Organometallics for Sustainability
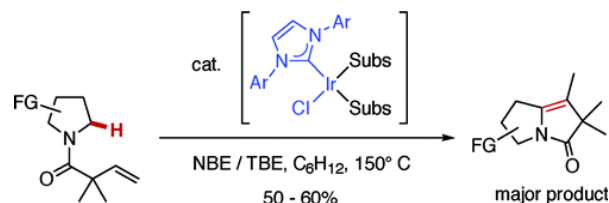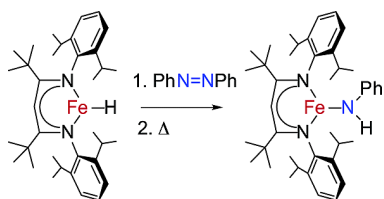## - Exploring Organometallics with P. J. Chirik's Work as Central Themes -

IUPAC Periodic Table of the Elements

N=N Bond Cleavage by a Low-Coordinate Iron(II) Hydride Complex

P. L. Holland et al.
J. Am. Chem. Soc. **2003**, *125*, 15752

Cross-Coupling of sp^3 C-H Bonds in Alkenes: Catalytic Cyclization of Alkene-Amide Substrates

D. Sames et al.
J. Am. Chem. Soc **2004**, *126*, 6556

Contents

[1] Dinitrogen Cleavage and Functionalization by Carbon Monoxide Promoted by a Hafnium Complex

P. J. Chirik et al.
Nature Chemistry **2010**, 2, 30
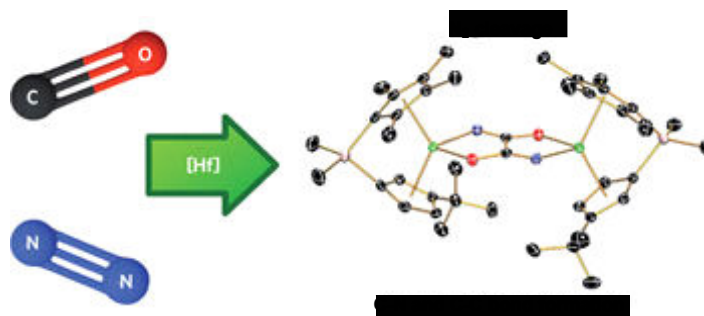
[2] Iron-Catalyzed, Hydrogen-Mediated Reductive Cyclization of 1,6-Enynes and Diynes: Evidence for Bis(imino)pyridine Participation
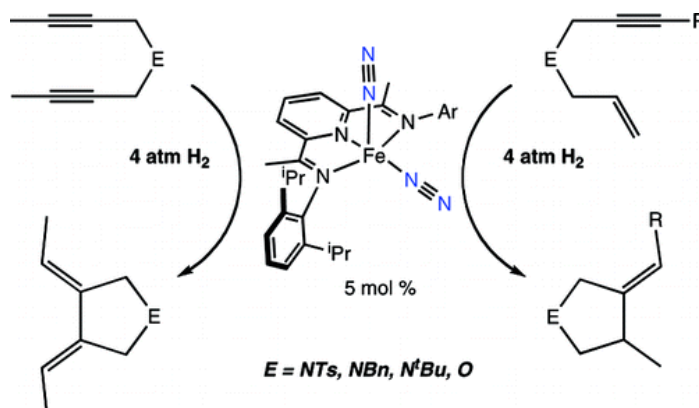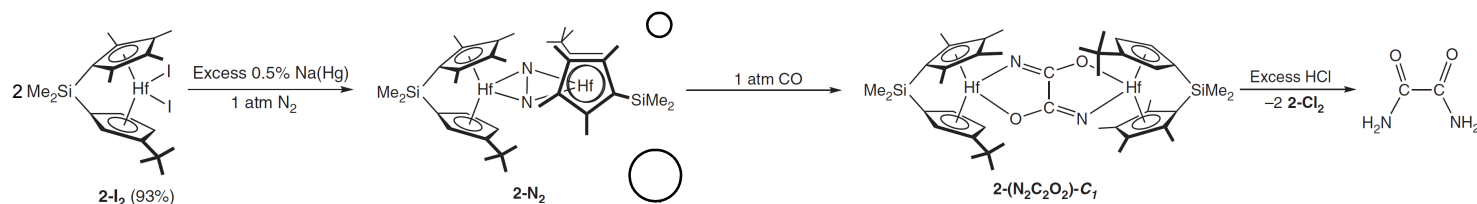
P. J. Chirik et al.
J. Am. Chem. Soc. **2009**, *131*, 8772

E = NTs, NBn, N^{t}Bu, O

[1] Dinitrogen Cleavage and Functionalization by Carbon Monoxide Promoted by a Hafnium Complex

(1) Overview

A new method for the cleavage of atmospheric N_2 and homologation by a hafnium complex that operates at ambient temperature and mild pressures

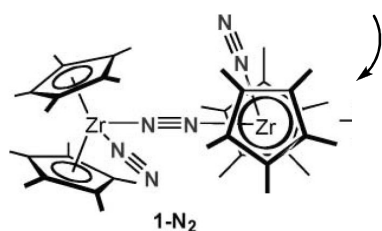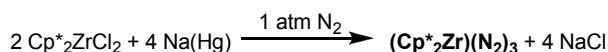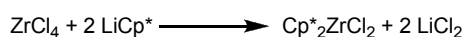

(2) Background

N_2

- 78 % of the Earth's atmosphere
- its non-polality, high ionizing potential, strong triple bond render it a typically inert molecule
- efficient chemical methods for the assemble of N-C bonds using N_2 are attractive
- **Haber-Bosch process**: N_2 (g) + $3H_2$ (g) $\rightleftharpoons$ $2NH_3$ (g)
  140 million tons/year, sustaining 40% of the world population
  harsh conditions: 400 ~ 650 °C, 200 ~ 400 atm

- "Chatt-mechanism"
  coordinated dinitrogen is functionalized by addition of strong electrophiles, typically proton donors such as mineral acids.
- Chirk's group sought to develop methods to elaborate coordinated N_2 with **non-polar reagents**, such as dihydrogen
- molecular nitrogen is **not a good ligand**
- even binding N_2 to metal complex in solution was a decades-long challenge

(3) Precedents and Related Studies

[Related Study 1]
Preparation of a Dinitrogen Complex of Bis(pentamethylcyclopentadienyl)zirconium(II). Isolation and Protonation Leading to Stoichiometric Reduction of Dinitrogen to Hydrazine

$$ZrCl_4 + 2\ LiCp^* \longrightarrow Cp^*_2ZrCl_2 + 2\ LiCl_2$$

$$2\ Cp^*_2ZrCl_2 + 4\ Na(Hg) \xrightarrow{1\ atm\ N_2} (Cp^*_2Zr)(N_2)_3 + 4\ NaCl$$

- first zirconocene dinitrogen complex (**1-N_2** = **$(Cp^*_2Zr)(N_2)_3$**)
- both terminal and bridging, **end-on** coordinated N_2 ligand
- N≡N bond lengths only slightly elongated from free N_2
- **neutral [N_2]^0** formulation was most appropriate
- exposure **1-N_2** to H_2 induces N_2 loss and formation of the zirconocene-H_2 complex

1-N_2

[Related Study 2-1]
Synthesis of Singly and Doubly Bridged *ansa*-Zirconocene Hydrides. Formation of an Unusual Mixed Valence Trimeric Hydride by Reaction of H_2 with {(Me$_2$Si)$_2$(η^5-C$_5$H$_3$)$_2$}Zr(CH$_3$)$_2$ and Generation of a Dinitrogen Complex by Reaction of N_2 with a Zirconocene Dihydride

rac-BpZrH$_2$ *rac*-[BpZr]$_2$N$_2$
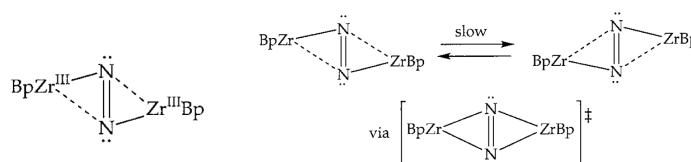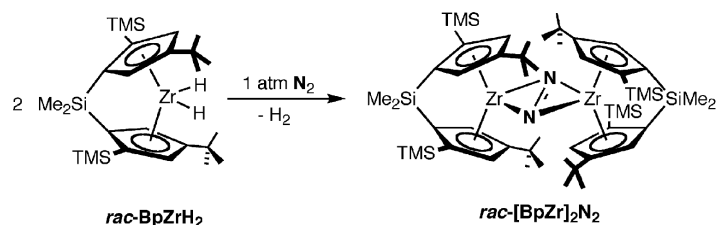
- ***ansa*-zirconocene complex:**
  two cyclopentadienyl rings are tethered by a bridging moiety configurational stability, control of the substituents' orientation
- *ansa*-ziconocene complex dihydride in the presence of N_2 undergoes facile thermal reductive elimination of H_2 and forms the **side-on** bound dinitrogen complex
- conversion of an early transition metal hydride to a dinitrogen complex is rather rare

- N-N bond length inidicates an important contribution from **[N_2]$^{2-}$** resonance form
- antiferromaganetic d^1, Zr (III) centers must be invoked to account for the apparent diamagnetism
- slow, **thermal reductive elimination** of dihydrogen followed by rapid trapping by dinitrogen
- *ansa*-bridge promotes reductive elimination
  (in a non-bridged analogue, no reductive elimination of H_2 observed)
- probably due to **reduced electron-donating ability**

The Electronic Influence of Ring Substituents and *Ansa* Bridges in Zirconocene Complexes as Probed by Infrared Spectroscopic, Electrochemical, and Computational Studies
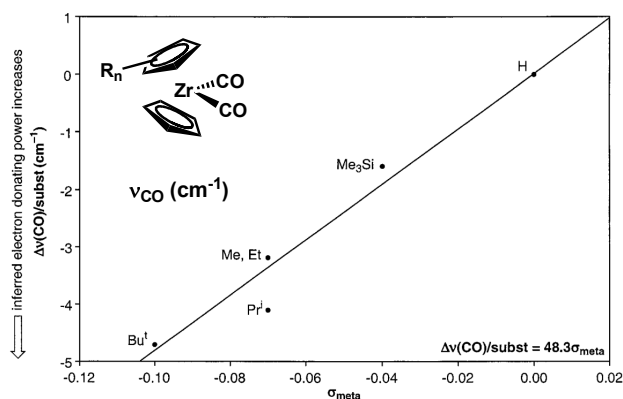
- ν_{CO} **stretching frequency** of a metal carbonyl complex provides a simple means of assessing the **electron density on the metal center**
- overall electron-donating influence of the substituents follows the sequence;
  t-Bu > *i*-Pr > Et > Me > Me$_3$Si > H

- for **unbridged** substituents:
  ν_{CO} on a per substituent basis correlates well with Hammet σ_{meta} parametes suggestig the influence of these substituents is via a simple inductive effect

$\Delta\nu(CO)/subst = 48.3\sigma_{meta}$
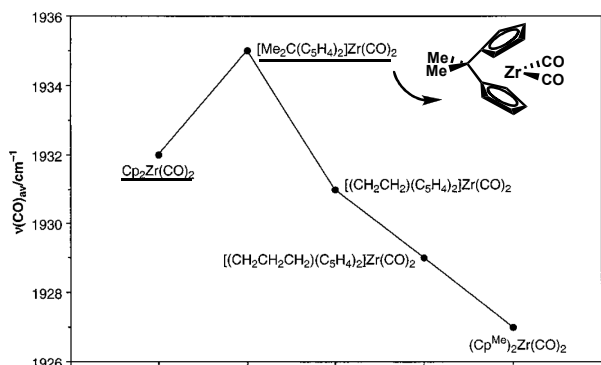
- however, for **bridged** systems....
- [Me$_2$C] and [Me$_2$Si] *ansa* bridges resulted in an increase in ν_{CO}
- these substituents have **electron withdrawing** influence on the Cp rings in contrast to the case of non-bridged substituents
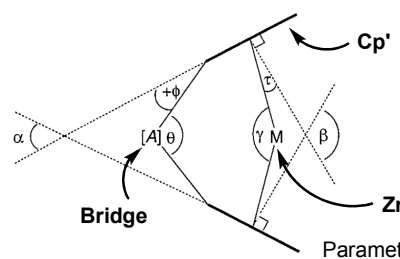
Parameters to define metallocene geometries
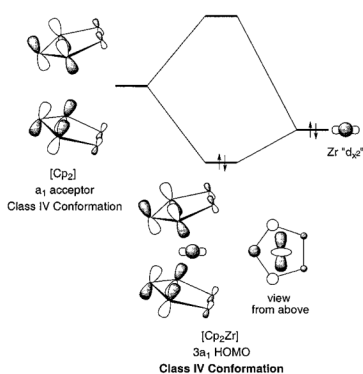
Figure 15
Back-bonding interaction between
"the filled d$_{x2}$ orbital" and
"the cyclpentadienyl ligand acceptor orbital"
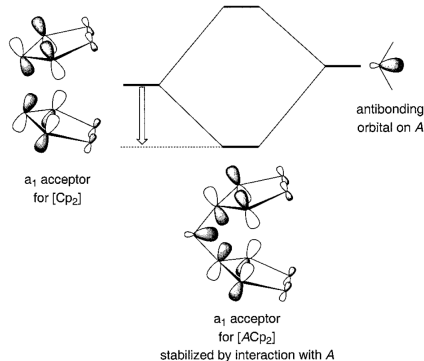
Figure 17
Stabilization of the combined cyclopentadienyl ligand a$_1$ acceptor orbital by the bridging atom

- interpretation by MO caluclations

- *Figure 15*
  + Zr d$_{x2}$ interacts with Cp's acceptor orbital
  + this interaction represents σ back-donation
  + bridging reinforces this interaction
- *Figure 17*
  + antibonding orbital on bridging atom decrese the energy a$_1$ acceptor orbital

- *ansa*-type zirconocene
  - increased reductive elimination of H$_2$ due to electron-withdrawing effect by the bridging
  - less favorable for N$_2$ activation itself

Hydrogenation and Cleavage of Dinitrogen to Ammonia with a Zirconium Complex

2-Cl$_2$

1 atm N$_2$
xs 0.5 % Na(Hg)
- 2 NaCl

2-N$_2$
d(N-N): 1.377(3) Å
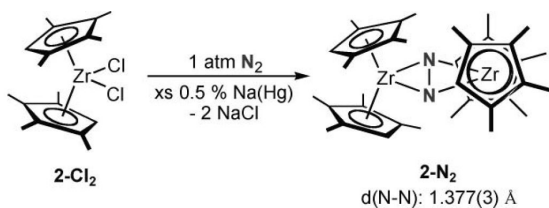
- going back to unbridged zirconocene complex
- systematic variation of the cyclopentyadienyl methyl substituents, expecting altered reactivity
- attempt with the complex **laking one methyl** from Cp* moiety
- affording **side-on** dinitrogen complex; N-N length 1.38 Å (cf. free N$_2$ 1.10 Å)
- consistent with **four electron reduction**
- 65.3 ° twist of the dimer - the dihedral angle between two planes formed

2-N$_2$: M = Zr

1 atm H$_2$

23 °C

2-N$_2$H$_4$: M = Zr
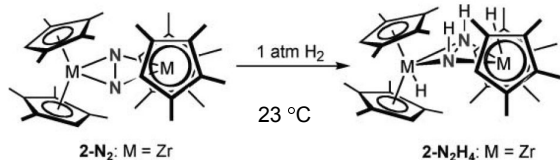
- dinitrogen hydrogenation with **2-N$_2$** was attempted
- 1 atm H$_2$, 23 °C; formation of hydrido zirconocene diazenido complex **2-N$_2$H$_4$**
- continued hydrgenation at 85 °C afforded ca. 10 % **NH$_3$** along with zirconocene dihydride complex

[Related Study 3-2]
On the Origin of Dinitrogen Hydrogenation Promoted by $[(\eta^5\text{-}C_5Me_4H)_2Zr]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$

Cp*(C_5Me_4H)ZrI$_2$ $\xrightarrow[\text{KC}_8]{\text{N}_2}$ **4** $\xrightarrow[\text{- 3 N}_2]{\text{1 atm H}_2}$ 2 **5**

"mixed ring"

- how about the reaction with "mixed ring" zirconocene complex **4** ?
  => **end-on** complex formed, no reduction of N_2 with H_2 gas

LUMO

HOMO

1   **6**

- **interpretation by MO caluculations**

  6: model complex $[(\eta^5\text{-}C_5H_5)_2Zr]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$
  where the **dihedral angle was confined to 0 °**

- LUMO: in-phase liniar combination (LC) of two zirconocene $1a_1$ orbitals
  which is suited to incoming H_2
- HOMO: out-of-phase LC of two zirconocene $1a_1$ orbitals engaged in
  π-bonding with a π^* orbital of the N_2 ligand
- reministent of group 4 transition metal imido complex, Zr=N character
- HOMO of **6**: does not have appropiate symmetry to engage in significant
  backbonding with N_2 ligand

[Related Study 3-3]
**How Many Methyl Groups in $[(\eta^5\text{-}C_5Me_nH_{5-n})_2Zr]_2(\mu_2,\eta^2,\eta^2\text{-}N_2)$ Are Needed for Dinitrogen Hydrogenation ?
A Theoretical Study**

end-on

• = H or R

side-on

- previous experimental results
  n = 5   end-on   no hydrogenation   Bercaw *JACS* **1974**
  n = 4   side-on   hydrogenation   Chirik *Nature* **2004**

- caluculations in this research
  n = 1 ~ 4 side-on complex is more stable
  n = 5   end-on complex is more stable owing to
  steric repulsion between five methyl groups

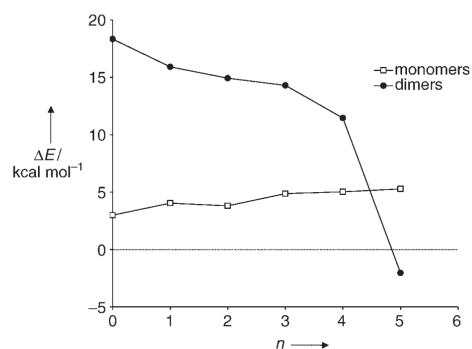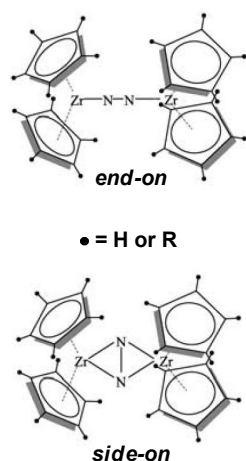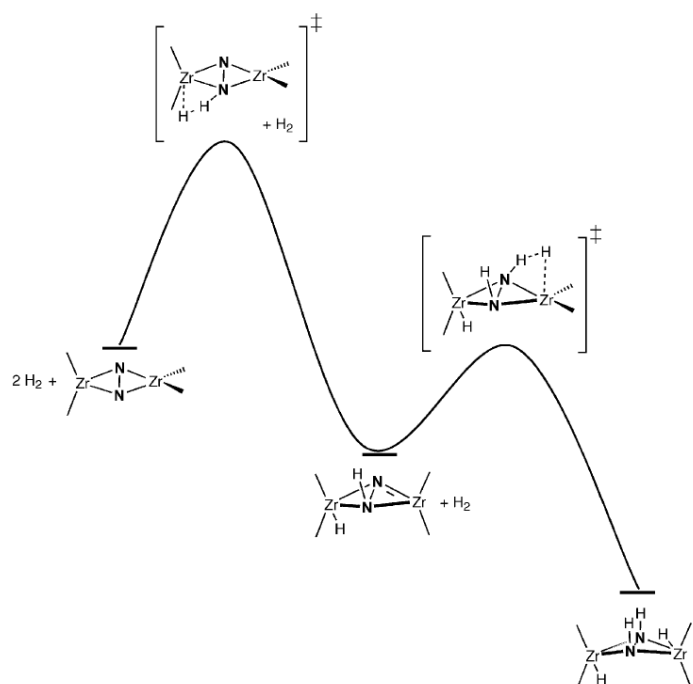**Figure 2.** Energy difference, $\Delta E = (E_{\text{end-on}} + ZPE_{\text{end-on}}) - (E_{\text{side-on}} + ZPE_{\text{side-on}})$, between the end-on- and the side-on-coordinated complexes $[(Cp')_2Zr(N_2)]$ and $[(Cp')_2Zr(N_2)Zr(Cp')_2]$ as a function of the number of methyl groups, *n*.

[Related Study 3-4]
**Kinetics and Mechanism of N_2 Hydrogenation in Bis(cyclopentadienyl) Zirconium Complexes and
Dinitrogen Functionalization by 1,2-Adition of a Saturated C-H Bond**

- several mechanistic studies
  - kinetics: first-order dependence on H_2 concentration
  - KIE: normal primary isotope effect
  - large negative entropies of activation
  => first H_2 addition being rate determining step
     through an ordered transition structure where H-H bond
     scission is simultaneous with Zr-H and N-H bond formation

- imido-like character of the side on N_2 zirconocene complex was confirmed
  also by the 1,2-addition of a saturated C-H bond in the ligand

$2 H_2 +$

$+ H_2$

2-N$_2$: R = Me
3-N$_2$: R = Ph
+ isomer
$\xrightarrow[\text{2 days}]{65\ ^\circ C}$
4: R = Me
5: R = Ph

N-C Bond Formation Promoted by a Hafnocene Dinitrogen Complex:
Comparison of Zirconium and Hafnium Congeners
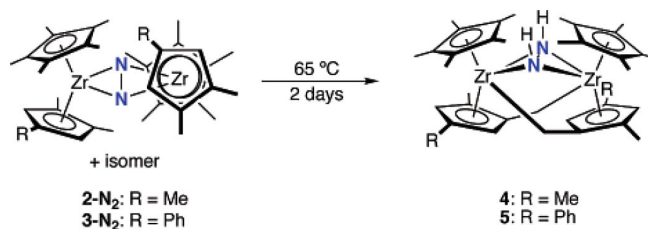
- attempt to expand the scope of 1,2-addition to include
  nitrogen-carbon forming reactions
- treatment of **1-N$_2$** with PhNCO produced complex mixture
  87 % of the gas expected for the loss of 1 equiv of free N$_2$

(1)

1-N$_2$: M = Zr
2-N$_2$: M = Hf

Observed for Zr only
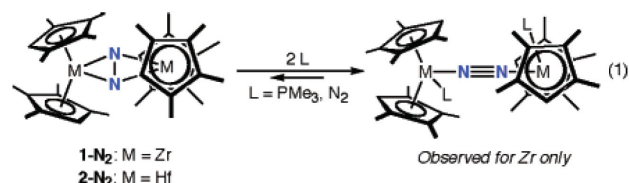
- competitive ligand-induced **side-on, end-on isomerization** proceeded?
- addition of 2 equiv of PMe$_3$ to **1-N$_2$** afforded **end-on** N$_2$ complex
- more strongly activated side-on N$_2$ complex was targeted

- **Hf** congeners **2-N$_2$**
- addition of 10 equiv of PMe$_3$ to **1-N$_2$** resulted in no change
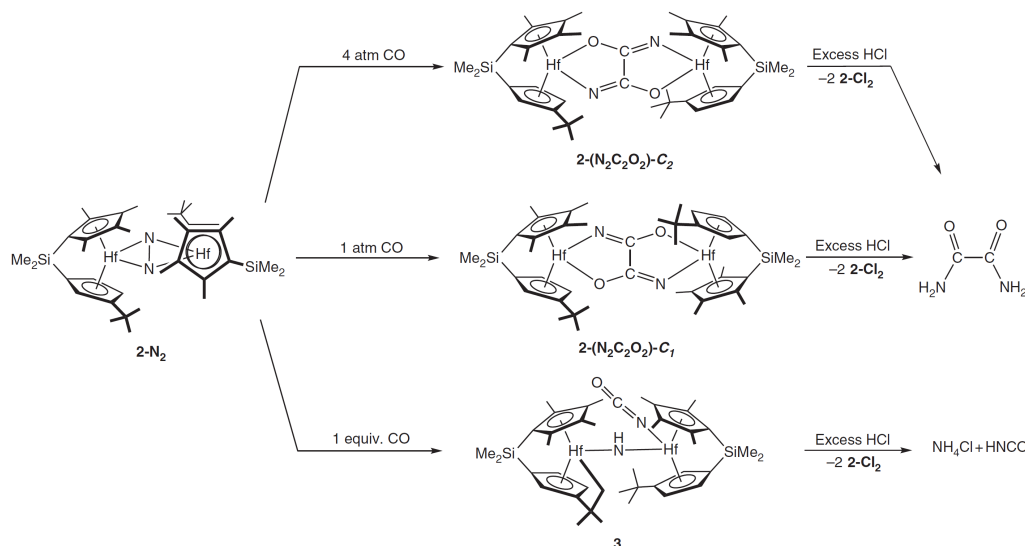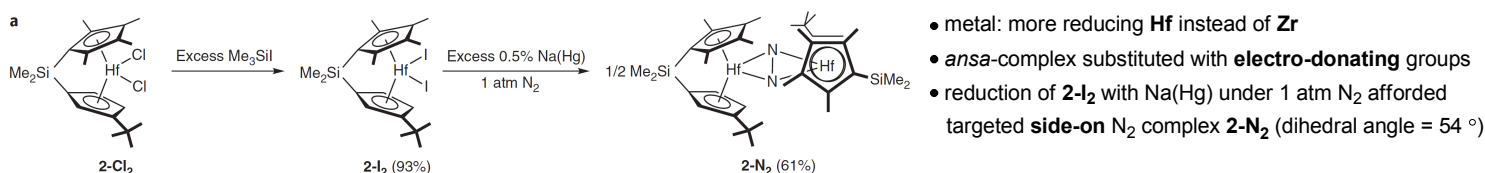- greater N$_2$ reduction imparted by the more reducing third-row metal

- with **2-N$_2$**, C-N bond formation was successful
- C=N cycloaddition to Zr=N bond
- C=O insertion into the newly formed Hf-N bond

- potentially rich dinitrogen functionalization chemistry is possible
  via [2 + 2] cycloaddition of activated π-systems
  if deleterious side-on, end-on isomerization can be suppressed.


2-N$_2$

[2 + 2] cycloaddition

PhNCO

C = O insertion

PhNCO

[2 + 2] cycloaddition

3 PhNCO

4

3

---
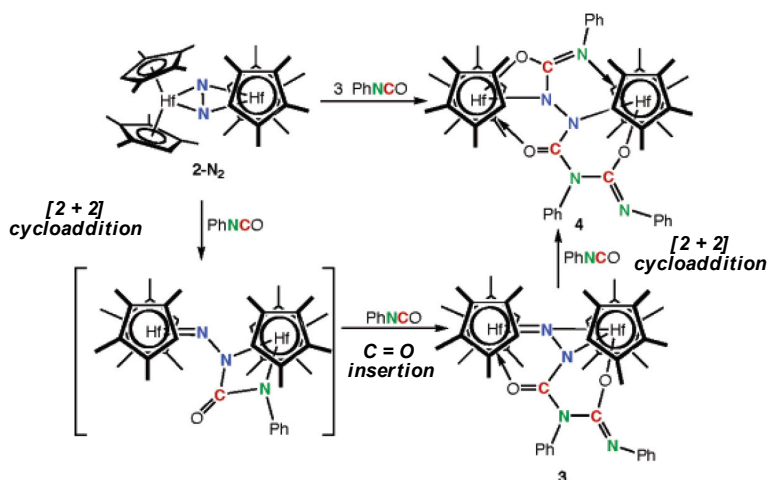
(4) Thematic Research
Dinitrogen Cleavage and Functionalization by Carbon Monoxide Promoted by a Hafnium Complex

2-Cl$_2$ →Excess Me$_3$SiI→   **2-I$_2$** (93%)   →Excess 0.5% Na(Hg), 1 atm N$_2$→   **2-N$_2$** (61%)

- metal: more reducing **Hf** instead of **Zr**
- *ansa*-complex substituted with **electro-donating** groups
- reduction of **2-I$_2$** with Na(Hg) under 1 atm N$_2$ afforded
  targeted **side-on** N$_2$ complex **2-N$_2$** (dihedral angle = 54 °)

2-N$_2$

4 atm CO →   **2-(N$_2$C$_2$O$_2$)-C$_2$**   →Excess HCl, −2 **2-Cl$_2$**→

1 atm CO →   **2-(N$_2$C$_2$O$_2$)-C$_1$**   →Excess HCl, −2 **2-Cl$_2$**→   H$_2$NC(O)-C(O)NH$_2$

1 equiv. CO →   **3**   →Excess HCl, −2 **2-Cl$_2$**→   NH$_4$Cl + HNCO

Figure 2 | Various N$_2$ cleavage products from the addition of CO to a benzene-d_6 solution of 2-N$_2$. In each case, a product derived from CO-induced bond cleavage was observed. For the hafnocene oxamidide compounds, protonation with a Brønsted acid furnished free oxamide.

- 4 atm CO, toluene as solvent,
  C_2 symmetric hafnium oxiamidide **2-(N$_2$C$_2$O$_2$)-C$_2$** (y. 82%)
- reducing the CO pressure to 1 atm
  an isomeric hafnium product (C_1 symmetry) **2-(N$_2$C$_2$O$_2$)-C$_2$** (y. 73%)
- the oxamidide ligand arises from cleavage of N$_2$ coupled with C-N
  bond formation and homologation of CO
- unprecedent transformation: strong-field CO ligand to metal N$_2$ complexes
  typically results in N$_2$ loss and formation of the corresponding metal
  (di)carbonyl derivative

- following protonolysis also confirmed N-N bond cleavage coupled with
  N-C and C-C bond formation
- **2-(N$_2$C$_2$O$_2$)** + HCl -> **2-Cl$_2$** + H$_2$NC(O)-C(O)NH$_2$ (oxiamide)
- free oxiamide could also be liberated using weaker acids such as ethanol

- a slight excess CO: cyclometallated complex **3** was formed
- N-N bond cleavage, N-C bond formation and C-H bond activation
  in a single step
- protonolysis of **3** with gaseous HCl yielded NH$_4$Cl
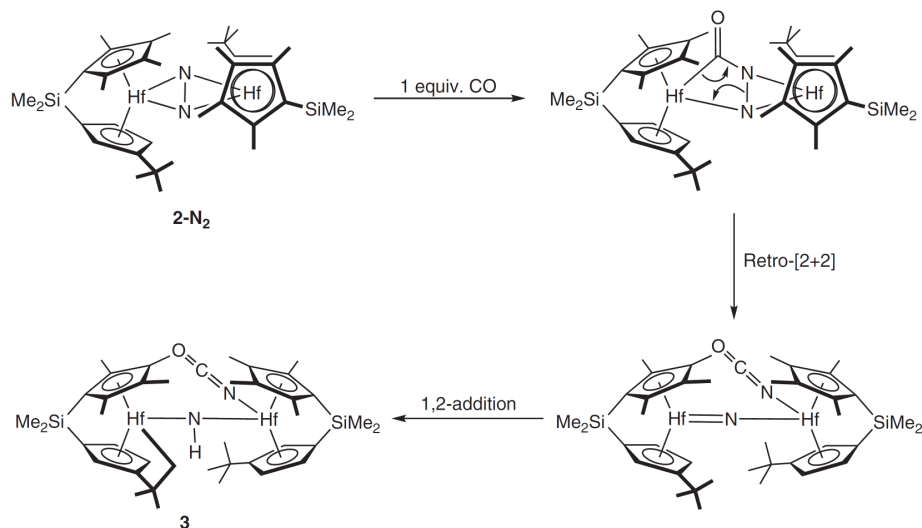
Figure 6 | Proposed mechanism for the carbonylation of 2-N₂ with one equivalent of CO to form 3. Carbonyl insertion precedes the retro-[2 + 2] event, which is responsible for cleavage of the N–N bond. Subsequent 1,2-addition of a C–H bond of a tert-butyl substituent yields the observed product.

- formal insertion of CO into one of the hafnium-nitrogen bond most likely one that is distal from the *t*-Bu group
- retro [2 + 2] cycloaddition effects N-N bond cleavage and generates isocyanate ligand, along with a bridging hafnocene nitride

- hafnium-nitrogen multiple bond promotes the intramolecular C-H activation of *t*-Bu substituents on Cp' ring by 1,2-addition to furnish **3**

---

(5) Appendix

Structure and Chemistry of Bis(cyclopentadienyl)-ML$_n$ Complexes

R. Hoffmann et al. *J. Am. Chem. Soc.* **1976**, *98*, 1729
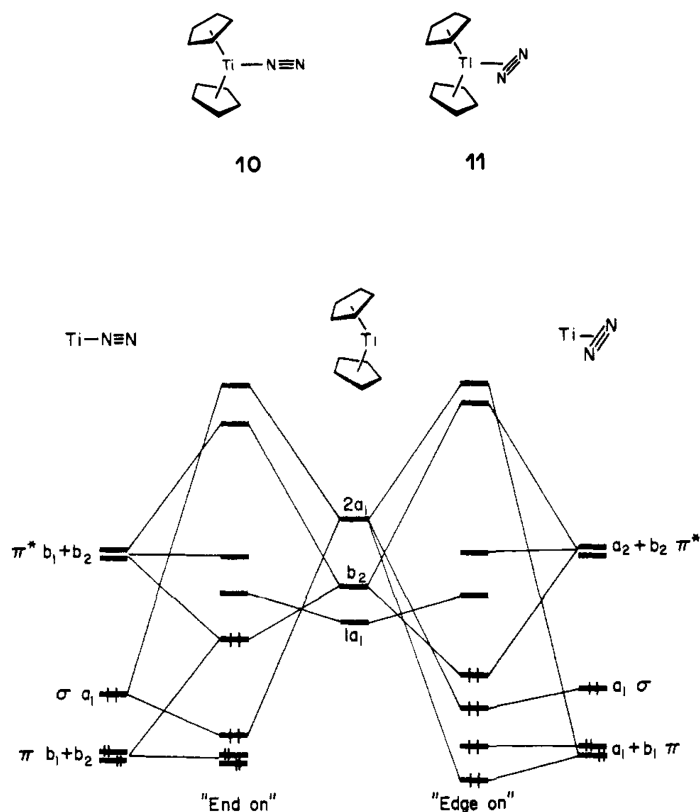
Figure 6. Interaction diagram for "end on" (left) and "edge on" (right) Cp₂TiN₂.

### Theoretical Prediction of a New Dinitrogen Reduction Process: Utilization of Four Dihydrogen Molecules and a Zr₂Pt₂ Cluster

D. G. Musaev *J. Phys. Chem. B* **2004**, *108*, 10012

SCHEME 1: Schematic Presentation of "Donation" and "Back-donation" Contributions on M−N₂ Interaction
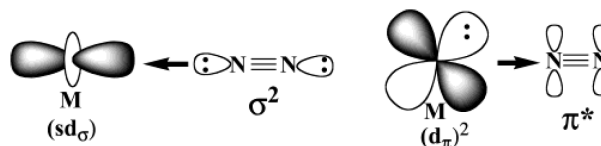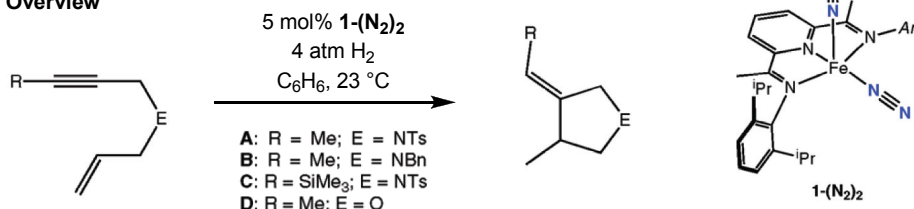

SCHEME 2: Possible Coordination Modes of the Dinitrogen Molecule in the Mono- and Dinuclear Transition Metal Complexes
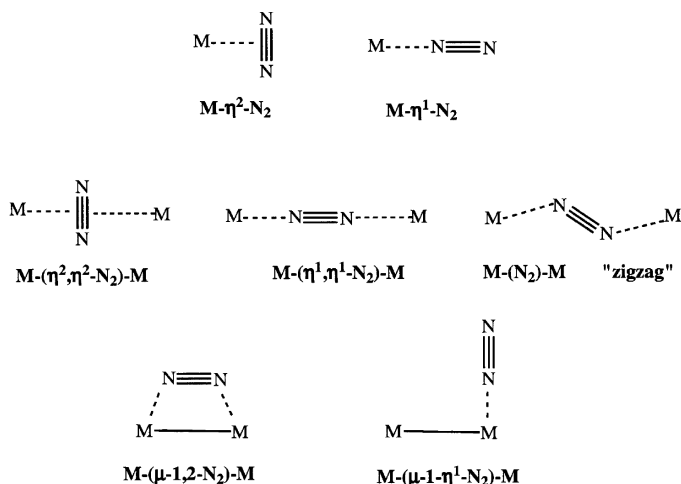
[2] Iron-Catalyzed, Hydrogen-Mediated Reductive Cyclization of 1,6-Enynes and Diynes: Evidence for Bis(imino)pyridine Ligand Participation

(1) Overview

R—≡—_/—E

5 mol% **1-(N₂)₂**
4 atm H₂
C₆H₆, 23 °C
→

A: R = Me; E = NTs
B: R = Me; E = NBn
C: R = SiMe₃; E = NTs
D: R = Me; E = O

1-(N₂)₂

Iron-catalyzed hydrogen-mediated reductive cyclization of enynes and diynes with turnover frequencies comparable to those of established precious metal catalysts

(2) Background

+ Catalytic bond forming reaction mediated by homogenous transition metal complex: indispensable tool

+ In many cases, the best catalysts rely on the scarest elements (Rh, Ir, Pt, etc...)

+ Attempts to replace noble metal catalysts to more abundant and benign metal catalysts.

(3) Related Studies

[Related Study 1]
Pentacarbonyliron(0) Photocatalyzed Hydrogenation and Isomerization of Olefins

**Table VIII.** Fe(CO)₅ Photoassisted Hydrogenation of Olefins[a]

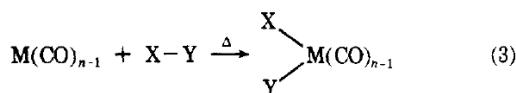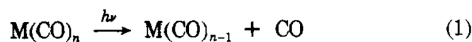| Starting olefin	Irradiation time, min	Product (% conversion)
Ethylene[b]	60	Ethane (16.7)
Propylene[c]	60	Propane (46.7)
cis-3-Hexene	60	n-Hexane (30.8)
2-Methyl-2-butene	60	2-Methylbutane (26.9)
cis-3-Methyl-2-pentene	110	3-Methylpentane (32.0)
2,3-Dimethyl-2-butene	60	2,3-Dimethylbutane (13.6)
Cyclopentene	60	Cyclopentane (47.0)
Cyclohexene	60	Cyclohexane (33.1)
Cycloheptene[d]	60	Cycloheptane (53.2)
cis-Cyclooctene[d]	60	Cyclooctane (53.5)
1-Methylcyclopentene	60	Methylcyclopentane (26.3)
Methylenecyclopentane	70	Methylcyclopentane (40.0)
1,2-Dimethylcyclopentene	60	No reaction
1,2-Dimethylcyclohexene	60	No reaction
α-Methylstyrene	60	No reaction
2,3-Pentadiene	60	No reaction
2-Cyclohexen-1-one	180	Cyclohexanone (4.1)
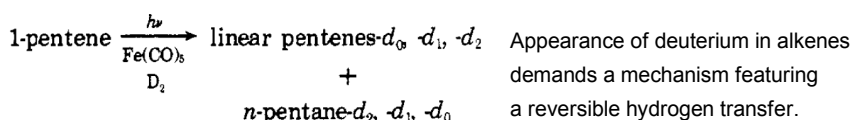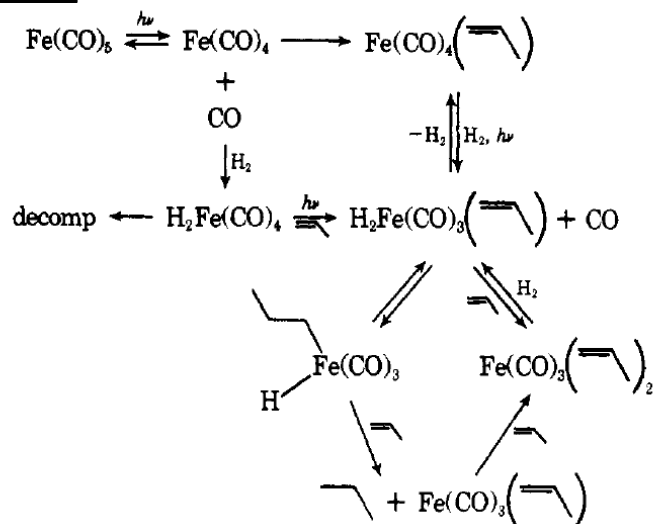
conditions: near-UV, 25 °C, benzene as solvent, H₂ at 10 psi

(a) General Reactivity of Transition Metal-Carbonyl Complexes

$$M(CO)_n \xrightarrow{h\nu} M(CO)_{n-1} + CO \qquad (1)$$

$$M(CO)_{n-1} + L \xrightarrow{\Delta} M(CO)_{n-1}L \qquad (2)$$

$$M(CO)_{n-1} + X-Y \xrightarrow{\Delta} \overset{X}{\underset{Y}{}}M(CO)_{n-1} \qquad (3)$$
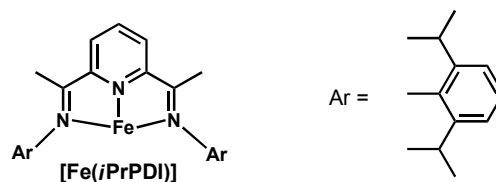
Unsaturated iron-carbonyl complex Fe(CO)₃ is the proposed active species:

=> introduction of a terdentate bis(imino)pyridine chelate

may allow thermal access to a catalytically active iron complex [Fe(*i*PrPDI)]
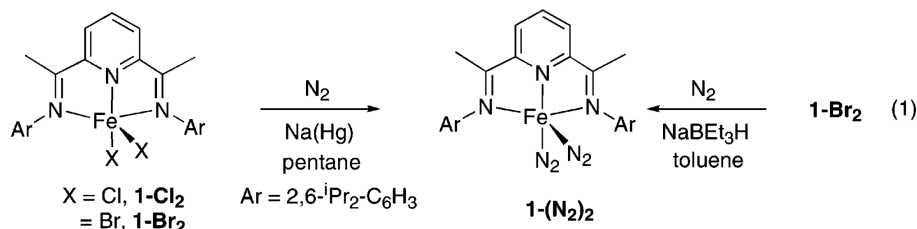
Initial expectations:

+ ease of synthesis, modulality

+ well-documented success in catalysis

+ stabilization of electron-rich Fe(0) complex by π-acidity of the ligand

(b) A Mechanistic Study

1-pentene $\xrightarrow[D_2]{\underset{Fe(CO)_5}{h\nu}}$ linear pentenes-d_0, -d_1, -d_2
+
n-pentane-d_2, -d_1, -d_0

Appearance of deuterium in alkenes demands a mechanism featuring a reversible hydrogen transfer.

(c) Prop▮▮▮▮nism

$$Fe(CO)_5 \rightleftharpoons Fe(CO)_4 \longrightarrow Fe(CO)_4\left(\overset{}{=}\right)$$

[reaction scheme showing iron carbonyl intermediates]

$$decomp \longleftarrow H_2Fe(CO)_4 \rightleftharpoons H_2Fe(CO)_3\left(\overset{}{=}\right) + CO$$

$$Fe(CO)_3 \qquad Fe(CO)_3\left(\overset{}{=}\right)_2$$

$$\searrow + Fe(CO)_3\left(\overset{}{=}\right)$$

[Fe(*i*PrPDI)]

Ar = 2,6-diisopropylphenyl

[Related Study 2]
Preparation and Molecular Electronic Structure of Iron(0) Dinitrogen and Silane Complexes and Their Application to Catalytic Hydrogenation and Hydrosilation

[structure of 1-Cl₂ / 1-Br₂] $\xrightarrow[\text{pentane}]{\underset{\text{Na(Hg)}}{N_2}}$ [structure of **1-(N₂)₂**] $\xleftarrow[\text{toluene}]{\underset{\text{NaBEt}_3\text{H}}{N_2}}$ **1-Br₂** (1)

X = Cl, **1-Cl₂**
= Br, **1-Br₂**

Ar = 2,6-*i*Pr₂-C₆H₃

1-(N₂)₂

highly active catalyst for the polymerization of ethylene
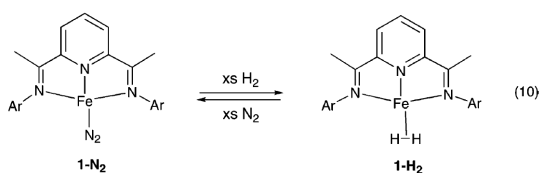M. Brookhart et al. *JACS* **1998**, *120*, 4049

• conditions: 4 atm H$_2$, 22 °C, 1.25 M in toluene

Table 2. Olefin Hydrogenation with 0.3 mol % **1-(N$_2$)$_2$**

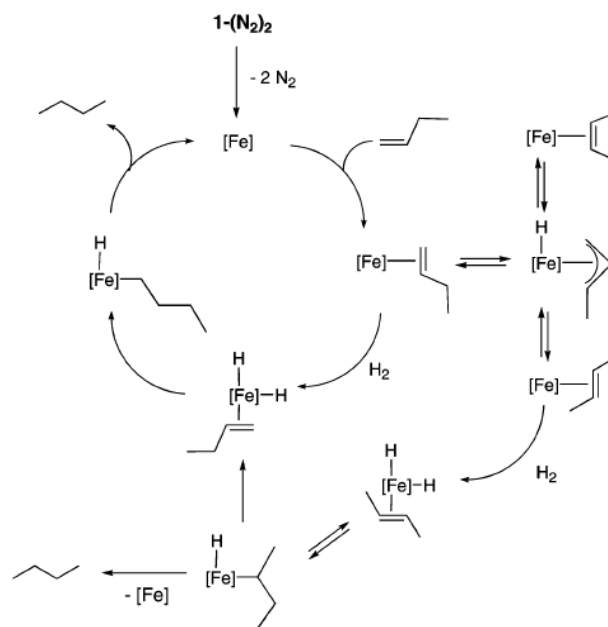| Substrate	time (min)[a]	tof (mol/hr)[b]
(alkene)	12	1814
Ph (alkene)	16	1344
(cyclohexene)	380	57
Ph (alkene)	210	104
(1,5-hexadiene)	60	363
(terpinene ring)	210	104[c]
MeO$_2$C ⟶ CO$_2$Me	360	3.3[d]

[a] Time required to reach >98% conversion as judged by GC. [b] Determined on the basis of the time required to reach completion. [c] The product is (+)-p-menth-1-ene. [d] A 5 mol % concentration of **1-(N$_2$)$_2$**.

• the actitvity for 1,5-hexadiene is slightly reduced from 1-hexane
• preferential hydrogenation of the *gem*-disubstituted over the trisubstituted
• high activity in non-polar solvents

Figure 9. Proposed mechanism for catalytic hydrogenation with **1-(N$_2$)$_2$**.

(10)

• exposure of **1-N$_2$** to 1 atm H$_2$ afforded iron(0) dihydrogen complex

=> the electon withdrawing character of the *i*-PrPDI ligand renders the iron center sufficiently electron deficient to inhibit oxidative addition of H$_2$?
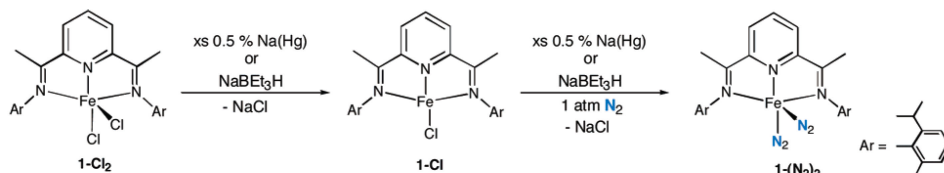
- -
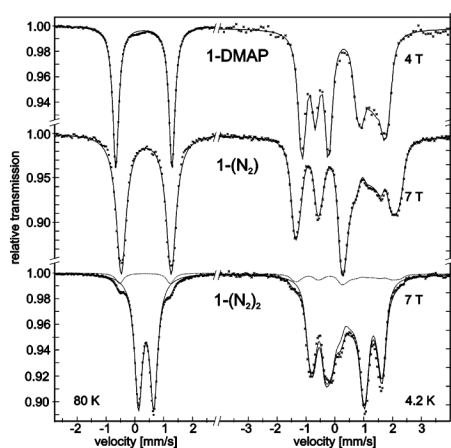
[Related Study 3]
Electronic Structure of Bis(imino)pyridine Iron Dichloride, Monochloride, and Neutral Ligand Complexes:
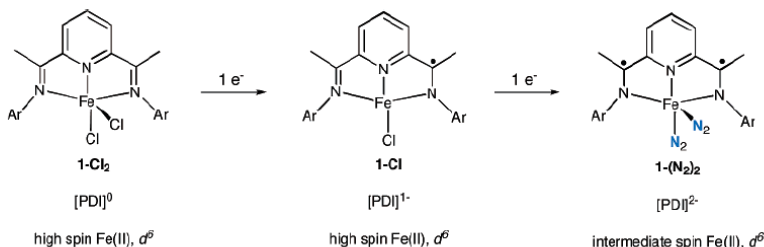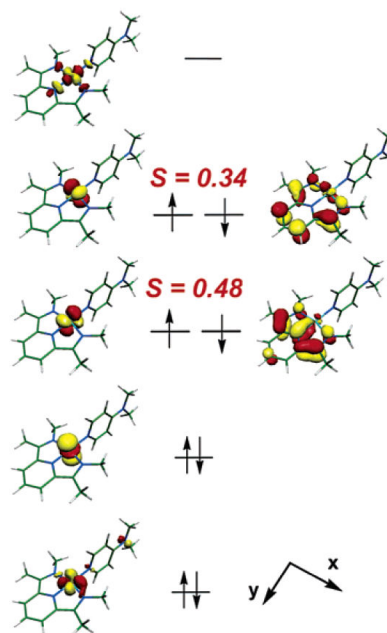**A Combined Structual Spectroscopic and Computational Study**

Figure 1. Reduction of (*i*PrPDI)FeCl$_2$ (**1-Cl$_2$**).

Figure 11. Mössbauer spectra of **1-DMAP**, **1-(N$_2$)**, and **1-(N$_2$)$_2$** recorded at 80 K in zero-field (left column) and at 4.2 K with applied fields as indicated (right column). The lines are fits with Lorentzian doublets for the zero-field spectra and magnetic simulations for $S = 0$ with the usual nuclear Hamiltonian for the magnetic spectra. The Mössbauer parameters are given in the text or in Table 6. The dotted lines in the spectra from **1-(N$_2$)$_2$** represent a 7.5% contamination with **1-(N$_2$)**.

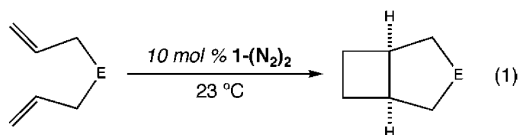**Figure 14.** Summary of the electronic structure of bis(imino)pyridine iron compounds.

• one electron reduction of **1-Cl** in the presence of weak fields ligands such as DMAP or N$_2$ results in reduction of the bis(imino)pyridine chelate, furnishing dianionic [PDI]$^{2-}$ fragment complexed to an intermediate ferrous ion

8

Iron-Catalyzed [2π + 2π] Cycloaddition of α,ω-Dienes : The Imporatance of Redox-Active Supporting Ligands

(a) Main Experimental Results

• some substrates, such as E = SiMe₂, and those with internal olefins (allyl-*tert*-butylcrotylamine or tertbutyldicrtylamine): not successful

Table 1. [2π + 2π] Cycloaddition of α,ω-Dienes[a]

	E	time (min)	conversion (%)	TOF (h⁻¹)	ΔG° (kcal/mol)	ΔH° (kcal/mol)	ΔS° (eu)
1	CH₂	300	92	1.8	−9.4	−13.2	−12.6
2	SiMe₂	300	0	0	−6.2	−10.9	−15.8
3	NH[b]	300	0	0	−11.4	−15.3	−12.7
4	N−Bn	26	90	21[c]	−14.0	−17.4	−11.3
5	N-*t*Bu	<5	>95	>240[d]	−18.3	−21.0	−9.5
6	NBoc	300	24	0.5	−15.5	−18.6	−10.3
7	C(CO₂Et)₂	141	>95	4	−16.3	−19.1	−9.4

[a] Conditions: 0.5 mL of a 0.010 M C₆D₆ solution of **1-(N₂)₂**, 10 equiv of substrate, 23 °C. [b] Stoichiometric reaction (vide infra). [c] 90% conversion; diminishes after 26 min owing to product inhibition (see text). [d] >95% in <5 min.

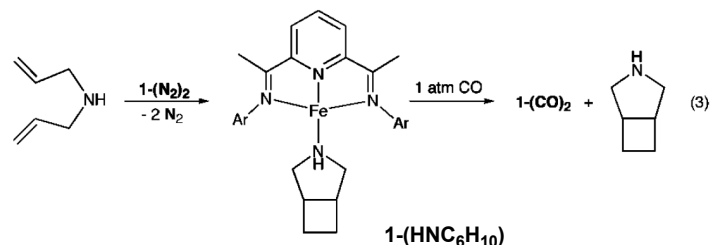• the stereochemistry of the catalytic [2π + 2π] reaction
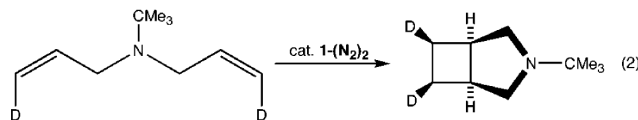
no isotopic scrambling, affording only one isotopomer product

(b) Mechanistic Study (1)

Entry 3

1-(HNC₆H₁₀)

• only stoichiometric cyclization, cleanly affording **1-(HNC₆H₁₀)**
• E = N*t*-Bu: **1-(N₂)₂** was recovered
• E = NBn: **1-(BnNC₆H₁₀)** was identified following turnover

=> product inhibition dictates the rate of catalytic turnover

• the metrical parameters and NMR spectroscopic data of **1-(HNC₆H₁₀)** are analogous to those **1-DMAP**, where computational, spectroscopic, and structural data established an intermediate spin (S_Fe = 1) ferrous center complexed by dianion [*i*-PrPDI]²⁻
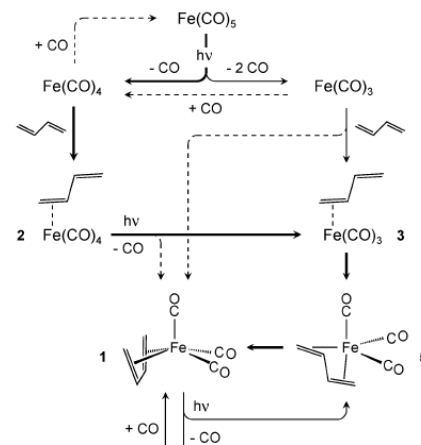
(c) Mechanistic Study (2)

• the reaction with 1,3-butadiene which would unlikely to undergo cycloaddition
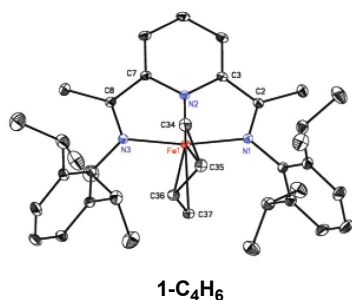
1-C₄H₆

• the iron-butadiene compound **1-C₄H₆** was formed
• a rare example of *trans*-butadiene
• two electron reduced bis(imino)pyridine complex

=> these data support Fe(II) complexed by [*i*PrPDI]²⁻ rather than an Fe(0) ion with a neutral chelate.

On trans-butadiene iron complex:
Organometallics, **2006**, *25*, 2705

(d) Proposed Mechanism
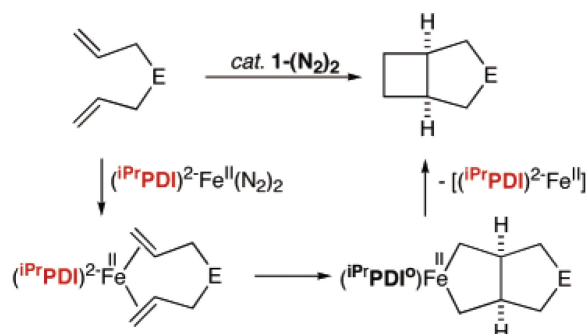

• substitution of the N₂ ligands by the diene

• based on the properties of **1-(C₄H₆)**, the oxidation states of the iron are maintained as ferrous throughout the process

• C-C coupling to form the matallocycle

• formal reductive elimination

(4) Thematic Research
Iron-Catalyzed, Hydrogen-Mediated Reductive Cyclization of 1,6-Enynes and Diynes:
Evidence for Bis(imino)pyridine Ligand Participation

(a) Preliminary Study:
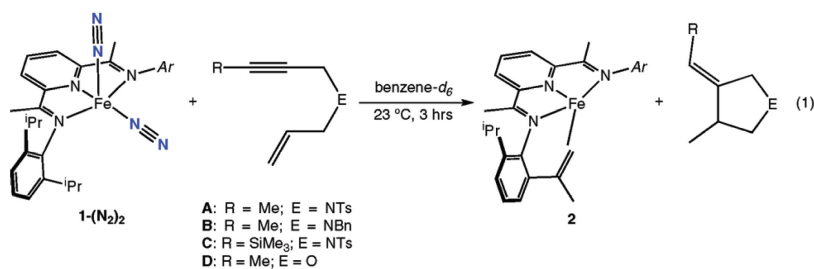
- **stoichiometric** reaction of 1,6-enynes with **1-(N$_2$)$_2$**
- conditions: 23 °C, 3hr, in benzene-d_6
- complete consumption of both starting materials
- product: 3,4-disubstituted pyrrolidine with only one (Z)-alkene
  the intramolecular olefin complex **2**
- overall, dehydrogenation of an *i*-Pr aryl substituents promotes
  iron-mediated reductive enyne cyclization.

(b) Further Attempt: H$_2$ as the Stoichometric Terminal Reductant

Table 1. Hydrogen-Mediated Enyne Cyclization^a
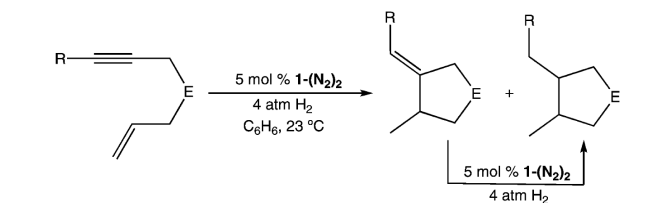
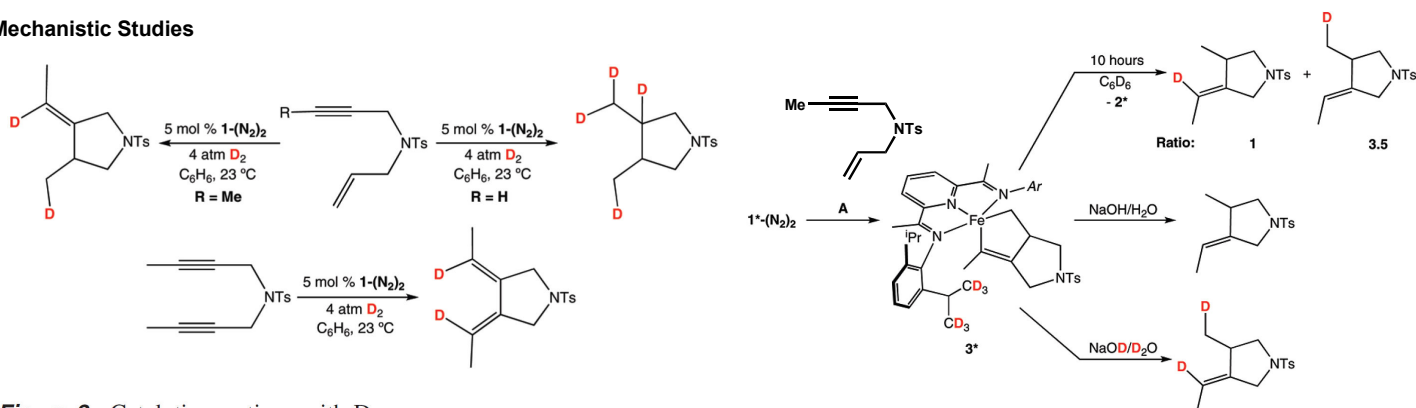| entry	E	R	time (min)	yield (%)^b	TOF (h^{-1})^c	cis/trans (saturated)
1	N^{t}Bu	H	180	68	6.7	>99:1
2	NTs	H	60	79	20.0	75:25
3	NBn	H	180	71	6.7	>99:1
4	NCH$_2$C$_6$Me$_5$	H	180	57^d	4.9	>99:1
5	NTs	Me	180	79	6.7	−
6	NBn	Me	180	71	6.7	−
7	NTs	SiMe$_3$	540	82	2.2	−
8	O	H	360	95	3.3	61:39^f
9	O	Me	180	62	6.7	−
10	(EtCO$_2$)$_2$C	H	180	74^e	6.7	79:21

^{a} Conditions: 4 atm H$_2$ at 23 °C. ^{b} Isolated yield. ^{c} Determined at >95% conversion by ^{1}H NMR spectroscopy and 99% GC−MS. ^{d} Reduced alkyne compound (16%) was observed. ^{e} Reduced alkyne complex (26%) was observed. ^{f} After 24 h, 53% conversion to the 3,4-dimethyltetrahydrofuran was found.

- **2** reacts cleanly with H$_2$ to yield a catalytically active iron-H$_2$ complex
- facile hydrogen-mediated cyclization with TOF comparable to those
  of Rh catalysts
- R = H; continued stirring led to the reduction of the exo-methylene,
  preference for the formation of cis-diastereomers over trans ones
- R ≠ H; only the unsaturated products were observed
  (reductance of **1-(N$_2$)$_2$** to hydrogenate unactivated trisubstituted alkenes
  was previously observed)

(c) Extention to Diyne Substrates

E: E = NTs (95%)
F: E = NBn (97 %)
G: E = NPh (67 %)
H: E = C(CO$_2$Et)$_2$ (58 %)

(d) Mechanistic Studies
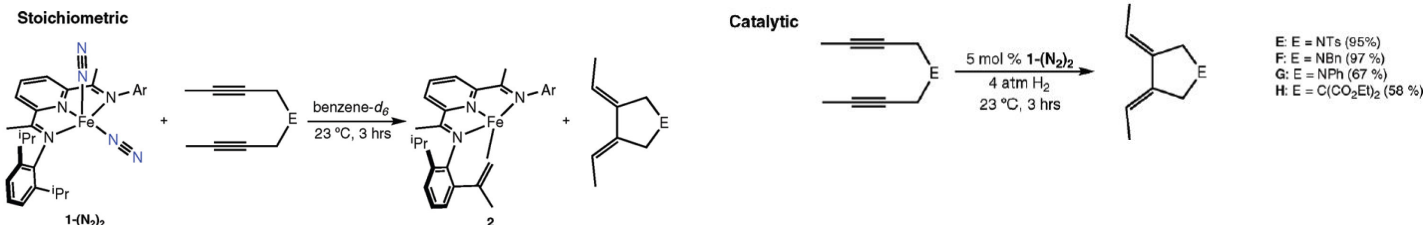
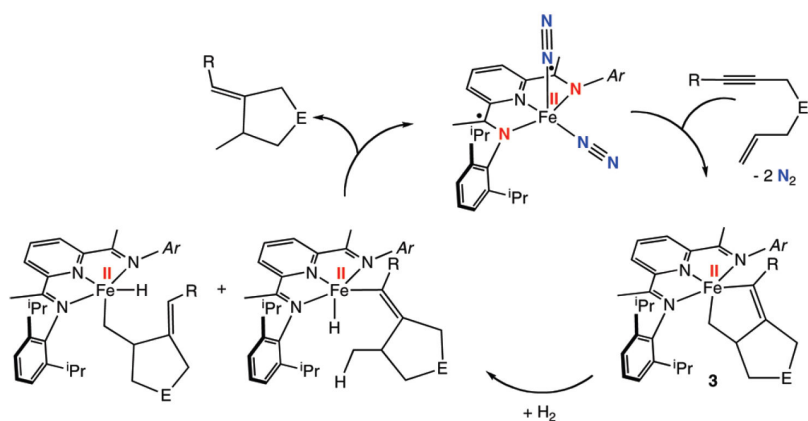**Figure 2.** Catalytic reactions with D$_2$ gas.

- the catalytic reaction with D$_2$ gas
- **enyne (R = Me):** labels exclusively in the methyl and vinyl
  position of the exo alkenyl substituents
- **enyne (R = H)** : d_4-isotopologue, additional deuterium incorporation
  arising from deuteration of the exo methylene pyrrolidine
  intermediate
- **diynes** : pyrrolidine-d_2 with the two labels in the vinyl positions of
  the product

- Comparison of the reactions with **3** and **3***; KIE k_H/k_D = 6.0(2)
  => C-H bond breaking event in the turnover-limiting step

Figure 3. Detection of catalytic intermediates and isotopic-labeling studies.

- the **stoichiometric** reaction with the labelled iron dinitrogen complex
  1*-(N$_2$)$_2$ where the isopropyl methyl substituents were deuterated
- reaction with enyne **A** resulted in complete and exclusive conversion
  into two pyrrolidine-d_1 isotopers
  => transfer hydrogenation from isopropyl aryl substituted
- paramagnetic (S = 2) intermediate, iron-metallocycle **3*** was observed.
  at this point, no isotpoic scrambling from isopropyl methyl groups
- degradation studies of **3***;
  with NaOH/H$_2$O: no deuterium incorporation in the product
  with NaOD/D$_2$O: deuterium incorporation

(e) Proposed Mechanism

- coordination of the substrate to the iron complex
- cyclometallation to form **3**
  (cyclization of the substrate upon addition of the catalyst is rapid)
- on the basis of the previous study, they believe reductive cyclization to form the C-C bond involves electron transfer and formal **oxidation of the bis(imino)pyridine chelate** rather than the iron center
- observation of **3** and the KIE results suggest that the next hydrogenation step is turnover limiting
- hydrogenation of **3** can occur either at alkyl or alkenyl position
- H$_2$ addition step can occur by **OA/RE** or by **σ-bond metathesis** to form new C-H and Fe-H bonds
- reductive elimination of a carbon-hydrogen bond forms the product
- ferrous oxidation state is preserved throughout the catalytic cycle

Figure 4. Proposed mechanism for the iron-catalyzed, hydrogen-mediated enyne cyclization.

- the redox activity of the [*i*PrPDI] ligand **preserves the ferrous oxidation state throughout the cycle** and may **prevent complications from Fe(0) precipitation** that are observed with other (e.g., Ni) metallocycles.
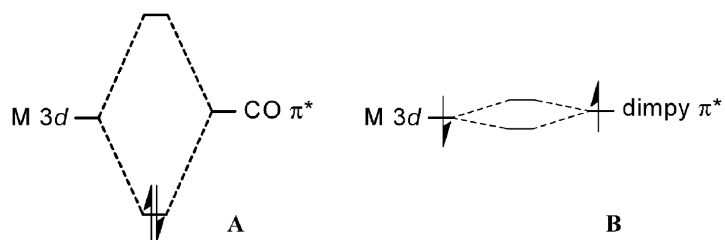
- -

(f) On PDI ligands
Ligand-centered reactivity in diiminepyridine complexes
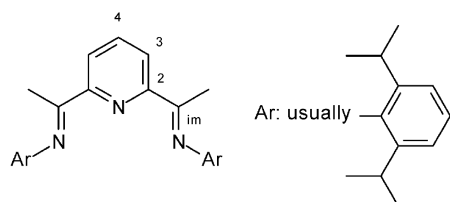
Scheme 1 Structure of the dimpy ligand, showing the adopted atom numbering scheme.

- extended π-system
- two low-lying π*-orbitals which are basically the combination of the two imine π* orbital, with siginificant participation of the central pyridine ring

Fig. 1 Lowest π* orbitals of dimpy.

Fig. 2 Schematic representation of orbital interactions in (A) metal–CO and (B) metal–dimpy complexes.
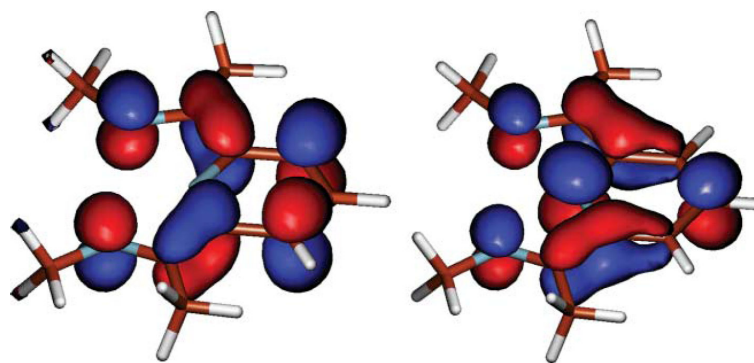
- different nature of metal-ligand from that of **classical π-acceptor** like **CO**
- in the case of **CO**
  π* LUMO is concentrated on the carbon atom directly bound to the metal
  large overlap between metal d and liand π* orbitals, resulting in a mainly covalent backdonation-type interaction
- in the case of **PDI ligand**
  π* orbitals are very localized, direct d-π* overlap is much smaller
  => the interaction will have the character of an intramolecular single-electron transfer