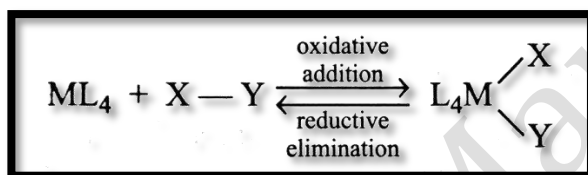


Oxidative Addition and Reductive Elimination:

One of the most important classes of reactions in organometallic chemistry is termed oxidative addition. In these reactions a coordinatively unsaturated complex in a relatively low oxidation state undergoes a formal oxidation by two units (loss of two electrons) and at the same time increases its coordination number by two.

An example is the reaction of *Vaska's complex* with molecular hydrogen. In this instance, iridium is oxidized from +1 to +3 and at the same time the coordination number of the complex increases from 4 to 6. The reverse reaction, in which H₂ is lost from the complex, involves reduction of iridium from +3 to +1 and a decrease in coordination number from 6 to 4. This process is called reductive elimination.

This specific example of oxidative addition/reductive elimination may be generalized as follows:



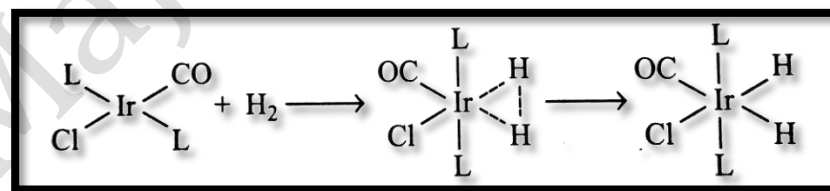
Requirements:

1. In order for oxidative addition to occur, vacant coordination sites must be available. A six-coordinate complex is not a good candidate unless it loses ligands during the course of the reaction making available a site for interaction.

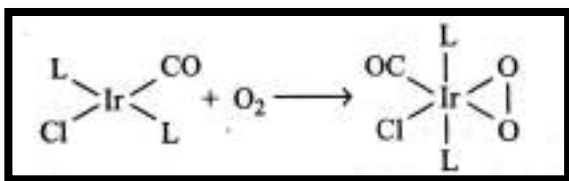
2. A further requirement is that suitable orbitals be available for bond information. An 18-electron complex such as [Fe(CO)₄]²⁻ has only four ligands but addition of X-Y would require the use of antibonding orbitals, which of course is not energetically favorable.

Mechanism:

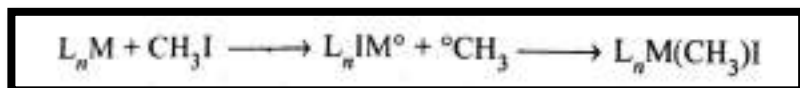
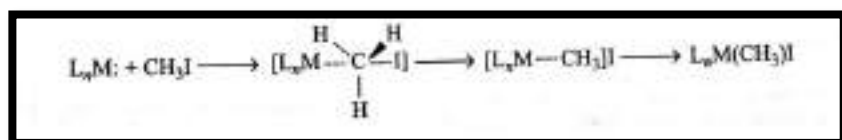
Mechanisms for oxidative additions vary according to the nature of X-Y. If X-Y is nonpolar, as in case of H₂, a concerted reaction leading to a three-centered transition state is most likely.



Nonclassical complexes of dihydrogen may be thought of as complexes in an arrested transition state and their existence provides strong support for a concerted reaction mechanism. Dioxygen, another non-polar molecule, also adds reversibly to Vaska's complex, but in this case the X-Y bond is not completely broken. The bond order of O₂ is reduced from two to essentially one.

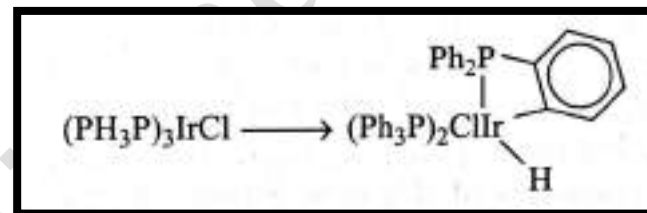


If X-Y is an electrophilic polar molecule such as CH_3I , oxidative addition reactions tend to proceed by $\text{S}_{\text{N}}2$ mechanisms involving two-electron transfer or via radical, one-electron transfer mechanisms.



3. Other factors besides a vacant coordination site are important in determining the tendency for a complex to undergo oxidative addition. The ease of oxidation (usually d^8 to d^6 with formal loss of two electrons), the relative stability of coordination number 4 compared to 5 or 6, and the strength of new bonds created (M-X and M-Y) relative to the bond broken (X-Y) all must be considered. Oxidation of the metal is easier for electron-rich systems than for electron-poor ones; hence oxidative addition is more likely for low-valent metals. The case of oxidation increases from top to bottom within a triad $[\text{Co}(\text{I}) < \text{Rh}(\text{I}) < \text{Ir}(\text{I})]$ and the tendency toward five-coordination decreases from left to right across a transition series $[\text{Os}(\text{O}) > \text{Ir}(\text{I}) > \text{Pt}(\text{II})]$.

4. Cleavage of the H-H bond by transition metal complexes suggests that similar reactions may be possible with C-H and C-C bonds. In fact it has been known for a number of years that coordinated triphenylphosphine can undergo intramolecular cyclometallation.

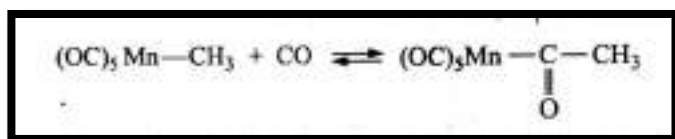


This reaction is also called orthometallation because it is the ortho carbon of the phenyl groups that participates. Although most common with phenyl groups of phosphines or phosphites, examples involving alkyl groups are also known.

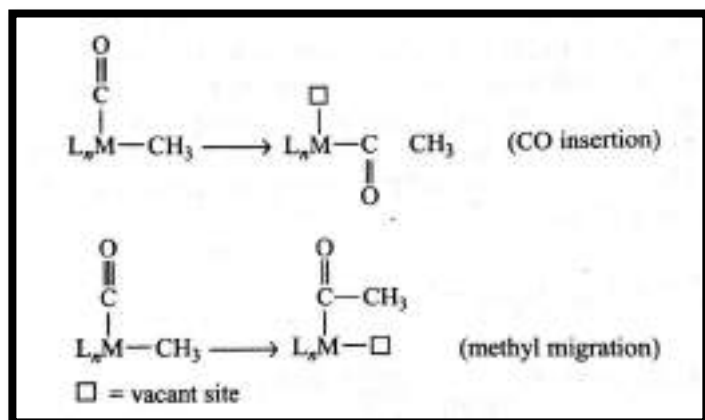
Insertion and Elimination:

Oxidative addition reactions lead to products that appear to have had a metal atom inserted into a bond, but the term insertion has generally been reserved for reactions which do not involve changes in metal oxidation state. These reactions are enormously important in catalytic cycles. Special emphasis in this section will be given to the insertion of carbon monoxide into metal-carbon bond and to the insertion of ethylene into metal-hydrogen bond.

A classic example of a CO insertion reaction (called migratory insertion) is found in the following reaction:



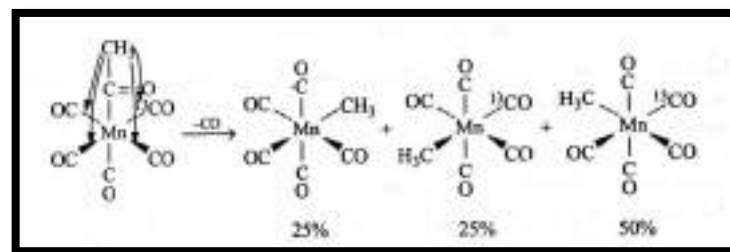
The product of this reaction appears to have formed by insertion of a CO group into an Mn-CH₃ bond. The reverse of this reaction is called decarbonylation but may also be called deinsertion or, more broadly, elimination. Infrared studies with ¹³CO have revealed that the reaction proceeds by migration of the methyl ligand rather than by CO insertion.



At first glance, these two processes may seem to be indistinguishable. However, careful consideration of the results of the infrared study will reveal otherwise. The reaction of ¹³CO with CH₃Mn(CO)₅ yields cis-(CH₃CO)Mn(¹³CO(CO)₄) as the exclusive product. None of the tagged CO is found in the acetyl group, which establishes that the reaction is not an

intermolecular insertion, i.e., no reaction occurs between gaseous CO and the M-C bond. Furthermore, none of the ¹³CO ends up trans to the acetyl group. This is an extremely important observation because it establishes that the CO ligands in the product do not scramble to give a statistical distribution. Additional mechanistic information can be gained by studying the reverse reaction, i.e., decarbonylation of cis-(CH₃CO)Mn(¹³CO)(CO)₄ because the mechanism of the two reactions must be the reverse of each other according to the principle of microscopic reversibility.

Experimentally it is found that 25% of the product is devoid of tagged CO, 25% of the product has ¹³CO trans to CH₃ and 50% of the product has ¹³CO cis to CH₃. Therefore CO insertion must be eliminated as a mechanistic possibility. A methyl migration mechanism, however, is consistent with these experimental results.



The methyl group as it migrates may displace the ¹³CO ligand to give product containing no ¹³CO (25%); it may displace either of the two CO ligands adjacent to the tagged CO to give the product with CH₃ cis to ¹³CO (50%); or it may

displace the CO ligand trans to the tagged CO to give the trans product (25%). This result has been further supported by carbon-13 NMR.

The validity of this mechanism has been demonstrated for a number of "CO insertion" reactions. Thus when chemists use the term CO insertion, they usually mean alkyl migration. Several things to keep in mind when considering reaction of this type are (1) it involves ligand which are cis to one another, (2) in the course of the reaction a vacant coordination becomes available, and (3) the reverse reaction cannot occur unless a ligand is first eliminated.

At this point it is fair to ask, what is the driving force for carbonyl insertion? These reactions involve breaking a metal-carbon bond and formation of a carbon-carbon bond. In addition, a bond is formed between the metal and the incoming Lewis base (CO in the foregoing examples, but frequently a phosphine or an amine). The enthalpy change, ΔH , for the reaction



has been calculated as $-54 + 8 \text{ kJ mol}^{-1}$. The less energy required to break the M-R bond and the more energy released when the C-C and M-C bonds are formed, the more favorable will be the reaction. Since gaseous CO is captured, it would be expected that the entropy change would inhibit spontaneity, but even so, the larger negative enthalpy term is dominant.