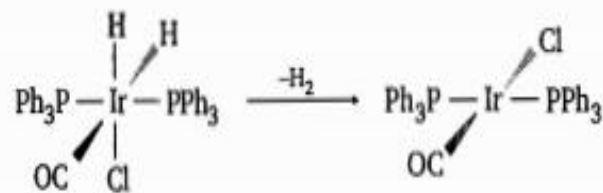
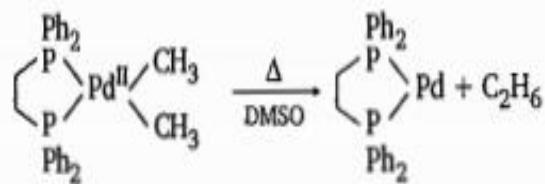
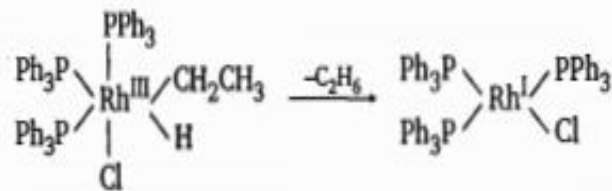
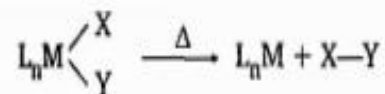
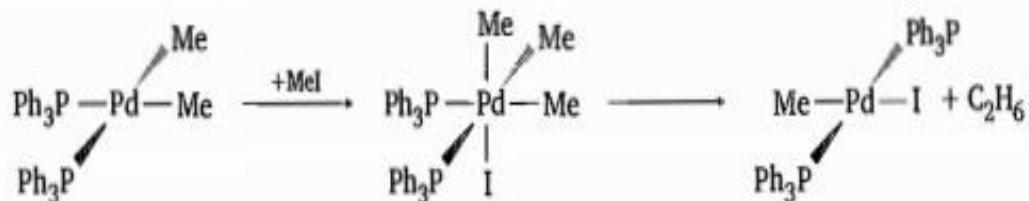


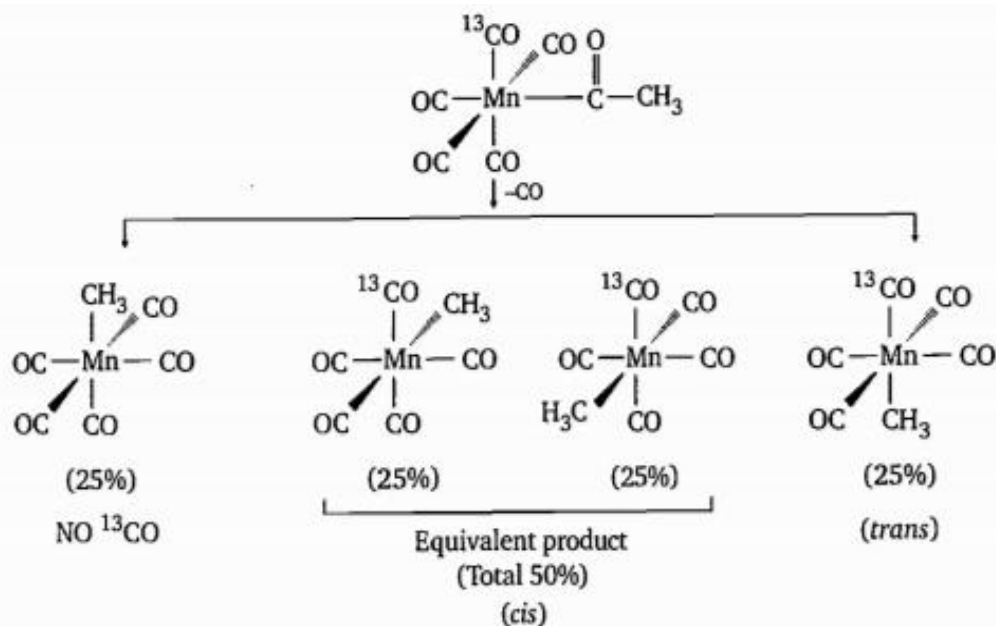
## Reductive Elimination

The reaction in which two *cis* ligands bound to metal couple together and leave the metal and the formal oxidation of the metal is reduced by two units is called a reductive elimination reaction. The reductive elimination reaction is the reverse of the oxidative addition reactions. Some examples are :



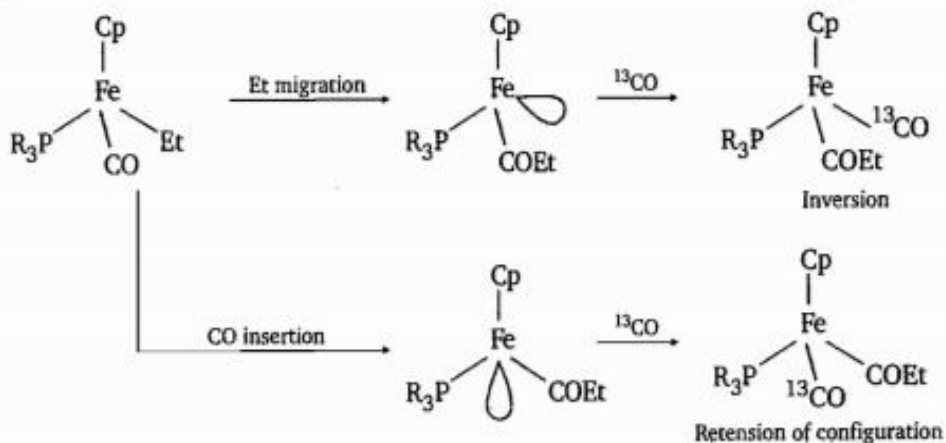
Some times the molecule eliminated is different from the one added oxidatively. For example,





Since the alkyl migration is consistent with these experimental results, therefore, when the term CO insertion is used, it often means that there is alkyl migration.

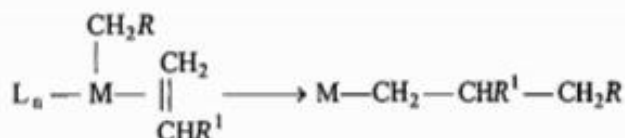
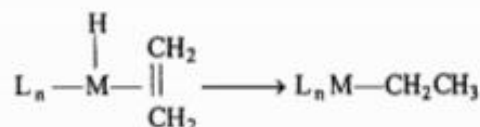
Another important evidence in favour of the migratory insertion is the stereochemical evidence.



When the reaction is carried out in  $\text{CH}_3\text{NO}_2$ , the product with inversion centre is formed which is consistent with Et migration.

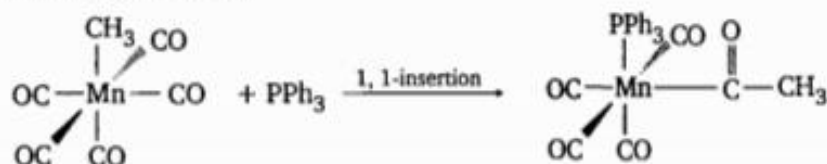
### Insertion of Alkenes

The migratory insertion of an alkene into  $\text{M}-\text{H}$  or  $\text{M}-\text{R}$  bond results in the conversion of a coordinated alkene to a  $\sigma$ -bonded alkyl group. This reaction involves migration of an H or alkyl group and results in carbon chain growth.



The H or alkyl group is migrated to the  $\beta$ -carbon of the alkene to form the metal alkyl complex. It is to be noted that CO insertion occurs into M—R bond but not in M—H bond. The insertion reactions can be classified into (1) 1,1-insertion (2) 1,2-insertion.

In 1,1-insertion reactions, the metal and the migrated ligand make the bonds to the same atom of the unsaturated ligand such as CO.



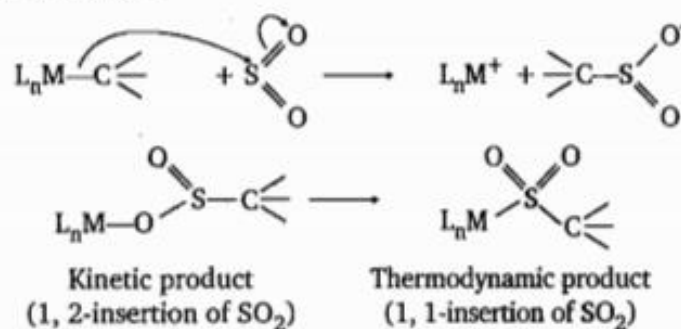
The insertion of CO into metal-alkyl bond of  $\text{CH}_3\text{Mn}(\text{CO})_5$  is also an example of 1,1-insertion.

In 1,2-insertion reactions, the metal and the migrated ligand make bonds to the adjacent atoms of the unsaturated ligand. Insertion of an alkene into M—H or M—R bond is an example of 1,2-insertion.

In general,  $\eta^1$ -ligands tend to favour 1,1-insertion whereas the  $\eta^2$ -ligands tend to favour 1,2-insertion.

$\text{SO}_2$  is an example which can undergo both 1,1- and 1,2-insertions. It is a strong electrophile with a vacant orbital on sulphur and therefore, it can attack even  $18e$  complexes.

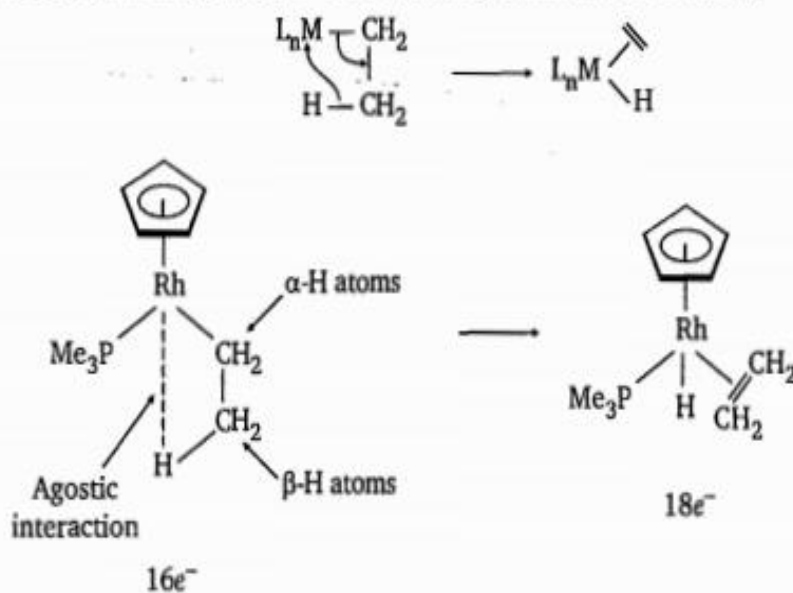
As an electrophile it can attack at the  $\alpha$ -carbon of the alkyl group from the side-opposite of the metal and forms an alkyl sulfinato ion,  $\text{RSO}_2^-$  with inversion at carbon. Since the negative charge is present on oxygen, kinetically oxygen of this ion can bound to the metal to form O-bound sulfinato complex. Since S is softer than O, therefore, the thermodynamic product is usually the S-bound sulfinato with soft metal. It can be concluded that in this reaction sequence  $\text{SO}_2$  first undergoes 1, 2 insertion and then 1, 1 insertion.



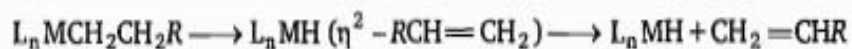
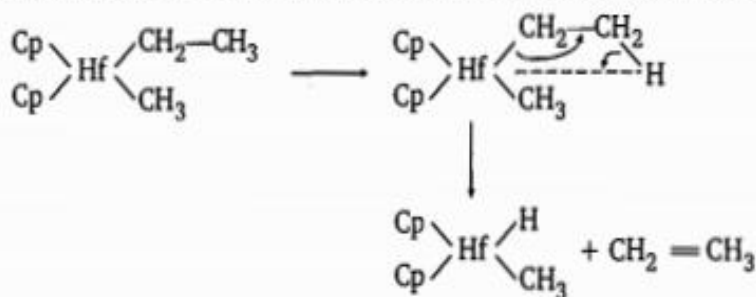
## $\beta$ -H Elimination

$\beta$  - hydrogen elimination is the reverse of the alkene insertion. It involves the transfer of  $\beta$  -hydrogen atom from the alkyl group to the metal and the conversion of the  $\sigma$  -alkyl group to the  $\pi$  -bonded alkene, *i.e.*, C—H bond is activated. The first step involves a cyclic intermediate with an

agostic M—H—C interaction. The agostic interaction is a three centred two electron ( $3c - 2e$ ) interaction between the metal M and a C—H bond in a ligand attached to metal.

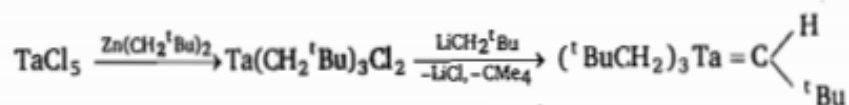


$\beta$  -elimination is responsible for the decomposition of some metal alkyl complexes.

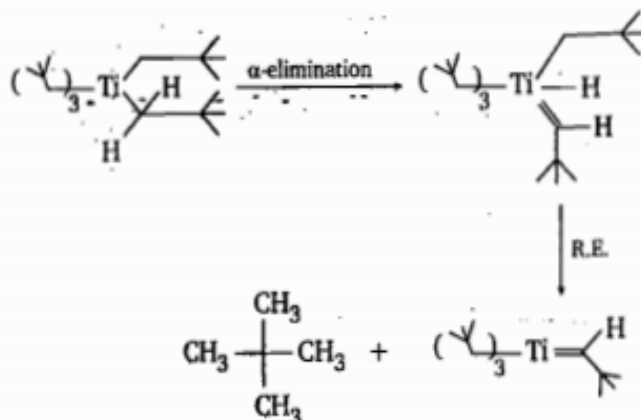
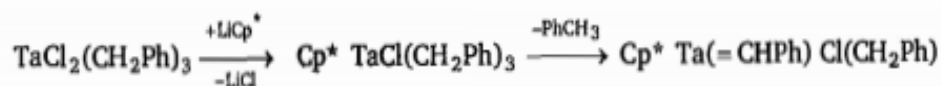
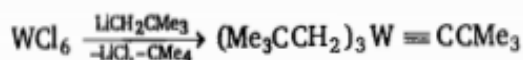


## $\alpha$ -H Abstraction

The alkyl complexes of early transition metals containing one or two  $\alpha$  -hydrogens but not  $\beta$  -hydrogens in alkyl groups may undergo  $\alpha$  -hydrogen abstraction to give carbene or carbyne complexes.



Abstraction of a two  $\alpha$  -H atoms gives a carbyne complex.



The  $\beta$  -elimination gives an alkene, a stable compound that dissociates from the metal. Whereas the methylene ligand formed from the  $\alpha$  -elimination is very unstable in the free state and therefore does not dissociate from the metal.