ACTIVATION OF MOLECULAR NITROGEN WITH TRANSITION METAL COMPLEXES

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HABER-BOSCH PROCESS

- **Catalytic steam reforming**

$$CH_4 + H_2O \xrightarrow{W} CO + 3H_2$$

- **Water gas shift reaction**

$$CO + H_2O \xrightarrow{W} CO_2 + H_2$$

- **Catalytic NH_3 formation**

$$N_2 + 3H_2 \xrightarrow{W} 2\ NH_3$$

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

Fe or Ru oxide cat

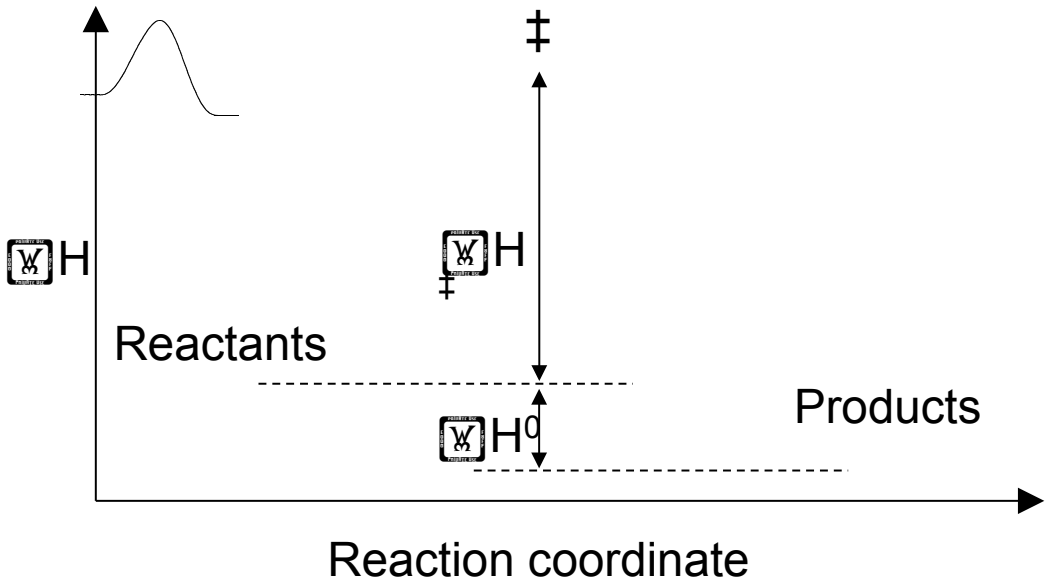
$N_2 + 3H_2 \rightleftharpoons 2\ NH_3$

Thermodynamics are favorable...

$\Delta H_f^0 = -46.1$ kJ/mol

but large kinetic barrier

$N \equiv N \quad \Delta H^0 = 944$ kJ/mol



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)*

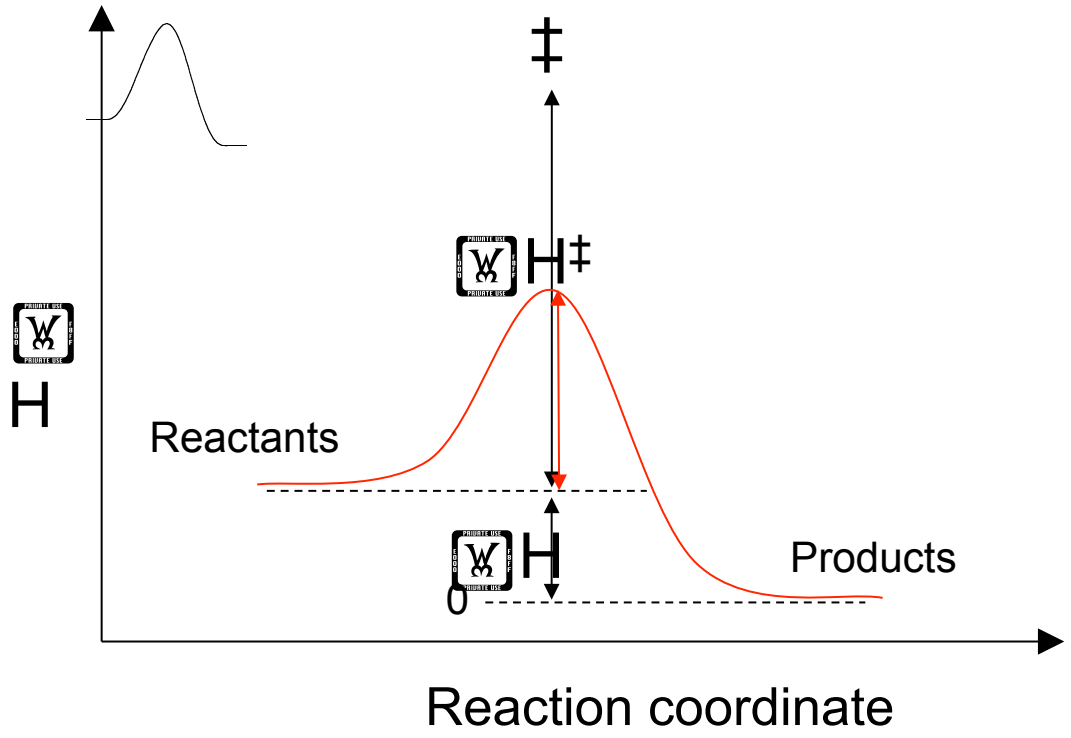
  125°C, yield is 91%.

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

NEED CATALYST

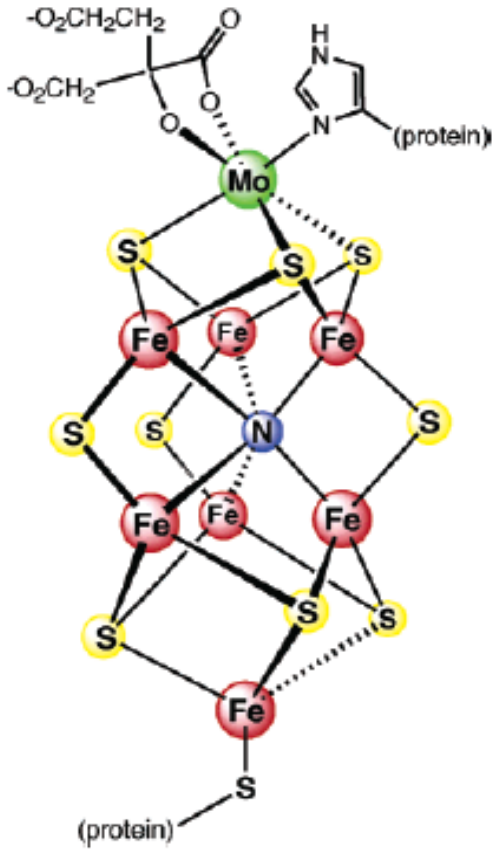
TO LOWER KINETIC BARRIER

CATALYZED VS UNCATALYZED REACTION



BIOLOGICAL NITROGEN FIXATION

NITROGENASE ENZYMES (Fe, Mo, V)



Plants:

N_2 from air

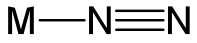
↓ Enzyme (= catalyst) + protons + electrons

$NH_3 + H_2$

M. D. Fryzuk, *Chem. Rev.* 2004, 104, 385;

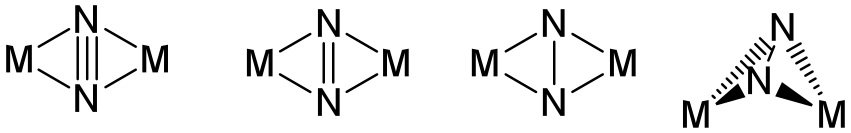
ACTIVATION OF N_2 BY BINDING TO COMPLEXES

End-on Monometallic

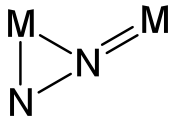


End-on Bimetallic

Side-on Bimetallic



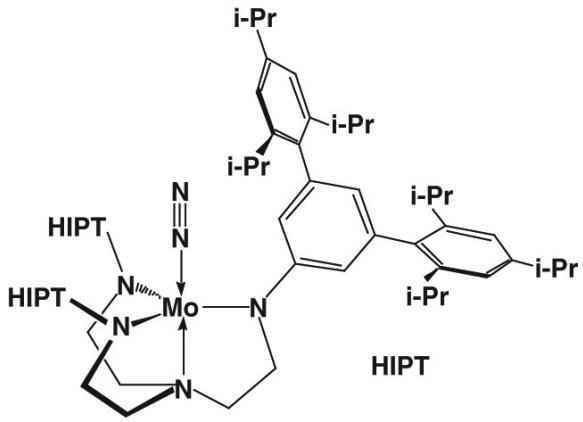
Side-on End-on Bimetallic



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

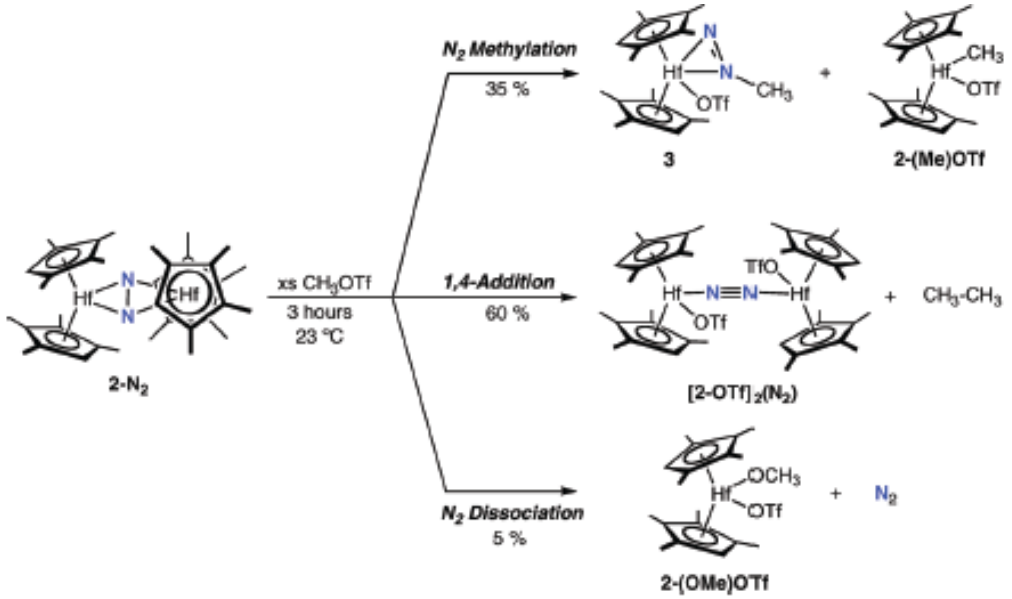
M. D. Fryzuk, *Chem. Rev.* 2004, 104, 385; *Acc. Chem. Res.* 2009, 42, 127

ACTIVATION AND CLEAVAGE OF N_2

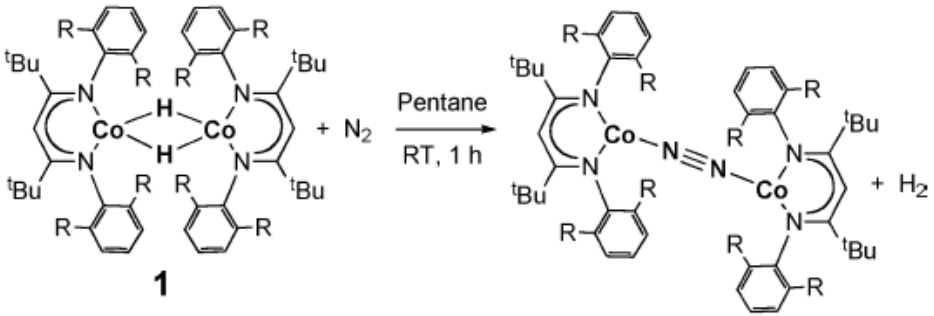


Cat for N_2 to NH_3 - 4 cycles

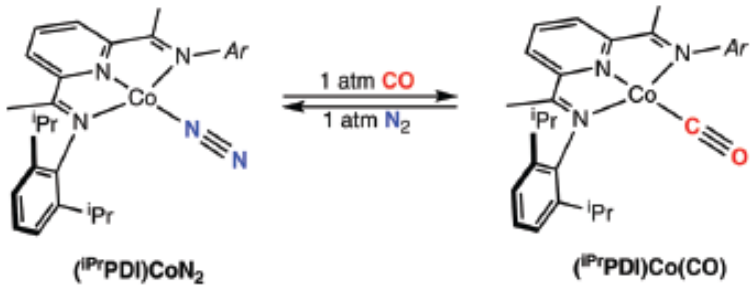
Yandulov, Schrock *Science* 2003, 301, 76



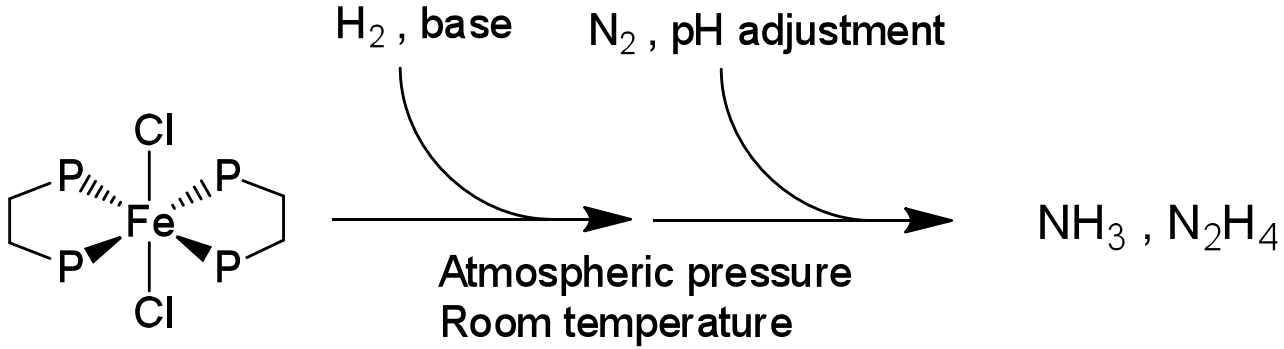
Chirik et al, JACS 2009, 14903; 2010, 1676

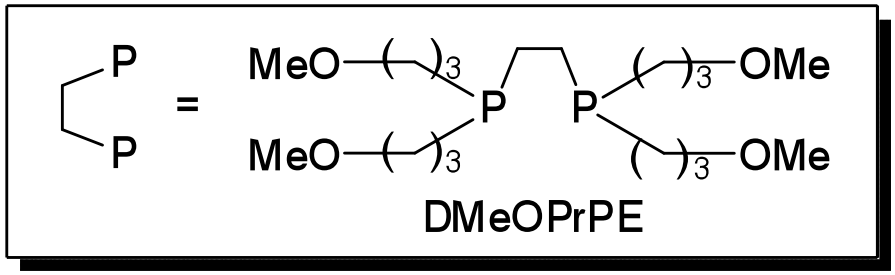


Holland et al, JACS 2009, 10804



REDUCTION OF N_2 TO NH_3 AT IRON

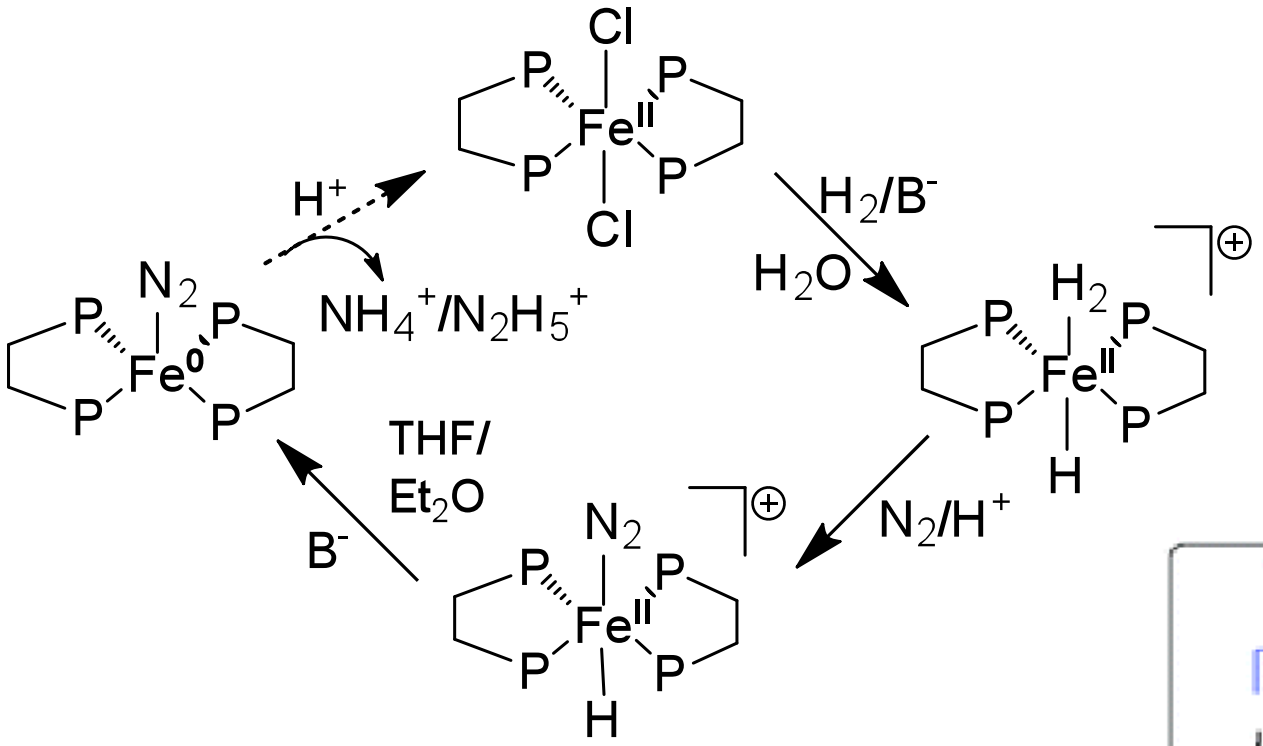


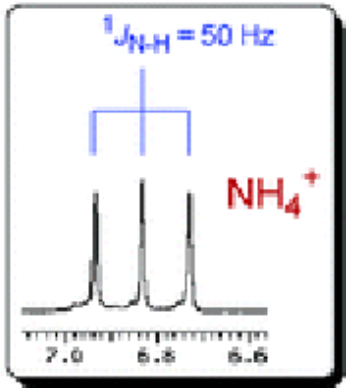


1,2-bis(bis(methoxypropyl)phosphino)ethane)

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

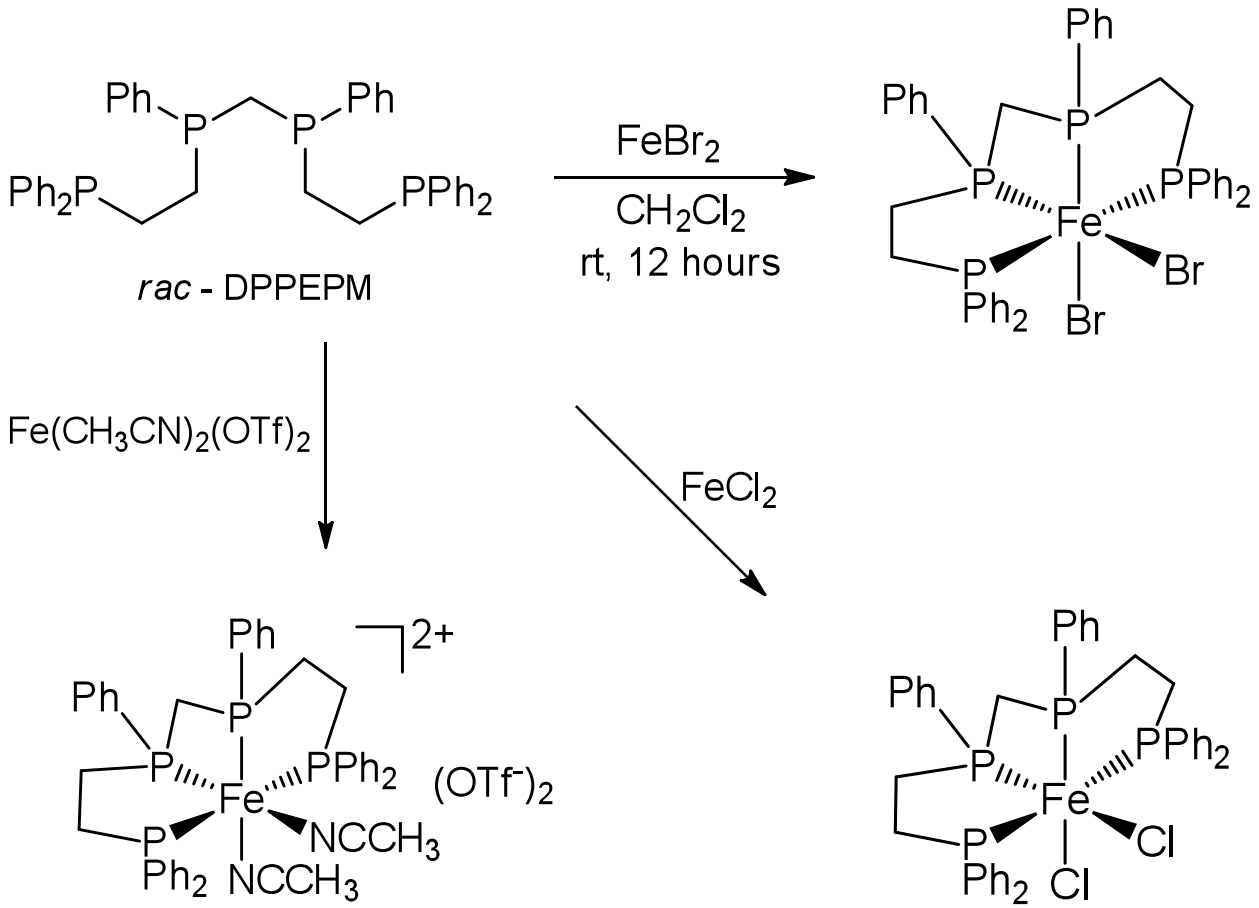
•Encourage temporary dissociation of one coordinating atom to allow binding of reactants (nitrogen, hydrogen)

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

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

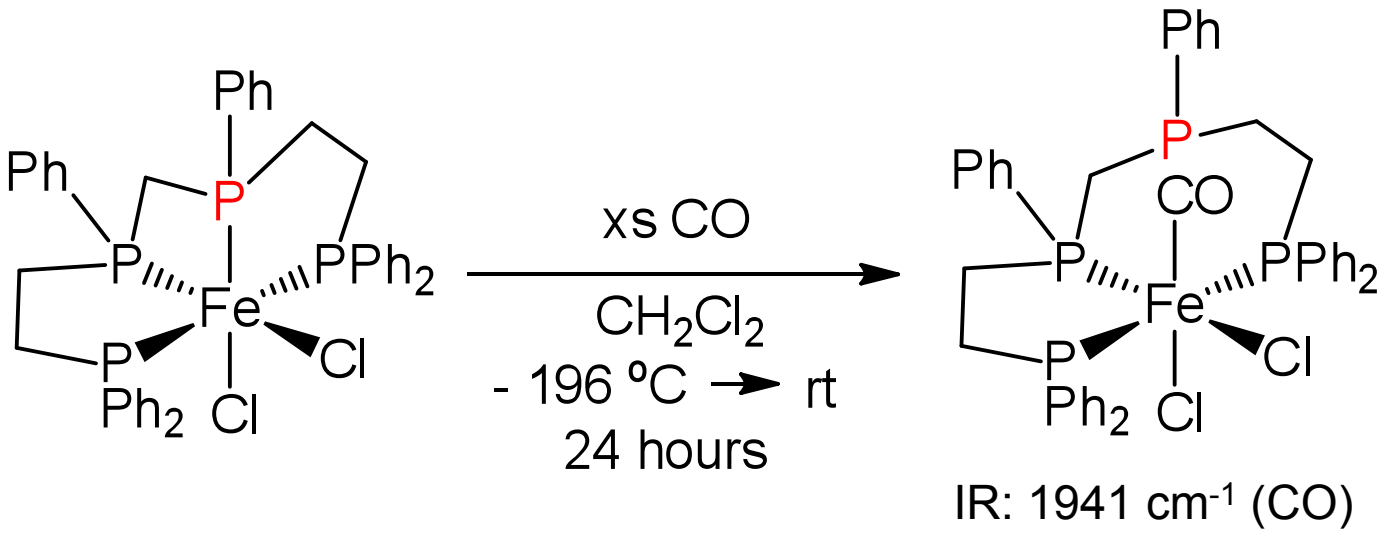
DPPEPM, DPPEPE

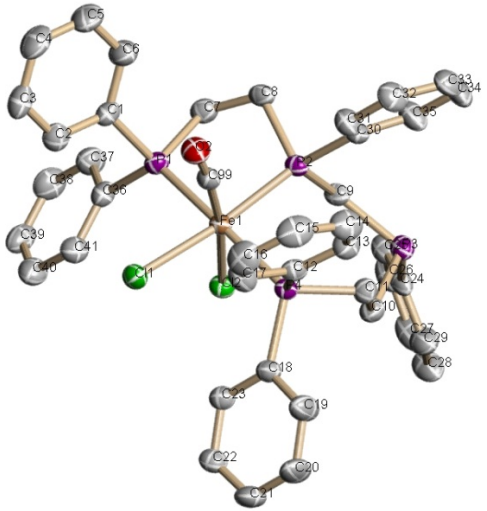
SYNTHESIS OF IRON COMPLEXES



Cis-geometry is common for this ligand!

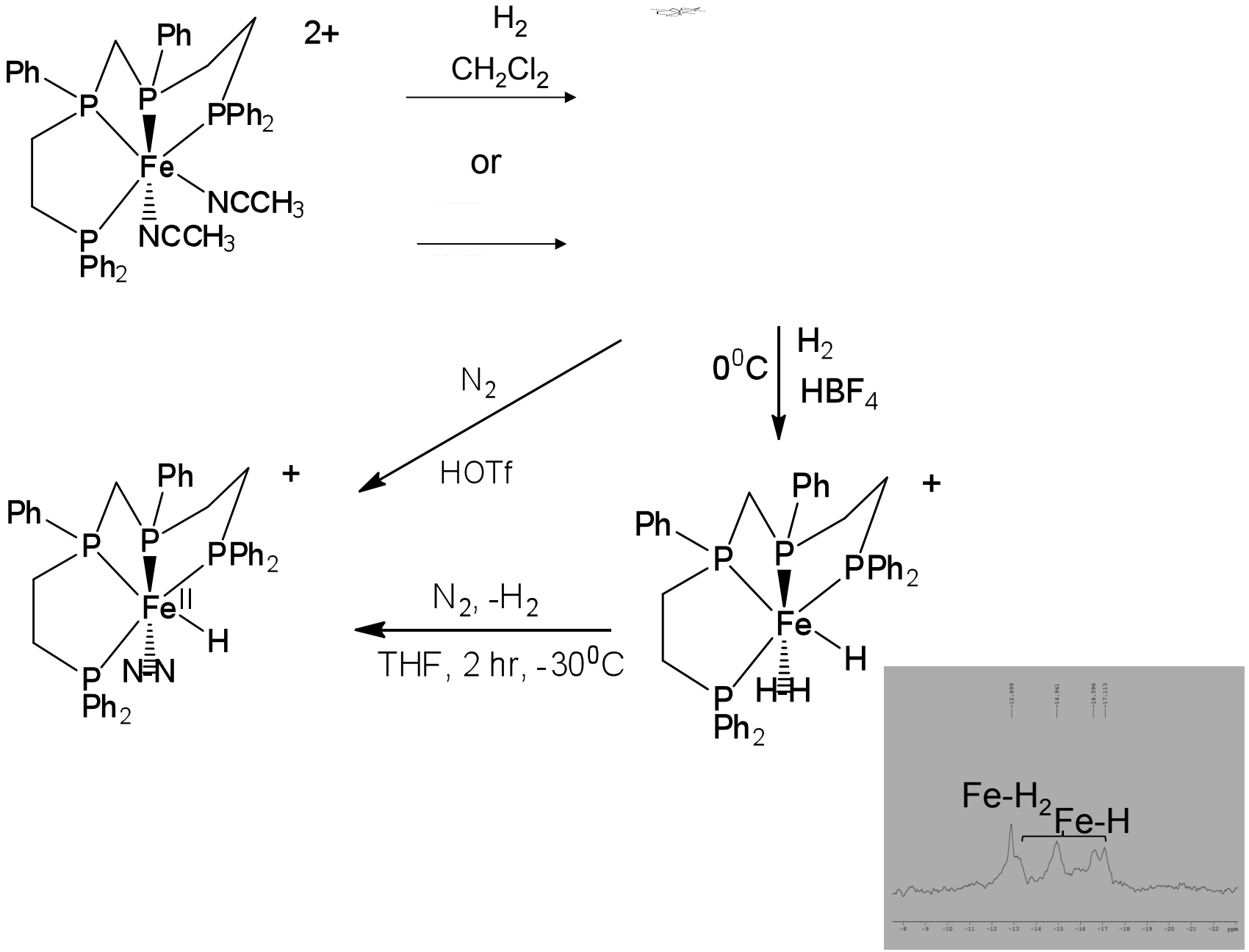
WEAK COORDINATION POSITION





CO displaces one of four P-atoms

INDIVIDUAL STEPS – PRELIMINARY EXPERIMENTS



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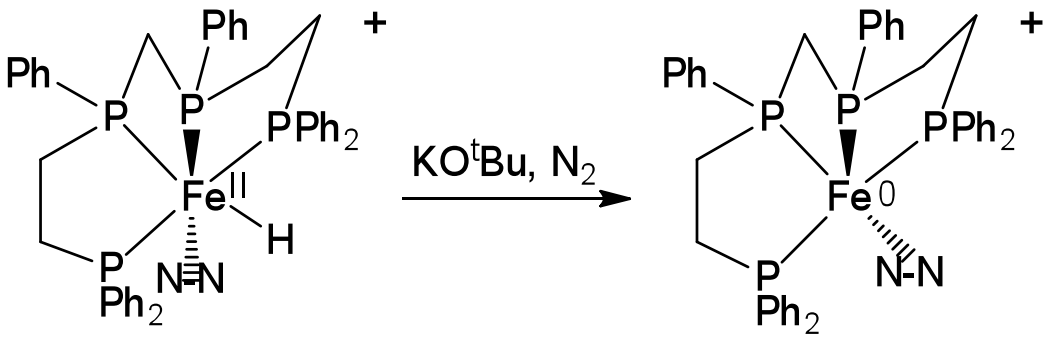


xs HOTf

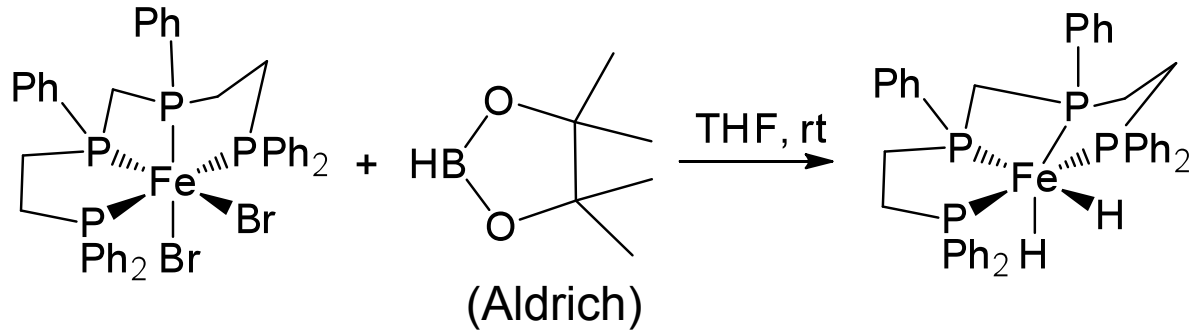
Light-green solution

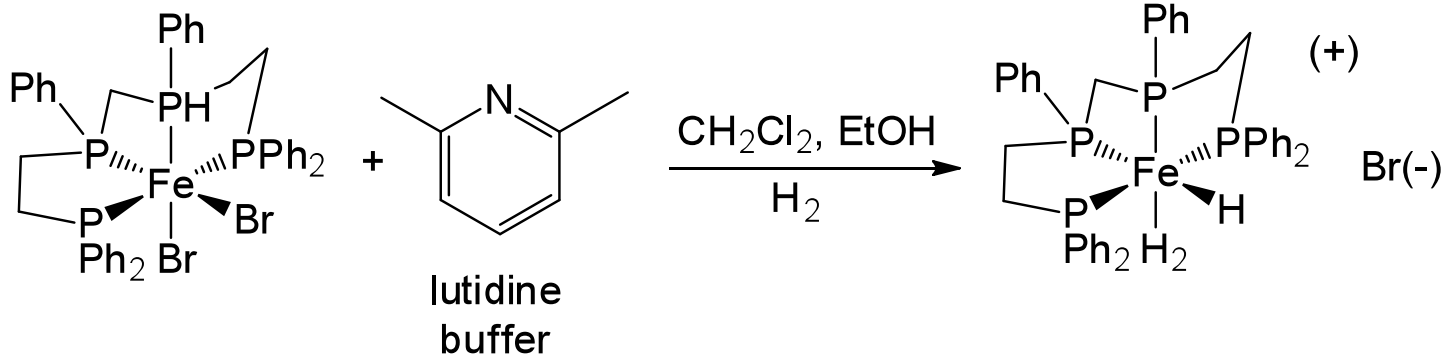
No NH_3 in NMR

But:

No decomposition in 3 days

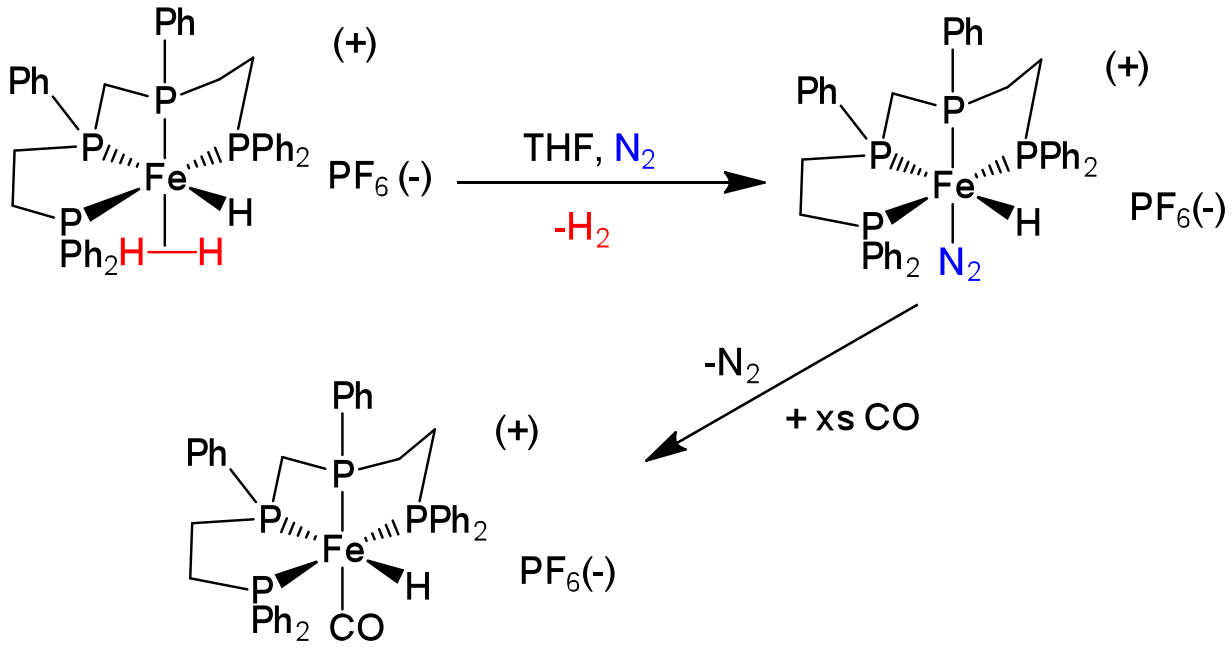
NOVEL ROUTES TO INTERMEDIATES





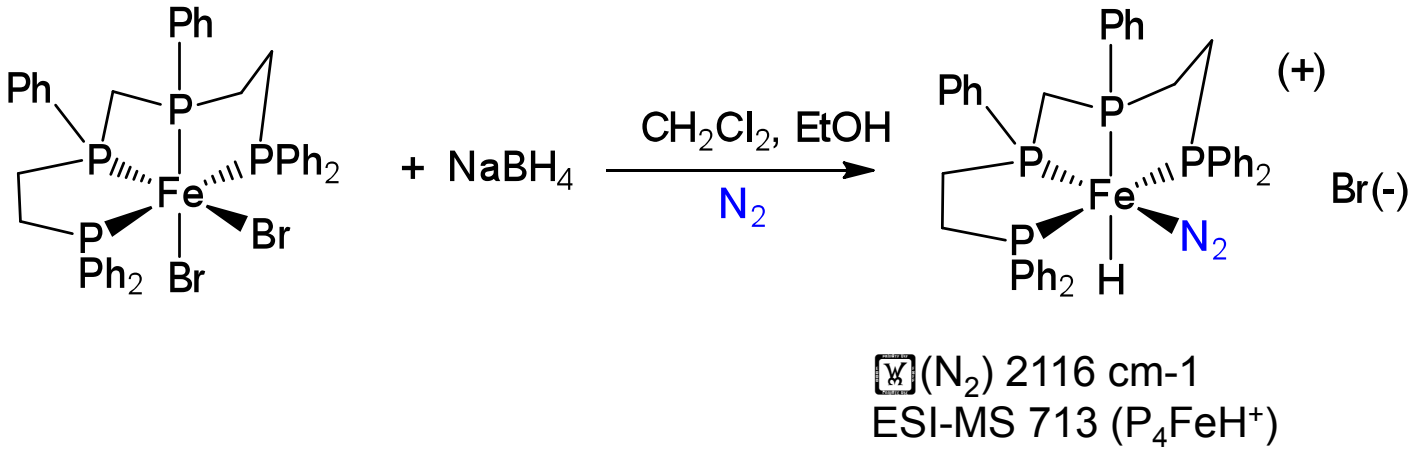
NOVEL ROUTES TO INTERMEDIATES

Characterization

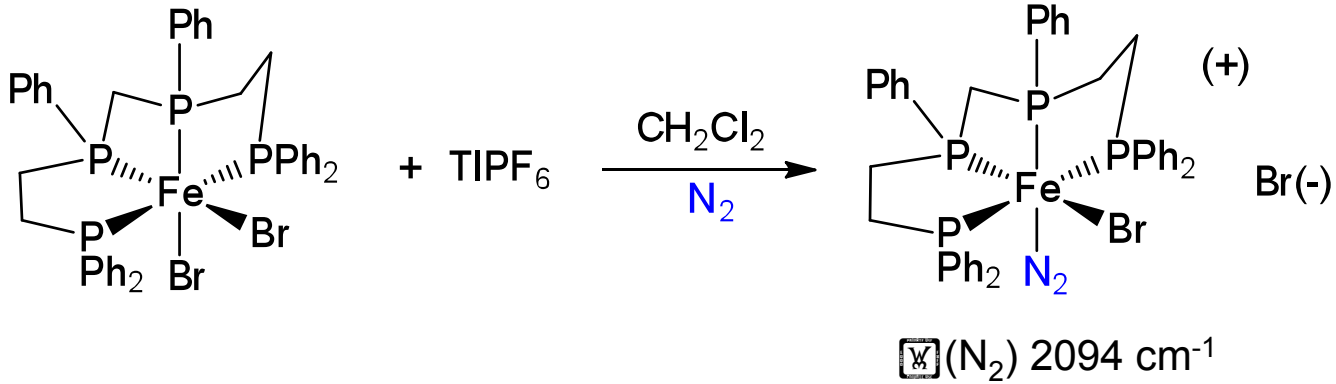


Have crystal
No structure yet

NOVEL ROUTES TO INTERMEDIATES

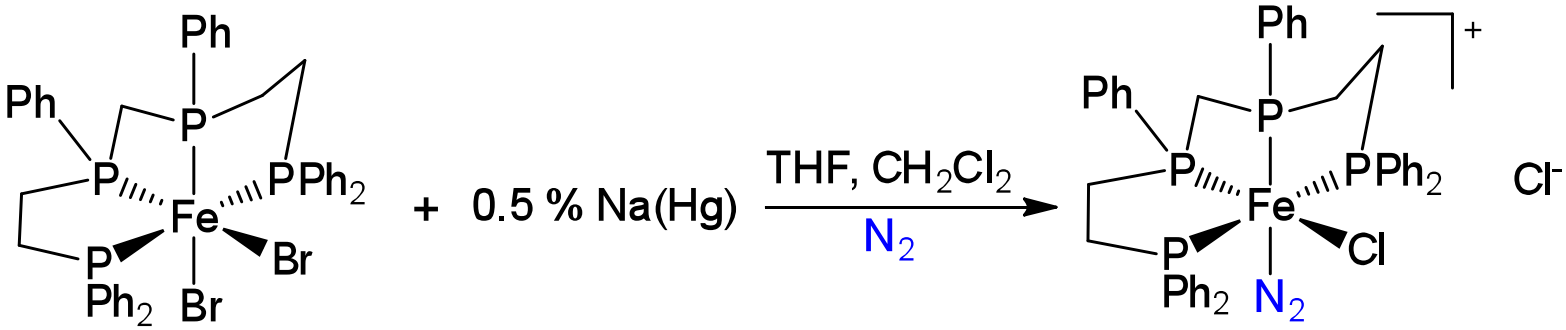


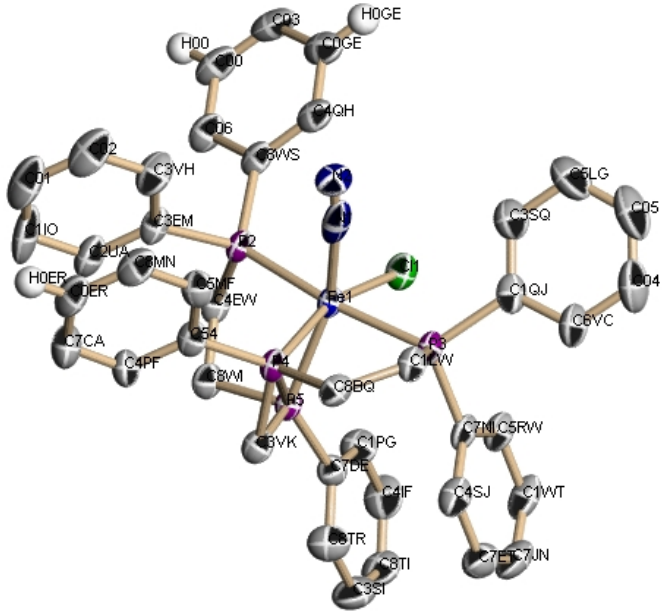
ν(N$_2$) 2116 cm-1
ESI-MS 713 (P_4FeH^+)



ν(N$_2$) 2094 cm^{-1}

FINALLY!


Ph
Ph
P
P
PPh2
Fe
Br
P
Ph2
Br
+ 0.5 % Na(Hg)
THF, CH2Cl2
N2
Ph
Ph
P
P
PPh2
Fe
Cl
P
Ph2
N2
+
Cl-


H0GE
C03
H00
C0GE
C4QH
C06
C3VH
C3EM
C2UA
C3MN
H0ER
C5MF
C4EW
C7CA
C4PF
C54
C8VM
C8BQ
C3VK
C1PG
C7DE
C4IF
C8TR
C8TI
C3SI
C5RW
C4SJ
C1WT
C7E7C7JN
C1QJ
C6VC
C3SQ
C5LG
C05
C04

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
-$(P_4)FeBr_2$ 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

Aaron Sadow

Funding: Iowa Energy Center

RUTHENIUM ANALOG