# INSERTION AND ELIMINATION
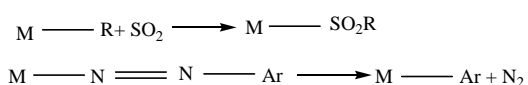
M. Sc. Sem.-IV (organomettalic)
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- Insertion and its reverse Elimination combine and transform the Ligands within the coordination sphere.
- ultimately expel these transformed ligands to form free organic compounds.
- In insertion a coordinated 2e ligand A=B
- Into M-X bond as M-(AB)-X.

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- There are two types of insertion -1,1 and 1,2.
- The metal and the X Ligand end up bound to the same (1,1) or adjcent (1,2) atom of an L-type ligand.
- The type of insertion observed in any given case depends on the nature of the 2e insering ligand. For exampale, COgives only 1,1 insertion: that is, boththe M and the X group end up attachet to the CO carbon.
- On the other hand, ethylene give only 1,2 insertion, in witch the M and the X end up of adjacent atom of what was the 2e ligand.
- In general, $\eta^1$ ligands tend to give 1,1 insertion and $\eta^2$ ligand give 1,2 insertion.
- SO$_2$ is the only common ligand that can only give both type of insertion; as a ligand, SO$_2$ can be $\eta^1$ or $\eta^2$ (S, O).

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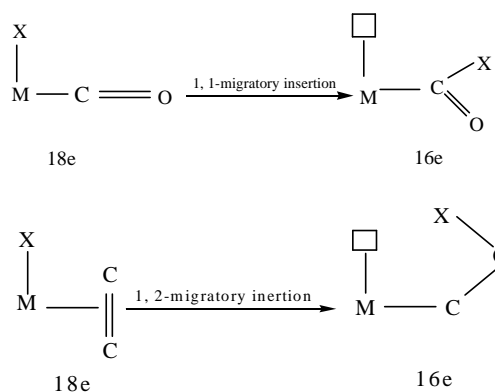
liganis only one of the two possible direction is obseerved in partice, probably because this direction is strongly favored thermodynamically. For example, SO$_2$ commanly insert into M-R bond to give alkyl sulfinate complexes, but thise rarely      eliminate SO$_2$.

Conversely, diazoarene complexes readily eliminate N$_2$ but N$_2$ has not yet been observed to insert into a metal – aryl bond.

$$M \longrightarrow R + SO_2 \longrightarrow M \longrightarrow SO_2R$$

$$M \longrightarrow N \equiv N \longrightarrow Ar \longrightarrow M \longrightarrow Ar + N_2$$

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- The immediate precursor to the final insertion product usually has both the 1e and 2e ligands coordinated. This means that a net 3e set of ligands is converted to a 1e insertion product (ionic model: 4e $\longrightarrow$ 2e), so that a 2e vacant site is generated by the insertion. This site can be occupied by an external 2e ligand and the insertion product trapped. Conversely, the elimination requires a vacant first dissociates. The insertion also requires a cis arrangement of the 1e and 2e ligands, while the elimination generates a cis

arrangement of these ligands. The formal oxidation state does not change during the reaction;

The below given reaction show the typical case of CO insertion.



(7.5)

$\triangle\ OS = 0$

$\triangle\ (e\ count) = -2$

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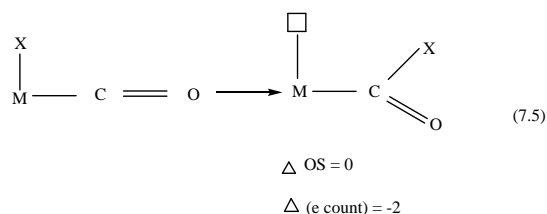
One way to show the insertion reactions is to consider that the X ligand migrates with M-X bonding electrons (e.g., $H^-$ or $Me^-$ )
to attack the л orbital of the A=B ligand.

# REACTIONS INVOLVING CO

CO shows a strong tendency to insert into metal-alkyl bonds to give acyls. The reaction has been carefully studied for a number of systems. Although the details may differ, most follow the pattern set by the best-known case:

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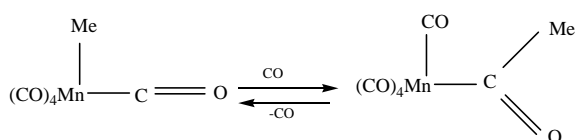


The mechanism of migratory insertion shown in the fig. below applies in many cases. The alkyl group in the reagent (Rgt) undergoes a migration to the CO to give an acyl intermediate that is trapped by added ligand, L, to give the final product.

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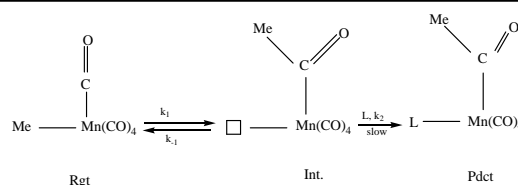


The kinetics in this situation are reminiscent of dissociative substitution except that the 2e site is formed at the metal in the migratory step, not by loss of a ligand. Using the usual steady-state method, the rate is given by:

$$Rate = \frac{-d[Rgt]}{dt} = \frac{k_1 k_2 [L][Rgt]}{k_{-1} + k_2[L]}$$

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• There are three possible regimes, all of which are found in real cases:

1. If $k_{-1}$ is very small relative to $k_2[L]$, [L] cancels and the equation reduces to:

$$Rate = \frac{-d[Rgt]}{dt} = k_1[Rgt]$$

Because $k_{-1}$ is small, L always traps the intermediate; this means the rate of the overall reaction is governed by $k_1$ and we have a first- order reaction.

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2. If $K_{-1\ is}$ very large relative to $k_2$ [L] ,then the equation becomes

Rate = -d[Rgt]/dt = $k_1 k_2$ [L][Rgt] / $k_{-1}$

**In this case the intermediate always go back to the starting reagent**

**And the second step, attack by L, which governs overall rate so we have second order kinetics.**

**3.** **If k-1 is comparable to k2 [L], then the situation is more complicated and the equqtion is usually rewritten as**

**4.** **Rate=-d[Rgt]/dt =kobs [Rgt]**

When incoming ligand is CO the product contains only one labeled CO which is cis to newly formed acetyl group

The methyl group migrates to the coordinated CO, rather than free CO attacking the Mn-Me bond.

$[Mn(CO)_5]^-$ $\xrightarrow[-Cl]{MeC^*OCl}$

(where $C^* = {}^{13}C$).