M.Sc Chemistry
Inorganic Chemistry
Semester-II

Course Title: Chemistry of d and f block elements

Course Code: 201-B

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Inorganic Group III and IV

REFERENCE BOOKS:

1. Electronic Spectra of Transition Metal Complexes by D. Sutton

2. Introduction to Ligand Field Theory: Figgis

3. Concise Inorganic Chemistry by J. D. Lee

Metal Carbonyls

Purcell and Kotz Page 1026
Atkins Pg 532-536 (ENP)

Electron Neutrality Principle

- According to the **electro neutrality principle** given by Pauling, the atoms in a molecule share the electron pairs to the extent such that charge on each of the atom remains close to zero.
- The first attempt to bonding in transition metal complexes was made by Sidgwick who extended the octet theory of G.N. Lewis to coordination compounds. Ligands (lewis bases); metal ion (lewis acid)
- Stability was assumed to be attendant to a noble gas configuration for the metal.
- The sum of electrons on metal + electrons donated from ligands was called eeffective atomic number EAN.
- eg: 36 (Kr), 54 (Xe)

18 electron Rule

- When metal achieves an outershell configuration of ns^2 $(n-1)d^{10}np^6$, there wil be 18 electrons in the valence orbitals and a closed, stable configurtion.

- This rule of thumb, which is referred as the 18 electron rule has the advantage of being the same for all rows of periodic chart, eliminating the need to remmber different EAN for each noble gas.

- Metal carbonyls follow this rule, therefore it has a considerable usefulness as a tool for predicting formulas of stable compounds.

Metal Carbonyls (Synergic Bonding)

- Transition metals in low oxidation state form complex with neutral ligands eg: CO, PR3, alkenes.
- CO ⟶ **Metal Carbonyl Compounds**

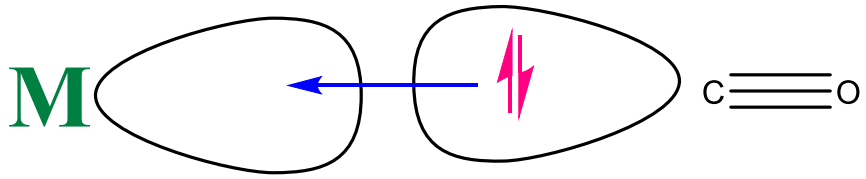
Π ACCEPTOR BONDING MODEL:

- **Metal Centre acts as a lewis acid. CO donates electrons to the metal**

(M ⟵ CO) Metal Centre σ-Bonding

(Metal lower oxidation State +1, -0, -1)

σ donation



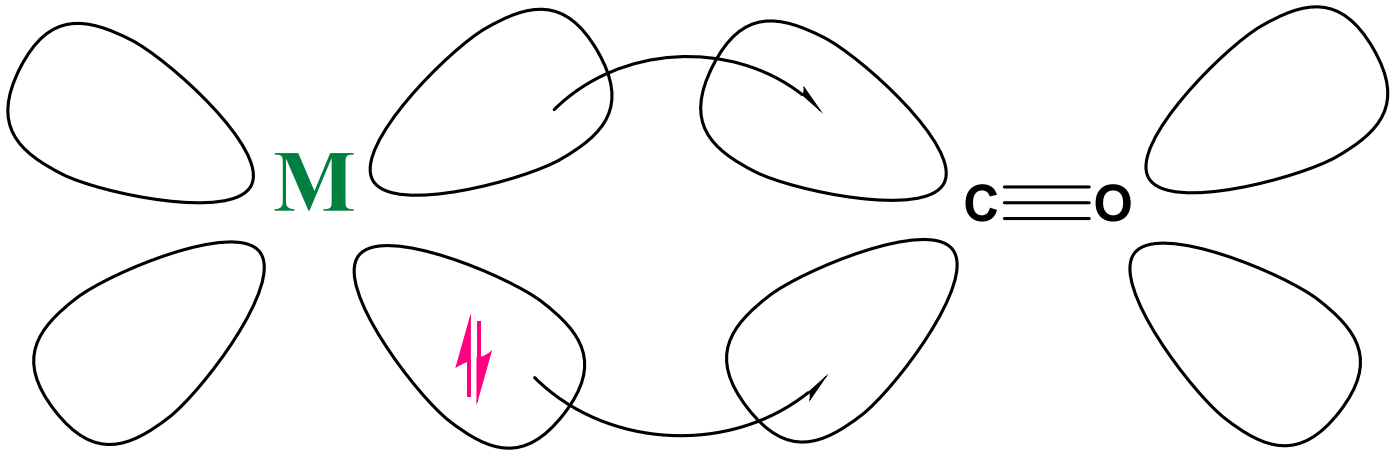
Empty dsp^2 hybrid orbital **∏ bonding orbital**

σ bond:

Empty dsp2 hybrid orbital ⟵ ∏ Filled Ligand

Transition metal having filled d orbital back donates electrons into empty antibonding molecular orbital of CO; Π acid complex.

Π bond: Filled d orbitals ⟶ Π* Ligand MO



Back donation of electrons from filled d orbitals of metal to empty antibonding orbitals of CO

SYNGERGIC BONDING: Energy released when σ bond is formed is reinforced for back bonding. σ donation leads to charge in metal centre which is reinforced back Π back donation.

SYNERGIC BONDING IN METAL CARBONYLS

As a result of synergic bonding, M-C bond strength increases, while **C≡O** bond strength decreases.

Metal Carbonyl	IR Stretching Frequency (cm-1)	Charge on complex
$[Mn(CO)_6]^+$	2090	+1
$[Ni(CO)_4]$	2060	0
$[Cr(CO)_6]$	2000	0
$[Co(CO)_4]^-$	1890	-1
$[Fe(CO)_4]^{2-}$	1790	-2

$CO > MCO > M_2CO > M_3CO$

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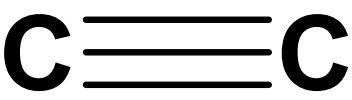
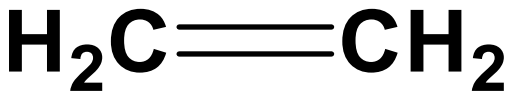
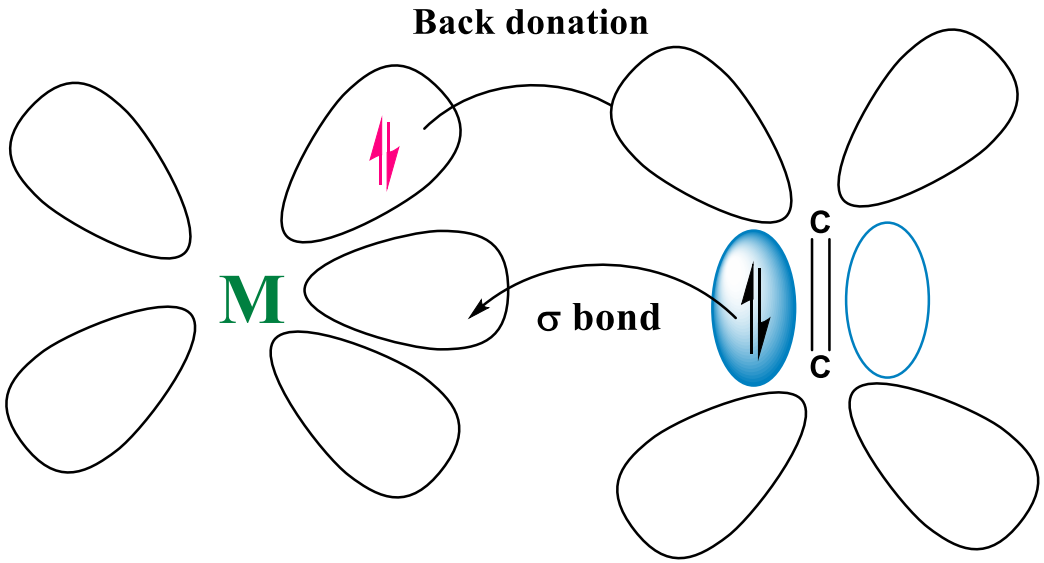


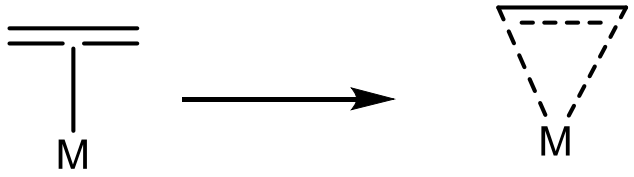
Alkyne



Alkene

Act as σ donor





3 centered bond

Dewar Chatt Duncansen Model