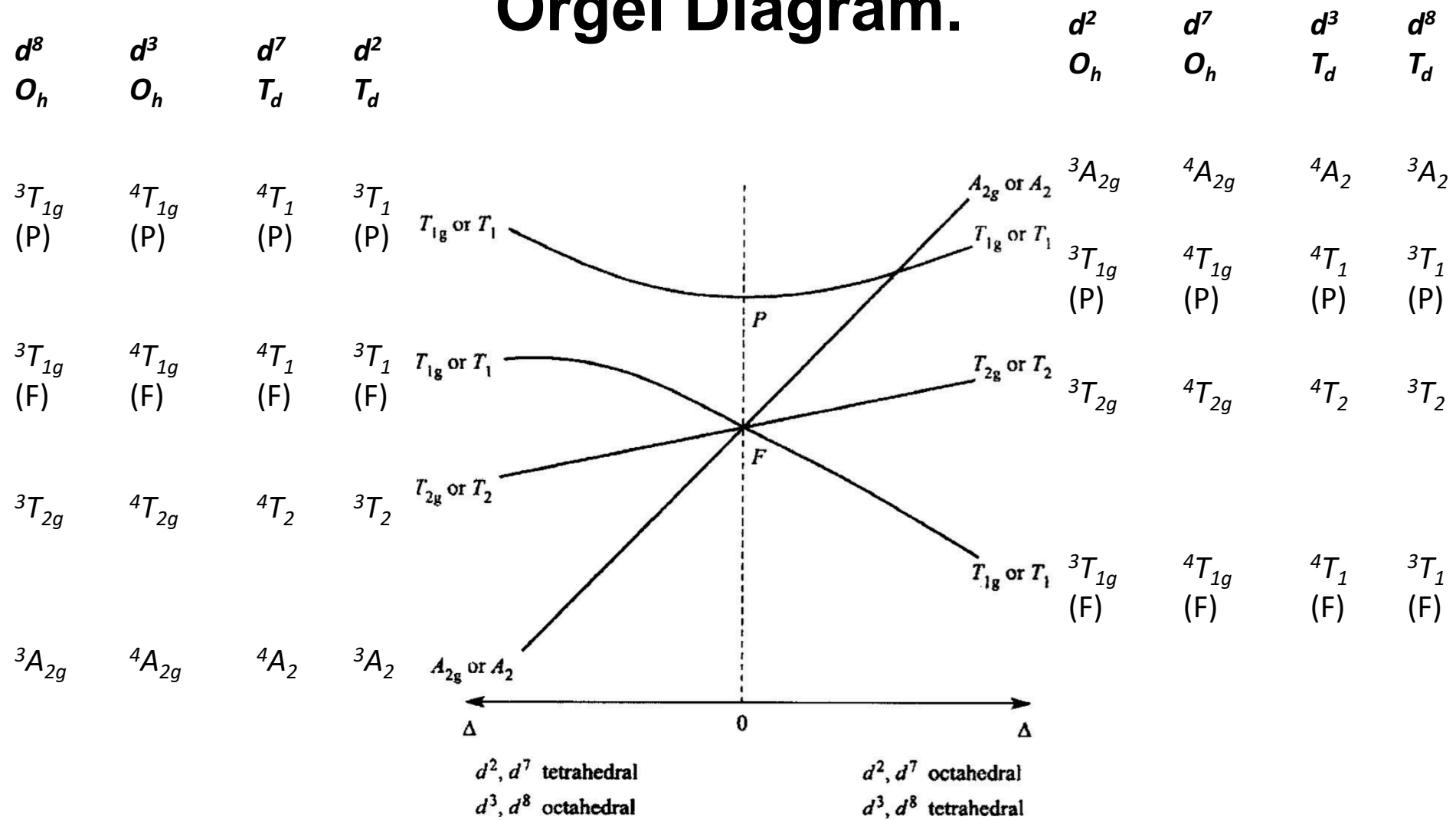


# Term Symbols.

$d^n$	$d^1$	$d^2$	$d^3$	$d^4$	$d^5$	$d^6$	$d^7$	$d^8$	$d^9$	$d^{10}$
Term Symbol	$^2D$	$^3F$	$^4F$	$^5D$	$^6S$	$^5D$	$^4F$	$^3F$	$^2D$	$^1S$

Term	Irreducible Representation
$S$	$A_{1g}$
$P$	$T_{1g}$
$D$	$E_g + T_{2g}$
$F$	$A_{2g} + T_{1g} + T_{2g}$
$G$	$A_{1g} + E_g + T_{1g} + T_{2g}$
$H$	$E_g + 2T_{1g} + T_{2g}$
$I$	$A_{1g} + A_{2g} + E_g + T_{1g} + 2T_{2g}$

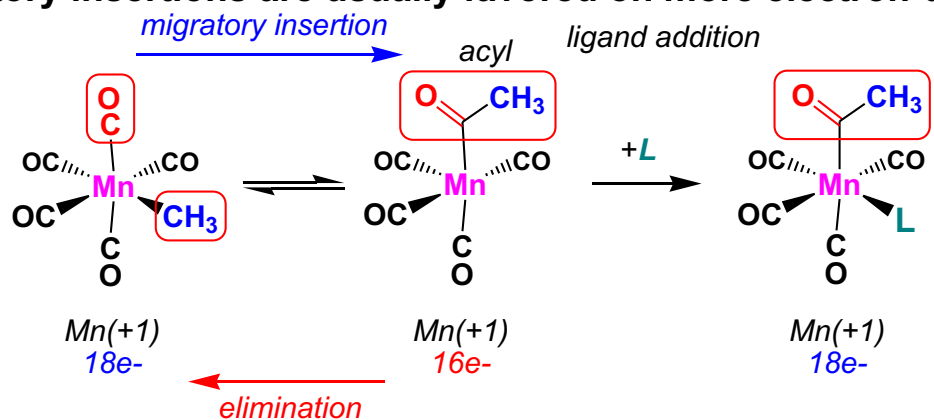
# Orgel Diagram.

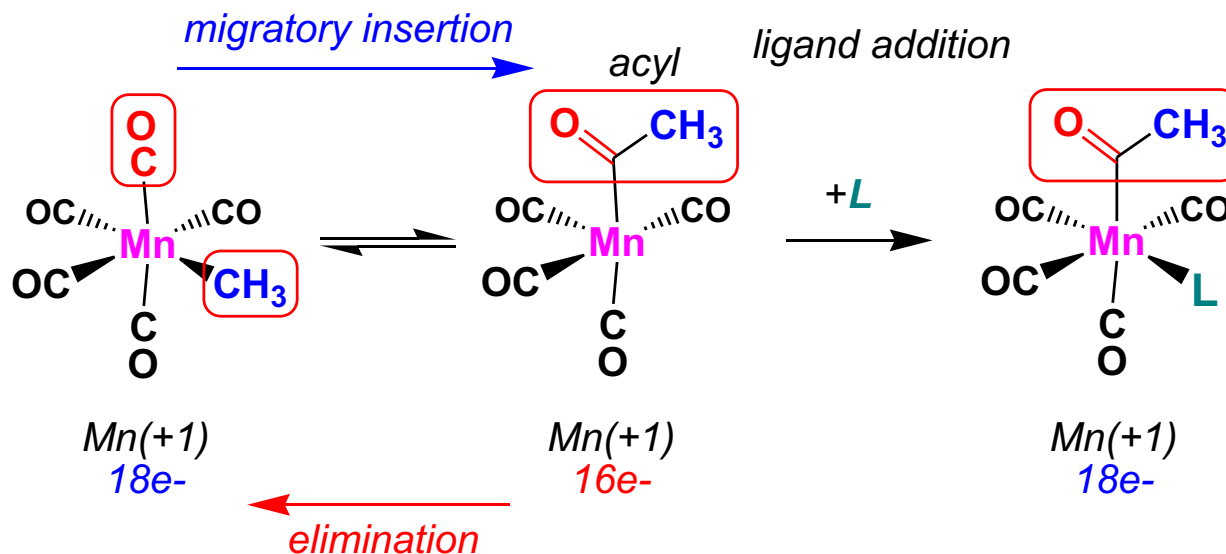


A **migratory insertion** reaction is when a **cisoidal anionic** and **neutral** ligand on a metal complex couple together to generate a new coordinated **anionic** ligand. This new anionic ligand is composed of the original neutral and anionic ligands now bonded to one another. **There is NO change in the oxidation state or d electron-count of the metal center.** But the overall electron-count on the metal **decreases** by **2e<sup>-</sup>**. The empty orbital generated by the migratory insertion reaction can enable the reverse of a **migratory insertion** reaction, which is called an **elimination** reaction (discussed in the next section). To stop the reverse elimination reaction from occurring after a **migratory insertion**, one often adds a neutral ligand to coordinate to this empty orbital thus stopping the **elimination** reaction from occurring. This is sometimes called the trapping ligand.

### General Features:

- 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.,  $\beta$ -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.



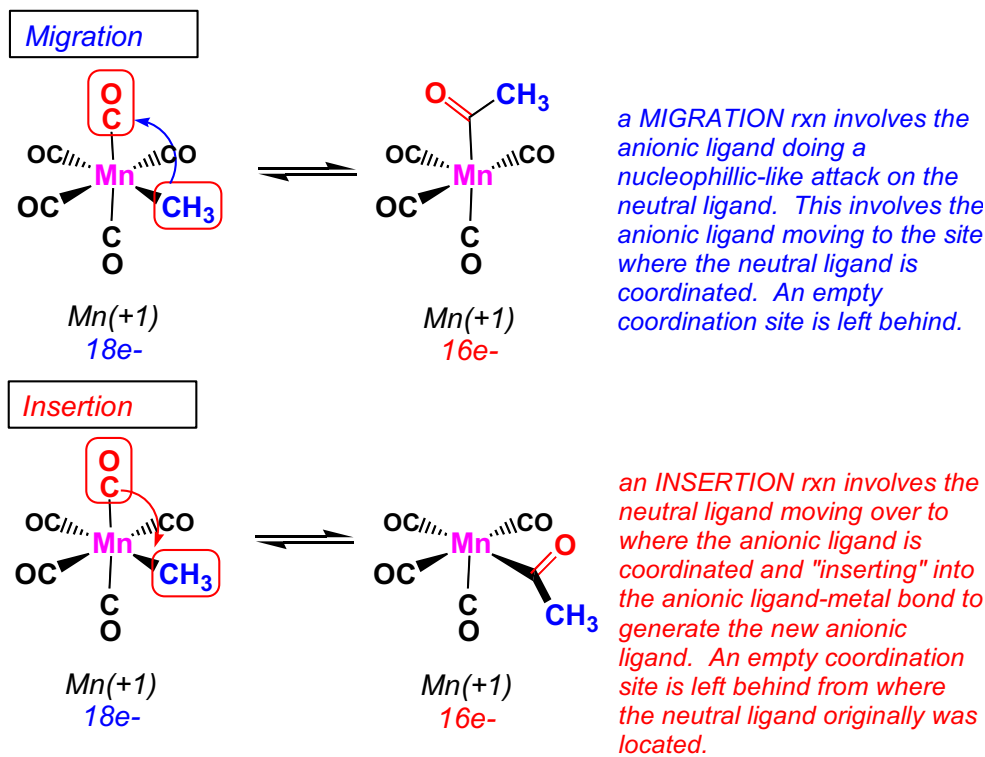


**Anionic:**  $H^-$ ,  $R^-$  (alkyl),  $Ar^-$  (aryl), acyl-,  $O_2^-$  (oxo)

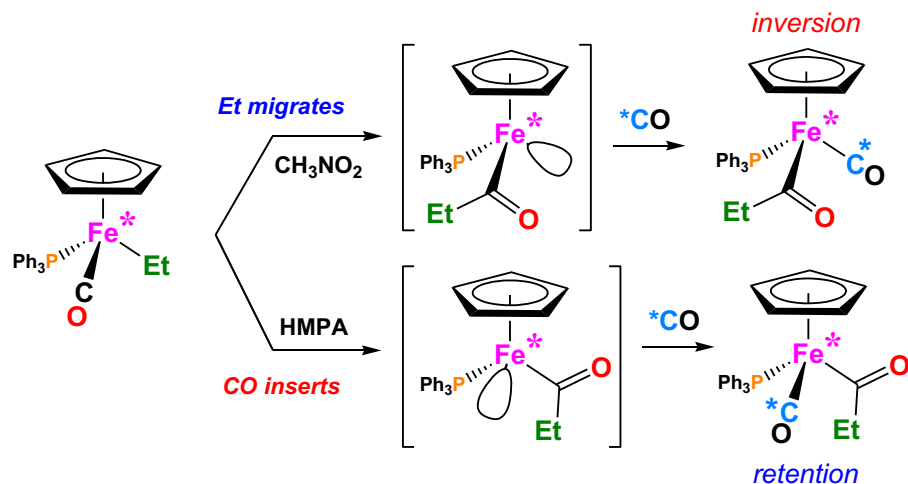
**Neutral:** CO, alkenes, alkynes, carbenes

# Migration vs. Insertion

There are two different “directions” that a migratory insertion can occur. A migration is when the anionic ligand moves and performs a nucleophilic-like intramolecular attack on the electrophilic neutral ligand. An insertion is when the neutral ligand moves and “inserts” into the bond between the metal and anionic ligand. Both of these pathways are illustrated below:



While most systems studied have been shown to do migrations, both are possible. The following example shows a system where both are very similar in energy and the solvent used favors one or the other.



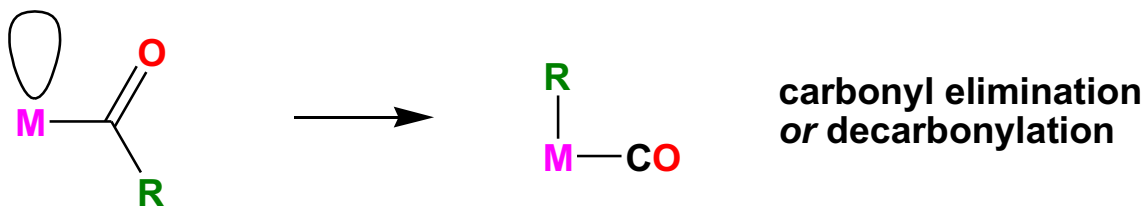
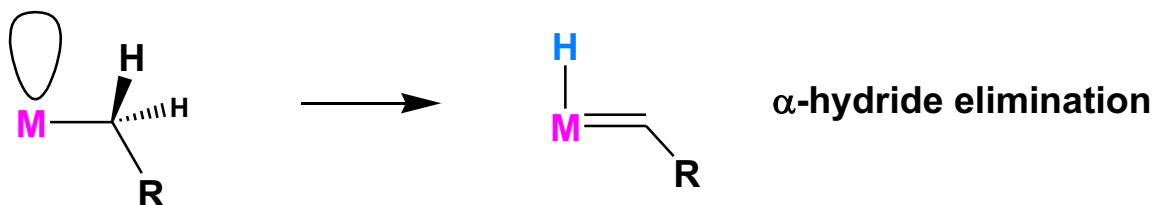
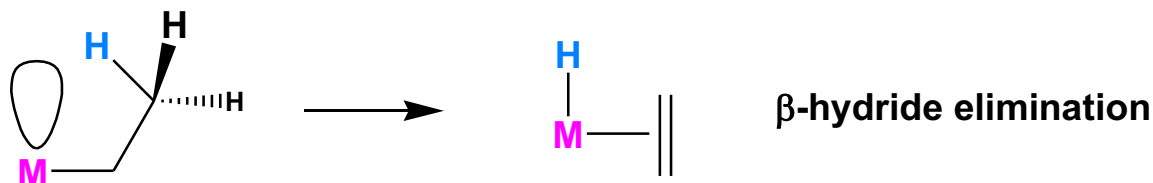
We generally do NOT worry about the exact pathway, that is why we use the redundant term “*migratory insertion*” to indicate that either directional pathway is fine and we don’t know (or care) exactly how the reaction is proceeding. Many organometallic chemists short-cut this and just say *insertion* reaction. They do not usually mean that they know what the mechanism is.

## Eliminations

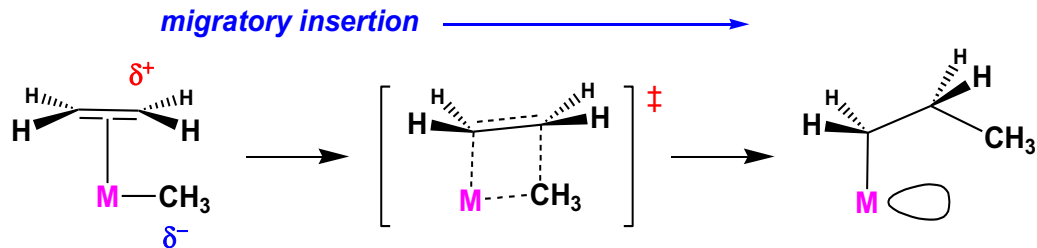
Elimination reactions are just the reverse of migratory insertion reactions. The various common elimination reactions are as follows:

The key points to remember are:

- 1) No change in formal oxidation state (exception: alkylidenes)
- 2) You must have an empty orbital that is cisoidal to the group that you are doing an elimination reaction on. Alternatively, a cisoidal labile ligand that can easily dissociate to open up an empty orbital.



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 rxn is very difficult:

One reason for this is that the C-C s-bond is surrounded by more reactive C-H bonds that short-circuit the attack on the C-C bond and can instead give a  $\beta$ -hydride elimination. The directed nature of the  $sp^3$  hybridized C-C s-bond also makes overlap with the empty metal orbital quite difficult

