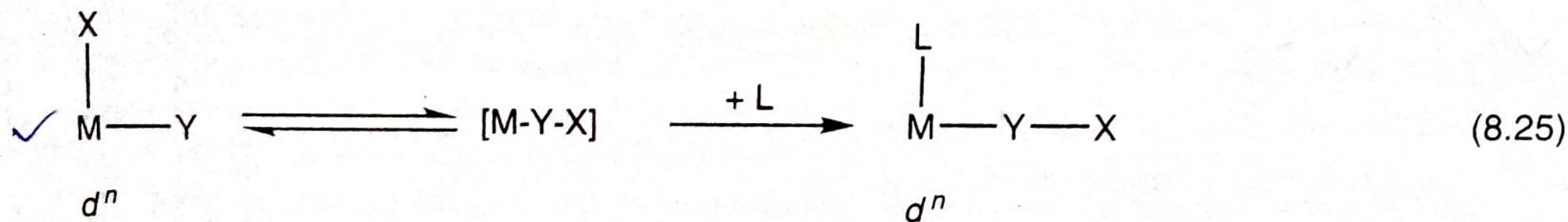


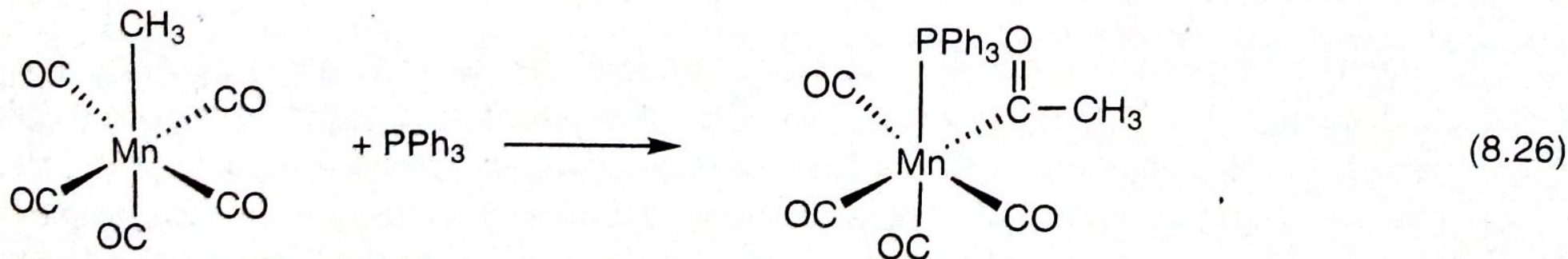
8.3 MIGRATORY INSERTION REACTIONS

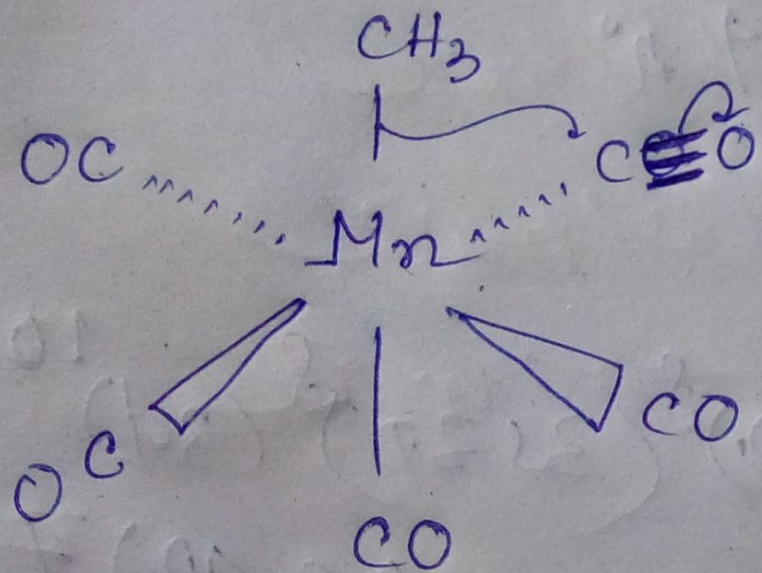
Oxidative addition and substitution reactions allow us to assemble 1e or 2e ligands on the metal. With insertion and its reverse reaction, de-insertion or extrusion, these ligands can be combined and transformed within the coordination sphere of the metal. The ligands can then be expelled to obtain the organic products.

Insertion broadly describes a reaction in which any atom or group is inserted between two other atoms initially bound together. Another ligand L usually occupies the vacant site that is created by the insertion. The incoming ligand L, may be any Lewis base, including the solvent.

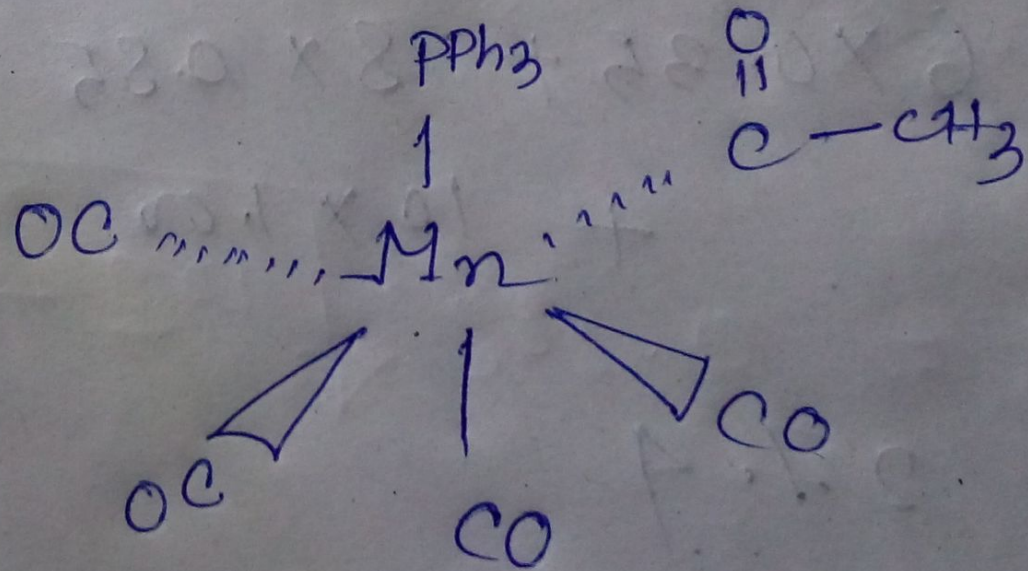
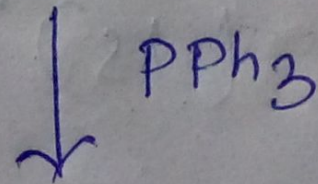


Y = CO, C=C, -C≡C-, arene; X = H, R, Ar, -COR

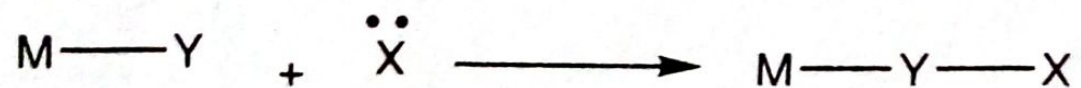




→ Intermediate



These *intramolecular* reactions are sometimes referred to as 'migratory insertions' to distinguish them from the *intermolecular* attack of a nucleophile X: on the coordinated ligand M-Y. This is discussed in detail, later in this chapter.



The general features of migratory insertions are specified below.

- A vacant coordination site is generated during a migratory insertion occurring in the forward direction. A trapping ligand is often needed to coordinate to the vacant site in

order to stop the reverse reaction from taking place and to regain the initial electron count.

• The groups undergoing migratory insertion must be *cisoidal* to one another. When the *cis* sites are blocked (for example, in tetradentate macrocycles), both the forward as well as the reverse reactions are inhibited.

• There is no change in the formal oxidation state of the metal (unless the inserting group is alkylidene or alkylidyne).

• Migratory insertions are usually favoured on more electron deficient metal centres.

Between two alkyl groups, the one which is more electron rich makes the better nucleophile for migrating to the electron deficient CO ($n\text{-alkyl}^- > \text{PhCH}_2^-$).

- Migratory insertion can be brought about by ligands other than CO. Ligands which are better donors are ideal for displacing the alkyl group for migratory insertion (for example, $\text{PMe}_3 > \text{PPh}_3$).
- When the migratory ligand 'X' is chiral, the reaction usually proceeds with retention of configuration at that chiral carbon. Racemisation occurs in a few cases because of free radical mechanism.
- Insertions are reversible, but in practice only one direction is observed.
- Cases where X migrates on to Y and where Y inserts into the M-X bond are known.

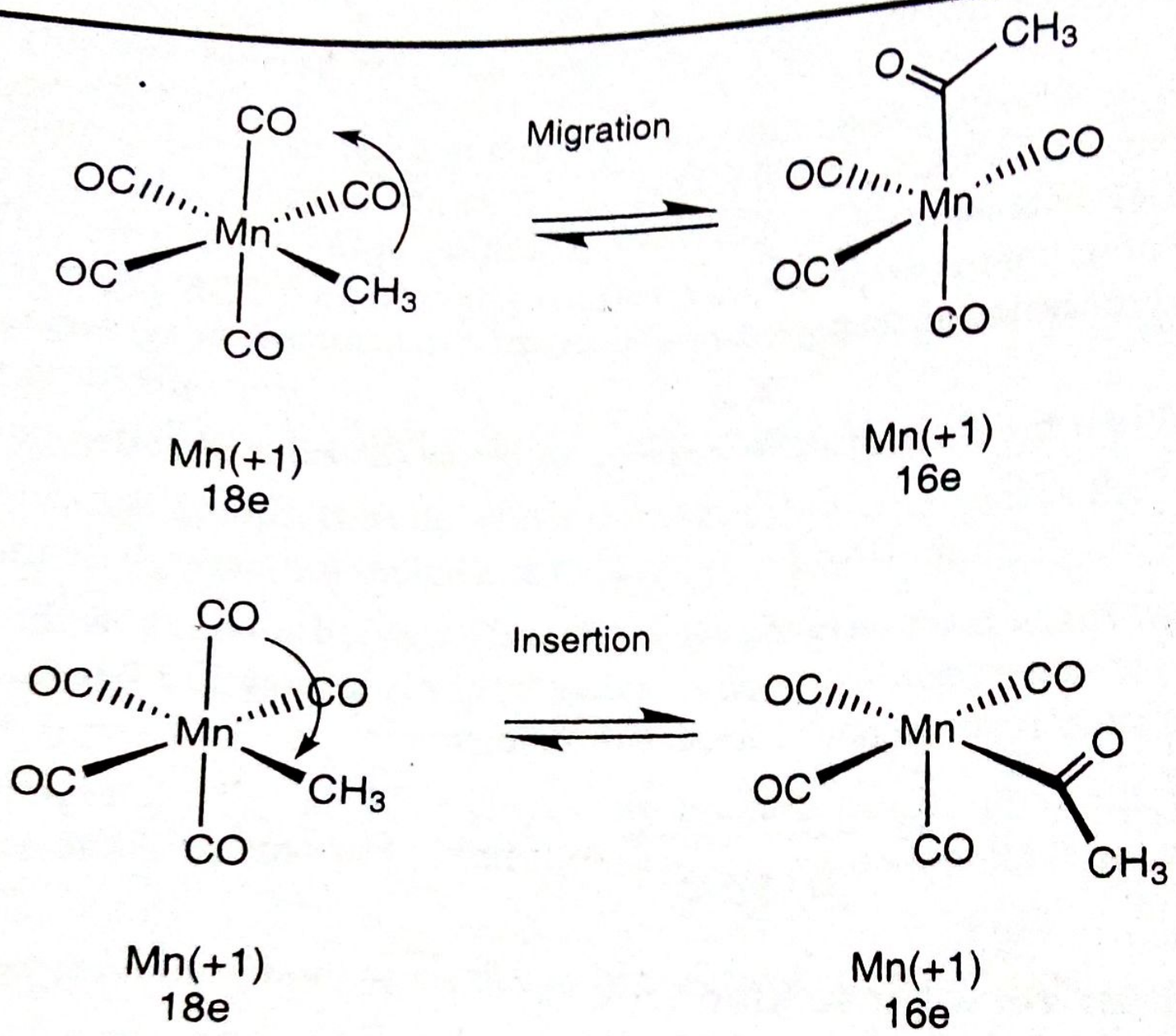
• The position of equilibrium of the reaction depends upon the strength of the M-X, M-Y and M-(YX) bonds.

- One electron oxidation of the starting complex, X-M-Y, often speeds up the reaction; a Lewis acid can often promote the rate of reaction.

8.3.3 Migration Versus Insertion

There are two different ways to visualise a migratory insertion. A migration occurs when the anionic ligand moves and performs a nucleophilic-like *intramolecular* attack on the electrophilic neutral ligand. An insertion occurs when the neutral ligand moves and gets inserted into the bond between the metal and the anionic ligand. Both of these pathways are illustrated in Scheme 8.2.

Most systems studied have been shown to

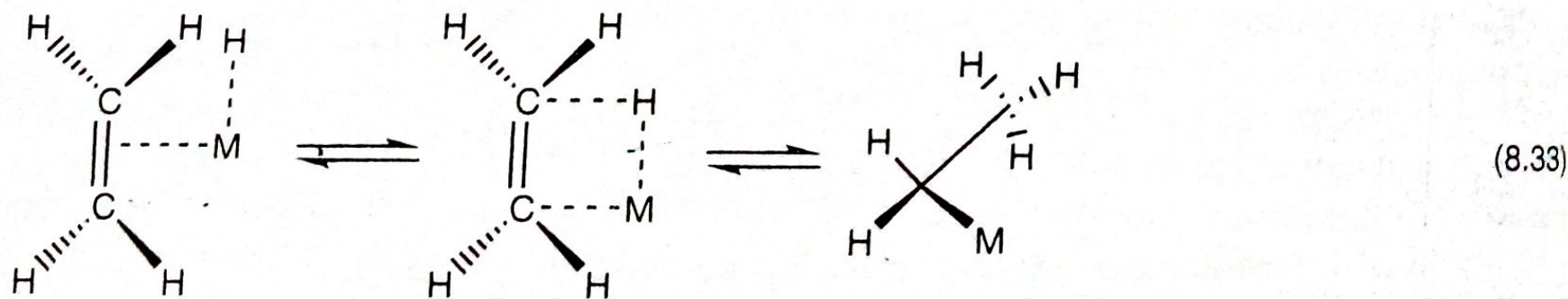


Scheme 8.3 Migration versus insertion

8.3.4 Insertion of Alkenes

The migratory insertion of an alkene into the M-H or M-R bond is one of the important steps in many multistep stoichiometric and catalytic reactions. But migratory insertion of this kind is rarely observed directly. The alkyl-carbonyl migratory insertions, as discussed above, are promoted by Lewis acids and 1e oxidations, but such effects have not been well studied in olefin insertions.

The *intramolecular* insertion of a hydride to the coordinated olefin is an obligatory step in many important reactions like olefin hydrogenation and hydroformylation. A general representation of hydride-olefin insertions is given below.



It is important to keep the following points in mind.

- The hydride is transferred to the β carbon of the alkene to form the metal alkyl complex. The hydride, the metal and the alkene must become coplanar during the reaction, that is, the addition is *cis* and has a four centered transition state as shown in Eq. 8.33
 - The stereochemistry at both carbons is retained since it is *syn* addition.
- ✓ CO insertion occurs in M-R bonds but not in M-H bonds; alkene insertion on the other hand, is very facile in M-H bonds but it is not so common in an M-R bond. ✓ Considering the C-H and C-C bond strengths and the overall thermodynamics of the reaction, it seems

✓ β -Hydrogen elimination is the reverse of alkene insertion and it represents the chief decomposition pathway of transition metal alkyl complexes (see Chapter 7). Since the forward as well as the backward reactions are quite facile, complexes which contain both the olefin and the hydride (*cis* disposition) are quite rare.

✓ For many alkenes, the insertion and β -hydride elimination reactions can be considered to be in equilibrium. The position of the equilibrium is decided by the overall thermodynamics of the particular system and it depends strongly on the nature of the alkene. For simple alkenes, the equilibrium lies towards the left (since β -hydrogen elimination is equally important) but for alkenes with electron withdrawing groups like C_2F_4 , the alkyl group is particularly stable and the equilibrium lies entirely to the right.

8.2.5 β -Hydrogen Elimination Versus Reductive Elimination