Hydride and dihydrogen are both 2e\(^-\) donors, H\(^-\) (1s\(^2\)) and H\(_2\) (\(\sigma_{1s^2}\))

Hydride complexes are synthesized by:

1. Replace halide with hydride using hydride transfer reagents:

   \[
   \text{LnM-X} \xrightarrow{\text{"H-"}} \text{LnM-H} + \text{X}^- \\
   \text{e.g., LiAlH}_4, \text{NaBH}_4
   \]

2. Heterolytic cleavage of a dihydrogen complex:

   \[
   \text{H-H} \xrightarrow{\text{:B}} [\text{LnM-H}]^- + \text{BH}^+ 
   \]

3. Oxidative-addition of hydrogen to a metal complex:

   \[
   \text{L-Ir}^{\text{III}}\text{Cl} + \text{H}_2 \rightarrow \text{L-Ir}^{\text{III}}\text{Cl} \quad \text{where } L = \text{PR}_3 
   \]

There are some general features of H\(_2\) oxidative-addition:

- cis addition
- 16e\(^-\) complexes or less add H\(_2\) (since 2e\(^-\)s are added to the metal complex)
- bimolecular rate law (rate = k [IrL\(_2\)Cl(CO)] [H\(_2\)])
- \(\Delta H^\ddagger = 11\) kcal/mol (little H–H stretch in the transition state recall that BDE(H\(_2\)) = 104 kcal/mol), and a \(\Delta S^\ddagger = 21\) eu
- rate decreases along the series X\(^-\) = I\(^-\) > Br\(^-\) > Cl\(^-\) (100 : 14 : 0.9)
- little isotope effect, \(k_H / k_D = 1.09\)
For the oxidative-addition reaction, there are two possibilities for the transition state:

1. an H$_2$ intermediate
2. a three-center transition state

Both reaction pathways are viable for oxidative-addition (and the reverse reaction, reductive-elimination).

For some metal complexes, the “arrested” addition product can be isolated—the dihydrogen complex is obtained as a stable species that can be put in a bottle. Kubas first did this in 1984 with the following reaction:
Several observables identify this as an authentic dihydrogen complex vs. a dihydride:

- \(d(H—H) = 0.84 \text{ Å}\) (as measured from neutron diffraction). This distance is near the bond distance of free \(H_2\), \(d(H—H) = 0.7414 \text{ Å}\).
- A symmetric \(H_2\) vibration is observed, \(\nu(H—H) = 2,690 \text{ cm}^{-1}\), as compared to \(\nu(H—H) = 4,300 \text{ cm}^{-1}\) in free \(H_2\).
- \(J_{HD} = 33 \text{ Hz}\) (vs 43 Hz in HD). For a dihydride complex \(J_{HD} \approx \text{ few Hz}\).

There is a delicate balance between a dihydrogen and dihydride complex:

\[
W(CO)_3(PR_3)_2 + H_2 \rightarrow \begin{array}{c}
\text{OC} \\
\text{C} \\
\text{H}
\end{array}
\begin{array}{c}
\text{PR}_3 \\
\text{O}
\end{array}
\]

From dynamic NMR measurements at 300 °C: \(k_1 = 63 \text{ s}^{-1}\) (\(\Delta G^\ddagger = 15.2 \text{ kcal/mol}\))

\(k_{-1} = 12.4 \text{ s}^{-1}\) (\(\Delta G^\ddagger = 16.0 \text{ kcal/mol}\))

Therefore the equilibrium constant is \(K_{eq} = 5.0\).

Ancillary ligands play an important role in determining the energetic balance between the dihydrogen and dihydride complexes. For instance, replacement of the 3 COs in the Mo version of Kubas’ original complex with PR3s furnishes the dihydride as the energetically favored complex.

The delicate balance between dihydrogen and dihydride complex can be understood with orbital comparisons to ethylene complexes. An ethylene complex is balanced.
energetically between a metallocyclopropane (all σ complex) and the olefin π complex.

\[ \text{H} - \text{C} = \text{C} - \text{H} \quad \text{M} \quad = \quad \text{H} - \text{C} = \text{C} - \text{H} \]

σ-bond: filled 2e⁻ π bond donates into empty d_{2z} / p_z

\[ \text{H} - \text{C} = \text{C} - \text{H} \quad \text{M} \quad = \quad \text{H} - \text{C} = \text{C} - \text{H} \]

π-bond: empty π* of ethylene accepts 2e⁻'s from metal dπ orbital

A similar situation arises for H₂ complexes. The frontier ligand orbitals in this case are σ(H₂) and σ*(H₂).

\[ \text{H} - \text{H} \quad \text{H} - \text{H} \]

σ-bond

\[ \text{H} - \text{H} \quad \text{H} - \text{H} \]

π-bond

Note: if metal too electron rich, π-back donation into H₂ σ* orbital will lead to H–H cleavage and hence dihydride formation
More quantitatively,

Thus the M–H$_2$ $\pi$ interaction is important for stabilizing the dihydrogen complex, but too much $\pi$-backbonding will break the H–H bond.
Reactivity

(1) Isomerization

\[ L_nM-H \xrightarrow{-L} L_{n-1}M-H \xrightarrow{+L} \text{insertion} \xrightarrow{\beta-H \text{ elim}} L_{n-1}M \]

or \[ \text{or} \]

\[ \xrightarrow{\beta-H \text{ elim}} \]

(2) Hydrogenation of Alkenes and Alkynes

\[ L = \text{neutral and exchangeable} \]

\[ \text{Ph-} \]

\[ \text{H} \]
(3) Alkene Insertion

\[
\begin{align*}
L_nM & \quad \leftrightarrow \quad L_nM - H \quad \leftrightarrow \quad L_{n-1}M + H \quad \rightarrow \quad L_nM - CH_2CH_3 \\
\end{align*}
\]

\(M - H \approx 60 \text{ kcal/mol} \quad M - C \quad 35-40 \text{ kcal/mol} \)
\(P(C=C) \quad 64 \text{ kcal/mol} \quad C - H \quad 98 \text{ kcal/mol} \)
\(~124 \text{ kcal/mol} \quad 133-138 \text{ kcal mol} \)

\(\Delta H = -9 \text{ to } -14 \text{ kcal/mol} \) (but there is an unfavorable entropic term). Thus the overall process is near thermoneutral and typically forward and reverse reactions are run with equal facility.

(4) Brønsted acid/base chemistry

\[
\begin{align*}
\text{L, L}^\prime & = \text{CO, NO, PR}_3 \\
\end{align*}
\]