Amineboranes for Hydrogen Storage

Michael Heinekey
University of Washington

UW

Karen Goldberg

Melanie C. Denney

Vincent Pons

Travis Hebden

Denise Mery

Brandon Dietrich

UNC

Maurice Brookhart

Inigo Göttker-Schnetmann

Barcelona

Augusti Lledos, Jose Lluch

PNNL

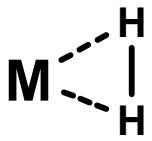
Tom Autrey, John Linehan

Crystallography:

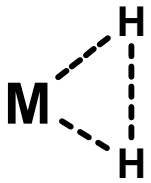
Antonio DiPasquale, Arnie Rheingold (UCSD)

Tom Koetzle, Paula Piccoli, Art Schultz (Argonne)

.



dihydrogen



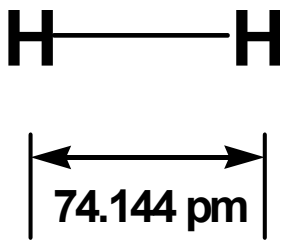
elongated dihydrogen

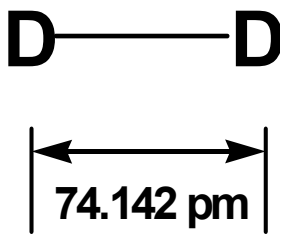
dihydride

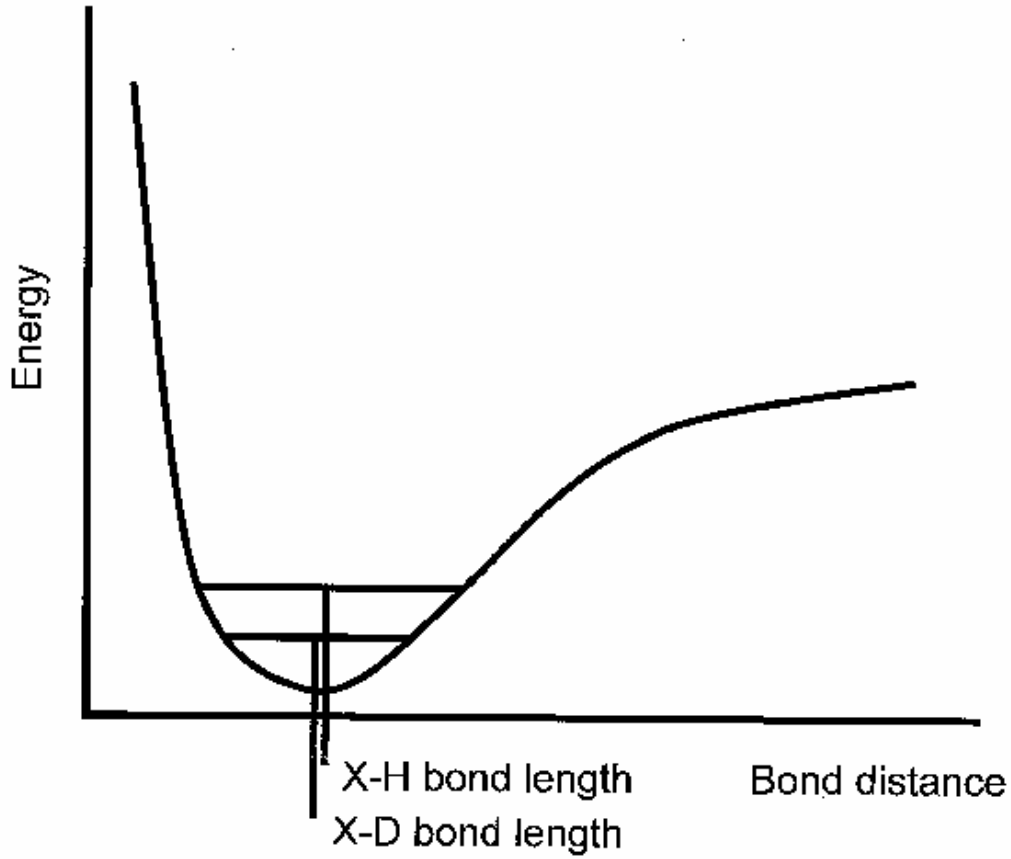
What do we mean by Structure**?**

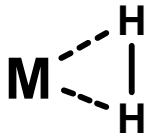
- A set of bond distances and bond angles
- Generally, a static concept
- For stable molecules, structure is usually independent of temperature

Does structure depend upon mass?

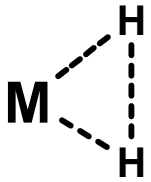





Energy
X-H bond length
X-D bond length
Bond distance



dihydrogen



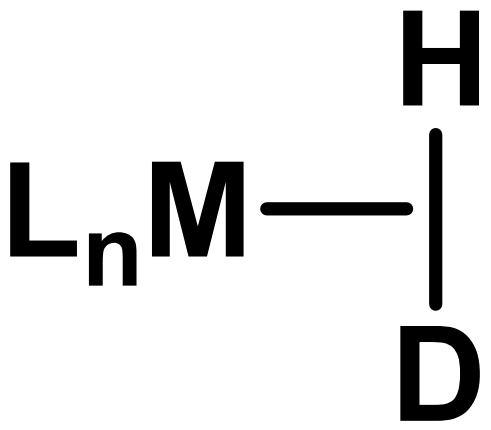
elongated dihydrogen

dihydride

Characterization of H_2 Complexes by ^1H NMR

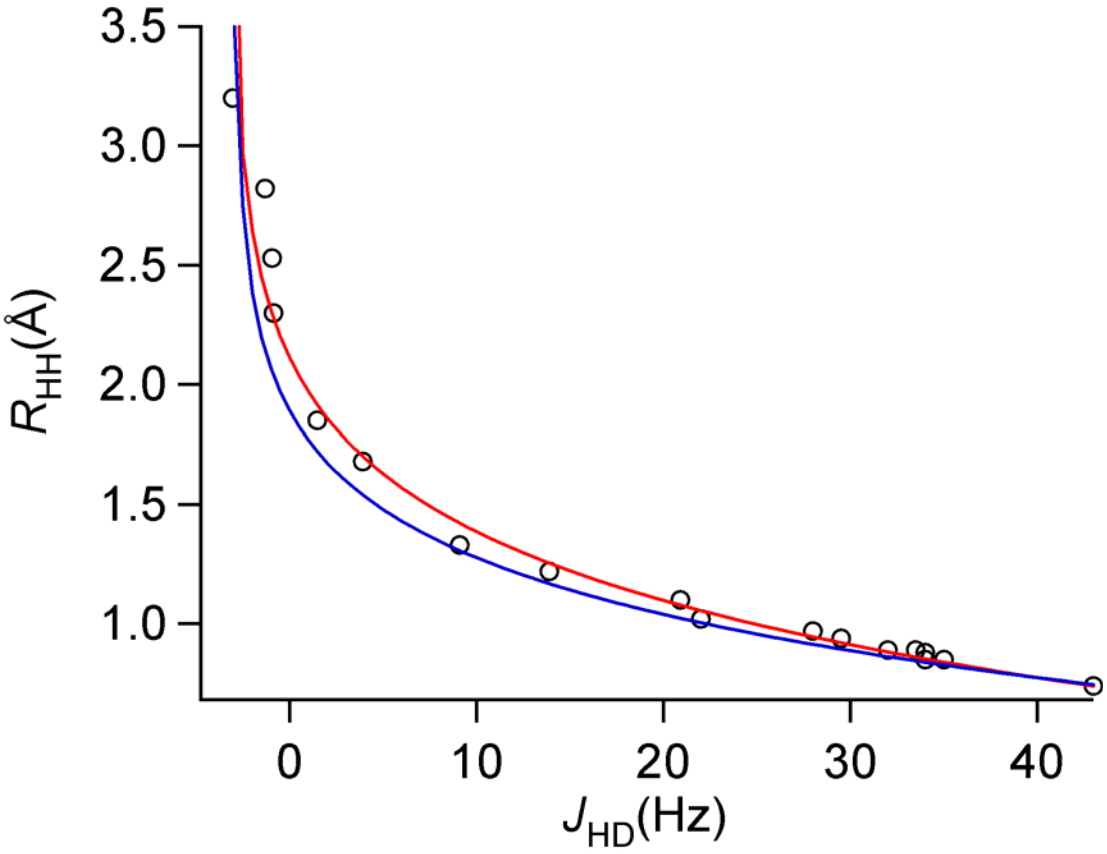
- "Hydride" resonances at high field

- Deuterium: nuclear spin I = 1
- → observation of a 1:1:1 triplet in the ^1H spectrum

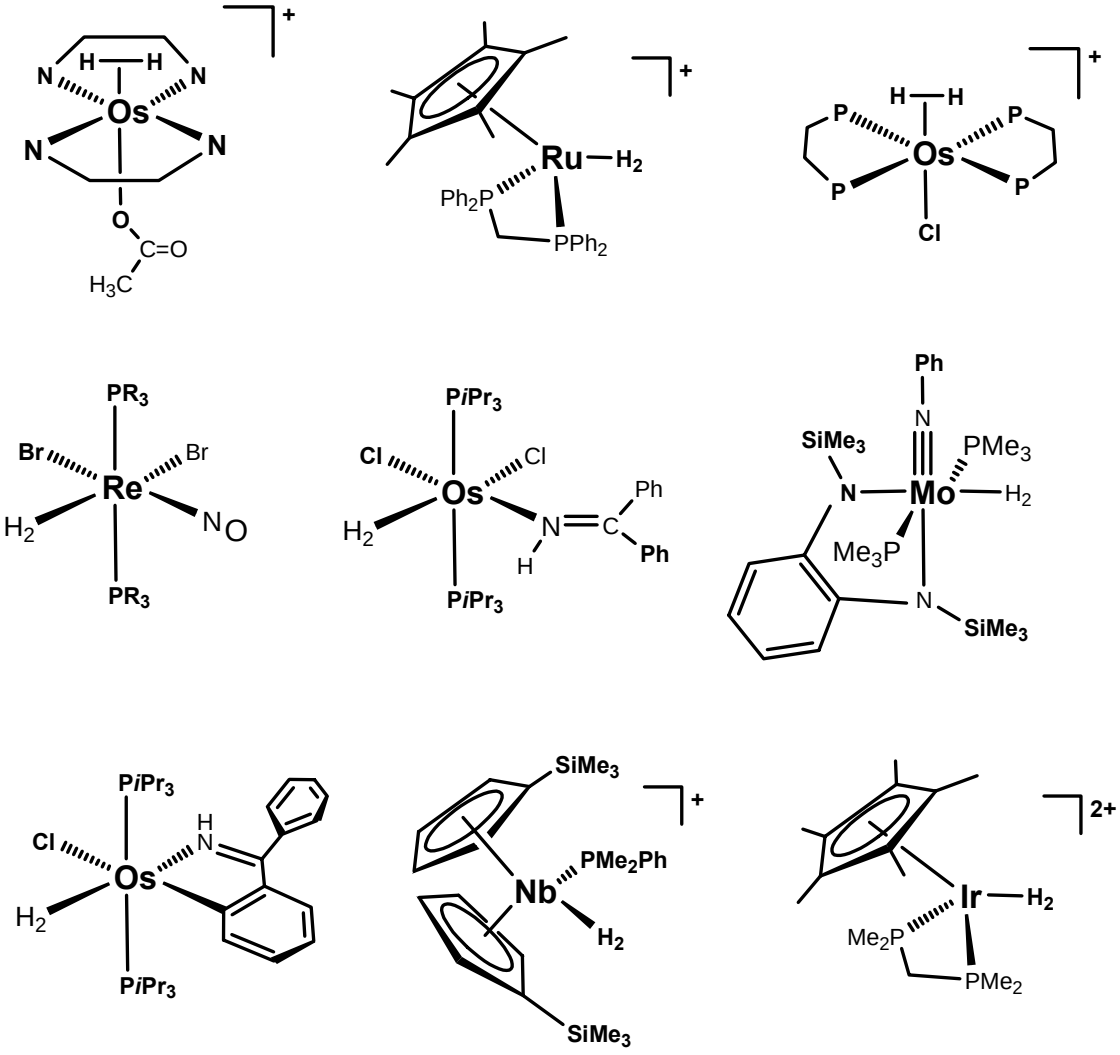


- 25 Hz < J_{HD} < 35 Hz
  (HD gas: J_{HD} = 43 Hz)

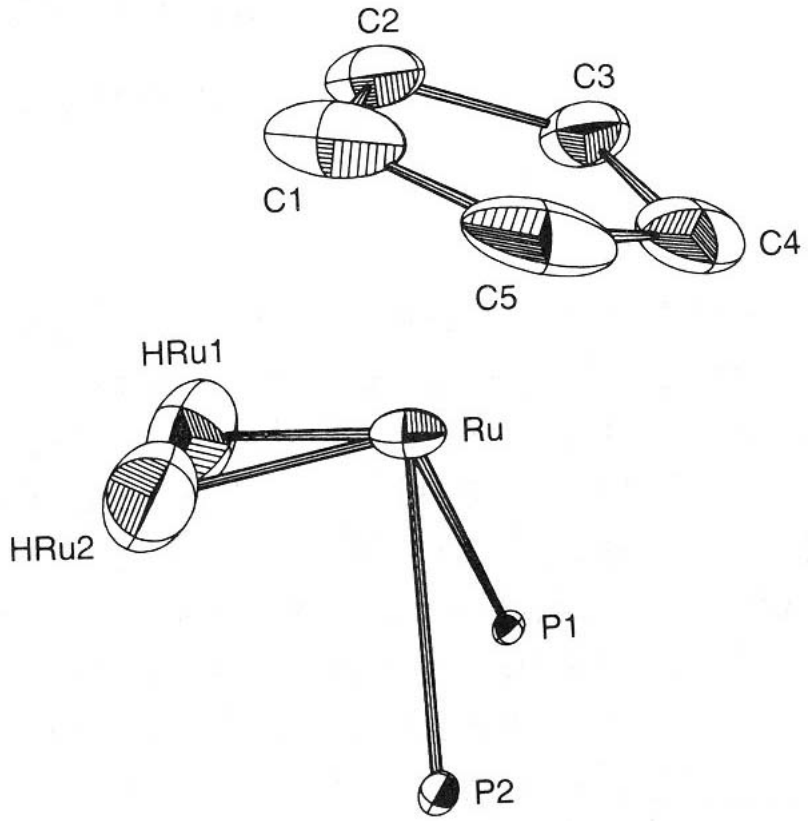
- dH-H = 1.44 – 0.0168 J_{HD}



D. M. Heinekey, V. Pons *et. al. J. Am. Chem. Soc.* 2004, *126*, 8813.



Chem. Soc. Rev. **2004**, *33*, 175-182



W. T. Klooster, T. F. Koetzle, G. Jia, T. P. Fong, R. H. Morris and A. Albinati, *J. Am. Chem. Soc.* 1994, *116*, 7677.

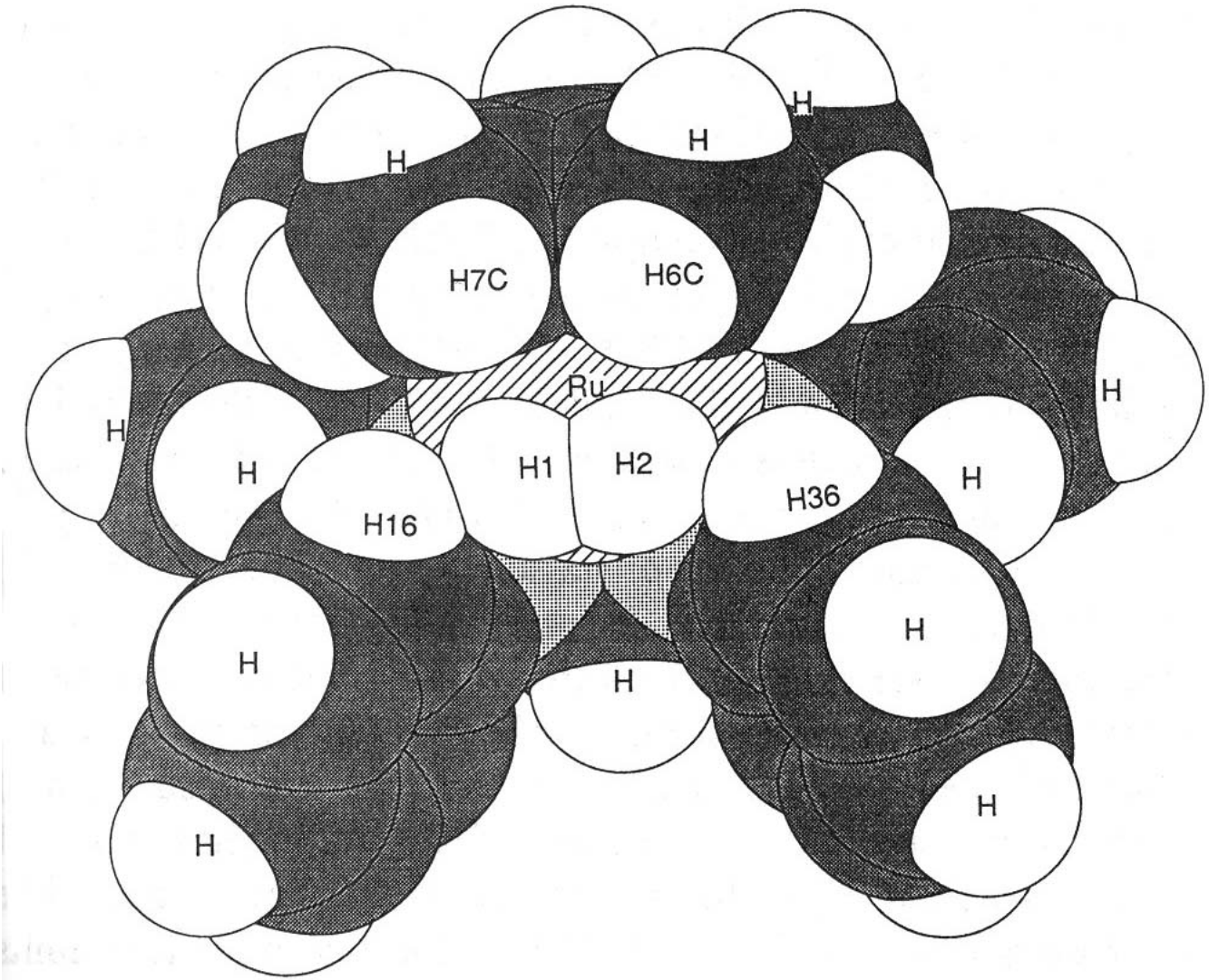
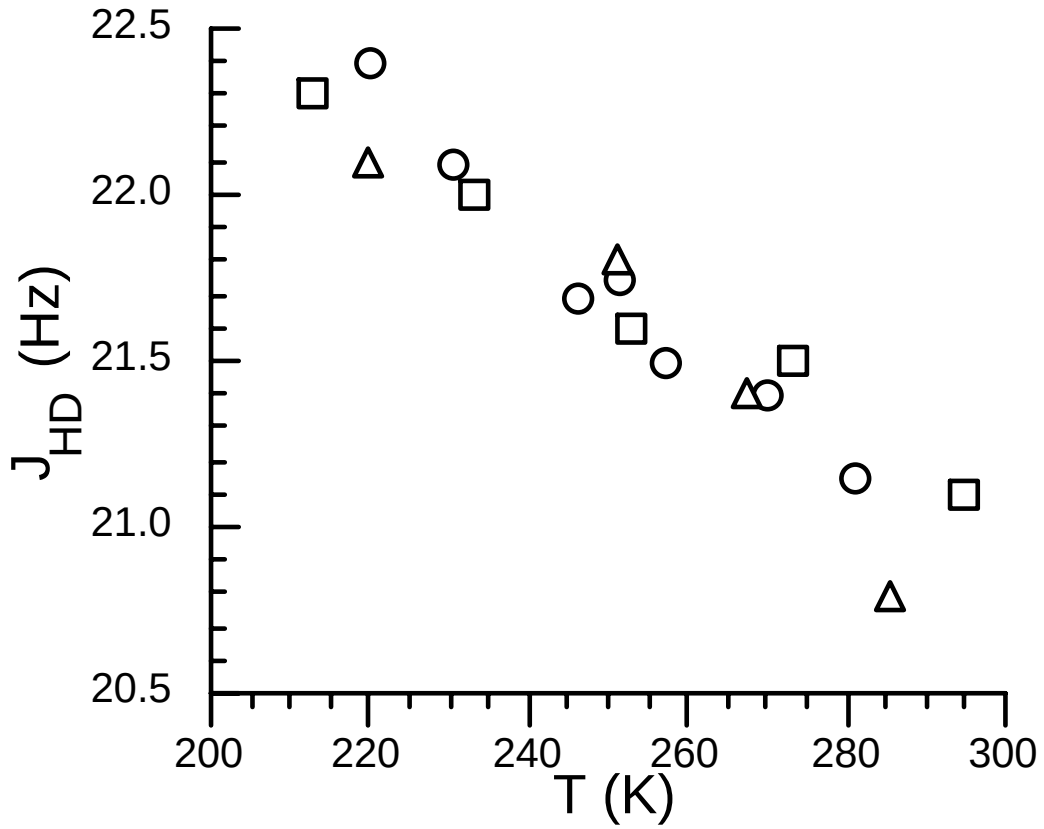
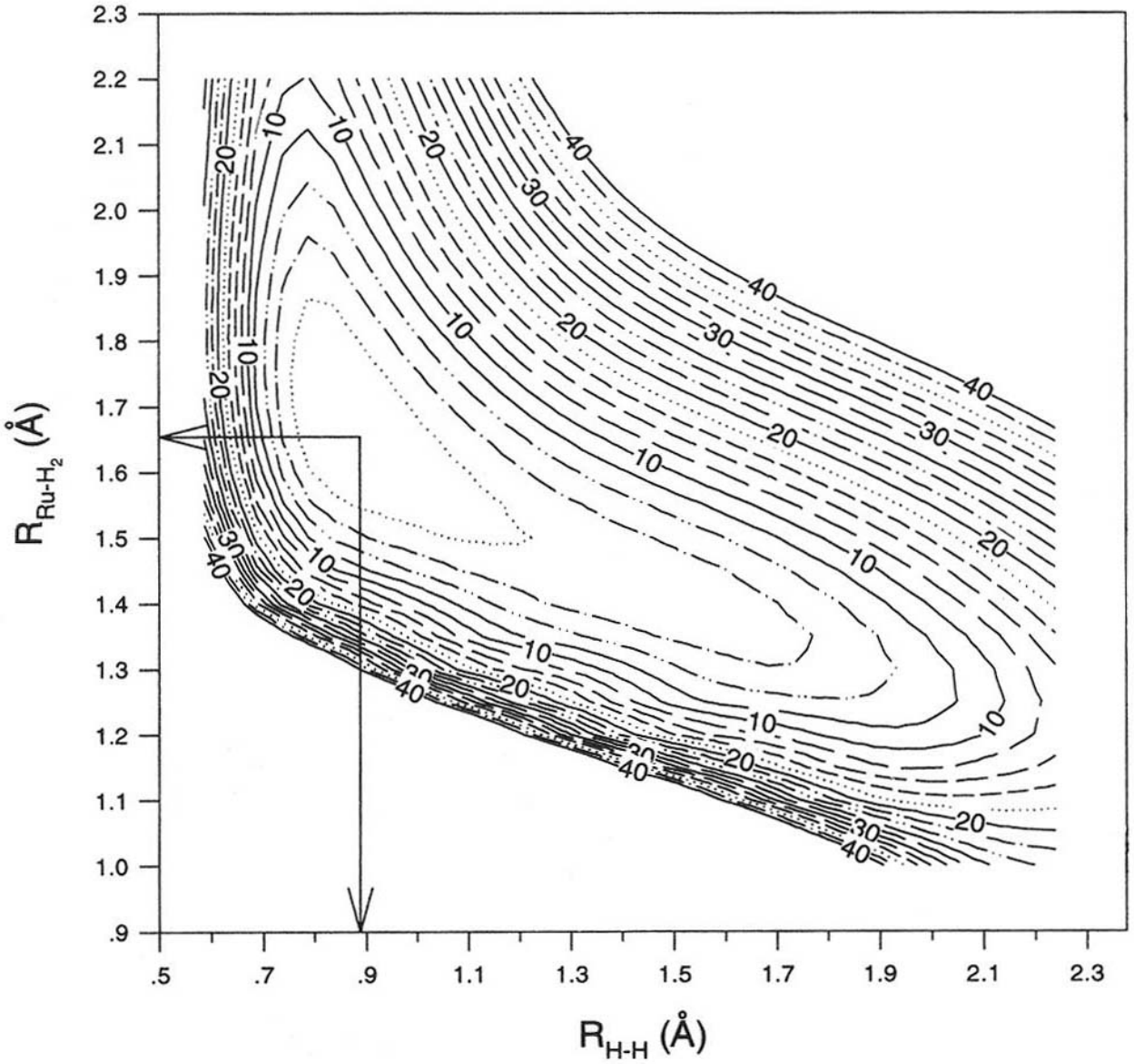

H
H
H
H7C
H6C
Ru
H
H
H1
H2
H
H16
H36
H
H
H
H
H
H

Table 3. Coupling Constants ^1J(H,D) of $[Ru(H\cdots D)(C_5Me_5)(dppm)]BF_4$ in CD_2Cl_2 as Determined by ^1H NMR Spectroscopy at 400 MHz

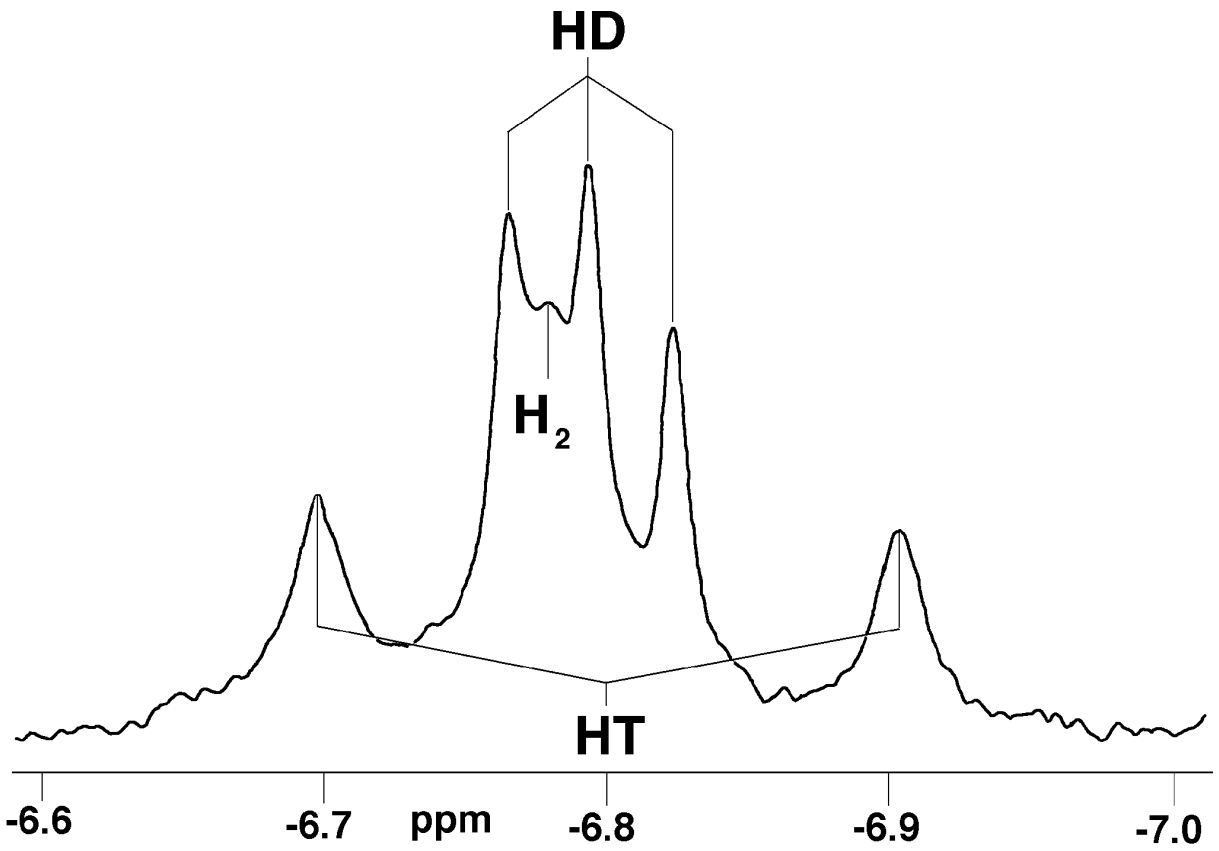
temp, K	^1J(H,D), Hz
295	21.1 ± 0.2
273	21.5 ± 0.1
253	21.6 ± 0.2
233	22.0 ± 0.1
213	22.3 ± 0.2



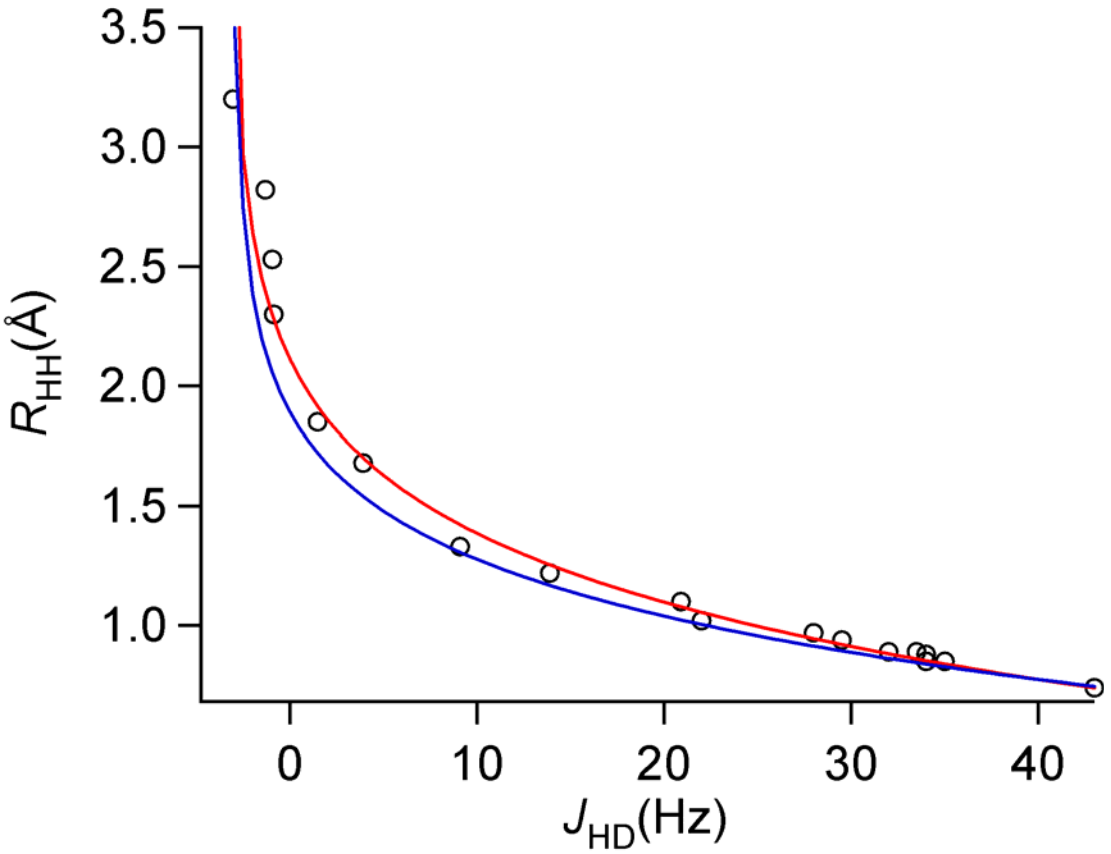
J. K. Law, H. Mellows and D. M. Heinekey
J. Am. Chem. Soc. 2001, ***123*, 2085**

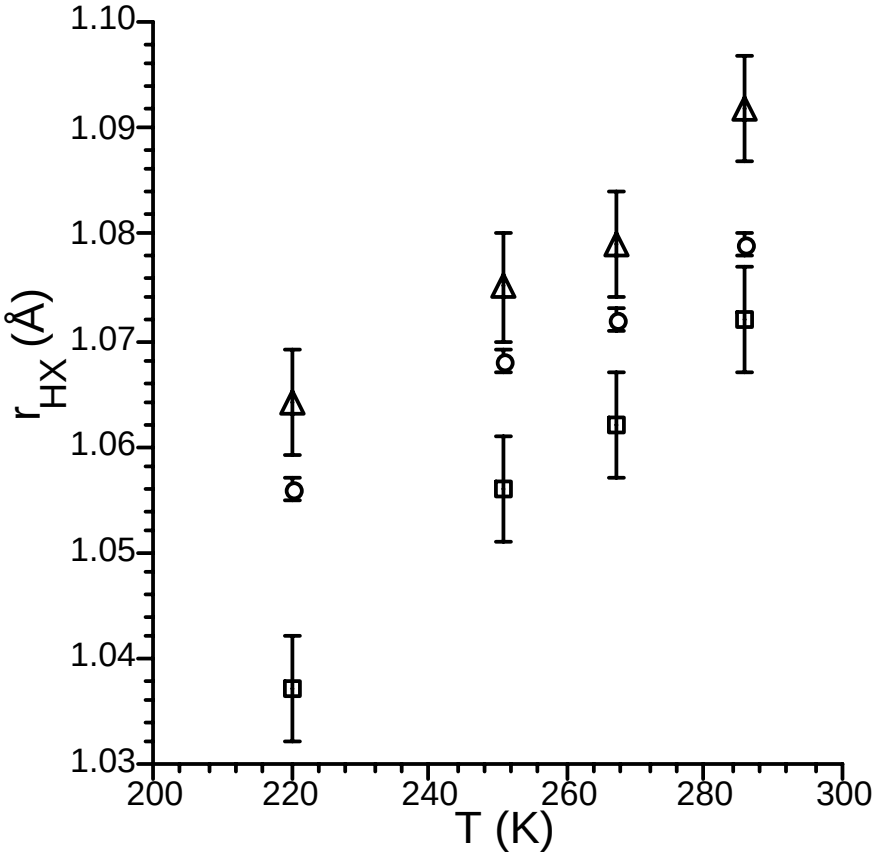


Lledos *et. al. J. Am. Chem. Soc.* **1997**, *119*, 9840



^{1}H NMR spectrum (hydride region) of a sample partially labeled with D and T

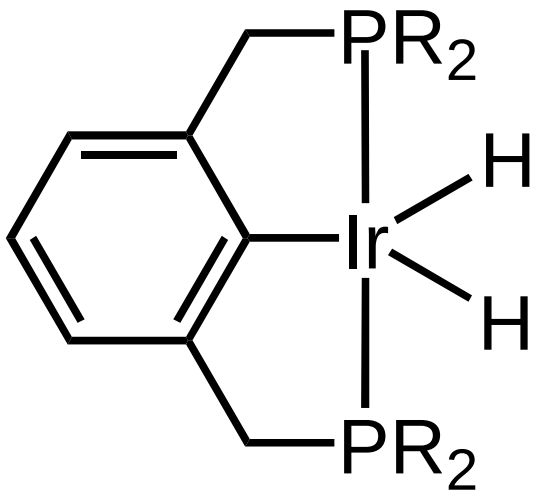

3.5
3.0
2.5
2.0
1.5
1.0
R_{HH}(Å)
0
10
20
30
40
J_{HD}(Hz)



HX distances derived from J_{HD}, J_{HT} and J_{DT}

Law, J. K.; Mellows, H.; Heinekey, D. M. *J. Am. Chem. Soc.* 2002, *124*, 1024

(pincer)Ir(H)2 complexes are active alkane dehydrogenation catalysts.*



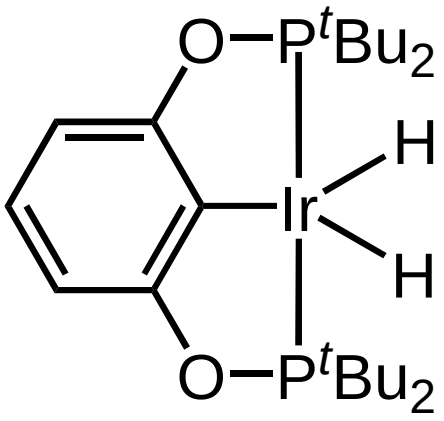
Structure?

In Silico: dH-H = 1.66 Å

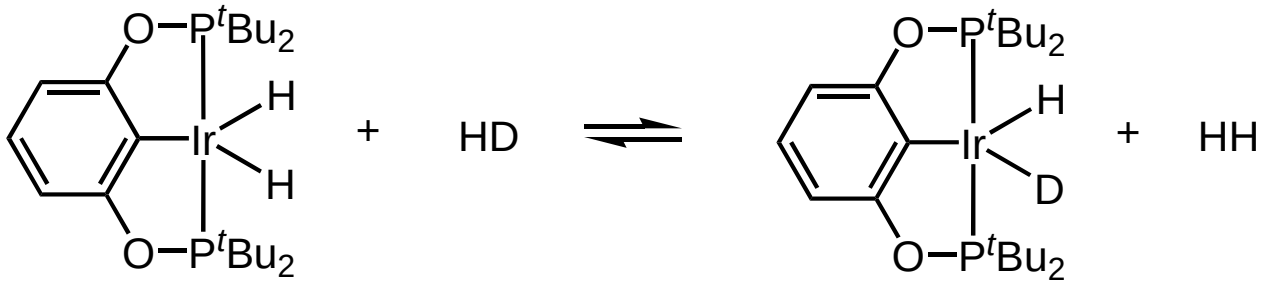
Niu and Hall, *J.Am. Chem. Soc.* **1999**, *121*, 3992.

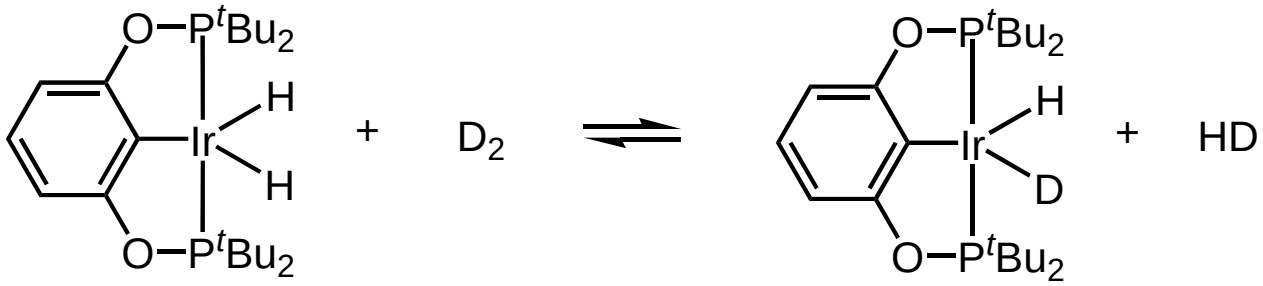
*e.g. Jensen et al. *Chem. Comm*.**1999**, 2443; Goldman et al. *J. Am. Chem. Soc.* **2002,** *124*, 11404; Brookhart et al. *J. Am. Chem. Soc.* **2004***, 126,* 1804*;* Jensen et al. *Inorg. Chim. Acta*. **2004,** *357*, 2953

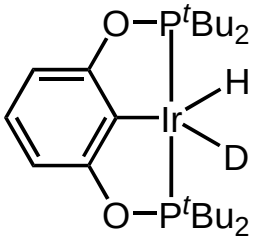
Most active catalyst for alkane dehydrogenation:



"(POCOP)Ir(H)$_2$"

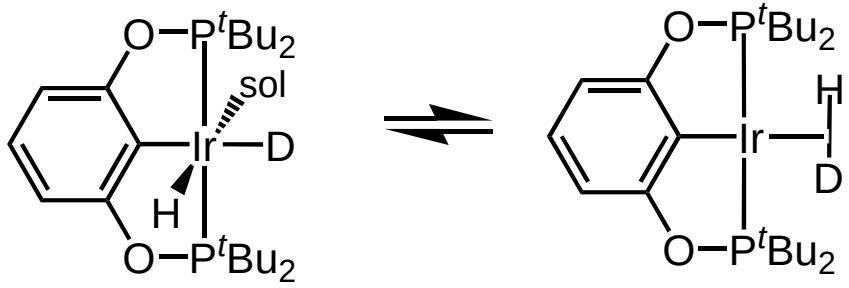

O–P^{t}Bu$_2$
H
Ir
H
O–P^{t}Bu$_2$
+
HD
O–P^{t}Bu$_2$
H
Ir
D
O–P^{t}Bu$_2$
+
HH


O–P^{t}Bu$_2$
H
Ir
H
O–P^{t}Bu$_2$
+
D$_2$
O–P^{t}Bu$_2$
H
Ir
D
O–P^{t}Bu$_2$
+
HD



J_{HD} = 7.5 Hz(pentane); T dependent

J_{HD} = zero ! (CH_2Cl_2)

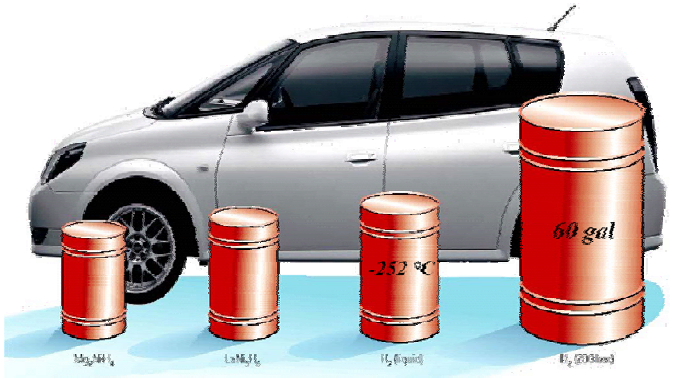


President's Hydrogen Fuel Initiative

The Hydrogen Fuel Initiative aims to reverse America's growing dependence on foreign oil by developing the technology needed for commercially viable hydrogen-powered fuel cells.

"With a new national commitment, our scientists and engineers will overcome obstacles to taking these cars from laboratory to showroom so that the first car driven by a child born today could be powered by hydrogen, and pollution-free.."

— President Bush, State of the Union Address, January 28, 2003



One obstacle is hydrogen storage ...what is needed?

Appropriate thermodynamics, High storage capacity (High gravimetric and volumetric densities), Fast kinetics, Long lifetime, Effective heat transfer, High mechanical strength and durability,Safe

http://www1.eere.energy.gov/hydrogenandfuelcells/presidents_initiative.html

Ammonia Borane as a H_2 Storage Material

DOE Storage Targets

	2010	2015
Target wt% usable H_2	6.0	9.0
Vol. density ($kgH_2.m^{-3}$)	45	80

Storage Potential of Ammonia Borane

H_2 Released	**1**	**2**	**3**
Wt% H_2	6.5	13.0	19.6
Vol. density	48	96	145
Product	$[H_2NBH_2]_n$	$[HNBH]_n$	$[NB]_n$

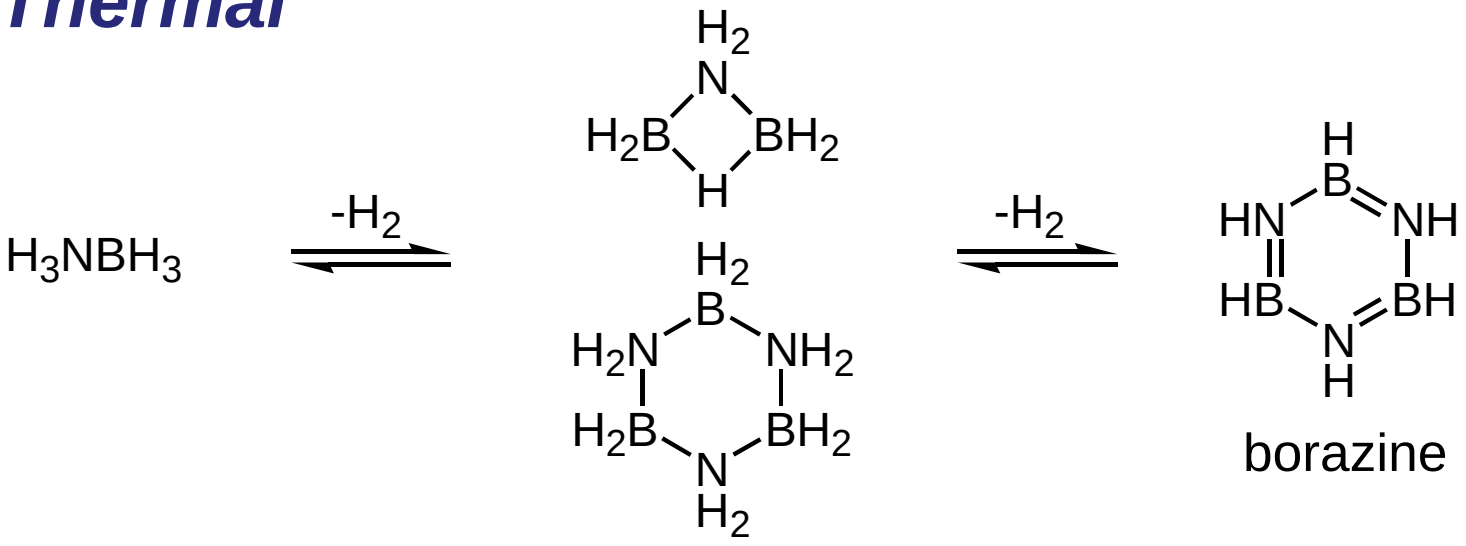
Appropriate Thermodynamics

- Gas phase calculations predict ammonia borane dehydrogenation is near thermoneutral.*
- Important for reversibility.

*Dixon, D. A.; Gutowski, M. *J. Phys. Chem. A* **2005**, *109*, 5129.

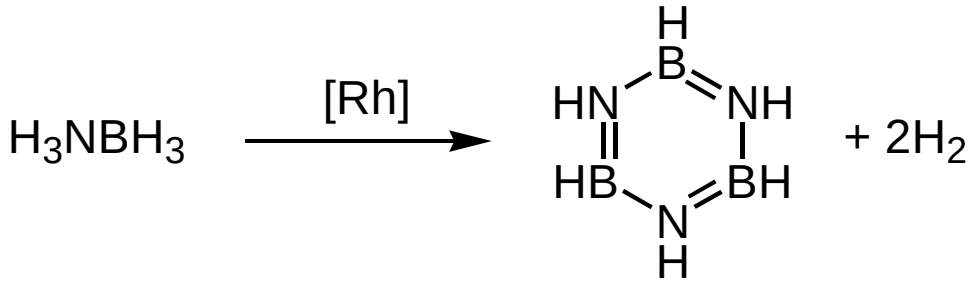
Dehydrogenation of Ammonia Borane

Thermal



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

Catalyzed



0.6 mol% catalyst

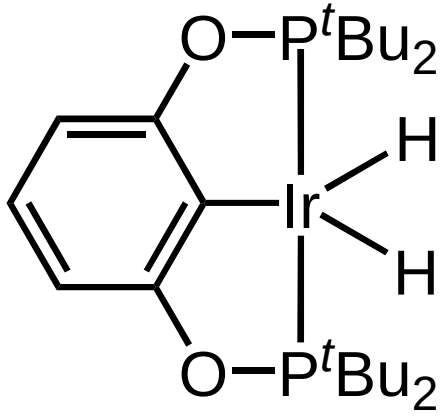
48 – 84 hours at 45 ºC

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

A Better Catalyst Choice?

$$n\ NH_3BH_3 \xrightarrow[THF,\ rt]{[catalyst]} [NH_2BH_2]_n + n\ H_2$$

- Amineboranes are isoelectronic with alkanes.
- (pincer)Ir$(H)_2$ complexes are active alkane dehydrogenation catalysts.*

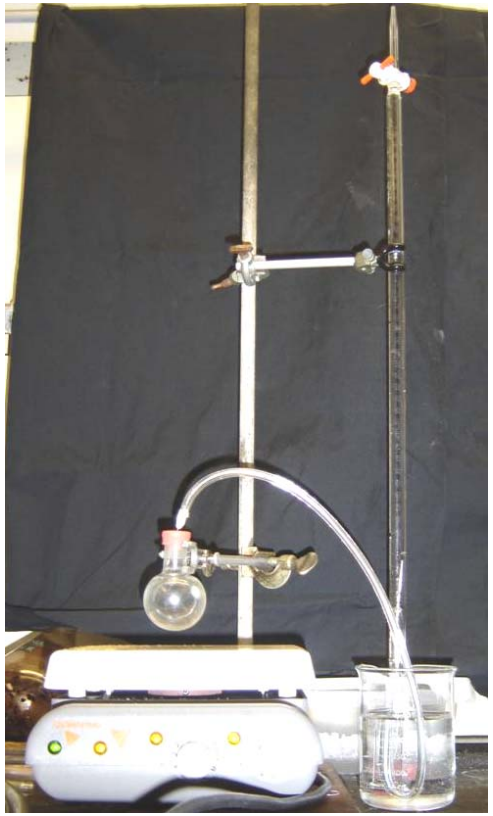


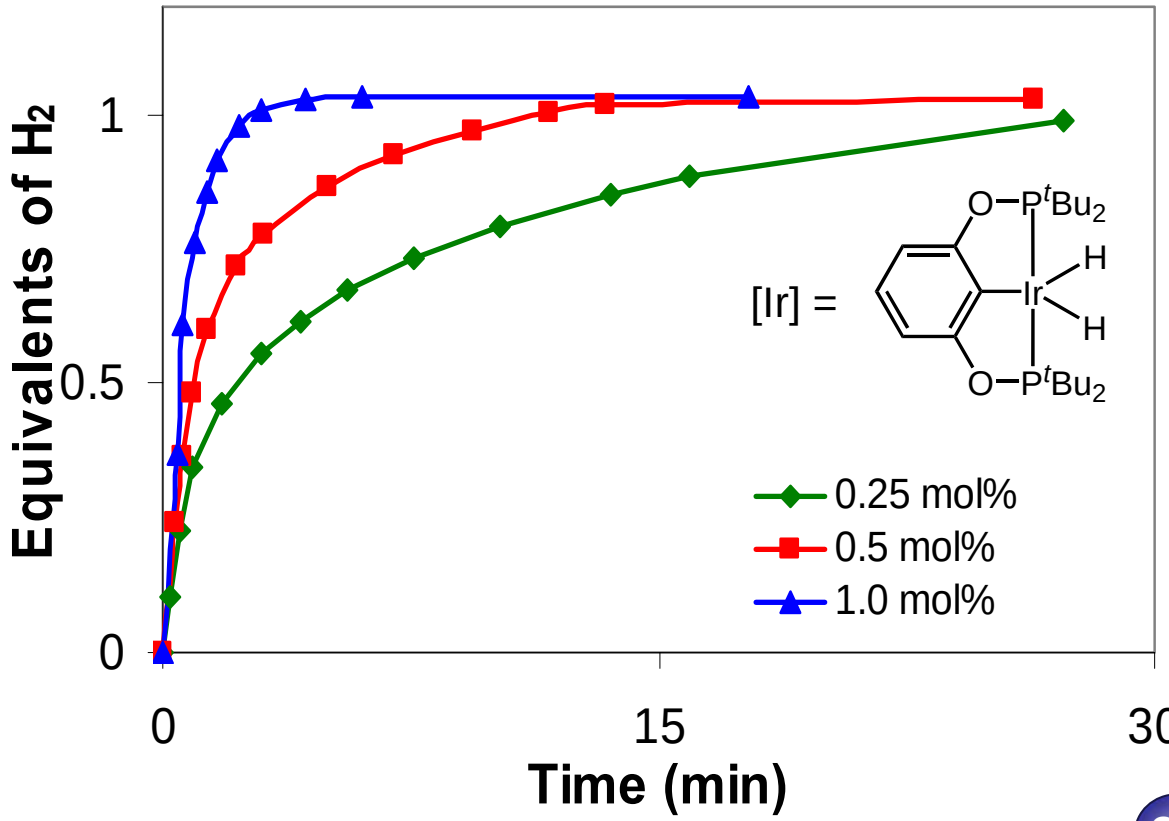
"(POCOP)Ir$(H)_2$"

*e.g. Jensen et al. *Chem. Comm.***1999**, 2443; Goldman et al. *J. Am. Chem. Soc.* **2002,** *124*, 11404; Brookhart et al. *J. Am. Chem. Soc.* **2004***, 126,* 1804*;* Jensen et al. *Inorg. Chim. Acta*. **2004,** *357*, 2953

Quantification of Hydrogen

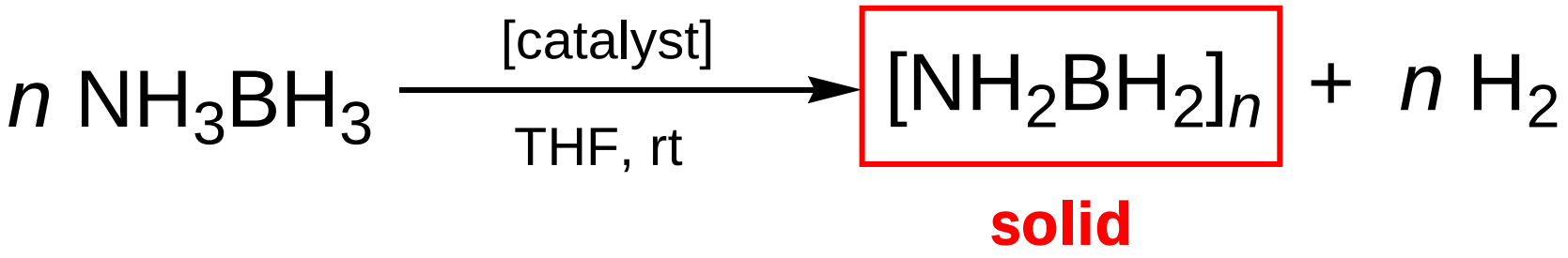
$$n\ NH_3BH_3 \xrightarrow[THF,\ rt]{[Ir]} [NH_2BH_2]_n + n\ H_2$$



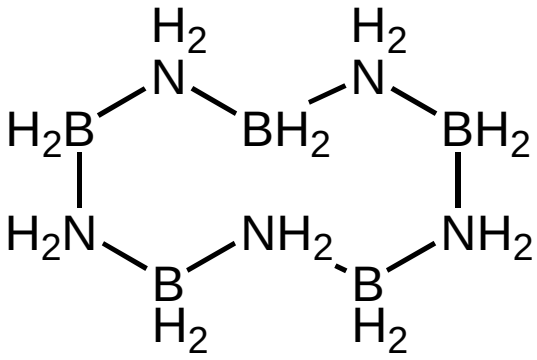


Demonstration of H_2 Release

Characterization of Solid Product



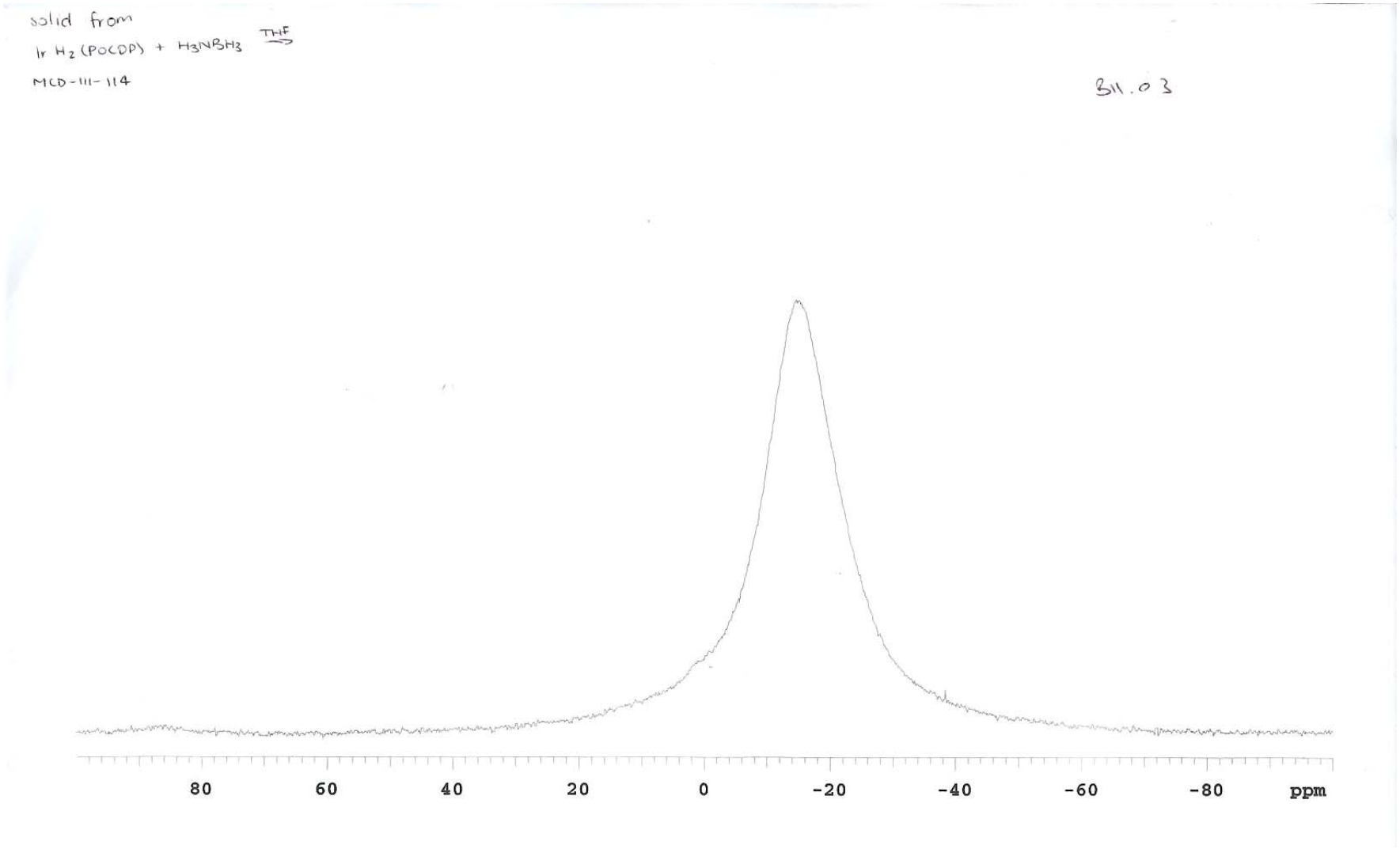
- Solid state ^{11}B NMR.
- Infrared spectroscopy.
- Powder X-ray diffraction.
- Non-volatile product should not poison fuel cell.



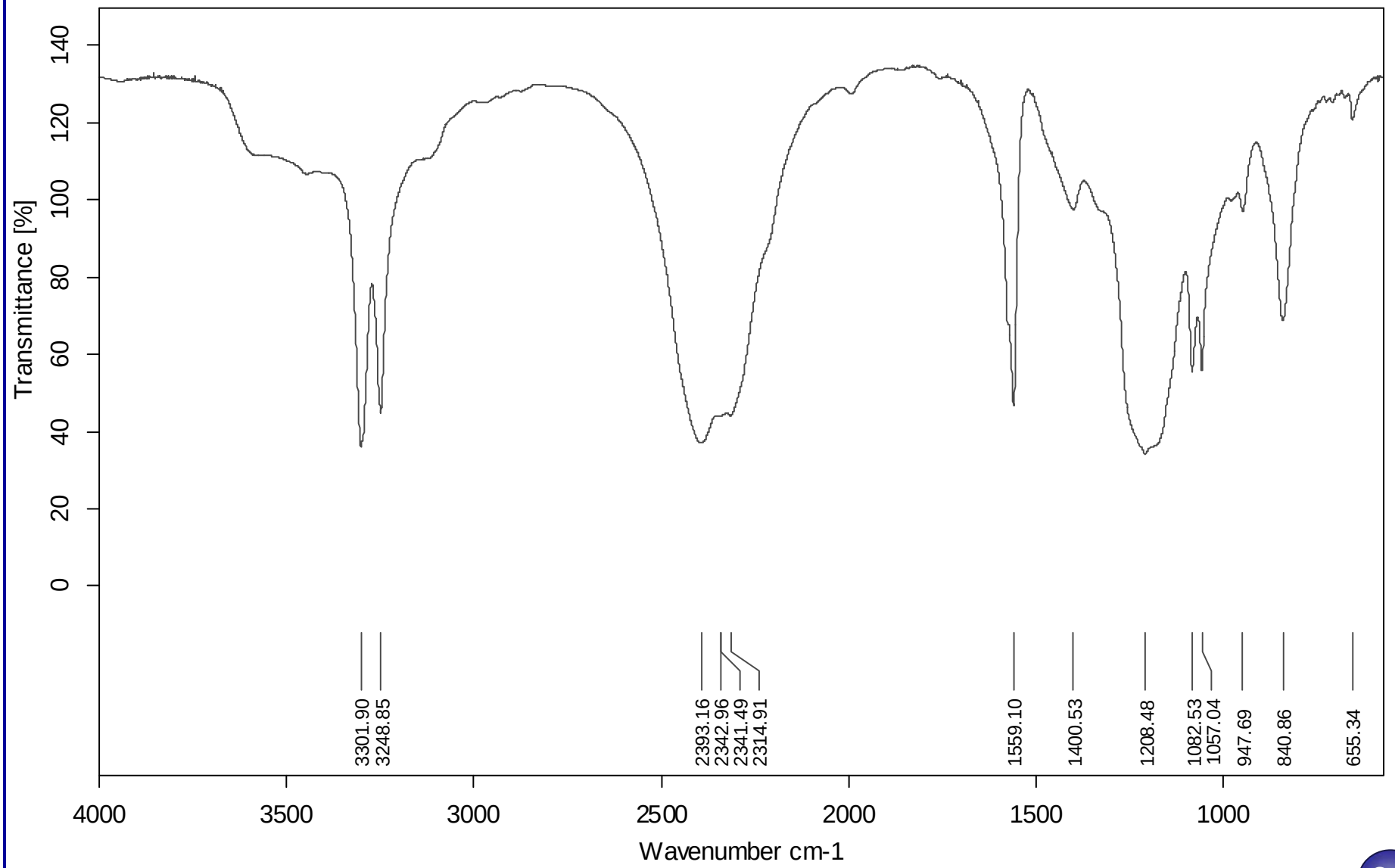
$n = 5$

Böddeker, K. W.; *et al. J. Am. Chem. Soc.* **1966**, *88*, 4396

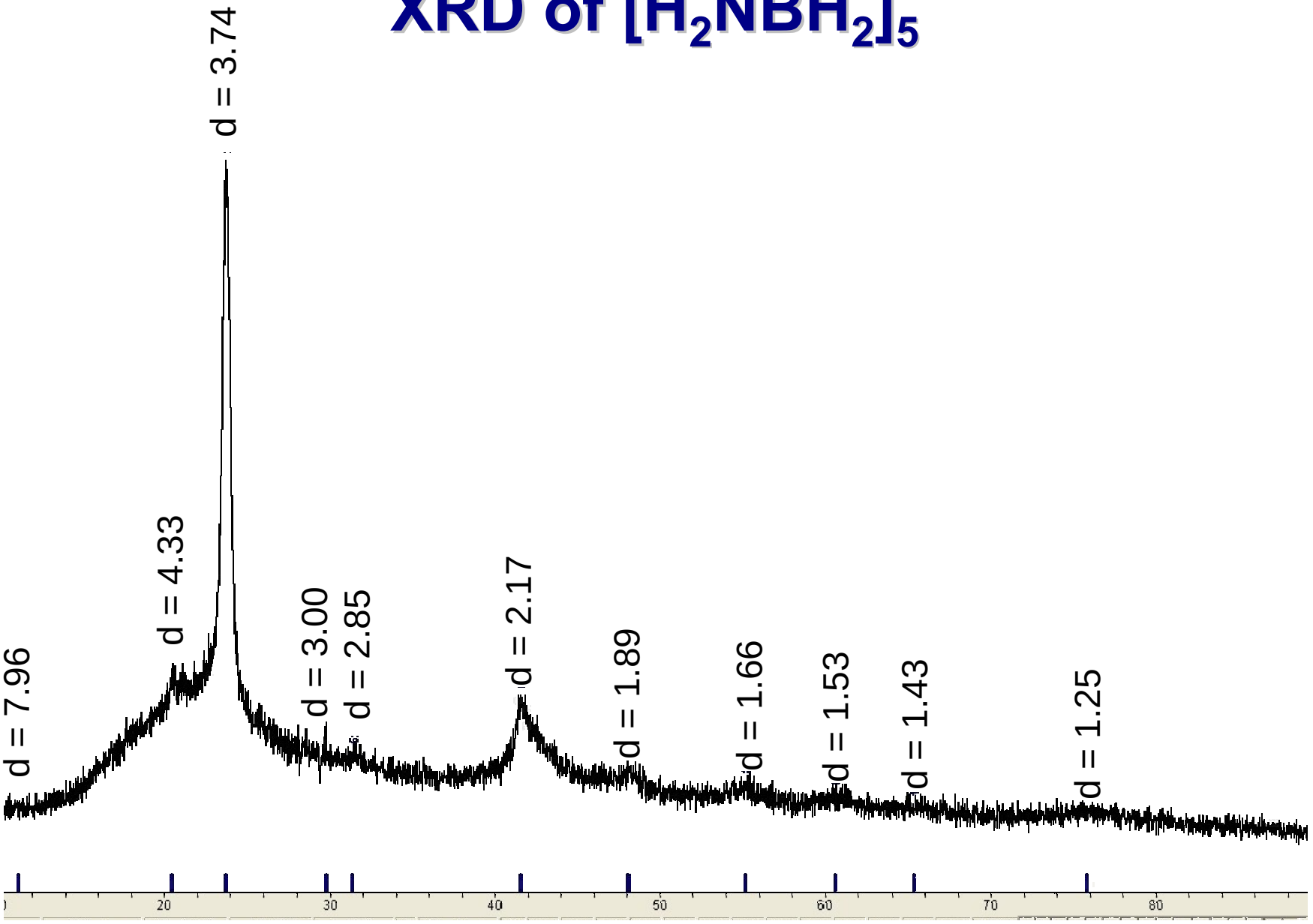
Solid State ^{11}B NMR of $[BH_2NH_2]_5$



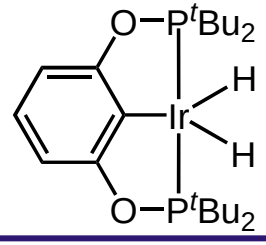
IR of $[BH_2NH_2]_5$



XRD of $[H_2NBH_2]_5$



Comparison with Previous Best Catalyst

	$[Rh(1,5\text{-}COD)(\mu\text{-}Cl)]_2$*	
Catalyst Loading	0.6 mol%	0.5 mol%
Temperature (ºC)	**45**	**25**
H_2 evolved (equiv.)	2	1
Products	Borazine	$[H_2NBH_2]_n$
Time	**48 – 84 hr**	**< 15 min**

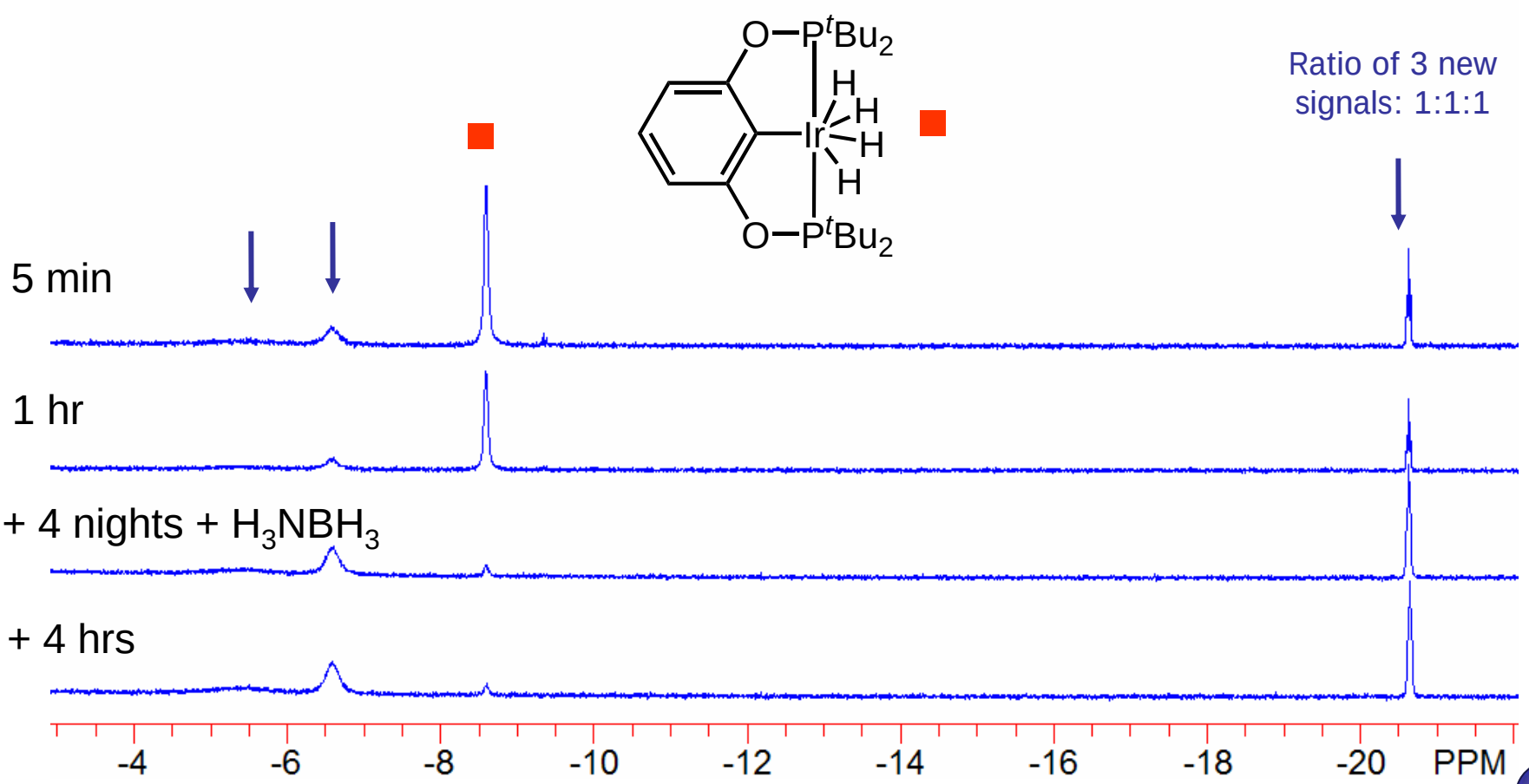
At least 200 fold increase in reaction rate over previous best.

*Manners *et al. J. Am. Chem. Soc.* **2003**, *125*, 9424.

Formation of Catalytically Dormant Species

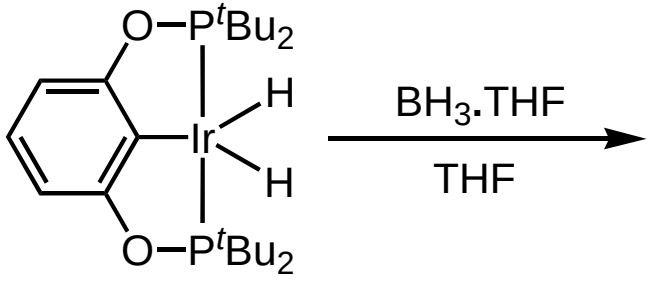
$$5\ H_3NBH_3 \xrightarrow[THF,\ rt]{(POCOP)IrH_2} [H_2NBH_2]_5 + 5\ H_2$$

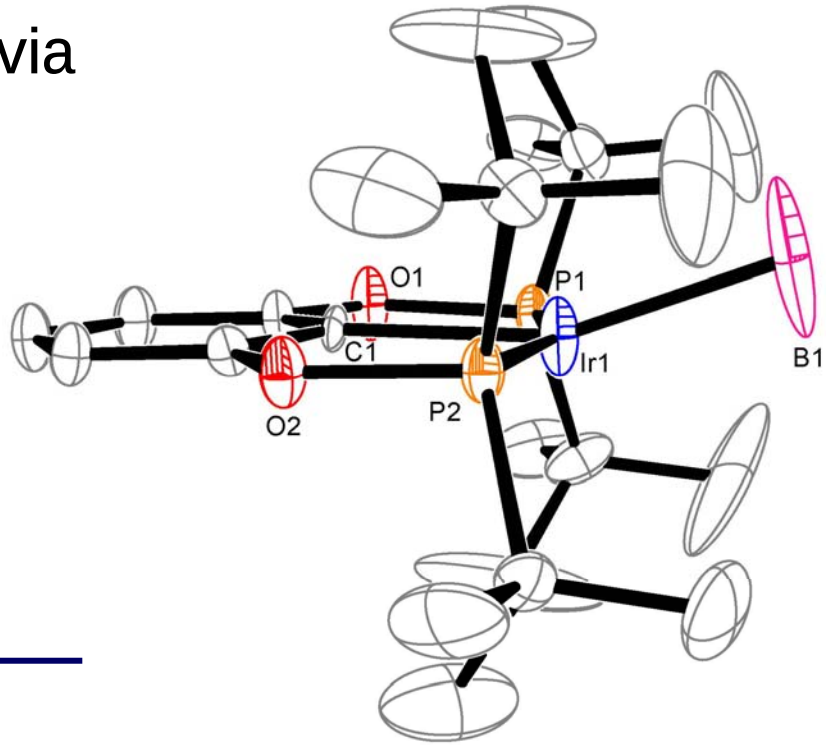
^{1}H NMR: Hydride region



Identification of Dormant Species

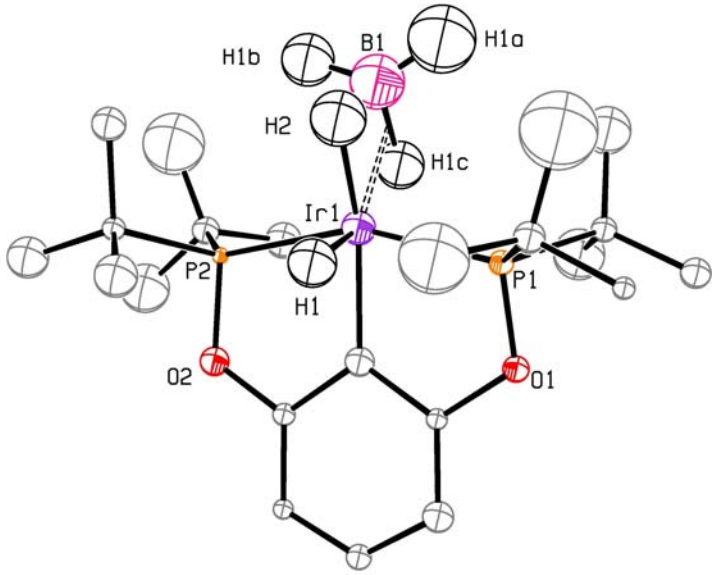
Same compound is formed via





	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)

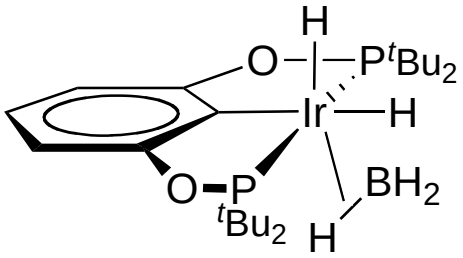
Neutron Structure

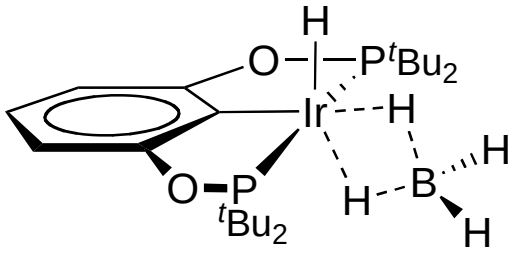


Bond Lengths (Å)

Ir1-B1	2.37(3)
Ir1-P1	2.29(2)
Ir1-P2	2.31(2)
Ir1-C1	1.99(2)
Ir1-H1	1.61(4)
Ir1-H2	1.74(4)
Ir1-ctr	2.02(1)
B1-H1a	1.18(8)
B1-H1b	1.22(5)
B1-H1c	1.45(5)
B1-H2	1.74

$(POCOP)Ir(BH_3)(H)_2$ or $(POCOP)Ir(BH_4)(H)$

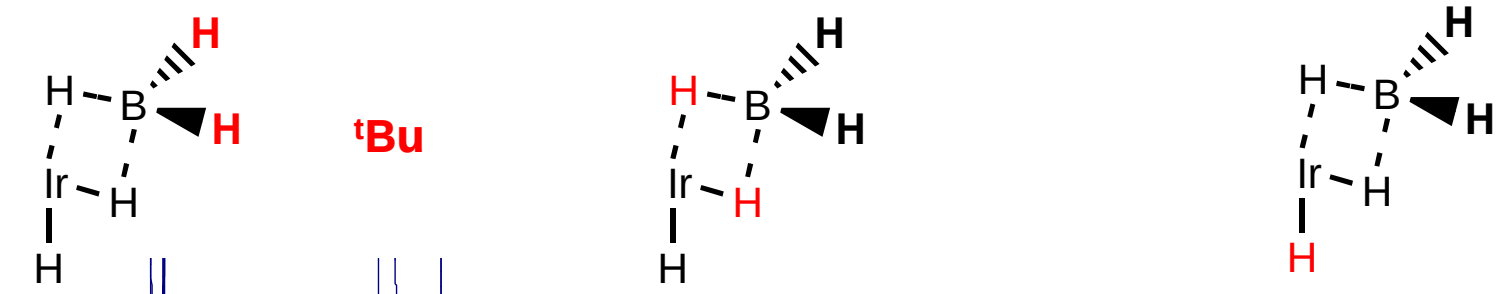


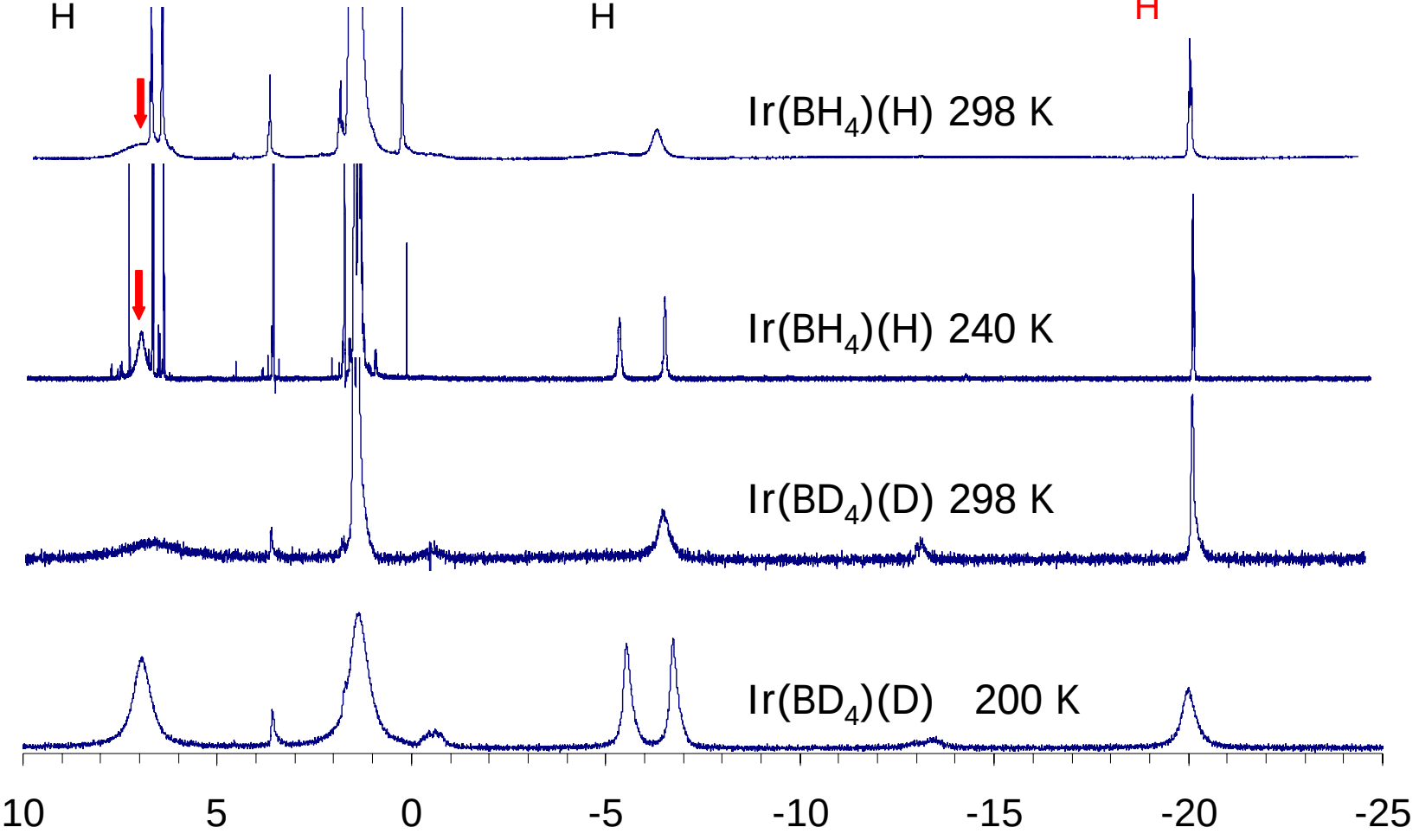


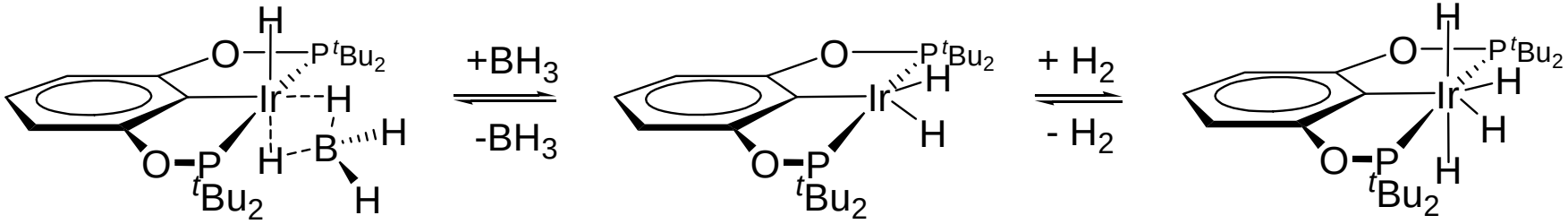
*ctr is the center of the B1 – H1C bond

IR: B-H stretches at 2466(s), 2441(s), 2285(s) and 2219 cm^{-1}(m) and Ir-H at 1930 cm^{-1}(m)

NMR of Ir(BD$_4$)D Analogue



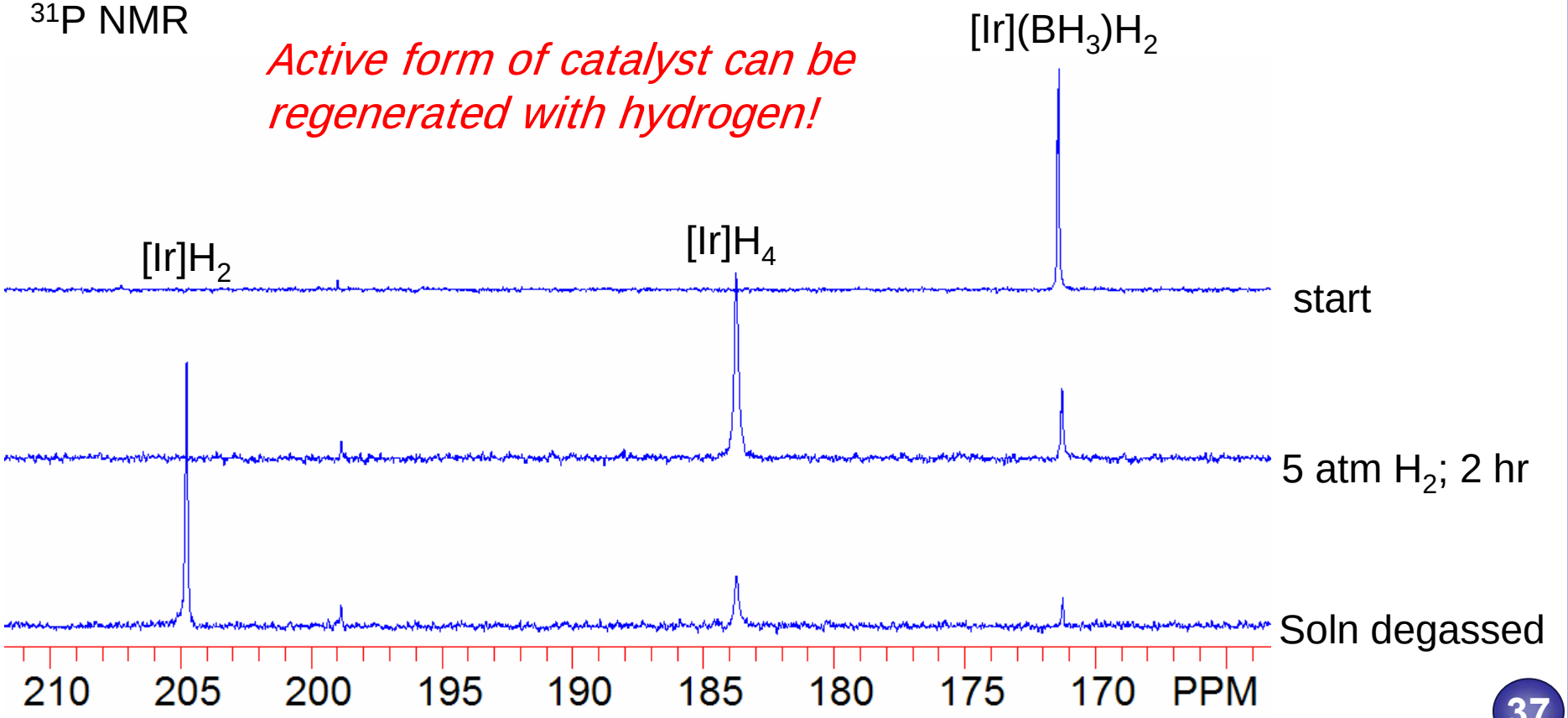




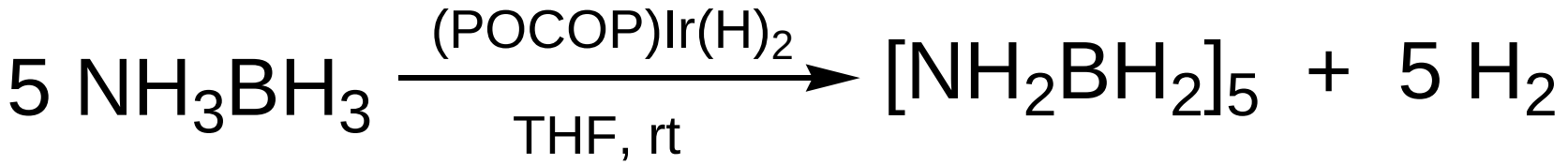
DORMANT **ACTIVE** **ACTIVE**

^{31}P NMR

Active form of catalyst can be regenerated with hydrogen!



Dehydrogenation of Ammonia Borane



- ✓ Efficient catalyst discovered.
- ✓ Reaction proceeds under mild conditions.
- ✓ Non-volatile $[NH_2BH_2]_5$ formed.
- ✓ Regeneration of active catalyst using hydrogen.

- Reversibility?

New (last week) solution calorimetry data from PNNL:

$$NH_3BH_3 \longrightarrow 1/5\ (NH_2BH_2)_5 + H_2$$

$$\Delta H = -28\ kJ/mol$$

Acknowledgements

DOE Center of Excellence For Chemical Hydrogen Storage