

10.2: Insertion and Elimination Reactions

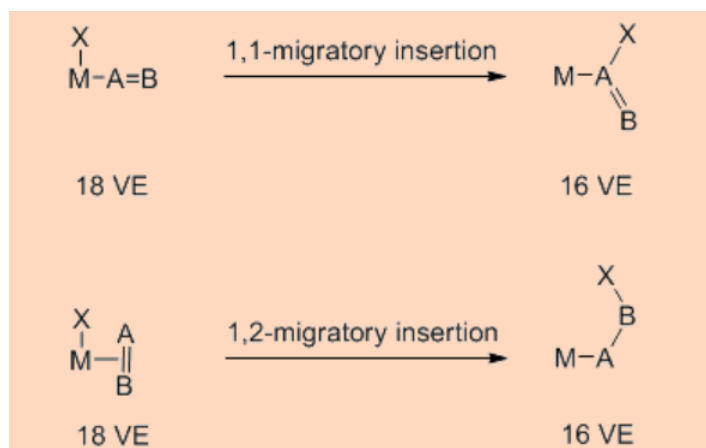
Learning Objectives

In this lecture you will learn the following

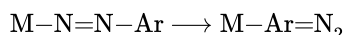
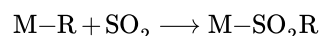
- The insertion and elimination reactions.
- The various mechanistic pathways by which these reactions proceed.
- Their relevance in some important catalytic cycles.

Unlike what we have learned about the oxidative addition and the reductive elimination reactions, that facilitate the addition or removal of 1-electron and 2-electron ligands on to a metal center, the insertion and the elimination reactions perform the subsequent transformation of these ligands from within the same coordination sphere of a metal. Thus, in an insertion reaction a metal bound 2 electron $A=B$ type of a ligand can insert on to a $M-X$ bond resulting in a new metal bound 1-electron ligand like, $M-A-B-X$, which is formed as a result of the formations of the $M-A$ and $B-X$ bonds. The insertion reaction thus leads to the generation of one vacant site created at the initial metal bound $A=B$ site. Thus a primary requirement for reverse elimination reaction to occur is the presence of a *cis* vacant site.

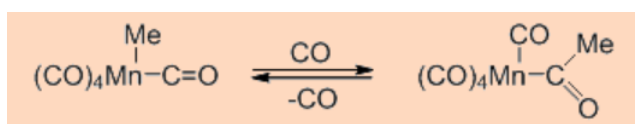
Insertions are of two types, 1,1-insertion and 1,2-insertion. In 1,1-insertion both the metal M and the ligand X of the $M-X$ bond end up on the same atom like in the $M-A(X)-B$ moiety formed after the insertion of the $A=B$ molecule in the $M-X$ bond, whereas in the 1,2-insertion, these end up on the adjacent atoms like in the $M-A-B-X$ moiety formed after the insertion of the $A=B$ molecule in the $M-X$ bond. The type of insertion depends on the type of the ligand undergoing the insertion like η^1 -ligand showing 1,1-insertion and η^2 -ligands showing 1,2-insertion. For example, the CO ligand exclusively undergoes 1,1-insertion while the C_2H_4 ligand undergoes 1,2-insertion. The SO_2 ligand remains the only exception as it can bind by both η^1 -(by S -donor site) and η^2 -(by S - and O -donor sites) modes and thus shows both type of insertions.



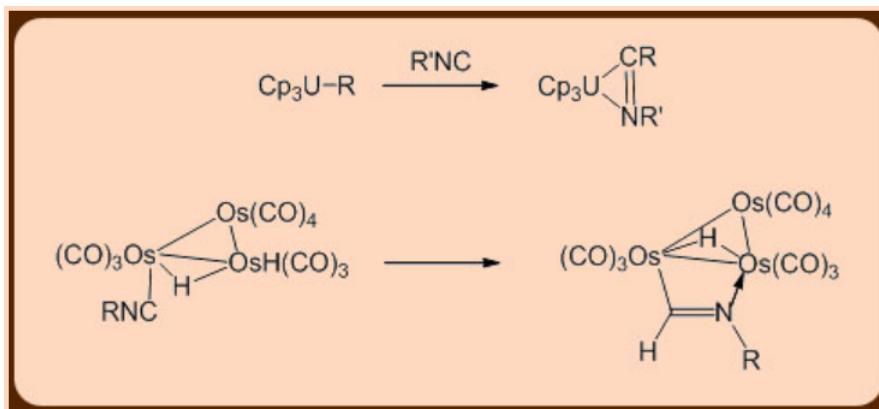
Though the insertion and the elimination reactions are mutually reversible, owing to the thermodynamical reasons one is favored over the other. For example, SO_2 is known to insert into the $M-R$ bond with no report of its elimination is known of it, while for N_2 ligand, no report of its insertion is known but it's elimination from a $M-N=N-R$ bond is known.



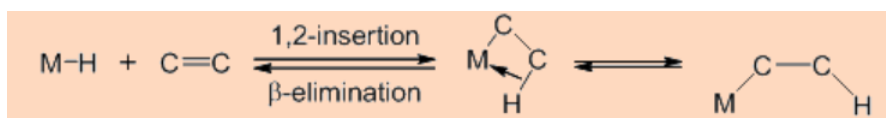
The CO ligand inserts readily into a metal-alkyl bond. Sterically demanding substituents (R) is found to accelerate the reaction as a bulky R group in an acyl moiety in the final $M-CO-R$ bond is far removed from the metal center than that in the starting $M-R$ bond.



Isonitriles readily insert into M-R and M-H bonds giving η^2 -bound iminoacyls.

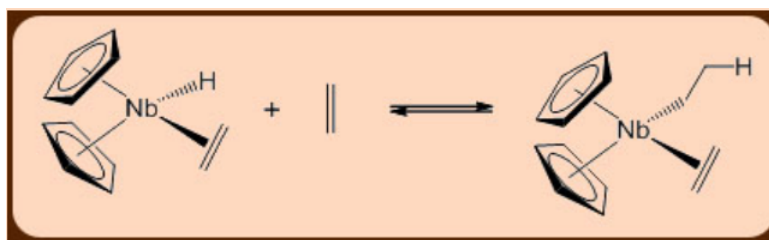


Olefins usually insert across a M-H bond and such insertions are of relevance to the commercially important olefin polymerization process. In certain cases the 1,2-insertions of olefins give species exhibiting agostic interactions.



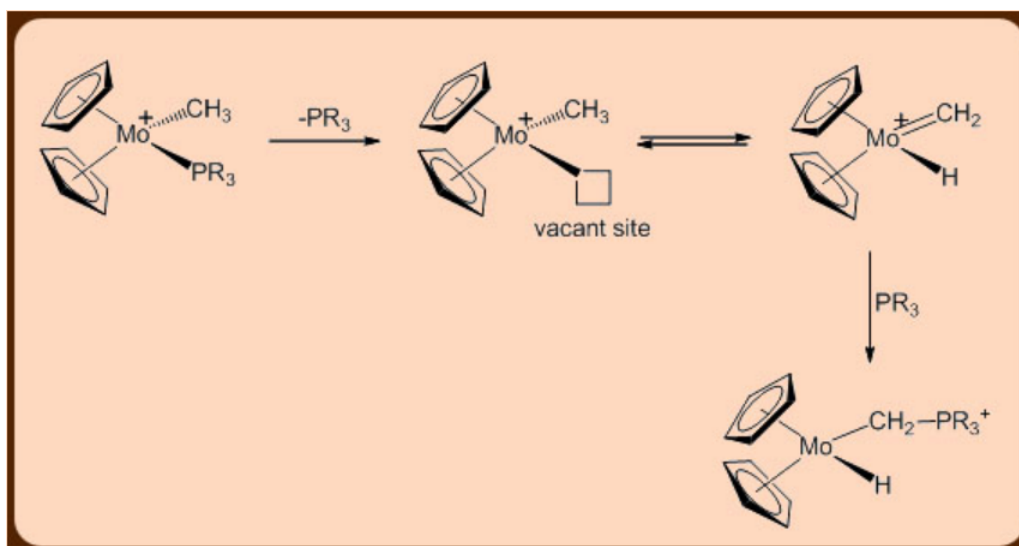
β -Elimination

β -elimination is just a reverse of 1,2-insertion and is a major cause of decomposition of metal alkyl bond having a β -hydrogen atom. A pre-requisite for the β -elimination reaction to occur is the presence of an adjacent vacant site next to the metal alkyl bond undergoing the β -elimination. The β -elimination step results in the formation of a metal hydride species that also contain a metal bound olefin moiety.



α -elimination

In absence of a β -hydrogen, a metal bound alkyl moiety may undergo the cleavage of a C-H bond at the α , γ and δ positions. For example, a methyl moiety may α -eliminate to give a metal bound methylene hydride moiety.



Problems

1. Give an example of a ligand that undergo 1,1-insertion.

Ans: CO

2. Give an example of a ligand that undergo 1,2-insertion.

Ans: C_2H_4

3. Give an example of a ligand that undergo both the 1,1-insertion and the 1,2-insertion reactions.

Ans: C_2H_4

Self Assessment test

1. On what type of bonds does CO insertion usually occur?

Ans: Metal-alkyl (M-R) bonds.

2. On what type of bonds does isonitrile insertion usually occur?

Ans: Metal-alkyl (M-R) and the metal-hydride (M-H) bonds.

3. On what type of bonds does C_2H_4 insertion usually occur?

Ans: Metal-hydride (M-H) bonds.

4. State an important requirement for the occurrence of an elimination reaction.

Ans: The presence of an adjacent vacant site.

Summary

Insertion and elimination reactions are important sequences that carryout transformation of the metal bound ligands to the corresponding product from within the same coordination sphere of the metal center and thus together represent key steps of an overall catalytic cycle. The insertions are highly ligand dependent and may proceed by 1,1-insertion and 1,2-insertion mechanisms. Elimination reactions are just reverse of the insertion reactions and they too may proceed by several pathways. The two pathways that are commonly observed are the β -elimination and the α -eliminations, even though other type of elimination pathways exists.

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