Hydrides and Dihydrogen as Ligands: Lessons from Organometallic Chemistry

Lecture 7
Schematic representation of physisorption and chemisorption of Hydrogen on a nickel metal surface.

(a) Different Exposed planes, edges; (b) steps and kinks from irregularities.
Hydrogenation of alkenes on supported metal involves $\text{H}_2$ dissociation and migration of H-atoms to an adsorbed ethene molecule. (Paul Sabatier, 1890)

**Mechanism:** All isotopomers are seen, therefore highly reversible prior to loss of the ethane.

Volcano diagrams relate stability of products on surface: Temp. for a set rate of release vs. the Enthalpy. *Intermediate values of $\Delta H_f$, with the rate being a combination of the rate of adsorption and the rate of desorption gives best catalyst.*

The Goldilock’s Effect
Isolobal Analogies: R. Hoffmann

CH₃

CH₂

CH

d⁷-ML₅

d⁷-ML₄

d⁷-ML₃
Isolobal species: H, Methyl, M(CO)’s

*Note that electrons can be added to or subtracted from each member of the isolobal group and still maintain isolobalilty—for example, $\text{CH}^+ \rightarrow \text{Mn(CO)}^+ \rightarrow \text{Co(CO)}_4$. 

\[ \text{H} \quad \text{H}^+ \quad \text{H}^2- \quad \text{B} \quad \text{P} \quad \text{OC} \quad \text{Co} \quad \text{Co}^2- \quad \text{Fe} \quad \text{Mn} \]

\[ \text{H}_3\text{C} \quad (\text{OC})_5\text{Mn} \quad (\text{OC})_4\text{Co} \]

\[ \text{C} \quad \text{N} \quad \text{P} \quad \text{OC} \quad \text{Co} \quad \text{Fe} \]

\[ \text{Mn} \quad \text{Co} \quad \text{Fe} \]
Feed-stock CH₃OH

Metal production M

-C-C-
Margarine

Fuel

NH₃
Fertilizers
plastics
Synthesis of Organometallic Complex Hydrides

• Reaction of MCO with OH\(^-\), H\(^-\), or CH\(_2\)CHR\(_2\)
  
  \[
  \begin{align*}
  \text{M(CO)}_n + \text{OH}^- & = \text{M(CO)}_{n-1}(\text{COOH})^- = \text{HM(CO)}_{n-1}^- + \text{CO}_2 \\
  \text{M(CO)}_n + \text{H}^- & = \text{M(CO)}_{n-1}(\text{C(=O)H})^- = \text{HM(CO)}_{n-1}^- + \text{CO} \\
  \text{M(CO)}_n\text{CH}_2\text{CHR}_2 & = \text{HM(CO)}_{n-1}^- + \text{CH}_2\text{=CR}_2 + \text{CO}
  \end{align*}
  \]

• Protonation of MCO anion*
  
  \[
  \begin{align*}
  \text{M(CO)}_n^- + \text{H}^+ & = \text{M(CO)}_n\text{H}
  \end{align*}
  \]

• Hydrogenation of MCO dimer**: 
  
  \[
  \begin{align*}
  \text{M}_2(\text{CO})_{2n} + \text{H}_2 & = \text{M(CO)}_n\text{H}
  \end{align*}
  \]

• Oxidative addition of H\(_2\) to (typically) d\(^8\) metal
  
  \[
  \begin{align*}
  \text{M(PR}_3)_3\text{X} + \text{H}_2 & = \text{M(CO)}_n\text{X(H)}_2
  \end{align*}
  \]

* Oxidative addition of a proton. If a dianion, the resultant MCO hydride will be anionic and may react as a hydride transfer reagent.

** The resultant neutral hydride may have acidic characteristics (i.e., the hydrogen may be removed by a base (reductive deprotonation)
7 $[(\mu-\text{H})\text{W}_2(\text{CO})_{10}]^-$

8 $[\text{ReH}_9]^{2-}$

12 $[\text{Ru(H)}_2(\text{H}_2)(\text{PCyp}_3)_2]$, Cyp = cyclo-\text{C}_5\text{H}_9

9 $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$, Ph = C$_6$H$_5$

10 $[\text{IrCl(H)}_2\text{CO(PPh}_3)_2]$

11 $[\text{W(CO)}_3(\text{H}_2)(\text{PPr}_3)_2]$
Properties of the M-H functionality

• Stereochemically active

• M-H distance range (3d transition metals): 1.5 - 1.7 Å

• M-H stretch: 2100 – 1600 cm⁻¹

• M-H hydride resonance: typically upfield, -1 to -20 ppm, but little correlation with electron density

• M-H Bond Dissociation Energy: 60 -100 kcal/mol (Contrast M-C BDE of ca. 26-30 kcal/mol)

• Homolytic cleavage can initiate radical chain reactions

• Acid/Base character: Varies. HCo(CO)₄ is strong acid, pKₐ <1; HFe(CO)₄⁻ is weak; Cp₂W(H)₂ forms Lewis Base/Acid adduct with AlMe₃.

• Proton loss is slow as in carbon-based acids.
# Acidity of MCO Hydrides

$$\text{HM(CO)}_n + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{M(CO)}_n^-$$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{HCo(CO)}_4$</td>
<td>~2</td>
</tr>
<tr>
<td>$\text{HCo(CO)}_3\text{PPh}_3$</td>
<td>$1 \times 10^{-7}$</td>
</tr>
<tr>
<td>$\text{HMn(CO)}_5$</td>
<td>$8 \times 10^{-8}$</td>
</tr>
<tr>
<td>$\text{HRe(CO)}_5$</td>
<td>very weak</td>
</tr>
<tr>
<td>$\text{H}_2\text{Fe(CO)}_4$</td>
<td>$3 \times 10^{-5}$ ; $1 \times 10^{-14}$</td>
</tr>
<tr>
<td>$\text{CpCr(CO)}_3\text{H}$</td>
<td>$10^{-13.3}$</td>
</tr>
<tr>
<td>$\text{CpMo(CO)}_3\text{H}$</td>
<td>$10^{-13.9}$</td>
</tr>
<tr>
<td>$\text{CpW(CO)}_3\text{H}$</td>
<td>$10^{-16.1}$</td>
</tr>
</tbody>
</table>
### Metal Carbonyl Anions: Nucleophilicity

\[
\{M\}CO^- + RX \rightarrow RM(CO) + X^-
\]

\[
\text{Rate} = k [MCO][RX]
\]

<table>
<thead>
<tr>
<th>Anion</th>
<th>CN Anion</th>
<th>Product</th>
<th>CN</th>
<th>Relative nucleophilicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpFe(CO)$_2$</td>
<td>5</td>
<td>CpFe(CO)$_2$R</td>
<td>6</td>
<td>7.0 x 10$^6$</td>
</tr>
<tr>
<td>CpRu(CO)$_2$</td>
<td>5</td>
<td>CpRu(CO)$_2$R</td>
<td>6</td>
<td>7.5 x 10$^6$</td>
</tr>
<tr>
<td>CpNi(CO)$^-$</td>
<td>4</td>
<td>CpNi(CO)R</td>
<td>5</td>
<td>5.5 x 10$^6$</td>
</tr>
<tr>
<td>Ru(CO)$_5$</td>
<td>5</td>
<td>Ru(CO)$_5$R</td>
<td>6</td>
<td>2.5 x 10$^4$</td>
</tr>
<tr>
<td>CpW(CO)$_3$</td>
<td>6</td>
<td>CpW(CO)$_3$R</td>
<td>7</td>
<td>~500</td>
</tr>
<tr>
<td>Mn(CO)$_5$</td>
<td>5</td>
<td>Mn(CO)$_5$R</td>
<td>6</td>
<td>77</td>
</tr>
<tr>
<td>CpMo(CO)$_3$</td>
<td>6</td>
<td>CpMo(CO)$_3$R</td>
<td>7</td>
<td>67</td>
</tr>
<tr>
<td>CpCr(CO)$_3$</td>
<td>6</td>
<td>CpCr(CO)$_3$R</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>Co(CO)$_4$</td>
<td>4</td>
<td>RCo(CO)$_4$</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>V(CO)$_6$</td>
<td>6</td>
<td>RV(CO)$_6$</td>
<td>7</td>
<td>&lt;&lt; 1</td>
</tr>
<tr>
<td>Fe(CO)$_4^{2-}$</td>
<td>4</td>
<td>RFe(CO)$_4^{2-}$</td>
<td>5</td>
<td>&gt;&gt; 7.0 x 10$^6$</td>
</tr>
</tbody>
</table>
Another electron rich metal center: Also reacts with Organic Electrophiles: Vaska’s Complex
The M-H Bond Functionality: Reactivity

- **Formal reduction of M oxidation state by 2; electron withdrawing ligands stabilize M oxidation state is unchanged; electron donating ligands stabilize**
  - M reduced by 1; can yield H\(_2\) or initiate radical rxns
  - M oxidation state is unchanged; electron donating ligands stabilize
# Nucleophilicity/Hydricity of Anionic MCO Hydrides

## Table I. Rate Constants for the Reaction of \([\text{PPN}]\text{HW(CO)}_5\) with RX in THF Solution at 26.0 °C

<table>
<thead>
<tr>
<th>RX</th>
<th>(k_2 \times 10^3) s(^{-1}) M(^{-1})</th>
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<tr>
<td>(n)-C(_4)H(_9)I</td>
<td>&gt;10</td>
<td>2-C(_4)H(_9)Br</td>
<td>1.79 (± 0.05)</td>
</tr>
<tr>
<td>(n)-C(_4)H(_9)Br</td>
<td>3.31 (± 0.13)</td>
<td>(t)-C(_4)H(_9)Br</td>
<td>2.81 (± 0.16)</td>
</tr>
<tr>
<td>(n)-C(_4)H(_9)Cl</td>
<td>(b)</td>
<td>1-bromoadamantane</td>
<td>0.268 (± 0.014)</td>
</tr>
<tr>
<td>C(_6)H(_5)CH(_2)Cl</td>
<td>1.68 (± 0.09)</td>
<td>C(_6)H(_5)Br</td>
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<tr>
<td>C(_6)H(_5)COCl</td>
<td>&gt;10</td>
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<td>&gt;10</td>
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\(^a\) Reactions were run under pseudo-first-order conditions with RX in 20-fold excess.  \([\text{HW}^-]\) = 0.005 M. Errors calculated at 90% confidence limit. \(^b\) No reaction.
Hydride Transfer Reactivity

\[
\text{HM(CO)}_n^- + \text{RX} \rightarrow \text{XM(CO)}_n^- + \text{RH}
\]

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*a* Reactions were run under pseudo-first-order conditions with RX in 20-fold excess. [HW\(^-\)] = 0.005 M. Errors calculated at 90% confidence limit. \( b \) No reaction.

**Chart I. Reactivity of Anionic Metal Carbonyl Hydrides**

As Established for the Reaction

\[
\text{[M]}^+ + \text{RX} \rightarrow \text{[M]}X^- + \text{RH}^a
\]

For \( R = 1^\circ \) \((n\)-BuBr\)

\( cis\)-HW(CO)\(_4\)P(OMe)\(_3\)\(^-\) > \( cis\)-HCr(CO)\(_4\)P(OMe)\(_3\)\(^-\) > \sim 50\)

\( HW(CO)_5^- > CpV(CO)_5H^- > HCr(CO)_5^- > 3.31 (± 0.13) 2.20 (± 0.06) 1.79 (± 0.05) \)

\( HRu(CO)_5^- >> HFe(CO)_5^- 1.0 \)

For \( R = 3^\circ \) \((t\)-BuBr\)

\( HCr(CO)_5^- > HW(CO)_5^- > cis\)-HCr(CO)\(_4\)P(OMe)\(_3\)\(^-\) > 3.17 (± 0.08) 2.81 (± 0.16) 0.81 (± 0.05) \)

\( CpV(CO)_5H^- > cis\)-HW(CO)\(_4\)P(OMe)\(_3\)\(^-\) >> HFe(CO)_5^- 0.33 (± 0.03) 0.21 (± 0.01) \)

*a* Values cited are second-order rate constants, \( k_2 \times 10^3\) s\(^{-1}\) M\(^{-1}\), measured in THF solution at 26.0 °C for bis(triphenylphosphine)nitrogen(1+) salts of the hydrides. Errors calculated at the 90% confidence limit. \( b \) No reaction.

*Organometallics, 1984, 3, 646*
Suppose one protonates the anionic metal hydride of \( \text{HW(CO)}_5^- \). Is it possible that the resultant \( \text{H}_2 \) would remain bound to the metal?

Heinekey, JACS, 2005, 850-851;
Heinekey, JACS, 2006, 2615-2620
The $\eta^2$-Dihydrogen as Ligand Story

Figure 1. Geometry of the W(CO)$_3$(P-\textit{i}-Pr)$_3$(\textit{\eta}^2-H$_2$) molecule with hydrogen atoms of the P-\textit{i}-Pr$_3$ groups omitted for clarity. The positions of the two hydrogen atoms shown were derived from neutron data while heavy-atom positions are from $-100(5)$ °C X-ray data.

The $\eta^2$-H$_2$ Complexes

- Typically d$^6$, Oh structures of Cr$^0$, Mo$^0$, W$^0$, Fe$^{II}$, Ru$^{II}$, Ir$^{III}$.

- Bonding: Delicate Balance Required for Stability

$\sigma$ - donor  $\sigma^*$ acceptor  $\text{M}^{2+}(\text{H}^-)_2$

- Examples of $\eta^2$-H$_2$ complexes

Kubas, LANL

Morris, U. Toronto

Crabtree, Yale
Every Molecule Has a Story: The $\eta^2$-H$_2$ Complexes

- stability towards H$_2$ dissociation
- oxidative addition to dihydride

Kubas, LANL

- strong acid
- CNH ligand

Morris, U. Toronto

- resonance forms
- H/D exchange

Crabtree, Yale
Homogeneous Catalysis: Hydrogenation of Alkenes: Wilkinson's catalyst and (one of several versions of) the mechanism.