Hydride and Dihydrogen Ligands

- First Hydride Complex = $[FeH_2(CO)_4]$ – Hieber, 1931
- First Dihydrogen Complex = $[Mo(H_2)(CO)_3(PCy_3)_2]$ – Kubas, 1983

Characterization of Metal-Hydrides:

- ^1H NMR → 0 to –60 ppm for non d^0-complexes (0 to +10 for d^0)
  → coupling to M (*e.g.* Pt or Rh) or co-ligands (*e.g.* PR_3 can be useful)
  → T_1 (dipole-dipole) α r^6 → > 100 ms
- IR → ν(M-H) = 2200-1500 cm^{-1}, but can be weak (therefore unreliable) – deuterium labeling can help
- X-Ray → Hydrides difficult to detect and M–H underestimated.
- Neutron Diffraction → V. Useful, but not readily available; large crystals required (1 mm^3 vs 0.01 mm^3)

Early TM Hydrides = hydridic

$[Cp^*_2ZrH_2]$

Late TM Hydrides = can be quite acidic (especially with low valent metals)

$[H_2Fe(CO)_4]$ - pKa 4.4

$[HCo(CO)_4]$ - pKa <0.4

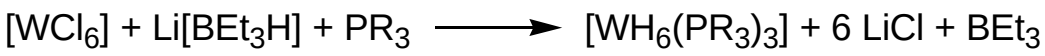
$MeCO_2H$ - pKa 4.75

F_3CCO_2H - pKa 0.2

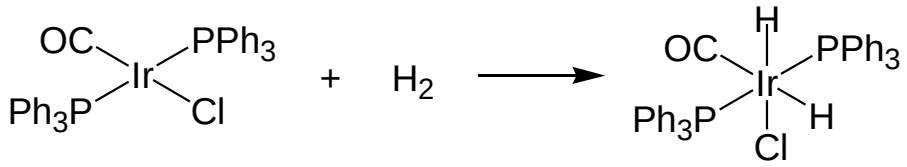
Synthesis of Hydride and Dihydrogen Ligands

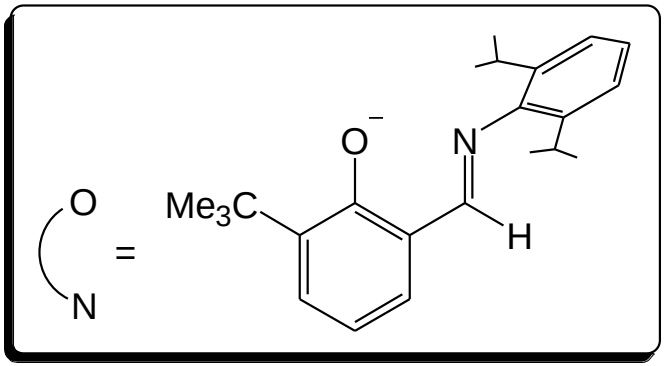
Protonation :

From H^- donors:

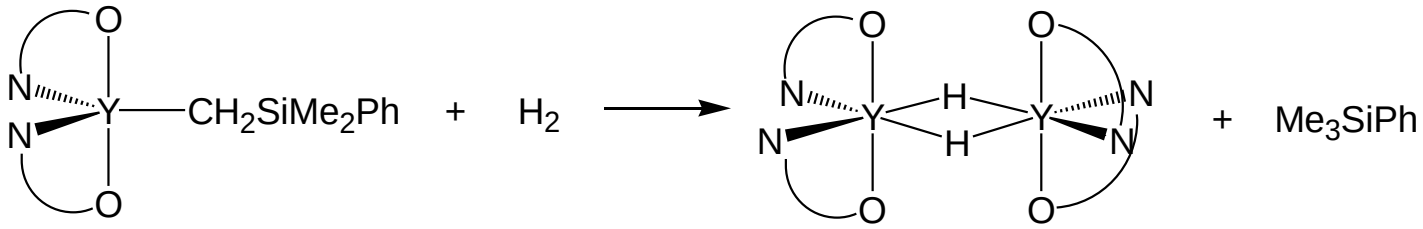


By Oxidative Addition (e.g. from H_2 or $HSiR_3$ or HBR_2)



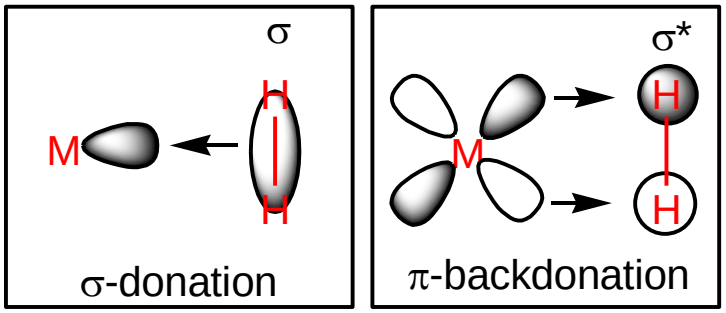


By σ-Bond Metathesis (typically early TM alkyl + H_2)



Hydride and Dihydrogen Ligands

- $M(H_2)$ = a type of σ-complex
- ν(H-H) = 2300-2900 cm^{-1} but often weak
- ^1H NMR = 0 to –10 ppm (often broad)
- T_1(dipole-dipole) α r^6 → <40 ms



- $^1J_{H,D}$ for M(HD) = 20-30 Hz, versus 43 Hz for free HD and ~1Hz for M(H)(D)
- Both interactions weaken the H–H bond
- Typical H-H distances in M–(H_2) complexes are 84-90 pm (*vs* 74 pm in free H_2)
- Metals capable of strong π-backdonation and with an accessible oxidation state 2 units higher (e.g. Ir^{I} → Ir^{III}) can break the H–H bond to give a dihydride.