Solutions for Chemical Hydrogen Storage: Dehydrogenation of B-N and C-C Bonds

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Project ID # ST056

Overview

Timeline

- **Start: FY 05**
- **End: FY 09**
- **Status: Complete**

Budget

- **Total project funding**
  - $1.1 M DOE share
  - $0.28 M cost share
- **Funding received in FY09**
  - $262,900
- **Funding for FY10**
  - No Cost Extension

Barriers

- **System Weight and Volume**
- **H_2 Charging/Discharging Rate**
- **System Cost**
- **Regeneration Processes**

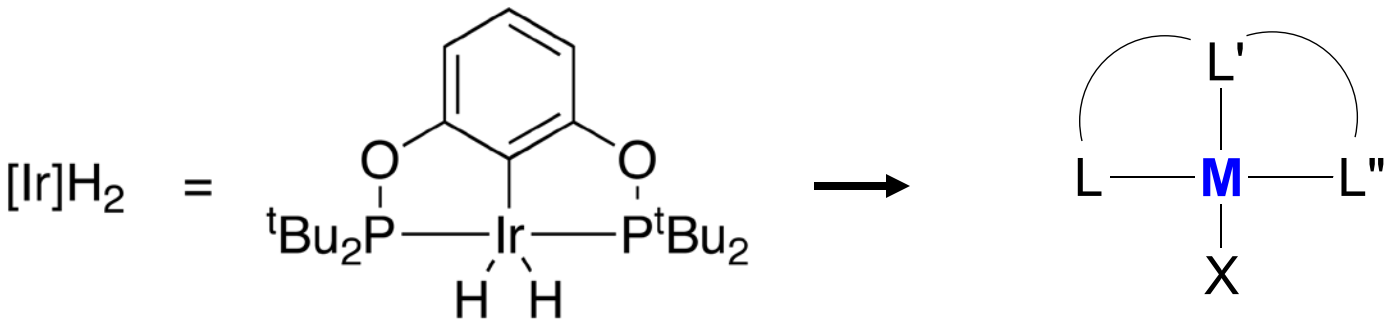
Partners

- **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 inexpensive non-platinum group metals such as cobalt and iron
- **Optimize catalysts to meet DOE target goals for H_2 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



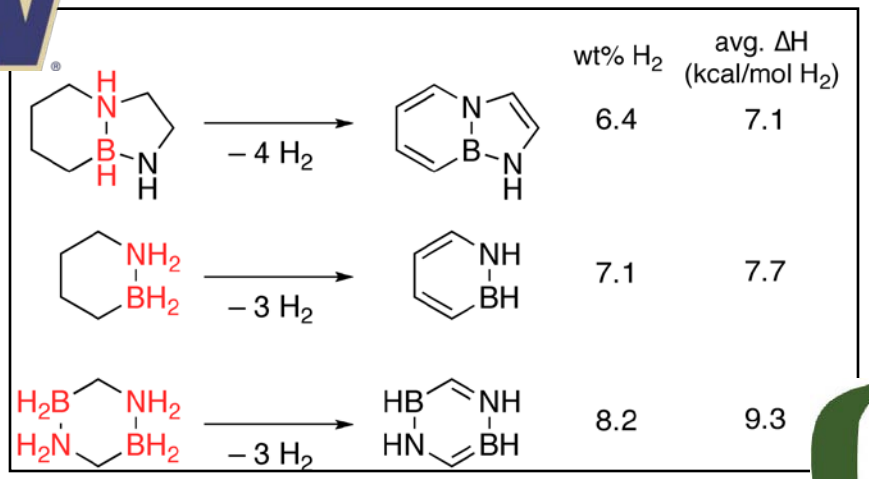
Highly active catalyst

Basic Tridentate Ligand Motif

- **Synthesis of new metal catalysts based on the tridentate ligand motif**
  - Replace iridium 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 model CBN materials prepared by U of Oregon for dehydrogenation of B-N and C-C bonds.



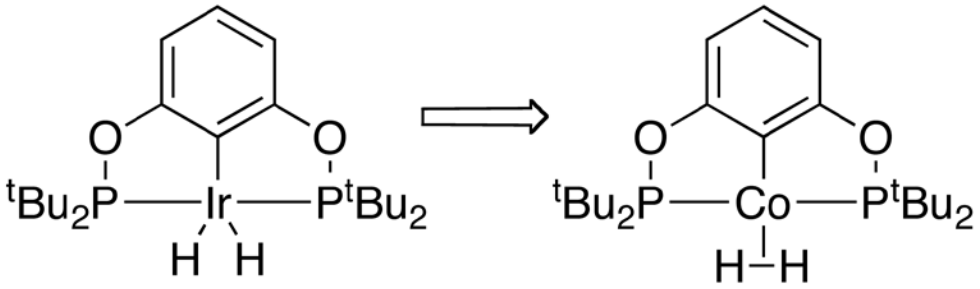
Distinct from Air Products approach

- 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 2009

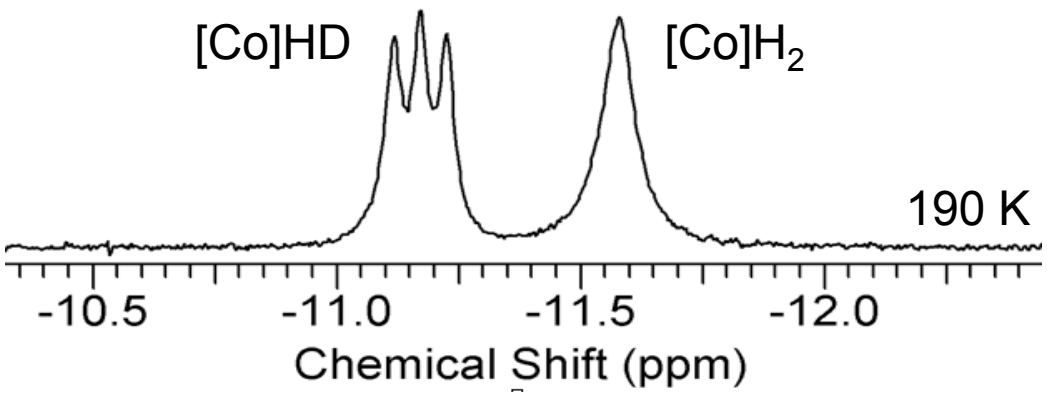
- **Characterized various (POCOP)CoX complexes**
  - Synthesized and characterized the first-row metal analog of the iridium system
- **Explored non-PGM catalyst leads**
  - Focused on synthesizing cobalt complexes
  - Also investigating nickel and iron based systems
- **Collaborated with the University of Oregon on CBN material studies**
  - Received three model CBN compounds that we have begun to study for BN and CC bond dehydrogenation
- **Targeted and began synthesis of potential CBN dehydrogenation catalysts**

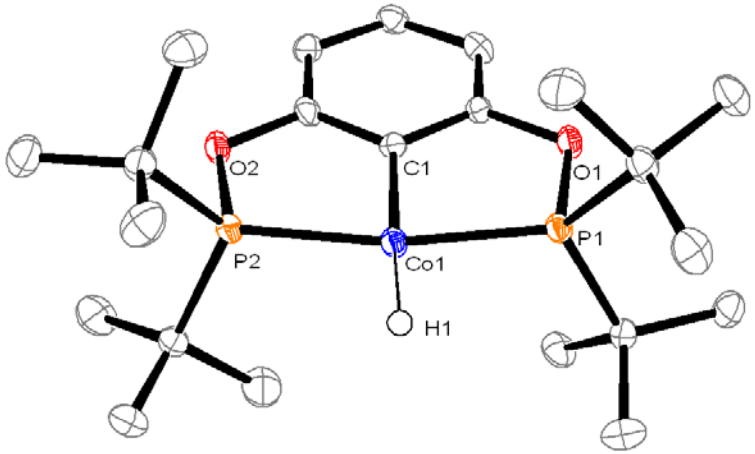
Synthesis and Characterization of (POCOP)CoH_2 and (POCOP)CoH



J_{HD} = 28 Hz, r_{HH} = 0.95 Å

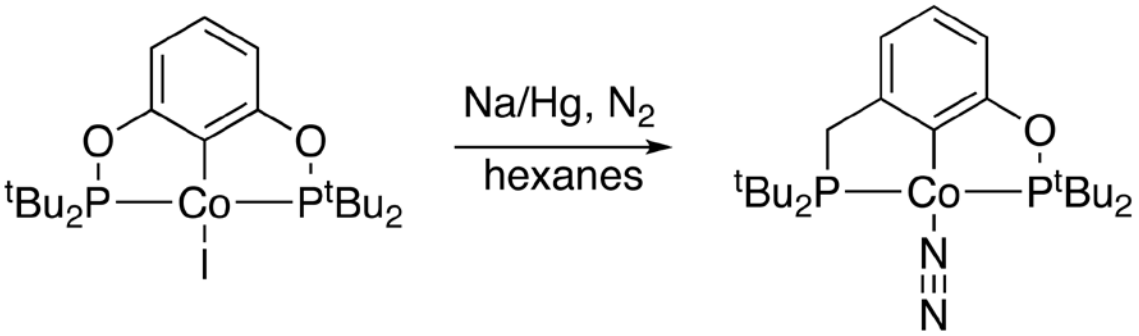
At RT (POCOP)CoH_2 decomposes to (POCOP)CoH





The direct cobalt analog to the iridium system can be synthesized, however, this cobalt species is only stable at low temperatures

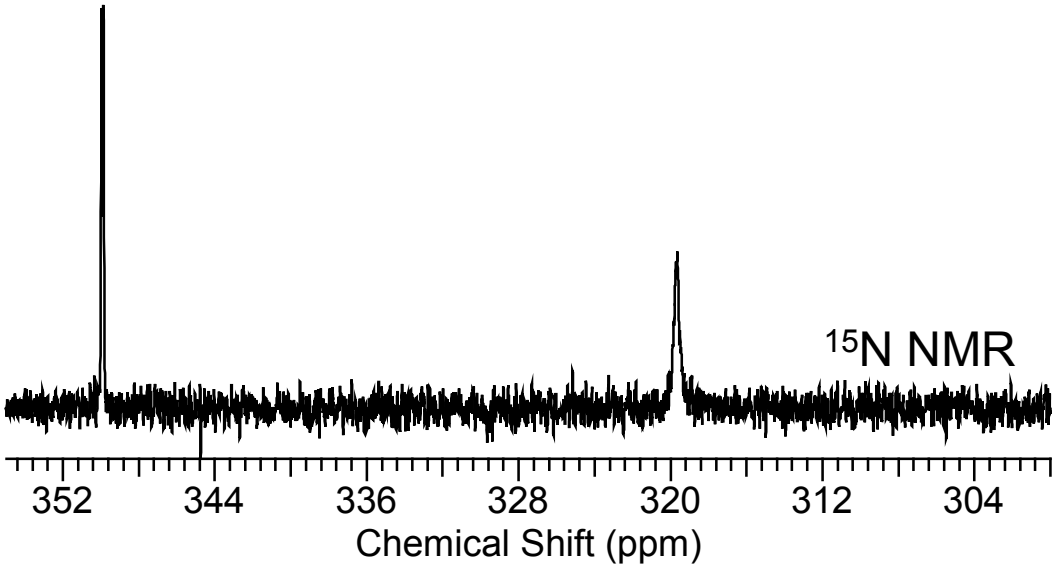
Synthesis and Characterization of $(POCOP)CoN_2$

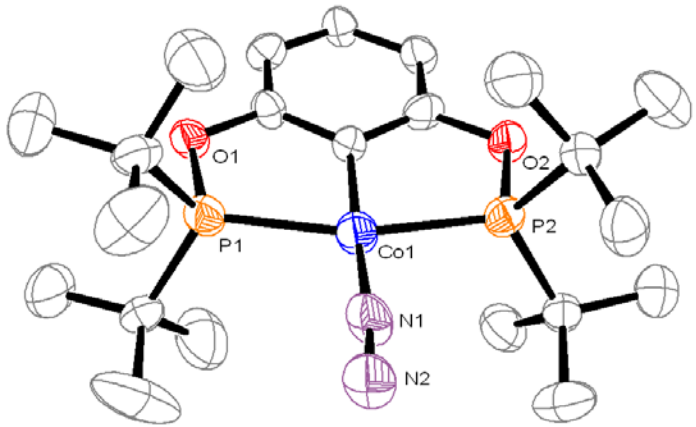


89% yield

$^{14}N_2$ ν_{NN} = 2027 cm^{-1}

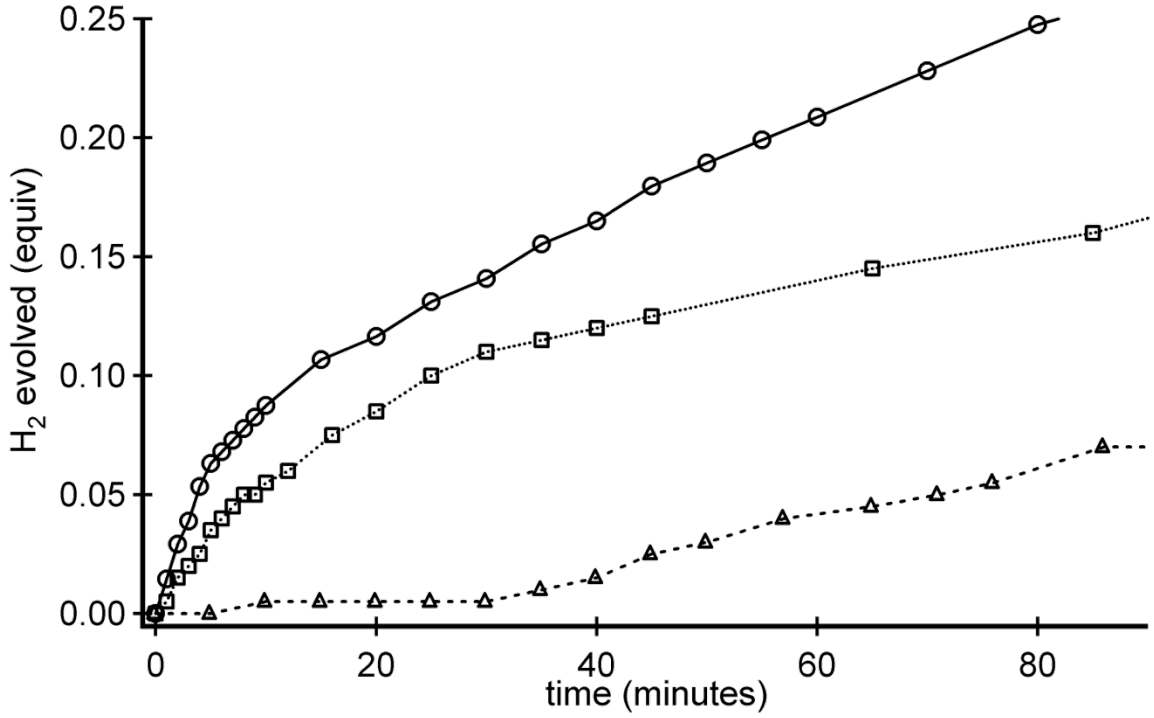
$^{15}N_2$ ν_{NN} = 1960 cm^{-1}

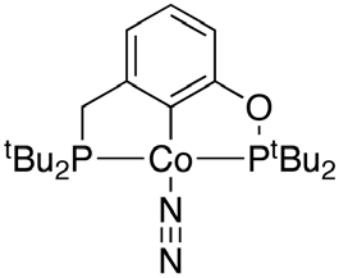


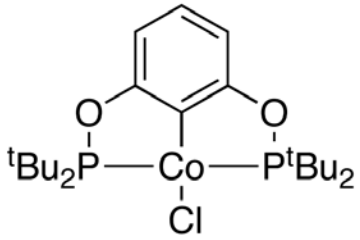


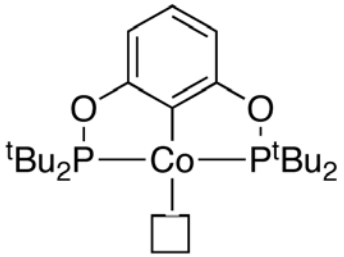
$(POCOP)CoN_2$ can be synthesized in high yield and is stable at RT.

Summary of (POCOP)CoX Reactivity



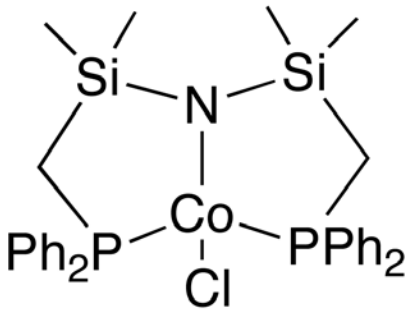




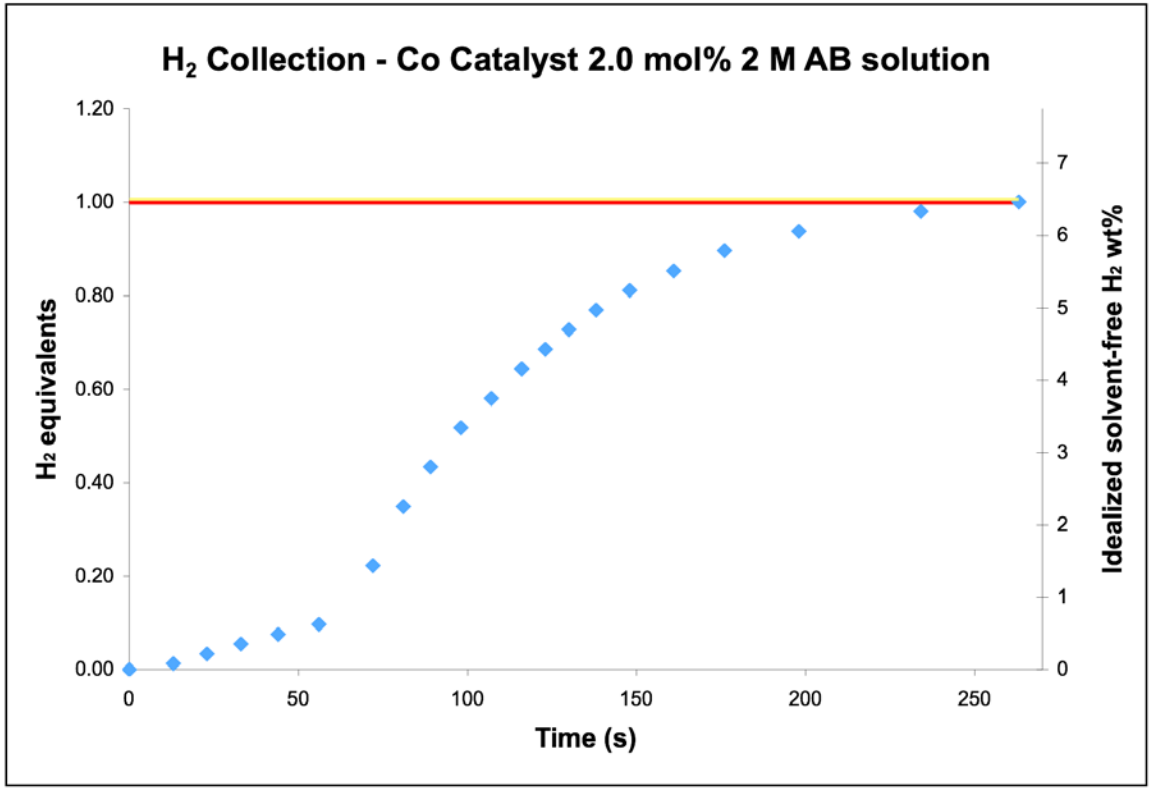


(POCOP)CoH is unreactive with AB and eventually decomposes.
(POCOP)CoN_2 exhibits the best dehydrogention activity, but rate is low.

Previously Reported (PNP)CoCl

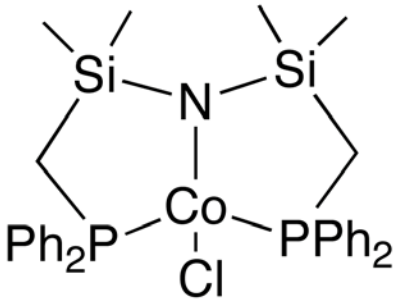


- Fastest reported 1st row metal catalyst
- Decomposes under reaction conditions

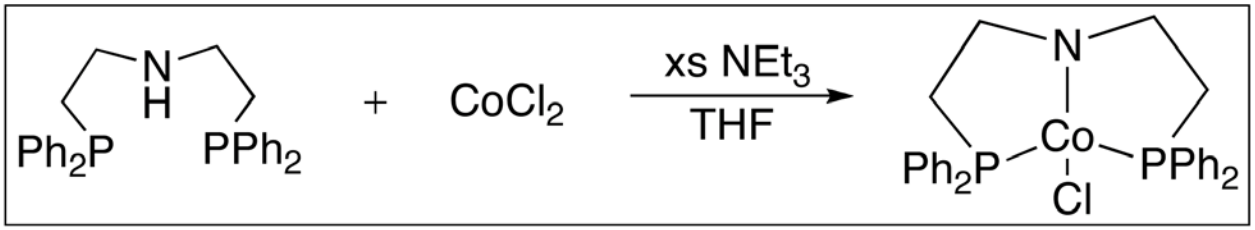


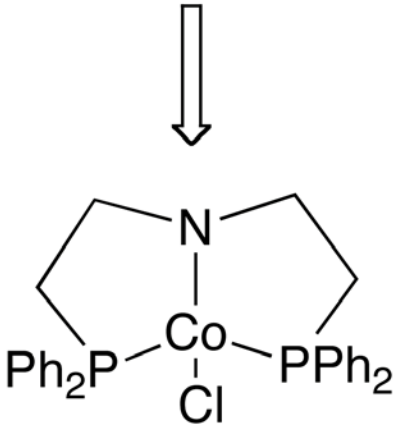
This is the fastest reported first-row metal catalyst for AB dehydrogenation.

Synthesis of a More Robust (PNP)CoX complex

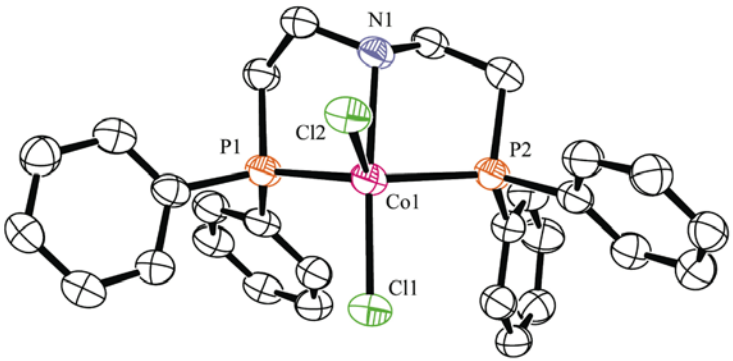


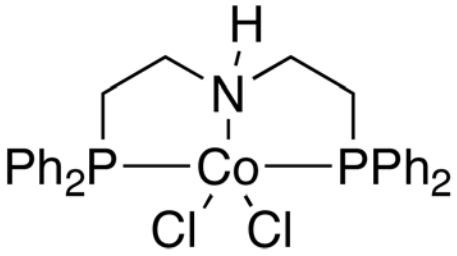
Proposed Synthesis





These reaction conditions led to isolation of the 5-coordinate species

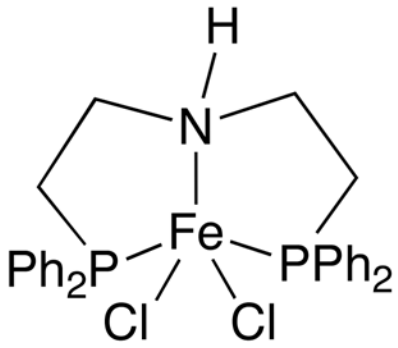


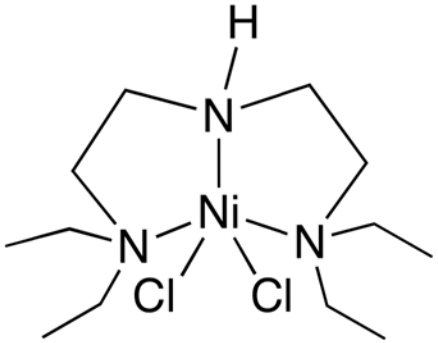


An analog of the (PNP)CoCl system has been synthesized and characterized. Dehydrogenation studies with this material are in progress.

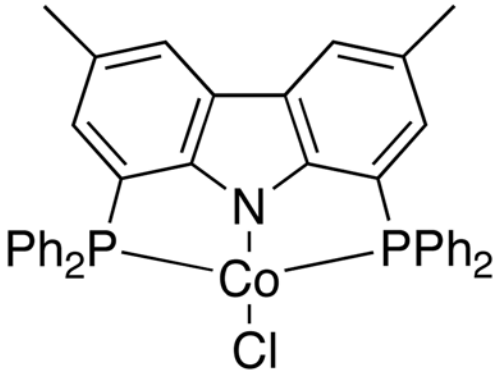
Other non-PGM Catalysts Tested

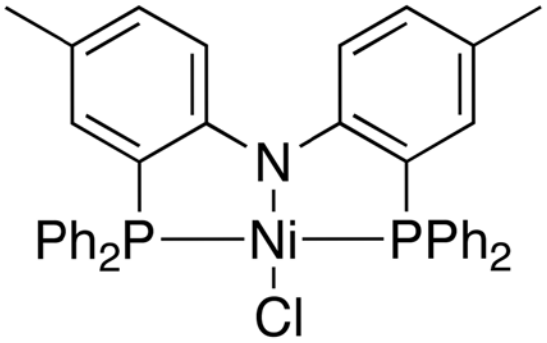
The tridentate pincer ligand motif has shown good activity for AB dehydrogenation in Ir and Co precatalysts.





JACS **1966**, 88(7), 1394



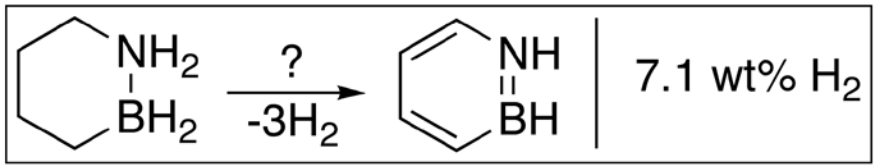


Organometallics **2003**, 22(15), 3007

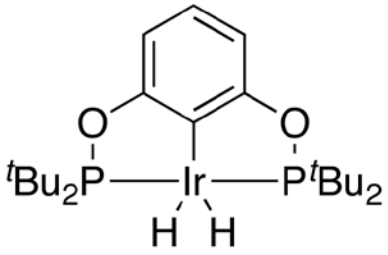
We have synthesized and tested a variety of first-row metal complexes. All complexes exhibit low activity and limited stability as AB dehydrogenation catalysts.

Model CBN Compounds Received from U of Oregon

Target Compound



Initial catalyst studied



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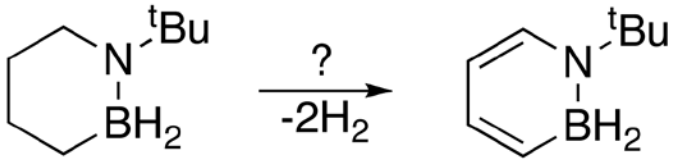
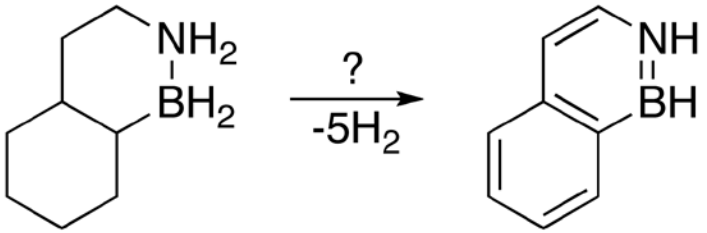
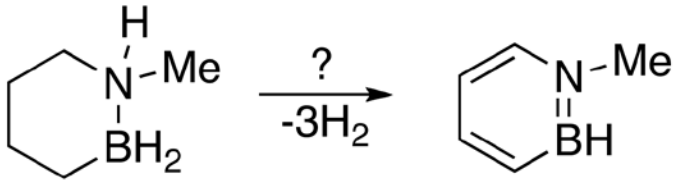
Model Compounds Received and Proposed Dehydrogenation Reactions

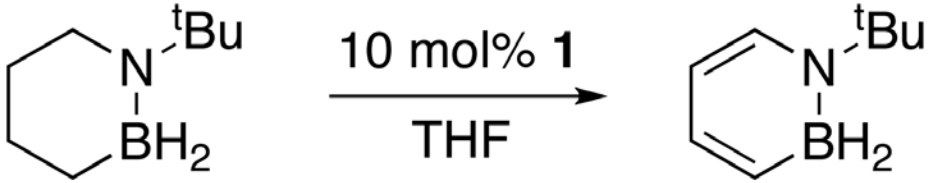




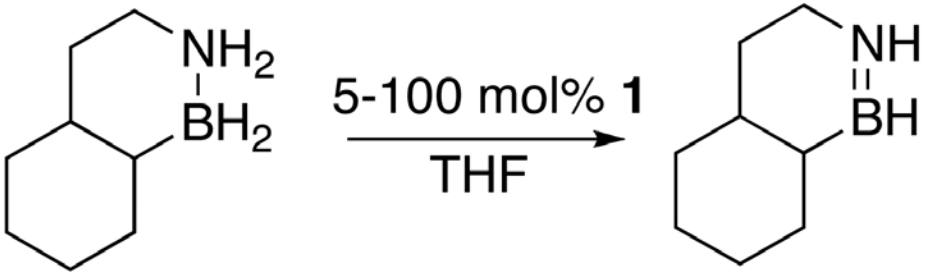


The $(POCOP)IrH_2$ complex is a known dehydrogenation catalyst that has shown the ability to dehydrogenate both BN and CC bonds.

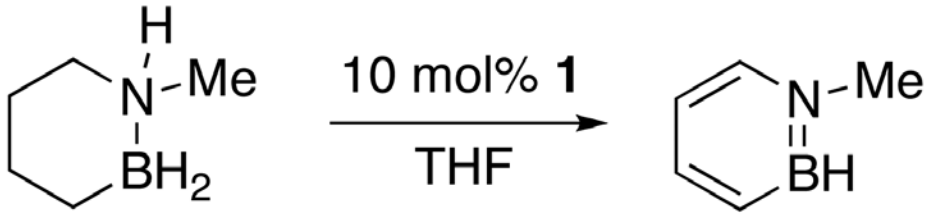
Summary of Observed Dehydrogenation Activity



Only trace amounts of product are observed



One equivalent H_2 is generated, no CC bond dehydrogenation observed



Reaction in progress

The (POCOP)IrH_2 catalyst dehydrogenates these CBN materials. However, only trace CC bond dehydrogenation has been observed.

Future Work

- **CBN Materials**
  - Now focused on developing catalysts for CBN material dehydrogenation
  - Transfer knowledge gained from these studies to explore first-row metal complexes for CBN dehydrogenation

Collaborations with Center Partners

- **University of Oregon**
  - Working closely with Oregon to investigate reactivity of new CBN materials

- **LANL**
  - Collaborating with LANL on the rehydrogenation of spent fuel from AB dehydrogenation.

Project Summary

- **Relevance**
  - BN compounds have significant potential as hydrogen storage materials which can meet DOE goals
- **Approach**
  - Develop catalysts for dehydrogenation of BN systems
  - Investigate different BN materials and systems
  - Optimize systems to meet DOE weight and volume, H_2 discharge rate, and system cost targets
- **Accomplishments**
  - Characterized 1st row analogs of the (POCOP)Ir catalyst
  - Modified the fastest known first-row metal catalyst for better stability
  - Collaborated with the U of Oregon on development and testing of CBN materials
  - Targeted potential CBN dehydrogenation catalysts
- **Collaboration**
  - Collaborations with groups at the University of Oregon and LANL
- **Future Work**
  - Develop CBN dehydrogenation catalysts