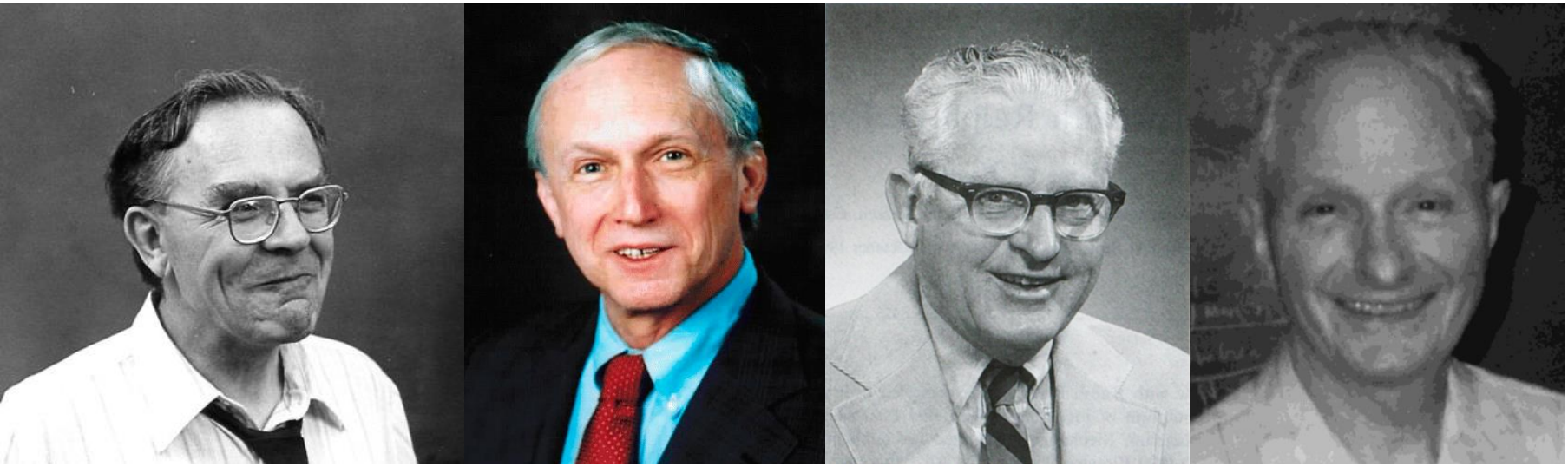
Transition Metal Hydrides: More Than You Wanted To Know

N. Ian Rinehart
SED Group Meeting
06/27/2018

Wilkinson *Norton* *Pearson* *Ibers*



Outline

1. Scope of talk
2. History: discovery, controversy, paradigm
   i. Synthesis of transition metal hydrides
   ii. Nature of the transition metal-hydride bond
3. Hydricity
4. Brønsted acidity
5. Transition metal hydride hydrogen atom transfer
6. Summary

Applications of Transition Metal Hydrides

Hydrogenation

Hydrofunctionalization

Energy storage and fuel cell applications

Water/Gas Shift

Imine reduction

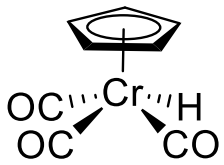
Conjugate reduction

Heck reaction

Nocera, *Chem. Rev.*, **2010**, 110, 6474

Types of Hydrides and Scope of Discussion

Transition Metal Hydride Complexes

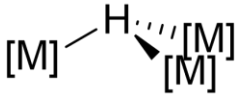


Interstitial Hydrides or Binary Lattice Solids

$LiAlH_4$, NaH, LiH, RaNi, H_2/Pd

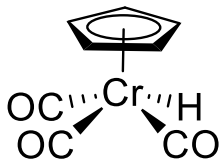
μ^2-bonding hydrides

μ^3-bonding hydrides



Types of Hydrides and Scope of Discussion

Transition Metal Hydride Complexes



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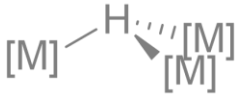


Discovery

Walter Hieber 1931

$$Fe(CO)_5 \xrightarrow[2.\ H^+]{1.\ 2OH^-} Fe(CO)_4H_2 + CO_3^{2-}$$

$FeH_2(CO)_4$

"Foul-smelling **pale-yellow oil** that **explodes violently** on contact with air...We can almost consider it a '**pseudonickelcarbonyl**' in that the FeH_2 almost behaves as a pseudo-nickel atom'"

1934

$$2Co(CO)_4 \cdot L \xrightarrow{2H^+} CoH(CO)_4 + Co^{2+}$$

$$2CO + L + 0.5H_2$$

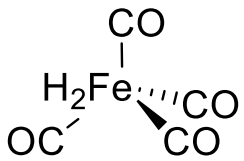
L= amine or alcohol

$$3Co(CO)_4 \xrightarrow{2H_2O} 2Co(CO)_4H + Co(OH)_2$$

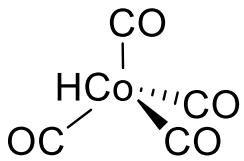
$$4CO$$

W. Hieber and F. Leutert, *Naturwissenschaften*, **1931**, 19. 360;
Z. Anorg. Allg. Chem., **1932**, 204, 145
Z. Elektrochem., **1934**, 40, 158.

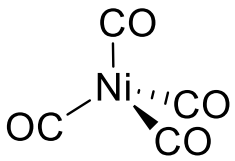
Controversy on the Nature of Transition Metal Hydrides



Hieber, 1931



Hieber, 1934

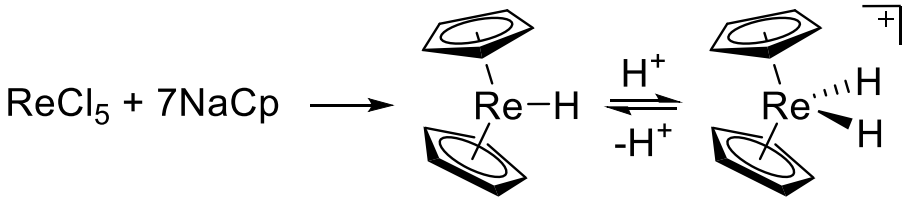


Mond, 1890

Later, on the basis of 2 IR peaks and 4 RAMAN peaks, concluded T_d symmetry (T_2's IR-allowed)

"Stereochemically inactive hydrogen" hypothesis prevailed into 1950's

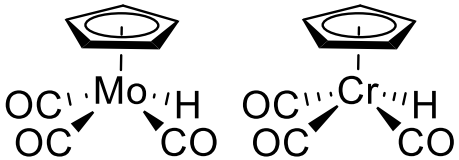
Wilkinson 1955



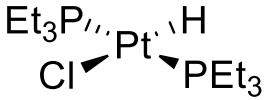
Tenable ^{1}H NMR evidence

Does not lose H_2(g)

Fischer, Hafner, Stahl 1955



Chatt, Duncanson, Shaw 1957



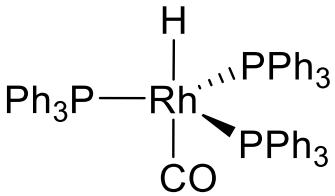
W. Hieber and F. Leutert, *Naturwissenschaften*, **1931**, 19. 360; *Z. Elektrochem.,* **1934**, 40, 158.
Wilkinson, G., *J. Am. Chem. Soc.,* **1955**, 77, 3421

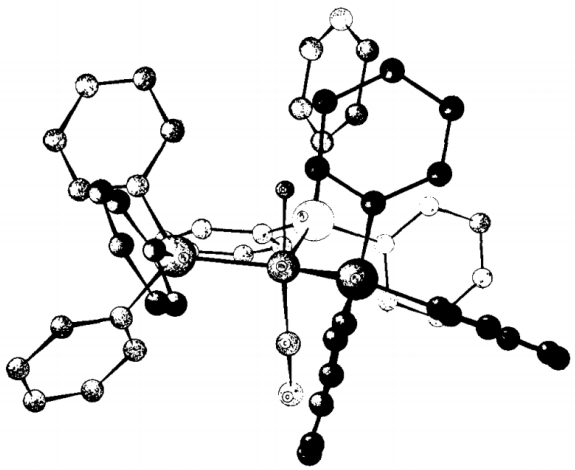
Chatt, Duncanson, Shaw, *Proc. Chem. Soc.,* **1957**, 343
Fischer, Hafner, Stahl, *Z. Anorg. Allg. Chem.,* **1955**, 282, 47

Incontrovertible Evidence for “Normal” M-H Covalent Bonding

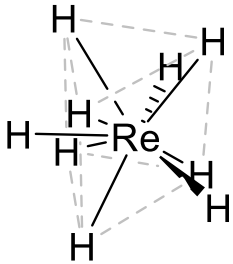
- Early evidence provided through ^{1}H NMR spectroscopy
- XRD limitation: data doesn’t pinpoint H atoms; they’re implied
- Neutron diffraction provided irrefutable proof of normal covalent bond lengths for T.M. Hydrides

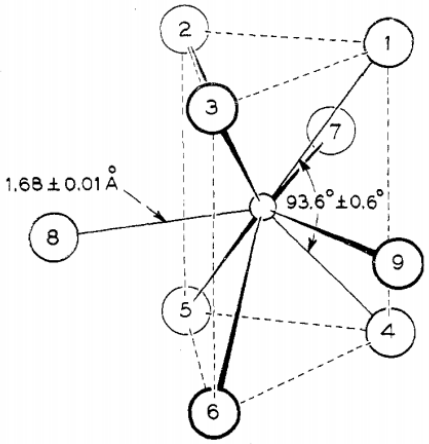
LaPlaca & Ibers 1963





Ginsberg 1964

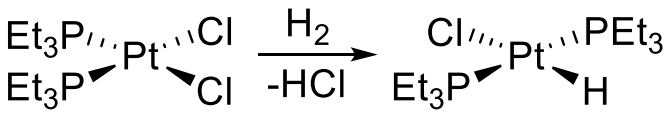


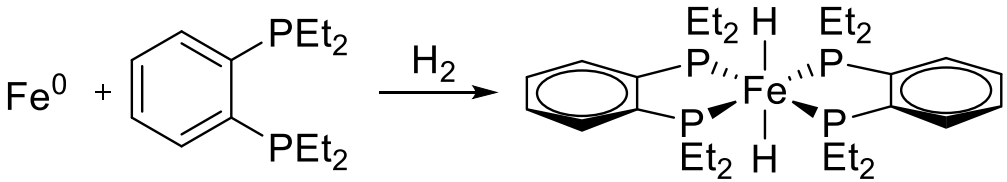


S. C. Abrahams, A. P. Ginsber, K. Knox, *Inorg. Chem.,* **1964**, 3, 558
S.J. LaPlaca, J.A. Ibers, *J. Am. Chem. Soc.*, **1963**, *85,* 3501

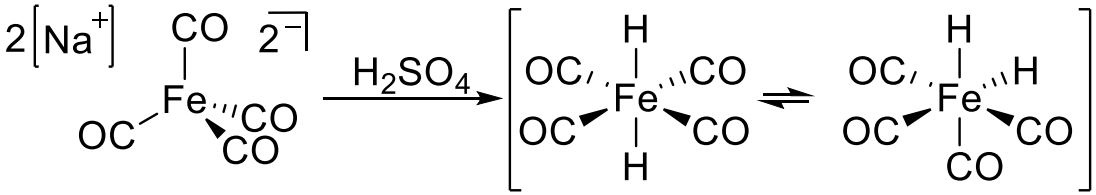
Brief Overview of Transition Metal Hydride Synthesis

Hydrogenation





Protonation

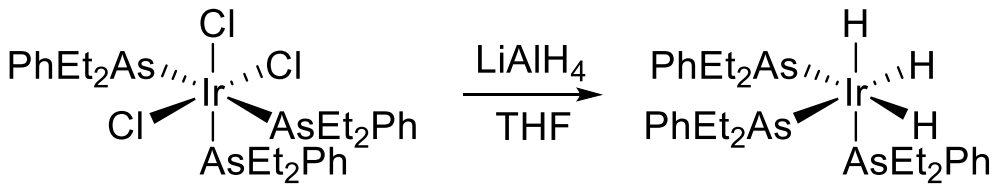


N.B.: Ternary T.M. carbonyl hydrides show stereochemical non-rigidity

D.S. Moore, S.D. Robinson, *Chem. Soc. Rev.*, **1983**,12, 415-452

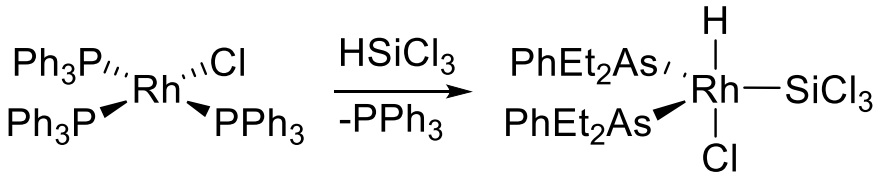
Brief Overview of Transition Metal Hydride Synthesis

Reduction of Metal Halides



N.B.: other common reducing agents include ROH, N_2H_4, $NaBH_4$, HCO_2H, H_3PO_2, $H_2S_2O_4$, $R_2Al(H/OR)$

Oxidative Addition of Main Group Hydrides



D.S. Moore, S.D. Robinson, *Chem. Soc. Rev.*, **1983**,12, 415-452

Bonding in TM Hydrides

Table 2 *Enthalpy contributions D(M—X) for M—X bonds (X = H, Me, or Cl) in some transition metal complexes*

Complex	$\bar{D}(M—X)$ kJ mol^{-1}		
	X = H	Me	Cl
$TiX_2(C_5Me_5)_2$	242		
$MoX_2(C_5H_5)_2$	258.7		
	251.4	149.5	304.2
$WX_2(C_5H_5)_2$	286.8		
	305.2	197.8	346.0
$MnX(CO)_5$	*ca.* 300	*ca.* 130	*ca.* 300
$[FeX(CO)_4]^-$	*ca.* 310		
$CoX(CO)_4$	*ca.* 290		
$IrX_2Cl(CO)(PR_3)_2$	*ca.* 240—255		

General Trend: $\Delta H_{M\text{-}H}$ is stronger than $\Delta H_{M\text{-}C}$ and comparable to $\Delta H_{M\text{-}Cl}$

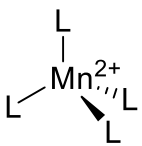
Robinson, S.D., Moore, D.S., *Chem. Soc. Rev.*, **1983**,12, 415-452
Pearson, R.G., *Chem. Rev.*, **1985**, 85, 41-49

Electronegativity and Bond Polarization

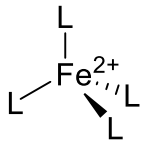
Pauling: $$\Delta\chi = \frac{1}{\sqrt{eV}}\sqrt{BDE_{AB} - \frac{BDE_{AA} + BDE_{BB}}{2}}$$

Modern method: $$\chi_i = 0.105n^* \left({}^{I_m}/_{R}\right)^{0.5} \Big/ r_i + 0.863$$

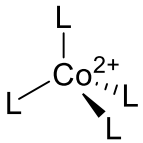
n* is the valence quantum number
I_m is the electron affinity for ion
R is the Rydberg constant
r_i is the ionic radius



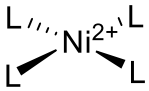
Pauling: 1.55
Xue prediction: 1.349



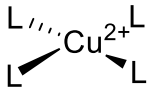
Pauling: 1.83
Xue prediction: 1.376



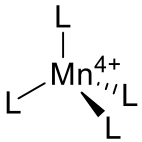
Pauling: 1.88
Xue prediction: 1.426



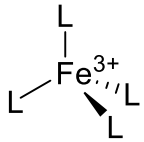
Pauling: 1.91
Xue prediction: 1.470



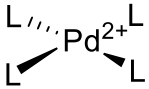
Pauling: 1.90
Xue prediction: 1.486



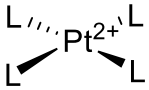
Pauling: 1.55
Xue prediction: 2.189



Pauling: 1.83
Xue prediction: 1.726



Pauling: 2.20
Xue prediction: 1.483



Pauling: 2.28
Xue prediction: 1.586

Xue, Keyan, J. Phys. Chem. A, **2006**, 110, 11332.

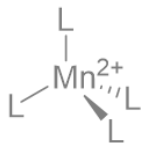
Bond Polarization

Pauling: $$\Delta\chi = \frac{1}{\sqrt{eV}}\sqrt{BDE_{AB} - \frac{BDE_{AA} + BDE_{BB}}{2}}$$

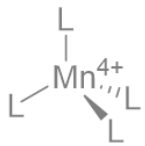
Modern meth

n* is the valence quantum number
I_m is the electron affinity for ion
nt

"The transition-metal-hydrogen bond is very similar to the carbon-hydrogen bond. Both are of low polarity [compared to alkali-hydride bonds] and can react as H+, H, or H- donors for that reason. The tendency to behave in one way or another depends on stabilization of the resulting anionic, radical, or cationic species."



Pauling: 1.55
Xue prediction: 1.34



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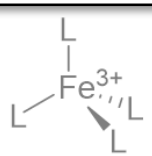

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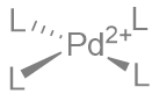

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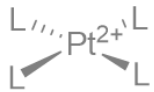

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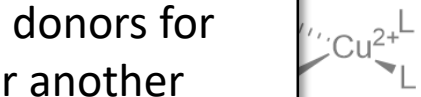

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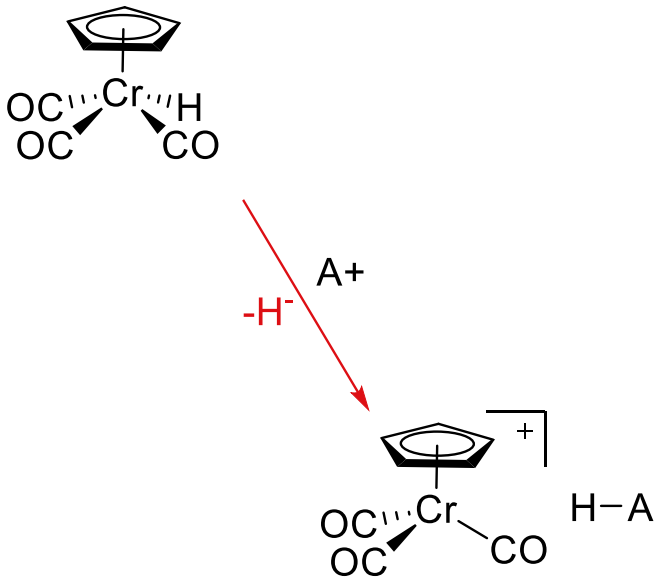
Pearson, R.G., *Chem Rev.*, **1985**, 85, 41.
Xue, Keyan, J. Phys. Chem. A, **2006**, 110, 11332.

Hydricity

Transition Metal Hydride Complexes

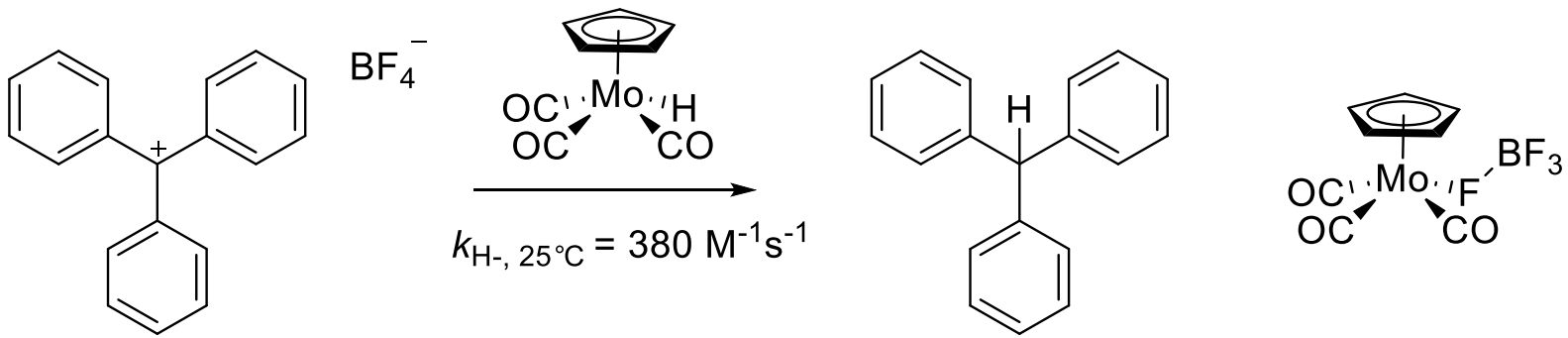


Hydricity of Transition Metal Hydrides

Definition of Hydricity

$$L_nM{-}H \longrightarrow ML_n^{+} + H^{-}$$

Endergonic state function: ΔG^{o}_{H-}

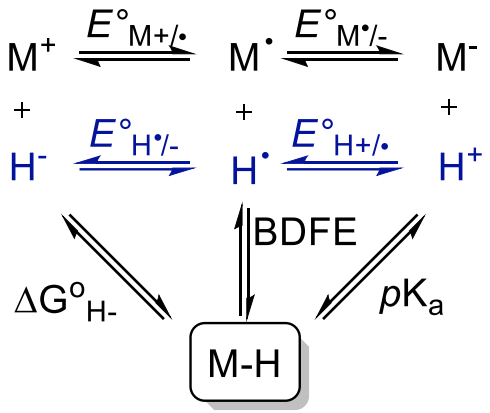


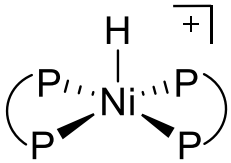
-Example of concerted hydride transfer to hydride acceptor
-Thermodynamic measurement compromised by irreversibility and non-innocence of BF_4^- ligand

Cheng, Bullock, *J. Am. Chem. Soc.,* **1998**, 120, 13121
Ibid, *Inorg. Chem.,* **2006**, 45, 4712

Measuring Hydricity

Full Thermodynamic Scheme





55.3 kcal/mol
depe

Example of determining hydricity indirectly:

- Cyclic Voltammetry used to determine *E*° values
- Acid/Base titrations used to determine pK_a
- The rest can be deduced
- Blue values are established standards

N.B.: Thermodynamic cycles *only work for state functions*

This means:

-need to account for all chemical steps

-must be at equilibrium/reversible (including *E*°)

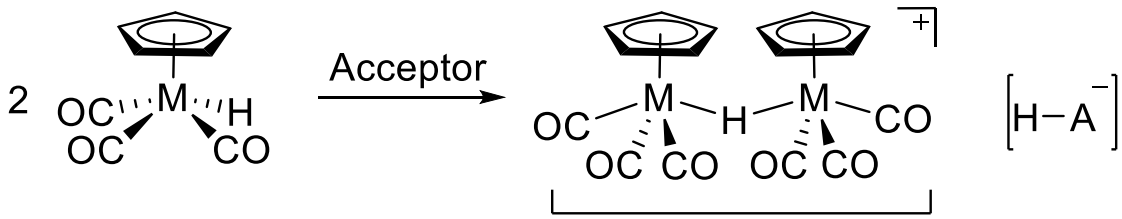
In practice:

Ni/Pd/Pt, Co/Rh are well suited to CV methods

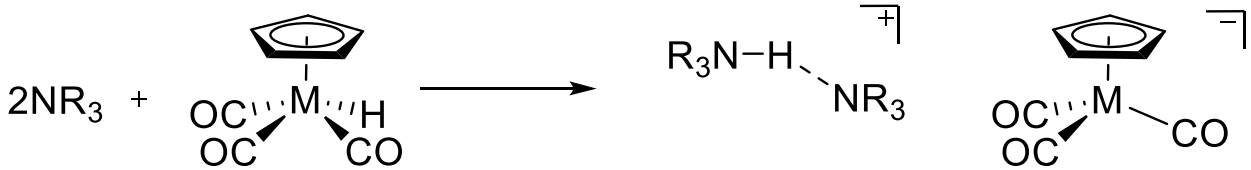
- reversible electrochemistry
- weak binding of MeCN (most common solvent)

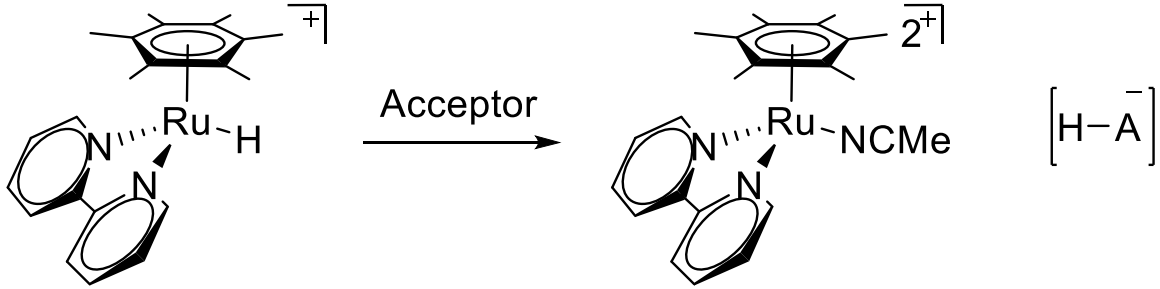
Appel, A.M., Miller, A.J., *Chem Rev.*, **2016**, 116, 8655.

Irreproducibility of Experimental Hydricity Values



Homoconjugation complicates ΔG^{o}_{H-} measurements

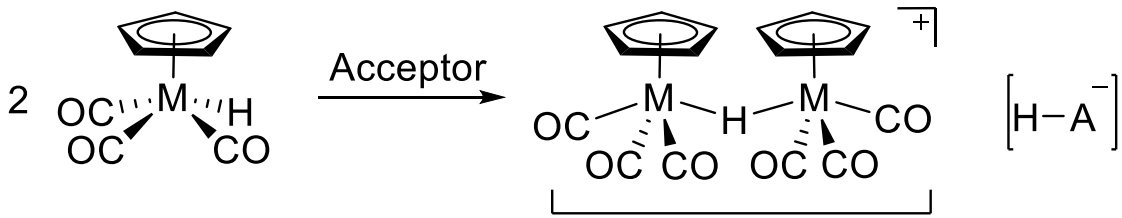




Solvent Coordination deviates ΔG_{obs} from ΔG_{H-}

Appel, A.M., Miller, A.J., *Chem Rev.*, **2016**, 116, 8655.

Irreproducibility of Experimental Hydricity Values



Homoconjugation complicates

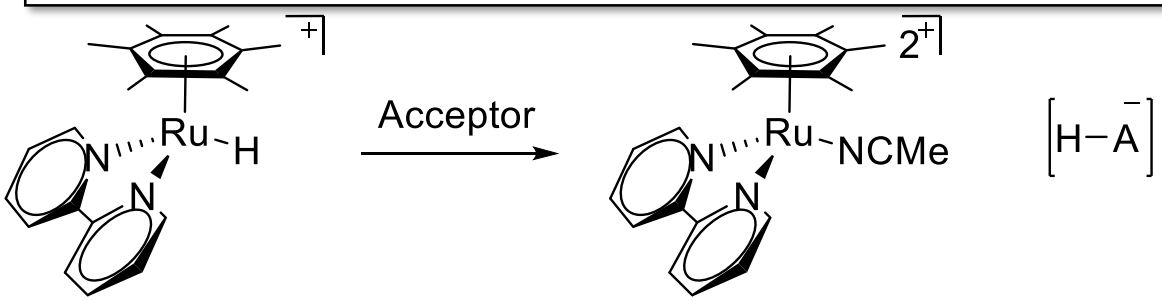
Most Common Errors Made in the Literature:

-Non-equilibrium measurements common

-Standard state deviations (e.g. H_2 not at 1 atm)

-Coordination of solvent

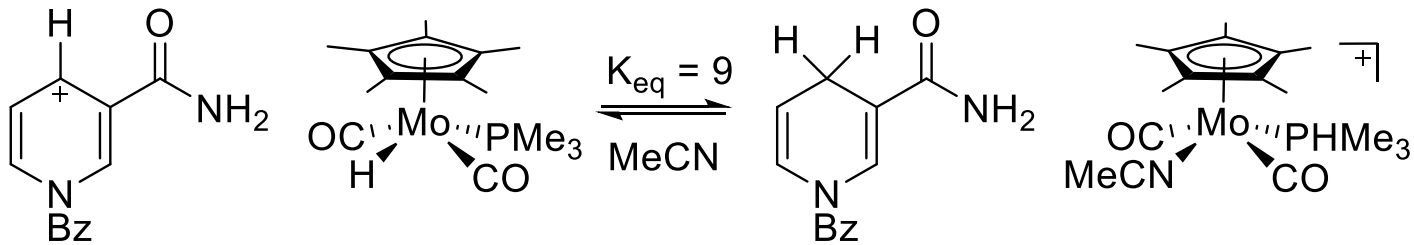
-Homoconjugation in products



Solvent Coordination deviates ΔG_{obs} from ΔG_{H-}

Appel, A.M., Miller, A.J., *Chem Rev.*, **2016**, 116, 8655.

Kinetic Hydricity: When Thermodynamics Aren't Enough



70 days to reach equilibrium, ΔG^{o}_{H-} 58 kcal/mol

-First measured hydricity was overestimated by 24 kcal/mol because the system never reached equilibrium

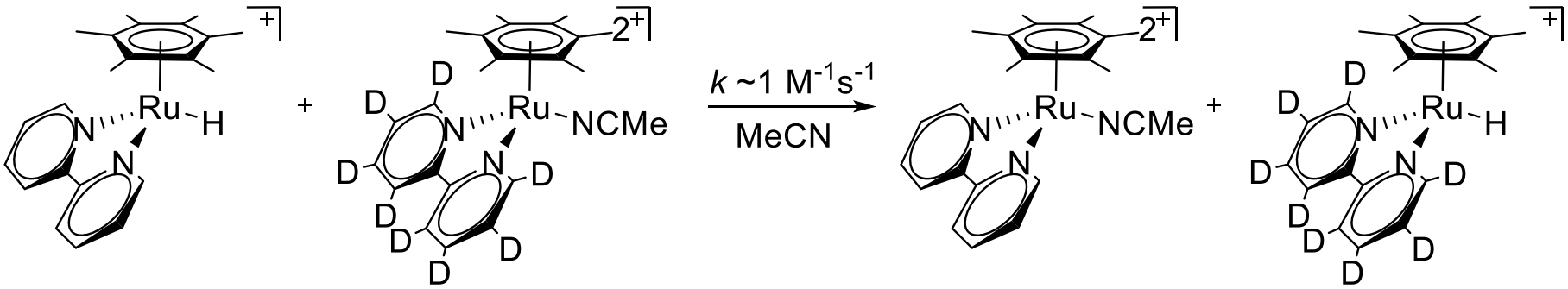
-in 2004, DuBois et al were more careful and accurately measured the hydricity

Bruno, *J. Am. Chem. Soc.*, **1999**, *121*, 2174

DuBois, *J. Am. Chem. Soc.*, **2004**, *126*, 2738

Probing Kinetic Hydricity via Pseudo-Self Exchange

Most feasible experiment to probe kinetic competence of hydride: start far-from-equilibrium and monitor the system approach it

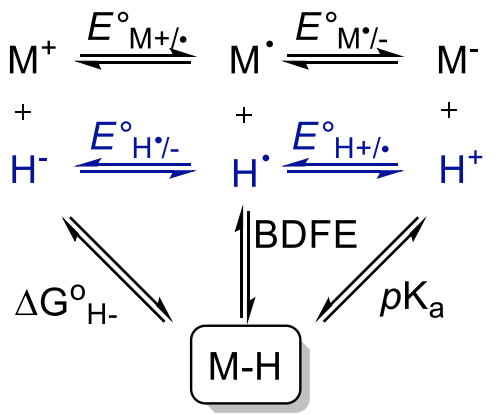


Rate constant order of magnitude indicates feasibility of measuring equilibrium value for hydricity determination

Shenvi, R.A., *Chem. Rev.*, **2016**, 116, 8912-9000

Thermochemical Cycles for Determining Hydricity

Full Thermodynamic Scheme



H_2 Heterolysis

$$HA \quad M\text{-}H \xrightleftharpoons{\Delta\Delta G^{o}_{H-}} H_2 \quad M^+ \quad A^-$$

$\Delta\Delta G^{o}_{H-} + \Delta G^{o}_{H-}(H_2) = \Delta G^{o}_{H-}(M\text{-}H)$

Also need to account for pKa of HA

Caveat:
-$\Delta\Delta G°_{H-}$ usually incorporates base, ligand, solvent, or (μ^2) H_2 binding that must be accounted for

Reaction with Hydride Acceptor

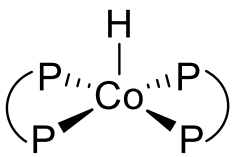
$$A \quad M\text{-}H \xrightleftharpoons{\Delta\Delta G^{o}_{H-}} HA^- \quad M^+$$

$\Delta\Delta G^{o}_{H-} + \Delta G^{o}_{H-}(A) = \Delta G^{o}_{H-}(M\text{-}H)$

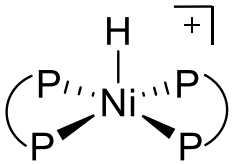
Caveat:
-$\Delta\Delta G°_{H-}$ must be small enough to measure relative quantities at equilibrium
-*system must reach equilibrium*

Appel, A.M., Miller, A.J., *Chem Rev.*, **2016**, 116, 8655.

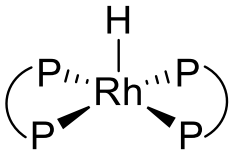
Hydricity Trends



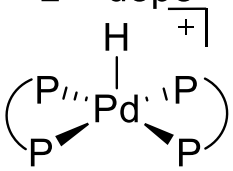
~50 kcal/mol



55.3 kcal/mol
L = depe



~30 kcal/mol



43.0 kcal/mol
L = depe

Down a group tends to increase hydricity

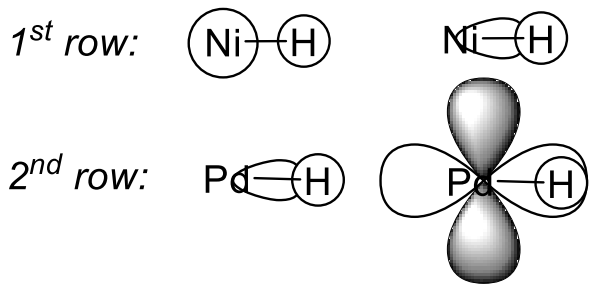
Isoelectronic complexes with lower charge are more hydridic

Late transition metals tend to be more hydridic (groups 4-7 vs. 8-11)

Note: solvent effects are *massive* and non-linear

Appel, A.M., Miller, A.J., *Chem Rev.*, **2016**, 116, 8655.

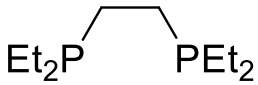
Orbital Overlap Affects Hydricity



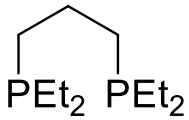
- Nickel uses more s-character
  - End up with tetragonal distortion, increases s-character in M-H bond → less reactive
- Palladium uses more d-character
  - 4d orbital more similar in energy than 5s, but still has poorer overlap & less stabilizing MO interaction → more reactive

D.S. Moore, S.D. Robinson, ***Chem. Soc. Rev.***, **1983**,12, 415-452

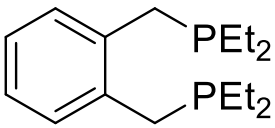
Bite Angle Effect on Hydricity



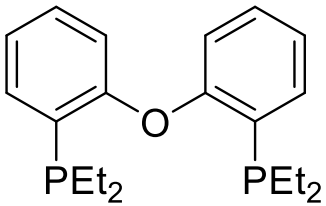
78°
depe



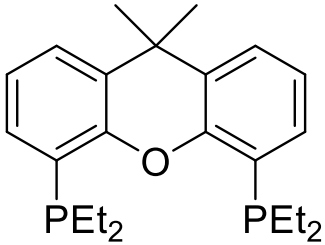
86°
depp



90°
depx

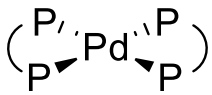


102°
depPE



111°
EtXantphos

P-Pd-P angle
= bite angle

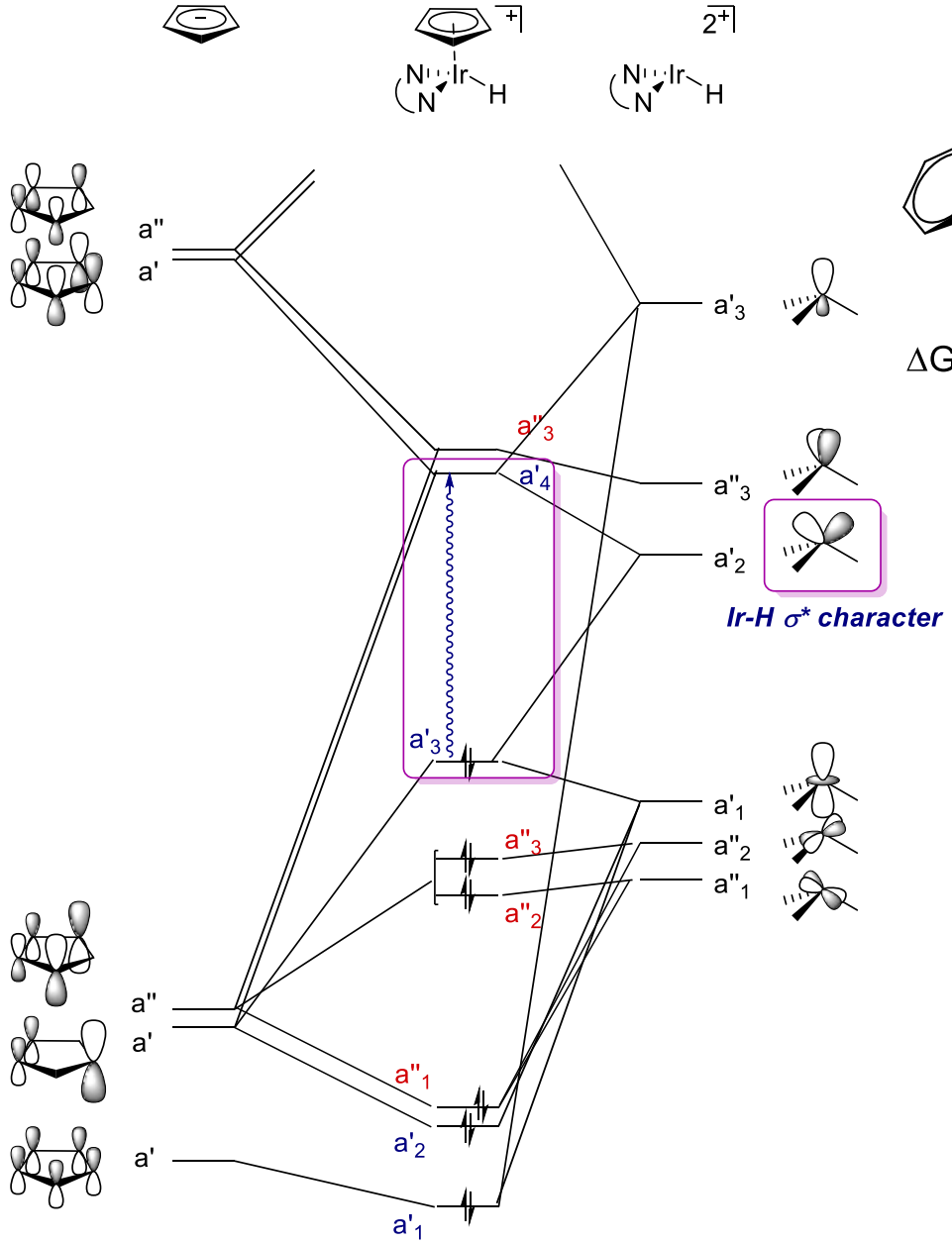


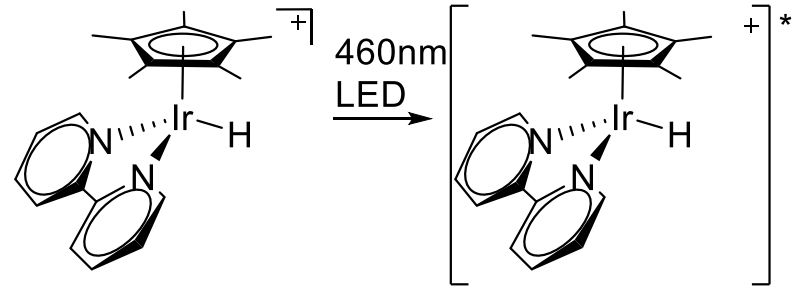
Bite Angle (degrees)	ΔG_{H^-} (kcal/mol)
78	43.2
86	54.7
90	61.5
102	66.4
111	70.4

Nonlinear correlation:
Larger bite angle → tetragonal distortion
Tetragonal distortion → increase M-H s-character

D.S. Moore, S.D. Robinson, ***Chem. Soc. Rev.***, **1983**,12, 415-452
DuBois, *J. Am. Chem. Soc.*, **2004**, *126,* 5502–5514

Photoexcited Hydricity





ΔG^{o}_{H-} 62.0 kcal/mol

ΔG^{o}_{H-}* 14.0 kcal/mol

Photoexcitation populates σ* orbital, which weakens the M-H bond/increasing hydricity

Miller, A.M., *J. Am. Chem. Soc.*, **2014**, 136, 14718

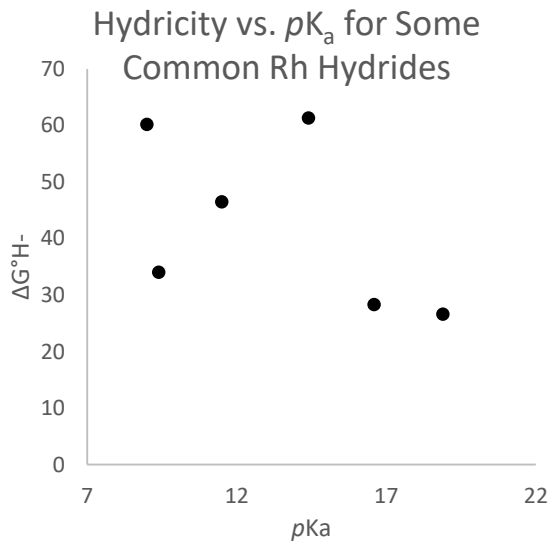
Albright, T. A. Electronic Structure of Organometallic Compounds. *Encycl. Inorganic Bioinorg. Chem.* **2011**.

Question

Are acidity and hydricity directly related?

- Intuitively, Brønsted acidity and hydricity ought to be inversely related
- In practice, that is a poor assumption
- Why? → Ligand sterics can distort coordination geometry and perturb hydricity with minimal impact on inductive effects from π-acidic ligands

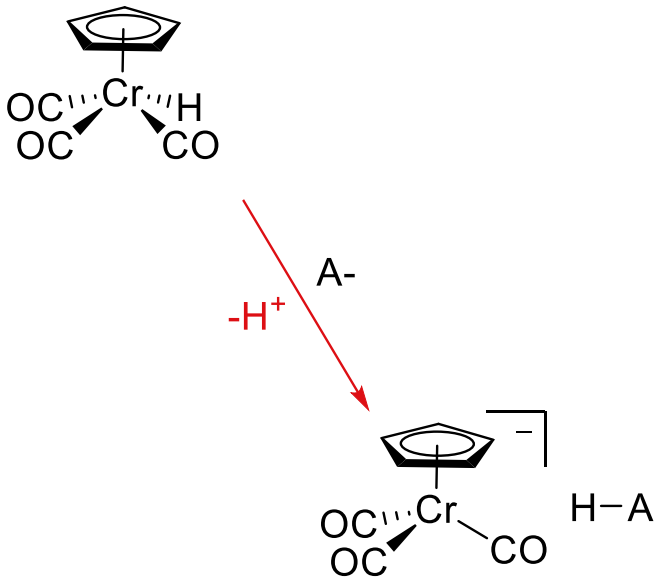
	pKa	Hyd
$Rh(dppe)_2H$	9	60.2
$Rh(dppb)_2H$	9.4	34
$Rh(depx)_2H$	11.5	46.5
$Rh(depp)_2H$	14.4	61.3
$Rh(depe)_2H$	16.6	28.3
$Rh(dmpe)_2H$	18.9	26.6



Morris, R.H., *J. Am. Chem. Soc.,* **2014**, 136, 1948-1959
Appel, Miller, Bullock, *Chem. Rev.,* **2016**, 116, 8655-8692

Brønsted Acidity

Transition Metal Hydride Complexes



Thermodynamic Brønsted Acidity

$$H{-}ML_n \rightleftharpoons ML_n^- \quad H^+$$

General trend:
-late TM's are more acidic, early TM's more hydridic
-"hard," electronegative ligands increase hydricity
-"soft," electropositive ligands increase acidity

Acidity decreases down a group

TABLE III. Brønsted Acidity of Transition-Metal Hydrides

hydride	pK_a
Water, 25 °C	
$HCo(CO)_4$	strong acid
$HCo(CO)_3(PPh_3)$	7.0
$HCo(CO)_3(P(OPh)_3)$	5.0
$HMn(CO)_5$	7.1
$H_2Fe(CO)_4$	$4.4 = pK_1$
	$\sim 14 = pK_2$
$HFe(NO)(CO)_3$	~5.1
$HV(CO)_6$	strong
$HV(CO)_5(PPh_3)$	6.8
$HM(PF_3)_4$, (M = Co, Rh, Ir)	strong
$HRe(CO)_5$	very weak
$HCo(dmgH)_2(PBu_3)$	10.5
$HRh(dmgH)_2(PPh_3)$	9.5
$HCo(CN)_5^-$	~20
Methanol, 25 °C	
$H_4Ru_4(CO)_{12}$	11.9
$H_4FeRu_3(CO)_{12}$	13.4
$H_2Ru_4(CO)_{13}$	14.7
$H_2FeRu_3(CO)_{12}$	14.3
$H_2Os(CO)_4$	14.7
$H_4Os_4(CO)_{12}$	12.0
$H_2Os_3(CO)_{12}$	14.5
$H_2Fe(CO)_4$	6.8
$H_4Ru_4(CO)_{11}P(OMe)_3$	13.6
$HCr(Cp)(CO)_3$	6.4
$HMo(Cp)(CO)_3$	7.2
$HW(Cp)(CO)_3$	9.0
$HNi(dppe)_2^+$	2.6
$HNi[P(OCH_3)_3]_4^+$	1.5
$HPd[P(OCH_3)_3]_4^+$	0.7
$HPt[P(OCH_3)_3]_4^+$	10.2
$HIr(CO)Cl(PPh_3)_2^+$	2.1
$HRh(CO)Cl(PPh_3)_2^+$	1.8
$HRh(dppe)(CH_3OH)_2^{2+}$	1.0
$HIr(CO)Br(PPh_3)_2^+$	2.6
$HIr(CO)I(PPh_3)_2^+$	2.8

Pearson, R.G., *Chem. Rev.*, **1985**, 85, 41-49

Thermodynamic Brønsted Acidity

π-acidic ligands increase acidity

σ-donor ligands attenuate acidity

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$HV(CO)_6$	strong
$HV(CO)_5(PPh_3)$	6.8
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$HRe(CO)_5$	very weak
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$HCo(CN)_5^-$	~20
Methanol, 25 °C	
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$HNi(dppe)_2^+$	2.6
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$HPd[P(OCH_3)_3]_4^+$	0.7
$HPt[P(OCH_3)_3]_4^+$	10.2
$HIr(CO)Cl(PPh_3)_2^+$	2.1
$HRh(CO)Cl(PPh_3)_2^+$	1.8
$HRh(dppe)(CH_3OH)_2^{2+}$	1.0
$HIr(CO)Br(PPh_3)_2^+$	2.6
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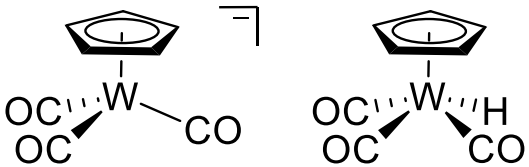
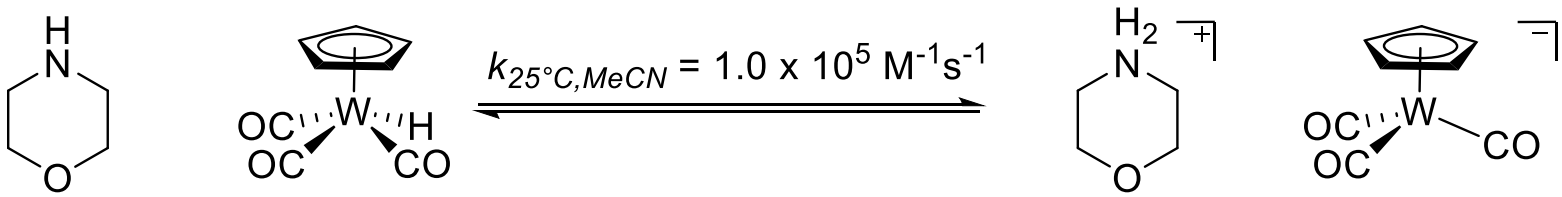
Pearson, R.G., *Chem. Rev.*, **1985**, 85, 41-49

Kinetic Acidity of TM Hydrides

$k_{25°C,MeCN}$ = 6.4 x 10^2 $M^{-1}s^{-1}$





pK_a = 16.1 K_{eq} = 2.9 pK_a = 16.6

Rates of proton transfer were extrapolated from activation parameters based on line broadening in ^{1}H NMR spectrum of well-resolved peaks

Norton, J.R., Jordan, R.F., *J. Am. Chem. Soc.*, **1982**, 104, 1255
D.S. Moore, S.D. Robinson, *Chem. Soc. Rev.*, **1983**,12, 415-452
Pearson, R.G., *Chem. Rev.*, **1985**, 85, 41-49

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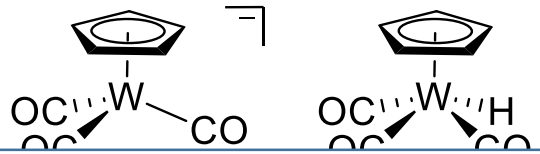

"Extensive electronic and structural rearrangement usually accompanies this stabilization. Rates of removal of protons by bases is unusually slow, because of this rearrangement."

pK_a = 16.1 K_{eq} = 2.9 pK_a = 16.6

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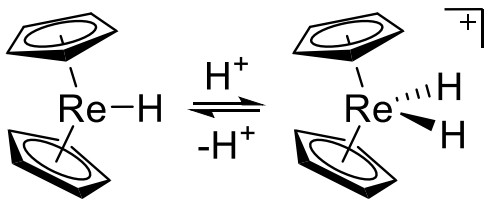
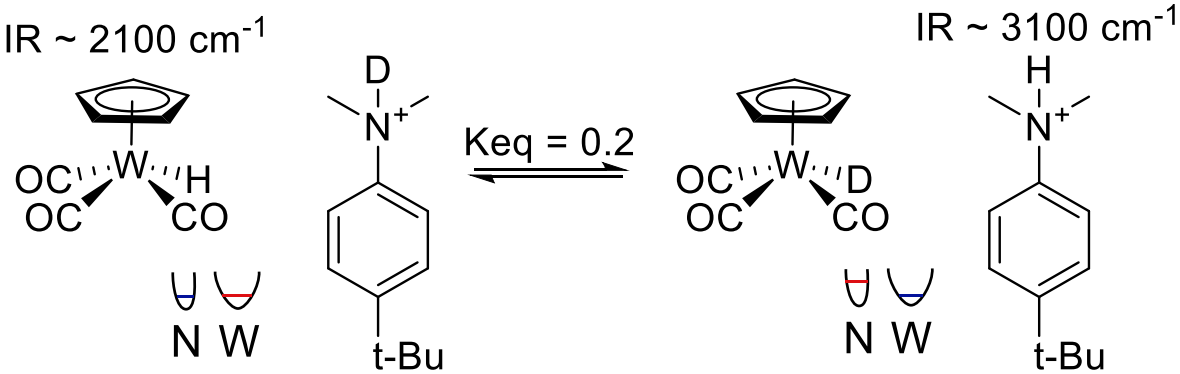
D.S. Moore, S.D. Robinson, *Chem. Soc. Rev.*, **1983**,12, 415-452
Pearson, R.G., *Chem. Rev.*, **1985**, 85, 41-49

Brønsted Basicity of TM Hydrides



Re-H has strong-field ligands and is quite hydridic, but not kinetically competent as a hydride donor



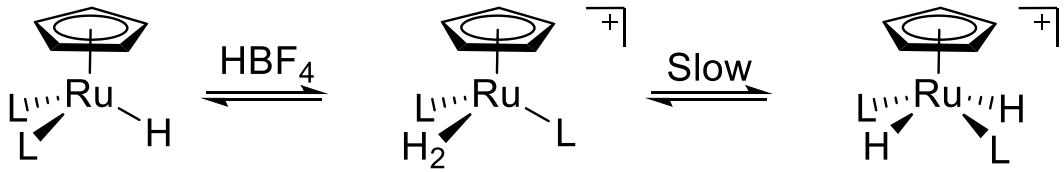
Exchange shows **kinetic competence** as Brønsted base: but *where is it protonating?*

Origin of EIE: bending and stretching modes are lower frequency for TM-H than MG-H

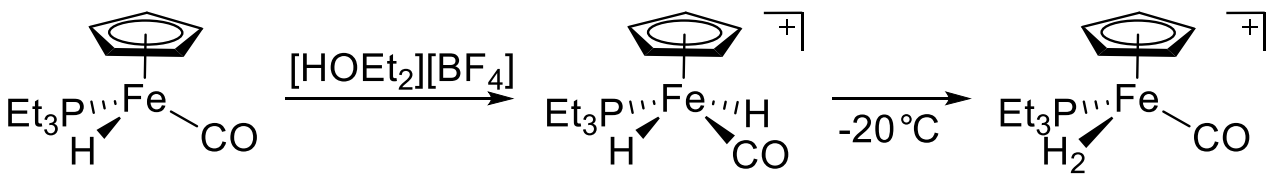
Papish, E. T.; Magee, M. P.; Norton, J. R. Protonation of Transition Metal Hydrides to Give Dihydrogen Complexes. Mechanistic Implications and Catalytic Applications. *Recent Adv. Hydride Chem. Publ. by Elsevier* **2001**, 39–74

Kinetic Site of Protonation: Metal vs Hydride

The Rule:

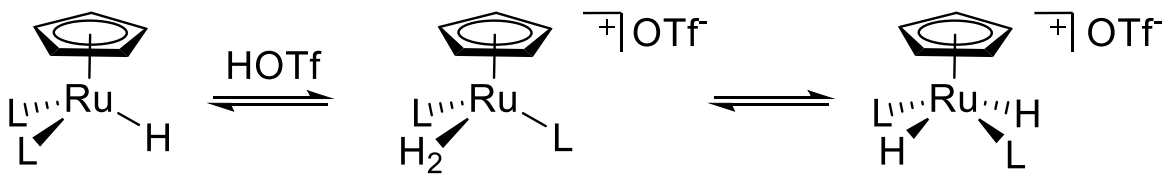


The Exception:

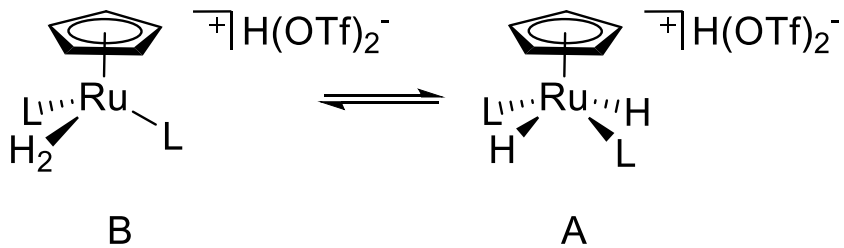


Papish, E. T.; Magee, M. P.; Norton, J. R. Protonation of Transition Metal Hydrides to Give Dihydrogen Complexes. Mechanistic Implications and Catalytic Applications. *Recent Adv. Hydride Chem. Publ. by Elsevier* **2001**, 39–74

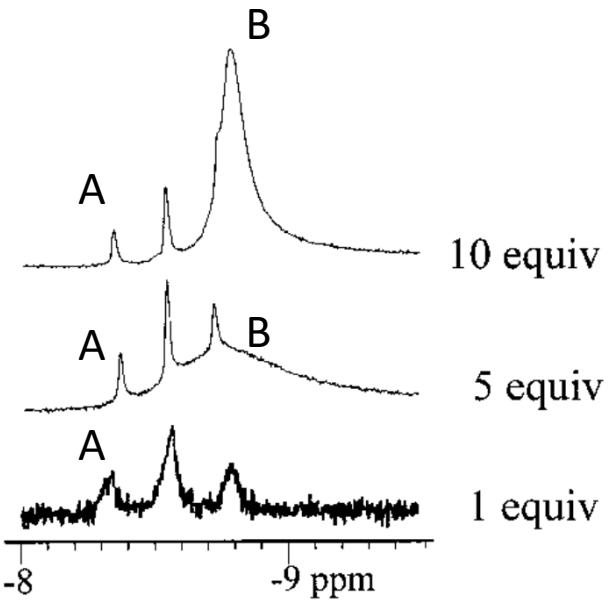
Kinetic Site of Protonation: Metal vs Hydride



Completely consumed, δ = -14ppm (t)

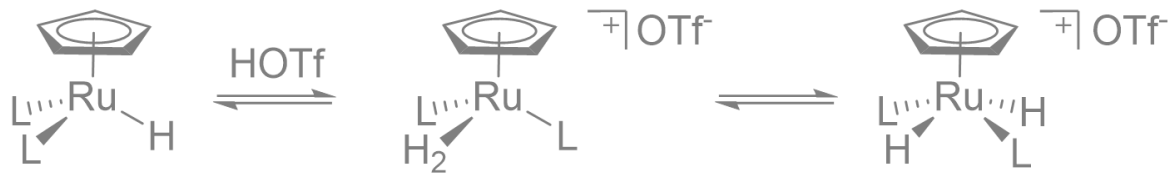


HOTf titration
NMR in CD_2Cl_2



Roddick, *Organometallics*, **1998,** 17, 5467
Morris, R.H., *Organometallics* **1992**,11, 161-171

Kinetic Site of Protonation: Metal vs Hydride



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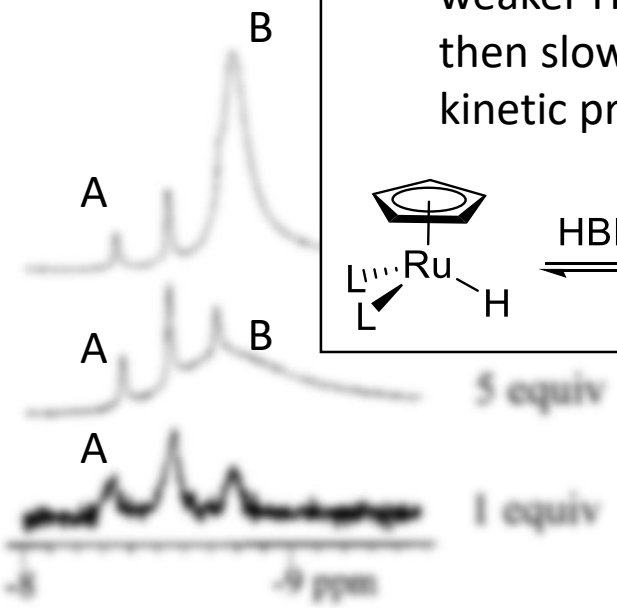
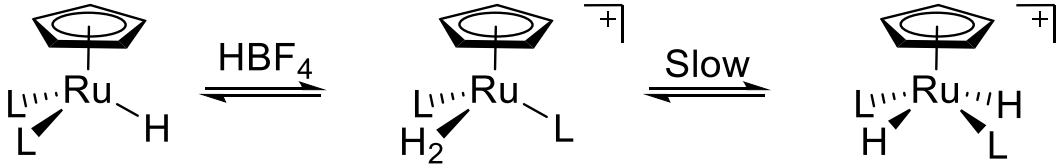
HOTf titration NMR in CD_2Cl_2

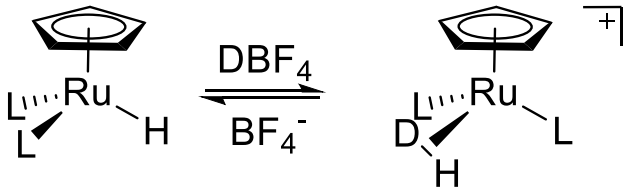


Note: Stoichiometric protonation with weaker HBF_4 led to formation of peak B, then slow evolution to A peaks → proof for kinetic protonation at hydride

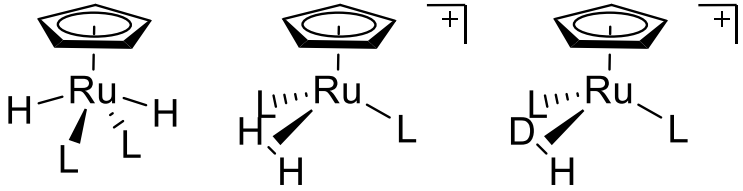


Roddick, *Organometallics*, **1998,** 17, 5467
Morris, R.H., *Organometallics* **1992**,11, 161-171

Kinetic Site of Protonation: Metal vs Hydride



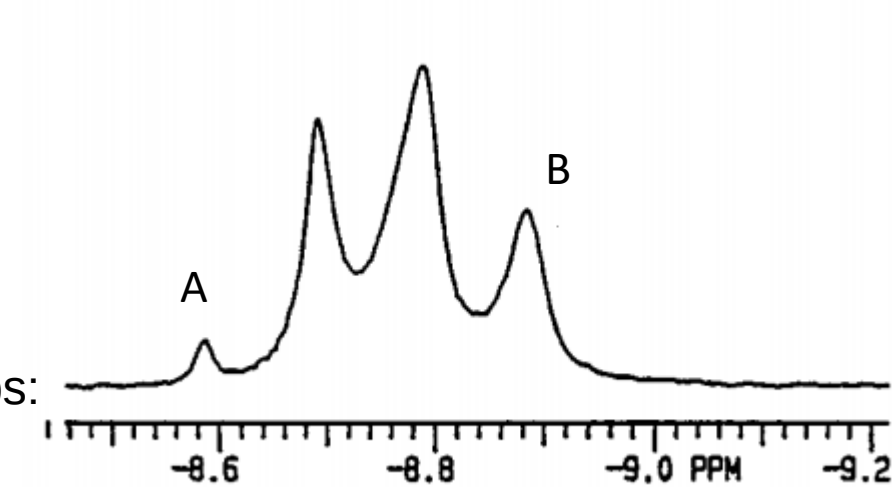
***J*(HD) 20-25Hz, 1:1:1 triplet**



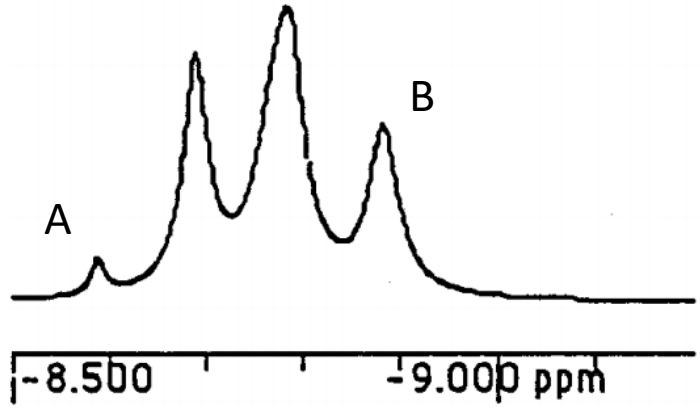
1 A | 3 B | 16 C

Characterization of peaks by inversion recovery:
T_1 for B is 69ms, for A it is 2.91s

Obs:



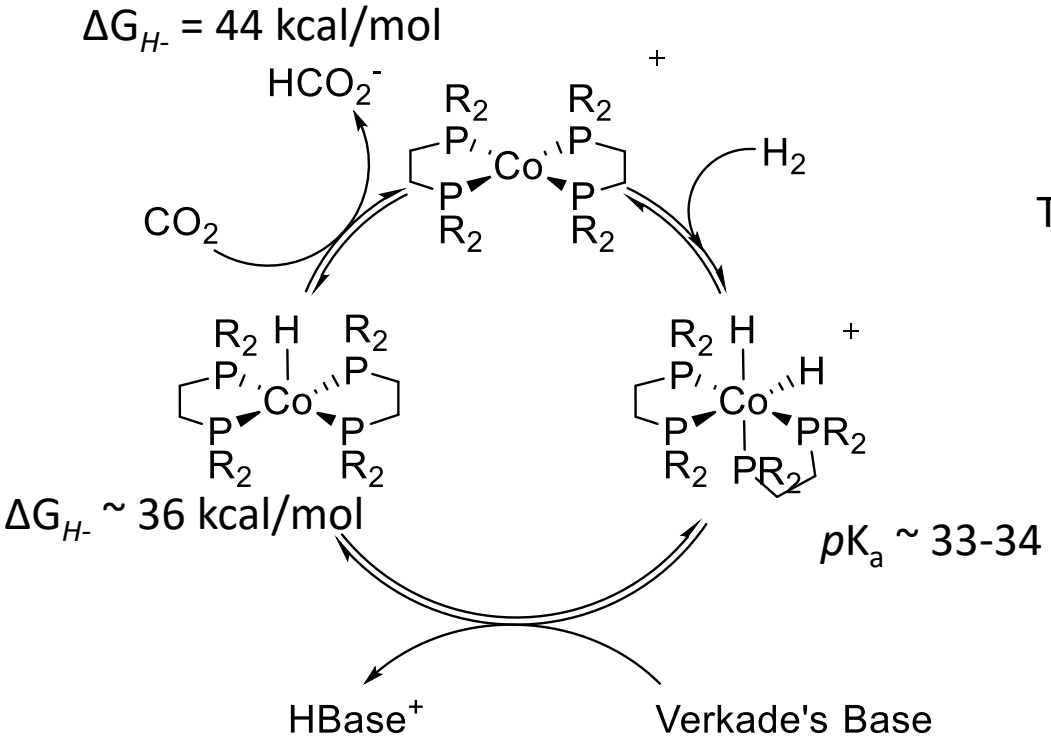
Calc:



Morris, R.H., *Organometallics* **1992**,11, 161-171
Roddick, *Organometallics*, **1998,** 17, 5467

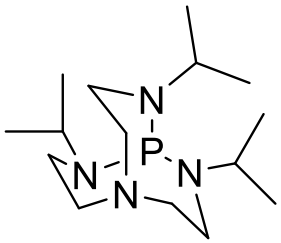
Application: CO_2 Hydrogenation

Deprotonating a $L_nCo(H)_2$ makes it far more hydridic and allows catalyst turnover



TOF 74,000 h^{-1} (20 atm 1:1 H_2/CO_2)

Note: a profound solvent effect makes the hydricities reverse order outside of MeCN and the catalyst can no longer reduce CO_2

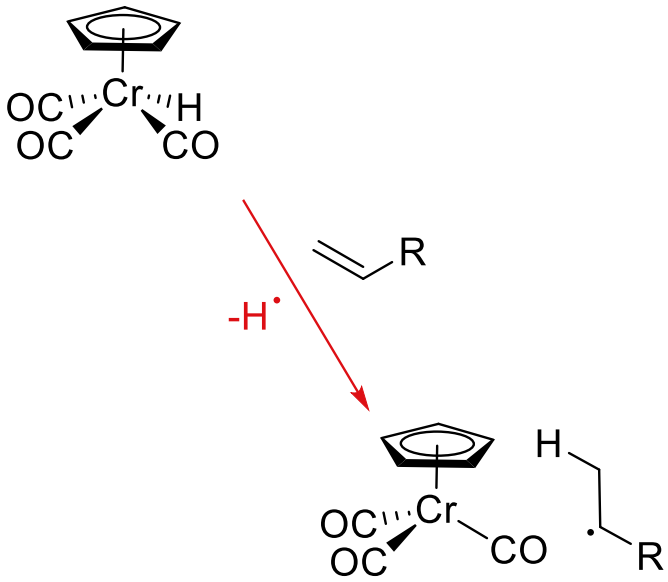


pK_a =33.6

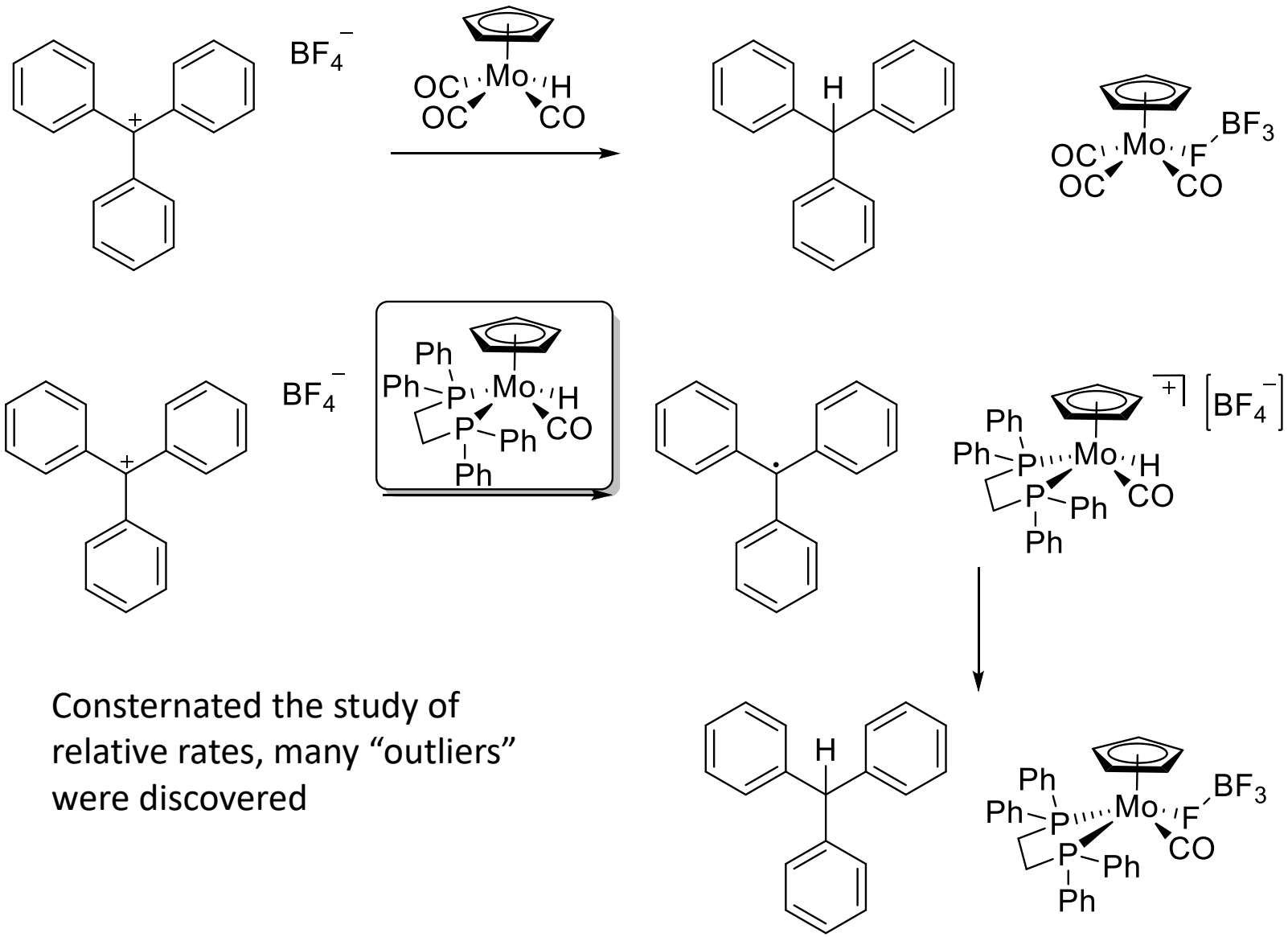
Linehan, J.C., Appel, A.M., *J. Am. Chem. Soc.,* **2013**, 135, 11533
Verkade, J.G., *J. Org. Chem.,* **2000**, 65, 5431

Transition Metal Hydride Hydrogen Atom Transfer (TM-H HAT)

Transition Metal Hydride Complexes



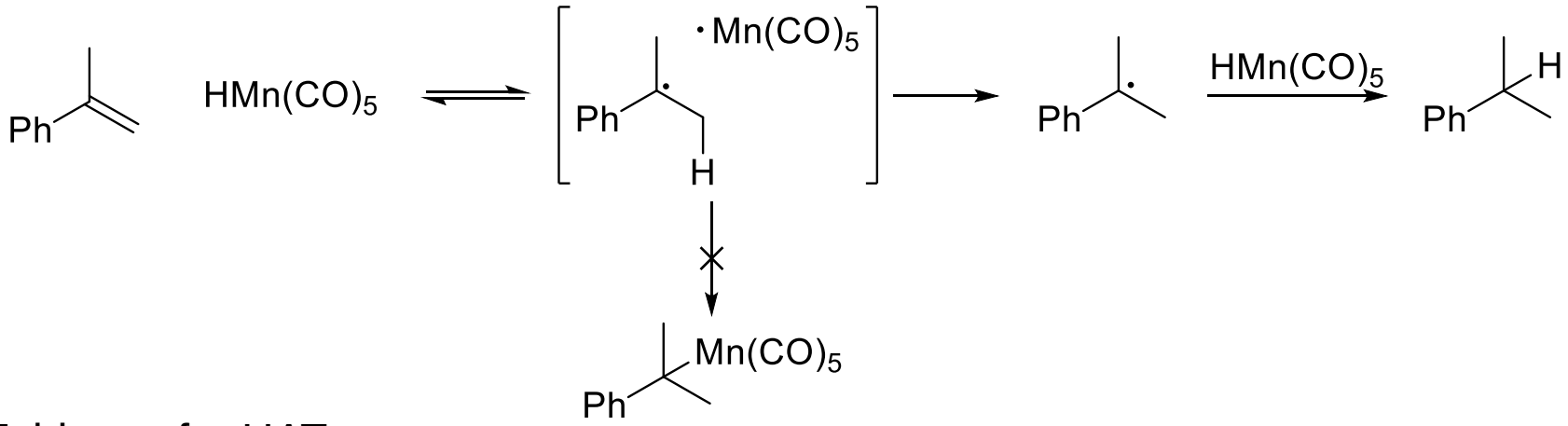
Transition Metal OSET/HAT



Consternated the study of relative rates, many “outliers” were discovered

Cheng, Bullock, *J. Am. Chem. Soc.*, **1998**, 120, 13121
Ibid, *Inorg. Chem.*, **2006**, 45, 4712

HAT of Transition Metal Hydrides



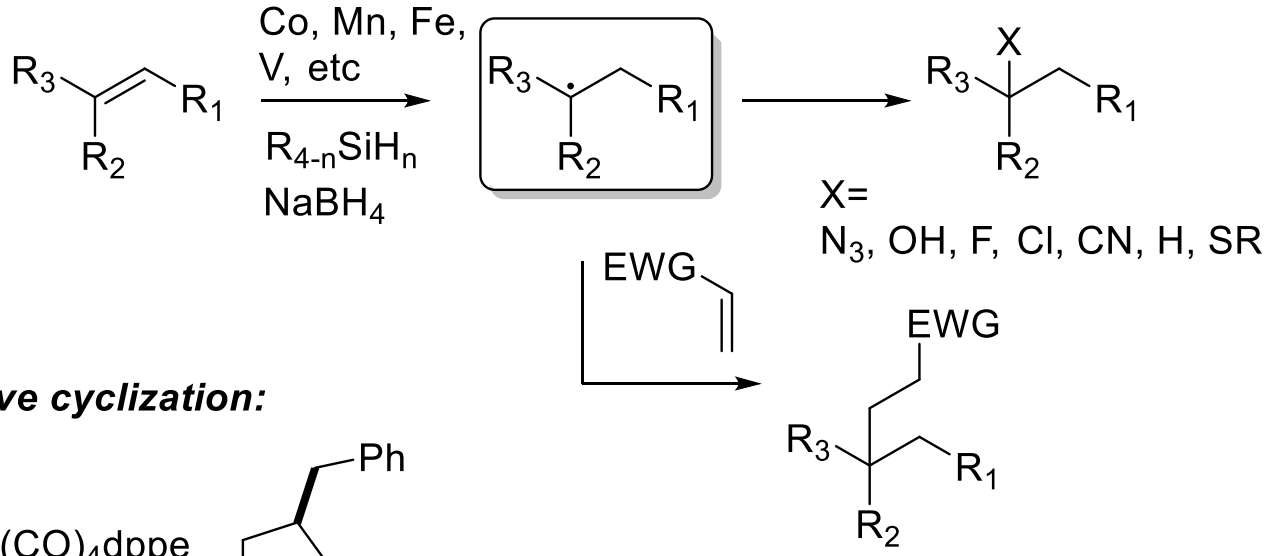
Evidence for HAT:

- CIDNP effect observed
  - Indicates presence of a SOMO at benzylic carbon
- H/D exchange with DMn(CO)5
  - Indicates pre-equilibrium/reversible HAT
- Inverse KIE (pre-equilibrium affected)
  - Consistent with RDS being cage escape

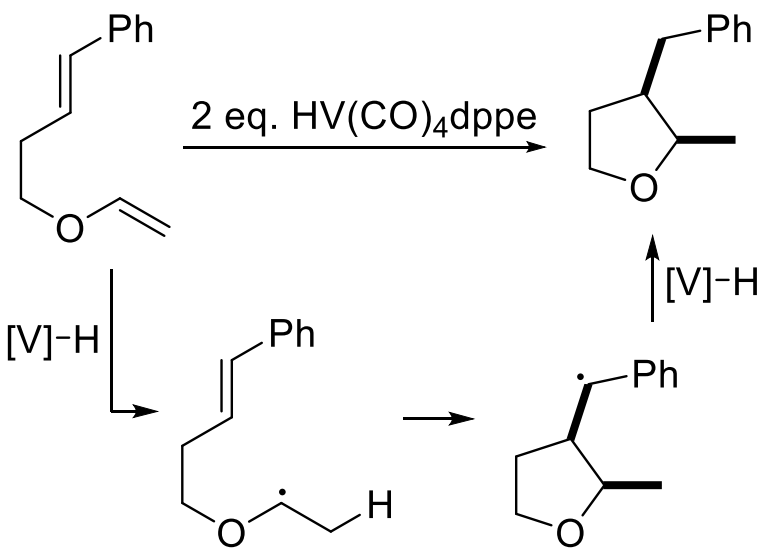
Jacobsen, Bergman, *J. Am. Chem. Soc.*, **1985**, *107*, pp 2023–2032
Sweaney, Halpern, *J. Am. Chem. Soc.*, **1977**, *99*, pp 8335–8337

HAT in Modern Methods

"Gentle" means to access alkyl radicals



Reductive cyclization:



Weak M-H slows olefin isomerization or recombination pathways

(first step is actually a pre-equilibrium)

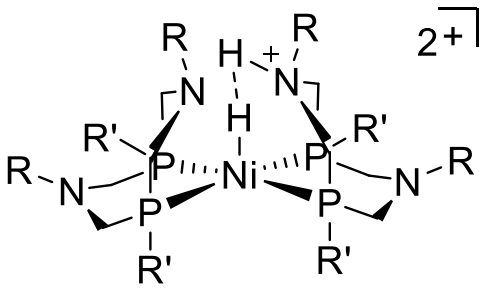
Norton, *J. Am. Chem. Soc.*, **2015,** 137, 1036
Baran, *J. Am. Chem. Soc.*, **2017**, 139, 2484
Shenvi, *Chem. Rev.* **2016**, 116, 8912

Summary

1. Transition metal hydride reactivity is profoundly affected by ligands, oxidation state, and periodic trends
   i. Strong donating ligands increase hydricity and decrease acidity
   ii. Withdrawing ligands decrease hydricity and increase acidity
   iii. Strain-induced distortions strongly affect hydricity
   iv. Higher oxidation states lower hydricity and raise acidity
   v. Late TM-Hs tend to be more acidic, early tend to be more hydritic
2. Hydrogen atom transfer (and PCET) are becoming widely accepted as operative mechanisms in many “hydrometallation” reactions
3. Most transition metal hydrides are actually Brønsted acidic

Questions?

Supplement: Water Electrolysis Catalysts



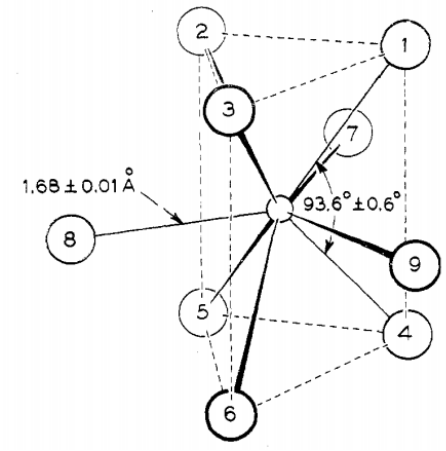
-TOF 3 x 10^7 s^{-1}
-in water
-400 mV overpotential

-Catalyst optimization required tuning of N bases to match the Brønsted basicity of the Ni^{II}-H/Ni^0

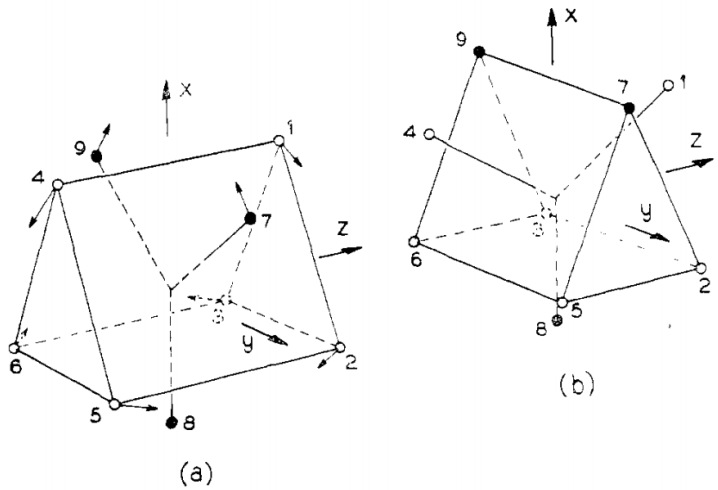
-If pendant amines are too basic, creates outer-sphere chelate → shuts down H_2 production

Bullock, R.M., *Inorg. Chem.,* **2016**, 55, 2, 445-460

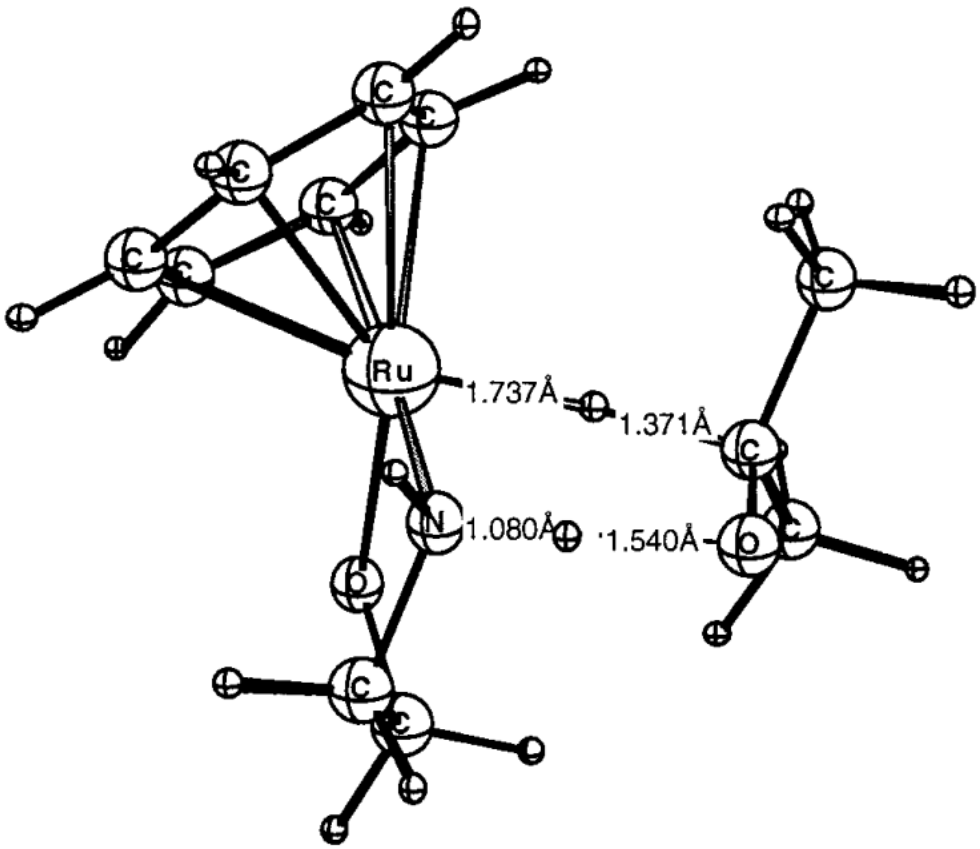
Supplement: K2ReH9 Exchange Mechanism

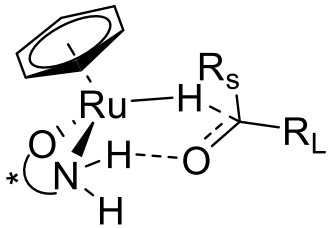


Mechanism of Exchange:



Supplement: Ionic Reduction





Hydride delivery is far more effective with a hydrogen bond to the carbonyl

Andersson, *J. Am. Chem. Soc.*, **1999**, 121, 9580

Supplement: Ionic Ketone Hydrogenation Mechanism