**Types of organometallic reactions:-**

- Ligand substitution.
- Oxidative addition (including orthometallation).
- Reductive elemination.
- Alkyl and hydrogen migration.
- β hydrogen elemination.
- α hydrogen abstruction.

Ligand substitution:-

Substitution of 'CO' ligand by another two electron donor e.g; PR_3 may occur by photochemical or thermal activation. Two standared methods are there—

i) Direct reaction of a metal carbonyl and incoming ligand.

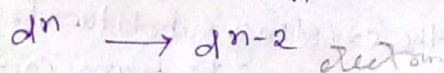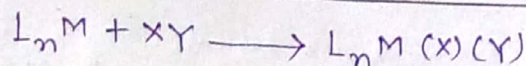ii) First by replacing a 'CO' by more labile ligand such as THF, CH_3CN etc followed by the final reaction.

e.g;
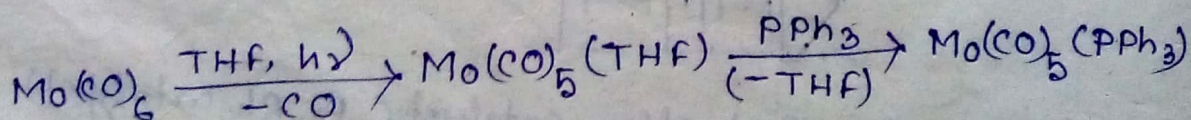
$$Mo(CO)_6 \xrightarrow[-CO]{THF,\ h\nu} Mo(CO)_5(THF) \xrightarrow[(-THF)]{PPh_3} Mo(CO)_5(PPh_3)$$

Oxidative addition and oxidative coupling:-

Addition of ligand, accompanied by oxidation of metal is called oxidative addition reaction.

$$L_nM + XY \longrightarrow L_nM(X)(Y)$$
$$d^n \longrightarrow d^{n-2} \text{ elec.}$$

⓵ features of this type of reaction :-

- formal oxidation state of 'M' is ~~increased~~ increased by 2 units.
- Transfer of two electron from the metal to incoming ligand breaks a bond in the incoming ligand to form two new anionic ligands.
- Co-ordination number of the metal is increased by 2 units.

⓵ Essential requirments :-

- Non bonding electron density on metal.
- Two vacant co-ordination site on reacting metal complex (L_nM) i.e; (co-ordinatively unsaturated).
- A metal ion with stable oxidation states separated by two units and the higher stable must be energetically stable and accessible

  oxidative addition of $Ir(I)$ to $Ir(III)$ is common, while $Fe(III)$ to $Fe(V)$ is possible but unlikely to occur.

- Oxidative addition occurs in transition metal complexes (square planar with d^8/d^{10} configuration).

  Oxidative addition is common for the following atoms —

Fe(0)	X	Ni(0)
Ru(0)	Rh(I)	Pd(II/0)
Os(0)	Ir(I)	Pt(II/0)
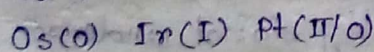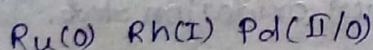
- Three major classes of compounds undergo oxidative addition –

i) Non polar and low polarity compound ($CH-H$, $H-SiR_3$, $R-H$, $Ar-H$, $R-SH$, X_2)

ii) polar compounds ($R-X$, $H-X$, $Ar-X$, $R-COX$, $CHCl_3$, $ROTS$, $R-SO_2X$)

iii) Ligands with π system (O_2, alkenes, alkynes).

⓵ Stereochemistry :-

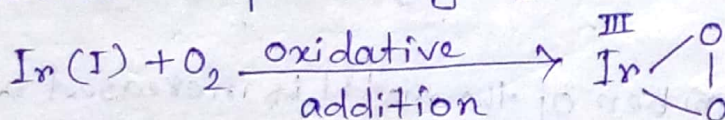Cis-addition :- Most polar compounds adds increament in cis manner.

Trans-addition:-

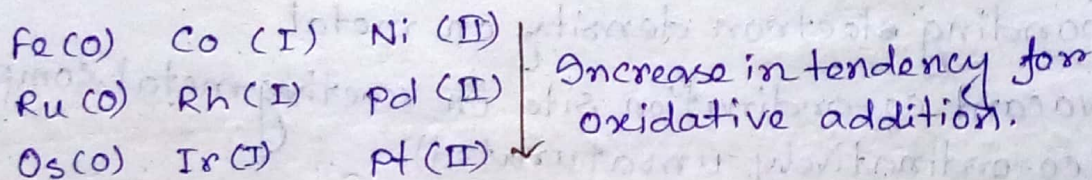Steric requirments of the existing substituents (bulky group Like PPh_3) can force to rearrange to trans configuration.

Similarly, polar molecule like CH_3I forms trans product, (Kinetically controlled, via SN^x type/ionic mechanism) which may convert to cis under thermodynamic condition.

• Unsaturated compound e.g; O_2 or alkenes forms metallacycle.

$$Ir(I) + O_2 \xrightarrow[\text{addition}]{\text{oxidative}} \overset{III}{Ir} \underset{O}{\overset{O}{\big<}} \Big|$$

ⓞ Trend:

Fe(0)	Co(I)	Ni(II)
Ru(0)	Rh(I)	Pd(II)
Os(0)	Ir(I)	Pt(II)

Increase in tendency for oxidative addition. ↓

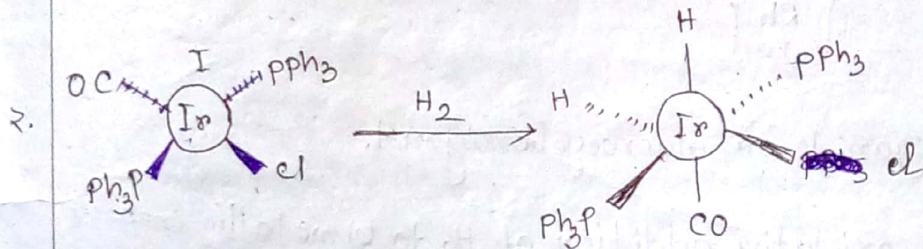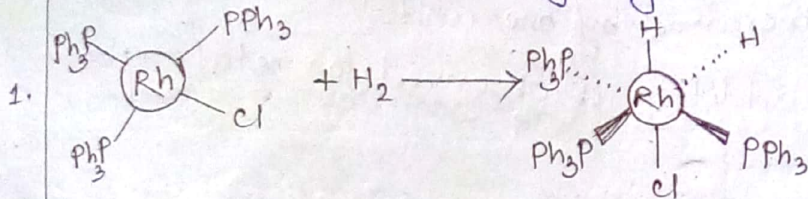← Increase in tendency for oxidative addition

• Presence of electron rich donor ligand around metal increases rate of addition.

• Complexes with 18 electron configuration can not undergo oxidative addition without expulsion of ligand.

$$Ru(CO)_4(PMe_3) + MeI \longrightarrow Ru(Me)(I)(CO)_3(PMe_3) + CO$$
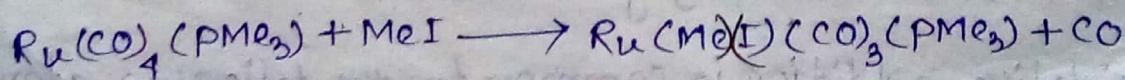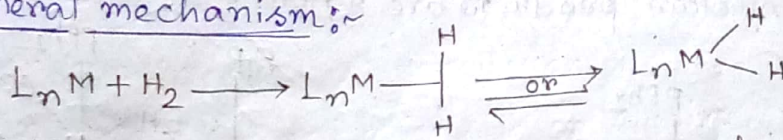
• Oxidative addition reaction can not occur on metal centre that are already in their higher oxidation state.

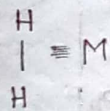• Complexes with d^0 metal usually do not undergo oxidative addition.
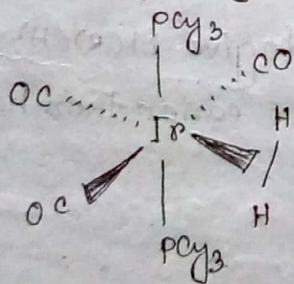
- **Oxidative addition of dihydrogen (H_2) :-**

1.

$$Ph_3P\text{–}Rh(PPh_3)(Cl)(PPh_3) + H_2 \longrightarrow$$

2.

$$\xrightarrow{H_2}$$

- **General mechanism:-**

$$L_n M + H_2 \longrightarrow L_n M\text{–}\underset{H}{\overset{H}{|}} \underset{\longleftarrow}{\overset{or}{\longrightarrow}} L_n M\big\langle{}^H_H$$

- Side on approach is preferred over end on.

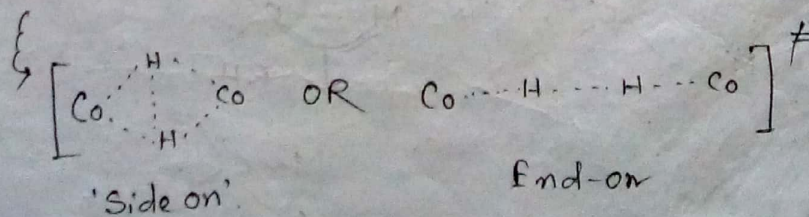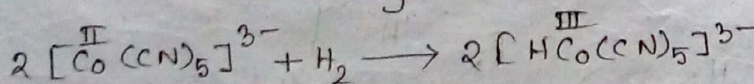$$\underset{H}{\overset{H}{|}} \equiv M$$

- Cis addition of H_2 has a low barrier i.e; generally less than 10 kcal/mole, where as trans addition of H_2 is forbidden and has a high energy barrier.

- First reported dihydrogen complex is given below

By 'Kubas'
Los Alamos National Lab
USA

- Oxidative addition of H_2 to two metal centres —

$$2\,[\overset{II}{Co}(CN)_5]^{3-} + H_2 \longrightarrow 2\,[\overset{III}{H Co}(CN)_5]^{3-}$$

$$\Bigg\{\bigg[Co\overset{\cdot\cdot H\cdot\cdot}{\underset{\cdot H\cdot}{\vdots}}Co\bigg] \quad OR \quad \Big[Co\cdots H\cdots H\cdots Co\Big]\Bigg\}^{\ddagger}$$

'Side on'   End-on

Probable transition state

- Two metal hydride products are formed, each with an oxidation state increased by one unit.

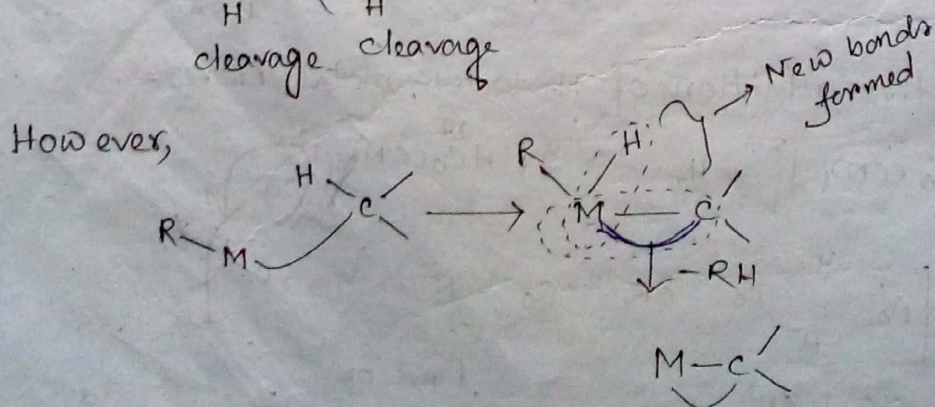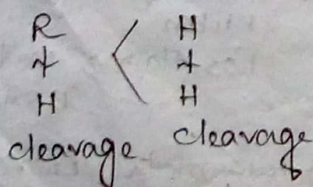- Such oxidative addition is observed for metal complexes of cobalt triad.

$$\left\{ \begin{array}{c} Co \\ Rh \\ Ir \end{array} \right\}$$
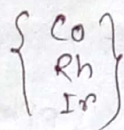
Ligand - cyanide or macrocyclic ligand.

- Example of oxidative addition of H_2 to bimetallic complexes to form dinuclear products are known —

$$\xrightarrow[\text{1atm, RT}]{H_2, \text{ toluene}}$$
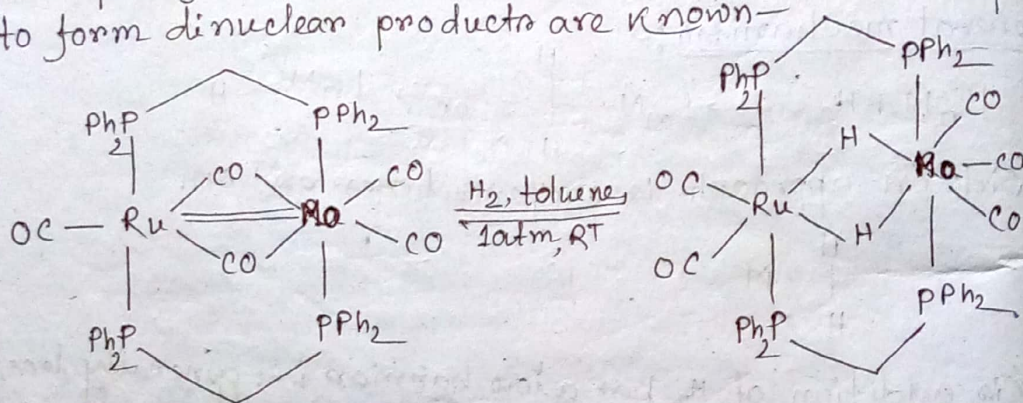
ⓐ Intramolecular oxidative addition : (C-H activation and cyclometallation)

Reaction of R-H with metal to give M(R)(H) is difficult.
(Homogeneous cleavage is more easier than heterogeneous cleavage).

$$\begin{array}{c} R \\ + \\ H \end{array} \left\langle \begin{array}{c} H \\ + \\ H \end{array} \right.$$

cleavage   cleavage

However,

→ New bonds formed

$$M-C\!\!\left\langle \right.$$

is facile and is called cyclometallation.

- The activation and cleavage of C-H bond is an important part of oxidative addition reaction.

$\left.\begin{array}{l} M-C \\ M-H \end{array}\right\}$ bond formation.
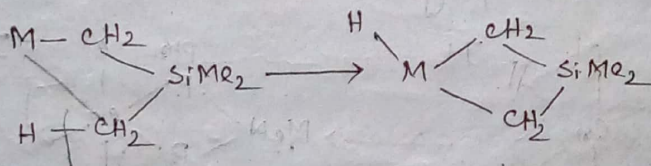
The various types of cyclometallation reaction leading to the formation of three, four and five membered rings are given below—

i) sp^3 hybridised carbon is attached to a phosphine/ cyclopenta diene or some other ligands.
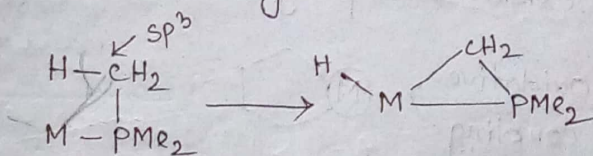
ii) The metal alkyl undergoes cyclisation.

iii) **Ortho metallation :—**

- Most common type of cyclometallation reaction.
- The ortho hydrogen of an aryl group in compounds such as aryl phosphines or phosphates, azobenzenes and other 'N' donors is often transferred or even lost.
- Oxidative addition is preceded by agostic interaction between the M and H atom ortho to the 'P' bound carbon.

e.g; cyclometallation involving PPh_3 of the complex $IrCl(PPh_3)_3$

Ortho metallation

Agostic interaction

Reductive elimination

$+$ HCl

$Ir(I)$, $16e^{\ominus}$

$18e$, $Ir(III)$

UNIQUE REACTIONS IN ORGANOMETALLIC CHEMISTRY
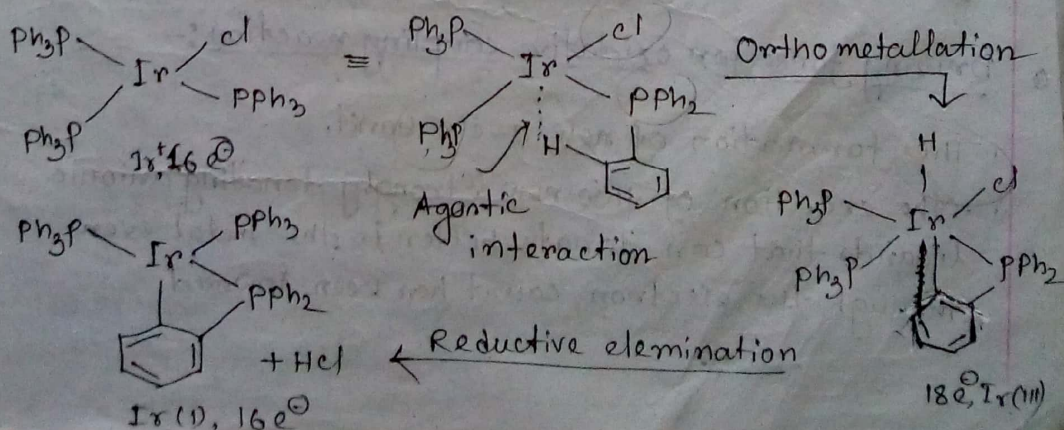
8.1 OXIDATIVE ADDITION AND OXIDATIVE COUPLING

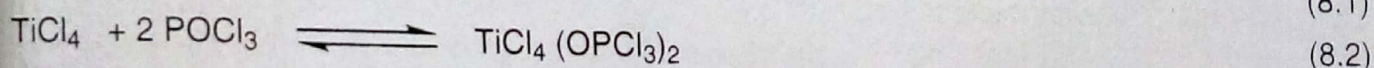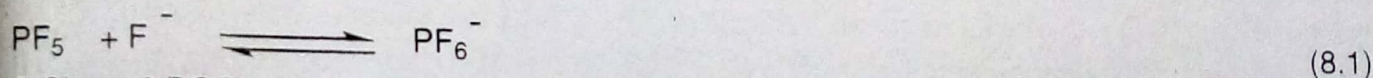Neutral or anionic nucleophiles can generally add on to coordinatively unsaturated molecules with or without the transition metal. These are simple addition reactions and indicate the Lewis acidic nature of the metal/central atom.

$$PF_5 + F^- \rightleftharpoons PF_6^- \tag{8.1}$$

$$TiCl_4 + 2\ POCl_3 \rightleftharpoons TiCl_4\ (OPCl_3)_2 \tag{8.2}$$

When addition of a ligand is accompanied by oxidation of the metal, it is called an oxidative addition reaction and is generally represented as

$$\underset{d^n}{L_nM} + XY \longrightarrow \underset{d^{n-2}}{L_n(X)(Y)M} \tag{8.3}$$
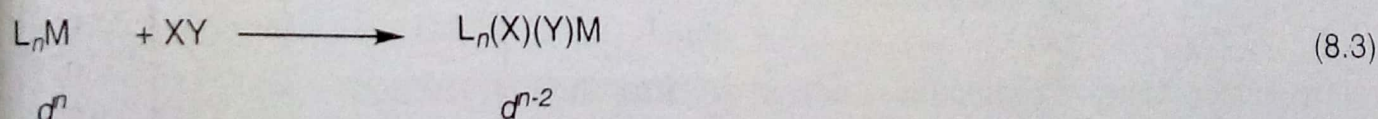
In this reaction, the formal oxidation state of the metal increases by two units. The transfer of two electrons from the metal to the incoming ligand breaks a bond in that ligand and forms two new anionic ligands. Hence, the coordination number of the metal also increases by two units.

For an oxidative addition to proceed, we must have:

- nonbonding electron density on the metal,
- two vacant coordination sites on the reacting complex (L_nM), that is, the complex must be coordinatively unsaturated, and
- a metal with stable oxidation states separated by two units; the higher oxidation state must be energetically accessible and stable.

For example, oxidative addition from Ir(I) to Ir(III) is common but an oxidative addition from Fe(III) to Fe(V), while possible, is unlikely to occur. The tendency of the complexes to undergo oxidative addition is governed by the electron density on the metal centre, that is, the ease with which metals can be oxidised. Such reactions are most common in transition metal complexes (mostly square planar) with the metal in d^8 and d^{10} electronic configurations, notably

Fe^0, Ru^0, Os^0, Rh^I, Ir^I, Pd^{II}, Pt^{II}, Ni^0 Pd^0 and Pt^0. An especially well-studied system is the square planar trans-$IrCl(CO)(PPh_3)_2$, well known as the Vaska's complex. Thus on adding Cl_2, a four coordinate d^8, 16 electron complex is converted to a six coordinate d^6, 18 electron product. The oxidation state of Ir increases from I to III. Consistent with this change, the stretching frequency of the CO increases from 1967 to 2075 cm^{-1}. The Cl–Cl bond is broken and two Ir–Cl bonds are formed.

Depending on the nature of the adding group (polar, nonpolar) as well as the type of mechanism involved (concerted, S_N2, free radical and ionic) one can get either *cis* addition products, a mixture of *cis* and *trans* addition products or in few cases *trans* addition products.

(8.4)
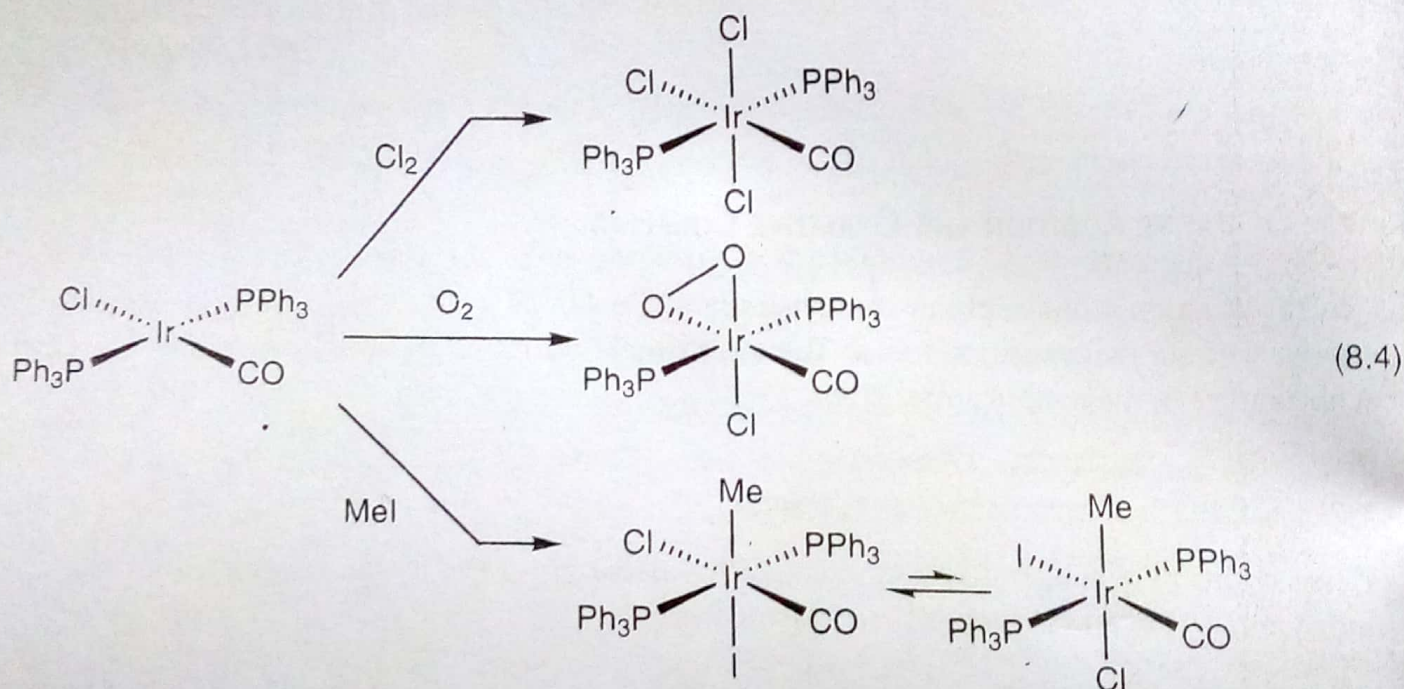
Three major classes of compounds undergo oxidative addition reaction:

(i) nonpolar and low polarity compounds (H–H, H–SiR$_3$, RH, ArH, RSH, X$_2$),
(ii) polar compounds (R–X, H–X, Ar–X, RCOX, CHCl$_3$, ROTs, RSO$_2$X), and
(iii) ligands with π systems (O$_2$, alkenes, alkynes).

Most of the nonpolar compounds such as H$_2$ or Cl$_2$ will add in the *cis* manner but steric requirements of the existing substituents (for example, a bulky group like PPh$_3$) can force it to rearrange to a *trans* configuration. In the same manner, ionic and S$_N2$ type mechanisms operating on polar molecules like MeI will form the kinetic controlled *trans* product which may convert to the *cis* product under thermodynamic conditions. However, unsaturated compounds like O$_2$ or
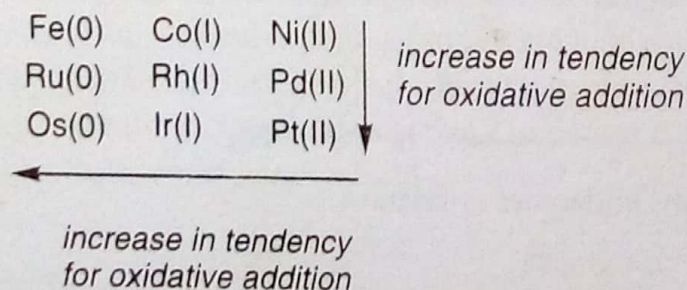

(8.5)
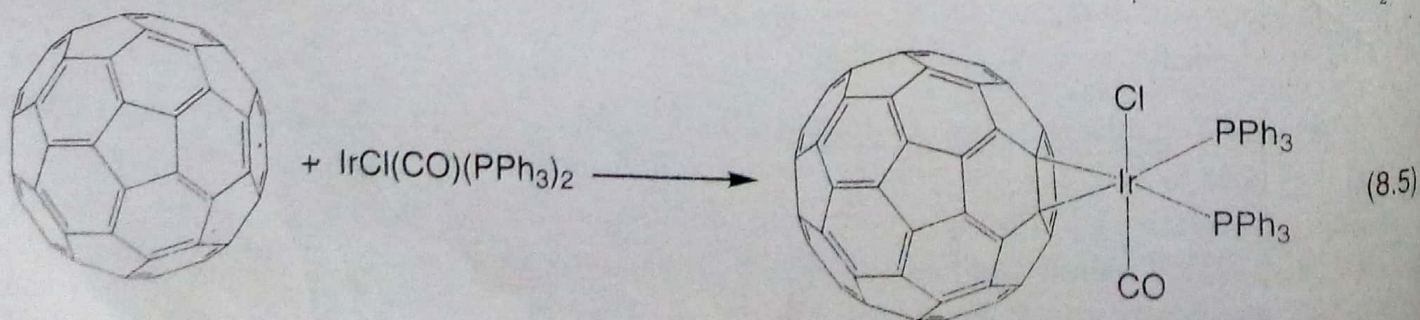
an alkyne will form a metallacycle; for example, in the reaction with molecular oxygen, Ir(I) is oxidised to Ir(III) and a three membered ring with single bonds is formed. Both C_{60} and C_{70} have also been found to undergo oxidative addition reactions with Vaska's complex (Eq. 8.5).

Several trends in the oxidative addition reaction have been noticed.

- The tendency of oxidative addition increases as one moves down in a group in the periodic table; for example, Ir^{2+} is easier to oxidise than Rh^{2+} which in turn is easier to oxidise than Co^{2+}.

- A low initial oxidation state is more favourable for oxidative addition to occur; for example, when all other factors are equal, Fe^0 is easier to oxidise than Co^I and this is easier to oxidise than Ni^{2+}. Fe(0), Co(I) and Ni (II) are isoelectronic metals. The presence of electron-rich donor ligands around the metal increases the rate of oxidative addition reaction. In comparing two or more metal complexes to find the most reactive one towards a particular substrate for oxidative addition, the metal centre having the strongest donor ligands, the fewest π acceptor ligands and the highest negative charge is picked.

- The possibility of oxidative addition of A–B to a metal M, depends on the relative strengths of the A–B, M–A and M–B bonds. For example, oxidative addition of an alkane is much less common than oxidative addition of an alkyl halide. In an alkane, the C–H bond is fairly strong compared to the M–H and M–R (R = alkyl) bonds. For isostructural d^8 complexes, the following trends are observed for oxidative addition.

$$
\begin{array}{lll}
\text{Fe(0)} & \text{Co(I)} & \text{Ni(II)} \\
\text{Ru(0)} & \text{Rh(I)} & \text{Pd(II)} \\
\text{Os(0)} & \text{Ir(I)} & \text{Pt(II)}
\end{array}
\quad \downarrow
\begin{array}{l}
\textit{increase in tendency} \\
\textit{for oxidative addition}
\end{array}
$$

←

increase in tendency
for oxidative addition

- Complexes with 18 electrons cannot undergo oxidative addition without the expulsion of a ligand.

$$Ru(CO)_4(PMe_3) + MeI \longrightarrow Ru(CH_3)(I)(CO)_3(PMe_3) + CO$$

Please note:

- Oxidative addition reactions cannot occur on metal centres that are already in their highest oxidation state. For example, Ta^{5+} cannot undergo oxidative addition to give Ta^{7+}. In these cases, a σ bond metathesis reaction is a likely alternative.

- Complexes with d^0 metals do not undergo oxidative addition reactions.

Therefore, the number of electrons in the starting and the final metal complexes are always counted to check out the overall electron count, the oxidation state of the metal and the number of d electrons.

8.1.1 Intramolecular Oxidative Addition: C—H Activation and Cyclometallation

The selective activation and subsequent functionalisation of C–H or C–C bonds under laboratory conditions has received a great deal of attention in recent years. The intermolecular oxidative addition – for example, the reaction of RH with M to give M(R)(H) – is rather difficult. On the other hand, the intramolecular oxidative addition reaction as described below is facile. Hence the activation and cleavage of the C–H bond is an important part of oxidative addition reactions.

Although there are many reactions that involve the cleavage of C–H bonds, only cyclometallation reactions will be discussed here. These are intramolecular C–H cleavage reactions that lead to the formation of MH + MC bonds. Sometimes only an M–C bond is formed when an alkyl or a hydride is transferred, which is then eliminated as an alkane or hydrogen.
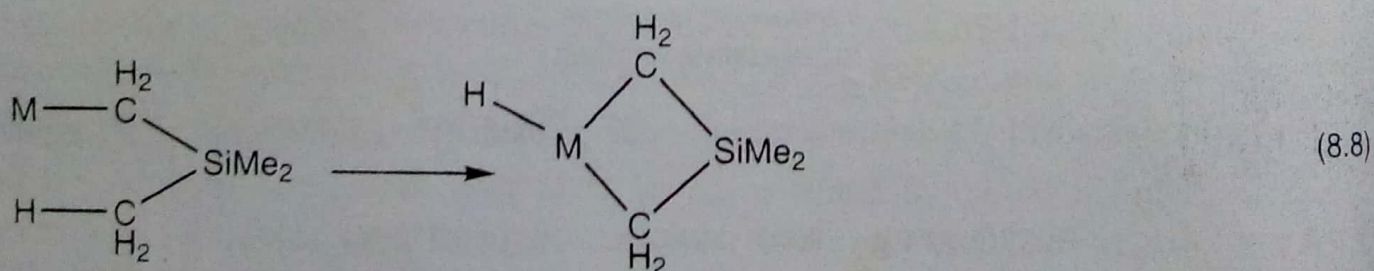
$$
\text{(8.6)}
$$
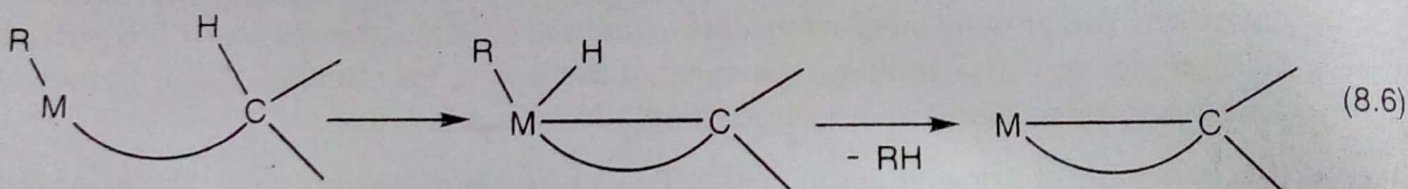
The various types of cyclometallation reactions that lead to the formation of 3, 4, 5 or 6 membered rings are given below.

(i) The sp^3 hybridised carbon is attached to a phosphine, cyclopentadiene or some other ligand.

$$
\text{(8.7)}
$$

(ii) The metal alkyl undergoes cyclisation.

$$
\text{(8.8)}
$$
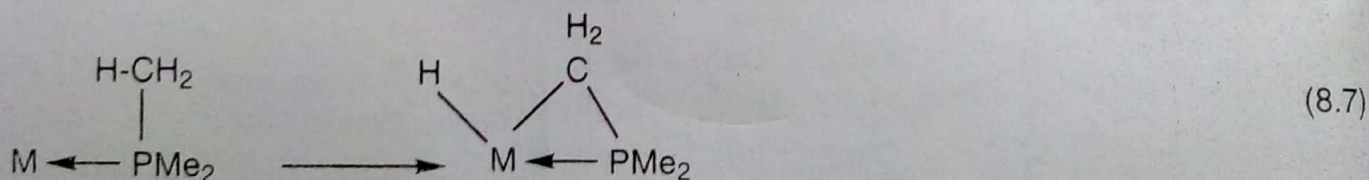
(iii) Orthometallation is the most common type of cyclometallation reaction. In this, the *ortho* hydrogen of an aryl group in compounds such as aryl phosphines or phosphates, azobenzene and other nitrogen donors is often transferred or even lost. The oxidative addition is preceded by an agostic interaction between the metal and the hydrogen atom *ortho* to the phosphorus bound carbon (Scheme 8.1).