

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 π -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. NH_2 , H_2O , CO and NO are examples of uncharged or neutral ligands, while OH^- , Cl^- , 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 π -bonding that supplements the σ -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 π -orbitals is called π -acidity or π -acceptor capacity.***

The term π -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 π -acceptor ligands are CO, NO isocyanides and certain unsaturated organic compounds.

Ligands which are isoelectronic with CO, such as NO^+ , CN^- , would be just as suitable for π -bonding, but the charge on the ligand has to be taken into consideration. Thus NO^+ with a positive charge is a stronger π -acceptor than CO, while CN^- is weaker one. Further, difference between 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, NO^+ , and 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 π -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.

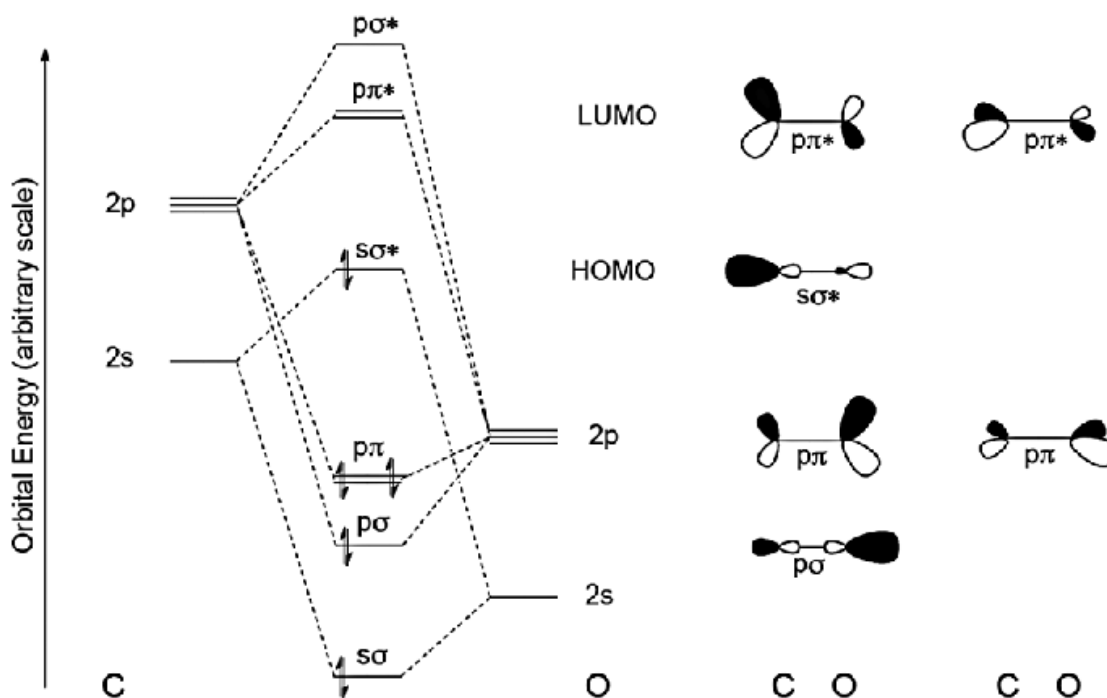
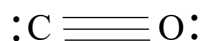


Figure 1: The molecular orbital diagram of CO molecule

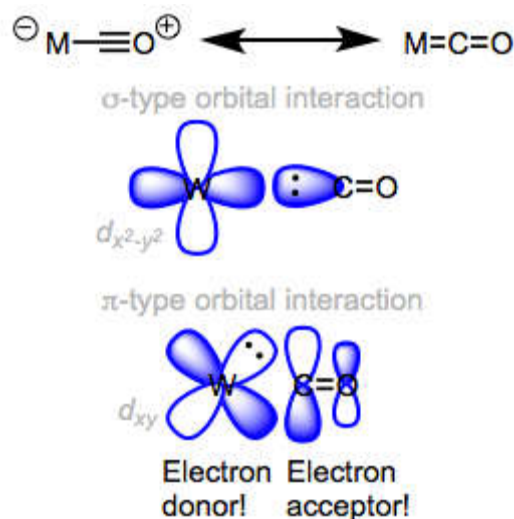
CO as π -Acid Ligand

CO provides a paradigm for bonding of π -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 the 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 cm^{-1} . However, in metal carboxyl the C - O stretching band is seen at 1850 to 2100 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 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 π^* 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 π^* orbitals on the ligands. The π^* 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.

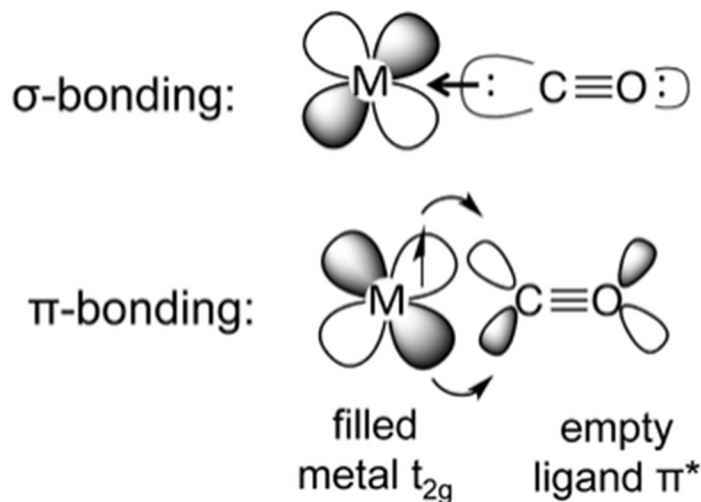


Figure 2: The overlap of a d-orbital on a metal with the antibonding π^* orbital on CO

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 π acceptors because of this receiving electron density donated from the metal to π^* 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 mayor 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 σ -electron donors.
- ii. The d-orbitals contain some electrons that can be involved in back donation to the π^* 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 π^* orbitals of the CO ligand by forming M - CO π 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 $\text{Ni}(\text{CO})_4$, $\text{M}(\text{CO})_5$, $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ and $\text{M}(\text{CO})_6$, ($\text{M} = \text{V}, \text{Cr}, \text{Mo}, \text{W}$). 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. The common binary metal carbonyls are listed in Table 5.1.

Effective Atomic Number Rule (The 18 Electron Rule)

The effective atomic number (EAN) rule (the 18-electron rule) put forward by Sidgwick and Bailey is observed by transition metal carbonyls which shows diamagnetic behavior. The only exception to EAN rule is vanadium hexacarbonyl which is paramagnetic in nature. The composition of stable binary metal carbonyls is largely predictable by EAN rule or the 18-electron rule. The EAN rule predicts that metal in the zero or other low oxidation state will gain electrons from a sufficient number of ligands so that the metal will achieve the electronic configuration of the next noble gas. For the first row transition metals, this means the krypton configuration with a total of 36 electrons.

A very large number of metal carbonyls including many anionic and cationic species, nitrosyl-, hydrogen and halogen substituted metal carbonyls conform to 18 electron rule. This rule can' also be formulated in terms of total number of electrons around the metal in which case this number is usually found to be 36, 54 or 86 corresponding to the atomic number of noble gases Kr, Xe and Rn. The metals are then said to obey the EAN rule.

Counting rules help to predict and understand the stoichiometry and structures of the binary metals Carbonyl. In counting the electrons around a single metal atom, follows these simple rules.

1. Count two electron for each CO.
2. Count one electron for each metal-metal bond.
3. Find the number of electrons that formally belong to the metal atom alone by
 - a. *adding up the charges on the ligands and changing the sign.*
 - b. *finding the metal oxidation number by adding this number to the total charge on the complex, &*
 - c. *subtracting the oxidation number from the valence electron count of the neutral metal.*
4. Add together the counts from steps 1 - 3.

Actually, there is ample evidence to indicate that the rule is followed in many other cases as well. For example, Zn^{2+} has 28 electrons, and receiving eight more electrons (two electrons form each of four ligands) as in $[Zn(NH_3)_4]^{2+}$ results in 36 electrons being around the Zn^{2+} . Similarly, Co^{3+} has 24 electrons, and six pairs of electrons from six ligands will raise the number to 36 (as in $[Co(CN)_6]^{3-}$). The vast majority of complexes containing Co^{3+} follow this trend. In the case of Cr^{3+} , the ion has 21 electrons, and gaining six pairs results in there being only 33 electrons around the chromium ion. For complexes of metal ions, the EAN rule is followed much more frequently by those metals in the latter part of the transition series.

The example of Cr^{3+} mentioned earlier that the "rule" is by no means always true. However, for complexes of metal in the zero oxidation state containing soft ligands such as CO, PR_3 , or alkenes, there is a strong tendency of the stable complexes to be those containing the number of ligands, predicted by EAN rule. Because the Ni atom has 28 electrons, we should expect eight more electrons to be added from four -ligands. Accordingly, the stable nickel carbonyl is $\text{Ni}(\text{CO})_4$. For chromium (0), which contains 24 electrons, the stable carbonyl is $\text{Cr}(\text{CO})_6$ as expected from the EAN rule. The six pairs of electrons from the six CO ligands brings to 36 the number of electrons around the chromium atom.

The Mn atom has 25 electrons. Adding five carbonyl groups would raise the number to 35, leaving the atom one electron short of the krypton configuration. If the single unpaired electron on one manganese atom is allowed to pair up with an unpaired electron on another to form a metal-metal bond, we have the formula $(\text{CO})_5 \cdot \text{Mn}-\text{Mn}(\text{CO})_5$ or $[\text{Mn}(\text{CO})_5]_2$ which is the formula for a manganese carbonyl that obeys the EAN rule.

Cobalt has 27 electrons, and adding eight more electrons (one pair from each of four CO ligands) brings the total to 35. Accordingly, forming a metal-metal bond using the remaining unpaired electrons would give $[\text{Co}(\text{CO})_4]_2$ or $\text{Co}_2(\text{CO})_8$ as the stable carbonyl compound. As we shall see, there are two different structures possible for $\text{Co}_2(\text{CO})_8$ both agreeing with the EAN rule. Based on the EAN rule, it might be expected that $\text{Co}(\text{CO})_4$ would not be stable, but the species $[\text{Co}(\text{CO})_4]^-$ obtained by adding an electron to $\text{Co}(\text{CO})_4$ would be stable. Actually, the $[\text{Co}(\text{CO})_4]^-$ ion is well known, and several derivatives containing it have been prepared.

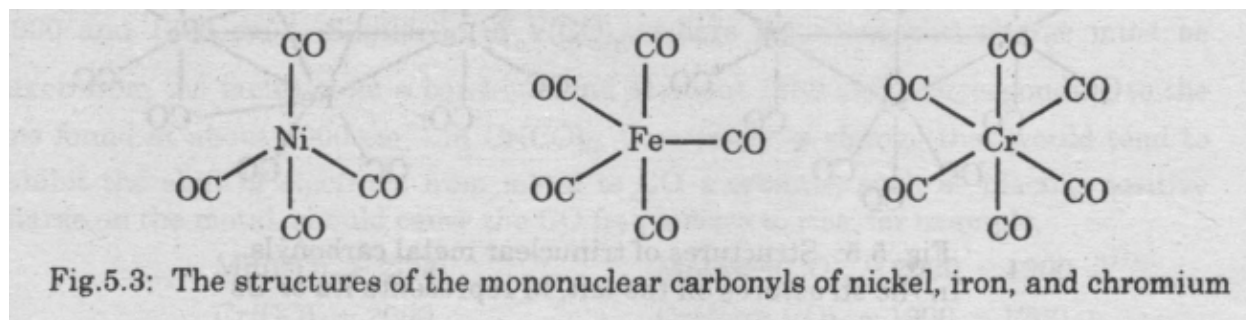
The EAN rule also applies to carbonyls of metal clusters. For example, in $\text{Fe}_3(\text{CO})_{12}$ there are eight electrons in the valence shells of the three Fe atoms, which gives a total of 24. Then, the 12 CO ligands contribute an electron pair, each which gives another 24 electrons and brings the total to 48. This gives an average of 16 per Fe atom, and the deficit must be made by the metal-metal bonds.

Since each atom contributes one electron to the bond, two bonds to other Fe atoms are required to give 18 electrons around each atom. As will be seen from the structure shown later, the structure of $\text{Fe}_3(\text{CO})_{12}$ has the three Fe atoms in a triangle with each bonded to two other Fe atoms. In a similar way, $\text{Co}_4(\text{CO})_{12}$ has 12 CO ligands contributing two each or a total of 24 electrons and four Co atoms that contribute 9 each or a total of 36 electrons. From both sources, the number of electrons available is 60, but for four metal atoms the number is 15 each. Therefore, to have each 18 each would require each Co atom to form bonds to three others. Such a structure is shown later in which the four Co atoms are arranged in a tetrahedron.

Although the 18-electron rule is not always followed, it does offer a logical basis for predicting the composition of many complexes. The arguments presented here can, of course, be extended to second- and third-row transition elements. The 18-electron rule is also of use in predicting the formulas of stable complexes containing carbonyl groups and other ligands, as might result from ligand substitution reactions. This is particularly important when a ligand (such as an alkene containing several double bonds) can donate different numbers of electrons depending on the number needed by the metal to achieve the configuration of the next noble gas.

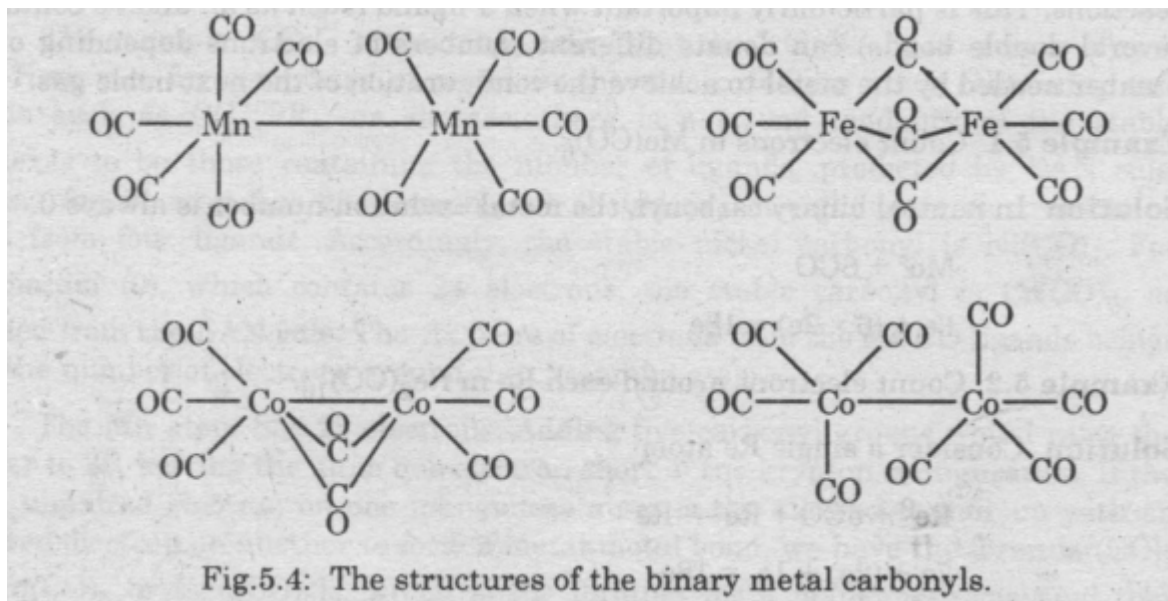
Structures of Metal Carbonyls

The mononuclear metal carbonyls contain only one metal atom, and they have comparatively simple structures. For example, nickel tetracarbonyl is tetrahedral. The pentacarbonyls of iron, ruthenium, and osmium are trigonal bipyramidal, whereas the hexacarbonyl of vanadium, chromium, molybdenum, and tungsten are octahedral. These structures are shown in Figure 5.3.

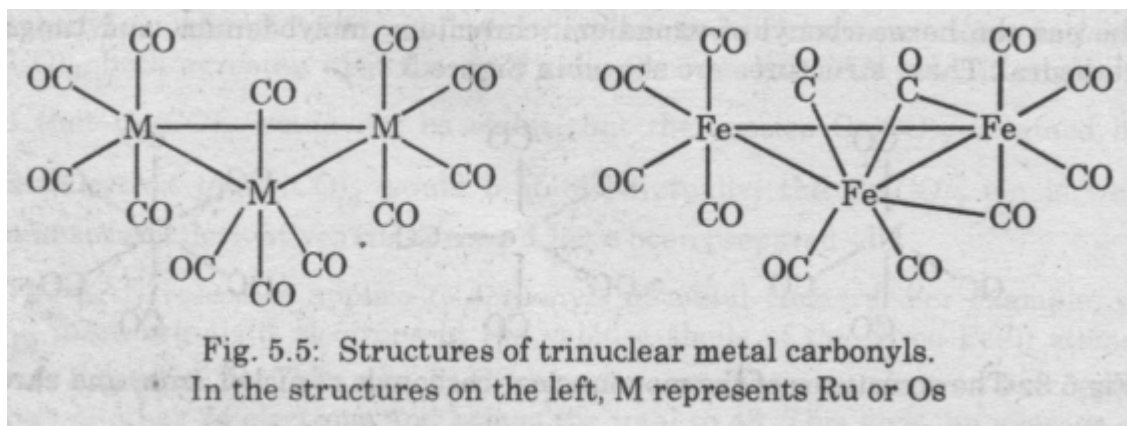


The structures of the dinuclear metal carbonyls (containing two metal atoms) involve either metal bonds or bridging CO groups, or both. For example, the structure of $\text{Fe}_2(\text{CO})_9$ (diron nonacarbonyl), contains three CO ligands that form bridges between the iron atoms, and each iron atom also has three other CO groups attached only to that atom.

Carbonyl groups that are attached to two metal atoms simultaneously are called bridging carbonyls, whereas those attached to only one metal atom are referred to as terminal carbonyl groups. The structures of $\text{Mn}_2(\text{CO})_{10}$ and $\text{Cr}_2(\text{CO})_{10}$ actually involve only a metal-metal bond, so the formulas are more correctly written as $(\text{CO})_5\text{M}-\text{M}(\text{CO})_5$. Two isomers are known for $\text{Co}(\text{CO})_8$. One has metal-metal bond between the cobalt atoms, the other has two bridging CO ligands and a metal-metal bond. Figure 5.4 shows the structures of the dinuclear metal carbonyls.



The structure for $\text{Mn}_2(\text{CO})_{10}$ is sometimes drawn to appear as if four CO ligands form a square plane around the Mn atom. In fact, the four CO groups do not lie in the same plane as the Mn atom. Rather, they lie about 12 pm from the plane containing the Mn on the side opposite the metal-metal bond.



Structures of the trinuclear,

tetranuclear, and higher compounds are best thought of as metal clusters containing either metal-metal bonds or bridging carbonyl groups. In some cases, both types of bonds occur. The structures of $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ are shown in Figure 5.5.

The structure of $\text{Fe}_3(\text{CO})_{12}$ also shown in Figure 5.5 contains a trigonal arrangement of Fe atoms, but it contains two bridging carbonyl

groups.

Carbonyls containing four metal atoms in the cluster are formed by Co, Rh, and Ir in which the metal atoms are arranged in a tetrahedron with 12CO ligands, nine in terminal positions and three that are bridging. These structures are shown in Figure 5.6.

