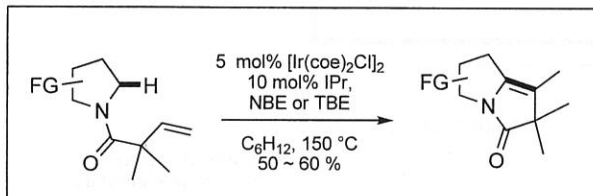


Bond Cleavage and Formation by Transition Metal Complexes

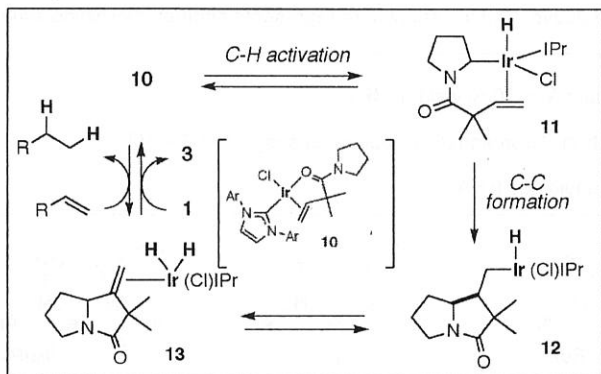
Artificial System: Pd, Rh, Ir, Ru etc.

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

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

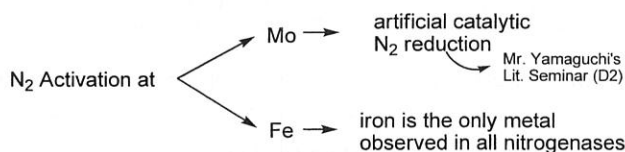
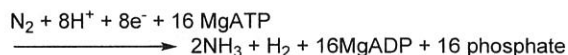
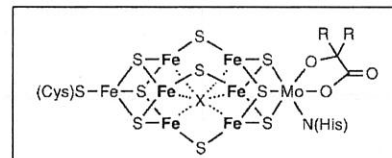


Proposed Mechanism

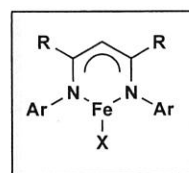


Nature: Fe, Cu, Mn, Co etc.

ex.
Iron-Molybdenum cofactor (FeMoco) in nitrogenase



P. L. Holland's group*: Model Iron Complex



Holland's model iron complex

Iron in FeMoco
High Spin
Low-Coordinate

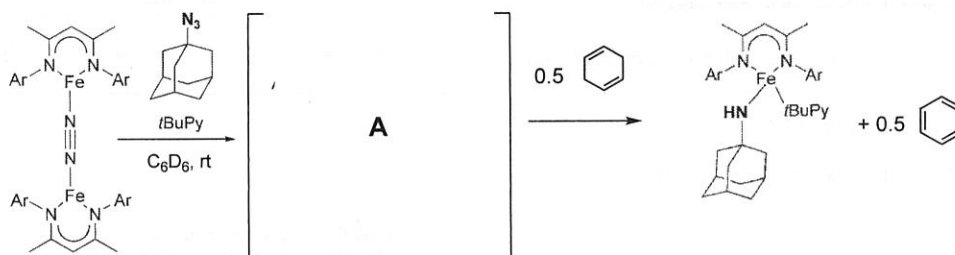
Model Iron Complex
bulky β -diketiminato ligand
three-coordinate, high spin

* Department of Chemistry, University of Rochester

Contents

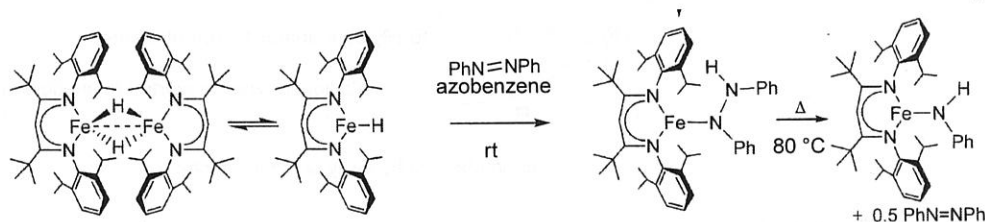
[1] Coordination-Number Dependency of Reactivity in an Imidoiron(III) Complex

P. L. Holland et al.
Angew. Chem. Int. Ed. 2006, 45, 6868



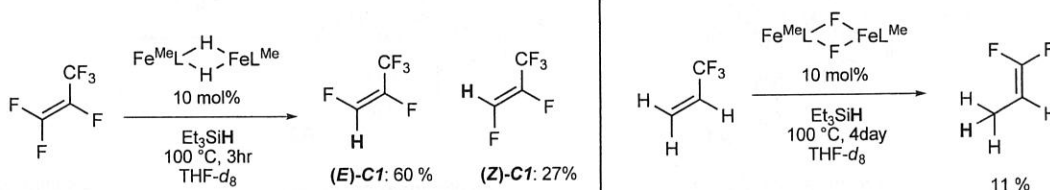
[2] N=N Bond Cleavage by a Low-Coordinate Iron(II) Hydride Complex

P. L. Holland et al.
J. Am. Chem. Soc. 2003, 125, 15752
J. Am. Chem. Soc. 2007, 129, 8112

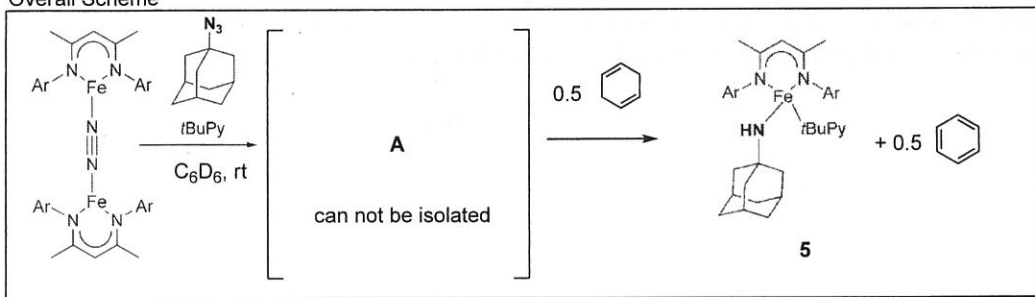


[3] Synthesis and Reactivity of Low-Coordinate Iron(II) Fluoride Complexes and Their Use in the Catalytic Hydrodefluorination of Fluorocarbons

P. L. Holland et al.
J. Am. Chem. Soc. 2005, 127, 7857

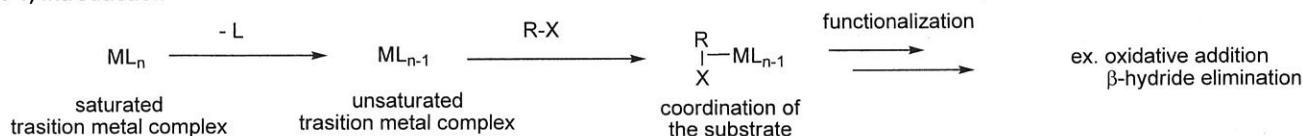


Overall Scheme



M=NR
 transition metal imido complex
 postulated roles in catalysis
 nitrogen fixation
 atom-, and group- transfer process

(1-1) Introduction



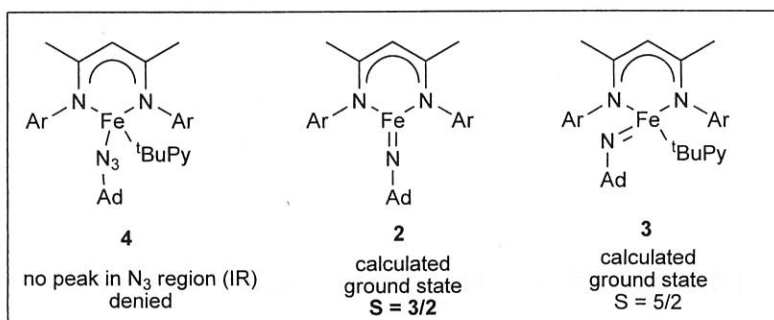
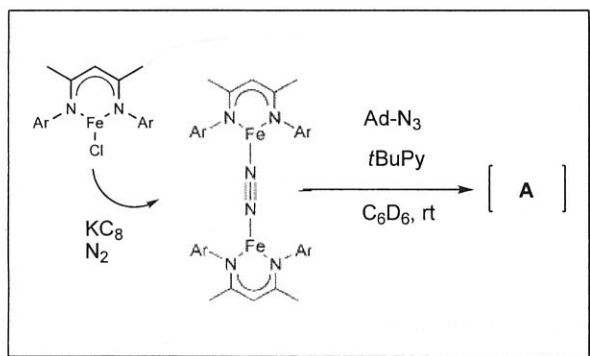
A typical situation where coordination number relates to the reactivity is described above. But the study here represents another interesting situation...

(1-2) Identification of the Intermediate A

Major product **A**: ~ 70 % yield (NMR)

EPR (Electron Paramagnetic Resonance) suggested $S = 3/2$

Possible candidates for **A**

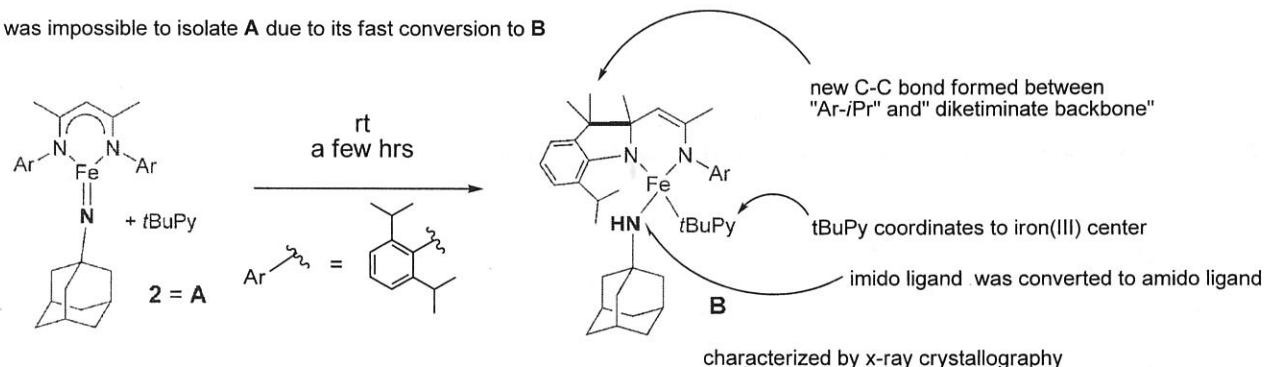


Other calculated spectral data of **2** match well with the experimental data

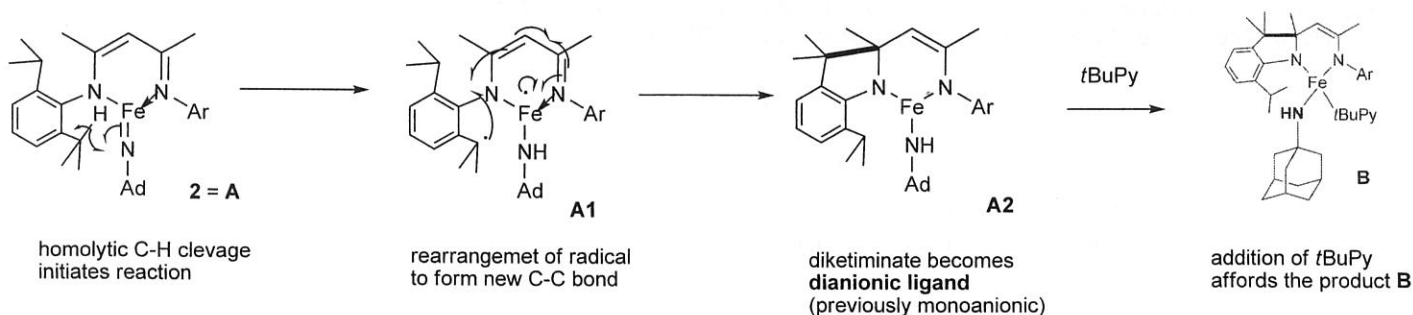
→ **2** should be **A**

(1-3) Study on the Decomposition Route of A

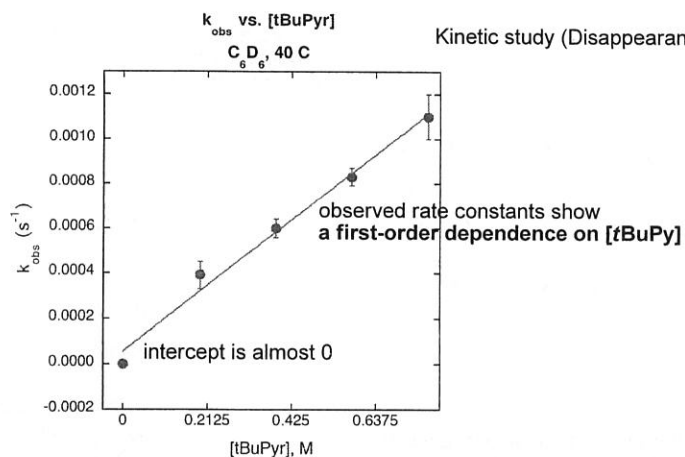
It was impossible to isolate **A** due to its fast conversion to **B**



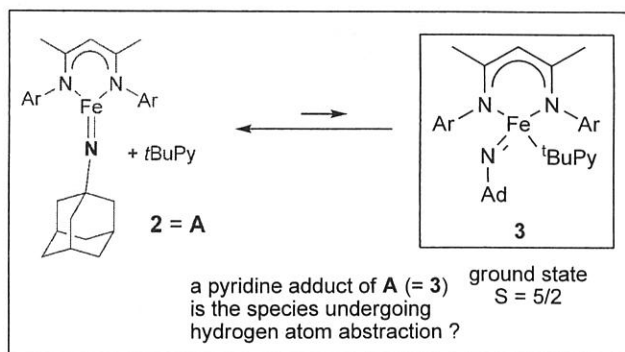
Working Hypothesis for the Mechanism (Revised later)



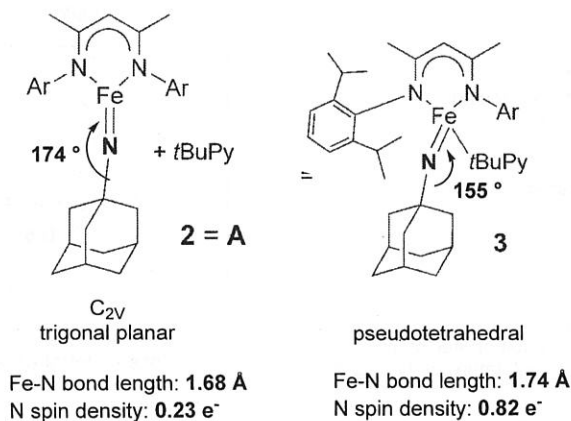
(1-4) Kinetic Study Suggested a Different Active Species



Kinetic study (Disappearance of **A** (= **2**)) was monitored with ¹H NMR



(1-5) Basics to Understand What Holland et al. Insist

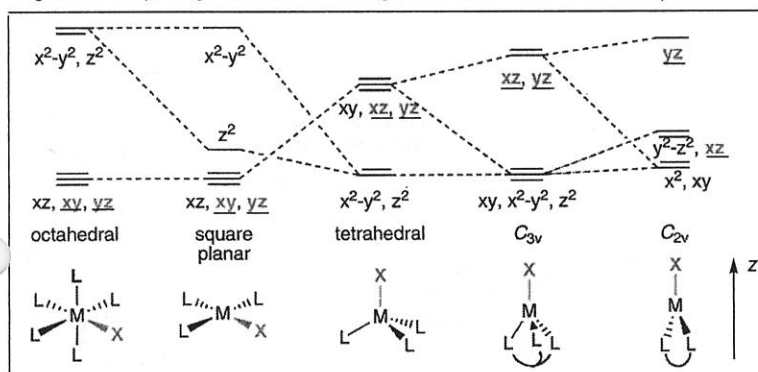


Basics for Imido Ligand

M. M. Abu-Omar et al.
Coord. Chem. Rev. 2003, 243, 83 and
The Organometallic HyperTextBook

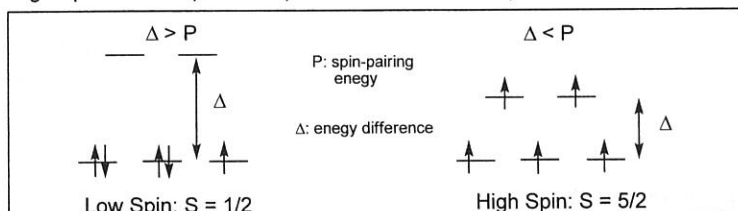
	bent	linear
	$L_nM=N\ddot{N}R$	$L_nM=\ddot{N}-R$
Hybridization at nitrogen	sp^2 $1\sigma + 1\pi$	sp $1\sigma + 2\pi$
Idealized bond angle	120°	180°
Electron donation		
NR ²⁻	4e ⁻	6e ⁻
neutral	2e ⁻	4e ⁻

Ligand-field splitting in some common geometries



underlined two d -orbital have the correct symmetry for π -interactions with the ligand labelled X

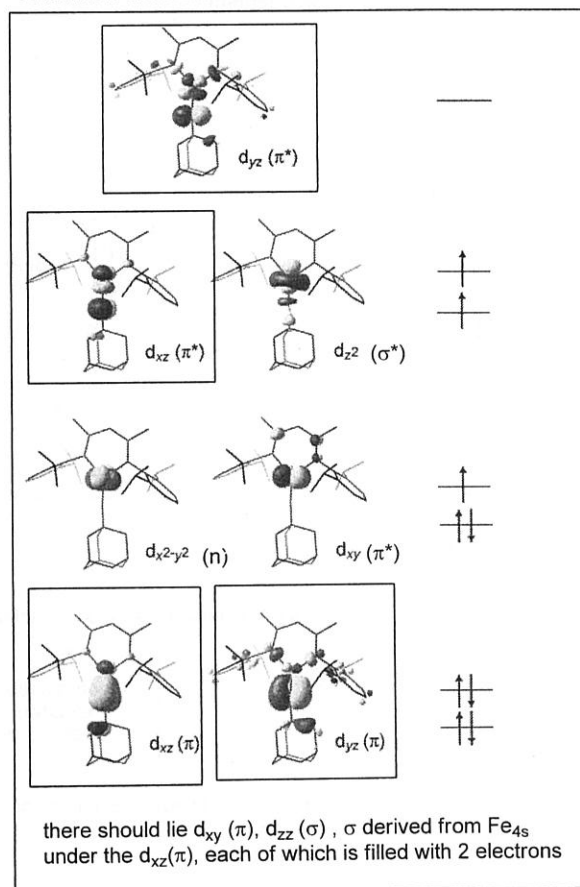
High Spin or Low Spin: example with octahedral complex, d^5



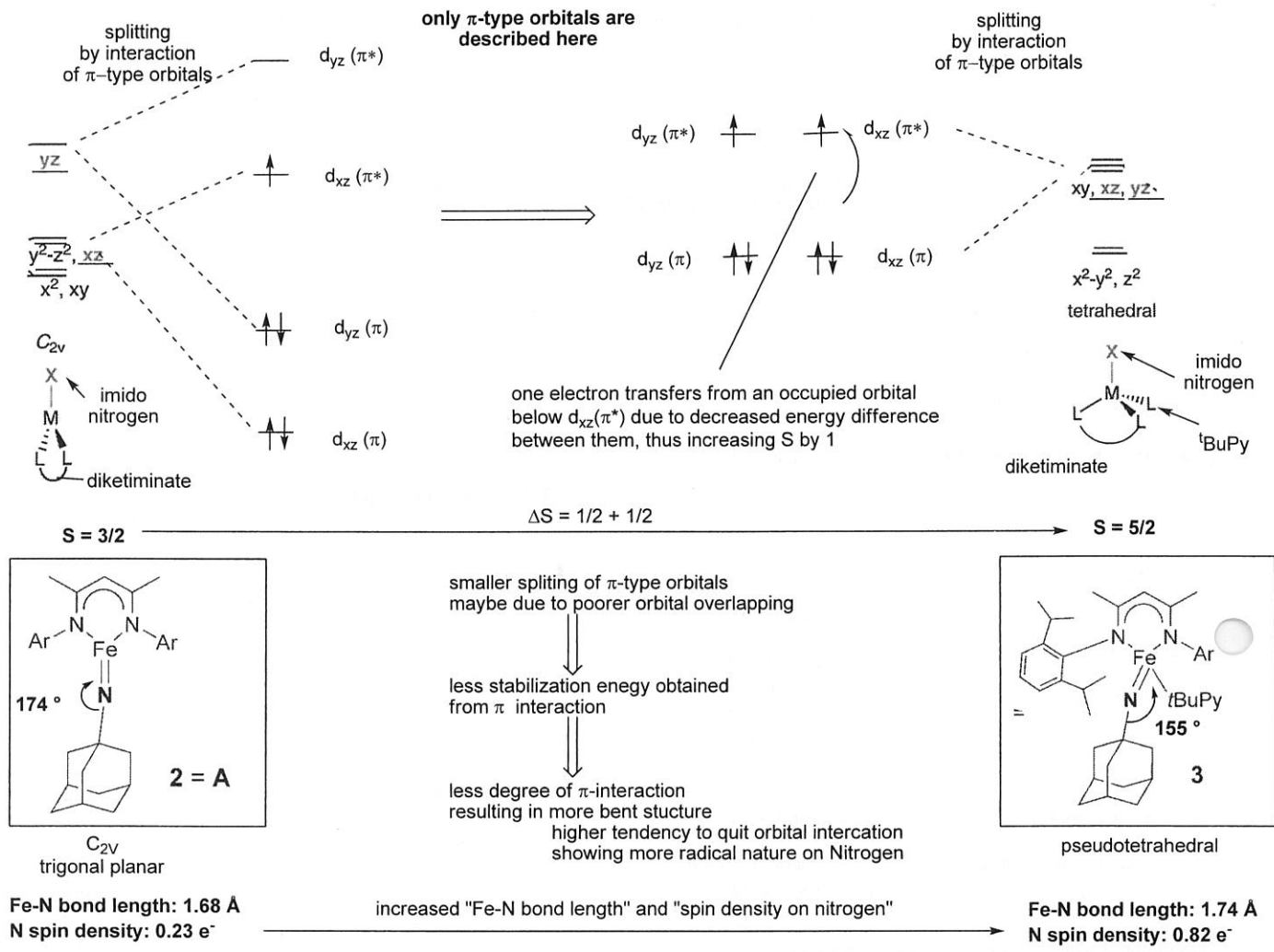
what Holland et al insist is....

In **3**, the geometry at iron is pseudotetrahedral, which results in a smaller splitting of the ligand-field orbitals (despite the increased coordination number) and hence an $S = 5/2$ ground state. As a result of populating the second π^* orbital in high-spin state of four-coordinate **3**, the Fe-N bond is lengthened to 1.74 Å. Binding of pyridine also causes substantial bending of the imido ligand. Finally, the nitrogen atom has much more density in four-coordinate in **3** than three-coordinate **2**.

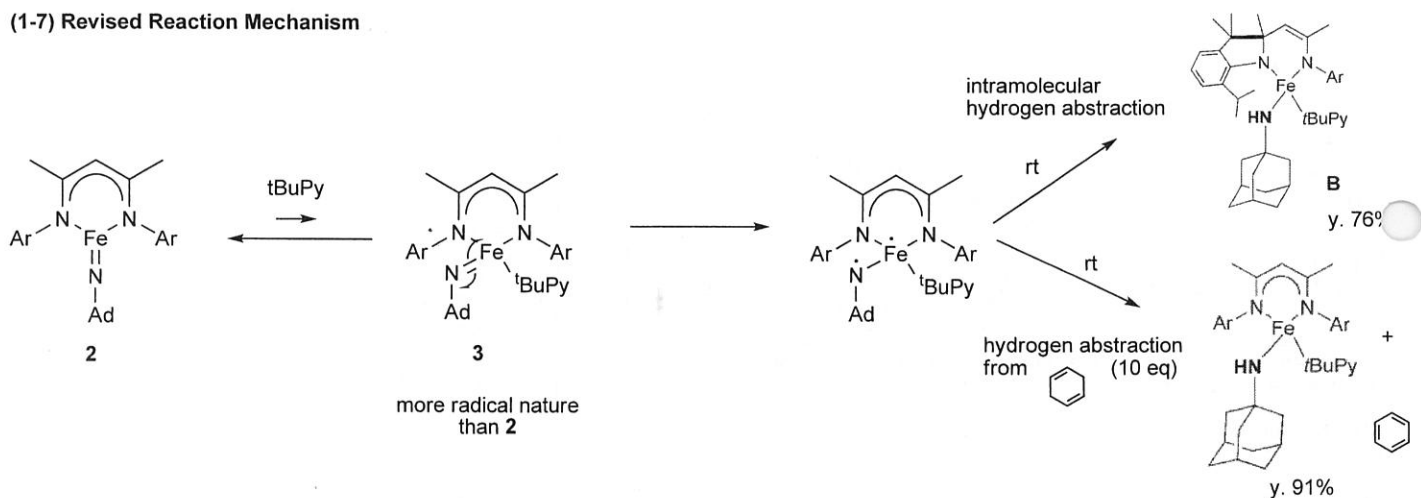
Calculated molecular orbitals of **A**



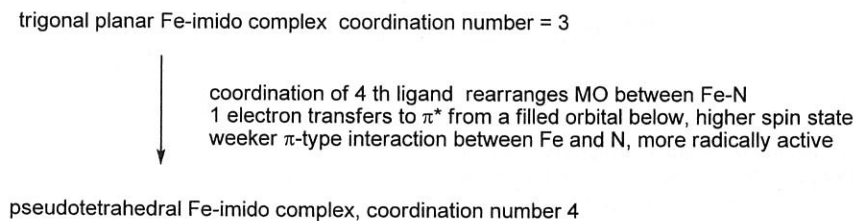
(1-6) Explanation for Different Reactivity between 2 and 3



(1-7) Revised Reaction Mechanism



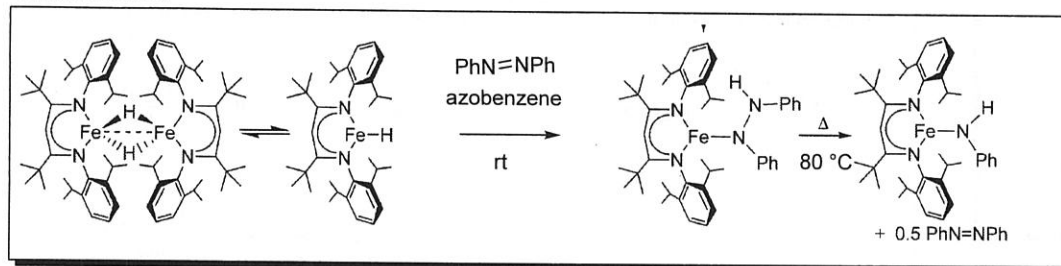
(1-8) Summary



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

P. L. Holland et al.
J. Am. Chem. Soc. **2003**, *125*, 15752
J. Am. Chem. Soc. **2007**, *129*, 8112

Overall Scheme

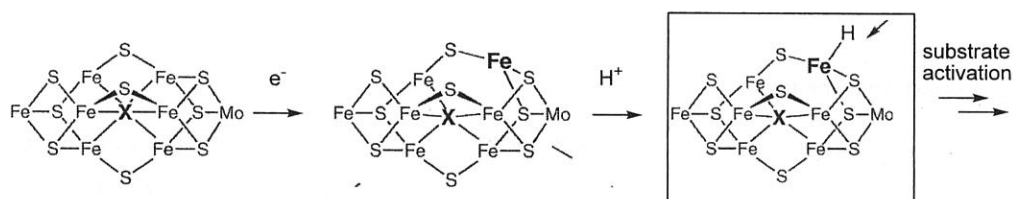


2step reductions of N=N

1st step: N=N to N-N
 2nd step: N-N to 2NH

(2-1) Background of the Research

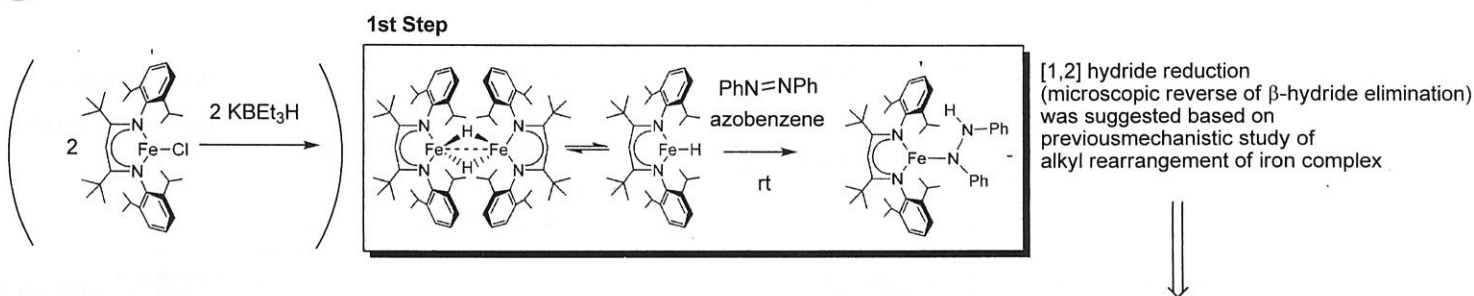
P. L. Holland et al.
Can. J. Chem. **2005**, *83*, 296



A proposed mechanism of nitrogenase N_2 reduction includes Fe-H as an active species

(2-2) Mechanistic Analysis of the First Reduction

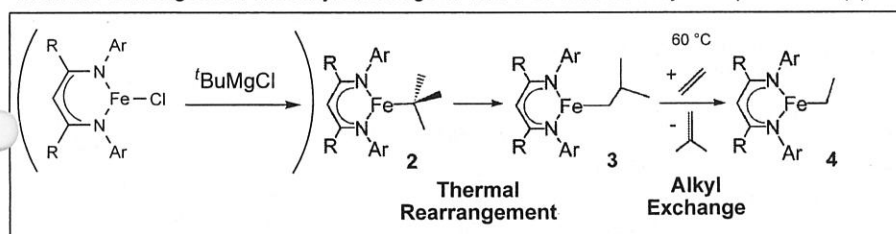
P. L. Holland et al.
J. Am. Chem. Soc. **2007**, *129*, 8112



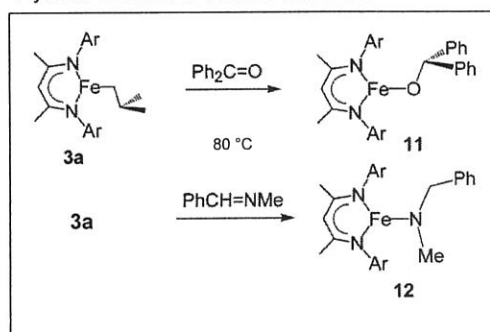
Ref. 2-1: Reversible Beta-Hydrogen Elimination of Three-Coordinate Iron(II) Alkyl Complexes: Mechanistic And Thermodynamic Studies

P. L. Holland et al.
Organometallics **2004**, *23*, 5226

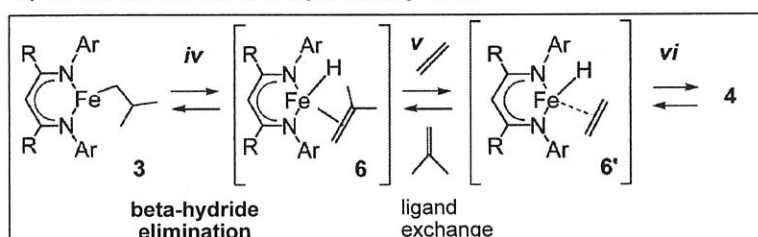
Thermal Rearrangement and Alkyl Exchange of Three-Coordinate Alkyl Complex of Iron(II)



Hydride Transfer to Ketone and Imine

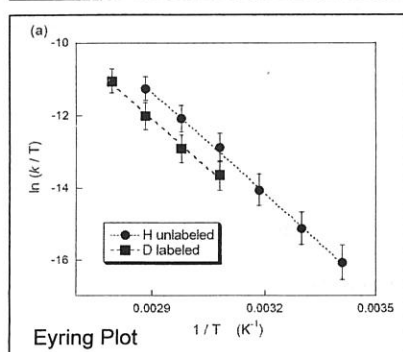


Speculated Mechanism for Alkyl Rearrangement



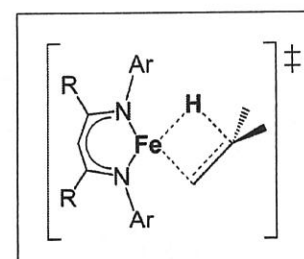
kinetic analysis of reaction suggested the mechanism via β -hydride elimination which is rate limiting step

kinetic isotope effect: $k_H/k_D = 2.2$
 (within the range of KIE for β -hydride elimination)

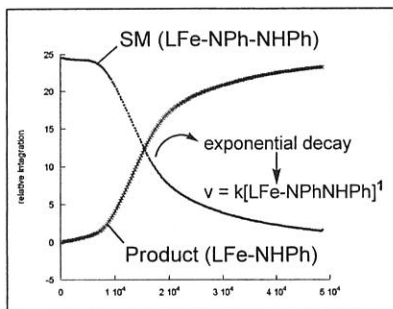
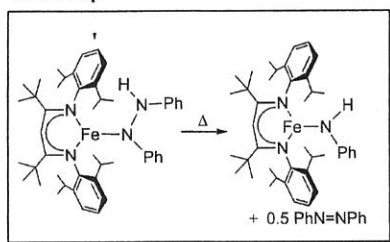


Eyring plot: negative ΔS^\ddagger
 consistent with limited motion in transition state in β -hydride elimination

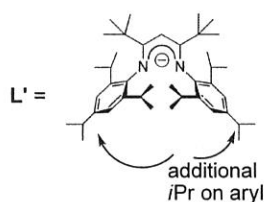
Speculated Transition State for Step iv



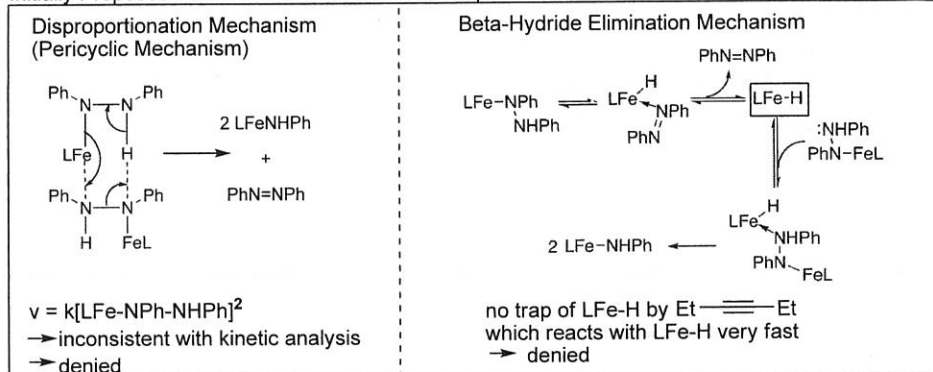
2nd Step



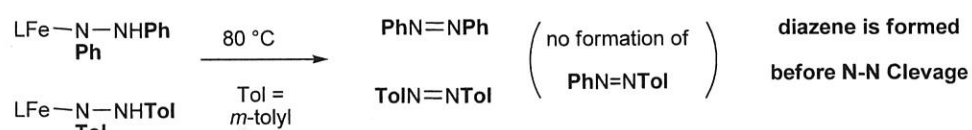
Kinetic Data for Conversion of LFe-NPhNHPH to LFe-NHPH



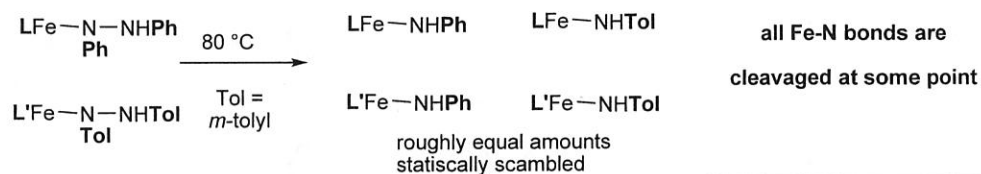
Initially Proposed Mechanisms for the Second Step



Crossover experiment

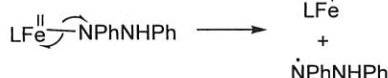


Double Crossover Experiment



(2-4) Proposed Reaction Mechanism of the Second Reduction

(2) Fe-N bond homolysis



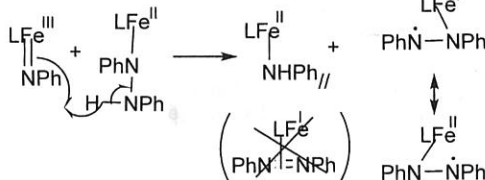
(6) LFe=NPh abstracts hydrogen atom from hydrazinyl radical



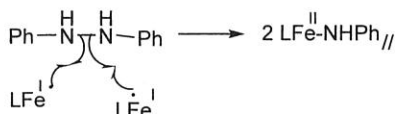
(3) Disproportionation of diphenylhydrazinyl radical



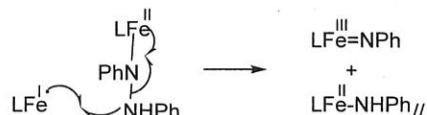
(7) LFe=NPh abstracts a hydrogen atom from LFe-NPhNHPH



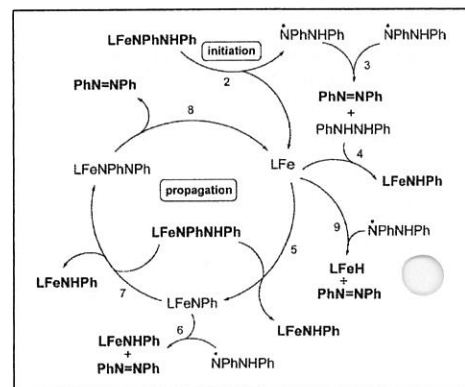
(4) Iron(I) LFe reacts with diphenylhydrazine



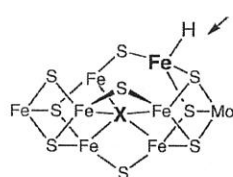
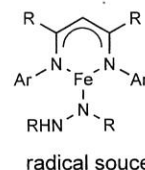
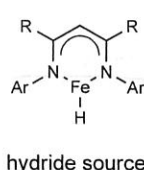
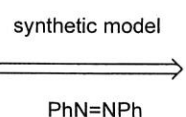
(5) LFe abstracts NHPH radical from LFe-NPhNHPH



(8) LFeNPhNHPH loses azobenzene to generate LFe



(2-5) Summary

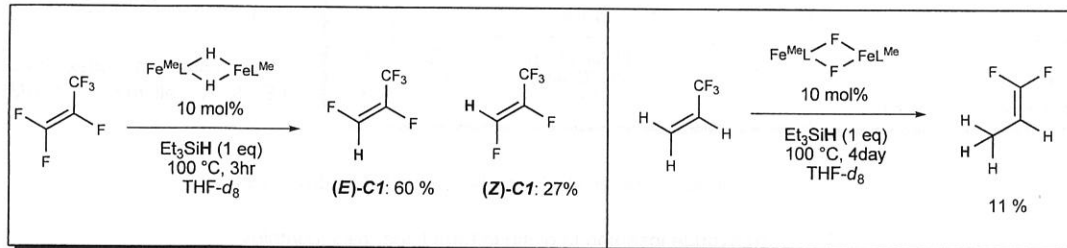
proposed Fe-H intermediate for N₂ reduction

two different active species for reduction

[3] Synthesis and Reactivity of Low-Coordinate Iron(II) Fluoride Complexes and Their Use in the Catalytic Hydrodefluorination of Fluorocarbons

P. L. Holland et al.
J. Am. Chem. Soc. 2005, 127, 7857

Overall Scheme



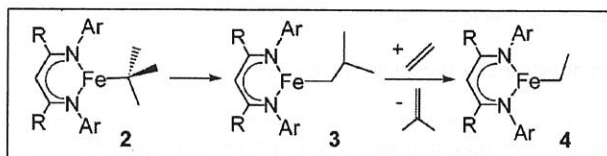
C-F : highly strong covalent bond
(cf. Mr. Yukawa's lit. seminar M1)

methods for chemically manipulating fluorocarbons to either degrade or add value to these materials

(3-1) Background of the Research

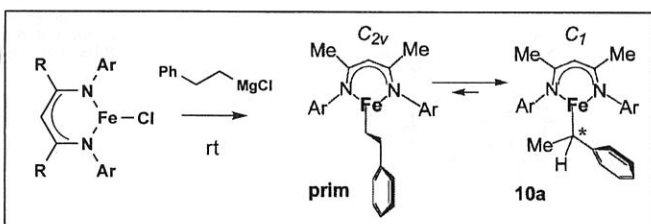
Ref. 3-1: Reversible Beta-Hydrogen Elimination of Three-Coordination Iron(II) Alkyl Complexes: Mechanistic and Thermodynamic Studies

P. L. Holland et al.
Organometallics. 2004, 23, 5226



Preference for **linear product** over branched product

Due to **steric influence** based on DFT calculation
(comparison between "normal ligand" and "less sterically hindered ligand")

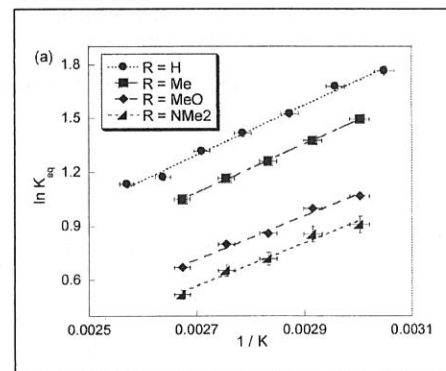


Preference for the **branched** over the linear in the case of ligands with specific electronic character

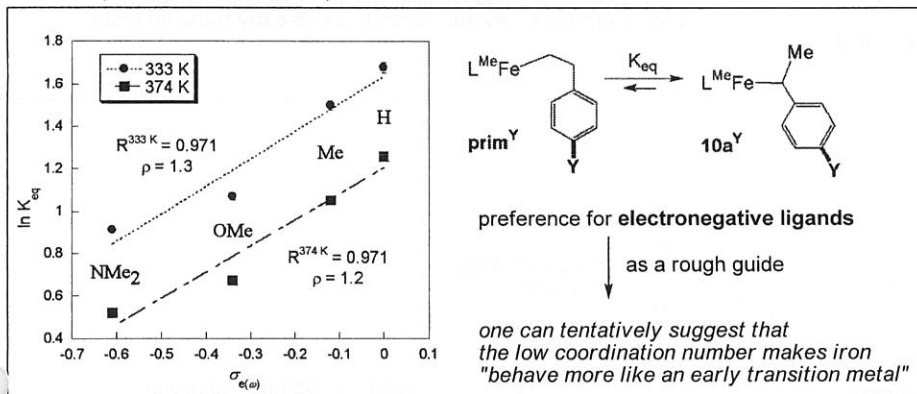
prim : **10a** = 1 : 9 (at 25 °C)

van't Hoff plot: $\Delta H^\circ = -2.8$ kcal/mol, $\Delta S^\circ = -4.9$ cal/mol
negative entropy: **10a** is more vibrationally restricted
entropic effect is overcome by the favorable enthalpic contribution

van't Hoff Plot

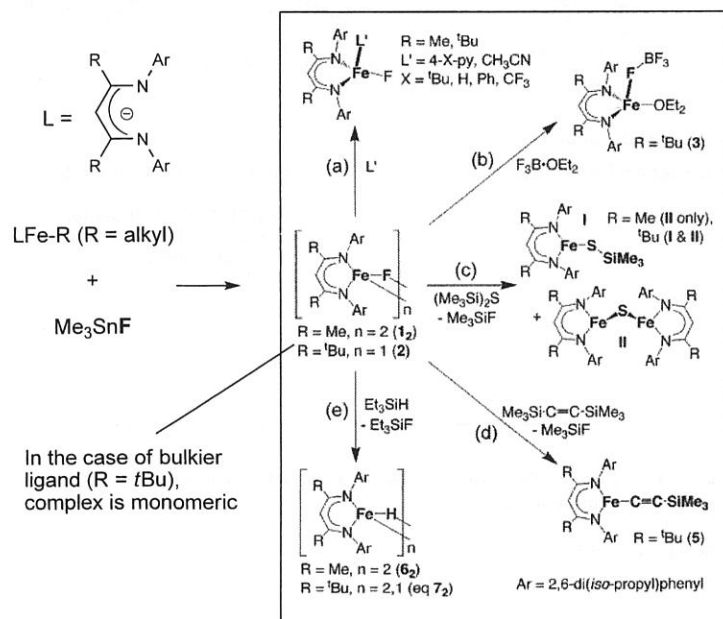


Hammett plot for isomerization equilibria between "linear" and "branched"



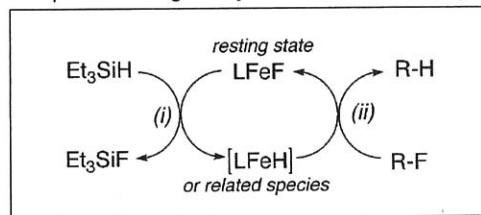
(3-2) Synthesis and Reactivity of Diketiminate Iron(II) Fluorides.

P. L. Holland et al.
J. Am. Chem. Soc. 2005, 127, 7857



- very short Fe-F bond suggested strong interaction between Fe and fluoride
- despite the strong Fe-F bond the exposed fluoride can be activated by boron and silicon reagents

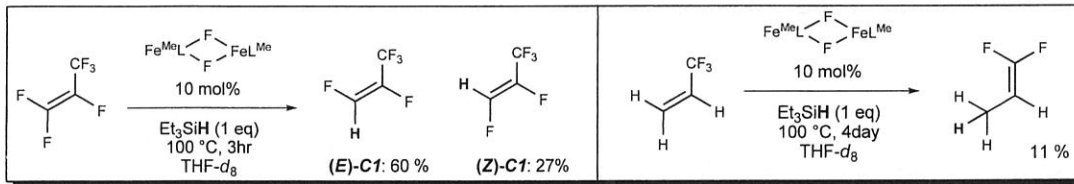
Blueprint for design of hydrodefluorination catalysis



- exchange of fluoride and hydride by the formation of strong Si-F bond
- extraction of fluoride from the substrate by strong affinity of LFe-X toward fluoride

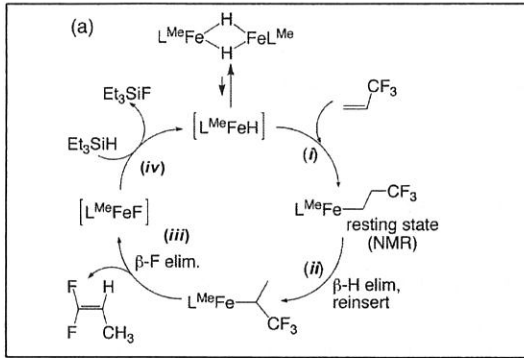
(3-3) Mechanistic Study of Catalytic Hydrodefluorination of Fluoroolefins

P. L. Holland et al.
J. Am. Chem. Soc. **2005**, *127*, 7857



No reaction with bulkier iron complex $L^t\text{-BuFe-F}$

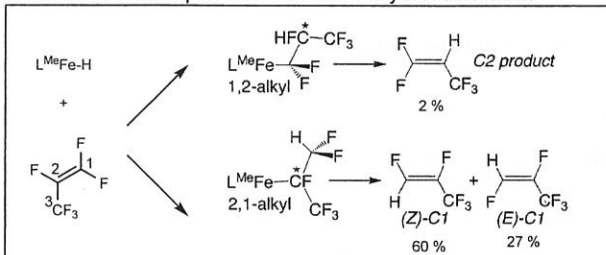
Resting state: complex similar to $L\text{Fe-R}$ ($R = \text{alkyl}$) (^1H , ^{19}F NMR)



Proposed Catalytic Cycle for the Second Dehydrofluorination

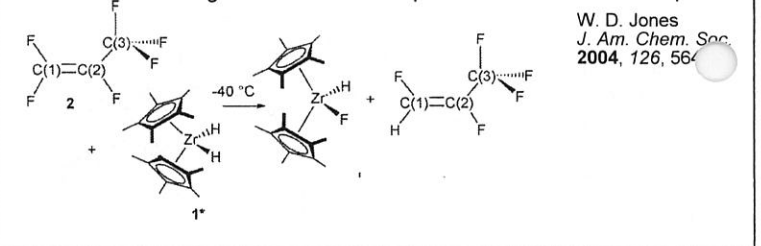
- (i) hydride insertion to olefin to form linear alkyl complex
- (ii) β -hydride elimination and reinsertion to afford branched complex not so favorable due to increased steric hindrance
- (iii) β -fluoride elimination maybe irreversible due to strong affinity of $L^{\text{Me}}\text{Fe-X}$ to F
- (iv) reformation of active $L\text{Fe-H}$ complex by Et_3SiH

Mechanistic Description on the First Dehydrofluorination



- regioselectivity in hydride insertion
 C_2 is less negative than $\text{C}_1 \Rightarrow$ hydride insertion at C_1
- stereoselectivity in β -fluoride elimination: no explanation

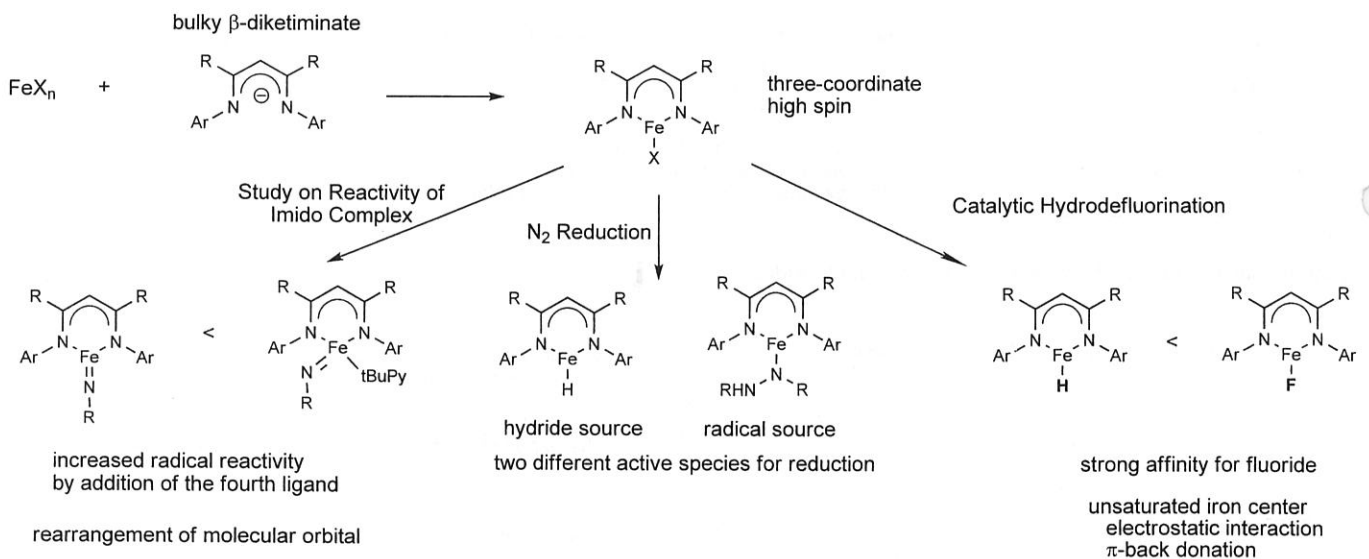
Defluorination of Perfluoropropene Using Cp^*ZrH_2 and Cp^*ZrHF : A Mechanism Investigation from a Joint Experimental-Theoretical Perspective



W. D. Jones
J. Am. Chem. Soc. **2004**, *126*, 564

- intermediacy of β -fluoride elimination in hydrodefluorination was suggested in several researches with **early transition metals**

Summary



Simplified Concept

