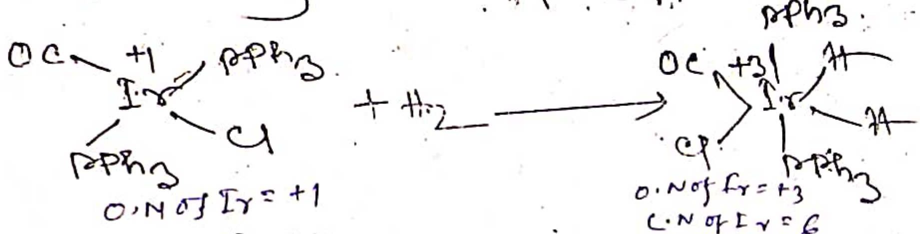
## Oxidative-Addition and Reductive-Elemination:

One of the most important classes of rxns in organometallic chemistry is formed oxidative addition. In these rxns a co-ordinatively unsaturated complex in a relatively low oxidation state undergoes a formal oxidation by two units and at the same time increases its co-ordination number by two.

An example of the rxn. of Vasca's complex with molecular $H_2$, In this case Ir is oxidised from +1 to +3 and at the same time the Co.No. of the complex increases from 4 to 6.



The reverse rxn, in which $H_2$ is lost from the complex, involves reduction of Ir from +3 to +1 and a decrease in Co. No. from 6 to 4. This process is called reductive-elemination. This specific example of oxidative addition or reductive elemination may be generalised as follows —

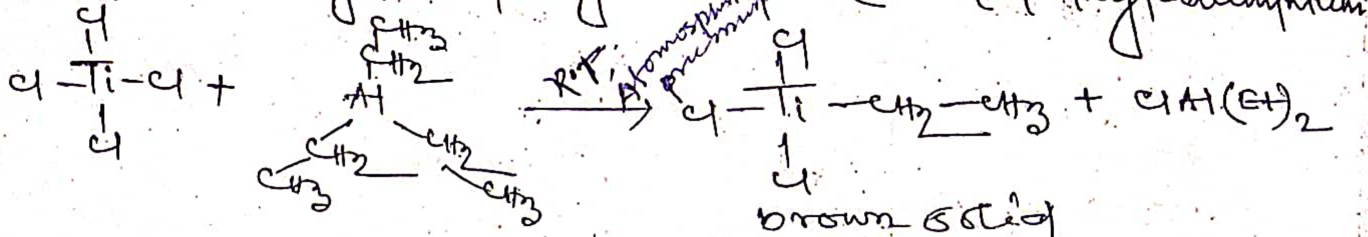
$$ML_4 + X-Y \underset{\text{Reductive elemination}}{\overset{\text{oxidative addition}}{\rightleftharpoons}} L_4M\begin{matrix}X\\Y\end{matrix}$$

In order for oxidative addition to occur, vaccant co-ordination sites must be available. A six co-ordinate complex is not a good candidate unless it losses ligands during the course of the rxn, making available a site for interaction. A further requirement is that suitable orbitals be available for bond formation. An 18-electrons complex such as $[Fe(CO)_4]^{2\ominus}$ has only four ligands but addition of X-Y would require the use of antibonding orbital which of cource is not energetically favourable.

# Polymerisation of alkenes and Zeigler-Natta Catalyst:

One of the great discoveries of organometallic chemistry was the catalysed polymerisation of alkenes at atmospheric pressure & at room tempr. Vast quantities of polyethelene and polypropelene are made by Zeigler-Natta Catalysis.

The Zeigler-Natta Catalyst is made by treating '$TiCl_4$' with triethylaluminium.



$$Cl-\overset{Cl}{\underset{Cl}{Ti}}-Cl + Al(CH_2CH_3)_3 \xrightarrow{R.T,\ \text{Atmospheric pressure}} Cl-\overset{Cl}{\underset{Cl}{Ti}}-CH_2-CH_3 + ClAl(Et)_2$$

brown solid
(Zeigler Natta catalyst)

**Principle:** In the Zeigler-Natta process, a transition metal halide like $TiCl_4$ is usually mixed with $Et_3Al$ in a hydrocarbon (eg: heptane) — the resulting brown mixture (Zeigler-Natta catalyst) can polymerise ethelene or propelene at room tempr and atmospheric pressure.

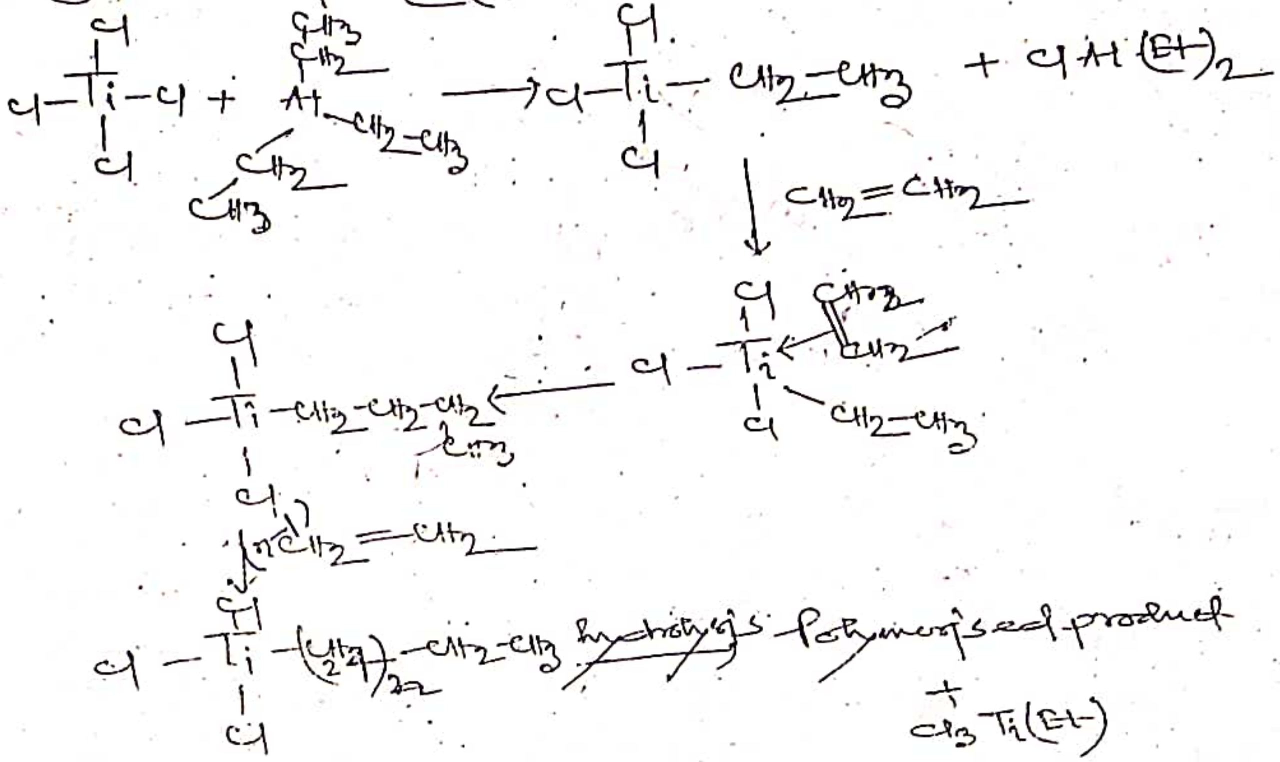
**Mechanism:**

i) At first $TiCl_4$ reacts with $Et_3Al$ to form the Zeigler-Natta catalyst.

ii) An ethelene molecule now co-ordinates ($\eta^2$) to the vacant site in the Ti atom on the surface of the catalyst.

iii) The ethelene is now interposed between the Ti − C bond with the ethyl group. This extends the carbon chain from ~~2~~ two to four and creats a further vacancy in the coordination site of Ti. Repeatation increases the carbon-chain length. As the process takes place on a surface, orientation of the attacking olefin is stereoselective.

e.g! With propelene ($CH_3-CH=CH_2$), the double bond will attached to the Ti leaving the methyl group pointed away from the surface. When the molecules gets incerted between the Ti – C bond, after migration it will always have the same orientation



After hydrolysis polyethelene is collected from the catalyst

**V.V.I** ● **Hydroformylation Rxn. (Oxo-process):**

The rxn. of an alkene with CO and $H_2$, catalysed by Co or Rodium salts to form an aldehyde is called hydroformylation. Sometime this process is also called OXO-process.

$$2R-CH=CH_2 + 2CO + 2H_2 \xrightarrow{Co_2(CO)_8} R-CH_2-CH_2-CHO + R-CH(CHO)-CH_3$$

The name hydroformylation arrises from the fact that in a formal sense a hydrogen atom and a formyl group are added across a double bond. The next result of the process is extention of the carbon chain by one and introduction of oxygen into the molecule.

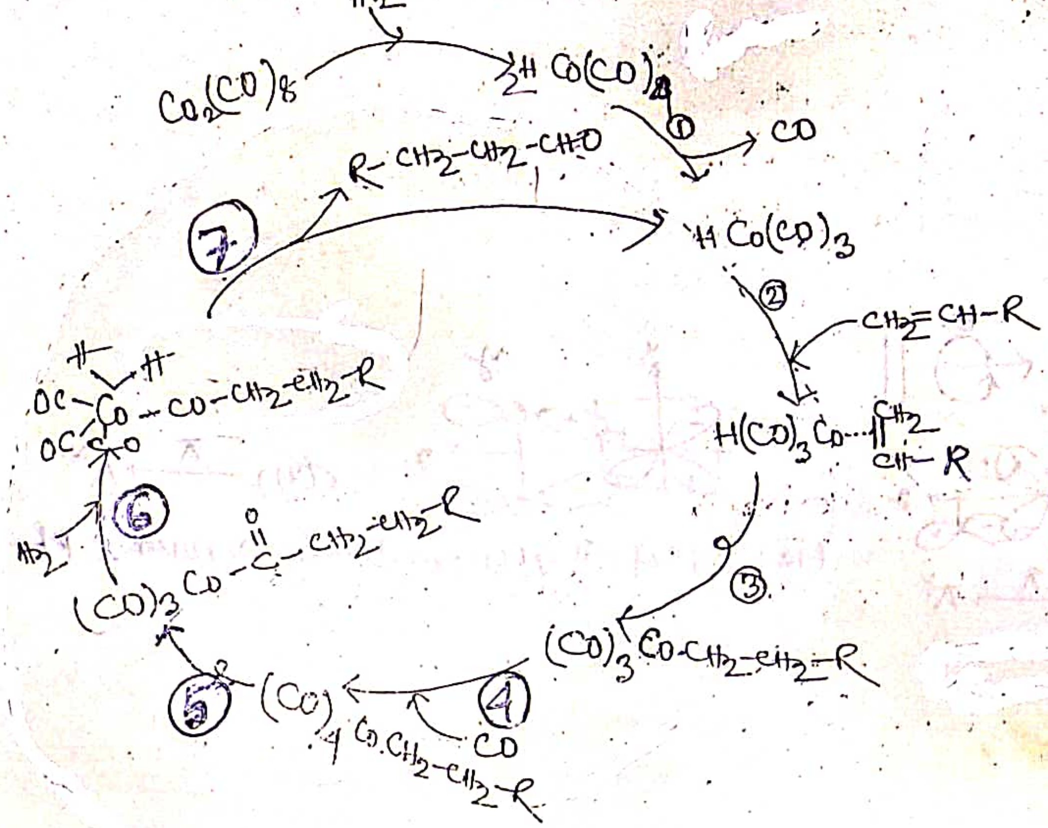


fig: Catalytic cycle for hydroformylation rxn.

① Ligand dissociation
② Substrate binding to vacant site
③ Alkyl or hydride migration and insertion
④ Binding of CO to the vacant site.
⑥ Oxidative addition ⑤ CO migration and insertion.
⑦ Reductive elimination

The most widely accepted mechanism for the catalytic cycle is shown above; We see that $Co_2(CO)_8$ reacts with $H_2$ to give $H-Co(CO)_4$ (an 18-electron species) which losses CO forming $HCo(CO)_3$ (a 16-electron species) an creating a vacant co-ordination site. Alkene coordination recreates an 18-electron complex which undergoes migratory insertion of olefin into Co–H bond thereby creating another 16-electron complex and another vacant co-ordination site to which CO can become co-ordinated. A CO ligand of $R-CH_2-CH_2-Co(CO)_4$ migrates to a position between the Co atom and the alkyl group. Rxn. with $H_2$ (oxidative addition) and then reductive elemination releases the aldehyde and regenerates the catalytic cobalt complex.