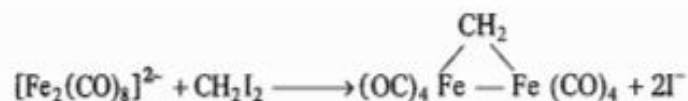


Synthesis of Metal Alkyl Complexes

1. By the Reaction of Metal Carbonylate Anions with Alkyl Halides :

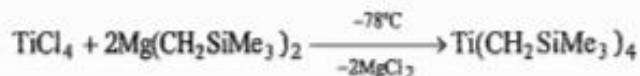
The metal carbonylate ions are strong nucleophiles and react readily with electrophiles such as alkyl halides. For example,



2. By Oxidative Addition :



3. By Alkylation of Metal Halides:

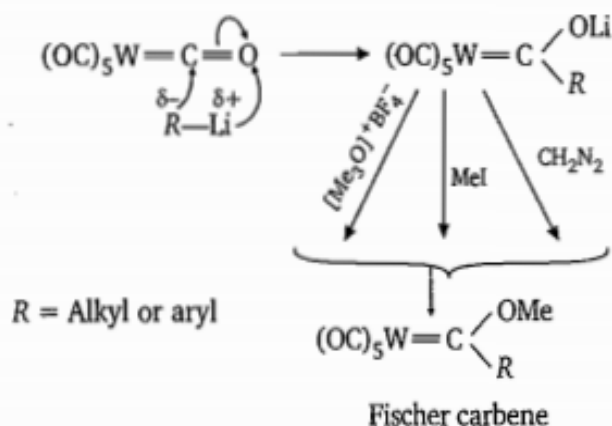


4. By the reaction of transition metal halide with organolithium, organomagnesium or organoaluminium (a nucleophilic attack on metal).

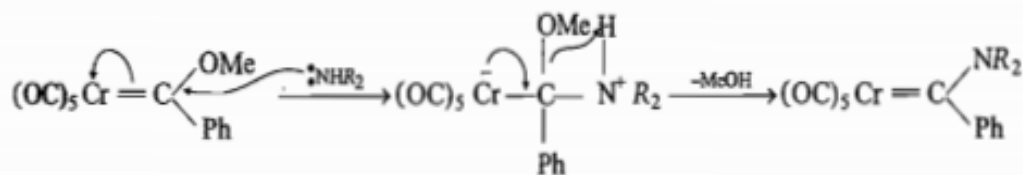


1. Fischer Carbenes

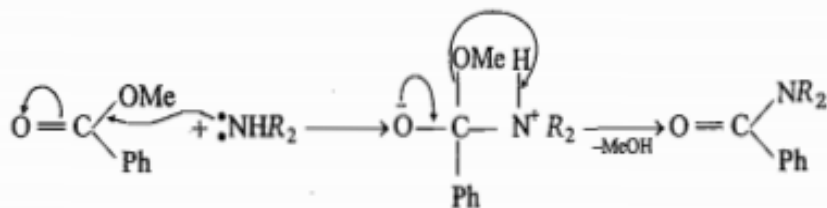
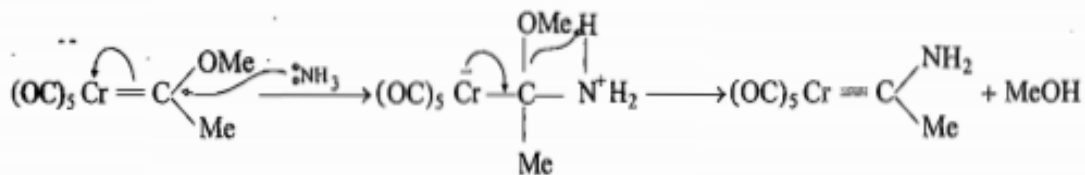
The first carbene complex was made by Fischer and **Massbol** in 1964. It was prepared by nucleophilic attack of alkyllithium on a carbon atom of hexacarbonyl tungsten, $W(CO)_6$ followed by alkylation.



The carbon atom in Fischer carbenes is electron deficient, therefore, it is attacked by nucleophiles. For examples, the attack of an amine on the electrophilic carbon atom of a Fischer carbene results in the displacement of the $-OR$ group to give a new carbene ligand.



If $(OC)_5Cr$ group is replaced with the oxygen atom, this reactions is seen to be aminolysis of esters to give amides.

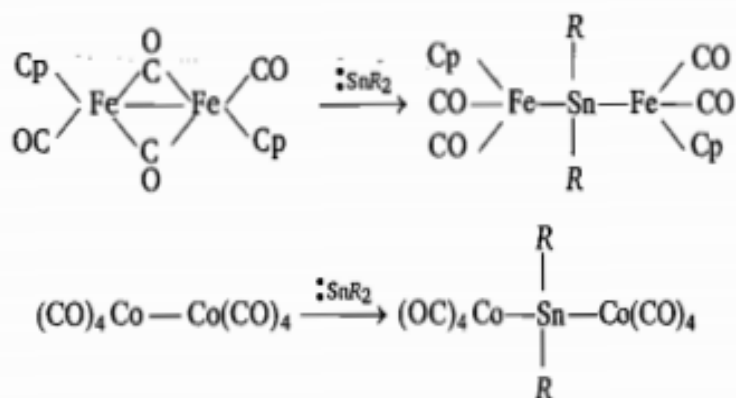


This reaction is favourable because nitrogen is not as electronegative as oxygen and its π donating ability exceeds that of oxygen.

The addition of carbon nucleophiles or alkenes forms metallacycles which can break down to a carbene and an alkene.

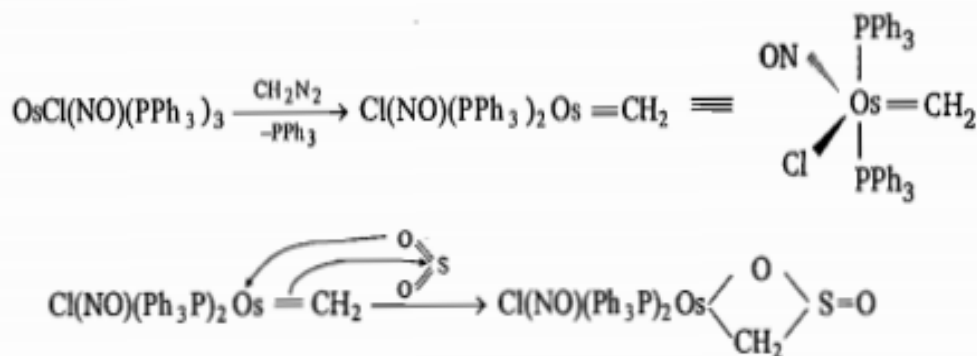
Insertion Reaction

Similar to carbene : CR_2 , $:\text{SnR}_2$ also behaves as carbene and shows insertion reactions. For examples.



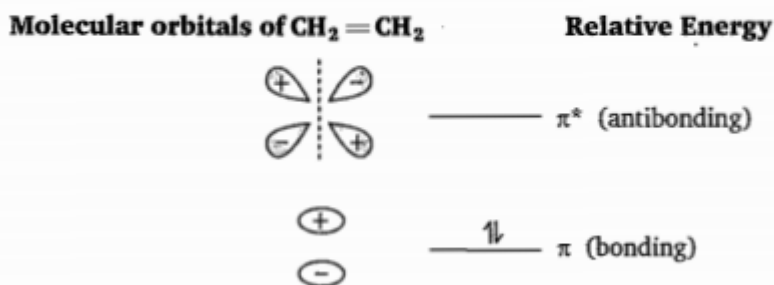
Carbenes Intermediate Between Fischer and Schrock Types

These are the carbenes which have properties intermediate between that of the Fischer and Schrock carbenes, because they react both with electrophiles such as SO_2 or H^+ and with nucleophiles such as CO or CNR . One of the most studied carbene is an osmium complex $\text{Cl}(\text{NO})(\text{PPh}_3)\text{Os}=\text{CH}_2$ which can be synthesised as shown in the following reaction:



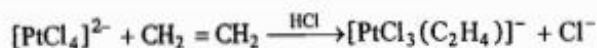
Metal Alkene Complexes

Ethylene is one of the simplest linear π -electron organic compound which has a single π bond resulting from the interactions of two $2p$ orbitals on its carbon atoms. Interaction of the two p orbitals results in the formation of one bonding and one antibonding π molecular orbitals.



The antibonding π -molecular orbital has one nodal plane perpendicular to the internuclear axis whereas the bonding π molecular orbital has no nodal plane. The π -bonding orbital is completely filled which is the HOMO and π^* antibonding orbital is unoccupied, which is the LUMO.

Probably the first and most well known alkene complex is Zeise's salt, $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$ that was discovered in 1827. Zeise isolated stable yellow crystals after refluxing alcoholic solution of $\text{K}_2[\text{PtCl}_4]$. Zeise's salt is really $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)] \cdot \text{H}_2\text{O}$ containing a water of crystallization. Zeise's salt is now made from the reaction of $\text{K}_2[\text{PtCl}_4]$ with ethylene.



The ethylene molecule occupies the fourth coordination site of the square planar complex with the C—C bond axis perpendicular to the square plane. The four C—H bonds in the ethylene complex are slightly bent away from the metal as shown in Fig. 5.14.

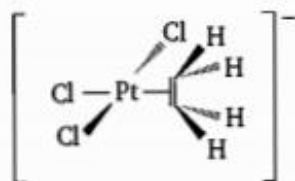


Fig. 5.14