

# CHEM – 465 Organometallic & Bio- inorganic Chemistry (Cr.03)

**Nature of metal-carbon bonds:** Compounds with Metal-Carbon single bonds; Compounds with Metal-Carbon  $\pi$ - bonds; Classification of organometallic compounds and 18- electron rule.

**Compounds of transition metals:** Single, double and triple bonds to carbon, (compound types, Acyls, Alkylidene complexes and alkylidyne complexes), delocalized hydrocarbon systems, (alkene, olefins, allyl and Butadienes), Alkyne complexes, Cyclic  $\pi$  complexes (four, five and six member rings),

**Fundamental Process in Reactions of Organotransition Metal Complexes:** Ligand Coordination & dissociation; Oxidative addition & reductive Eliminations; Insertion & Extrusion reactions; Reaction of Coordinated ligands, Applications of organometallic compounds in synthetic chemistry and industry.

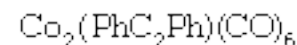
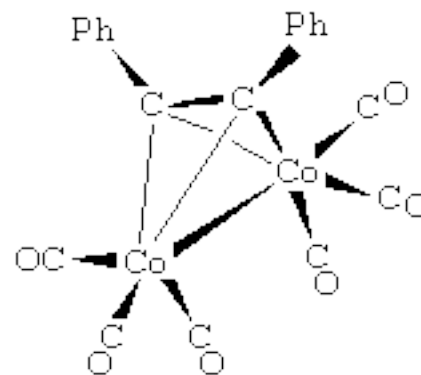
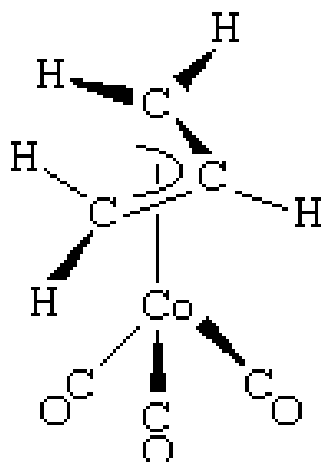
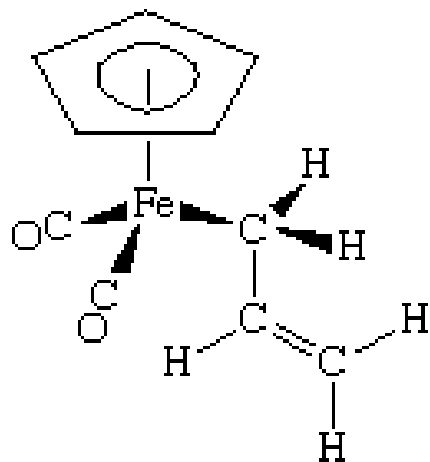
**Bio-Inorganic chemistry:** Essential elements, Biochemistry of iron (iron storage and transport), Haemoglobin and myoglobins, Cytochromes, other natural oxygen carrier, Biochemistry of other metals (Zn, Cu, Co, Cr, Ni, and V), Metal based drugs.

## **Recommended Books**

1. Huheey, J.E., Keiter, E.A. and Keiter, R.L. "Inorganic Chemistry: Principles of Structure and Reactivity", 7<sup>th</sup> Ed., Harper and Row, New York, (2010).
2. Garry L., Miessler, D. and Tarr, A. "Inorganic Chemistry" 3<sup>rd</sup> Edition, Pearson Education, Inc. NY (2004).

# Introduction

Organometallic compound, any member of a class of substances containing at least one metal-to-carbon bond in which the carbon is part of an organic group. The class includes such compounds as ferrocene, a remarkably stable compound in which an iron atom is sandwiched between two hydrocarbon rings.

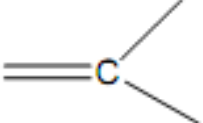
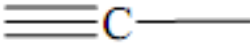

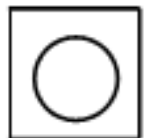

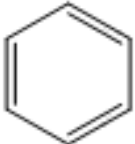




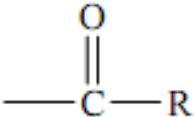
# Historical Perspective

- 1760 Louis Claude Cadet de Gassicourt investigates inks based on cobalt salts and isolates cacodyl from cobalt mineral containing arsenic
- 1827 William Christopher Zeise produces Zeise's salt; the first platinum / olefin complex
- 1848 Edward Frankland discovers diethylzinc
- 1863 [Charles Friedel](#) and James Crafts prepare organochlorosilanes
- 1890 Ludwig Mond discovers nickel carbonyl
- 1899 Introduction of Grignard reaction
- 1899 John Ulric Nef discovers alkynylation using sodium acetylides.
- 1900 Paul Sabatier works on hydrogenation organic compounds with metal catalysts. Hydrogenation of fats kicks off advances in food industry, see margarine
- 1909 Paul Ehrlich introduces Salvarsan for the treatment of syphilis, an early arsenic based organometallic compound
- 1912 Nobel Prize Victor Grignard and Paul Sabatier
- 1930 Henry Gilman works on lithium cuprates, see Gilman reagent
- 1951 Walter Hieber was awarded the Alfred Stock prize for his work with metal carbonyl chemistry.
- 1951 Ferrocene is discovered
- 1963 Nobel prize for Karl Ziegler and Giulio Natta on Ziegler-Natta catalyst
- 1965 Discovery of cyclobutadieneiron tricarbonyl
- 1968 Heck reaction
- 1973 Nobel prize Geoffrey Wilkinson and Ernst Otto Fischer on sandwich compounds

- 1981 Nobel prize Roald Hoffmann and Kenichi Fukui for creation of the Woodward-Hoffman Rules
- 2001 Nobel prize W. S. Knowles, R. Noyori and Karl Barry Sharpless for asymmetric hydrogenation
- 2005 Nobel prize Yves Chauvin, Robert Grubbs, and Richard Schrock on metal-catalyzed alkene metathesis
- 2010 Nobel prize Richard F. Heck, Ei-ichi Negishi, Akira Suzuki for palladium catalyzed cross coupling reactions

# Common Ligands in Organometallics

Formula	Names
CO	Carbonyl
	Carbene (Alkylidene)
	Carbyne (Alkylidyne)
	Cyclopropenyl (cyclo-C <sub>3</sub> H <sub>3</sub> )
	Cyclobutadien (cyclo-C <sub>4</sub> H <sub>4</sub> )
	Cyclopentdienyl (cyclo-C <sub>5</sub> H <sub>5</sub> )Cp)
	Benzene
	1,5-cyclooctadiene (1,5-COD)

$\text{H}_2\text{C}=\text{CH}_2$	Ethylene
$\text{HC}\equiv\text{CH}$	Acetylene
	$\pi$ -Alyl ( $\text{C}_3\text{H}_5$ ) Allyl
	Acyl

## Nature of metal-carbon bonds

The bonding interaction between metal and carbon in organometallic compounds must be ionic or covalent, localized or delocalized between one or more carbon atoms of an organic molecule or group and a transition, lanthanide, actinide or main group metal or metalloid atom. Accordingly, the organometallic compounds are of following types on the basis of the nature of metal-carbon bond :

**(a) Ionic organometallic compounds :** The organometallic compounds containing highly electropositive metals such as alkali metals, alkaline earth metals, lanthanides and actinides with electronegativity value equal to or less than 1 are predominantly ionic in nature. The carbon atom is negatively charged and the metal atom is positively charged in such compounds. The main binding force in such organometallic compounds is the electrostatic attractive force acting between the oppositely charged ions which is non-directional in nature. For example,  $\text{C}^{\ominus}\text{H}_3\text{K}^{\oplus}$  (methyl potassium) has  $\sim 51\%$  ionic character.  $\text{C}_5^{\ominus}\text{H}_5\text{Na}^{\oplus}$  (sodium cyclopentadienide) is also an ionic organometallic compound. The organometallic compounds of lithium, beryllium and magnesium are appreciably covalent in most of the cases on account of smaller size, greater charge-radius ( $e/r$ ) ratio and hence greater polarising power of  $\text{Li}^+$ ,  $\text{Be}^{++}$  and  $\text{Mg}^{++}$  ions.

**(b)  $\sigma$ -Bonded covalent organometallic compounds** : The organometallic compounds in which the carbon atom of the organic group is attached to metal by a normal covalent ( $\sigma$ ) bond, *i. e.*, two-centered, two-electron ( $2c - 2e$ ) bond are called  $\sigma$ -bonded covalent organometallic compounds. Such compounds are generally formed by *p*-block elements with electronegativity greater than 1 but less than 2.5.

Examples :  $B(CH_3)_3$ ,  $Al(CH_3)_3$ ,  $Si(CH_3)_4$ ,  $Pb(CH_3)_4$ , etc. However, *d*-block elements are also capable of forming  $\sigma$  bonded organometallic compounds.

Examples :  $W(CH_3)_6$ ,  $CH_3 - Mn(CO)_5$ ,  $[Ta(\eta^5 - C_5H_5)_2 (CH_3)_3]$ ,  $Ta(CH_3)_5$ .

The binary alkyls of non-transition elements are more stable than binary alkyls of transition elements. The latter decompose even at room temperature.



This is due to the fact that the binary alkyls or aryls of transition metals are coordinatively and electronically unsaturated. It provides an easy pathway to chemical decomposition/reaction.

In the  $\sigma$ -bonded covalent organometallic compounds, the singly occupied hybrid orbital of carbon atom of the organic group overlaps with the singly occupied hybrid orbital of the metal atom forming a  $2c - 2e$  bond. The shape of  $\sigma$ -bonded covalent organometallic compounds depends upon the type of hybridisation on metal atom.



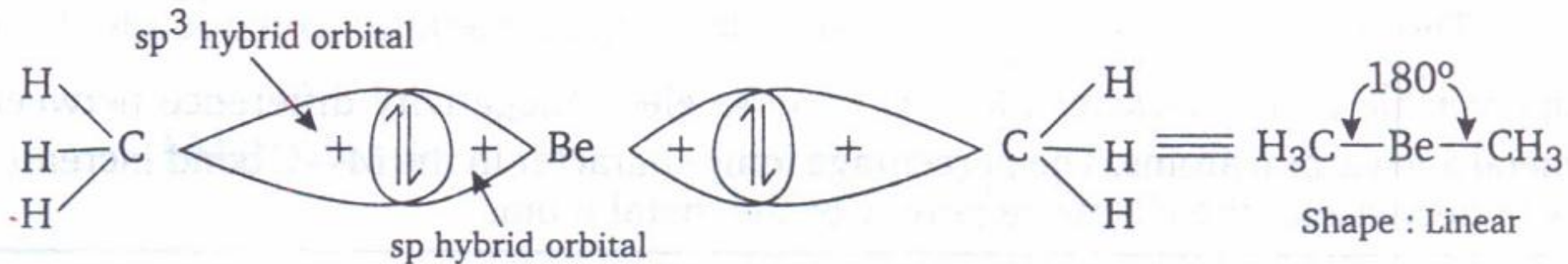
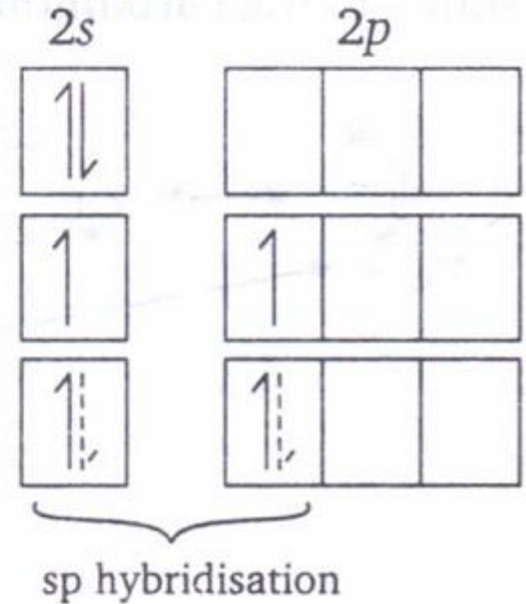


Valence shell electronic configuration (VSEC) of Be

atom in the ground state (G.S.)

VSEC of Be atom in the excited state (E.S.)

VSEC of Be atom in Be(CH<sub>3</sub>)<sub>2</sub> molecule

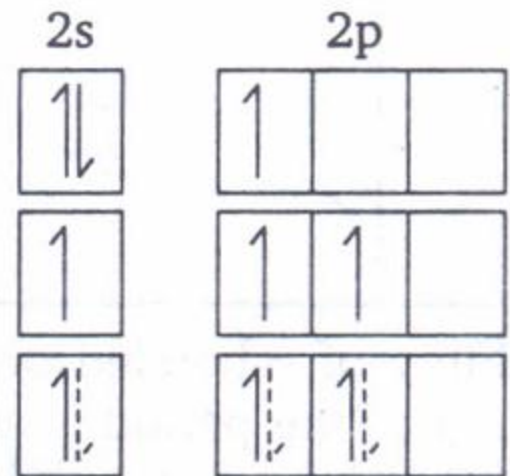


# $B(CH_3)_3$

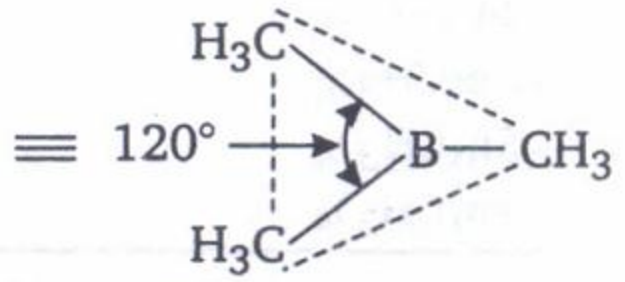
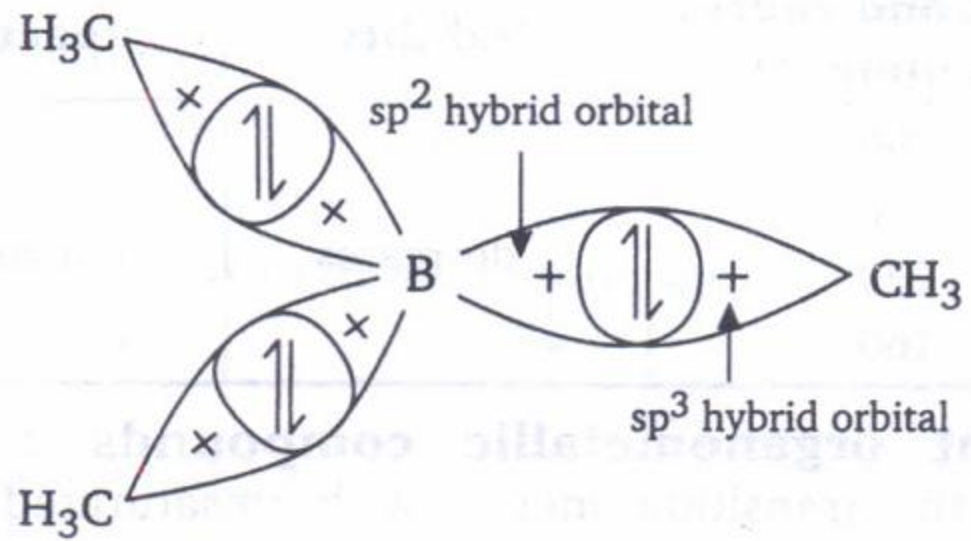
VSEC of B atom in the (G.S.)

VSEC of B atom in the (E.S.)

VSEC of B atom in  $B(CH_3)_3$  molecule



$sp^2$  hybridisation  
 $sp^2$  hybridisation



Shape : Triangular planar

The metal-carbon bonds of  $\sigma$ -bonded organometallic compounds have appreciable ionic character ( $M^{\delta+}-C^{\delta-}$ ) due to electronegativity difference between metal and carbon atoms. The percentage ionic character in the M—C bond increases with decrease in the electronegativity of the metal atom.

M—C bond	Electronegativity of metal atom	% ionic character
Si—C	1.8	12
Al—C	1.5	22
Mg—C	1.2	35
Na—C	1.0	47
K—C	0.9	51

The stability of  $\sigma$ -bonded organometallic compounds decreases on moving down the group of the periodic table due to decrease in M—C bond energy and, therefore, the reactivity increases in the same order.

Organometallic compound	M—C bond energy (kJ mole <sup>-1</sup> )	Stability	Reactivity
Si(CH <sub>3</sub> ) <sub>4</sub>	290	↓ decreases	↓ increases
Ge(CH <sub>3</sub> ) <sub>4</sub>	240		
Sn(CH <sub>3</sub> ) <sub>4</sub>	220		
Pb(CH <sub>3</sub> ) <sub>4</sub>	160		

**(c)  $\pi$ -Bonded covalent organometallic compounds :** In the organometallic compounds of the transition metals with unsaturated organic compounds/groups such as ethylene, acetylene, cyclopentadienyl, benzene, etc., there is interaction between the atomic orbitals (AOs) of the metal atom and the  $\pi$ -molecular orbitals (MOs) of the organic ligand. For example, in ferrocene,  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]$ , the atomic orbitals of iron atom interact with  $\pi$ -MOs of cyclopentadienyl rings forming the MOs of the ferrocene molecule.  $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$  is another example of such an organometallic compound.

## Bonding in Metal Carbonyls

Although CO possesses weaker Lewis basicity but it forms very stable complexes with almost all transition metals in their low oxidation states due to multiple nature of M–CO bonds supported by spectroscopic evidence. The formation of stable complexes by CO with the transition metals in their low oxidation states (low positive, zero or low negative) is attributed to the so called synergic bonding.  $\pi$ -acceptor ligands (e.g., CO) give large ligand field splitting. These ligands can stabilize the low positive, zero or even negative oxidation states of the metals due to the presence of vacant  $\pi^*$  orbitals in addition to lone electron pairs as shown in the MO diagram of CO.

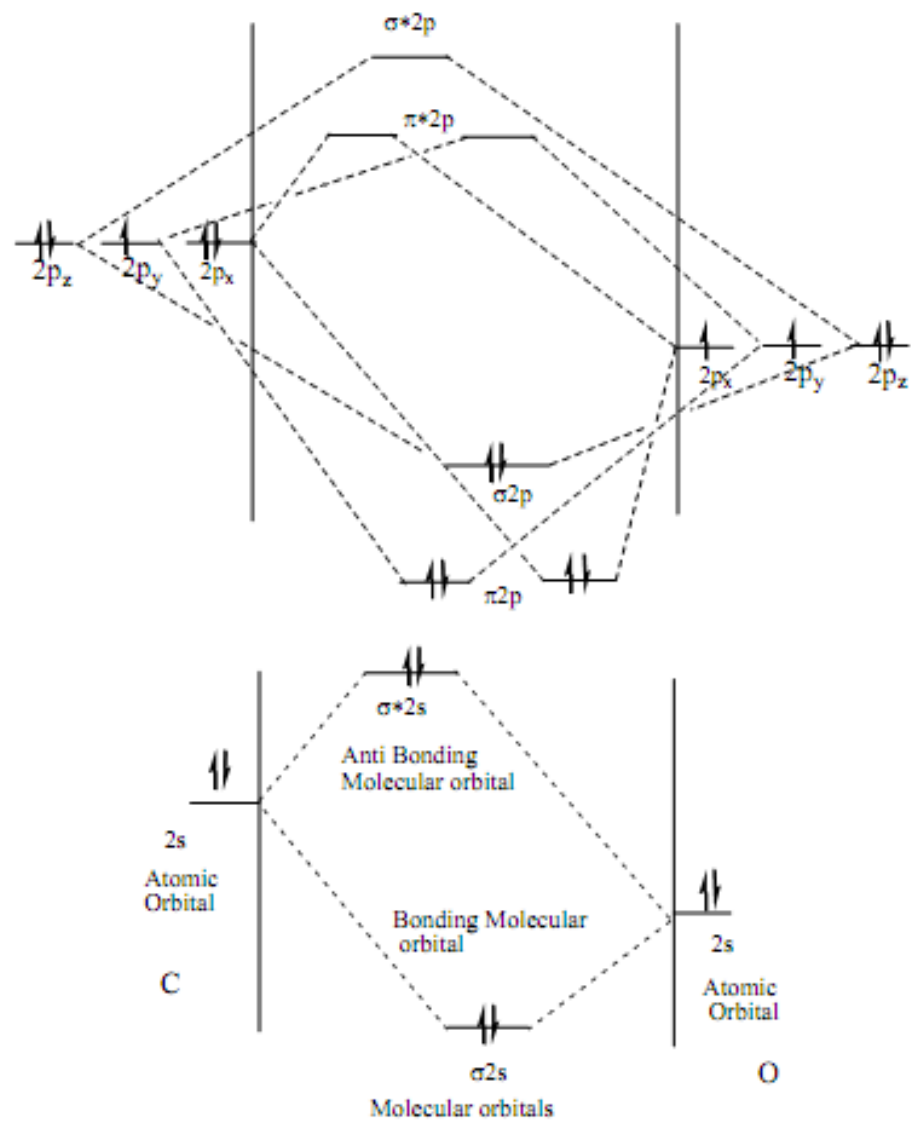
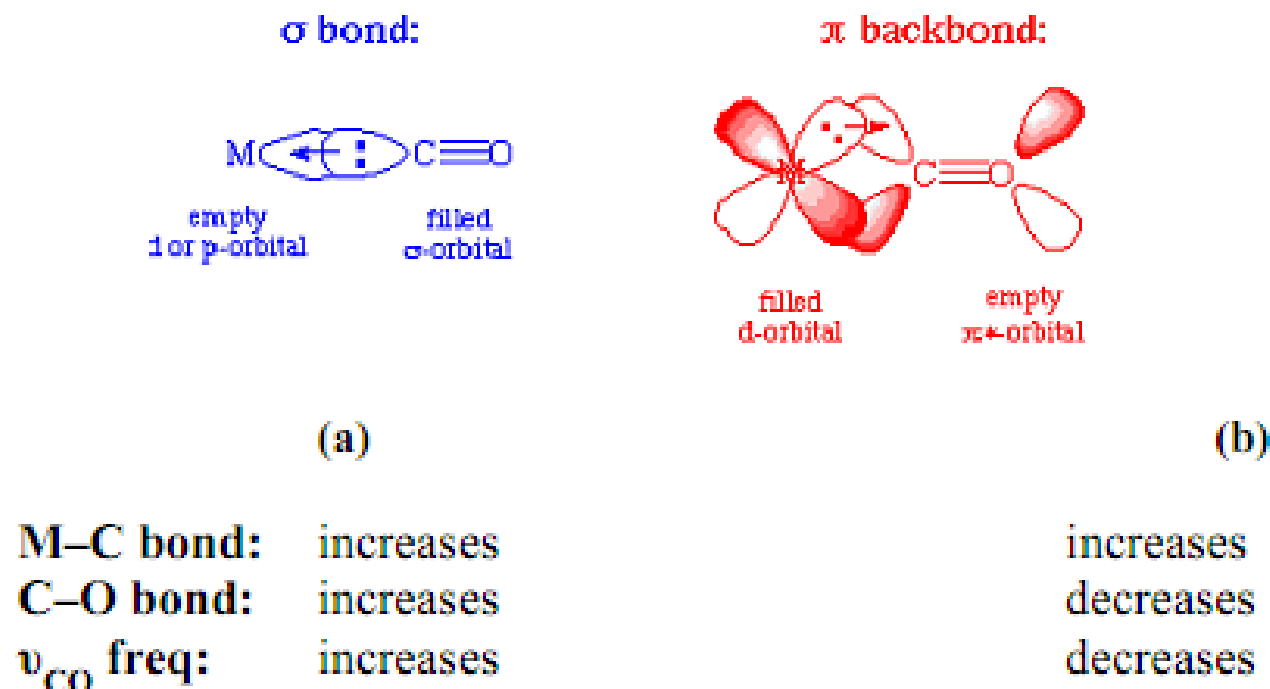


Figure: Molecular orbital diagram of CO showing vacant  $\pi^*_{2p}$  orbitals

Lone electron pairs are donated to vacant  $d$  orbitals of the transition metals in the low valent oxidation states which are incapable of retaining the charge density in their low oxidation states. The charge density received by the transition metal through sigma bonds is released back to vacant  $\pi^*$ - orbitals of the ligands as shown in figure below. This is called Pi bonding or back donation. The two components of this bonding are synergistic, the more sigma donation by the carbonyl (or other sigma-donors on the metal center), the stronger the pi-back bonding interaction.



**Figure:** Formation of  $\sigma$  and Pi bond in M–CO

Hence a metal–carbon  $\sigma$ –bond is formed by the overlap of filled  $sp$  hybrid orbital carbon and vacant hybrid orbital of metal; that is  $sp^3$  of Ni in  $\text{Ni}(\text{CO})_4$ ,  $dsp^3$  of Fe in  $\text{Fe}(\text{CO})_5$  and  $dsp^3$  of Fe in  $\text{Fe}(\text{CO})_5$ .  $\pi$ –bonds are formed simultaneously by overlapping of filled d-orbitals of metals with the  $\pi^*$ - orbitals of the CO groups. The dipole moment of M–C bond is found to be as low as 0.5D which suggests that no net charge density is shifted from CO to metal atom which explains the zero valent state of the metal atom. The formation of  $\sigma$ –bond is shown figure: x (a) while formation of  $\pi$ –bond is depicted in figure: x (b). The types of bonding in metal carbonyls is represented in simplified form in **figure x**.



The bond length and infrared spectral studies indicates favour the multiple nature of bonds and indicates that the structures (a) and (b) exists in equilibrium and actual structure of carbonyls is a hybrid of both structures. It can be concluded from the above discussion that back donation of electron density from metal to CO increases the M–C bond strength and decreases the bond length whereas  $\text{C} \equiv \text{O}$  bond length increases and bond becomes weaker.

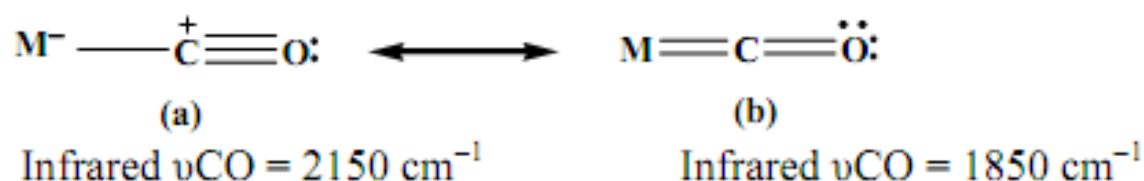
Infrared refers to that part of the electromagnetic spectrum between the visible and microwave regions ( $4000\text{--}400\text{ cm}^{-1}$ ). IR spectra are sometimes reported in  $\mu\text{m}$ , although another unit,  $\bar{\nu}$  (nu bar or *wave number*), is currently preferred. The energy of molecular vibrations corresponds to infrared part of the electromagnetic spectrum. The molecules possess characteristic vibration frequencies depending on the functional groups. The infrared spectra of metal carbonyls are useful in predicting the nature of bonding and molecular structures. The stretching frequencies of free CO and coordinated CO are different and their comparison enables us to draw certain conclusion about the structure of metal carbonyls.

In the IR, typical stretching frequencies are:

- Uncoordinated or "free" CO:  $2143\text{ cm}^{-1}$
- Terminal M-CO:  $2125\text{ to }1850\text{ cm}^{-1}$
- Doubly bridging ( $\mu_2$ ):  $1850\text{ to }1750\text{ cm}^{-1}$
- Triply bridging ( $\mu_3$ ):  $1675\text{ to }1600\text{ cm}^{-1}$
- Semi bridging: somewhere between terminal and  $\mu_2$ .



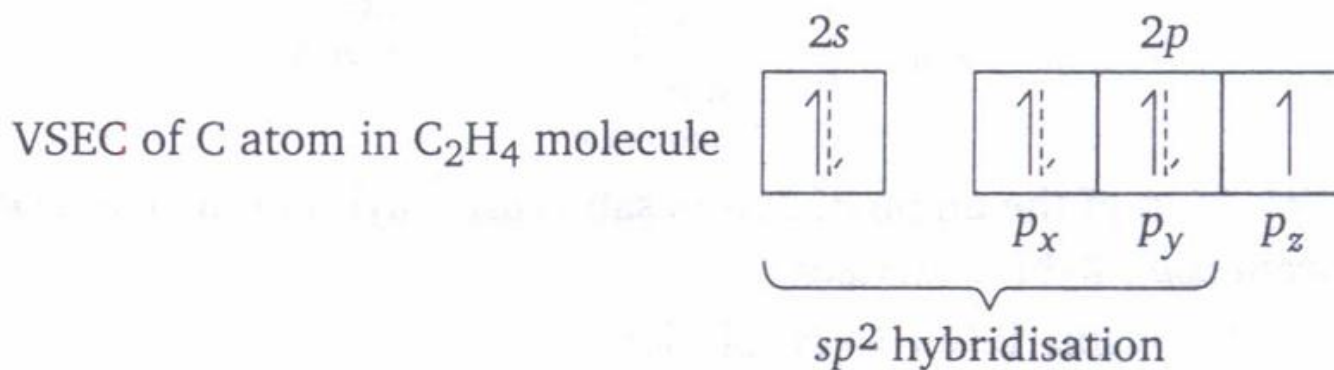
The free carbon monoxide has triple bond between C and O ( $C\equiv O$ ) and C to O bond order is three. In metal carbonyls, C to O bond order decreases due to charge density drift from d-orbitals of the metal to  $\pi^*$ -orbitals of CO and consequently infrared stretching frequency of CO ( $\nu_{CO}$  freq) also decreases to about  $2000\text{cm}^{-1}$ . The infrared stretching frequencies of CO ( $\nu_{CO}$  freq) in metal carbonyls depend on the extent of back of donation electron density from metal to CO, greater the back donation of electrons from metal to CO, greater will be decrease in  $\nu_{CO}$  frequency and *vice versa* and the structure (b) in figure below will be prominent. When the electrons of metal in d-orbitals are completely drifted to  $\pi^*$ -orbitals of CO, this will correspond to structure (b) and infrared  $\nu_{CO}$  frequency will be observed at about  $1850\text{ cm}^{-1}$ . If no charge density is drifted, there will be only structure (a)  $\nu_{CO}$  frequency will be observed at about  $2150\text{ cm}^{-1}$ .



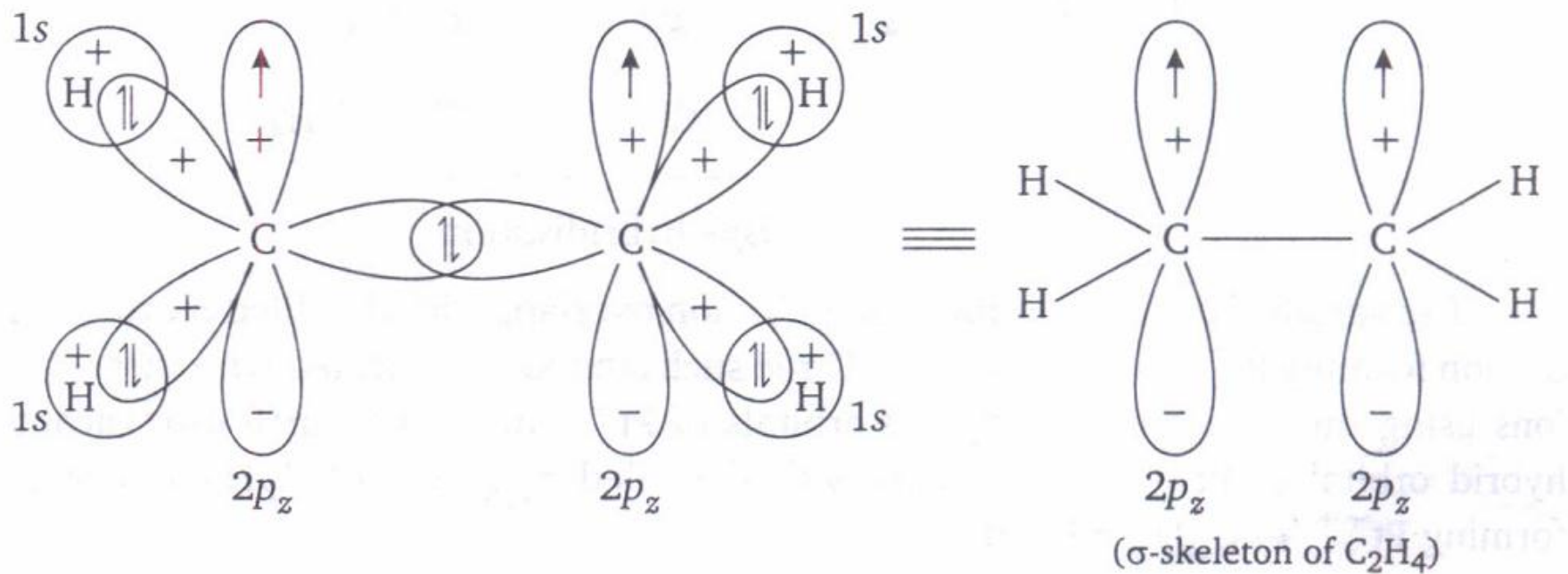
# Metal-Carbon $\pi$ - bonds

The nature of bonding between  $\text{Pt}^{++}$  ion and  $\text{C}_2\text{H}_4$  molecules in the anion of Zeise's salt can be explained nicely on the basis of Dewar-Chatt-Duncanson model developed in 1951–1953.

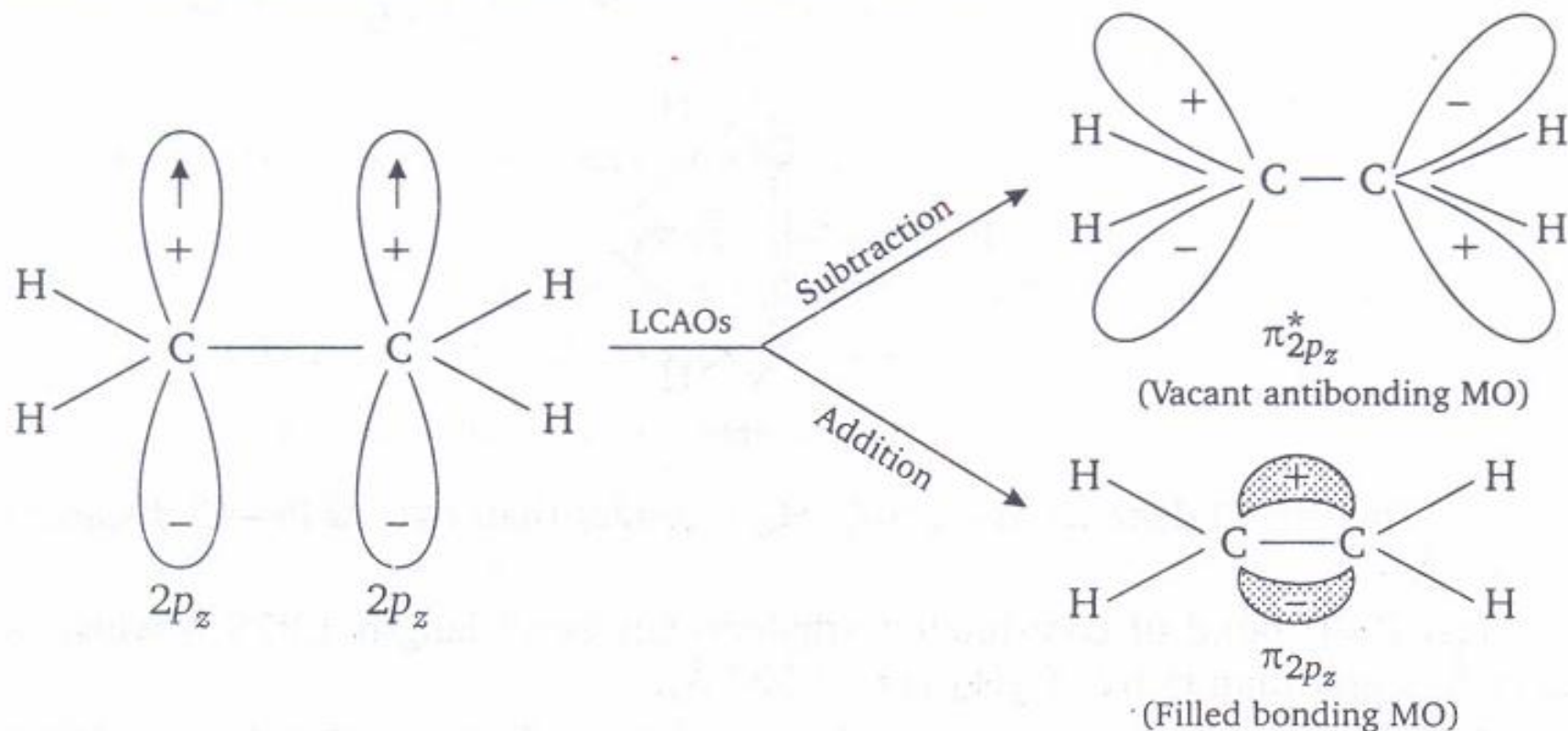
First of all, let us consider the nature of bonding in  $\text{C}_2\text{H}_4$  (ethylene) molecule. Each carbon atom of ethylene molecule ( $\text{CH}_2=\text{CH}_2$ ) is  $sp^2$  hybridised.

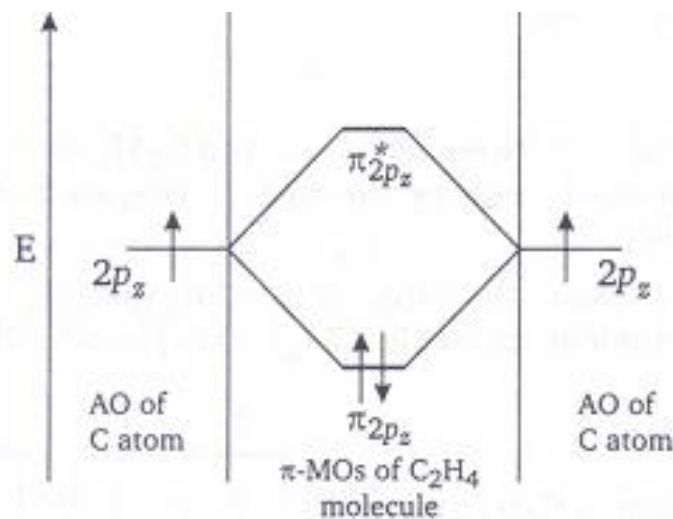


Each carbon atom forms three  $\sigma$  bonds—one with other carbon atom and two with H atoms using its three singly occupied  $sp^2$  hybrid orbitals as follows :



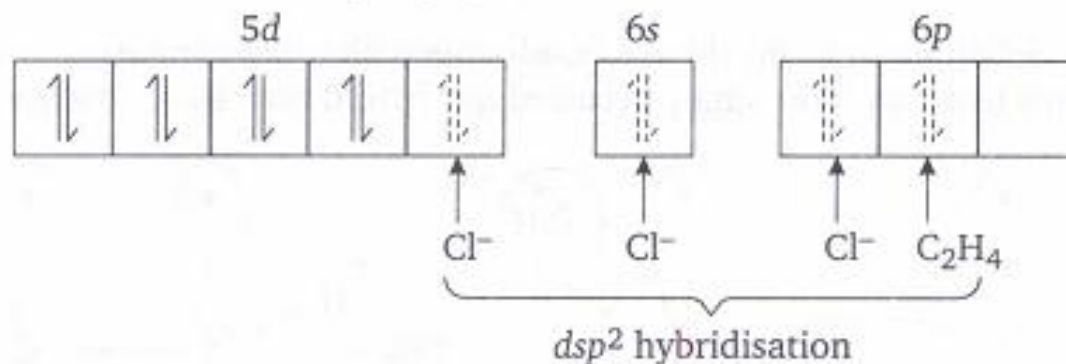
One singly occupied  $2p_z$  AO is left unused on each carbon atom  $\perp$  to the plane of  $C_2H_4$  molecule. These two parallel singly occupied  $2p_z$  AOs take part in the linear combination producing two  $\pi$ -MOs as follows :



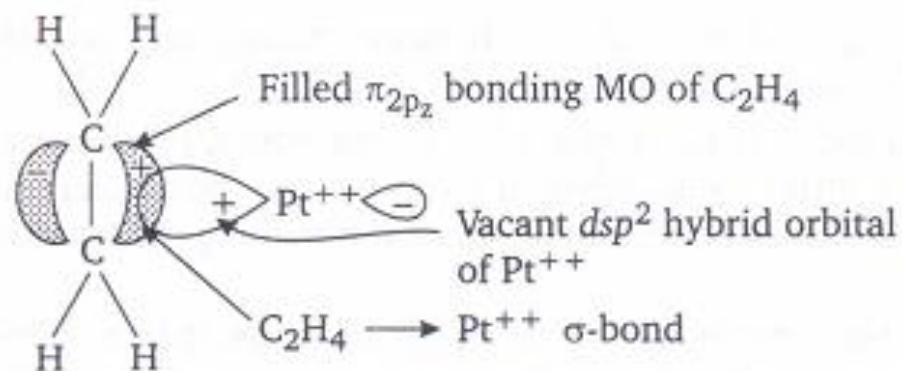


The  $\text{Pt}^{++}$  ion of the anion of Zeise's salt is  $dsp^2$  hybridised. Thus,  $\text{Pt}^{++}$  ion has four vacant  $dsp^2$  hybrid orbitals.

VSEC of  $\text{Pt}^{++}$  ion  $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^\ominus$  ion

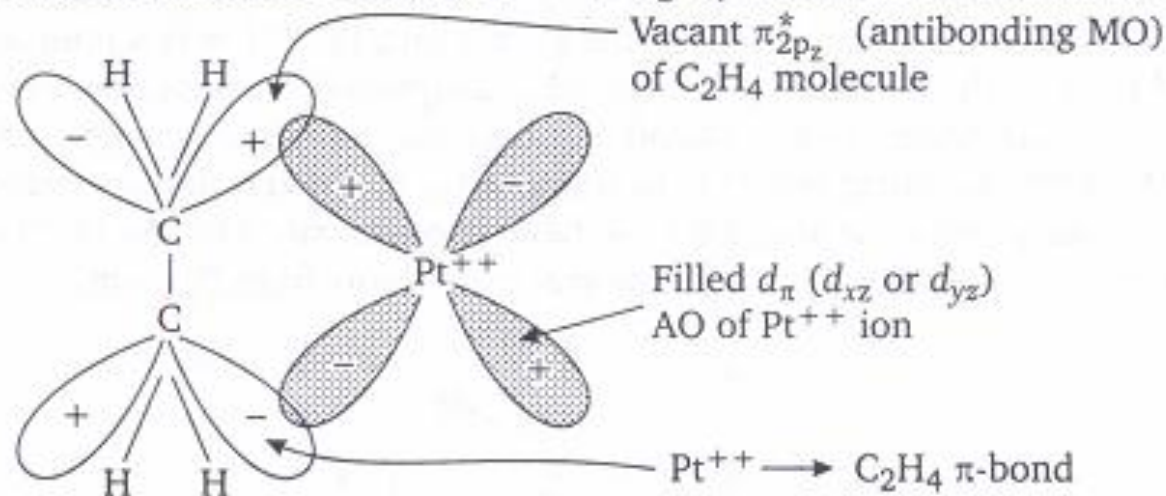


The vacant  $dsp^2$  hybrid orbital of  $\text{Pt}^{++}$  ion overlaps with the filled  $\sigma$ -orbital of  $\text{Cl}^-$  ion forming  $\text{Pt}^{++} \leftarrow \text{Cl}^-$   $\sigma$ -bond. Three such  $\sigma$  bonds are formed with three  $\text{Cl}^-$  ions using three vacant  $dsp^2$  hybrid orbitals of  $\text{Pt}^{++}$  ion. The fourth  $dsp^2$  vacant hybrid orbital of  $\text{Pt}^{++}$  ion overlaps with the filled  $\pi_{2p_z}$  MO of  $\text{C}_2\text{H}_4$  molecule forming  $\text{Pt}^{++} \leftarrow \text{C}_2\text{H}_4$   $\sigma$ -bond as follows :



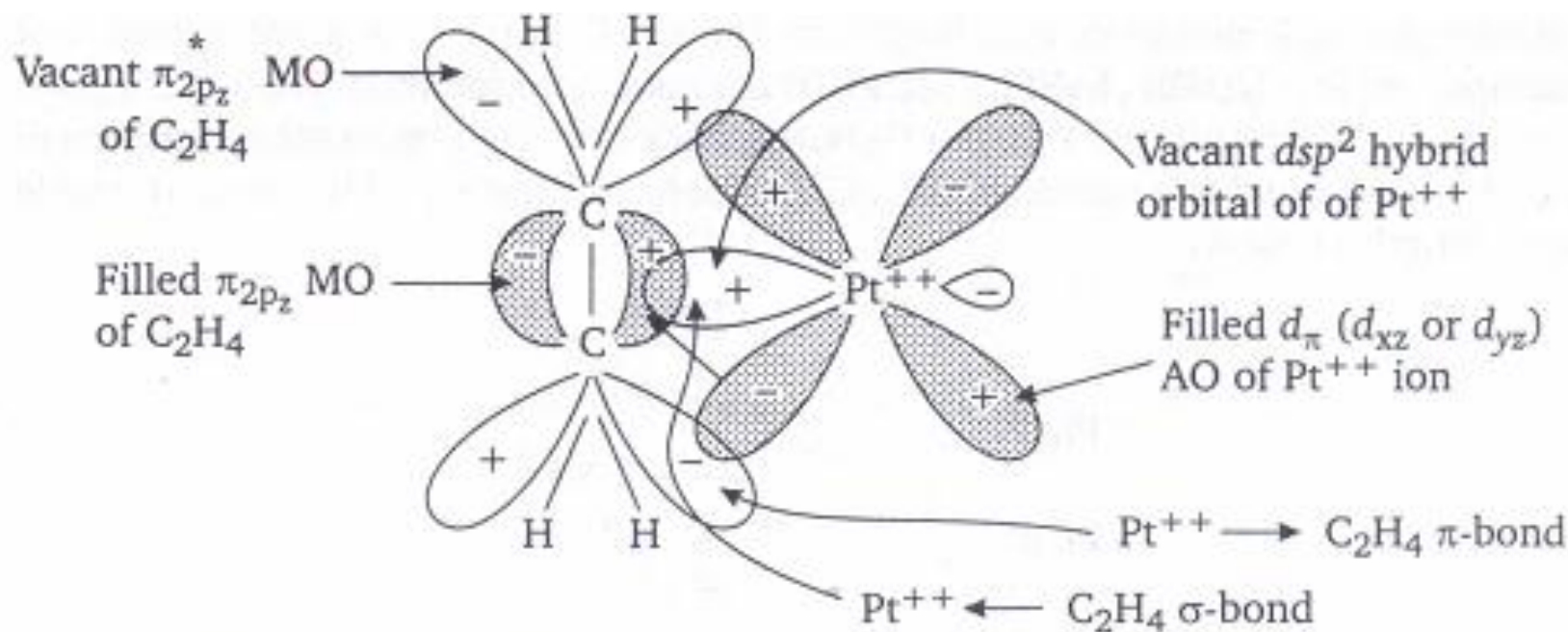
( $\sigma$ -Donation from the filled  $\pi_{2p_z}$  MO of ethylene into the vacant  $dsp^2$  hybrid orbital of  $Pt^{++}$  ion).

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



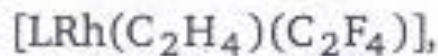
( $\pi$ -Back-donation from a filled  $d$  AO of  $Pt^{++}$  ion into the vacant  $\pi_{2p_z}^*$  MO of ethylene)

The  $Pt^{++} \leftarrow C_2H_4$   $\sigma$ -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



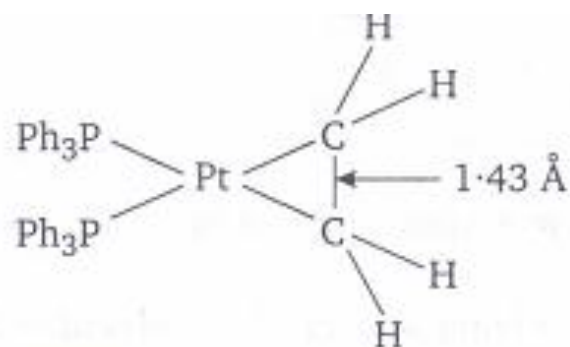
where L = acetylacetonato or Cp (Cyclopentadienyl)

the tetrafluoro ethylene molecule bonds more strongly and at a shorter distance ( $\text{Rh}-\text{C}=2.01 \text{ \AA}$ ) than does unsubstituted  $\text{C}_2\text{H}_4$  ( $\text{Rh}-\text{C}=2.17 \text{ \AA}$ ).

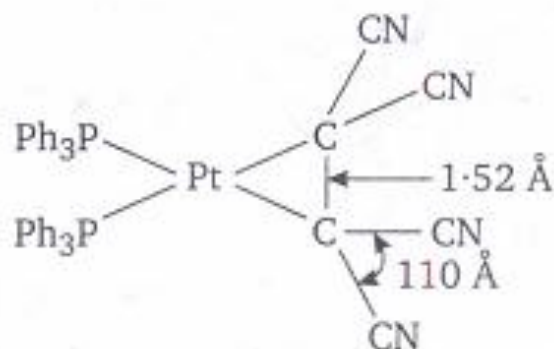
$\text{C}_2\text{F}_4$  is a poorer  $\sigma$ -donor but a better  $\pi$ -acceptor than  $\text{C}_2\text{H}_4$  on account of highly electronegative fluorine substituents. It indicates that the  $\pi$ -accepting ability of the alkene ligand is the most important factor in determining the bond-lengths in these compounds.

The  $\text{C}=\text{C}$  bond of the alkene lengthens on bonding to transition metal. The metal  $\leftarrow$  alkene  $\sigma$ -bond depletes the  $\text{C}=\text{C}$   $\pi$ -bond by partial transfer of these  $\pi$ -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  $\pi_{2pz}^*$  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,  $\text{Pt}^{++}$  ion is a poor  $\pi$ -donor (due to dipositive charge) and  $\text{C}_2\text{H}_4$  is a poor  $\pi$ -acceptor (due to less electronegative H atoms) and, therefore, the  $\text{C}-\text{C}$  bond of coordinated ethylene is lengthened only slightly (by  $0.038 \text{ \AA}$ ). 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  $\pi$ -donor and, therefore, the  $\text{C}-\text{C}$  bond becomes much longer ( $1.43 \text{ \AA}$ ) and H atoms are bent considerably out of the plane and away from Pt atom.



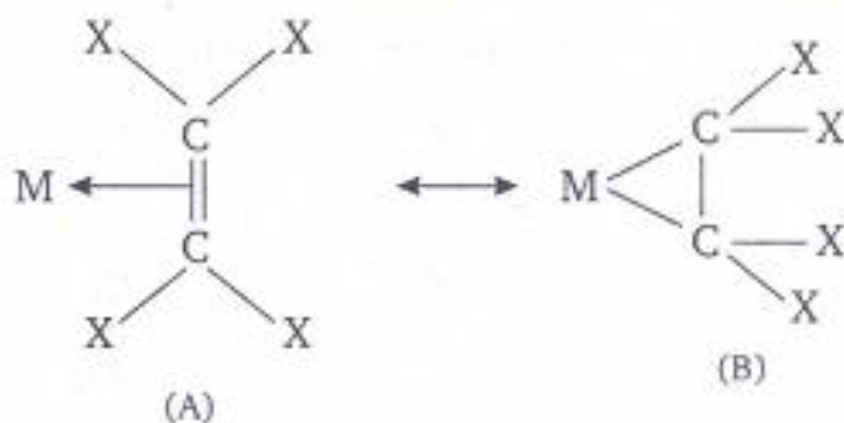


The presence of electron-withdrawing group on the  $\text{C}=\text{C}$  bond also encourages back donation and lengthens the  $\text{C}-\text{C}$  bond to a great extent. For example, in  $[\text{Pt}\{\text{C}_2(\text{CN})_4\}(\text{PPh}_3)_2]$ ,  $\text{Pt}(0)$  is a good  $\pi$ -donor and  $\text{C}_2(\text{CN})_4$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



At the same time,  $2\text{P}$  and  $2\text{C}$  that are bonded to  $\text{Pt}$  are almost coplanar.

Thus in the extreme cases where both  $\text{C}_2\text{X}_4 \rightarrow \text{M}$   $\sigma$ -bond and  $\text{C}_2\text{X}_4 \leftarrow \text{M}$   $\pi$ -bond have an order of one, the bonding can be represented by a simple valence bond structure (B) involving only two  $\sigma$ -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).



(A) represents alkene  $\rightarrow$  metal  $\sigma$ -bond only and (B) represents the extreme of complete back-bonding and mixing of  $\sigma$  and  $\pi$  orbitals to form two  $\sigma$ -bonds between metal and olefin. This view-point is useful to explain the following structural variables :

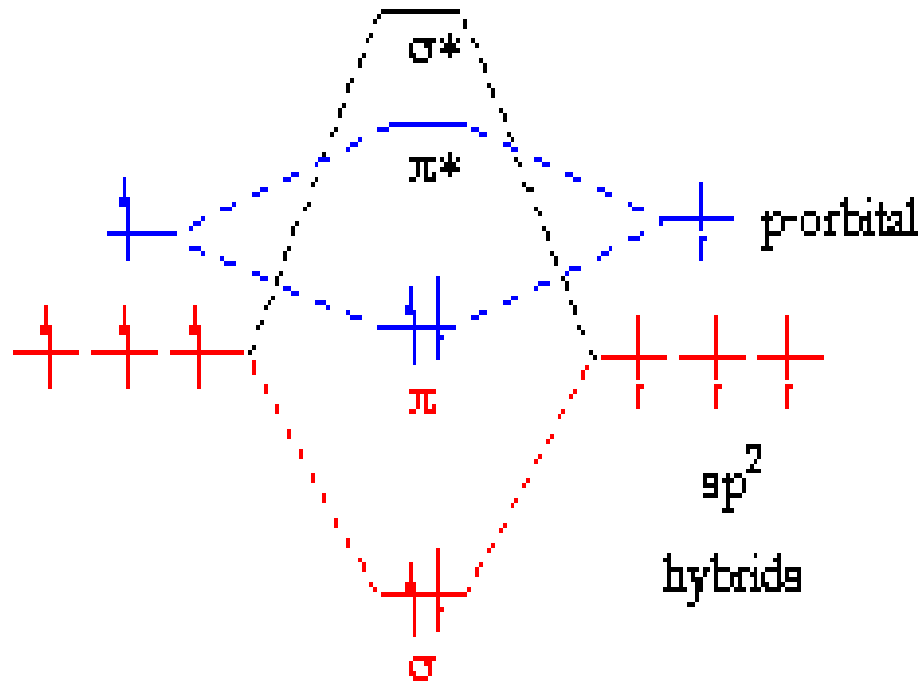
- (a) The increase in C—C bond-length
- (b) The bending of the substituents (X) away from the metal as back-bonding becomes more important. These two effects operate together as the electronegativity of X increases :

$$\Delta\beta = 2.09 \times \Delta l$$

where,  $\Delta\beta$  = Bending of substituents away from the metal atom.

$\Delta l$  = lengthening of C—C bond in pm.

# Metal-Carbon $\pi$ - bonds



MO diagram of ethene molecules