Metal Hydride Complexes

• Main group metal hydrides play an important role as reducing agents (e.g. LiH, NaH, LiAlH₄, LiBH₄).
• The transition metal M-H bond can undergo insertion with a wide variety of unsaturated compounds to give stable species or reaction intermediates containing M-C bonds.
• They are not only synthetically useful but are extremely important intermediates in a number of catalytic cycles and also in battery technologies.
Transition Metal Hydride Preparation

1. Protonation
   - requires an electron rich basic metal center

   $\text{[Fe(CO)}_4\text{]}^{2-} + \text{H}^+ \rightarrow \text{[HFe(CO)}_4\text{]}^- + \text{H}^+$
   $\rightarrow \text{H}_2\text{Fe(CO)}_4$

   $\text{Cp}_2\text{WH}_2 + \text{H}^+ \rightarrow \text{[Cp}_2\text{WH}_3\text{]}^+$

1. From Hydride donors
   - main group metal hydrides are typically used as donors.

   $\text{WCl}_6 + \text{LiBEt}_3\text{H} + \text{PR}_3 \rightarrow \text{WH}_6(\text{PR}_3)_3$
Transition Metal Hydride Preparation

1. Protonation
   - requires an electron rich basic metal center

   ![Reaction Diagram]

2. From Hydride donors
   - main group metal hydrides are typically used as donors.

   \[
   \text{WCl}_6 + \text{LiBEt}_3\text{H} + \text{PR}_3 \rightarrow \text{WH}_6(\text{PR}_3)_3
   \]
3. From $\text{H}_2$
   - via oxidative addition
   - requires a coordinatively unsaturated metal center

$$\text{IrCl}(\text{CO})(\text{PPh}_3)_2 + \text{H}_2 \rightarrow \text{IrH}_2\text{Cl}(\text{CO})(\text{PR}_3)_2$$

3. From a ligand (β-elimination)

$$\text{RuCl}_2(\text{PPh}_3)_3 + \text{KOCCHMe}_2 + \text{PPh}_3 \rightarrow$$

$$\text{RuH}_2(\text{PPh}_3)_4 + \text{Me}_2\text{CO} + \text{KCl}$$

$$\text{Cr}(\text{CO})_6 + \text{OH}^- \rightarrow [\text{Cr}(\text{CO})_5(\text{COOH})]^- \xrightarrow{-\text{CO}_2}$$

$$[\text{CrH}(\text{CO})_5]^- \xrightarrow{\text{Cr}(\text{CO})_6, -\text{CO}} [\text{(CO)}_5\text{Cr}-\text{H}-\text{Cr}(\text{CO})_5]^-$$
3. From H₂
   - via oxidative addition
   - requires a coordinatively unsaturated metal center

\[
\begin{array}{c}
\text{Ph}_3\text{P} \quad \text{Ir} \quad \text{Cl} \\
\text{OC} \quad \text{PPh}_3
\end{array}
\quad \xrightarrow{\text{H}_2} \quad
\begin{array}{c}
\text{Ph}_3\text{P} \quad \text{Ir} \quad \text{H} \\
\text{OC} \quad \text{PPh}_3 \quad \text{Cl}
\end{array}
\]

oxidative addition

3. From a ligand (β-elimination)

\[
\begin{array}{c}
\text{Ph}_3\text{P} \quad \text{Ru} \quad \text{Cl} \\
\text{Cl} \quad \text{PPh}_3
\end{array}
\quad +
\quad \begin{array}{c}
\text{O}^- \quad \text{K}^+ \\
\text{H}
\end{array}
\quad +
\quad 2\text{PPh}_3
\quad \rightarrow
\begin{array}{c}
\text{Ph}_3\text{P} \quad \text{Ru} \quad \text{H} \\
\text{H} \quad \text{PPh}_3 \quad \text{PPh}_3
\end{array}
\quad +
\quad \begin{array}{c}
\text{O} \\
\text{KCl}
\end{array}
\]

4. From a ligand (decarboxylation)

\[
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{OC} \quad \text{CO} \quad \text{CO}
\end{array}
\quad +
\quad \text{OH}^-
\quad \rightarrow
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO}
\end{array}
\quad +
\quad \begin{array}{c}
\text{CO}_2 \\
\text{Cr} \quad \text{CO}
\end{array}
\quad \rightarrow
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO} \quad \text{H}
\end{array}
\quad +
\quad \begin{array}{c}
\text{CO}_2 \\
\text{Cr} \quad \text{CO}
\end{array}
\quad \rightarrow
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO} \quad \text{H}
\end{array}
\quad +
\quad \begin{array}{c}
\text{Cr} \quad \text{CO}
\end{array}
\quad +
\quad \begin{array}{c}
\text{CO}_2
\end{array}
\]

\[
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO}
\end{array}
\quad +
\quad \text{Cr} \quad \text{CO}
\quad \rightarrow
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO}
\end{array}
\quad +
\quad \begin{array}{c}
\text{CO}_2
\end{array}
\]

\[
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO}
\end{array}
\quad +
\quad \text{Cr} \quad \text{CO}
\quad \rightarrow
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO}
\end{array}
\quad +
\quad \begin{array}{c}
\text{CO}_2
\end{array}
\]

\[
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO}
\end{array}
\quad +
\quad \text{Cr} \quad \text{CO}
\quad \rightarrow
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO}
\end{array}
\quad +
\quad \begin{array}{c}
\text{CO}_2
\end{array}
\]

\[
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO}
\end{array}
\quad +
\quad \text{Cr} \quad \text{CO}
\quad \rightarrow
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO}
\end{array}
\quad +
\quad \begin{array}{c}
\text{CO}_2
\end{array}
\]

\[
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO}
\end{array}
\quad +
\quad \text{Cr} \quad \text{CO}
\quad \rightarrow
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO}
\end{array}
\quad +
\quad \begin{array}{c}
\text{CO}_2
\end{array}
\]

\[
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO}
\end{array}
\quad +
\quad \text{Cr} \quad \text{CO}
\quad \rightarrow
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO}
\end{array}
\quad +
\quad \begin{array}{c}
\text{CO}_2
\end{array}
\]

\[
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO}
\end{array}
\quad +
\quad \text{Cr} \quad \text{CO}
\quad \rightarrow
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO}
\end{array}
\quad +
\quad \begin{array}{c}
\text{CO}_2
\end{array}
\]

\[
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO}
\end{array}
\quad +
\quad \text{Cr} \quad \text{CO}
\quad \rightarrow
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO}
\end{array}
\quad +
\quad \begin{array}{c}
\text{CO}_2
\end{array}
\]

\[
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO}
\end{array}
\quad +
\quad \text{Cr} \quad \text{CO}
\quad \rightarrow
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO}
\end{array}
\quad +
\quad \begin{array}{c}
\text{CO}_2
\end{array}
\]

\[
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO}
\end{array}
\quad +
\quad \text{Cr} \quad \text{CO}
\quad \rightarrow
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO}
\end{array}
\quad +
\quad \begin{array}{c}
\text{CO}_2
\end{array}
\]

\[
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO}
\end{array}
\quad +
\quad \text{Cr} \quad \text{CO}
\quad \rightarrow
\begin{array}{c}
\text{OC} \quad \text{Cr} \quad \text{CO} \\
\text{CO}
\end{array}
\quad +
\quad \begin{array}{c}
\text{CO}_2
\end{array}
\]
Transition Metal Hydride Reactivity

- Hydride transfer and insertion are closely related

- A metal hydride may have acidic or basic character depending on the electronic nature of the metal involved (and of course its ligand set).

- Early transition metal hydrides tend to carry significant negative charge on the H atom whereas later more electronegative transition metals favour a more positive charge on the H atom (the term Hydride should therefore not be taken literally).

- Reactivity can also depend upon the substrate, e.g. CpW(CO)$_3$H is a H$^+$ donor to simple bases, a H$^+$ donor to toward styrene and a H$^-$ donor to carbonium ions.
• HCo(CO)$_4$ is a strong acid (pK$_a$ ~ 8.5) due to the electron withdrawing effect of the σ-donating, π-accepting CO ligands on the Co(I) center. It is commonly used as a hydroformylation catalyst.
• An example of an isolable late transition metal hydride complex \([(\eta^6\text{-hmb})\text{Ru}^{II}\text{Hbpy}]^+\)
and its aqua derivative \([(\eta^6\text{-hmb})\text{Ru}^{II}\text{(OH}_2\text{)}\text{bpy}]^{2+}\)
(hmb = hexamethylbenzene)

Hayashi et al. J. Am. Chem. Soc., 2003, 125 (47), 14266-14267
Ogo et al. Organometallics, 2002, 21 (14), 2964-2969
• Applied in catalysis to promote ketone reduction e.g. acetone to isopropanol. The formate ion (HCO$_2^-$) is used as a source of H$^-$ with liberation of CO$_2$. 
The same catalyst can be used for reduction of \( \text{CO}_2 \) under the appropriate conditions.
Dihydrogen $\sigma$-complexes

- An electrophile $E^+$ can react with an X-H bond to give a $\sigma$-complex 1, in which the X-H bond acts as a 2e donor. (*not to be confused with $\sigma$-bonding Hydrides*)

- 1a and 1b show two common ways of representing 1. Coordination to $E^+$ alters the chemical properties of the X-H bond and can activate it either for nucleophilic attack at X or deprotonation.

- The X-H bond is always coordinated side-on to $E^+$, as in 1.
• **σ complexes** bind by donation of the X-H σ-bonding electrons in a 2e 3 center bond to the metal.

\[
\begin{align*}
&M\text{H} \\
&X
\end{align*}
\]

• \( X = \text{H, Si, Sn, B, or P} \ldots \text{at least one H must always be present.} \)

• The H atom has a small atomic radius and carries no lone pairs or other substituent's, allowing the hydrogen end of the X-H bond to approach close to the metal and so allow the filled M \( d\pi \) orbital to back-bond relatively strongly onto the lobe of the X-H \( \sigma^* \) orbital that is located on the H atom.
• **The bonding picture for a σ complex.**
  
  a) Only the $\Psi_1$ orbital which bonds over all three centers, is occupied. Occupation of $\Psi_2$ would lead to the opening of one edge of the triangle (nodal plane marked as a dotted line).
  
  b) In an M-(H-X) complex the electrons of the X-H $\sigma$ bond are donated to an empty metal d, orbital. This is analogous to the binding of the lone pair on NH$_3$ to a metal atom.
  
  c) Electron density from the M(d$\pi$) orbital is donated to the X-H $\sigma^*$ orbital (back-donation). This resembles M(d$\pi$) + CO($\pi^*$) back-donation and is unique to transition metal σ complexes.
• An isolable complex must have some backbonding, but **strong back-donation leads to cleavage of the X-H bond by oxidative addition to give an X-M-H complex.**

\[
\begin{align*}
\text{M} + \text{X-H} & \rightarrow \text{M}\leftrightarrow\text{X} \rightarrow \text{M} \rightarrow \text{M} + \text{X-H} \\
\end{align*}
\]

• In contrast, below is a four-electron system, where \(\Psi_2\) must be filled. As this molecular orbital has an antibonding interaction on one side of the triangle, formation of a linear structure is preferred.

\[
\text{B:} \quad \cdots \text{H} \rightarrow \text{A}
\]
• In complexes with weak back-bonding, the length of X-H bond is similar to that in free X-H.

• The acidity and electrophilicity of X-H can be strongly enhanced, however, because **σ** bonding reduces the electron density in the X-H unit.

• Stronger back-donation can lead to σ complexes with elongated X-H bonds and reduced electrophilicity of the X-H group.
Characterization Criteria for Dihydrogen Coordination

- Dihydrogen complexes have been characterized by X-ray, or, much better, neutron diffraction.
- An IR absorption at 2300–2900 cm\(^{-1}\) is assigned to the H–H stretch, but it is not always seen.
- The H\(_2\) resonance appears in the range 0 to \(-10\) δ \textit{in the} \(^1\)H NMR \textit{and is often broad}.
- \textit{The presence of an} H–H(D) \textit{bond is shown by} the H,D coupling constant of 20–34 Hz in the \(^1\)H NMR spectrum of the H–D analog. This compares with a value of 43 Hz for free HD and \(\sim 1\) Hz for classical H–M–D species.
- Coupling to \(^{31}\)P or the metal center normally is not resolved, even at low temperature.
- \(J_{HD}\) \textit{is often unobservable} in fluctional complexes that also contain hydrides.
- Crabtree developed a second criterion: proton relaxation time
- \(T_1\) \textit{was} anticipated to be unusually short (4-100 ms) for H\(_2\) ligands vs \(> 350\) ms for hydrides.
• In prototypical dihydrogen complexes, there are a number of cases where both 6-coordinate dihydrogen and 7-coordinate dihydride structures are reported to exist in dynamic equilibrium, indicating a delicate energetic balance between two quite different structures.

• For example, NMR observations establish that the dihydrogen complex $(\text{PCy}_3)_2\text{W(CO)}_3(\text{H}_2)$ is in equilibrium with the 7-coordinate dihydride complex $(\text{PCy}_3)_2\text{W(CO)}_3\text{H}_2$, with the dihydrogen form predominant.
H–H BOND DISTANCES FROM CRYSTALLOGRAPHY AND NMR

0.74 Å  0.8-0.9 Å  1.0–1.2 Å  1.36 Å  >1.6 Å
true H₂ complex  elongated H₂ complex  hydride
• The H-H distance of 0.82 Å observed by neutron diffraction is little changed from its value in free H$_2$ (0.74Å).

• Since the H-H bonds in most H$_2$ complexes are not stretched, it is not surprising that the activation energy for loss of H$_2$ (more generally X-H) is not usually large.

• Facile loss of X-H can be important in applications to catalysis, for example, because the resulting coordinatively unsaturated intermediates may be very reactive.
• We can also look at $\sigma$ complexes as being derived from the classical adduct $[L_nM(X)(H)]$ in which an attractive interaction between X and H causes these two ligands to approach one another.

• This description is more appropriate for "stretched" $\sigma$ complexes in which the X-H distance is substantially longer than in the free XH molecule.

• Eisenstein et al. have shown how hydridoligands even in classical dihydrides of type $[L_nMH_2]$ have a mutually attractive interaction not present in CH$_4$.

• Attractive interactions between ligands are likely to facilitate reactions such as reductive elimination and insertion - reactions in which two ligands must approach each other to reach the transition state.

• *By stabilizing the transition state for oxidative addition and reductive elimination the activation energy is thus lowered.* This helps explain the special facility of these reactions in transition metal complexes.
• Starting in the early 1980s, the activity in the area of C-H activation led to renewed interest in compounds with C-H-M bridges.

• In their 1983 review, Brookhart and Green directed attention to C-H-M systems, which they named agostic.
“We propose the term “agostic” which will be used to discuss the various manifestations of covalent interactions between carbon-hydrogen groups and transition metal centres in organometallic compounds. The word agostic will be used to refer specifically to situations in which a hydrogen atom is covalently bonded simultaneously to both a carbon atom and to a transition metal atom.”
Agostic Bonds

• The β C–H bond is bound to the metal in a way that suggests that the alkyl is beginning the approach to the transition state for β elimination.

• These agostic alkyls can be detected by X-ray or neutron crystal structural work and by the high-field shift of the agostic H in the proton NMR.

• The lowering of the $J(C,H)$ and $\nu(CH)$ in the NMR and IR spectra, respectively, on binding is symptomatic of the reduced C–H bond order in the agostic system.

• The reason that β elimination does not occur is that the d$^0$ Ti has no electron density to back donate into the $\sigma^*$ orbital of the C–H bond.

• This back donation breaks the C–H bond in the β-elimination reaction, much as happens in oxidative addition.
• Agostic binding of C−H bonds also provides a way to stabilize coordinatively unsaturated species.

• They are also found in transition states for reactions such as alkene insertion/β elimination either by experiment or in theoretical work.
Figure 2. Ortep drawing of $\text{W}($CO$)_3($PCy$_3)_2$ (30% thermal ellipsoids).