Transition Metal Hydrides: More Than You Wanted To Know

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SED Group Meeting
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Wilkinson  Norton  Pearson  Ibers
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

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
- $\mu^2$-bonding hydrides
  
  $\begin{array}{c}
  [M] \overset{\cdots}{\overset{H}{\cdots}} [M]
  \end{array}$

- $\mu^3$-bonding hydrides
  
  $\begin{array}{c}
  [M] \overset{H}{\cdots} [M]
  \end{array}$
Types of Hydrides and Scope of Discussion

**Transition Metal Hydride Complexes**

![Transition Metal Hydride Complex](image)

**Interstitial Hydrides or Binary Lattice Solids**

LiAlH₄, NaH, LiH, RaNi, H₂/Pd

- \( \mu^2 \)-bonding hydrides
  
  \[
  [M] \cdots H \cdots [M]
  \]

- \( \mu^3 \)-bonding hydrides
  
  \[
  [M] \cdots H \cdots [M]
  \]
**Walter Hieber 1931**

\[
\text{Fe(CO)}_5 \xrightarrow{1. \text{2OH}^-} \text{Fe(CO)}_4\text{H}_2 + \text{CO}_3^{2-} \\
\text{FeH}_2(\text{CO})_4
\]

"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**

\[
\begin{align*}
2\text{Co(CO)}_4\text{L} & \xrightarrow{2\text{H}^+} \text{CoH(CO)}_4 + \text{Co}^{2+} \\
& \quad 2\text{CO} + \text{L} + 0.5\text{H}_2
\end{align*}
\]

L = amine or alcohol

\[
3\text{Co(CO)}_4 \xrightarrow{2\text{H}_2\text{O}} 2\text{Co(CO)}_4\text{H} + \text{Co(OH)}_2
\]

4CO
Controversy on the Nature of Transition Metal Hydrides

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

Fischer, Hafner, Stahl 1955

Chatt, Duncanson, Shaw 1957

W. Hieber and F. Leutert, Naturwissenschaften, 1931, 19, 360; Z. Elektrochem., 1934, 40, 158.

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

Brief Overview of Transition Metal Hydride Synthesis

**Hydrogenation**

\[
\text{Et}_3\text{P} \quad \text{Pt} \quad \text{Cl} \quad \xrightarrow{\text{H}_2} \quad \text{Cl} \quad \text{Pt} \quad \text{P}\text{Et}_3
\]

\[
\text{Et}_3\text{P} \quad \text{Cl} \quad \xrightarrow{-\text{HCl}} \quad \text{Et}_3\text{P} \quad \text{H}
\]

\[
\text{Fe}^0 + \begin{array}{c}
\text{PEt}_2 \\
\text{PEt}_2
\end{array} \quad \xrightarrow{\text{H}_2} \quad \begin{array}{c}
\text{P} \\
\text{Fe} \\
\text{P}
\end{array} \quad \begin{array}{c}
\text{Et}_2\text{H} \\
\text{Et}_2\text{H} \\
\text{Et}_2\text{H}
\end{array}
\]

**Protonation**

\[
2\left[\text{Na}^+\right] \quad \text{CO} \quad \xrightarrow{\text{H}_2\text{SO}_4} \quad \begin{array}{c}
\text{OC} \\
\text{Fe} \\
\text{CO}
\end{array} \quad \xrightarrow{\text{H}_2\text{SO}_4} \quad \begin{array}{c}
\text{OC} \\
\text{H} \\
\text{Fe} \\
\text{CO}
\end{array}
\]

\[
\text{OC} \quad \text{Fe} \quad \text{CO} \quad \xrightarrow{\text{H}_2\text{SO}_4} \quad \begin{array}{c}
\text{OC} \\
\text{H} \\
\text{Fe} \\
\text{H} \\
\text{CO}
\end{array}
\]

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

Brief Overview of Transition Metal Hydride Synthesis

**Reduction of Metal Halides**

\[
\begin{align*}
\text{PhEt}_2\text{As} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Ir} \quad \text{Cl} \\
\text{AsEt}_2\text{Ph} & \quad \text{LiAlH}_4 \\
\text{THF} & \\
\text{PhEt}_2\text{As} & \quad \text{H} \quad \text{H} \\
\text{Ir} & \quad \text{H} \\
\text{AsEt}_2\text{Ph} & 
\end{align*}
\]

*N.B.: other common reducing agents include ROH, N\textsubscript{2}H\textsubscript{4}, NaBH\textsubscript{4}, HCO\textsubscript{2}H, H\textsubscript{3}PO\textsubscript{2}, H\textsubscript{2}S\textsubscript{2}O\textsubscript{4}, R\textsubscript{2}Al(H/OR)*

**Oxidative Addition of Main Group Hydrides**

\[
\begin{align*}
\text{Ph}_3\text{P} & \quad \text{Rh} \quad \text{Cl} \\
\text{Ph}_3\text{P} & \quad \text{PPPh}_3 \\
\text{HSiCl}_3 & \quad \text{PhEt}_2\text{As} \\
\text{Rh} & \quad \text{SiCl}_3 \\
\text{Cl} &
\end{align*}
\]

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

<table>
<thead>
<tr>
<th>Complex</th>
<th>$D(M\cdash X)$ kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$X = H$</td>
</tr>
<tr>
<td>TiX$_2$(C$_5$Me$_5$)$_2$</td>
<td>242</td>
</tr>
<tr>
<td>MoX$_2$(C$_5$H$_5$)$_2$</td>
<td>258.7</td>
</tr>
<tr>
<td>WX$_2$(C$_5$H$_5$)$_2$</td>
<td>251.4</td>
</tr>
<tr>
<td>MnX(CO)$_5$</td>
<td>ca. 300</td>
</tr>
<tr>
<td>[FeX(CO)$_4$]$^-_1$</td>
<td>ca. 310</td>
</tr>
<tr>
<td>CoX(CO)$_4$</td>
<td>ca. 290</td>
</tr>
<tr>
<td>IrX$_2$Cl(CO)(PR$_3$)$_2$</td>
<td>ca. 240--255</td>
</tr>
</tbody>
</table>

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

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

Modern method: \[ \chi_i = 0.105 n^* (I_m/R)^{0.5}/r_i + 0.863 \]

- \( n^* \) is the valence quantum number
- \( I_m \) is the electron affinity for ion
- \( R \) is the Rydberg constant
- \( r_i \) is the ionic radius

Modern method: $\chi_i = 0.105 n^* \left( \frac{I_m}{R} \right)^{0.5} + 0.863$.

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

$n^*$ is the valence quantum number

$I_m$ is the electron affinity for ion

$R$ is the Rydberg constant

$r_i$ is the ionic radius

$\Delta \chi$ is the difference in electron affinity.

“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.”


Hydricity

Transition Metal Hydride Complexes

\[
\begin{align*}
\text{OC} & \quad \text{Cr} \quad \text{H} \\
\text{OC} & \quad \text{CO} \\
\text{OC} & \quad \text{Cr} \\
\text{OC} & \quad \text{CO}
\end{align*}
\]

A+ \quad -H^- \quad \text{H}^-A
Hydricity of Transition Metal Hydrides

**Definition of Hydricity**

\[ L_nM-H \rightarrow ML_n^+ + H^- \]

*Endergonic state function: \( \Delta G^0_{H^-} \)*

Example of concerted hydride transfer to hydride acceptor

- Thermodynamic measurement compromised by irreversibility and non-innocence of BF\(_4^-\) ligand


Measuring Hydricity

Example of determining hydricity indirectly:
- Cyclic Voltammetry used to determine $E^\circ$ 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 $E^\circ$)

In practice:
Ni/Pd/Pt, Co/Rh are well suited to CV methods
- reversible electrochemistry
- weak binding of MeCN (most common solvent)

Irreproducibility of Experimental Hydricity Values

Homocoujugation complicates $\Delta G^0_{\text{H-}}$ measurements

Solvent Coordination deviates $\Delta G_{\text{obs}}$ from $\Delta G_{\text{H-}}$.

Irreproducibility of Experimental Hydricity Values

Most Common Errors Made in the Literature:
- Non-equilibrium measurements common
- Standard state deviations (e.g. H₂ not at 1 atm)
- Coordination of solvent
- Homoconjugation in products

Solvent Coordination deviates $\Delta G_{\text{obs}}$ from $\Delta G_H$. 

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.
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

Thermochemical Cycles for Determining Hydricity

Full Thermodynamic Scheme

\[
\begin{align*}
M^+ & \rightleftharpoons E^{\circ}_{M+/}\text{M}^- & M^- & \rightleftharpoons E^{\circ}_{M^-/}\text{M}^+ \\
+ & \rightleftharpoons E^{\circ}_{H^+/H^-} & + & \rightleftharpoons E^{\circ}_{H^-/H^+} \\
H^- & \rightleftharpoons \Delta G^{\circ}_{H^-} & H^+ & \rightleftharpoons \text{BDFE} \quad pK_a \\
\end{align*}
\]

\(\Delta G^{\circ}_{H^-}\)

\[\text{H}_2 \text{ Heterolysis}\]

HA \quad M-H \quad \frac{\Delta \Delta G^{\circ}_{H^-}}{\text{H}_2} \quad M^+ \quad A^- 

\[\Delta \Delta G^{\circ}_{H^-} + \Delta G^{\circ}_{H^-}(\text{H}_2) = \Delta G^{\circ}_{H^-}(\text{M-H})\]

Also need to account for \(pK_a\) of HA

\[\text{Reactorion with Hydride Acceptor}\]

A \quad M-H \quad \frac{\Delta \Delta G^{\circ}_{H^-}}{\text{HA}^-} \quad M^+ 

\[\Delta \Delta G^{\circ}_{H^-} + \Delta G^{\circ}_{H^-}(A) = \Delta G^{\circ}_{H^-}(\text{M-H})\]

Caveat:
-\(\Delta \Delta G^{\circ}_{H^-}\) usually incorporates base, ligand, solvent, or \((\mu^2)\) \(\text{H}_2\) binding that must be accounted for.

Caveat:
-\(\Delta \Delta G^{\circ}_{H^-}\) must be small enough to measure relative quantities at equilibrium.

\(-system\ must\ reach\ equilibrium\)

Hydricity Trends

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

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

**Bite Angle Effect on Hydricity**

\[
\begin{array}{c}
\text{Et}_2\text{P} & \text{PEt}_2 & \text{PEt}_2 \\
78^\circ & \text{depe} & \\
\text{PEt}_2 & \text{PEt}_2 & \text{PEt}_2 \\
86^\circ & \text{depp} & \\
\text{PEt}_2 & \text{PEt}_2 & \text{PEt}_2 \\
90^\circ & \text{depx} & \\
\text{PEt}_2 & \text{PEt}_2 & \text{PEt}_2 \\
102^\circ & \text{depPE} & \\
\text{PEt}_2 & \text{PEt}_2 & \text{PEt}_2 \\
111^\circ & \text{EtXantphos} & \\
\end{array}
\]

**Nonlinear correlation:**

Larger bite angle → tetragonal distortion

Tetragonal distortion → increase M-H s-character

**P-Pd-P angle**

\[
\begin{align*}
P-Pd-P \text{ angle} &= \text{ bite angle} \\
&= \begin{pmatrix} P & Pd & P \end{pmatrix}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Bite Angle (degrees)</th>
<th>( \Delta G_H^- ) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>78</td>
<td>43.2</td>
</tr>
<tr>
<td>86</td>
<td>54.7</td>
</tr>
<tr>
<td>90</td>
<td>61.5</td>
</tr>
<tr>
<td>102</td>
<td>66.4</td>
</tr>
<tr>
<td>111</td>
<td>70.4</td>
</tr>
</tbody>
</table>


Photoexcited Hydricity

Photoexcitation populates $\sigma^*$ orbital, which weakens the M-H bond/increasing hydricity

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.

<table>
<thead>
<tr>
<th>pKa</th>
<th>Hyd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(dppe)$_2$H</td>
<td>9</td>
</tr>
<tr>
<td>Rh(dppb)$_2$H</td>
<td>9.4</td>
</tr>
<tr>
<td>Rh(depx)$_2$H</td>
<td>11.5</td>
</tr>
<tr>
<td>Rh(depp)$_2$H</td>
<td>14.4</td>
</tr>
<tr>
<td>Rh(depe)$_2$H</td>
<td>16.6</td>
</tr>
<tr>
<td>Rh(dmpe)$_2$H</td>
<td>18.9</td>
</tr>
</tbody>
</table>

Thermodynamic Brønsted Acidity

H–MLₙ ⇌ MLₙ⁻ 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

<table>
<thead>
<tr>
<th>hydride</th>
<th>pKₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCo(CO)₄</td>
<td>strong acid</td>
</tr>
<tr>
<td>HCo(CO)₆(PPh₃)</td>
<td>7.0</td>
</tr>
<tr>
<td>HCo(CO)₆(P(OPh)₃)</td>
<td>5.0</td>
</tr>
<tr>
<td>HMn(CO)₆</td>
<td>7.1</td>
</tr>
<tr>
<td>H₂Fe(CO)₄</td>
<td>4.4 = pK₁</td>
</tr>
<tr>
<td></td>
<td>~14 = pK₂</td>
</tr>
<tr>
<td>HFe(NO)(CO)₃</td>
<td>~5.1</td>
</tr>
<tr>
<td>HV(CO)₆</td>
<td>strong</td>
</tr>
<tr>
<td>HV(CO)₆(PPh₃)</td>
<td>6.8</td>
</tr>
<tr>
<td>HM(PF₆)₄(M = Co, Rh, Ir)</td>
<td>strong</td>
</tr>
<tr>
<td>HRe(CO)₆</td>
<td>very weak</td>
</tr>
<tr>
<td>HCo(dmgh₂)₄(PBu₃)</td>
<td>10.5</td>
</tr>
<tr>
<td>HRh(dmgh₂)₄(PPh₃)</td>
<td>9.5</td>
</tr>
<tr>
<td>HCo(CN)₅⁻</td>
<td>~20</td>
</tr>
</tbody>
</table>

Methanol, 25 °C

<table>
<thead>
<tr>
<th>hydride</th>
<th>pKₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂Ru₄(CO)₁₂</td>
<td>11.9</td>
</tr>
<tr>
<td>H₂FeRu₃(CO)₁₂</td>
<td>13.4</td>
</tr>
<tr>
<td>H₂Ru₄(CO)₁₃</td>
<td>14.7</td>
</tr>
<tr>
<td>H₂FeRu₄(CO)₁₂</td>
<td>14.3</td>
</tr>
<tr>
<td>H₂Os(CO)₁₄</td>
<td>14.7</td>
</tr>
<tr>
<td>H₂Os₄(CO)₁₂</td>
<td>12.0</td>
</tr>
<tr>
<td>H₂Os₃(CO)₁₂</td>
<td>14.5</td>
</tr>
<tr>
<td>H₂Fe(CO)₁₄</td>
<td>6.8</td>
</tr>
<tr>
<td>H₂Ru₄(CO)₁₂P(OME)₃</td>
<td>13.6</td>
</tr>
<tr>
<td>HCr(Cp)(CO)₃</td>
<td>6.4</td>
</tr>
<tr>
<td>HMo(Cp)(CO)₃</td>
<td>7.2</td>
</tr>
<tr>
<td>HW(Cp)(CO)₃</td>
<td>9.0</td>
</tr>
<tr>
<td>HNi(dppe)₉⁺</td>
<td>2.6</td>
</tr>
<tr>
<td>HNi[P(OCH₃)₃]₄⁺</td>
<td>1.5</td>
</tr>
<tr>
<td>HPd[P(OCH₃)₃]₄⁺</td>
<td>0.7</td>
</tr>
<tr>
<td>HP⁺[P(OCH₃)₃]₄⁺</td>
<td>10.2</td>
</tr>
<tr>
<td>HIr(CO)Cl(PPh₃)₂⁺</td>
<td>2.1</td>
</tr>
<tr>
<td>HRh(CO)Cl(PPh₃)₂⁺</td>
<td>1.8</td>
</tr>
<tr>
<td>HRh(dppe)(CH₃OH)₂²⁺</td>
<td>1.0</td>
</tr>
<tr>
<td>HIr(CO)Br(PPh₃)₂⁺</td>
<td>2.6</td>
</tr>
<tr>
<td>HIr(CO)I(PPh₃)₂⁺</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Thermodynamic Brønsted Acidity

π-acidic ligands increase acidity

σ-donor ligands attenuate acidity

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<table>
<thead>
<tr>
<th>hydride</th>
<th>pK_a</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Water, 25 °C</strong></td>
<td></td>
</tr>
<tr>
<td>HCo(CO)_4</td>
<td>strong acid</td>
</tr>
<tr>
<td>HCo(CO)_3(PPh_3)</td>
<td>7.0</td>
</tr>
<tr>
<td>HCo(CO)_3(P(OH)_3)</td>
<td>5.0</td>
</tr>
<tr>
<td>HMn(CO)_5</td>
<td>7.1</td>
</tr>
<tr>
<td>H_2Fe(CO)_4</td>
<td>4.4 = pK_1</td>
</tr>
<tr>
<td></td>
<td>~14 = pK_2</td>
</tr>
<tr>
<td>HFes(NO)(CO)_3</td>
<td>~5.1</td>
</tr>
<tr>
<td>HV(CO)_6</td>
<td>strong</td>
</tr>
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<td>HV(CO)_5(PPh_3)</td>
<td>6.8</td>
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<td>HM(PF_6)_4, (M = Co, Rh, Ir)</td>
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<td>HCo(CN)_5^-</td>
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</tr>
<tr>
<td><strong>Methanol, 25 °C</strong></td>
<td></td>
</tr>
<tr>
<td>H_2Ru_4(CO)_12</td>
<td>11.9</td>
</tr>
<tr>
<td>H_4FeRu_3(CO)_12</td>
<td>13.4</td>
</tr>
<tr>
<td>H_2Ru_4(CO)_13</td>
<td>14.7</td>
</tr>
<tr>
<td>H_4FeRu_3(CO)_12</td>
<td>14.3</td>
</tr>
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<td>H_2Os(CO)_4</td>
<td>14.7</td>
</tr>
<tr>
<td>H_2Os_4(CO)_12</td>
<td>12.0</td>
</tr>
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</tr>
<tr>
<td>H_2Fe(CO)_4</td>
<td>6.8</td>
</tr>
<tr>
<td>H_2Ru_4(CO)_12P(OMe)_3</td>
<td>13.6</td>
</tr>
<tr>
<td>HCr(Cp)(CO)_3</td>
<td>6.4</td>
</tr>
<tr>
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<td>HRe(CO)Cl(PPh_3)_2+</td>
<td>1.8</td>
</tr>
<tr>
<td>HRe(dppe)(CH_3OH)_22+</td>
<td>1.0</td>
</tr>
<tr>
<td>HIr(CO)Br(PPh_3)_2+</td>
<td>2.6</td>
</tr>
<tr>
<td>HIr(CO)I(PPh_3)_2+</td>
<td>2.8</td>
</tr>
</tbody>
</table>

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


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

$k_{25^\circ C,MeCN} = 6.4 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$

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

$pK_a = 16.1$ \hspace{1cm} $K_{eq} = 2.9$ \hspace{1cm} $pK_a = 16.6$
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.

Kinetic Site of Protonation: Metal vs Hydride

The Rule:

\[
\begin{align*}
&\text{Ru}_\text{H}^+ \\
&\text{Ru}^\text{L}_\text{H} \\
&\text{Ru}^\text{L}_\text{H}_2
\end{align*}
\]

The Exception:

\[
\begin{align*}
&\text{Fe}^\text{Et}_3\text{P}_\text{H}^+ \\
&\text{Fe}^\text{Et}_3\text{P}_\text{HCO} \\
&\text{Fe}^\text{Et}_3\text{P}_\text{H}_2\text{CO}
\end{align*}
\]

Kinetic Site of Protonation: Metal vs Hydride

HOTf titration
NMR in CD$_2$Cl$_2$

\[ \delta = -14 \text{ppm (t)} \]

Roddick, *Organometallics*, 1998, 17, 5467
Kinetic Site of Protonation: Metal vs Hydride

HOTf titration
NMR in CD$_2$Cl$_2$

\[
\begin{align*}
\text{Note:} & \quad \text{Stoichiometric protonation with} \\
& \text{weaker HBF}_4 \text{ led to formation of peak B,} \\
& \text{then slow evolution to A peaks} \rightarrow \text{proof for} \\
& \text{kinetic protonation at hydride}
\end{align*}
\]
Kinetic Site of Protonation: Metal vs Hydride

\[ J(\text{HD}) \ 20-25\text{Hz}, \ 1:1:1 \ \text{triplet} \]

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

Morris, R.H., Organometallics 1992, 11, 161-171
Roddick, Organometallics, 1998, 17, 5467
Application: CO$_2$ Hydrogenation

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

$\Delta G_{H^-} = 44 \text{ kcal/mol}$

$\Delta G_{H^-} \approx 36 \text{ kcal/mol}$

$\text{pK}_a \approx 33-34$

TOF $74,000 \text{ h}^{-1}$ (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$_2$


Transition Metal Hydride Hydrogen Atom Transfer (TM-H HAT)
Consternated the study of relative rates, many “outliers” were discovered.

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

"Gentle" means to access alkyl radicals

\[
\begin{align*}
R_3 & \quad \text{Ph} \\
\text{Ph} & \quad [V]-H
\end{align*}
\]

Reductive cyclization:

Weak M-H slows olefin isomerization or recombination pathways

(first step is actually a pre-equilibrium)

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?
-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 $\rightarrow$ shuts down H$_2$ production

Supplement: K2ReH9 Exchange Mechanism

Mechanism of Exchange:
Hydride delivery is far more effective with a hydrogen bond to the carbonyl
Supplement: Ionic Ketone Hydrogenation Mechanism

(i) $\text{H}RHu-NH = \text{MOR}$

(ii) $\text{H}RHu-NM \rightarrow \text{ROH}$

(iii) $\text{H}RHu-NM \rightarrow [\text{M}_{\text{Me}Ph}O]$ +

(iv) $\text{H}RHu-NM \rightarrow [\text{Me}_{\text{Me}Ph}O]$

(v) $\text{H}RHu-NM \rightarrow \text{Me}_{\text{Me}Ph}O$

$\text{M} = \text{alkali metal cation}$