

Metal Hydrides

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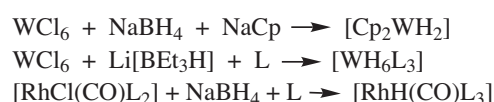
We know that main group hydrides such as LiAlH_4 and NaBH_4 are the common reducing agents used by organic chemists to reduce aldehydes, ketones and carboxylic acids. Transition metal hydrides act as good catalysts for hydrogenation, isomerization, hydroformylation and hydrocyanation of olefins. The coordination modes of the hydride ligand are as follows.

- (i) **Terminal (M-H)** - e.g. $\text{K}_2[\text{ReH}_9]$, $[\text{CoH}(\text{CO})_4]$, *trans* $[\text{PtHCl}(\text{PEt}_3)_2]$.
 - (ii) **Doubly bridging (M-H-M)** or $(\mu_2\text{-H})$ - e.g. $[(\text{OC})_5\text{W}(\mu\text{-H})\text{W}(\text{CO})_5]^-$.
 - (iii) **Triply bridging $(\mu_3\text{-H})$** - It bridges three metals or one triangular face of the tetrahedral metal cluster, e.g. $[\text{Re}_4(\text{CO})_{12}(\mu_3\text{-H})_4]^-$.
 - (iv) **Interstitial** - The H atom is placed at the centre of the metal cluster, e.g. octahedral complex ion, $[\text{HCo}_6(\text{CO})_{15}]^-$.
- A metal hydride exerts a strong *trans*-effect on the opposite ligand (L) and weakens the M–L bond, i.e. it labilises the *trans*-ligand.
 - The proton chemical shift (δ_{H}) of a metal hydride appears in the range of 0 to -25 ppm with respect to TMS. For example, the chemical shift (δ_{H}) of the hydride ligand of $[\text{HW}(\text{Cp})(\text{CO})_3]$, $[\text{HMn}(\text{CO})_5]$, $[\text{H}_2\text{Fe}(\text{CO})_4]$ and $[\text{HCo}(\text{CO})_4]$ are -7.5, -7.5, -11.2 and -10.7, respectively.
 - The IR absorption frequency of the M–H bond, $\nu(\text{M-H})$, appears in the region of 1500-2200 cm^{-1} ; it can be identified by converting it into a M–D group with D_2O . $\nu(\text{M-D}) = \nu(\text{M-H}) \div \sqrt{2}$

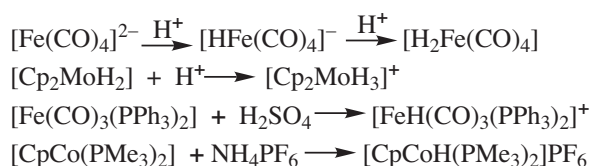
Synthesis of metal hydrides

Metal hydrides can be synthesized in various methods.

Using a hydride source – In order to form a stable metal hydride, stabilizing ligands such as PR_3 , CO and Cp⁻ groups are generally added. L = PPh_3



By protonation with acids - Basic metal centres and metal centres bonded with good electron donating ligands can be easily protonated with acids. Anionic complexes give neutral metal hydrides, while neutral complexes often yield cationic hydrides.



By oxidative addition of H_2 or HY - (Y = X, -CN, -SiR₃, -B(OR)₂, -NR₂, -SR group)

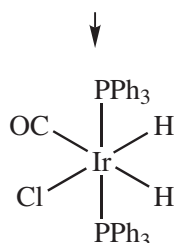
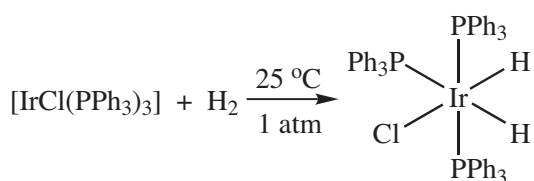
Polyhydrides

Transition metal hydrides containing three or more hydride ligands per metal atom are called multihydrides or polyhydrides. Some examples include $[\text{WH}_6(\text{PR}_3)_3]$, $\text{K}_2[\text{ReH}_9]$, $[\text{ReH}_5(\text{PR}_3)_3]$, $[\text{ReH}_7(\text{PR}_3)_2]$, $[\text{OsH}_4(\text{PR}_3)_3]$, and $[\text{IrH}_3(\text{PR}_3)_3]$. The presence of phosphine or cyclopentadienyl (Cp) ligands tend to stabilize these 18e-complexes. Most of the polyhydrides are fluxional at room temperature.

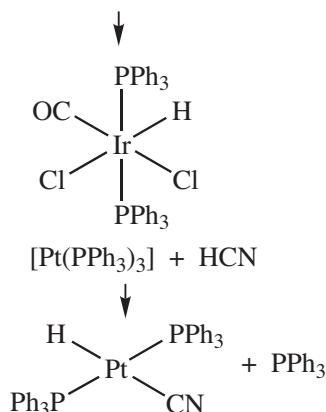
Properties of metal hydrides

- A metal hydride can be a H^+ donor to a base, H atom (H) donor to an olefin, and H^- donor to a cation.
- Acidity of a metal hydride depends upon the other co-ligands. $[\text{HCo}(\text{CO})_4]$ is a strong acid with a pK_a value of zero.

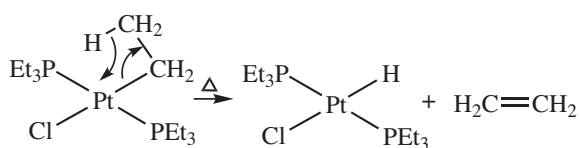
Addition of H₂ gives *cis*-dihydrides.



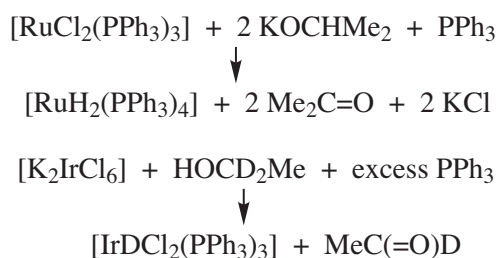
The H₂ addition gives *trans*-products.



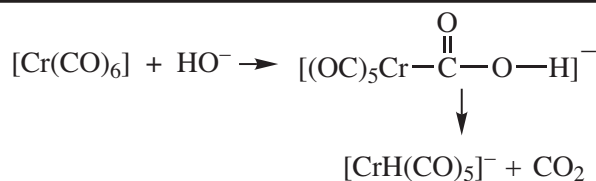
By β -hydride abstraction - Metal alkyls give metal hydrides and olefins, e.g.



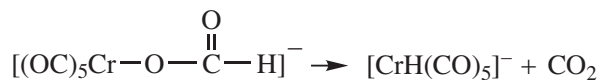
Metal alkoxides give metal hydrides with a loss of a ketone or aldehyde.



By reacting metal carbonyls with HO⁻ - Initially formed hydroxycarbonyl group loses CO₂ molecule to give the metal hydride.



Metal formate loses a CO₂ molecule to give the metal hydride.

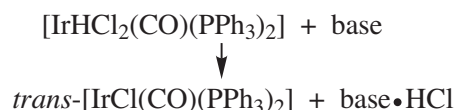


General reactions of metal hydrides

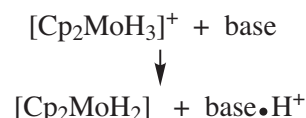
Metal hydrides undergo deprotonation (-H⁺), dehydrohalogenation (-HX), migratory insertion reactions with olefins, and protonation (+H⁺) as given below.

1. Deprotonation and dehydrohalogenation

A metal hydride can be deprotonated by a base such as Et₃N, Bu₃N, pyridine and sodium ethoxide.

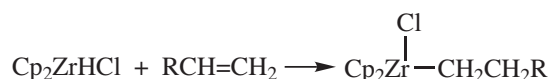


A base can be used to dehydrohalogenate a halogenohydride.

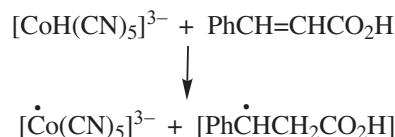


2. Migratory Insertion

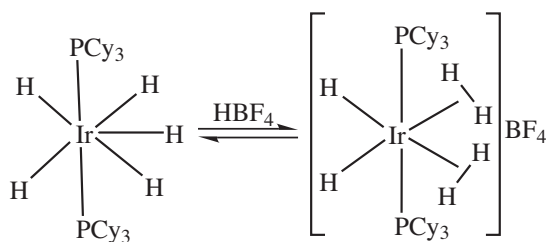
Hydride can migratory insert into an unsaturated molecule (i.e. the reverse of β -hydride abstraction and elimination of an olefin). For example,



3. *Hydrogen atom donation* - The Co(III) complex [CoH(CN)₅]³⁻ transfers a hydrogen atom (H[•]) to the activated double bond of cinnamic acid giving the 17e complex [Co(CN)₅]³⁻.

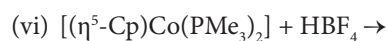
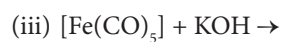


4. Preparation of dihydrogen complexes - HBF_4 reversibly protonates $[\text{IrH}_5(\text{PCy}_3)_2]$ to give $[\text{IrH}_2(\eta^2\text{H}_2)_2(\text{PCy}_3)_2]\text{BF}_4$.



Problems

1. Suggest the product(s) formed from the following reactions.



2. $[(\text{PhCH}_2\text{CH}_2)_2\text{Pt}(\text{OCH}_2\text{CH}_3)(\text{dppe})]$ gives an alkane (**A**), alkene (**B**), alcohol (**C**) and aldehyde (**D**) when it is heated in toluene at 100°C . Identify (**A**), (**B**), (**C**) and (**D**). $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ is a bidentate ligand.