

TRANSITION METAL π -COMPLEXES

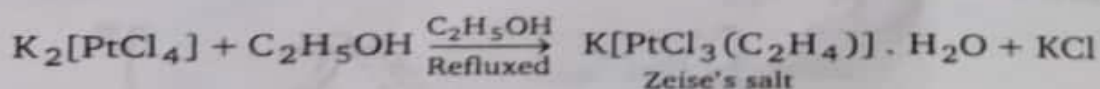
The molecules that have multiple bonds such as, $C=C$, $C\equiv C$, $N=O$, $N\equiv N$, etc. can form complexes with transition metals which are called π -complexes. The π -complexes of transition metals with unsaturated organic molecules such as alkenes, alkynes, arenes, etc. are quite important and these will be discussed in detail in this chapter.

4.1 TRANSITION METAL-ALKENE COMPLEXES

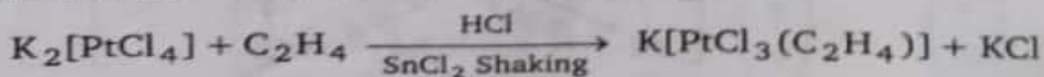
The complexes of transition metals with alkenes (*i.e.*, olefins) have been known since 1827 but they were not understood well until 1950s. In 1827, the Danish chemist W.C. Zeise isolated stable yellow crystals of platinum (II)-ethylene complex in Copenhagen. It was called Zeise's salt. But its exact composition was not known at that time. Later on, a number of transition metal-alkene complexes have been synthesised and characterized. However, Zeise's salt is still the most important transition metal-olefin complex.

4.1.1. Methods of Preparation

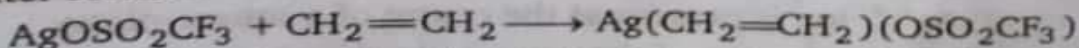
(a) Zeise's salt is isolated as stable yellow crystals when an ethanolic solution of potassium tetrachloroplatinate(II) is refluxed.



(b) Zeise's salt may also be obtained by prolonged shaking of a solution of $K_2[PtCl_4]$ in dilute HCl with ethylene. This reaction is generally slow. However, it can be speeded up by the addition of small amount of stannous chloride ($SnCl_2$).

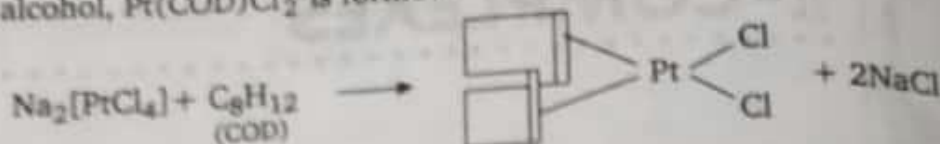


(c) Silver ions form similar alkene complexes which are water soluble.

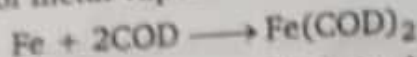


The formation of such complexes can be employed for the separation of alkenes from alkanes.

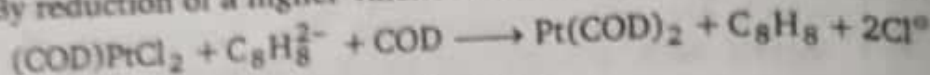
(d) When $\text{Na}_2[\text{PtCl}_4]$ is refluxed with *cis-cis-cycloocta-1, 5-diene* (COD) in *n*-propyl alcohol, $\text{Pt}(\text{COD})\text{Cl}_2$ is formed.



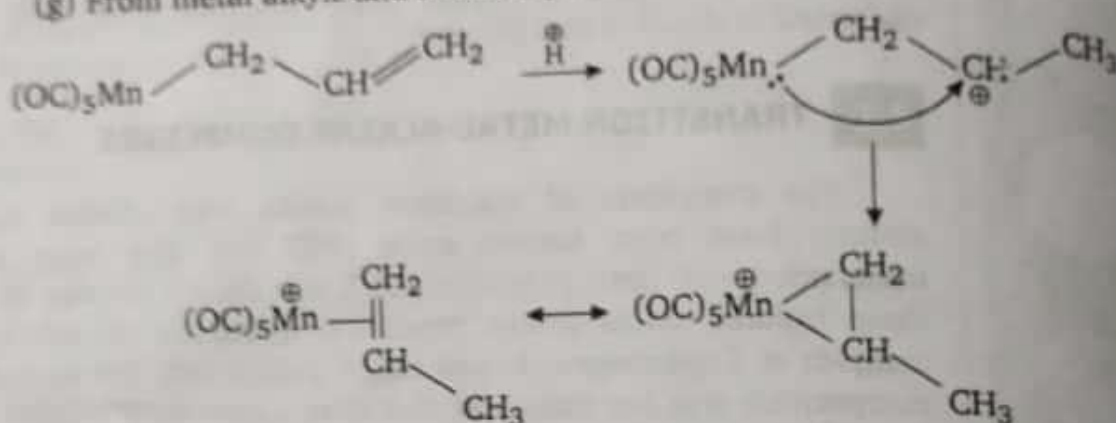
(e) By condensation of metal vapour with alkenes.



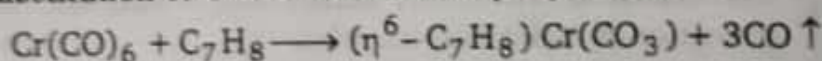
(f) By reduction of a higher-valent metal salt in the presence of alkene



(g) From metal alkyls and related species

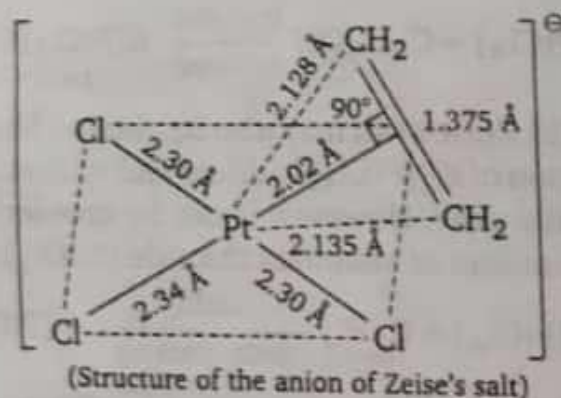


(h) By substitution of CO of metal carbonyl by alkene



4.1.2. Structure

The structure of the anion of Zeise's salt has been studied extensively by various methods including neutron diffraction technique. Its structure is given below :

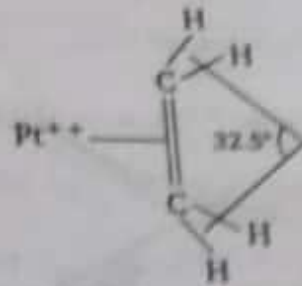


The main structural features of the anion of Zeise's salt are

- (i) Pt^{++} ion is present at the centre of a square-plane.
- (ii) Three corners of the square-plane are occupied by Cl^- ions.
- (iii) C_2H_4 occupies the fourth coordination site of the square-planar complex

with the $\text{C}=\text{C}$ bond \perp to the PtCl_3 plane, i.e., Pt -ligand plane and the centre of the $\text{C}=\text{C}$ bond lies on the square-plane corner.

between the normals to the CH_2 planes is 32.5° . It means, the H atoms of CH_2 groups of coordinated ethylene molecule bend away from the Pt^{++} ion.



(v) The Pt—Cl distance trans to C_2H_4 is longer than two *cis*-Pt—Cl distances by 0.04 \AA .

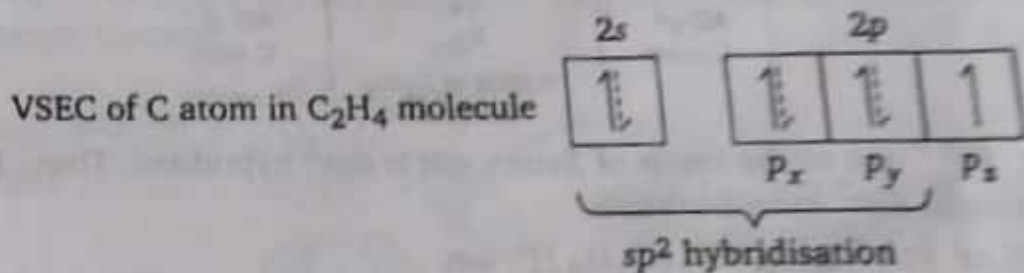
(vi) C=C bond of coordinated ethylene has bond length 1.375 \AA which is 0.038 \AA longer than in free C_2H_4 (i.e., 1.337 \AA).

(vii) The two carbon atoms of the coordinated C_2H_4 molecule are almost equidistant from the Pt^{++} ion.

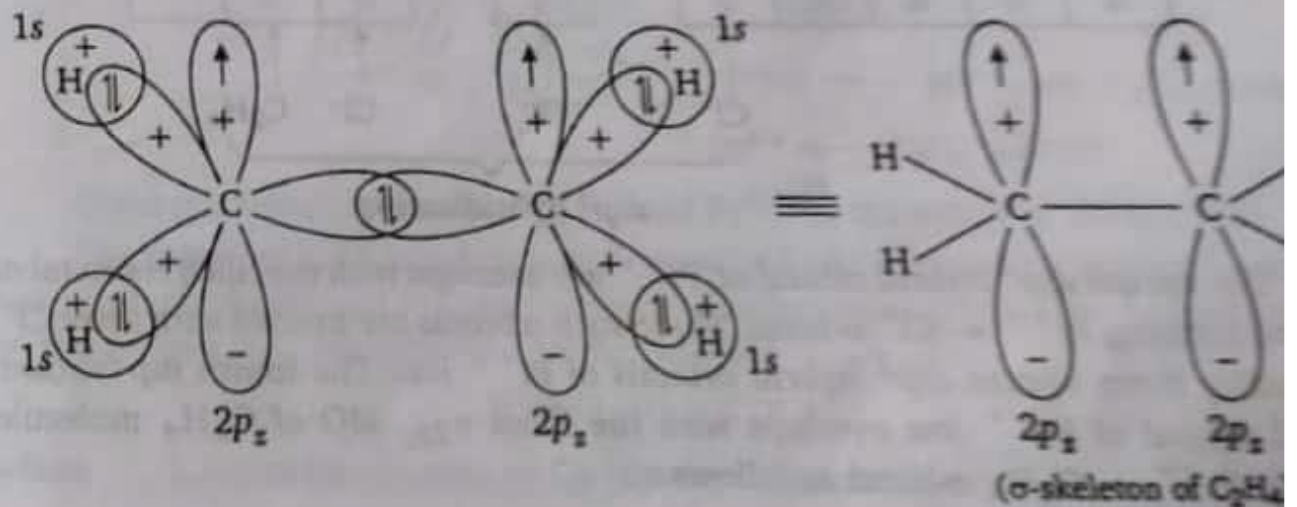
4.1.3. Bonding

The nature of bonding between Pt^{++} ion and C_2H_4 molecules in the anion of Zeise's salt can be explained nicely on the basis of Dewar-Chatt-Duncanson model developed in 1951–1953.

First of all, let us consider the nature of bonding in C_2H_4 (ethylene) molecule. Each carbon atom of ethylene molecule ($\text{CH}_2=\text{CH}_2$) is sp^2 hybridised.



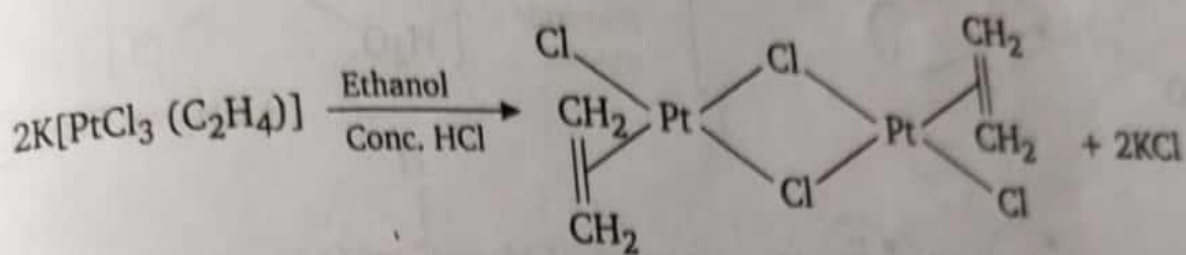
Each carbon atom forms three σ bonds—one with other carbon atom and two with H atoms using its three singly occupied sp^2 hybrid orbitals as follows :



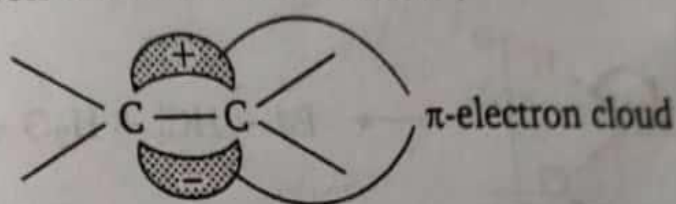
4.1.4. Properties

The Zeise's salt is a yellow coloured crystalline solid.

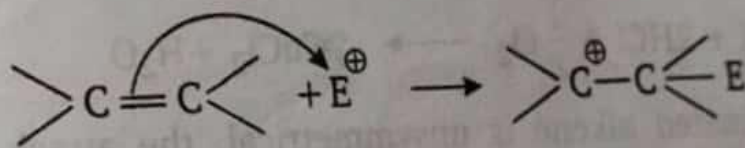
(i) When an ethanolic solution of Zeise's salt is treated with conc HCl, orange coloured dimer is formed.



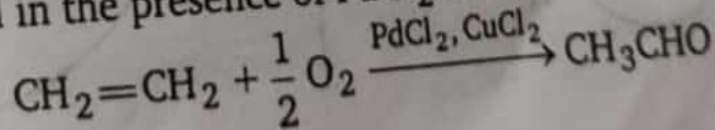
(ii) **Nucleophilic attack on coordinated alkene** : A free alkene molecule has π -electron cloud above and below :

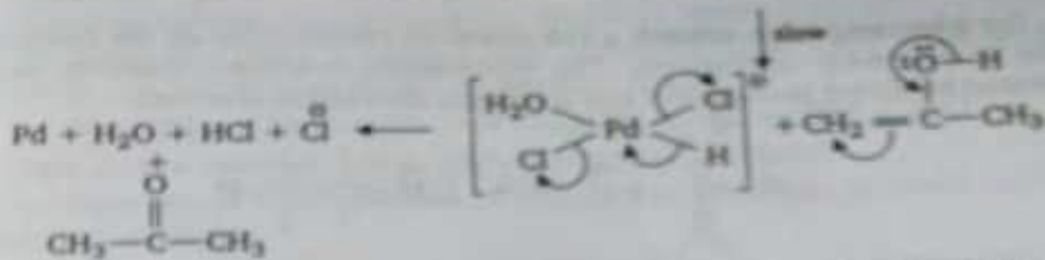


the molecular plane. Therefore, it is nucleophilic and it is attacked by an electrophile (E^+).

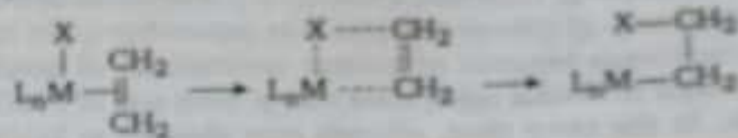


But the π -electron density in the coordinated alkene decreases due to the formation of alkene \rightarrow metal σ -bond. Therefore, the coordinated alkene becomes electron-deficient and it is readily attacked by nucleophiles such as H_2O , OH^{\ominus} , OMe^{\ominus} , CH_3COO^{\ominus} , $:NHMe_2$, Cl^{\ominus} etc. This property of metal-olefin complex is the basis of Wacker process for the aerial oxidation of alkene into carbonyl compound in the presence of $PdCl_2$ and $CuCl_2$ in dilute HCl.

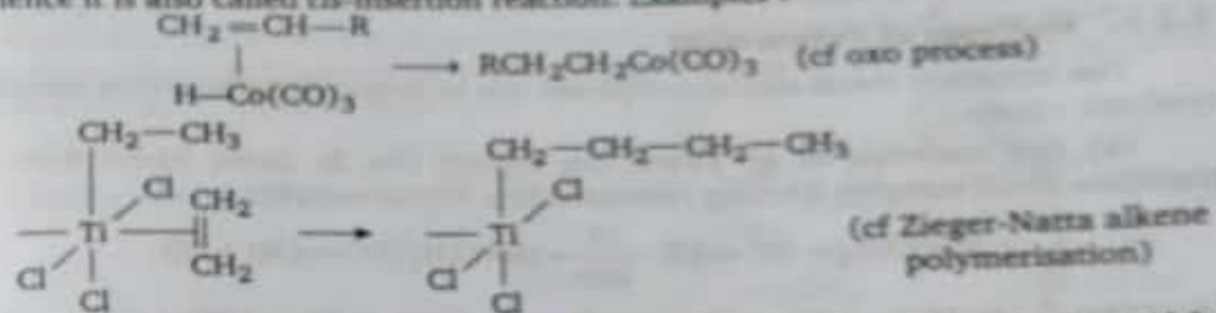




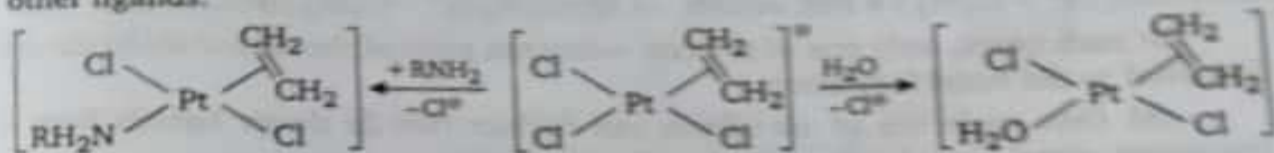
(iii) **Insertion reaction** : The alkene ligand coordinated to transition metal (M) has a tendency to be inserted into M—X bond where X is generally H atom or alkyl group. This 1, 2-insertion reaction proceeds through a four-centred transition state as follows :



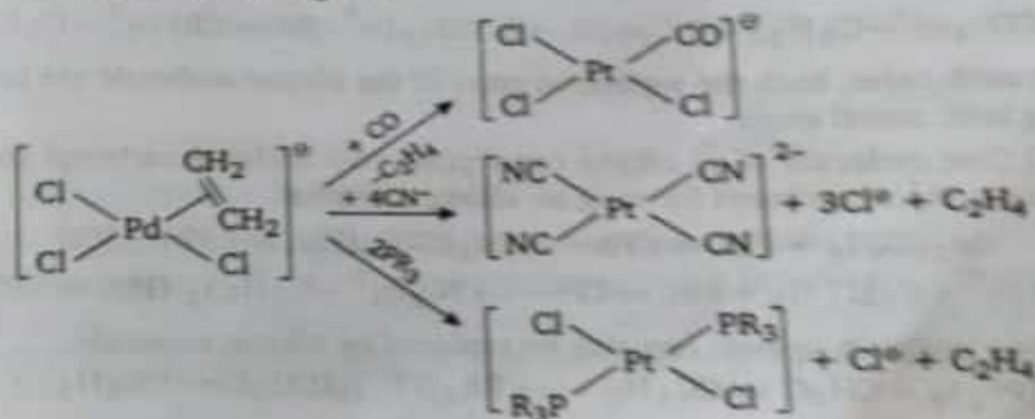
In this reaction, M and X are attached from the same side of C=C bond and hence it is also called *cis*-insertion reaction. Examples :



(iv) **Ligand substitution reaction** : The coordinated alkene ligand has high *trans*-effect. Therefore, the ligand *trans* to alkene can be easily replaced by other ligands.

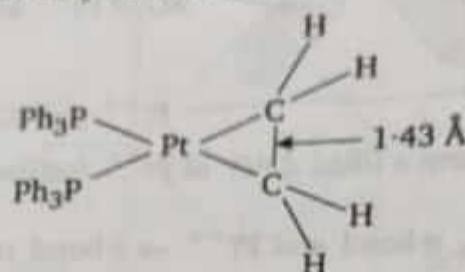


In some cases, the coordinated alkene molecule may also be replaced by strong ligands such as CO, CN⁻, PR₃ etc.

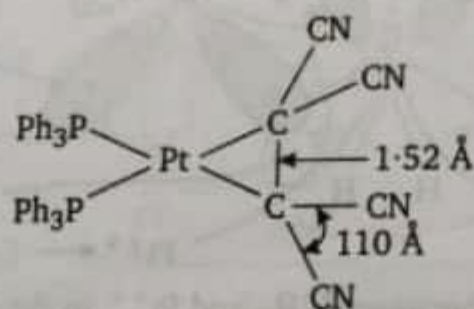


the tetrafluoro ethylene molecule bonds more strongly and at a shorter distance ($\text{Rh}-\text{C}=2.01 \text{ \AA}$) than does unsubstituted C_2H_4 ($\text{Rh}-\text{C}=2.17 \text{ \AA}$). C_2F_4 is a poorer σ -donor but a better π -acceptor than C_2H_4 on account of highly electronegative fluorine substituents. It indicates that the π -accepting ability of the alkene ligand is the most important factor in determining the bond-lengths in these compounds.

The $\text{C}=\text{C}$ bond of the alkene lengthens on bonding to transition metal. The metal \leftarrow alkene σ -bond depletes the $\text{C}=\text{C}$ π -bond by partial transfer of these π -electrons to the metal and hence slightly weakens and lengthens it. But the major factor in lengthening the $\text{C}=\text{C}$ bond is the strength of back-donation from the metal. As a result of this back-donation, electron density flows from the metal atom to π_{2p}^* MO of the $\text{C}=\text{C}$ group. It decreases the $\text{C}=\text{C}$ bond order and, therefore, the $\text{C}-\text{C}$ bond is weakened and lengthened. In the Zeise's salt, Pt^{+2} ion is a poor π -donor (due to dipositive charge) and C_2H_4 is a poor π -acceptor (due to less electronegative H atoms) and, therefore, the $\text{C}-\text{C}$ bond of coordinated ethylene is lengthened only slightly (by 0.038 \AA). But in $[\text{Pt}(\text{PPh}_3)_2(\text{CH}_2=\text{CH}_2)]$, $\text{Pt}(0)$ is rich in electron and is a good π -donor and, therefore, the $\text{C}-\text{C}$ bond becomes much longer (1.43 \AA) and H atoms are bent considerably out of the plane and away from Pt atom.



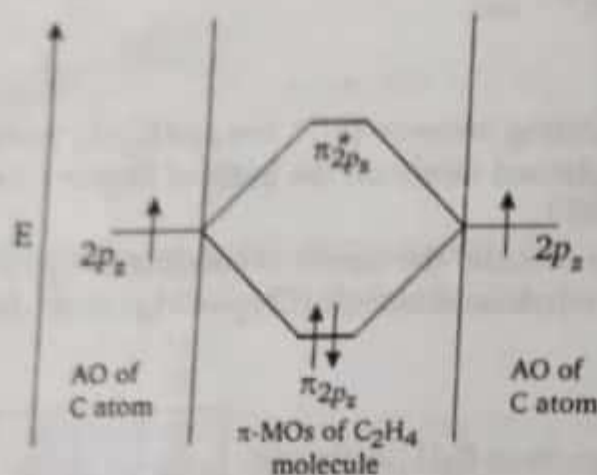
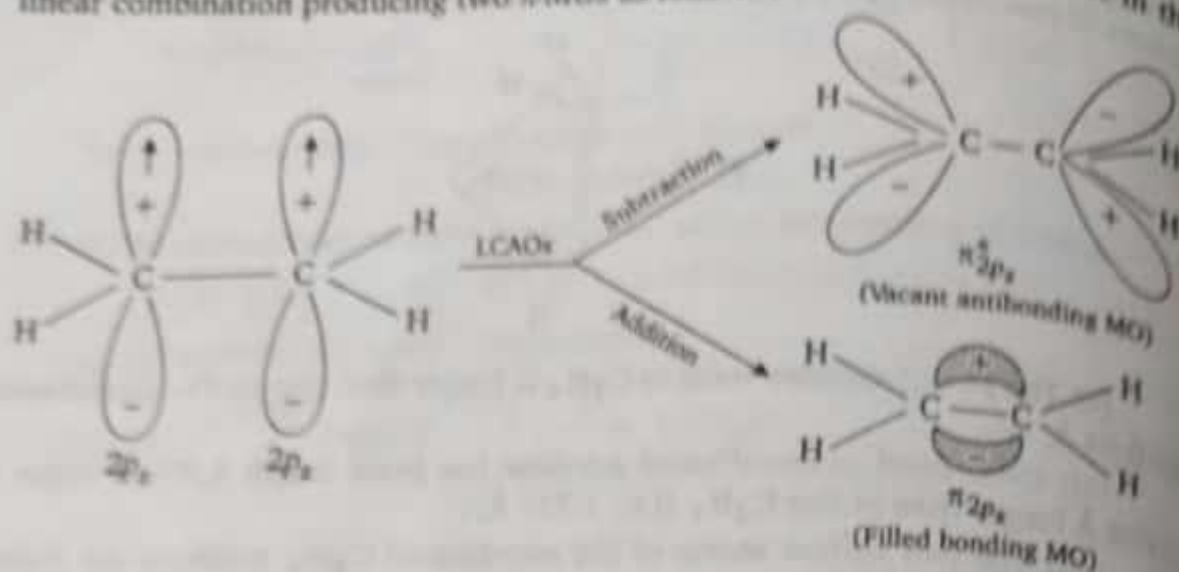
The presence of electron-withdrawing group on the $\text{C}=\text{C}$ bond also encourages back donation and lengthens the $\text{C}-\text{C}$ bond to a great extent. For example, in $[\text{Pt}(\text{C}_2(\text{CN})_4)(\text{PPh}_3)_2]$, $\text{Pt}(0)$ is a good π -donor and $\text{C}_2(\text{CN})_4$ is a good π -acceptor. As a result, the $\text{Pt}(0) \rightarrow \text{C}_2(\text{CN})_4$ back-donation becomes so prominent that the $\text{C}-\text{C}$ bond is lengthened to 1.52 \AA which is almost equal to the $\text{C}-\text{C}$ single bond-length (1.54 \AA).



At the same time, 2P and 2C that are bonded to Pt are almost coplanar.

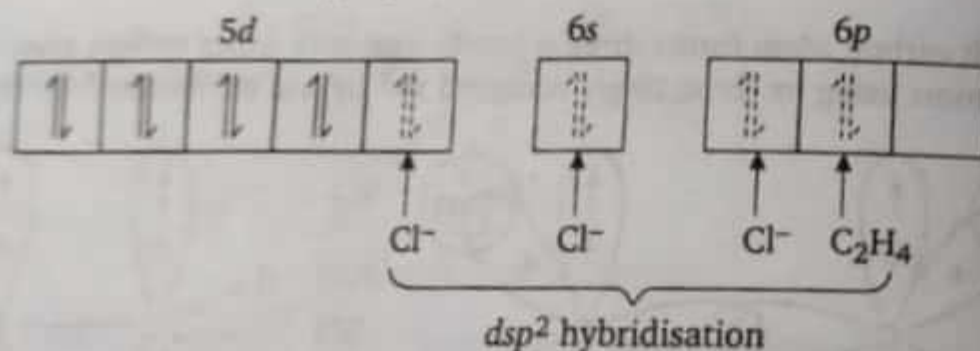
Thus in the extreme cases where both $\text{C}_2\text{X}_4 \rightarrow \text{M}$ σ -bond and $\text{C}_2\text{X}_4 \leftarrow \text{M}$ π -bond have an order of one, the bonding can be represented by a simple valence bond structure (B) involving only two σ -bonds with sp^3 hybridisation on carbon atom. Hence, the true structure of these transition metal-olefin complexes may be regarded as a resonance hybrid of (A) and (B).

One singly occupied $2p_x$ AO is left unused on each carbon atom \perp to the plane of C_2H_4 molecule. These two parallel singly occupied $2p_x$ AOs take part in the linear combination producing two π -MOs as follows :



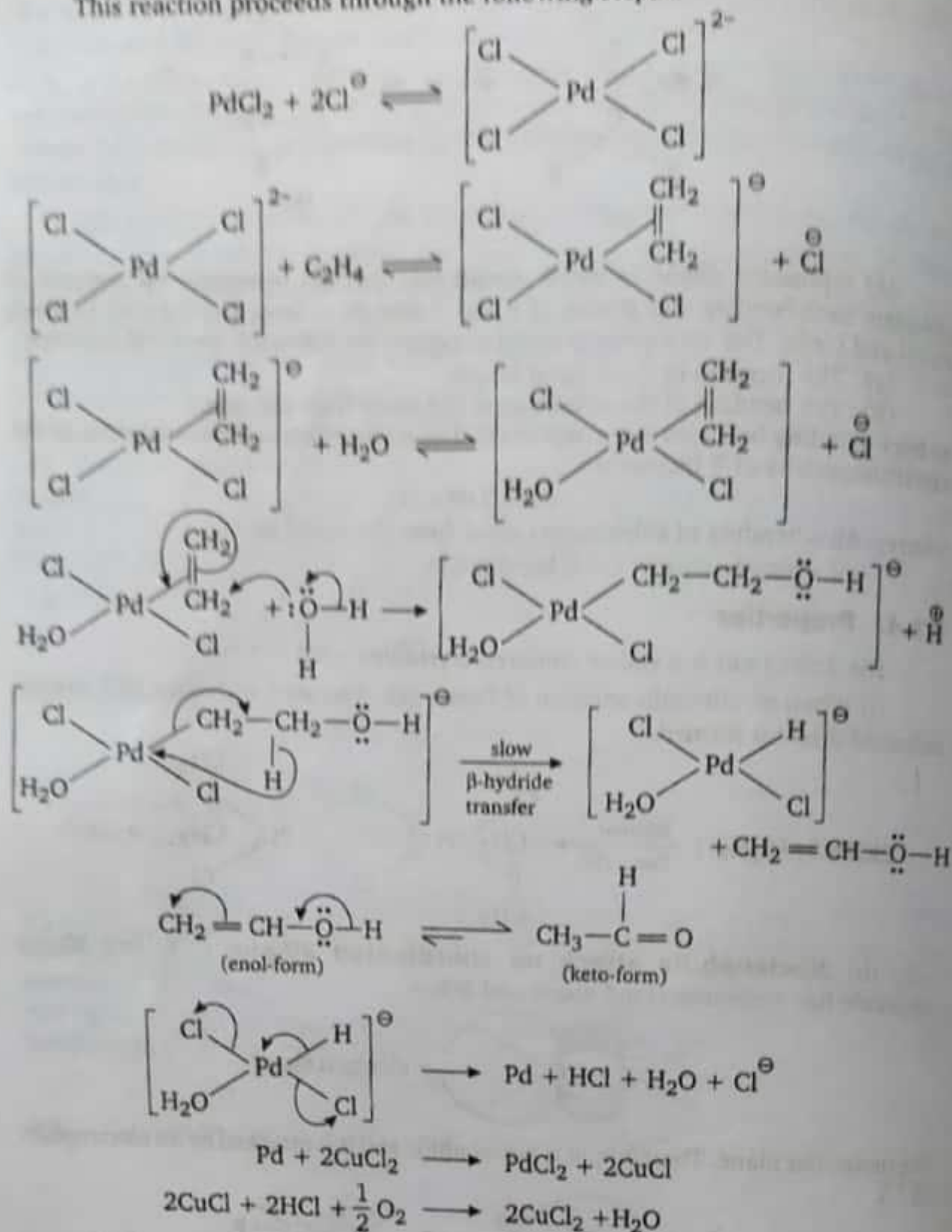
The Pt^{++} ion of the anion of Zeise's salt is dsp^2 hybridised. Thus, Pt^{++} ion has four vacant dsp^2 hybrid orbitals.

VSEC of Pt^{++} ion $[PtCl_3(C_2H_4)]^\ominus$ ion

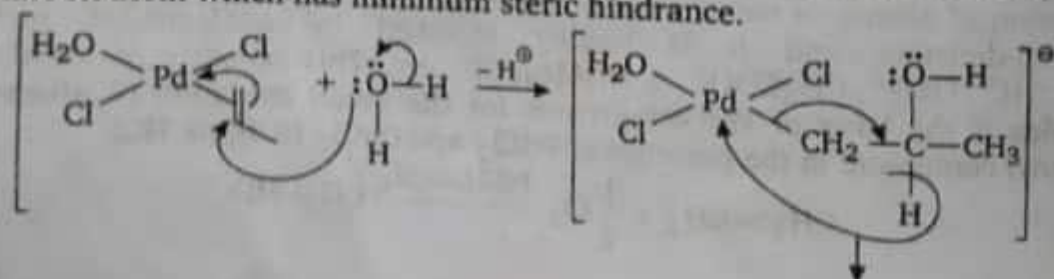


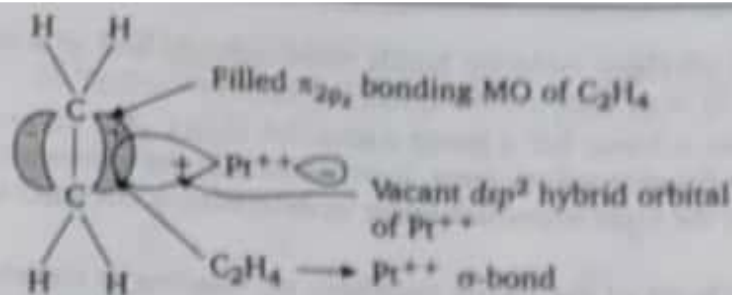
The vacant dsp^2 hybrid orbital of Pt^{++} ion overlaps with the filled σ -orbital of Cl^- ion forming $Pt^{++} \leftarrow Cl^-$ σ -bond. Three such σ bonds are formed with three Cl^- ions using three vacant dsp^2 hybrid orbitals of Pt^{++} ion. The fourth dsp^2 vacant hybrid orbital of Pt^{++} ion overlaps with the filled $\pi 2p_x$ MO of C_2H_4 molecule forming $Pt^{++} \leftarrow C_2H_4$ σ -bond as follows :

This reaction proceeds through the following steps :



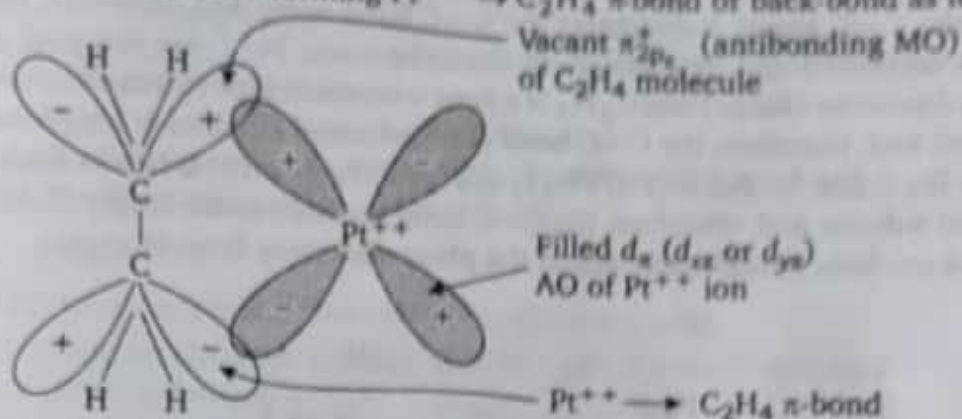
If the coordinated alkene is unsymmetrical, the attack by nucleophile is regioselective for the more substituted position so that the bulky Pd atom goes to that carbon atom which has minimum steric hindrance.





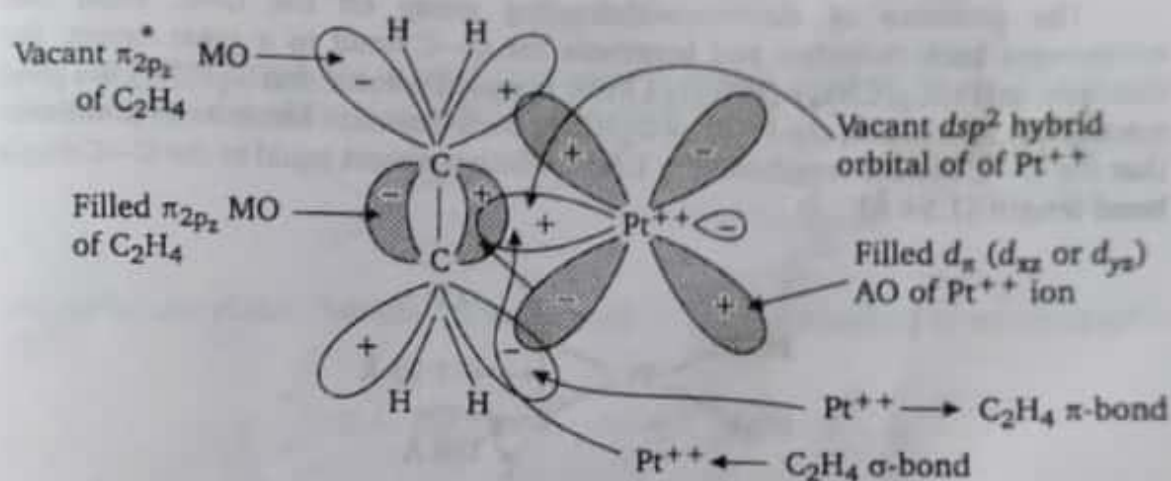
(σ -Donation from the filled π_{2p_z} MO of ethylene into the vacant dsp^2 hybrid orbital of Pt^{++} ion).

Now, the filled d_π (d_{xz} or d_{yz}) AO of Pt^{++} ion overlaps with the vacant $\pi_{2p_z}^*$ MO of ethylene molecule forming $Pt^{++} \rightarrow C_2H_4$ π -bond or back-bond as follows:



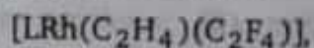
(π -Back-donation from a filled d AO of Pt^{++} ion into the vacant $\pi_{2p_z}^*$ MO of ethylene)

The $Pt^{++} \leftarrow C_2H_4$ σ -bond and $Pt^{++} \rightarrow \pi$ -bond reinforce each other. It is called synergic bonding.



(Synergic bonding between C_2H_4 and Pt^{++} in the anion of Zeise's salt)

The extent of back-bonding is undetermined and it varies depending upon the nature of substituents on $>C=C<$ bond, oxidation state of metal and other ligands on the metal atom. For example, in the complex



where L = acetylacetonato or Cp (Cyclopentadienyl)