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# Inorganic Chemistry in Hydrogen Storage and Biomass Catalysis

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Dave Thorn, Los Alamos National Laboratory

June 15, 2012

With special thanks to:

DOE Hydrogen Program, and the talented PIs and Co-Is in the Chemical Hydrogen Storage Center of Excellence (especially Bill Tumas, Tony Burrell, Tom Baker, John Gordon, Ben Davis, Andrew Sutton)

LANL LDRD and the Center for Enabling New Technologies through Catalysis (especially Susan Hanson, Andrew Sutton, Tom Baker, John Gordon [LANL]; Wes Borden, Dave Hrovat, Tom Cundari [UNT] )

# Inorganic Chemistry in Hydrogen Storage and Biomass Catalysis

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"Inorganic Chemistry in Hydrogen Storage and Biomass Catalysis"

Making or breaking C-H, B-H, C-C bonds has been at the core of catalysis for many years. Making or breaking these bonds to store or recover energy presents us with fresh challenges, including how to catalyze these transformations in molecular systems that are "tuned" to minimize energy loss and in molecular and material systems present in biomass. This talk will discuss some challenging transformations in chemical hydrogen storage, and some aspects of the inorganic chemistry we are studying in the development of catalysts for biomass utilization.

# The Hydrogen Storage Story

Chemical Hydrogen Storage Center of Excellence, 2003

Chose chemical systems that possess two key attributes:

- Inherent energy density  
(H<sub>2</sub> storage capacity) >6 wt% H<sub>2</sub>
- Favorable thermodynamics  
for H<sub>2</sub> release

DOE Targets for Onboard Hydrogen Storage Systems for Light-Duty Vehicles

Table 2 Technical Targets: Onboard Hydrogen Storage Systems				
Storage Parameter	Units	2010	2017	Ultimate
System Gravimetric Capacity: Usable, specific-energy from H <sub>2</sub> (net useful energy/max system mass) <sup>a</sup>	kWh/kg (kg H <sub>2</sub> /kg system)	1.5 (0.045)	1.8 (0.055)	2.5 (0.075)
System Volumetric Capacity: Usable energy density from H <sub>2</sub> (net useful energy/max system volume)	kWh/L (kg H <sub>2</sub> /L system)	0.9 (0.028)	1.3 (0.040)	2.3 (0.070)
Storage System Cost <sup>b</sup> :	\$/kWh net (\$/kg H <sub>2</sub> )	TBD (TBD)	TBD (TBD)	TBD (TBD)
• Fuel cost <sup>c</sup>	\$/gge at pump	3-7	2-4	2-4
Durability/Operability: • Operating ambient temperature <sup>d</sup>	°C	-30/50 (sun)	-40/60 (sun)	-40/60 (sun)
• Min/max delivery temperature	°C	-40/85	-40/85	-40/85
• Operational cycle life (1/4 tank to full) <sup>e</sup>	Cycles	1000	1500	1500
• Min delivery pressure from storage system; FC= fuel cell, ICE= internal combustion engine	bar (abs)	5 FC/35 ICE	5 FC/35 ICE	3 FC/35 ICE
• Max delivery pressure from storage system <sup>f</sup>	bar (abs)	12 FC/100 ICE	12 FC/100 ICE	12 FC/100 ICE
• Onboard Efficiency	%	90	90	90
• Well-to-Plant Efficiency	%	60	60	60
Charging / Discharging Rates: • System fill time (5 kg)	min	4.2	3.3	2.5
• Minimum full flow rate	(kg H <sub>2</sub> /min)	(1.2)	(1.5)	(2.0)
• Start time to full flow (20°C) <sup>g</sup>	(g)/kW	0.02	0.02	0.02
• Start time to full flow (-20°C) <sup>h</sup>	s	5	5	5
• Transient response 10%-90% and 90%-0% <sup>i</sup>	s	15	15	15
	s	0.75	0.75	0.75
Fuel Purity (H <sub>2</sub> from storage) <sup>j</sup> :	% H <sub>2</sub>	SAE J2719 and ISO/PDTS 14687-2 (99.97% dry basis)		
Environmental Health & Safety: • Permeation & leakage <sup>k</sup>	g/wh	Meets or exceeds applicable standards		
• Toxicity	-			
• Safety	-			
• Loss of useable H <sub>2</sub> <sup>l</sup>	(g)/kg H <sub>2</sub> stored	0.1	0.05	0.05

Useful constraints: 0.2778 kWh/MJ; 33.3 kWh/kg H<sub>2</sub>; 1 kg H<sub>2</sub> = 1 gal gasoline equivalent.

Note: The above targets are based on the lower heating value of hydrogen. Targets are for a complete system, including tank, material, valves, regulators, piping, mounting brackets, insulation, added cooling capacity, and/or other balance-of-plant components. All capacities are defined as useable capacities that could be delivered to the powerplant (i.e. fuel cell or internal combustion engine). All targets must be met at the end of service life (approximately 1,500 cycles or 5,000 operation hours, equivalent of 150,000 miles). Unless otherwise indicated, all targets are for both hydrogen internal combustion engine and for hydrogen fuel cell use, based on the low likelihood of power plant specific fuel being commercially viable. Commercial systems must meet manufacturing specifications for cycle life variation; see note [e] to cycle life below.

Revision 4.0

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[http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdf/s/targets\\_onboard\\_hydro\\_storage.pdf](http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdf/s/targets_onboard_hydro_storage.pdf)

[http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdf/s/targets\\_onboard\\_hydro\\_storage\\_explanation.pdf](http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdf/s/targets_onboard_hydro_storage_explanation.pdf)



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Slide 3

# The Hydrogen Storage Story

Tier	Chemical System	Research Focus
1	NaBH <sub>4</sub> /water (“Hydrogen on Demand” ®)	<i>More energy efficient synthesis of NaBH<sub>4</sub></i>
2	Other B-H systems, e.g. NH <sub>3</sub> BH <sub>3</sub>	Develop effective catalysts and systems for H <sub>2</sub> release; <b>develop energy-efficient regeneration</b>
3	“Other than boron” (C,N,O)-H {Si, P, Al}-H	<b>Identify systems with viable H<sub>2</sub> release thermodynamics, and develop enabling catalytic processes</b>

This talk:

- Systems other than boron
- Energy-efficient regeneration of NH<sub>3</sub>BH<sub>3</sub>

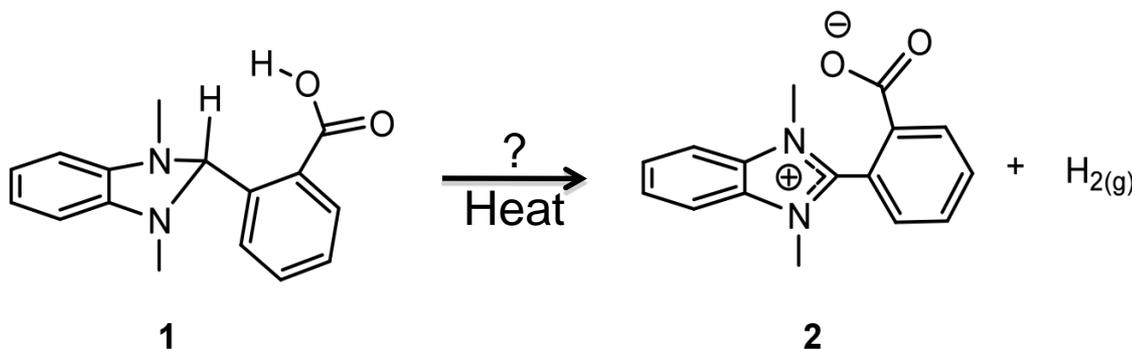
# Hydrogen Storage: Systems other than Boron

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- Dehydrogenation of e.g. decalin known for hydrogen storage, requires high grade heat ( $\Delta H$  ca. 17 kcal/mole of  $H_2$  at ca. 280 C for 1 atm pressure)
- The need for high-grade heat limits storage efficiency ( $\Delta H$  requires burning ca. 0.25 mole of  $H_2$  per mole of  $H_2$  released from decalin)
- *Efficient hydrogen storage using (C,N,O)-H requires new concepts*
  - Wuest et al
  - Crabtree et al
  - Cooper, Pez et al

# Heteroatom Organic Systems for Hydrogen Storage

- Borrowed from the literature: “especially good formal donors of hydride”



- “However, despite the juxtaposition of a hydridic C-H bond and a carboxylic acid .. It does not undergo intramolecular protonolysis to form H<sub>2</sub>.”

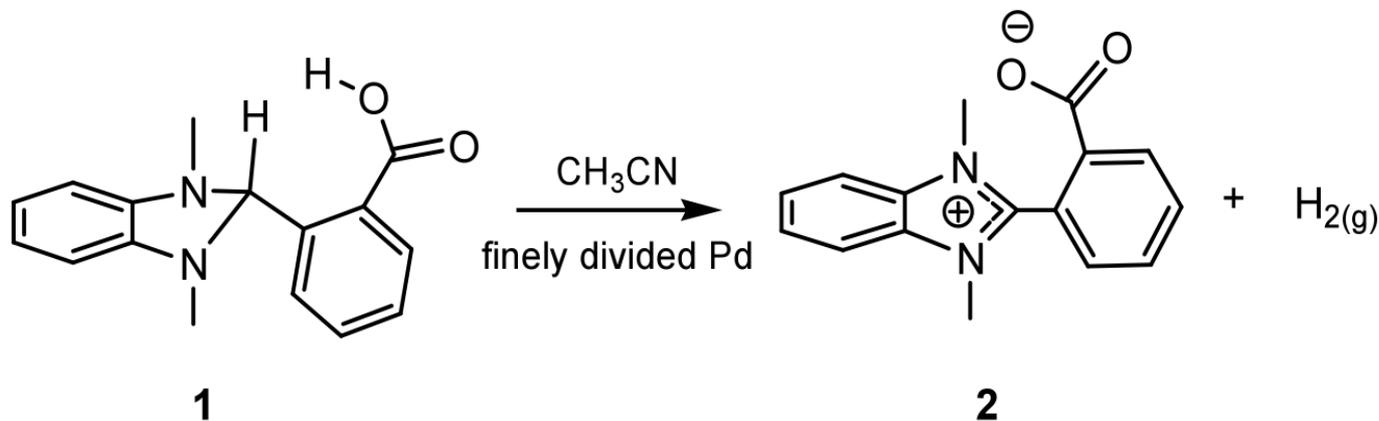
Can. J. Chem. 1996, 74, 689

- Regarding H<sub>2</sub> release from other, related, dihydrobenzimidazoles:  
“Unfortunately, this novel reaction ... is endothermic..”  
J. Org. Chem. 1988, 53, 1489

# Heteroatom Organic Systems for Hydrogen Storage

“Unfortunately, this novel reaction ... is endothermic..”

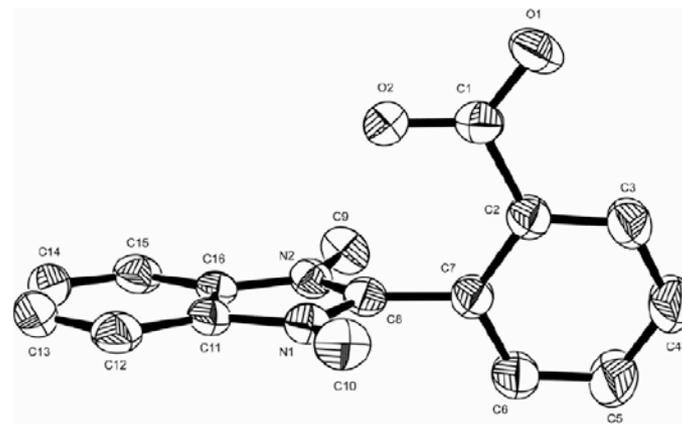
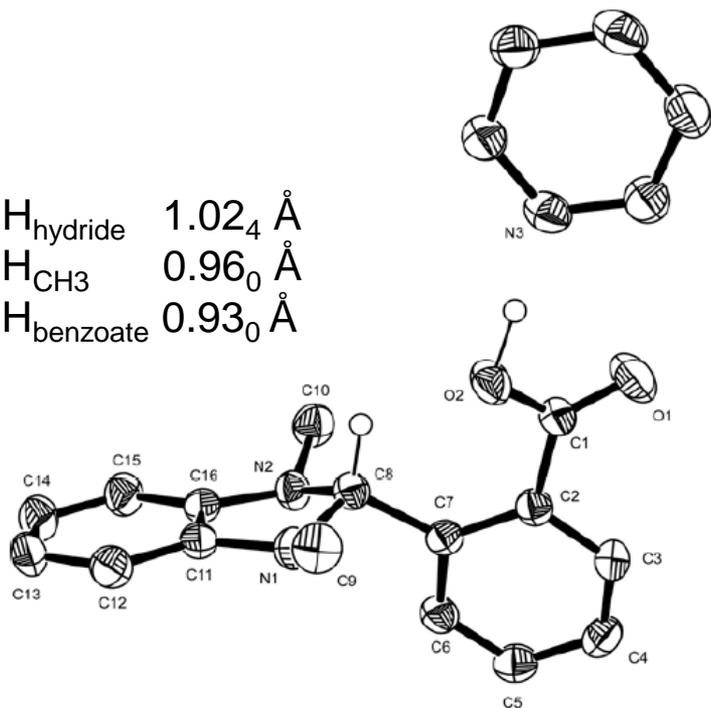
We suspected that the reaction was actually exergonic  
but that a suitable catalyst was needed to release H<sub>2</sub>,  
and found that Pd(0) is an effective catalyst (RT → 80 C)



# Heteroatom Organic Systems for Hydrogen Storage

Juxtaposition of a hydridic C-H bond and a carboxylic acid?

$\text{C-H}_{\text{hydride}}$  1.02<sub>4</sub> Å  
 $\text{C-H}_{\text{CH}_3}$  0.96<sub>0</sub> Å  
 $\text{C-H}_{\text{benzoate}}$  0.93<sub>0</sub> Å



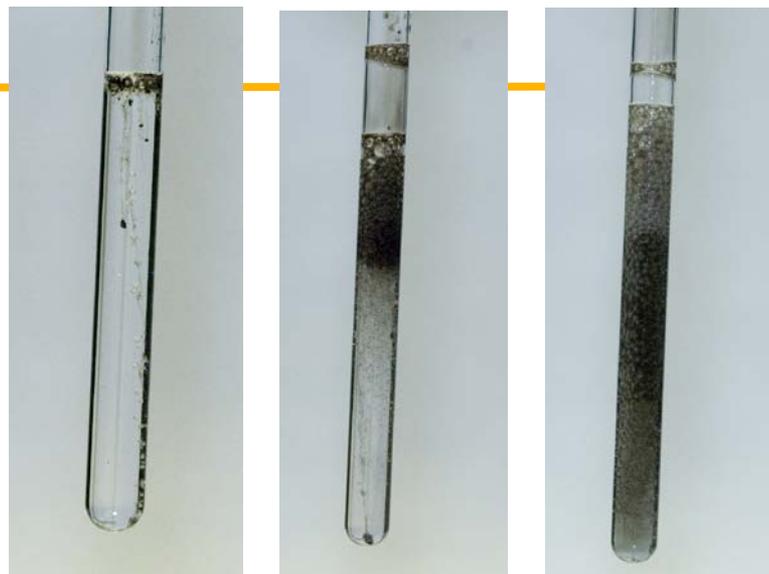
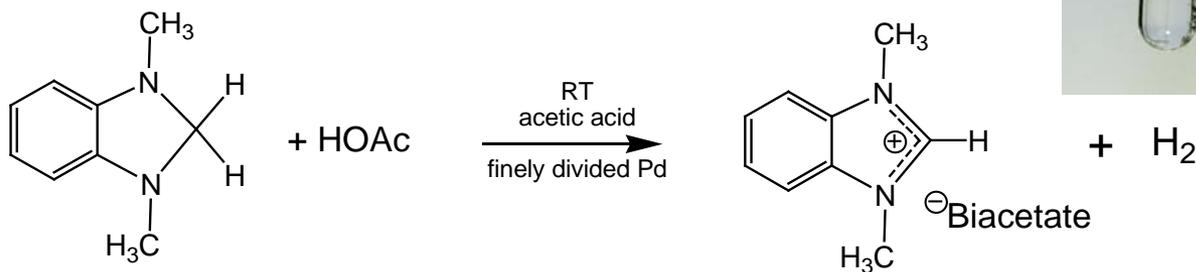
Compound 1, *recrystallized from pyridine*

Compound 2

# Heteroatom Organic Systems for Hydrogen Storage

- Next step:

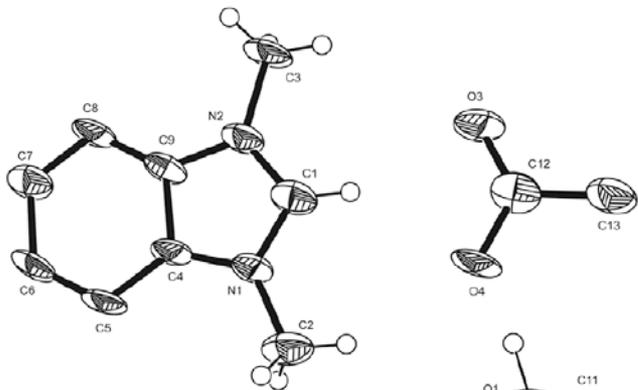
- H<sub>2</sub> storage density far too low (0.75% releasable H<sub>2</sub> in compound 1)
- eliminate benzoic acid group in favor of a lighter acid



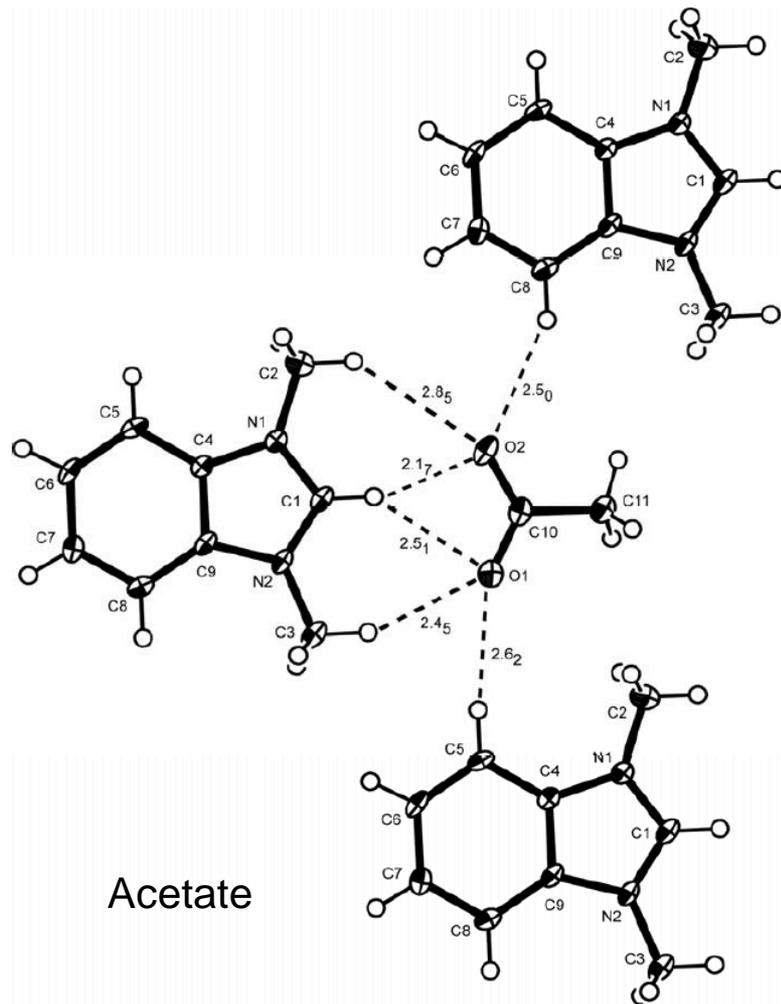
Hydrogen release is facile at room temperature (turnover rate ca. 30/min, mole/mole Pd)  
H<sub>2</sub> release is exothermic ( $\Delta H$  ca.  $-10(3)$  kcal/mole), exergonic ( $\Delta G$  ca.  $-17(5)$  kcal/mole),  
and irreversible with H<sub>2</sub> pressure alone  
Hydrogen yield is quantitative, but limited to 1 wt% H<sub>2</sub> by mwt of components

# Heteroatom Organic Systems for Hydrogen Storage

Crystal structures of carboxylate products:  
Potential CH...O hydrogen bonding,  
expressed in a coplanar "CH pocket" motif:



Biacetate

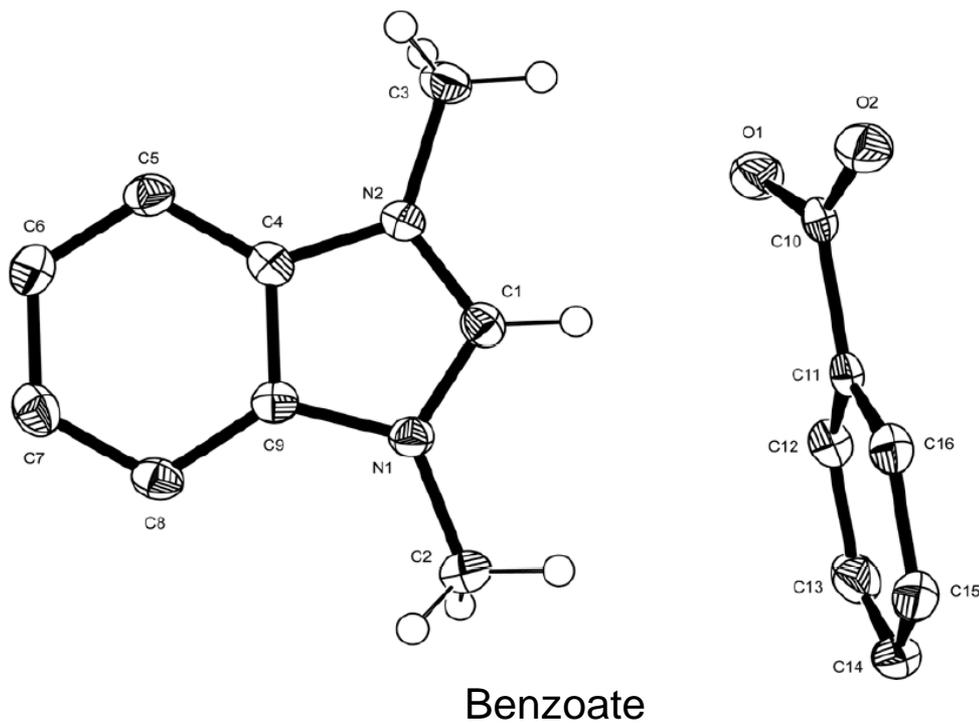


Acetate

# Heteroatom Organic Systems for Hydrogen Storage

How robust is the coplanar “CH pocket” motif in directing dimethylbenzimidazolium carboxylate structures?

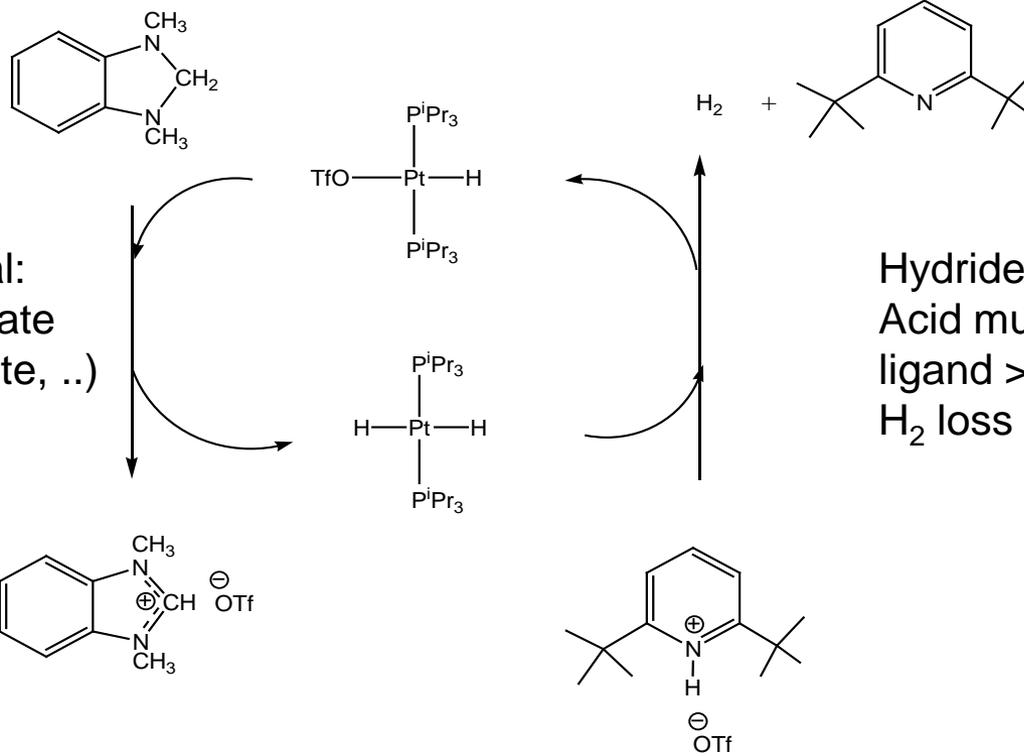
Not very ...



# Catalysis: Improve Reaction Rates

Catalysts: What potential in homogeneous catalysts?

- secondary C-H bonds traditionally difficult
- Wilkinson's catalyst, ruthenium-phosphine catalysts work, but slowly (< 2 turnover/min, 70 C)
- Found faster Pt-based homogeneous catalyst (ca. 1-10 turnovers/min at 20 C)



# Catalysis: *Why is it Necessary??*

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- Why doesn't the juxtaposition of the hydridic C-H bond and a carboxylic acid enable facile formation of H<sub>2</sub>?
- In part, kinetic barrier results from poor coupling of electron and proton transfer
- In part, this can be rationalized by (lack of) symmetry:
  - The covalent H-H bond requires a nearly equal participation of “valence bond” and “symmetric ionic” wavefunctions
  - Yet in a {hydride + proton} reaction the ionic contributions are highly asymmetric

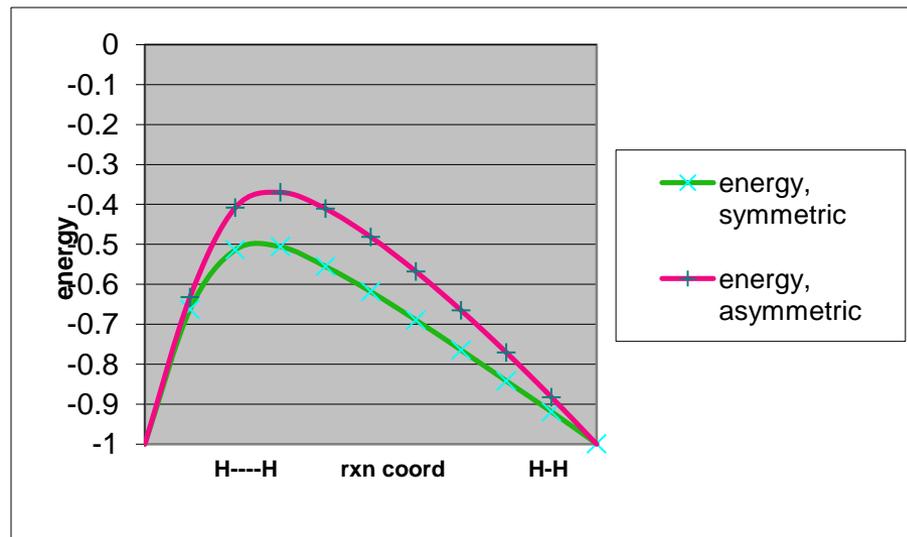
# Catalysis: *Why is it Necessary??*

- In a very simplistic model, the asymmetry of the ionic contributions in the starting compound impose an additional transition-state energy relative to the energy if the two hydrogen atoms were symmetric in the starting compound

- One way to make the two hydrogen atoms symmetrical, is to put them both on the same transition metal center

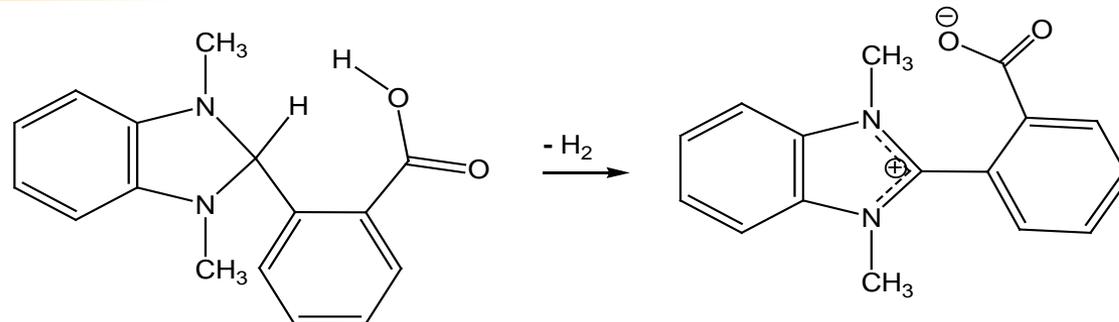
e.g.  $[\text{trans}-(\text{PR}_3)_2\text{Pt}(\text{H}_2)\text{H}]^+$

(Stahl, Labinger, Bercaw *Inorg. Chem.* 1998, 37, 2422)

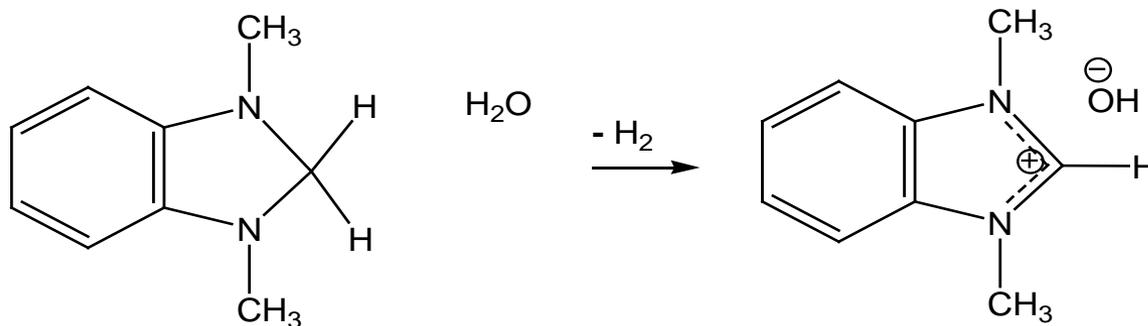


# Path to Improved Capacity

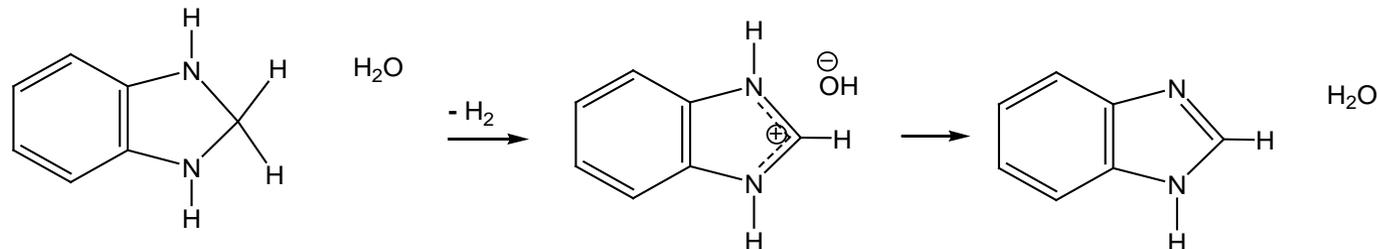
Parent system:  
0.75% H<sub>2</sub>



Replace C<sub>6</sub>H<sub>4</sub>COOH  
with H<sub>2</sub>O:  
1.2% H<sub>2</sub>

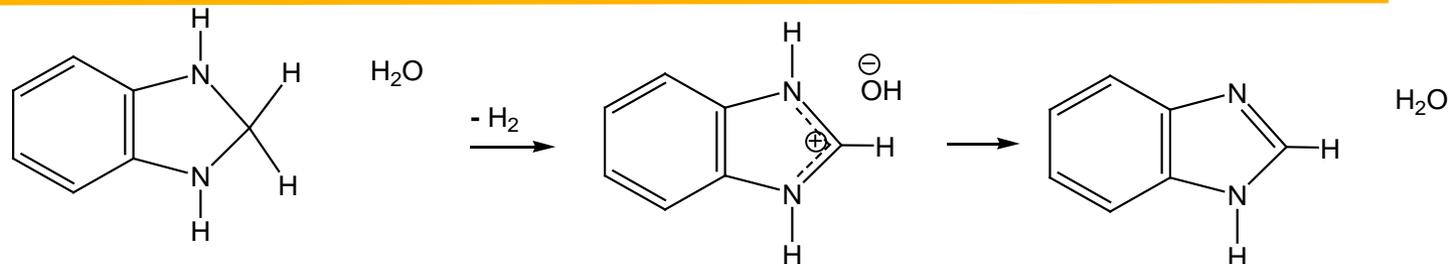


Replace N-CH<sub>3</sub>  
with N-H:  
1.5% H<sub>2</sub>

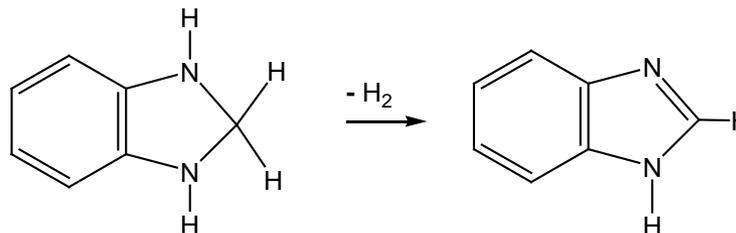


# And on paper, we can keep going ...

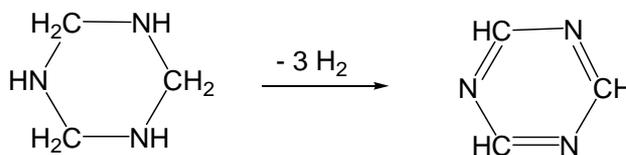
Replace N-CH<sub>3</sub>  
with N-H:  
1.5% H<sub>2</sub>



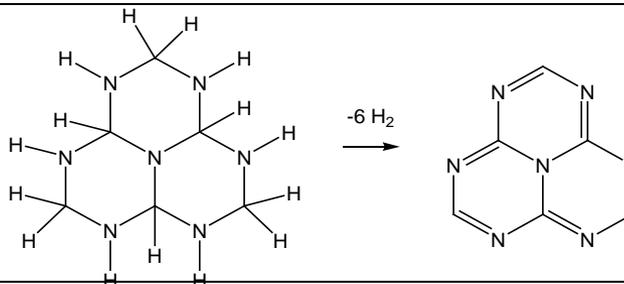
and the H<sub>2</sub>O becomes  
unnecessary:  
1.7% H<sub>2</sub>



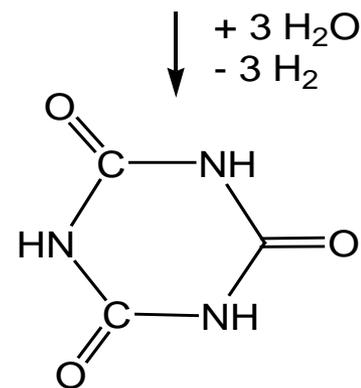
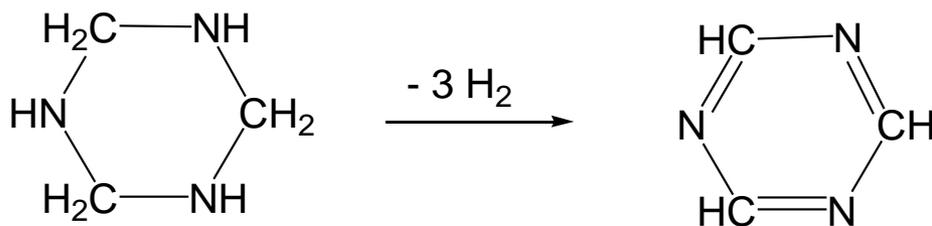
Then replace the benzo  
with additional  
-CH<sub>2</sub>NH- units:  
6.9% H<sub>2</sub>



If necessary,  
stabilize by fusion  
6.5% H<sub>2</sub>



# ... and keep going ...



and now bring back the H<sub>2</sub>O:

8.6% H<sub>2</sub>

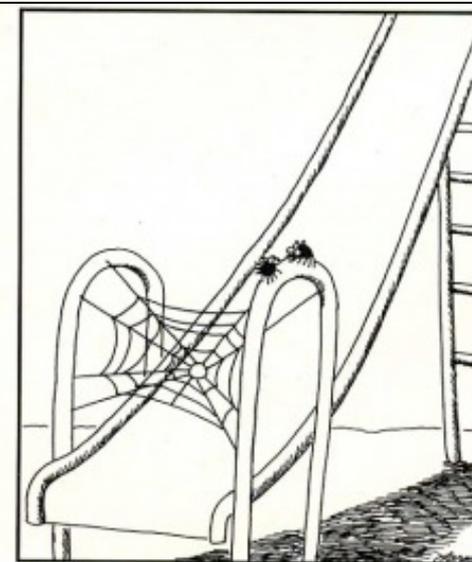
(13.9% H<sub>2</sub> if water is free)

- The big steps are

Getting the cyclo-(CH<sub>2</sub>NH)<sub>3</sub> system (or fused analogs) to work

Enabling the dehydrogenative urea formation

Improved catalysts for hydrogen evolution

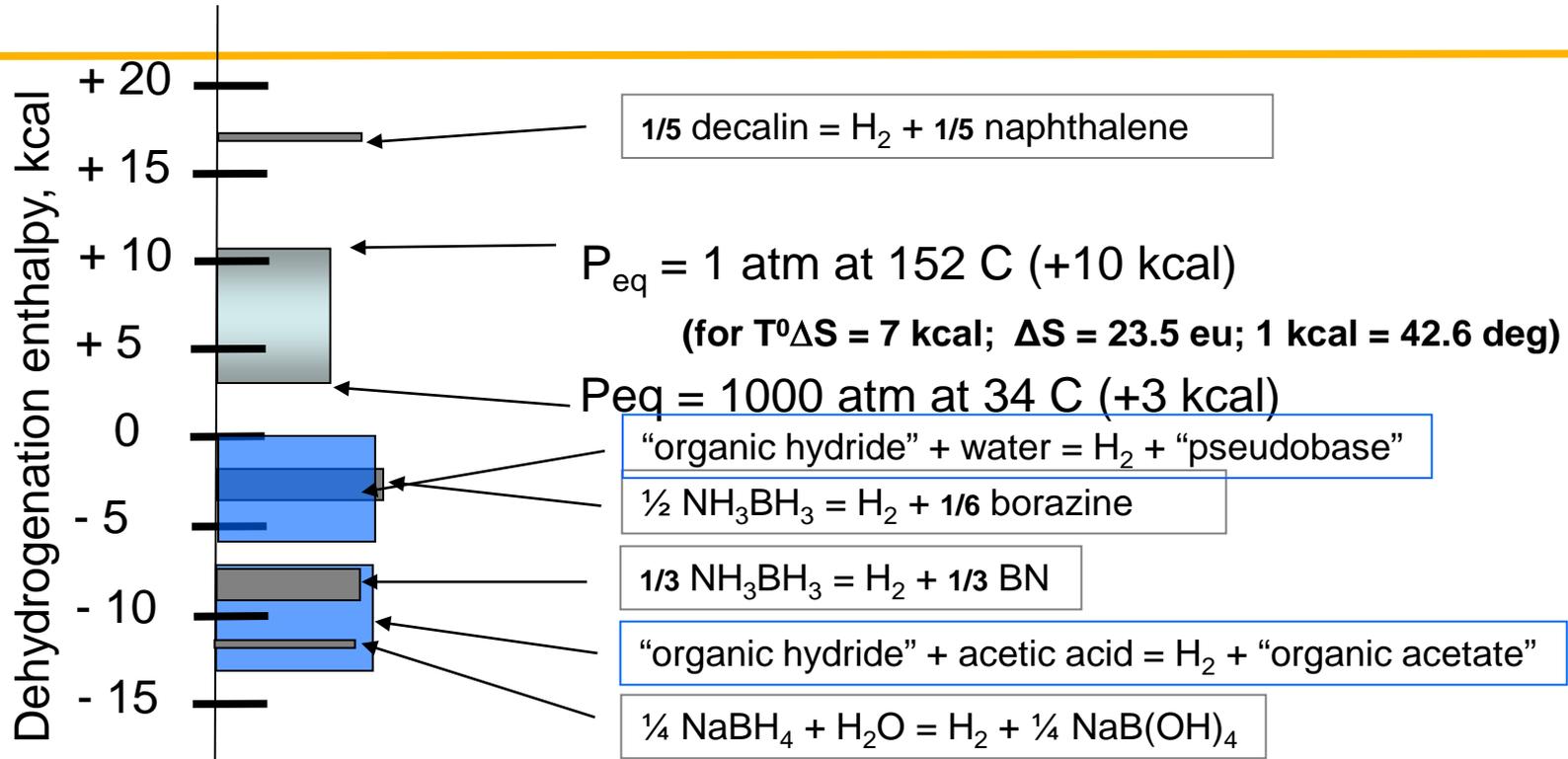


"If we pull this off, we'll eat like kings."

# Ammonia Borane Regeneration

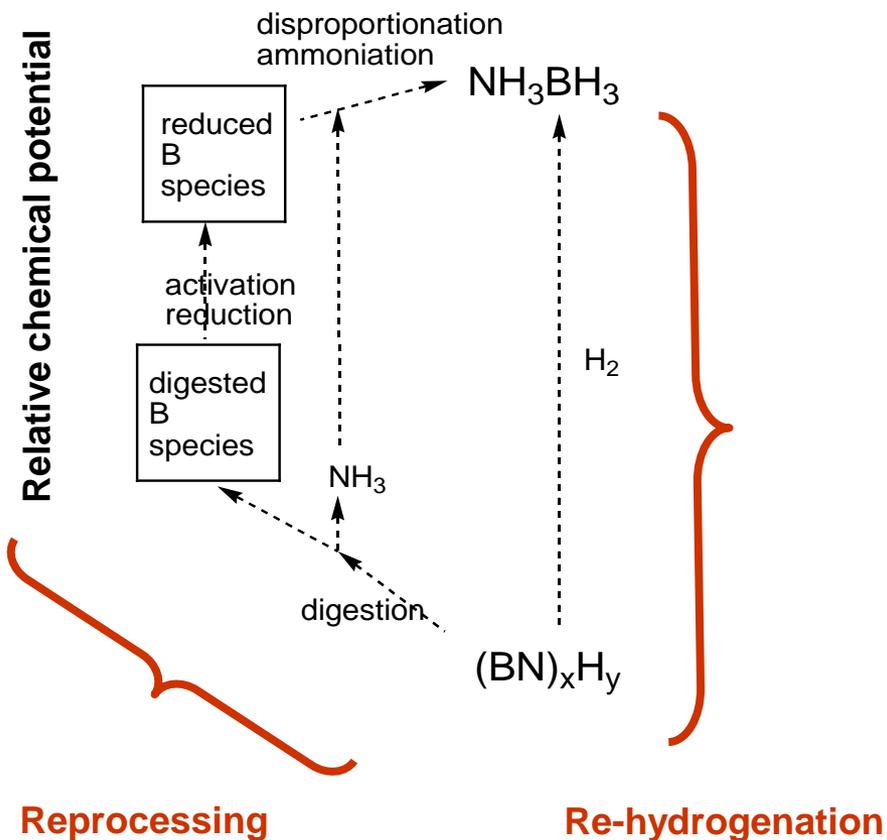
Tier	Chemical System	Research Focus
1	NaBH <sub>4</sub> /water (“Hydrogen on Demand” ®)	<i>More energy efficient synthesis of NaBH<sub>4</sub></i>
2	Other B-H systems, e.g. NH <sub>3</sub> BH <sub>3</sub>	Develop effective catalysts and systems for H <sub>2</sub> release; <b>develop energy-efficient regeneration</b>
3	“Other than boron” (C,N,O)-H {Si, P, Al}-H	<b><i>Identify systems with viable H<sub>2</sub> release thermodynamics, and develop enabling catalytic processes</i></b>

# Regeneration vs. Enthalpy



If  $\Delta H$  for dehydrogenation > ca. 10 kcal, requires too much on-board heat for storage  
 If < ca. 3 kcal, requires too much pressure to rehydrogenate  
 (If < 0, exothermic, requires at least 136,000 atm)

# Toward AB Regeneration



Toward minimally-costly reprocessing:

## Digestion

Agent competent to digest  $(\text{BN})_x\text{H}_x$ ,  
readily liberated from  $\text{NH}_3$   
Digested B species:  
readily reducible to BH species

## Reduction

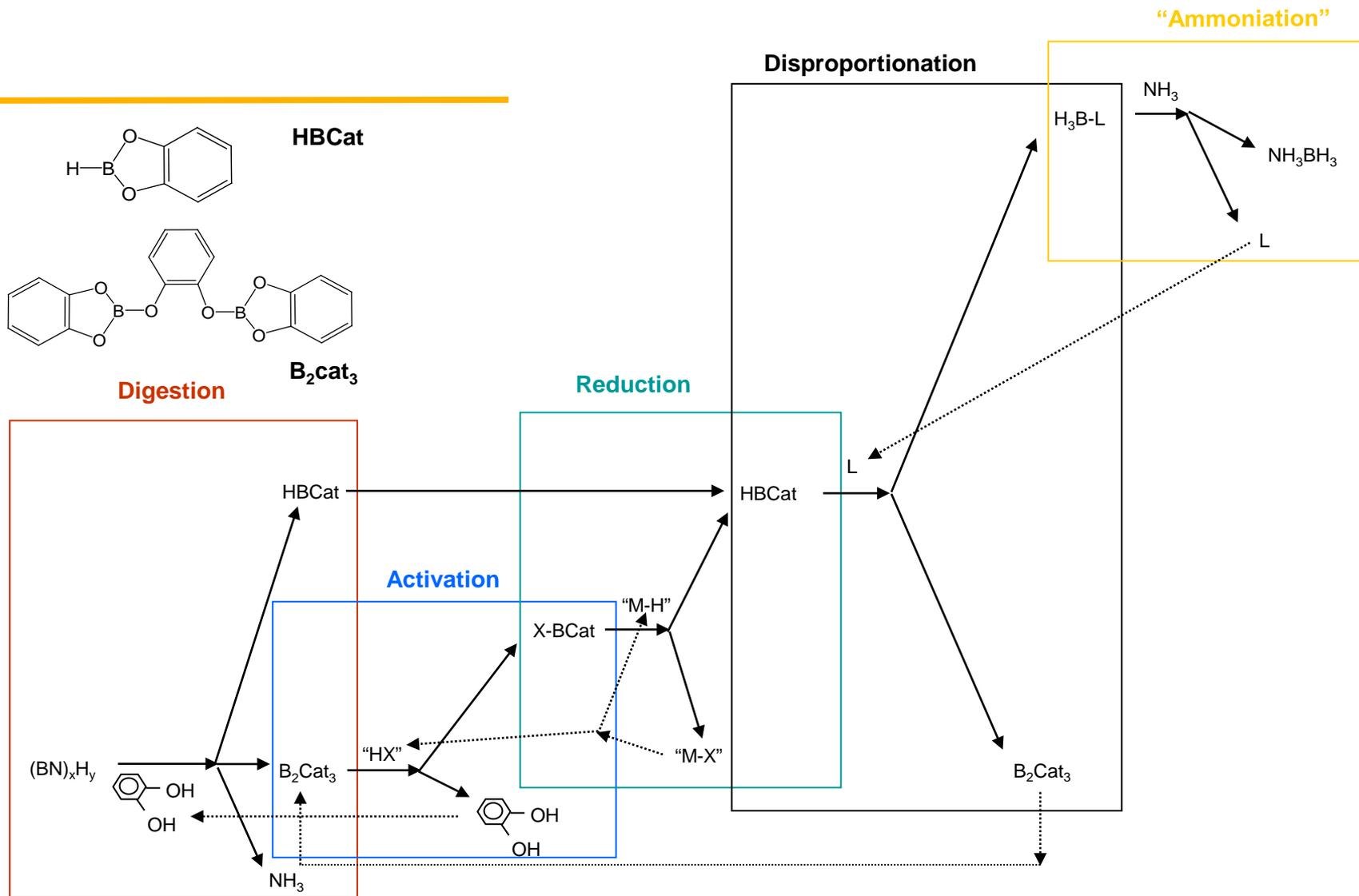
Competent reducing agent,  
inexpensive and energy-efficient,  
probably stops at  $\text{H}_{1,2}\text{B}$  entities

## Disproportionation, ammoniation

Drive all  $\text{H}_{1,2}\text{B}$  to  $\text{H}_3\text{B}$  entities,  
cleanly re-combine with  $\text{NH}_3$

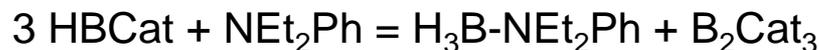
# Toward Efficient AB Regeneration: Scheme Alpha (2006)

Relative chemical potential



# AB Regeneration, Scheme Alpha: Disproportionation

L = NEt<sub>2</sub>Ph



Establishes equilibrium (THF solution)

$$K_{\text{eq}} \approx 0.15 \text{ M}^{-2} \text{ (60 C)}$$

$$\approx 1.6 \text{ to } 2.3 \text{ M}^{-2} \text{ (18 C)}$$

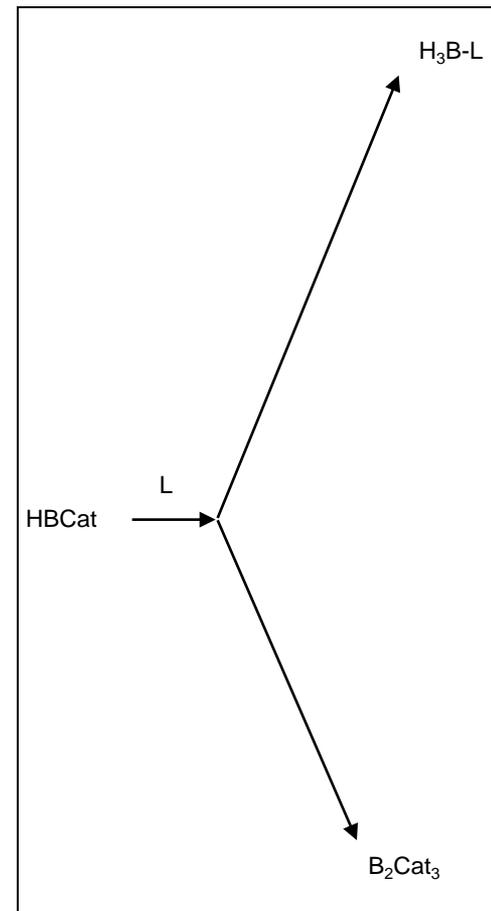
$$\Delta H \approx -10 \text{ to } -13 \text{ kcal,}$$

$$\Delta S \approx -35 \text{ to } -45 \text{ eu}$$

Slow to establish equilibrium ( $t_{1/2}$  O(hrs) )

Additional minor component observable  
could be  $(\text{NEt}_2\text{Ph})_2\text{BH}_2^+ \text{BCat}_2^-$   
(11B NMR -1 (t, H-coupled); +23 (s) )

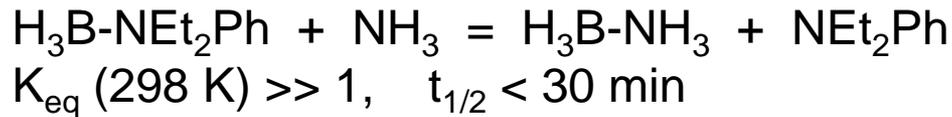
Disproportionation



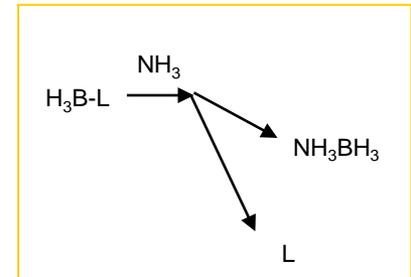
# AB Regeneration, Scheme Alpha: “Ammoniation”



L = NEt<sub>2</sub>Ph, quite promising



“Ammoniation”



# AB Regeneration, Scheme Alpha: Digestion/Activation

Activation:

$B(O-Z)_3$  is very difficult to reduce with “M-H” anything milder than alkali hydrides;

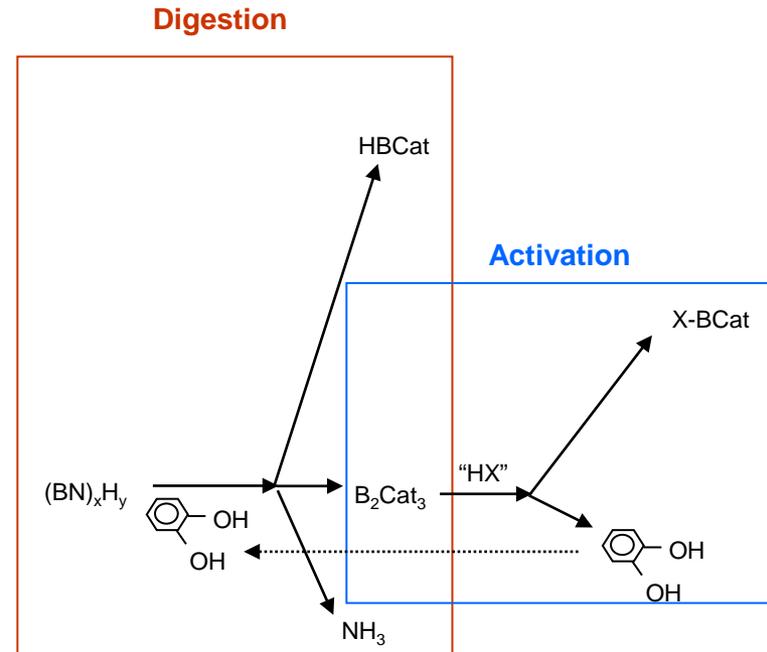
“activation” = conversion to more reactive B-X species

Another possibility: (Scheme Beta)

Digestion:

Catechol is reported to digest  $TiO_2$ ,  $SiO_2$

Reaction with borazine or spent AB, is problematic (lots of  $H_2$  formed, most residual B-H consumed)



# AB Regeneration, Scheme Alpha: Reduction

Reduction:

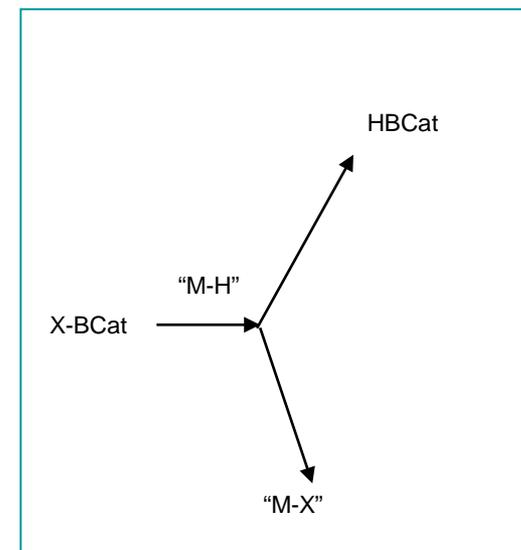
Cl-BCat readily reduces to HBCat using  $\text{HSnBu}_3$

“M-X” is then  $\text{ClSnBu}_3$ , which can be converted with  $\text{NaHCO}_2$  into  $\text{Bu}_3\text{Sn}(\text{formate})$  and subsequently thermally decarboxylated to  $\text{HSnBu}_3$

In a sense, the “thermodynamic reducing potential” required to regenerate B-H bonds is provided by a combination of the driving force of forming  $\text{NaCl}$  plus the enthalpic input from the thermal decarboxylation of  $\text{Bu}_3\text{Sn}(\text{formate})$

(Not often is heat “upgraded” to reducing potential !)

Reduction



# AB Regeneration, Scheme Alpha: Improvements Needed

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## Process simplification!

5-step process will be costly, even if each step is straightforward and efficient

Need to combine/integrate steps

e.g., if  $\text{NH}_3$  will promote disproportionation, we eliminate the need for “L” and for separate ammoniation step

## Step improvements:

Will need efficient digestion yet without significant waste of residual B-H

**“Activation” step will be troublesome/costly**

Disproportionation step is much too slow, catalyst needed

## Rigorous analysis:

How good does this overall route look under rigorous engineering and economic scrutiny?

# AB Regeneration, Scheme Beta

(Work by J. Gordon, A. Sutton, B. Davis)

## Get rid of catechol.

Two problems with catechol:

- (1) Loses too much of the residual B-H
- (2) Creates stable B-O bonds, which then require activation before reduction.

## Replaced catechol with benzenedithiol

Immediately fixes (2), improves (1), but forms a mixture of B-containing products

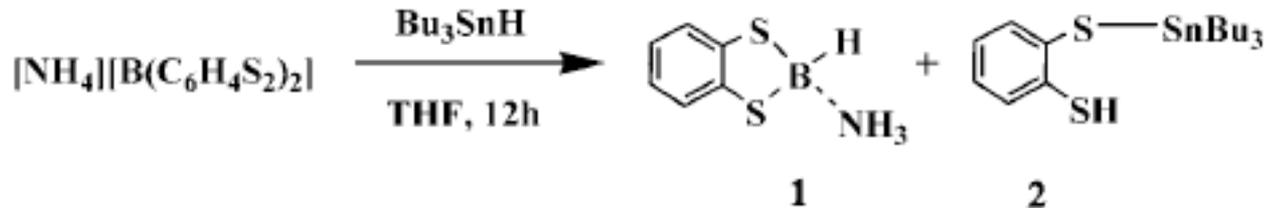


*Scheme 2.* Digestion of PB or borazine with benzenedithiol.

# AB Regeneration, Scheme Beta

Resolving this mixture of B-containing products:

Exploit reducing potential of  $\text{HSnBu}_3$



*Scheme 3.* Reduction of  $[\text{NH}_4][\text{B}(\text{C}_6\text{H}_4\text{S}_2)_2]$  with  $\text{Bu}_3\text{SnH}$ .

Now, all the B is converted to Compound 1

To complete the regeneration of ammonia borane, need to either drive further reduction or effect a disproportionation

Compound 1 required  $\text{H}_2\text{SnBu}_2$  for further reduction; or, exchange with  $\text{NMe}_3$  to enable use of  $\text{Bu}_3\text{SnH}$

# AB Regeneration, Scheme Beta

First successful demonstration of AB regeneration that didn't require going to e.g.  $\text{NaBH}_4$  or to gaseous  $\text{BCl}_3$

But, recall the filter of *Rigorous analysis:*

*How good does this overall route look under rigorous engineering and economic scrutiny?*

Lots of reagents consumed ( $\text{NaOH}$ ,  $\text{HCl}$ ) and waste generated even at 100% yields.

And, lots of  $\text{HSnBu}_3$  recycled (>28 pounds per pound of AB); overwhelming capital investment and handling costs

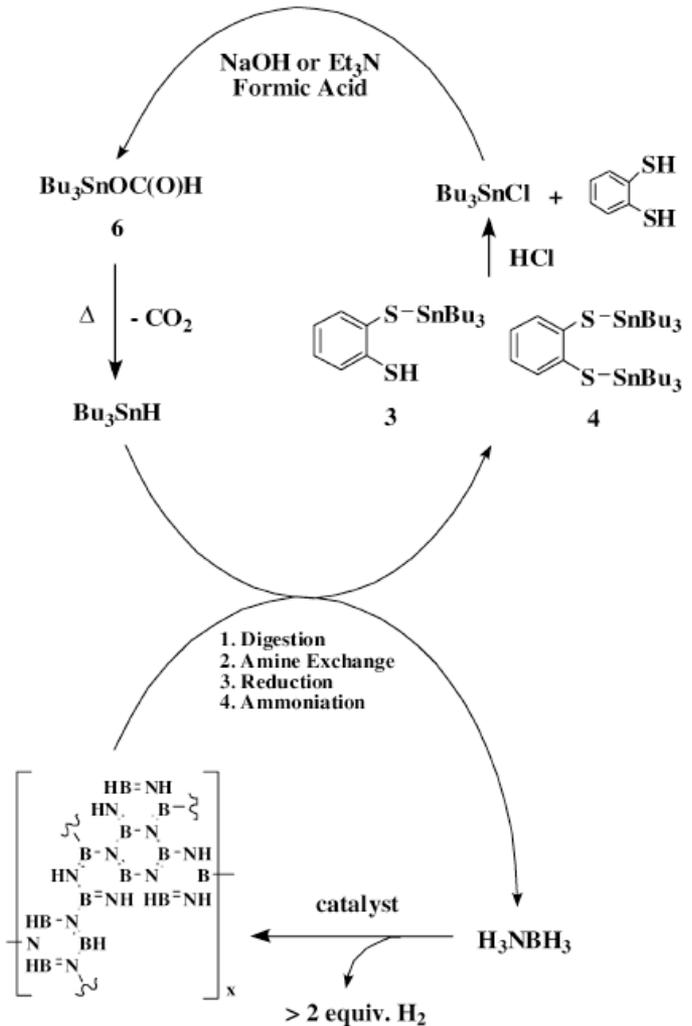


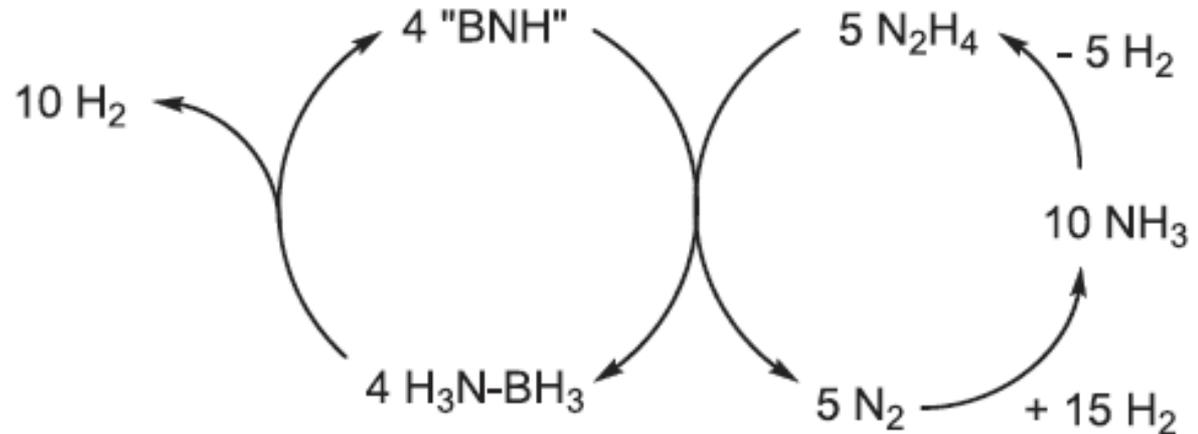
Fig. 1 Regeneration of AB with tin recycle and *ortho*-benzenedithiol recovery.

# AB Regeneration, Scheme Omega:

Needed a one-pot, one-shot reducing agent.

*Discovered the reaction with hydrazine in liquid NH<sub>3</sub>:  
Sutton et al, Science 2011, 331, 1426*

**Fig. 3.** Ideal overall reaction scheme for AB (H<sub>3</sub>N-BH<sub>3</sub>) regeneration from PB ("BNH") with hydrazine (N<sub>2</sub>H<sub>4</sub>).



This translates the challenge into

***What is the least costly and most efficient way to make hydrazine?***

And begs the question, Might not N-N/N-H bonds be an equally effective means of storing energy?

# Biomass for Energy / Vanadium Oxidation

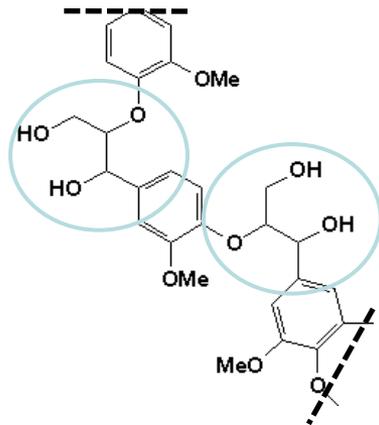
## *Energy:*

Use organic content of lignin for transportation fuels or non-petroleum feedstocks

Depolymerize lignin by oxidative C-C bond cleavage

Use air as the oxidant

$\beta$ -O-4 linkage



## *Vanadium:*

Earth-abundant element  
Can sustain widespread use in “energy economy”

V<sup>v</sup> known to oxidize C-H, C-C bonds

V<sup>iv</sup> known to re-oxidize in air

Known to bind alkoxides

# Vanadium in Oxidation Processes

---

One important industrial process: BUTOX



Catalyzed by vanadium phosphates

- bulk phase vanadyl pyrophosphate  $(\text{V}^{\text{IV}}\text{O})_2\text{P}_2\text{O}_7$ 
  - if bulk phase becomes e.g.  $\text{V}^{\text{V}}\text{OPO}_4$ , rates and yields deteriorate
  - actual oxidation performed by surface  $\text{V}^{\text{V}}$  species
- detailed mechanism elusive

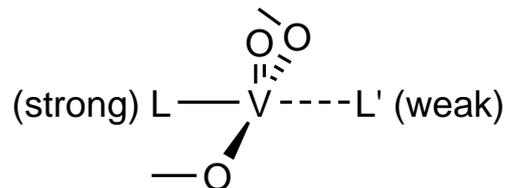
Our interests:

- *Improve understanding of oxidation by phosphate-ligated vanadium*
- **Study other coordination environments to discover faster oxidation processes**
- **Ultimately, develop a coordination environment capable of controlled C-C, C-O bond breaking for converting lignin to monomers**

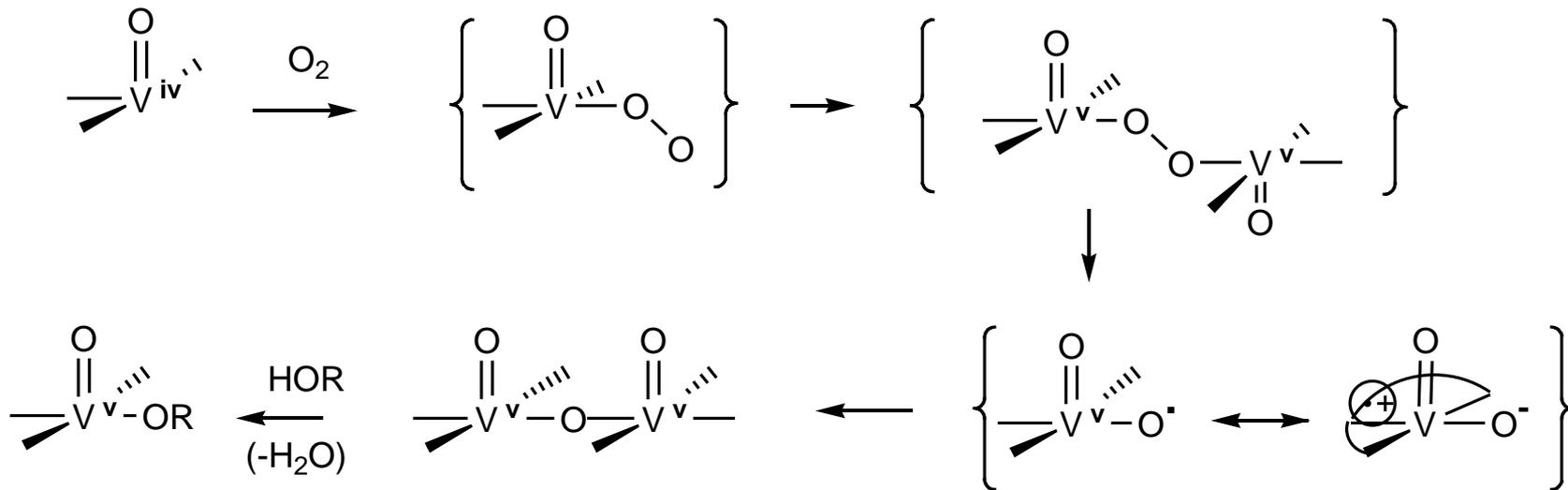
# Vanadium(iv): Reoxidizing with O<sub>2</sub>

Certain O=V<sup>iv</sup> compounds are very air-sensitive: O=V<sup>iv</sup> + x O<sub>2</sub> = O=V<sup>v</sup>-O-

Common structure:

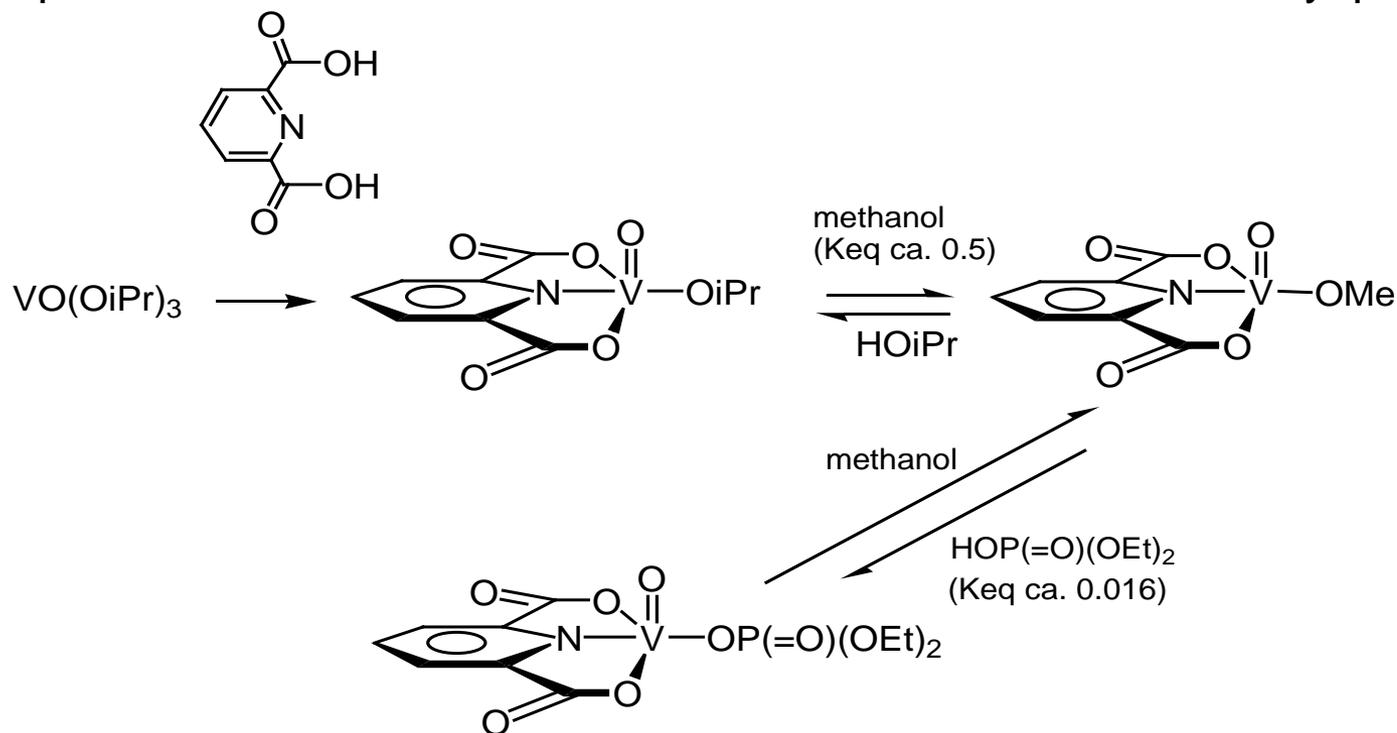


- Chemistry:



# V compounds with “O,N,O” supporting dipic ligand

Dipic allowed us to isolate the first “almost non-cluster” vanadyl phosphate compound



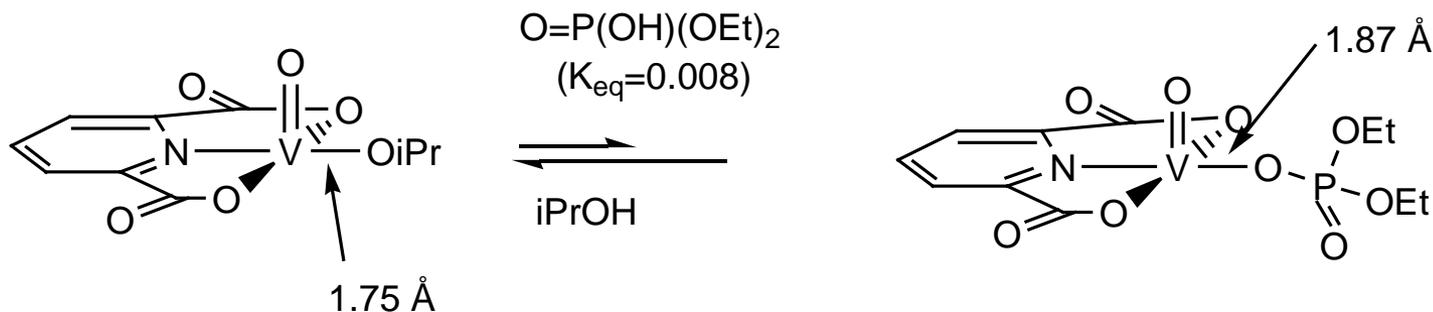
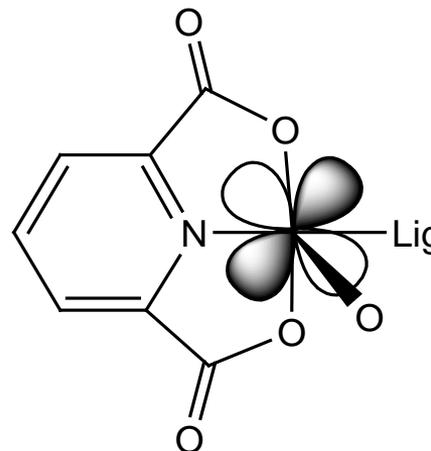
The unfavorable equilibrium with alcohols suggests that V-phosphate bonds may be kinetically labile with alcohols, and that the alcoholato form is key to oxidation chemistry

# Vanadyl Chemistry: Basal plane reactivity

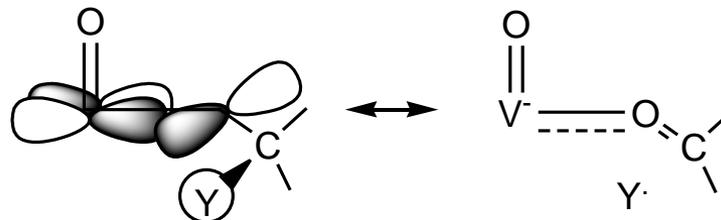
- Electron-withdrawing capacity of  $V^V$  expressed via in-plane dxy orbital

- Chemical consequences:

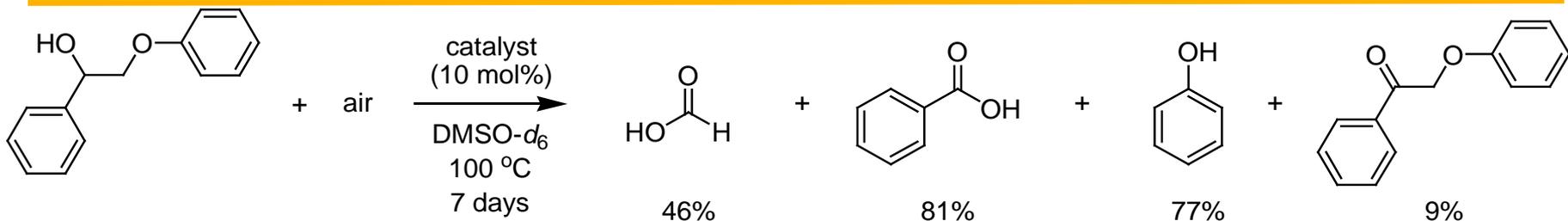
- preference for  $3^\circ > 2^\circ > 1^\circ$  alkoxy  $>$  OP (preferences reverse as  $V^V$  becomes less electron withdrawing)



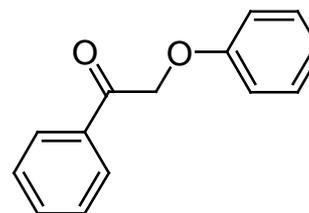
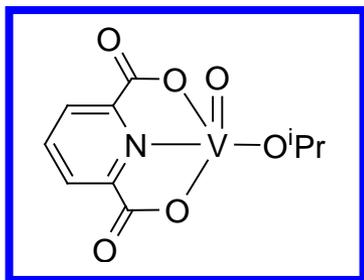
- activation of VOC-H, VOC-C



# Catalytic oxidation of lignin models



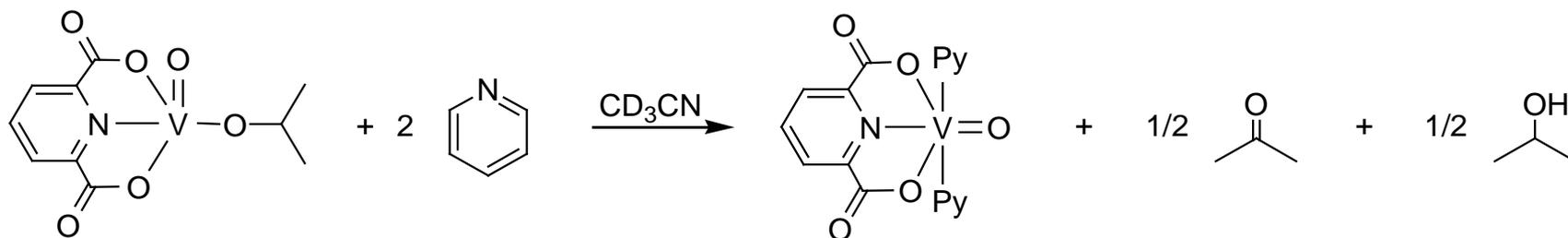
catalyst



Detected as an intermediate:  
~80% yield at 50% conversion

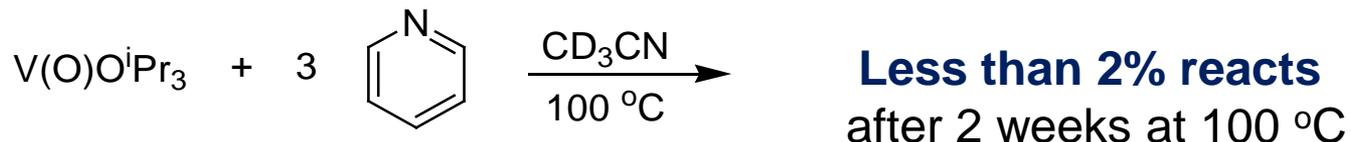
***Can we control C-H vs. C-C bond breaking on V<sup>v</sup>?***

# A Base-Assisted C-H Bond Activation Pathway?

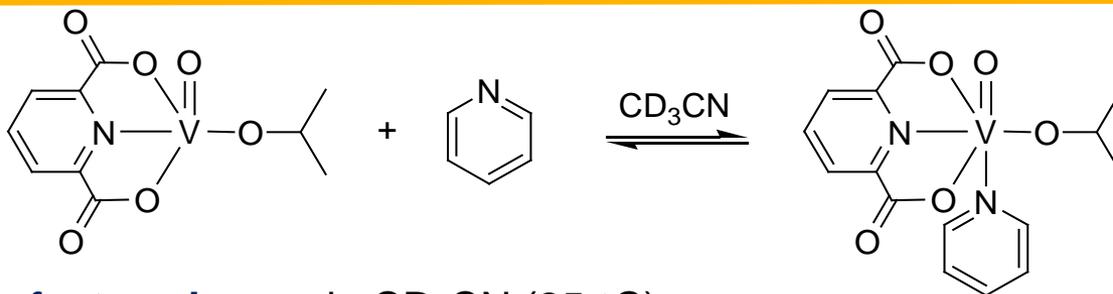


**With no added base:** no reaction (25 °C)  
*Less than 25% reacts after 3 weeks at 100 °C*

**The dipicolinate ligand is important:**

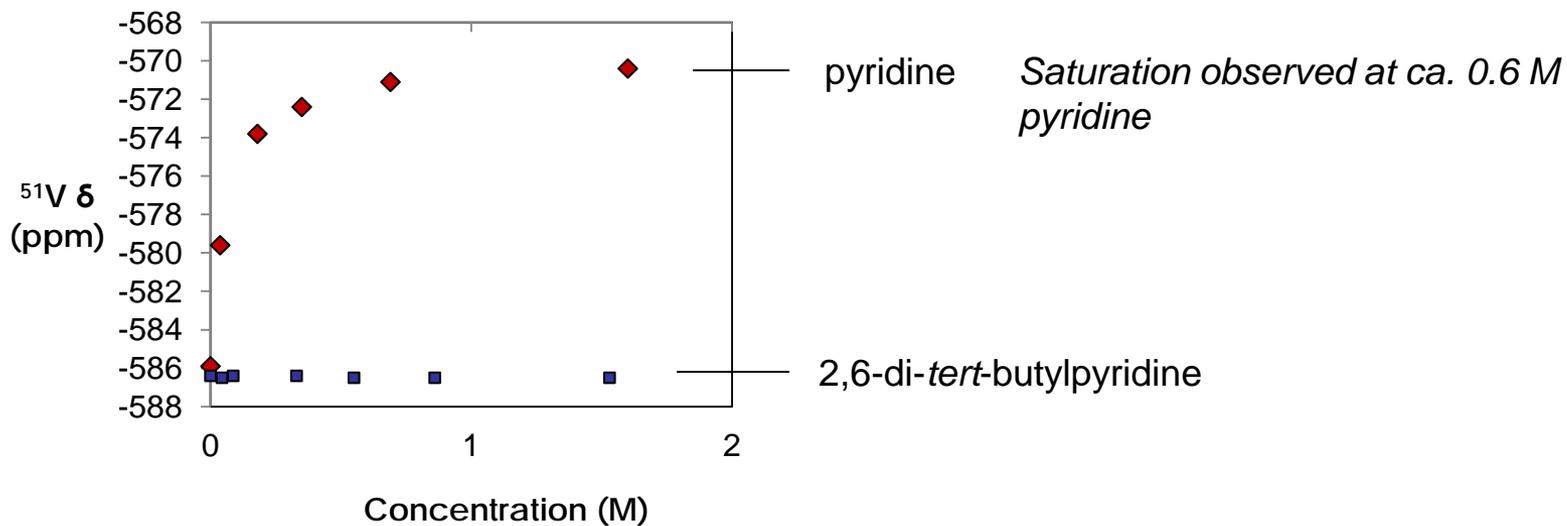


# Evidence for Pyridine Coordination

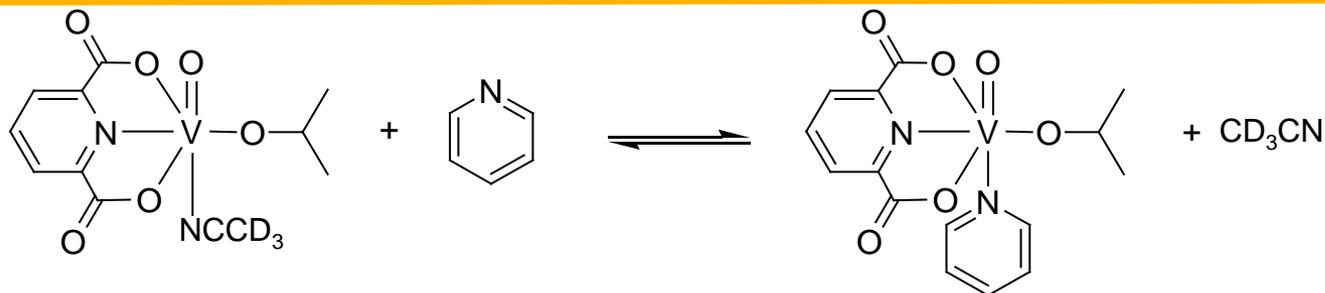


$^1\text{H}$  NMR: **fast exchange** in  $\text{CD}_3\text{CN}$  (25 °C)

$^{51}\text{V}$  NMR chemical shift vs. [pyridine]



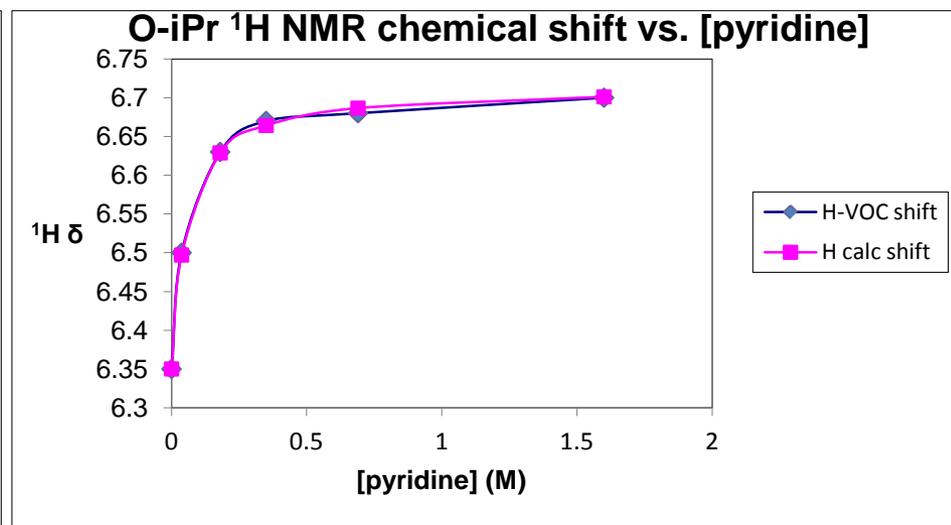
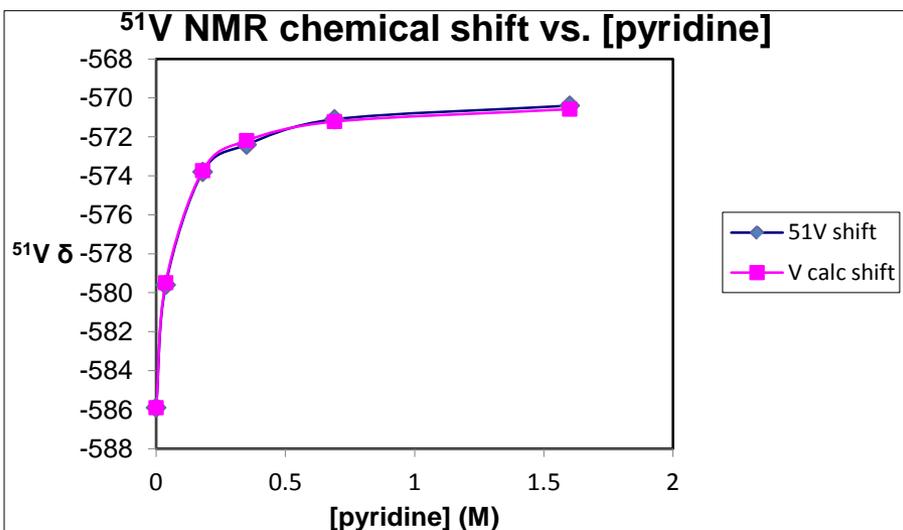
# Evidence for Pyridine Coordination



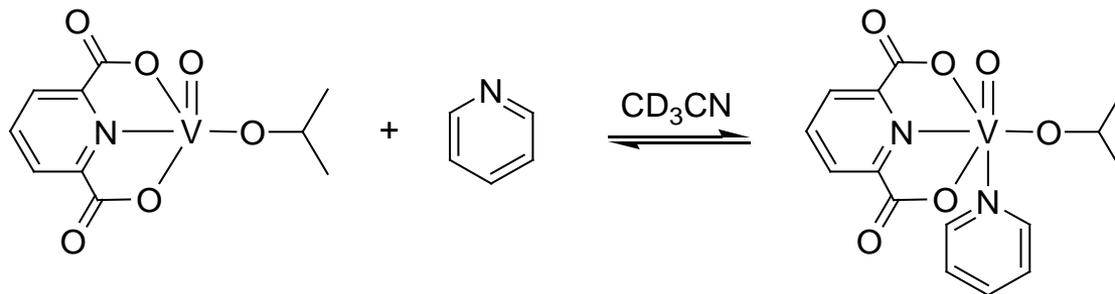
Assume acetonitrile coordination in absence of pyridine

NMR Chemical shifts fit to  $K_{eq} = [V\text{-pyr}][CD_3CN]/[V\text{-}CD_3CN][pyr]$  ca.  $352 \pm 22$  or  $\Delta G^{(298)} = -3.5$  kcal/mol

(if no acetonitrile coordination,  $K'_{eq} = 18(1) \text{ mol}^{-1}$  or  $\Delta G'^{(298)} = -1.7$  kcal/mol)



# Evidence for Pyridine Coordination



## Selected Bond Lengths ( $\text{\AA}$ ):

parent isopropoxide (dimer)

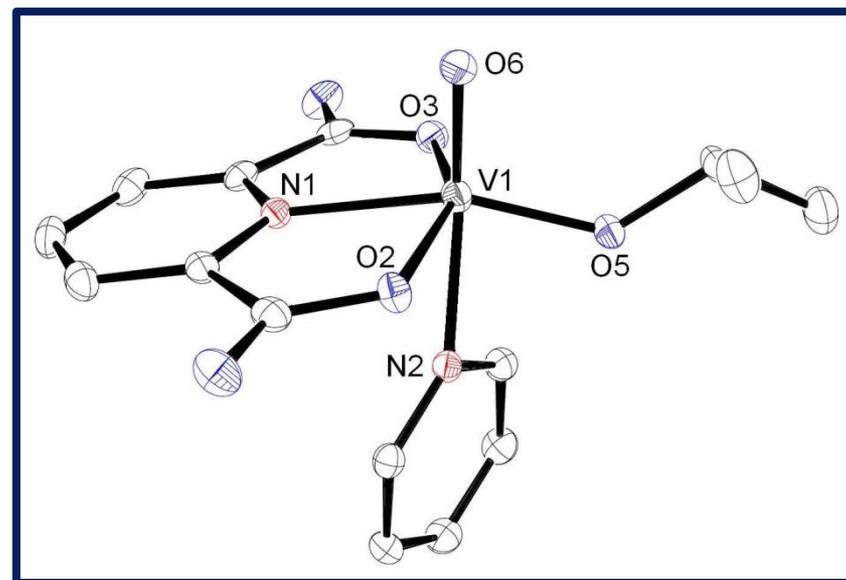
pyridine ligated

$V=O = 1.588(3)$

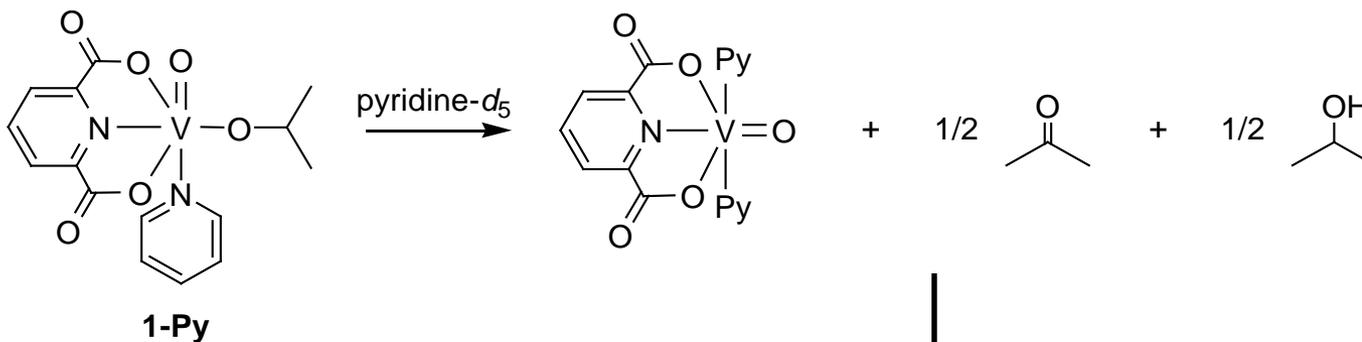
$V1-O6 = 1.585(1)$

$V-OiPr = 1.756(3)$

$V1-O5 = 1.755(1)$



# Kinetic Study of the Isopropanol Oxidation



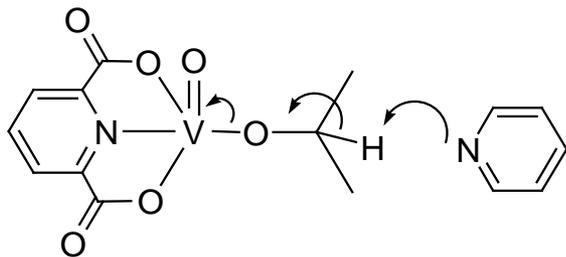
Reaction rate: First-order in V  
 Zero order in isopropanol  
 Approximately first-order in pyridine  
 (except nonzero intercept at [pyr] → 0)

$$\Delta H^\ddagger = 86(4) \text{ kJ/mol} = 25.5(1) \text{ kcal/mol}$$

$$\Delta S^\ddagger = -76(6) \text{ J/mol-deg} = -18(2) \text{ cal/mol-deg}$$

$$\Delta G^\ddagger(298) = 31(2) \text{ kcal/mol}$$

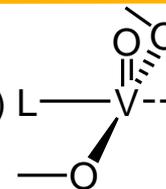
Suspect base-assisted removal of C-H



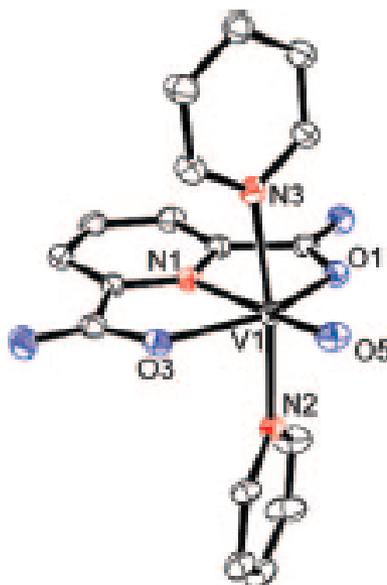
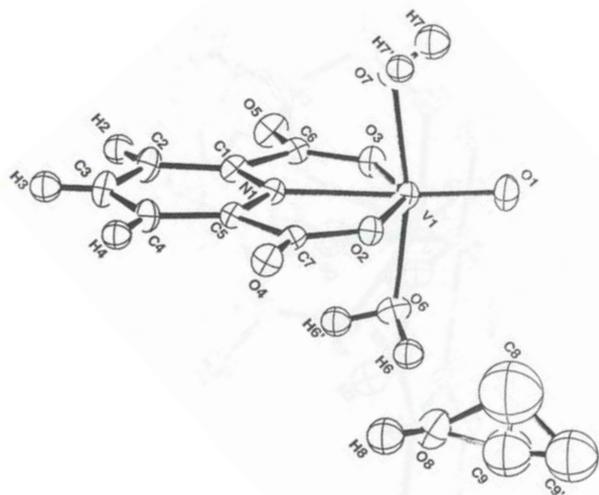
At 340 K:  $k_H/k_D = 5.7$

# Note: Good Stoichiometric Reaction $\neq$ Good Catalysis

“O=V(+4)(dipic)” is relatively air-stable: It’s not of the form (strong) L—V—L' (weak)



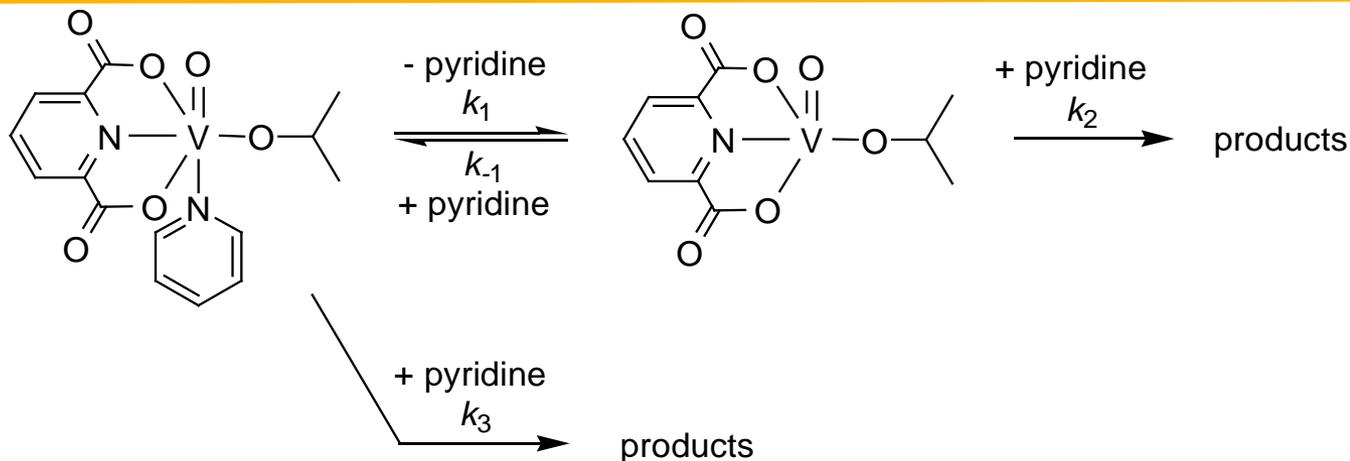
Isolated dihydrate and bis(pyridine) compounds,  
rearrange to N trans to vanadyl;  
the V-O(water/pyridine) ligands are relatively strongly bonded



Why dipic stays cis to vanadyl in isolated V(+5) compounds,  
but goes trans in V(+4),  
is not known

– but teaches us that we can’t always count on “O,N,O” staying cis

# Probable Reaction Mechanism



$$\text{rate} = k_3[1\text{-Py}][\text{pyridine}] + k_2k_1[1\text{-Py}]/k_{-1}$$

Satisfactory fit assuming both pathways are operating

But leaves one very interesting question:

- Product is exclusively  $\text{V}^{\text{IV}}$ ;  
 how do we accomplish a  $2 e^-$  oxidation  
 with a one-electron oxidant that exhibits first-order kinetics?

# Possible Reaction Mechanism: E2 by calculation

(U)B3LYP/6-31G\* Energy Differences( $\Delta E$ ) in kcal/mol at (U)B3LYP/6-31G\* Optimized Geometries

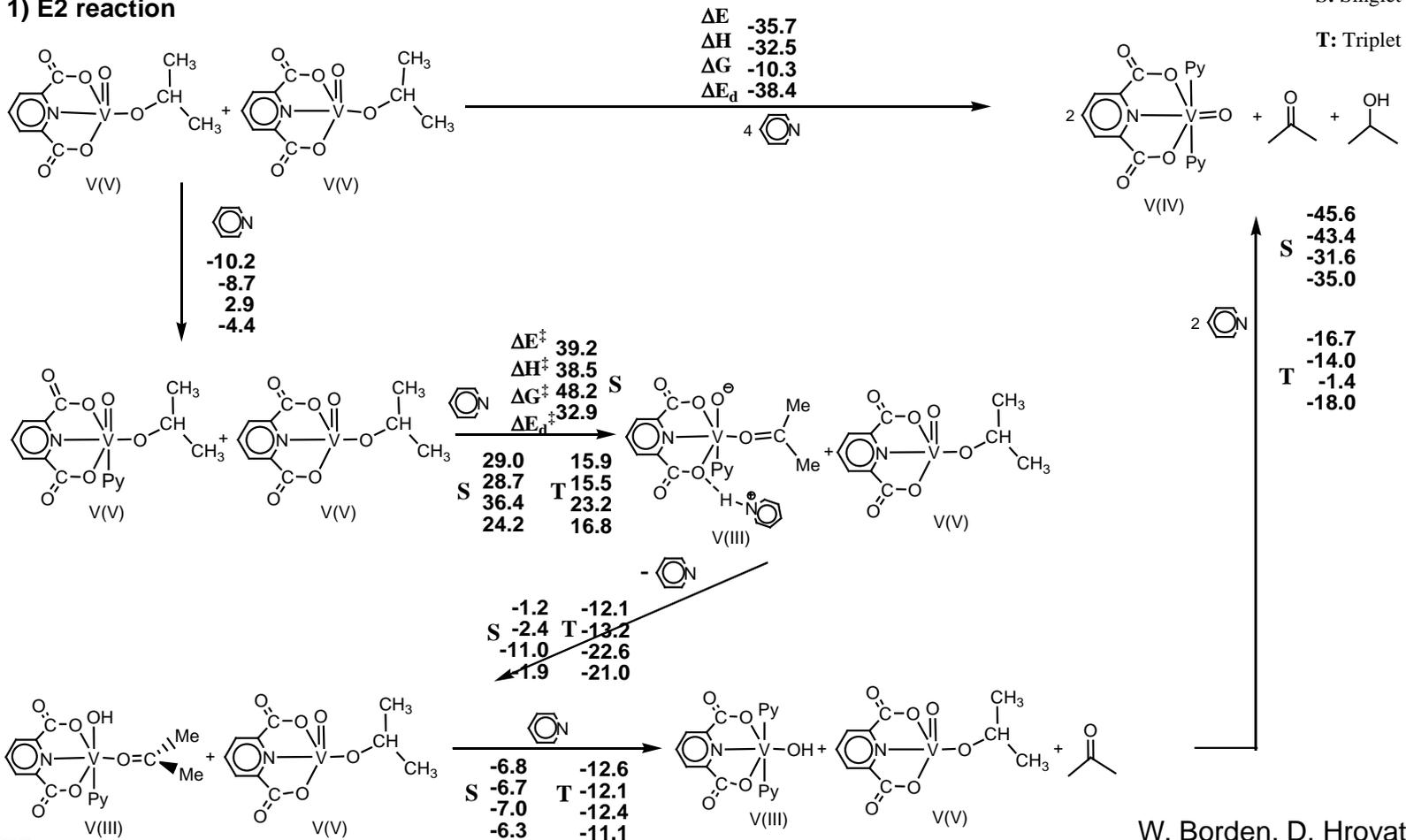
B3LYP/6-31G(d)  
Solvent effect-PCM\_DMSO

$\Delta E$	$\Delta H$	$\Delta G$	$\Delta E_d$
-35.7	-32.5	-10.3	-38.4

kcal/mol

Possible Mechanisms:

1) E2 reaction



# Possible Reaction Mechanism: E2 by calculation

---

Pyridine removes “H<sup>+</sup>” from isopropoxide, with concomitant V<sup>v</sup> -> V<sup>iii</sup>

V<sup>iii</sup> is more stable as a triplet than as a singlet but finding exact singlet/triplet crossover point has been difficult  
(compounded by dipic going from cis -> trans)

V<sup>iii</sup> rapidly conproportionates with remaining V<sup>v</sup> to make 2 V<sup>iv</sup>

However, this conproportionation is only ca. 1.4 kcal exergonic by calculation,  
relative to the overall oxidation reaction being 10 kcal exergonic by calculation

Two possible consequences:

- If V centers were surface-bound and could not conproportionate, reaction could still occur
- Conproportionation might be incomplete i.e. reversible

In C-H oxidation reactions, V<sup>iii</sup> has not been observed,  
and no evidence for incomplete conproportionation

However, in C-C oxidation (pinacol) V<sup>iii</sup> has been isolated

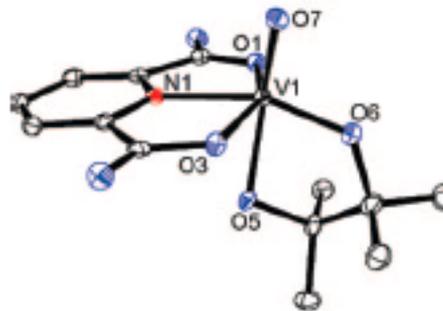
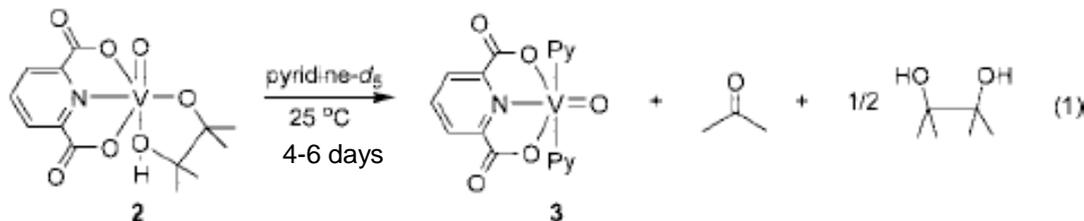
# C-C Bond Breaking: Oxidation of Pinacol

$d_{xy}$  orbital activates VOC-H  
(pyridine-assisted)

But what if there is no OC-H?

Using pinacol, discovered  $V^V$   
activates VOC-C

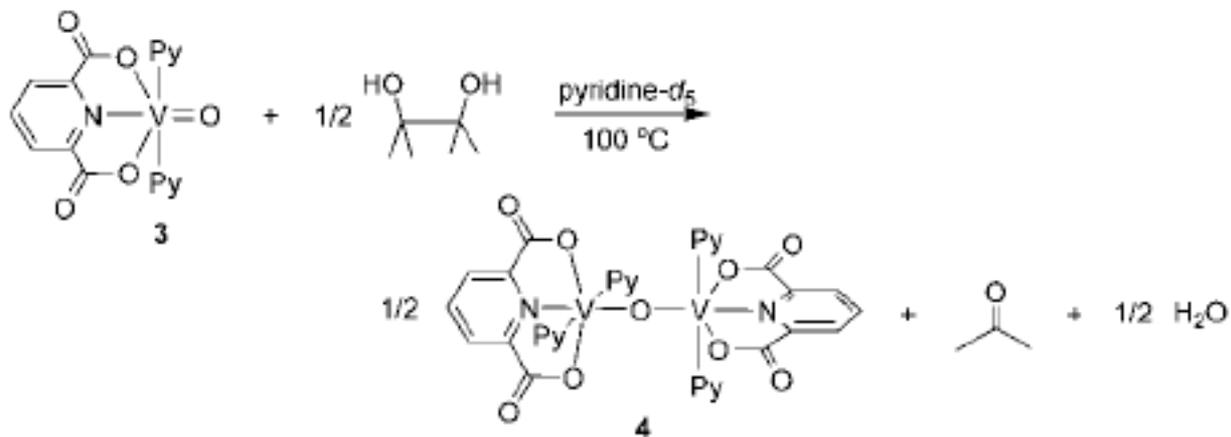
Starting pinacolato compound  
shows expected chelation to  
(dipic)vanadyl center



Reaction appears to go via 2-electron oxidation of the pinacol to give acetone +  $V^{III}$ , followed by rapid comproportionation with  $V^V$  to give two  $V^{IV}$  molecules (Hanson et al, *JACS* **2009**, 131, 428)

# C-C Bond Breaking: Oxidation of Pinacol

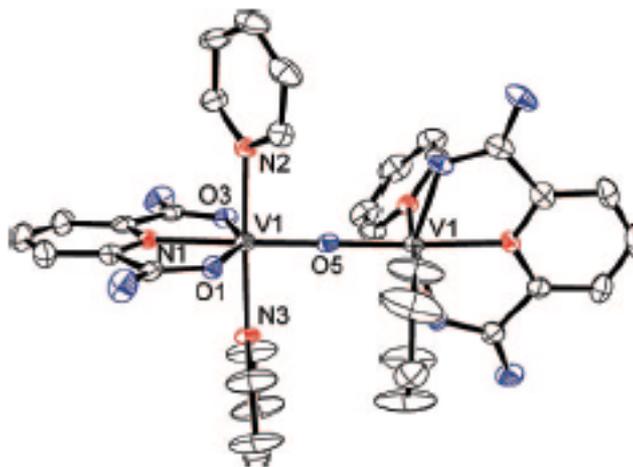
Unexpectedly, the  $V^{IV}$  compound reacts further with pinacol to give acetone +  $V^{III}$



Is  $V^{IV}$  reacting with pinacol via 2-electron oxidation to give  $V^{II}$ , followed by rapid comproportionation to give  $V^{III}$  ?

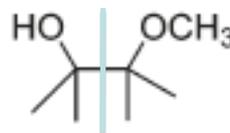
More probable:  
Pinacol drives disproportionation  
 $2 V^{IV} = V^{III} + V^{V}$  (pinacolato)

and the  $V^V$  oxidizes the pinacol as before



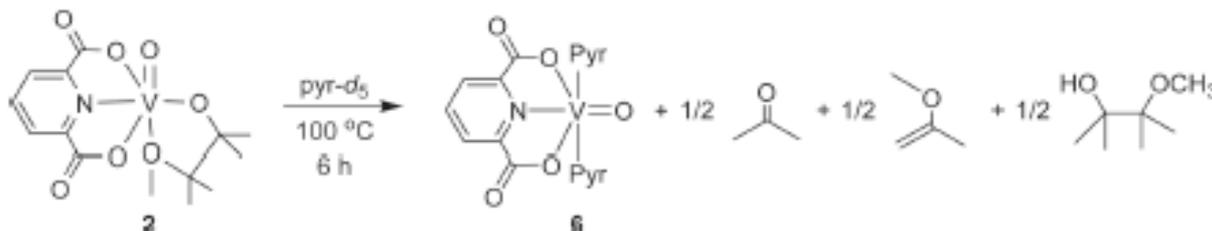
# C-C Bond Breaking: Oxidation of Pinacol-monoethers

What happens if the one of the pinacol hydroxyls is converted to an ether?



C-C bond breaking can no longer yield two ketones

Find however that C-C bond still breaks (first), making half an equivalent of ketone, with the  $\text{Me}_2\text{COME}$  fragment losing a C-H bond to give half an equivalent of vinyl ether (Hanson et al, *Inorg. Chem.* **2010**, *49*, 5611)



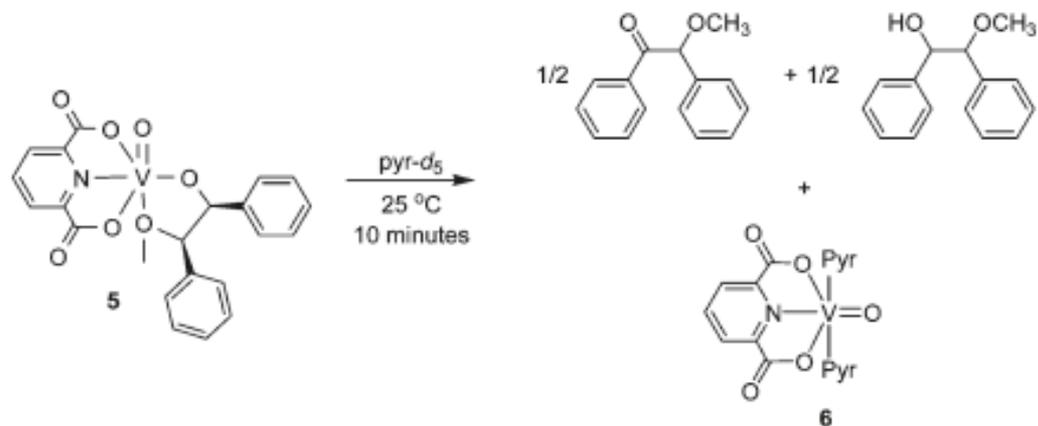
**Next question: If both OC-H and OC-C bonds are present, which does  $\text{V}^{\text{v}}$  activate?**

# C-C Bond Breaking: Oxidation of Pinacol-monoethers

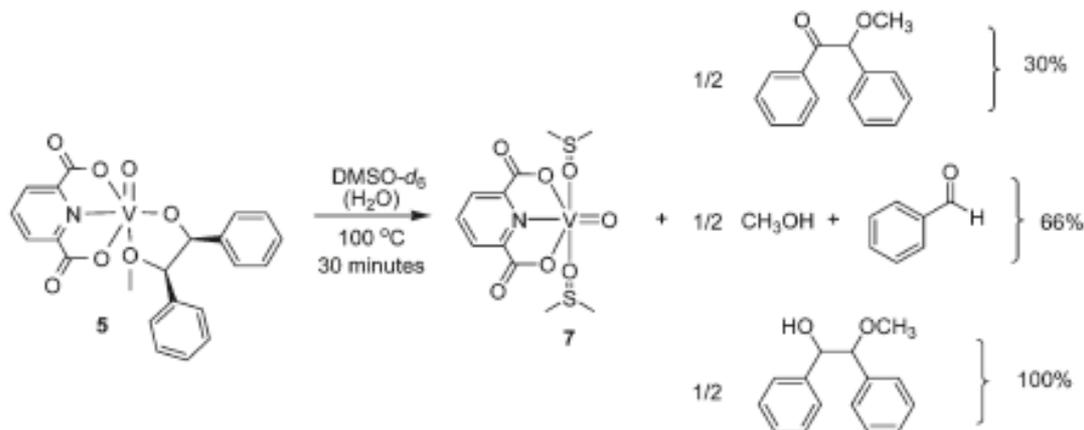
If both OC-H and OC-C bonds are present, which does V<sup>v</sup> break?

It depends!

For the oxidation of 1,2-diphenyl-2-methoxy-ethanol, If in pyridine solvent we see C-H bond breaking (facile)



If in DMSO, we see primarily C-C bond breaking (more difficult)



# Dependent on Solvent, and on Ligand

---

**In (dipic)V<sup>v</sup> compounds, pyridine promotes OC-H bond breaking  
(for substrates that have OC-H bonds)**

**Absent pyridine or other base, OC-H bond breaking is much slower,  
and OC-C bond breaking can become competitive**

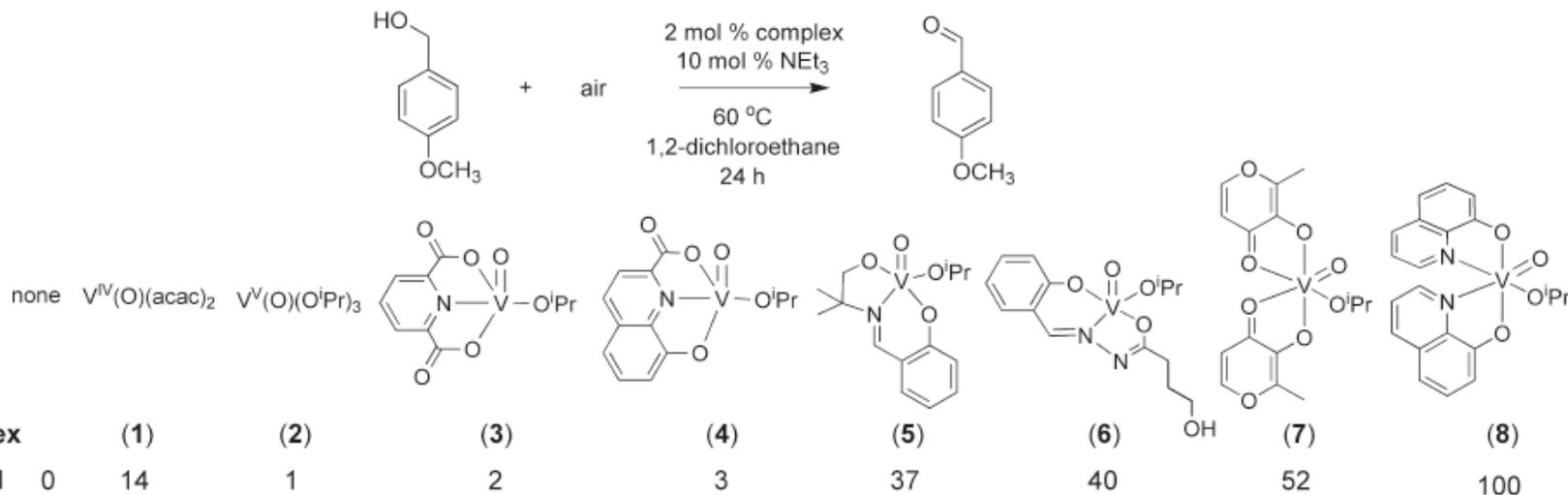
What effect does the ligand have on these processes?

# Ligand Effects on C-H Bond Breaking

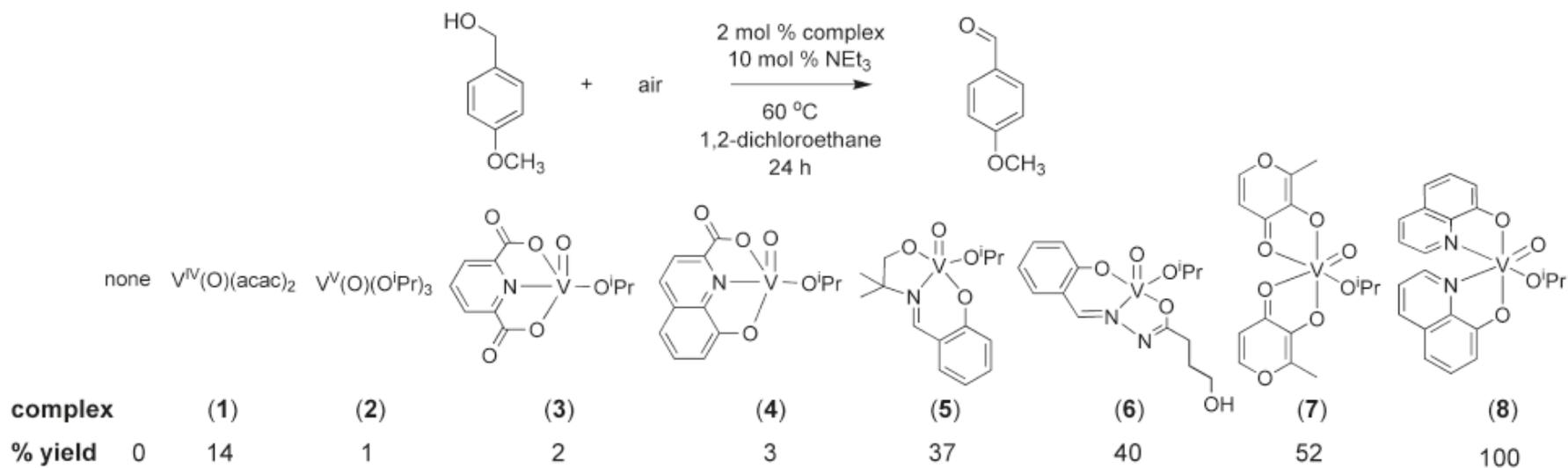
In (dipic)V<sup>V</sup> compounds, pyridine promotes OC-H bond breaking  
(rapid stoichiometric oxidation reaction)

However pyridine also complexes to (dipic)V<sup>IV</sup> product and inhibits aereal re-oxidation  
(makes net catalytic turnover very slow)

Examined ligands other than (dipic) in catalytic processes



# Ligand Effects on C-H Bond Breaking

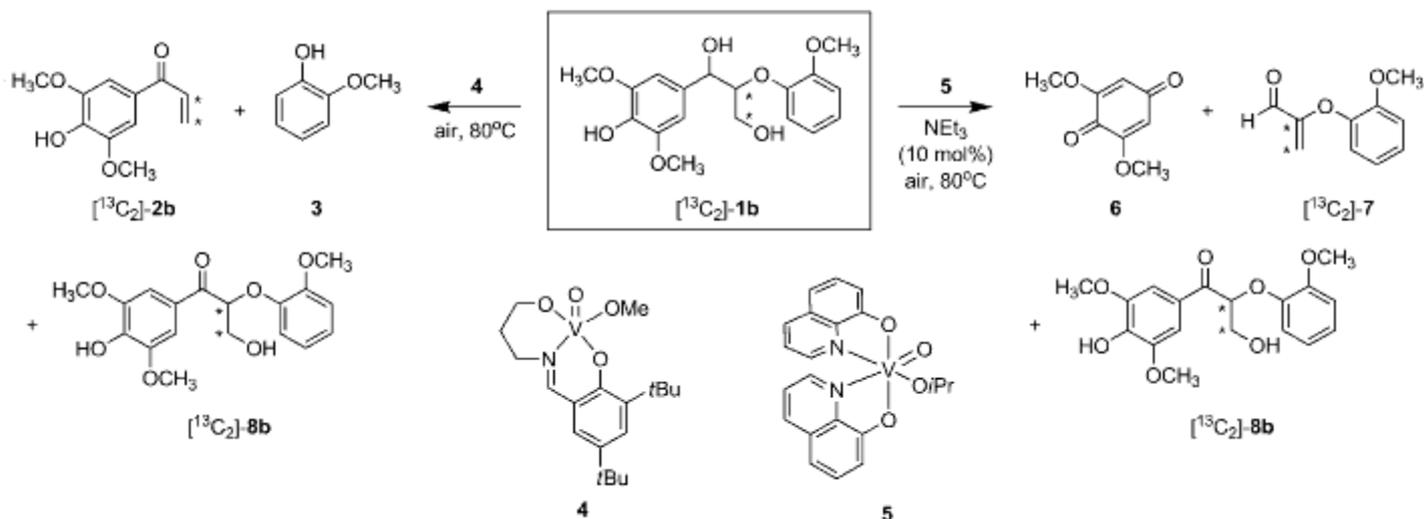


**(dipic)V (3) is woefully inadequate catalyst; other (O,N,O) and (O,N,O)-like ligands are more effective**

**At least three potential contributing reasons:**

- **(dipic)(V<sup>iv</sup>=O) goes trans, ancillary ligands inhibit reaction with O<sub>2</sub>**
- **alkoxy-containing (O,N,O) ligands increase electron density in (O,N,O)(V<sup>iv</sup>=O)**
- **nominally-tetradentate ligands promote reoxidation of V<sup>iv</sup>**

# Ligand Effects Convolved with Substrate Effects



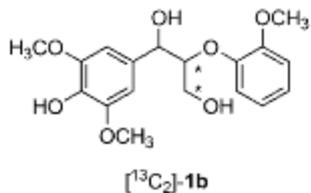
Compound **4** promotes C-H oxidation at the benzylic carbon, also promotes phenol elimination and dehydration (C-O bond breaking) (Son, Toste *Angew. Chem.* **2010**, 122, 439)

Compound **5** also oxidizes benzylic C-H, but also (new!) promotes C-C bond breaking at the  $\text{C}_{\text{phenyl}}\text{-C}_{\text{benzylic}}$  bond (Hanson et al, *Angew. Chem. Int. Ed.* **2012**, 51, 3410)

Our previous work had us expecting C-C bond breaking at  $\text{C}_\alpha\text{-C}_\beta$ , or  $\text{C}_\beta\text{-C}_\gamma$ .

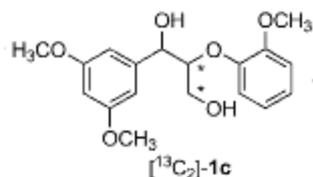
$\text{C}_{\text{phenyl}}\text{-C}_\alpha$  bond breaking is a new pattern for us; requires phenolic O-H

# Ligand Effects Convolved with Substrate Effects



with (O,N,O)V<sup>v</sup>, breaks C-H and C-O bonds

with (O,N;N,O)V<sup>v</sup>, breaks C<sub>phenyl</sub>-C<sub>α</sub> bond as well as C-H



only observe C-H, C-O bond breaking

Our original intent was to:

- Study other coordination environments to discover faster oxidation processes
- Develop a coordination environment capable of controlled C-C, C-O bond breaking for converting lignin to monomers

We have interesting progress but quite a way yet to go.