

# Metal Poly(Dihydrogen) Complexes for Hydrogen Storage

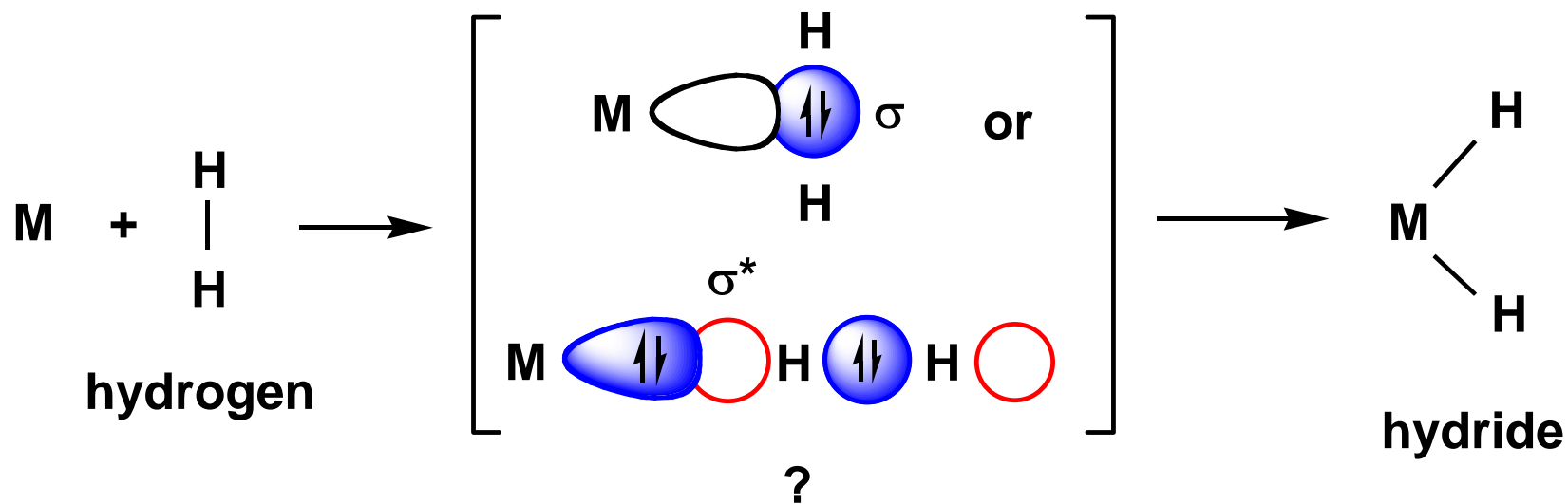
**Gregory J. Kubas and Jeffrey Cross**  
Los Alamos National Laboratory

**Juergen Eckert**

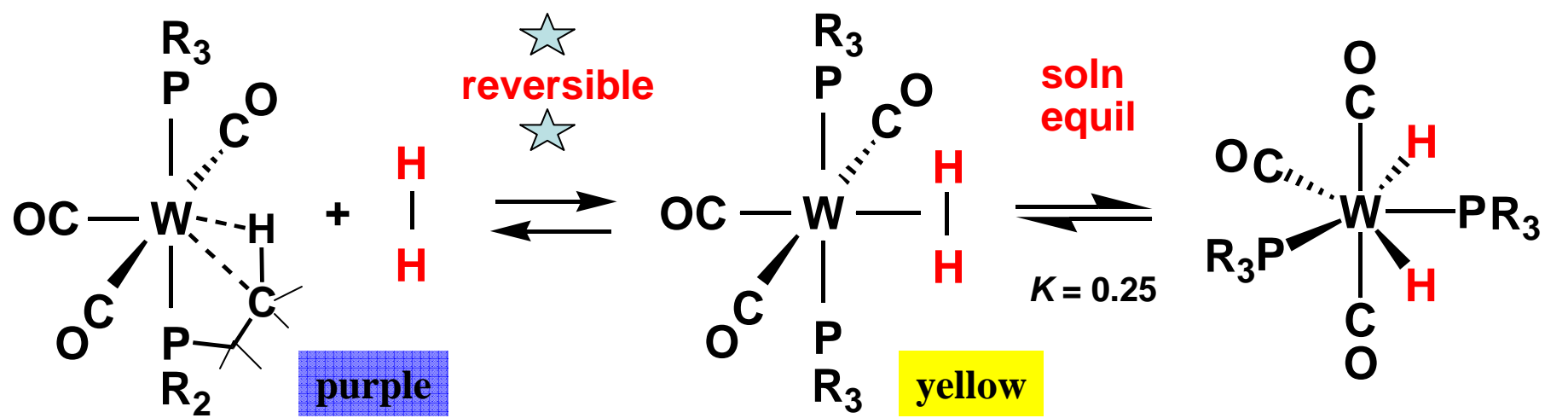
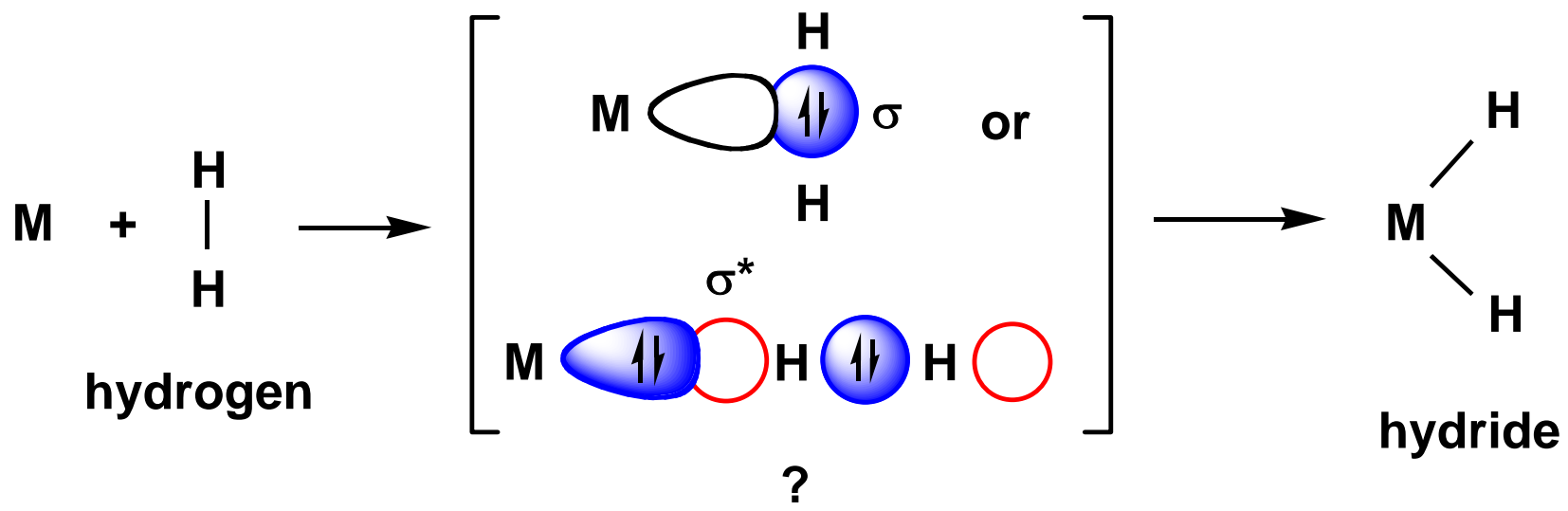


Materials Research Laboratory  
University of California Santa Barbara

**METALS BREAK H-H AND OTHER  $\sigma$  BONDS BUT NO ONE KNEW EXACTLY HOW!**



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16 e with agostic CH

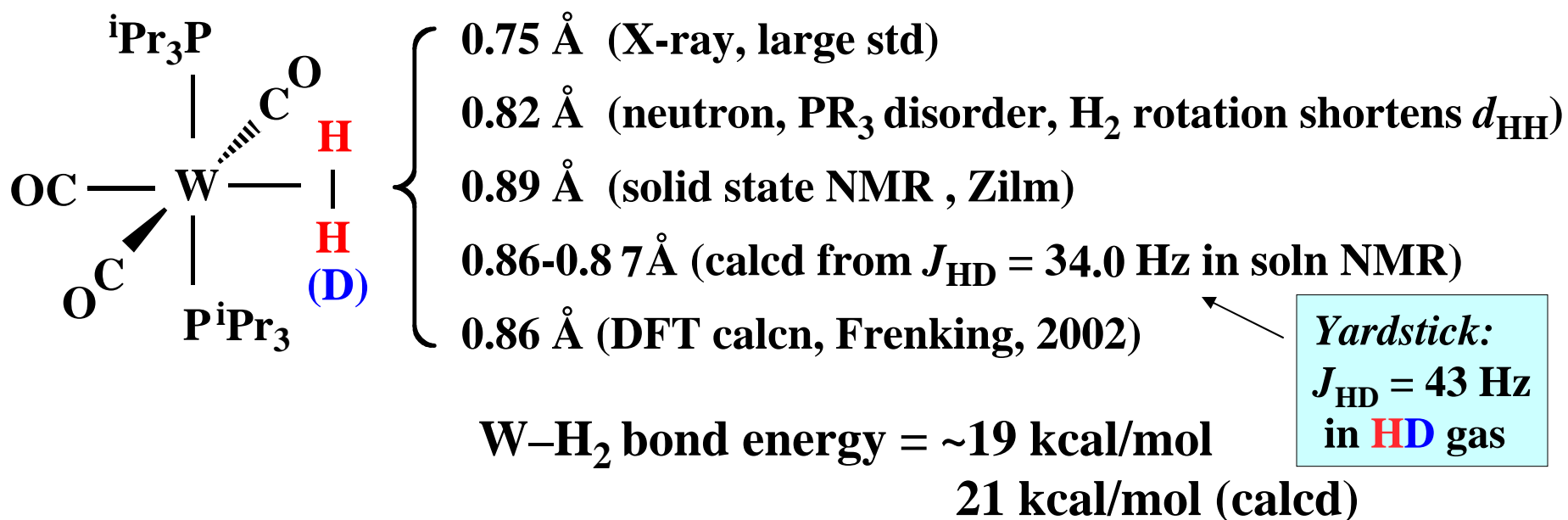
isolated as stable solid

oxidative addn of H<sub>2</sub>  
not isolated

## 22nd Anniversary of First Report of Dihydrogen Complex

Kubas, Ryan, Swanson, Vergamini, and Wasserman, *J. Am. Chem. Soc.*, **January, 1984**

Complexes were first prepared in 1979, but structure not confirmed until 1983

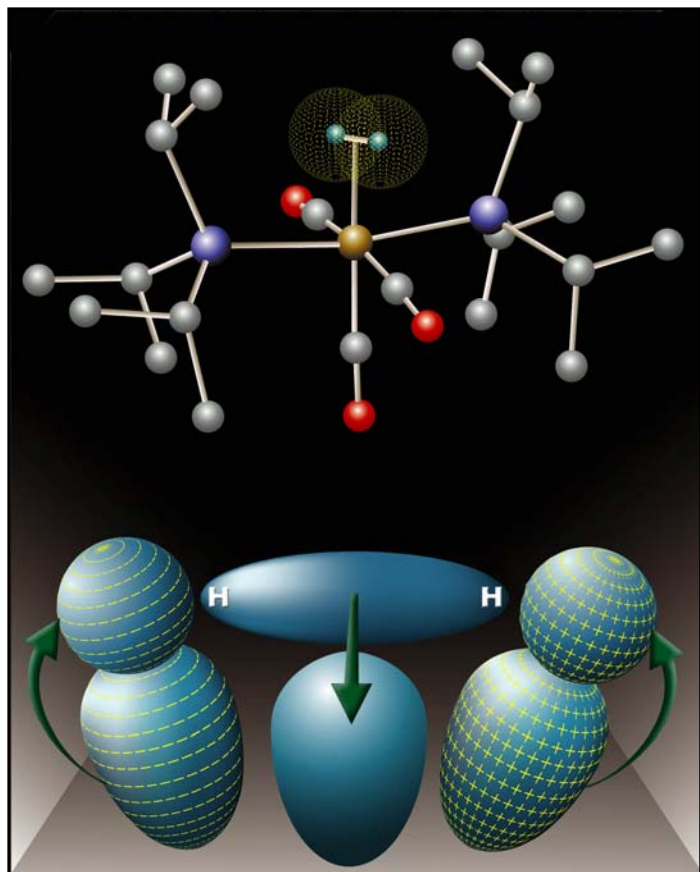


### Theoretical calculation:

Saillard and Hoffmann, *J. Am. Chem. Soc.*, **April, 1984**

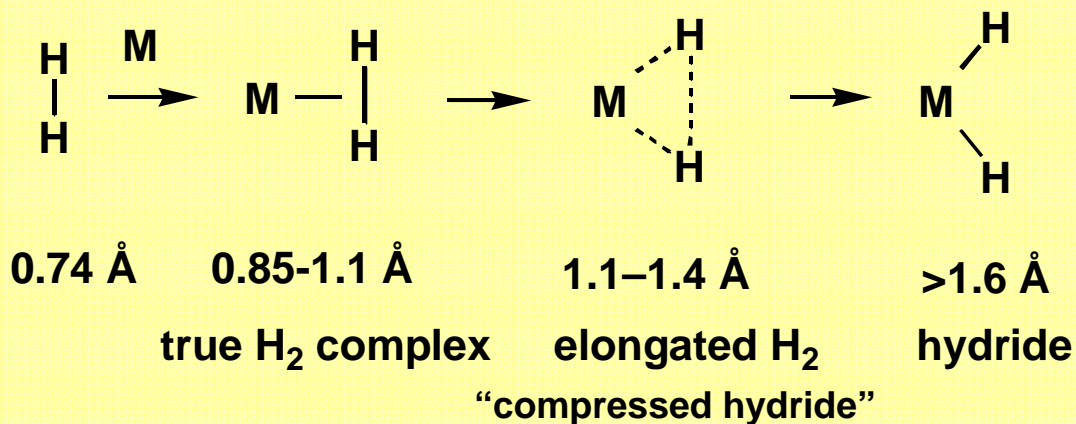
side-on ( $\eta^2$ ) bonding of H<sub>2</sub> in Cr(CO)<sub>5</sub>(H<sub>2</sub>) favored over end-on

# The field of M–H<sub>2</sub> $\sigma$ complexes has grown to feature:



**Bonding in  $W(CO)_3(P^iPr_3)_2(H_2)$ :**  
donation of the bonding electrons  
in  $H_2$  to a filled metal d orbital and  
backdonation to the antibonding  
orbital of  $H_2$

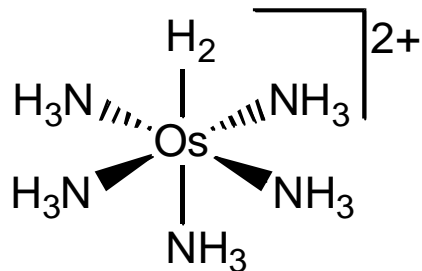
- >1200 papers published (~300 computational); 142 research groups (**six Nobel Laureates!**)
- ~660  $L_nM-H_2$  complexes (560 stable; ~250 Ru)
- Every transition metal from vanadium to platinum; main-group interactions also
- H–H distance varies from 0.85 to 1.6 Å
- $J(HD)$  varies inversely from 36 to 2 Hz



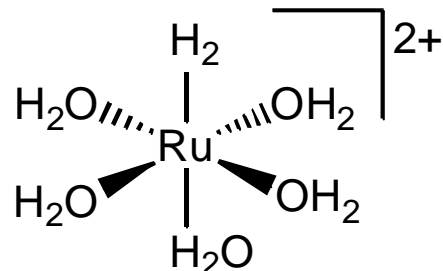
- Book: *Metal-Dihydrogen and  $\sigma$ -Bond Complexes*, G. J. Kubas, Kluwer Academic/Plenum, 2001

$\sigma$  complexes include  $M(Si-H)$ ,  $M(C-H)$ , etc

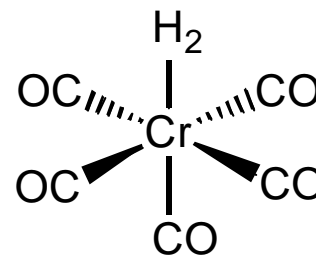
## HOMOLEPTIC AND OTHER NOVEL H<sub>2</sub> COMPLEXES



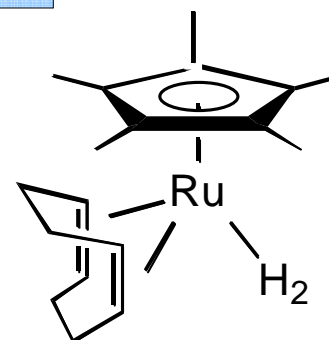
H-H = 1.34 Å for analogue [Taube]



Merbach

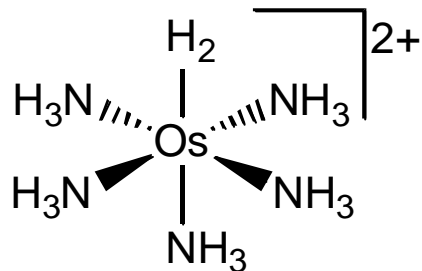


Heinekey

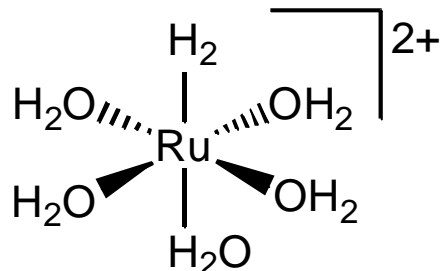


Jia and Lau

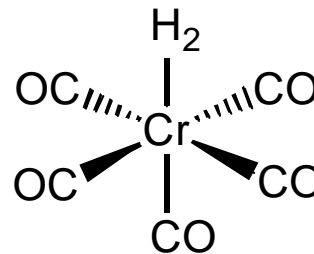
# HOMOLEPTIC AND OTHER NOVEL H<sub>2</sub> COMPLEXES



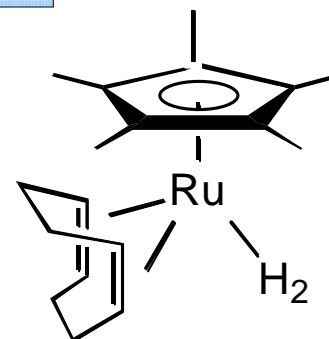
H-H = 1.34 Å for analogue [Taube]



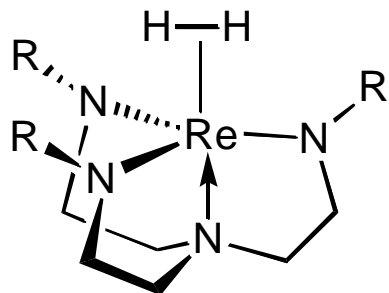
Merbach



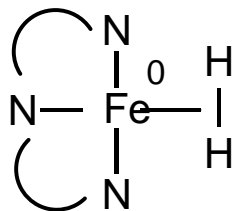
Heinekey



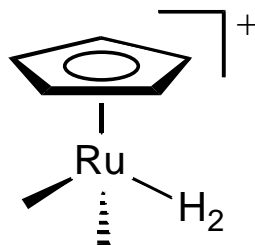
Jia and Lau



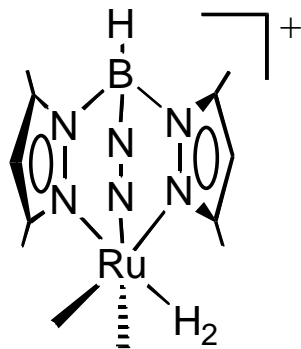
R = C<sub>6</sub>F<sub>5</sub> high valent: Re<sup>III</sup> [Schrock]



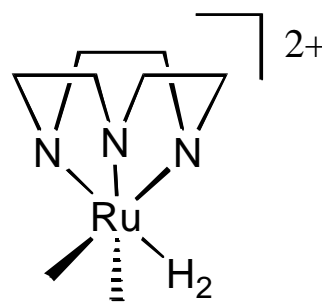
paramagnetic [Chirik, 2004]



Cp

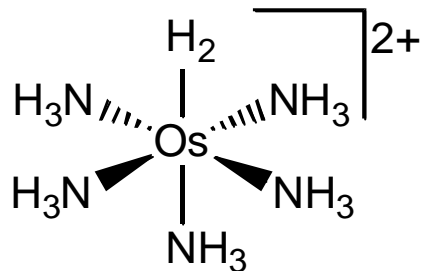


Tp

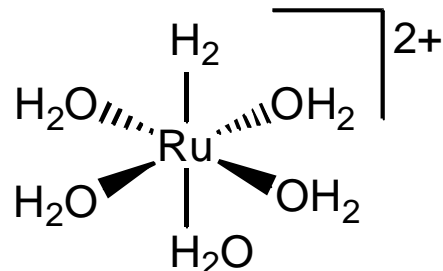


Cn

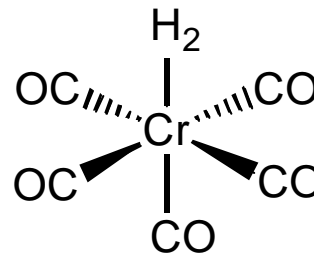
# HOMOLEPTIC AND OTHER NOVEL H<sub>2</sub> COMPLEXES



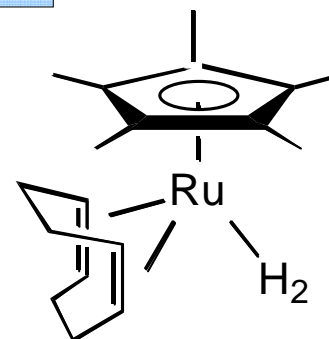
H-H = 1.34 Å for analogue [Taube]



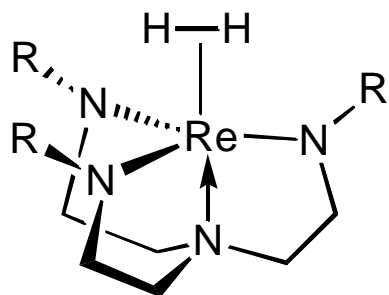
Merbach



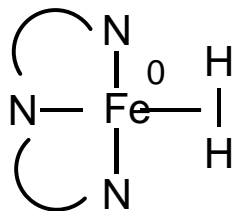
Heinekey



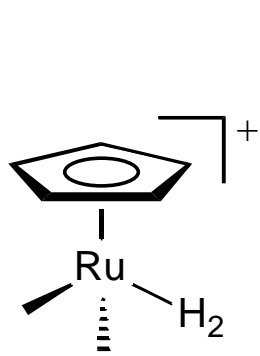
Jia and Lau



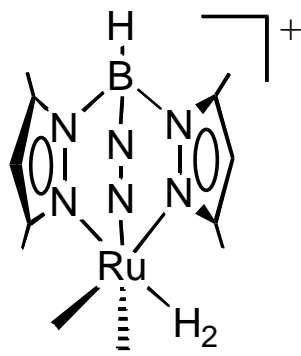
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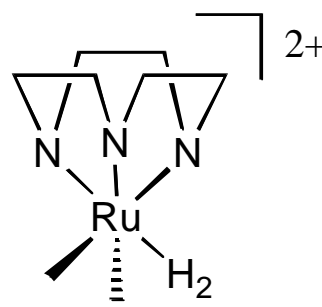
paramagnetic [Chirik, 2004]



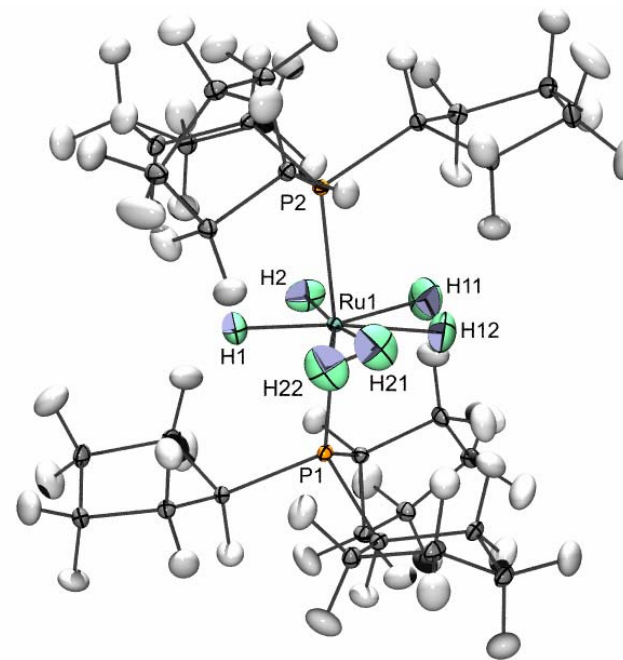
Cp



Tp



Cn



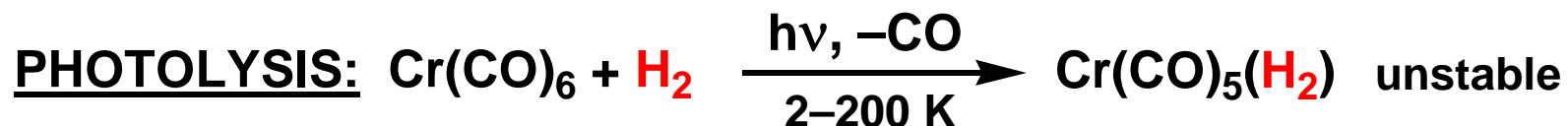
first neutron structure of a bis-H<sub>2</sub> complex

RuH<sub>2</sub>(H<sub>2</sub>)<sub>2</sub>[P(*c*-pentyl)<sub>3</sub>]<sub>2</sub>

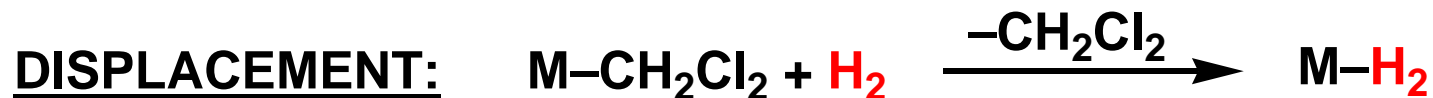
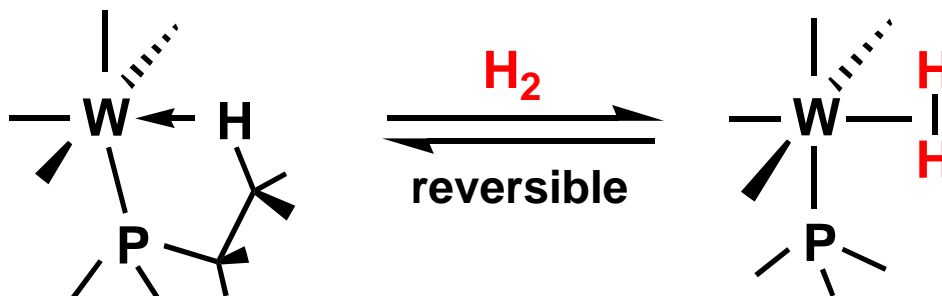
[JACS 2005, Chaudret and Sabo-Etienne]



## SYNTHETIC ROUTES TO H<sub>2</sub> COMPLEXES

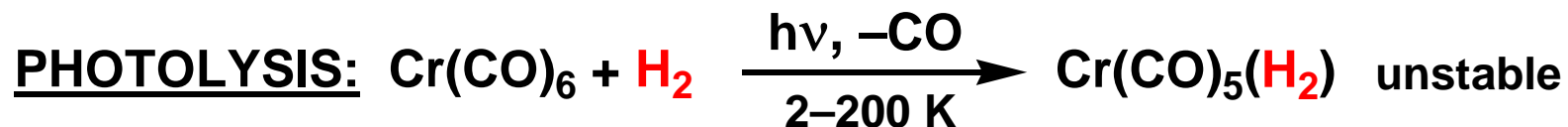


UNSATURATED  
PRECURSOR:  
(e. g. "agostic")

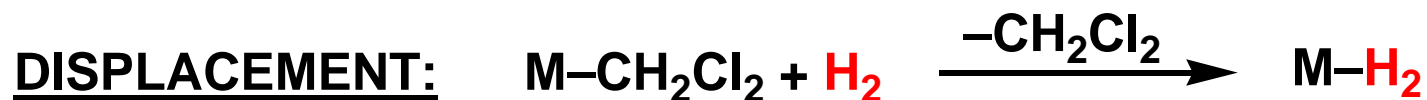
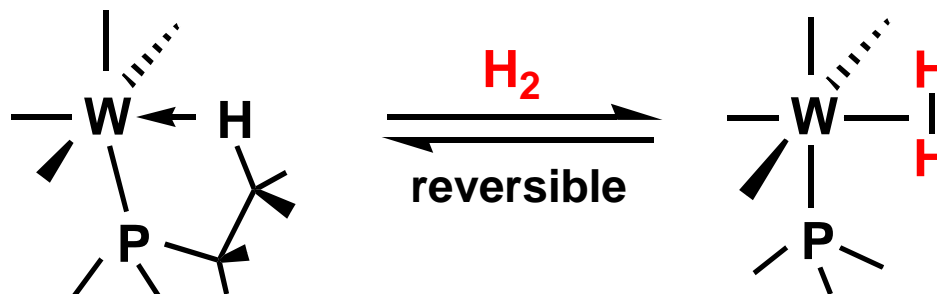


Binding of H<sub>2</sub> to metal complexes such as W(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub> is competitive with binding of water, i.e. an H<sub>2</sub> complex can be made by displacement of an H<sub>2</sub>O (aquo) ligand

## SYNTHETIC ROUTES TO H<sub>2</sub> COMPLEXES



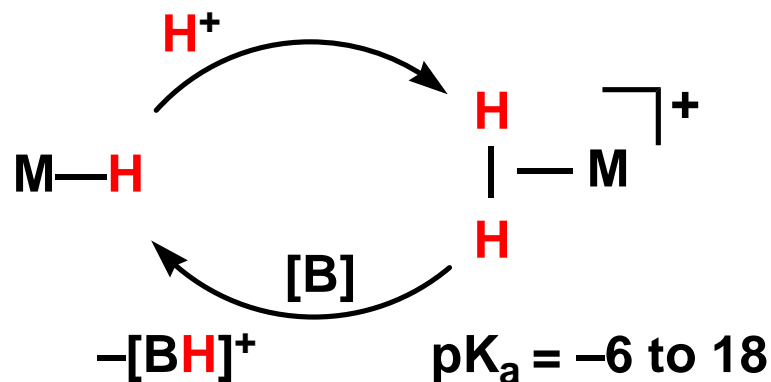
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PRECURSOR:**  
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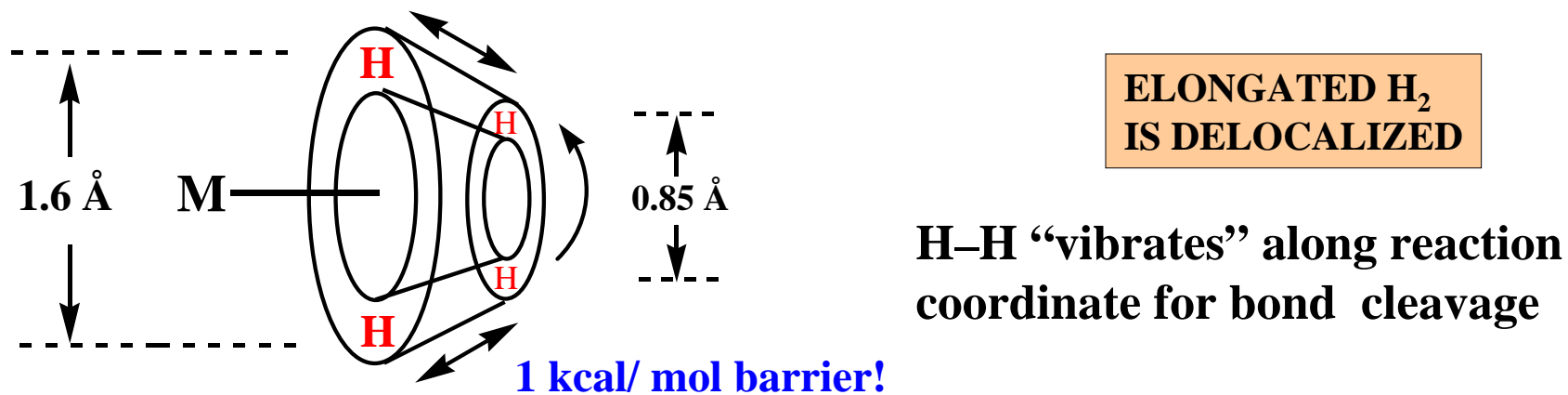
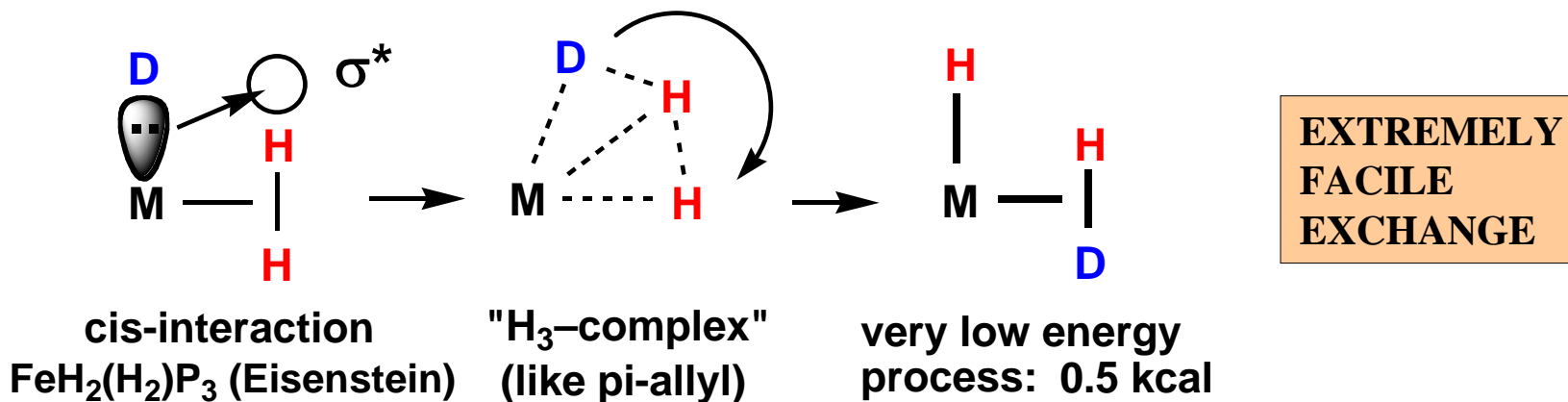
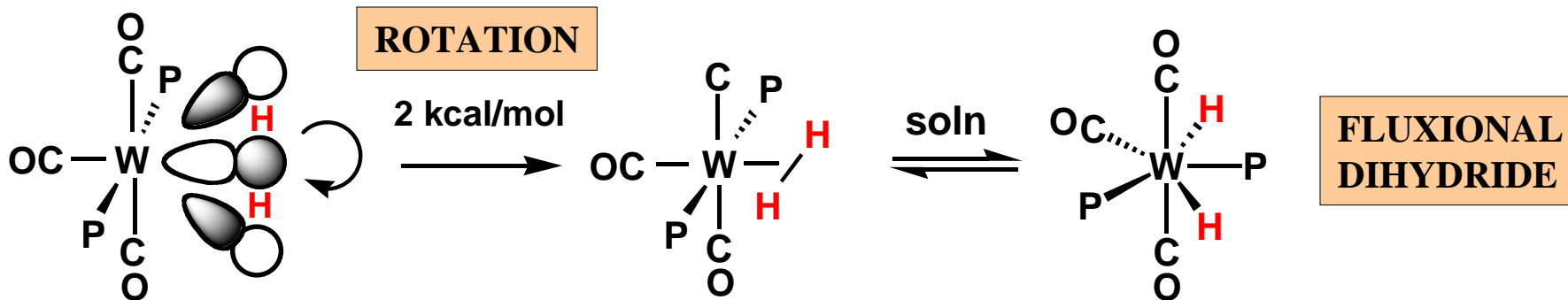
**PROTONATION OF HYDRIDE:**

by acids as weak as *ROH*

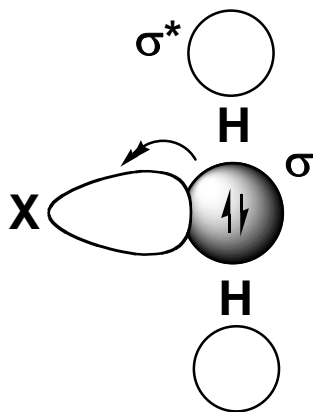
Deprotonation of bound H<sub>2</sub>  
by bases as weak as *Et<sub>2</sub>O*



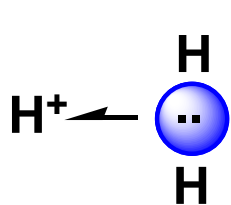
# H<sub>2</sub> IS THE MOST DYNAMIC LIGAND



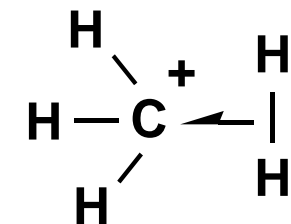
## H<sub>2</sub> IS A WEAK ELECTRON DONOR



X = M<sup>+</sup>, H<sup>+</sup>, etc



H<sub>3</sub><sup>+</sup>



carbocations

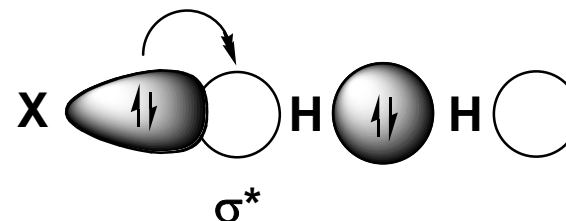
[Olah] CH<sub>5</sub><sup>+</sup>

[M(H<sub>2</sub>)<sub>n</sub>]<sup>+</sup>

gas-phase "naked" M cations

surface-M<sup>+</sup>(H<sub>2</sub>) [e.g. zeolites]

## H<sub>2</sub> IS A WEAK ELECTRON ACCEPTOR



"end-on"

X = O<sup>2-</sup>, halide, C=C, H-H, M ??

Cr<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>, -130 °C [Burwell, 1977]

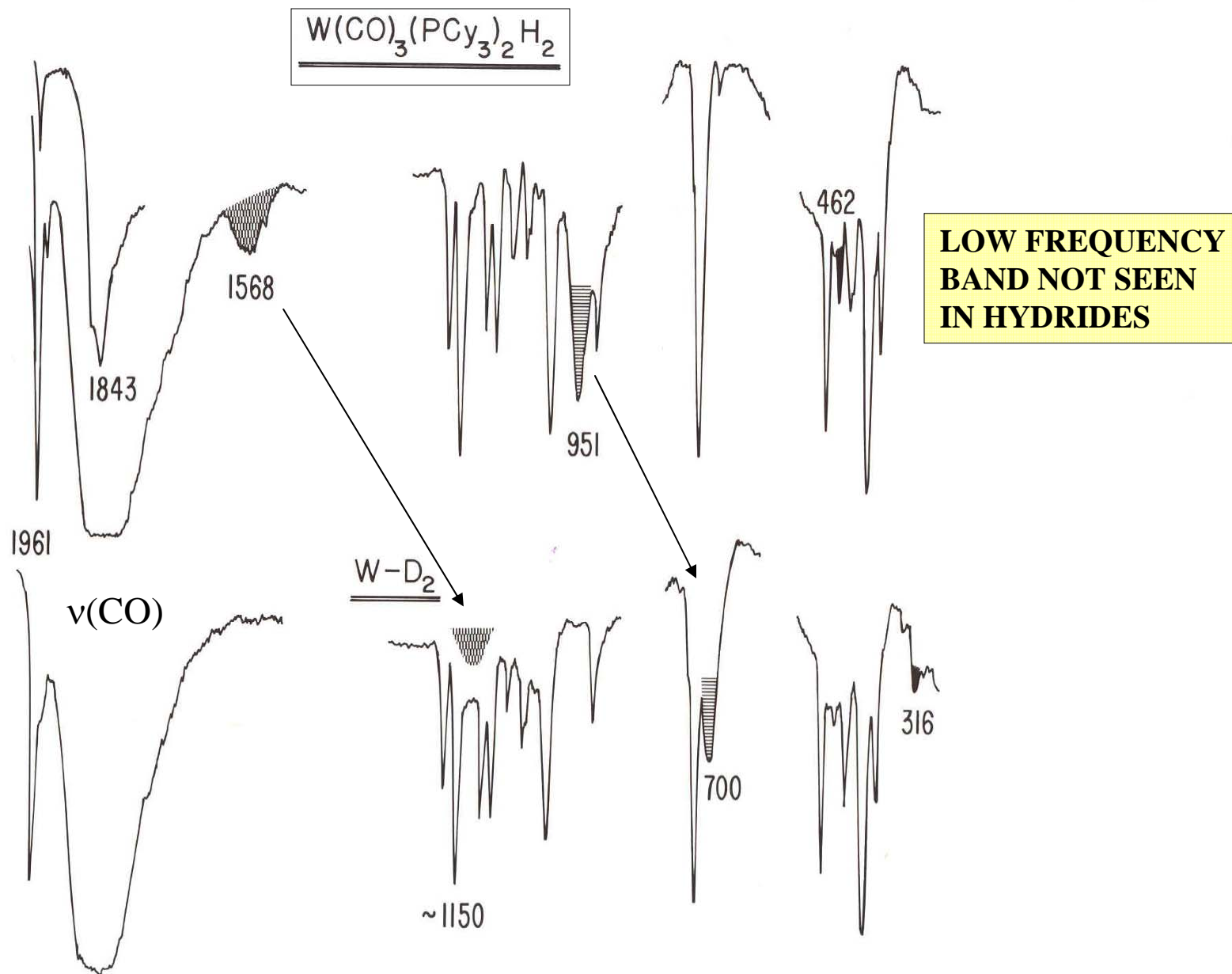
nanocrystalline MgO binds 1.8 wt%  
H<sub>2</sub> reversibly at 77 K and 13 atm H<sub>2</sub>

[Schwarz; Kubas]

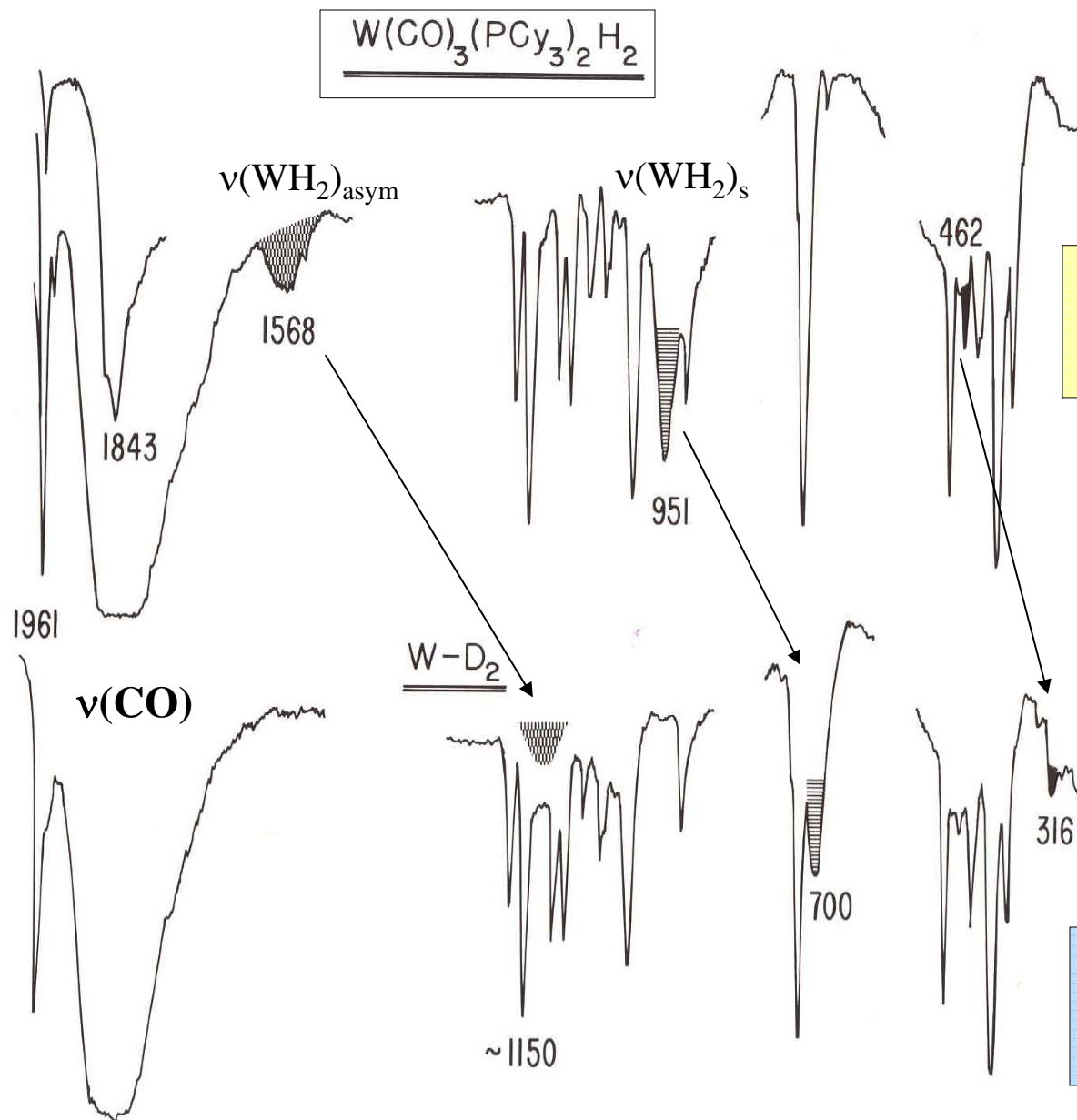
[Na<sup>+</sup>][Cl<sup>-</sup>] - H<sub>2</sub> weak interaction in  
low T matrix [Sweany]

C(nanotube)-H<sub>2</sub>

# FIRST CRUCIAL CLUE FOR METAL-DIHYDROGEN DISCOVERY INVOLVED "ROUTINE" INFRARED SPECTRA OF SOLID COMPLEX



# FIRST CRUCIAL CLUE FOR METAL-DIHYDROGEN DISCOVERY INVOLVED “ROUTINE” NUJOL MULL IR SPECTRA



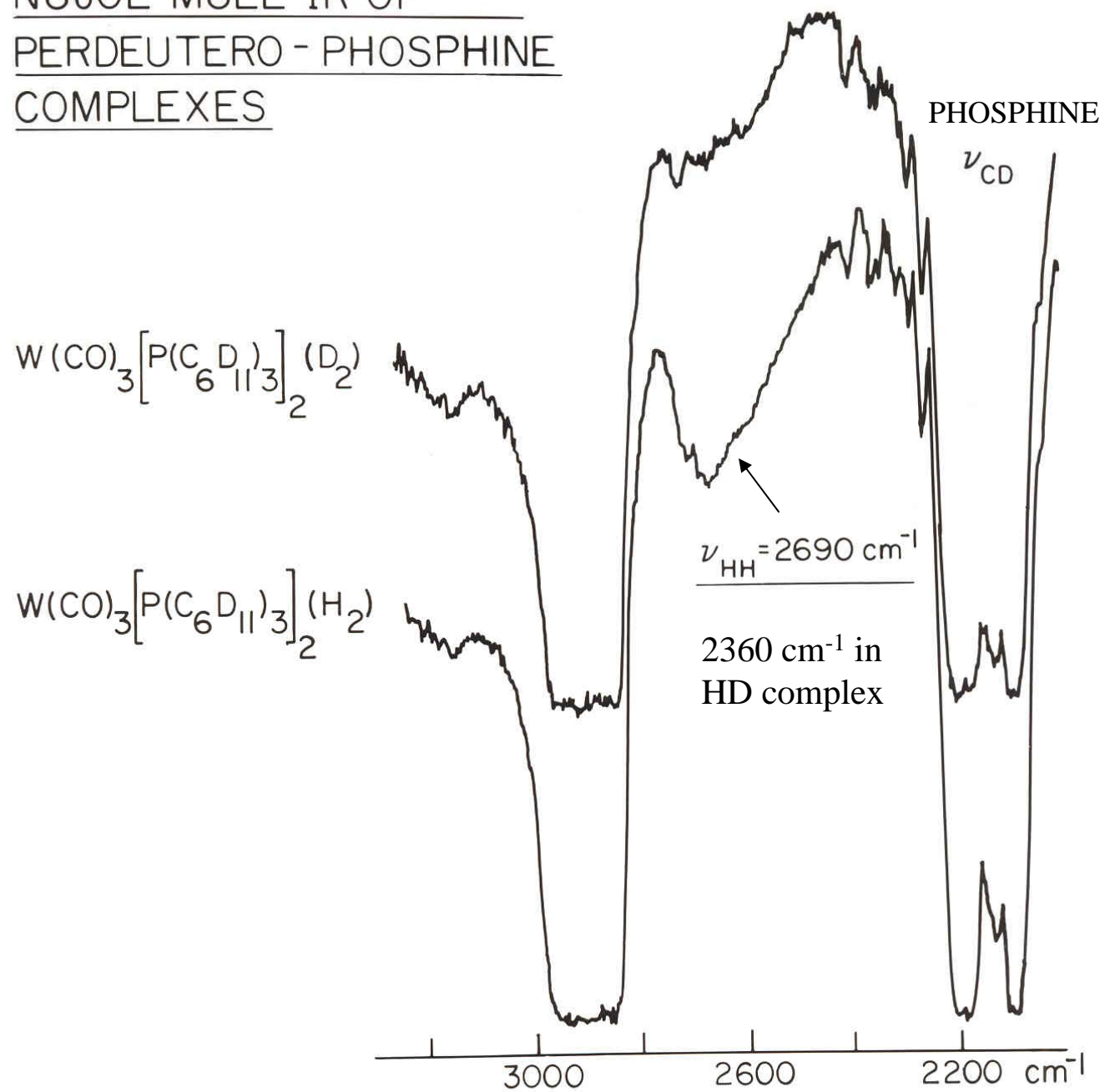
**LOW FREQUENCY DEFORMATION,  $\delta(\text{WH}_2)$ , NOT SEEN IN HYDRIDES**

**SHIFTS FOR W-D<sub>2</sub> TO REGION BELOW 400 cm<sup>-1</sup>**

**NON-ROUTINE IR INSTRUMENT**

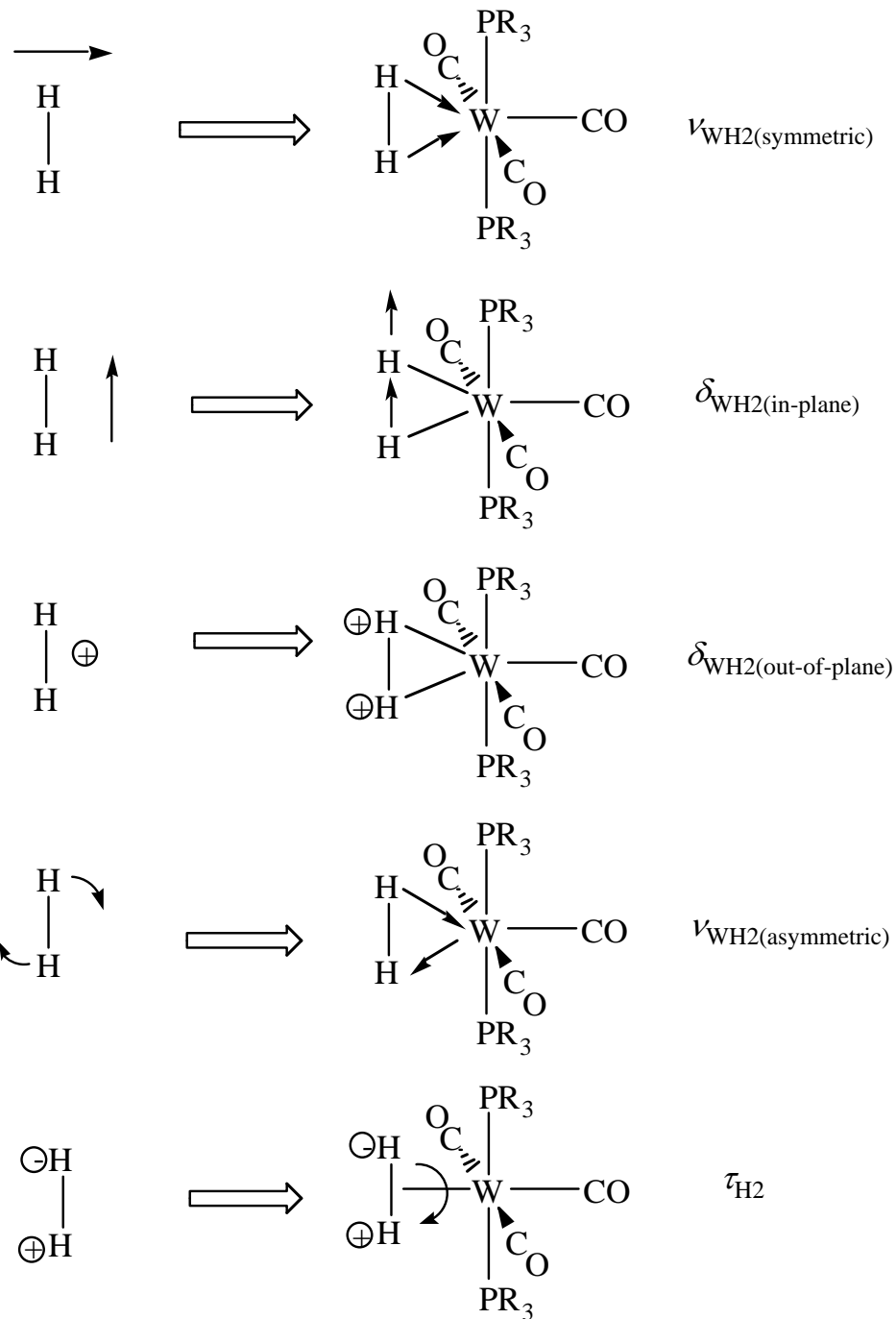
**“bonding of hydrogen to complexes may be novel”**  
---- *Chem. Comm.* 1980

NUJOL MULL IR OF  
PERDEUTERO - PHOSPHINE  
COMPLEXES



H-H stretch PLUS  $\Rightarrow$

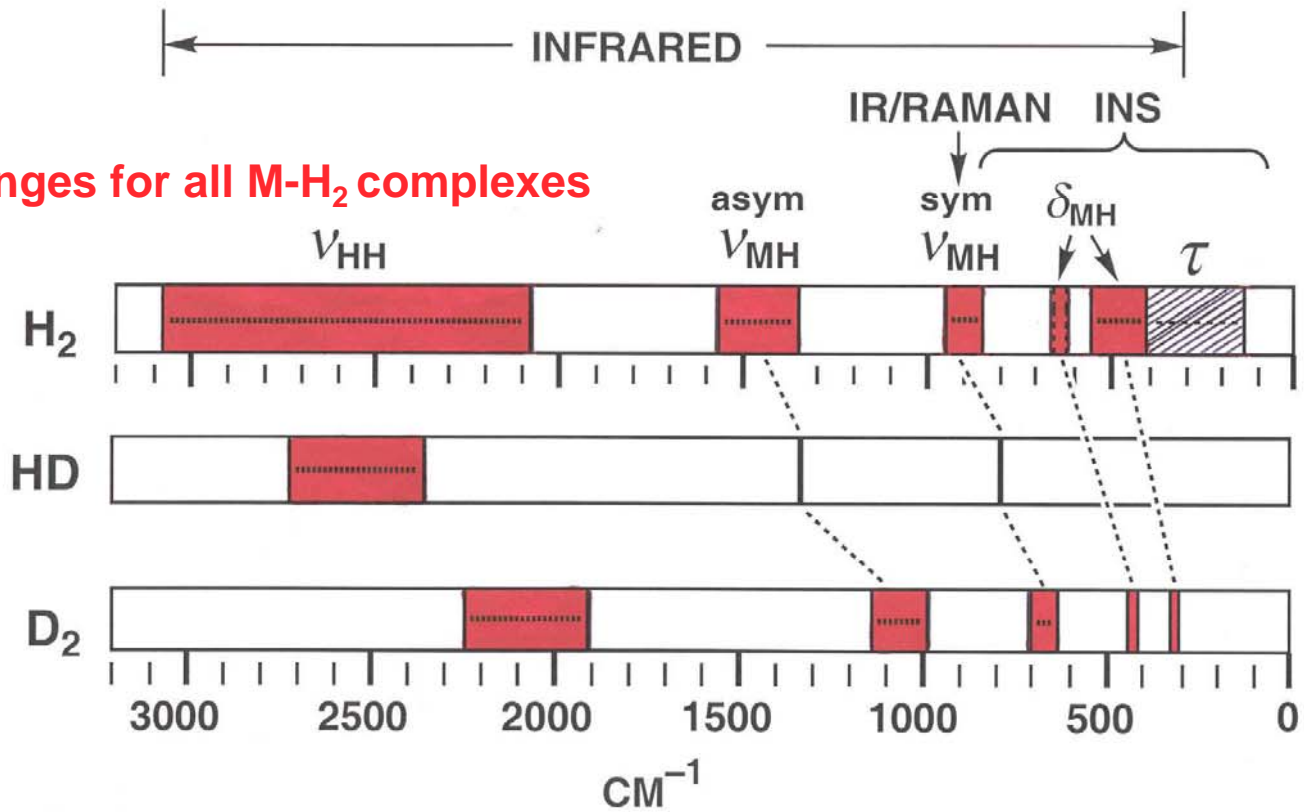
Six vibrational modes for bound dihydrogen versus two for atomically bound hydride



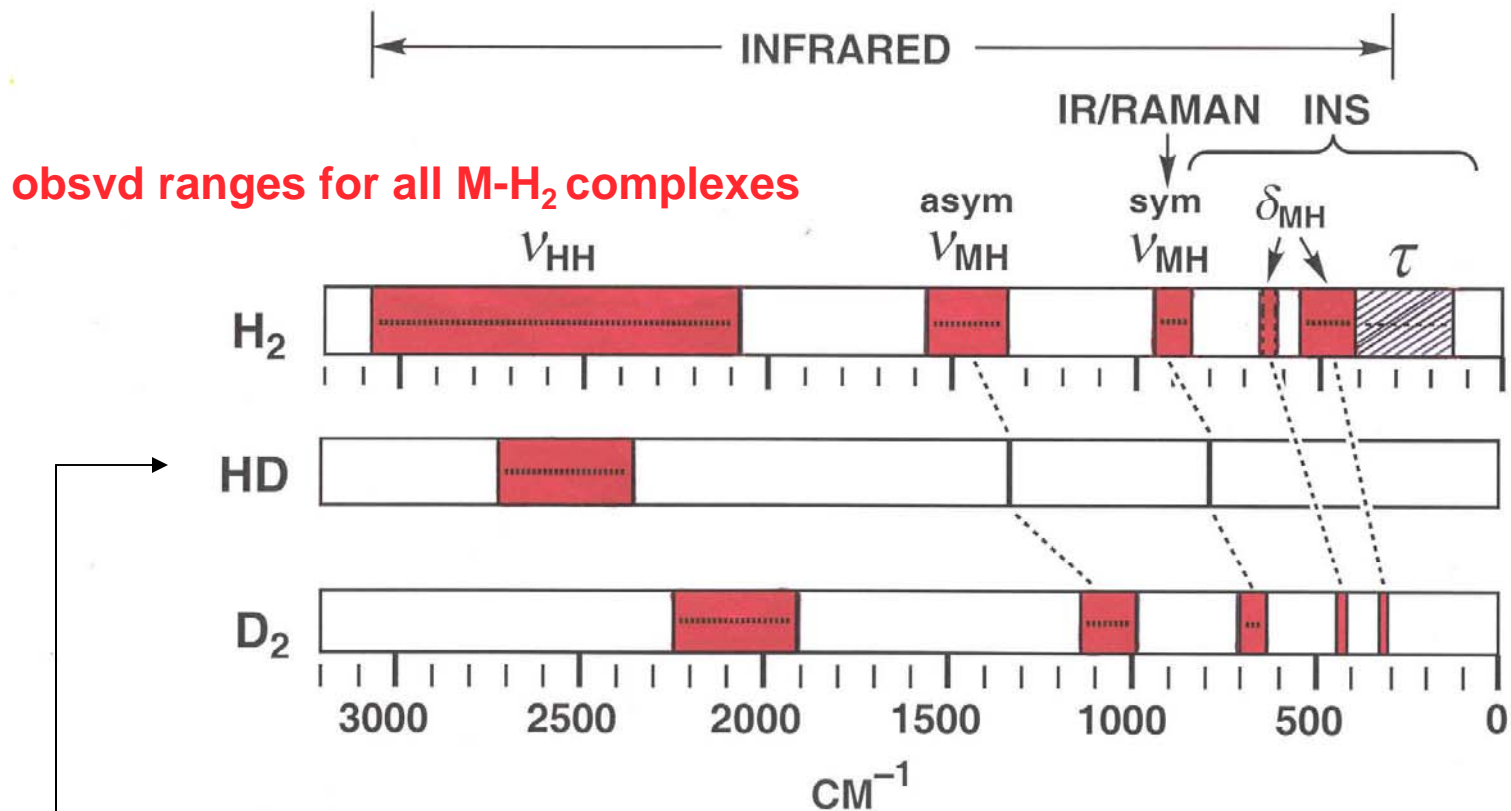


6 VIBRATIONAL MODES EXPECTED FOR  $M-\begin{matrix} H \\ | \\ H \end{matrix}$

obsvd ranges for all M-H<sub>2</sub> complexes

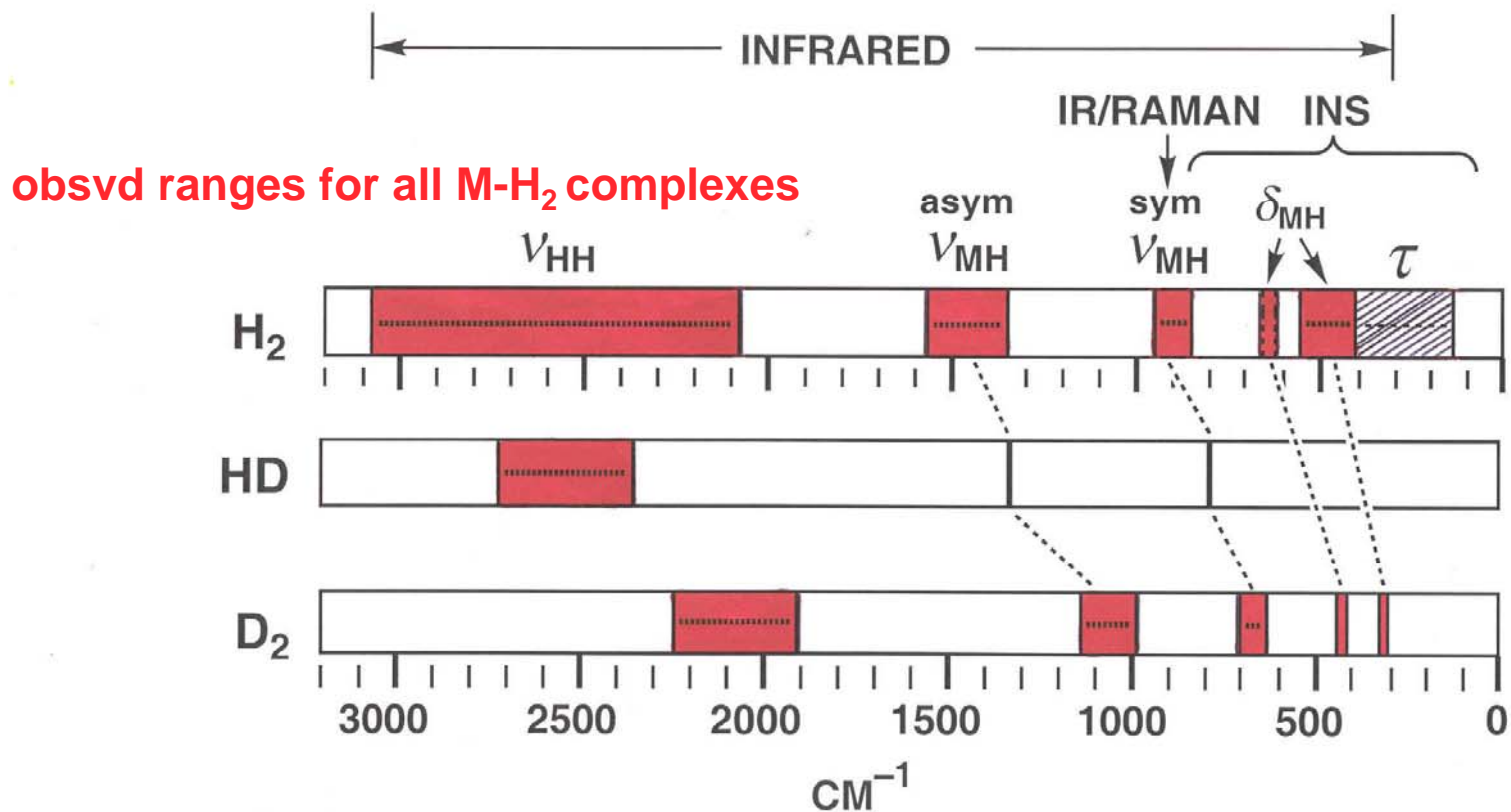


6 VIBRATIONAL MODES EXPECTED FOR  $\text{M}-\begin{matrix} \text{H} \\ | \\ \text{H} \end{matrix}$

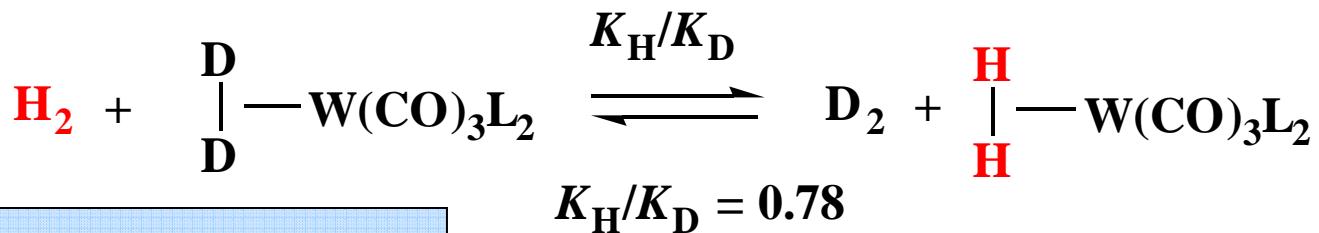


The frequencies of the bands for the  $\eta^2$ -HD complexes are in between those for the  $\eta^2$ -HH and  $\eta^2$ -DD species and not a superimposition of MH<sub>2</sub> and MD<sub>2</sub> bands as seen for classical hydrides.

6 VIBRATIONAL MODES EXPECTED FOR  $\begin{array}{c} \text{H} \\ | \\ \text{M}-\text{I} \\ | \\ \text{H} \end{array}$



SIX MODES LEADS TO INVERSE EQUILIBRIUM ISOTOPE EFFECT

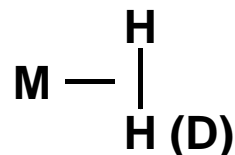


**D<sub>2</sub> binds stronger than H<sub>2</sub>**

[Bender, Kubas, Jones, Swanson, Hoff, JACS, 1997]

# Solution NMR Diagnostic for Dihydrogen Versus Hydride Structure

$^1\text{H}$  NMR {  
SIGNAL  
[ $T_1$ ]<sub>min</sub>  
 $J(\text{HD})$



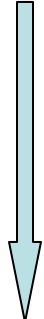
broad, uncoupled  
<40 ms  
1–35 Hz  
(43 Hz in HD gas)



sharp, coupled  
>100 ms  
< 1 Hz



# Comparison of H–H Distances Determined by Diffraction Methods and NMR

Complex	H–H Distance, Å		Solid state NMR	Soln NMR $J_{\text{HD}}$	Stability to H <sub>2</sub> loss
	X-ray	Neutron			
Cr(CO) <sub>3</sub> (PPr <sup>i</sup> ) <sub>2</sub> (H <sub>2</sub> )	0.67(5)			35	reversible
Cr(CO) <sub>3</sub> (PCy <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> )			0.85(1)		
Mo(CO) <sub>3</sub> (PCy <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> )			0.87(1)		
Mo(CO)(dppe) <sub>2</sub> (H <sub>2</sub> )		0.736(10)	0.88(1)	34	
W(CO) <sub>3</sub> (PPr <sup>i</sup> ) <sub>2</sub> (H <sub>2</sub> )	0.75(16)	0.82(1)	0.89(1)	33.5	
W(CO) <sub>3</sub> (PCy <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> )			0.89(1)		
[FeH(H <sub>2</sub> )(dppe) <sub>2</sub> ] <sup>+</sup>	0.87(3)	0.816(16)	0.90(1)	32	
[CpRu(dppm)(H <sub>2</sub> )] <sup>+</sup>	1.01			21.9	irreversibly bound H <sub>2</sub>
[CpRu(dmpe)(H <sub>2</sub> )] <sup>+</sup>			1.02(1)	22	

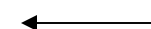
Distance needs correction for the effects of hydrogen librational motion.

$$d_{\text{HH}} = 1.44 - 0.0168J_{\text{HD}} \text{ \AA}$$

$$d_{\text{HH}} = 1.42 - 0.0167J_{\text{HD}} \text{ \AA}$$

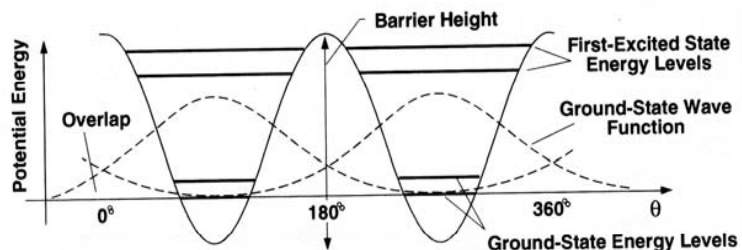
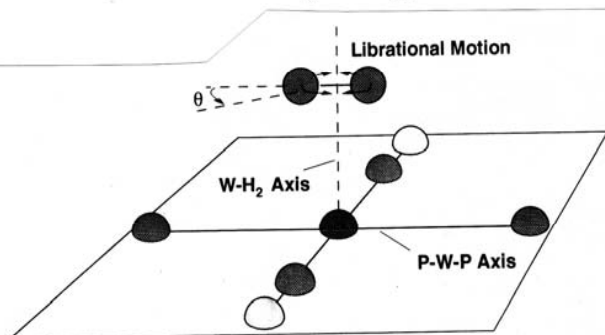
[Heinekey]

[Morris]



# Planar Rotation of Molecular Hydrogen

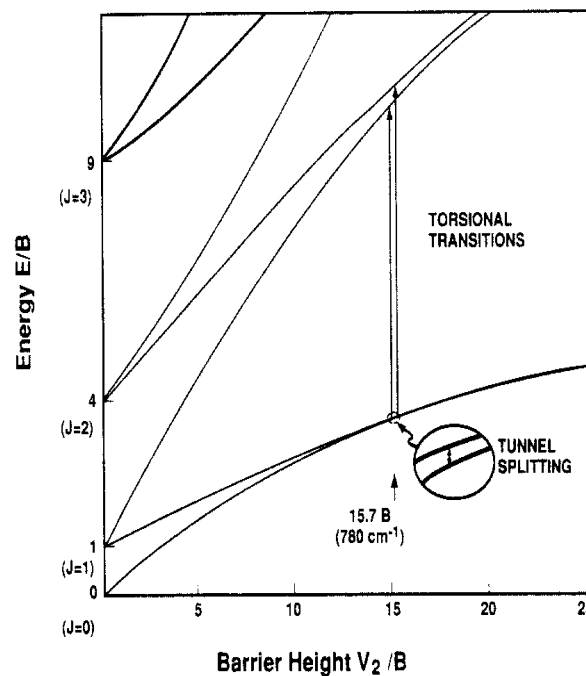
## Model for Dihydrogen Rotation



$$\left( -B \frac{\partial^2}{\partial \phi^2} + \frac{1}{2} V_2 \cos 2\phi \right) \psi = E \psi$$

$$E_J = BJ^2 \text{ if } V_2 = 0$$

## Molecular Hydrogen Complexes



Energy level spacing differs appreciably from that for 3-D rotation

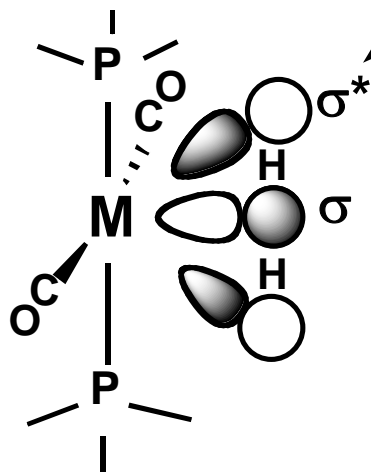
Deduce chemical binding of H<sub>2</sub>?

# ROTATIONAL BARRIER OF THE H<sub>2</sub> LIGAND

ABSOLUTE EVIDENCE FOR NONCLASSICAL  
DIHYDROGEN COORDINATION VERSUS CLASSICAL  
HYDRIDE LIGANDS

DETERMINED IN COLLABORATION WITH JUERGEN  
ECKERT AT LANL AND UCSB BY INELASTIC NEUTRON  
SCATTERING (INS) METHODS

rotational tunneling spectroscopy  
(quantummechanical rotation)



EVIDENCE FOR M → H<sub>2</sub> σ\* BACKBONDING

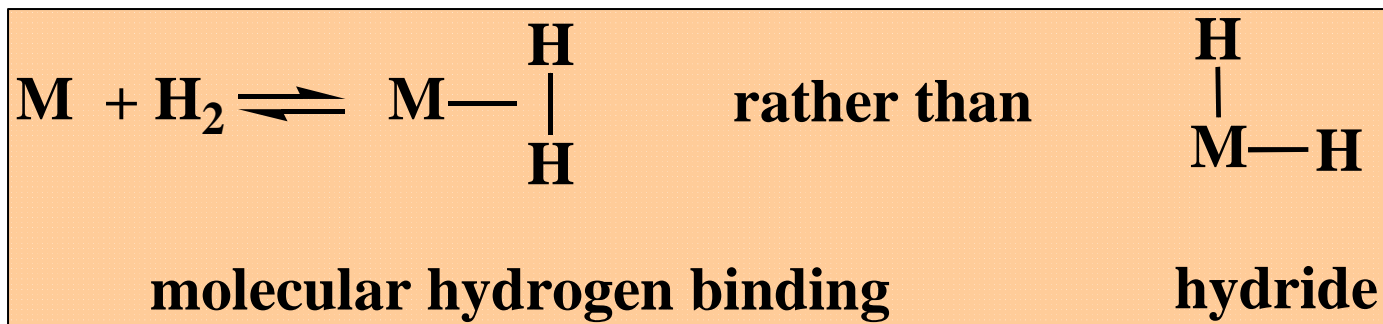
FOR M(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>):

<u>M</u>	<u>BARRIER (kcal)</u>
Cr	1.3
Mo	1.7
W	2.2

ECKERT HAS ALSO DETERMINED BARRIERS FOR H<sub>2</sub>  
BINDING TO ZEOLITES AND METAL ORGANIC  
FRAMEWORK COMPLEXES (MOF'S)

## DIHYDROGEN COMPLEXES FOR HYDROGEN STORAGE

*Chemisorption* of MOLECULAR hydrogen on light atom structures should give *reversibly* bound H<sub>2</sub>



“M” could also be an oxide or other light main group atom


H–H bond is very strong (104 kcal/mol) and completely breaking it to form hydrides costs a lot of energy. *This is avoided for molecular H<sub>2</sub> binding.*

*Multiple* H<sub>2</sub> binding on inexpensive transition metals such as iron may be possible to give >6% H<sub>2</sub>:





## H<sub>2</sub> STORAGE ON NANOCRYSTALLINE MgO

Calculations (Hermansson [*J. Chem. Phys.* 1998, 7515) suggested that H<sub>2</sub> molecules adhere to the (111) surface of MgO with binding energy of 124 kJ/mole. We tested adsorption of H<sub>2</sub> onto commercial nanocrystalline MgO, which stores very little H<sub>2</sub> at RT but a lot reversibly at 77 K. 

Using surface area = 600 m<sup>2</sup>/g, the theoretical monolayer hydrogen density of 1.3 x 10<sup>-5</sup> mole-H/m<sup>2</sup>, at a pressure of 10,000 torr (13 Atm) and 77 K, the MgO adsorbs the equivalent of 2.5 H<sub>2</sub> monolayers.

QuickTime™ and a  
TIFF (LZW) decompressor  
are needed to see this picture.

Sieverts apparatus  
Schwarz, Los Alamos

This indicates crevices store additional hydrogen. The enhancement storage factor of 2.5 is ~4 times smaller than that found in carbon (nanotubes, etc)

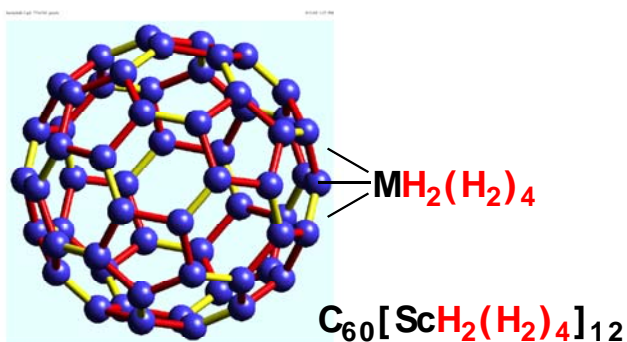
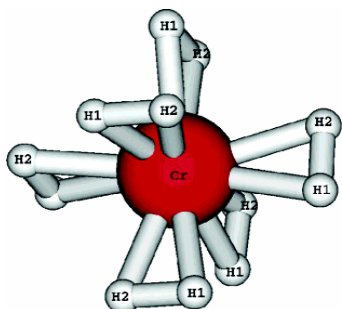
# Molecular chemisorption of $H_2$ : preserve easy kinetics of (ad/de)sorption with stronger binding

Can we tune the guest-host interaction of the hydrogen molecule into the range between physisorption and (dissociative) chemisorption - i.e. that of the molecular hydrogen complexes ? (: 10-20 kJ/mol) - AND make materials with enough of these sites ??

Create highly porous material with many (unsaturated) metal binding sites  
(Cheetham et al. : Ni-5sulfoisophthalate, next)

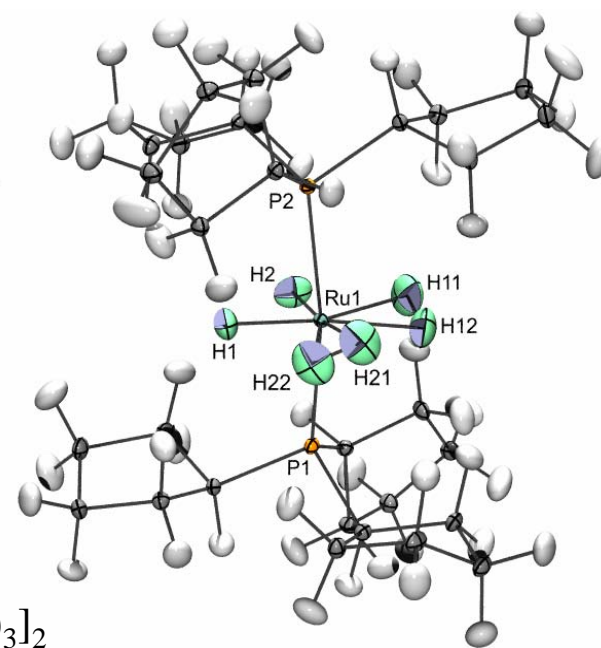
AND

Support metal-(multiple-)dihydrogen complexes in porous material seems "easy" in theory (below); organometallic example (right)



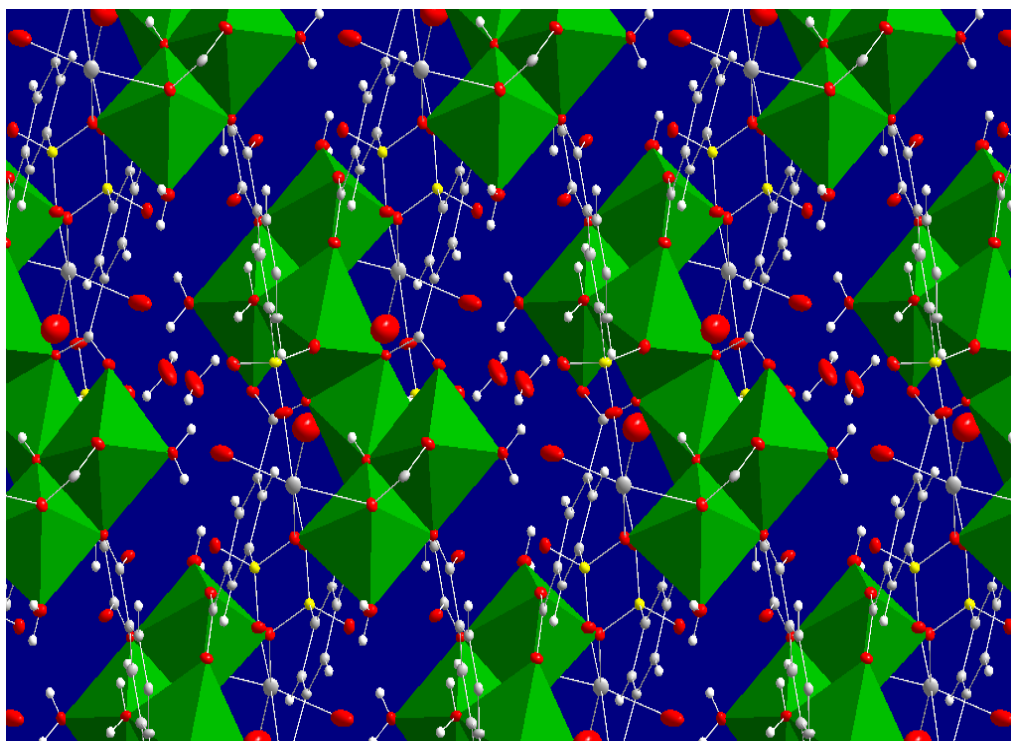
Heben; Dillon

L. Gagliardi and P. Pyykko, JACS 126, 15014 (2004)



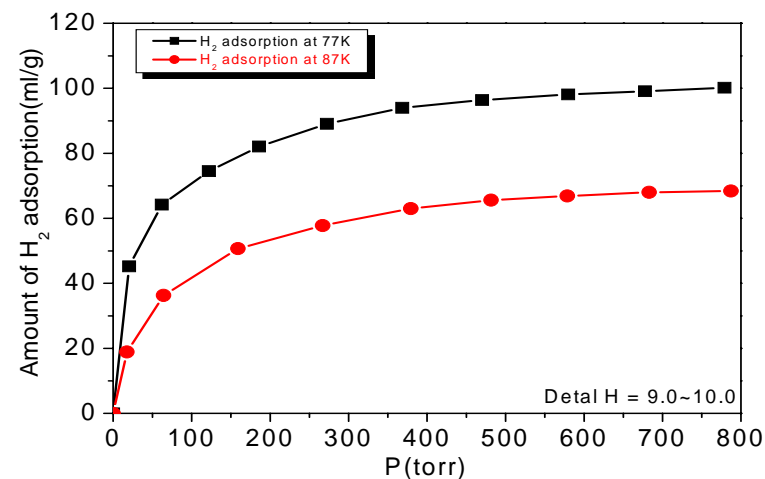
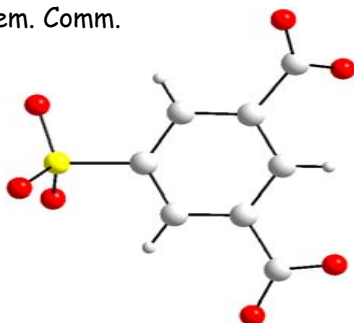
Chaudret, Sabo-Etienne et al, JACS 2005

# A thermally stable Nickel 5-Sulfoisophthalate with remarkable H<sub>2</sub> sorption properties

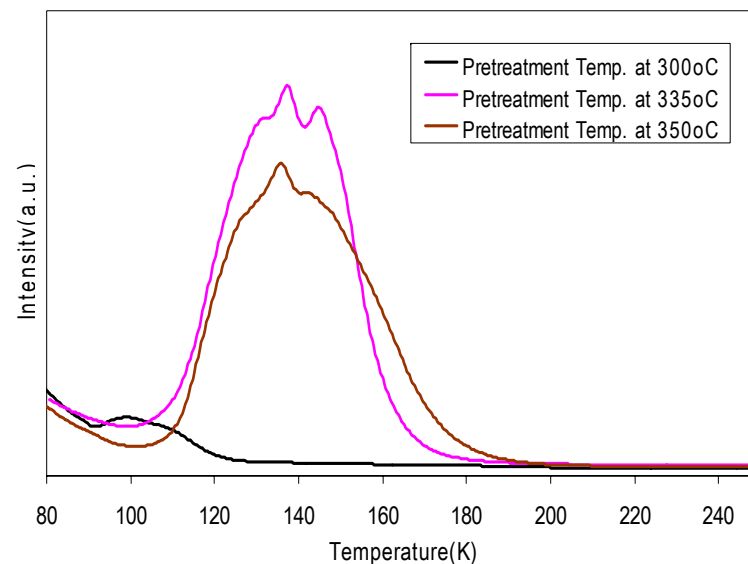


D.S. Kim, P. M. Forster, R. L. Toquin, A. K. Cheetham, Chem. Comm. 2005

5-Sulfoisophthalate



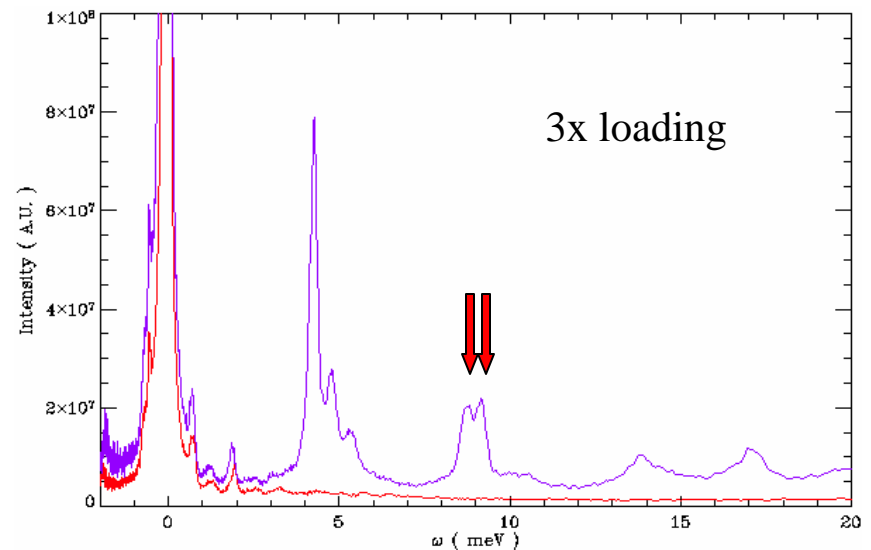
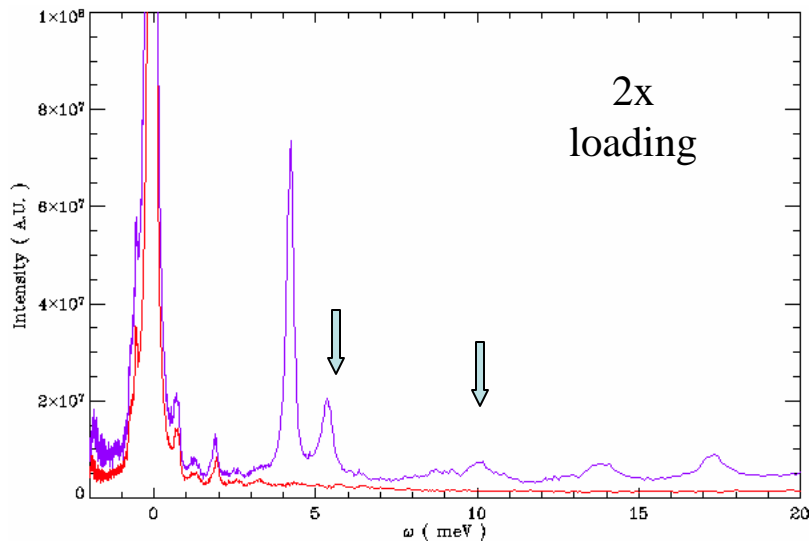
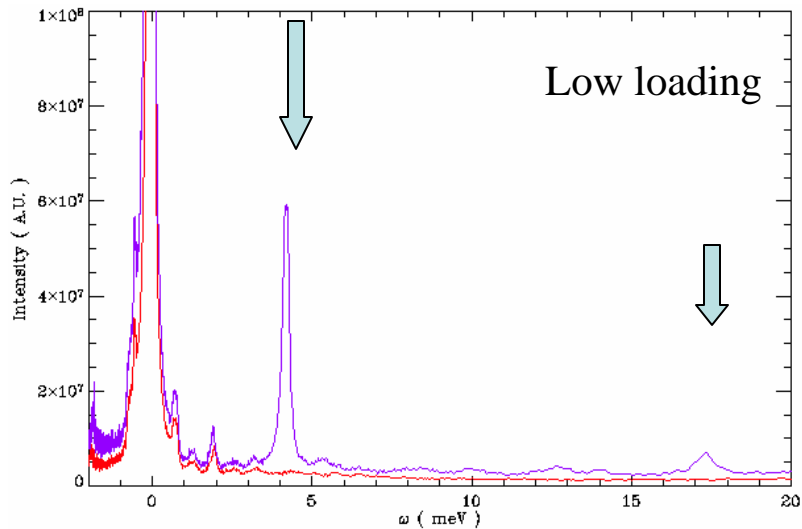
Ni-SIPA dehydrated at 335 C



# Rotational tunneling spectra of H<sub>2</sub> in Nickel 5-Sulfoisophthalate

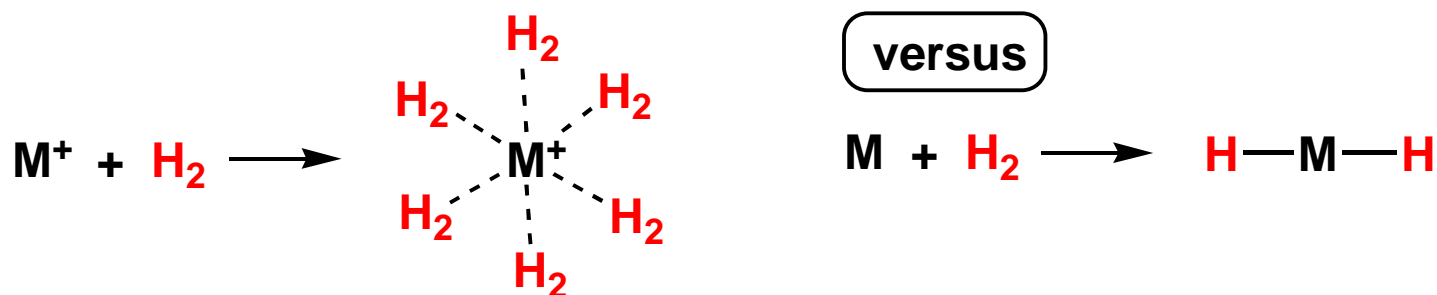
(QENS, IPNS(ANL), April 2005)

several well-defined binding sites with strong guest-host interaction  
( $\gg$  than carbons or MOF-5)  
sites with planar rotation  
chemisorbed H<sub>2</sub> at unsaturated Ni sites  
and 3-D rotation physisorbed H<sub>2</sub>



## H<sub>2</sub> BINDING TO “NAKED” METAL IONS AND ATOMS

Unstable “naked” metal cations, [M(H<sub>2</sub>)<sub>n</sub>]<sup>+</sup> studied in gas phase by Bowers using ion-beam and mass spec techniques to give H<sub>2</sub> binding energies



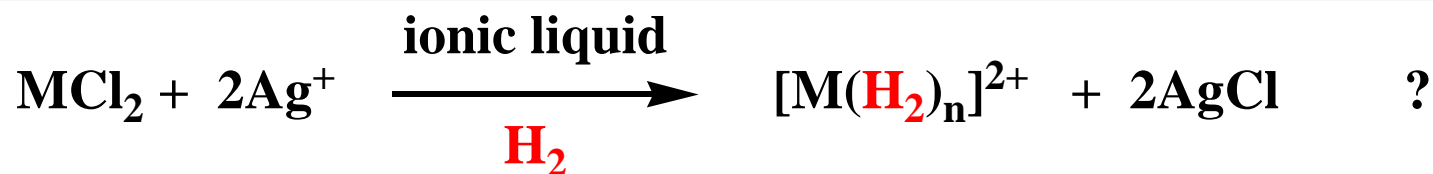
Comparison of Experimental Binding Energies ( $\pm 0.4$ - $1.4$  kcal/mol) for [M]<sup>+</sup> + L  $\rightarrow$  [M(L)<sub>n</sub>]<sup>+</sup> for L = H<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>.

ion	L	n = 1	n = 2	n = 3	n = 4	.....	n = 6-10
[Ti(L) <sub>n</sub> ] <sup>+</sup>	H <sub>2</sub>	10.0	9.7	9.3	8.5		>20% H <sub>2</sub>
[V(L) <sub>n</sub> ] <sup>+</sup>	H <sub>2</sub>	10.2	10.7	8.8	9.0		
[Cr(L) <sub>n</sub> ] <sup>+</sup>	H <sub>2</sub>	7.6	9.0	4.7	3.4		
[Mn(L) <sub>n</sub> ] <sup>+</sup>	H <sub>2</sub>	1.90	1.65	1.4	1.2		
[Fe(L) <sub>n</sub> ] <sup>+</sup>	H <sub>2</sub>	16.5	15.7	7.5	8.6		
	CH <sub>4</sub>	13.6	23.2	23.7	17.7		
	N <sub>2</sub>	12.9	19.8	10.8	13.6		

Pd(H<sub>2</sub>)<sub>3</sub> and Mo(H<sub>2</sub>)<sub>n</sub> studied in low T matrices by Lester Andrews

## "Naked Metal Ion" Generation and Reaction with H<sub>2</sub>

Synthesize highly unsaturated species that would bind multiple H<sub>2</sub> as in known gas phase naked metal ions:



M = Fe or other "light" first row transition metal

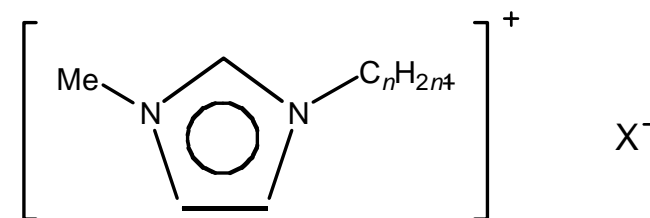
anions for ionic liquid and Ag salt are "noncoordinating"

also likely to form:  $[\text{MH}_2(\text{H}_2)_n]$

bimetallic bridging halide species M-Cl-Ag

$[\text{M}(\text{anion})_2(\text{H}_2)_n]$  — great precursor

alkane complexes

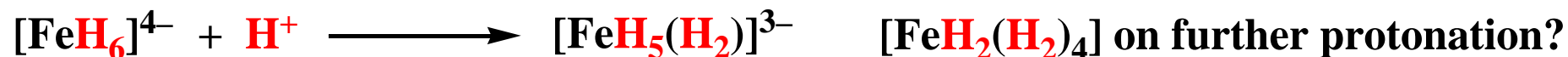
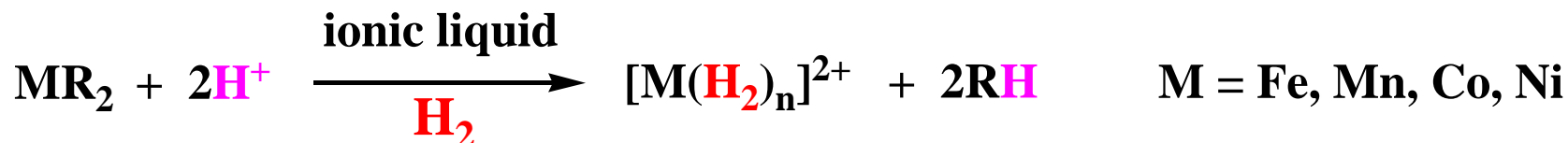


- I  $n = 4$ ,  $\text{X} = [\text{PF}_6]$ ; [bmim][PF<sub>6</sub>]
- II  $n = 4$ ,  $\text{X} = [(\text{CF}_3\text{SO}_2)_2\text{N}]$ ; [bmim][Tf<sub>2</sub>N]
- III  $n = 2$ ,  $\text{X} = [(\text{CF}_3\text{SO}_2)_2\text{N}]$ ; [emim][Tf<sub>2</sub>N]

typical ionic liquid

## "Naked Metal Ions" and Hydrogen-Rich Complexes for Hydrogen Storage

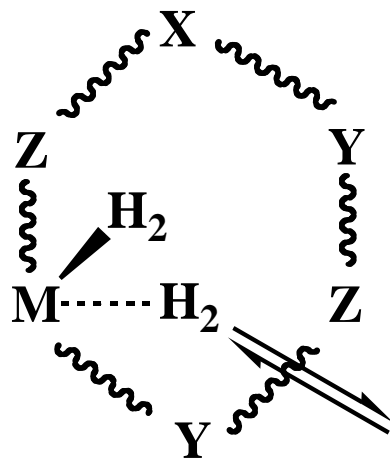
Synthesize highly unsaturated **first-row** metal species with **multiple H<sub>2</sub>** ligands via metal alkyl, aryl, or hydride complexes



[Linn]

Protonation of hydride by acid with low-coordinating anion

If unstable, embed H<sub>2</sub>-rich species into nanoporous media (zeolites, MOF)



X, Y, Z = light main-group atoms:

e.g. Li, Be, B, C, N, O, F

H<sub>2</sub> gas rapidly diffuses in and out

Dissociation pressure ~1-100 atm

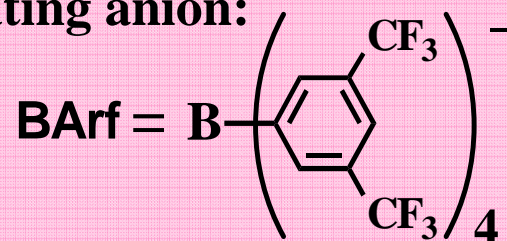
# Protonation of Aryl and Hydride Complexes

**Iron-aryl complex:**

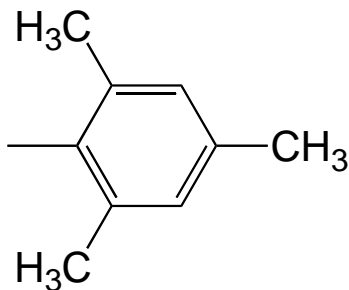
$\text{Fe}_2(\text{mesityl})_4 + \text{H}_2$  gives no reaction

$\text{Fe}_2(\text{mesityl})_4 + \text{H}[\text{BArf}]$  forms oily precipitate in toluene

low coordinating anion:



mesityl =





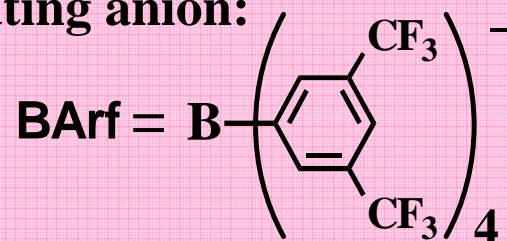
# Protonation of Aryl and Hydride Complexes

**Iron-aryl complex:**

$\text{Fe}_2(\text{mesityl})_4 + \text{H}_2$  gives no reaction

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low coordinating anion:



**HYDRIDE**

2.7 atm

**Linn complex---** soluble in organics!

Linn & Gibbins, *J. Organomet. Chem.*, **554**, 171(1998)

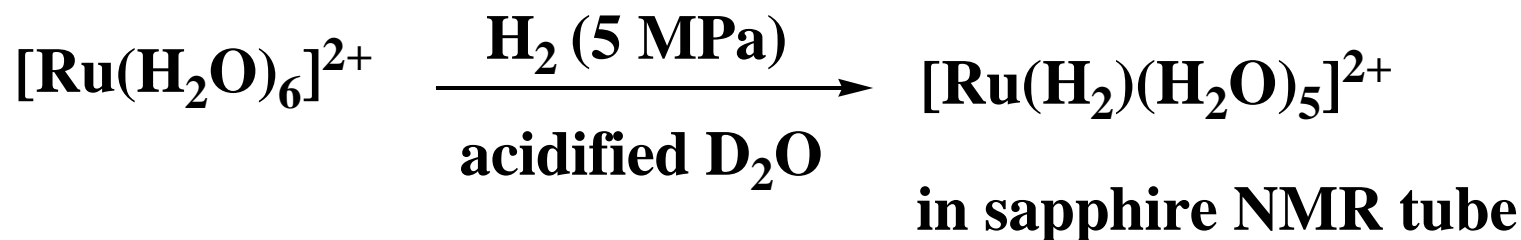
*Inorganic Synth.* in press

$[\text{FeH}_6]^{4-} + \text{H}[\text{BArf}]$  gives reaction in THF at RT (no gas evolution)

broad NMR signals (paramagnetic impurity?)

Further reactions will be carried out at low T under  $\text{H}_2$

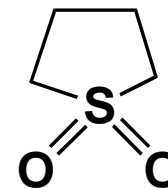
## Synthesis of H<sub>2</sub> Complexes from Classic Aquo Complexes



Merbach, *Chem. Comm.* **1998**, 2303;  
*Inorg. Chim. Acta* **2006**, 1795

$J(\text{HD}) = 31.2 \text{ Hz}$

Can this be done for iron analogue? We are examining reaction of  $[\text{Fe}(\text{H}_2\text{O})_6][\text{triflate}]_2$  with H<sub>2</sub> in sulfolane solvent and monitoring by IR (paramagnetic system)



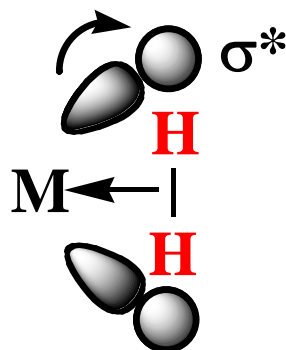
# DUAL PATHWAYS FOR $\sigma$ BOND CLEAVAGE

heterolytic cleavage

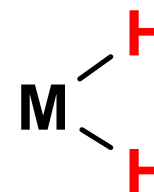


electrophilic M

oxidation state of M  
does not change



homolytic cleavage

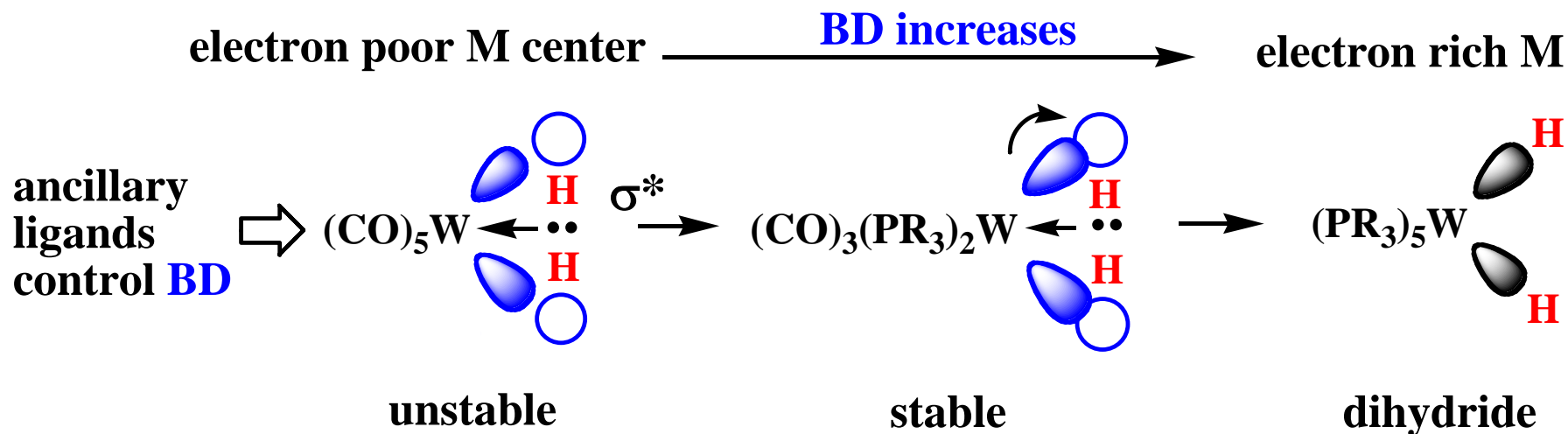


nucleophilic M

oxidative addition

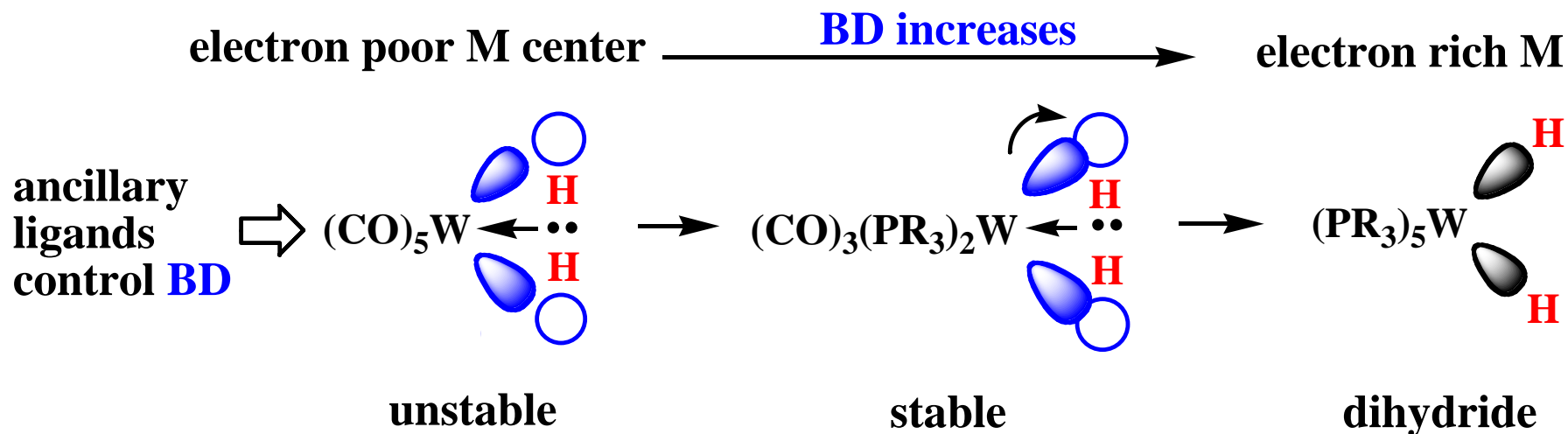
oxidation state of metal  
increases by 2

# Backdonation (BD) is critical to stability of H<sub>2</sub> complexes and H-H cleavage

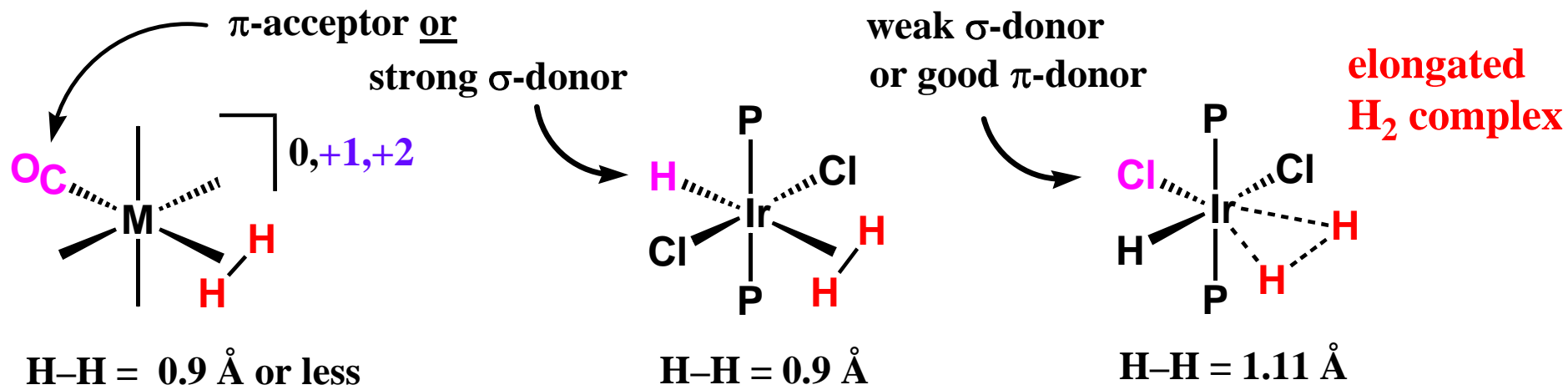


H<sub>2</sub> is a good acceptor ligand, much as an olefin

# Backdonation (BD) is critical to stability of H<sub>2</sub> complexes and H-H cleavage

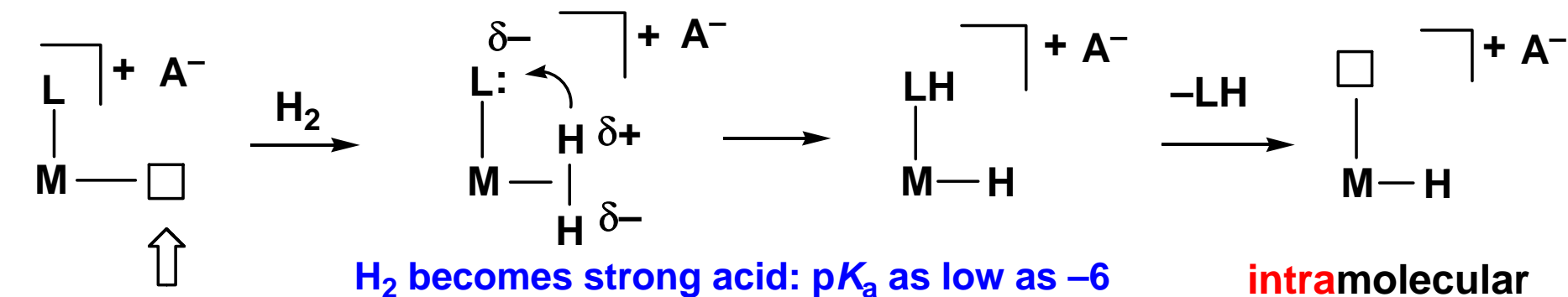


$\sigma$  complex favored by **strong trans ligand** and **positive charge**:  
(and heterolytic cleavage of H<sub>2</sub>)



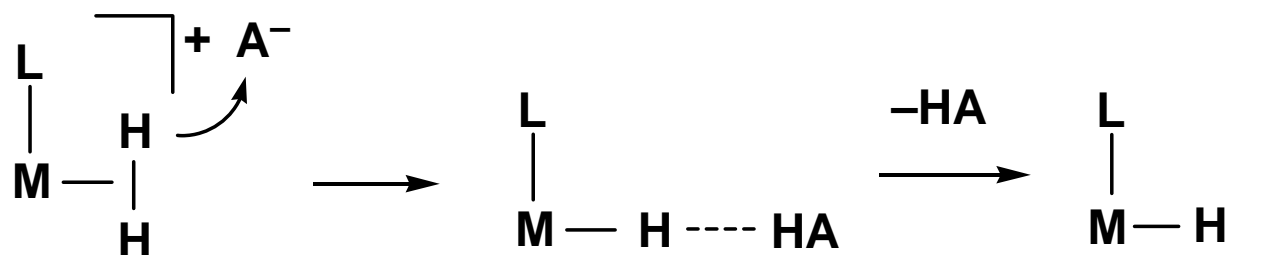
CO ligand trans to H<sub>2</sub>

# HETEROLYTIC CLEAVAGE OF HYDROGEN ON CATIONIC CENTERS



coordinatively  
 unsaturated site  
 or weak ligand

**all reactions  
 are reversible**

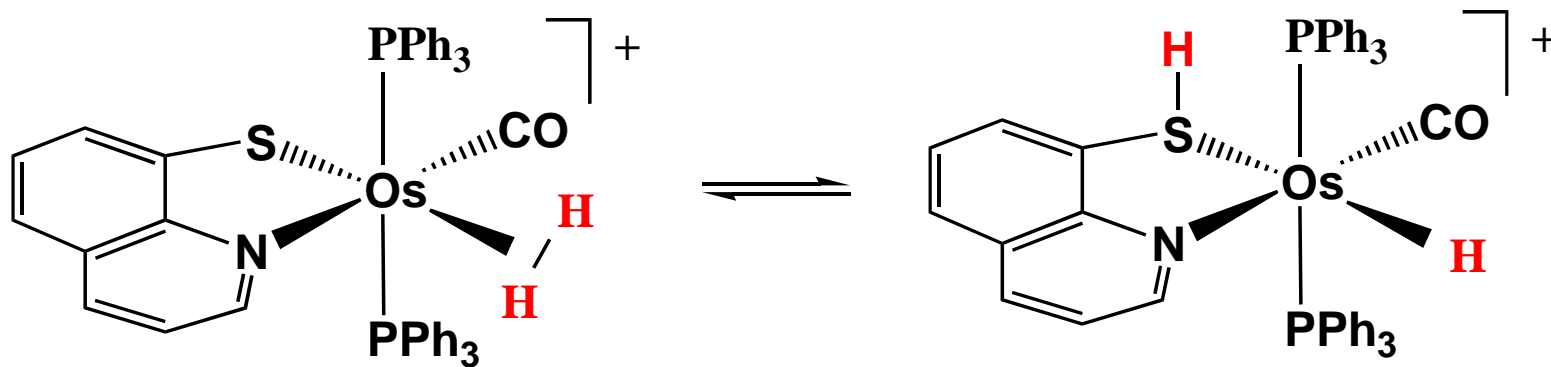


**dihydrogen bond**

**intramolecular**

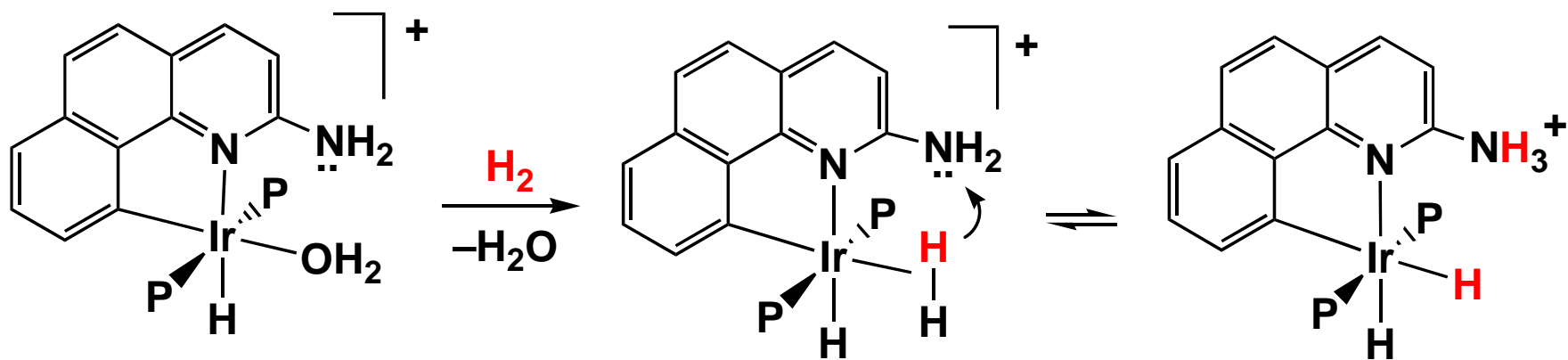
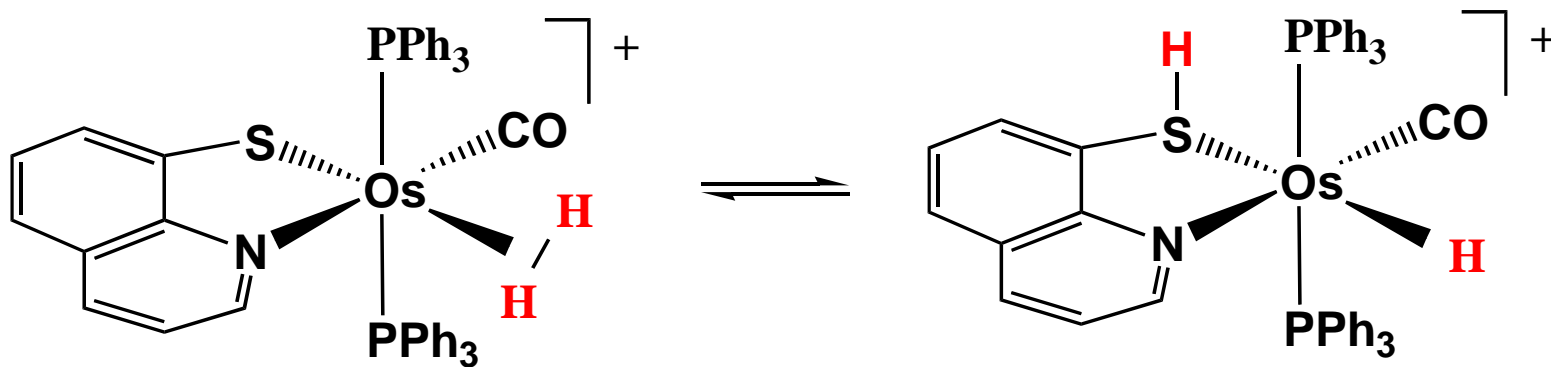
**L = ligand      A = anion = Cl, etc**

## INTRAMOLECULAR HETEROLYTIC CLEAVAGE OF H<sub>2</sub>



**Morris:** estimated pK<sub>a</sub> values of coordinated alkanethiol ligands of 5–10  
**& Schlaf** mimics heterolytic splitting of H<sub>2</sub> on metal sulfides in HDS catalysis

## INTRAMOLECULAR HETEROLYTIC CLEAVAGE OF H<sub>2</sub>

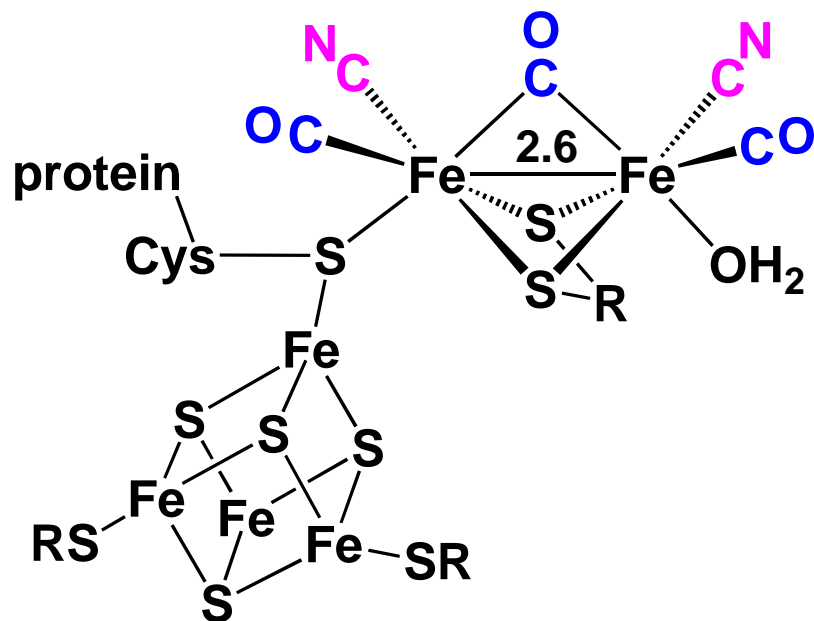


Crabtree: mimics biological splitting of H<sub>2</sub> on Fe sites in hydrogenases



# HYDROGENASE ENZYMES

Nature's ancient, efficient catalysts for H<sub>2</sub> production/consumption



3-4 billion years old

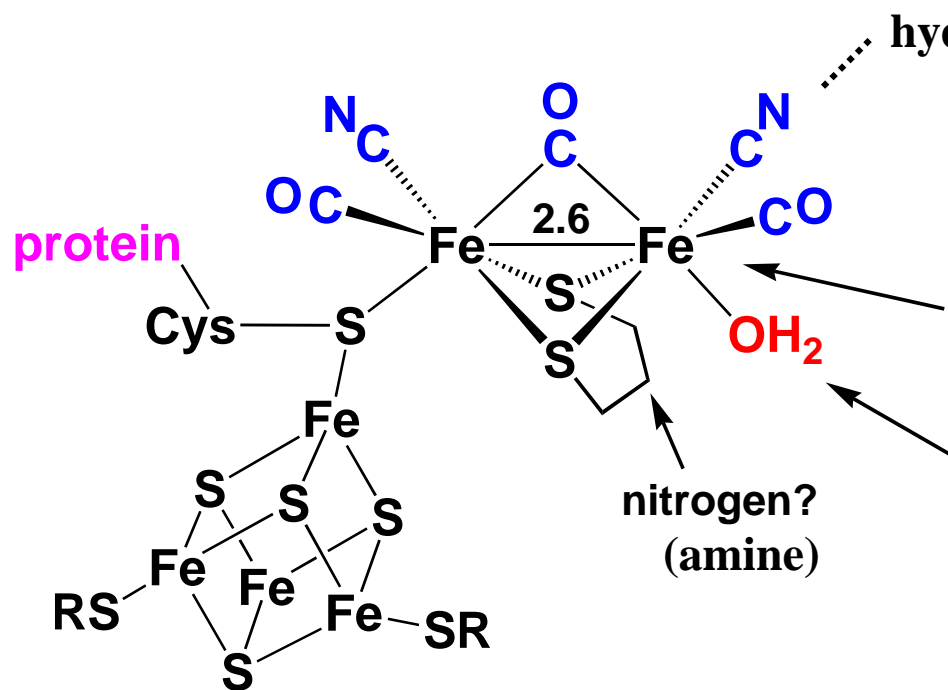
Organometallic active site

CO and CN ligands-- first time observed in biology. Why present?

*Clostridium Pasteurianum*

X-ray: John Peters, 1998

# THE ORGANOMETALLIC ASPECTS OF HYDROGENASES



Fe-S cubane cluster  
for electron transfer

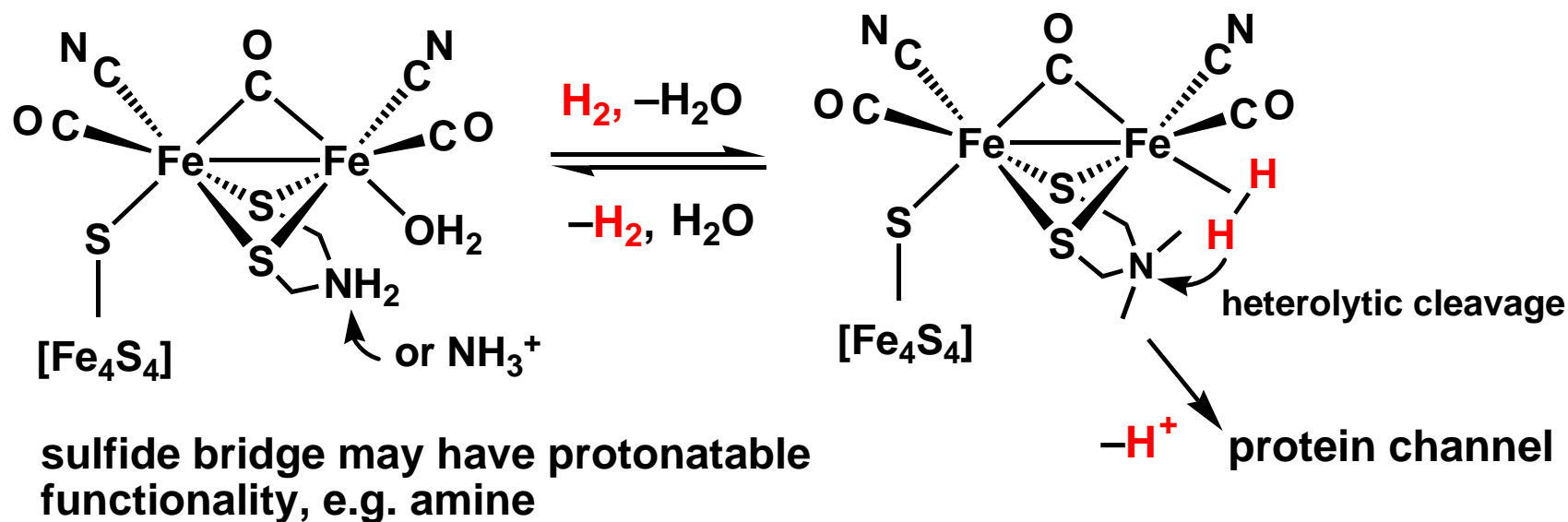
Closest model: Pickett, et. al.  
Nature 2005, 433, 610

hydrogen bonding to protein

- Active site attached at only **one point**
- **CO** and **CN** ligands on low-spin Fe<sup>II</sup>
- Metal-metal bonds why dinuclear?
- Intramolecular heterolysis of **H<sub>2</sub>** ostensibly at this site  
CO can displace **H<sub>2</sub>O**; can **H<sub>2</sub>**?  
**H<sub>2</sub>** is slightly stronger ligand than **H<sub>2</sub>O** on W(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>
- Mimic active site for H<sub>2</sub> production?

Nature doing organometallic  
catalysis eons ago!

## A POSSIBLE MECHANISM FOR HYDROGENASE

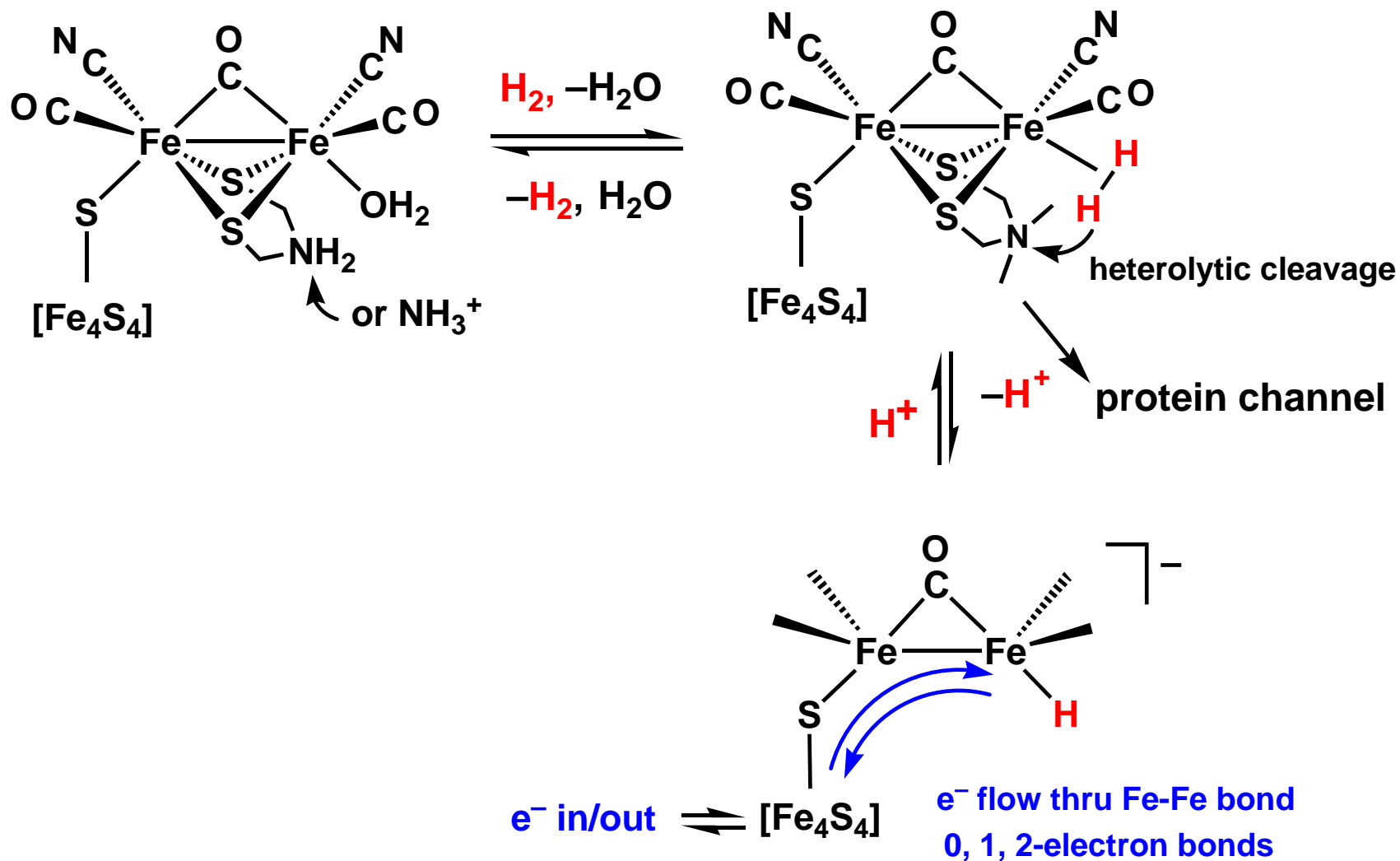


Darensbourg, *JACS* 2001, 3268

**CO** ligands needed to make iron less electron-rich (electrophilic), favoring both molecular binding and heterolysis of H<sub>2</sub>

**CN** ligands (strong ligand field) needed to keep iron in a low-spin Fe(II) state (diamagnetic), favoring strong binding of CO

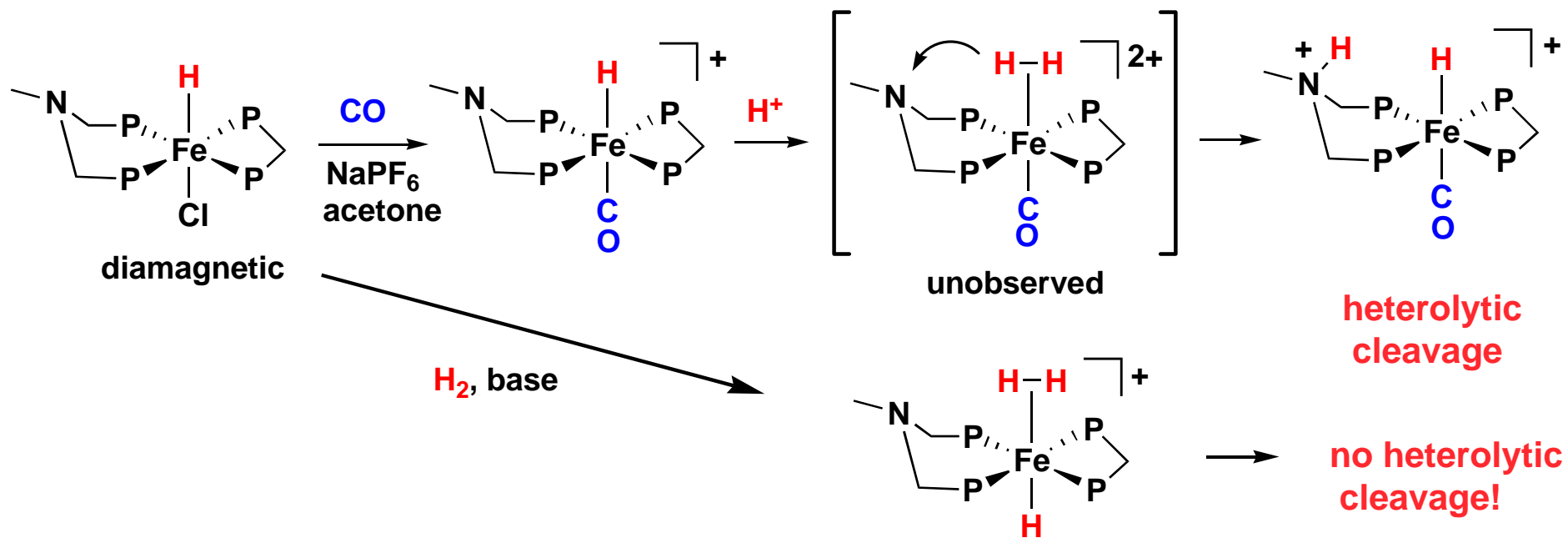
# A POSSIBLE MECHANISM FOR HYDROGENASE





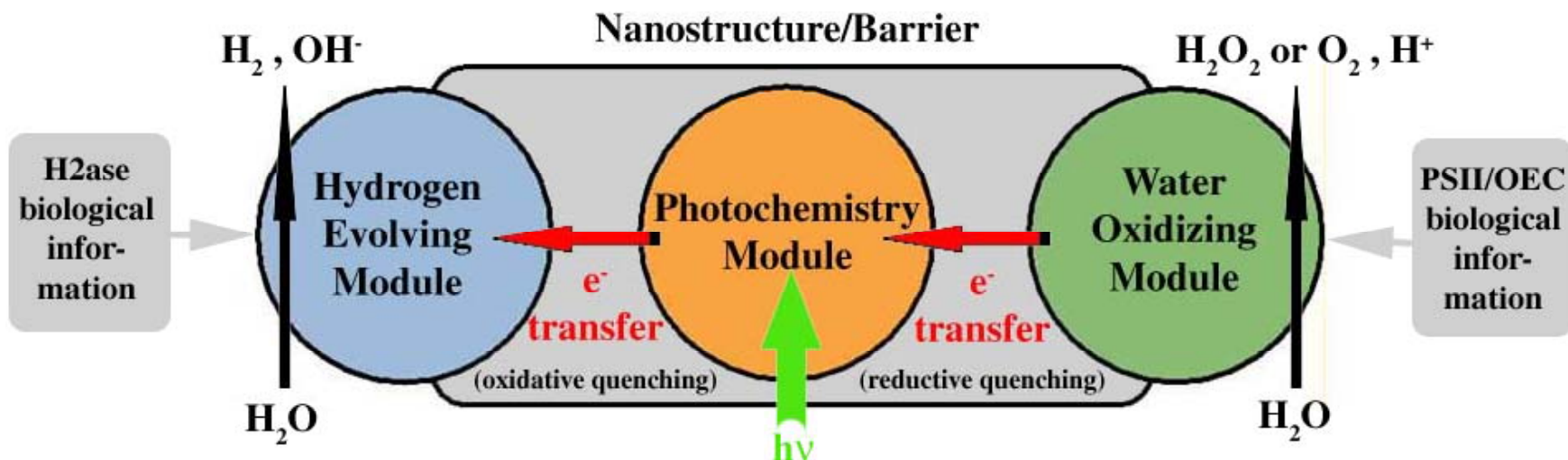
# HETEROLYSIS OF H<sub>2</sub> ON Fe-DIPHOSPHINE COMPLEXES

Dan Dubois, Mary Rakowski DuBois, *Organomet.* 2005, 2481

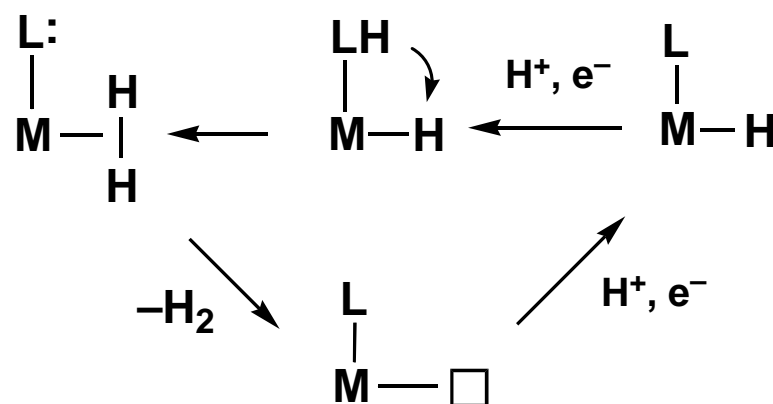


**CO ligand favors heterolytic cleavage of H<sub>2</sub>!**

# Biomimetic Hydrogen Production by Photoinitiated Transition Metal Catalysis



- Directly links efficient photoreceptor with  $H_2$  producing biocatalyst *at the molecular level*.
- Use abundant metals such as iron as catalysts rather than expensive, foreign-dependent metals such as platinum



hydrogen  
evolving  
module

mononuclear complex?  
 $L-M = \text{RS-Fe}(\text{CN})(\text{CO})_2(\text{Y})$

$\square$  = coordinatively unsaturated site or water ligand

## **COWORKERS AND COLLABORATORS**

**JEFF CROSS**

*POSTDOC*

**MARCEL SCHLAF**

*SABBATICAL*

**JUERGEN ECKERT**

*NEUTRON SCATTERING*

**BRIAN SCOTT**

*CRYSTALLOGRAPHY*

**RICARDO SCHWARZ**

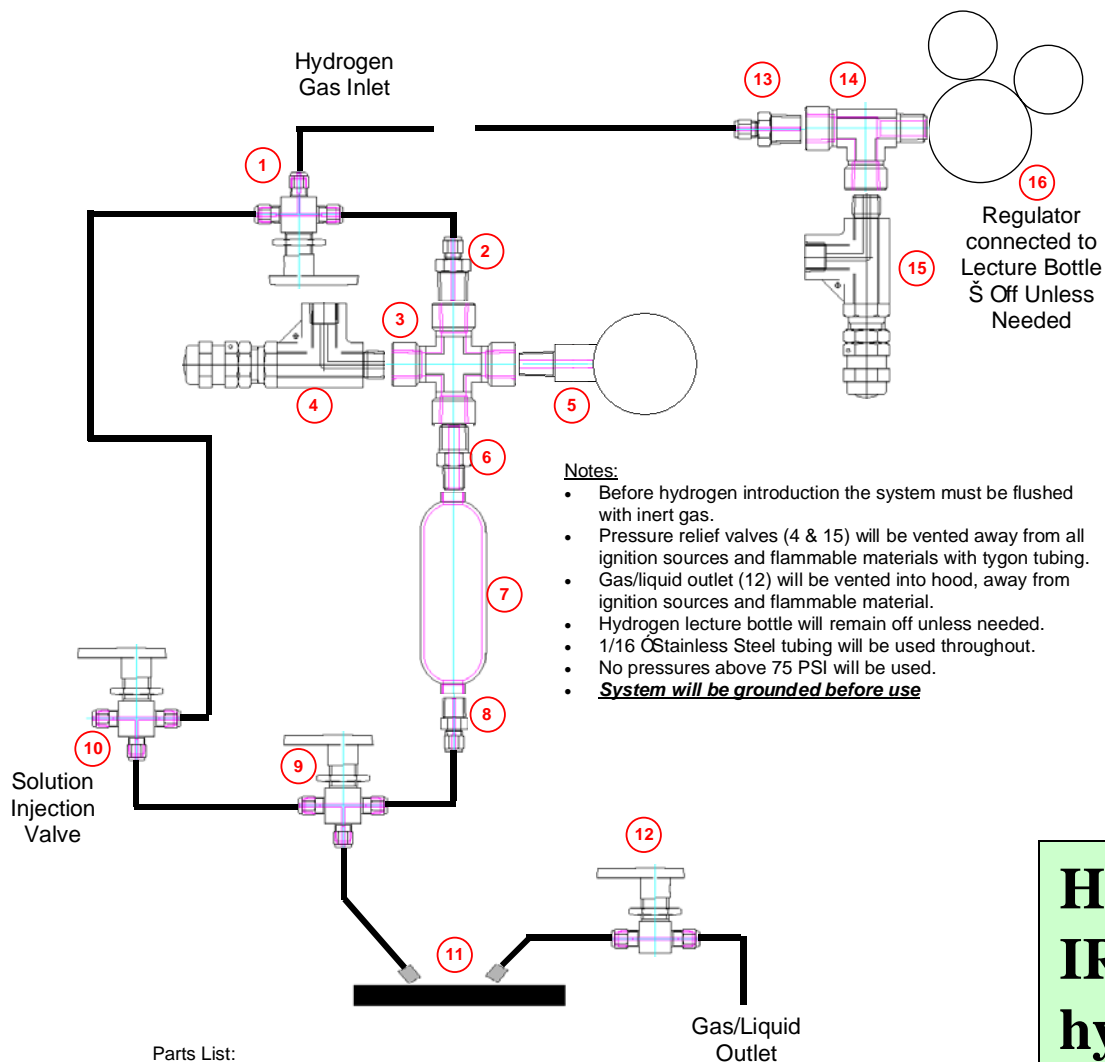
*HYDROGEN STORAGE*

Quantum™ and e  
THE EPCO logo  
are marks of the EPCO group

**FUNDING**

**Department of Energy, Basic Energy Sciences, Chemical Sciences  
Office of Energy Efficiency and Renewable Energy**



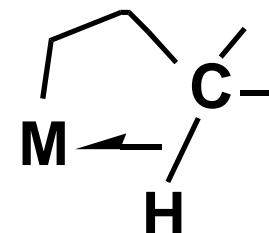
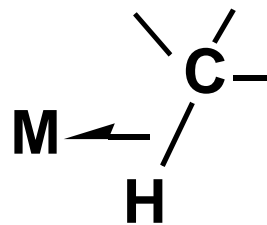
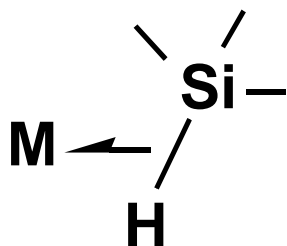
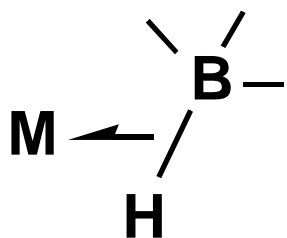
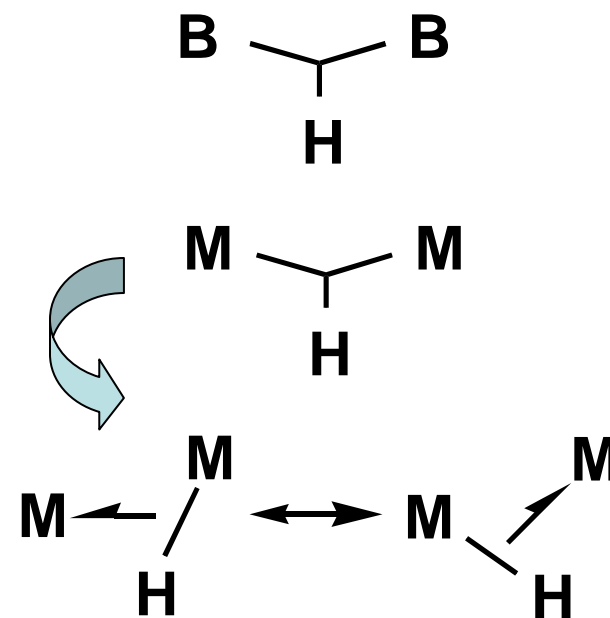
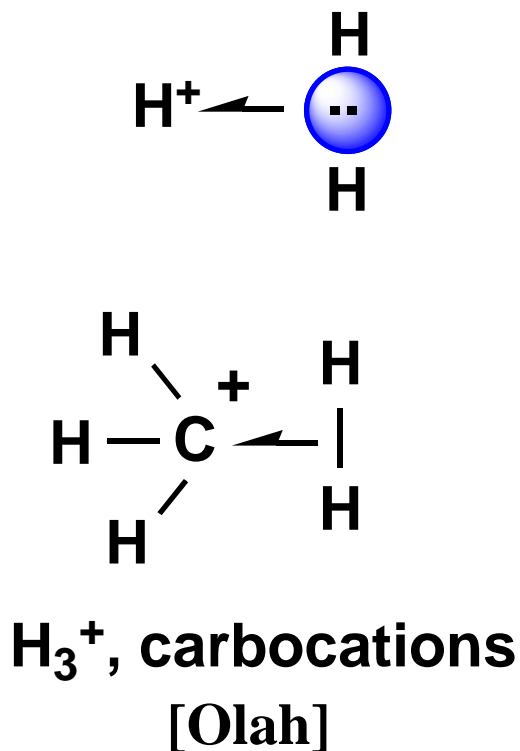
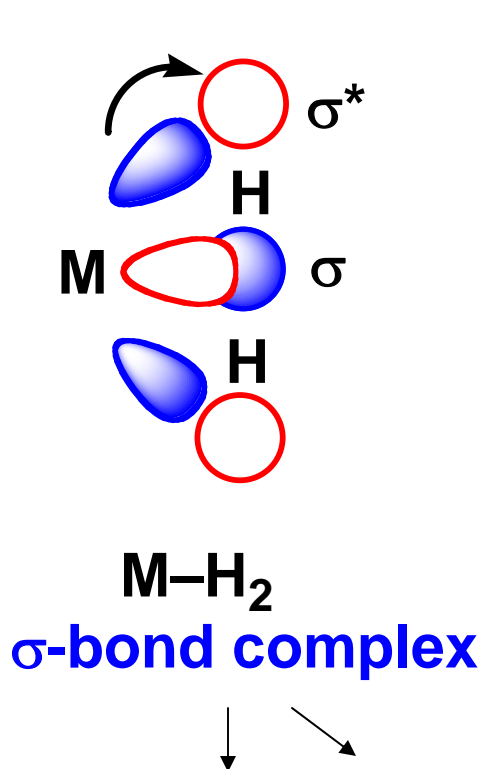


## High pressure solution IR apparatus for monitoring hydrogen reactions

### Parts List:

1. Swagelok SS-41SX1, 3-way valve, 1/16" tube
2. Swagelok SS-100-1-4, Adapter, 1/8" NPT-F / 1/16" tube
3. Swagelok SS-4-CS, Cross, 1/8" NPT-F
4. Swagelok SS-RL3M4-F4, Relief Valve set at 120 PSI
5. Swagelok PGI-63C-PG100, Pressure gauge, 0 to 100 PSI
6. Swagelok SS-4-HRN-2, Reducing adapter, 1/8" NPT-M / 1/8" NPT-M
7. Swagelok 304L-HDF2-40, Double-ended sample cylinder, 40 mL, 1/8" NPT-F
8. Swagelok SS-100-1-2, Adapter, 1/8" NPT-F / 1/16" tube
9. Swagelok SS-41SX1, 3-way valve, 1/16" tube
10. Swagelok SS-41SX1, 3-way valve, 1/16" tube
11. Thermo-Electron Heated HATR flow cell for Spectra-Tech ARK, 500 psi rating, up to 200C rating
12. Swagelok SS-41S1, 2-way valve, 1/16" tube
13. Swagelok SS-100-1-4, Adapter, 1/8" NPT-F / 1/16" tube
14. Swagelok SS-4-ST, Street Tee, 1/8" NPT
15. Swagelok SS-RL3M4-F4, Relief Valve set at 120 PSI
16. Lecture Bottle Regulator

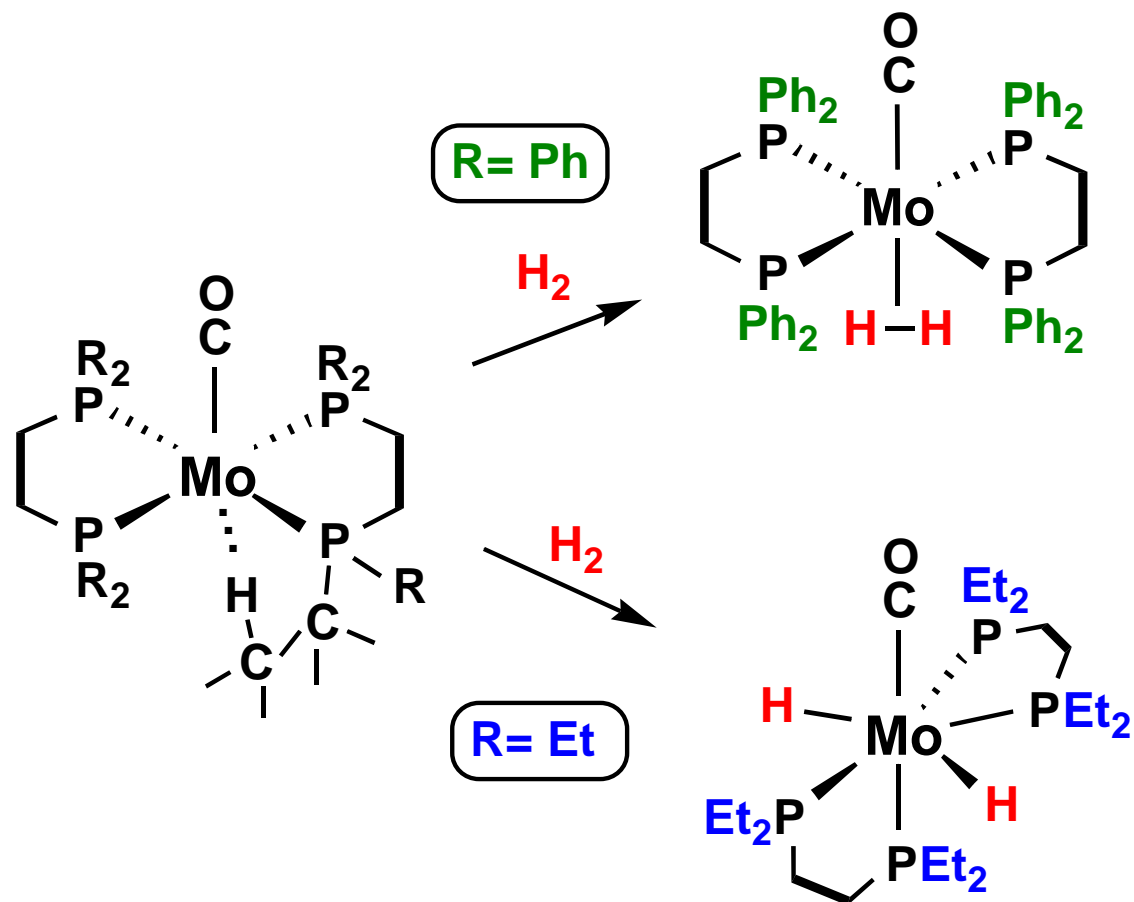
# NONCLASSICAL 3-CENTER TWO-ELECTRON BONDS



not isolated at RT

agostic

# Dihydrogen Versus Dihydride Binding is Very Finely-Tuned Electronically



*octahedral d<sup>6</sup> Mo<sup>0</sup>*

H-H = 0.88 Å

$J_{\text{HD}} = 34 \text{ Hz}$

oxidative  
addition to a  
dihydride

change of substituent  
on phosphine breaks H-H

*cationic Mn analogue  
is H<sub>2</sub> complex*



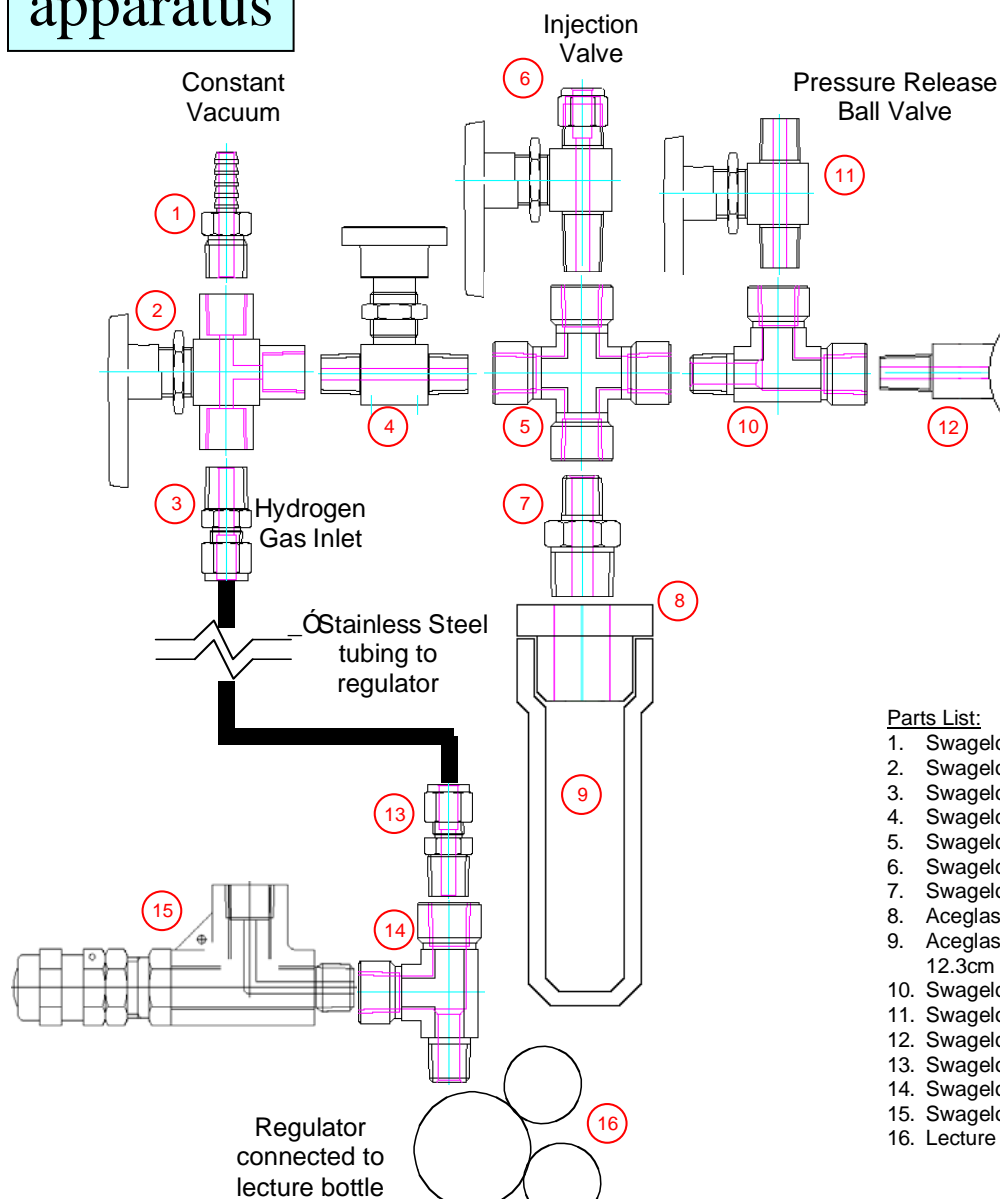
2.7 atm H<sub>2</sub>

**Linn complex--- soluble in organics!**

Linn & Gibbins, *J. Organomet. Chem.*, **554**, 171(1998)

*Inorganic Synth.* in press

apparatus



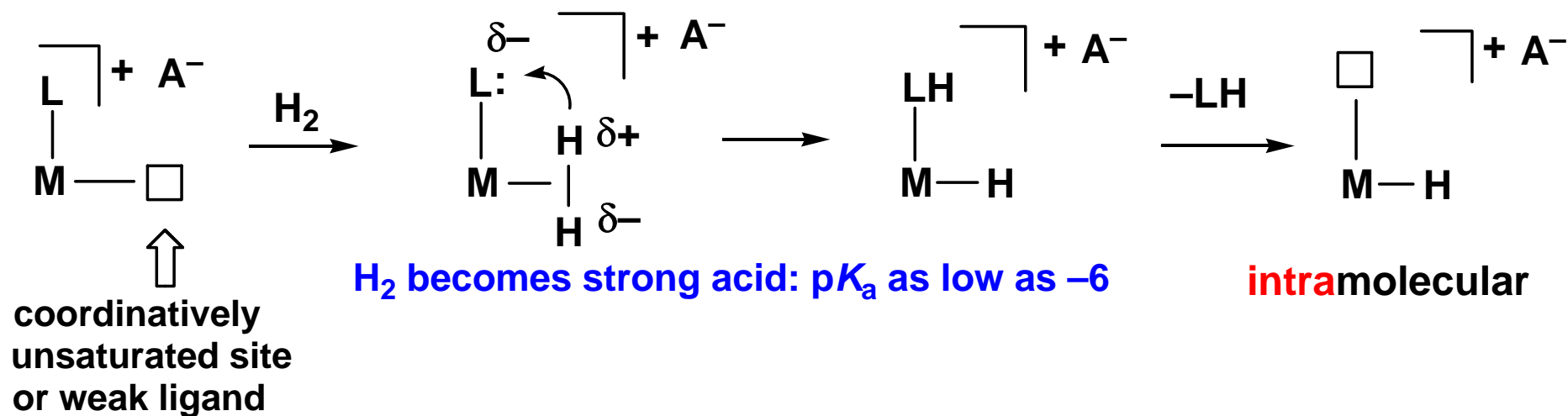
Notes:

1. Continuous vacuum at vacuum connection (1) when hydrogen in use.
2. Before hydrogen introduction the system must be under inert gas or vacuum conditions.
3. Pressure relief ball valve (11) will be vented away from all ignition sources and flammable materials with tygon tubing.
4. Apparatus will have line-of-sight protection (blast shield) while in use.
5. Hydrogen lecture bottle will remain off unless needed.
6.  $\varnothing$ Stainless Steel tubing between apparatus and regulator
7. Injection valve (6) will remain closed above ~15 PSI gas pressure. No reagent introduction will be done above this pressure.
8. No pressures above 75 PSI will be used.
9. **System will be grounded before use**

Parts List:

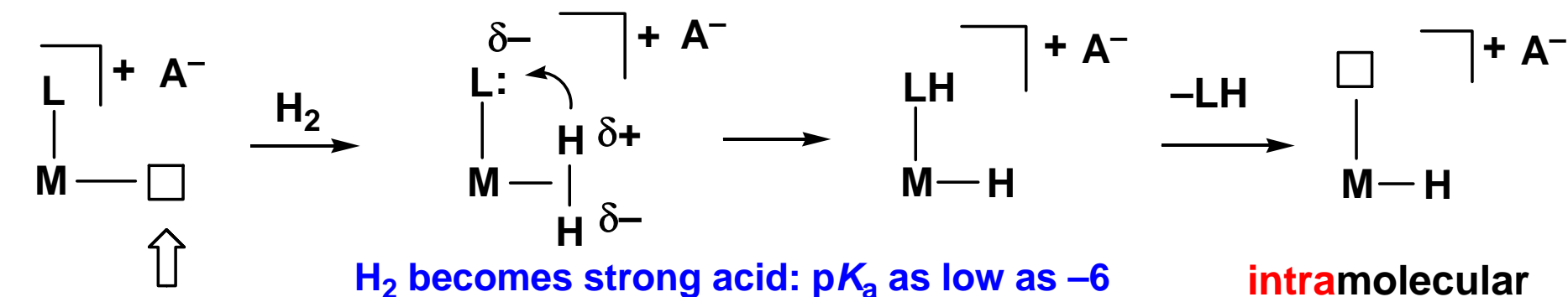
1. Swagelok SS-4-HC-1-4, Barbed hose connection
2. Swagelok SS-43XGF4, 3-way ball valve,  $\varnothing$  NPT-F
3. Swagelok SS-400-1-4, Adapter,  $\varnothing$ NPT-F /  $\varnothing$ tube
4. Swagelok SS-4H2, Needle valve, 1/4 $\varnothing$ NPT-M
5. Swagelok SS-4-CS, Cross,  $\varnothing$  NPT-F
6. Swagelok SS-43M4-S4, 2-way ball valve,  $\varnothing$  NPT-M to  $\varnothing$ tube
7. Swagelok SS-8-HRN-4, Reducing adapter,  $\varnothing$  NPT-M to  $\varnothing$ NPT-M
8. Aceglass 5844-104, #25 Ace-thread to  $\varnothing$ NPT-F PTFE Swagelok Adapter
9. Aceglass 8648-249, 77ML #25 150psi Pressure tube with front-seal plug, 12.3cm long, 38.1mm O.D.
10. Swagelok SS-4-ST, Street tee,  $\varnothing$ NPT
11. Swagelok SS-43M4, 2-way ball valve,  $\varnothing$  NPT-M
12. Swagelok PGI-63C-PG100, Pressure gauge, 0 to 100 PSI
13. Swagelok SS-400-1-4, Adapter,  $\varnothing$ NPT-F /  $\varnothing$ tube
14. Swagelok SS-4-ST, Street tee,  $\varnothing$ NPT
15. Swagelok SS-RL3M4-F4, Relief Valve set at 120 PSI
16. Lecture Bottle Regulator

# HETEROLYTIC CLEAVAGE OF HYDROGEN ON CATIONIC CENTERS

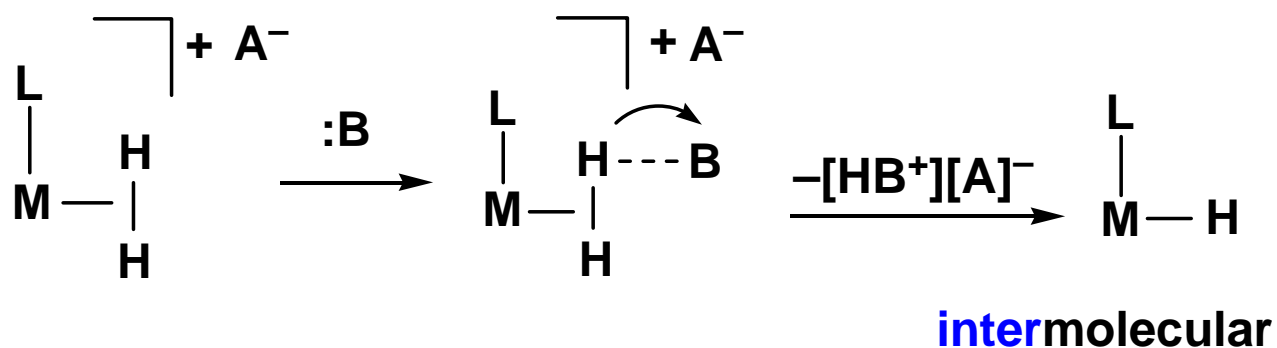
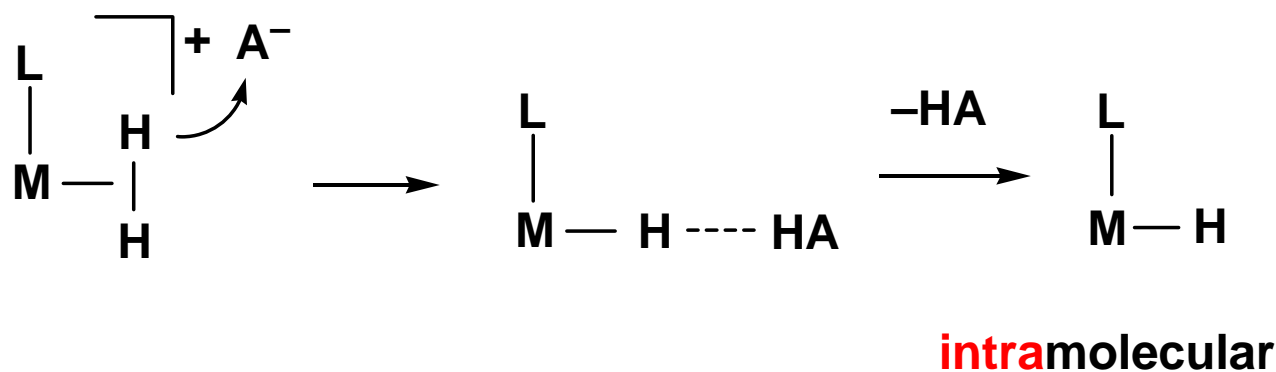


all reactions  
are reversible

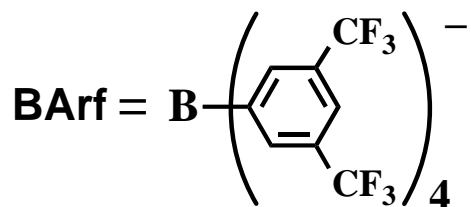
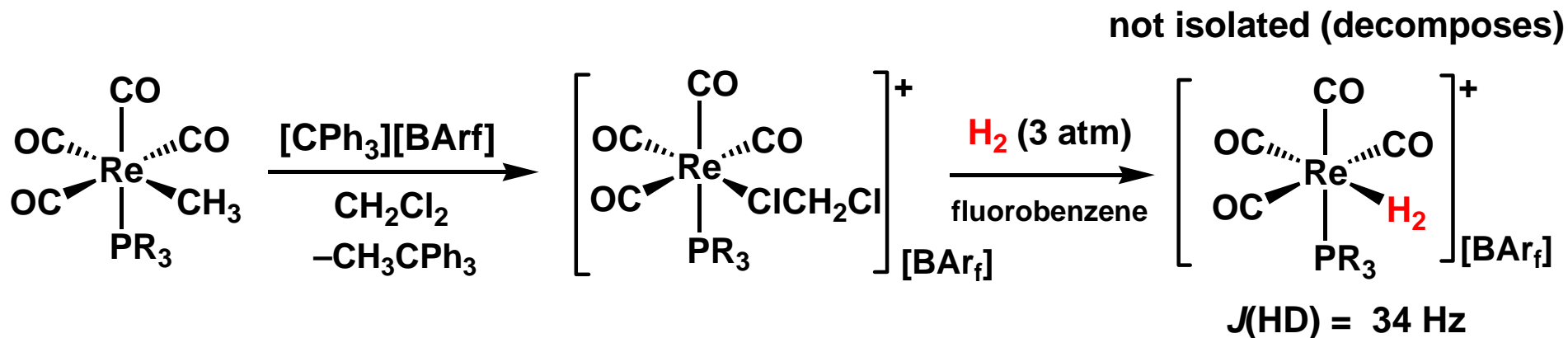
# HETEROLYTIC CLEAVAGE OF HYDROGEN ON CATIONIC CENTERS



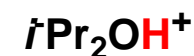
all reactions are reversible



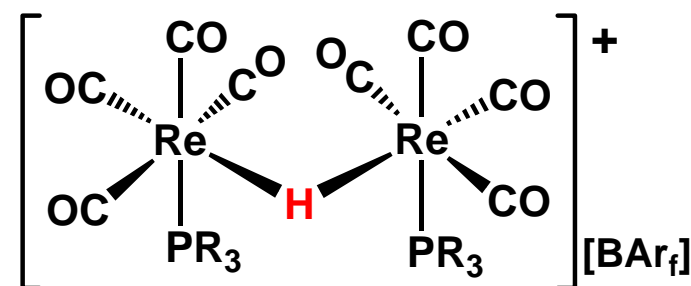
# HETEROLYTIC CLEAVAGE OF H<sub>2</sub> ON HIGHLY ELECTROPHILIC CENTERS



acidic H<sub>2</sub> ligand  
protonates ethers



+



pK<sub>a</sub> of bound H<sub>2</sub> is 1 to -2

**W(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>)** can be deprotonated only by  
**neutral** strong bases such as Cu(OR)(PR<sub>3</sub>)

**cationic**  
**[W(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>)<sup>+</sup>** generated electrochemically  
is a strong acid and protonates THF

Bruns, et.al. *Inorg. Chem.* 1995, 34, 663