

# Pi-Acceptor Ligands

## Introduction

A characteristic feature of the d-block transition metal atoms is their ability to form complexes with a variety of neutral molecules (e.g. carbon monoxide, isocyanides, substituted phosphines, arsines, nitric oxide etc.) and with various molecules with delocalized  $\pi$ -orbitals such as pyridine, 1,10-phenanthroline etc. Very diverse type of complexes exist, ranging from binary molecular compounds, such as  $\text{Cr}(\text{CO})_6$  to complexes ions such as  $[\text{Fe}(\text{CN})_5\text{CO}]^{2-}$ ,  $[\text{Mo}(\text{CO})_5\text{I}]^-$  etc.

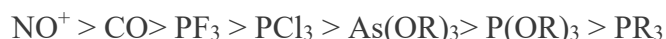
When we examine the enormous range of complexes that are known, it sometimes seems that if any metal can form any type of the complex. This is not necessarily the case, and there are some general trends that are followed. Complexes form as a result of the attraction of the metal ion for electron pairs on the ligands (electron pair donor or nucleophiles). *Ligands* are the charged or uncharged electron pair donor atoms or molecules which are bonded to the central metal atom or ions.  $\text{NH}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$  and  $\text{NO}$  are examples of uncharged or neutral ligands, while  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{O}^+$  etc. are charged ligands.

One of the most important consideration is what types of orbitals are available on the metal ion to accept electron pairs. If a metal ion has at least two empty d-orbitals, it is possible to form a set of  $d^2sp^3$  hybrid orbitals so that six pairs of electrons can be accommodated. A second important consideration in the formation of complexes is the charge to size ratios of the metal ion. Ions of high charge and small size (high charge density) have the greatest affinity for electron pairs and can generally accommodate the greater build-up of negative charge that results from the acceptance of electron pairs. As a general rule metal ions of high charge tend to form complexes in which the coordination numbers are higher, especially if they are larger ions from second and third transition series.

In majority of the complexes, the metal ions are in low positive, zero or even negative formal oxidation state. It is a characteristics of the ligands now under discussion that they can stabilize low oxidation states. This property is associated with the fact that these ligands have vacant n-orbitals in addition to lone pairs. These vacant orbitals accept electron density from filled metal orbitals to form a type of  $\pi$ -bonding that supplements the  $\sigma$ -bonding arising from lone-pair donation. High electron density on the metal ion can thus be delocalized onto the ligands. *The ability of the ligands to accept electron density into low-lying empty  $\pi$ -orbitals is called  $\pi$ -acidity or  $\pi$ -acceptor capacity.*

The term  $\pi$ -acidity is derived from the Lewis acid concept where a species capable of accepting lone pair of electrons is called an acid. The typical examples of  $\pi$ -acceptor ligands are  $\text{CO}$ ,  $\text{NO}$  isocyanides and certain unsaturated organic compounds.

Ligands which are isoelectronic with CO, such as  $\text{NO}^+$ ,  $\text{CN}^-$ , would be just as suitable for  $\pi$ -bonding, but the charge on the ligand has to be taken into consideration. Thus  $\text{NO}^+$  with a positive charge is a stronger  $\pi$ -acceptor than CO, while  $\text{CN}^-$  is weaker one. Further, difference between  $\text{CN}^-$  and CO as ligands arises from the fact that the former combines with cation rather than uncharged atoms. However, there is enough in common between complexes of CO,  $\text{NO}^+$ , and  $\text{CN}^-$  to justify their treatment together. Based on the study of many mixed carbonyl complexes, it is possible to compare the ability of various ligands to accept back donation. When this is done, it is found that the ability to accept back donation decreases in the order.



The most important  $\pi$ -acceptor ligand is carbon monoxide. The transition metal derivatives of CO are called "*carbonyls*". Many carbonyl are of considerable structural interest as well as being important industrially and in catalytic and other reaction Carbonyl derivatives of at least one type are known for all of the transition metals. In this chapter we shall discuss the chemistry of some important carbonyl and their derivatives in detail.

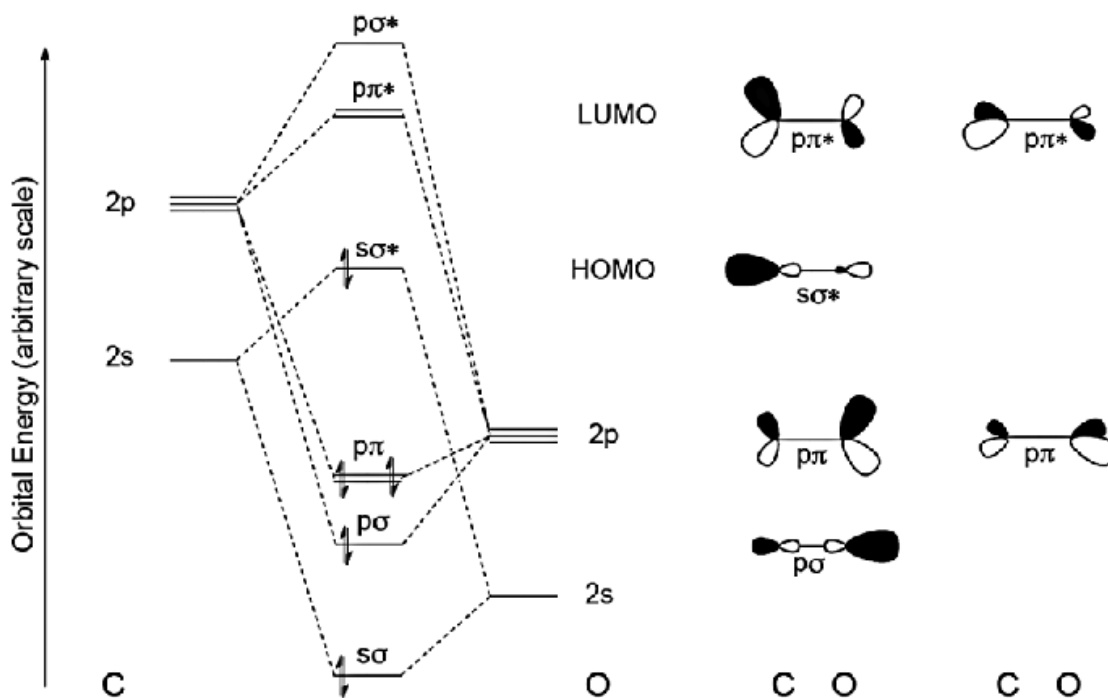
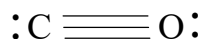


Figure 1: The molecular orbital diagram of CO molecule

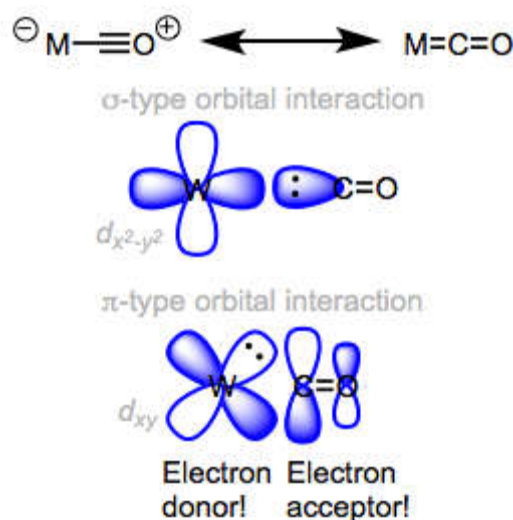
### CO as $\pi$ -Acid Ligand

CO provides a paradigm for bonding of  $\pi$ -acid ligands to metals. The valence-bond (VB) structure of CO shows two nonbonding electron pairs with a triple bond between C and O.



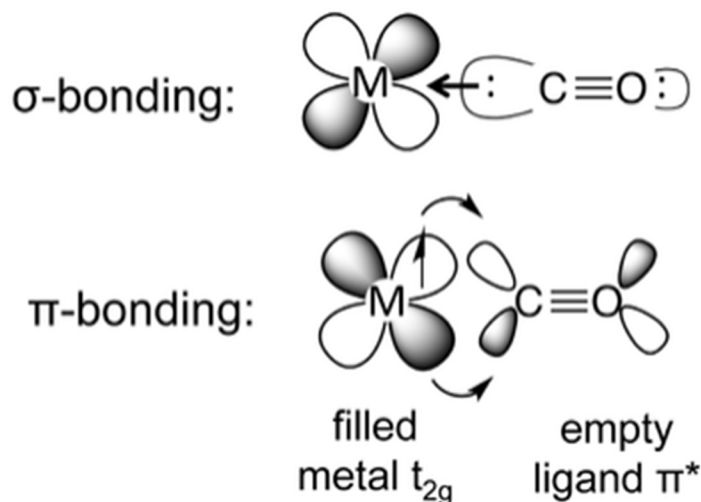
The formal charge on the oxygen atom is +1, whereas on the carbon atom is -1. Although the electronegativity of oxygen is considerably higher than that of carbon, these formal charges are consistent with the dipole moment (0.12D) with the carbon being at the negative end of the dipole. The carbon end of CO molecule is thus a softer electron donor, and it is the carbon atom that is bound to the metal. The molecular orbital description of bonding in CO is shown in Fig.1.

The bond order in CO molecule is given in terms of the number of electrons in bonding orbitals and the number in the antibonding orbitals. The bond order is 3 for CO, i.e. a triple bond exists in CO molecule. For gaseous CO in which the triple bond exists, the C - O stretching is observed at  $2143 \text{ cm}^{-1}$ . However, in metal carbonyl the C - O stretching bond is seen at  $1850$  to  $2100 \text{ cm}^{-1}$  for terminal CO groups. The shift of the CO stretching band upon coordination to metals reflects a slight reduction in the bond order resulting from back donation of electron density from the metal to the CO. However, bridging carbonyl groups normally show an absorption band in the  $1700$  to  $1850 \text{ cm}^{-1}$  range.



The molecular orbitals of CO are populated as shown in Fig 1 and the molecule is diamagnetic. However, the next higher unpopulated molecular orbitals are the  $\pi^*$  orbitals. By virtue of accepting several pairs of electron from the ligands, the metal acquires a negative formal charge. In order to remove part of this negative charge from the metal, the electron density is donated back from the metal to the  $\pi^*$  orbitals on the ligands. The  $\pi^*$  orbital on the CO have appropriate symmetry to effectively accept this electron density, resulting in a slight double bond character to the M - CO bond and a slight reduction from triple bond character in the CO ligand.

Figure 2 shows the orbital interaction that permits back donation to occur. The valence bond approach to this multiple bonding can be shown in terms of the resonance structures.



**Figure 2:** The overlap of a  $d$ -orbital on a metal with the antibonding  $\pi^*$  orbital on CO

Because the electron bonding density is flowing from the metal onto the ligands, this donation is known as *back donation*. It is in the reverse direction to that in the normal donation of electrons in forming coordinate bonds. The term *back bonding* is sometimes used instead of *back donation*, but it is not as descriptive because the ligands are functioning as acceptors of electron density from the metal. The essential feature of the electron donation is that there must be an acceptor, which in this case is ligand. The ligands are referred to as  $\pi$  acceptors because of this receiving electron density donated from the metal to  $\pi^*$  orbitals. Back donation results in increasing the bond order between the metal and ligand, so as it results in additional bonding.

### Binary Metal Carbonyls

Binary carbonyls are the simple class of  $n$ -acid complexes. The compounds formed by the combination of CO molecules with transition metals' atoms in low oxidation states are called metallic carbonyls. In binary metal carbonyls only metal atoms and carbonyls ligands are present. Although there are many complexes known that contain both carbonyls and other ligands (mixed carbonyl complexes). A remarkable characteristics of these compounds is that because the ligands are neutral molecules, the metals are present in the zero oxidation state. Depending on the net charge on the other ligands, the metal may or may not be in the zero oxidation state. In any event, the metal in the metal carbonyls occur in low oxidation states because of the favorable interaction of the soft ligands (Lewis bases) with metals in low oxidation states (soft Lewis acids).

Generally, the metals that form stable carbonyl complexes are those in the first transition series from V to Ni, in the second row from Mo to Rh, and in the third

row from W to Ir. There are several reasons for these being the metals most often found in carbonyl complexes:

- i. These metals have one or more d-orbitals that are not completely filled so they can accept electron pairs from the  $\sigma$ -electron donors.
- ii. The d-orbitals contain some electrons that can be involved in back donation to the  $\pi^*$  orbitals on the CO ligands.
- iii. The metals are generally in zero oxidation state or at least a low oxidation state as they behave as soft Lewis acids, making it favourable to bond to a soft Lewis base like CO.

Metal atom in metal carbonyls is in low oxidation state. This is because of the fact that there is high electron density on the metal atom in its low oxidation state than its higher oxidation. Thus, since metal is electropositive in nature, it would feel more comfortable, if some of the excess electron density present on the metal atom gets transferred to the vacant  $\pi^*$  orbitals of the CO ligand by forming M - CO  $\pi$  bond.

### **Classification of Metal Carbonyls**

Metal carbonyls have been classified into following classes:

#### **(i) Mononuclear Carbonyls**

The carbonyls containing only one metal atom per molecule are called mononuclear or monomeric carbonyls. Examples are  $\text{Ni}(\text{CO})_4$ ,  $\text{M}(\text{CO})_5$ ,  $\text{CM} = \text{Fe, Ru, Os}$  and  $\text{M}(\text{CO})_6$ , ( $\text{M} = \text{V, Cr, Mo, W}$ ). They have general formula  $\text{M}(\text{CO})_x$  ( $X = 4$  to  $6$ ).

#### **(ii) Binuclear Carbonyls**

The carbonyls that contain two metal atoms in one molecule of the metal carbonyl are called binuclear carbonyls. They have general formula  $\text{M}_2(\text{CO})_x$  ( $X = 8$  to  $10$ ). Examples are  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Fe}_2(\text{CO})_9$ ,  $\text{Co}_2(\text{CO})_8$  etc.

#### **(iii) Polynuclear Carbonyls**

The carbonyls which contains more than two metal atoms in a molecule are called polynuclear carbonyls. Examples are  $\text{Fe}_3(\text{CO})_{12}$ ,  $\text{Os}_3(\text{CO})_{12}$ ,  $\text{Co}_4(\text{CO})_{12}$  etc.