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P. J. Chirik et al.
Nature Chemistry 2010, 2, 30

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Evidence for Bis(imino)pyridine Participation

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J. Am. Chem. Soc. 2009, 131, 6772
[1] Dinitrogen Cleavage and Functionalization by Carbon Monoxide Promoted by a Hafnium Complex
P. J. Chirik et al. Nature Chemistry 2010, 2, 30

(1) Overview
A new method for the cleavage of atmospheric N₂ and homologation by a hafnium complex that operates at ambient temperature and mild pressures

(2) Background

- 78% of the Earth’s atmosphere
- its non-polarity, high ionizing potential, strong triple bond render it a typically inert molecule
- efficient chemical methods for the assembly of N-C bonds using N₂ are attractive
- Haber-Bosch process: N₂(g) + 3H₂(g) ⇌ 2NH₃(g)
  
 140 million tons/year, sustaining 40% of the world population harsh conditions: 400 ~ 650 °C, 200 ~ 400 atm

N₂

- "Chatt-mechanism" coordinated dinitrogen is functionalized by addition of strong electrophiles, typically proton donors such as mineral acids.
- Chirik’s group sought to develop methods to elaborate coordinated N₂ with non-polar reagents, such as dihydrogen
- molecular nitrogen is not a good ligand
- even binding N₂ 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

J. E. Bercaw et al., J. Am. Chem. Soc. 1974, 96, 6229

ZrCl₄ + 2 LiCp⁺ → Cp²⁺ZrCl₂ + 2 LiCl₂

2 Cp²⁺ZrCl₂ + 4 Na(Hg) + 1 atm N₂ → (Cp²⁺Zr)(N₂)₃ + 4 NaCl

- first zirconocene dinitrogen complex (1-N₂ = (Cp²⁺Zr)(N₂)₃
- both terminal and bridging, end-on coordinated N₂ ligand
- Nₐ = N bond lengths only slightly elongated from free N₂
- neutral [N₂]¹⁻ formulation was most appropriate
- exposure 1-N₂ to H₂ induces N₂ loss and formation of the zirconocene-H₂ complex

[Related Study 2-1]
Synthesis of Singly and Doubly Bridged ansa-Zirconocene Hydrides. Formation of an Unusual Mixed Valence Trimeric Hydride by Reaction of H₂ with {(Me₅Si)₂(η⁵-C₅H₅)Zr(CH₃)₂ and Generation of a Dinitrogen Complex by Reaction of N₂ with a Zirconocene Dihydride

J. E. Bercaw et al., Organometallics 2001, 20, 534

- ansa-zirconocene complex: two cyclopentadienyl rings are tethered by a bridging moiety configurational stability, control of the substituents’ orientation
- ansa-zirconocene complex dihydride in the presence of N₂ undergoes facile thermal reductive elimination of H₂ 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 indicates an important contribution from [N₂]²⁻ resonance form
- antiferromagnetism d¹, 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 H₂ 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

- $\nu_{\text{CO}}$ 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: $\text{t-Bu} > \text{i-Pr} > \text{Et} > \text{Me} > \text{Me}_2\text{Si} > \text{H}$

- for unbridged substituents: $\nu_{\text{CO}}$ on a per substituent basis correlates well with Hammet $\sigma_{\text{meta}}$ parameters suggesting the influence of these substituents is via a simple inductive effect

- however, for bridged systems...
  - $[\text{Me}_2\text{C}]$ and $[\text{Me}_2\text{Si}]$ ansa bridges resulted in an increase in $\nu_{\text{CO}}$
  - these substituents have electron withdrawing influence on the Cp rings in contrast to the case of non-bridged substituents

Figure 15
Back-bonding interaction between the filled $d_{x^2}$ 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 calculations
- **Figure 15**
  + Zr d$_{x^2}$ interacts with Cp's acceptor orbital
  + this interaction represents back-donation
  + bridging reinforces this interaction
- **Figure 17**
  + antibonding orbital on bridging atom decrease the energy $a_1$ acceptor orbital

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

[Related Study 3-1]
Hydrogenation and Cleavage of Dinitrogen to Ammonia with a Zirconium Complex

- going back to unbridged zirconocene complex
- systematic variation of the cyclopentadienyl methyl substituents, expecting altered reactivity
- attempt with the complex taking one methyl from Cp* moiety
- affording side-on dinitrogen complex; N-N length 1.38 Å (cf. free $\text{N}_2$ 1.10 Å)
- consistent with four electron reduction
  - 65.3° twist of the dimer - the dihedral angle between two planes formed
  - dinitrogen hydrogenation with 2-$\text{N}_2$ was attempted
  - 1 atm $\text{H}_2$, 23 °C; formation of hydrido zirconocene diazenido complex $2\text{-N}_2\text{H}_2$
  - continued hydrogenation at 85 °C afforded ca. 10 % NH$_3$ along with zirconocene dithydride complex
On the Origin of Dinitrogen Hydrogenation Promoted by [(η⁵-C₅Me₅H)₂Zr]₂(µ₂,η²,η²-N₂)

- how about the reaction with "mixed ring" zirconocene complex 4?
  => end-on complex formed, no reduction of N₂ with H₂ gas

- interpretation by MO calculations
  6: model complex [(η⁵-C₅H₅)₂Zr]₂(µ₂,η²,η²-N₂) where the dihedral angle was confined to 0°

LUMO: in-phase linear combination (LC) of two zirconocene 1a orbitals which is suited to incoming H₂
HOMO: out-of-phase LC of two zirconocene 1a orbitals engaged in π-bonding with a π* orbital of the N₂ ligand
reminiscent of group 4 transition metal imido complex, Zr-N character
HOMO of 6: does not have appropriate symmetry to engage in significant backbonding with N₂ ligand

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How Many Methyl Groups in [(η⁵-C₅Me₅)₂Zr]₂(µ₂,η²,η²-N₂) Are Needed for Dinitrogen Hydrogenation?
A Theoretical Study

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

- calculations 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

---

Kinetics and Mechanism of N₂ Hydrogenation in Bis(cyclopentadienyl) Zirconium Complexes and Dinitrogen Functionalization by 1,2-Addition of a Saturated C-H Bond

- several mechanistic studies
- kinetics: first-order dependence on H₂ concentration
- KIE: normal primary isotope effect
- large negative entropies of activation
  => first H₂ 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 N₂ zirconocene complex was confirmed also by the 1,2-addition of a saturated C-H bond in the ligand
Comparison of Zirconium and Hafnium Congeners

• attempt to expand the scope of 1,2-addition to include nitrogen-carbon forming reactions
• treatment of 1-N₂ with PhNCO produced complex mixture
  87% of the gas expected for the loss of 1 equiv of free N₂
• competitive ligand-induced side-on, end-on isomerization proceeded?
• addition of 2 equiv of PMe₃ to 1-N₂ afforded end-on N₂ complex
• more strongly activated side-on N₂ complex was targeted

• Hf congeners 2-N₂
• addition of 10 equiv of PMe₃ to 1-N₂ resulted in no change
• greater N₂ reduction imparted by the more reducing third-row metal

• with 2-N₂: 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.

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

- metal: more reducing Hf instead of Zr
- ansa-complex substituted with electro-donating groups
- reduction of 2-I₂ with Na(Hg) under 1 atm N₂ afforded targeted side-on N₂ complex 2-N₂ (dihedral angle = 54°)

- 4 atm CO, toluene as solvent, C₂ symmetric hafnium oxiamidide 2-(N₂C₂O₂)₂-C₂ (y. 82%)
- reducing the CO pressure to 1 atm an isomeric hafnium product (C₁ symmetry) 2-(N₂C₂O₂)₂-C₂ (y. 73%)
- the oxiamide ligand arises from cleavage of N₂ coupled with C-N bond formation and homologation of CO
- unprecedented transformation: strong-field CO ligand to metal N₂ complexes typically results in N₂ 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-(N₂C₂O₂)₂ + HCl → 2-Cl₂ + H₂NC(O)C(O)NH₂ (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 NH₄Cl

Figure 2 | Various N₂ cleavage products from the addition of CO to a benzene-d₆ solution of 2-N₂. 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.
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

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.

(5) Appendix

Structure and Chemistry of Bis(cyclopentadienyl)-MLₙ Complexes

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

Figure 6. Interaction diagram for “end on” (left) and “edge on” (right) Cp₂TiN₂.
Iron-Catalyzed, Hydrogen-Mediated Reductive Cyclization of 1,6-Enynes and Diynes: Evidence for Bis(imino)pyridine Ligand Participation

P. J. Chirik et al
J. Am. Chem. Soc. 2009, 131, 8772

(1) Overview

5 mol% 1-(N₂)₂
4 atm H₂
C₆H₆, 23 °C

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

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 scarcest 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

(a) General Reactivity of Transition Metal-Carbonyl Complexes

Starting olefin | Irradiation time, min | Product (% conversion)
--- | --- | ---
Ethylene | 60 | Ethane (16.7)
Propylene | 60 | Propyne (46.7)
2-Methyl-2-butene | 60 | 2-Methylbutane (26.9)
3-Methyl-2-pentene | 110 | 3-Methylpentane (32.0)
2,3-Dimethyl-2-butene | 60 | 2,3-Dimethylbutane (13.6)
Cyclohexene | 60 | Cyclohexane (33.1)
Cycloheptene | 60 | Cycloheptane (53.2)
Cyclooctene | 60 | Cyclooctane (53.5)
1-Methylcyclopentene | 60 | Methylcyclopentane (26.3)
Methylcylocyclopentane | 70 | Methylcyclopentane (40.0)
2-Methylcyclopentene | 60 | No reaction
2,3-Dimethylcyclohexene | 60 | No reaction
2,3-Pentadiene | 60 | No reaction
2-Cyclohexen-1-one | 180 | Cyclohexanone (41)

(b) A Mechanistic Study

1-pentene → linear pentenes
+n-pentane
Appearance of deuterium in alkenes demands a mechanism featuring a reversible hydrogen transfer.

(c) Proposed mechanism

Fe(CO)₅ ⇌ Fe(CO)₄(ether)
CO
H₂
Fe(CO)₃Ar + CO
Fe(CO)₃Ar
H₂
Fe(CO)₃Ar
Fe(CO)₃Ar

Unsaturated iron-carbonyl complex Fe(CO)₅ is the proposed active species:
=> introduction of a terdentate bis(imino)pyridine chelate may allow thermal access to a catalytically active iron complex [Fe(PrPDI)]

Initial expectations:
+ ease of synthesis, modularity
+ well-documented success in catalysis
+ stabilization of electron-rich Fe(0) complex by π-acidity of the ligand

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

X = Cl, 1-Cl₂
= Br, 1-Br₂
N₂ → ArNa(Hg)pentane
1-Br₂
N₂ → NaBEt₃Htoluene
X = Br, 1-Br₂
N₂ → NaBEt₃Htoluene
1-Br₂

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>
<thead>
<tr>
<th>Solvent</th>
<th>time min(^a)</th>
<th>rate (mol/hr)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph</td>
<td>12</td>
<td>1814</td>
</tr>
<tr>
<td>Ph</td>
<td>16</td>
<td>1344</td>
</tr>
<tr>
<td>Ph</td>
<td>380</td>
<td>57</td>
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<td>Ph</td>
<td>210</td>
<td>104</td>
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<tr>
<td>Ph</td>
<td>60</td>
<td>363</td>
</tr>
<tr>
<td>Ph</td>
<td>210</td>
<td>104</td>
</tr>
<tr>
<td>Ph</td>
<td>360</td>
<td>3.3(^c)</td>
</tr>
</tbody>
</table>

\(^a\) 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-nona-1,5-ene. \(^d\) A 5 and 9% concentration of 1-(N\(_2\))\(_2\)

the activity 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

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

\(\Rightarrow\) the electron 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 Structural Spectroscopic and Computational Study

P. J. Chirik et al.
J. Am. Chem. Soc.
2006, 128, 13901

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

(a) Main Experimental Results

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

<table>
<thead>
<tr>
<th>E</th>
<th>time (min)</th>
<th>conversion (%)</th>
<th>TOF (h⁻¹)</th>
<th>ΔG° (kcal/mol)</th>
<th>ΔH° (kcal/mol)</th>
<th>ΔS° (eu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>300</td>
<td>92</td>
<td>1.8</td>
<td>-9.4</td>
<td>-13.2</td>
<td>-12.6</td>
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<tr>
<td>SiMe₂</td>
<td>300</td>
<td>0</td>
<td>0.62</td>
<td>-10.9</td>
<td>-15.8</td>
<td></td>
</tr>
<tr>
<td>NH₂</td>
<td>300</td>
<td>0</td>
<td>0.62</td>
<td>-11.4</td>
<td>-15.3</td>
<td>-12.7</td>
</tr>
<tr>
<td>N–Bn</td>
<td>26</td>
<td>90</td>
<td>21c</td>
<td>-14.0</td>
<td>-17.4</td>
<td>-11.3</td>
</tr>
<tr>
<td>N–Bu</td>
<td>&lt; 5</td>
<td>&gt; 95</td>
<td>240d</td>
<td>-18.3</td>
<td>-21.0</td>
<td>-9.5</td>
</tr>
<tr>
<td>NBoc</td>
<td>300</td>
<td>24</td>
<td>0.5</td>
<td>-15.5</td>
<td>-18.6</td>
<td>-10.3</td>
</tr>
<tr>
<td>C(CO₂Et)₂</td>
<td>141</td>
<td>&gt; 95</td>
<td>4</td>
<td>-16.3</td>
<td>-19.1</td>
<td>-9.4</td>
</tr>
</tbody>
</table>

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

(b) Mechanistic Study (1)

Entry 3

only stoichiometric cyclization, cleanly affording 1-(HNC₆H₁₀)

E = N-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 (SFe = 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

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.

(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 metallocycle

formal reductive elimination
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 \( \text{1-} \text{(N2}_2 \text{)} \)
- conditions: 23 °C, 3 hr, in benzene-\( \text{d}_6 \)
- complete consumption of both starting materials
- product: 3,4-disubstituted pyrrolidine with only one (Z)-alkene
- the intramolecular olefin complex 

(b) Further Attempt: \( \text{H}_2 \) as the Stoichiometric Terminal Reductant

- \( \text{2} \) reacts cleanly with \( \text{H}_2 \) to yield a catalytically active iron-H\( \text{2} \) complex
- facile hydrogen-mediated cyclization with TOF comparable to those of Rh catalysts
- \( \text{R} = \text{H} \); continued stirring led to the reduction of the exo-methylene, preference for the formation of cis-diastereomers over trans ones
- \( \text{R} = \text{H} \); only the unsaturated products were observed

(c) Extention to Diyne Substrates

- the stoichiometric reaction with the labelled iron dinitrogen complex 1*-(\text{N2}_2) where the isopropyl methyl substituents were deuterated
- reaction with enyne \text{A} resulted in complete and exclusive conversion into two pyrrolidine-\text{d}_1 isotopers

(d) Mechanistic Studies

- the catalytic reaction with \( \text{D}_2 \) gas
- **enyne** \( \text{R} = \text{Me} \): labels exclusively in the methyl and vinyl position of the exo alkynyl substituents
- **enyne** \( \text{R} = \text{H} \): \text{d}_4-isotopologue, additional deuterium incorporation arising from deuteration of the exo methylene pyrrolidine intermediate
- **diynes** : pyrrolidine-\text{d}_2 with the two labels in the vinyl positions of the product

- Comparison of the reactions with 3 and 3*; KIE \( k_\text{H}/k_\text{D} = 6.0(2) \) => C-H bond breaking event in the turnover-limiting step

Figure 2. Catalytic reactions with \( \text{D}_2 \) gas.

<table>
<thead>
<tr>
<th>entry</th>
<th>( \text{E} )</th>
<th>( \text{R} )</th>
<th>time (min)</th>
<th>yield (%)(^\text{a})</th>
<th>TOF (h(^{-1}))(^\text{b})</th>
<th>cis/trans (saturated)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>( \text{N}^\text{Bu} )</td>
<td>( \text{H} )</td>
<td>180</td>
<td>68</td>
<td>6.7</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>2</td>
<td>( \text{NTS} )</td>
<td>( \text{H} )</td>
<td>60</td>
<td>79</td>
<td>20.0</td>
<td>75:25</td>
</tr>
<tr>
<td>3</td>
<td>( \text{NBn} )</td>
<td>( \text{H} )</td>
<td>180</td>
<td>71</td>
<td>6.7</td>
<td>&gt;99:1</td>
</tr>
<tr>
<td>4</td>
<td>( \text{NCH}_2\text{C}_6\text{Me}_5 )</td>
<td>( \text{H} )</td>
<td>180</td>
<td>57(^\text{c})</td>
<td>4.9</td>
<td>&gt;99:1</td>
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<td>5</td>
<td>( \text{NTS} )</td>
<td>( \text{Me} )</td>
<td>180</td>
<td>79</td>
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<td>( \text{Me} )</td>
<td>180</td>
<td>71</td>
<td>6.7</td>
<td>-</td>
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<tr>
<td>7</td>
<td>( \text{NTS} )</td>
<td>( \text{SiMe}_3 )</td>
<td>540</td>
<td>82</td>
<td>2.2</td>
<td>-</td>
</tr>
</tbody>
</table>

\( \text{a} \) Conditions: 4 atm \( \text{H}_2 \) at 23 °C. \( \text{b} \) Isolated yield. \( \text{c} \) Determined at >95% conversion by \( ^1\text{H} \) NMR spectroscopy and 99% GC–MS. Note: Reduced alkene complex (26%) was observed. After 24 h, 53% conversion to the intramolecular olefin complex \( \text{2} \) was found.

Figure 3. Detection of catalytic intermediates and isotopic-labeling studies.
(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
- H₂ 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

![Proposed mechanism for the iron-catalyzed, hydrogen-mediated enyne cyclization.](image)

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

- the redox activity of the [iPrPDI] 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 diminepyridine complexes

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

![Structure of the dimpy ligand, showing the adopted atom numbering scheme.](image)

Scheme 1 Structure of the dimpy ligand, showing the adopted atom numbering scheme.

- different nature of metal-ligand from that of classical σ-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 ligand 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

![Lowest π* orbitals of dimpy.](image)

Fig. 1 Lowest π* orbitals of dimpy.

![Schematic representation of orbital interactions in (A) metal–CO and (B) metal–dimpy complexes.](image)

Fig. 2 Schematic representation of orbital interactions in (A) metal–CO and (B) metal–dimpy complexes.