

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

Nature of metal-carbon bonds: Compounds with Metal-Carbon single bonds; Compounds with Metal-Carbon π - 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 π 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

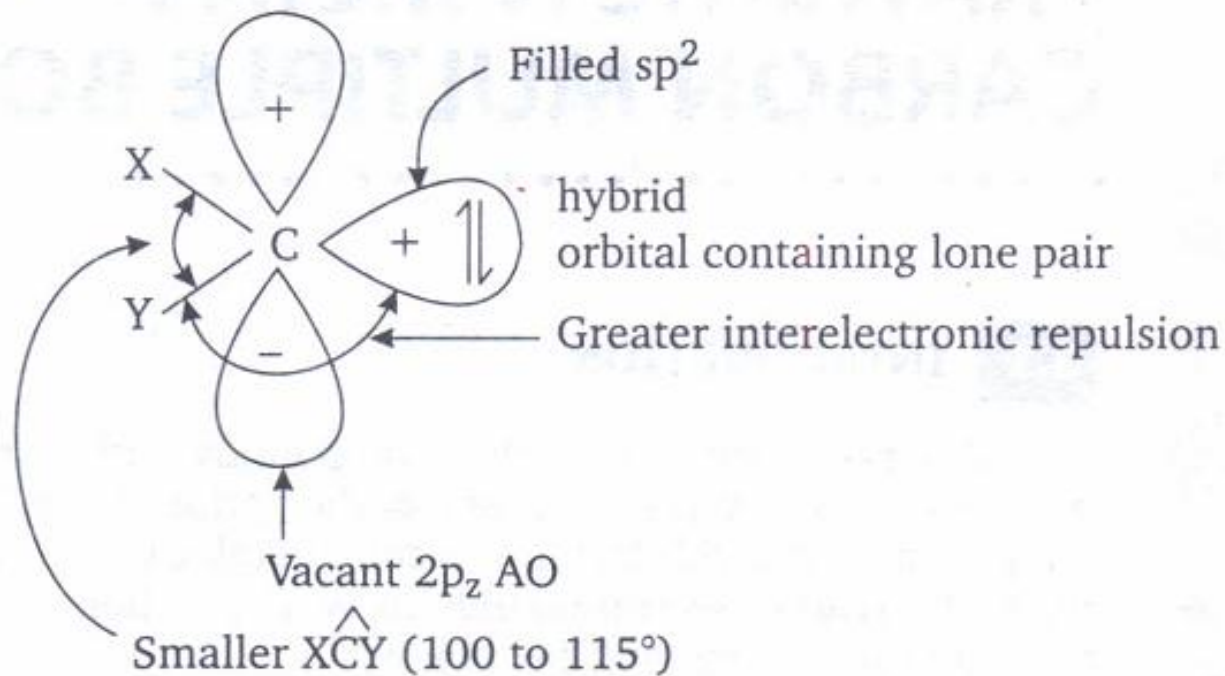
1. Huheey, J.E., Keiter, E.A. and Keiter, R.L. "Inorganic Chemistry: Principles of Structure and Reactivity", 7th Ed., Harper and Row, New York, (2010).
2. Garry L., Miessler, D. and Tarr, A. "Inorganic Chemistry" 3rd Edition, Pearson Education, Inc. NY (2004).

Metal-Carbon π - bonds (Metal- Carbon double bond)

The complex compounds in which a metal atom is bonded to carbon atom by a double ($M=C$) bond are called alkylidene complexes.

The carbene ligands have divalent neutral carbon atom with two unshared electrons distributed between two non-bonded orbitals. There are two types of carbenes.

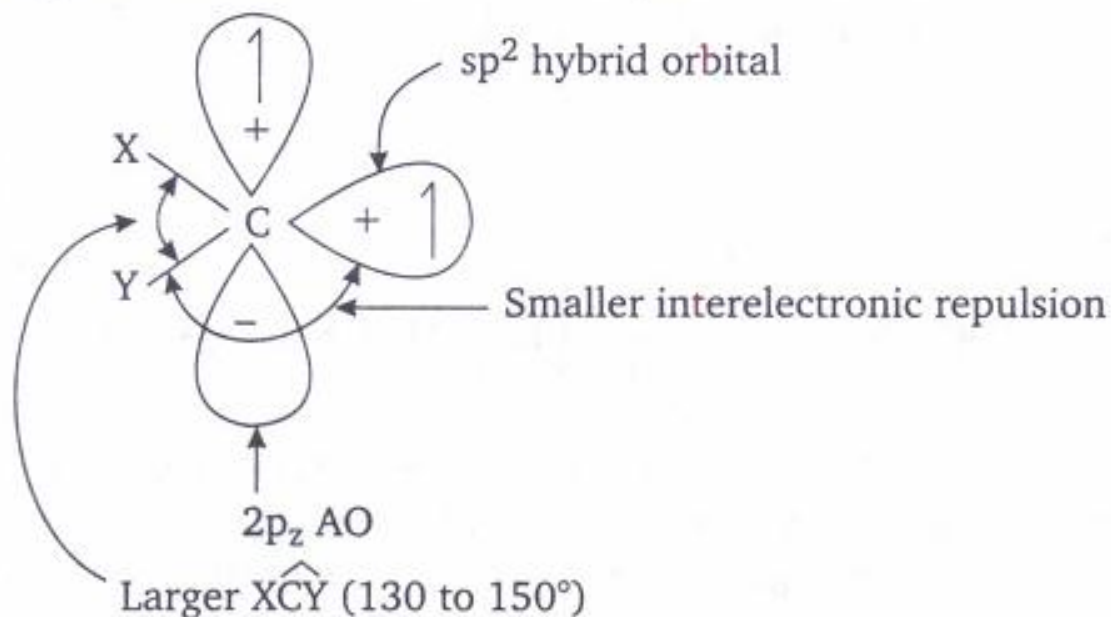
(a) Singlet Carbene : It has no unpaired electrons. It has a lone pair of electrons in sp^2 hybrid orbital.



Resultant spin-angular momentum quantum number,

$$\begin{array}{l|l}
 S = \Sigma m_s & \text{Spin-multiplicity} = 2S + 1 \\
 = +\frac{1}{2} - \frac{1}{2} = 0 & = 2 \times 0 + 1 = 1
 \end{array}$$

(b) Triplet Carbene : It has two unpaired electrons.



Resultant spin-angular momentum quantum number,

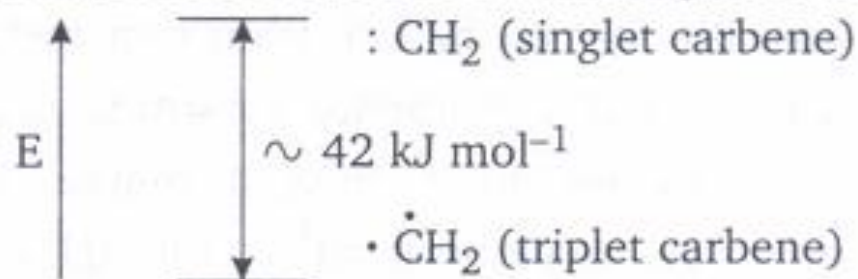
$$S = \sum m_s = \frac{1}{2} + \frac{1}{2} = 1$$

Spin-multiplicity, $2S + 1 = 2 \times 1 + 1 = 3$

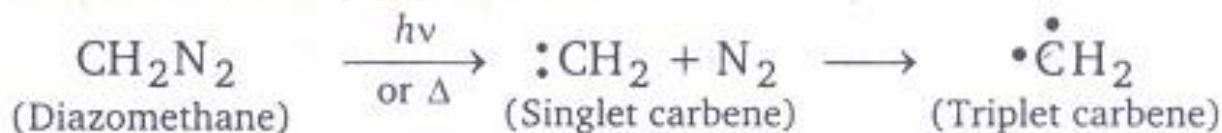
The carbon atom is sp^2 hybridised in both singlet and triplet carbenes. In the singlet carbene, the XCY bond angle is expected to be 120° . But is generally in the range 100 to 115° . This is due to stronger lone pair-bond pair repulsion than bond pair-bond pair repulsion.

Singlet carbenes :	: CH ₂	: CCl ₂	: CBr ₂
Bond angle :	103°	100°	114°

In the triplet carbene, there are two unpaired electrons—one in sp^2 hybrid orbital and another is $2p_z$ AO. The single unpaired electron causes weaker inter-electronic repulsion than pair of electrons. This is why is $\angle X\overset{\cdot}{C}Y$ bond angle in triplet carbene is larger (130 to 150°). For example, the HCH bond angle in triplet methylene ($\cdot\text{CH}_2$) is 136°. The esr spectral studies and various other evidences suggest that the triplet carbene is more stable than singlet carbene by $\sim 42 \text{ kJ mol}^{-1}$.

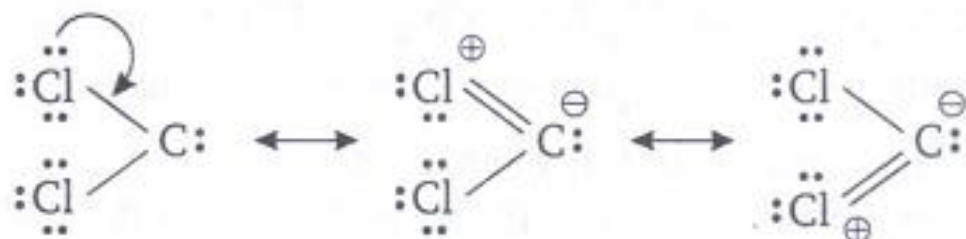


This is due to the fact that some energy is to be supplied to pair up two electrons in a single orbital. It is called pairing energy. It increases the energy and decreases the stability of singlet carbene.

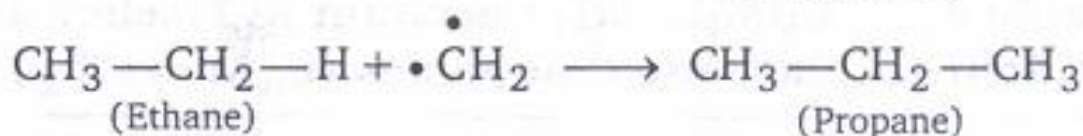
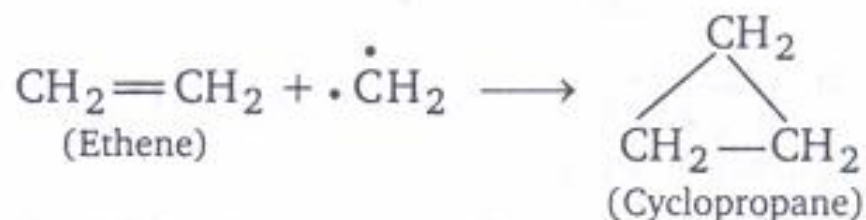


Carbene formed is initially in singlet state which transforms into more stable triplet state rapidly. However, the ground state for dichlorocarbene has been found to be the singlet state.

This is due to the fact that the singlet state of dichlorocarbene is stabilized by Cl atoms through π -donation into the empty $2p_z$ AO of carbene carbon.



Carbenes are rarely stable in the free state. For example, $\cdot\dot{\text{C}}\text{H}_2$ (methylene or carbene) is a transient species. It reacts rapidly with a wide variety of substances including alkanes.



Carbenes are both kinetically and thermodynamically very less stable. This is why carbenes have very strong ability to be coordinated to metal atoms because the dissociation of transition metal-carbene complexes is not favourable energetically.

Metal-Carbon π - bonds (Metal- Carbon triple bond)

The organometallic compounds in which a transition metal atom is bonded to a carbon atom by a triple bond ($M\equiv C$) are called transition metal-alkylidyne complexes.

The alkylidyne complexes were prepared first of all by Fischer in 1973. Thereafter, a number of alkylidyne complexes have been synthesised and characterised.

Structure and Bonding

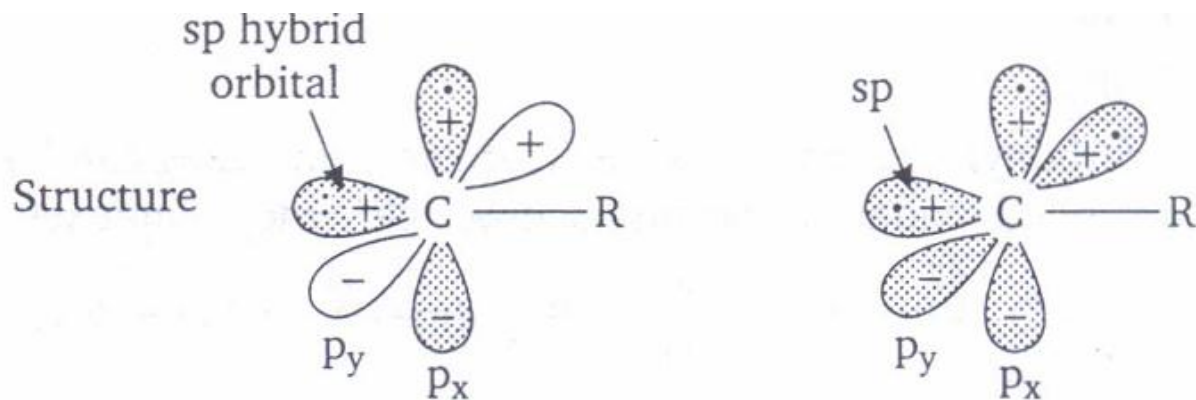
The structures of transition metal carbyne complexes have been determined by various means *viz.*, X-diffraction studies, IR and NMR spectral studies, etc. These studies suggest that the $M\equiv C-C$ linkage of carbyne complexes is linear due to sp hybridisation on middle carbon atom. The $M-C-C$ bond angle is $\sim 180^\circ$. However, the $M-C-C$ bond angle deviates from 180° in some cases, *e.g.*, $trans-I(OC)_4W\equiv C-Ph$ has an angle of 162° . The $M\equiv C$ bond is very short.

For first transition series, $M\equiv C$ bond length = 1.65 – 1.75 Å

For second and third transition series, $M\equiv C$ bond length = 1.75 – 1.90 Å

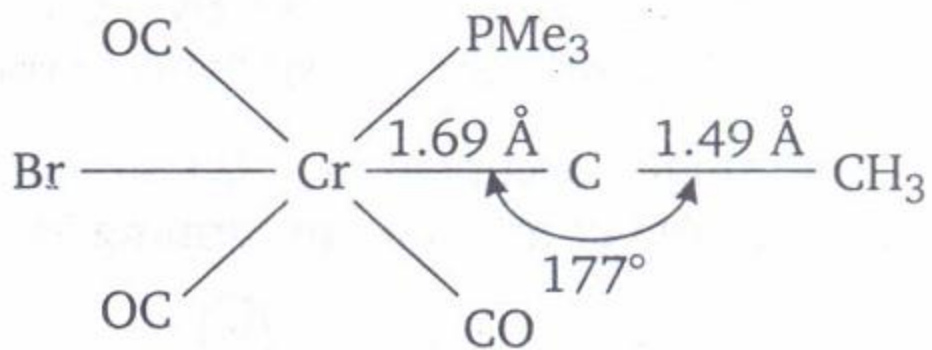
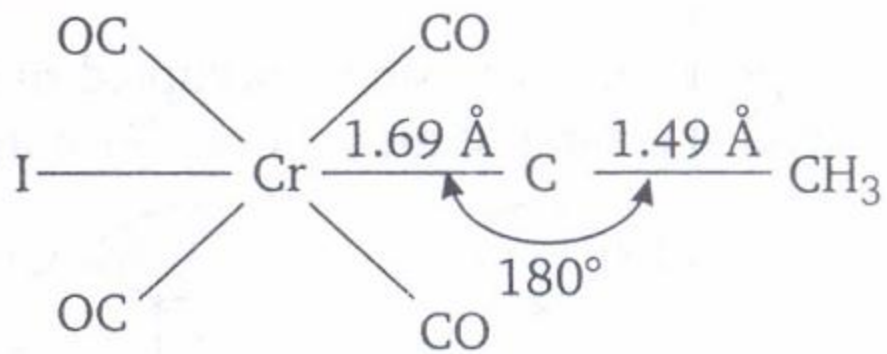
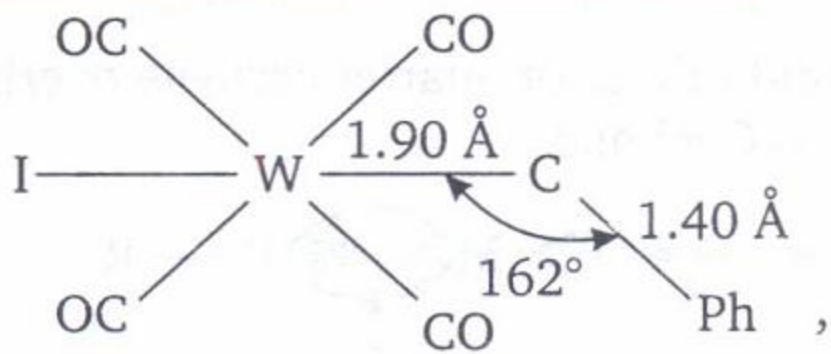
The force constants for $M\equiv C$ bonds are comparable to those for $M\equiv N$ bonds.

Like carbenes, the carbyne ligands are of two types:

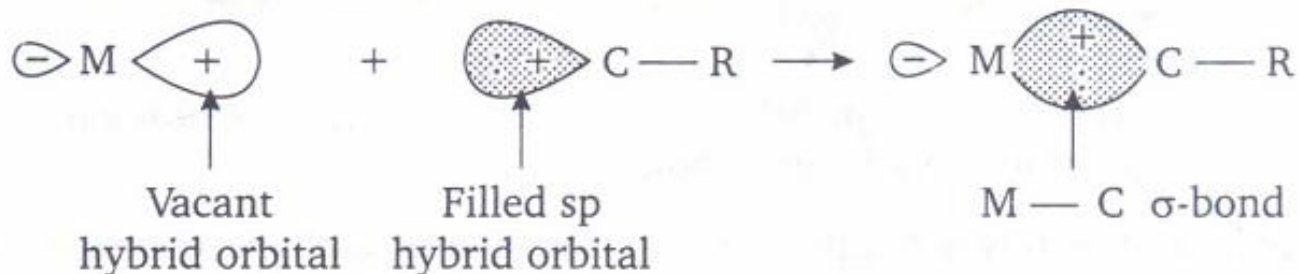


Name	Doublet carbyne	Quartet carbyne
Resultant spin quantum number	$S = \frac{1}{2}$	$S = \frac{3}{2}$
Spin-multiplicity	$2S + 1 = 2$	$2S + 1 = 4$
No. of unpaired electrons	1	3

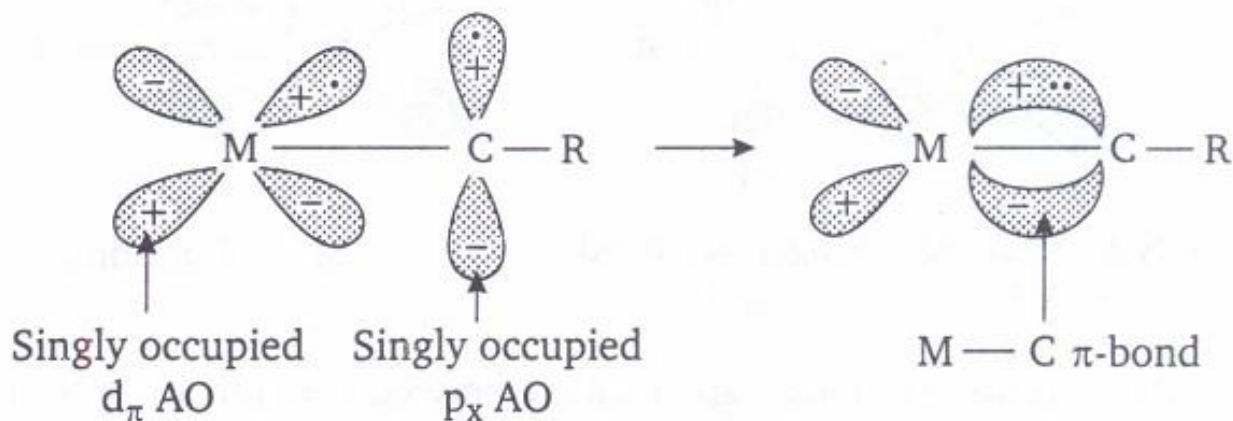
The carbon atom of both the types of carbynes are sp hybridised. The doublet carbyne has a lone pair of electrons in sp hybrid orbital and an unpaired electron in one of the two remaining p AOs. Thus, one p AO remains vacant. On the other hand, the carbon atom of the quartet carbyne has three unpaired electrons—one each in sp hybrid orbital and p_x and p_y atomic orbitals.



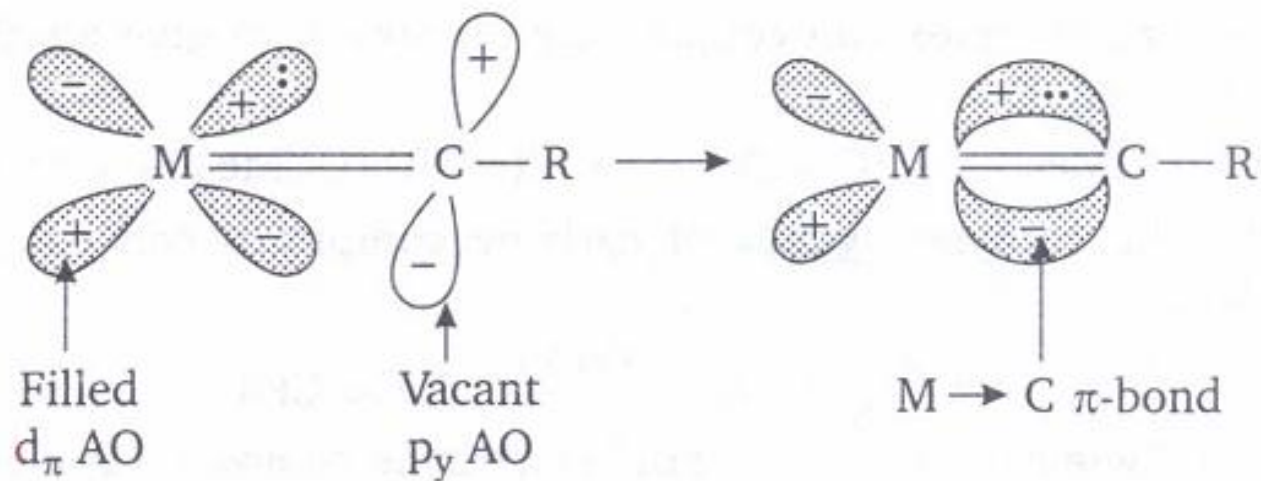
The doublet carbyne ligand of Fischer carbyne complexes acts as $3e$ donor ligand, *i. e.*, LX type ligand. The filled sp hybrid orbital of doublet carbyne overlaps with vacant hybrid orbital of metal atom forming $M \leftarrow C$ σ bond.



The singly occupied p_x AO of doublet carbyne carbon atom overlaps with singly occupied d_π AO of metal forming $M-C$ π bond. It is called $d_\pi - p_\pi$ bond.

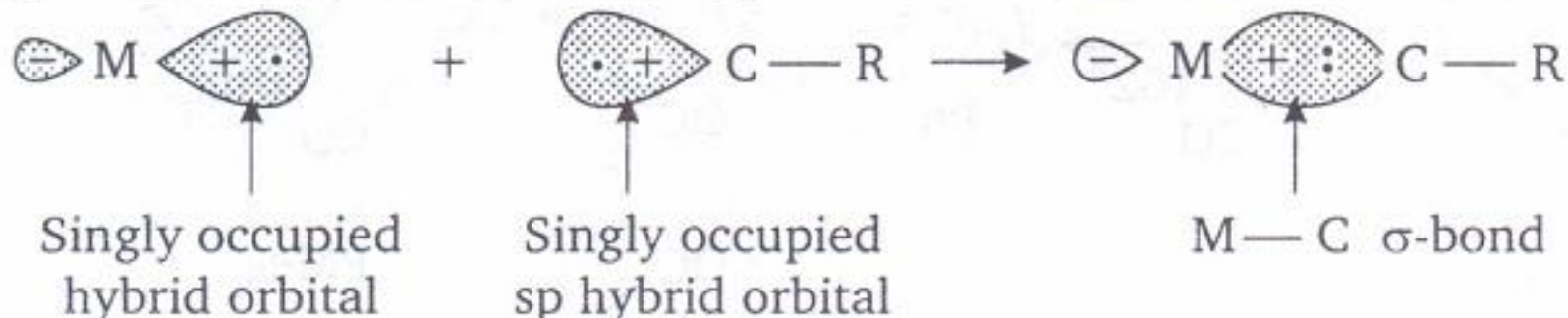


The vacant p_y AO of doublet carbyne carbon atom overlaps with filled d_π AO of metal atom forming $M \rightarrow C$ π bond. It is called $d_\pi - p_\pi$ bond or back bond.

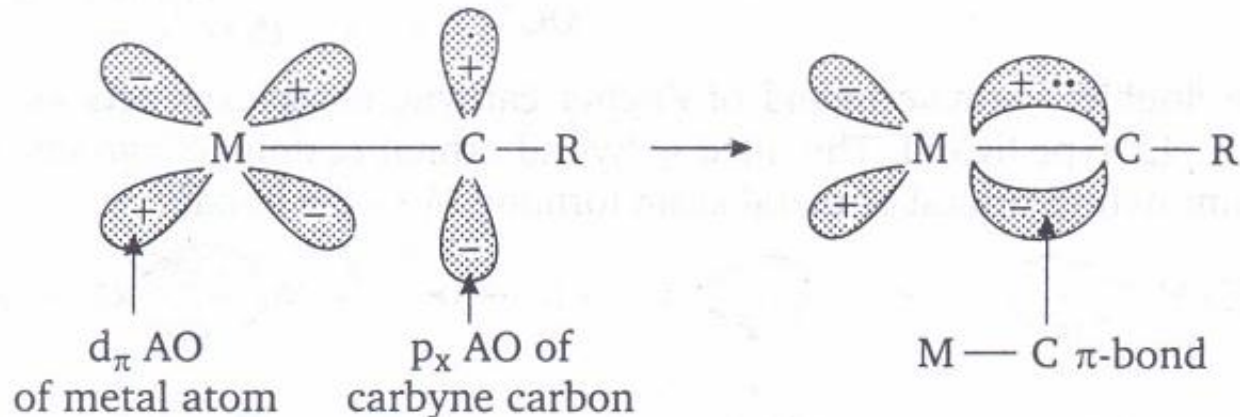


Thus, three covalent bonds are formed between metal atom and carbene carbon atom in Fischer carbene complexes.

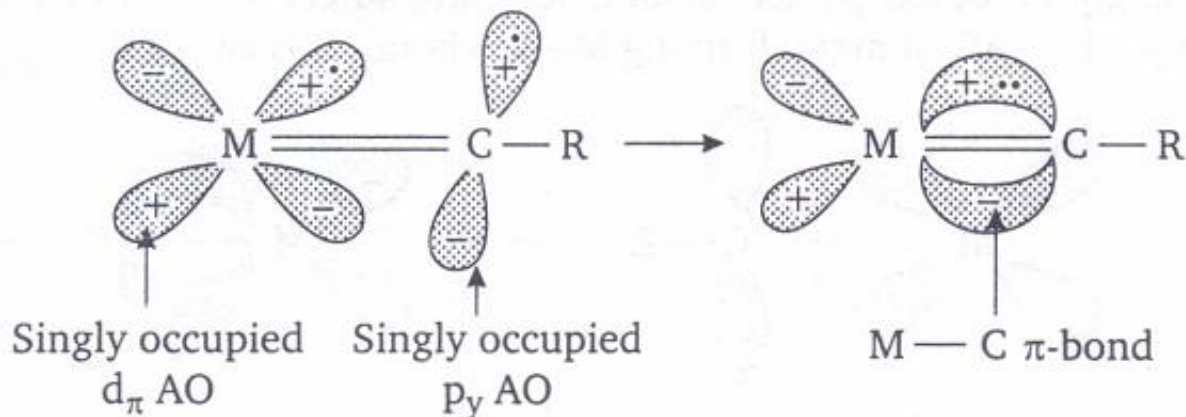
In the Schrock carbene complexes, quartet carbenes are involved which have three unpaired electrons. The quartet carbene also acts as a $3e$ donor ligand. But it is a X_3 type ligand. The singly occupied sp hybrid orbital of quartet carbene overlaps with hybrid orbital of metal atom forming $M-C$ σ bond.



The singly occupied p_x AO of quartet carbyne overlaps with the singly occupied d_{π} AO of metal atom forming M—C $d_{\pi} - p_{\pi}$ bond.



Similarly, the singly occupied p_y AO of quartet carbyne overlaps with the singly occupied d_{π} AO of metal atom forming another M—C $d_{\pi} - p_{\pi}$ bond.



Thus, three covalent bonds are formed between metal atom and carbyne carbon atom in Schrock carbyne complexes.