

Solutions for Chemical Hydrogen Storage: Hydrogenation/ Dehydrogenation of B-N Bonds

PIs: Karen Goldberg and Mike Heinekey

**Co-workers: Tony St. John, Brandon
Dietrich, Travis Hebden, Steve Matthews
(partners in the Chemical Hydrogen
Storage Center)**

**Project ID #
STP_17_Goldberg**

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- **Start: FY 05**
- **End: FY 09**
- **80% Complete**

Budget

- **Total project funding**
 - \$1.1 M DOE share
 - \$0.28 M cost share
- **Funding received in FY08**
 - \$246,820
- **Funding for FY09**
 - \$300,000

Barriers

- **System Weight and Volume**
- **H₂ Charging/Discharging Rate**
- **System Cost**
- **Regeneration Processes**

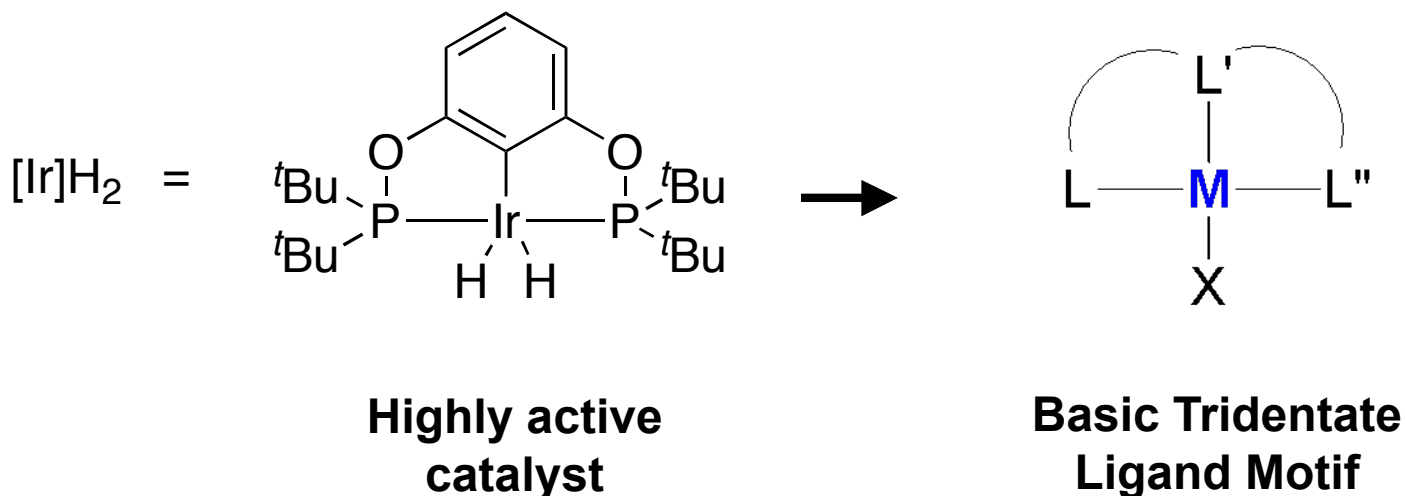
Partners

- **University of Oregon**
- **University of Alabama**
- **Pacific Northwest National Laboratory (PNNL)**
- **Los Alamos National Laboratory (LANL)**

Objectives

- **Develop cost-effective metal catalysts for the dehydrogenation of BN hydrogen storage materials**
 - Focus on cheap widely available non-platinum group metals such as cobalt and iron
- **Optimize catalysts to meet DOE target goals for H₂ discharging rates from BN materials**
- **Collaborate with the U of Oregon to develop systems based on novel CBN materials**
 - Identify and investigate catalysts capable of dehydrogenating both B-N and C-C bonds
 - Investigate the potential of direct regeneration of spent CBN fuels

Approach

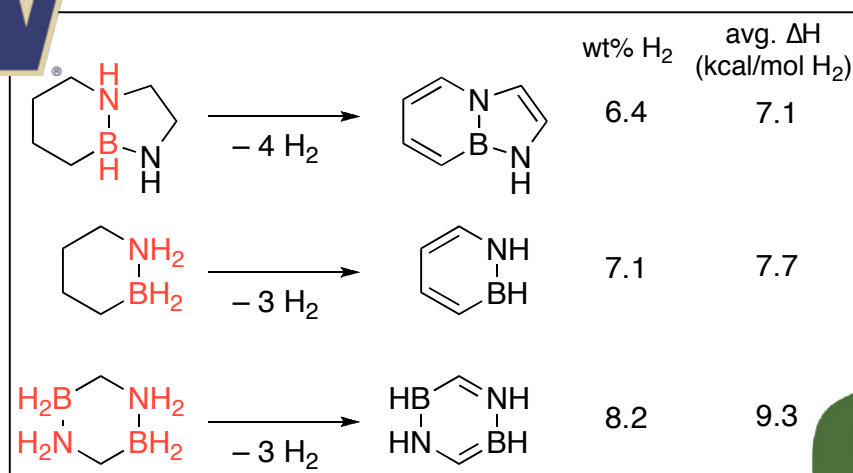


- **Synthesis of new metal catalysts based on the tridentate ligand motif**
 - Replace Ir with inexpensive metal
 - Tune L, L', L'' and X to achieve high activity and catalyst stability

Approach

- Measure rates and extents of hydrogen release from BN and CBN materials
- Investigate systems where spent fuel can potentially be regenerated
 - Identify CBN compounds that have favorable thermodynamics (collaboration with U of Alabama)
 - Screen catalysts with target CBN materials prepared by U of Oregon and investigate rehydrogenation of B-N and C-C bonds.

W



O

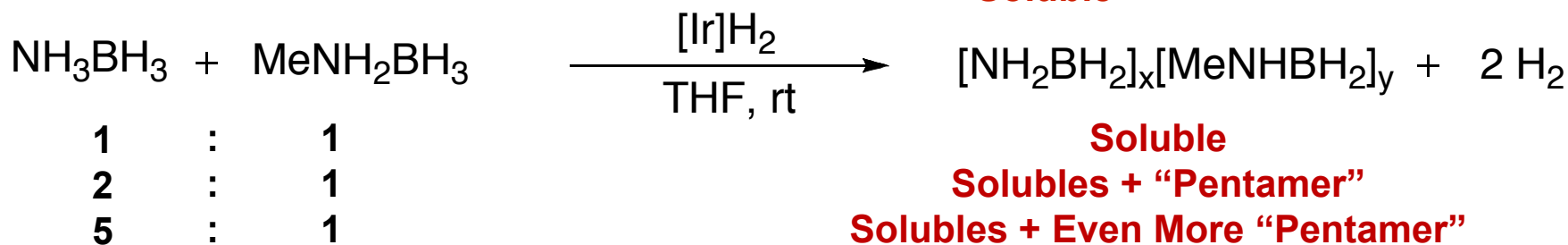
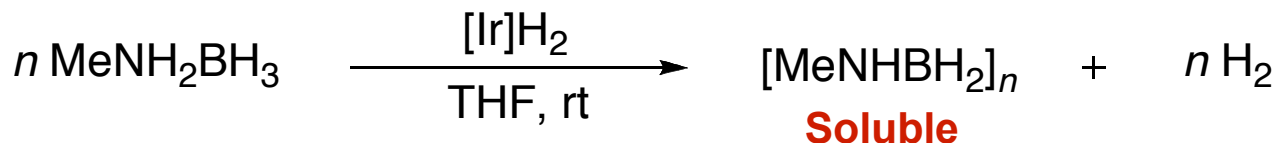
Distinct from Air Products approach

- contains boron
- lower average ΔH
- one CC is replaced by BN
- lower activation energy in some of the steps
- synergistically combines features of ammonia borane and cyclic systems

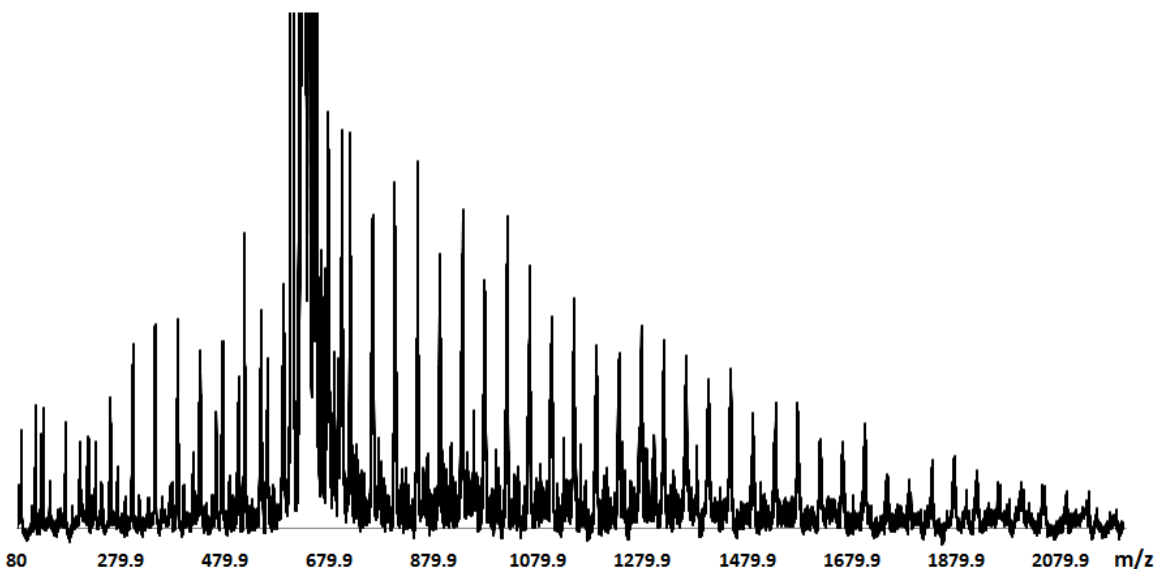
Key Accomplishments for 2008

- **Collaborated with the University of Oregon on CBN materials**
 - Transferred synthetic portion of effort to U of Oregon
 - Began screening CBN materials provided by U of Oregon for dehydrogenation activity with known AB dehydrogenation catalyst
- **Identified soluble products in models of liquid spent fuel: iridium catalyzed dehydrogenation of ammonia borane (AB) and methylamine borane (MeAB) mixtures**
 - Identified soluble products as mixtures of oligomers of varying chain lengths
 - Observed cross-linked products in the mixed AB/MeAB containing both (NH_2BH_2) and $(\text{CH}_3\text{NHBH}_2)$ units
 - Demonstration of an important capability for characterization of liquid spent fuels – Collaboration with LANL
- **Successfully extended highly active (POCOP)Ir motif to a first row metal (cobalt)**
- **Optimized the previously reported cobalt pre-catalyst and targeted more robust ligand motifs**

Identifying Soluble Products in Models of Liquid Spent Fuels



ESI-MS of MeAB Oligomers

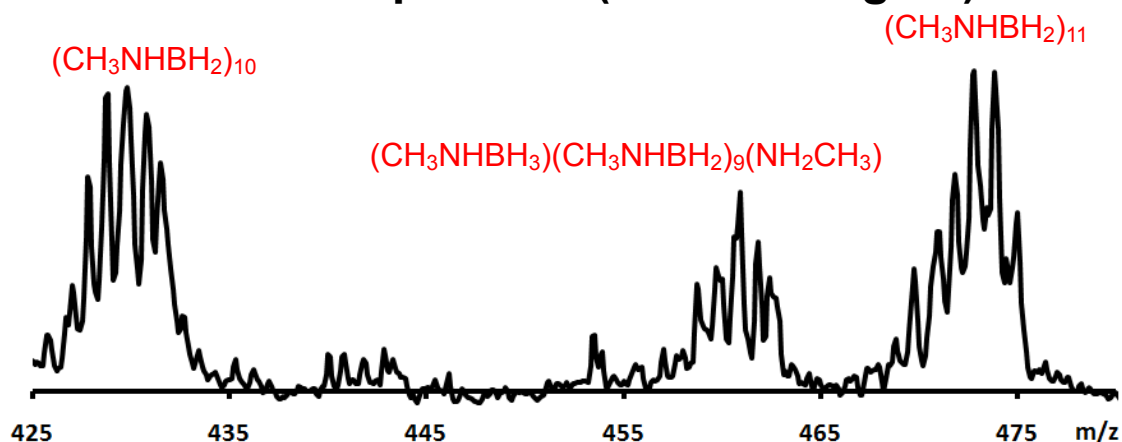


Soluble iridium-catalyzed
dehydrogenation products of
MeAB and mixtures of AB/MeAB
can be identified using Electro-
spray Ionization Mass
Spectrometry (ESI-MS) techniques

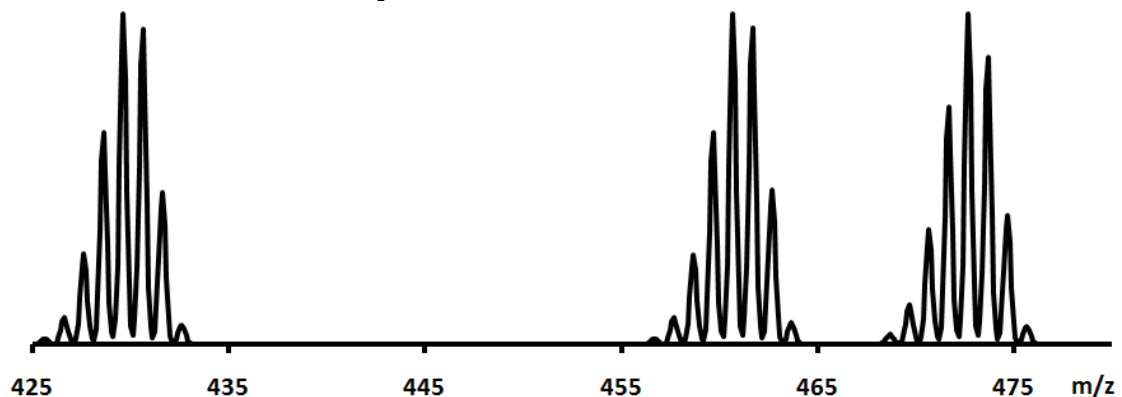
Identifying Soluble Products

- Soluble products are mixtures of oligomers
- Gel Permeation Chromatography (GPC) experiments in collaboration with PNNL confirm oligomeric species
- Concurrent work by Manners *et al.* suggests oligomer / polymer distribution is concentration dependent

Actual ESI-MS Spectrum (selected region)



Simulation of Spectrum

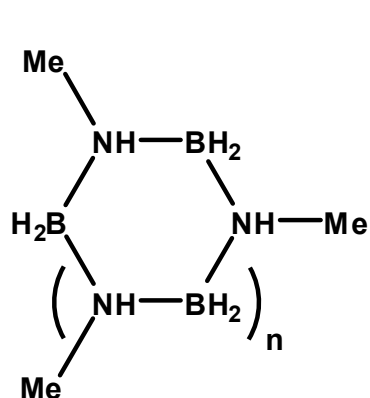


Soluble iridium-catalyzed dehydrogenation products are mixtures of oligomers of varying molecular weights

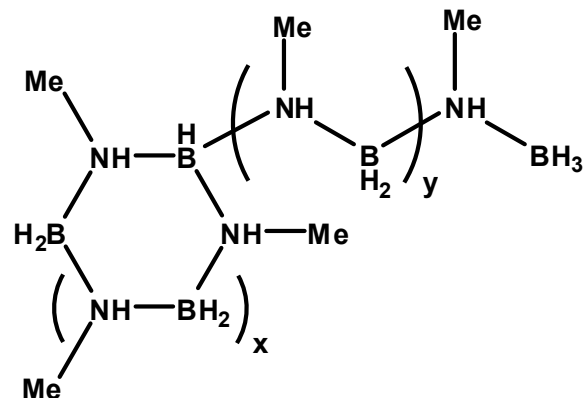
Identifying Soluble Products

MeAB Soluble Products

Cyclic Products -
 $(\text{CH}_3\text{NHBH}_2)_n$

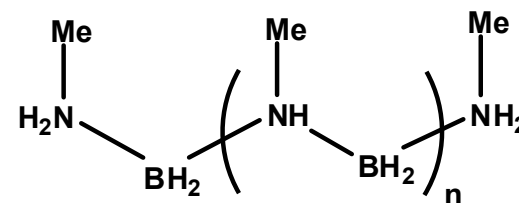


Macrocycles



Cycles with branching

Acyclic Products -
 $(\text{CH}_3\text{NH}_2\text{BH}_2)(\text{CH}_3\text{NHBH}_2)_n$
 (CH_3NH_2)



Linear

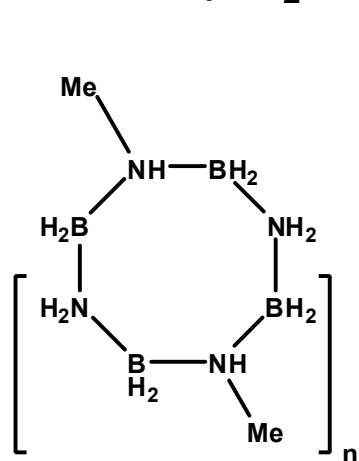
Branched Products
also Possible

Both cyclic and acyclic dehydrogenation products are observed in the MeAB products.

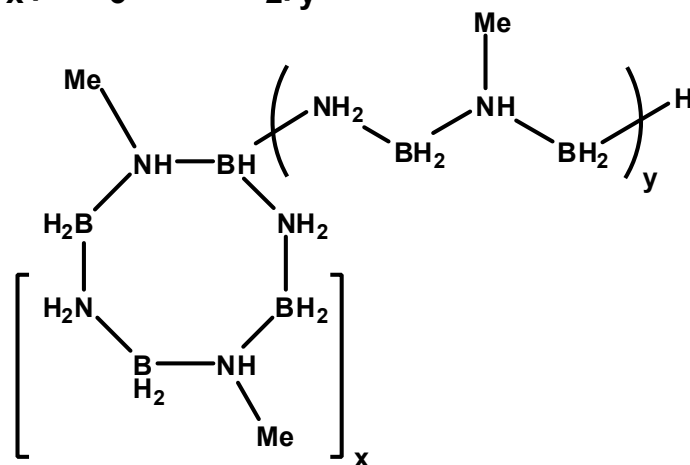
Identifying Soluble Products

Mixed AB/MeAB Soluble Products

Cyclic -

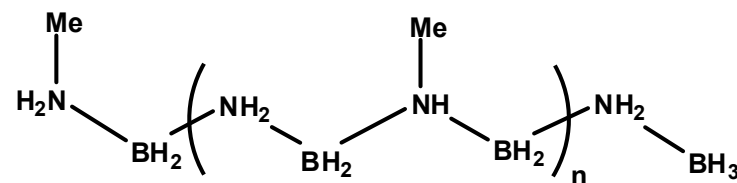
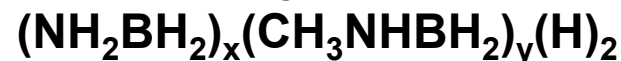


Macrocycles



Cycles with branching

Acyclic -

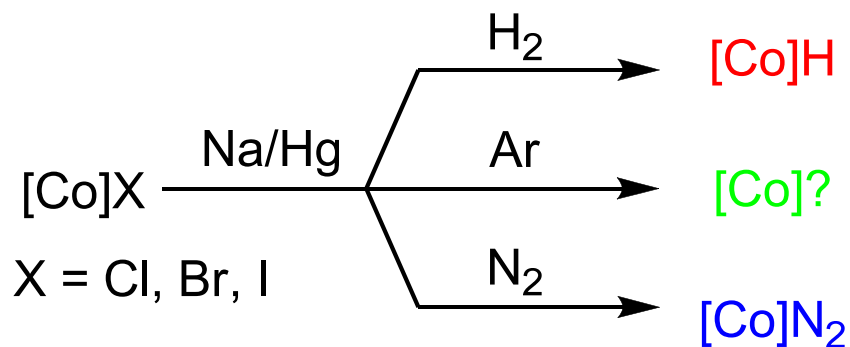
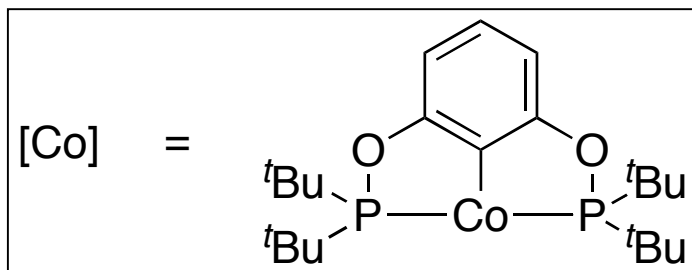


Linear

Branched Products
also Possible

Both cyclic and acyclic dehydrogenation products are observed in the mixed AB/MeAB reactions. Cross-linked products containing both (NH_2BH_2) and $(\text{CH}_3\text{NHBH}_2)$ fragments in a ~1:1 ratio are observed.

Extending (POCOP)Ir to the 1st Row

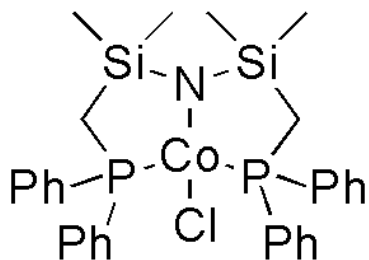


- [Co]H: Reaction with AB afforded minimal dehydrogenation
- [Co]?: Reaction with AB led to dehydrogenation of AB (< 1 eq.) and loss of catalyst activity
- [Co]N₂: Was found to be an active dehydrogenation catalyst for AB. [Co]N₂ was present in solution following the reaction, along with a solid precipitate (pentamer).

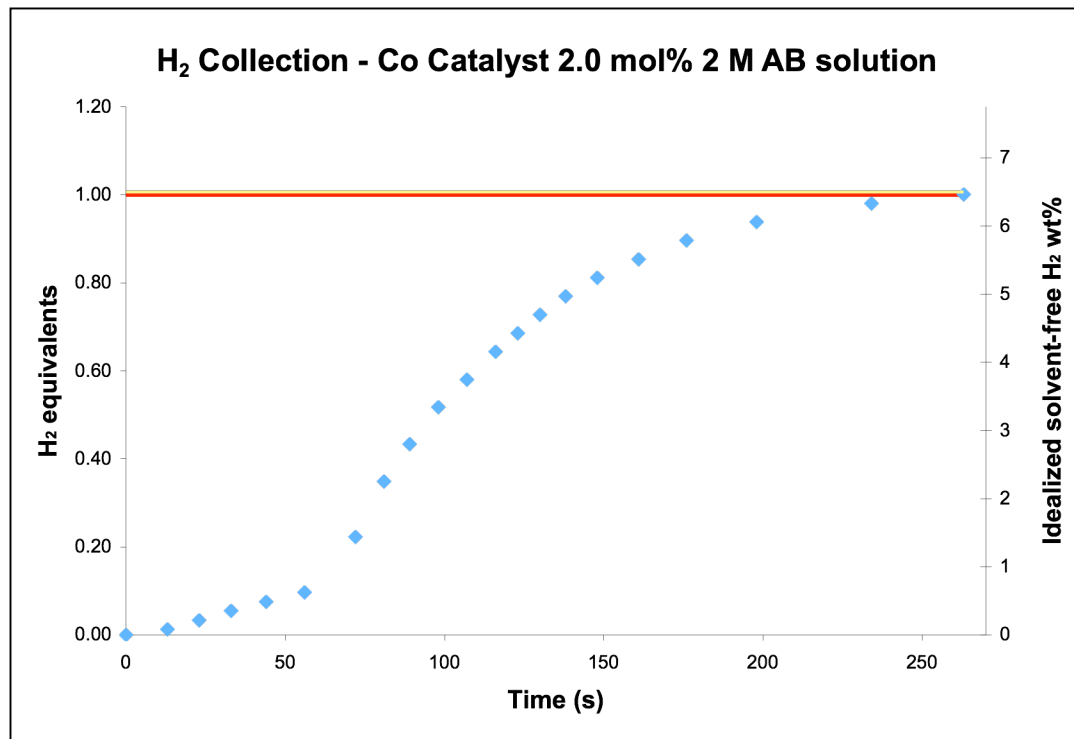
A first row analog of the highly successful (POCOP)Ir catalyst which is active for the dehydrogenation of AB has been identified.

Characterization of the active catalyst and collection of rate data is ongoing.

Optimization of Cobalt Catalyst



•After formation of the active species one equivalent of H₂ is generated within 3 min

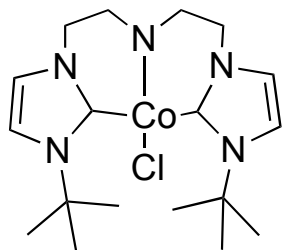


The lifetime of the active catalyst is limited
-Evidence of ligand backbone degradation

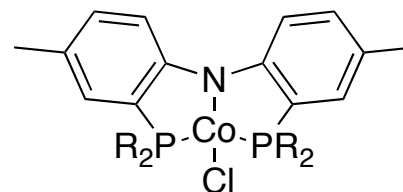
Optimization of cobalt catalyst resulted in dehydrogenation activity approaching the Ir system

Design of More Robust Catalysts

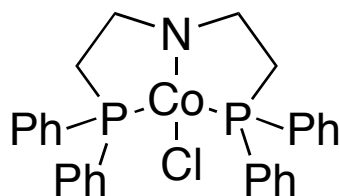
The tridentate pincer ligand motif has shown good activity for AB dehydrogenation in Ir and Co precatalysts.



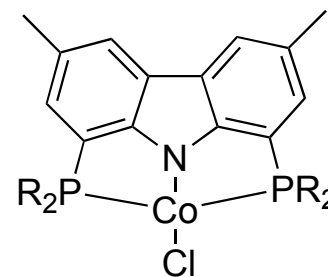
•Carbene based system proved to be an ineffective catalyst



•PNP complex exhibits improved stability at 60 °C



•A potentially more robust analog of the highly active Si containing catalyst

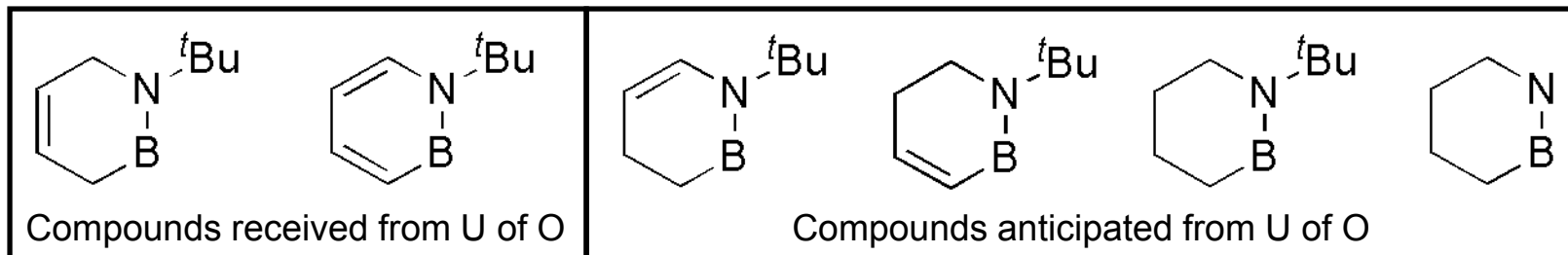


•Carbazole based system may display greater thermal stability

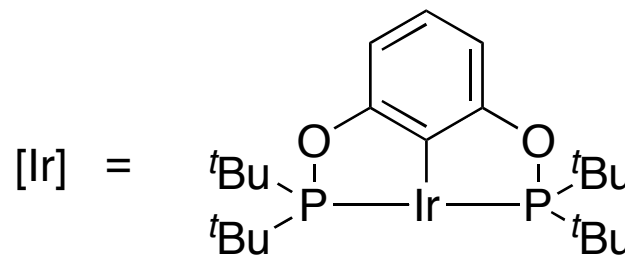
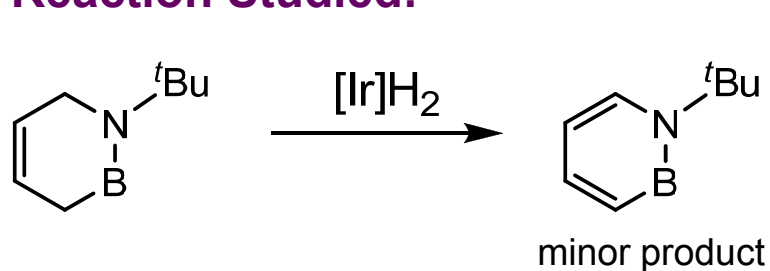
Higher temperatures give improved dehydrogenation. This strategy is being pursued with appropriately designed catalysts

Dehydrogenation of CBN heterocycles

Calculations (U of Alabama) indicate that dehydrogenation of CBN compounds will be endothermic resulting in overall thermodynamics close to thermoneutral. This will allow direct regeneration of the spent material.



Reaction Studied:



**[Ir]H₂ is able to dehydrogenate the received material; yields are low.
Search for useful catalysts of CBN dehydrogenation is currently underway**

Future Work

- **CBN Materials**

- Collaboration with U of Oregon in synthesis, dehydrogenation and rehydrogenation of CBN materials

- **Characterization of liquid spent fuels in collaboration with LANL**

- **Development of new transition metal catalysts**

- Shift metal emphasis
 - Focus has shifted from Ir based catalysts to Co, Fe
- New Ligand Designs
 - Modify current ligand designs to increase dehydrogenation activity of metal complexes and make complexes more robust at higher temperatures
 - Investigate ligands capable of participating in ionic dehydrogenation mechanisms

Collaborations with Center Partners

- **PNNL**
 - GPC experiments with soluble MeAB and mixed AB/MeAB dehydrogenation products
- **University of Oregon**
 - Working closely with Oregon to investigate reactivity of new CBN materials
- **University of Alabama**
 - Collaborated on obtaining calculations of thermodynamics of CBN target fuels

Project Summary

- **Relevance**
 - BN and CBN compounds have significant potential as hydrogen storage materials which can meet DOE goals
- **Approach**
 - Develop catalysts for dehydrogenation of BN and CBN systems
 - Investigate different BN/CBN materials and systems
 - Optimize systems to meet DOE weight and volume, H₂ discharge rate, and system cost targets
- **Accomplishments**
 - Identified soluble products of mixed MeAB/AB systems
 - Synthesized direct 1st row metal analog of highly active Ir system
 - Optimized previously reported highly active Co system
 - Started active collaboration with U of Oregon towards testing new CBN fuels
- **Collaboration**
 - Collaborations with groups at PNNL, LANL, University of Alabama, and University of Oregon
- **Future Work**
 - Develop cheap 1st row metal catalysts with robust ligand backbones
 - Study dehydrogenation of new CBN materials provided by U of Oregon