# Reactions of Organometallic Compounds

Oxidative Addition

Oxidative addition reactions are among the most important reactions in organometallic chemistry. An Oxidative addition reaction involves :

1. The addition of a molecule $X-Y$ with cleavage of $X-Y$ single bond to a coordinatively unsaturated compound in a relatively low oxidation state.
2. Formal oxidation of metal by two units and at the same time increase in metal coordination number by 2.

$$L_nM + X - Y \longrightarrow L_nM\Big\langle{}^X_Y$$
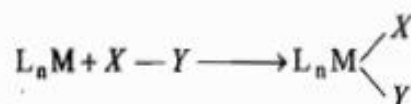
Addition of a multiply bonded species with reduction in the bond order to form a metallacycle is also an oxidative addition reaction.

$$L_nM + X - C {=\!=} C - Y \longrightarrow L_nM\Big\langle{}^{C}_{C}{}^{X}_{Y}$$
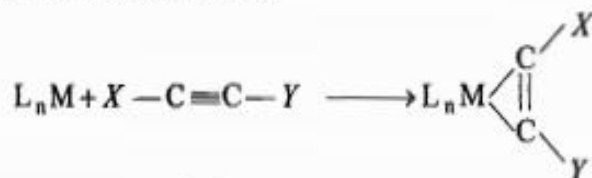
Addition of a C—H bond in an ortho-metallation step is also an oxidative addition reaction.

Mechanisms for Oxidative Addition Reactions

Depending upon the nature of X—Y, oxidative addition reactions may undergo by the following mechanisms:

(1) Concerted Reaction : If X—Y is non-polar such as H_2, O_2 then it undergoes oxidative addition reaction through concerted or three centred transition state. Concerted oxidative addition reaction is an associative reaction in which the incoming ligand X—Y first binds as a σ complex and then undergoes X—Y bond breaking resulting in strong back donation of two electrons from the metal into the σ-antibonding molecular orbital of X—Y ligand.

$$L_nM + X—Y \longrightarrow L_nM—\overset{X}{\underset{Y}{|}} \longrightarrow L_nM\overset{X}{\underset{Y}{\diagdown}}$$
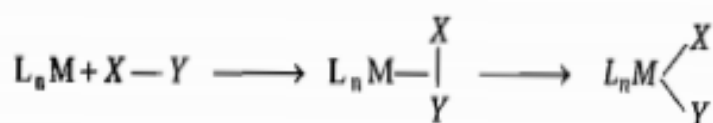
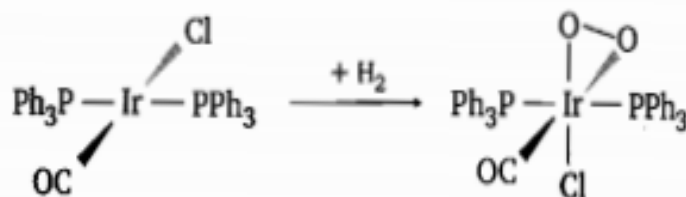The second step really involves the oxidation of metal because two electrons are formally transferred to σ-antibonding of X—Y. Some examples of concerted reaction of Vaska's complexes are :

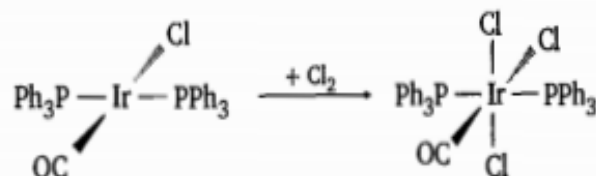**(i)** Oxidative addition of H_2 on Vaska's complex :
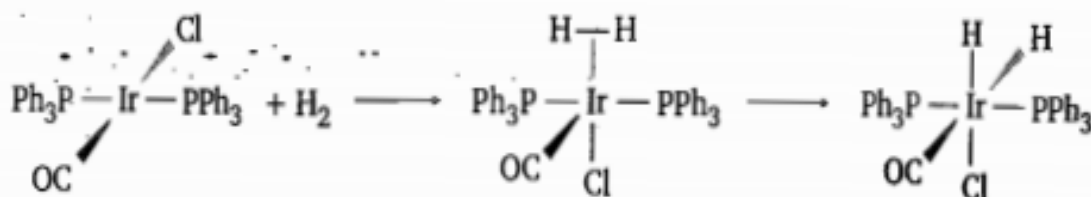
(ii) Oxidative addition of O_2 on Vaska's complex :

In this reaction O—O bond is not completely broken but the bond order of O_2 is reduced from 2 to 1.

(iii) Oxidative addition of halogen (X_2) on Vaska's complex :

(iv) Oxidative addition of alkenes and alkynes on Vaska's complex :
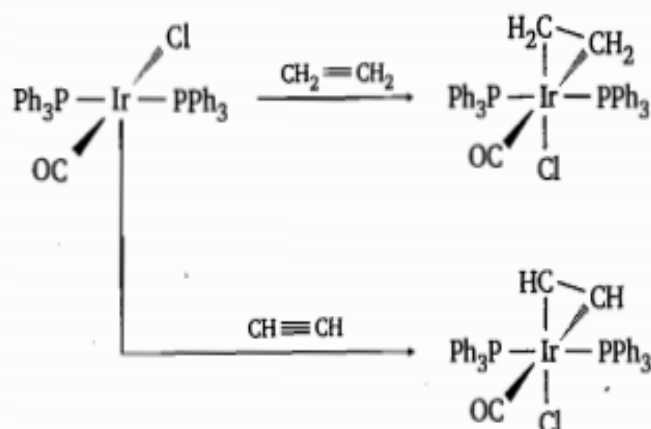
In these reactions, the *trans* (CO)Cl set of ligands become *cis* in the product. In the TBP transition state the strong π-acceptor CO ligand occupies the equatorial position.

(v) Oxidative addition of methane :
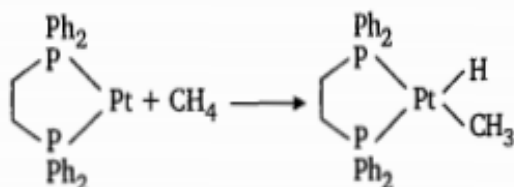
(2) S_{N^2} and Radical Reactions : If $X-Y$ is an electrophilic polar molecule such as alkyl halides (CH_3Cl, CH_3Br, CH_3I), oxidative addition reactions proceed by S_{N^2} mechanism involving two electron transfer or via radical, one electron transfer mechanism. In S_{N^2} mechanism, the electron pair of metal of L_nM directly attacks at the least electronegative atom of $X-Y$ molecule and provides a electron pair to σ-antibonding molecular orbital formally to break $X-Y$ molecule into X^- and Y^- ions. The L_nM compound itself oxidized to L_nM^{2+}.

$$L_nM: + CH_3I \longrightarrow L_nM \cdots C \cdots I \longrightarrow [L_nM(CH_3)]I$$

with H, H, H around the central C

$$\longrightarrow [L_nM(CH_3)]I$$

$$Ph_3P - Ir - PPh_3 + CH_3I \longrightarrow Ph_3P - Ir - PPh_3$$

with Cl, OC substituents on left Ir; H_3C, Cl, OC, Cl substituents on right Ir
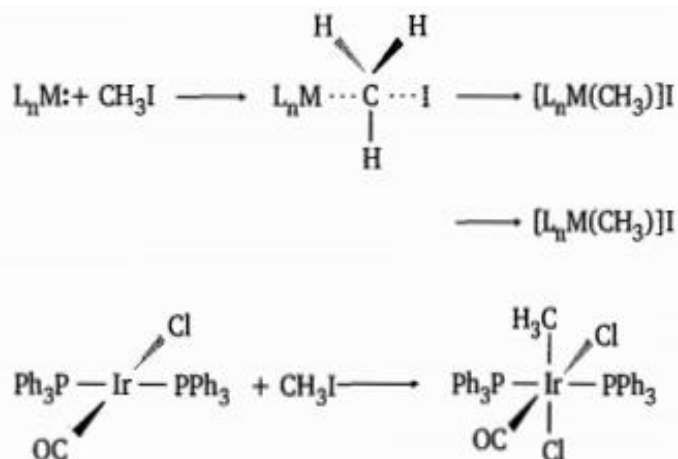
Like concerted reactions, these reactions are also second order reactions but they are accelerated in polar solvents. R and X may be *cis* or *trans* to one another in the final product as expected for the recombination of the ion pair formed in the first step. In the reaction (1) the product is *trans*, because the *trans* effect of CH_3 group is high and therefore, it prefers the position *trans* to the vacant site in the 16 electron square pyramidal intermediate. It is to be noted that in polar solvents, the molecules that dissociates are not restricted to occupy the *cis* position.

The radical mechanism may proceed in two ways—the non-chain and the chain mechanisms.

The more nucleophilic the metal (higher electron density on metal, low oxidation state of metal), greater will be its reactivity in S_{N2} oxidative addition. For example, $Ni(PR_3)_4$ undergoes oxidative addition more faster than $Ni(PAr_3)_4$. Increase in steric hindrance on carbon leads to decrease in the rate of oxidative addition. Therefore reactivity of alkyl halides follow the order :

$$MeI > EtI > i\text{-}PrI$$

The non-chain reaction involves the addition of alkyl halides, RX to $Pt(PPh_3)_3$ (where R = Me, Et and X = I, R = $PhCH_2$, X = Br). In non-chain oxidative addition, one electron from M is transferred to the σ-antibonding orbital of RX to form M^+ and RX^-. First X^- is coordinated to M^+ forming MX and R radicals. These radicals readily recombine to give the product.

$$L_nM + CH_3I \longrightarrow L_nI\dot{M} + \dot{C}H_3 \longrightarrow L_nM(CH_3)I$$

For example,

$$Pt(PPh_3)_3 \xrightarrow{Fast} Pt(PPh_3)_2 + PPh_3$$

$$Pt(PPh_3)_2 + MeI \xrightarrow{slow} \dot{P}t(PPh_3)_2^+ + \dot{M}eI^- \xrightarrow{slow} \dot{P}t(PPh_3)_2I + \dot{M}e \xrightarrow{fast} MePt(PPh_3)_2I$$
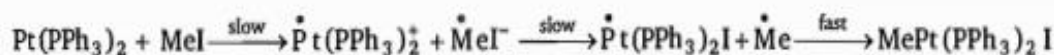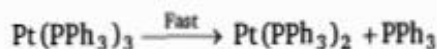
For a given alkyl halide, rate of oxidative addition reaction increases with increasing basic character of metal and the order of reactivity of alkyl halide is :

$$RI > RBr > RCl$$

The rate of oxidative addition reaction increases with increasing stability of alkyl radical :

$$3° > 2° > 1° > Me$$

The radical chain reaction occurs mainly between EtBr or $PhCH_2Br$ and Vaska's complex as shown below :

$$R^• + Ir(CO)Cl(PPh_3)_2 \longrightarrow R\overset{•}{Ir^{II}}(CO)Cl(PPh_3)_2 \xrightarrow{+RX} RXIr^{III}(CO)Cl(PPh_3)_2 + R^•$$

$$R^• + R^• \longrightarrow R_2$$

(3) Ionic Mechanisms : Hydrogen halides are dissociated in polar solvents to give proton (H^+) and halide ions (X^-) which add to metal complexes in separate steps. Usually the complex in which the metal is in low oxidation state and the ligands are basic enough, gets protonated followed by the addition of halide ion to form the final product.

$$Pt(PPh_3)_4 + H^+ \xrightarrow{-PPh_3} [HPt(PPh_3)]^+ \xrightarrow[-PPh_3]{+Cl^-} [HPt(PPh_3)_2Cl]$$
$$18e^-, d^{10}, \qquad\qquad 16e, d^8, \qquad 16e^-, d^8, \text{ square planar}$$
$$\text{Tetrahedral} \qquad\qquad \text{square planar}$$

Rate of reaction $= k$ [complex] $[H^+]$

There are some rare cases in which the halide ion binds first followed by protonation of the intermediate. These reactions are accelerated by electron acceptor ligands and by the net positive charge on the complex ion.

$$[Ir(cod)_4L_2]^+ + Cl^- \longrightarrow [Ir(cod)L_2Cl] \xrightarrow{+H^+} [HIr(cod)L_2Cl]^+$$
$$16e^-, d^8, \text{ square planar} \qquad 18e^-, d^8, \text{ TBP} \qquad 18e^-, d^6, \text{ octahedral}$$

Rate $= k$ [complex] $[Cl^-]$

Lewis acids such as $RCOOH$ and $HgCl_2$ also react by same mechanism.

$$Ir(CO)ClL_2 \xrightarrow{RCOOH} [HIr(OCOR)(CO)L_2Cl]$$
$$\xrightarrow{HgCl_2} [Ir(HgCl)Cl_2(CO)L_2]$$