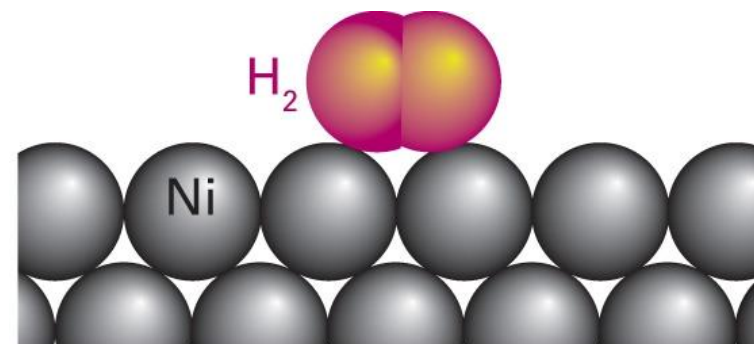


*Hydrides and Dihydrogen
as Ligands: Lessons from
Organometallic Chemistry*

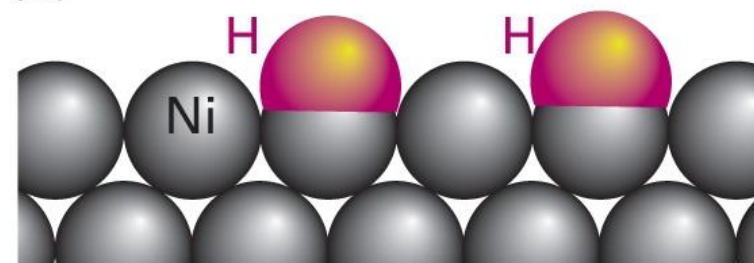
Lecture 7

Schematic representation of physisorption and chemisorption of Hydrogen on a nickel metal surface

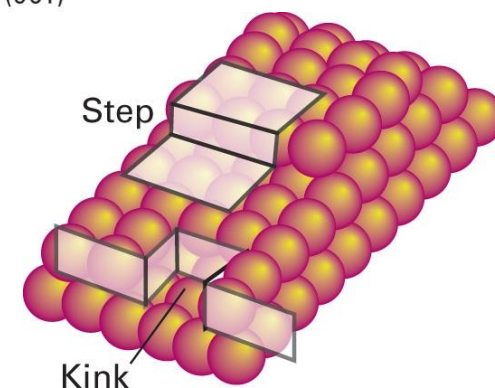
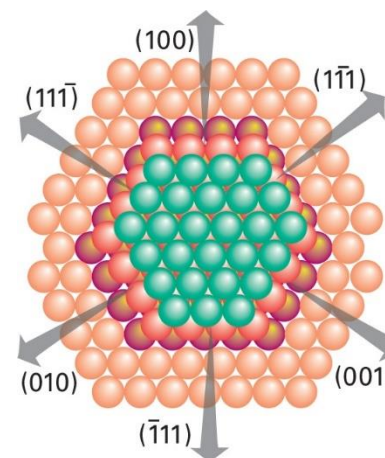
Diverse sites exposed on a Metal surface—a) different Exposed planes, edges; b) steps And kinks from irregularities



(a)



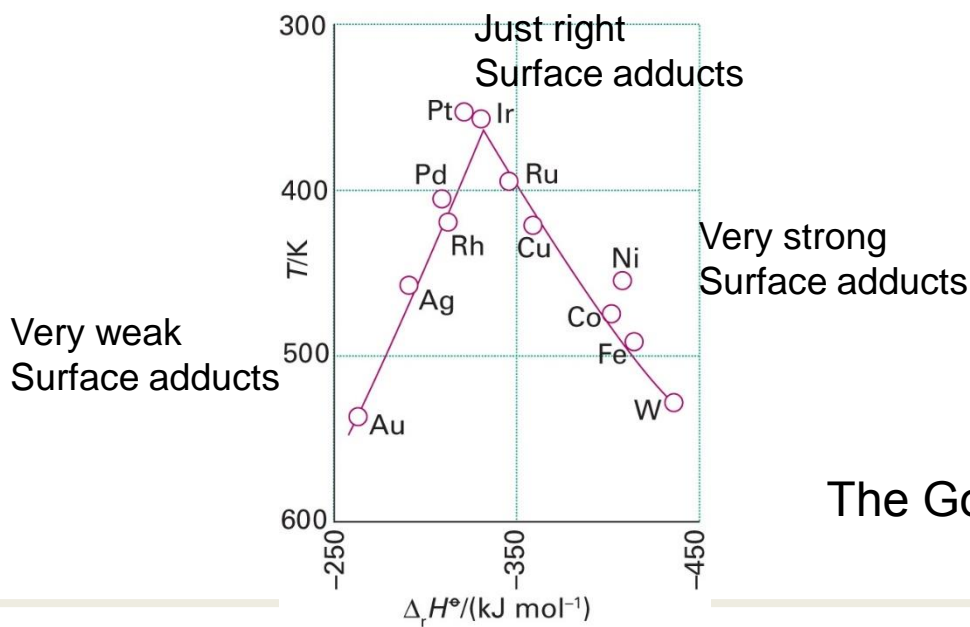
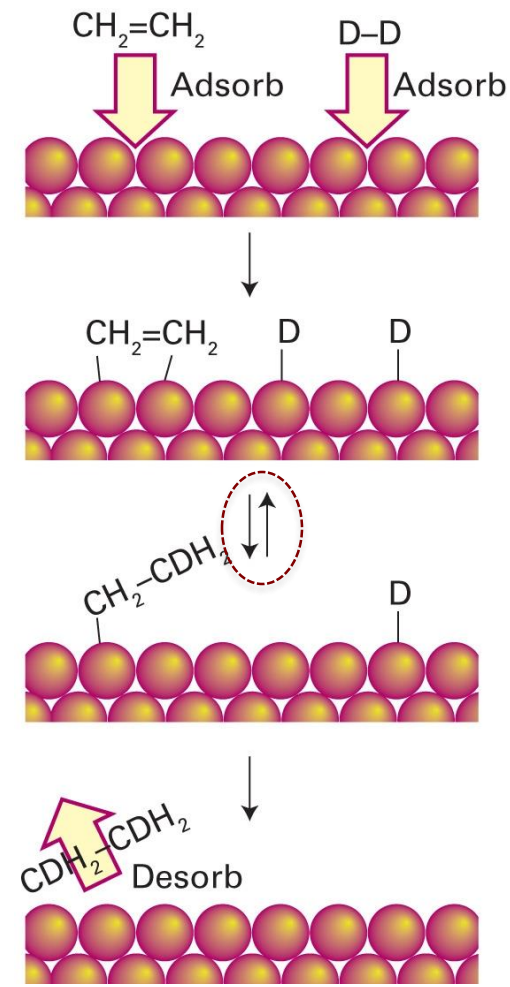
(b)



Hydrogenation of alkenes on supported metal
 Involves H₂ dissociation and migration of H-atoms
 to an adsorbed ethene molecule. (Paul Sabatier, 1890)

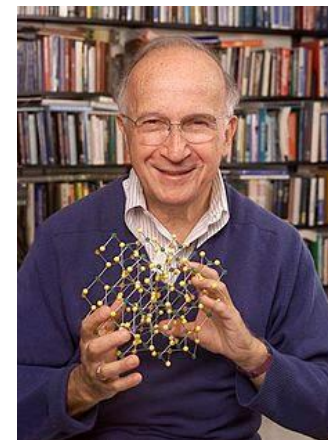
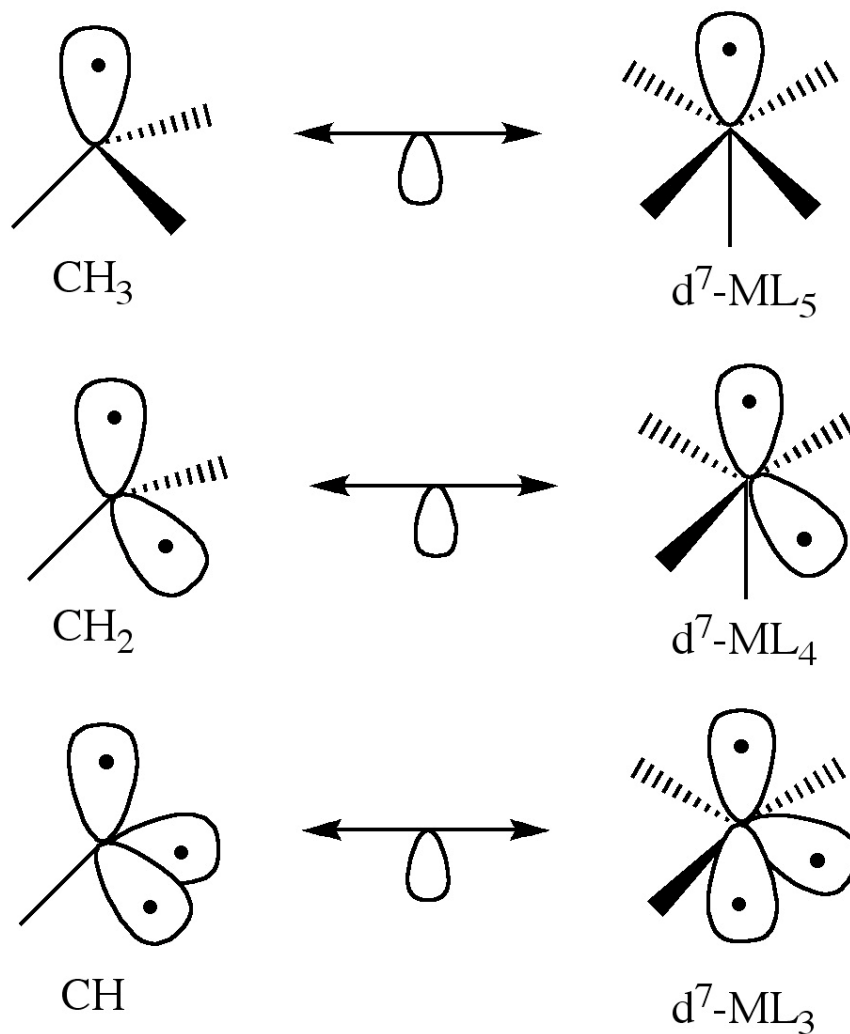
Mechanism: All isotopomers are seen, therefore highly Reversible prior to loss of the ethane.

Volcano diagrams relate stability of products on Surface: Temp. for a set rate of release vs. the Enthalpy. *Intermediate values of ΔH_f , with the rate being a combination of the rate of adsorption and the rate of desorption gives best catalyst.*

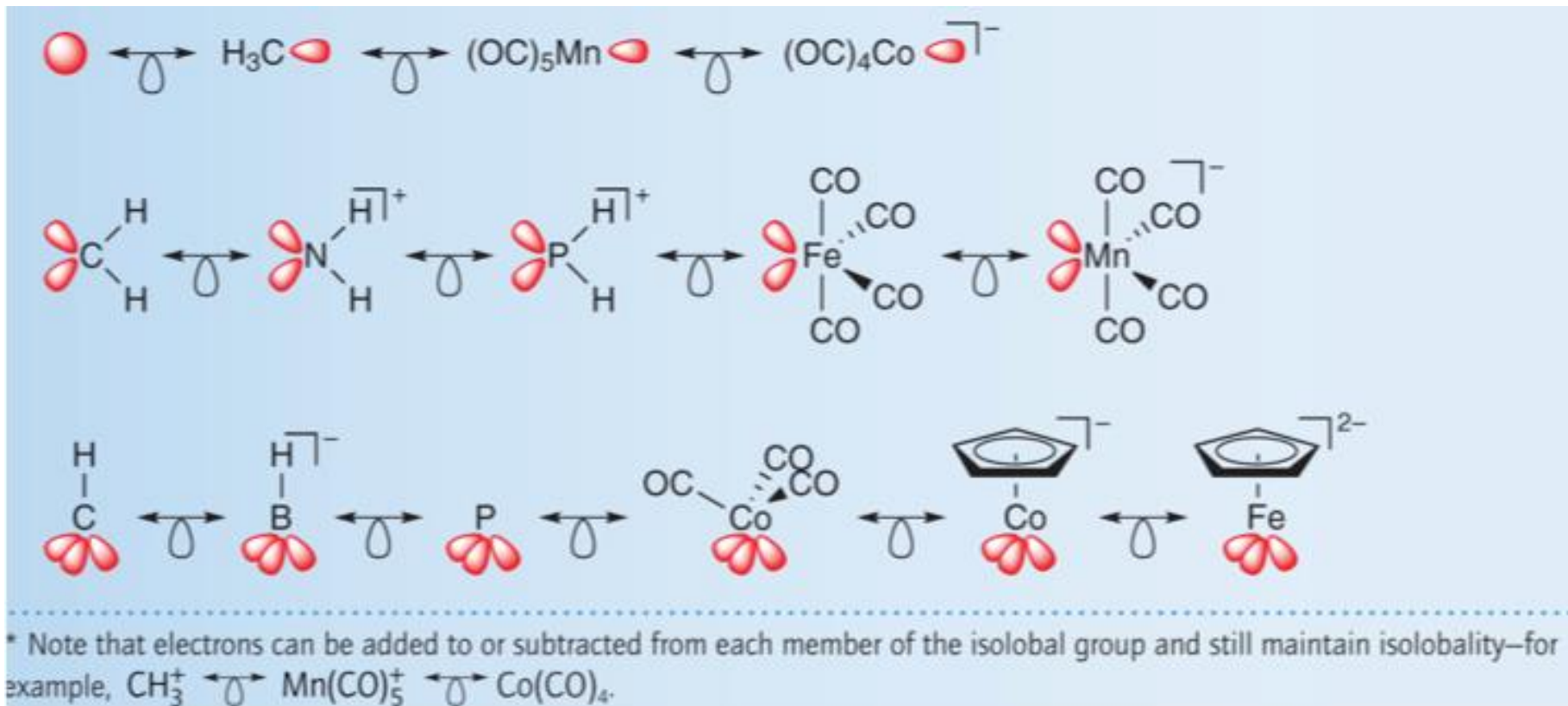


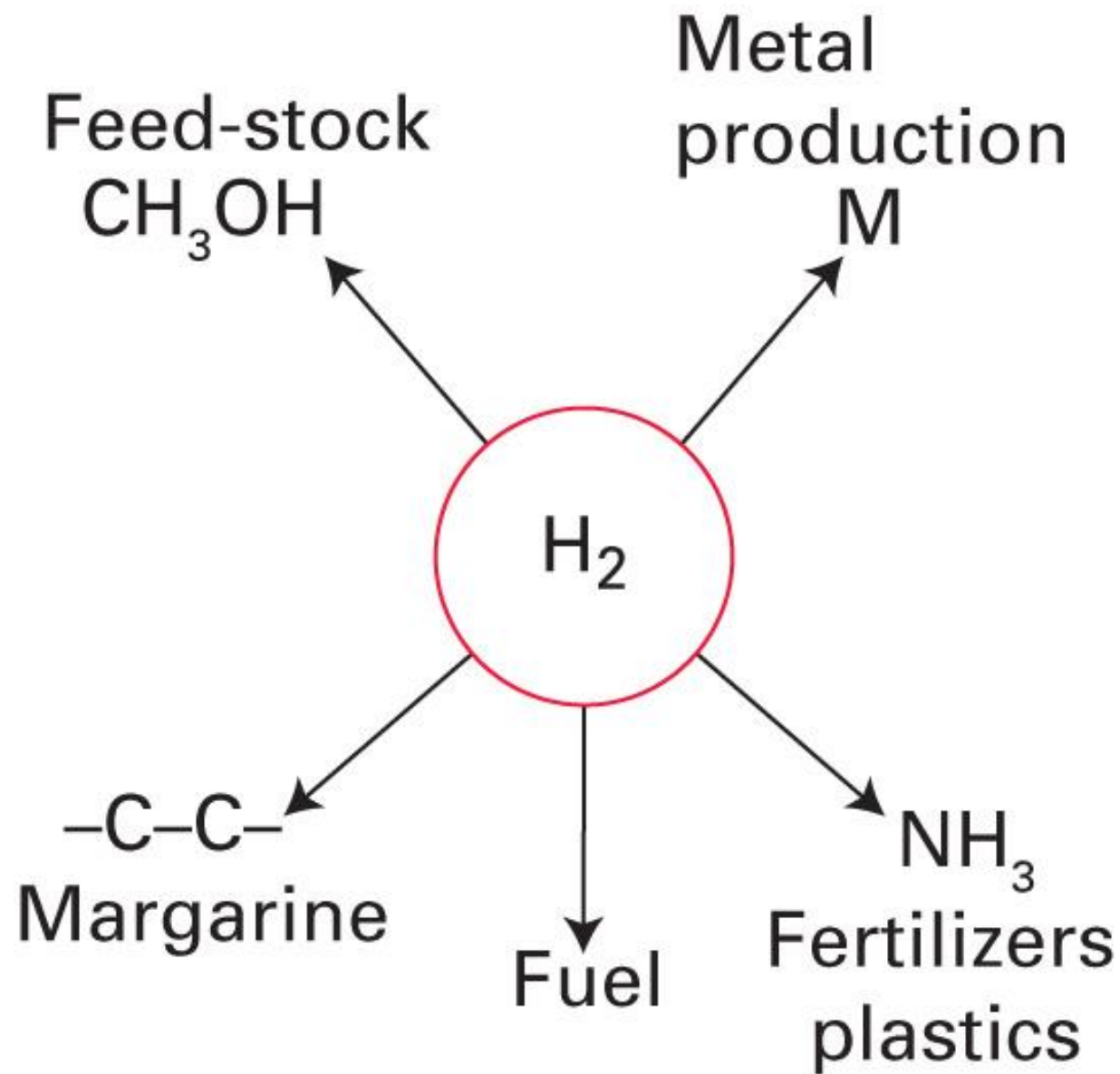
The Goldilock's Effect

Isolobal Analogies: R. Hoffmann



Isolobal species: H, Methyl, M(CO)'s



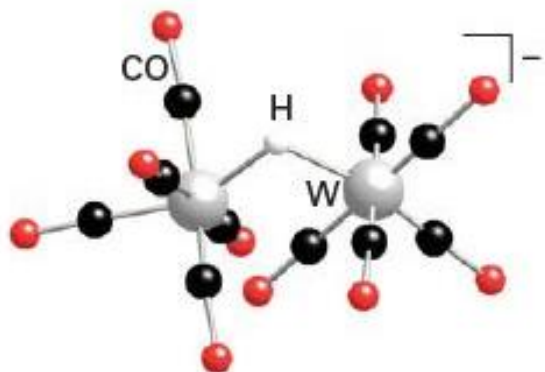


Synthesis of Organometallic Complex Hydrides

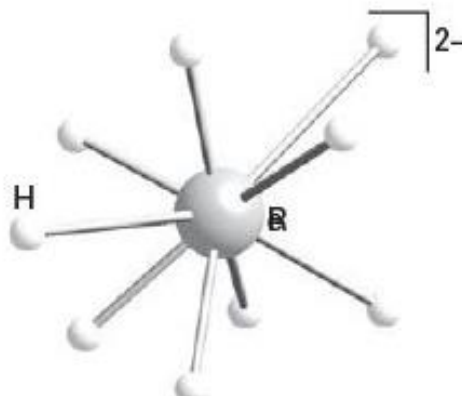
- Reaction of MCO with OH^- , H^- , or CH_2CHR_2
 - $\text{M}(\text{CO})_n + \text{OH}^- = \text{M}(\text{CO})_{n-1}(\text{COOH})^- = \text{HM}(\text{CO})_{n-1}^- + \text{CO}_2$
 - $\text{M}(\text{CO})_n + \text{H}^- = \text{M}(\text{CO})_{n-1}(\text{C}(\text{=O})\text{H})^- = \text{HM}(\text{CO})_{n-1}^- + \text{CO}$
 - $\text{M}(\text{CO})_n\text{CH}_2\text{CHR}_2 = \text{HM}(\text{CO})_{n-1}^- + \text{CH}_2=\text{CR}_2 + \text{CO}$
- Protonation of MCO anion*
 - $\text{M}(\text{CO})_n^- + \text{H}^+ = \text{M}(\text{CO})_n\text{H}$
- Hydrogenation of MCO dimer**:
 - $\text{M}_2(\text{CO})_{2n} + \text{H}_2 = \text{M}(\text{CO})_n\text{H}$
- Oxidative addition of H_2 to (typically) d^8 metal
 - $\text{M}(\text{PR}_3)_3\text{X} + \text{H}_2 = \text{M}(\text{CO})_n\text{X}(\text{H})_2$

*Oxidative addition of a proton. If a dianion, the resultant MCO hydride will be anionic and may react as a hydride transfer reagent.

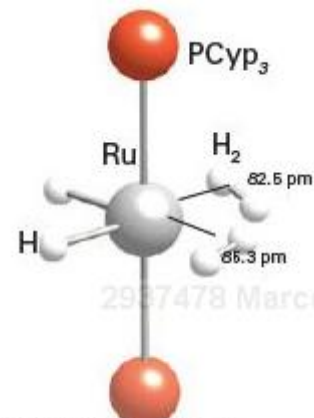
**The resultant neutral hydride may have acidic characteristics (i.e., the hydrogen may be removed by a base (reductive deprotonation))



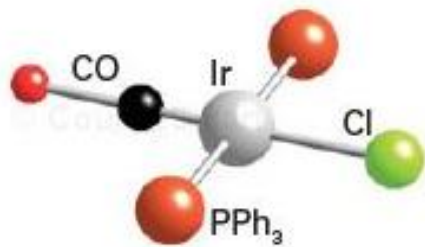
7 $[(\mu\text{-H})\text{W}_2(\text{CO})_{10}]^-$



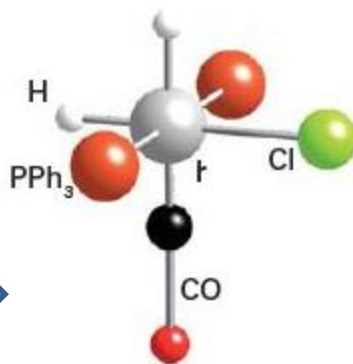
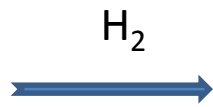
8 $[\text{ReH}_9]^{2-}$



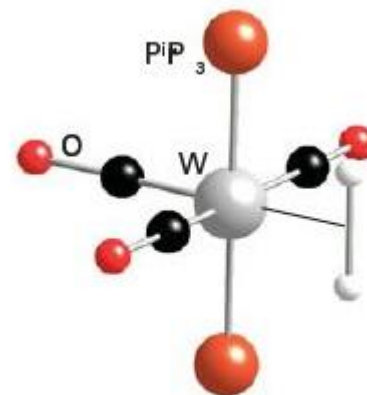
12 $[\text{Ru}(\text{H})_2(\text{H}_2)(\text{PCyp}_3)_2]$, Cyp = *cyclo*- C_6H_9



9 $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$, Ph = C_6H_5



10 $[\text{IrCl}(\text{H})_2\text{CO}(\text{PPh}_3)_2]$

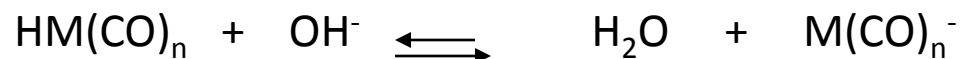


11 $[\text{W}(\text{CO})_3(\text{H}_2)(\text{P}^i\text{Pr}_3)_2]$

Properties of the M-H functionality

- Stereochemically active
- M-H distance range (3d transition metals): 1.5 -1.7 Å
- M-H stretch: 2100 – 1600 cm⁻¹
- M-H hydride resonance: typically upfield, -1 to -20 ppm, but little correlation with electron density
- M-H Bond Dissociation Energy: 60 -100 kcal/mol (Contrast M-C BDE of ca. 26-30 kcal/mol)
- Homolytic cleavage can initiate radical chain reactions
- Acid/Base character: Varies. HCo(CO)₄ is strong acid, pK_a <1; HFe(CO)₄⁻ is weak; Cp₂W(H)₂ forms Lewis Base/Acid adduct with AlMe₃.
- Proton loss is slow as in carbon-based acids.

Acidity of MCO Hydrides



	K_a
HCo(CO)_4	~ 2
$\text{HCo(CO)}_3\text{PPh}_3$	1×10^{-7}
HMn(CO)_5	8×10^{-8}
HRe(CO)_5	very weak
$\text{H}_2\text{Fe(CO)}_4$	$3 \times 10^{-5} ; 1 \times 10^{-14}$
$\text{CpCr(CO)}_3\text{H}$	$10^{-13.3}$
$\text{CpMo(CO)}_3\text{H}$	$10^{-13.9}$
$\text{CpW(CO)}_3\text{H}$	$10^{-16.1}$

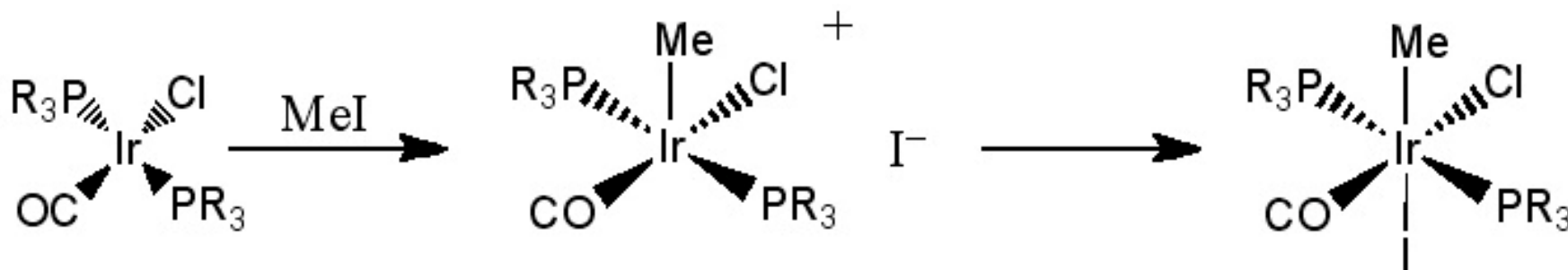
Metal Carbonyl Anions: Nucleophilicity



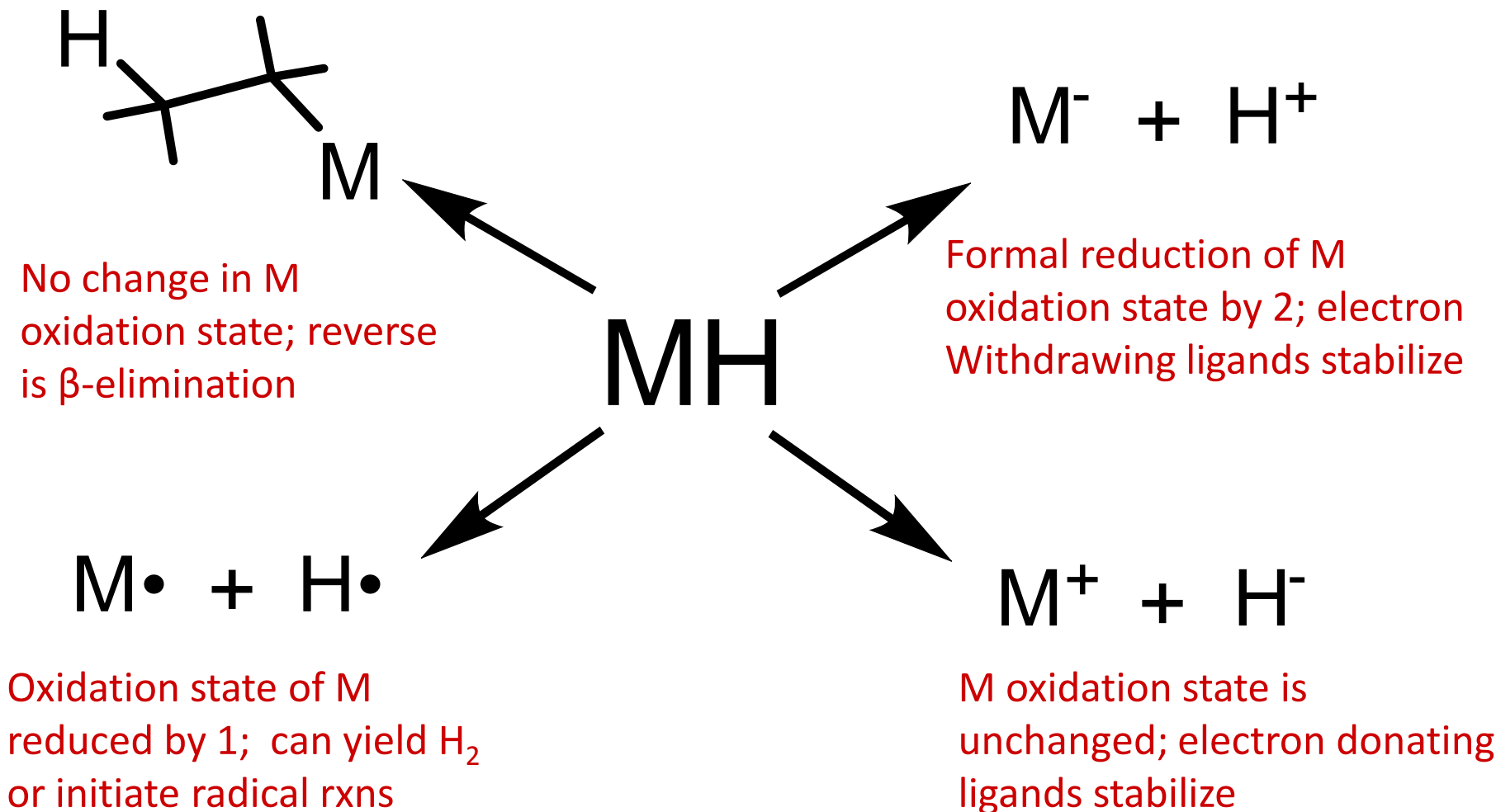
$$\text{Rate} = k [MCO][RX]$$

Anion	CN Anion	Product	CN	Relative nucleophilicity
$CpFe(CO)_2^-$	5	$CpFe(CO)_2R$	6	7.0×10^6
$CpRu(CO)_2^-$	5	$CpRu(CO)_2R$	6	7.5×10^6
$CpNi(CO)^-$	4	$CpNi(CO)R$	5	5.5×10^6
$Ru(CO)_5^-$	5	$Ru(CO)_5R$	6	2.5×10^4
$CpW(CO)_3^-$	6	$CpW(CO)_3R$	7	~ 500
$Mn(CO)_5^-$	5	$Mn(CO)_5R$	6	77
$CpMo(CO)_3^-$	6	$CpMo(CO)_3R$	7	67
$CpCr(CO)_3^-$	6	$CpCr(CO)_3R$	7	4
$Co(CO)_4^-$	4	$RCo(CO)_4$	5	1
$V(CO)_6^-$	6	$RV(CO)_6$	7	$\ll 1$
$Fe(CO)_4^{2-}$	4	$RFe(CO)_4^-$	5	$\gg 7.0 \times 10^6$

Another electron rich metal center: Also reacts with Organic Electrophiles: Vaska's Complex



The M-H Bond Functionality: Reactivity



Nucleophilicity/Hydricity of Anionic MCO Hydrides

Table I. Rate Constants for the Reaction of [PPN]HW(CO)₅ with RX in THF Solution at 26.0 °C^a

RX	$k_2 \times 10^3$ s ⁻¹ M ⁻¹	RX	$k_2 \times 10^3$ s ⁻¹ M ⁻¹
<i>n</i> -C ₄ H ₉ I	> 10	2-C ₄ H ₉ Br	1.79 (± 0.05)
<i>n</i> -C ₄ H ₉ Br	3.31 (± 0.13)	<i>t</i> -C ₄ H ₉ Br	2.81 (± 0.16)
<i>n</i> -C ₄ H ₉ Cl	<i>b</i>	1-bromoadamantane	0.268 (± 0.014)
C ₆ H ₅ CH ₂ Cl	1.68 (± 0.09)	C ₆ H ₅ Br	0.369 (± 0.045)
C ₆ H ₅ COCl	> 10	C ₆ H ₅ CH ₂ Br	> 10

^a Reactions were run under pseudo-first-order conditions with RX in 20-fold excess. [HW⁻] = 0.005 M. Errors calculated at 90% confidence limit. ^b No reaction.

Hydride Transfer Reactivity



Table I. Rate Constants for the Reaction of [PPN]HW(CO)₅ with RX in THF Solution at 26.0 °C^a

RX	$k_2 \times 10^3$ s ⁻¹ M ⁻¹	RX	$k_2 \times 10^3$ s ⁻¹ M ⁻¹
<i>n</i> -C ₄ H ₉ I	>10	2-C ₄ H ₉ Br	1.79 (±0.05)
<i>n</i> -C ₄ H ₉ Br	3.31 (±0.13)	<i>t</i> -C ₄ H ₉ Br	2.81 (±0.16)
<i>n</i> -C ₄ H ₉ Cl	<i>b</i>	1-bromoadamantane	0.268 (±0.014)
C ₆ H ₅ CH ₂ Cl	1.68 (±0.09)	C ₆ H ₅ Br	0.369 (±0.045)
C ₆ H ₅ COCl	>10	C ₆ H ₅ CH ₂ Br	>10

^a Reactions were run under pseudo-first-order conditions with RX in 20-fold excess. [HW⁻] = 0.005 M. Errors calculated at 90% confidence limit. ^b No reaction.

$$\text{Rate} = k_2[\text{HM}^-][\text{RX}]$$

Chart I. Reactivity of Anionic Metal Carbonyl Hydrides As Established for the Reaction [M]H⁻ + RX → [M]X⁻ + RH^a

For R = 1° (*n*-BuBr)

cis-HW(CO)₄P(OMe)₃⁻ > *cis*-HCr(CO)₄P(OMe)₃⁻ > ~50 ~30
 HW(CO)₅⁻ > CpV(CO)₃H⁻ > HCr(CO)₅⁻ > 3.31 (±0.13) 2.20 (±0.06) 1.79 (±0.05)
 HRu(CO)₄⁻ >> HFe(CO)₄⁻
 1.0 *b*

For R = 3° (*t*-BuBr)

HCr(CO)₅⁻ > HW(CO)₅⁻ > *cis*-HCr(CO)₄P(OMe)₃⁻ > 3.17 (±0.08) 2.81 (±0.16) 0.81 (±0.05)
 CpV(CO)₃H⁻ > *cis*-HW(CO)₄P(OMe)₃⁻ >> HFe(CO)₄⁻
 0.33 (±0.03) 0.21 (±0.01) *b*

^a Values cited are second-order rate constants, $k_2 \times 10^3$ s⁻¹ M⁻¹, measured in THF solution at 26.0 °C for bis(tri-phenylphosphine)nitrogen(1+) salts of the hydrides. Errors calculated at the 90% confidence limit. ^b No reaction.

Suppose one protonates the anionic metal hydride of $HW(CO)_5^-$. Is it possible that the resultant H_2 would remain bound to the metal?

Heinekey, JACS, 2005, 850-851;
Heinekey, JACS, 2006, 2615-2620

The η^2 -Dihydrogen as Ligand Story

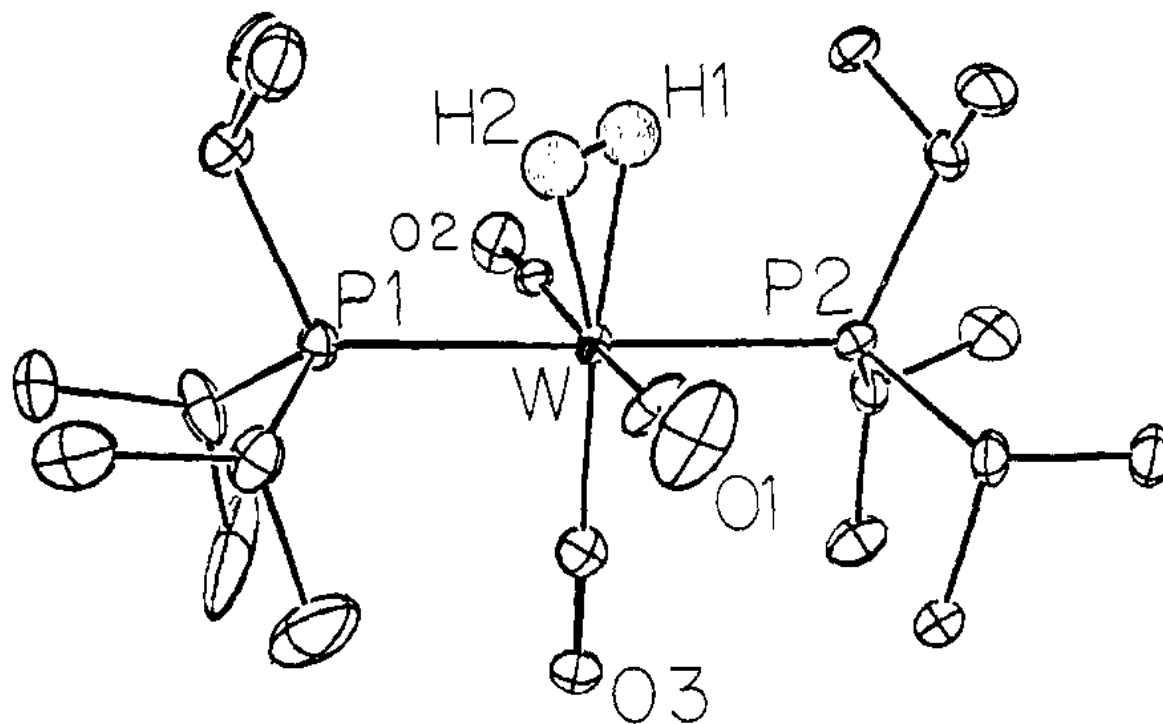
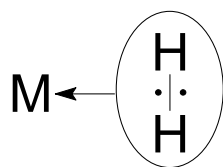


Figure 1. Geometry of the $W(CO)_3(P\text{-}i\text{-}Pr)_2(\eta^2\text{-}H_2)$ molecule with hydrogen atoms of the $P\text{-}i\text{-}Pr_3$ groups omitted for clarity. The positions of the two hydrogen atoms shown were derived from neutron data while heavy-atom positions are from $-100(5)^\circ\text{C}$ X-ray data.

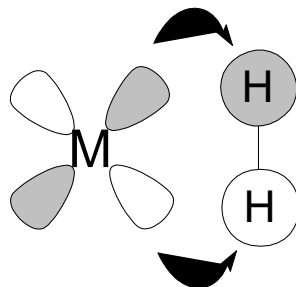
Kubas, *JACS*, **1984**, *10*, 451.

The $\eta^2\text{-H}_2$ Complexes

- Typically d^6 , Oh structures of Cr^0 , Mo^0 , W^0 , Fe^{II} , Ru^{II} , Ir^{III} .
- Bonding: Delicate Balance Required for Stability



σ - donor



σ^* acceptor



$\text{M}^{2+}(\text{H}^-)_2$



Kubas, LANL

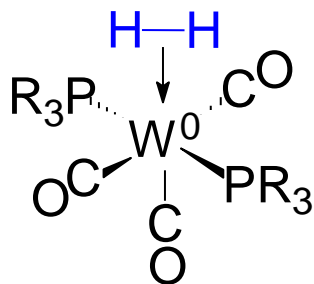


Morris, U. Toronto

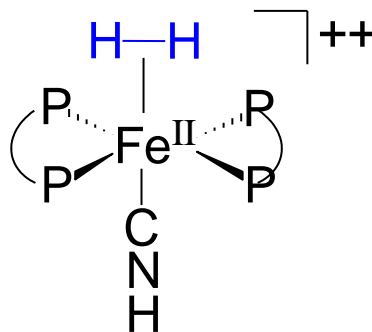


Crabtree, Yale

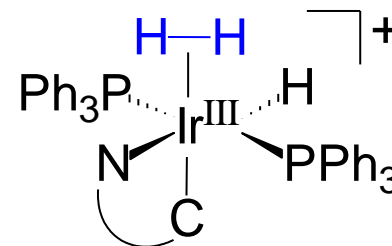
- Examples of $\eta^2\text{-H}_2$ complexes



Kubas

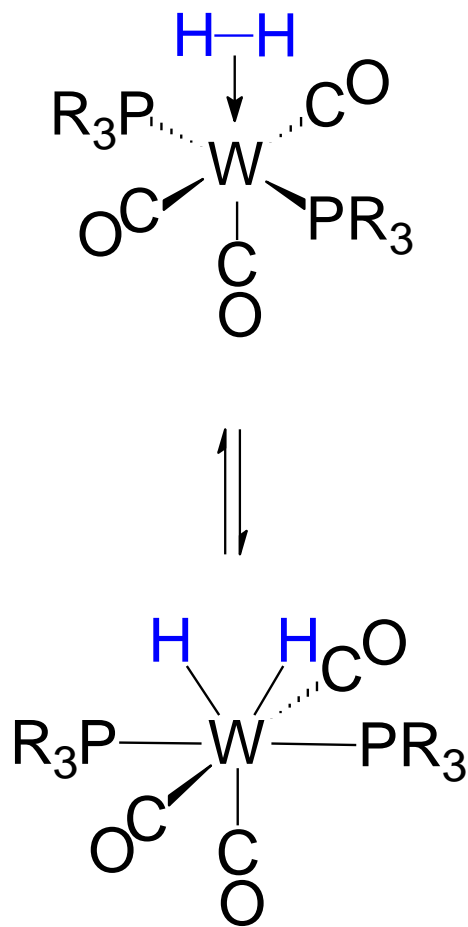


Morris



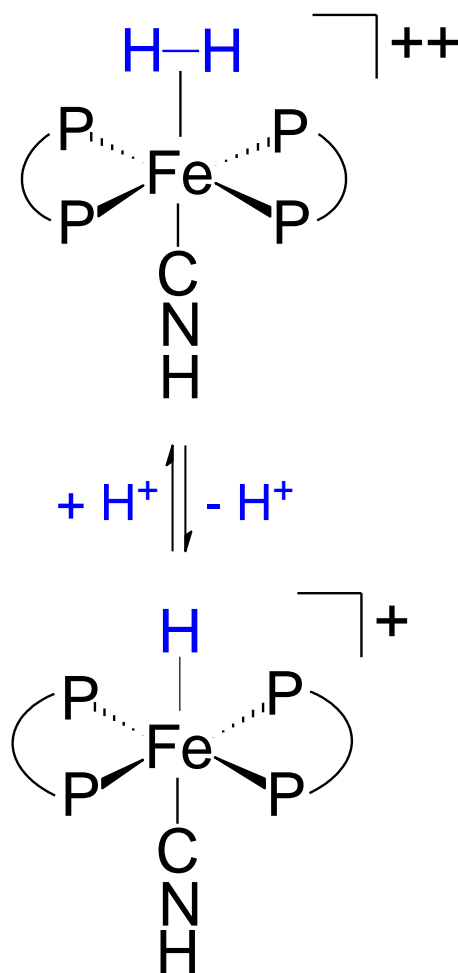
Crabtree

Every Molecule Has a Story: The η^2 -H₂ Complexes



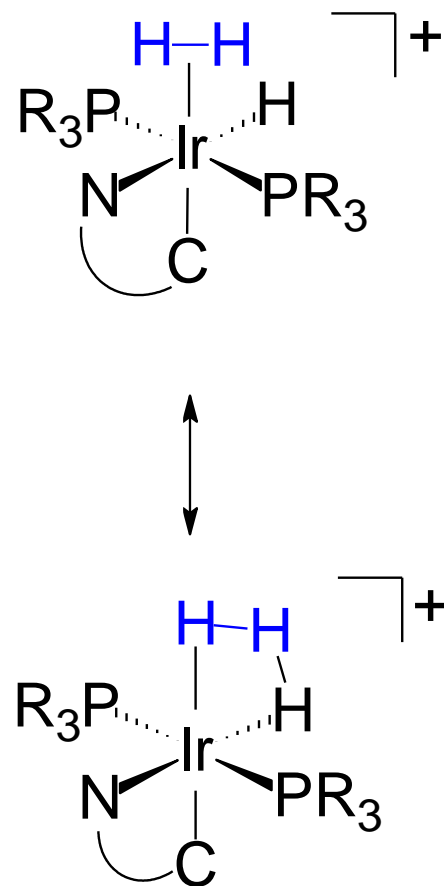
- stability towards H₂ dissociation
- oxidative addition to dihydride

Kubas, LANL



- strong acid
- CNH ligand

Morris, U. Toronto



- resonance forms
- H/D exchange

Crabtree, Yale

Homogeneous Catalysis: Hydrogenation of Alkenes: Wilkinson's catalyst and (one of several versions of) the mechanism

