Chapter 2

Metal Carbonyls and Clusters

Metal Carbonyls :

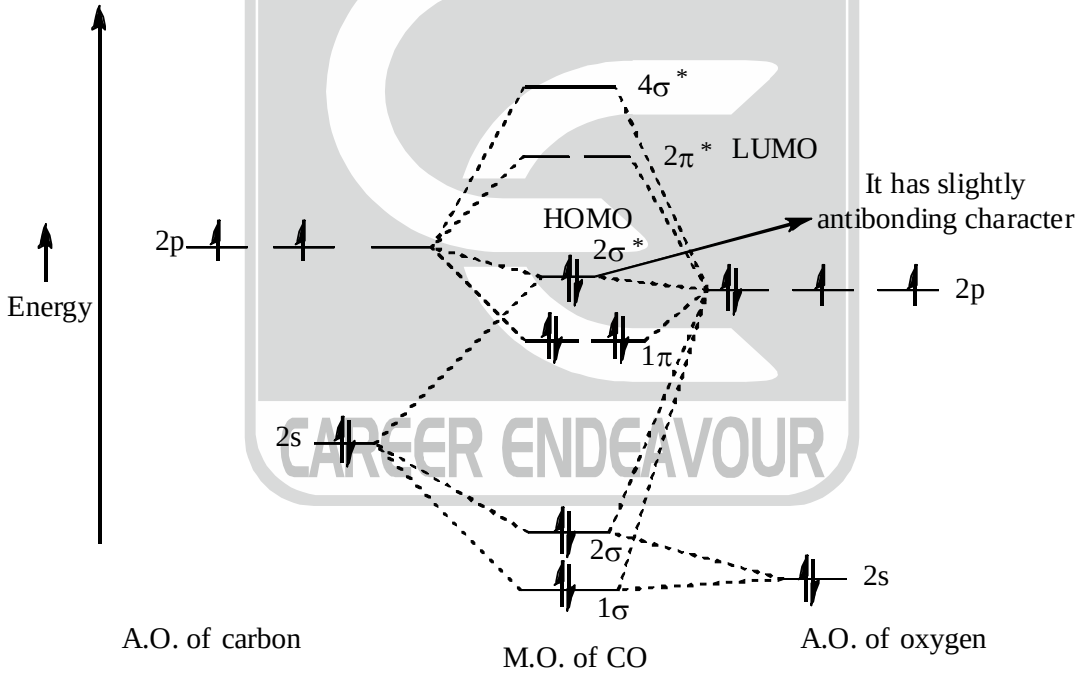
Metal carbonyls are those compounds which contain carbonyl (CO) as a ligand bonded to metal. Some properties of metal carbonyls are

(1) This CO group is a weak σ donar and strong π acceptor.

$$M \xleftarrow[\sigma \text{ bond}]{} CO$$

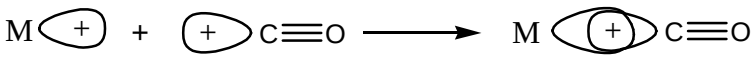
(2) Metal should be in low oxidation state CO stablises low oxidation state

MOLECULAR ORBITAL DIAGRAM OF CO

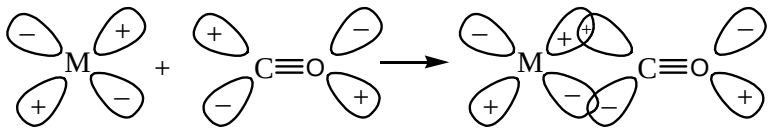


BONDING IN METAL CARBONYLS :

(1) σ- Bond :



(2) π- Back Bonding : π back bonding utilises in filled d orbital of metal & empty π^* orbital of CO



π-bond

This type of bonding where both π and σ bond help (reinforce) each other is called synergistic bonding during σ-bond formation CO donates electron density to the metal. As a result of which –ve charge on the metal increases. Metal can remove this excess electron density by π back bonding from a filled d-orbital of metal to empty π^* orbital of CO.

CLASSIFICATION OF METAL CARBONYLS:

1. On the basis of ligand present in metal carbonyls they can be classified as

M.C.

Homoleptic carbonyl complex Heteroleptic carbonyl complex

Homoleptic : Complex containing only carbonyl as a ligand)

e.g. $Rh_6(CO)_{16}$, $Mn_2(CO)_{10}$, $W(CO)_6$ etc.

Heteroleptic : $M + CO's$ + other ligands.

e.g. $Fe(CO)_3(PPh_3)_2$, $Ni(CO)_3(PPh_3)$, $W(CO)_3(PPh_3)$ etc.

2. On the basis of metal present in metal carbonyls, they can be classified as

M.C.

HNCC LNCC

$M \geq 4$ $M \leq 4$

(High nuclearity carbonyl complex (Low nuclearity carbonyl complex

M = 4 is a border line case.

SPECTRAL PROPERTY OF METAL CARBONYLS:

I.R. SPECTROSCOPY OF METAL CARBONYLS:

$$v = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}\ cm^{-1}$$

Where k is the stiffness (strength) of the bond, whereas μ is reduced mass and $\mu = \frac{m_1 m_2}{m_1 + m_2}$

It is clear from above equation that $v \propto \sqrt{k}$ and $v \propto \frac{1}{\sqrt{\mu}}$

$v_{C\equiv 0}\,(\text{free})\ 2143\ cm^{-1}$

$v_{(CO)^+} = 2184\ cm^{-1}$

$v_{C-O}\,(\text{terminal}) = 2120 - 1850\ cm^{-1}$

$v_{C-O}\,(\text{bridging}) = 1850 - 1750\ cm^{-1}$

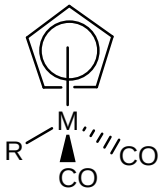
$\mu^3\ v_{C-O} = 1730 - 1620\ cm^{-1}$

i.e. free CO stretching frequency comes at 2143 cm^{-1}, when metal is bonded to CO, π- back bonding from metal occurs to carbonyl, increasing M – C bond order (increases from single to double) and decreasing CO bond order from triple to double). As a result of this the stretching frequency decreases.

Note : v_{C-C} decreasing order $-C\equiv C- > \diagup C=C\diagdown > -C-C-$

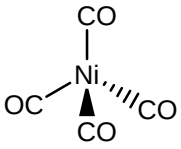
IR BANDS FOR METAL CARBONYLS:

If a molecules has C_{2V} or C_s point group than the number of IR bands = number of CO's present in that molecules.

e.g. 

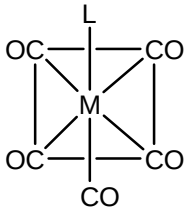
$\sigma_v \Rightarrow C_s$

So, two-IR bands



due to high symmetry

only one-IR bands

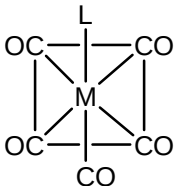
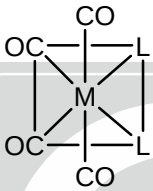
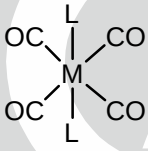
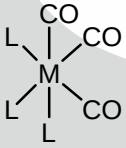
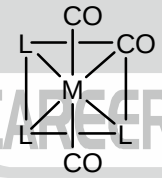
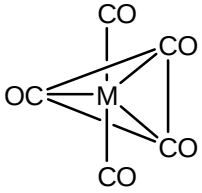
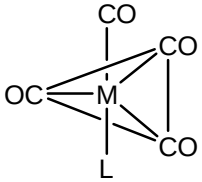
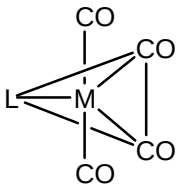


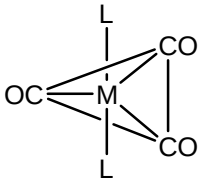
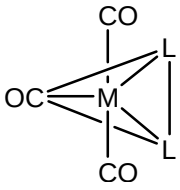
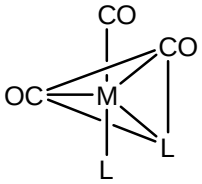
due to high symmetry

Only one-IR band for all CO

M = Cr, Mo, W

NUMBER OF IR BAND OF METAL CARBONYLS:

Complex	Isomer	Structure	Point group	Number of IR bands
$M(CO)_5L$			C_{4V}	3
$M(CO)_4L_2$	cis		C_{2V}	4
$M(CO)_4L_2$	trans		D_{4h}	1
$M(CO)_3L_3$	facial		C_{3V}	2
$M(CO)_3L_3$	meridonial		C_{2V}	3
$M(CO)_5$			D_{3h}	2
$M(CO)_4L$	Axial		C_{3V}	3
$M(CO)_4L$	Equatorial		C_{2V}	4

$M(CO)_3L_2$	Axial		D_{3h}	1
$M(CO)_3L_2$	Equatorial		C_{2V}	3
$M(CO)_3L_2$	one equatorial and one axial		Cs	3

FACTOR AFFECTING ν_{C-O} :

(1) Charge of the metal:

Greater the –ve charge on the metal stronger will be the back π – bonding , hence lower will be the ν_{C-O} structure due to weak CO bond and vice versa.

(2) Presence of other Ligand on metal:

(a) σ- donor : Presence of σ bonded ligand on a metal like NH_3, Pyridine. Increase electron density on the metal, so π-back bonding increases and ν_{C-O} decreases.

(b) π– acceptor Ligands: π-acceptor ligands decreases the electron density on metal. So, π-back bonding is decreases and ν_{C-O} increases.

e.g. **(i)** ν_{C-O} in decreasing order?

(1) $\left[Mn(CO)_6\right]^+$ (2) CO (3) $H_3O^+ \leftarrow CO$ (4) $\left[v(CO)_6\right]^-$

Soln: 3 > 2 > 1 > 4

(ii) Arrange the following in the decreasing order of back donation.

$Cr(CO)_6$, $\left[Ti(CO)_6\right]^{2-}$, $\left[Mn(CO)_6\right]^+$, $\left[Ir(CO)_6\right]^{3+}$ and $\left[V(CO)_6\right]^-$

Soln. As we know that if an electron density increases on the metal the back, donation (back π – bonding) will also increase so, the order will be

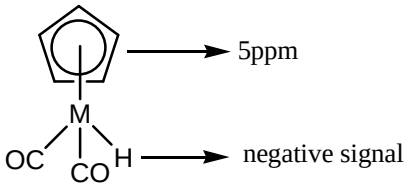
$$\left[Ir(CO)_6\right]^{3+} > \left[Mn(CO)_6\right]^+ > \left[Cr(CO)_6\right] > \left[V(CO)_6\right]^- > \left[Ti(CO)_6\right]^{2-}$$

^{1}H NMR SPECTROSCOPY OF METAL CARBONYL :

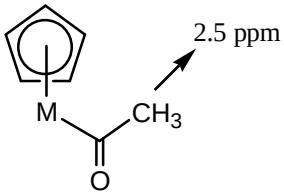
In ^{1}H NMR if there is any signal in negative chemical shift that clearly indicates that there is a metal hydride band.

$\left[HFe(CO)_4\right]^- = -9$ ppm

$\left[HMn(CO)_5\right]^- = H - Mn$ –7.5 ppm

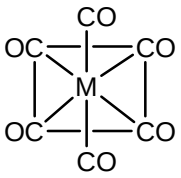


two ^{1}HNMR signals



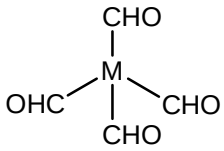
^{13}C NMR SPECTROSCOPY OF METAL CARBONYL :

(i)



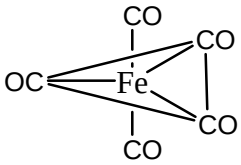
one signal in ^{13}C NMR due to high symmetrical structure

(ii)



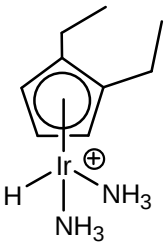
one signal in ^{13}C NMR due to high symmetrical structure

(iii)



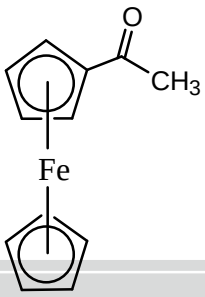
one signal in ^{13}C NMR due to Barey Pseudo rotation

(iv)



five ^{13}C NMR signals

(v)



six ^{13}C NMR signal

Note : ^{13}C NMR spectrum of organometallic complex occur in region $(M-R)$ – 40 to 20 δppm

Example: The carbonyl resonance in ^{13}C NMR spectrum of $\left[\eta^5 CpRh(CO)\right]_3$, $\left[^{103}Rh, I=\frac{1}{2}100\%\right]$.

Shows a triplet at – 65ºC. Showing (due) to presence of –

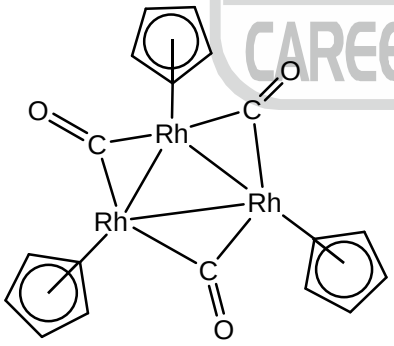
(a) terminal CO

(b) μ^2 – CO

(c) μ^3 – CO

(d) μ^5 – Cp

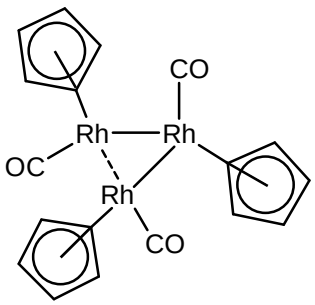
Soln. **First :**



CO bind to two Rh. So, shows a triplet

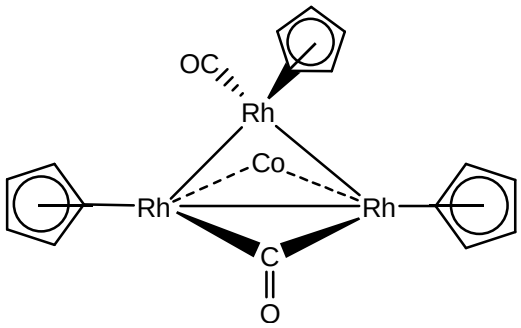
$2\times\frac{1}{2}\times 2+1=3$

Second :



Both structures are possible but the question conditions are fulfill by first one.

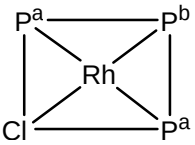
Third :



than all carbons of CO would be in different environment and we will get 3 signal.

Hence, first structure predict the correct data. So, correct option is (b)

^{31}P NMR SPECTROSCOPY OF ORGANOMETALLIC COMPOUND :

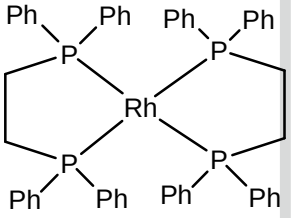
$Rh(PPh_3)_3Cl$ 

where, P = PPh_3

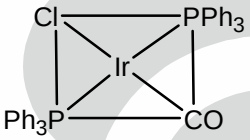
Then two types of P present. So, we will get two signals in ^{31}P NMR.

$2P^a \rightarrow$ doublet of doublet

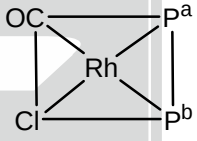
$2P^b \rightarrow$ triplet of doublet



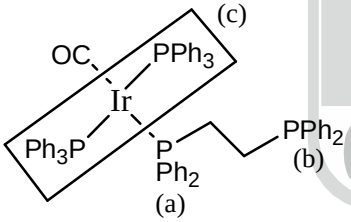
one signal
doublet of 4-p due to Rh coupling



one signal of two phosphorus (same environment)



$P^a \rightarrow$ doublet of doublet
$P^b \rightarrow$ doublet of doublet



3 signals are obtained

$P^a \rightarrow$ singlet

$P^b \rightarrow$ singlet

$P^c \rightarrow$ singlet

PREPARATION OF METAL CARBONYL:

(1) Direct Reaction :

$$Ni + 4\,CO \xrightarrow[25^oC]{1\ bar} Ni(CO)_4$$

$$Fe + 5CO \xrightarrow[150^oC]{100\ bar} Fe(CO)_5$$

(2) Reductive Carbonylation : This uses as reducing agent to convert a metal from high oxidation to low oxidation state along with CO.

(a) Using a Reducing Agent :

$$MCl_3 + \underset{\text{reducing agent}}{Al} + n\,CO \longrightarrow M(CO)_n + AlCl_3$$

$$CrCl_3 + Al + 6\,CO \longrightarrow Cr(CO)_6 + AlCl_3$$

$$MoCl_5 + 5\,Na + 6\,CO \longrightarrow Mo(CO)_6 + 5\,NaCl$$

(b) By reducing CO itself : Using CO as a reducing agent

$$CO \rightarrow CO_2$$

$$OsO_4 + CO \xrightarrow[125°C/75\ atm]{MeOH} Os_3(CO)_{12} + 4CO_2$$

(3) Using Photochemical / Thermal Reaction : Generally use for binuclear carbonyls :

$$Fe(CO)_5 \xrightarrow[AcOH]{h\nu} Fe_2(CO)_9 + CO$$

$$2CO_2(CO)_8 \xrightarrow{70°C} CO_4(CO)_{12} + 4CO$$

REACTIONS OF METAL CARBONYLS:

1. Associative Mechanism SN^2 :

$$LnM(CO) \xrightarrow[slow]{+Y} LnM\begin{matrix}CO\\ \diagup\\ \diagdown\\ Y\end{matrix} \xrightarrow[-CO]{fast} LnMY$$

Dissociative Mechanism SN^1:

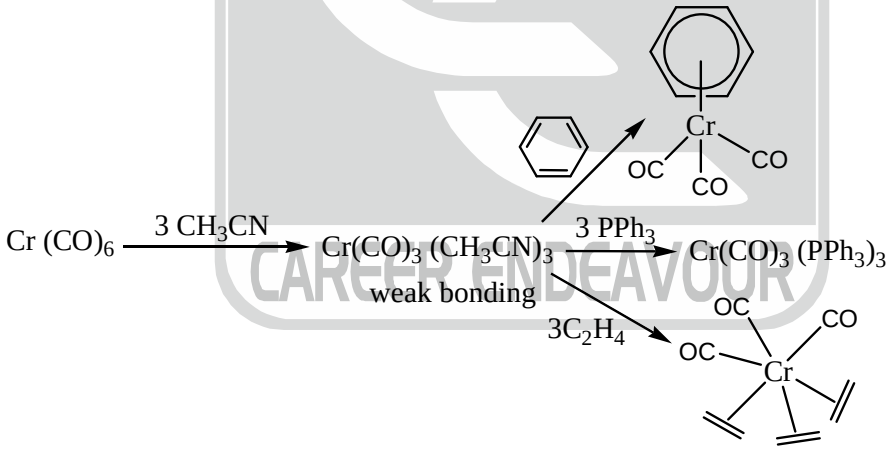
$$LnM-CO \underset{+CO,\ k_{-1}}{\overset{-CO,\ k_1}{\rightleftharpoons}} LnM \xrightarrow{+Y,\ k_2} LnM-Y$$

An 18 electron species undergo nucleophilic substitution by dissociative or SN^1 mechanism where as 16 or 17 electron species of carbonyl undergo associative mechanism .

$$\underset{18\ e^-}{Fe(CO)_5} \xrightarrow[\Delta]{:PPh_3} \underset{16e^-}{Fe(CO)_4} + CO \xrightarrow{:PPh_3} Fe(CO)_4PPh_3$$

$$\underset{17e^-}{V(CO)_6} \xrightarrow[slow]{:PPh_3} V(CO)x, PPh_3 \xrightarrow{-CO} V(CO)_5(PPh_3)$$

(2) Activation : Activate by some heating substance methyl cyanide :



(3) Carbonylate Anions: Negatively charged carbonyl :

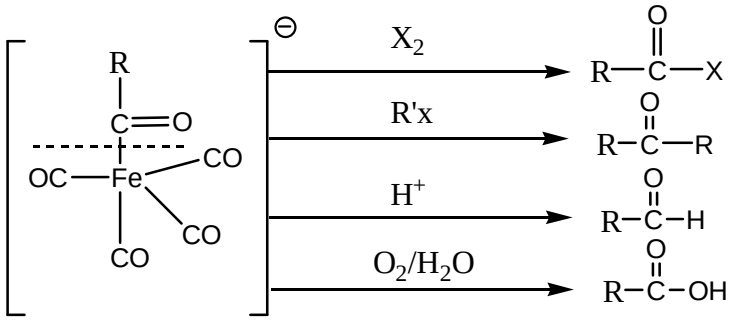
$$Mn_2(CO)_{10} \xrightarrow{2Na} 2\ Na[\ Mn(CO)_5]$$

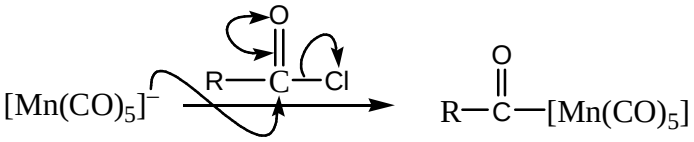
$$Co_2(CO)_8 \xrightarrow{2Na} 2Na\left[Co(CO)_4\right]$$

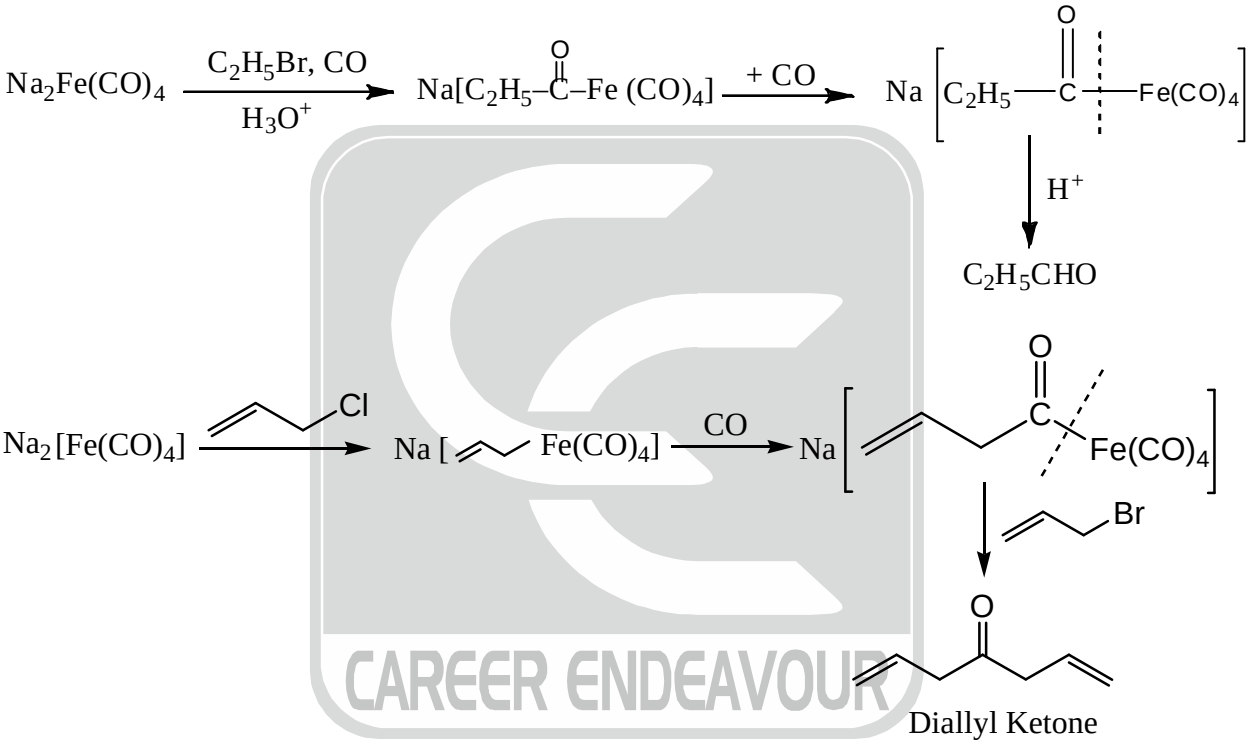
$$\underset{18e^-}{Fe_2(CO)_9} \xrightarrow{2Na} Na_2\ Fe(CO)_4$$

(4) Collmann Reagent: $Na_2\ [Fe(CO)_4]$

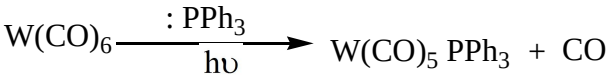
$$Na_2\ [Fe(CO)_4] \xrightarrow[Rx]{-Nax} [RFe(CO)_4]^{\ominus} \xrightarrow[CO]{insertion} \left[\begin{matrix}R\\ |\\ C=O\\ |\\ Fe(CO)_4\end{matrix}\right]^{\ominus}$$







(5) Photochemical Reaction : Used for monosubstitution :



(6) Using π- bonding Ligand :