

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

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Overview

Timeline

- Start: FY 05
- End: FY 09
- 25% complete

Budget

- Total funding
 - \$1.1 M DOE share
 - \$ 0.28 M cost share
- DOE FY05:
\$155K(partial)
- DOE FY06: \$ 200 K

Barriers

- Weight and volume
- Efficiency
- Regeneration Processes

Amineboranes offer high H₂ storage capacity in principle, but thermal H₂ release is slow and inefficient. Effective catalysts for dehydrogenation/hydrogenation of BN compounds are needed.

Partners

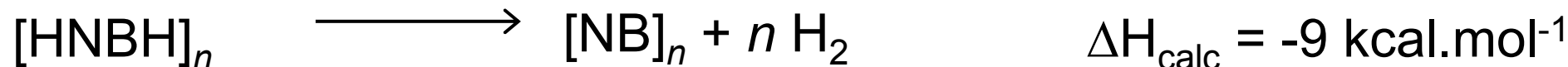
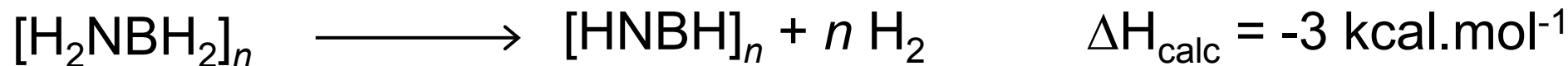
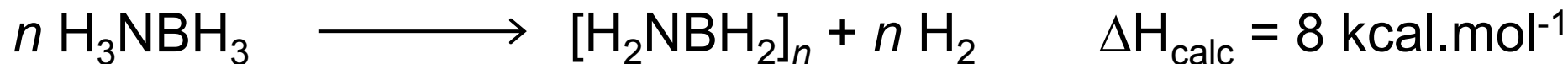
DOE Center of Excellence for
Chemical Hydrogen
Storage

Objectives

- To understand the interaction of BN compounds with transition metals
- To develop Platinum group metal(PGM) based catalysts for dehydrogenation and rehydrogenation of BN compounds
- To determine thermodynamic parameters for hydrogenation/dehydrogenation
- To develop non PGM catalysts

Ammonia Borane as a H₂ Storage Material

Appropriate Thermodynamics



Near thermoneutral reactions important for reversibility.

Ammonia Borane as a H₂ Storage Material

DOE Storage Targets

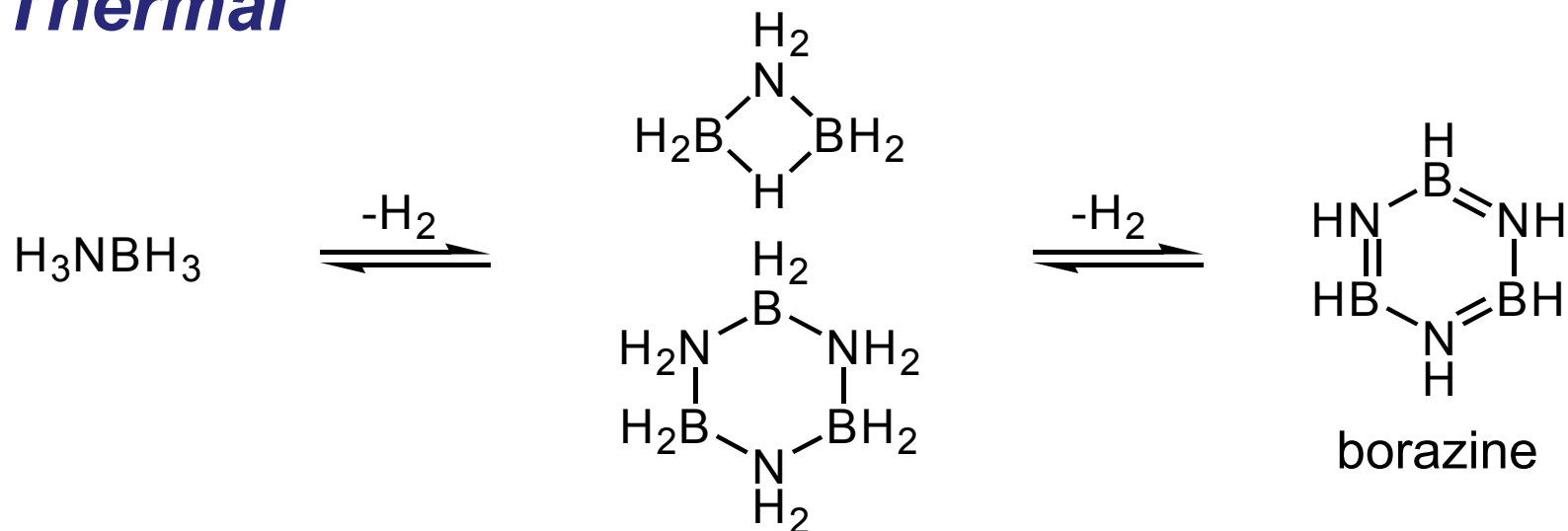
	2010	2015
Target wt%	6.0	9.0

Storage Potential of Ammonia Borane

H₂ Released	1	2	3
Wt% H₂	6.5	13.0	19.6
Product	[H ₂ NBH ₂] _n	[HNBH] _n	[NB] _n

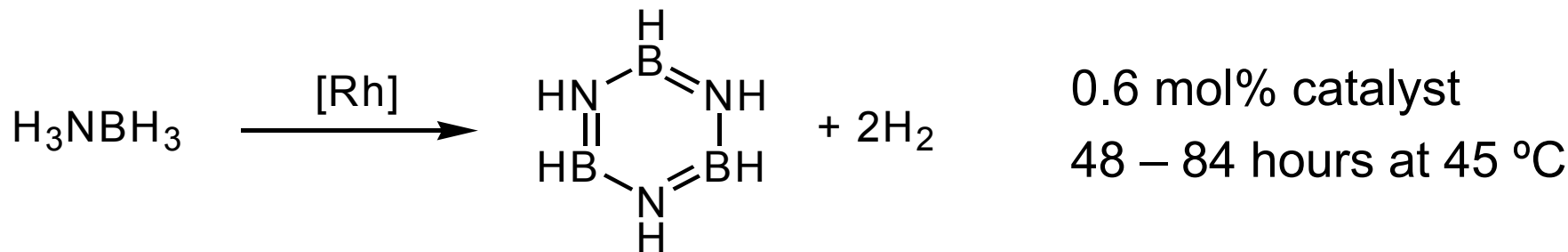
Dehydrogenation of Ammonia Borane

Thermal



Wang, J. S.; Geanangel, R. A. *Inorg. Chim. Acta* **1988**, 148, 185.

Catalyzed



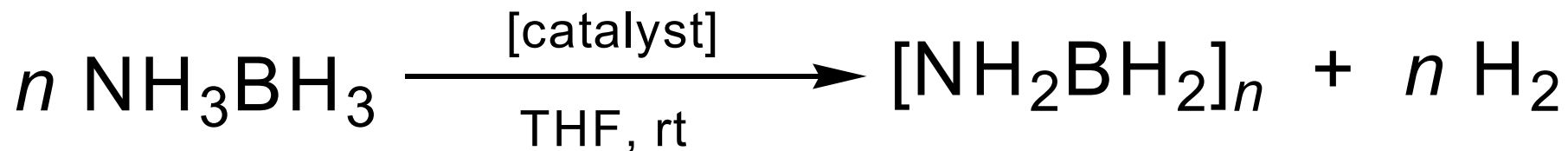
Jaska, C. A.; Manners, I. *J. Am. Chem. Soc.* **2004**, 126, 9776.

Approach

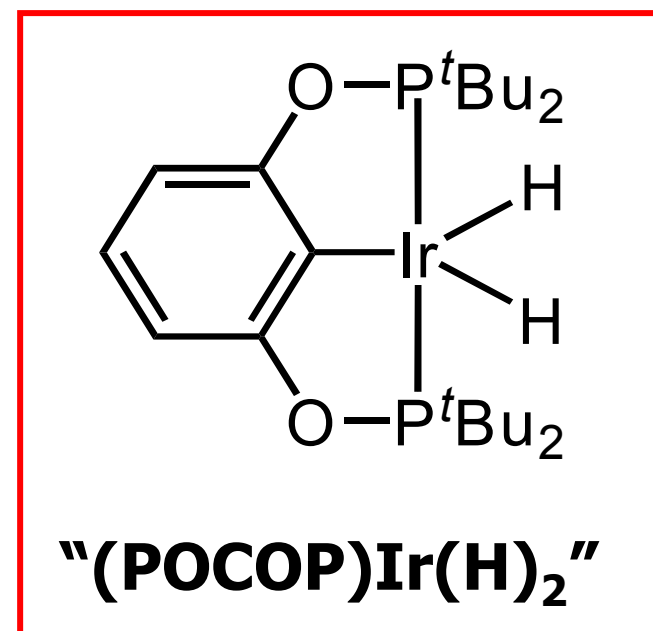
- We seek to develop catalysts to accelerate dehydrogenation/rehydrogenation of amine boranes, eg.



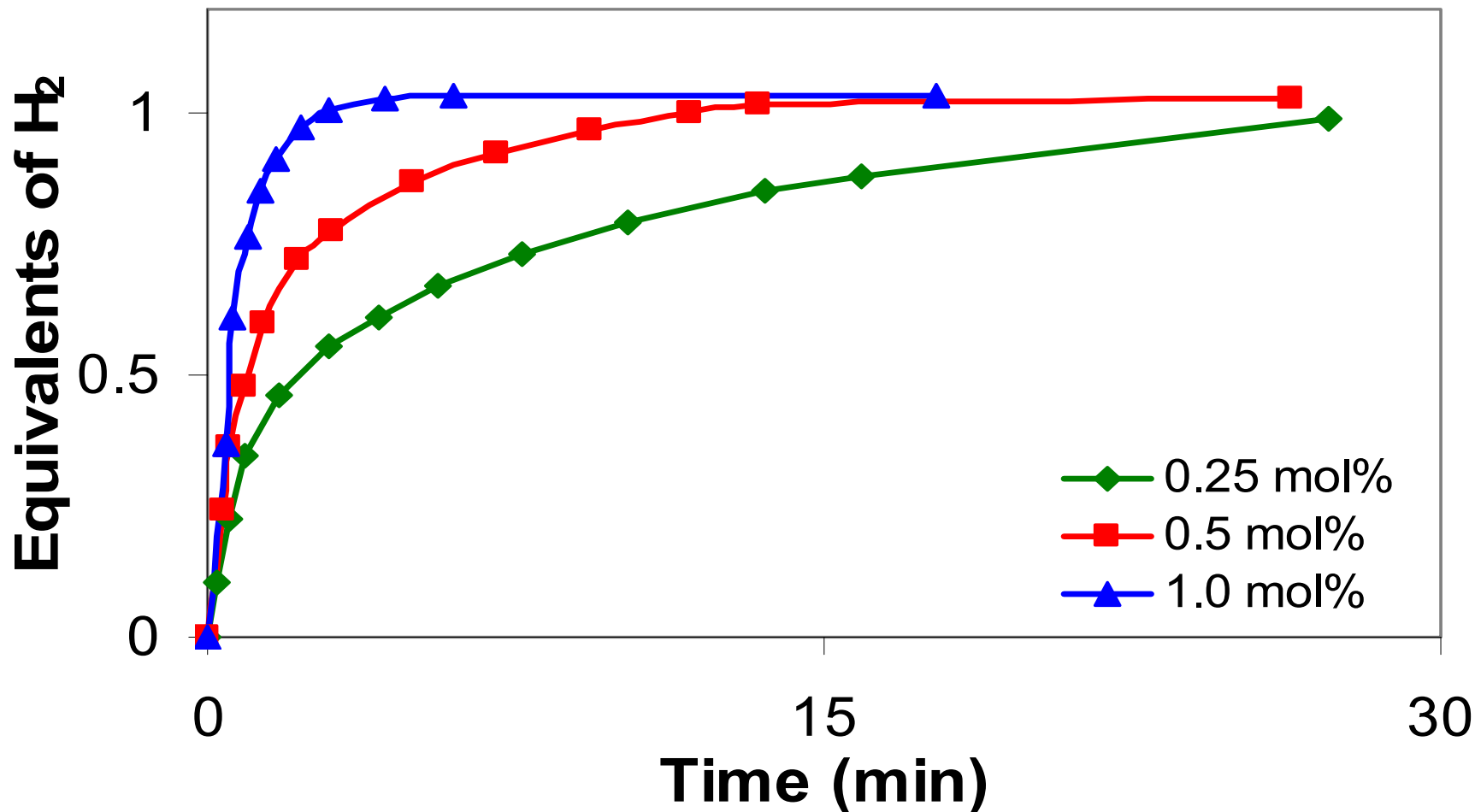
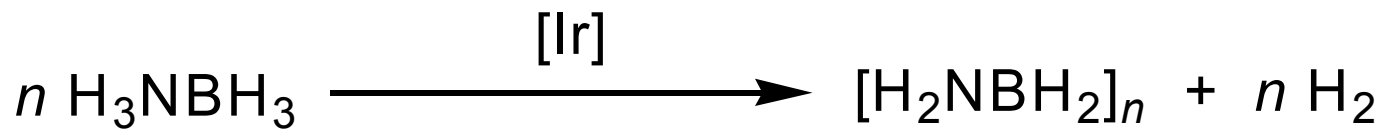
Results: Catalyst Choice



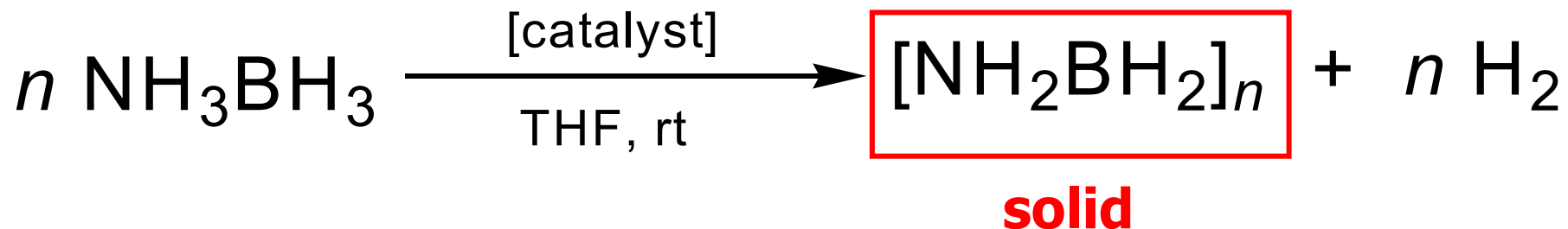
- (POCOP)Ir(H)₂ already known to be an effective *alkane* (transfer) dehydrogenation catalyst.
- Amineboranes are isoelectronic with alkanes.



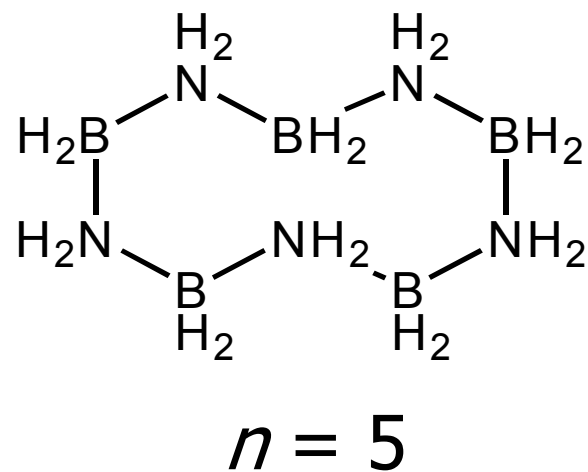
Evolution of Hydrogen



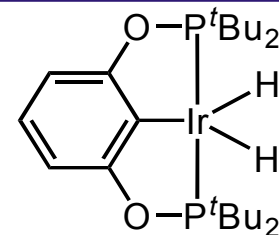
Characterization of Solid Product



- Single well characterized non-volatile product
- All other reported reactions of this type lead to mixtures including borazine



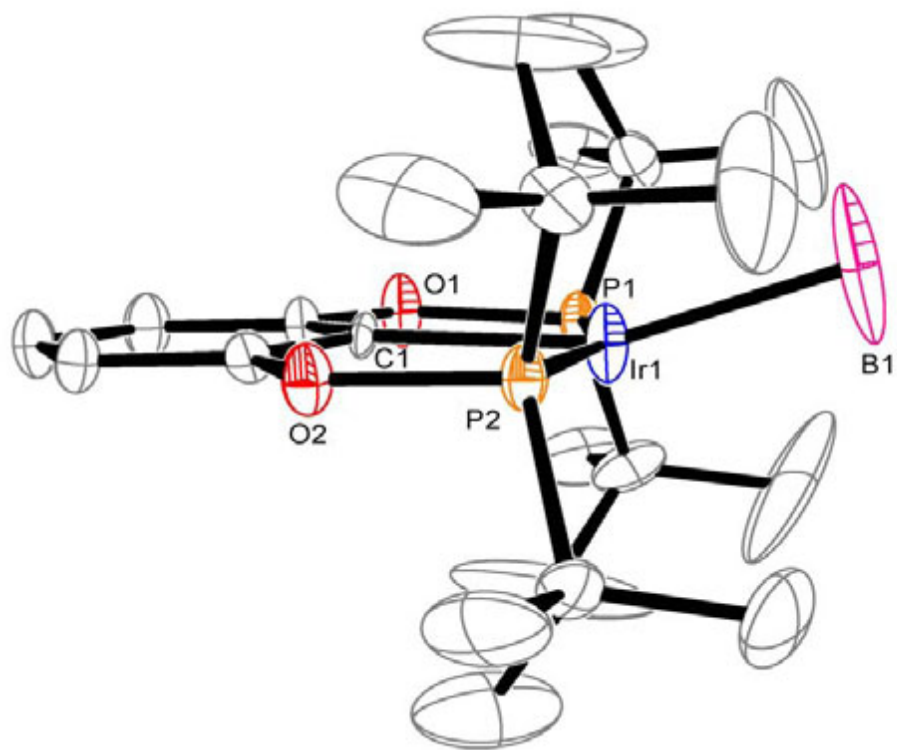
Comparison with Previous Best Catalyst



Catalyst Loading	0.6 mol%	0.5 mol%
Temperature (°C)	45	25
H₂ evolved (equiv.)	2	1
Products	Borazine	[H ₂ NBH ₂] ₅
Time	48 – 84 hr	< 15 min

At least 200 fold increase in reaction rate over previous best.

- Eventually, the Ir catalyst converts to a dormant form:



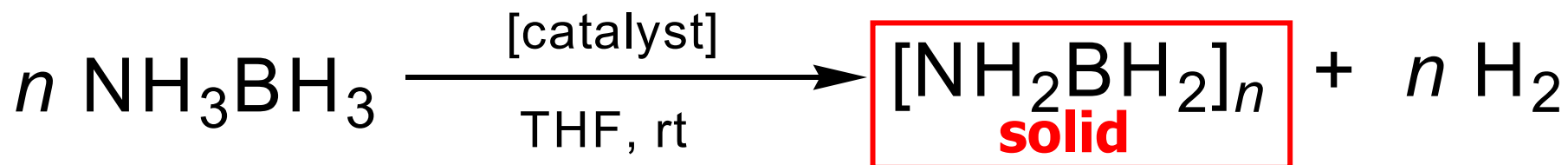
Future Work

- In collaboration with PNNL, use calorimetry to accurately measure the heat of reaction for the dehydrogenation reaction. This is critical to validate computational work and to evaluate reversibility.
- Explore ligand variations with Ir for better catalysis.
- Define the mechanism of the reaction; use mechanistic insight to guide catalyst development
- Study rehydrogenation reactions.
- Develop non PGM catalysts with less expensive metals such as Fe, Co and Ni.

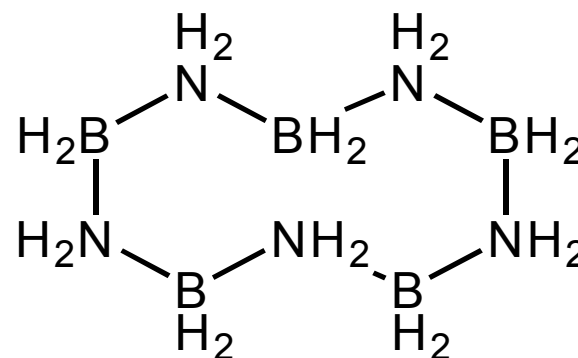
Summary

- We have developed an extraordinarily active dehydrogenation catalyst with activity orders of magnitude greater than the prior art.
- The catalyst is well defined and active indefinitely in the presence of hydrogen.
- In contrast to previous reports of complex mixtures, our Ir catalyst gives a single non-volatile BN containing product.

Backup Data: Characterization of Solid Product



- Solid state ^{11}B NMR.
- Infrared spectroscopy.
- Powder X-ray diffraction.



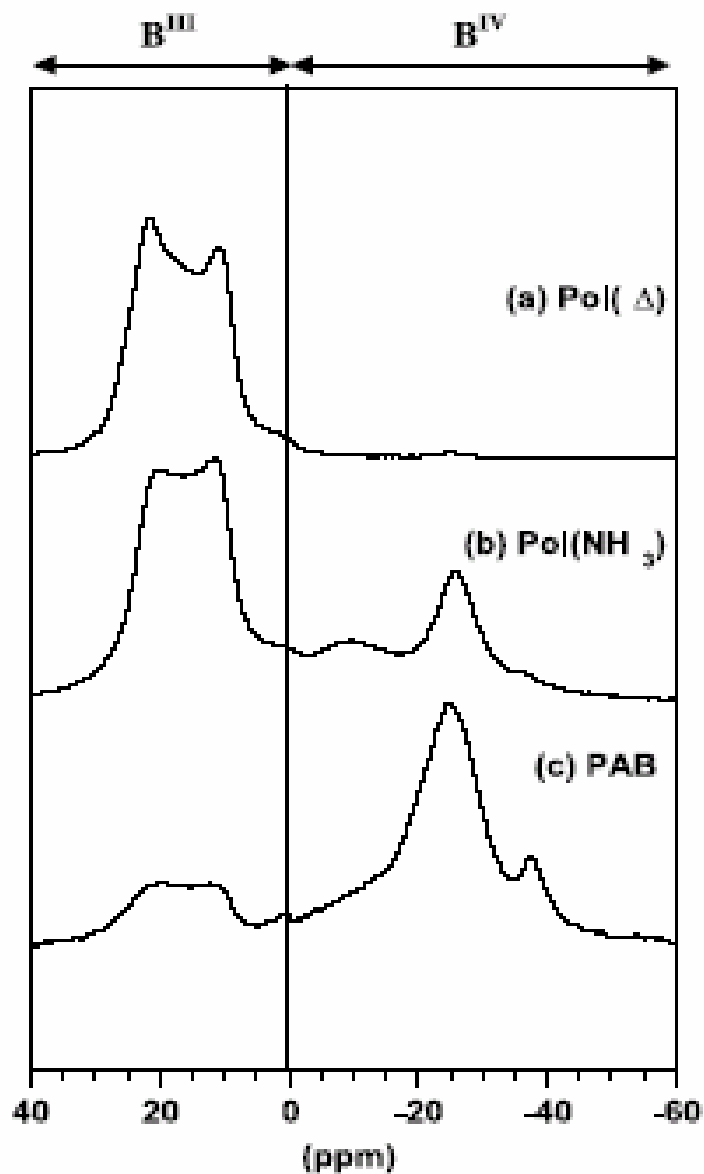


Fig. 5. ^{11}B MAS NMR spectra of the three polymers recorded at 9.4 T.

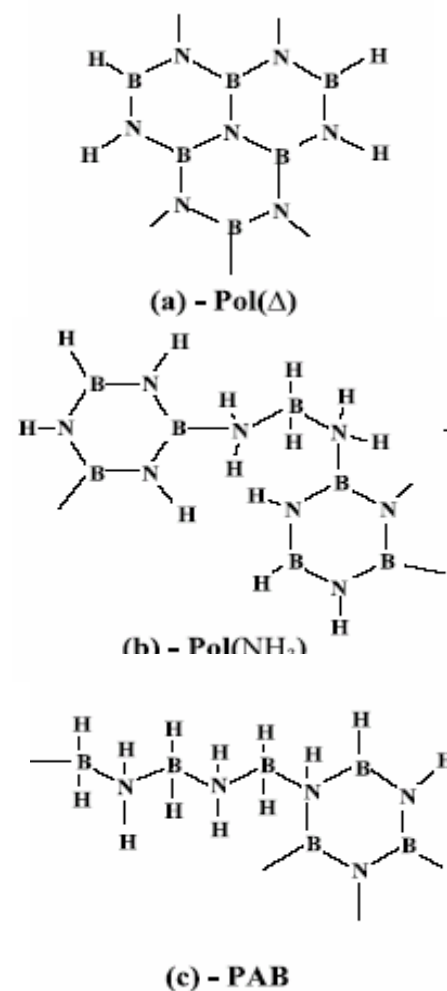
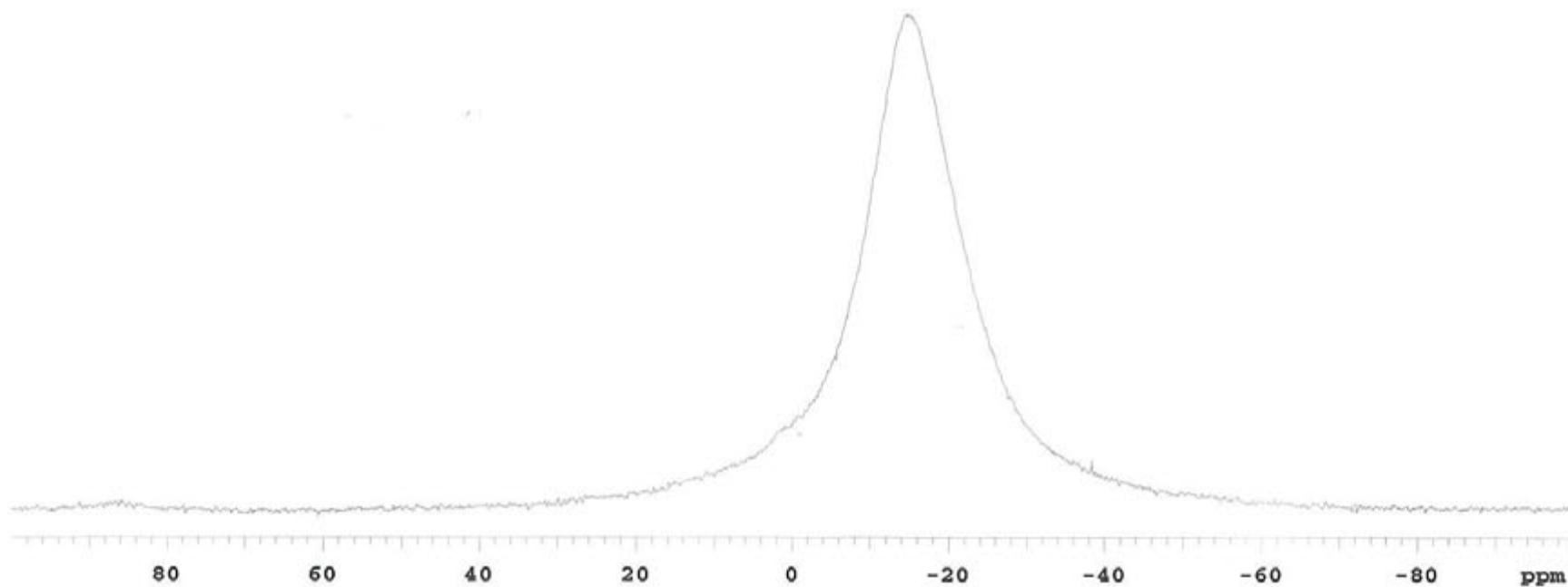


Fig. 8. Schematic representation of the three polymers structures, based on NMR results.

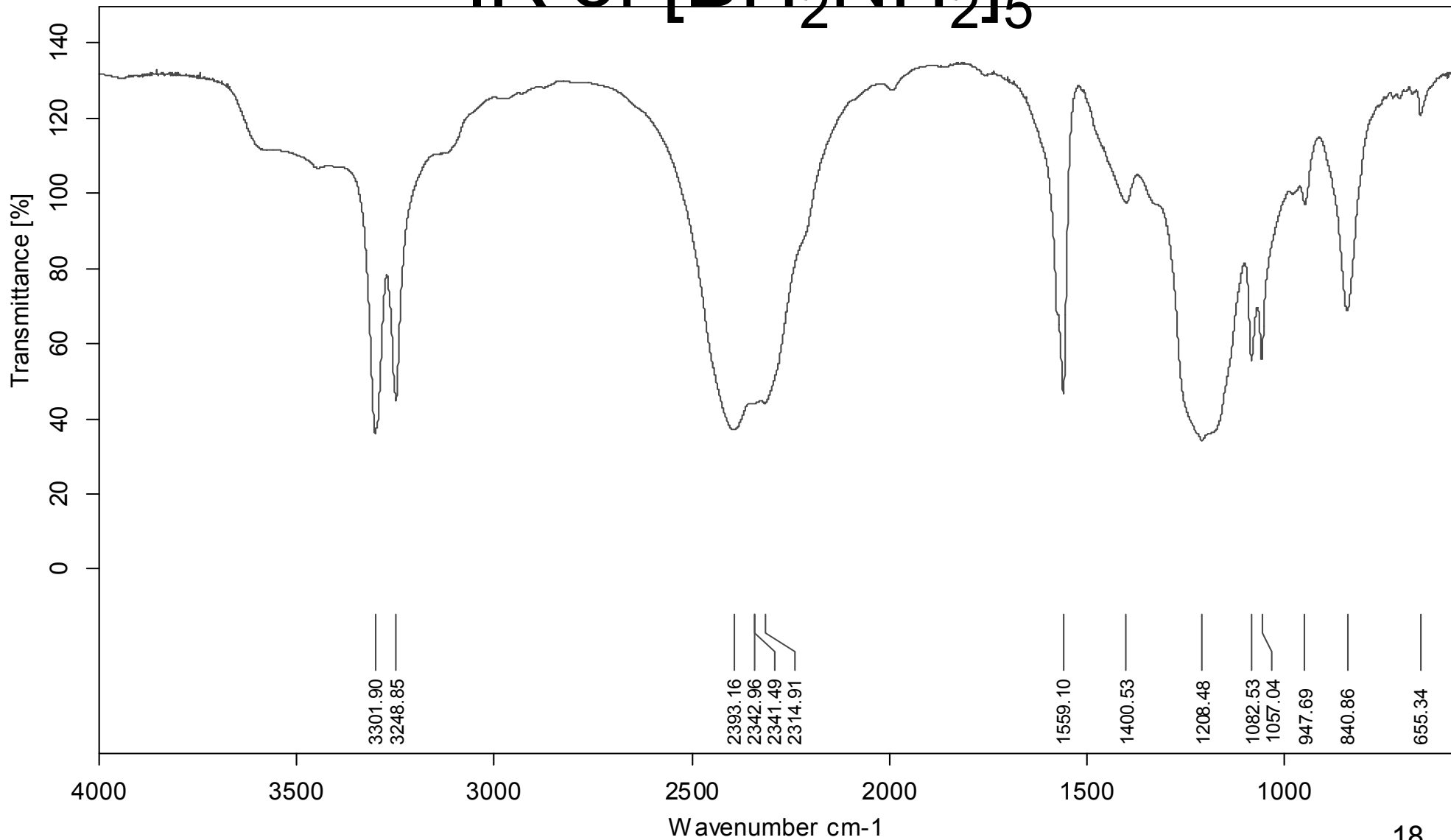
Solid State ^{11}B NMR of $[\text{BH}_2\text{NH}_2]_5$

solid from
Ir H₂ (POCOP) + H₃NBH₃ $\xrightarrow{\text{THF}}$
MCD-111-114

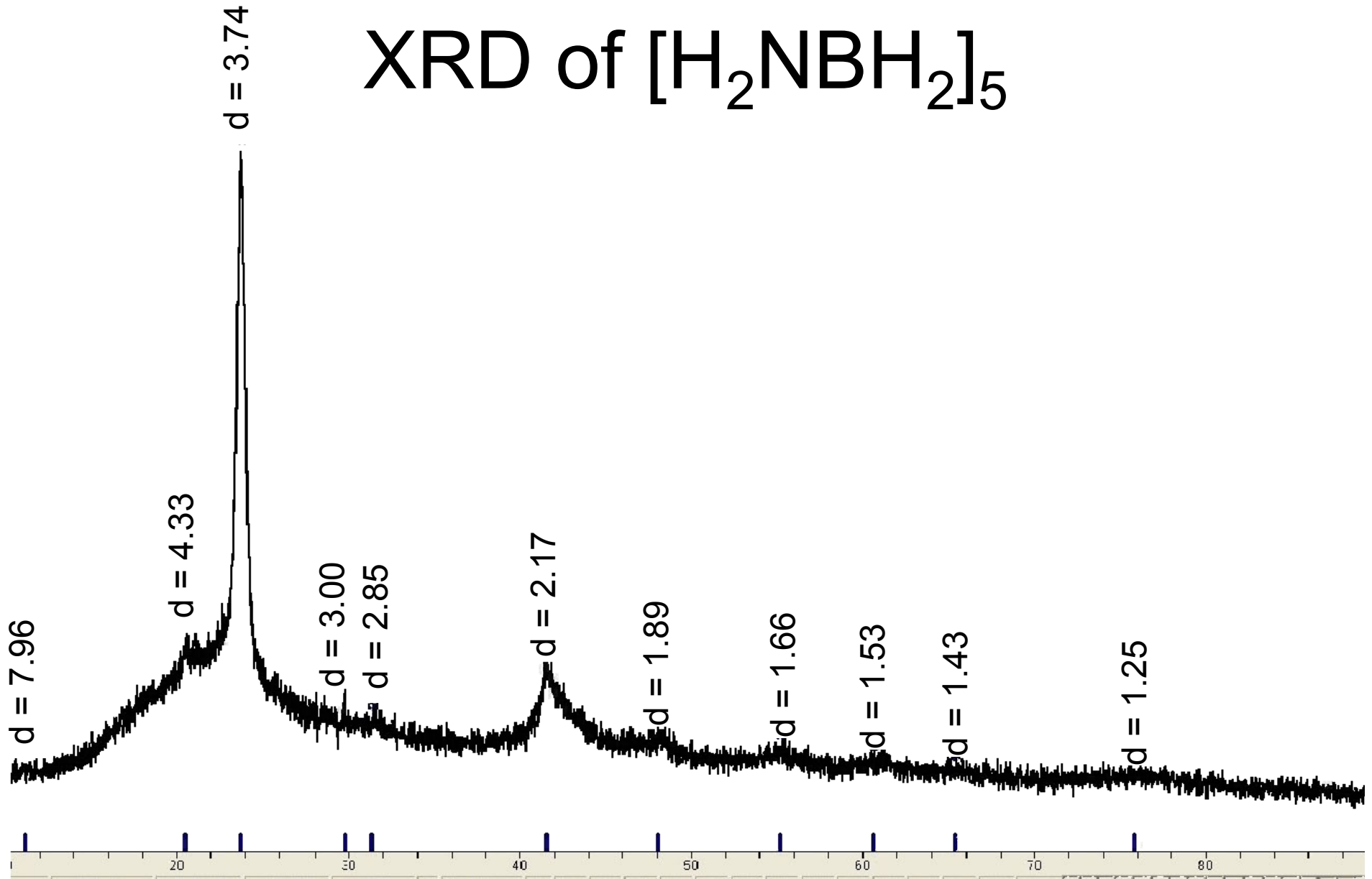
B11.03

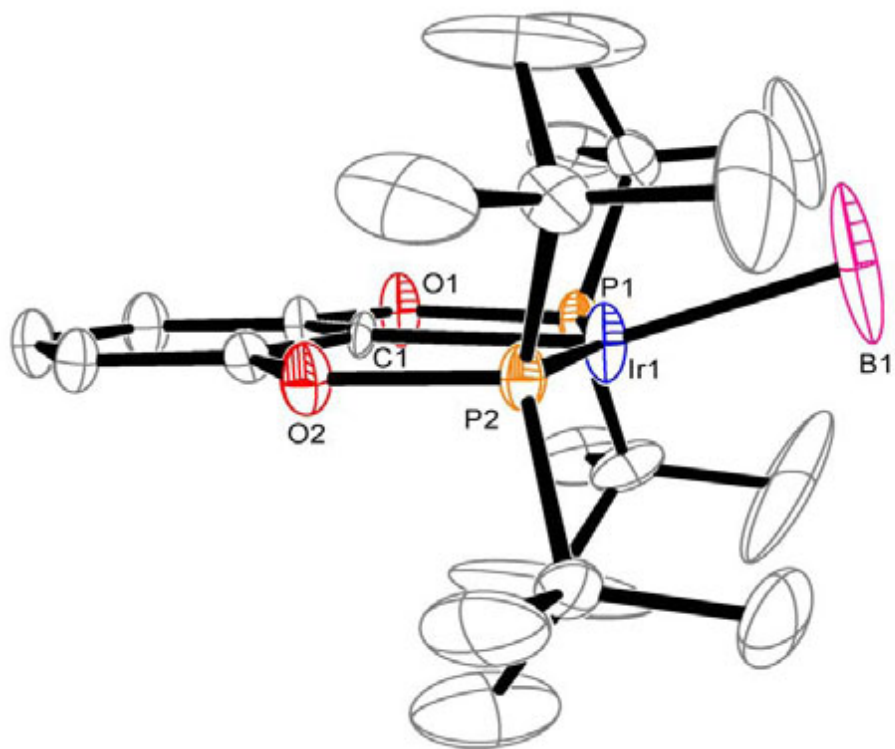


IR of $[\text{BH}_2\text{NH}_2]_5$

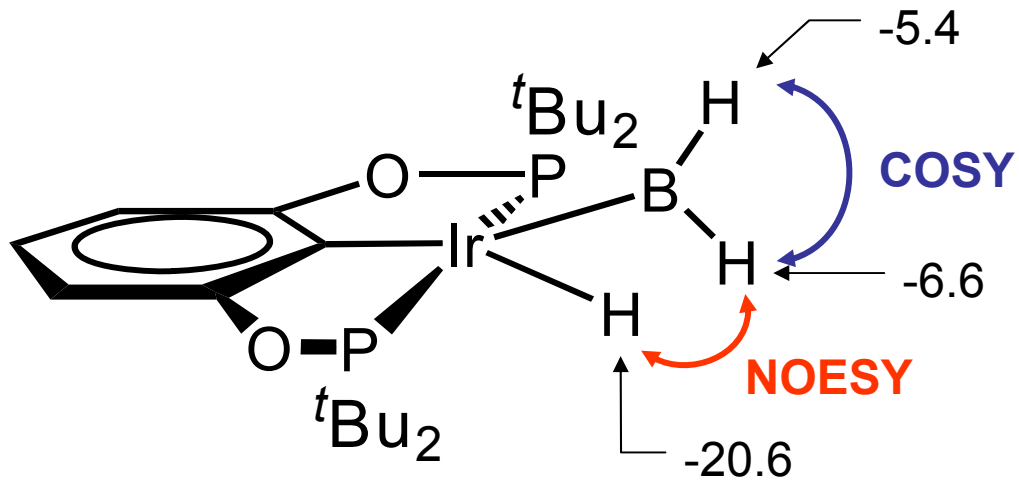


XRD of $[H_2NBH_2]_5$





Bond Length (Å)	
Ir(1)-B(1)	2.185(9)
Ir(1)-P(1)	2.3137(14)
Ir(1)-P(2)	2.3122(14)
Ir(1)-C(1)	2.032(4)



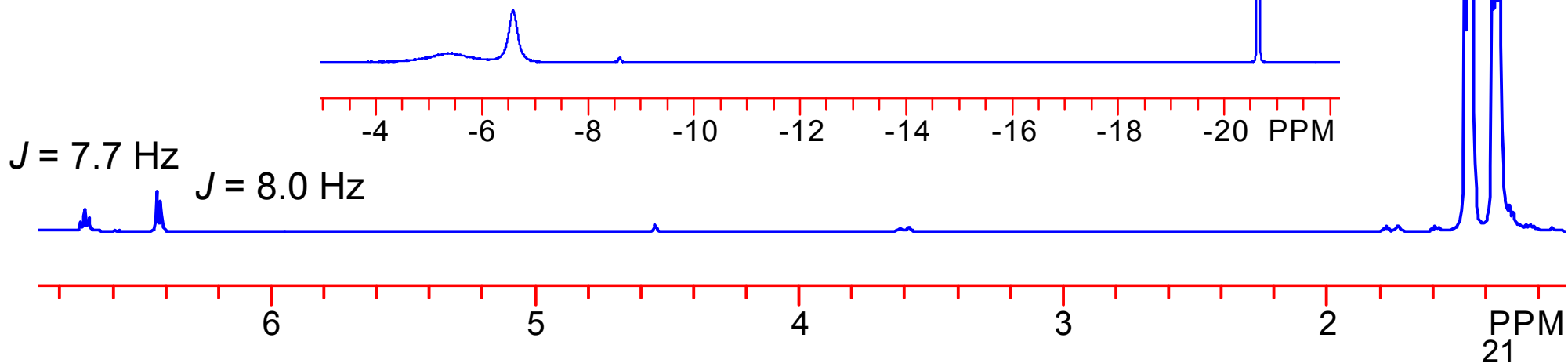
$^{31}\text{P} = 171.6 \text{ ppm}$
 $^{11}\text{B} = 13 \text{ ppm}$

$J = 7.7 \text{ Hz}$

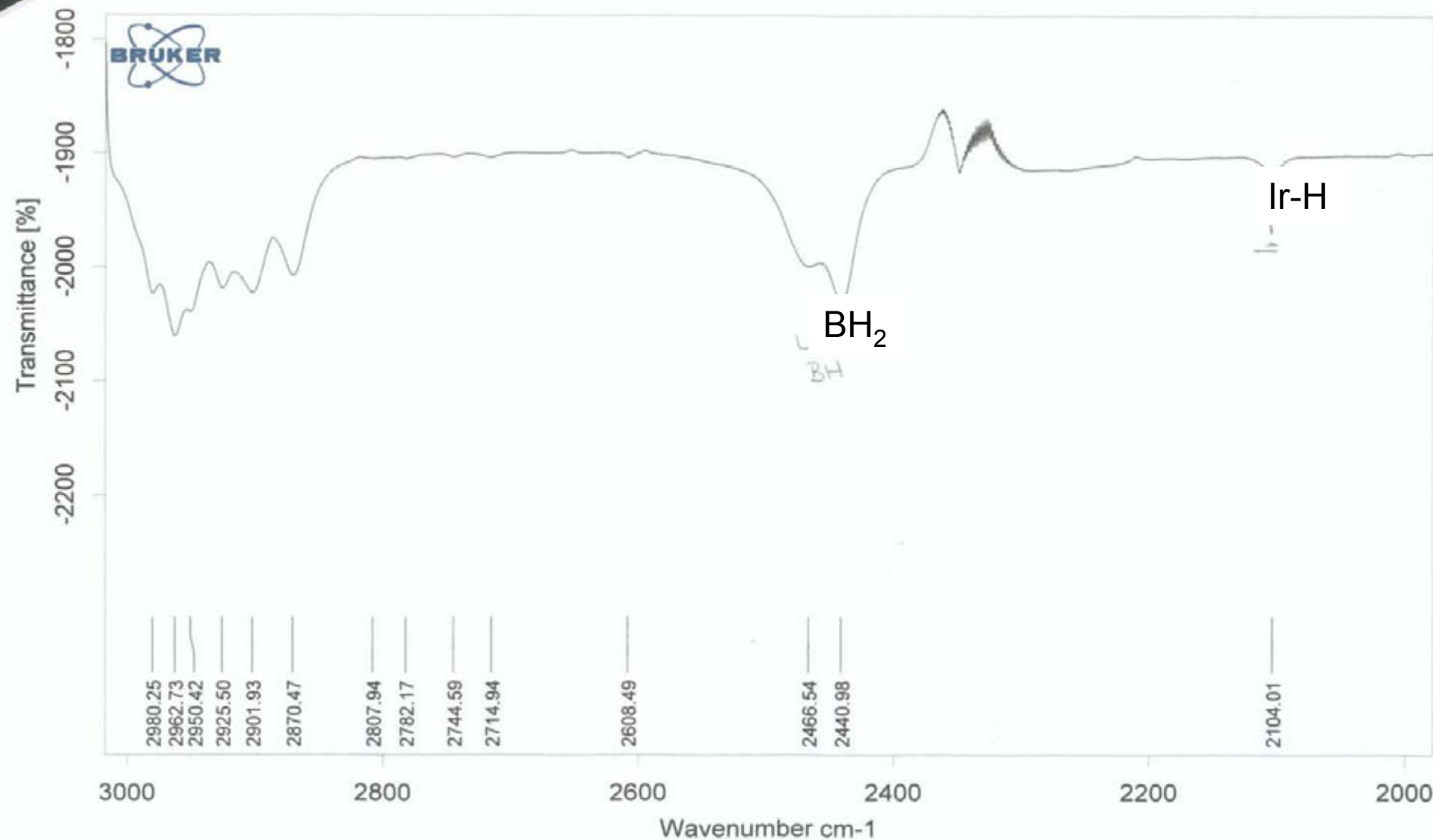
$J = 5.7 \text{ Hz}$

$J = 26 \text{ Hz}$

^1H NMR in $\text{THF-}d_8$



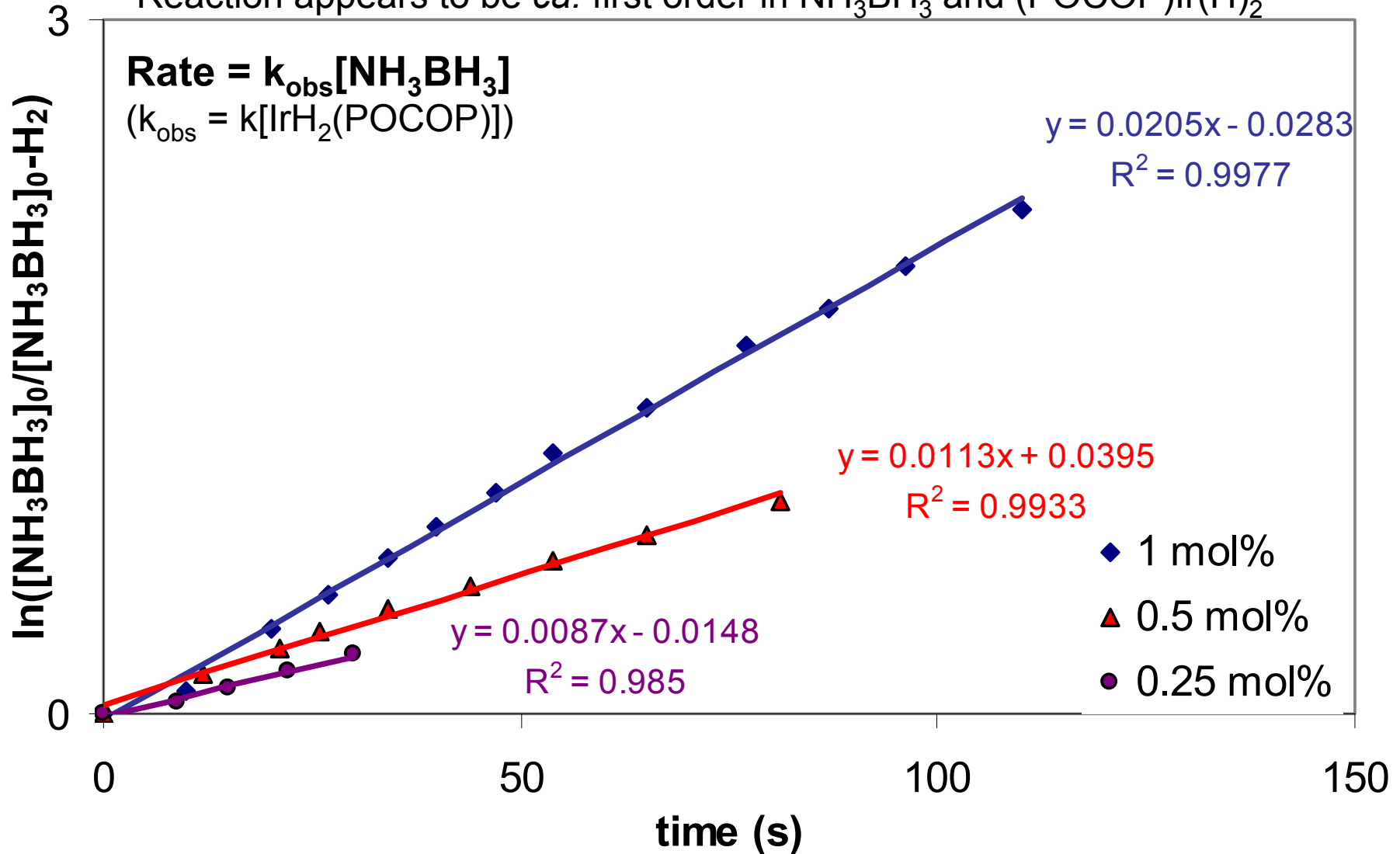
IR spectrum of (POCOP)IrH(BH₂)

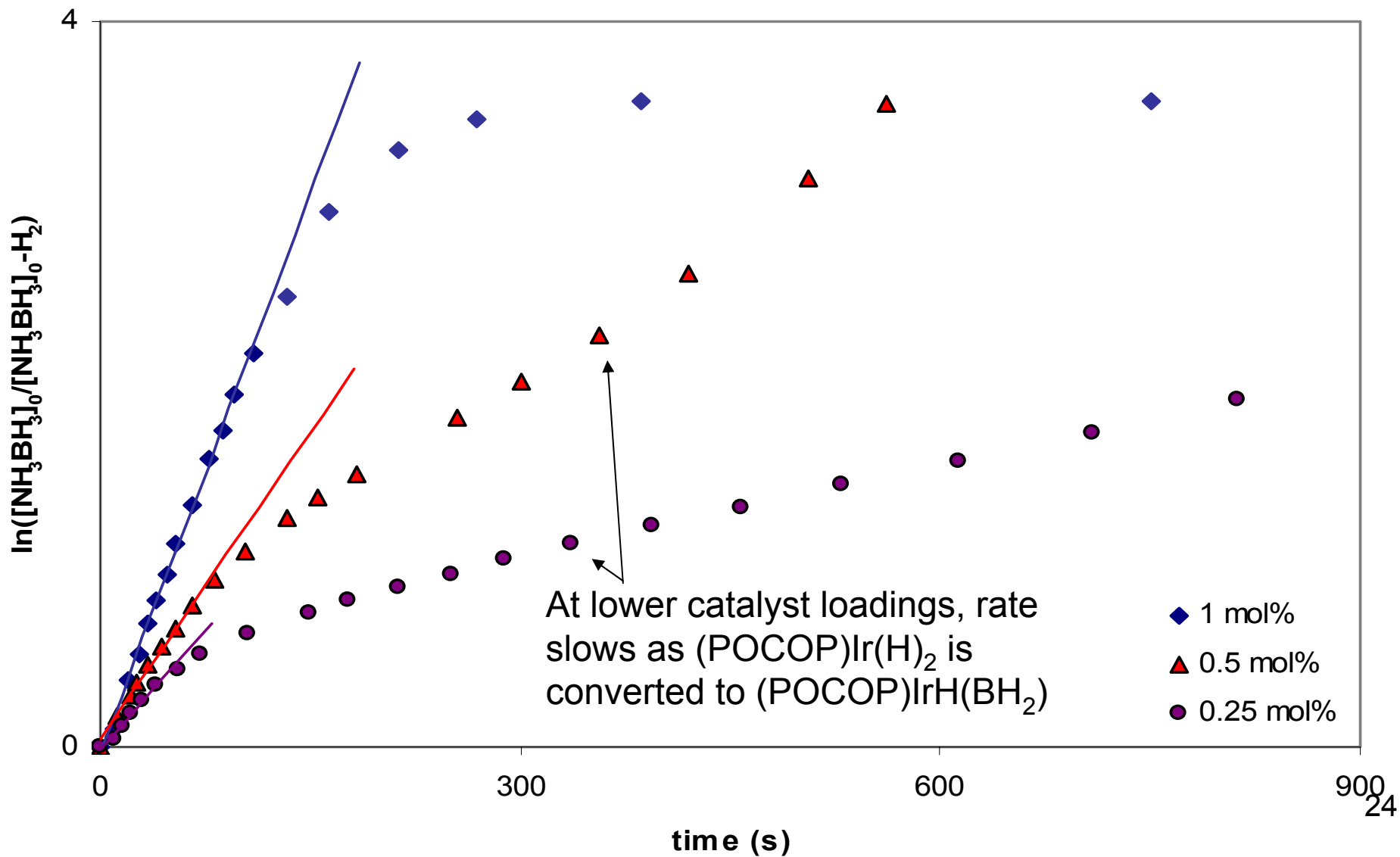


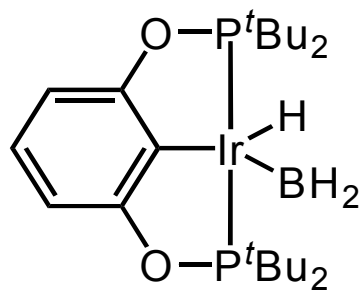
Solution in C₆H₆

Initial Rates

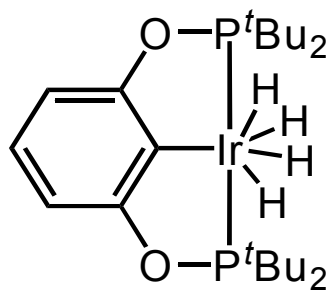
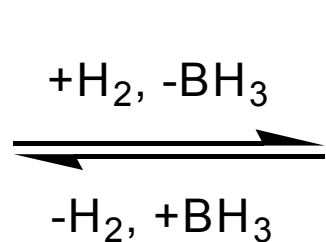
Reaction appears to be *ca.* first order in NH_3BH_3 and $(\text{POCOP})\text{Ir}(\text{H})_2$



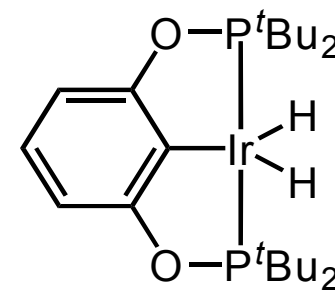
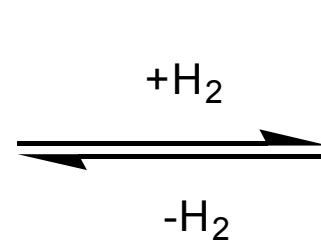




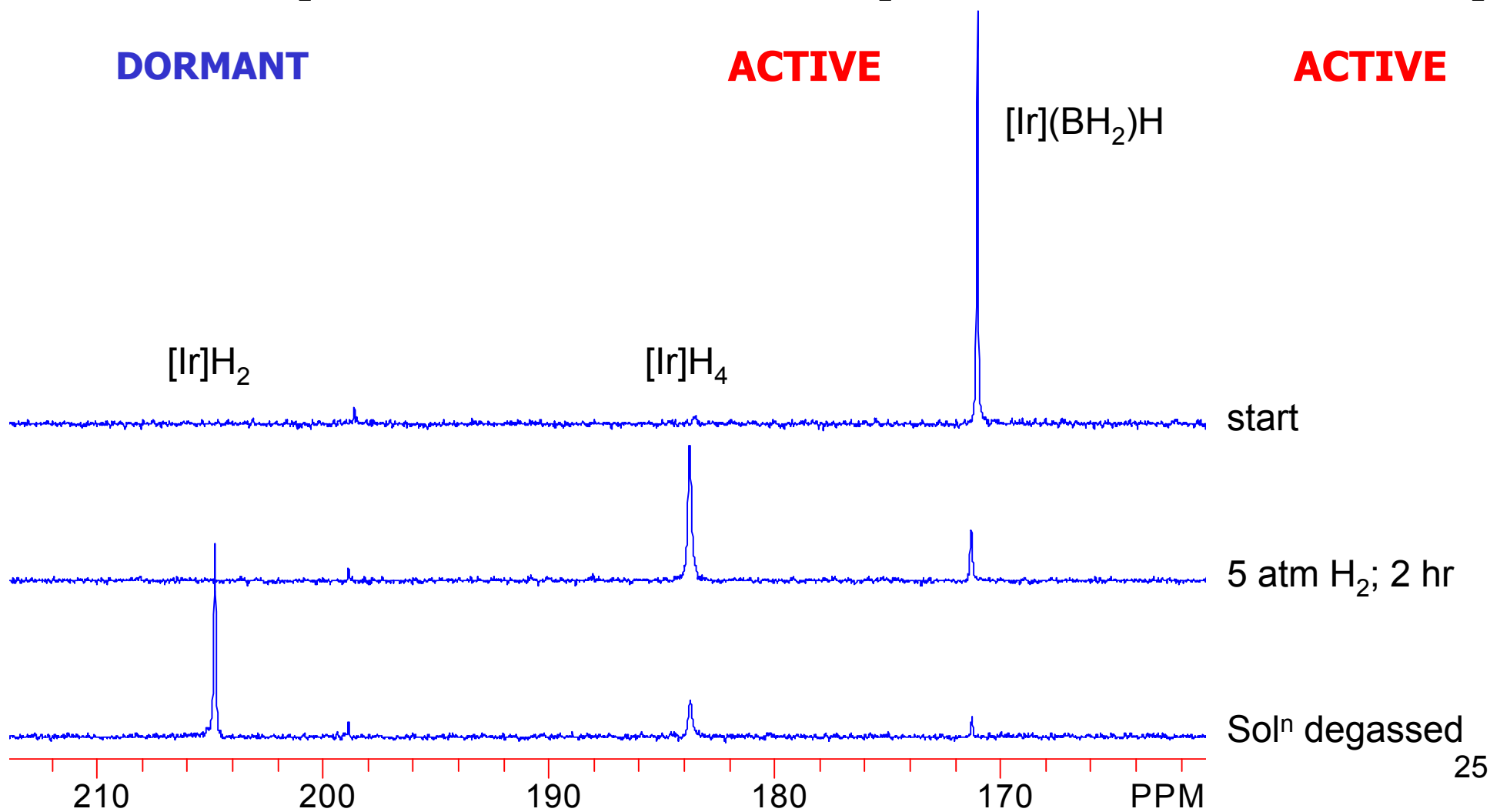
DORMANT



ACTIVE



ACTIVE



Publications and Presentations

Paper on the Ir catalyst submitted to J. Am. Chem. Soc.

Critical Assumptions and Issues

- Computational work suggests that the hydrogenation/dehydrogenation of BN compounds is reversible. This needs to be verified by experiment. Thermodynamic data for these complexes is very limited.
- The formation of volatile borazine must be avoided for fuel cell applications. Most catalysts generate mixtures including borazine.
- The cost of amine borane must be brought down.