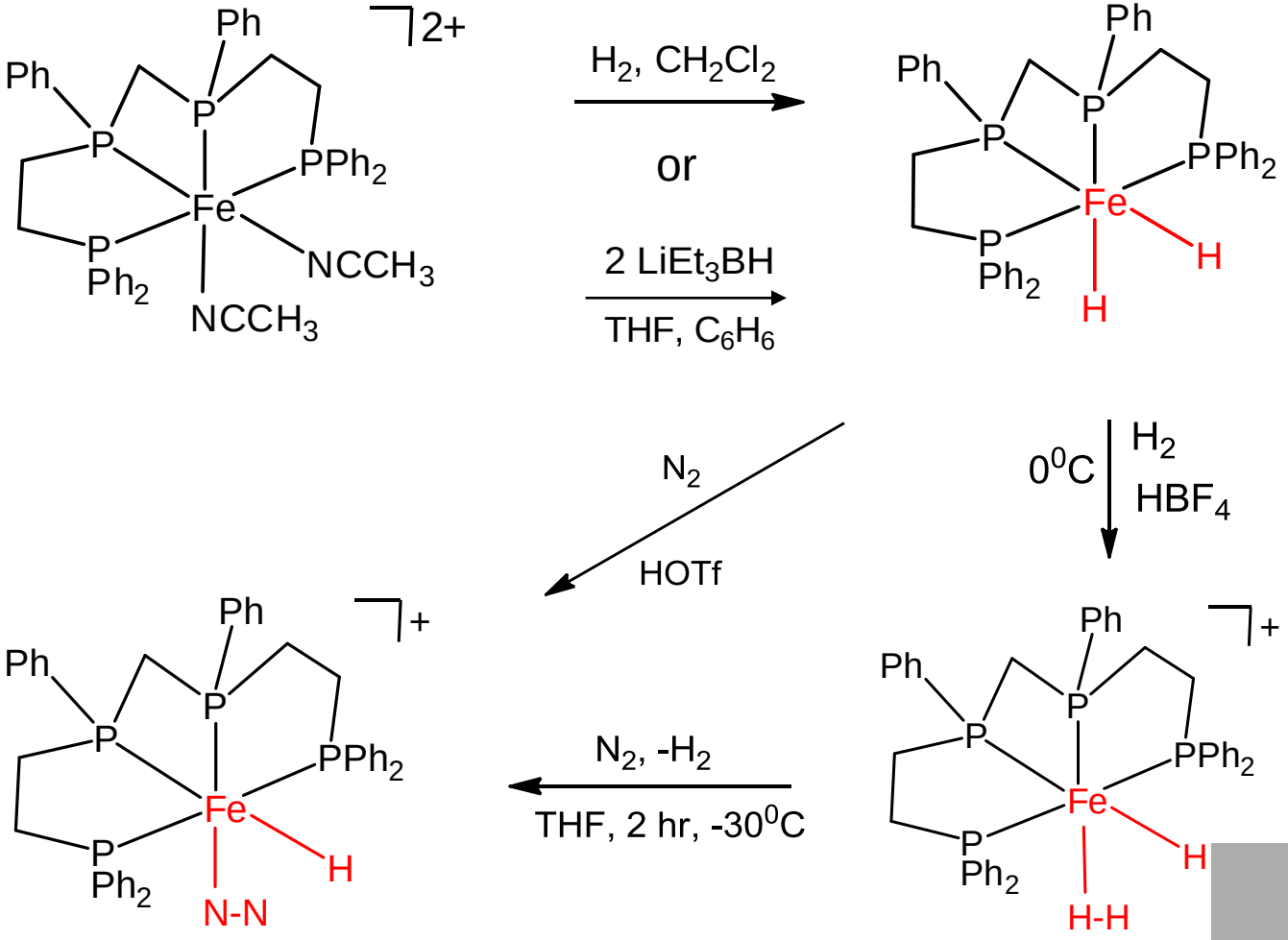


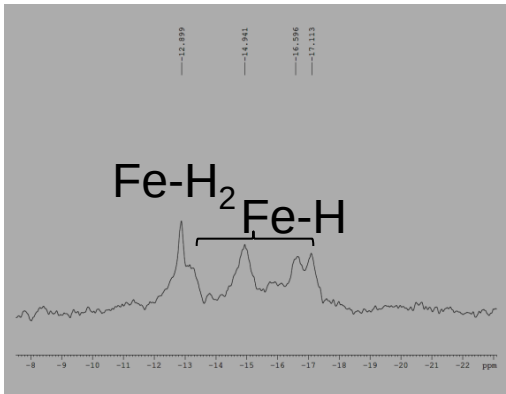
IR: 1941 cm^{-1} (CO)



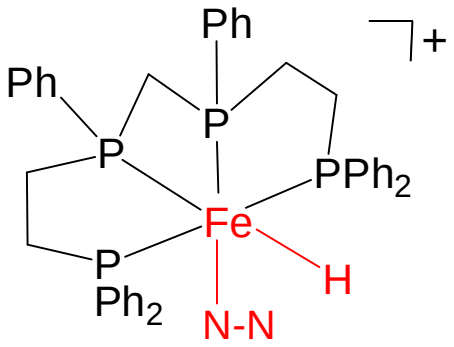
CO displaces one of four P-atoms

INDIVIDUAL STEPS – PRELIMINARY EXPERIMENTS

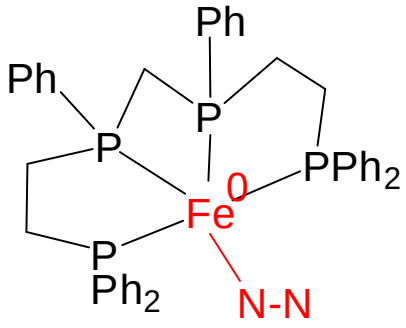




INDIVIDUAL STEPS – PRELIMINARY EXPERIMENTS



KO^tBu, N_2



Brown solution

xs HOTf

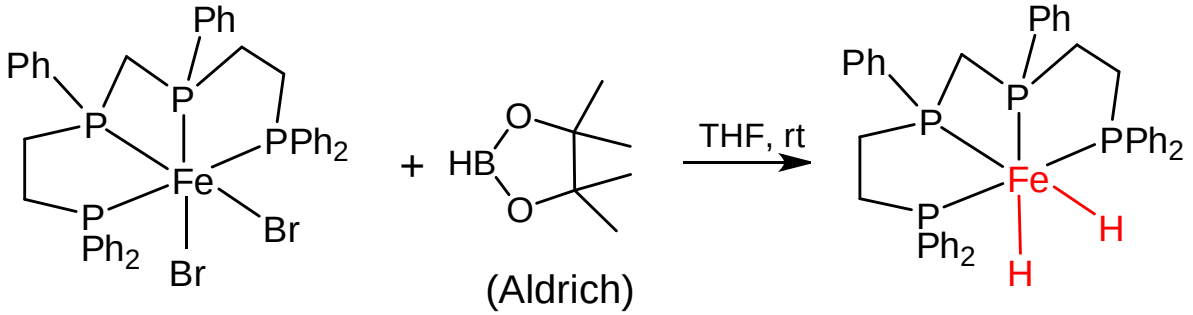
Light-green solution
No NH_3 in NMR
Still has coordinated N_2
But:
No decomposition in 3 days

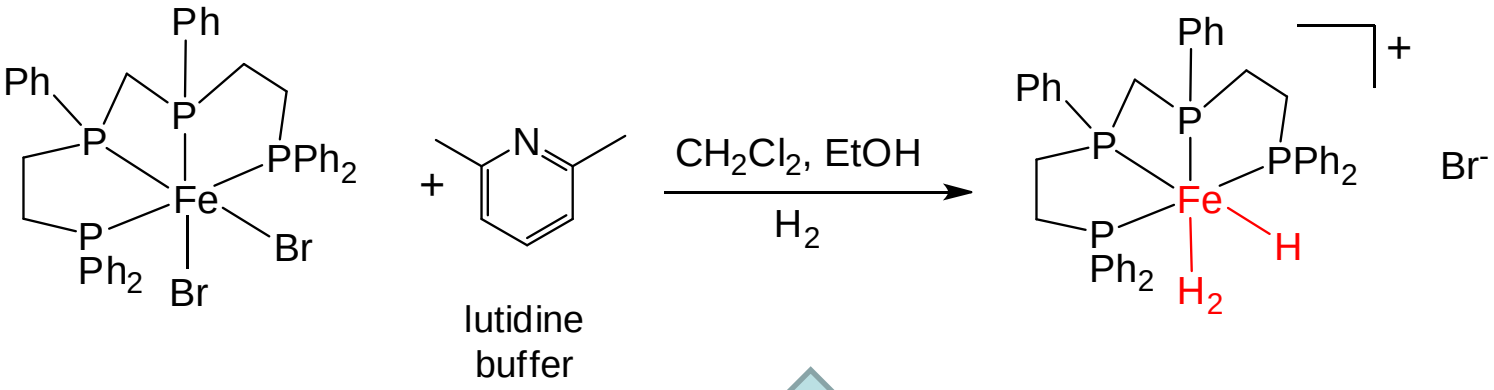
Vacuum, r. t.

N_2, -45^0C

Orange solution

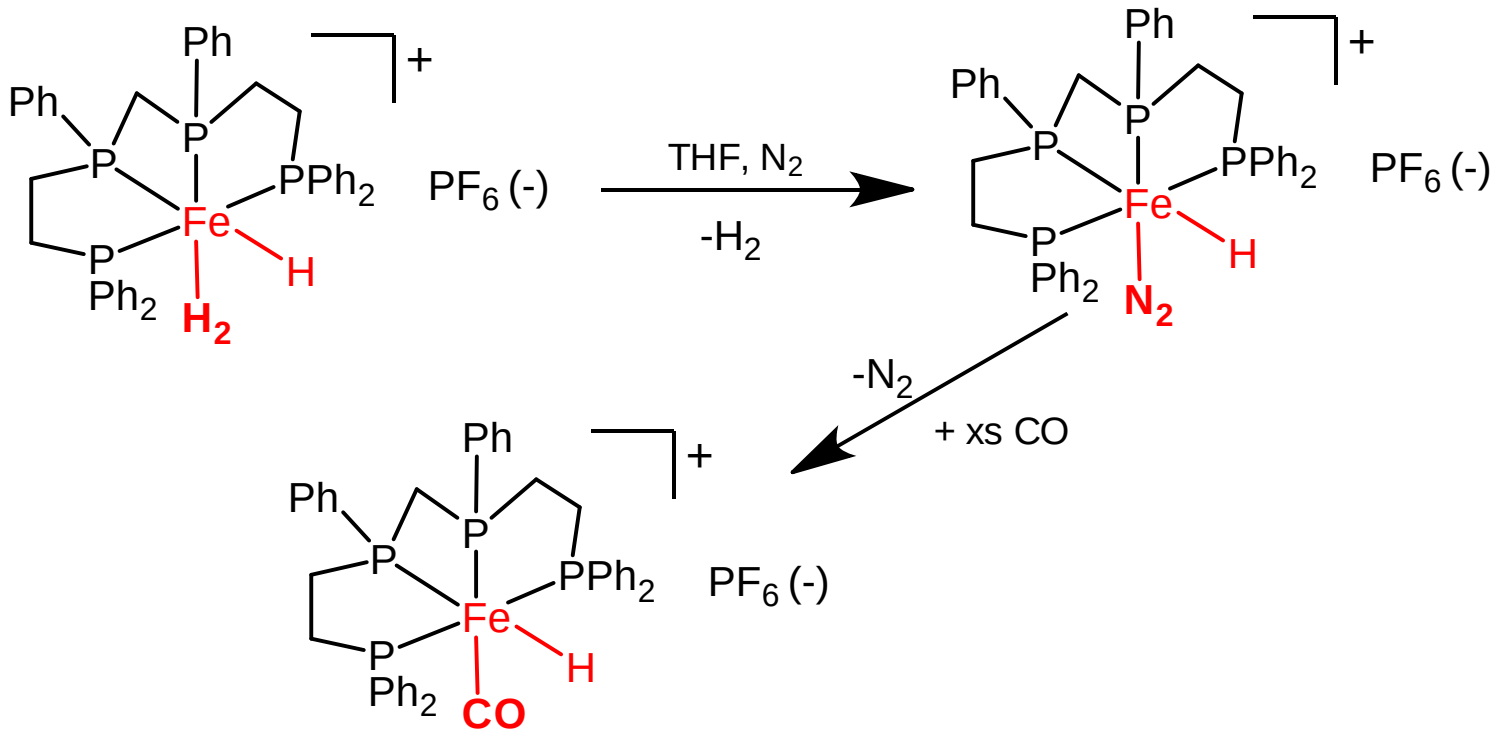
NOVEL ROUTES TO INTERMEDIATES





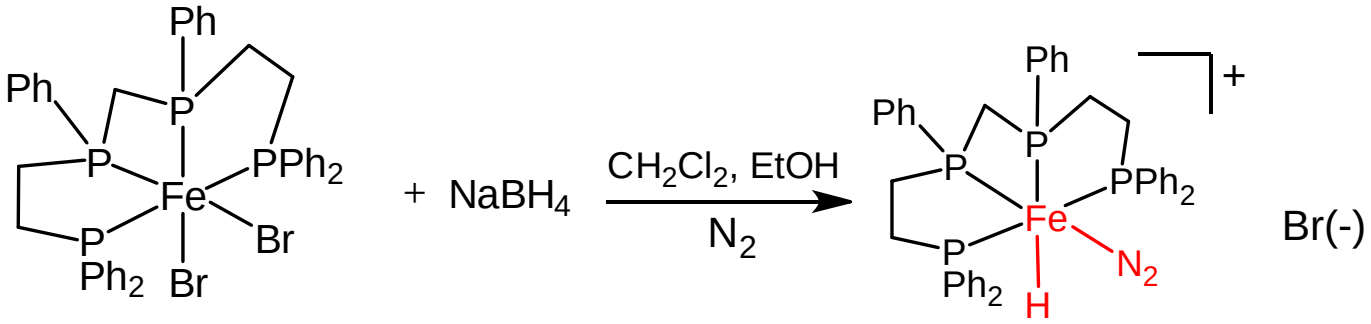
NOVEL ROUTES TO INTERMEDIATES

Characterization



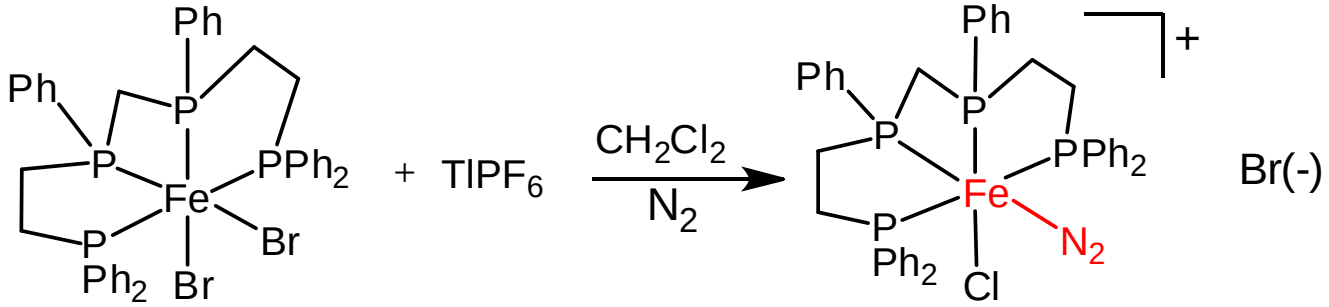
Have crystal
No structure yet

NOVEL ROUTES TO INTERMEDIATES



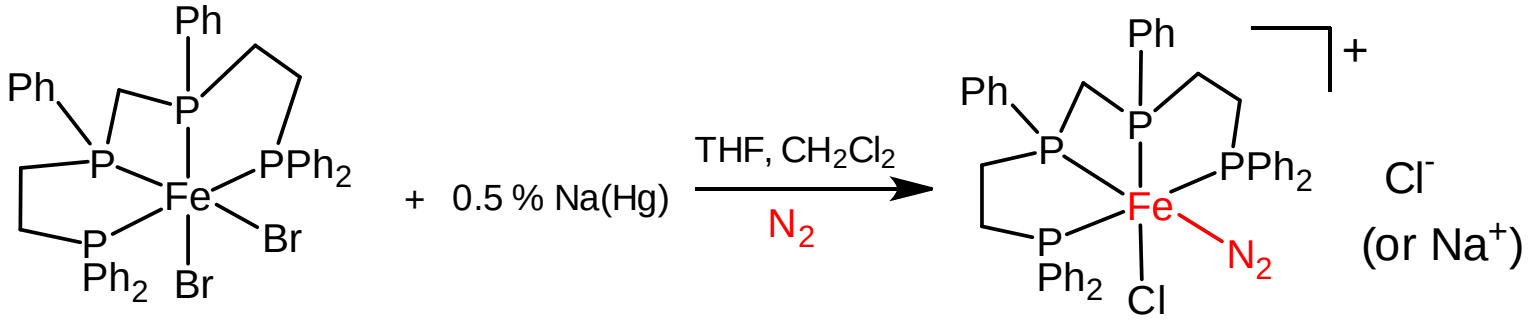
$\upsilon(N_2)$ 2116 cm-1

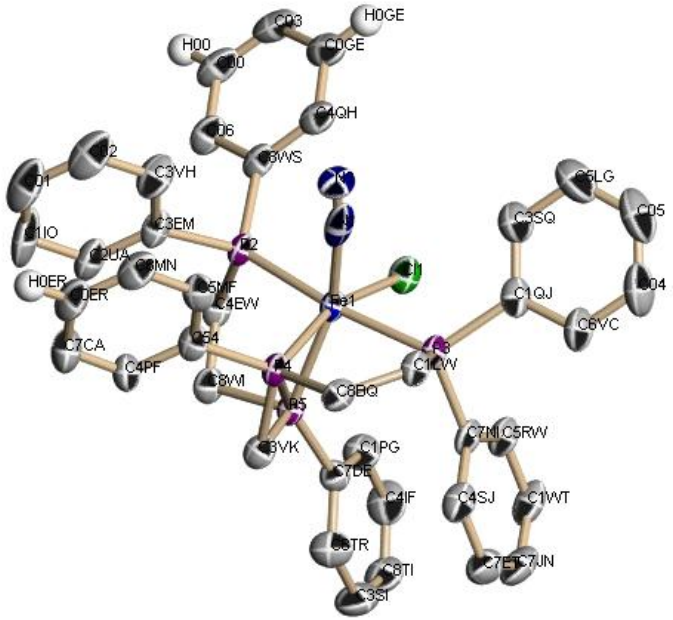
ESI-MS 713 (P_4FeH^+)



$\upsilon(N_2)$ 2094 cm^{-1}

CRYSTAL





Fe(0) or Fe(II)?

$\upsilon(N_2)$ 2094 cm^{-1} supports Fe(II)

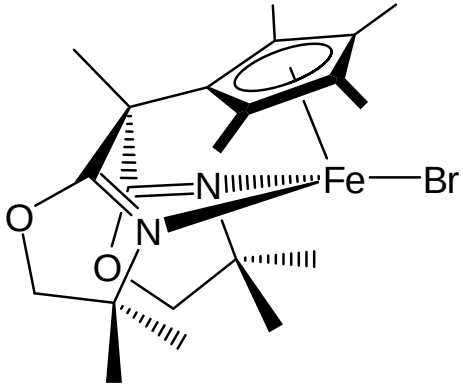
IN THE MEANTIME…

Bis-(4,4’ oxazoline)-based cyclopentadienyl ligand

Electron rich, negatively charged

Dissociable nitrogen provides free coordination site

Oxygen can act as internal base



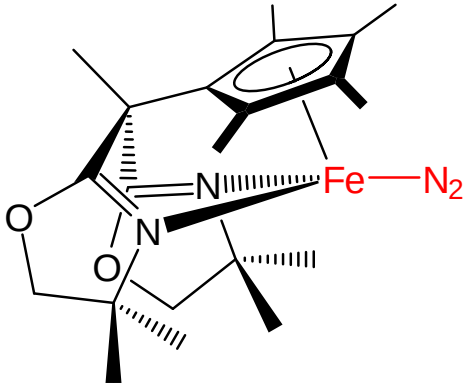
Dark yellow

Na(Hg)

THF, N_2

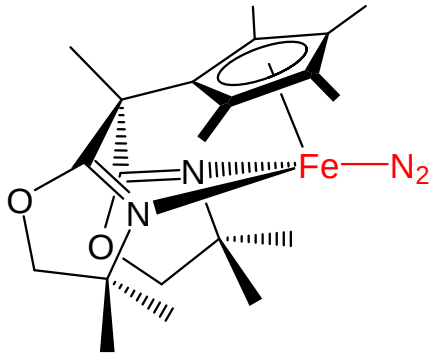
Green product

IR stretch: 1973 cm^{-1}



probably Fe^0

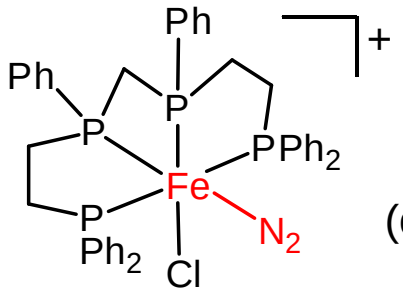
FUTURE



$\upsilon(N_2)$ 1973 cm^{-1}

H_2, H^+ →

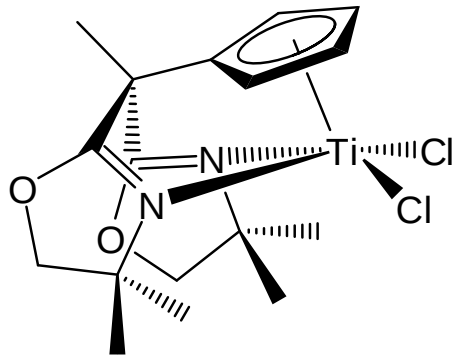
- Establish proper conditions
- Look for reduced product
- NH_3, N_2H_4….



Cl^- (or Na^+)

$\upsilon(N_2)$ 2094 cm^{-1}

- Further reduction to weaken N-N bond
- Reactions with H^+, H_2



- Reduction + N_2
- Make N_2 complex
- Expect significant reactivity

CONCLUSIONS

Fe(II) DPPEPM complexes

- have *cis* geometry – expect it to be beneficial for reactivity
- React with H_2 and N_2 under appropriate conditions
- (P4)$FeBr_2$ reacts with H_2 in lutidine buffers to give (P4)Fe(H)$(H_2)^+$
- Reversible binding of N_2 observed
- N_2-binding confirmed by X-ray crystal structure
- Reaction of $Fe^0(N_2)$ + H^+ does not cause loss of ligand

Fe(II) bis-oxazoline-cyclopentadienyl

- Nitrogen is partly reduced
- IR stretch: 1973 cm^{-1}

Expect this ligand to also yield reactive complexes of other metals (Ti, Zr….)

Aaron Sadow

Funding: Iowa Energy Center

RUTHENIUM ANALOG