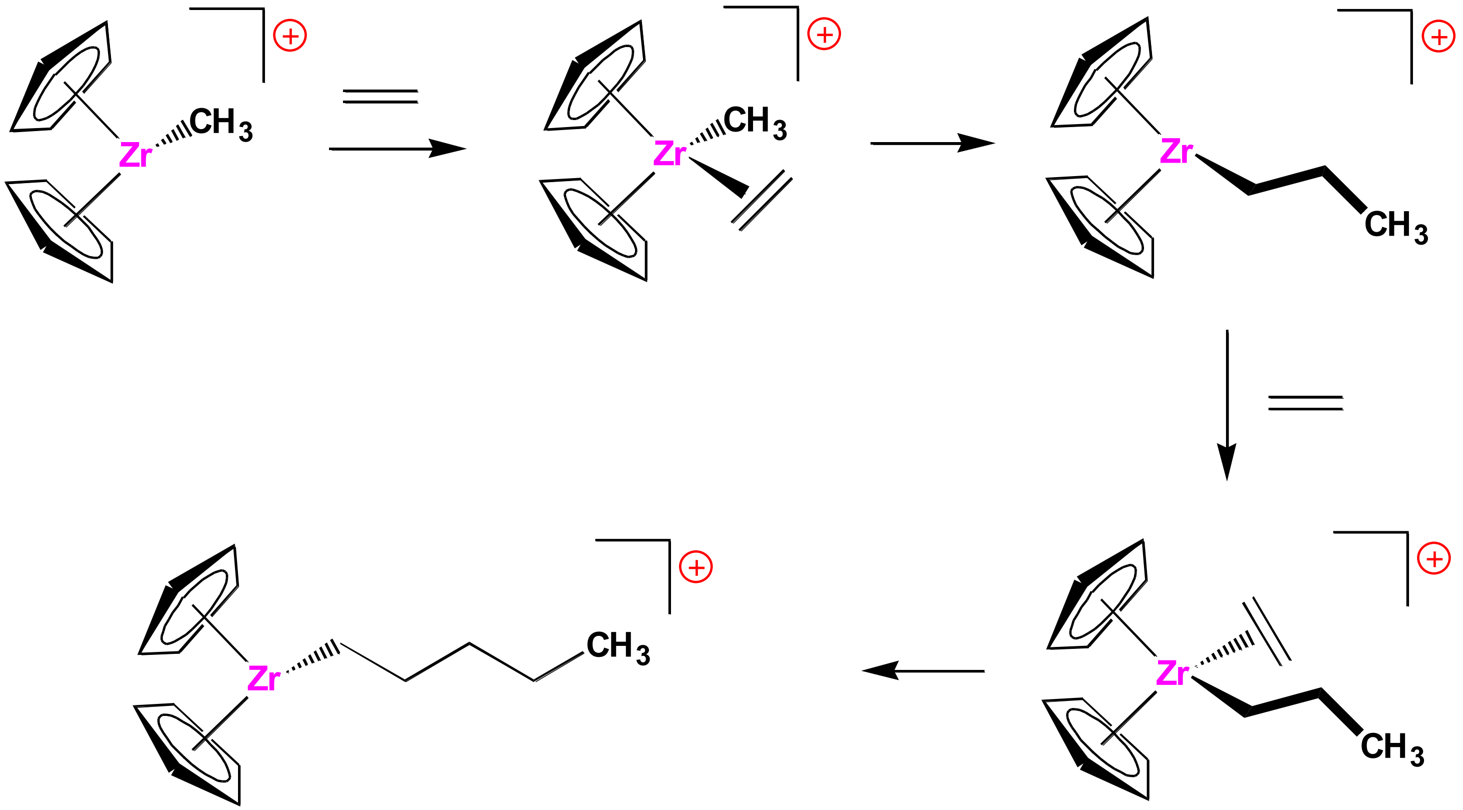
Alkene Migratory Insertions



General Features of Migratory Insertions:

1) No change in formal oxidation state (exception: alkylidenes)
2) The two groups that react must be cisoidal to one another

3) A vacant coordination site is generated by the migratory insertion. Therefore, a vacant site is required for the back elimination reaction (e.g., b-hydride elimination). A trapping ligand is often needed to coordinate to the empty site formed from a migratory insertion in order to stop the back elimination reaction.

4) Migratory insertions are usually favored on more electron-deficient metal centers.

The following are common **anionic** and **neutral** ligands that can do ***migratory insertion*** reactions with one another:

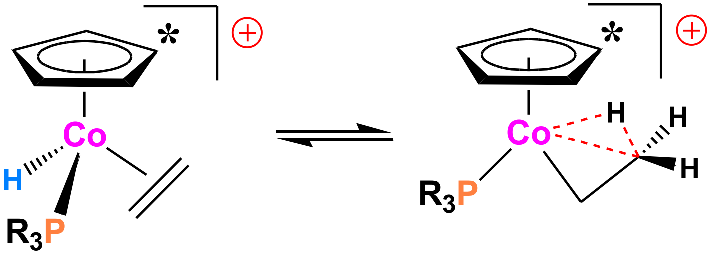
Anionic: H^-, R^- (alkyl), Ar^- (aryl), $acyl^-$,

Neutral: CO, alkenes, alkynes, carbenes

CO and alkyl migratory insertions (as shown on previous slide) are extremely important and are often generically referred to as **carbonylation** reactions.

Hydride and CO migratory insertions to produce formyl groups are not common due to the *thermodynamic instability* of the formyl-metal interaction.

Agostic C-H to Metal Interactions – “Frozen Migratory Insertion” or Intermediate

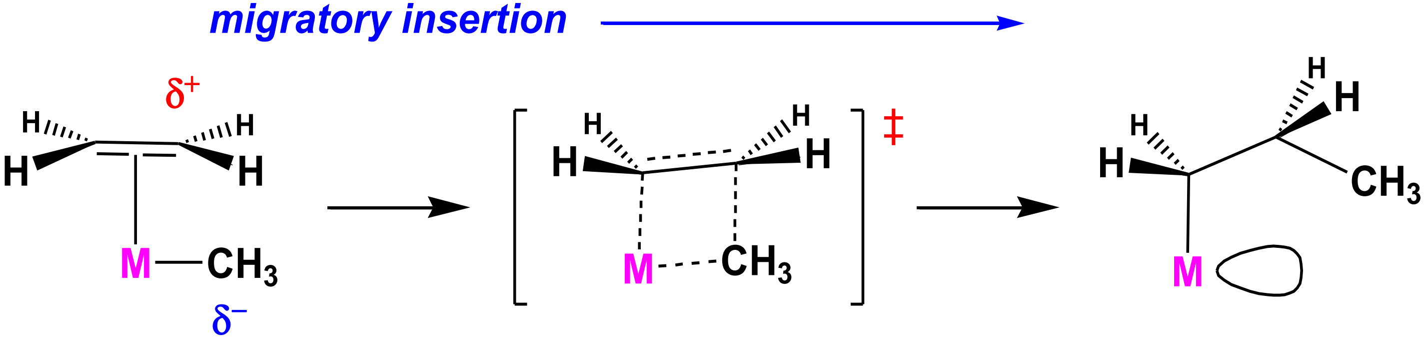


One of the C-H bonds of the methyl group is within bonding distance to the Co center.
This is called an ***Agostic*** *C-H bond interaction.*

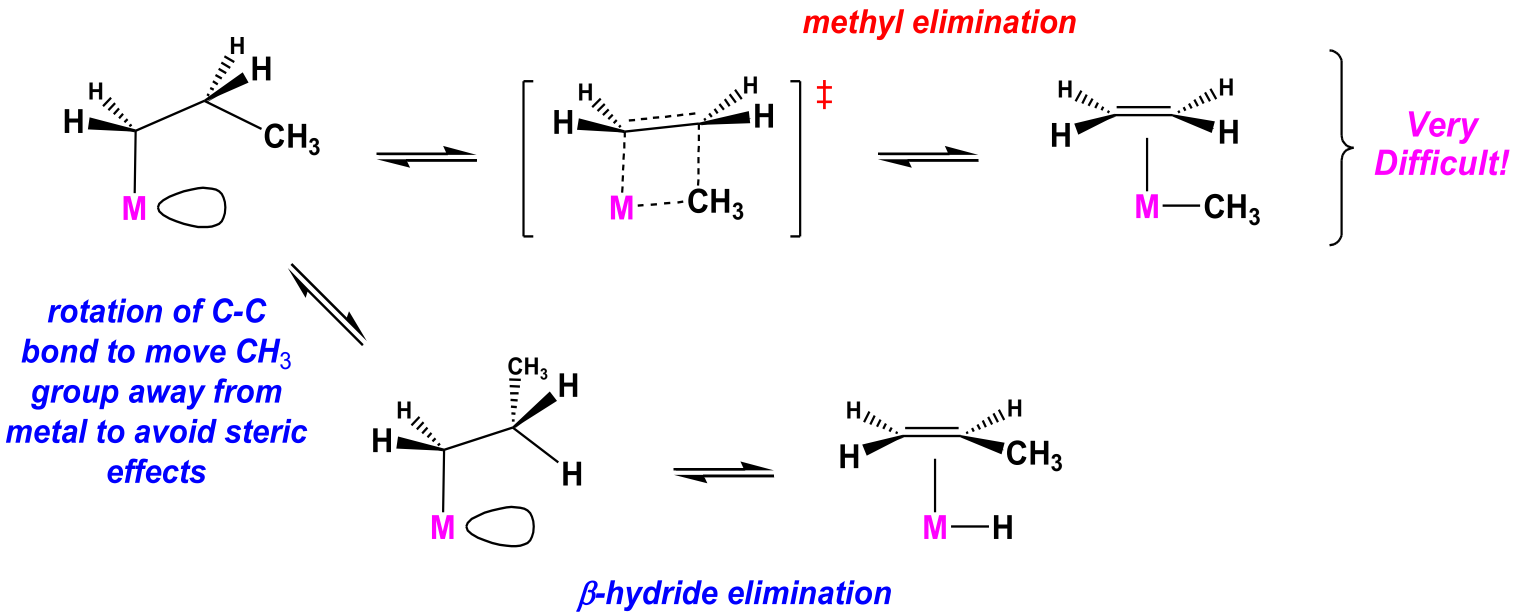
Because the C-H bond is sharing some of its σ-bond electron density with the metal, the C-H bond is *weakened*. This produces some relatively clear-cut spectroscopic characteristics:

1) $\nu_{C\text{-}H}$ infrared stretching frequency is lowered to the mid-2500 cm^{-1} region from a normal value of 2900-3000 cm^{-1}
2) the $J_{C\text{-}H}$ coupling constant in the ^{13}C NMR is lowered to around 70-90 Hz from a normal value of 150 Hz.
3) the ^{1}H chemical shift of the agostic proton is in the –10 to –15 ppm region, much like a metal-hydride resonance.

migratory insertion



But the reverse **methyl elimination** rxn is very difficult:

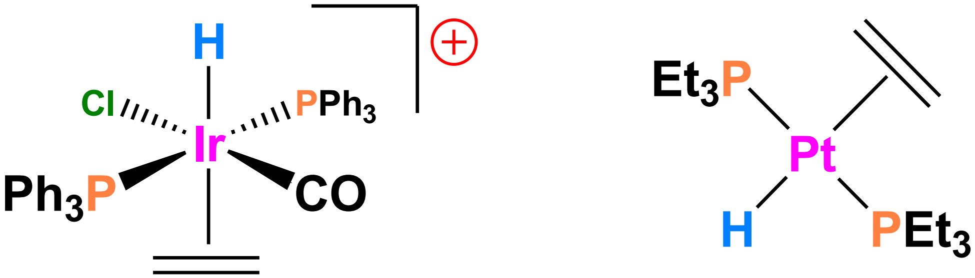

methyl elimination

Very Difficult!

rotation of C-C bond to move CH_3 group away from metal to avoid steric effects

β-hydride elimination

Problem: Why don't either of the complexes shown below do alkene-hydride migratory insertions at room temperature?



Problem: Sketch out and label the two mechanistic steps (in the correct order) that are occurring for the following reaction.