Metal Hydride Complexes

- Main group metal hydrides play an important role as reducing agents (e.g. LiH, NaH, LiAlH4, LiBH4).
- The transition metal M-H bond can undergo insertion with a wide variety of unsaturated compounds to give stable species or reaction intermediates containing M-C bonds
- They are not only synthetically useful but are extremely important intermediates in a number of catalytic cycles and also in battery technologies.

Transition Metal Hydride Preparation

1. Protonation
   - requires an electron rich basic metal center

$$[Fe(CO)_4]^{2-} \xrightarrow{H^+} [HFe(CO)_4]^- \xrightarrow{H^+} H_2Fe(CO)_4$$

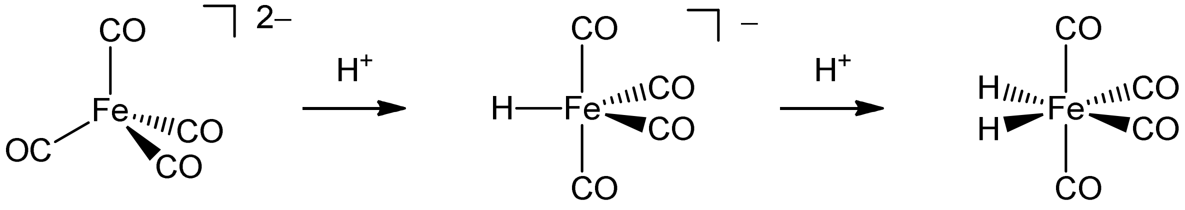
$$Cp_2WH_2 \xrightarrow{+H^+} [Cp_2WH_3]^+$$

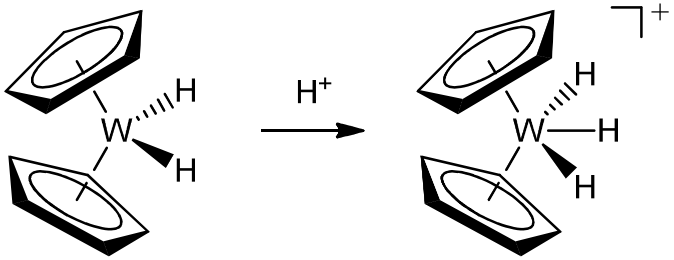
1. From Hydride donors
   - main group metal hydrides are typically used as donors.

$$WCl_6 + LiBEt_3H + PR_3 \longrightarrow WH_6(PR_3)_3$$

Transition Metal Hydride Preparation

1. Protonation
   - ➢ requires an electron rich basic metal center





2. From Hydride donors
   - ➢ main group metal hydrides are typically used as donors.

$$WCl_6 + LiBEt_3H + PR_3 \longrightarrow WH_6(PR_3)_3$$

3. From H_2
    - via oxidative addition
    - requires a coordinatively unsaturated metal center

$$\mathrm{IrCl(CO)(PPh_3)_2} \xrightarrow{\mathrm{H_2}} \mathrm{IrH_2Cl(CO)(PR_3)_2}$$

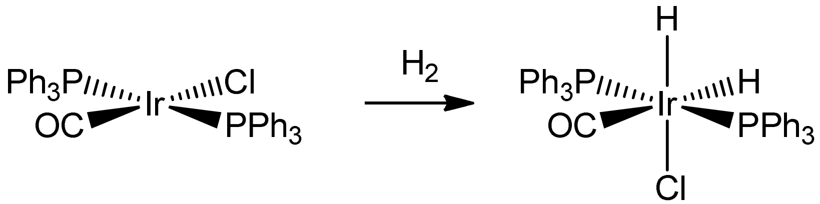
3. From a ligand (β-elimination)

$$\mathrm{RuCl_2(PPh_3)_3 + KOCHMe_2 + PPh_3} \longrightarrow$$
$$\mathrm{RuH_2(PPh_3)_4 + Me_2CO + KCl}$$

$$\mathrm{Cr(CO)_6 + OH^-} \longrightarrow \mathrm{[Cr(CO)_5(COOH)]^-} \xrightarrow{-\mathrm{CO_2}}$$

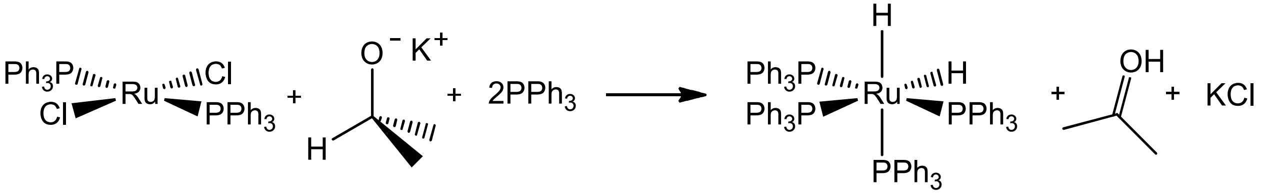
$$\mathrm{[CrH(CO)_5]^-} \xrightarrow{\mathrm{Cr(CO)_6},\ -\mathrm{CO}} \mathrm{[(CO)_5Cr{-}H{-}Cr(CO)_5]^-}$$

3. From H_2
   - via oxidative addition
   - requires a coordinatively unsaturated metal center

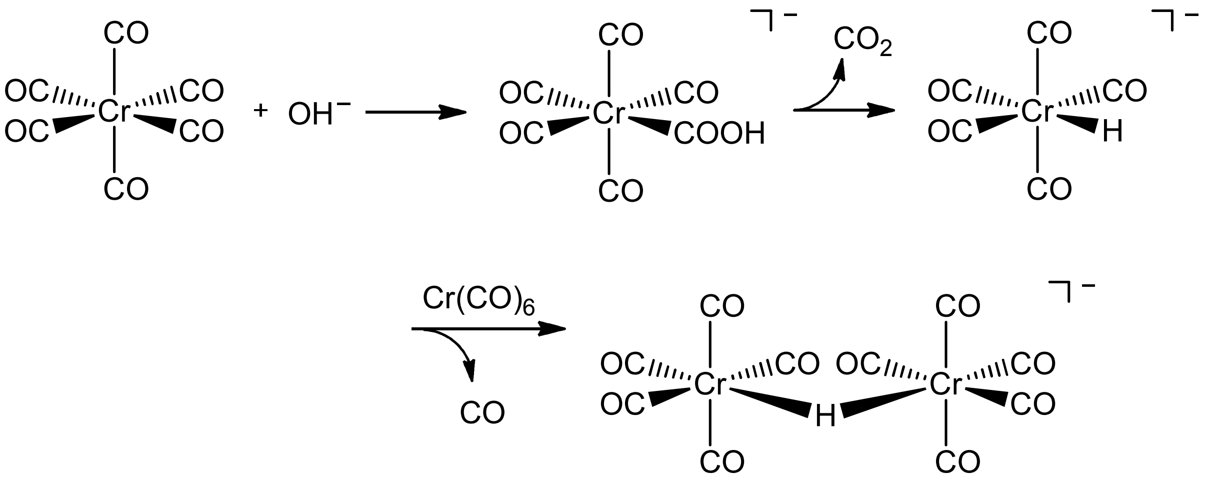


oxidative addition

3. From a ligand (β-elimination)

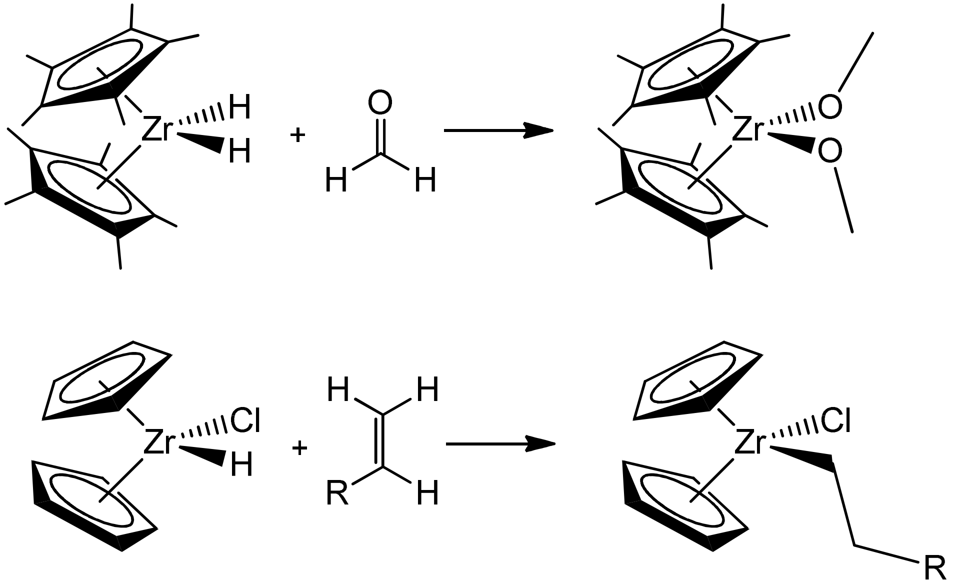


4. From a ligand (decarboxylation)



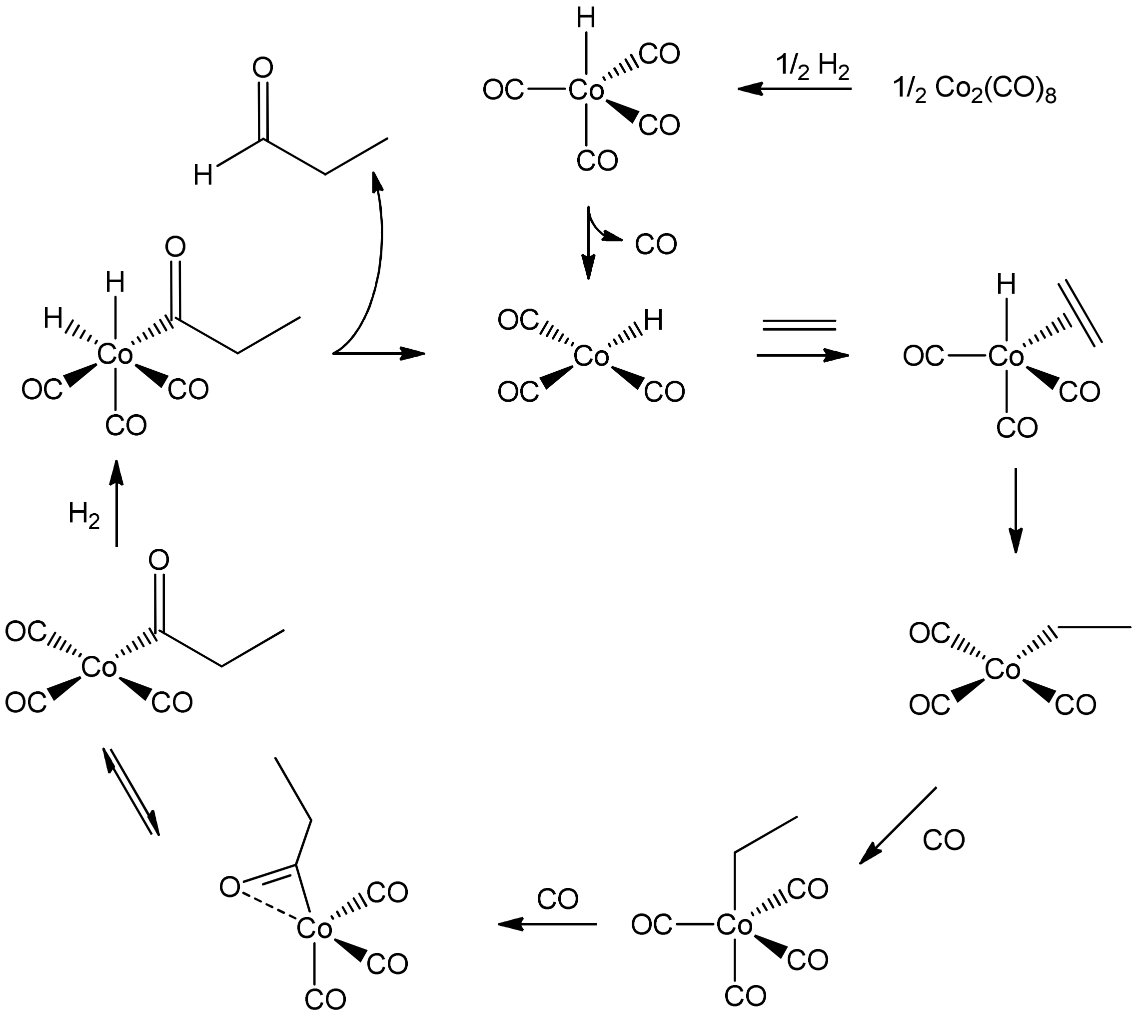
Transition Metal Hydride Reactivity

- Hydride transfer and insertion are closely related



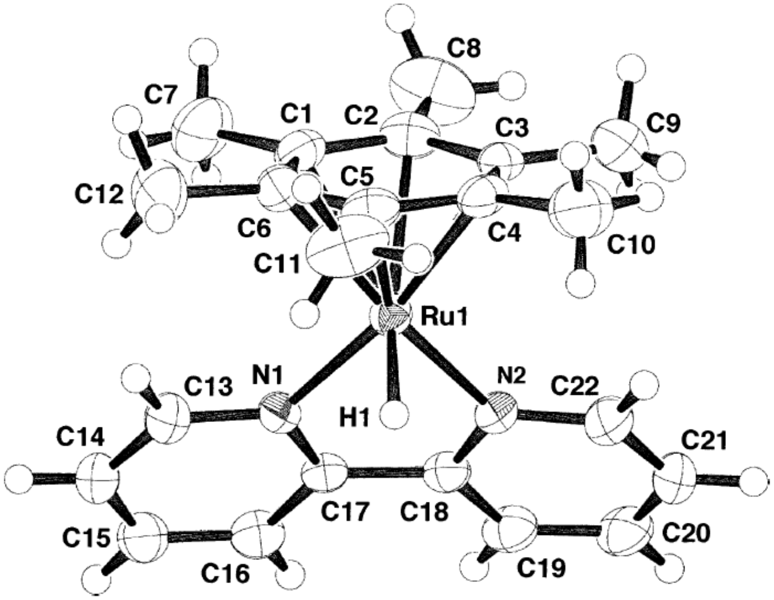
- A metal hydride my have acidic or basic character depending on the electronic nature of the metal involved (and of course its ligand set).
- Early transition metal hydrides tend to carry significant negative charge on the H atom whereas later more electronegative transition metals favour a more positive charge on the H atom (the term Hydride should therefore not be taken literally).
- Reactivity can also depend upon the substrate, e.g. $CpW(CO)_3H$ is a H^+ donor to simple bases, a $H^\bullet$ donor to toward styrene and a H^- donor to carbonium ions.

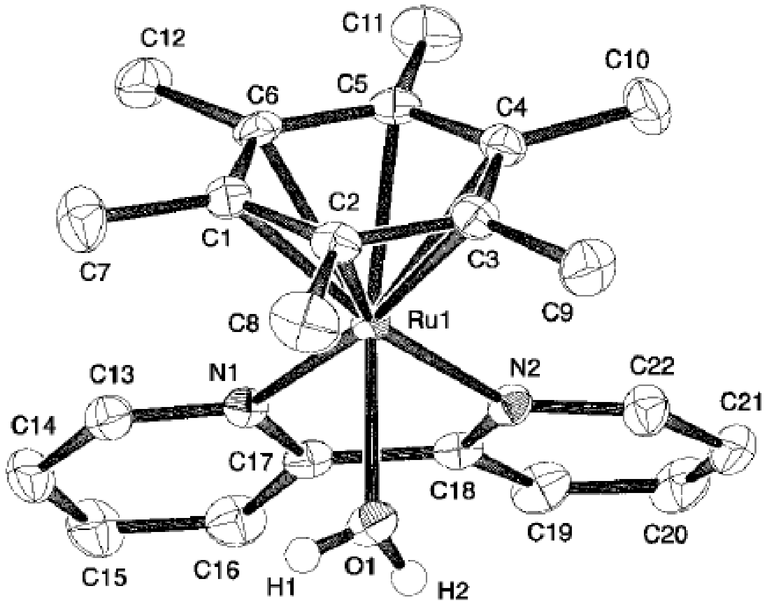
- $HCo(CO)_4$ is a strong acid (pK_a ~ 8.5) due to the electron withdrawing effect of the σ-donating, π-accepting CO ligands on the Co(I) center. It is commonly used as a hydroformylation catalyst.



- An example of an isolable late transition metal hydride complex $[(\eta^6\text{-hmb})\text{Ru}^{II}\text{Hbpy}]^+$ and its aqua derivative $[(\eta^6\text{-hmb})\text{Ru}^{II}(\text{OH}_2)\text{bpy}]^{2+}$

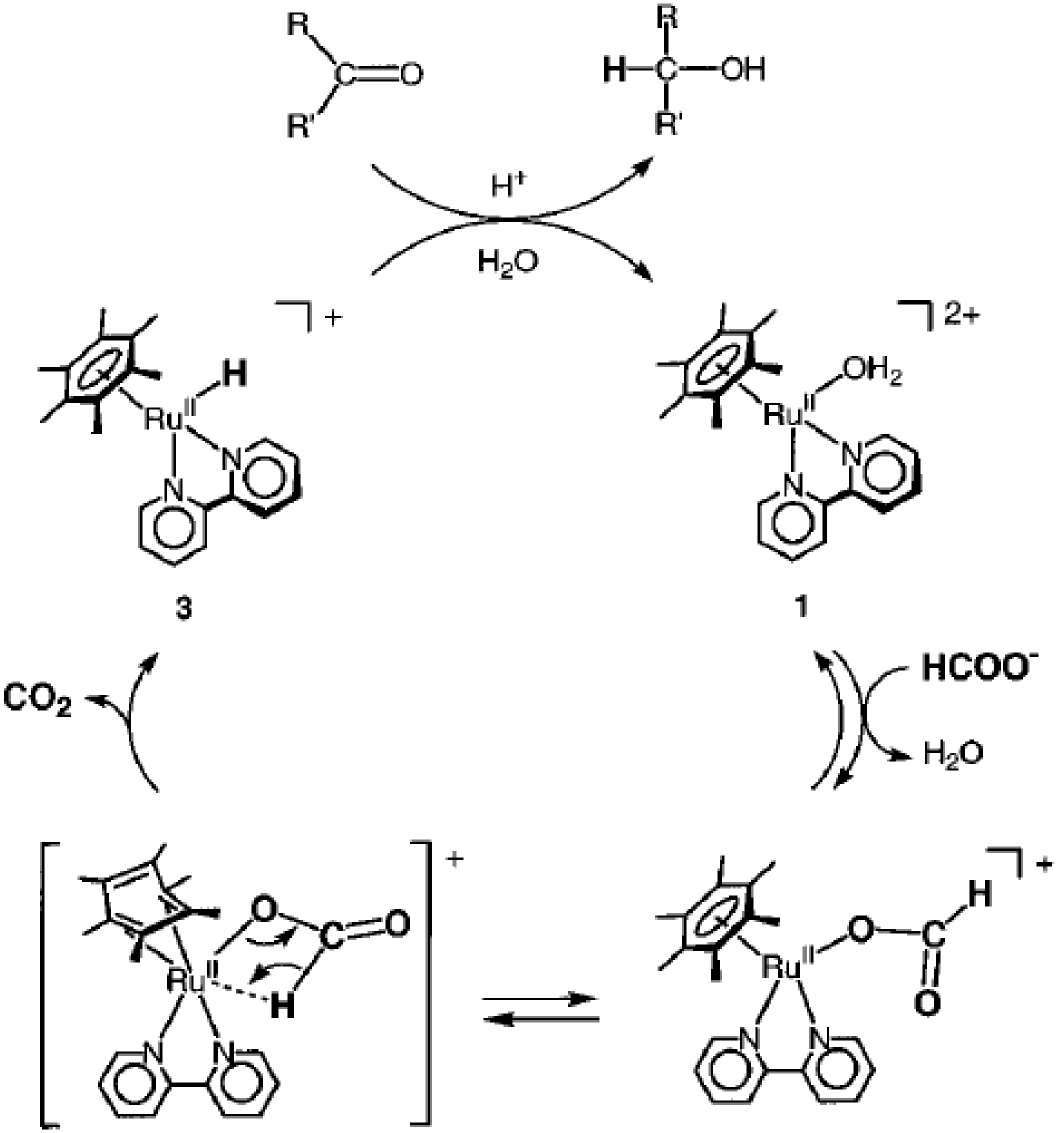
  (hmb = hexamethylbenzene)



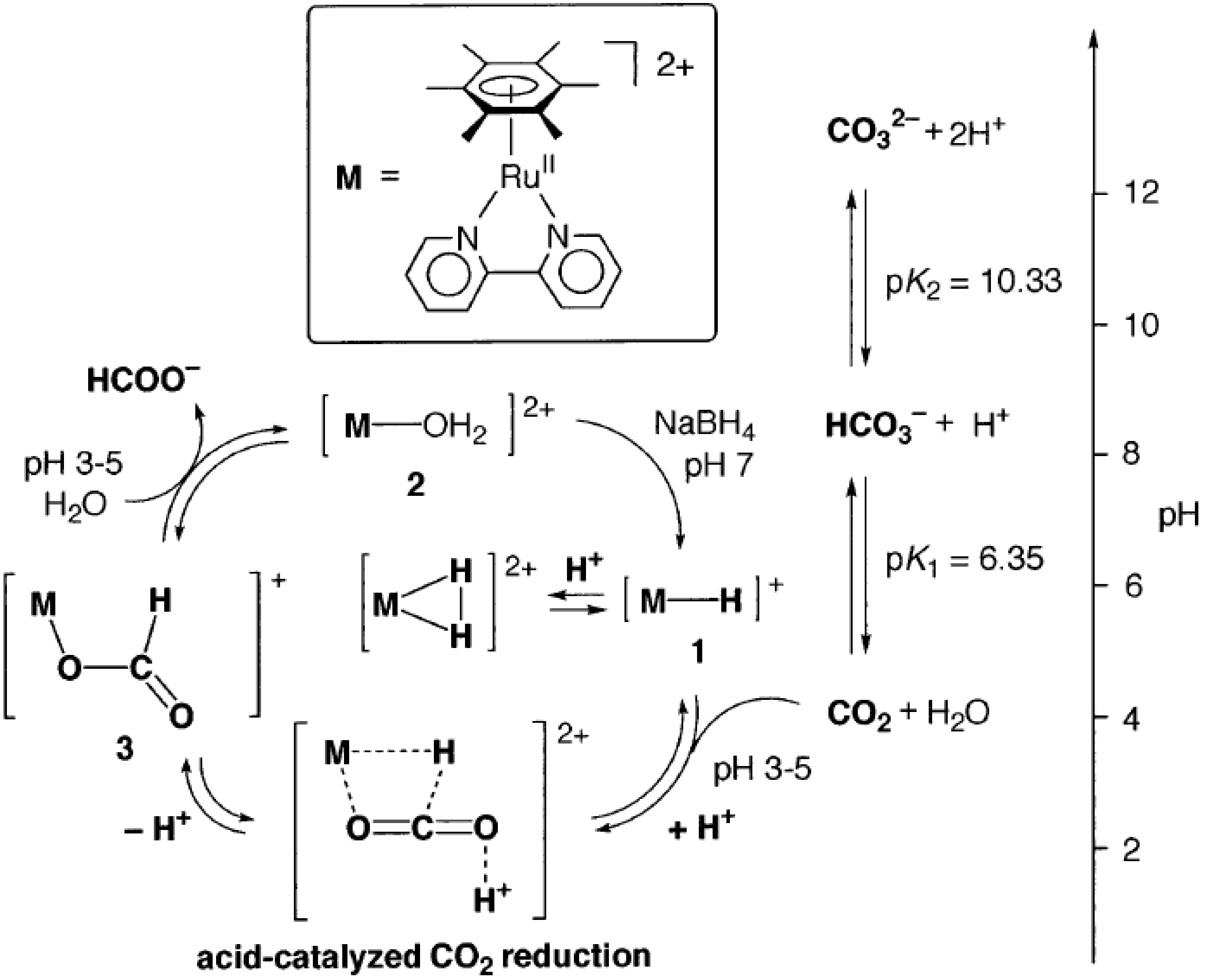


Hayashi et al. J. Am. Chem. Soc., 2003, 125 (47), 14266-14267
Ogo et al. Organometallics, 2002, 21 (14), 2964-2969

- Applied in catalysis to promote ketone reduction e.g. acetone to isopropanol. The formate ion (HCO_2^-) is used as a source of H^- with liberation of CO_2.

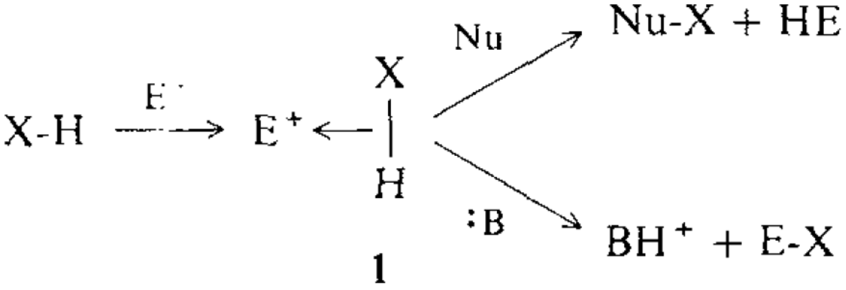


- The same catalyst can be used for reduction of CO_2 under the appropriate conditions.



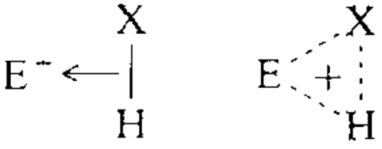
Dihydrogen σ-complexes

- An electrophile E^+ can react with an X-H bond to give a ***σ complex 1**, in which the X-H bond acts as a 2e donor.* ***(not to be confused with σ-bonding Hydrides)***



1

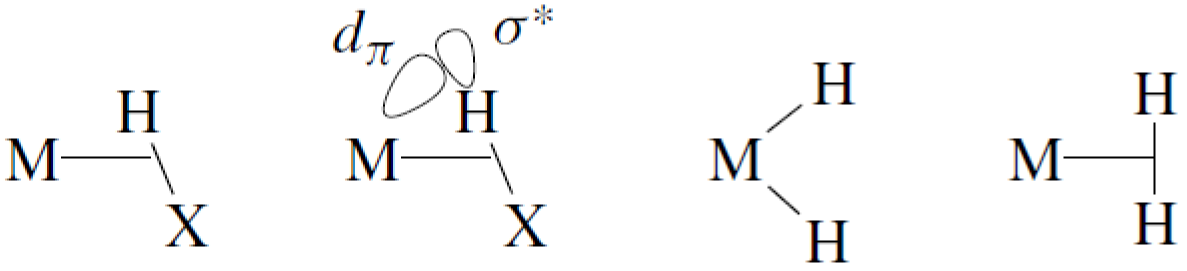
- *1 a* and 1 b show two common ways of representing **1**. Coordination to E^+ alters the chemical properties of the X-H bond and can activate it either for nucleophilic attack at X or deprotonation.



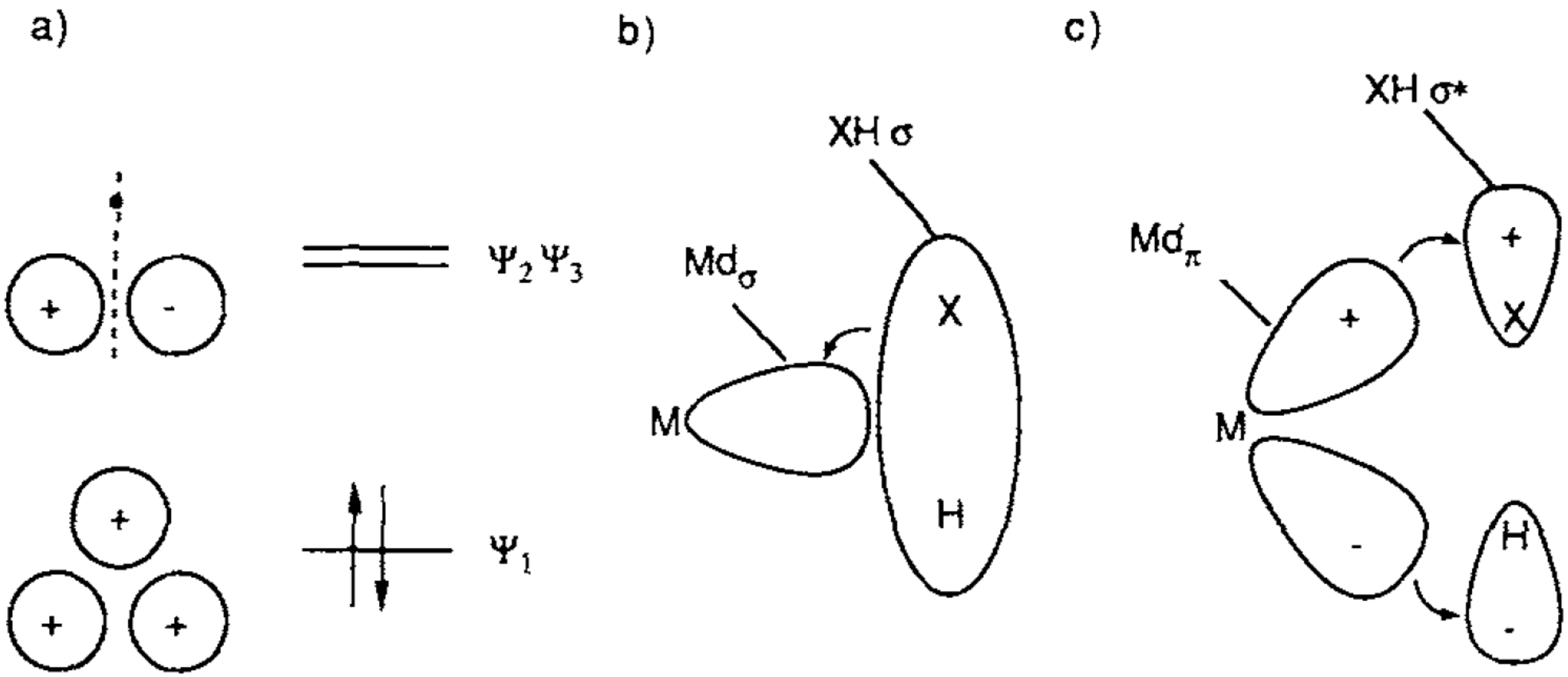
1a **1b**

- **The X-H bond is always coordinated side-on to E^+**, as in **1**.

- ***σ complexes*** **bind by donation of the X-H σ-bonding electrons in a 2e 3 center bond to the metal.**



- X = H, Si, Sn, B, or P…..***at least one H must always be present***.
- The H atom has a small atomic radius and carries no lone pairs or other substituent's, allowing the hydrogen end of the X-H bond to approach close to the metal and so allow the filled M dπ orbital to back-bond relatively strongly onto the lobe of the X-H σ* orbital that is located on the H atom.



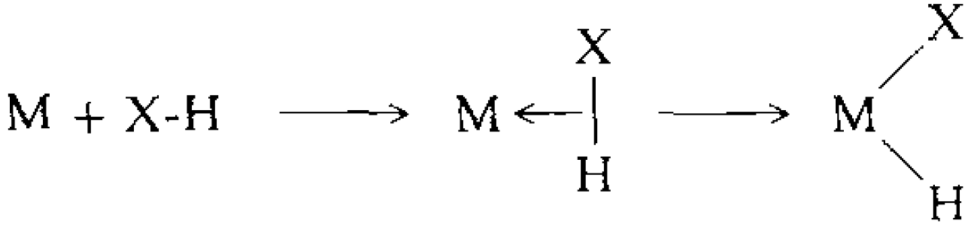
- **The bonding picture for a σ complex.**

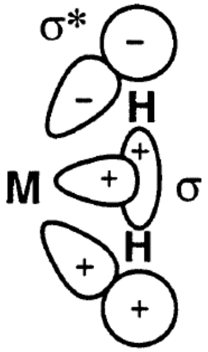
a) Only the Ψ_1 orbital which bonds over all three centers, is occupied. Occupation of Ψ_2 would lead to the opening of one edge of the triangle (nodal plane marked as a dotted line).

b) In an M-(H-X) complex the electrons of the X-H σ bond are donated to an empty metal d, orbital. This is analogous to the binding of the lone pair on NH_3 to a metal atom.

c) Electron density from the M(dπ) orbital is donated to the X-H σ* orbital (back-donation). This resembles M(dπ) + CO(π*) back-donation and is unique to transition metal σ complexes.

- An isolable complex must have some backbonding, but **strong back-donation leads to cleavage of the X-H bond by oxidative addition to give an X-M-H complex**.



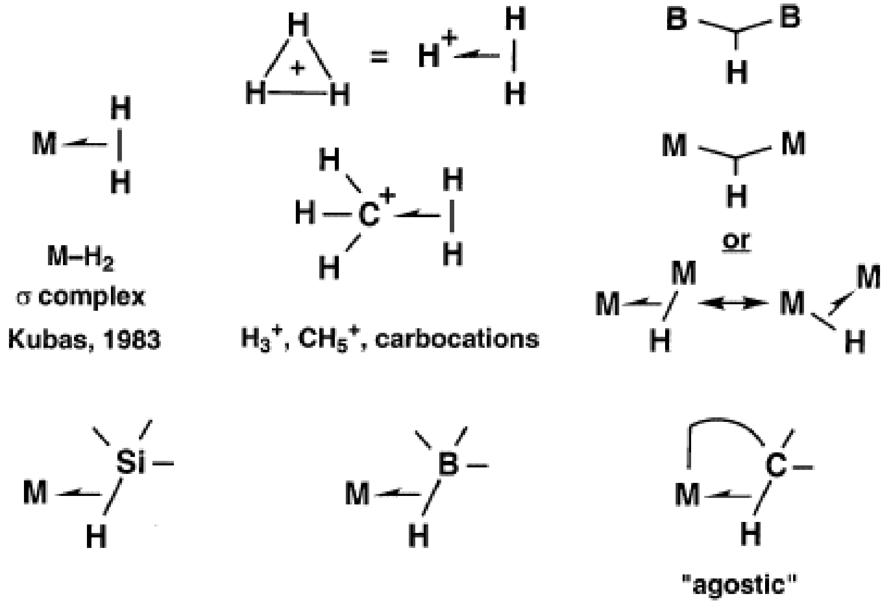


- In contrast, below is a four-electron system, where Ψ_2 must be filled. As this molecular orbital has an antibonding interaction on one side of the triangle, formation of a linear structure is preferred.

B: - - - - H — A

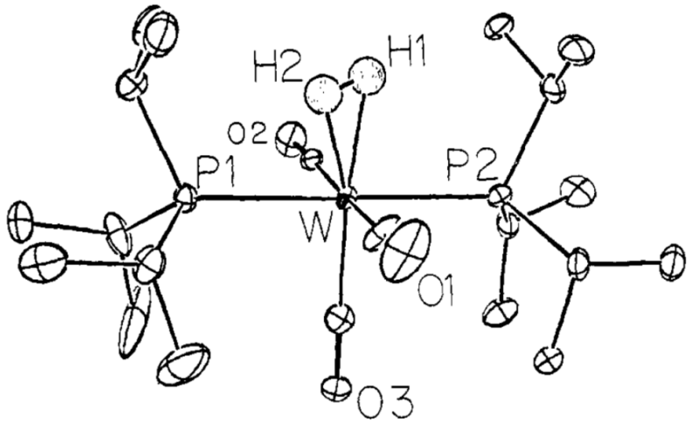
- In complexes with weak back-bonding, the length of X-H bond is similar to that in free X-H.
- The acidity and electrophilicity of X-H can be strongly enhanced, however, because ***σ bonding reduces the electron density in the X-H unit***.
- Stronger back-donation can lead to σ complexes with elongated X-H bonds and reduced electrophilicity of the X-H group.

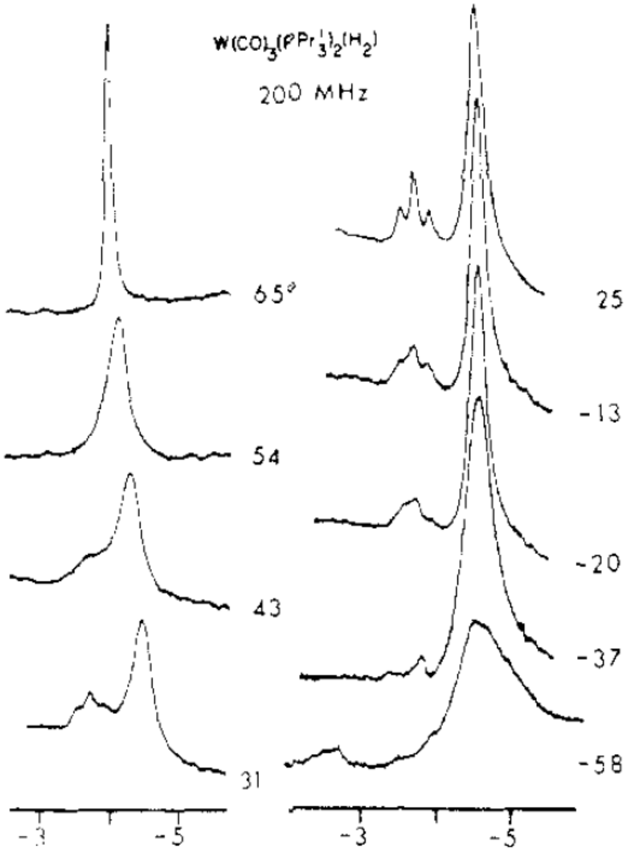
NONCLASSICAL 3-CENTER, 2-ELECTRON (3c-2e) BONDS



Characterization Criteria for Dihydrogen Coordination

- Dihydrogen complexes have been characterized by X-ray, or, much better, neutron diffraction.
- An IR absorption at 2300–2900 cm^{-1} is assigned to the H−H stretch, but it is not always seen.
- The H_2 resonance appears in the range 0 to −10 δ *in the* ^1H *NMR and is often broad.*
- *The presence of an H−H(D) bond is* shown by the H,D coupling constant of 20–34 Hz in the 1H NMR spectrum of the H−D analog. This compares with a value of 43 Hz for free HD and ∼1 Hz for classical H−M−D species.
- Coupling to ^{31}P or the metal center normally is not resolved, even at low temperature.
- J_{HD} *is often unobservable* in fluctional complexes that also contain hydrides.
- Crabtree developed a second criterion: proton relaxation time
- T_1 *was* anticipated to be unusually short (4-100 ms) for H_2 ligands vs > 350 ms for hydrides.



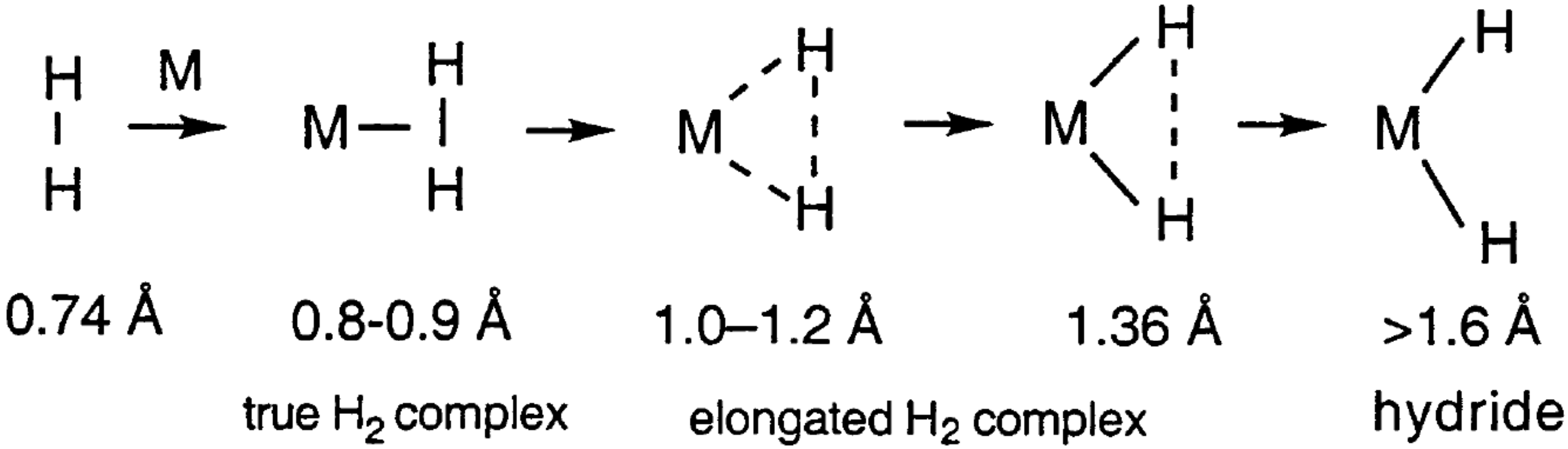


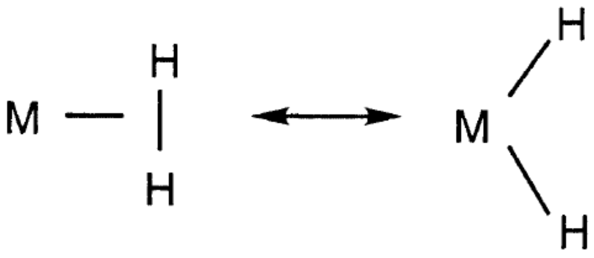
- In prototypical dihydrogen complexes, there are a number of cases where both 6-coordinate dihydrogen and 7-coordinate dihydride structures are reported to exist in dynamic equilibrium, indicating a delicate energetic balance between two quite different structures.

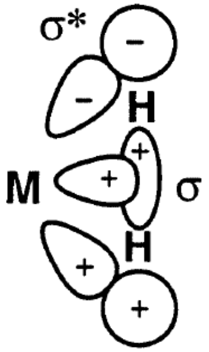
- For example, NMR observations establish that the ***dihydrogen*** complex $(PCy_3)_2W(CO)_3(H_2)$ is in equilibrium with the ***7-coordinate dihydride complex*** $(PCy_3)_2W(CO)_3H_2$, with the dihydrogen form predominant.

G. J. Kubas. R. R. Ryan, B. I. Swanson, P. J. Vergamini, H. J. Wasserman. J. Am. Chem. Soc. 1984. 106,451 -452;

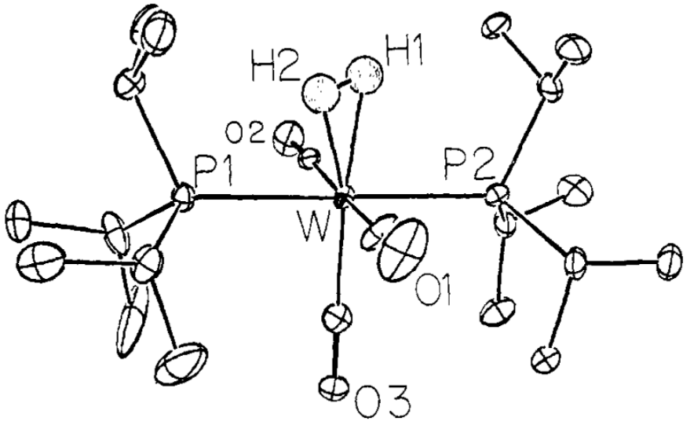
H–H BOND DISTANCES FROM CRYSTALLOGRAPHY AND NMR



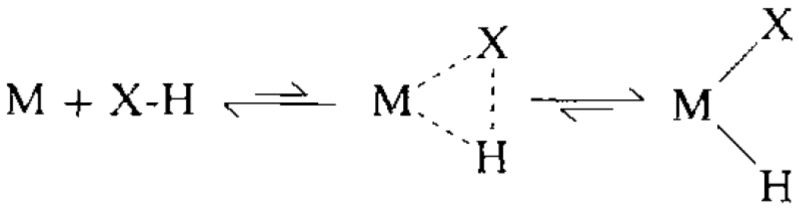




- The H-H distance of 0.82 A observed by neutron diffraction is little changed from its value in free H_2 (0.74A).
- Since the H-H bonds in most H_2 complexes are not stretched, it is not surprising that the activation energy for loss of H_2 (more generally X-H) is not usually large.
- Facile loss of X-H can be important in applications to catalysis, for example, because the resulting coordinatively unsaturated intermediates may be very reactive.

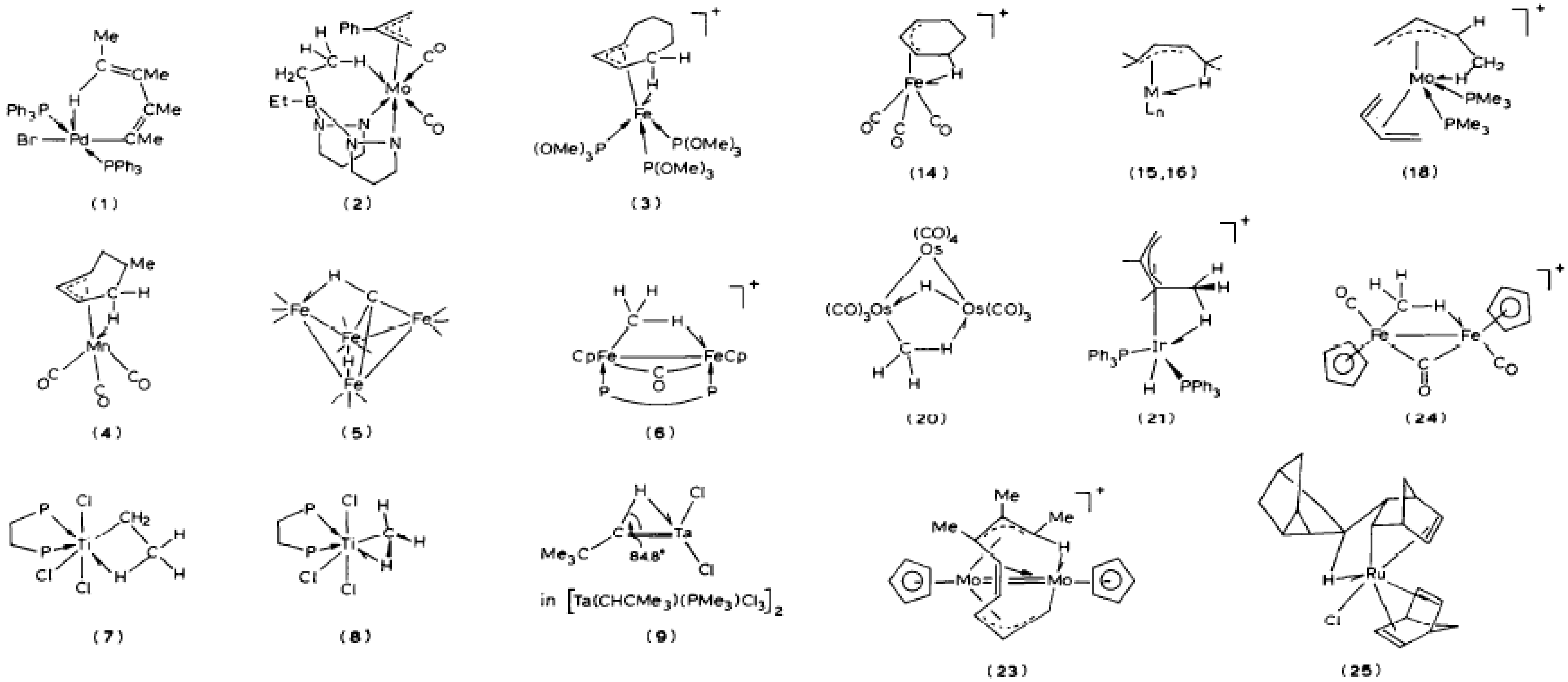


- We can also look at σ complexes as being derived from the classical adduct [$L_nM(X)(H)$] in which an attractive interaction between X and H causes these two ligands to approach one another.
- This description is more appropriate for "stretched" σ complexes in which the X-H distance is substantially longer than in the free XH molecule.



- Eisenstein et al. have shown how hydrido ligands even in classical dihydrides of type [L_nMH_2] have a mutually attractive interaction not present in CH_4
- Attractive interactions between ligands are likely to facilitate reactions such as reductive elimination and insertion - reactions in which two ligands must approach each other to reach the transition state.
- ***By stabilizing the transition state for oxidative addition and reductive elimination the activation energy is thus lowered***. This helps explain the special facility of these reactions in transition metal complexes.

- Starting in the early 1980s, the activity in the area of C-H activation led to renewed interest in compounds with C-H-M bridges.
- In their 1983 review, Brookhart and Green directed attention to C-H-M systems, which they named agostic.

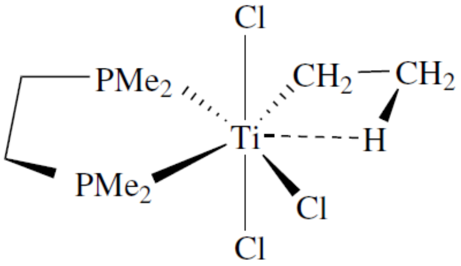


Journal of Organometallic Chemistry, 250 (1983) 395-408

“We propose the term “agostic” which will be used to discuss the various manifestations of covalent interactions between carbon-hydrogen groups and transition metal centres in organometallic compounds. The word agostic will be used to refer specifically to situations in which a hydrogen atom is covalently bonded simultaneously to both a carbon atom and to a transition metal atom.”

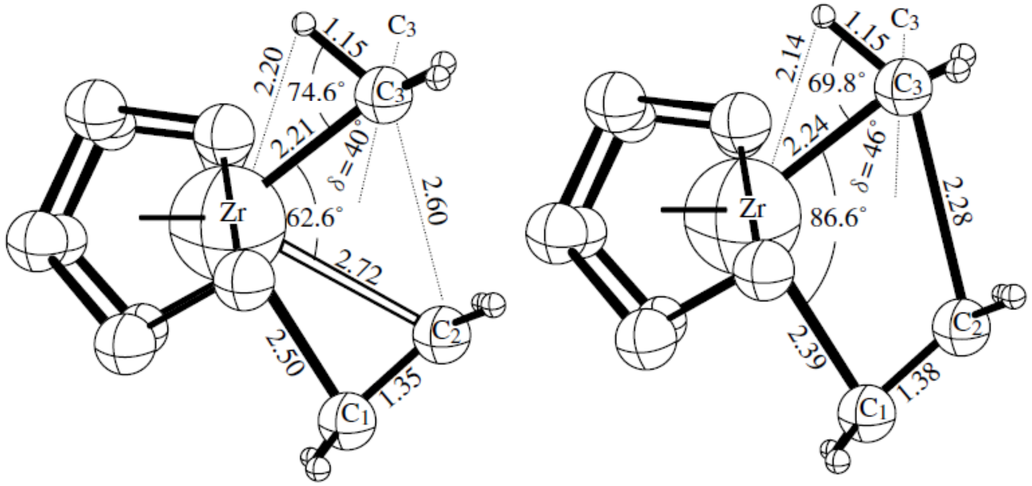
Agostic Bonds

- The **β C−H** bond is bound to the metal in a way that suggests that the alkyl is beginning the approach to the transition state for β elimination.
- These agostic alkyls can be detected by X-ray or neutron crystal structural work and by the high-field shift of the agostic H in the proton NMR.
- The lowering of the *J*(C,H) and *ν*(CH) in the NMR and IR spectra, respectively, on binding is symptomatic of the reduced C−H bond order in the agostic system.



- The reason that β elimination does not occur is that the d^0 Ti has no electron density to back donate into the σ∗ orbital of the C−H bond.
- This back donation breaks the C−H bond in the β-elimination reaction, much as happens in oxidative addition.

- Agostic binding of C−H bonds also provides a way to stabilize coordinatively unsaturated species.
- They are also found in transition states for reactions such as alkene insertion/β elimination either by experiment or in theoretical work.



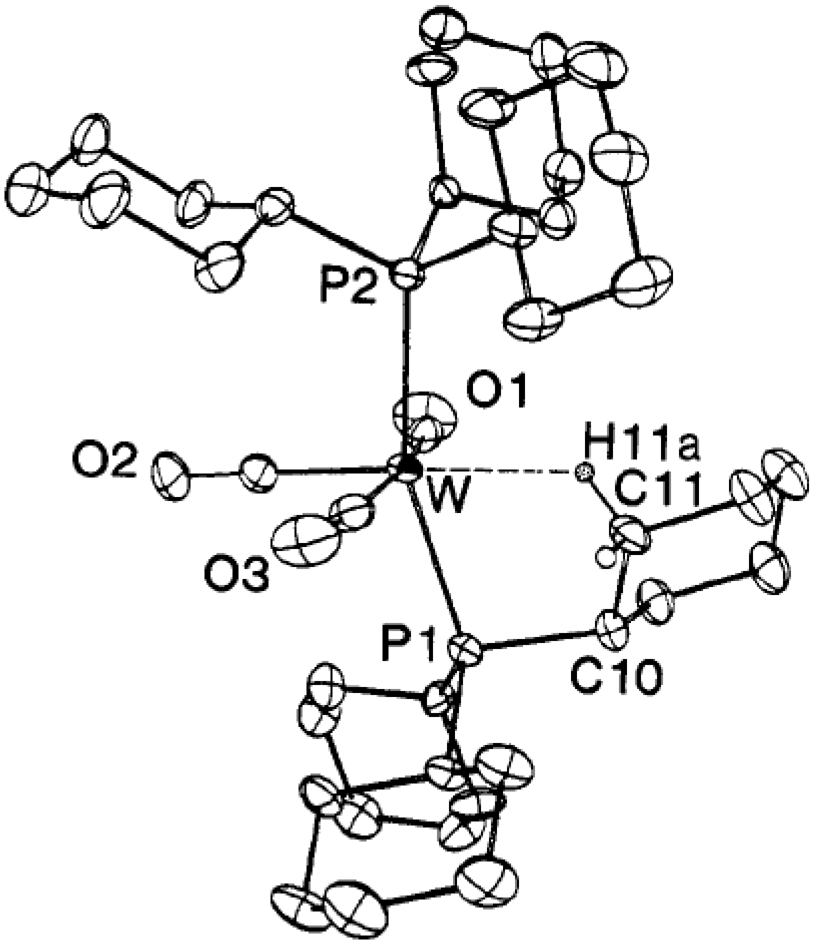


Figure 2. Ortep drawing of $W(CO)_3(PCy_3)_2$ (30% thermal ellipsoids).

ChemComm

Cite this: *Chem. Commun.*, 2011, **47**, 7989–7991

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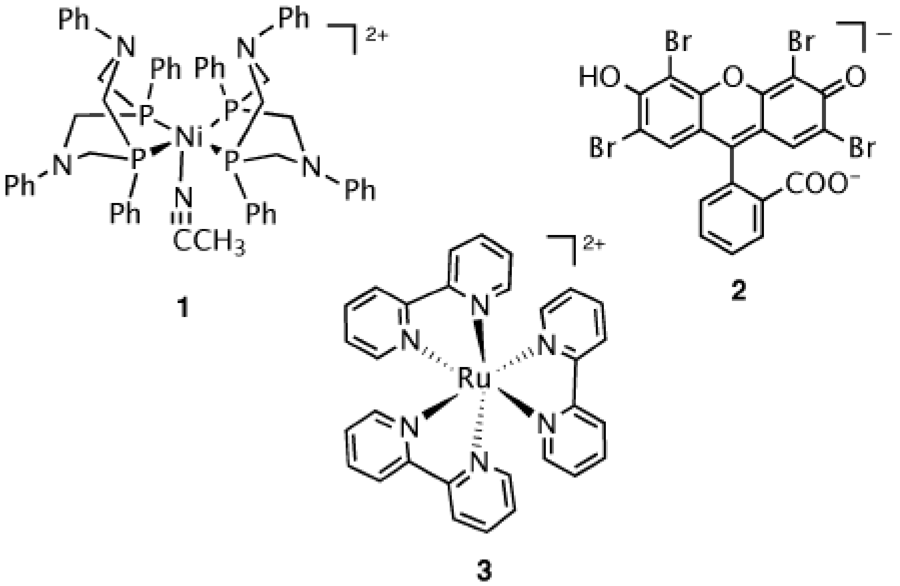
COMMUNICATION

A stable molecular nickel catalyst for the homogeneous photogeneration of hydrogen in aqueous solution†

Matthew P. McLaughlin, Theresa M. McCormick, Richard Eisenberg* and Patrick L. Holland*



Scheme 1 Complexes in the photocatalytic system: (1) $[Ni(P_2^{Ph}N_2^{Ph})_2]^{2+}$, (2) Eosin Y, (3) $[Ru(bpy)_3]^{2+}$.