UG part II
(Hons) + (Subsidiary)
First transition series

Complex formation in different oxidation states.

- The tendency of an ion to form complexes depends upon its size ; the smaller the size of an ion , the greater is its tendency to form complexes.
- Complexes of Scandium
- The size of Sc^{3+} ion is smaller than that of other ions of this group. It therefore , readily forms complex ions , as for example. $[ScF_6]^{3-}$, $[Sc(bipy)_3]^{+}$, $[Sc(DMOS)_3]^{3+}$ etc.

Where bipy → bipyridyl
DMSO → dimethyl sulphoxide.

- Some bidentate chelating agents such as $C_2O_4^{2-}$ and acac (acetyl acetonate anion) are also known to form chelates with Sc^{3+} such as $[Sc(C_2O_4)_2]^-$, $[Sc(acac)_3]$ etc.

Complexes of Ti(IV)

- The colorimetric estimation of TiO^{2+} or $[Ti(OH)_2]^{2+}$ in aqueous solution is carried out by the addition of H_2O_2 to the solution when an orange colour is developed due to the formation of a peroxo complex of Ti^{4+} whose probable formula is $[Ti(O_2)OH\cdot(H_2O)_n]^{+}$

- The O_2^{2-} ion is attached with Ti as peroxo group.
- Ti(IV) halides, $TiCl_4$ and TiF_4 react with HCl and HF respectively to give hexa co-ordinate complex ions.

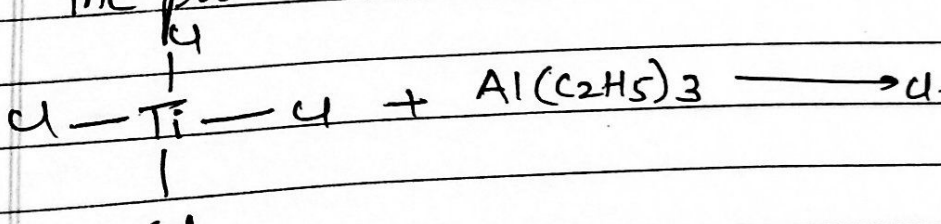
$$TiCl_4 + 2HCl \longrightarrow H_2[TiCl_6]$$
$$TiF_4 + 2HF \longrightarrow H_2[TiF_6]$$

- The tetrahalides also react with amines, phosphines and arsines to give hexa co-ordinate complexes as for example $TiF_4 \cdot 2PPh_3$.
- Tetraalkyl ammonium chloride reacts with $TiCl_4$ to give $[Et_4N]^+[TiCl_5]^-$ which contains five-co-ordinated Ti^{4+} in its anion.
- In the complex $[Ti(NO_3)_4]$, the co-ordination number of Ti^{4+} is 8 since NO_3 group is bidentate in this complex.

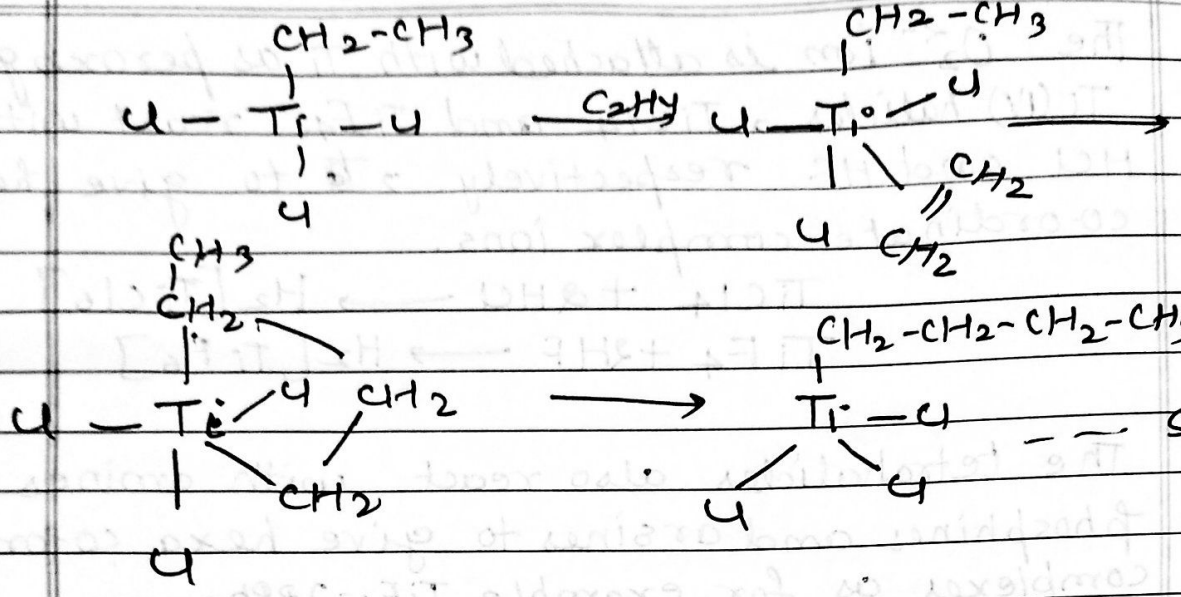
Organometallic compounds of Titatnium

- When $TiCl_4$ is added to $Al(C_2H_5)_3$ in hexane it yields a brown solid known as Ziegler-Natta catalyst which is employed in conversion of ethene to straight chain polymer polyethene.

The probable mechanism is as follows.

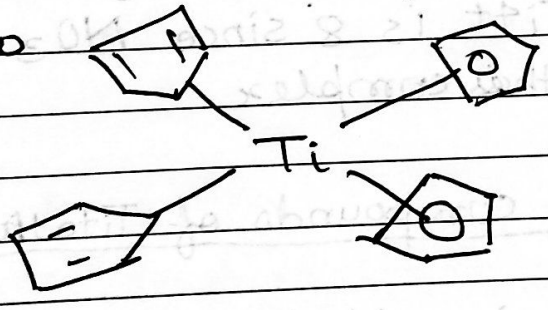


Zeigler-Natta catalyst



- Several Stable cyclopentadienyls such as $[Ti(\eta^5-(C_5H_5)_2(CO)_2]$, $Ti(\eta^5-C_5H_5)_2]$ etc. are known.

- More interesting are the compounds in which Ti is attached to four C_5H_5 rings as shown below



- Some alkyls and aryls of Ti are also known but these are quite unstable.