

**Project Number:** DOE-NMSU-15996

**Project Title:** Nitrogen Atom Transfer from High Valent Iron Nitrides

**DOE Grant Number:** DE-FG02-08ER15996

**PI:** Michael D. Johnson, New Mexico State University

**Contact Information:** Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces NM 88003. Tel: (575) 646-3627. E-mail: [johnson@nmsu.edu](mailto:johnson@nmsu.edu).

**Co-PI:** Jeremy M. Smith, Indiana University

**Contact Information from August 1, 2013:** Department of Chemistry, Indiana University, 800 E. Kirkwood Ave., Bloomington IN 47405. E-mail: [smith962@indiana.edu](mailto:smith962@indiana.edu).

**Postdoc Name:** Wei-Tsung Lee

**Student Names:** Salvador Muñoz, Song Xu, Anne Hickey.

**Collaborators:** Haobin Wang (New Mexico State), Diane A. Dickie (New Mexico/Sandia), Martin L. Kirk (New Mexico), Joshua Telser (Roosevelt), Karsten Meyer (Erlangen-Nürnberg, Germany), Brian M. Hoffman (Northwestern), Mu-Hyun Baik (KAIST), Michael D. Johnson (New Mexico State)

**Period of Execution:** 8/15/14-8/14/15

**Yearly Budget:** \$155,000

**Significant Achievements:** (1) Structural and spectroscopic characterization of the first isolable iron(V) complex; (2) Hydrocarbon functionalization through nitrogen atom transfer

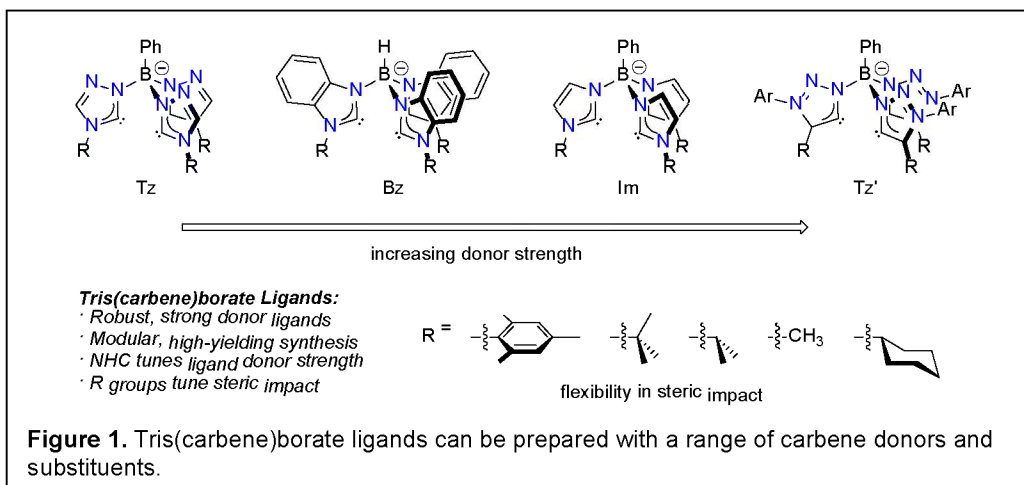
**Interest to DOE:** Organonitrogen compounds such as aziridines are useful species for organic synthesis, but there are few efficient methods for their synthesis. Using iron nitrides to catalytically access these species may allow for their synthesis in an energy- and atom-efficient manner. Moreover, since metal nitrides can be prepared from N<sub>2</sub>, developing new methods for nitrogen atom transfer from iron nitride complexes may lead to methods for preparing organonitrogen compounds directly from N<sub>2</sub>, without the need for preparing ammonia as an intermediate compound. Similarly, the reactivity of other metal-ligand multiple bonds may lead to new catalytic methods for substrate functionalization.

The development of new ligand frameworks is important to these goals, as they allow for the stabilization of unusual oxidation states and ligands, as well as providing a method for inducing previously unknown reactivity. In particular, strongly donating ligands that stabilize low coordination environments are expected to provide ready access to higher oxidation states as well as activate electron-accepting ancillary ligands.

## Research Results

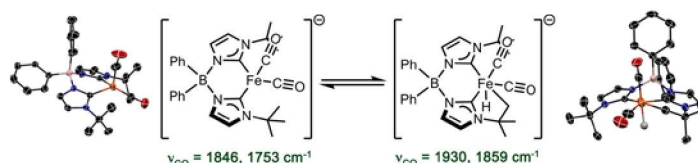
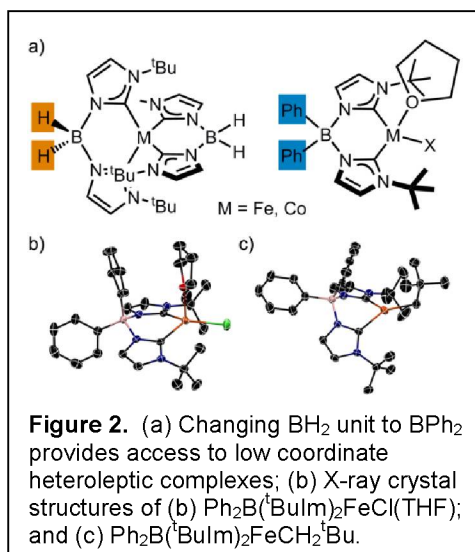
### 1. New Ligands

**1.1. Tris(carbene)borates:** New tripodal ligands containing stabilized carbenes other than imidazol-2-ylidenes have been prepared and their donor strengths evaluated from the frequency of  $\nu_{\text{NO}}$  in  $\{\text{NiNO}\}$  derivatives. Specifically, we have reported more weakly donating tris(carbene)borate ligands based on 1,2,4-triazol-3-ylidene (Tz) and benzimidazol-2-ylidene (Bz) donor groups (Fig. 1), and a more strongly donating variant based on mesoionic 1,2,3-triazol-4-ylidenes (Tz'). Additionally, we have prepared tris(imidazol-2-ylidene)borates with a wide range of substitution patterns, which allow for precise tuning of both steric and electronic properties.



**1.2. Bis(carbene)borates:** Building on the success of tris(carbene)borates for stabilizing unusual coordination environments and engendering new chemistry, we have initiated research into the development of analogous bidentate ligands (Fig. 2). Initial studies using a bidentate dihydrobis(carbene)borate ligand have been complicated by the formation of undesired homoleptic complexes containing two bis(carbene)borates. This problem was solved through the use of diphenylbis(carbene)borate ligands which provide access to four-coordinate complexes of Fe and Co, and three-coordinate Ni and Cu without evidence for the formation of homoleptic complexes.

In unpublished work, we have investigated the reductive chemistry of the bis(carbene)borate complex  $\text{Ph}_2\text{B}^t\text{Bulm}_2\text{FeCl}(\text{THF})$ . Most interestingly, reduction in the presence of CO leads to a formally Fe(0) complex that undergoes reversible C-H activation of the supporting ligand (Fig. 3). To our knowledge, this is a unique

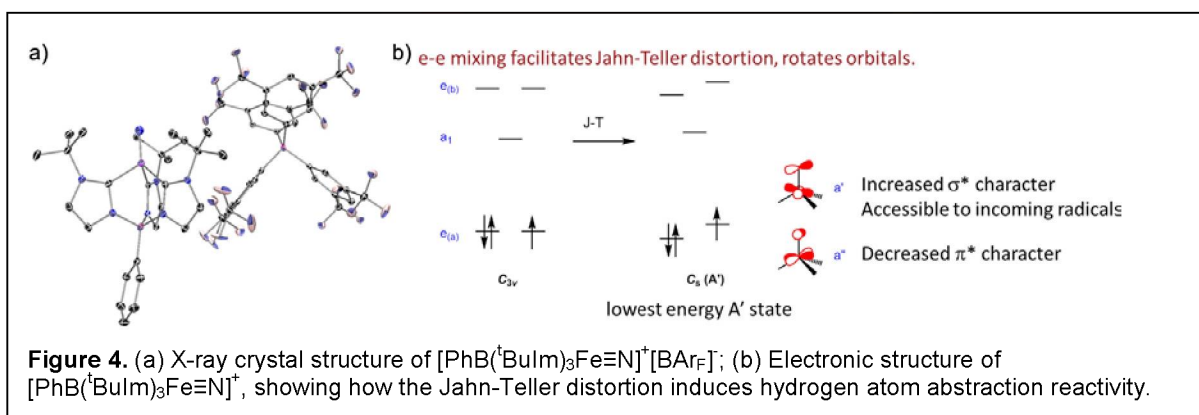


**Figure 3.** Equilibrium involving intramolecular C-H oxidative addition. Crystal structures of both complexes are shown, counterion omitted for clarity.

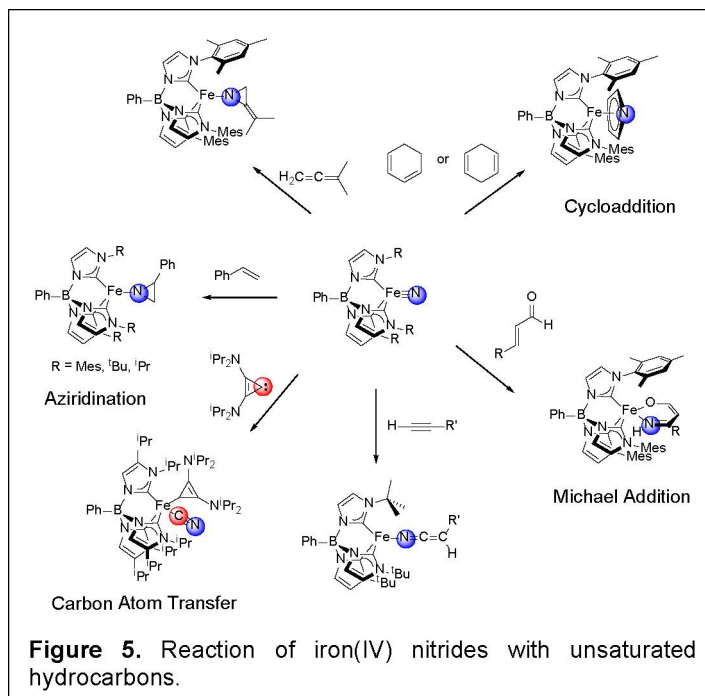
example of system in which both the reactant and product of a C-H activation reaction have been structurally characterized. Preliminary computational investigations suggest that this reaction involves a spin state change from high spin ( $S = 1$ ) to low spin ( $S = 0$ ), with C-H activation occurring on the singlet surface.

## 2. Synthesis and Reactivity of Iron Nitrides

Building from our synthesis and characterization of isolable iron(IV) nitride complexes, we have subsequently reported an isolable Fe(V) nitride,  $[\text{PhB}(\text{Bulm})_3\text{Fe}\equiv\text{N}]^+[\text{Bar}_\text{F}]^-$  (Fig. 4). In collaboration with the groups of Brian Hoffman (Northwestern) and Martin Kirk (University of New Mexico), we have undertaken detailed spectroscopic measurements (EPR, ENDOR) of the Fe(V) nitrido complex. These measurements, in combination with electronic structure calculations, show that the  $C_{3v} \rightarrow C_s$  distortion of the complex is primarily due to an extremely strong Jahn-Teller interaction that overwhelms the spin-orbit coupling. A key component of the Jahn-Teller distortion is considerable mixing of the  $d_{x^2-y^2}/d_{xy}$  ( $e_{(a)}$ ) and  $d_{xz}/d_{yz}$  ( $e_{(b)}$ ) orbitals. This distortion is proposed to drive the hydrogen atom abstraction chemistry of this complex.

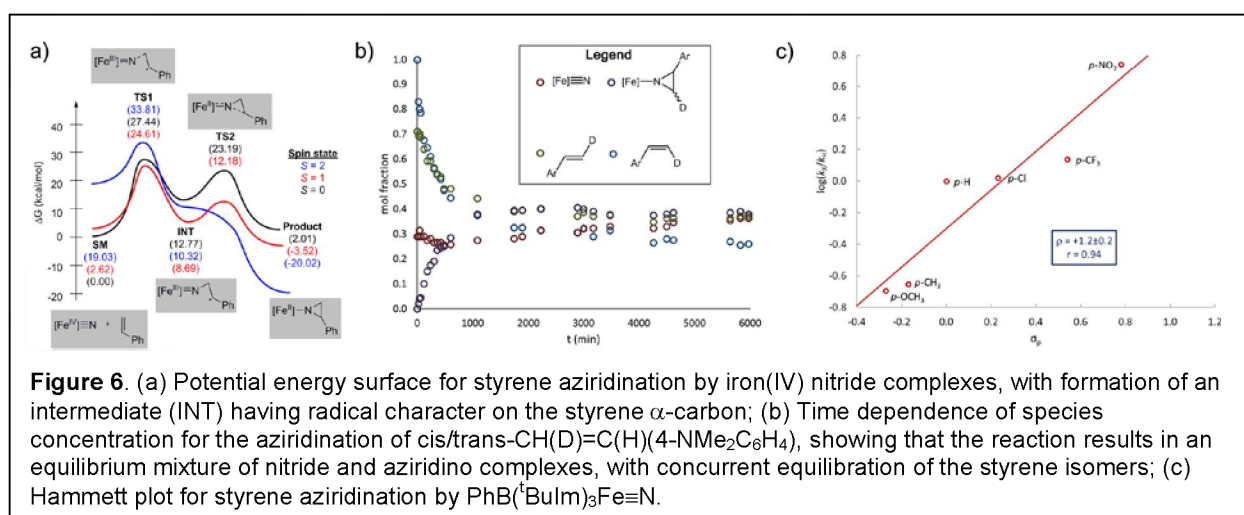


Building on earlier work on nitrogen atom transfer to phosphines, CO and isocyanides, we have undertaken a comprehensive investigation into the reactivity of iron(IV) nitride complexes with unsaturated hydrocarbons (Fig. 5). Reaction selectivity depends on the tris(carbene)borate substituent, with the nitride complex  $\text{PhB}(\text{MesIm})_3\text{Fe}\equiv\text{N}$  showing the greatest range of reactivity. Thus, this complex reacts with bulky styrenes and allenes to yield aziridino ligands, cyclic dienes to provide pyrrolides and enones to give ketiminate ligands. The high reactivity of this complex is due in part to the accessibility of the metal center with this ligand since in many cases the product has a higher coordination number than the nitride starting material. Many of these reactions are previously unknown modes of reactivity for transition metal nitrides.



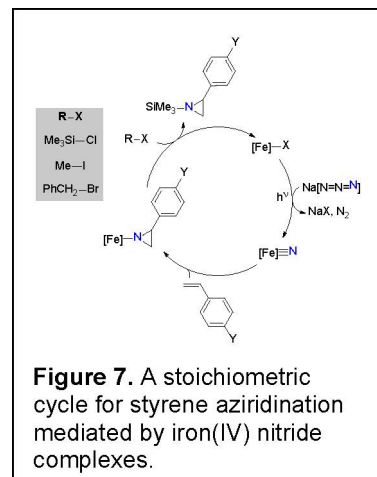
While  $\text{PhB}^t\text{Bulm}_3\text{Fe}\equiv\text{N}$ , in which the metal center is better shielded from the environment, does not show the same diversity of reactivity, this complex reacts cleanly with a wider range of styrenes to provide the corresponding aziridino complexes, one of which has been structurally characterized. Additionally, this complex also reacts with terminal alkynes to provide azaallene ( $\text{PhB}^t\text{Bulm}_3\text{Fe}-\text{N}=\text{C}=\text{C}(\text{H})\text{R}$ ), another mode of reactivity that was previously unknown nitride reaction. Preliminary reactivity investigations reveal an even larger substrate scope for  $\text{PhB}^t\text{Pr}_2\text{Im}_3\text{Fe}\equiv\text{N}$ , which even reacts with tetrasubstituted alkenes. This complex also abstracts a carbon atom from a stabilized cyclopropylidene to provide a cyanide ligand.

Given the synthetic value of aziridines, particularly in organic chemistry, we have undertaken a comprehensive investigation into the aziridination mechanism using a combination of experimental and theoretical methods. Although the reaction landscape is complicated by the accessibility of multiple spin states, theoretical calculations reveal aziridination follows a stepwise pathway in which both steps are reversible (Fig. 6 a): (1) radical attack of the nitride on the alkene yields an imido intermediate having radical character on the styrene  $\alpha$  carbon (Figure 6 a, INT), which is followed by (2) ring closure to yield the iron(II) aziridino product.



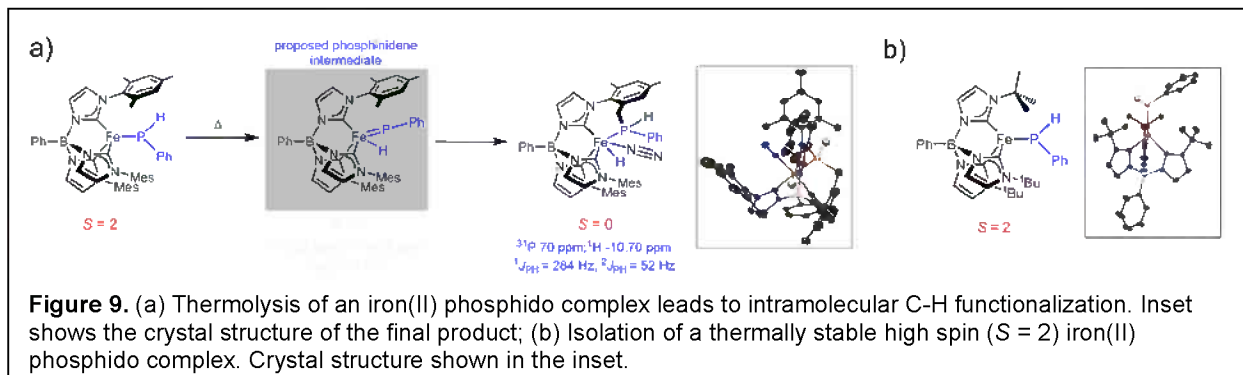
Two key experimental observations demonstrate the reversible, stepwise nature of the aziridination reaction. Firstly, the aziridino complex  $\text{PhB}^t\text{Bulm}_3\text{Fe}-\text{N}(\text{CH}_2\text{CHPh})$  reacts with *para*-substituted styrenes ( $p\text{-C}_6\text{H}_4\text{X})\text{CH}=\text{CH}_2$  to form the corresponding aziridino product  $\text{PhB}^t\text{Bulm}_3\text{Fe}-\text{N}(\text{CH}_2\text{CH}(\text{C}_6\text{H}_4\text{X}))$  and styrene, i.e., aziridine cross-metathesis. Secondly, the reaction of  $\text{PhB}^t\text{Bulm}_3\text{Fe}\equiv\text{N}$  with a mixture of *cis*- and *trans*- $((p\text{-C}_6\text{H}_4\text{R}))\text{CH}=\text{CH}(\text{D})$  leads to thermal equilibration of these isomers in addition to formation of the aziridino product (Fig. 6 b). Initial rate measurements with *para*-substituted styrenes show that electron-poor styrenes react more rapidly than electron-rich styrenes ( $\rho = 1.2$ , Fig. 6 c), and thus the aziridination mechanism is reminiscent of a radical addition reaction, where the nitride has nucleophilic character.

The aziridino complexes  $\text{PhB}^t\text{Bulm}_3\text{Fe}-\text{N}(\text{CH}_2\text{CH}(\text{C}_6\text{H}_4\text{R}))$  reacts with a range of electrophiles to provide *N*-functionalized aziridines (Fig. 7). For example,  $\text{PhB}^t\text{Bulm}_3\text{FeN}(\text{CH}_2\text{CHPh})$  reacts with  $\text{Me}_3\text{SiCl}$  to quantitatively provide  $\text{PhB}^t\text{Bulm}_3\text{FeCl}$  and the aziridine  $\text{Me}_3\text{SiN}(\text{CH}_2\text{CHPh})$ . The latter compound, which was identified by  $^1\text{H}$  NMR spectroscopy, is readily



hydrolyzed by water to yield  $\text{HN}(\text{CH}_2\text{CHPh})$ , which was characterized by  $^1\text{H}$  NMR spectroscopy and ESI mass spectrometry. Analogous results were obtained with the alkylating agents MeI and  $\text{PhCH}_2\text{Br}$ , leading to formation of the aziridines  $\text{MeN}(\text{CH}_2\text{CHPh})$  and  $\text{PhCH}_2\text{N}(\text{CH}_2\text{CHPh})$ , respectively.

In summary, tris(carbene)borate iron(IV) nitride complexes react with a range of styrenes to yield the corresponding iron(II) aziridino complexes. The aziridine heterocycles can be liberated from the metal concomitant with *N*-functionalization, closing a synthetic cycle for styrene aziridination. This suggests that a catalytic cycle may be in sight, where an important advantage



of this methodology is the ability to selectively functionalize the aziridine nitrogen atom, particularly with a proton, without the need for preformed nitrenes. Additionally, the aziridination reaction does not require very oxidizing conditions, in fact the nitride complexes are poor oxidants, with  $E(\text{Fe}^{\text{IV}}/\text{Fe}^{\text{III}}) < -2.2$  V vs  $\text{Fc}^+/\text{Fc}$ .

#### Publications resulting from this work.

1. Muñoz, III, S.B.; Lee, W.-T.; Dickie, D.A.; Scepaniak, J.J.; Subedi, D.; Pink, M.; Johnson, M.D.; Smith, J.M. "Styrene Aziridination by Iron(IV) Nitrides" *Angew. Chem. Int. Ed.* **2015**, 54, 10600-10603. DOI: 10.1002/anie.201503773