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.
$[\text{ReH}_9]\text{K}_2$
Metal Hydride Preparation

1. Protonation (requires an electron rich basic metal center)

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

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

2. From Hydride donors (main group metal hydrides)

\[
\text{WC}l_6 + \text{LiBEt}_3\text{H} + \text{PR}_3 \rightarrow \text{WH}_6(\text{PR}_3)_3
\]
3. From $\text{H}_2$ (via oxidative addition – requires a coordinatively unsaturated metal center)

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

4. From a ligand ($\beta$-elimination)

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

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

$$\text{Cr(CO)}_6 + \text{OH}^- \rightarrow [\text{Cr(CO)}_5(\text{COOH})]^- \rightarrow [\text{CrH(CO)}_5]^- \rightarrow [((\text{CO})_5\text{Cr}−\text{H}−\text{Cr(\text{CO})}_5]^-$$
• Hydride transfer and insertion are closely related

\[
\begin{align*}
\text{Cp}_2^*\text{ZrH}_2 + \text{CH}_2\text{O} & \rightarrow \text{Cp}_2^*\text{Zr(OMe)}_2 \\
\text{Cp}_2\text{ZrHCl} + \text{RCH}=\text{CH}_2 & \rightarrow \text{Cp}_2\text{ZrCl(CH}_2 - \text{CH}_2\text{R)}
\end{align*}
\]

• 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. \(\text{CpW(CO)}_3\text{H} \) is a \( \text{H}^+ \) donor to simple bases, a \( \text{H}^+ \) donor to toward styrene and a \( \text{H}^- \) donor to carbonium ions.
• HCo(CO)$_4$ is a strong acid due to the electron withdrawing effect of the $\sigma$-donating, $\pi$-accepting CO ligands on the Co(I) center.

• With $\sigma$-donating, $\pi$-donating ligands the hydride can become quite basic and reactive towards $H^-$ transfer.

• An example of an isolable late transition metal hydride complex \([\eta^6\text{-hmb})\text{Ru}^{II}\text{Hbpy}]^+\) and its aqua derivative \([\eta^6\text{-hmb})\text{Ru}^{II}(\text{OH}_2)\text{bpy }]^{2+}\) (hmb = hexamethylbenzene)
Applied in catalysis to promote ketone reduction e.g. acetone to isopropanol. The formate ion ($\text{HCO}_2^-$) is used as a source of $\text{H}^-$ with liberation of $\text{CO}_2$. 
The same catalyst can be used for reduction of 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)*

$$
\begin{align*}
X-H & \xrightarrow{E^+} E^+ \xleftarrow{\text{Nu}} \text{Nu-X} + \text{HE} \\
& \xrightarrow{\text{B}} \text{BH}^+ + \text{E-X}
\end{align*}
$$

- 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.

$$
\begin{align*}
\text{E}^- & \xleftarrow{\text{H}} X \xrightarrow{E^+} \text{E}^+ \\
& \xleftarrow{\text{H}} X
\end{align*}
$$

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

\[
\begin{align*}
\text{M} & \quad \sigma^* \\
H & \quad d_\pi \\
X & \\
\end{align*}
\]

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

- The H atom has a small atomic radius and carries no lone pairs or other substituents, 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.

\[
M + X-H \rightarrow M \xleftarrow{\text{X}} H \rightarrow M \xrightarrow{\text{X}} H
\]

• 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.

\[
B : \cdots H \longrightarrow A
\]
• 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 \( \sigma \) bonding reduces the electron density in the X-H unit.
• Stronger back-donation can lead to \( \sigma \) 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 $\delta$ in the $^1$H NMR and is often broad.
- The presence of an H–H(D) bond is shown by the H,D coupling constant of 20–34 Hz in the 1H 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.
- $J_{HD}$ is often unobservable in fluctional complexes that also contain hydrides.
- Crabtree developed a second criterion: proton relaxation time
- $T_1$ 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 $(\text{PCy}_3)_2\text{W}(\text{CO})_3(\text{H}_2)$ is in equilibrium with the 7-coordinate dihydride complex $(\text{PCy}_3)_2\text{W}(\text{CO})_3\text{H}_2$, with the dihydrogen form predominant.

H–H BOND DISTANCES FROM CRYSTALLOGRAPHY AND NMR

H
\[ \rightarrow \]
M
\[ \rightarrow \]
M–H
\[ \rightarrow \]
M
\[ \rightarrow \]
M
\[ \rightarrow \]
M

0.74 Å 0.8–0.9 Å 1.0–1.2 Å 1.36 Å >1.6 Å
true H\(_2\) complex elongated H\(_2\) complex hydride

M
\[ \rightarrow \]
M
\[ \rightarrow \]
M

\[ \sigma^* \]

\[ \sigma \]
• The H-H distance of 0.82 Å observed by neutron diffraction is little changed from its value in free H₂ (0.74Å).

• Since the H-H bonds in most H₂ complexes are not stretched, it is not surprising that the activation energy for loss of H₂ (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 hydrido ligands 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.

![Agostic Bond](image)

- 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 $\text{W(CO)}_3\text{(PCy}_3\text{)}_2$ (30% thermal ellipsoids).