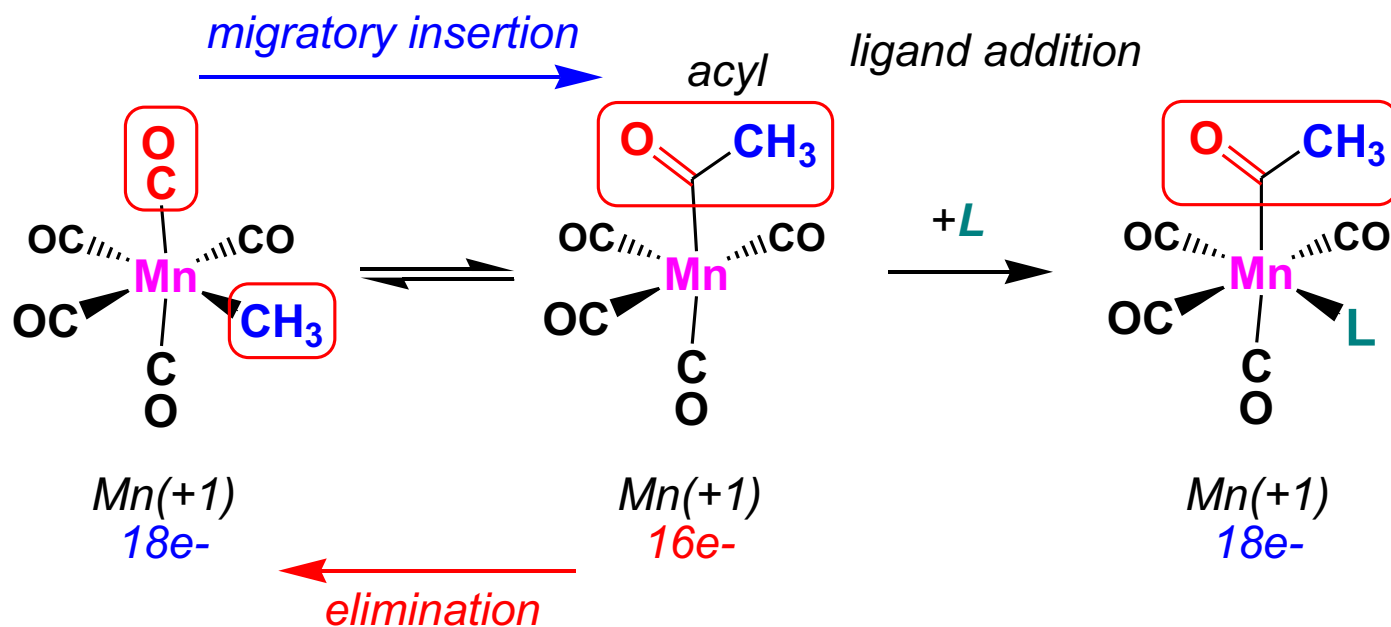


Migratory Insertion

In a *migratory insertion* reaction, a **cisoidal anionic** and *neutral* ligand on a metal complex couple together to generate a new coordinated *anionic* ligand.

There is **NO** change in the *oxidation state* of the metal center.

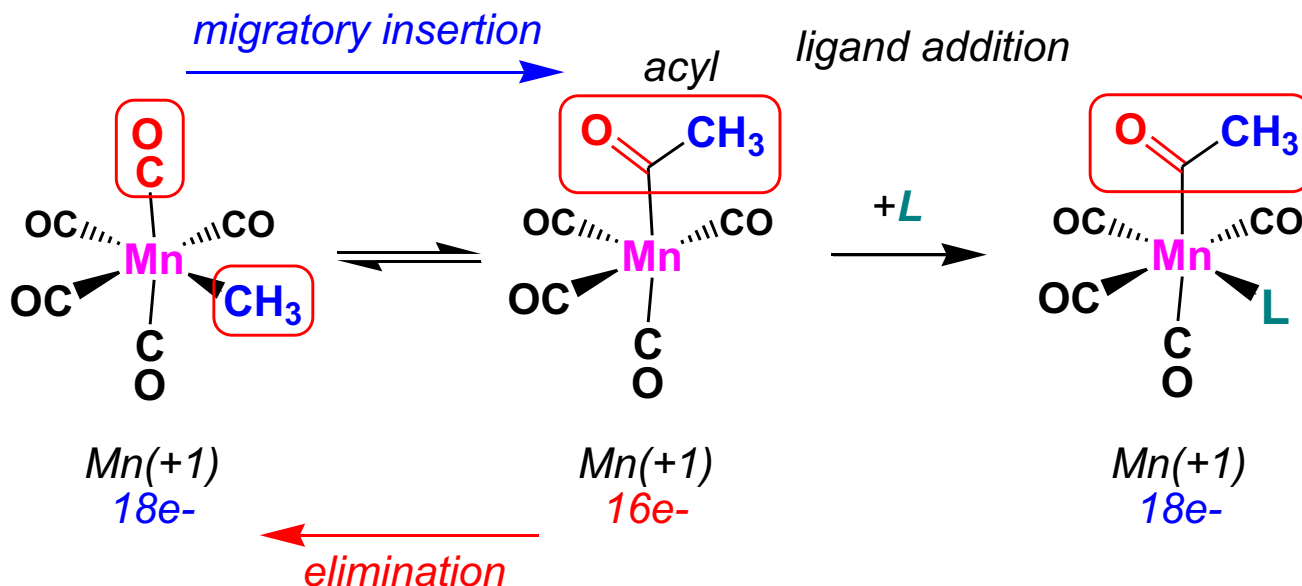
But the overall electron-count on the metal **decreases** by $2e^-$.



Migratory Insertion

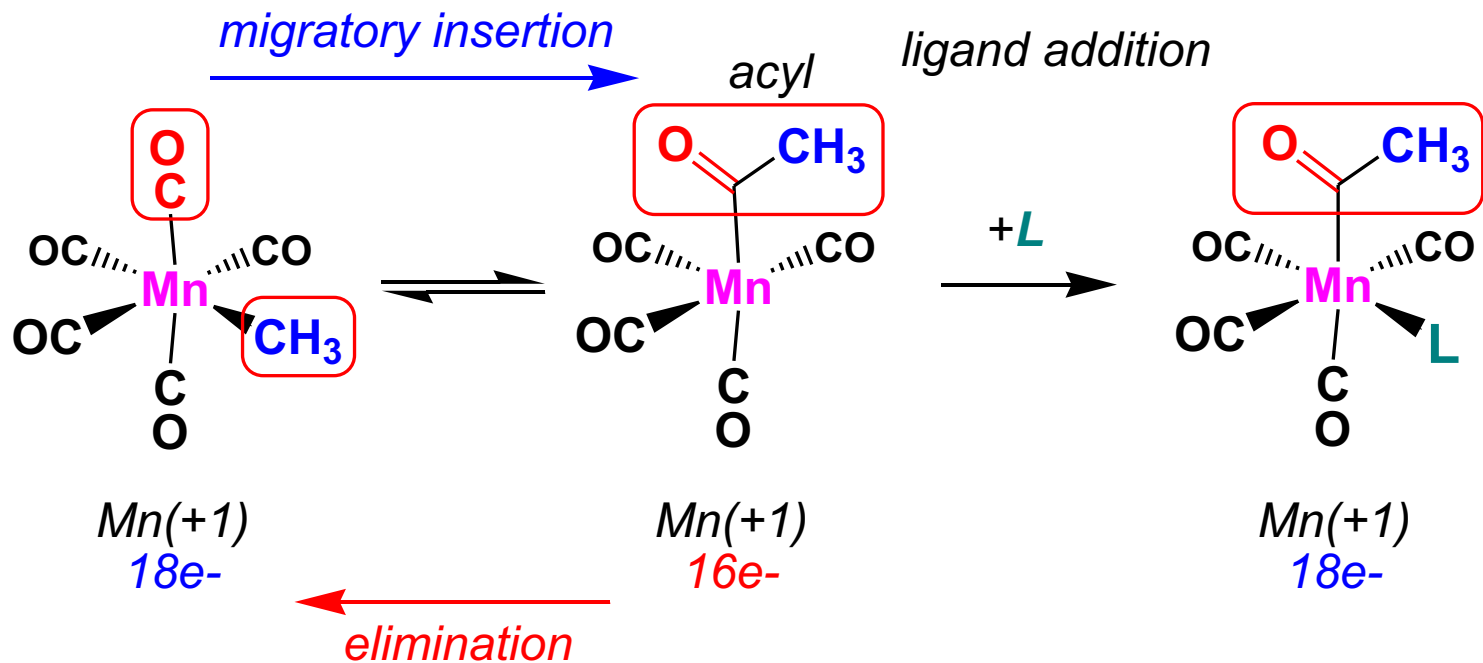
The empty orbital generated by the migratory insertion reaction can enable the reverse of a *migratory insertion* reaction, which is called an *elimination* reaction.

The reverse elimination reaction can be prevented from occurring, if one often adds a neutral ligand (trapping ligand) to coordinate to this empty orbital.



Migratory Insertion – *General Features*

- 1) No change in formal oxidation state
- 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 reverse elimination reaction. 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.



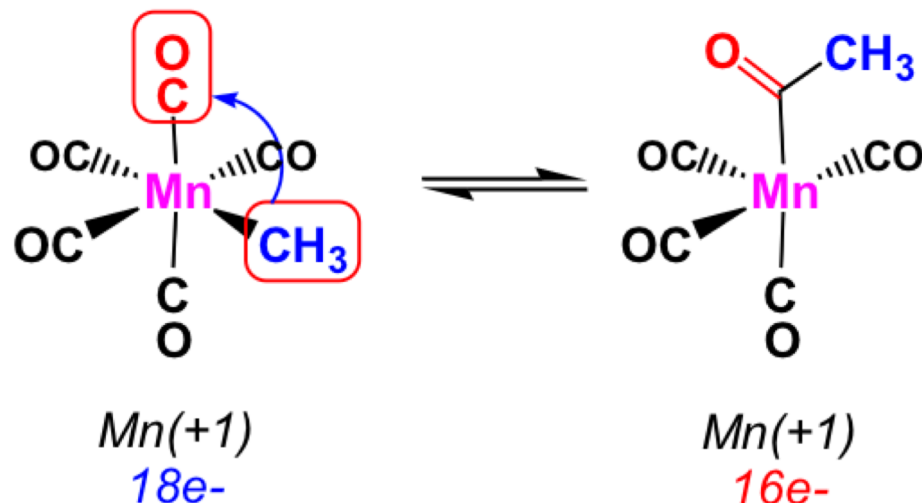
Anionic: H-, R- (alkyl), Ar- (aryl), acyl-, O_2^- (oxo)

Neutral: CO, alkenes, alkynes, carbenes

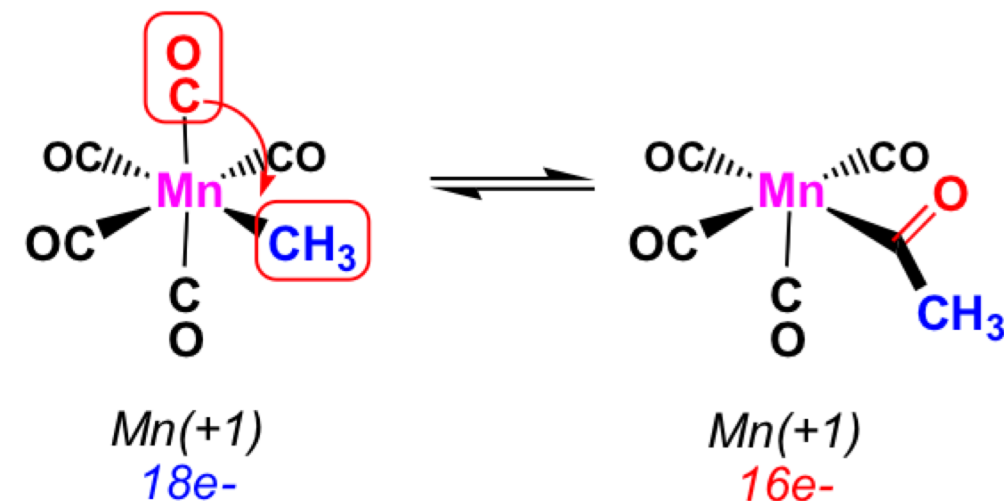
Migration Vs. Insertion

There are two different “directions” that a migratory insertion can occur.

Migration



Insertion

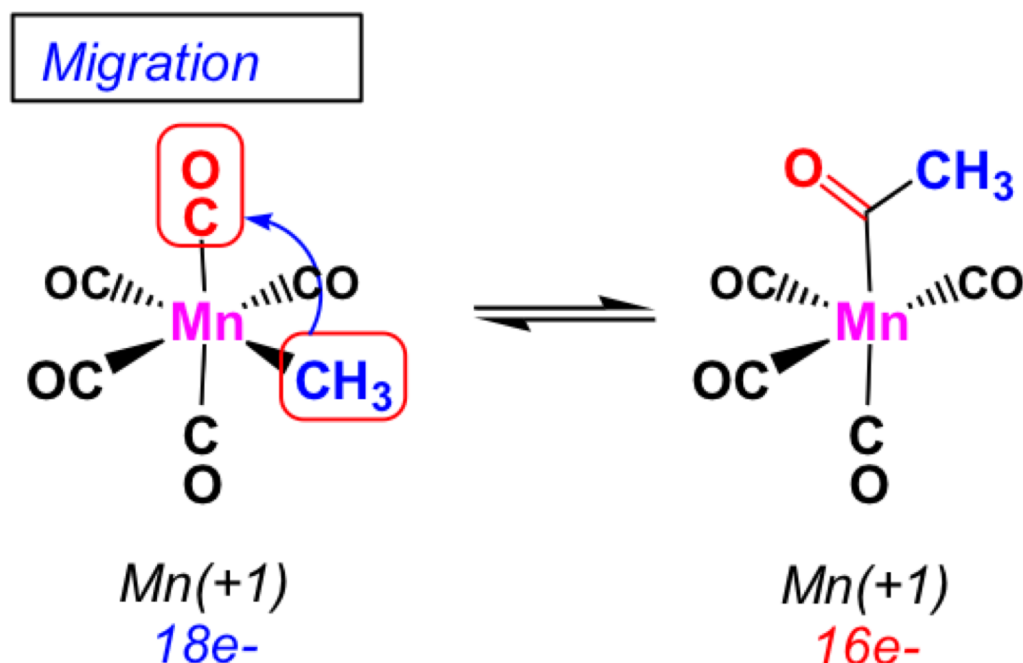


Migration Vs. Insertion

A **migration** is when the anionic ligand moves and performs a nucleophilic-like intramolecular attack on the electrophilic neutral ligand.

This involves the anionic ligand moving to the site where the neutral ligand was initially present.

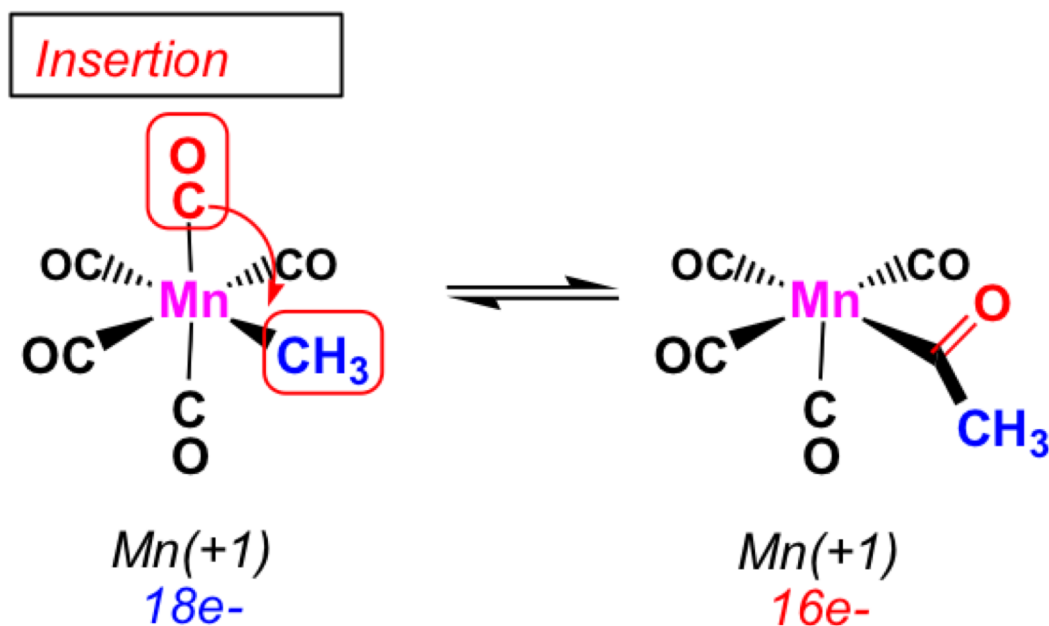
A new anionic ligand is generated. An empty coordination site is left behind (*where the old anion was originally present*).



Migration Vs. Insertion

An insertion is when the neutral ligand moves and “inserts” into the bond between the metal and anionic ligand.

A new anionic ligand is generated. An empty coordination site is left behind (*where the neutral ligand was originally present*).

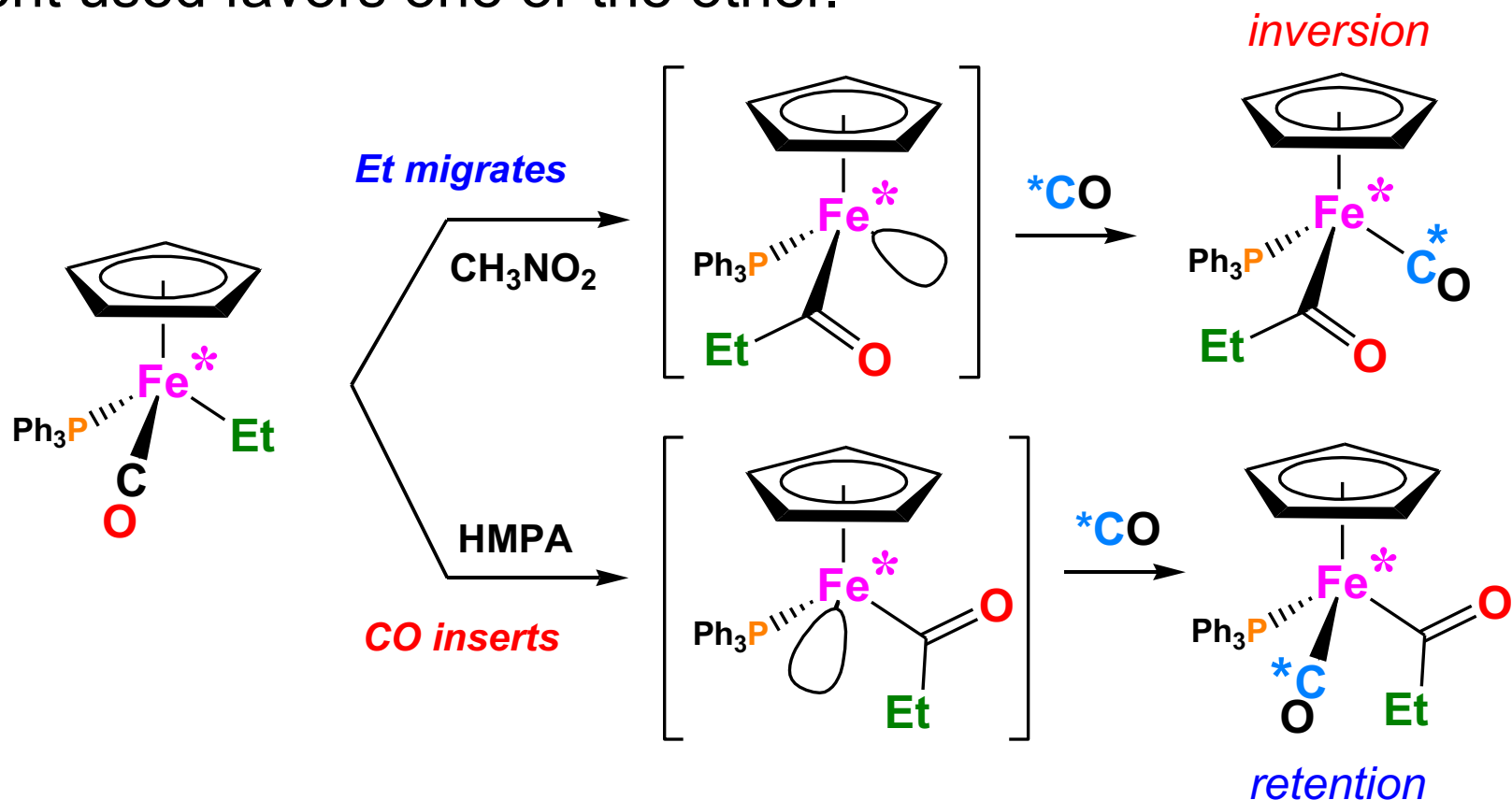


Generally one does NOT worry about the exact pathway, that is why the redundant term “*migratory insertion*” is used to indicate that either directional pathway is fine.

Migration Vs. Insertion

The following example is an exception and shows a system where both migration and insertion have a significant impact on the outcome of the reaction.

Here migration and insertion are very similar in energy and the solvent used favors one or the other.

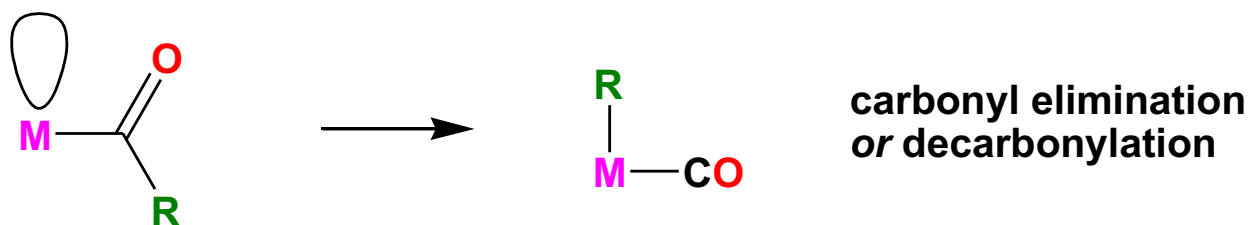
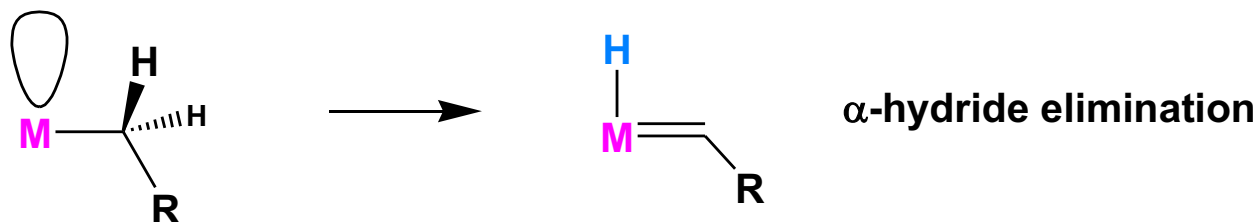
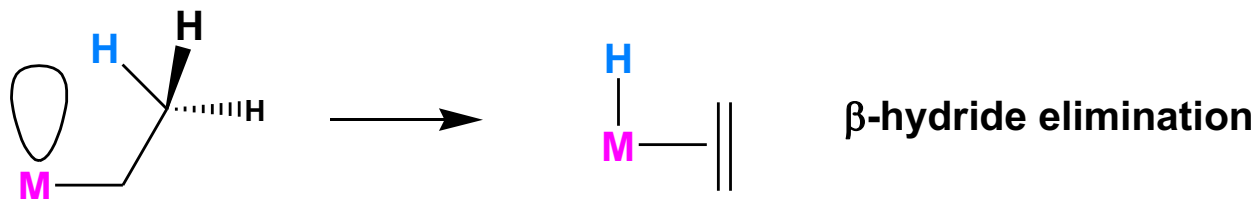


Elimination Reaction

Elimination reactions are just the **reverse** of migratory insertion reactions. Some points to remember:

No change in formal oxidation state

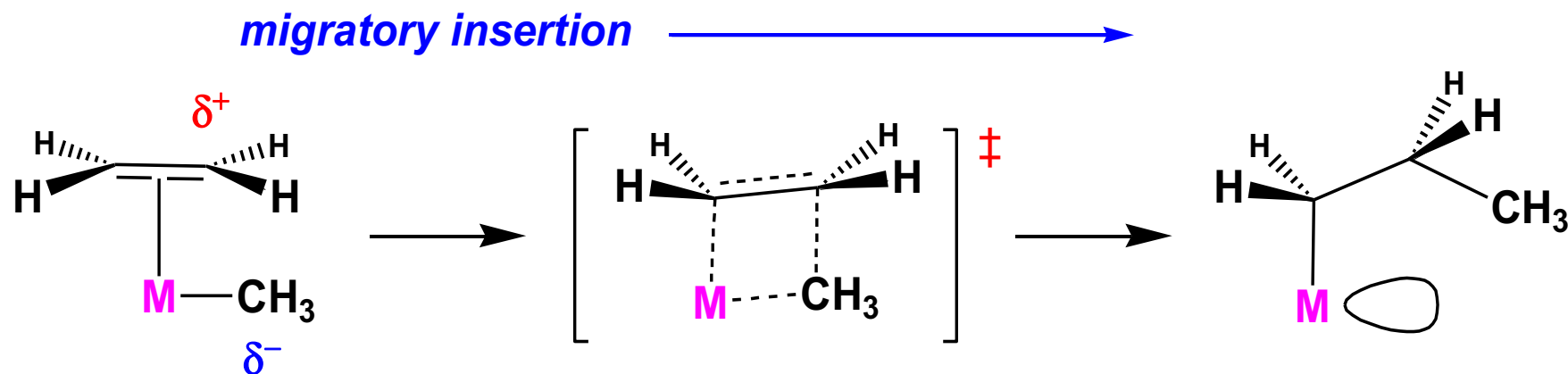
One must have an empty orbital (or an easily dissociate able labile ligand) that is cisoidal to the group that does an elimination.



Elimination Reaction

One of the hardest elimination reactions is the breaking of a C-C bond.

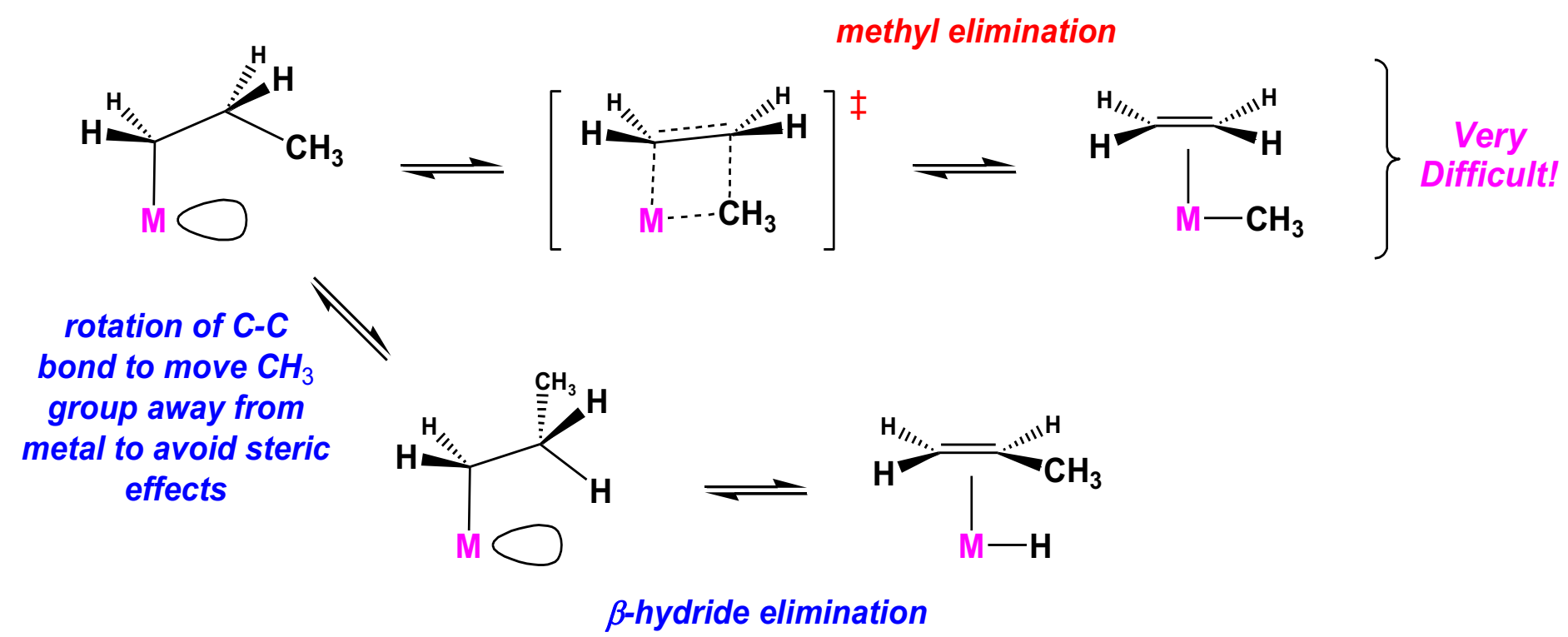
For example the following **migratory insertion** is quite common and plays a critical role in polymerization catalysis:



But the reverse **methyl elimination** reaction is very difficult

Elimination Reaction

The C-C σ -bond is surrounded by more reactive C-H bonds that are more prone to attack rather than the C-C bond. This results in a β -hydride elimination. The directed nature of the sp^3 hybridized C-C σ -bond also makes overlap with the empty metal orbital quite difficult



Hydroformylation

