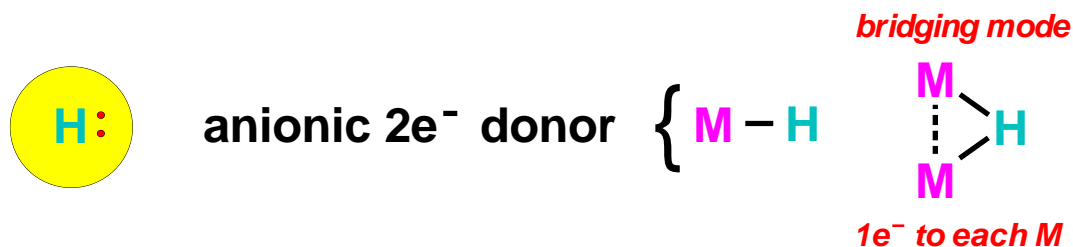


Hydride Ligands



Hydride nomenclature comes from the NMR behavior:

$M-H \sim -5 \text{ to } -25 \text{ ppm}$ *for d¹ d⁹ metals!!*
upfield shift indicates "hydridic" chemical nature

$HCo(CO)_4$ $^1H \text{ NMR} = -10.7 \text{ ppm}$

BUT: $HCo(CO)_4$ $H^+ + Co(CO)_4^-$
strong acid in H₂O, MeOH
similar to HCl !!

d⁰ $Cp^*_2ZrH_2$ $\delta = +7.5 \text{ ppm}$

d¹⁰ $[HCu\{P(p\text{-tolyl})_3\}]_6$ $\delta = +3.5 \text{ ppm}$

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.

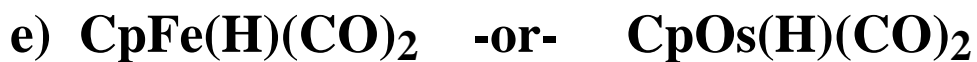
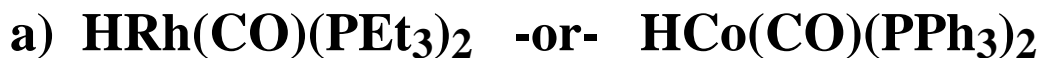
IR Spectra: $M-H$ $2200 - 1600 \text{ cm}^{-1}$ } can be very weak or absent
 $M_2(\mu-H)$ $1600 - 800 \text{ cm}^{-1}$ } broader (weak or absent)

Late Transition Metals: tend to be more "protic"
Early Transition Metals: tend to be more "hydridic"
 (plenty of exceptions; charge on complex important)

pK_a Values for Transition Metal Hydrides in Various Solvents

Metal Hydride Complex	Solvent		
	H ₂ O	MeOH	CH ₃ CN
HV(CO) ₆	strong acid		
HV(CO) ₅ (PPh ₃)	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 (PMe ₃)			26.6
HMn(CO) ₅			15.1
HRe(CO) ₅			~21
H ₂ Fe(CO) ₄	4.0		11.4
H ₂ Ru(CO) ₄			18.7
H ₂ Os(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 (PPh ₃)	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
H ₄ Ru ₄ (CO) ₁₂		11.7	
H ₄ Os ₄ (CO) ₁₂		12.3	
H ₂ Ru ₄ (CO) ₁₃		11.1	

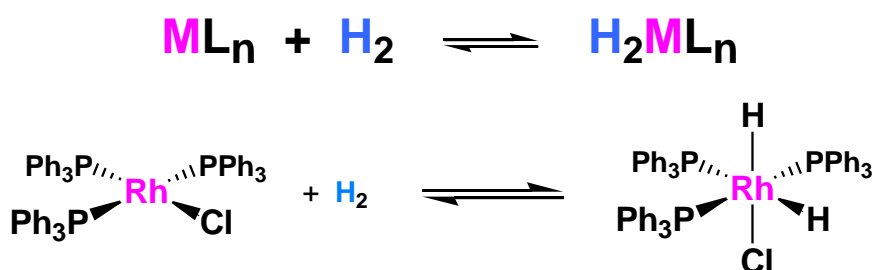
Problem: Which of the following pairs of metal hydrides is the most acidic (lowest pK_a)?



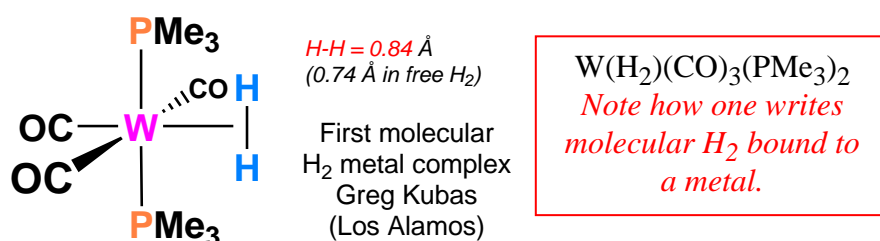
Structural Features:

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.

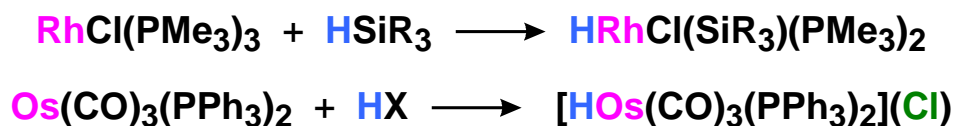
Synthesis: For moderately electron-rich metals with 2 or more d electrons, the **oxidative addition** of molecular H₂ to the metal center is quite common and very important for catalysis:



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



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



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