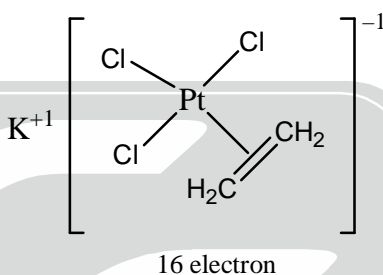


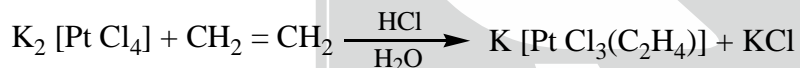
Metallocenes

METAL OLEFIN COMPLEX: ZEISE'S SALT:



Potassium trichloro (η^2 -ethylene) Platinate (II)

Zeise's salt is first organometallic compound of transition elements.

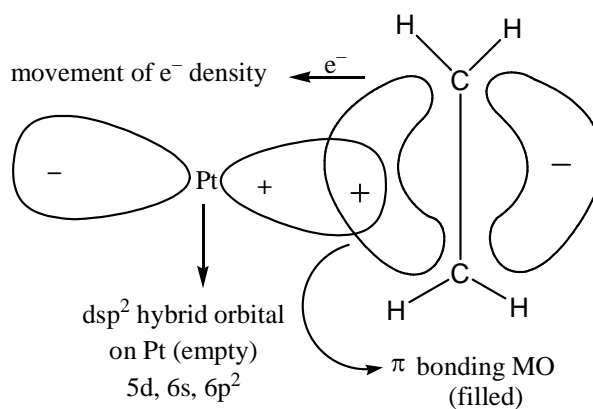


Structure : Square planar complex.

C-C bond exist perpendicular to the Pt. It forms a square planar complex where ethylene forms the fourth coordination site with the C = C bond axis is perpendicular to the square planar.

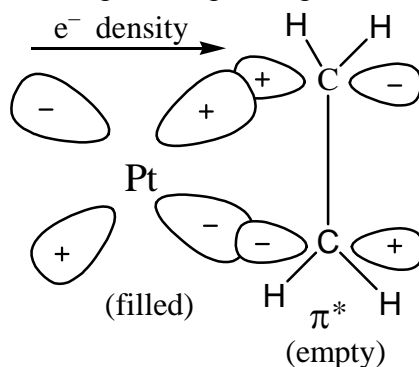
DEWAR CHATT –DUNCANSON THEORY:

(1) σ - bonding :



The σ bond formed by overlapping by filled π bonding MO of ethylene to empty dsp^2 hybridise orbital of Pt, and e^- density shifted from ethylene to Pt.

π - Back Bonding : The back donation of electron density from the metal to the π^* orbital of ethylene reduces its bond order and hence results in the weakening and lengthening of C–C bond.

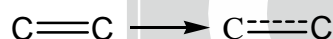


So, ethylene molecule interacts with metal both as a σ -donor through C–C π orbital and as a π -acceptor through the C–C π^* orbital.

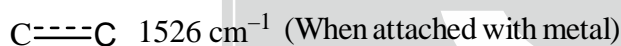
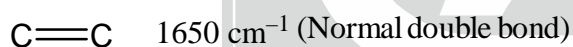
Consequences :

1. C = C bond length increased from 1.34 Å to 1.37 Å

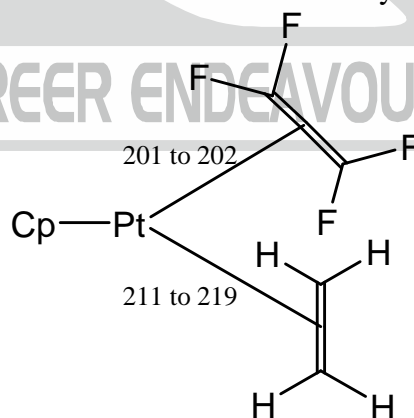
The increase in bond length due to donation of π electron density from ethylene system to metal and acceptance of electrons in antibonding orbital which destabilise the system and bond length increase and bond order decreases.



2. IR spectroscopy : Stretching frequency decreases means bond becomes weak.



3. Because of the π back-bonding substituent on alkene move away from the C = C double bond.



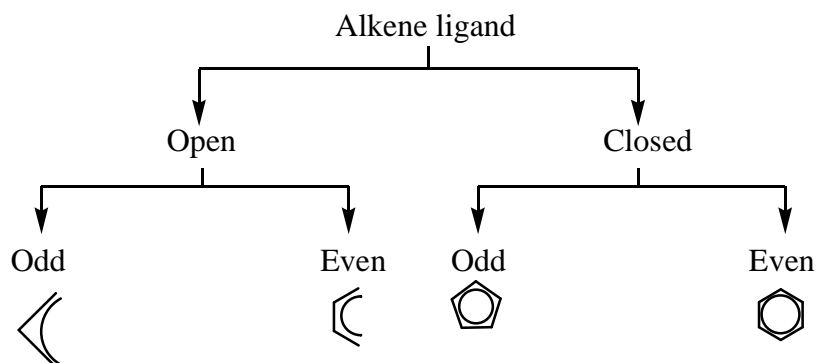
because presence of electronegative element on alkene will increase the back bonding from metal and metal alkene back bond length will decrease.

In extreme cases when metal is very much electron rich and alkene contain very much electron withdrawing ligands then backbonding is so severe (high) then perpendicular alkene lies in the same plane with the metal and other ligands.

4. All Pt–Cl bond length are not equal. The Pt–Cl bond which is trans to ethylene is slightly elongated due to greater trans effect of ethylene.

Reaction of metal bound alkene

Davies, Mingos and Green rule (DMG rule):



(1) Even ligands are attacked preferably to odd ligands

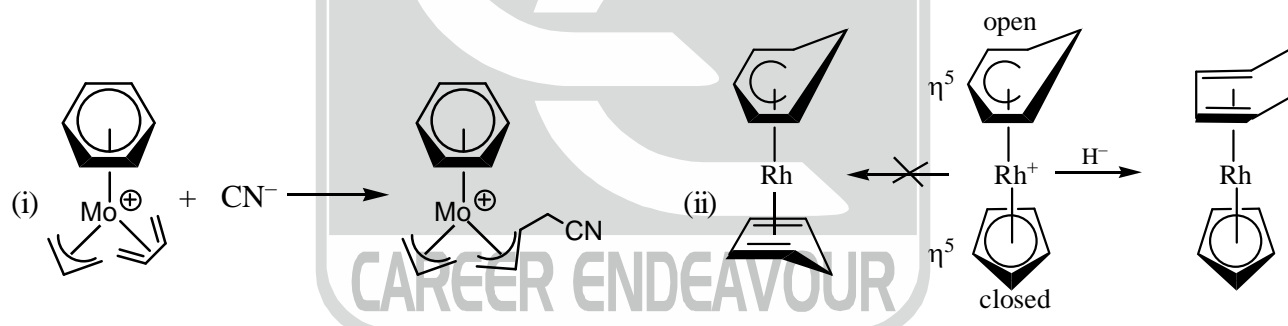
(2) Open ligands are attacked preferably to cyclic ligands

(3) The attack preferably occurs on the terminal carbon of the ligand in the polyenes and open polyenyls.

The reactivity of ligands—



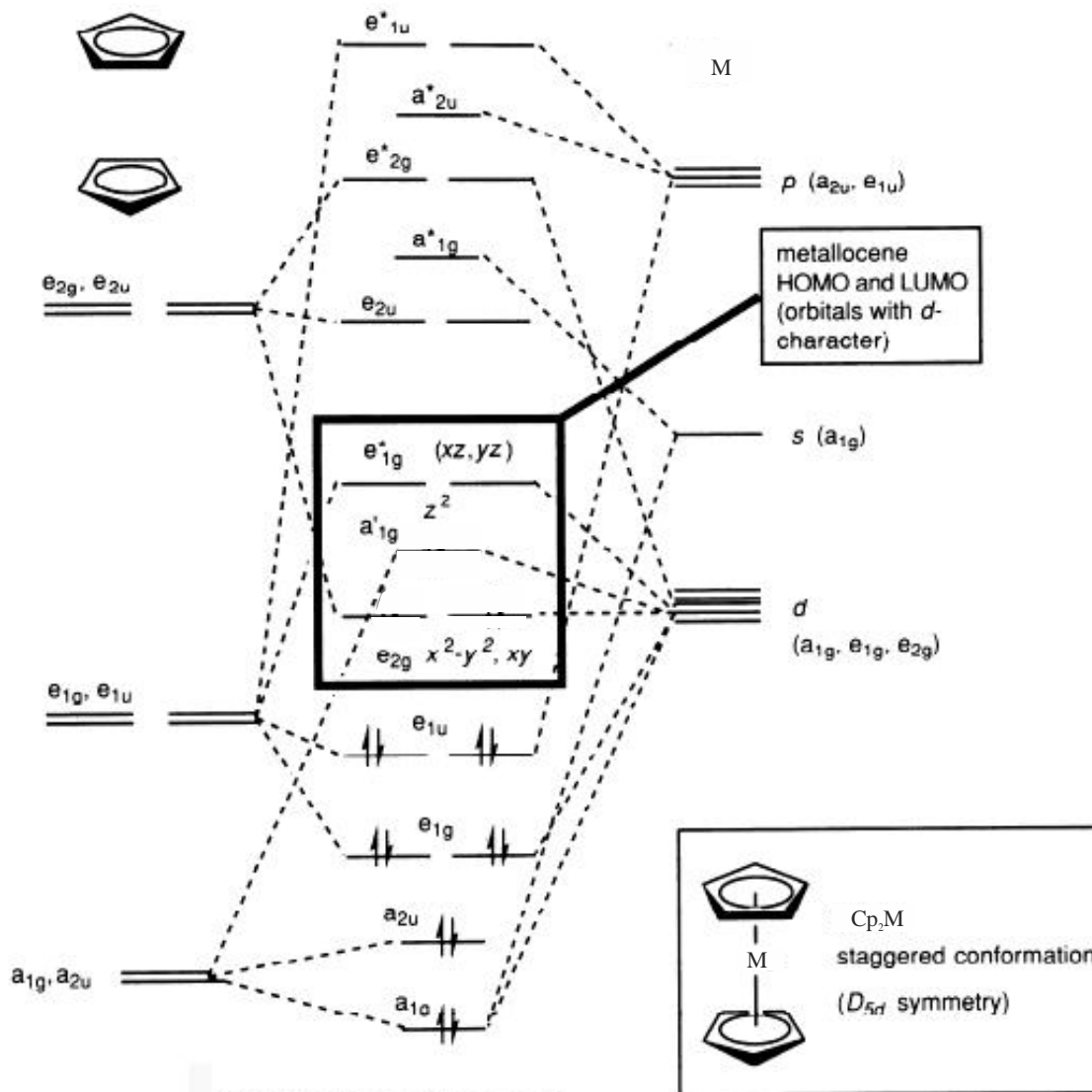
For example:



METALLOCENE (Sandwich Compound)

The compound in which two Cp rings as well as metal are present. Here, M = V (Vadanocene), Co(Cobaltocene), Ni(Nickelocene), Fe(ferrocene), etc.

Molecular orbital diagram of Metallocene:



MO diagram of Metallocene

Compound	No. of unpaired e ⁻	Electronic configuration	Dipole moment
(1) Cp ₂ V	\uparrow a _{1g} \uparrow e _{2g}	e _{2g} ² a _{1g} ¹	3.87
(2) Cp ₂ Cr	\uparrow a _{1g} \uparrow e _{2g}	e _{2g} ³ a _{1g} ¹	2.83
(3) Cp ₂ Mn (exception)	\uparrow e _{1g} [*] \uparrow a _{1g} \uparrow e _{2g}	e _{2g} ² a _{1g} ¹ e _{1g} ^{*2}	5.92