



1971 Born in Chicago, Illinois
1993 B.S. in Chemistry at the University of Chicago (G. Hillhouse)

- *synthetic methods in inorganic chemistry: stabilization of reactive species such as HN=NH and HNO*
- 2 publications

1994 Marshall Scholar at the University of Nottingham (J.J. Turner)

- *physical inorganic chemistry: photochemical generation and detection of short-lived transients by rapid time-resolved methods*
- 2 publications

1998 Ph.D. at the Massachusetts Institute of Technology (C.C. Cummins)

- *activation and functionalization of small molecules using low coordinate tris-amido molybdenum and titanium complexes*
- 6 publications

1998-1999 Miller Postdoctoral Fellow at the University of California, Berkeley (T.D. Tilley)

- *synthesis and employment of novel phosphine, silane, and phosphino silane ligands relevant to late metal Si-C, Si-H, C-H, and C-C bond breaking and forming processes*
- 3 publications

1999-2004 Assistant Professor, Caltech

2004-2006 Associate Professor, Caltech

2006 Professor, Caltech

2007-2010 W.M. Keck Professor of Energy, MIT

2010-present Bren Professor of Chemistry, Caltech

- 142 publications to date as a principal investigator

Mentorship:

Ph.D. Students in Academia:

Theodore A. Betley, Ph.D. **2005** (Professor, Harvard U.)
David M. Jenkins, Ph.D. **2005** (Associate Prof., U. Tennessee)
Connie C. Lu, Ph.D. **2006** (Associate Prof., U. Minnesota)
Christine M. Thomas, Ph.D. **2006** (Associate Prof., Brandeis U.)
Neal P. Mankad, Ph.D. **2009** (Assistant Prof., U. Illinois at Chicago)

Postdoctoral Associates in Academia:

Louise A. Berben (Associate Prof., U.C. Davis)
William H. Harman (Assistant Prof., U.C. Riverside)
Xile Hu (Professor, EPFL)
David Lacy (Assistant Prof., U. Buffalo)
Yunho Lee (Associate Professor, KAIST)
Cora E. MacBeth (Assistant Prof., Emory U.)
Mark P. Mehn (Assistant Prof., U. Wyoming)

Marc-Etienne Moret (Assistant Prof., U. Utrecht)

Eric Rivard (Associate Prof., U. Alberta)

Nathaniel Szymczak (Assistant Professor, U. Michigan)

Christopher Uyeda (Assistant Professor, Purdue U.)

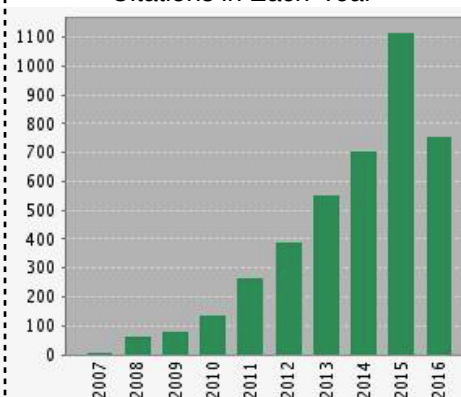
Research interests:

1. *Multi electron redox reactions of small molecule substrates with first row transition metals*
2. *Dicopper cores as multi-electron redox shuttles and photochemical reductants*
3. *Electrocatalytic hydrogen evolution at positive potentials*
4. *Zwitterionic approach to catalysis mediated at late transition metal centers*

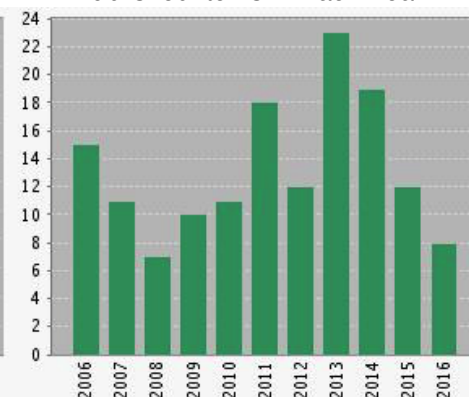
Top cited (in sum) papers:

1. Benchmarking Heterogeneous Electrocatalysts for the Oxygen Evolution reaction *JACS* **2013**, *135*(45), 16977. (433 citations; 108/yr)
2. Electrocatalytic hydrogen evolution at low overpotentials by cobalt macrocyclic glyoxime and tetraimine complexes *JACS* **2007**, *129*(29), 8988. (327 citations; 33/yr)
3. E-Type Delayed Fluorescence of a Phosphine-Supported Cu-2(μ -NAr₂)₂ Diamond Core: Harvesting Singlet and Triplet Excitons in OLEDs *JACS* **2010**, *132*(27), 9499. (182 citations; 26/yr)
4. Electrocatalytic Hydrogen Evolution in Acidic Water with Molecular Cobalt Tetraazamacrocycles *JACS* **2012**, *134*(6), 3164. (137 cit.; 27/yr)
5. Catalytic conversion of nitrogen to ammonia by an iron model complex *Nature* **2013**, *501*(7465), 84. 134 (36/yr)

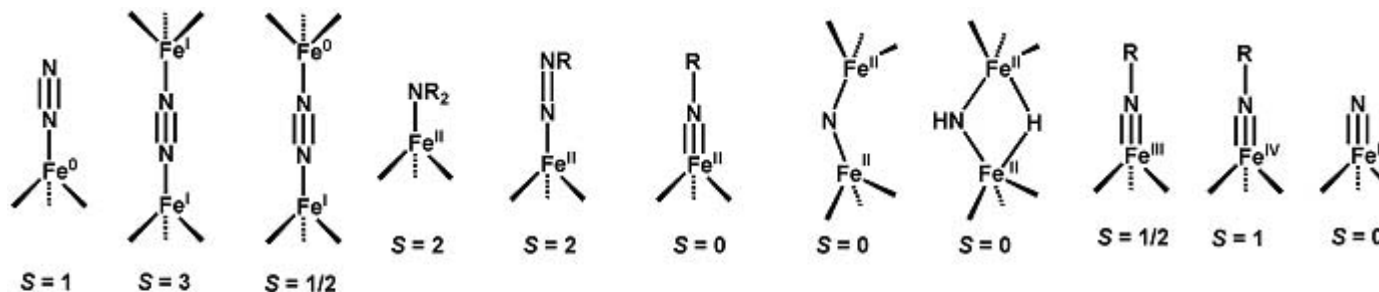
Citations in Each Year



Published Items in Each Year



1. Multi-electron redox reactions of small molecule substrates using late first row transition metals



Well-defined multi-electron redox processes established using these L_3Fe-N_x platforms:



Metals of interest: Mn, Fe, Co, Ni, Cu

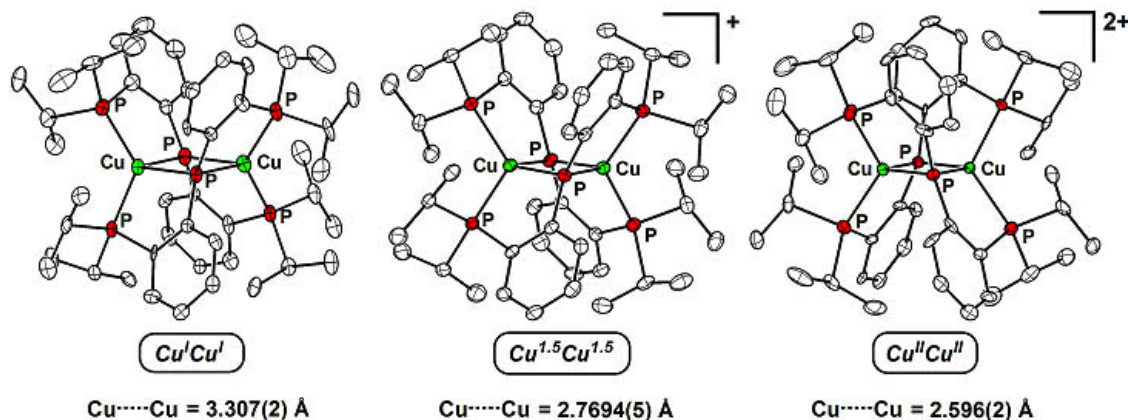
This area of work **expands understanding about the chemistry that is accessible by mid-to-late transition metals**, (including unusual binding modes, redox processes and spin states.)

eg.) Pseudotetrahedral iron complexes are ubiquitous in metalloenzymes, and in synthesis and catalysis, and had been assumed (at the start of Peters' independent career in 1999) to only populate high spin ground states ($S=2$ for Fe^{2+} and $S=5/2$ for Fe^{3+}). However, Peters' research has characterized a variety of pseudotetrahedral Fe^0 , Fe^{+1} , Fe^{+2} , Fe^{+3} , and Fe^{+4} complexes that are capable of 1, 2, and 3 electron redox processes, and in so doing can access low spin ground states stabilized by multiply bonded ligand types (e.g. $Fe=NR$ and $Fe=N$).

Detailed structural and electronic characterization of these complexes has improved fundamental understanding of inorganic metallo-complex behaviour.

Applications include understanding of the role of iron in **nitrogen fixation** (nitrogenase) and the use of redox rich Fe, Co, Ni and Cu systems in other multi-electron transformations (**hydrogen evolution** via H^+ protonation, **C-1** (i.e. CO and CO_2) **reduction**).

2. Dicopper cores as multi-electron redox shuttles and photochemical reductants



This work explores **bimetallic copper systems** that combine **unusual 2-electron redox activity** with exceptional **luminescence**.

eg) The Peters group has prepared synthetic Cu_2N_2 and Cu_2P_2 (N=amide and P=phosphide) which exhibit two fully reversible 1-electron redox processes, which is unknown for other synthetic copper systems. Isolation and characterization of all three accessible oxidation states (Cu^ICu^I , $\text{Cu}^{1.5}\text{Cu}^{1.5}$, and $\text{Cu}^{II}\text{Cu}^{II}$) is possible because of a "local distorted tetrahedral geometry that is flexibly maintained at each copper center regardless of the oxidation state sampled by the system." Nature employs copper with soft sulfur and hard oxygen ligands similarly in bimetallic cofactors in numerous copper-containing metalloenzymes, so this research improves understanding of how the nature of the bridging ligand affects redox and spin states.

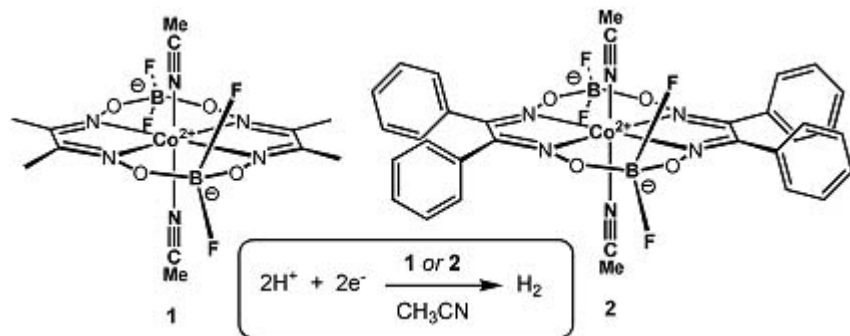
eg) Synthetic Cu^ICu^I systems also exhibit very unusual luminescence behaviour (high quantum efficiency and long lifetime), and in combination with a relatively low redox couple (for the $\text{Cu}^I\text{Cu}^I/\text{Cu}^{1.5}\text{Cu}^{1.5}$ redox couple), and energy of the E^{0-0} transition mean that these dicopper systems show promise as excellent photoreductants. The Peters group is studying the photophysics and structure/function relationship of these and related CuZn bimetallic systems.

Relevant papers:

- JACS* **2004**, *126*, 2885. (Initial disclosure of a Cu_2N_2 core supported by an $[\text{SNS}]^-$ ligand)
- JACS* **2004**, *126*, 2885. (Highly emissive Cu_2N_2 core supported by a $[\text{PNP}]^-$ ligand)
- JACS* **2005**, *127*, 16032. (Cu_2P_2 core with a 3 e- redox window)
- Inorg. Chem.* **2007**, *46*(18), 7244. (Long-lived efficient emission from mononuclear $[\text{PN}]^-$ Cu complexes)
- JACS* **2008**, *130*, 3478. (Structure/Electronic structure studies of Cu_2N_2 and Cu_2P_2 complexes)
- JACS* **2009**, *131*, 3878. (Cu^I amido and aminyl radical complexes)
- Inorg. Chem.* **2009**, *48*(15), 7026. (EPR studies of Cu_2N_2 diamond cores)
- JACS* **2010**, *132*, 9499 (E-type delayed fluorescence of a Cu_2N_2 core: harvesting excitons in OLEDs)
- Chem. Comm.* **2010**, *46*, 3690. (Efficient luminescence from Cu^I arylamidophosphines)

(see "Supplementary" section for papers which discuss C-S/N/O cross-coupling methodology that employs Cu catalysts)

3. Electrocatalytic hydrogen evolution at positive potentials



The goal of this research is to develop **hydrogen evolution catalysts that operate at potentials as close to the thermodynamic potential** (defined 0 V vs. NHE) as possible using abundant metals (Fe, Co, Ni). Peters along with Caltech and MIT collaborations ultimately also wants these catalysts to be able to either produce or consume H_2 based on the applied potential. (Hydrogenase enzymes employ Fe and Ni to mediate key H_2 evolution and consumption steps.)

Peters also looks to redirect H^+/e^- currency to acceptor substrates of interest (i.e. CO_2) rather than evolving H_2 and to develop a viable water-splitting device based upon molecular catalyst components.

Selected relevant papers:

- Chem. Comm.* **2005**, 4723. (HER with $\text{Co}(\text{dmgBF}_2)_2$ in MeCN at -0.28 V vs SCE)
- JACS* **2007**, *129*, 8988. (HER at low overpotentials with Co macrocyclic glyoxime and tetraimine complexes)
- Chem. Comm.* **2009**, *44*, 6729. (HER with redox rich dicobalt macrocycles)
- Chem. Comm.* **2010**, *46*, 398. (HER with a cobalt tetraimine catalyst adsorbed on electrode surfaces)
- JACS* **2007**, *129*, 8988. (HER with a Co bis(iminopyridine) complex))
- JACS* **2012**, *134*, 3164. (HER with Co tetraazamacrocycles)
- JACS* **2013**, *135*, 2023. (NO_2^- reduction to N_2O with a CoMg complex)
- JACS* **2013**, *135*, 16977. (Benchmarking heterogeneous catalysts for the OER; with T.F. Jaramillo)
- Inorg. Chem.* **2014**, *53*, 4980. (Electrocatalytic CO_2 reduction with a Co catalyst)
- JACS* **2015**, *137*, 4860. (A study pertaining to the putative Co-H of Shrauzer's cobaloxime, a HER catalyst)
- JACS* **2015**, *137*, 4347. (Benchmarking HER and OER catalysts for solar water splitting devices; with T.F. Jaramillo)
- J. Phys. Chem. C* **2015**, *119*, 4645. (CO_2 activation by a $[\text{CoN}_4\text{H}(\text{MeCN})]^\text{II}$ complex)
- J. Mat. Chem.* **2016**, *4*, 3068. (Benchmarking nanoparticulate metal oxide electrocatalysts for the alkaline water oxidation reaction; with T.F. Jaramillo)
- Electrocatalysts* **2016**, *7*, 87. (Evaluating HER Co and Ni catalyst under elevated H_2 and CO pressure)
- ACS Catalysis* **2016**, ASAP (A study of the energy cost/kinetic barrier correlation in the HER via a Co(pyridine-diimine-dioxime) catalyst; with T.F. Miller)

4. Zwitterionic approach to catalysis at late transition metal centers



This area of research studies **organometallic zwitterions as mediators of stoichiometric and catalytic reaction transformations**.

By incorporating a partially insulated borate counter-anion into the auxiliary ligand architecture, Peters preserves *accessible coordination sites at highly electrophilic transition metal centers* (c.f. non-coordinating counterions).

The Peters group is interested in understanding through charge/structure/function studies how the cationic charge affects a given transformation.

For selected relevant papers, see:

JACS **2002**, *124*, 5272 (Catalytic copolymerization of CO and C₂H₄ with a Pd^{II} zwitterion)

ACIE **2003**, *42*, 2385 (A zwitterionic Rh catalyst for H-E (E=C,Si,B) additions to olefins)

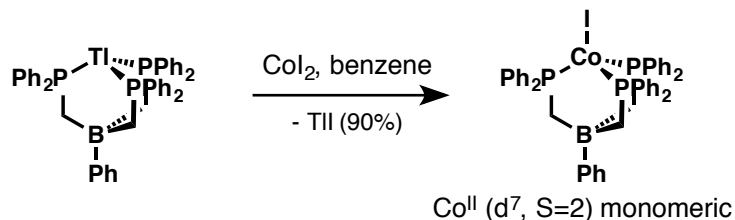
JACS **2004**, *126*, 15818 (Amine activation mediated by a zwitterionic Pd^{II} center)

Organometallics **2005**, *24*, 5858. (Comparative studies with zwitterionic Pt^{II} bis(pyrazolyl)borate and 2,2'-bipyridylborate ligands)

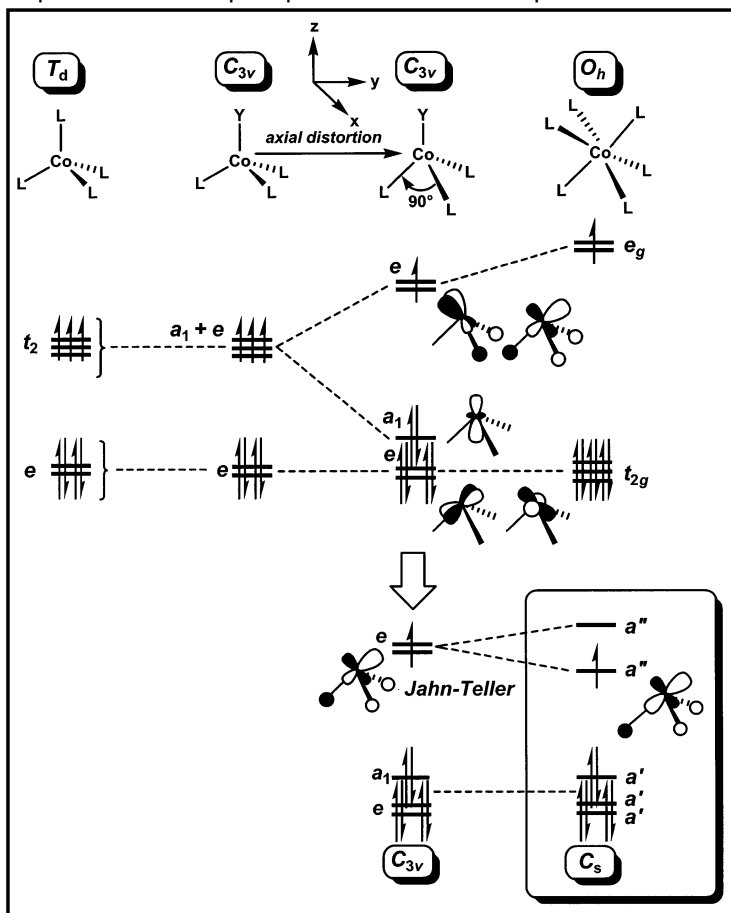
Idea: Unusual ligand geometries/electronic states result in interesting reactivity. aka. How might one access low spin 1st row TM complexes?

1. *Synthesis of a Low Spin Cobalt(II) system in a Distorted Tetrahedral Geometry. JACS 2002, 124, 15336*

Background: Prior to this work, the only known low spin (S=2) Co^{II} complexes adopted a square planar geometry, and all known tetrahedral Co^{II} complexes had high spin S=4 ground states. This was the *first example of a 4 coordinate tetrahedral Co(II) low spin complex*.



Explanation of unique spin state for this Co^{II} pseudotetrahedral complex:



- the combination of the very strong field ligand, PhBP₃⁻, and axial distortion away from tetrahedral geometry (which stabilizes the a₁ orbital and is geometrically enforced) result in an inverted ligand, where the d_{x²-y²} and d_{z²}-derived orbitals lie above the d_{xy}, d_{yz}, d_{xy}-derived orbitals

For further discussion of spin-crossover behaviour in d⁷ pseudotetrahedral Co(II) ions, see:

JACS **2003**, *125*, 11162.

JACS **2005**, *127*, 7148.

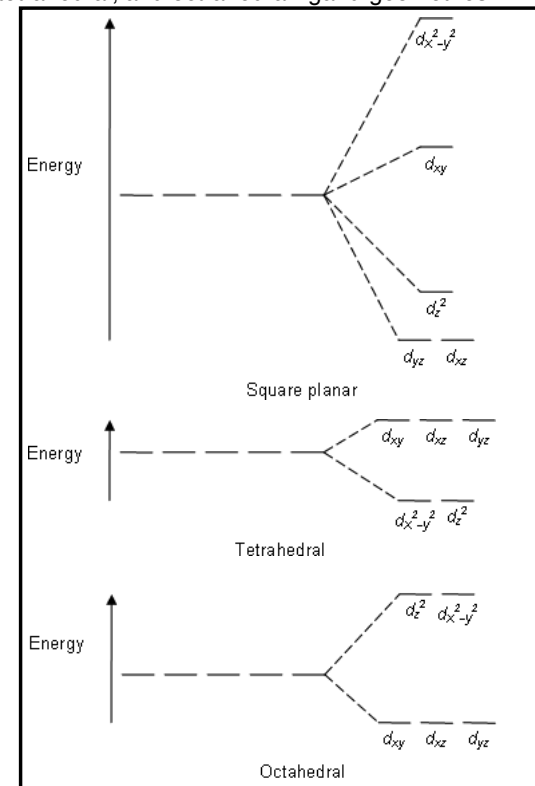
For a review: *Coord. Chem. Rev.* **2011**, *255*, 920

For iron complexes, see:

Inorg. Chem. **2016**, *55*, 3894.

-Br and Cl analogues also prepared and exist as μ-Br/Cl dimers in solid state, but predominately as monomers in solution (some dimerization at low T)
- The Br/Cl dimers are 5-coordinate, high spin, square pyramidal while the monomers are 4-coordinate, high spin, pseudotetrahedral
- characterized by SQUID, EPR, optical spectra, and X-ray

c.f. Normal relative orbital energies for square planar, tetrahedral, and octahedral ligand geometries



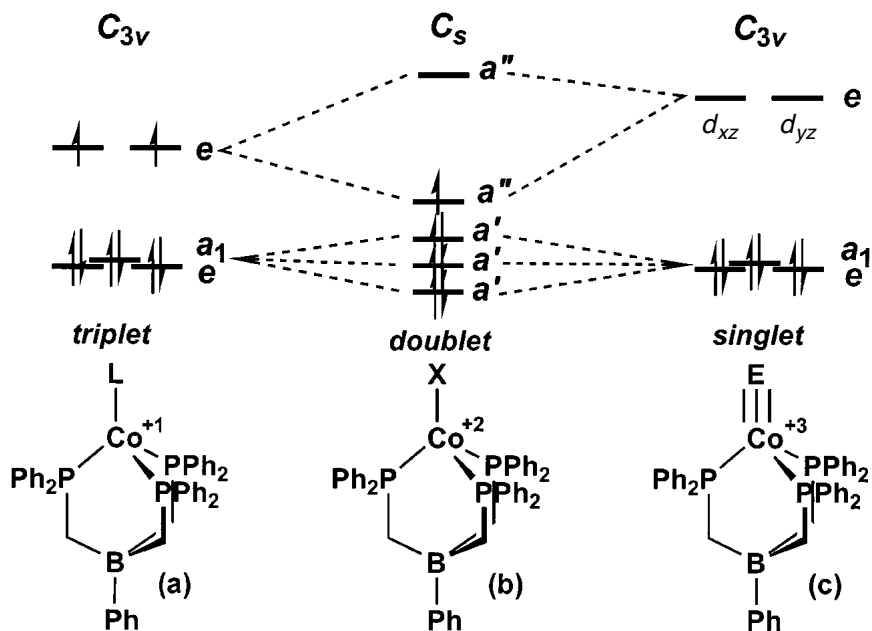
Chem. Rev. **2016**, *116*(14), 8173. (discussion of inverted ligand fields)

Chem. Comm. **2001**, *40*, 5083 (TI transmetalation)

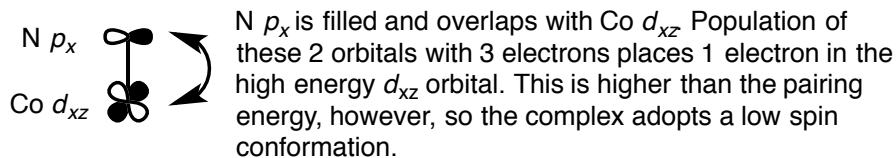
Context: Late first-row transition metals multiply bonded to N and O were rare and poorly understood/characterized prior to Peters' work.

2. Reactivity of $[\text{PhBP}_3\text{Co}]$ ($S=2$), pseudotetrahedral

The $S=2$ pseudotetrahedral geometry of PhBP_3CoI suggested that it should in principle, be possible to replace the iodide ligand by a divalent, strongly π -donating ligand to form an 18-electron, closed-shell configuration. i.e.)

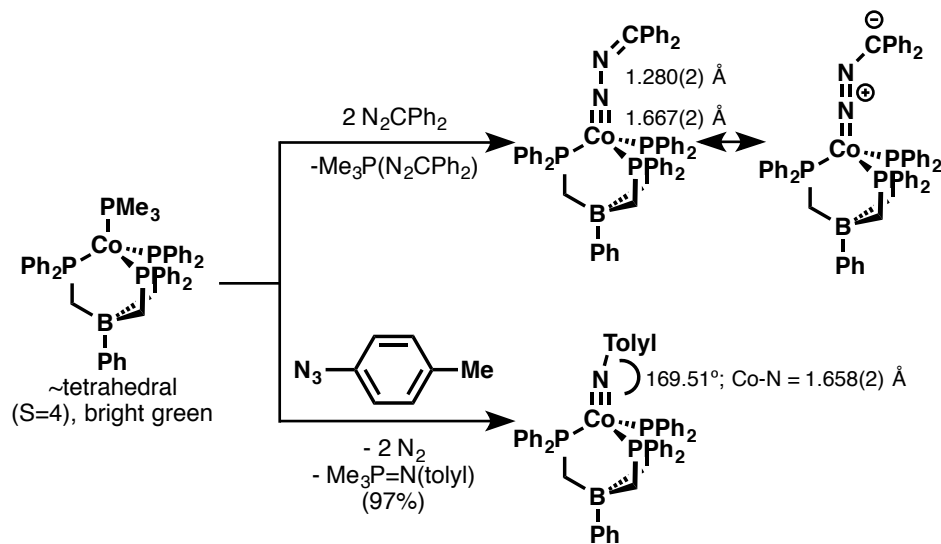
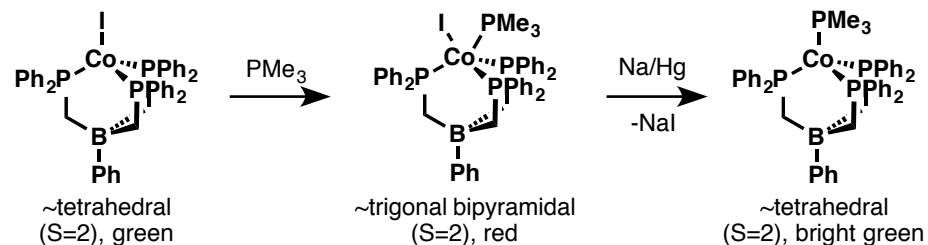


- axial π -interactions of $E=N$ (lone pairs in the nitrogen p-orbitals destabilize the orbitals of d_{xz} and d_{yz} parentage, increasing their energy and allowing the $\text{PhBP}_3\text{Co}=\text{NAr}$ complex to adopt a low spin ground state electronic configuration. That is:



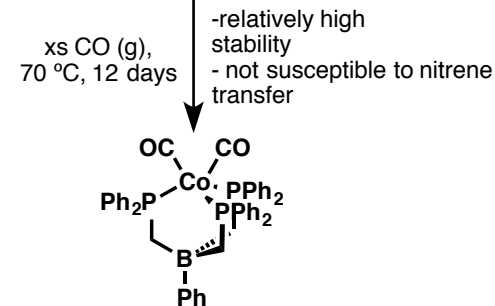
JACS 2002, 124, 11238 (formation of terminal Co(III) imido complex).

Indeed, installation of a terminal nitrido functionality is possible:



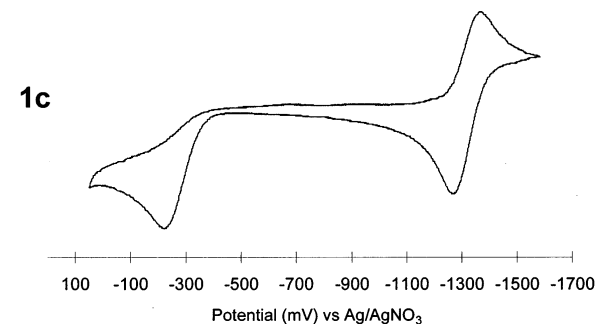
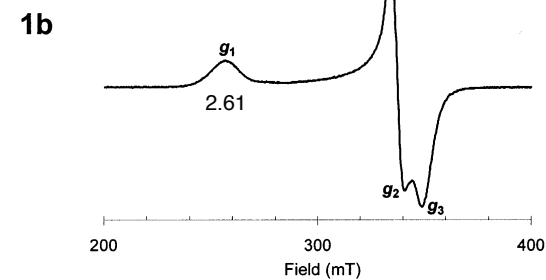
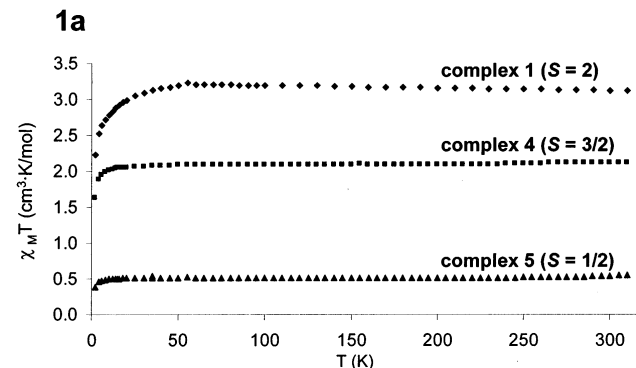
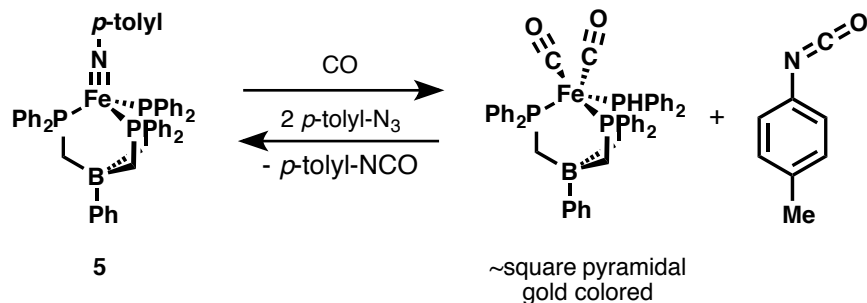
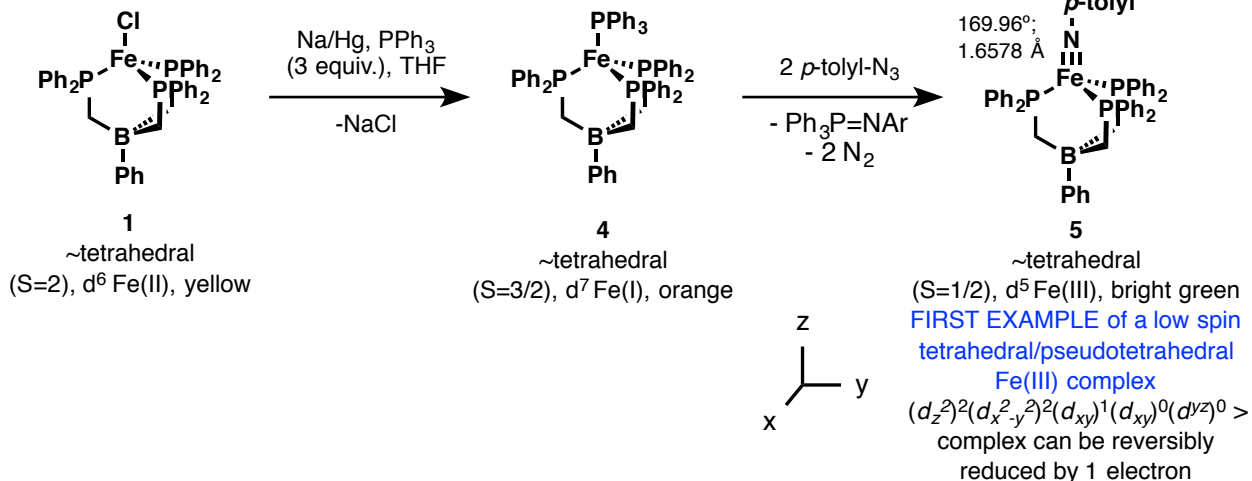
Standard bond lengths:

- N-N = 1.35 Å (aromatic)
- N=N = 1.25 Å
- N≡N = 1.16 Å
- C-N = 1.47 Å
- C=N = 1.25 Å
- C≡N = 1.16 Å
- C-C = 1.54 Å
- C=C = 1.34 Å
- C≡C = 1.20 Å

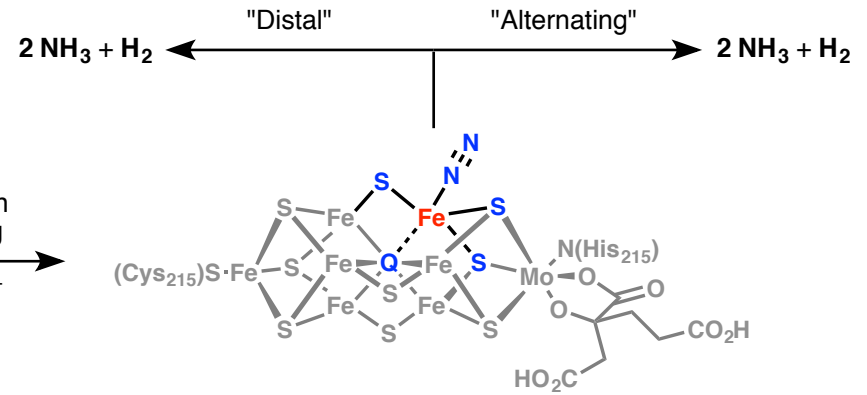
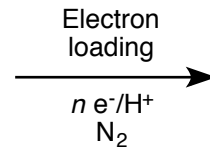
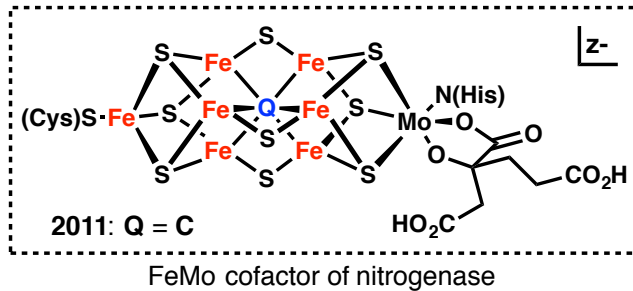
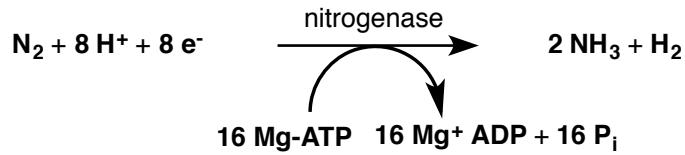


Context: Low valent iron, sulfur-ligated Fe(I) and Fe(II) play a critical role in small molecule reduction chemistry (eg. N_2). Towards N_2 reduction, the ability for a metal complex to accommodate a π -acidic N_2 ligand, as well as π -basic functionalities derived from N_2 (e.g., N^3- , NH_2^{2-}) at a single site in one key feature of competent N_2 -reducing molybdenum systems (Schrock). Peters set out to access well-defined N_2 -reducing iron complexes.

3. *Synthesis of a Low Spin d^5 Iron Imide.* JACS 2003, 125, 322.



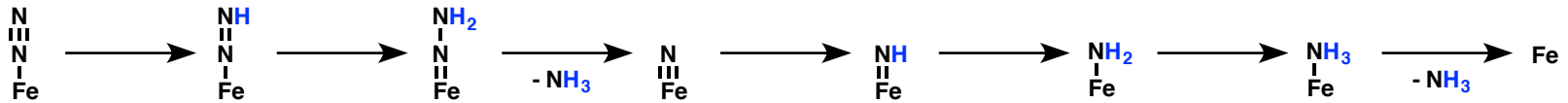
Fundamental question: *What is the role of Fe in the FeMo cofactor?*



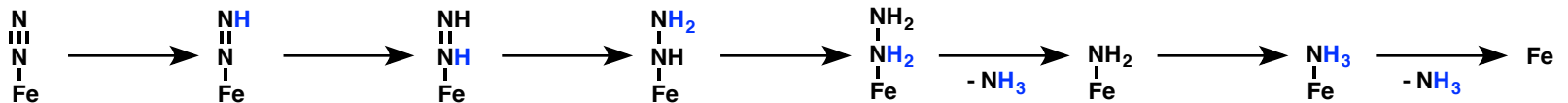
In 1992, there was not thought to be an atom at Q. In 2002, atom Q was proposed to be nitrogen. Finally, in 2011, atom Q was shown to be carbon atom. (*Science* **2011**, 334, 940; **2011**, 334, 974.) The Peters group is deeply interested in understanding the role of iron in nitrogenase.

What is the pathway for N_2 reduction by iron? How does it work? (*Nature* **2013**, 501, 84.)

a) "Distal" pathway (*Chem. Rev.* **1978**, 78, 589.)

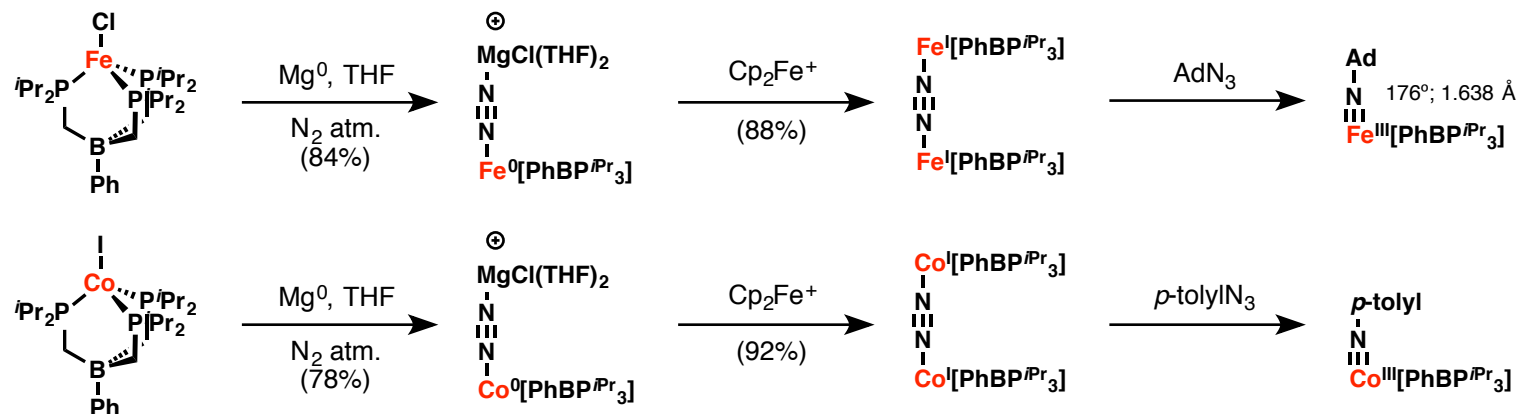


b) "Alternating" pathway (*Annu. Rev. Biochem.* **2009**, 78, 701.)

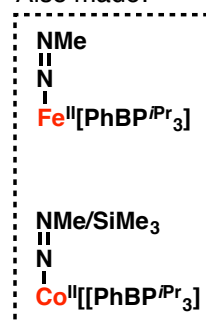


Iron is the only TM essential to all nitrogenases, but the exact site(s) of N_2 coordination and reduction were poorly understood. Jonas Peters' group synthesized a large variety of Fe (and Co) complexes and studied their reactivity in the presence of N_2 , H_2 , and related conditions. The following discussion highlights key discoveries in this area in chronological order.

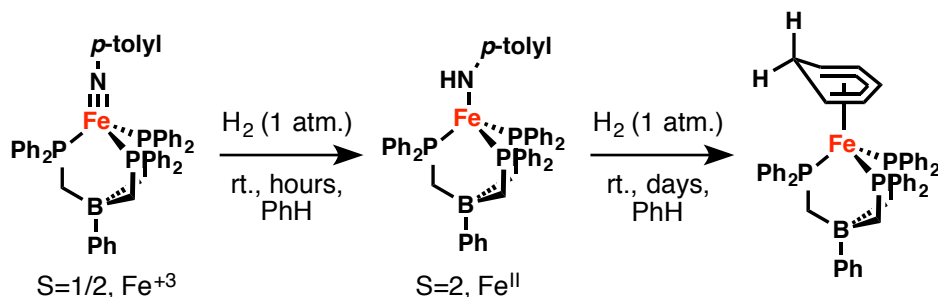
- Formation of Fe and Co bound N_2 complexes. *JACS* **2003**, *125*, 10782
Selected reactions:



Also made:



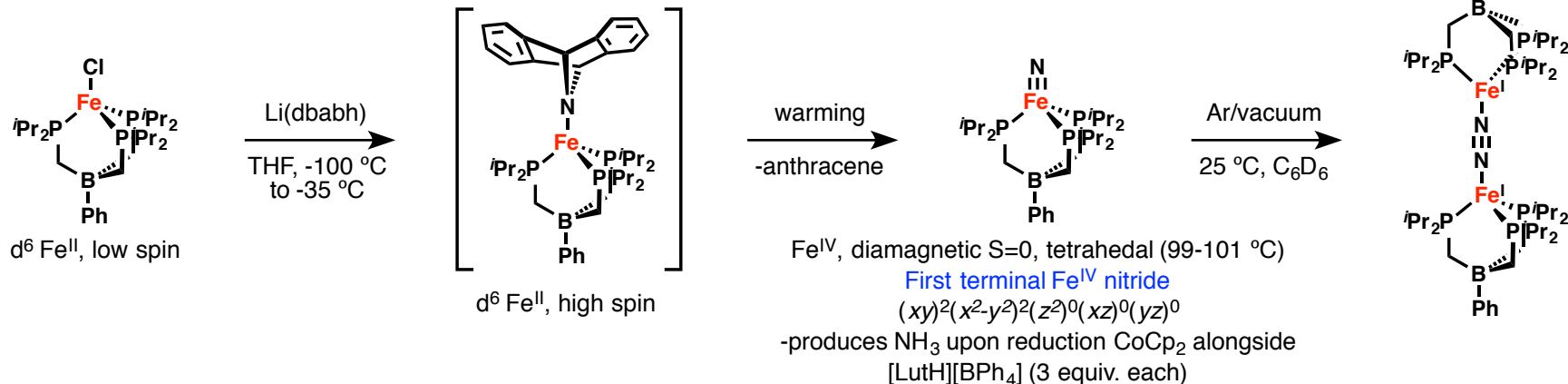
- Reaction of an Fe^{III} imide with hydrogen. *JACS* **2004**, *126*, 4538



Mechanism appears to involve initial addition of H_2 to the Fe(III)imide, bimolecular loss of H_2 , a second addition of H_2 to generate an unobservable Fe^{II}-H with loss of *p*-Me-aniline. The Fe^{II}-H then adds to benzene to form an Fe^{II} cyclohexadienyl species.

- Showed that an iron imide could be reduced with H_2 in a well-defined, stepwise process. (see *Inorg. Chem.* **2004**, *43*, 7474. for olefin hydrogenation with $[\text{PhBP}^i\text{Pr}_3\text{Fe-H}_x]$ species)

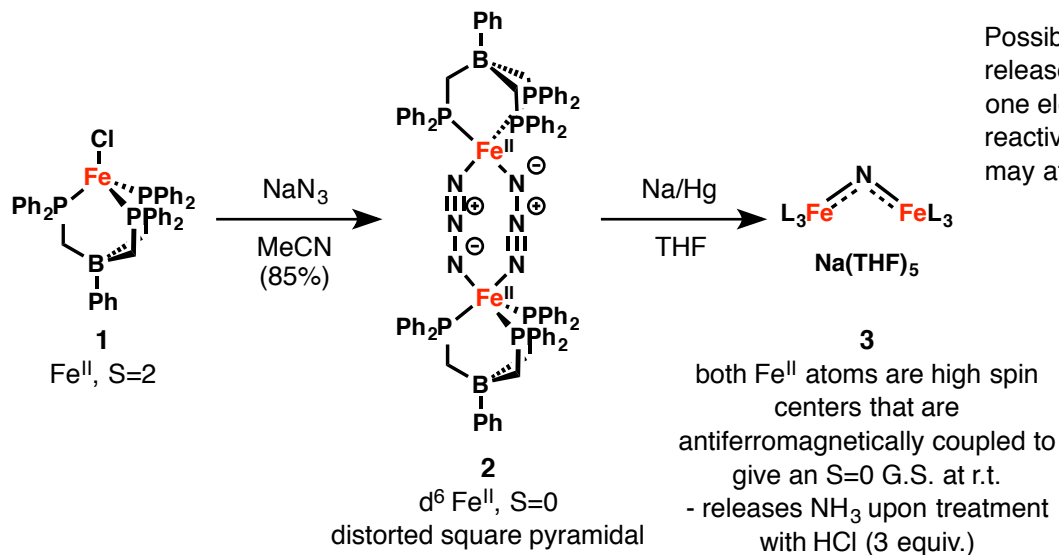
Formation of the first terminal Fe^{IV} nitride and dimerization to an $\text{Fe}^{\text{I}}\text{-N}_2\text{-Fe}^{\text{I}}$ complex. *JACS* **2004**, 126, 6252.



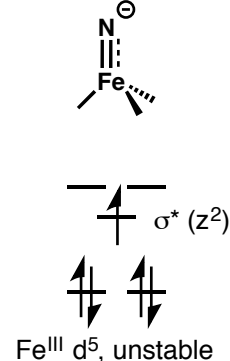
Undergoes bimolecular condensation via nitride coupling ($6 e^-$ redox process). This suggests that the reverse reaction may be possible by the principle of microscopic reversibility.

Importance: Supports possibility of reduction of N_2 to NH_3 by successive H^+/e^- transfer steps (e.g., $\text{Fe}^{\text{I}}\text{-N}_2 + 3\text{H}^+ + 3e^- \rightarrow \text{Fe}^{\text{IV}}\equiv\text{N} + \text{NH}_3$)

Formation of ground-state singlet $\text{L}_3\text{Fe}(\mu\text{-N})\text{-FeL}_3$ and $\text{L}_3\text{Fe}(\text{NR})$. *JACS* **2005**, 127, 1913. (see *Inorg. Chem.* **2006**, 45(18), 7417 and *Inorg. Biochem.* **2006**, 100, 634 for further structural analysis of Fe and Co imido and nitrido bonds)



Possible mechanism: Na/Hg reduces **2** to its corresponding anion with release of N_2 (g). A plausible byproduct of this would be $\text{L}_3\text{Fe}^{\text{III}}\equiv\text{N}^-$, which has one electron in a high lying a_1 (σ^*) antibonding orbital and is therefore highly reactive. This species may react with an Fe^{II} center of **2** to displace azide, or may attack an azide ligand itself.

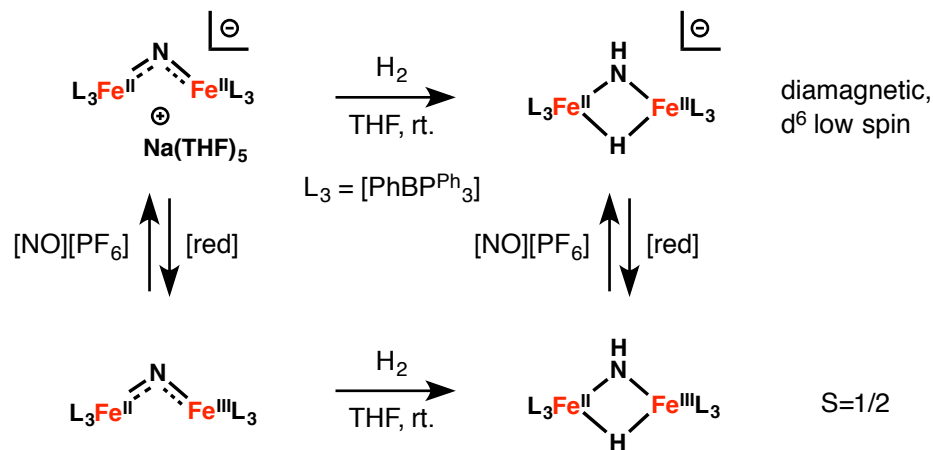


-a potent reductant: -1.3 V vs. Fc^+/Fc . ($\text{Cp}_2\text{Co} = -1.3 \text{ V}$)

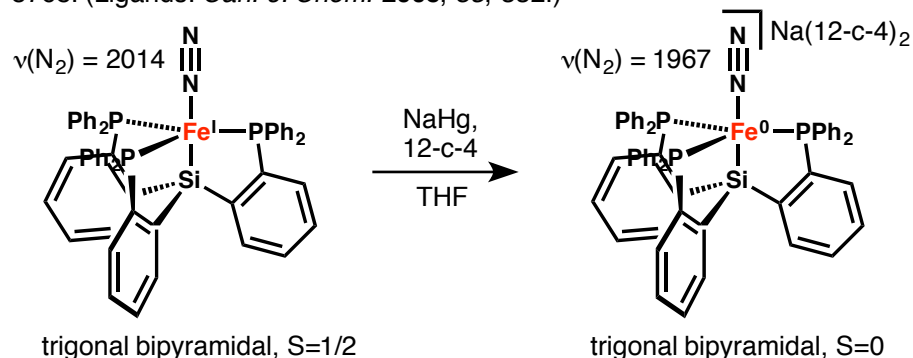
For reference:
 $< -2.5 \text{ V}$ (very strong reductant)
 -1.5 to -2.5 V (strong)
 -0.5 to -1.5 V (mild)
 $> -0.5 \text{ V}$ (weak)

Chem. Rev. **1996**, 96(2), 877.

Bridging iron nitrides stabilized by [PhBP₃] ligands mediate H₂ activation under mild conditions (1 atm. H₂, r.t.). *JACS* **2005**, *127*, 13146.

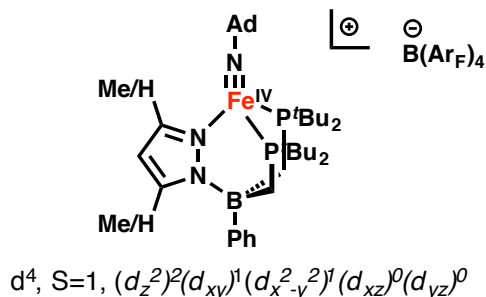


Access to mononuclear terminally bound Fe^I-N₂ species. *ACIE* **2007**, *46*, 5768. (Ligands: *Can. J. Chem.* **2005**, *83*, 332.)



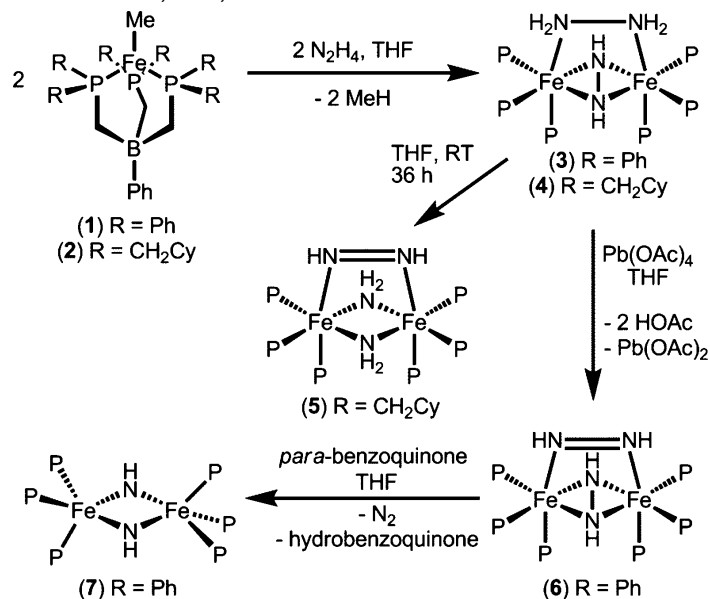
Use of bulkier [SiR₃]- (R=Ph, iPr) ligands allowed formation of mononuclear terminally bound Fe^I-N₂ species (c.f. linear μ -N₂ dimer formation with [PhBP₃]Fe species; *Inorg. Chem.* **2007**, *46*, 5720). Addition of HCl/BF₄ to the Fe^I complex resulted in low yields of NH₃ and N₂H₄; yields increased with addition of CrCl₂/Cp₂ or CrCp*₂. Competitive H⁺ reduction to H₂.

Terminal cationic Iron(IV) imide. *JACS* **2006**, *128*, 4956.



The new ligand system, [PhBP^tBu₂(pz')], allows access to iron imides in +3 and +4 oxidation states. (With the [PhBP^R]₃] ligand system, only +2 and +3 oxidation state were accessible.) The authors reason that the ability of this ligand system to stabilize a higher Fe oxidation state may be due to:
a) a cathodic shift in the Fe^{IV/III} potential which may lend stability to the borate unit of the ligand. (aka, more e⁻ rich ligand allows for [O] at less positive potentials)
b) the lower symmetry of the [PhBP^tBu₂(pz')] ligand which is more compatible with a d⁴ triplet electronic configuration.

Fe systems bearing parent N₂H₄, N₂H₂²⁻, N₂H₂, NH₂⁻ and NH₂²⁻ ligands. *JACS* **2009**, *131*, 10358.

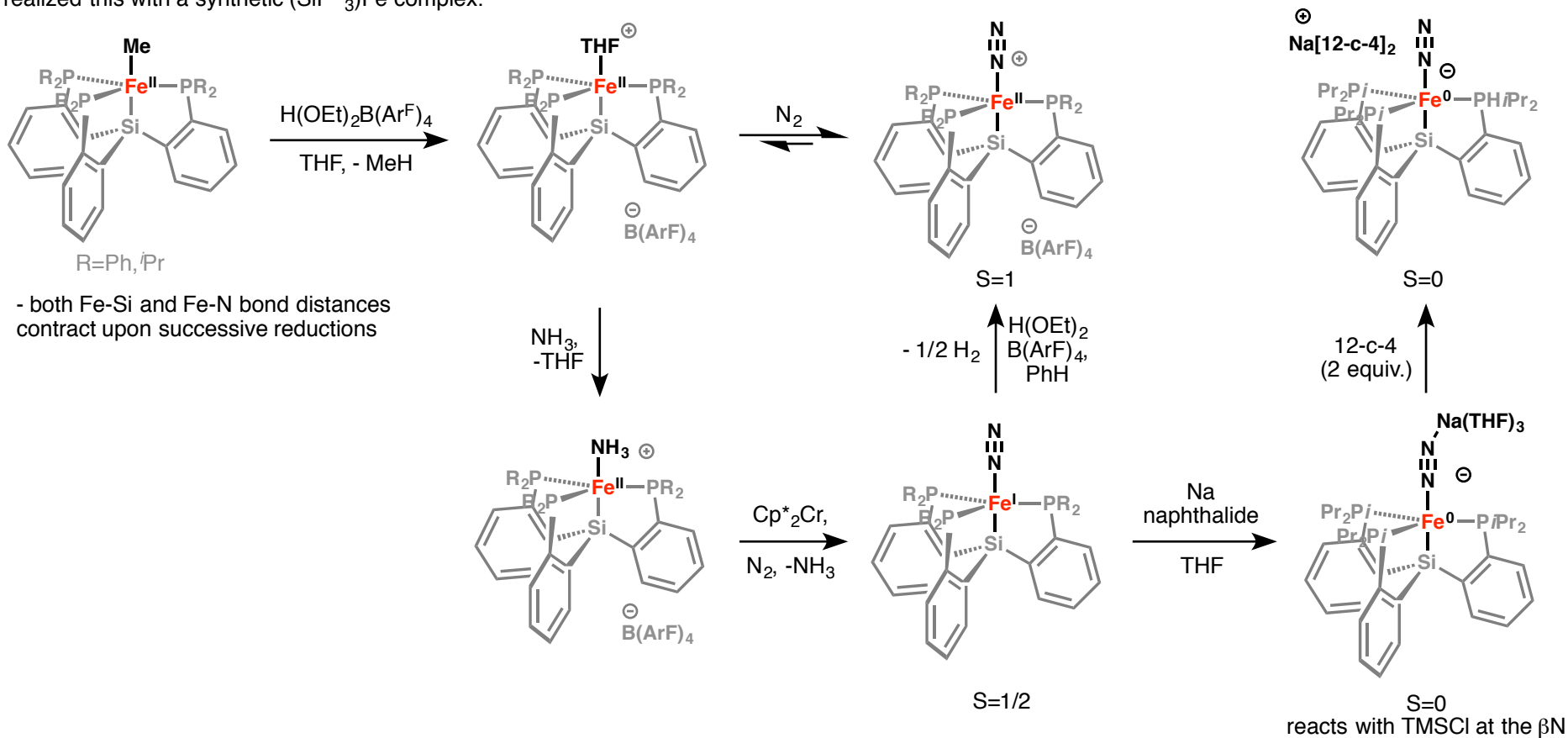


- diiron species may be involved in reductions of N_xH_y species by nitrogenase. These complexes serve as model systems.

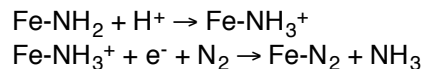
(For further work on Fe-N_xH_y species, see *ACIE* **2011**, *50*, 3446; *Inorg. Chem.* **2012**, *51*, 10043)

Triggering N_2 re-uptake by a NH_3 bound Fe species. *Nature. Chem.* **2010**, 2(7), 558.

In order for *catalytic* reduction of N_2 to NH_3 to occur with an iron-based catalyst, it is necessary for N_2 (a π -acidic ligand) to displace NH_3 . This paper realized this with a synthetic $(SiPR_3)Fe$ complex.

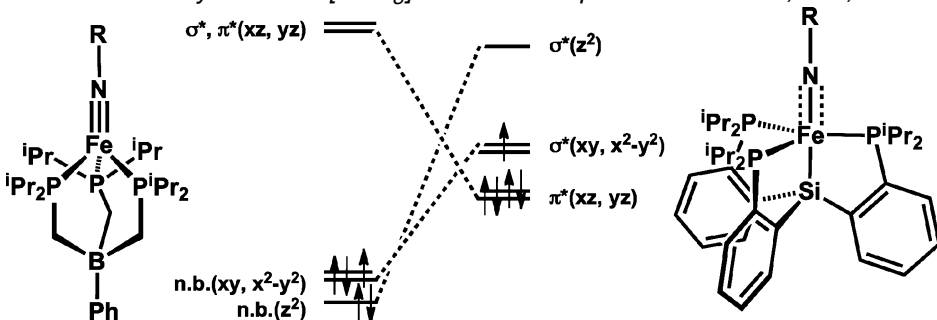


Importance: established viability of displacing a π -basic amine ligand with a π -basic dinitrogen ligand, which is relevant to nitrogenase



Further reactivity of a TBP $[\text{SiP}^{\text{R}}_3]\text{Fe}$ nitride complex. *JACS* **2010**, *132*, 4083.

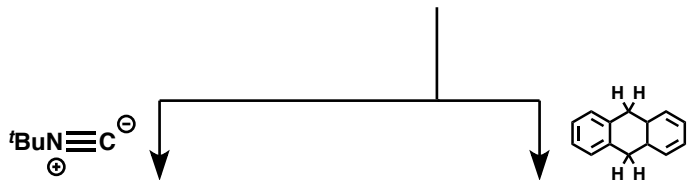
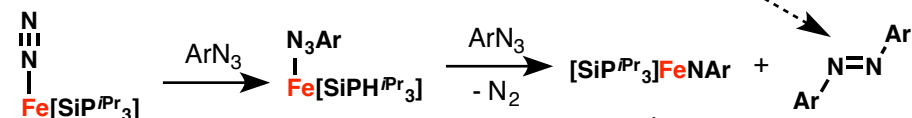
Use of Iron Metallaboratranes. *ACIE* **2011**, *50*, 2063.



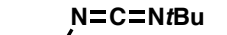
The presence of a ligand trans to the imido group shifts the Fe atom into the L_3 plane and leads to population of the π^*_{FeN} set which decreases Fe-N bond order/strength. Since TBP systems with a higher e^- count often dissociate the apical ligand and distort towards the more stable pseudotetrahedral geometry, the Peters group was interested in looking at the effect that this TBP ligand system would have on a FeNR species.

Indeed, these TBPFe species exhibit rich chemistry! (see *JACS* **2012**, *134*, 6695 for related $[\text{SiP}^{\text{R}}_3]\text{Ru}^{\text{I}}$ chemistry)

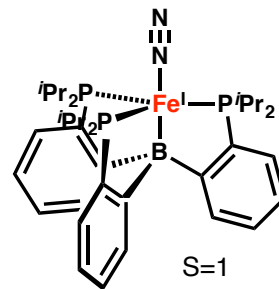
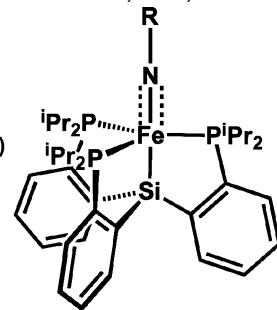
via bimolecular Fe nitrene coupling ($4 e^-$ process)



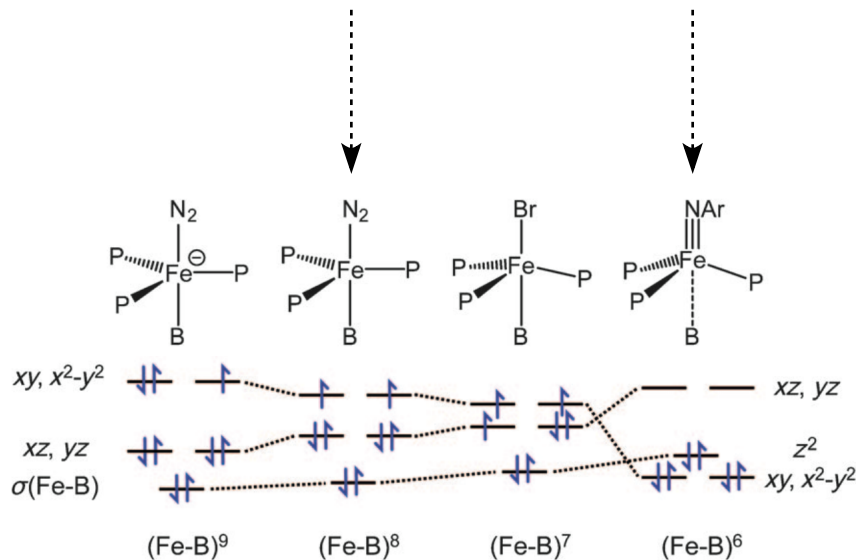
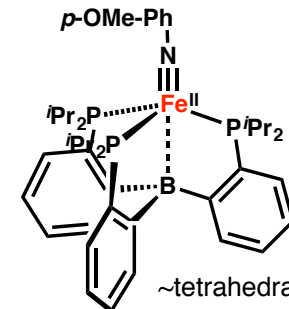
"Two-state reactivity" could explain the rich chemistry observed here. *Acc. Chem. Res.* **2000**, *33*(3), 139.



via nitrene transfer
($2 e^-$ process)

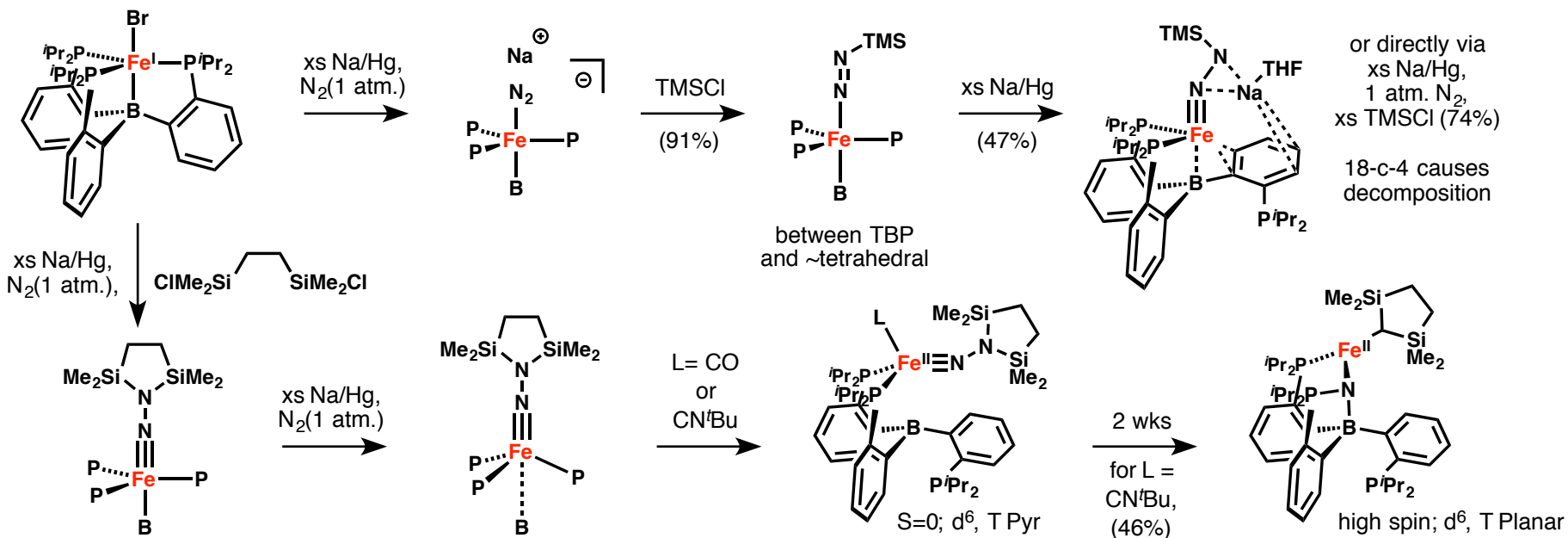


not stable if Si instead of B
(empty B σ stabilizes filled Fe d_{z^2} HOMO)

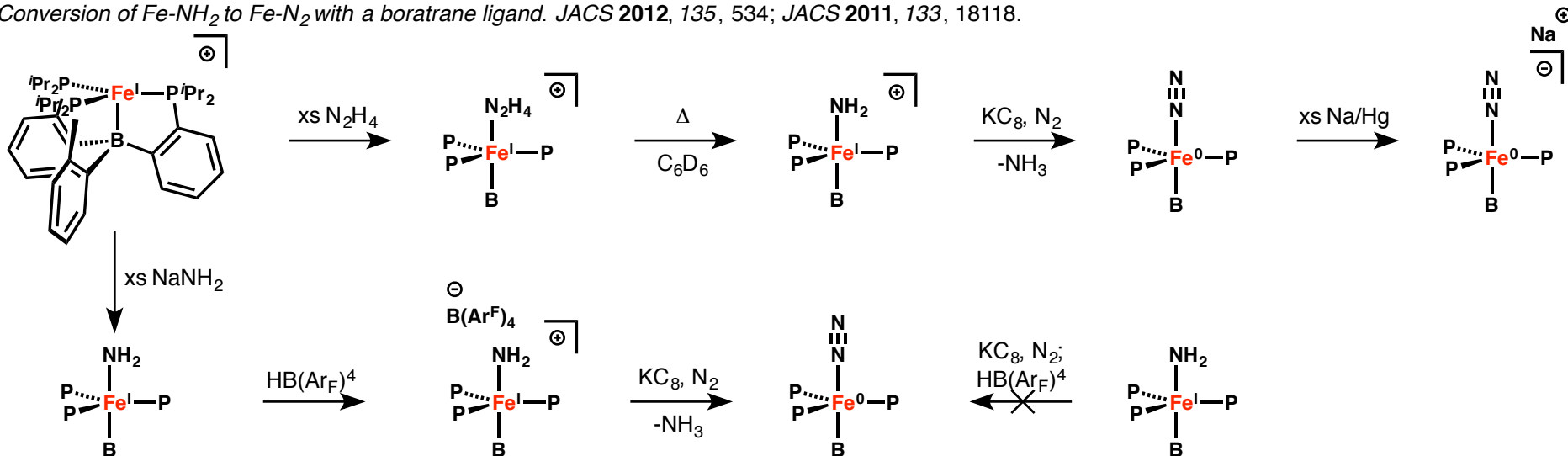


The use of the tetraboratranes ligand stabilizes both low-valent iron dinitrogen complexes and a mid-valent imido species due to its ability to shuttle between trigonal-bipyramidal and pseudotetrahedral geometries by elongation of the apical Fe-B bond. This stabilization makes a $4e^-$ redox shuttle possible ($0 \leftrightarrow \text{IV}$).

*N*₂ functionalization at Iron Metallaboranes. *JACS* **2011**, *133*, 18118. Importance: represents a series of transformations which result in full scission of the N≡N bond occurs! i.e. Fe-N₂ → Fe-NN=NH → Fe≡N-NH₂. The Fe-B coordinative flexibility affords another redox step and thereby further N₂ functionalization.

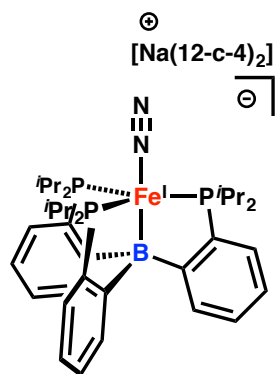
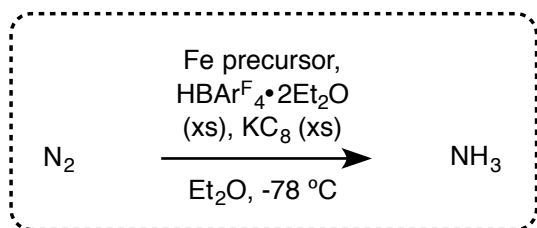


Conversion of Fe-NH₂ to Fe-N₂ with a boratrane ligand. *JACS* **2012**, *135*, 534; *JACS* **2011**, *133*, 18118.

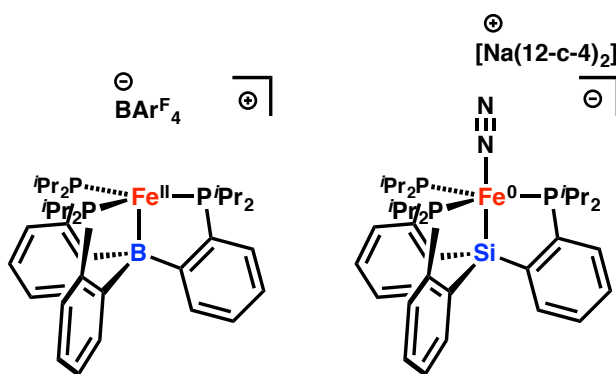


All Fe^I complexes are high spin, S=3/2! This demonstrates remarkable ability of this [BP^{iPr}₃] ligand to stabilize high spin states at iron.

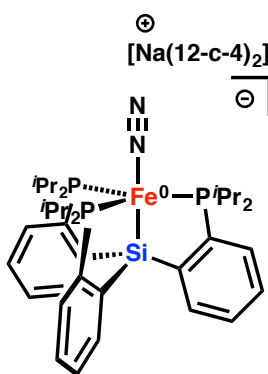
Catalytic conversion of nitrogen to ammonia. *Nature* **2013**, *501*, 84.



1 (yields 7.0 equiv.)



2 (6.2 equiv.)



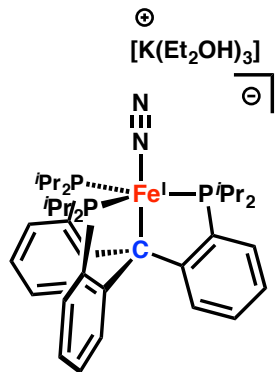
3 (0.7 equiv.)

Entry	Fe precursor	NH ₃ equiv./Fe†
1	[(TPB)Fe(N ₂)] [Na(12-crown-4) ₂]	7.0 ± 1‡
2	[(TPB)Fe][BARF ₄]	6.2
3	[(SiP ^{i-Pr} ₃)Fe(N ₂)] [Na(12-crown-4) ₂]	0.7
4	(TPB)(μ-H)Fe(N ₂)(H)	0.5
5	FeCl ₂ ·1.5THF	<0.1
6	FeCl ₃	<0.1
7	Cp ₂ Fe	<0.2
8	Fe(CO) ₅	<0.1
9	None	<0.1

Variations on standard conditions using [(TPB)FeN₂][Na(12-crown-4)₂]

Entry	Variation	NH ₃ equiv./Fe†
10	HOTf as acid	0.4
11	[Lutidinium][BARF ₄] as acid	<0.1
12	HCl as acid	<0.1
13	Cp* ₂ Co as reductant	0.6
14	Cp* ₂ Cr as reductant	<0.2
15	K metal as reductant	0.4

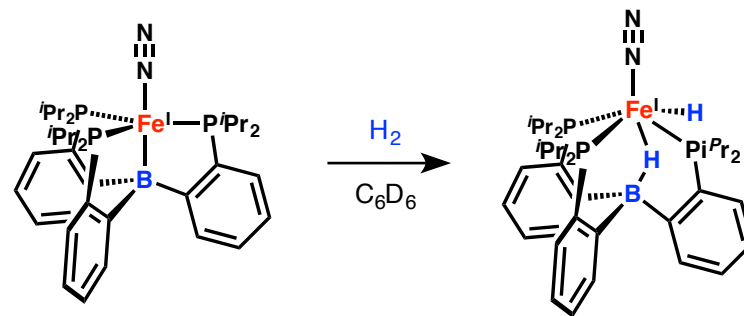
C-anchor analog. *PNAS* **2013**, *110*, 15898; *JACS* **2014**, *136*, 1105.



yields 4.6 equiv. of NH₃ per Fe

The relative activity: B > C > Si trends with Fe-B/C/Si axial bond flexibility.

The carbide ligand in FeMoco may similarly facilitate N₂ reduction by serving as a flexible trans ligand, allowing the adjacent iron center to sample pseudotetrahedral, trigonal pyramidal, trigonal bipyramidal and similar geometries as required to stability various Fe oxidation states and N_xH_y coordinating modes.

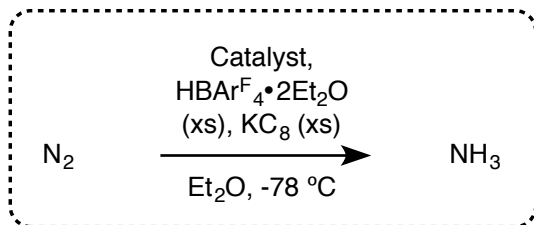


4 (0.5 equiv.)
Ineffective for catalytic N₂ reduction.

4 forms from 1 in presence of KC₈ and HBARF₄·Et₂O

Catalyst poisoning? 4 was originally reported in *Organometallics* **2013**, *32*, 3053.

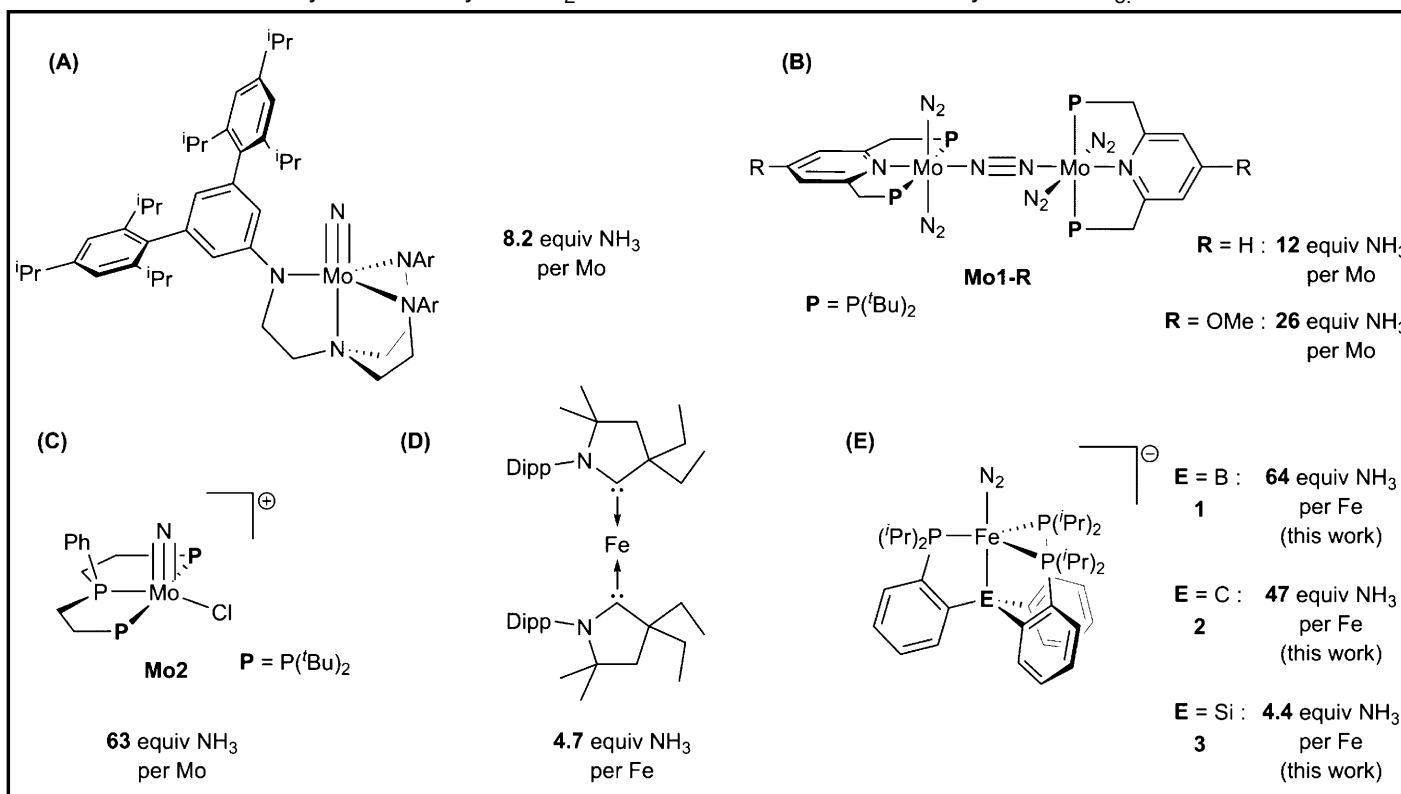
⁵⁷Fe Mössbauer freeze-quench data; further insights and improvement. *JACS* **2016**, *138*, 5341.



Notable findings:

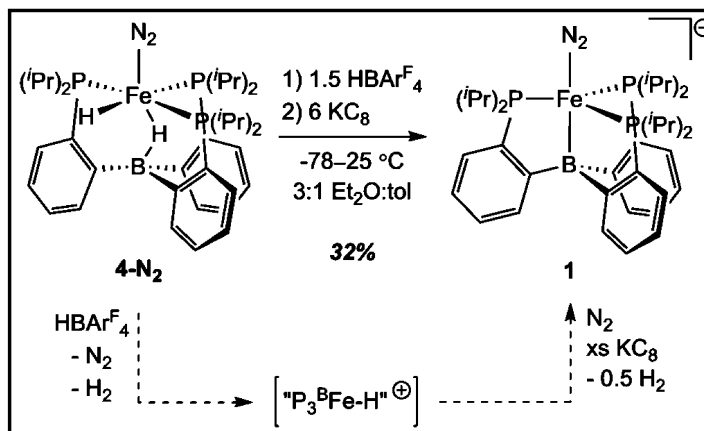
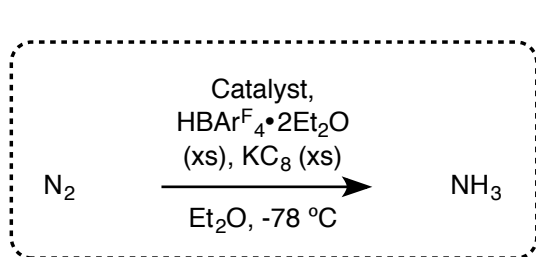
- acid purity and good mixing of N₂ into solution are required for improved turnover
- catalysis of hydrogen evolution is competitive with N₂ fixation, especially for Fe complex **3**
- NH₃ inhibits the reaction
- the reaction is first order in Fe catalyst, indicating that a single Fe site is responsible for catalysis

Synthetic catalyst for N₂ fixation with maximum observed yields of NH₃.



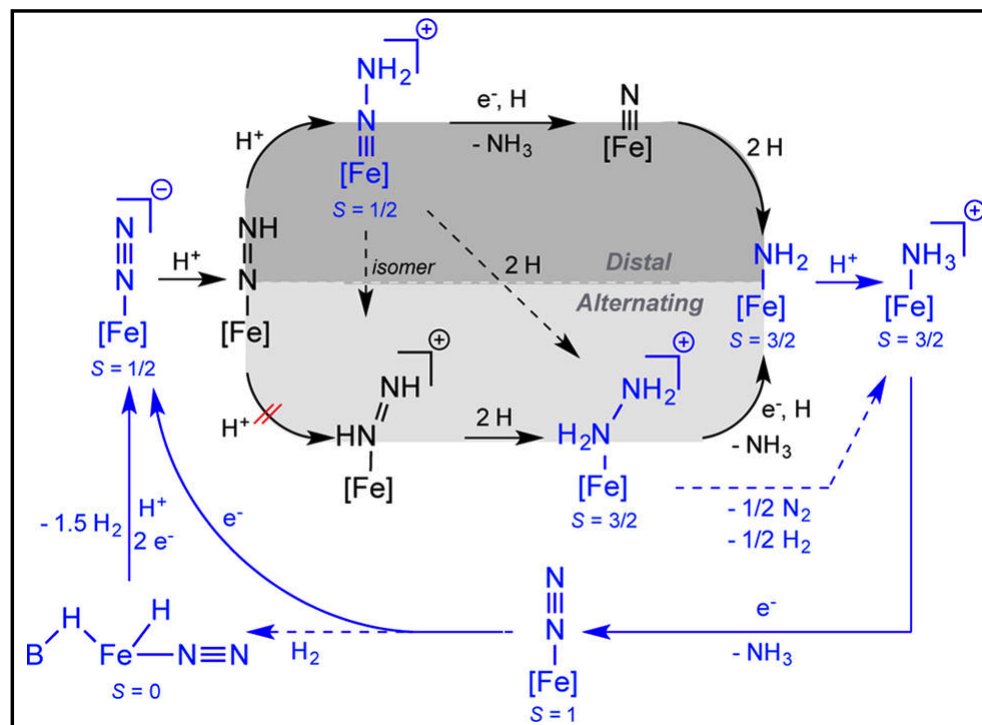
(A) *Science* **2003**, *301*, 76.; *JACS* **2014**, *126*, 6150. (B) *Nat. Chem.* **2011**, *3*, 120.; *Nat. Commun.* **2014**, *5*, 3737.; *JACS* **2014**, *136*, 9719. (C) *JACS* **2015**, *137*, 5666. (D) *ACIE* **2015**, *54*, 532. (E) *JACS* **2016**, *138*, 5341.

⁵⁷Fe Mössbauer freeze-quench data; further insights and improvement. continued... JACS 2016, 138, 5341.



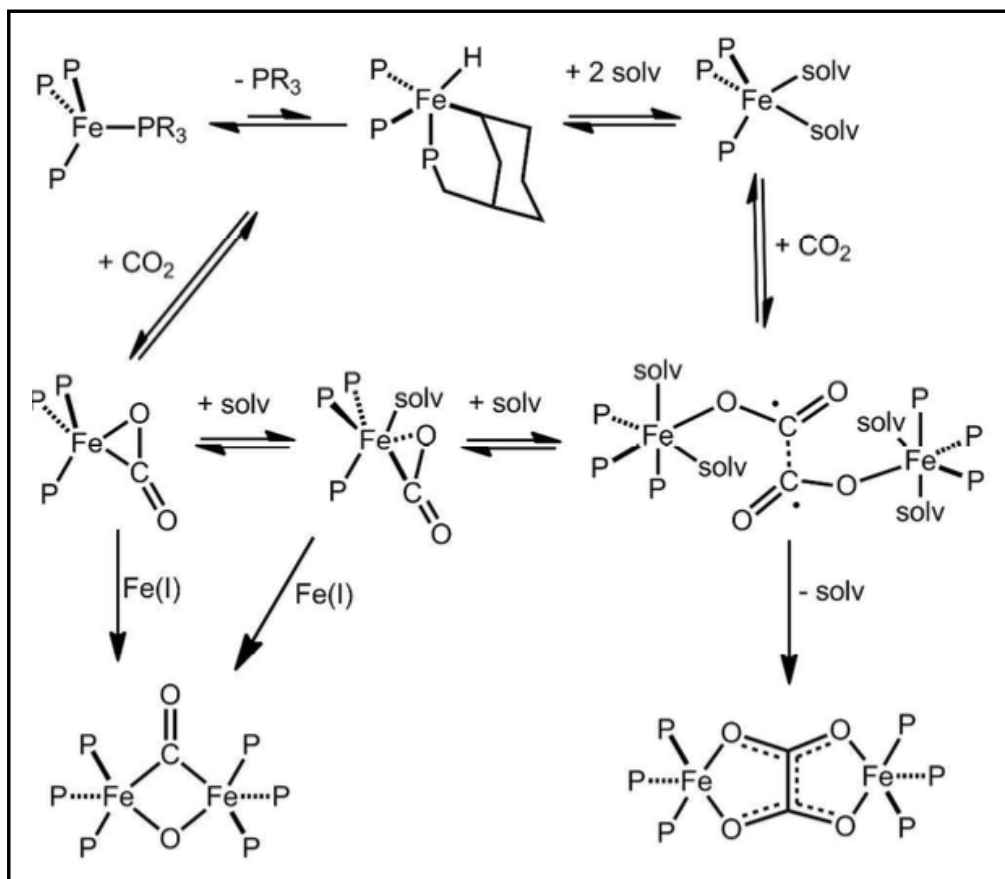
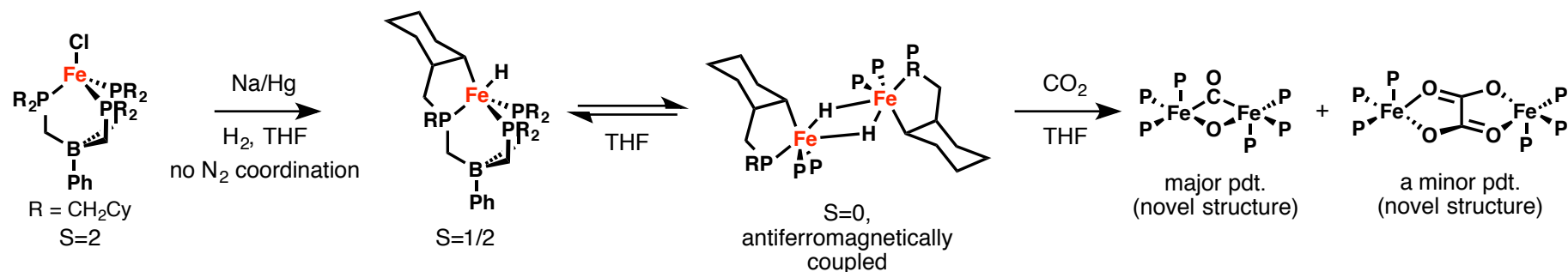
- 4-N₂ is the catalyst's resting state.
- Solubility was an issue

Possible catalytic scenarios:



Blue species are fully characterized.

Reactivity with CO_2 . *JACS* **2007**, *129*, 4; *Chem. Sci.* **2013**, *4*, 4042 (full paper); (see also *Inorg. Chem.* **2015**, *54*, 5124.)

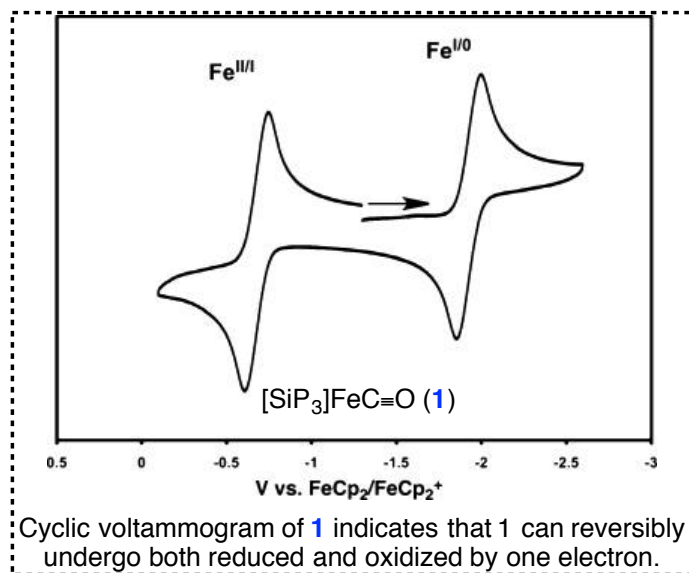
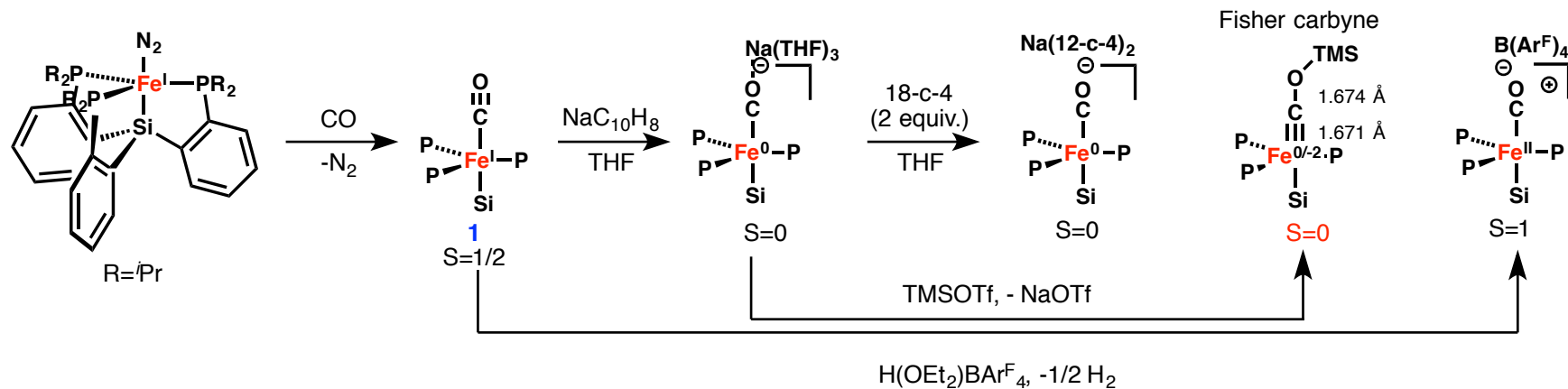


The product distribution (C-C coupling vs. C-O cleavage) is determined by the ability of solvent to coordinate to the $\text{Fe}(\text{I})$ center.

Coordinating solvents favor C-C coupling.

C-C coupling appears to occur from an electronically saturated " $\text{Fe}^{\text{I}}\text{-CO}_2^*$ " species.

Reactivity with CO. JACS 2011, 133, 4438.



Chemistry pertaining to reduction of C-1 units:

JACS 2013, 135, 12583 (Fe carbyne that releases olefin upon hydrogenation)
ACIE 2016, Just Accepted (Proton-Coupled Reduction of Fe-CN to CH_4 and NH_3)

Additional Fe-N chemistry.

ACIE **2006**, 45, 776. (Reaction of Fe nitride with silanes)

JACS **2013**, 135, 4938. (H₂ and Si-H bond addition across FeNNR₂ intermediates)

ACIE **2014**, 53, 8427. (Fe⁰ and Co⁰ supported by cyclic alkyl amino carbenes)

ACIE **2015**, 54, 532. (Low-T N₂ binding by 2-coordinate L₂Fe⁰ enables reductive trapping of L₂FeN₂⁻ and NH₃ generation)

JACS **2016**, 138, 4243. (Demonstration of a hybrid distal-to-alternating pathway for N₂ reduction with an [SiP^R₃]Fe complex)

Fe-S chemistry.

JACS **2011**, 133, 8440. (Dinitrogen complexes of sulfur-ligated iron)

ACIE **2014**, 53, 5978. (Low-spin pseudotetrahedral iron(I) sites in Fe₂(μ-S) complexes)

JACS **2015**, 137, 7310. (Diiron bridged-thiolate complexes that bind N₂ at the Fe(II)Fe(II), Fe(II)Fe(I), and Fe(I)Fe(I) redox states)

Fe-H chemistry.

Inorg. Chem. **2004**, 43, 7474. (Use of FeH_x species for hydrogenation)

JACS **2005**, 127, 13146. (Heterolytic H₂ activation mediated by low-coordinate Fe complexes)

ACIE **2006**, 45, 776. (An η³-H₂SiR₂ adduct of [PhB(CH₂iPr)₃]Fe^{II}H)

JACS **2011**, 133, 16366. (A nonclassical Fe^I-H₂ adduct.)

Organometallics **2013**, 32, 3053. (Heterolytic H₂ cleavage and catalytic hydrogenation with an Iron metallaboratrane)

JACS **2014**, 136, 13853 (10⁶ fold increase in N₂-binding affinity of a Fe₂(μ-H)₂ core upon reduction to a mixed-valence Fe(II)Fe(I) state)

Inorg. Chem. **2015**, 54, 5124. (Reduction of CO₂ with Fe-H species.)

Co-H chemistry.

JACS **2012**, 134, 14158. (Chemistry of Co-H₂ species)

JACS **2013**, 135, 15310. (Cobalt activation of H₂ and related chemistry)

JACS **2014**, 136, 14998. (Chemistry of Co-H₂ species)

Ni-H/B/Si chemistry.

Inorg. Chem. **2004**, 43(15), 4645. ([PhBP^R₃]Ni chemistry)

JACS **2011**, 134, 5080. (Addition of H₂ reversibly across a N-B unit)

Chem. Sci. **2012**, 3, 1313. (N₂ and H₂ adducts of cationic Ni^{II})

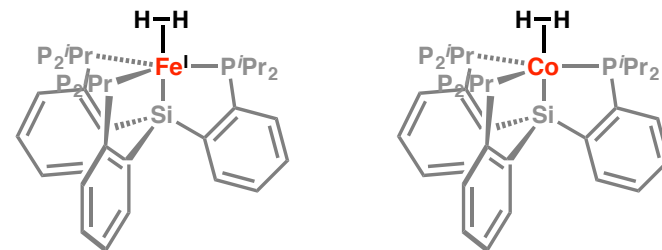
Chem. Sci. **2013**, 4(1), 157. (Access to formally Ni(I) states in a NiZn system)

JACS **2014**, 136, 13672. (Boryl-M bonds facilitate Co/Ni-catalyzed olefin reduction)

ACIE **2014**, 53, 1081. (A d¹⁰ Ni-H₂ adduct as an intermediate in H₂ oxidative addition across a Ni-B bond)

Chem. Sci. **2014**, 5, 590. (Ni-B complex catalyzed Si-H activation and hydrosilylation)

Organometallics **2016**, 5(35), 686. (H atom exchange between H₂ and SiH on a low valent Ni center)



Use of copper as a cross-coupling catalyst in collaboration with Greg Fu.

- Science* **2012**, *338*, 647. (Photoinduced Cu-catalyzed Ullman C-N coupling; with G. Fu)
JACS **2013**, *135*, 9548. (Photoinduced Cu-catalyzed ArSH + ArI/Br cross coupling; with G. Fu.)
JACS **2013**, *135*, 13107. (Expansion of the Photoinduced Cu-catalyzed Ullman C-N coupling; with G. Fu)
ACIE **2013**, *52*, 5129. (Photoinduced Cu-catalyzed C-N cross couplings; with G. Fu)
JACS **2014**, *136*, 2162. (Photoinduced Cu-catalyzed alkylation of amide with 2° alkyl halides; with G. Fu)
Chem. Sci. **2014**, *5*, 2831. (Photoinduced Cu-catalyzed ArOH + ArI cross coupling; with G. Fu)
JACS **2015**, *137*, 13902. (Photoinduced Cu-catalyzed cyanation with 2° alkyl halides; with G. Fu)
Chem. Sci. **2016**, *7*, 4091. (Mechanistic investigation of Cu-catalyzed ArSH + ArI/Br cross coupling; with G. Fu)
Science **2016**, *351*, 681. (Asymmetric photoinduced Cu-catalyzed C-N cross couplings; with G. Fu)

Other first row transition metal chemistry.

- Dalton Trans.* **2006**, 1347 (Facially coordinated borohydride complexes with Fe)
Chem. Comm. **2008**, 1061. ([Ph₂BP^R₂]Cu chemistry)
Inorg. Chem. **2008**, *47*, 4579. (Electronic structure of diimine Fe complexes shows ligands are redox active.)
ACIE **2014**, *53*, 8427. (2-coordinate Fe⁰ and Co⁰ complexes supported by cyclic(alkyl)(amino)carbenes)
Inorg. Chem. **2015**, *54*, 9256. (Evaluating Co complexes for N₂ to NH₃ reduction)
Organometallics **2015**, *34*, 4741. (E-H bond activations and silylation catalysis with Fe and Co metalloboranes)
Inorg. Chem. **2015**, *54*, 9229. (A perspective on small molecule activation)

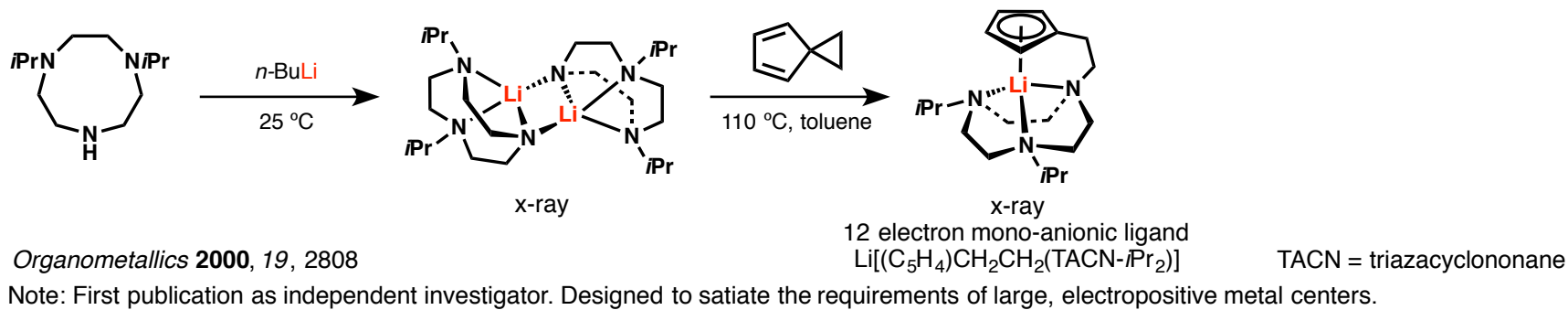
Second and third row transition metal chemistry.

- Inorg. Chem.* **2005**, *44*, 1713. (Excited state properties of cyclometallated Ir^{III} species)
Chem. Comm. **2010**, 46, 6554. (Ligand design for Pd and Pt centers to generate homo- and heteropolymetallic motifs)
ACIE **2010**, *49*, 4088. (Well-defined Ru^I and Os^I metalloradicals)
Inorg. Chem. **2012**, *51*, 16. (A homologous series of Co, Rh and Ir metalloradicals bearing the [SiP^R₃] ligand)
JACS **2012**, *134*, 6695. (A [SiP^R₃]Ru^I metalloradical catalyzes azoarene formation from aryl azides)
Chem. Eur. J. **2015**, *21*, 8497. (Reduction of CO₂ by a Mo catalyst)

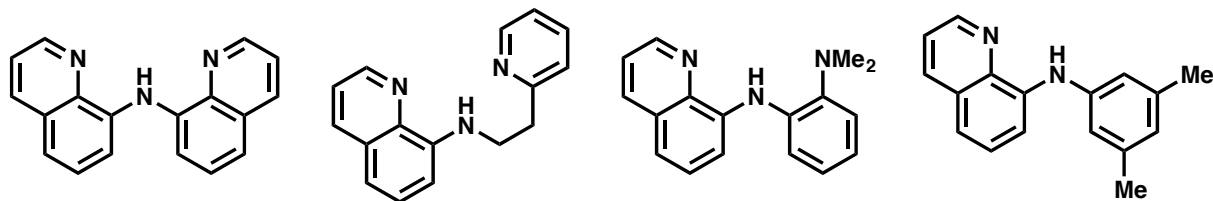
Spectroscopy contributions.

- Inorg. Chim. Acta* **2008**, *361*, 1157. (Changes induced in Fe⁰ to Fe^{IV} complexes by XAS photochemistry can facilitate structural assignment)
JACS **2007**, *134*, 12637. (Modelling the signatures of hydrides in metalloenzymes with ENDOR analysis of H-bridged Fe complexes)

1. Uni-negative, multidentate ligands

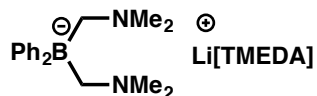


2. Pincer-like amido ligands (based on 8-amino quinoline)



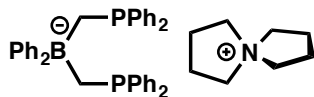
Inorg. Chem. **2001**, *40*, 5083 (Li, Pt, Pd, Ni, Tl complexes). Prepared by Pd catalyzed C-N cross-coupling.
Organometallics **2002**, *21*, 1753; *JACS* **2003**, *125*, 8870 (Pt^{II} complexes and chemistry)
Inorg. Chem. **2008**, *47*, 11570. (chemistry with Fe, Ru and Os)

3. (Dialkylamino)borate anionic ligands

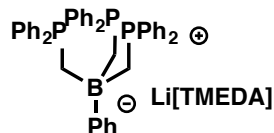


Inorg. Chem. **2002**, *41*, 6541 (formation of N-chelated rhodium(I) zwitterions).
Polyhedron **2004**, *23*, 2901; *Chem. Comm.* **2008**, 1061. (Cu^I complexes and chemistry)

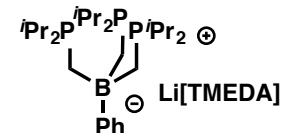
4. Anionic bis- and tris-(phosphino)borate ligands (latter extensively used to support Fe, Co and Ni chemistry)



JACS **2001**, *123*, 5100 (stabilizes reactive cationic Pt^{II} complexes)
Inorg. Chem. **2003**, *42*, 5055
(full paper on bis(phosphino)borates)

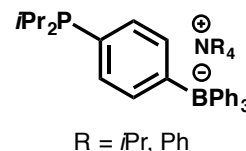
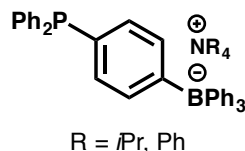
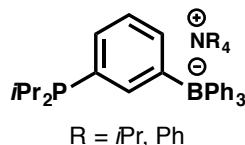
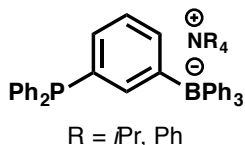


Chem. Comm. **2001**, *40*, 5083
(forms stable Tl(I) complex, which can be used for clean deliver of the [PhBP₃] ligand to other metals, eg. forms a low spin [PhBP₃]Co^I complex)
Polyhedron **2004**, *23*, 489. (related Pt species)



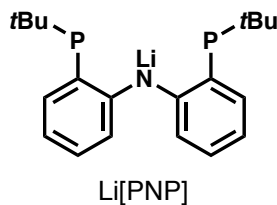
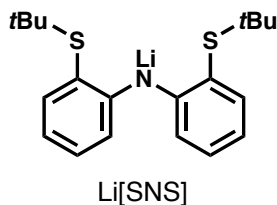
Inorg. Chem. **2003**, *42*(17), 5074
(forms coordinatively unsaturated complexes with Fe^{II}, Co^{II} and Ru^{II})
Inorg. Chem. **2006**, *45*, 8597.
(chemistry of [PhBP^{iPr}]Mn complexes)

5. (Phosphino)tetraphenylborate ligands



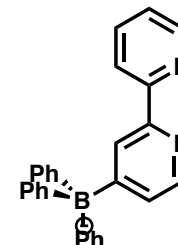
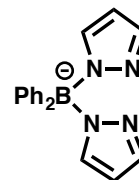
Inorg. Chem. **2004**, *43*, 8. These anionic, electron-releasing phosphines that incorporate a borate counteranion within the ligand framework are able to promote Suzuki cross-coupling of aryl chloride substrates.

6. Bis(sulfanyl)amide and bis(phosphine)amide ligands.



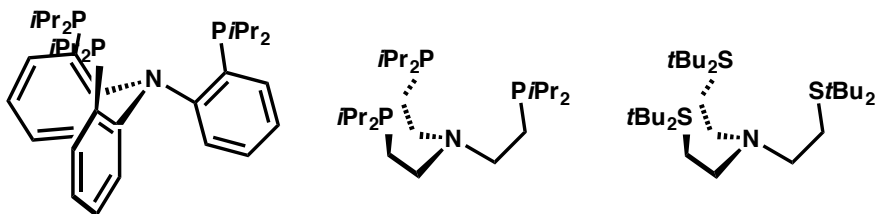
JACS **2004**, *126*, 2885; *JACS* **2005**, *127*, 2030. (Used to form Cu₂N₂ complexes with remarkable photophysical properties)

7. Anionic bis(pyrazolyl)borate and 2,2'-dipyridylborate ligands



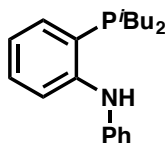
Organometallics **2005**, *24*, 5858. (A comparative study of these with the bis-(phosphino)borate ligand using Pt(II) species)

8. Tris(phosphine)amine and tris(thioether)amine ligands (Sacconi type ligands).



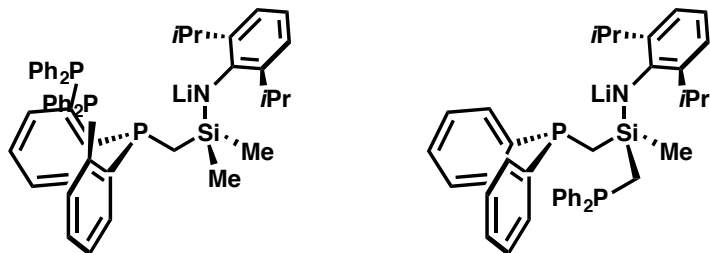
Can. J. Chem. **2005**, *83*, 332. (supports Fe for N₂ chemistry)

9. Amidophosphine ligands.



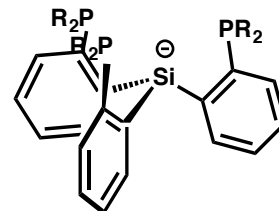
Inorg. Chem. **2007**, *46*(18), 7244. (Emissive properties in Cu complexes)

10. Tripodal amido-polyphosphine hydrid ligands.



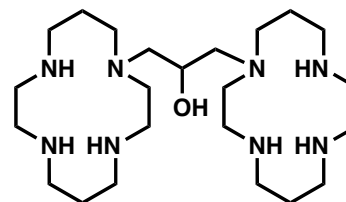
Chem. Comm. **2006**, 1613. (supports Co and Fe metals; charge is on an X-type ligand, rather than the ligand's backbone)

11. Tris(phosphino)silyl ligands (derivatives of Sacconi type ligands).



ACIE **2007**, *46*, 5768. (1st use; enables Fe-N₂ chemistry)
Inorg. Chem. **2009**, *48*, 2507. (supports Fe, Co, and Ir in N₂ chemistry)
Organometallics **2009**, *28*, 3744. (E-H (E=H,C,Si,Ge) bond activation with Ru)
JACS **2010**, *132*, 13975. (allows 4 coordinate TP Pt(II) and Pd(II) complexes)

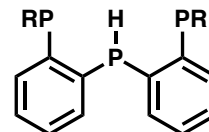
12. Cyclam ligand.



cyclam₂iPrOH

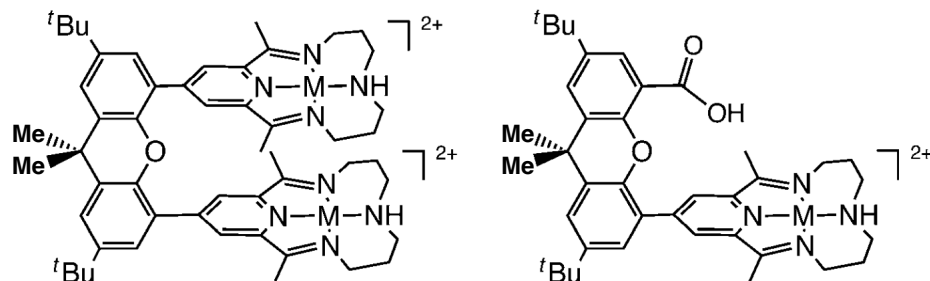
Inorg. Chem. **2008**, *47*, 11669.
(Forms high spin Fe and Mn complexes. The Mn complex is an excellent H₂O₂ disproportionation catalyst; of interest to H₂O oxidation)

13. Phosphido pincer ligand.



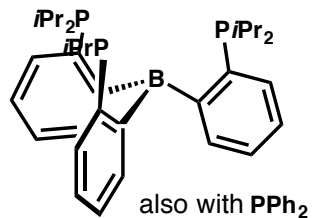
Dalton. Trans. **2011**, *40*, 9026. (phosphido pincer complexes of Pt)
Organometallics **2008**, *27*, 5741. (phosphido pincer complexes of Pd)

14. Pacman and Hangman Metal Tetrazamacrocycles.



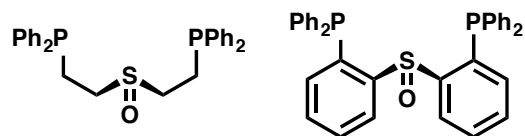
ChemSusChem **2013**, *6*, 1541. (when M=Zn, Co, relevant to HER.)

15. Tris(phosphino)boryl ligands (derivatives of Sacconi type ligands).



JACS **2013**, *135*, 15310; *JACS* **2014**, *136*, 13672. (bis-phosphino-boryl ligand, Co and Ni chemistry)

16. Diphosphinosulfinyl $S(O)P_2$ Pincer-type ligands.



Organometallics **2012**, *3*, 5213 (Supports M=Rh, Ir, Ni, Pd, and Pt)

Crystal Field Theory is "a model that describes the breaking of degeneracies of electron orbital states, usually d or f orbitals, due to a static electric field produced by a surrounding charge distribution." - Wikipedia article on "Crystal Field Theory".

Concepts to know:

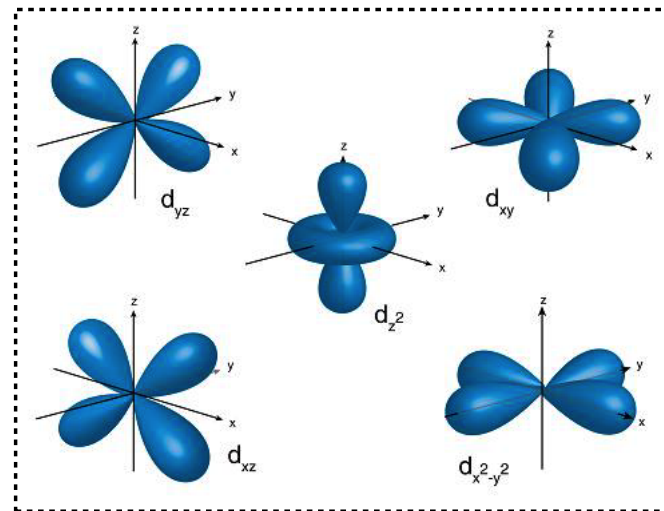
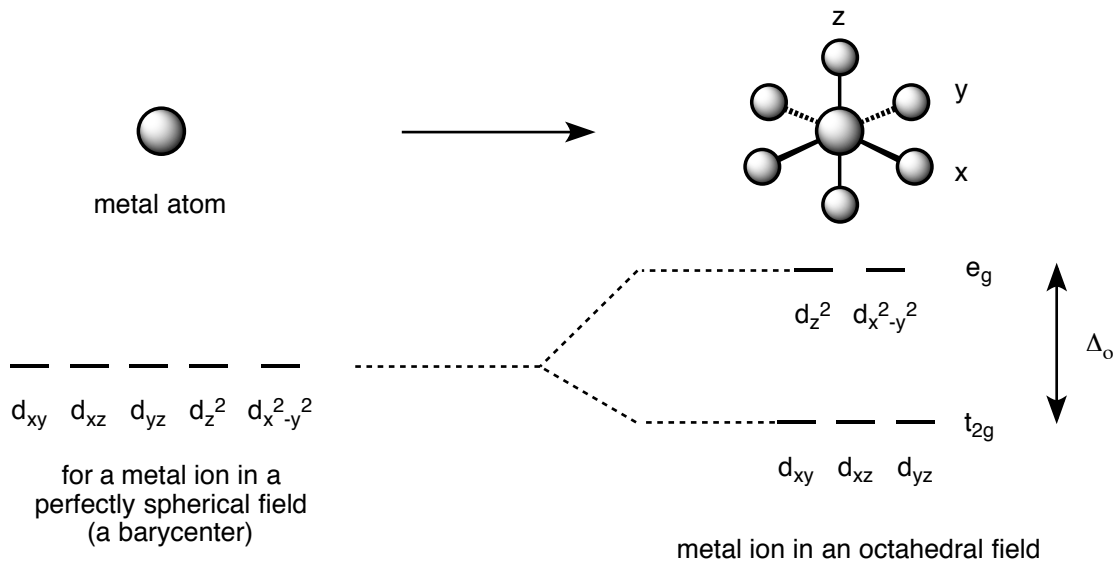
- 1) the crystal field
- 2) high spin vs. low spin complexes
- 3) factors which affect the crystal field splitting

1) The Crystal Field (example):

For a naked metal atom (i.e. no ligands), all five metal d orbitals are degenerate.

When ligands enter a metal ion's field, the metal's d-orbitals which overlap with ligands are destabilized due to electronic repulsion. Those which overlay best are most strongly destabilized.

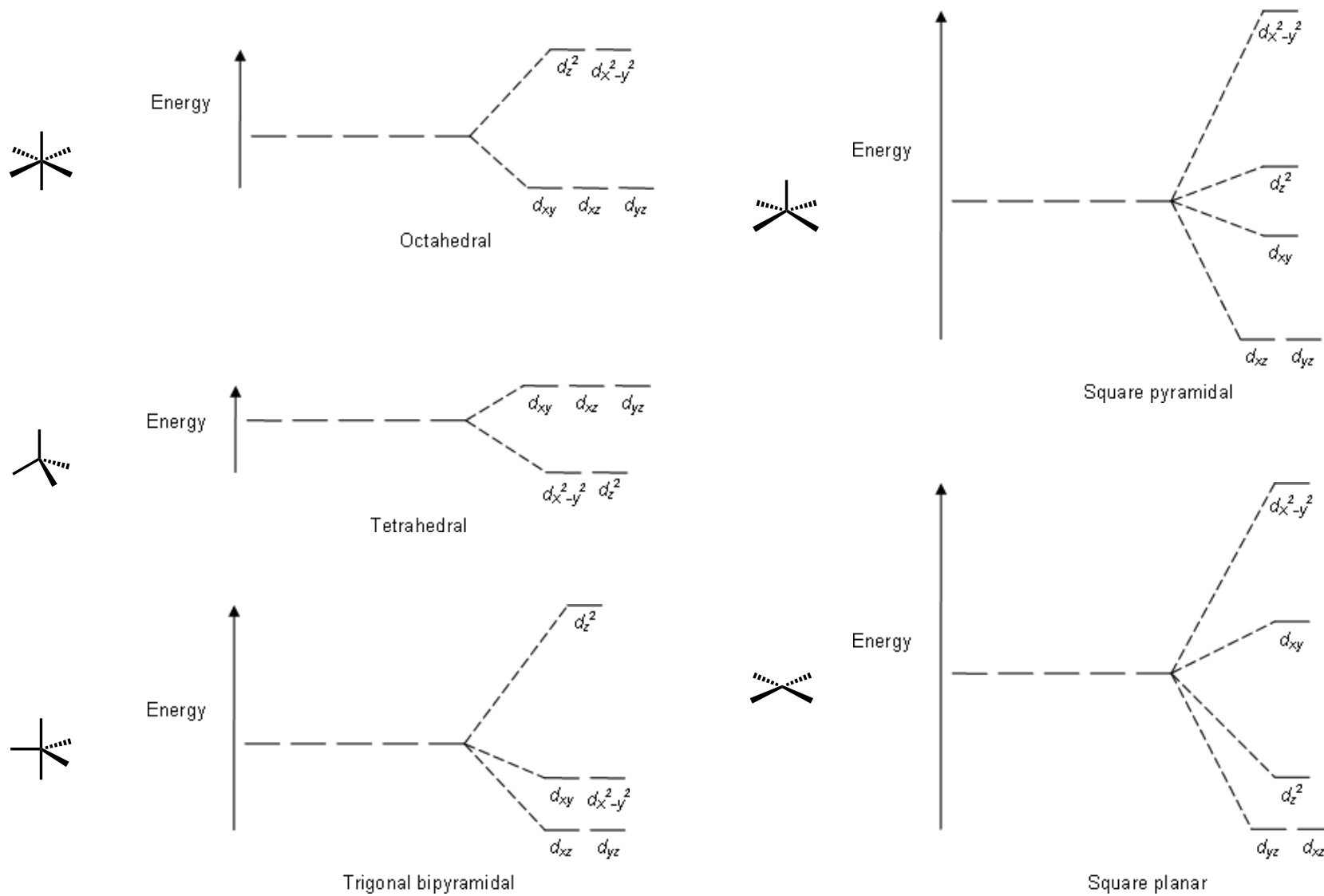
eg) a metal atom in an octahedral ligand field



<https://socratic.org/chemistry/the-electron-configuration-of-atoms/arrangement-of-electrons-in-orbitals-spd-and-f>

Question: What does the crystal field of a metal ion with a square planar geometry look like?

Common crystal field diagrams particularly relevant to this group meeting:



Metal complexes generally adopt a ligand geometry which maximizes the CFSE.

Crystal field stabilization energy (CFSE)

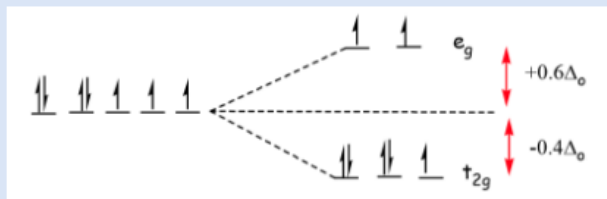
$$CFSE = \Delta E = E_{\text{ligand field}} - E_{\text{isotropic field}}$$

CFSE depends on:

- geometry, which changes the d-orbital splitting patterns
- number of d-electrons
- spin pairing energy
- ligand character

Example 1: CFSE for a high Spin d^7 complex

Consider a high spin d^7 octahedral complex. The splitting pattern and electron configuration for both isotropic and octahedral ligand fields are compared below.



The energy of the isotropic field ($E_{\text{isotropic field}}$) is

$$E_{\text{isotropic field}} = 7 \times 0 + 2P = 2P$$

The energy of the octahedral ligand field ($E_{\text{ligand field}}$) is

$$E_{\text{ligand field}} = (5 \times -2/5\Delta_o) + (2 \times 3/5\Delta_o) + 2P = -4/5\Delta_o + 2P$$

So via equation 1, the CFSE is

$$\begin{aligned} CFSE &= E_{\text{ligand field}} - E_{\text{isotropic field}} \\ &= (-4/5\Delta_o + 2P) - 2P \\ &= -4/5\Delta_o \end{aligned}$$

Factors which affect the crystal field splitting.

- 1) the nature of the metal ion
 - 2nd and 3rd row transition metals have large crystal field splittings than 1st row transition metals
- 2) the metal's oxidation state
 - higher oxidation states lead to larger splittings

Spectrochemical series for first row transition metals: $Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Cr^{3+} < V^{3+} < Co^{3+}$

- 3) the arrangement of ligands surrounding the metal ion
- 4) the nature of the ligands surrounding the metal ion (strong field vs. weak field)

Spectrochemical series for ligands:

$I^- < Br^- < SCN^- < Cl^- < F^- \leq OH^- , ONO^- < OH_2 < NCS^- < NCCH_3 < NH_3 , py < NO_2^- < CN^- , NO , CO$
weak-field ligands (π -donors and weak σ donors) strong field ligands (π -acceptors and strong σ -donors)

High spin complexes result from a small crystal field splitting and low spin complexes from a large crystal field splitting.

Examples:



Examples:

