

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

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Project ID # **ST10**

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Project Overview

Timeline

- Start: FY 05
- End: FY 09
- 60% Complete

Budget

- Total project funding
 - \$1.3 M DOE share
 - \$0.33 M Contractor share
- Funding received in FY07
 - \$250K
- Funding for FY08
 - \$250K

Barriers

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

Partners

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

Objectives

Center-wide effort directed toward the use of amine boranes (BN materials) as on-board vehicular hydrogen storage materials

UW Project Objectives are:

- **Develop cost-effective metal catalysts for the dehydrogenation of BN hydrogen storage materials**
 - *Utilize inexpensive and widely available system components*
- **Optimize catalysts to meet DOE target goals for H₂ discharging rates from BN materials**
 - *Achieve rapid rates of dehydrogenation at mild temperatures*
- **Identify and develop new BN materials to address challenges for automotive H₂ storage materials**
 - *Materials must meet DOE gravimetric and volumetric H₂ density goals*
 - *Optimal materials will be those for which the dehydrogenated (spent) fuel can be directly regenerated on-board by reaction with hydrogen*

Key Accomplishments of Past Year

UW Objectives for past year:

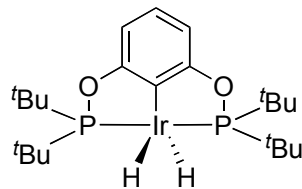
- Use rational design methods to improve stability and activity of non-precious metal catalysts for ammonia borane (AB) dehydrogenation
- Evaluate methylamine borane (MeAB) and mixed AB:MeAB systems for potential of direct regeneration of spent fuel
- Develop viable targets for alternative BN materials

Summary of UW Accomplishments for past year:

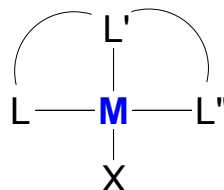
- Demonstrated success of rational ligand modification in significantly improving stability and activity (by 20-fold) of a cobalt catalyst.
- Found that a tridentate ligand design is valuable in catalyst stability and activity
- Demonstrated that the enthalpies of dehydrogenation of MeAB and 1:1 AB/MeAB mixtures are too exothermic to allow direct regeneration of spent fuel (collaboration with PNNL)
- Downselected AB:MeAB liquid mixtures
- Found with straight chain CBN material that BN dehydrogenation occurs rapidly but C-C bond is not affected.
- Identified and have begun synthetic development for new CBN targets which are predicted to have more favorable thermodynamics for on-board regeneration of spent fuel (collaboration with U of Alabama)

Approach Overview

- Rationally Design Lower Cost Metal Catalysts for AB Dehydrogenation

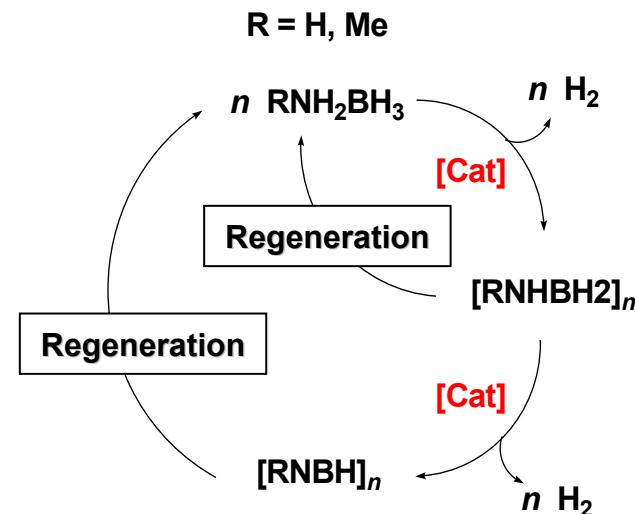


Highly active
Ir catalyst



- Replace Ir with inexpensive M
- Tune L, L', L'' and X for high activity and catalyst stability

- Measure rates and extents of hydrogen release from BN materials with different catalysts
- Determine viability of direct recharging of spent fuel with H₂ of different BN materials (enthalpy measurements, collaboration with PNNL)
- Identify, prepare and study new BN materials which approach DOE weight targets and for which the spent fuel can be easily recharged (collaboration with U of Alabama)

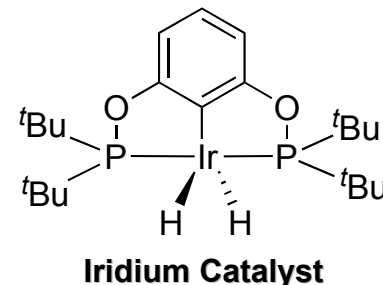
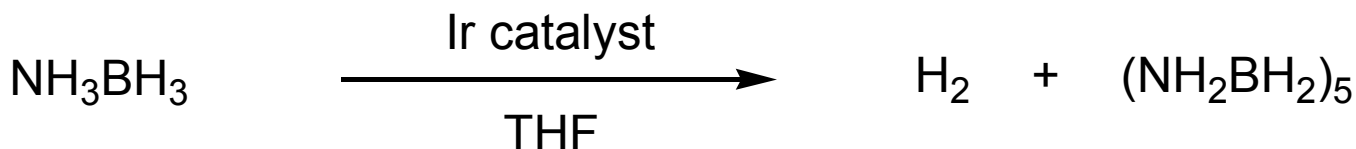


Results from the Past Year

- **Rational design of low-cost catalysts for dehydrogenation of BN materials**
- **Consideration of AB and MeAB materials for on-board hydrogen storage and issues of regeneration**
- **New CBN Materials - Towards Direct Regeneration**

Previous Work In Brief:

Dehydrogenation of BN compounds using an Iridium Catalyst



- **Utilization of Iridium catalyst for dehydrogenation of BN compounds**

- **Benefits**

- Fastest reported catalyst for dehydrogenation of AB
- Dehydrogenates a variety of BN compounds at similar rates to form oligomeric products
 - AB - *insoluble* oligomeric product
 - MeAB – *soluble* oligomeric/polymeric product
 - 1:1 AB/MeAB – *soluble* cooligomer/copolymer product
- Rapid reaction allows for experimental determination of thermodynamics for BN materials

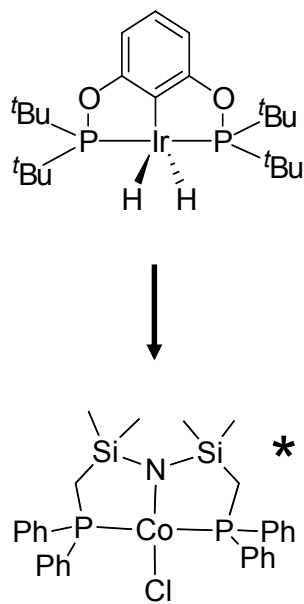
- **Drawbacks**

- Iridium is expensive and availability is limited
- Only 1 equivalent of H₂ is released

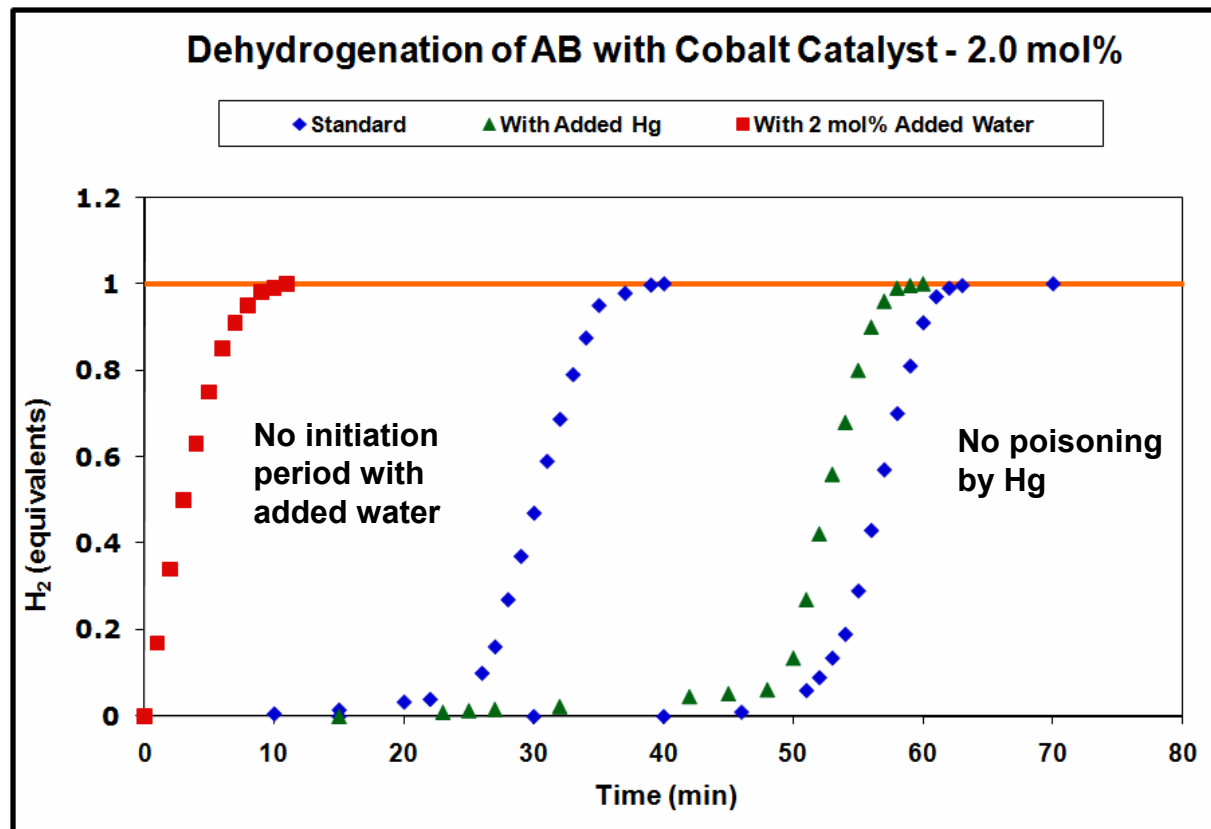
Iridium catalyzed dehydrogenation is still the fastest reported and within an order of magnitude of meeting DOE targets for discharging rate

Key will be to use highly successful Ir catalyst to guide the design of lower cost catalysts using more widely available metals

Rational Catalyst Design: Dehydrogenation of AB with Co Analog of the Ir Catalyst



* Co compound reported by Fryzuk, 1998



- One equivalent of H₂ is released within 10 min at RT
- Catalyst decomposes under reaction conditions at 60 °C

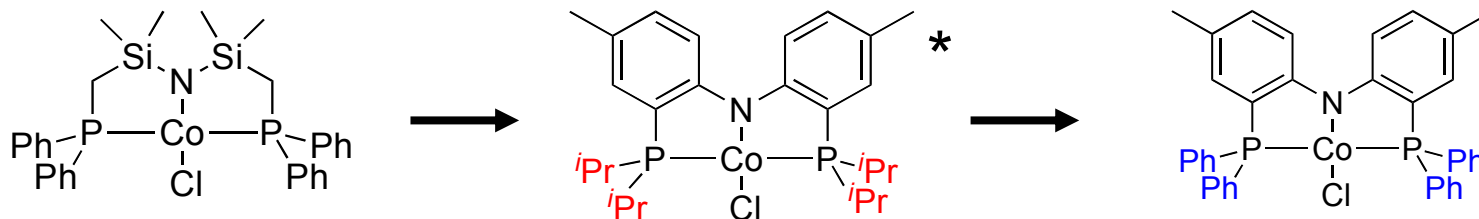
Demonstrated high activity for AB dehydrogenation using a cheaper first-row transition metal analog to the iridium catalyst

Co catalyst decomposes at 60 °C – More robust catalysts are needed

Rational Catalyst Design:

Synthesis of a more robust cobalt catalyst and subsequent ligand modification to increase reactivity

Modifying ligands can lead to increased stability and reactivity



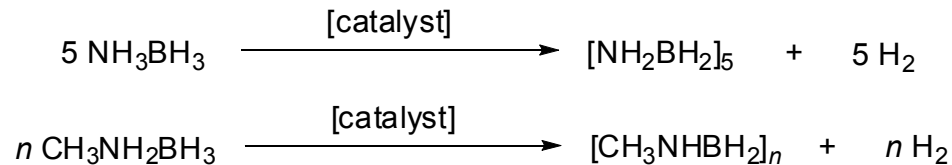
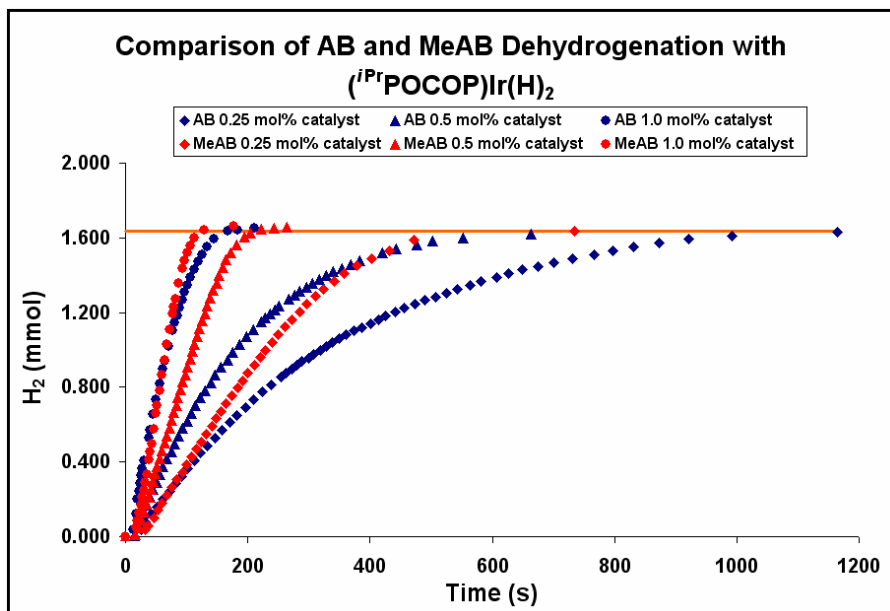
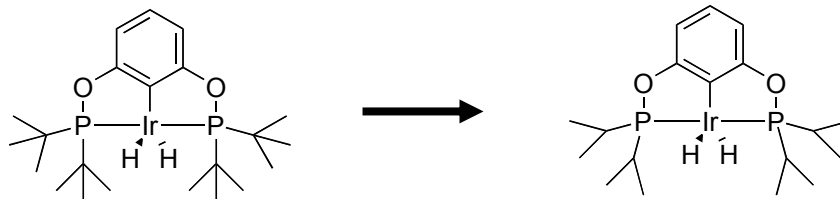
AB dehydrogenation	Si-N-Si	<i>iPr</i>	Ph
Equivalents H ₂ Generated	One	One	One
Stability at 60 °C - Reaction Conditions	Unstable	Stable	Stable
Induction Period	Variable	None	None
Reaction Time - RT	15 min	48 hrs	6 hrs
Reaction Time - 60 °C	-	24 hrs	70 min

Rational ligand modification was used effectively to increase stability of catalyst under high temperature reaction conditions. Further ligand modification was used to increase activity 20-fold.

* Mendiola 2006

Rational Catalyst Design: Changing Sterics Affects Reactivity

Modifying sterics of ancillary groups on ligands influences the kinetic dependence on different substrates

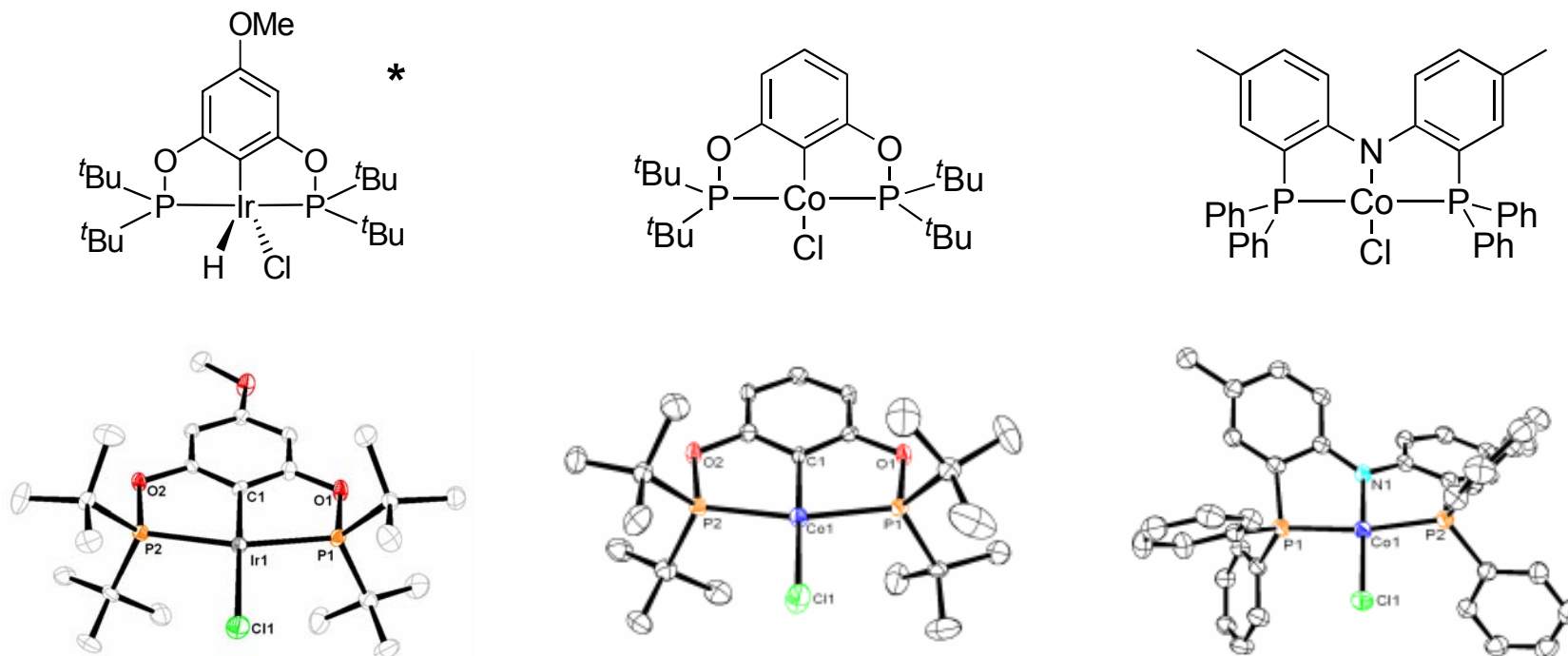


	AB	MeAB
$(tBuPOCOP)Ir(H)_2$	First-Order in AB	First Order in MeAB
$(iPrPOCOP)Ir(H)_2$	First-Order in AB	Zero-Order in MeAB

Changing the steric bulk of the ligand on the catalyst can affect the kinetic behavior of the reaction with different BN substrates

Structures of Cobalt Catalysts: Metal Center Environments Similar to Iridium

Determined specific ligand motif may be key to reactivity



*Brookhart 2004

Several metal complexes which are active catalysts for AB dehydrogenation share a similar tridentate pincer ligand framework. Continued development of catalysts with this basic ligand design is a promising path

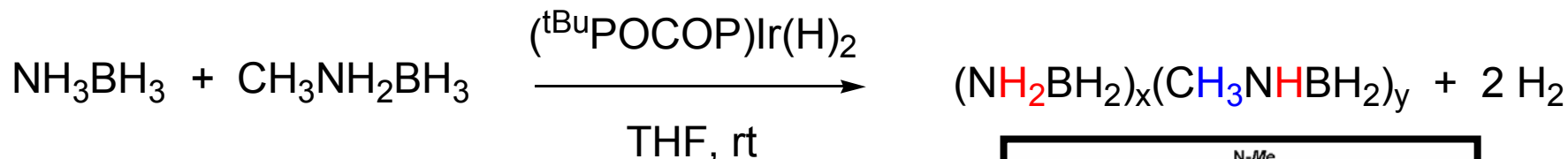
Rational Catalyst Design: Key Accomplishments

- **Identified a cobalt catalyst that approaches activity of iridium catalyst but is not stable at elevated temperatures**
- **Utilized rational catalyst design to identify a more robust cobalt catalyst, however reduced activity was observed**
- **Synthesized a cobalt complex with a modified ligand structure to obtain a similarly robust catalyst that showed a 20-fold increase in reactivity and is within two orders of magnitude of iridium catalyst rate**
- **Recognized the tridentate ligand structure of these metal complexes may play an important role in catalyst activity**
 - **Demonstrated that modifications of ancillary groups on the tridentate ligands can change activity and kinetic behavior with different substrates**

Addressing Oligomer Solubility: Mixed AB/MeAB Dehydrogenation Reactions

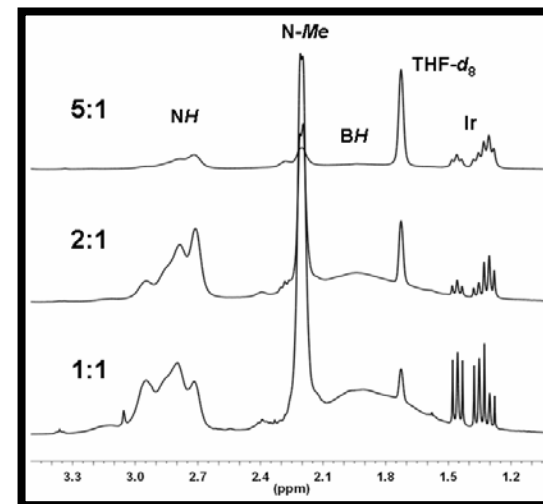
Last year showed MeAB and 1:1 AB:MeAB gave soluble oligomeric products....

Question: Can we increase overall weight % by using higher ratios of AB:MeAB and still get soluble oligomers?



1 : 1
2 : 1
5 : 1

Different oligomers are produced but a 1:1 ratio of dehydrogenated AB/MeAB is maintained regardless of initial ratios of AB and MeAB which are present.



In each case integrations show a ratio of 3 NH protons to 3 CH protons

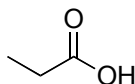
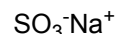
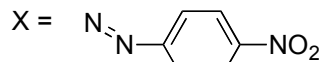
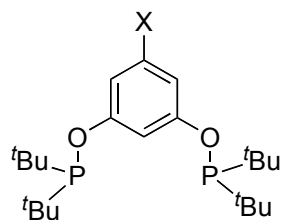
Discovered that the AB/MeAB ratio in the soluble co-oligomer product is limited to 1:1 with iridium catalyst

Addressing System Gravimetric Density:

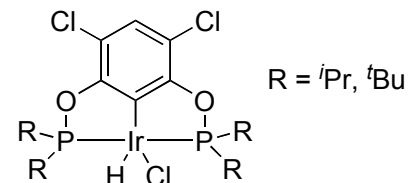
Investigation of Catalysts for the Dehydrogenation of Liquid AB/MeAB Mixtures



Efforts to develop soluble catalysts for this reaction:



Polar ligand targets



New Ir complexes

Path was downselected as syntheses of these polar ligand targets were challenging and focus in center shifted away from liquid AB:MeAB mixtures

Development of catalysts soluble in neat AB/MeAB mixtures has been halted, however, similar strategies may be needed in the future for Co catalysts with CBN materials currently under development

Feasibility of Direct Regeneration

Thermodynamic Studies

Using fast Ir catalysts, DSC calorimetry experiments were performed to evaluate enthalpies of dehydrogenation
(In collaboration with PNNL)

	AB (Previous Results)	MeAB	AB:MeAB (1:1)
ΔH (kcal·mol ⁻¹) (2.5 mol% Ir at 30 °C)	-6.7 ± 0.6	-6.8 ± 0.6	-6.7 ± 0.1

Dehydrogenation of AB and MeAB is too exothermic to allow direct regeneration – New BN materials would be required

Use of AB and MeAB as hydrogen storage materials would require the development of off-board regeneration techniques

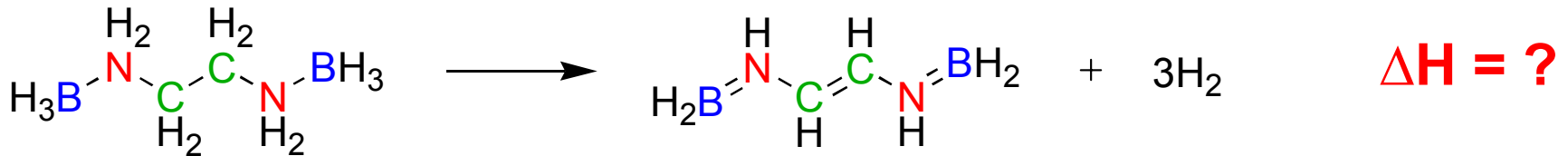
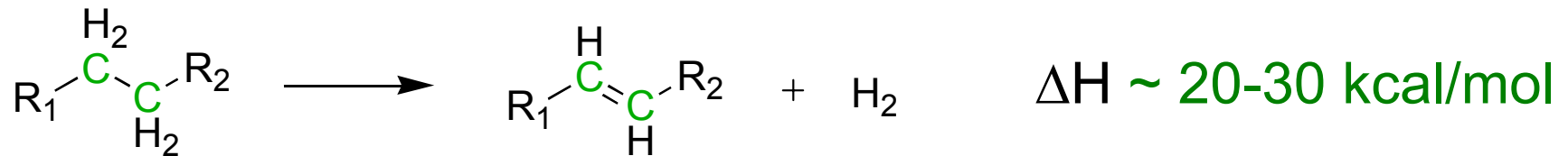
Evaluation of the potential for direct regeneration of spent BN hydrogen storage materials is feasible with fast iridium catalyst and this technique can be used for general screening of BN materials.

AB and MeAB

Key Accomplishments

- **Demonstrated the soluble AB/MeAB copolymers only form in a 1:1 ratio with iridium ^tBuPOCOP catalyst**
- **Downselected development of highly polar ligands for liquid AB:MeAB mixtures**
- **Determined that MeAB and mixed AB/MeAB dehydrogenation is too exothermic for direct regeneration of spent fuel**

CBN Materials

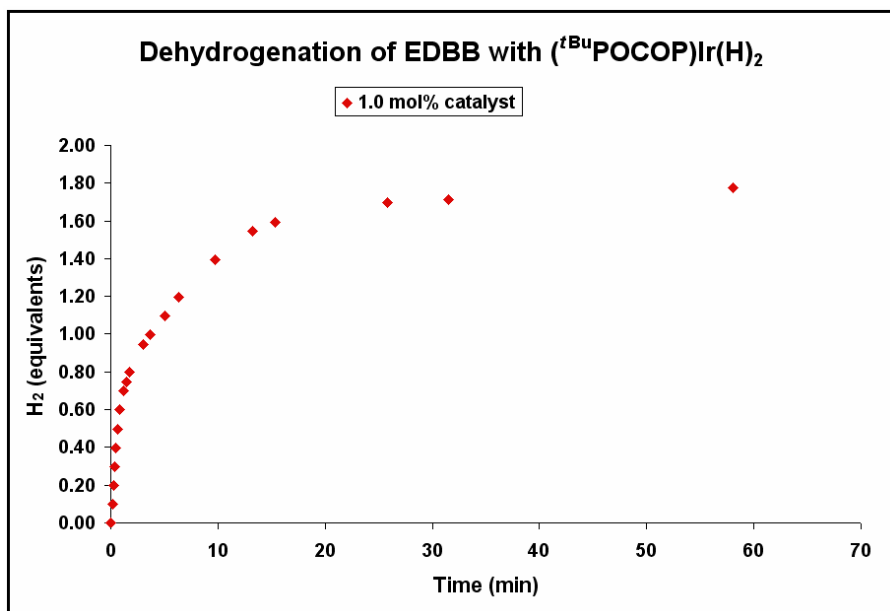
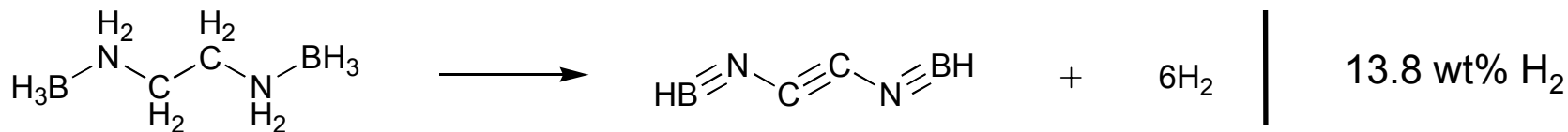


Combining *exothermic* dehydrogenation of B-N bonds with *endothermic* dehydrogenation of C-C bonds may lead to more favorable thermodynamics for regeneration

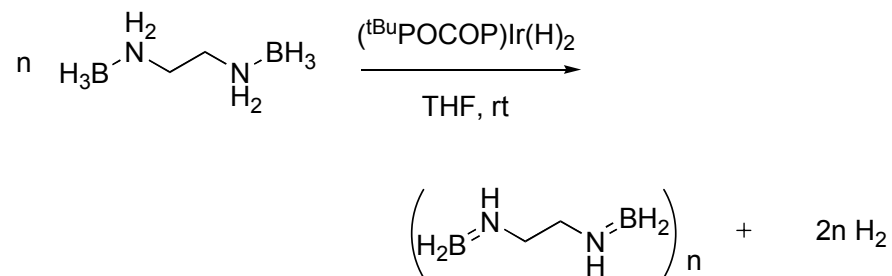
CBN systems where both B-N and C-C bonds undergo dehydrogenation could provide hydrogen storage materials which can be regenerated directly on-board the vehicle with molecular hydrogen.

Towards Favorable Thermodynamics

CBN Materials - Ethylenediamine Bisborane (EDBB)



Observed:

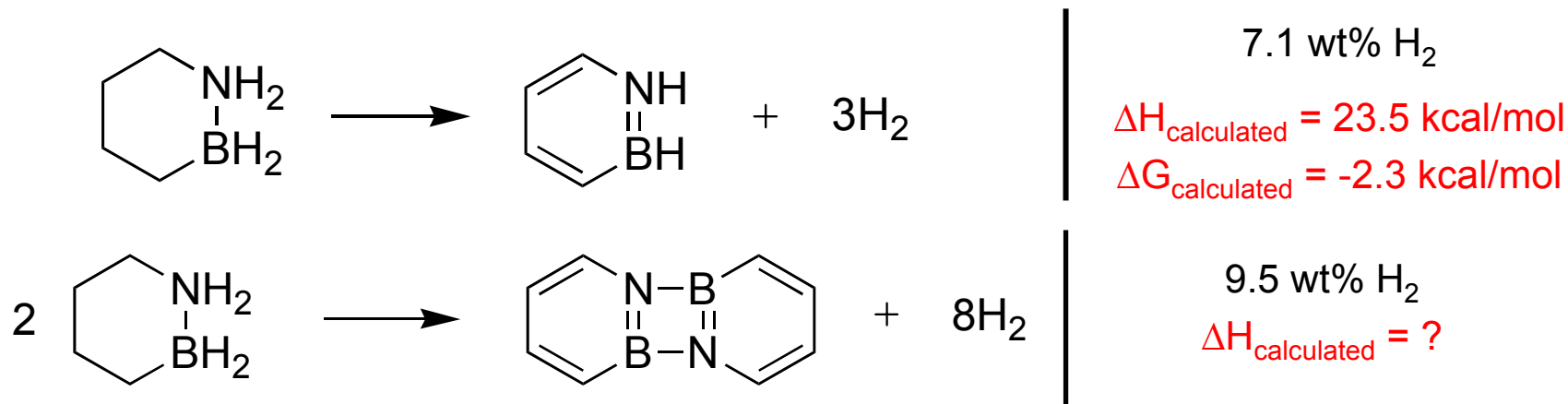


- Only 2 equiv of H₂ per substrate molecule
- No dehydrogenation of C-C Bond

**C-C bond dehydrogenation was not observed in this system.
Further efforts will focus on systems where other factors may favor C-C
bond dehydrogenation**

Towards Favorable Thermodynamics

CBN Materials - 1,2-azaboracyclohexane



•1,2-azaboracyclohexane

- Mixed CBN material that may activate C-C bond toward dehydrogenation
- Has the potential to be directly regenerated**
 - Center partners (U of Alabama) have calculated the thermodynamics of dehydrogenation using G3MP2 modeling at 298 K
- Synthesis of C₄H₁₂BN is at the last step of a multi-step procedure

Mixed CBN compounds should allow the coupling of exothermic B-N dehydrogenation with endothermic C-C dehydrogenation for more favorable thermodynamics

Cyclic CBN structures may promote C-C bond dehydrogenation due to increased resonance stability of product

Towards Direct Regeneration: Key Accomplishments

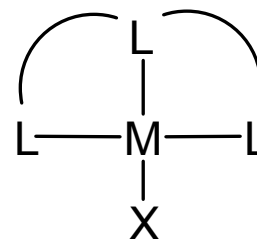
- **Developed concept of combining exothermic B-N dehydrogenation with endothermic C-C bond dehydrogenation to approach desirable thermodynamics to accommodate direct rehydrogenation of spent fuel**
- **Established experimentally that direct conjugation of C-C bond to B-N bond is not enough to promote C-C bond dehydrogenation**
- **Targeted new CBN material with a structure that should lead to more facile dehydrogenation of C-C bonds**
- **Collaborated with U of Alabama to obtain computational insight into the thermodynamics of dehydrogenation of CBN compounds**
- **Developed synthetic methods to obtain novel CBN targets with potential for direct rehydrogenation of spent fuel**

Future Work

Rational Design of New First-Row Metal Catalysts Development of New CBN Materials

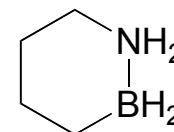
- **Continued development of metal complexes using promising tridentate pincer-ligand motif**

- Ligand modification of cobalt catalysts will be pursued with goal to approach and ultimately exceed activity of iridium catalyst
- Continue efforts to develop new analogues using inexpensive metals



- **Exploration of materials designed for more facile regeneration of spent materials**

- Concentrate on CBN materials as dehydrogenation of C-C bonds in addition to B-N should lead to more favorable thermodynamics

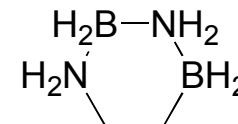


- **Identify most promising targets**

- Collaborate with center partners (U of Alabama) to identify the most promising materials through computational studies

- **Develop new synthetic methods for obtaining these CBN compounds**

- Most target CBN compounds are unknown in the literature



- **Collaborate with center partners (PNNL) to measure thermodynamics of dehydrogenation of CBN materials**

Project Summary

- **Relevance**

- UW Research is focused on meeting DOE targets through:
 - developing suitable BN and CBN materials (high H₂ gravimetric and volume %) that can release hydrogen and be directly regenerated with hydrogen on board
 - developing cost-effective catalysts that can promote release of hydrogen quickly from the above materials

- **Approach**

- Rational design of economically viable transition metal catalysts based on known highly active catalysts
- Investigation of catalytic activity of new metal complexes in promoting the dehydrogenation of BN and novel CBN materials
- Synthesis and investigation of new CBN materials to develop systems that are viable for on-board regeneration of spent fuels

Project Summary

- **Technical Accomplishments** (*relevance for on-board storage goals*)
 - Synthesized low cost cobalt catalysts that approach iridium catalyst activity (*system cost barriers*)
 - Successfully demonstrated that modification of ligands can be used to improve stability and activity of cobalt catalysts (*operating temperature range, rates of hydrogen release*)
 - Produced *soluble* dehydrogenated 1:1 AB/MeAB oligomers (*facilitation of processing of spent fuel*)
 - Determined direct regeneration of AB and MeAB (*spent fuel*) is not viable via enthalpy measurements
 - Proposed new CBN materials predicted to have more favorable thermodynamics for direct regeneration and syntheses are in progress (*recharging of spent fuel*)
- **Collaborations**
 - Collaborated with PNNL to measure the thermodynamics of dehydrogenation of MeAB and mixed AB/MeAB systems
 - Worked jointly with U of Alabama to identify CBN materials that have more favorable calculated thermodynamics
 - Consulted with LANL on catalyst development

Project Summary

- **Future Work**

- Continue to develop and optimize inexpensive first-row transition metal catalysts based on knowledge gained from current iridium and cobalt catalysts. Use ligand modification (sterics and electronics) to promote higher activity and catalyst stability.
- Continue collaboration with center partners to identify CBN compounds that contain high wt%'s of H₂ and are expected to have favorable thermodynamics of dehydrogenation
- Work on development of viable and cost effective synthetic methods for obtaining these novel CBN compounds
- Distribute knowledge of methods and CBN compounds to other center members for investigations of dehydrogenation and rehydrogenation