**Hydride Ligands**



Hydride nomenclature comes from the NMR behavior:

M-H ~ 5 to 25 ppm ***for d1  d9 metals!!***

*upfield shift indicates “hydridic” chemical nature*

HCo(CO)4 1H NMR = 10.7 ppm

***BUT:*** HCo(CO)4  H+ + Co(CO)4

*strong acid in H2O, MeOH*

*similar to HCl !!*

***d0*** Cp\*2ZrH2  = + 7.5 ppm

***d10*** [HCu{P(*p*-tolyl)3}]6  = + 3.5 ppm

The presence of partially filled ***d*** orbitals on the transition metal has a considerable shielding effect (moves the chemical shift of the NMR resonance to more negative ppm) on the hydride 1H NMR chemical shift position.

**IR Spectra:** M-H 2200 - 1600 cm1 } can be very weak or absent

M2(-H) 1600 - 800 cm1 } broader (weak or absent)

Late Transition Metals (especially cationic): tend to be more **“protic”**

Early Transition Metals: tend to be more **“hydridic”**

(plenty of exceptions; charge on complex very important)

**pK*a* Values for Transition Metal Hydrides in Various Solvents**

|  |  |  |  |
| --- | --- | --- | --- |
|  |  | Solvent |  |
| Metal Hydride Complex | H2O | MeOH | CH3CN |
| HV(CO)6 | strong acid |  |  |
| HV(CO)5(PPh3) | 6.8 |  |  |
| CpCrH(CO)3 |  | 5.4 | 13.3 |
| CpMoH(CO)3 |  | 6.2 | 13.9 |
| Cp\*MoH(CO)3 |  |  | 17.1 |
| CpWH(CO)3 |  | 8.0 | 16.1 |
| CpWH(CO)2(PMe3) |  |  | 26.6 |
| HMn(CO)5 |  |  | 15.1 |
| HRe(CO)5 |  |  | ~21 |
| H2Fe(CO)4 | 4.0 |  | 11.4 |
| H2Ru(CO)4 |  |  | 18.7 |
| H2Os(CO)4 |  | 15.2 | 20.8 |
| CpFeH(CO)2 |  |  | 19.4 |
| Cp\*FeH(CO)2 |  |  | 26.3 |
| CpRuH(CO)2 |  |  | 20.2 |
| HCo(CO)4 | strong acid | strong acid | 8.4 |
| HCo(CO)3{P(OPh)3} | 5.0 |  | 11.4 |
| HCo(CO)3(PPh3) | 7.0 |  | 15.4 |
| HNi[P(OMe)3]4+ |  | 1.5 | 12.3 |
| HPd[P(OMe)3]4+ |  | 1.0 | 8.0 |
| HPt[P(OMe)3]4+ |  | 10.2 | 18.5 |
| H4Ru4(CO)12 |  | 11.7 |  |
| H4Os4(CO)12 |  | 12.3 |  |
| H2Ru4(CO)13 |  | 11.1 |  |

**Problem: Which of the following pairs of metal hydrides is the most acidic (lowest pKa )?**

**a) HRh(CO)(PEt3)2 -or- HCo(CO)(PPh3)2**

**b) HMn(CO)5 -or- HRe(CO)5**

**c) Cp2V(H)(NCMe) -or- [Ru(C6H6)(CO)2(H)]+**

**d) [HNi(CO)2(dmpe)]+ -or- [HPt(CO)2{P(OMe)3}2]+**

**e) CpFe(H)(CO)2 -or- CpOs(H)(CO)2**

Structural Features:

Hydride is the smallest ligand and as a result, M-H distances are typically quite short: 1.8 to about 1.5 Å, depending on the metal. Periodic trends are followed, as noted for phosphine-metal distances. Hydrides can be quite difficult to observe via X-ray diffraction (the most common technique used to determine structures) due to the very small number of electrons on the hydride vs. adjacent atoms, especially the metal. Therefore, neutron diffraction studies are considered best for accurately locating and identifying hydrides on metal centers.

Synthesis: For moderately electron-rich metals with 2 or more d electrons, the oxidative addition of molecular H2 to the metal center is quite common and very important for catalysis:

**MLn + H2  H2MLn**



Occasionally, if the metal center has the right amount of electron density (not too much, not too little) molecular H2 complexes can form:



W(H2)(CO)3(PMe3)2

*Note how one writes molecular H2 bound to a metal.*

Hydrides can also be formed from the oxidative addition of “active” hydrogen sources such as silanes (HSiR3) or acids:

**RhCl(PMe3)3** + **HSiR3  HRhCl(SiR3)(PMe3)2**

**Os(CO)3(PPh3)2** + **HX  [HOs(CO)3(PPh3)2](Cl)**

Naturally, hydride sources like LiAlH4, borohydrides, or even NaH can be used to substitute off more weakly coordinated ligands like halides.