Student Corner

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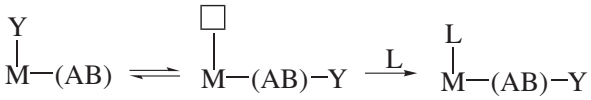
Insertion and deinsertion reactions

K Sarath D Perera

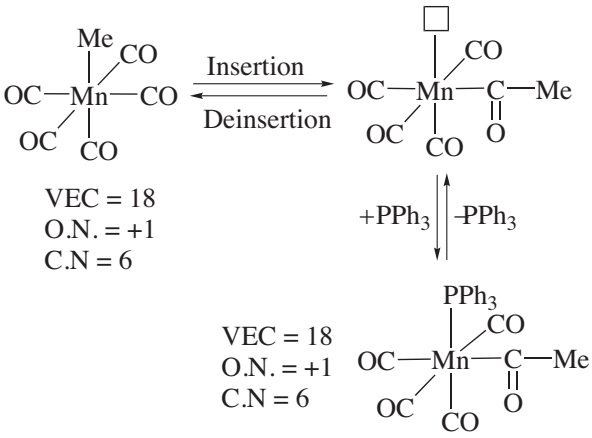
Senior Professor in Chemistry, Department of Chemistry, The Open University of Sri Lanka

In an insertion reaction, Y gets transferred on to a ligand (AB). This can be considered as a **migration reaction** as shown below.



Hence, these types of reactions are also known as **migratory insertion reactions**. In almost all cases, Y is a **mono anionic ligand** while AB is a neutral ligand with a multiple bond between A and B. Often, the first step of the insertion or migration reaction can be reversible; coordination of a suitable incoming ligand (L) make the process irreversible. The reaction of $[MnMe(CO)_5]$ with 1 equiv. of PPh_3 gives cis-$[Mn(COMe)(PPh_3)(CO)_4]$.

Mechanism of this simple, two-step insertion reaction is as follows:



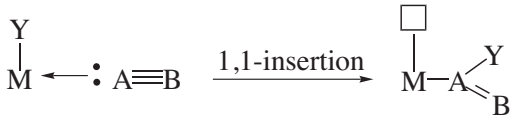
During this process, the oxidation number (O.N.), coordination number (C.N.), and VEC of the metal **remain unchanged.**

First, methyl group migrates on to CO ligand which is situated at ***cis* position** to form an acetyl group, and then PPh_3 group fills that vacant site. Therefore, PPh_3 group and acetyl group are ***cis* to each other**.

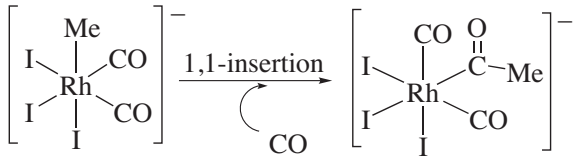
1,1-Insertion

Insertion can be either 1,1-insertion or 1,2-inserton.

In 1,1-insertion, AB ligand is a neutral, **η^1-type** ligand with a multiple bond such as CO and isonitriles. Due to the migration of Y on to A, both M and Y are bonded to A atom to give anionic ligand -A(=B)Y, and a vacant site on the metal.

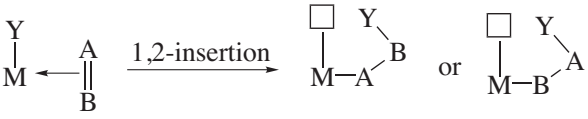


In the Monsanto process, before the final reductive elimination of MeCOI, the Me group migrates on to a CO ligand and the vacant site generated on Rh(III) is filled by another CO ligand.

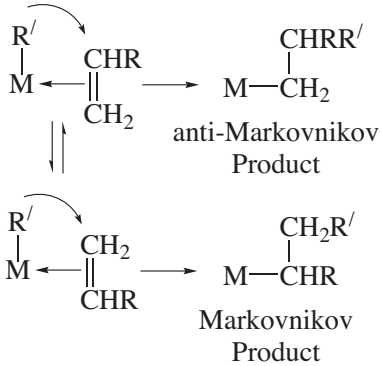


1,2-Insertion

In this case, ligands which are coordinated to a metal atom in the **η^2-fashion**, such as **alkenes** and **alkynes** undergo 1,2-insertion reaction as they contain double/ triple bonds.



However, with unsymmetrical olefins, formation of two types of products (**Markovnikov** and **anti-Markovnikov**) is possible during this reaction.

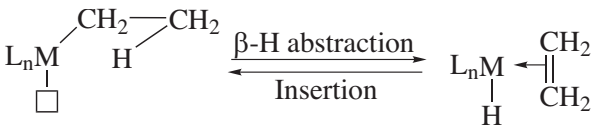


The product depends on the properties of the metal and ligands attached to it.

Deinsertion

Deinsertion can be simply known as the **reverse** or **opposite** reaction of the insertion reaction. To take place deinsertion reactions, there should be either a vacant site in the cis position of the metal centre, or coordinatively saturated metal should lose a ligand to generate a vacant site.

Deinsertion is somewhat similar to **β-hydride abstraction** by a metal centre: as the β-H of the alkyl group migrates to fill a vacant site in the metal centre.



Some examples for deinsertion of N_2, CO_2 or SO_2 are given below. These reactions take place by the action of heat or light. (L = PPh_3)

$$[PtPh(N{=}NPh)L_2] \rightarrow [PtPh_2L_2] + N_2$$

$$[Rh(CO_2Ph)L_3] \rightarrow [RhPhL_3] + CO_2$$

$$[(OC)_2CpFeSO_2Ph] \rightarrow [(OC)_2CpFePh] + SO_2$$

Problems

1. Suggest products for the following insertion and deinsertion reactions.

   (i) $[Cp^*_2ZrMe_2] + CO \rightarrow$

   (ii) $[Cp_2MoH(\eta^2\text{-}C_2H_4)]^+ + PMe_3 \rightarrow$

   (iii) $[CpCo(Et)PMe_3]^+ \rightarrow$ deinsertion

2. Suggest a suitable mechanism for the following reaction.

   $[MnMe(CO)_5] + CF_2{=}CF_2 \rightarrow [MnCF_2CF_2Me(CO)_5]$

3. Draw the structures of **A**, **B** and **C** of the following reaction scheme.

   $$[Mn_2(CO)_{10}] \xrightarrow[(i)]{Na} \mathbf{A} \xrightarrow[(ii)]{MeCOCl} \mathbf{B} \xrightarrow[(iii)]{\triangle} \mathbf{C}$$

   (**A**, **B** & **C** are 18e-complexes; (i) Reduction; (ii) Substitution; (iii) Deinsertion)