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.* $K_2[ReH_9]$, $[CoH(CO)_4]$, *trans* $[PtHCl(PEt_3)_2]$.

(ii) **Doubly bridging** (M-H-M) or (μ_2-H) - *e.g.* $[(OC)_5W(\mu\text{-}H)W(CO)_5]^-$.

(iii) **Triply bridging** (μ_3-H) - It bridges three metals or one triangular face of the tetrahedral metal cluster, *e.g.* $[Re_4(CO)_{12}(\mu_3\text{-}H)_4]^-$.

(iv) **Interstitial** - The H atom is placed at the centre of the metal cluster, *e.g.* octahedral complex ion, $[HCo_6(CO)_{15}]^-$.

Polyhydrides

Transition metal hydrides containing three or more hydride ligands per metal atom are called multihydrides or polyhydrides. Some examples include $[WH_6(PR_3)_3]$, $K_2[ReH_9]$, $[ReH_5(PR_3)_3]$, $[ReH_7(PR_3)_2]$, $[OsH_4(PR_3)_3]$, and $[IrH_3(PR_3)_3]$. 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 ($H^{\cdot}$) donor to an olefin, and H^- donor to a cation.
- Acidity of a metal hydride depends upon the other co-ligands. $[HCo(CO)_4]$ is a strong acid with a pK_a value of zero.
- 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 $[HW(Cp)(CO)_3]$, $[HMn(CO)_5]$, $[H_2Fe(CO)_4]$ and $[HCo(CO)_4]$ are -7.5, -7.5, -11.2 and -10.7, respectively.
- The IR absorption frequency of the M—H bond, ν(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. $\nu(M—D) = \nu(M—H) \div \sqrt{2}$

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

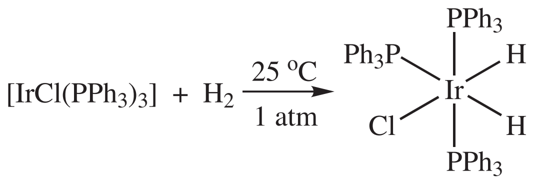
$$WCl_6 + NaBH_4 + NaCp \rightarrow [Cp_2WH_2]$$
$$WCl_6 + Li[BEt_3H] + L \rightarrow [WH_6L_3]$$
$$[RhCl(CO)L_2] + NaBH_4 + L \rightarrow [RhH(CO)L_3]$$

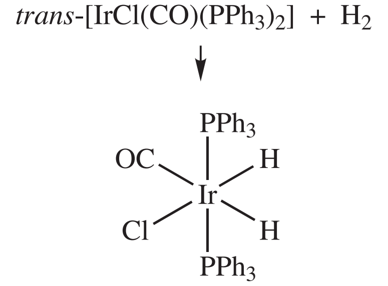
By protonation with acids - Basic metal centres and metal centres bonded with good electron donating ligands can be easily protonated with acids. Anionic complexes give neutral metal hydrides, while neutral complexes often yield cationic hydrides.

$$[Fe(CO)_4]^{2-} \xrightarrow{H^+} [HFe(CO)_4]^- \xrightarrow{H^+} [H_2Fe(CO)_4]$$
$$[Cp_2MoH_2] + H^+ \rightarrow [Cp_2MoH_3]^+$$
$$[Fe(CO)_3(PPh_3)_2] + H_2SO_4 \rightarrow [FeH(CO)_3(PPh_3)_2]^+$$
$$[CpCo(PMe_3)_2] + NH_4PF_6 \rightarrow [CpCoH(PMe_3)_2]PF_6$$

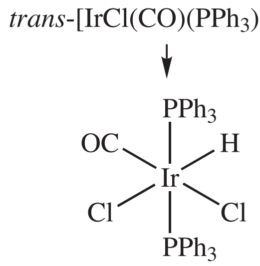
By oxidative addition of H_2 or HY - (Y= X, -CN, $-SiR_3$, $-B(OR)_2$, $-NR_2$, -SR group)

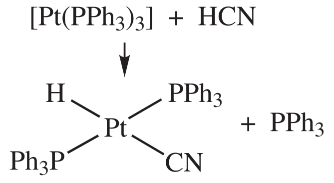
Addition of H_2 gives *cis*-dihydrides.



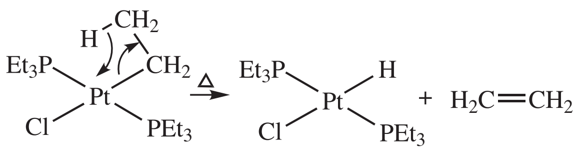


The HY addition gives *trans*-products.





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

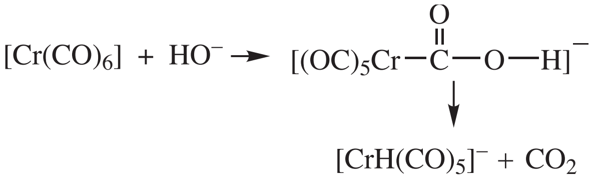


Metal alkoxides give metal hydrides with a loss of a ketone or aldehyde.

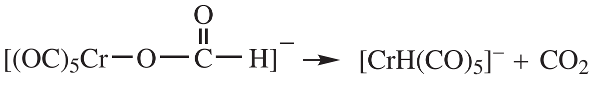
$$[RuCl_2(PPh_3)_3] + 2\ KOCHMe_2 + PPh_3 \downarrow [RuH_2(PPh_3)_4] + 2\ Me_2C{=}O + 2\ KCl$$

$$[K_2IrCl_6] + HOCD_2Me + \text{excess } PPh_3 \downarrow [IrDCl_2(PPh_3)_3] + MeC({=}O)D$$

By reacting metal carbonyls with HO⁻ - Initially formed hydroxycarbonyl group loses CO_2 molecule to give the metal hydride.



Metal formate loses a CO_2 molecule to give the metal hydride.



$$[(OC)_5Cr{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H]^{-} \rightarrow [CrH(CO)_5]^{-} + CO_2$$

General reactions of metal hydrides

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

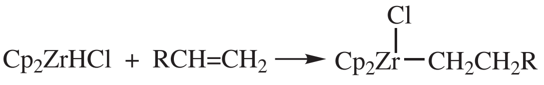
1. *Deprotonation and dehydrohalogenation*
   A metal hydride can be deprotonated by a base such as Et_3N, Bu_3N, pyridine and sodium ethoxide.

$$[IrHCl_2(CO)(PPh_3)_2] + \text{base} \downarrow trans\text{-}[IrCl(CO)(PPh_3)_2] + \text{base}{\bullet}HCl$$

   A base can be used to dehydrohalogenate a halogenohydride.

$$[Cp_2MoH_3]^+ + \text{base} \downarrow [Cp_2MoH_2] + \text{base}{\bullet}H^+$$

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,

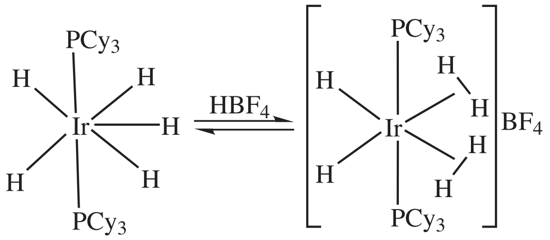


$$Cp_2ZrHCl + RCH{=}CH_2 \longrightarrow Cp_2\overset{\overset{\displaystyle Cl}{|}}{Zr}{-}CH_2CH_2R$$

3. *Hydrogen atom donation* - The Co(III) complex $[CoH(CN)_5]^{3-}$ transfers a hydrogen atom ($H^{\cdot}$) to the activated double bond of cinnamic acid giving the 17e complex $[{}^{\cdot}Co(CN)_5]^{3-}$.

$$[CoH(CN)_5]^{3-} + PhCH{=}CHCO_2H \downarrow [\dot{C}o(CN)_5]^{3-} + [Ph\dot{C}HCH_2CO_2H]$$

4. *Preparation of dihydrogen complexes* - HBF_4 reversibly protonates $[IrH_5(PCy_3)_2]$ to give $[IrH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]BF_4$.



Problems

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

(i) $[(\eta^5\text{-}C_5Me_5)ZrHCl] + HC{\equiv}CH \rightarrow$

(ii) $[(\eta^5\text{-}C_5Me_5)WH(CO)_3] + HBF_4 \rightarrow$

(iii) $[Fe(CO)_5] + KOH \rightarrow$

(iv) $[RhEt(CO)_3] \rightarrow$ (heat)

(v) $[Co_2(CO)_8] + H_2 \rightarrow$

(vi) $[(\eta^5\text{-}Cp)Co(PMe_3)_2] + HBF_4 \rightarrow$

2. $[(PhCH_2CH_2)Pt(OCH_2CH_3)(dppe)]$ 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**). dppe = $Ph_2PCH_2CH_2PPh_2$ is a bidentate ligand.

Student Corner

Hydrogenation of olefins

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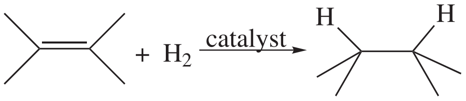
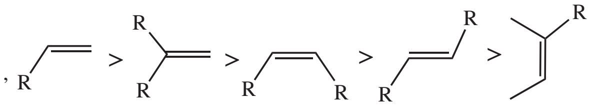
Hydrogenation of olefins is one of the simplest reactions, where two hydrogen atoms add across a carbon-carbon double bond to give an alkane.



The ease of this reaction decreases with the increasing steric hindrance at the olefin as shown below.



Heterogeneous hydrogenation catalysts

They are present in a phase different from that of the reactants. Here, the reaction takes place at the surface of an insoluble solid catalyst. Some examples are 1% platinum on activated carbon or alumina, 5% ruthenium on activated carbon, and Raney nickel. When homogeneous catalysts are chemically attached to a solid surface, they are called heterogenized homogeneous catalysts.

Homogeneous hydrogenation catalysts

The activity of homogeneous catalysts can be adjusted by changing the type and size of the ligands around the metal. Some simple homogeneous hydrogenation catalysts or precursors include: $[M_2(cod)_2Cl_2]$ (M = Rh, Ir), $[Ir(cod)(pyridine)(PPh_3)]PF_6$, $[RhClL_3]$, $[RuHClL_3]$ and $[RhH(CO)L_3]$, where L = PPh_3 and cod = cyclooctadiene.

Asymmetric hydrogenation can be achieved by using chiral ligands such as DIOP, binaphthyl (BINAP), ferrocenyl (PPFA), phosphinooxazoline (PHOX) ligands *etc*. Some commercial processes of asymmetric hydrogenation are the synthesis of (i) L-Dopa (dihydroxy phenylalanine), used in the treatment of Parkinson's disease; (ii) the pain reliever Naproxen; (iii) N-acetyl L phenylalanine, the synthetic precursor to the sweetener aspartame *etc*.

Sources of hydrogen

Hydrogenation is one of the most extensively studied reactions using homogeneous catalysts. Dihydrogen (H_2), BH_4^-, HX and HCO_2H are the sources of hydrogen. Here, we will consider reduction reactions of olefins with **dihydrogen** in the presence of a suitable catalyst.

Dihydrogen can be activated *via* three methods. They are, (i) **oxidative addition** (ii) **heterolytic activation** & (iii) **homolytic activation**. General reactions for these