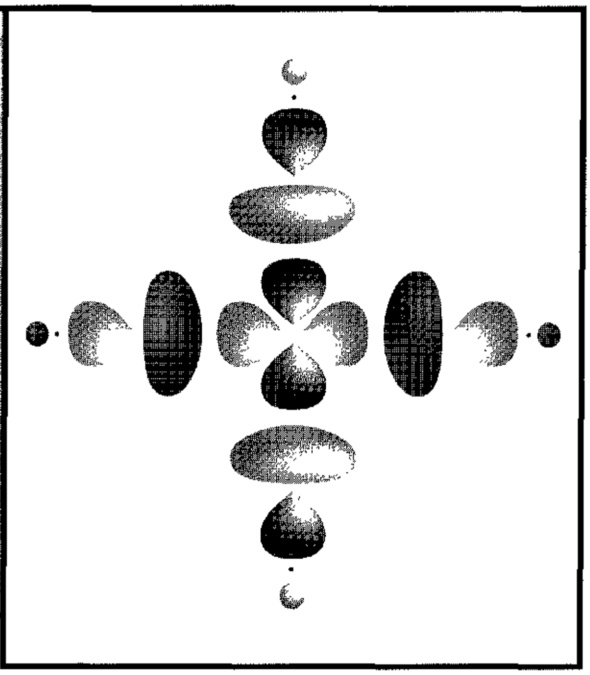
CHAPTER
13
Organometallic Chemistry



Organometallic chemistry, the chemistry of compounds containing metal-carbon bonds, has grown enormously as a field of study during the past four decades. It encompasses a wide variety of chemical compounds and their reactions, including compounds containing both σ and π bonds between metal atoms and carbon; many cluster compounds, containing one or more metal-metal bonds; and molecules of structural types unusual or unknown in organic chemistry. In some cases, reactions of organometallic compounds bear similarities to known organic reactions, and in other cases they are dramatically different. Aside from their intrinsically interesting nature, many organometallic compounds form useful catalysts and consequently are of significant industrial interest. In this chapter, we describe a variety of types of organometallic compounds and present descriptions of organic ligands and how they bond to metals. Chapter 14 continues with an outline of major types of reactions of organometallic compounds and how these reactions may be combined into catalytic cycles. Chapter 15 discusses parallels that may be observed between organometallic chemistry and main group chemistry.

Certain organometallic compounds bear similarities to the types of coordination compounds already discussed in this text. $Cr(CO)_6$ and $[Ni(H_2O)_6]^{2+}$, for example, are both octahedral. Both CO and H_2O are σ-donor ligands; in addition, CO is a strong π acceptor. Other ligands that can exhibit both behaviors include CN^-, PPh_3, SCN^-, and many organic ligands. The metal-ligand bonding and electronic spectra of compounds containing these ligands can be described using concepts discussed in Chapters 10 and 11. However, many organometallic molecules are strikingly different from any we have considered previously. For example, cyclic organic ligands containing delocalized π systems can team up with metal atoms to form **sandwich compounds**, such as those shown in Figure 13-1.

A characteristic of metal atoms bonded to organic ligands, especially CO, is that they often exhibit the capability to form covalent bonds to other metal atoms to form **cluster compounds**.[1] These clusters may contain only two or three metal atoms or as many as several dozen; there is no limit to their size or variety. They may contain single,

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[1] Some cluster compounds are also known that contain no organic ligands.

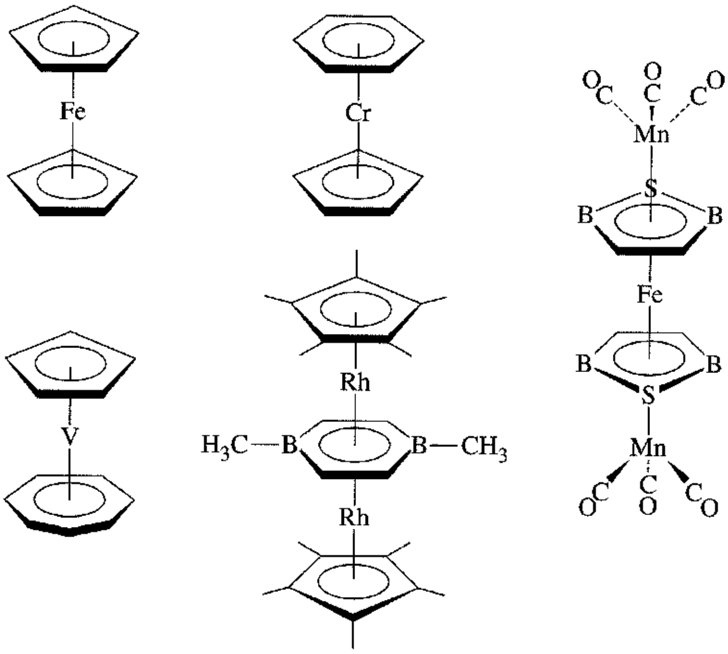

FIGURE 13-1 Examples of Sandwich Compounds.

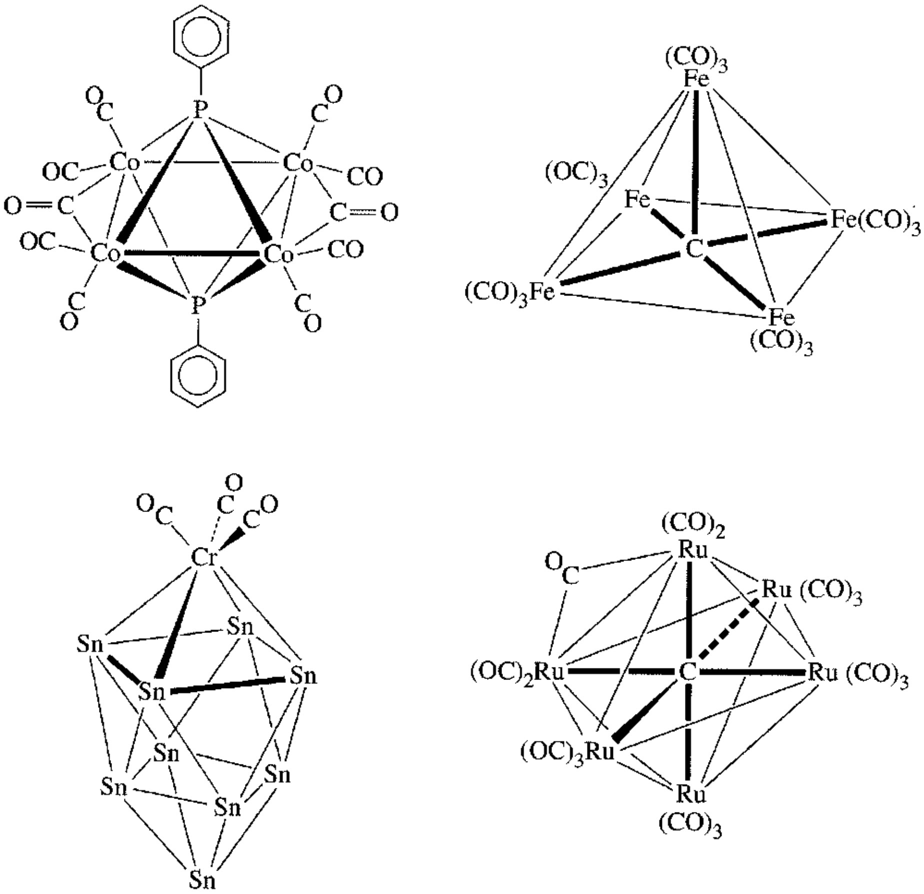

FIGURE 13-2 Examples of Cluster Compounds.

double, triple, or quadruple bonds between the metal atoms and may in some cases have ligands that bridge two or more of the metals. Examples of metal cluster compounds containing organic ligands are shown in Figure 13-2; clusters will be discussed further in Chapter 15.

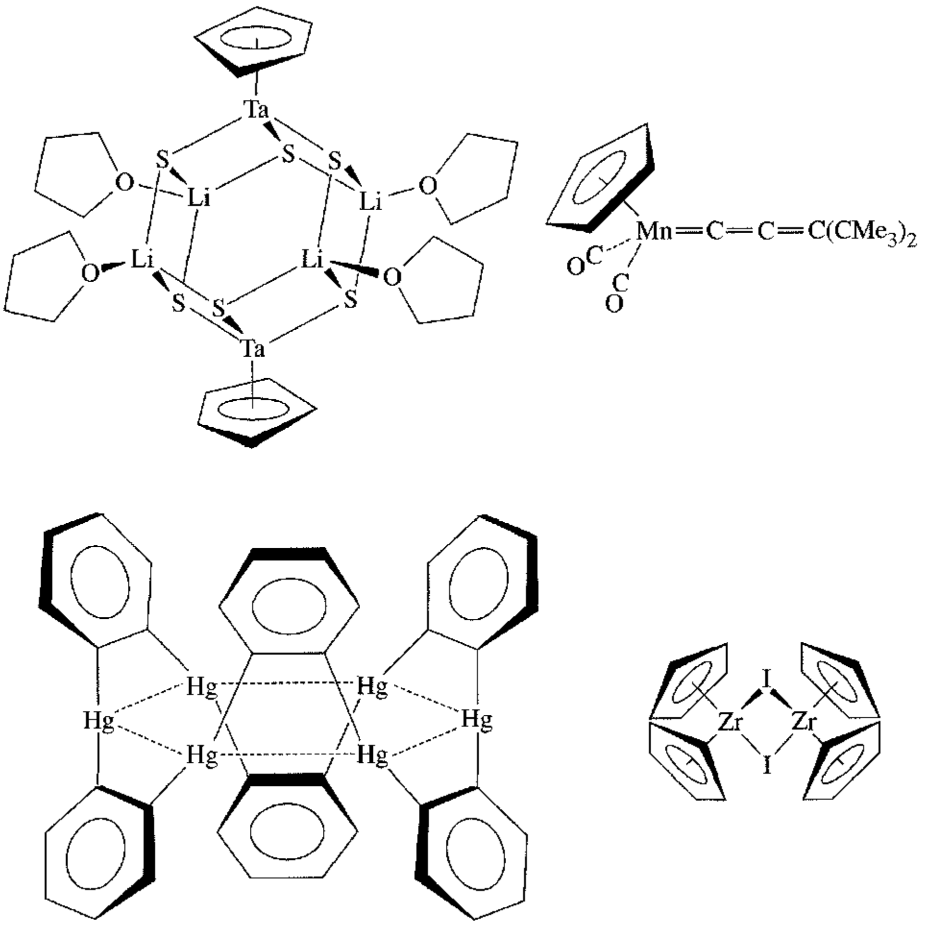

FIGURE 13-3 More Examples of Organometallic Compounds.

Carbon itself may play quite a different role than commonly encountered in organic chemistry. Certain metal clusters encapsulate carbon atoms; the resulting carbon-centered clusters, frequently called **carbide clusters**, in some cases contain carbon bonded to five, six, or more surrounding metals. The traditional notion of carbon forming bonds to, at most, four additional atoms, must be reconsidered.[2] Two examples of carbide clusters are included in Figure 13-2.

Many other types of organometallic compounds have interesting structures and chemical properties. Figure 13-3 shows several additional examples of the variety of molecular structures encountered in this field.

Strictly speaking, the only compounds classified as organometallic are those that contain metal-carbon bonds, but in practice complexes containing several other ligands similar to CO in their bonding, such as NO and N_2, are frequently included. (Cyanide also forms complexes in a manner similar to CO, but is usually considered a classic, nonorganic ligand.) Other π-acceptor ligands, such as phosphines, often occur in organometallic complexes, and their chemistry may be studied in association with the chemistry of organic ligands. In addition, dihydrogen, H_2, participates in important aspects of organometallic chemistry and deserves consideration. We will include examples of these and other nonorganic ligands as appropriate in our discussion of organometallic chemistry.

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[2] A few examples of carbon bonded to more than four atoms are also known in organic chemistry. See, for example, G. A. Olah and G. Rasul, *Acc. Chem. Res.*, **1997**, *30*, 245.

13-1 HISTORICAL BACKGROUND

The first organometallic compound to be reported was synthesized in 1827 by Zeise, who obtained yellow needle-like crystals after refluxing a mixture of $PtCl_4$ and $PtCl_2$ in ethanol, followed by addition of KCl solution.[3] Zeise correctly asserted that this yellow product (subsequently dubbed Zeise's salt) contained an ethylene group. This assertion was questioned by other chemists, most notably Liebig, and was not verified conclusively until experiments performed by Birnbaum in 1868. However, the structure of the compound proved elusive and was not determined until more than 100 years later![4] Zeise's salt was the first compound identified as containing an organic molecule attached to a metal using the π electrons of the former. It is an ionic compound of formula $K[Pt(C_2H_4)Cl_3]\cdot H_2O$; the structure of the anion, shown in Figure 13-4, is based on a square plane, with three chloro ligands occupying corners of the square and the ethylene occupying the fourth corner, but perpendicular to the plane.

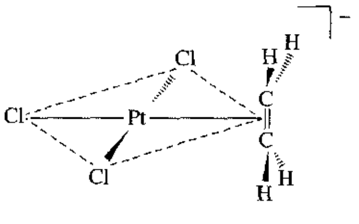
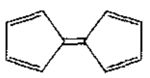


FIGURE 13-4 Anion of Zeise's Compound.

The first compound to be synthesized containing carbon monoxide as a ligand was another platinum chloride complex, reported in 1867. In 1890, Mond reported the preparation of $Ni(CO)_4$, a compound that became commercially useful for the purification of nickel.[5] Other metal CO (carbonyl) complexes were soon obtained.

Reactions between magnesium and alkyl halides, performed by Barbier in 1898 and 1899, and subsequently by Grignard,[6] led to the synthesis of alkyl magnesium complexes now known as Grignard reagents. These complexes often have a complicated structure and contain magnesium-carbon σ bonds. Their synthetic utility was recognized early; by 1905, more than 200 research papers had appeared on the topic. Grignard reagents and other reagents containing metal-alkyl σ bonds (such as organozinc and organocadmium reagents) have been of immense importance in the development of synthetic organic chemistry.



Fulvalene

Organometallic chemistry developed slowly from the discovery of Zeise's salt in 1827 until around 1950. Some organometallic compounds, such as Grignard reagents, found utility in organic synthesis, but there was little systematic study of compounds containing metal-carbon bonds. In 1951, in an attempt to synthesize fulvalene, shown in the margin, from cyclopentadienyl bromide, Kealy and Pauson reacted the Grignard reagent *cyclo*-C_5H_5MgBr with $FeCl_3$, using anhydrous diethyl ether as the solvent.[7] This reaction did not yield the desired fulvalene but rather an orange solid of formula $(C_5H_5)_2Fe$, ferrocene:

$$\textit{cyclo}\text{-}C_5H_5MgBr + FeCl_3 \longrightarrow \underset{\text{ferrocene}}{(C_5H_5)_2Fe}$$

The product was surprisingly stable; it could be sublimed in air without decomposition and was resistant to catalytic hydrogenation and Diels-Alder reactions. In 1956, X-ray diffraction showed the structure to consist of an iron atom sandwiched between two parallel C_5H_5 rings,[8] but the details of the structure proved controversial. The initial study indicated that the rings were in a staggered conformation (D_{5d} symmetry). Electron diffraction studies of gas phase ferrocene, on the other hand, showed the rings to be

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[3] W. C. Zeise, *Ann. Phys. Chem.*, **1831**, *21*, 497–541. A translation of excerpts from this paper can be found in G. B. Kauffman, ed., *Classics in Coordination Chemistry*, Part 2, Dover, New York, 1976, pp. 21–37. A review of the history of the anion of Zeise's salt, including some earlier references, has recently been published. See D. Seyferth, *Organometallics*, **2001**, *20*, 2.

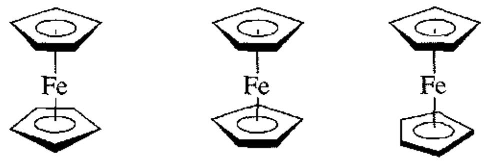
[4] R. A. Love, T. F. Koetzle, G. J. B. Williams, L. C. Andrews, and R. Bau, *Inorg. Chem.*, **1975**, *14*, 2653.

[5] L. Mond, *J. Chem. Soc.*, **1890**, *57*, 749.

[6] V. Grignard, *Ann. Chim.*, **1901**, *24*, 433. An English translation of most of this paper is in P. R. Jones and E. Southwick, *J. Chem. Ed.*, **1970**, *47*, 290.

[7] T. J. Kealy and P. L. Pauson, *Nature*, **1951**, *168*, 1039.

[8] J. D. Dunitz, L. E. Orgel, and R. A. Rich, *Acta Crystallogr.*, **1956**, *9*, 373.



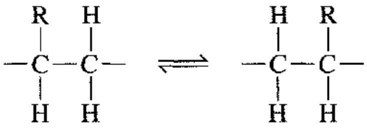
D_{5d} Staggered rings D_{5h} Eclipsed rings D_5 Skew rings

FIGURE 13-5 Conformations of Ferrocene.

eclipsed (D_{5h}), or very nearly so. More recent X-ray diffraction studies of solid ferrocene have identified several crystalline phases, with an eclipsed conformation at 98 K and with conformations having the rings slightly twisted (D_5) in higher temperature crystalline modifications (Figure 13-5).[9]

The discovery of the prototype sandwich compound ferrocene rapidly led to the synthesis of other sandwich compounds, of other compounds containing metal atoms bonded to the C_5H_5 ring in a similar fashion, and to a vast array of other compounds containing other organic ligands. Therefore, it is often stated, and with justification, that the discovery of ferrocene began the era of modern organometallic chemistry, an area that continues to grow rapidly.[10]

Finally, a history of organometallic chemistry would be incomplete without mention of what surely is the oldest known organometallic compound, vitamin B_{12} coenzyme. This naturally occurring cobalt complex, whose structure is illustrated in Figure 13-6, contains a cobalt–carbon σ bond. It is a cofactor in a number of enzymes that catalyze 1,2 shifts in biochemical systems:



$$\begin{array}{cc} R & H \\ | & | \\ -C- & C- \\ | & | \\ H & H \end{array} \rightleftharpoons \begin{array}{cc} H & R \\ | & | \\ -C- & C- \\ | & | \\ H & H \end{array}$$

The chemistry of vitamin B_{12} is described briefly in Chapter 16.

13-2 ORGANIC LIGANDS AND NOMENCLATURE

Some of the most common organic ligands are shown in Figure 13-7.

Special nomenclature has been devised to designate the manner in which some of these ligands bond to metal atoms; several of the ligands in Figure 13-7 may bond through different numbers of atoms, depending on the molecule in question. The number of atoms through which a ligand bonds is indicated by the Greek letter η (eta) followed by a superscript indicating the number of ligand atoms attached to the metal. For example, because the cyclopentadienyl ligands in ferrocene bond through all five atoms, they are designated η^5-C_5H_5. The formula of ferrocene may therefore be written $(\eta^5\text{-}C_5H_5)_2Fe$ (in general we will write hydrocarbon ligands before the metal). In written or spoken form, the η^5-C_5H_5 ligand is designated the pentahaptocyclopentadienyl ligand. *Hapto* comes from the Greek word for fasten; therefore, pentahapto means "fastened in five places." C_5H_5, probably the second most frequently encountered ligand in organometallic chemistry (after CO), most commonly bonds to metals through five

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[9] E. A. V. Ebsworth, D. W. H. Rankin, and S. Cradock, *Structural Methods in Inorganic Chemistry*, Blackwell Scientific, Oxford, 1987.

[10] A special issue of the *Journal of Organometallic Chemistry* (**2002**, *637*, 1) was recently devoted to ferrocene, including recollections of some involved in its discovery; a brief summary of some of these recollections has appeared in *Chem. Eng. News*, December 3, 2001, p. 37.

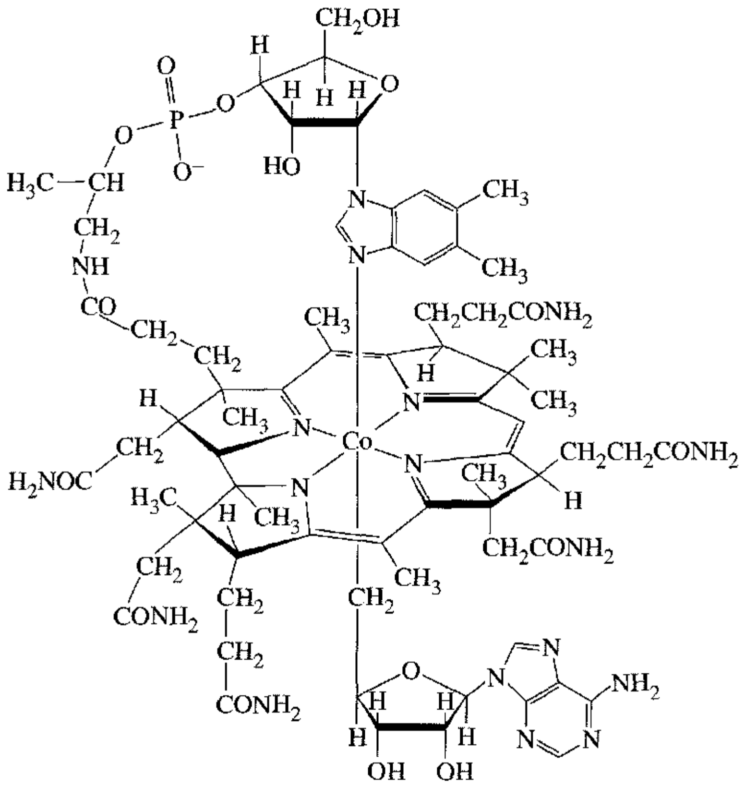


FIGURE 13-6 Vitamin B_{12} Coenzyme.

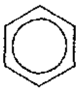
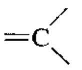
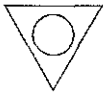
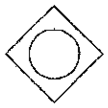
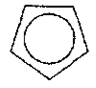
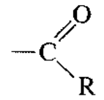
Ligand	*Name*	*Ligand*	*Name*
CO	Carbonyl		Benzene
	Carbene (alkylidene)		
$\equiv$C—	Carbyne (alkylidyne)		1,5-cyclooctadiene (1,5-COD) (1,3-cyclooctadiene complexes are also known)
	Cyclopropenyl (*cyclo*-C_3H_3)	$H_2C{=}CH_2$	Ethylene
		$HC{\equiv}CH$	Acetylene
			π-Allyl (C_3H_5)
	Cyclobutadiene (*cyclo*-C_4H_4)	$-CR_3$	Alkyl
	Cyclopentadienyl (*cyclo*-C_5H_5)(Cp)		Acyl

FIGURE 13-7 Common Organic Ligands.

positions, but under certain circumstances may bond through only one or three positions. As a ligand, C_5H_5 is commonly abbreviated Cp.

The corresponding formulas and names are designated according to this system as follows:[11]

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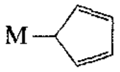
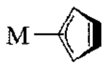
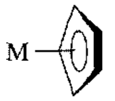
[11] For ligands having all carbons bonded to a metal, sometimes the superscript is omitted. Ferrocene may therefore be written (η-$C_5H_5)_2$Fe and dibenzenechromium (η-$C_6H_6)_2$Cr. Similarly, π with no superscript may occasionally be used to designate that all atoms in the π system are bonded to the metal (for example, (π-$C_5H_5)_2$Fe).

Number of Bonding Positions	*Formula*	*Name*	
1	η^1-C_5H_5	monohaptocyclopentadienyl	
3	η^3-C_5H_5	trihaptocyclopentadienyl	
5	η^5-C_5H_5	pentahaptocyclopentadienyl	

As in the case of other coordination compounds, bridging ligands, which are very common in organometallic chemistry, are designated by the prefix μ, followed by a subscript indicating the number of metal atoms bridged. Bridging carbonyl ligands, for example, are designated as follows:

Number of Atoms Bridged	*Formula*
None (terminal)	CO
2	μ_2-CO
3	μ_3-CO

13-3
THE 18-ELECTRON RULE

In main group chemistry, we have encountered the octet rule in which the electronic structures of many main group compounds can be rationalized on the basis of a valence shell requirement of 8 electrons. Similarly, in organometallic chemistry, the electronic structures of many compounds are based on a total valence electron count of 18 on the central metal atom. As in the case of the octet rule, there are many exceptions to the 18-electron rule,[12] but the rule nevertheless provides some useful guidelines to the chemistry of many organometallic complexes, especially those containing strong π-acceptor ligands.

13-3-1 COUNTING ELECTRONS

Several schemes exist for counting electrons in organometallic compounds. We will describe two of these. First, here are two examples of electron counting in 18-electron species:

EXAMPLES

$Cr(CO)_6$ A Cr atom has 6 electrons outside its noble gas core. Each CO is considered to act as a donor of 2 electrons. The total electron count is therefore:

Cr		6 electrons
6(CO)	6 × 2 electrons =	12 electrons
	Total =	18 electrons

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[12] A variation on the 18-electron rule, often called the effective atomic number (EAN) rule, is based on electron counts relative to the total number of electrons in noble gases. The EAN rule gives the same results as the 18-electron rule and will not be considered further in this text.

$Cr(CO)_6$ is therefore considered an 18-electron complex. It is thermally stable; for example, it can be sublimed without decomposition. $Cr(CO)_5$, a 16-electron species, and $Cr(CO)_7$, a 20-electron species, on the other hand, are much less stable and are known only as transient species. Likewise, the 17-electron $[Cr(CO)_6]^+$ and 19-electron $[Cr(CO)_6]^-$ are far less stable than the neutral, 18-electron $Cr(CO)_6$.

The bonding in $Cr(CO)_6$, which provides a rationale for the special stability of many 18-electron systems, will be discussed in Section 13-3-2.

(η^5-C_5H_5)Fe(CO)$_2$Cl Electrons in this complex may be counted in two ways:

Method A (Donor Pair Method)
This method considers ligands to donate electron pairs to the metal. To determine the total electron count, we must take into account the charge on each ligand and determine the formal oxidation state of the metal.

Pentahapto-C_5H_5 is considered by this method as $C_5H_5^-$, a donor of 3 electron pairs; it is a 6-electron donor. As in the first example, CO is counted as a 2-electron donor. Chloride is considered Cl^-, a donor of 2 electrons. Therefore, $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ is formally an iron(II) complex. Iron(II) has 6 electrons beyond its noble gas core. Therefore, the electron count is

Fe(II)	6 electrons
η^5-$C_5H_5^-$	6 electrons
2 (CO)	4 electrons
Cl^-	2 electrons
Total =	18 electrons

Method B (Neutral Ligand Method)
This method uses the number of electrons that would be donated by ligands *if they were neutral.* For simple inorganic ligands, this usually means that ligands are considered to donate the number of electrons equal to their negative charge as free ions. For example,

Cl is a 1-electron donor (charge on free ion $= -1$)
O is a 2-electron donor (charge on free ion $= -2$)
N is a 3-electron donor (charge on free ion $= -3$)

We do not need to determine the oxidation state of the metal to determine the total electron count by this method.

For $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$, an iron *atom* has 8 electrons beyond its noble gas core. η^5-C_5H_5 is now considered as if it were a neutral ligand (a 5-electron π system), in which case it would contribute 5 electrons. CO is a 2-electron donor and Cl (counted as if it were a neutral species) is a 1-electron donor. The electron count is

Fe atom	8 electrons
η^5-C_5H_5	5 electrons
2 (CO)	4 electrons
Cl	1 electron
Total =	18 electrons

Many organometallic complexes are charged species, and this charge must be included in determining the total electron count. The reader may wish to verify (by either method of electron counting) that $[Mn(CO)_6]^+$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ are both 18-electron ions.

In addition, metal-metal bonds must be counted. A metal-metal single bond counts as one electron per metal, a double bond counts as two electrons per metal, and so forth. For example, in the dimeric complex $(CO)_5Mn{-}Mn(CO)_5$ the electron count per manganese atom is (by either method):

Mn	7 electrons
5 (CO)	10 electrons
Mn—Mn bond	1 electron
Total =	18 electrons

TABLE 13-1
Electron Counting Schemes for Common Ligands

Ligand	*Method A*	*Method B*
H	2 (H^-)	1
Cl, Br, I	2 (X^-)	1
OH, OR	2 (OH^-, OR^-)	1
CN	2 (CN^-)	1
CH_3, CR_3	2 (CH_3^-, CR_3^-)	1
NO (bent M—N—O)	2 (NO^-)	1
NO (linear M—N—O)	2 (NO^+)	3
CO, PR_3	2	2
NH_3, H_2O	2	2
=CRR′ (carbene)	2	2
$H_2C{=}CH_2$ (ethylene)	2	2
CNR	2	2
=O, =S	4 (O^{2-}, S^{2-})	2
η^3-C_3H_5 (π-allyl)	2 ($C_3H_5^+$)	3
≡CR (carbyne)	3	3
≡N	6 (N^{3-})	3
Ethylenediamine (en)	4 (2 per nitrogen)	4
Bipyridine (bipy)	4 (2 per nitrogen)	4
Butadiene	4	4
η^5-C_5H_5 (cyclopentadienyl)	6 ($C_5H_5^-$)	5
η^6-C_6H_6 (benzene)	6	6
η^7-C_7H_7 (cycloheptatrienyl)	6 ($C_7H_7^+$)	7

Electron counts for common ligands according to both schemes are given in Table 13-1.

EXAMPLES

Both methods of electron counting are illustrated for the following complexes.

	Method A		*Method B*	
$ClMn(CO)_5$	Mn(I)	6 e^-	Mn	7 e^-
	Cl^-	2 e^-	Cl	1 e^-
	5 CO	10 e^-	5 CO	10 e^-
		18 e^-		18 e^-
$(\eta^5$-$C_5H_5)_2Fe$ (ferrocene)	Fe(II)	6 e^-	Fe	8 e^-
	2 η^5-$C_5H_5^-$	12 e^-	2 η^5-C_5H_5	10 e^-
		18 e^-		18 e^-
$[Re(CO)_5(PF_3)]^+$	Re(I)	6 e^-	Re	7 e^-
	5 CO	10 e^-	5 CO	10 e^-
	PF_3	2 e^-	PF_3	2 e^-
	+ charge	*	+ charge	−1 e^-
		18 e^-		18 e^-

* Charge on ion is accounted for in assignment of oxidation state to Re.

The electron counting method of choice is a matter of individual preference. Method A includes the formal oxidation state of the metal; Method B does not. Method B may be simpler to use for ligands having extended π systems; for example, η^5 ligands have an electron count of 5, η^3 ligands an electron count of 3, and so on. Because neither description describes the bonding in any real sense, these methods should, like the Lewis electron-dot approach in main group chemistry, be considered primarily electron

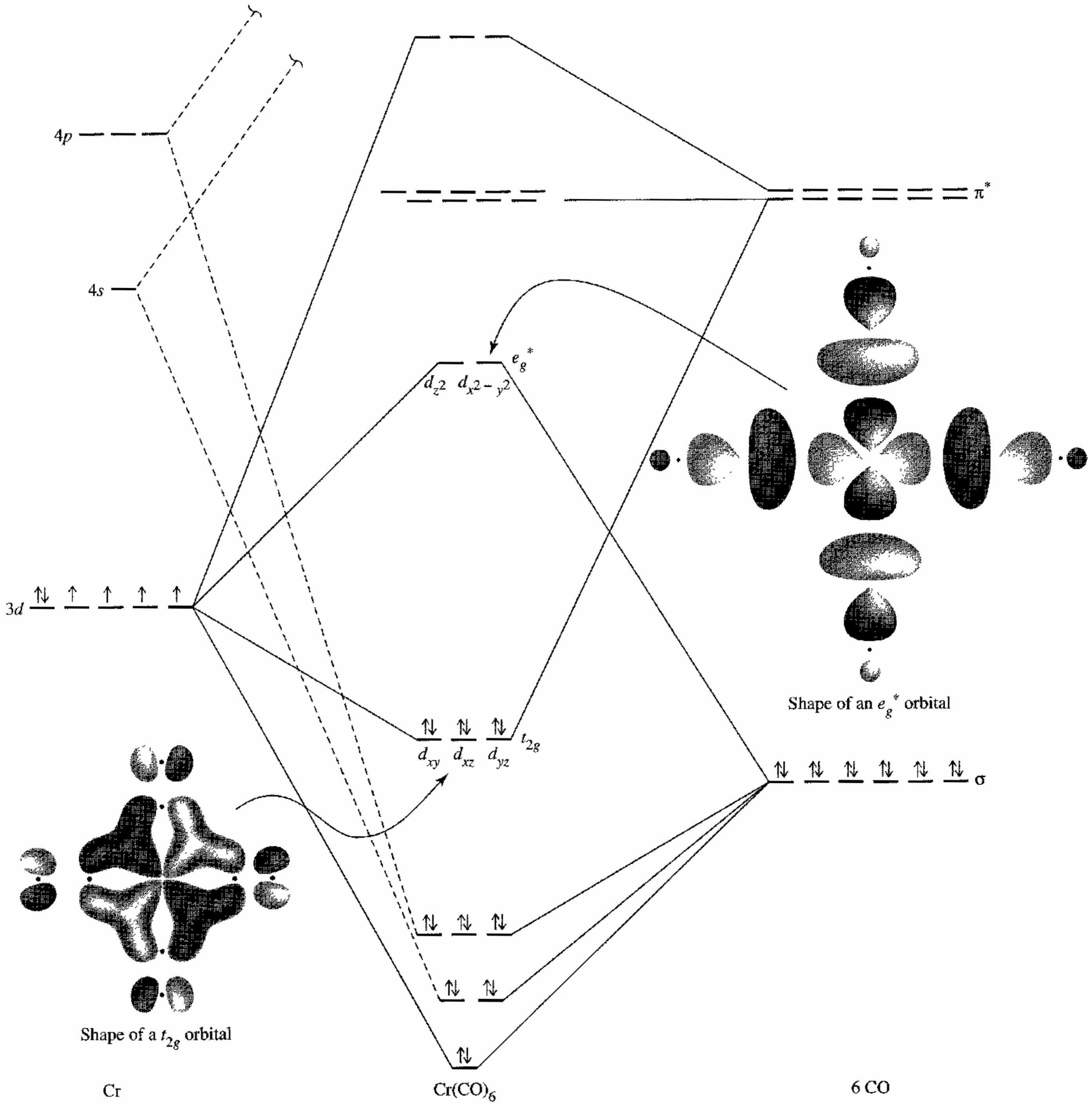

FIGURE 13-8 Molecular Orbital Energy Levels of $Cr(CO)_6$. (Adapted with permission from G. O. Spessard and G. L. Miessler, *Organometallic Chemistry*, Prentice Hall, Upper Saddle River, NJ, 1997, pp. 53–54, Figs. 3-2 and 3-3.)

or more electrons to $Cr(CO)_6$ would populate the e_g orbitals, which are antibonding; the consequence would be destabilization of the molecule. Removal of electrons from $Cr(CO)_6$ would depopulate the t_{2g} orbitals, which are bonding as a consequence of the strong π-acceptor ability of the CO ligands; a decrease in electron density in these orbitals would also tend to destabilize the complex. The result is that the 18-electron configuration for this molecule is the most stable.

By considering 6-coordinate molecules of octahedral geometry, we can gain some insight as to when the 18-electron rule can be expected to be most valid. $Cr(CO)_6$

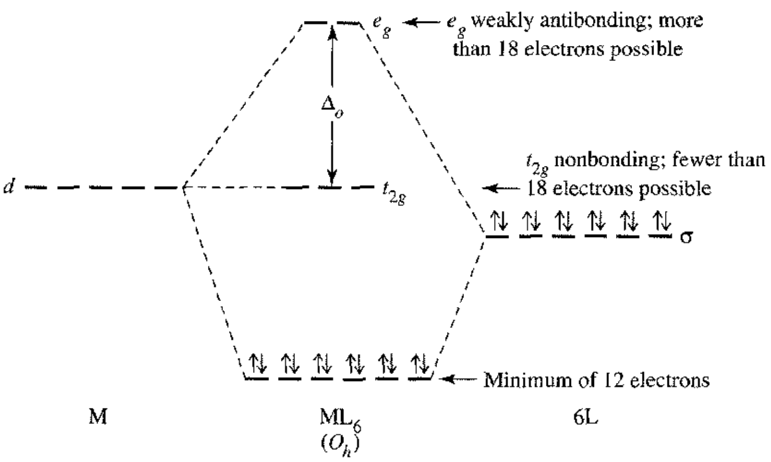

FIGURE 13-9 Exceptions to the 18-Electron Rule.

obeys the rule because of two factors: the strong σ-donor ability of CO raises the e_g orbitals in energy, making them considerably antibonding (and raising the energy of electrons in excess of 18); and the strong π-acceptor ability of CO lowers the t_{2g} orbitals in energy, making them bonding (and lowering the energies of electrons 13 through 18). Ligands that are both strong σ donors and π acceptors should therefore be the most effective at forcing adherence to the 18-electron rule. Other ligands, including some organic ligands, do not have these features and consequently their compounds may or may not adhere to the rule.

Examples of exceptions may be noted. $[Zn(en)_3]^{2+}$ is a 22-electron species; it has both the t_{2g} and e_g orbitals filled. Although en (ethylenediamine) is a good σ donor, it is not as strong a donor as CO. As a result, electrons in the e_g orbitals are not sufficiently antibonding to cause significant destabilization of the complex, and the 22-electron species, with 4 electrons in e_g orbitals, is stable. An example of a 12-electron species is TiF_6^{2-}. In this case, the fluoride ligand is a π donor as well as a σ donor. The π-donor ability of F^- destabilizes the t_{2g} orbitals of the complex, making them slightly antibonding. The species TiF_6^{2-} has 12 electrons in the bonding σ orbitals and no electrons in the antibonding t_{2g} or e_g orbitals. These examples of exceptions to the 18-electron rule are shown schematically in Figure 13-9.[13]

The same type of argument can be made for complexes of other geometries; in most, but not all, cases there is an 18-electron configuration of special stability for complexes of strongly π-accepting ligands. Examples include trigonal-bipyramidal geometry (e.g., $Fe(CO)_5$) and tetrahedral geometry (e.g., $Ni(CO)_4$). The most common exception is square-planar geometry, in which a 16-electron configuration may be the most stable, especially for complexes of d^8 metals.

13-3-3 SQUARE-PLANAR COMPLEXES

Examples of square-planar complexes include the d^8, 16-electron complexes shown in Figure 13-10. To understand why 16-electron square-planar complexes might be especially stable, it is necessary to examine the molecular orbitals of such a complex. An energy diagram for the molecular orbitals of a square-planar molecule of formula ML_4 (L = ligand that can function as both σ donor and π acceptor) is shown in Figure 13-11.[14]

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[13] P. R. Mitchell and R. V. Parish, *J. Chem. Ed.*, **1969**, *46*, 311.

[14] Figure 10-15 shows a more complete diagram.

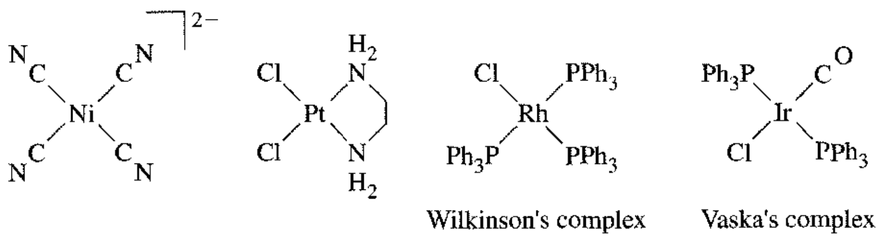

FIGURE 13-10 Examples of Square-Planar d^8 Complexes.

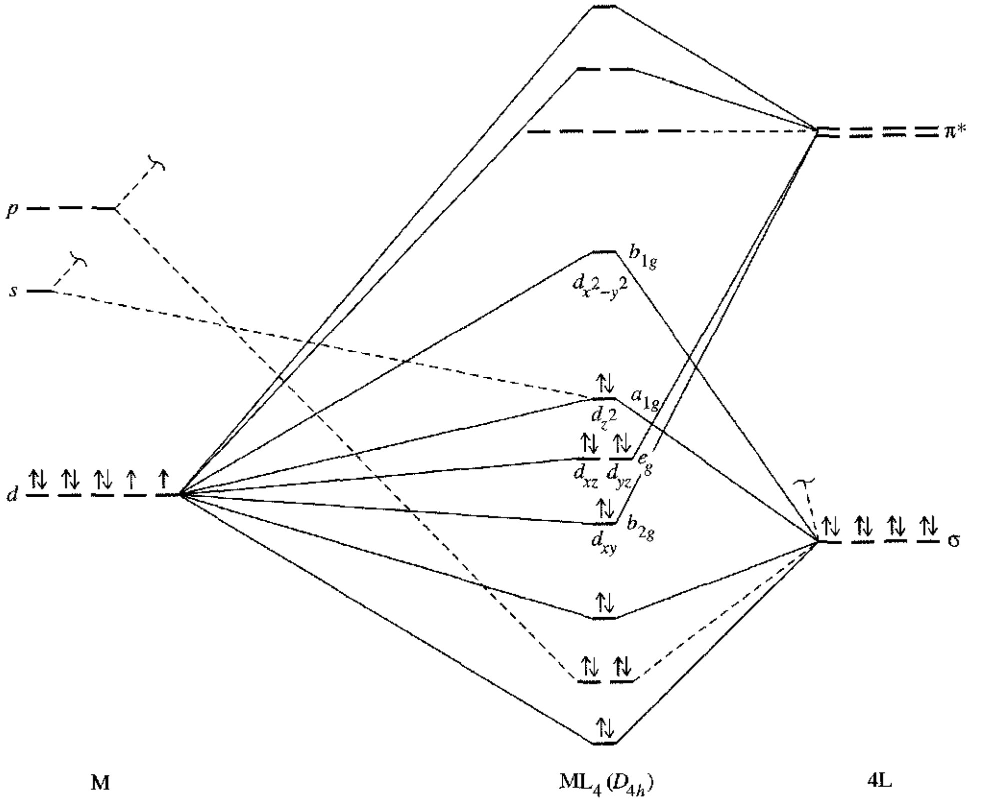

FIGURE 13-11 Molecular Orbital Energy Levels for a Square-Planar Complex.

The four lowest energy molecular orbitals in this diagram result from bonding interactions between the σ-donor orbitals of the ligands and the $d_{x^2-y^2}$, d_{z^2}, p_x, and p_y orbitals of the metal. These molecular orbitals are filled by 8 electrons from the ligands. The next four orbitals are either slightly bonding, nonbonding, or slightly antibonding (derived primarily from d_{xz}, d_{yz}, d_{xy}, and d_{z^2} orbital of the metal).[15] These orbitals are occupied by a maximum of 8 electrons from the metal.[16] Additional electrons would occupy an orbital derived from the antibonding interaction of a metal $d_{x^2-y^2}$ orbital with the σ-donor orbitals of the ligands (the $d_{x^2-y^2}$ orbital points directly toward the ligands; its antibonding interaction is therefore the strongest). Consequently, for square-planar complexes of ligands having both σ-donor and π-acceptor characteristics, a 16-electron configuration is more stable than an 18-electron configuration. Sixteen-electron square-planar complexes

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[15] The d_{z^2} orbital has A_{1g} symmetry and interacts with an A_{1g} group orbital. If this were the only metal orbital of this symmetry, the molecular orbital labeled d_{z^2} in Figure 13-11 would be antibonding. However, the next higher energy s orbital of the metal also has A_{1g} symmetry; the greater the degree to which this orbital is involved, the lower the energy of the molecular orbital.

[16] The relative energies of all four of these orbitals depend on the nature of the specific ligands and metal involved; in some cases, as shown in Figure 10-15, the ability of ligands to π donate can cause the order of energy levels to be different than shown in Figure 13-11.

may also be able to accept one or two ligands at the vacant coordination sites (along the *z* axis) and thereby achieve an 18-electron configuration. As will be shown in the next chapter, this is a common reaction of 16-electron square-planar complexes.

EXERCISE 13-3

Verify that the complexes in Figure 13-10 are 16-electron species.

Sixteen-electron square-planar species are most commonly encountered for d^8 metals, in particular for metals having formal oxidation states of 2+ (Ni^{2+}, Pd^{2+}, and Pt^{2+}) and 1+ (Rh^+, Ir^+). Square-planar geometry is also more common for second- and third-row transition metal complexes than for first-row complexes. Some square-planar complexes have important catalytic behavior. Two examples of square-planar d^8 complexes that are used as catalysts are Wilkinson's complex and Vaska's complex, shown in Figure 13-10.

13-4

LIGANDS IN ORGANOMETALLIC CHEMISTRY

Hundreds of ligands are known to bond to metal atoms through carbon. Carbon monoxide forms a very large number of metal complexes and deserves special mention, along with several similar diatomic ligands. Many organic molecules containing linear or cyclic π systems also form numerous organometallic complexes. Complexes containing such ligands will be discussed next, following a brief review of the π systems in the ligands themselves. Finally, special attention will be paid to two types of organometallic compounds of recent interest: carbene complexes, containing metal-carbon double bonds, and carbyne complexes, containing metal-carbon triple bonds.

13-4-1 CARBONYL (CO) COMPLEXES

Carbon monoxide is the most common ligand in organometallic chemistry. It serves as the only ligand in binary carbonyls such as $Ni(CO)_4$, $W(CO)_6$, and $Fe_2(CO)_9$ or, more commonly, in combination with other ligands, both organic and inorganic. CO may bond to a single metal or it may serve as a bridge between two or more metals. In this section, we will consider the bonding between metals and CO, the synthesis and some reactions of CO complexes, and examples of the various types of CO complexes.

Bonding

It is useful to review the bonding in CO. The molecular orbital picture of CO, shown in Figure 5-14, is similar to that of N_2. Sketches of the molecular orbitals derived primarily from the 2*p* atomic orbitals of these molecules are shown in Figure 13-12.

Two features of the molecular orbitals of CO deserve attention. First, the highest energy occupied orbital (the HOMO) has its largest lobe on carbon. It is through this orbital, occupied by an electron pair, that CO exerts its σ-donor function, donating electron density directly toward an appropriate metal orbital (such as an unfilled *d* or hybrid orbital). Carbon monoxide also has two empty π^* orbitals (the lowest unoccupied, or LUMO); these also have larger lobes on carbon than on oxygen. A metal atom having electrons in a *d* orbital of suitable symmetry can donate electron density to these π^* orbitals. These σ-donor and π-acceptor interactions are illustrated in Figure 13-13.

The overall effect is synergistic. CO can donate electron density via a σ orbital to a metal atom; the greater the electron density on the metal, the more effectively it can

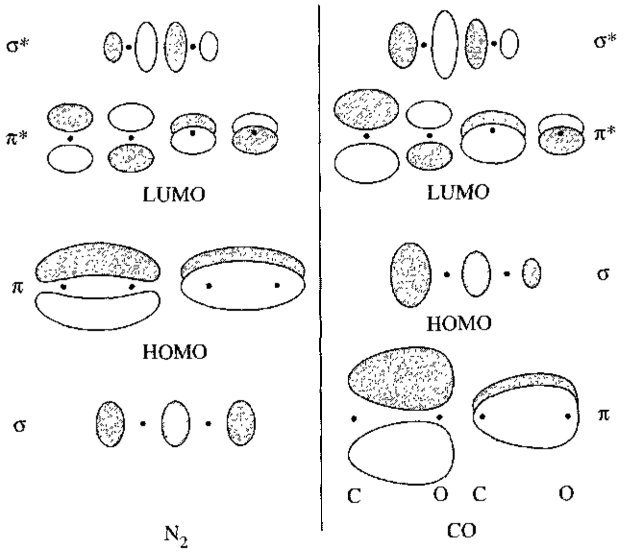

FIGURE 13-12 Selected Molecular Orbitals of N_2 and CO.

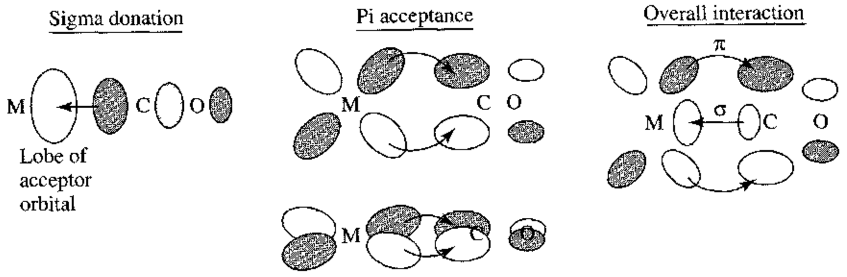

FIGURE 13-13 σ and π Interactions Between CO and a Metal Atom.

return electron density to the π* orbitals of CO. The net effect can be strong bonding between the metal and CO; however, as will be described later, the strength of this bonding depends on several factors, including the charge on the complex and the ligand environment of the metal.

EXERCISE 13-4

N_2 has molecular orbitals rather similar to those of CO, as shown in Figure 13-12. Would you expect N_2 to be a stronger or weaker π acceptor than CO?

If this picture of bonding between CO and metal atoms is correct, it should be supported by experimental evidence. Two sources of such evidence are infrared spectroscopy and X-ray crystallography. First, any change in the bonding between carbon and oxygen should be reflected in the C—O stretching vibration as observed by IR. As in organic compounds, the C—O stretch in organometallic complexes is often very intense (stretching the C—O bond results in a substantial change in dipole moment), and its energy often provides valuable information about the molecular structure. Free carbon monoxide has a C—O stretch at 2143 cm^{-1}. $Cr(CO)_6$, on the other hand, has its C—O stretch at 2000 cm^{-1}. The lower energy for the stretching mode means that the C—O bond is weaker in $Cr(CO)_6$.

The energy necessary to stretch a bond is proportional to $\sqrt{\frac{k}{\mu}}$, where k = force constant and μ = reduced mass; for atoms of mass m_1 and m_2, the reduced mass is given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

The stronger the bond between two atoms, the larger the force constant; consequently, the greater the energy necessary to stretch the bond and the higher the energy of the corresponding band (the higher the wavenumber, in cm^{-1}) in the infrared spectrum. Similarly, the more massive the atoms involved in the bond, as reflected in a higher reduced mass, the less energy necessary to stretch the bond and the lower the energy of the absorption in the infrared spectrum.

Both σ donation (which donates electron density from a bonding orbital on CO) and π acceptance (which places electron density in C—O antibonding orbitals) would be expected to weaken the C—O bond and to decrease the energy necessary to stretch that bond.

Additional evidence is provided by X-ray crystallography. In carbon monoxide, the C—O distance has been measured at 112.8 pm. Weakening of the C—O bond by the factors described above would be expected to cause this distance to increase. Such an increase in bond length is found in complexes containing CO, with C—O distances approximately 115 pm for many carbonyls. Although such measurements provide definitive measures of bond distances, in practice it is far more convenient to use infrared spectra to obtain data on the strength of C—O bonds.

The charge on a carbonyl complex is also reflected in its infrared spectrum. Five isoelectronic hexacarbonyls have the following C—O stretching bands (compare with $\nu(CO) = 2143\ cm^{-1}$ for free CO):[17]

Complex	*ν(CO), cm⁻¹*
$[Ti(CO)_6]^{2-}$	1748
$[V(CO)_6]^-$	1859
$Cr(CO)_6$	2000
$[Mn(CO)_6]^+$	2100
$[Fe(CO)_6]^{2+}$	2204

Of these five, $[Ti(CO)_6]^{2-}$ has the metal with the smallest nuclear charge; this means that titanium has the weakest ability to attract electrons and the greatest tendency to back-donate electron density to CO. Alternatively, the formal charges on the metals increase from −2 for $[Ti(CO)_6]^{2-}$ to +2 for $[Fe(CO)_6)]^{2+}$. The titanium in $[Ti(CO)_6]^{2-}$, with the most negative formal charge, has the strongest tendency to donate to CO. The consequence is strong population of the π^* orbitals of CO in $[Ti(CO)_6]^{2-}$ and reduction of the strength of the C—O bond. In general, the more negative the charge on the organometallic species, the greater the tendency of the metal to donate electrons to the π^* orbitals of CO and the lower the energy of the C—O stretching vibrations.

EXERCISE 13-5

Predict which of the complexes $[V(CO)_6]^-$, $Cr(CO)_6$, and $[Mn(CO)_6]^+$ has the shortest C—O bond.

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[17] The positions of the C—O stretching vibrations in the ions may be affected by interactions with solvents or counterions, and solid and solution spectra may differ slightly.

How is it possible for cationic carbonyl complexes such as $[Fe(CO)_6]^{2+}$ to have C—O stretching bands even higher in energy than those in free CO? It has been argued that in such complexes the CO ligand does not have π-acceptor activity and that the HOMO of CO, a σ orbital that is slightly antibonding with respect to the carbon-oxygen bond, acts as a donor to the metal. If this orbital were to act as a donor, there would be a decrease in the population of the HOMO and a consequent strengthening of the carbon-oxygen bond. However, calculations have demonstrated that it is much more likely that donation from the HOMO to the metal in cationic complexes is insignificant in comparison with the polarization effect caused by the metal cation.[18]

In free CO, the electrons are polarized toward the more electronegative oxygen. For example, the electrons in the π orbitals are concentrated nearer to the oxygen atom than to the carbon. The presence of a transition metal cation tends to reduce the polarization in the C—O bond by attracting the bonding electrons:

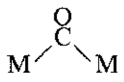
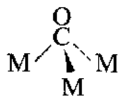
$$\overset{\delta+}{C}\equiv\overset{\delta-}{O} \qquad\qquad M^{n+} \longleftarrow \overset{\delta+}{C}\equiv\overset{\delta-}{O}$$

The consequence is that the electrons in the positively charged complex are more equally shared by the carbon and the oxygen, giving rise to a stronger bond and a higher energy C—O stretch.

Bridging modes of CO

Although CO is most commonly found as a terminal ligand attached to a single metal atom, many cases are known in which CO forms bridges between two or more metals. Many such bridging modes are known; the most common are shown in Table 13-2.

TABLE 13-2
Bridging Modes of CO

Type of CO	*Approximate Range for ν (CO) in Neutral Complexes (cm^{-1})*
Free CO	2143
Terminal M—CO	1850–2120
Symmetric[a] μ_2—CO 	1700–1860
Symmetric[a] μ_3—CO 	1600–1700

NOTE: [a] Asymmetrically bridging μ_2- and μ_3-CO are also known.

The bridging mode is strongly correlated with the position of the C—O stretching band. In cases in which CO bridges two metal atoms, both metals can contribute electron density into π* orbitals of CO to weaken the C—O bond and lower the energy of the stretch. Consequently, the C—O stretch for doubly bridging CO is at a much

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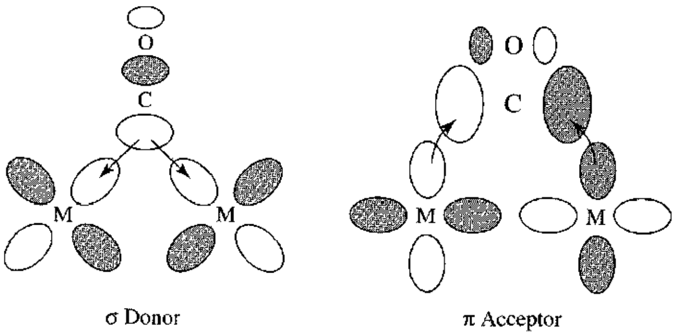
[18] A. S. Goldman and K. Krogh-Jespersen, *J. Am. Chem. Soc.*, **1996**, *118*, 12159.



σ Donor

π Acceptor

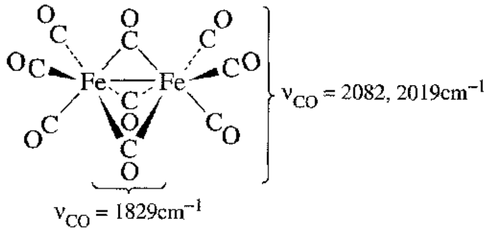
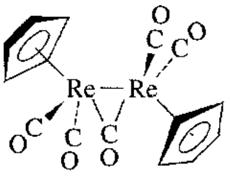


FIGURE 13-14 Bridging CO.

lower energy than for terminal COs. An example is shown in Figure 13-14. Interaction of three metal atoms with a triply bridging CO further weakens the C—O bond; the infrared band for the C—O stretch is still lower than in the doubly bridging case. (For comparison, carbonyl stretches in organic molecules are typically in the range 1700 to 1850 cm^{-1}, with many alkyl ketones near 1700 cm^{-1}.)

Ordinarily, terminal and bridging carbonyl ligands can be considered 2-electron donors, with the donated electrons shared by the metal atoms in the bridging cases. For example, in the complex



the bridging CO is a 2-electron donor overall, with a single electron donated to each metal. The electron count for each Re atom according to method B is

Re	7 e$^-$
η^5-C_5H_5	5 e$^-$
2 CO (terminal)	4 e$^-$
$\frac{1}{2}$(μ_2-CO)	1 e$^-$
M—M bond	1 e$^-$
Total =	18 e$^-$

A particularly interesting situation is that of nearly linear bridging carbonyls such as in $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2$. When a sample of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ is heated, some carbon monoxide is driven off; the product, $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2$, reacts readily with CO to reverse this reaction:[19]

$$\underset{1960,\ 1915\ \text{cm}^{-1}}{[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2} \overset{\Delta}{\rightleftharpoons} \underset{1889,\ 1859\ \text{cm}^{-1}}{[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2} + 2\,CO$$

---

[19] D. S. Ginley and M. S. Wrighton, *J. Am. Chem. Soc.*, **1975**, *97*, 3533; R. J. Klingler, W. Butler, and M. D. Curtis, *J. Am. Chem. Soc.*, **1975**, *97*, 3535.

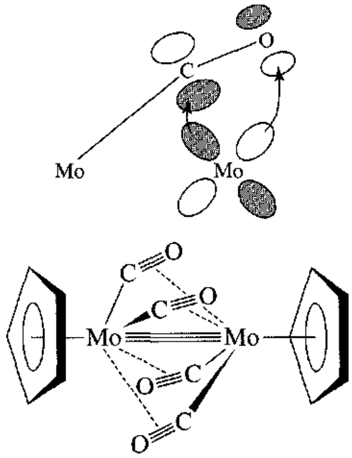


FIGURE 13-15 Bridging CO in $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2$.

This reaction is accompanied by changes in the infrared spectrum in the CO region, as listed above. The Mo—Mo bond distance also shortens by approximately 100 pm, consistent with an increase in the metal-metal bond order from 1 to 3. Although it was originally proposed that the "linear" CO ligands may donate some electron density to the neighboring metal from π orbitals, subsequent calculations have indicated that a more important interaction is donation from a metal *d* orbital to the π^* orbital of CO, as shown in Figure 13-15.[20] Such donation weakens the carbon-oxygen bond in the ligand and results in the observed shift of the C—O stretching bands to lower energies.

Additional information on infrared spectra of carbonyl complexes is included in Section 13-7 at the end of this chapter.

Binary carbonyl complexes

Binary carbonyls, containing only metal atoms and CO, are numerous. Some representative binary carbonyl complexes are shown in Figure 13-16. Most of these complexes obey the 18-electron rule. The cluster compounds $Co_6(CO)_{16}$ and $Rh_6(CO)_{16}$ do not obey the rule, however. More detailed analysis of the bonding in cluster compounds is necessary to satisfactorily account for the electron counting in these and other cluster compounds. This will be discussed in Chapter 15.

One other binary carbonyl does not obey the rule, the 17-electron $V(CO)_6$. This complex is one of a few cases in which strong π-acceptor ligands do not succeed in requiring an 18-electron configuration. In $V(CO)_6$, the vanadium is apparently too small to permit a seventh coordination site; hence, no metal-metal bonded dimer, which would give an 18-electron configuration, is possible. However, $V(CO)_6$ is easily reduced to $[V(CO)_6]^-$, a well-studied 18-electron complex.

EXERCISE 13-6

Verify the 18-electron rule for five of the binary carbonyls [other than $V(CO)_6$, $Co_6(CO)_{16}$ and $Rh_6(CO)_{16}$] shown in Figure 13-16.

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[20] A. L. Sargent and M. B. Hall, *J. Am. Chem. Soc.*, **1989**, *111*, 1563, and references therein.

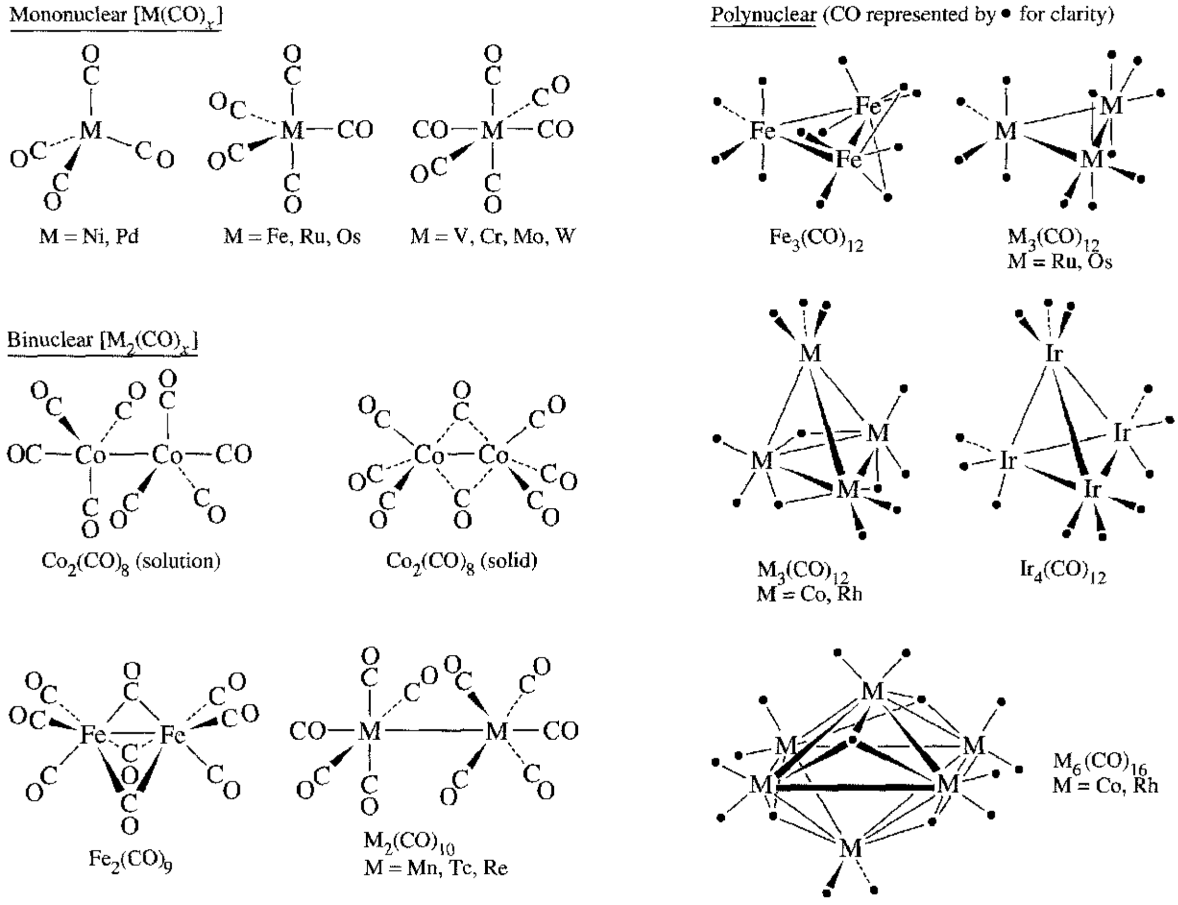

FIGURE 13-16 Binary Carbonyl Complexes.

An interesting feature of the structures of binary carbonyl complexes is that the tendency of CO to bridge transition metals decreases in going down the periodic table. For example, in $Fe_2(CO)_9$ there are three bridging carbonyls, but in $Ru_2(CO)_9$ and $Os_2(CO)_9$ there is a single bridging CO. A possible explanation is that the orbitals of bridging CO are less able to interact effectively with transition metal atoms as the size of the metals increases.

Binary carbonyl complexes can be synthesized in many ways. Several of the most common methods are as follows:

1. Direct reaction of a transition metal with CO. The most facile of these reactions involves nickel, which reacts with CO at ambient temperature and 1 atm:

$$Ni + 4\,CO \longrightarrow Ni(CO)_4$$

$Ni(CO)_4$ is a volatile, extremely toxic liquid that must be handled with great caution. It was first observed in Mond's study of the reaction of CO with nickel valves.[21] Because the reaction can be reversed at high temperature, coupling of the forward and reverse reactions has been used commercially in the Mond process for obtaining purified nickel from ores. Other binary carbonyls can be obtained from direct reaction of metal powders with CO, but elevated temperatures and pressures are necessary.

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[21] L. Mond, *J. Chem. Soc.*, **1890**, *57*, 749.

2. Reductive carbonylation: reduction of a metal compound in the presence of CO and an appropriate reducing agent. Examples are

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

$$Re_2O_7 + 17\,CO \longrightarrow Re_2(CO)_{10} + 7\,CO_2$$

(CO acts as a reducing agent in the second reaction; high temperature and pressure are required.)

3. Thermal or photochemical reaction of other binary carbonyls. Examples are

$$2\,Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9 + CO$$

$$3\,Fe(CO)_5 \xrightarrow{\Delta} Fe_3(CO)_{12} + 3\,CO$$

The most common reaction of carbonyl complexes is CO dissociation. This reaction, which may be initiated thermally or by absorption of ultraviolet light, characteristically involves loss of CO from an 18-electron complex to give a 16-electron intermediate, which may react in a variety of ways, depending on the nature of the complex and its environment. A common reaction is replacement of the lost CO by another ligand to form a new 18-electron species as product. For example,

$$Cr(CO)_6 + PPh_3 \xrightarrow[\text{or } h\nu]{\Delta} Cr(CO)_5(PPh_3) + CO$$

$$Re(CO)_5Br + en \xrightarrow{\Delta} \textit{fac}\text{-}Re(CO)_3(en)Br + 2\,CO$$

This type of reaction therefore provides a pathway in which CO complexes can be used as precursors for a variety of complexes of other ligands. Additional aspects of CO dissociation reactions will be discussed in Chapter 14.

Oxygen-bonded carbonyls

This section would not be complete without mentioning one additional aspect of CO as a ligand: it can sometimes bond through oxygen as well as carbon. This phenomenon was first noted in the ability of the oxygen of a metal-carbonyl complex to act as a donor toward Lewis acids such as $AlCl_3$, with the overall function of CO serving as a bridge between the two metals. Many examples are now known in which CO bonds through its oxygen to transition metal atoms, with the C—O—metal arrangement generally bent. Attachment of a Lewis acid to the oxygen results in significant weakening and lengthening of the C—O bond and a corresponding shift of the C—O stretching vibration to lower energy in the infrared. This shift is typically between 100 and 200 cm^{-1}. Examples of O-bonded carbonyls (sometimes called isocarbonyls) are shown in Figure 13-17. The physical and chemical properties of oxygen-bonded carbonyls have been reviewed.[22]

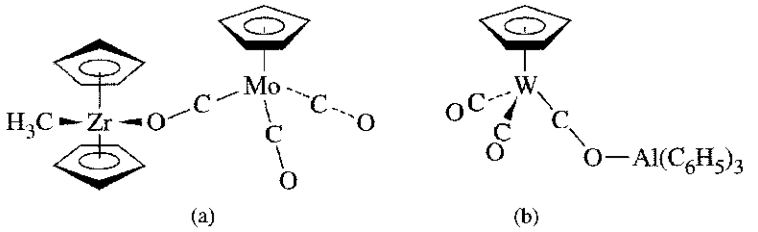

FIGURE 13-17 Oxygen-bonded Carbonyls.

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[22] C. P. Horwitz and D. F. Shriver, *Adv. Organomet. Chem.*, **1984**, *23*, 219.

13-4-2 LIGANDS SIMILAR TO CO

Several diatomic ligands similar to CO are worth brief mention. Two of these, CS (thiocarbonyl) and CSe (selenocarbonyl), are of interest in part for purposes of comparison with CO. In most cases, synthesis of CS and CSe complexes is somewhat more difficult than for analogous CO complexes, because CS and CSe do not exist as stable, free molecules and do not, therefore, provide a ready ligand source.[23] Therefore, the comparatively small number of such complexes should not be viewed as an indication of their stability. Thiocarbonyl complexes are also of interest as possible intermediates in certain sulfur transfer reactions in the removal of sulfur from natural fuels. In recent years, the chemistry of complexes containing these ligands has developed more rapidly as avenues for their synthesis have been devised.

CS and CSe are similar to CO in their bonding modes in that they behave as both σ donors and π acceptors and can bond to metals in terminal or bridging modes. Of these two ligands, CS has been studied more closely. It usually functions as a stronger σ donor and π acceptor than CO.[24]

Several other common ligands are isoelectronic with CO and, not surprisingly, exhibit structural and chemical parallels with CO. Two examples are CN^- and N_2. Complexes of CN^- have been known even longer than carbonyl complexes. For example, blue complexes (Prussian blue and Turnbull's blue) containing the ion $[Fe(CN)_6]^{3-}$ have been used as pigments in paints and inks for approximately three centuries. Cyanide is a stronger σ donor and a somewhat weaker π acceptor than CO; overall, it is close to CO in the spectrochemical series. Unlike most organic ligands, which bond to metals in low formal oxidation states, cyanide bonds readily to metals having higher oxidation states. As a good σ donor, CN^- interacts strongly with positively charged metal ions; as a weaker π acceptor than CO (largely a consequence of the negative charge of CN^-), cyanide is not as able to stabilize metals in low oxidation states. Therefore, its compounds are often studied in the context of classic coordination chemistry rather than organometallic chemistry.

The recent discovery that hydrogenase enzymes contain both CO and CN^- bound to iron has stimulated interest in complexes containing both ligands. Remarkably, only two iron complexes containing both CO and CN^- and a single iron atom, $[Fe(CO)(CN)_5]^{3-}$ (reported in 1887) and $[Fe(CO)_4(CN)]^-$ (reported in 1974), were known before 2001. Both the *cis* and *trans* isomers of $[Fe(CO)_2(CN)_4]^{2-}$ and *fac*-$[Fe(CO)_3(CN)_3]^-$ have recently been prepared by simple pathways. Two of the mixed ligand complexes can be prepared using $Fe(CO)_4I_2$ as starting material:[25]

$$Fe(CO)_4I_2 \xrightarrow{3\,CN^-} fac\text{-}[Fe(CO)_3(CN)_3]^- \xrightarrow{CN^-} cis\text{-}[Fe(CO)_2(CN)_4]^{2-}$$

The complex *trans*-$[Fe(CO)_2(CN)_4]^{2-}$ can be made simply by the addition of cyanide to a solution of $FeCl_2$ under an atmosphere of CO:[26]

$$FeCl_2(aq \text{ or } CH_3CN) + 4\,CN^- \xrightarrow{CO} trans\text{-}[Fe(CO)_2(CN)_4]^{2-}$$

Dinitrogen is a weaker donor and acceptor than CO. However, N_2 complexes are of great interest, especially as possible intermediates in reactions that may simulate natural processes of nitrogen fixation.

[23] E. J. Moltzen and K. J. Klabunde, *Chem. Rev.*, **1988**, *88*, 391, provides a detailed review of CS chemistry.

[24] P. V. Broadhurst, *Polyhedron*, **1985**, *4*, 1801.

[25] J. Jiang and S. A. Koch, *Inorg. Chem.*, **2002**, *41*, 158.

[26] J. Jiang and S. A. Koch, *Angew. Chem., Int. Ed.*, **2001**, *40*, 2629; T. B. Rauchfuss, S. M. Contakes, S. C. N. Hsu, M. A. Reynolds, and S. R. Wilson, *J. Am. Chem. Soc.*, **2001**, *123*, 6933; S. M. Contakes, S. C. N. Hsu, T. B. Rauchfuss, and S. R. Wilson, *Inorg. Chem.*, **2002**, *41*, 1670.

NO complexes

Although not an organic ligand, the NO (nitrosyl) ligand deserves discussion here because of its similarities to CO. Like CO, it is both a σ donor and π acceptor and can serve as a terminal or bridging ligand; useful information can be obtained about its compounds by analysis of its infrared spectra. Unlike CO, however, terminal NO has two common coordination modes, linear (like CO) and bent. Examples of NO complexes are shown in Figure 13-18.

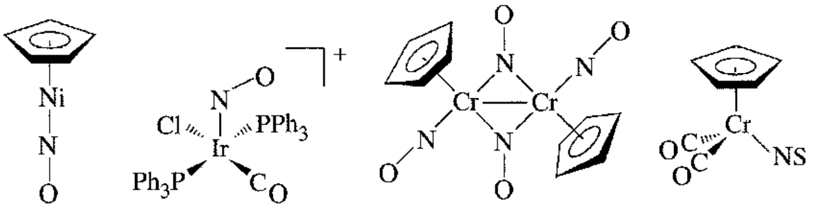
A formal analogy is often drawn between the linear bonding modes of both ligands. NO^+ is isoelectronic with CO; therefore, in its bonding to metals, linear NO is considered by electron-counting scheme A as NO^+, a 2-electron donor. By the neutral ligand method (B), linear NO is counted as a 3-electron donor (it has one more electron than the 2-electron donor CO).

The bent coordination mode of NO can be considered to arise formally from NO^-, with the bent geometry suggesting sp^2 hybridization at the nitrogen. By electron-counting scheme A, therefore, bent NO is considered the 2-electron donor NO^-; by the neutral ligand model, it is considered a 1-electron donor.

Although these electron-counting methods in NO complexes are useful, they do not describe how NO actually bonds to metals. The use of NO^+, NO, or NO^- does not necessarily imply degrees of ionic or covalent character in coordinated NO; these labels are simply convenient means of counting electrons.

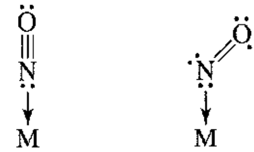
Useful information about the linear and bent bonding modes of NO is summarized in Figure 13-19. Many complexes containing each mode are known, and examples are also known in which both linear and bent NO occur in the same complex. Although linear coordination usually gives rise to N—O stretching vibrations at a higher energy than the bent mode, there is enough overlap in the ranges of these bands that infrared spectra alone may not be sufficient to distinguish between the two. Furthermore, the manner of packing in crystals may bend the metal—N—O bond considerably from 180° in the linear coordination mode.

One compound containing only a metal and NO ligands is known, $Cr(NO)_4$, a tetrahedral molecule that is isoelectronic with $Ni(CO)_4$.[27] Complexes containing bridging



Linear Bent Bridging NS complex

FIGURE 13-18 Examples of NO and NS Complexes.



	Linear	Bent
M—N—O angle	165°—180°	119°—140°
ν (N-O) in neutral molecules	1610—1830 cm^{-1}	1520—1720 cm^{-1}
Electron donor count	2 (as NO^+) 3 (as neutral NO)	2 (as NO^-) 1 (as neutral NO)

FIGURE 13-19 Linear and Bent Bonding Modes of NO.

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[27] Compounds containing only a single ligand, such as NO in $Cr(NO)_4$ and CO in $Mo(CO)_6$, are called homoleptic compounds.

nitrosyl ligands are also known, with the neutral bridging ligand formally considered a 3-electron donor. One NO complex, the nitroprusside ion, $[Fe(CN)_5(NO)]^{2-}$, has been widely used as a vasodilator in the treatment of high blood pressure. Its therapeutic effect is a consequence of its ability to release its NO ligand; the NO itself acts as the vasodilating agent.

In recent years, several dozen compounds containing the isoelectronic NS (thionitrosyl) ligand have been synthesized; one of these is shown in Figure 13-18. Infrared data have indicated that, like NO, NS can function in linear, bent, and bridging modes. In general, NS is similar to NO in its ability to act as a π-acceptor ligand; the relative π-acceptor abilities of NO and NS depend on the electronic environment of the compounds being compared.[28]

13-4-3 HYDRIDE AND DIHYDROGEN COMPLEXES

The simplest of all possible ligands is the hydrogen atom; similarly, the simplest possible diatomic ligand is H_2. It is perhaps not surprising that these ligands have gained attention by virtue of their apparent simplicity, as models for bonding schemes in coordination compounds. Moreover, both ligands have played important roles in the development of applications of organometallic chemistry to organic synthesis, and especially catalytic processes. Although the hydrogen atom (ordinarily designated the hydride ligand) has been recognized as an important ligand for many years, the significance of the dihydrogen ligand has become recognized only relatively recently.

Hydride complexes

Although hydrogen atoms form bonds with nearly every element, we will consider specifically coordination compounds containing H bonded to transition metals.[29] Because the hydrogen atom only has a 1*s* orbital of suitable energy for bonding, the bond between H and a transition metal must by necessity be a σ interaction, involving metal *s*, *p*, and/or *d* orbitals (or a hybrid orbital). As a ligand, H may be considered a 2-electron donor as hydride ($:H^-$, method A) or a 1-electron neutral donor (H atom, method B).

Although some transition metal complexes containing only the hydride ligand are known—an example of some structural interest is the 9-coordinate $[ReH_9]^{2-}$ ion (Figure 9-33), the classic example of a tricapped trigonal prism[30]—we are principally concerned with complexes containing H in combination with other ligands. Such complexes may be made in a variety of ways. Probably the most common synthesis is by reaction of a transition metal complex with H_2. For example,

$$Co_2(CO)_8 + H_2 \longrightarrow 2\,HCo(CO)_4$$

$$trans\text{-}Ir(CO)Cl(PEt_3)_2 + H_2 \longrightarrow Ir(CO)Cl(H)_2(PEt_3)_2$$

Carbonyl hydride complexes can also be formed by the reduction of carbonyl complexes, followed by the addition of acid. For example,

$$Co_2(CO)_8 + 2\,Na \longrightarrow 2\,Na^+[Co(CO)_4]^-$$

$$[Co(CO)_4]^- + H^+ \longrightarrow HCo(CO)_4$$

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[28] H. W. Roesky and K. K. Pandey, *Adv. Inorg. Chem. Radiochem.*, **1983**, *26*, 337.

[29] G. J. Kubas, *Comments Inorg. Chem.*, **1988**, *7*, 17; R. H. Crabtree, *Acc. Chem. Res.*, **1990**, *23*, 95; G. J. Kubas, *Acc. Chem. Res.*, **1988**, *21*, 120.

[30] S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, **1964**, *3*, 558.

One of the most interesting aspects of transition metal hydride chemistry is the relationship between this ligand and the rapidly developing chemistry of the dihydrogen ligand, H_2.

Dihydrogen complexes

Although complexes containing H_2 molecules coordinated to transition metals had been proposed for many years, the first structural characterization of a dihydrogen complex did not occur until 1984, when Kubas and coworkers synthesized $M(CO)_3(PR_3)_2(H_2)$ (M = Mo, W; R = cyclohexyl, isopropyl).[31] Subsequently, many H_2 complexes have been identified, and the chemistry of this ligand has developed rapidly.[32]

The bonding between dihydrogen and a transition metal can be described as shown in Figure 13-20. The σ electrons in H_2 can be donated to a suitable empty orbital on the metal (such as a *d* orbital or hybrid orbital), and the empty σ* orbital of the ligand can accept electron density from an occupied *d* orbital of the metal. The result is an overall weakening and lengthening of the H—H bond in comparison with free H_2. Typical H—H distances in complexes containing coordinated dihydrogen are in the range of 82 to 90 pm, in comparison with 74.14 pm in free H_2.

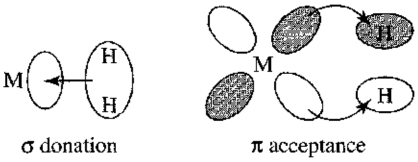

FIGURE 13-20 Bonding in Dihydrogen Complexes.

This bonding scheme leads to interesting ramifications that are distinctive from other donor-acceptor ligands such as CO. If the metal is electron rich and donates strongly to the σ* of H_2, the H—H bond in the ligand can rupture, giving separate H atoms. Consequently, the search for stable H_2 complexes has centered on metals likely to be relatively poor donors, such as those in high oxidation states or surrounded by ligands that function as strong electron acceptors. In particular, good π acceptors such CO and NO can be effective at stabilizing the dihydrogen ligand.

EXERCISE 13-7

Explain why $Mo(PMe_3)_5H_2$ is a dihydride (contains two separate H ligands), but $Mo(CO)_3(PR_3)_2(H_2)$ contains the dihydrogen ligand (Me = methyl, *R* = isopropyl).

Dihydrogen complexes have frequently been suggested as possible intermediates in a variety of reactions of hydrogen at metal centers. Some of these reactions are steps in catalytic processes of significant commercial interest. As this ligand becomes more completely understood, the applications of its chemistry are likely to become extremely important.

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[31] G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini, and H. J. Wasserman, *J. Am. Chem. Soc.*, **1984**, *106*, 451.

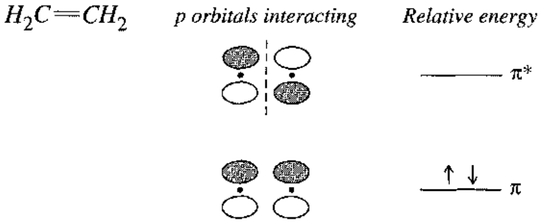
[32] J. K. Burdett, O. Eisenstein, and S. A. Jackson, "Transition Metal Dihydrogen Complexes: Theoretical Studies," in A. Dedieu, ed., *Transition Metal Hydrides*, VCH, New York, 1992, pp. 149–184.

13-4-4 LIGANDS HAVING EXTENDED π SYSTEMS

Although it is relatively simple to describe pictorially how ligands such as CO and PPh_3 bond to metals, explaining bonding between metals and organic ligands having extended π systems can be more complex. For example, how are the C_5H_5 rings attached to Fe in ferrocene, and how can 1,3-butadiene bond to metals? To understand the bonding between metals and π systems, we must first consider the π bonding within the ligands themselves. In the following discussion, we will first describe linear and then cyclic π systems, after which we will consider how molecules containing such systems can bond to metals.

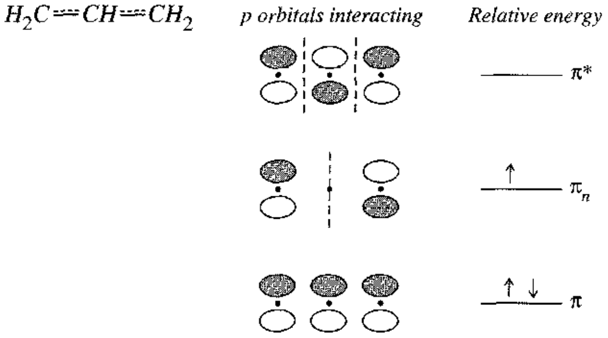
Linear π systems

The simplest case of an organic molecule having a linear π system is ethylene, which has a single π bond resulting from the interactions of two $2p$ orbitals on its carbon atoms. Interactions of these p orbitals result in one bonding and one antibonding π orbital, as shown:



The antibonding interaction has a nodal plane perpendicular to the internuclear axis, but the bonding interaction has no such nodal plane.

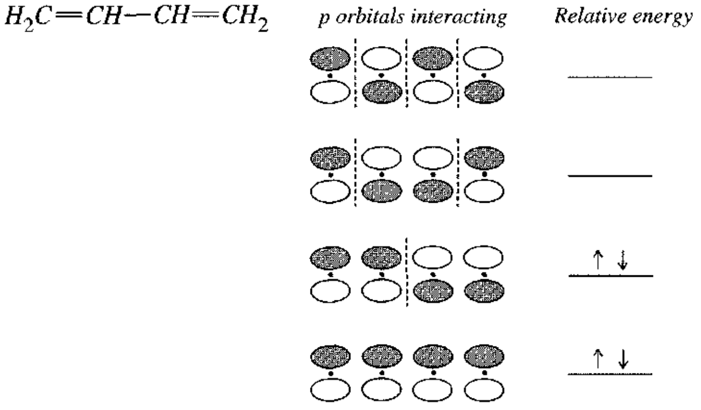
Next is the three-atom π system, the π-allyl radical, C_3H_5. In this case, there are three $2p$ orbitals to be considered, one from each of the carbon atoms participating in the π system. The possible interactions are as follows:



The lowest energy π molecular orbital for this system has all three p orbitals interacting constructively, to give a bonding molecular orbital. Higher in energy is the nonbonding orbital (π_n), in which a nodal plane bisects the molecule, cutting through the central carbon atom. In this case, the p orbital on the central carbon does not participate in the molecular orbital; a nodal plane passes through the center of this π orbital and thereby cancels it from participation in the molecular orbital. Highest in energy is the antibonding π^* orbital, in which there is an antibonding interaction between each neighboring pair of carbon p orbitals.

The number of nodes perpendicular to the carbon chain increases in going from lower energy to higher energy orbitals; for example, in the π-allyl system, the number of nodes increases from zero to one to two from the lowest to the highest energy orbital. This is a trend that will also appear in the following examples.

One more example should suffice to illustrate this procedure. 1,3-Butadiene may exist in *cis* or *trans* forms. For our purposes, we will treat both §as linear systems; the nodal behavior of the molecular orbitals is the same in each case as in a linear π system of four atoms. The $2p$ orbitals of the carbon atoms in the chain may interact in four ways, with the lowest energy π molecular orbital having all constructive interactions between neighboring p orbitals, and the energy of the other π orbitals increasing with the number of nodes between the atoms.


$H_2C{=}CH{-}CH{=}CH_2$

Similar patterns can be obtained for longer π systems; two more examples are included in Figure 13-21. As in the other examples, the number of π molecular orbitals is equal to the number of carbons in the π system.

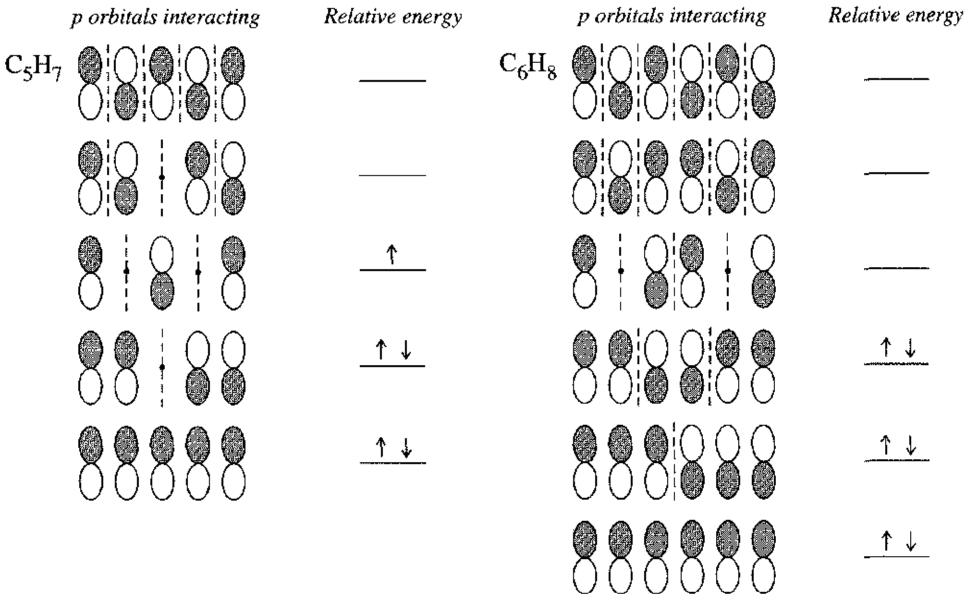
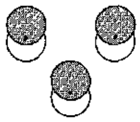


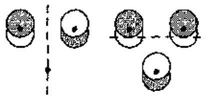
FIGURE 13-21 π Orbitals for Linear Systems.

Cyclic π systems

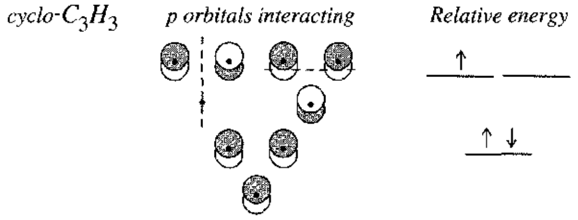
The procedure for obtaining a pictorial representation of the orbitals of cyclic π systems of hydrocarbons is similar to the procedure for the linear systems described above. The smallest such cyclic hydrocarbon is *cyclo*$-C_3H_3$. The lowest energy π molecular orbital for this system is the one resulting from constructive interaction between each of the $2p$ orbitals in the ring:



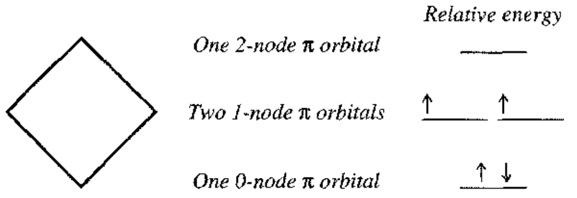
Because the number of molecular orbitals must equal the number of atomic orbitals used, two additional π molecular orbitals are needed. Each of these has a single nodal plane that is perpendicular to the plane of the molecule and bisects the molecule; the nodes for these two molecular orbitals are perpendicular to each other:



These molecular orbitals have the same energy; π molecular orbitals having the same number of nodes in cyclic π systems of hydrocarbons are degenerate (have the same energy). The total π molecular orbitals diagram for *cyclo*-C_3H_3 can therefore be summarized as follows:



A simple way to determine the p orbital interactions and the relative energies of the cyclic π systems that are regular polygons is to draw the polygon with one vertex pointed down. Each vertex then corresponds to the relative energy of a molecular orbital. Furthermore, the number of nodal planes perpendicular to the plane of the molecule increases as one goes to higher energy, with the bottom orbital having zero nodes, the next pair of orbitals a single node, and so on. For example, this scheme predicts that the next cyclic π system, *cyclo*-C_4H_4 (cyclobutadiene), would have molecular orbitals as follows:[33]



Similar results are obtained for other cyclic π systems; two of these are shown in Figure 13-22. In these diagrams, nodal planes are disposed symmetrically. For example, in *cyclo*-C_4H_4 the single-node molecular orbitals bisect the molecule through opposite sides; the nodal planes are oriented perpendicularly to each other. The 2-node orbital for this molecule also has perpendicular nodal planes.

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[33] This approach predicts a diradical for cyclobutadiene (one electron in each 1-node orbital). Although cyclobutadiene itself is very reactive (P. Reeves, T. Devon, and R. Pettit, *J. Am. Chem. Soc.*, **1969**, *91*, 5890), complexes containing derivatives of cyclobutadiene are known. At 8 K, cyclobutadiene itself has been isolated in an argon matrix (O. L. Chapman, C. L. McIntosh, and J. Pacansky, *J. Am. Chem. Soc.*, **1973**, *95*, 614; A. Krantz, C. Y. Lin, and M. D. Newton, *J. Am. Chem. Soc.*, **1973**, *95*, 2746).

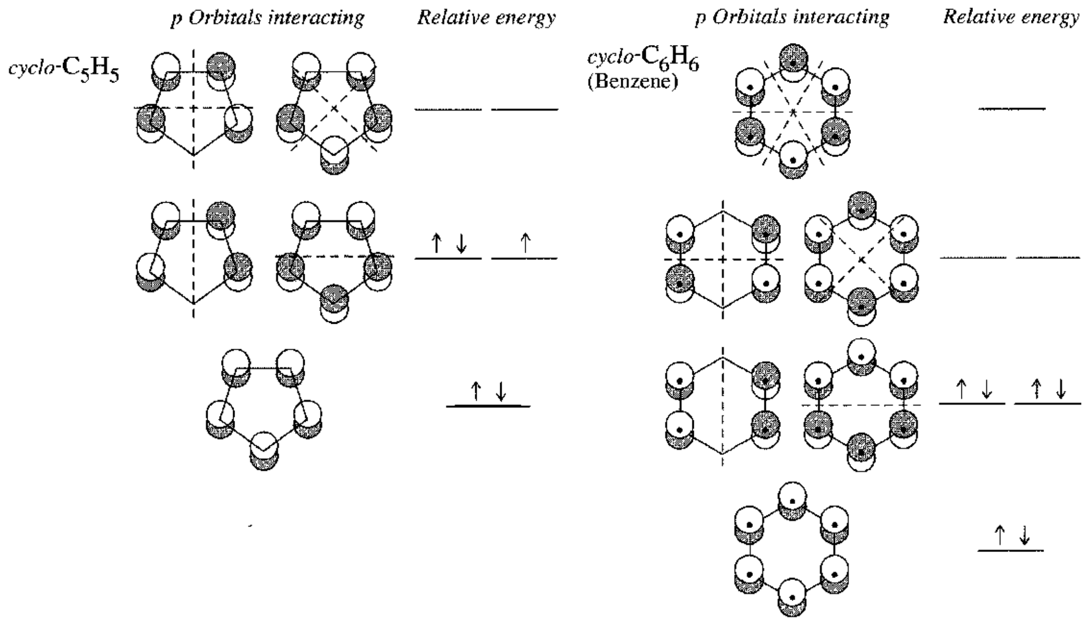


FIGURE 13-22 Molecular Orbitals for Cyclic π Systems.

This method may seem oversimplified, but the nodal behavior and relative energies are the same as those obtained from molecular orbital calculations. The method for obtaining equations for the molecular orbitals of cyclic hydrocarbons of formula C_nH_n (n = 3 to 8) is given by Cotton.[34] Throughout this discussion we have shown not the actual shapes of the π molecular orbitals, but rather the p orbitals used. The nodal behavior of both sets (the π orbitals and the p orbitals used) is identical and therefore sufficient for the discussion of bonding with metals that follows.[35]

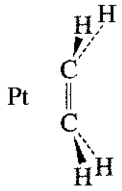
13-5 BONDING BETWEEN METAL ATOMS AND ORGANIC Π SYSTEMS

We are now ready to consider metal-ligand interactions involving such systems. We will begin with the simplest of the linear systems, ethylene, and conclude with the classic example of ferrocene.

13-5-1 LINEAR π SYSTEMS

π-Ethylene complexes

Many complexes involve ethylene, C_2H_4, as a ligand, including the anion of Zeise's salt, $[Pt(\eta^2\text{-}C_2H_4)Cl_3]^-$, one of the earliest organometallic complexes. In such complexes, ethylene most commonly acts as a sidebound ligand with the following geometry with respect to the metal:



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[34] F. A. Cotton, *Chemical Applications of Group Theory*, 3rd ed., Wiley-Interscience, 1990, pp. 142-159.

[35] Diagrams of many molecular orbitals for linear and cyclic π systems can be found in W. L. Jorgenson and L. Salem, *The Organic Chemist's Book of Orbitals*, Academic Press, New York, 1973.

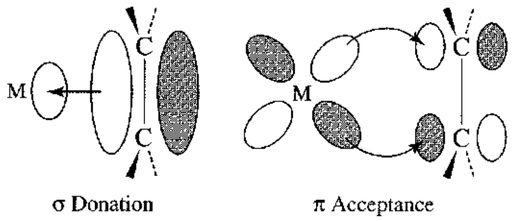


FIGURE 13-23 Bonding in Ethylene Complexes.

The hydrogens in ethylene complexes are typically bent back away from the metal, as shown. Ethylene donates electron density to the metal in a σ fashion, using its π-bonding electron pair, as shown in Figure 13-23. At the same time, electron density can be donated back to the ligand in a π fashion from a metal *d* orbital to the empty π* orbital of the ligand. This is another example of the synergistic effect of σ donation and π acceptance encountered earlier with the CO ligand.

If this picture of bonding in ethylene complexes is correct, it should be in agreement with the measured C—C distance. The C—C distance in Zeise's salt is 137.5 pm in comparison with 133.7 pm in free ethylene. The lengthening of this bond can be explained by a combination of the two factors involved in the synergistic σ-donor, π-acceptor nature of the ligand: donation of electron density to the metal in a σ fashion reduces the π-bonding electron density within the ligand, weakening the C—C bond. Furthermore, the back-donation of electron density from the metal to the π* orbital of the ligand also reduces the C—C bond strength by populating the antibonding orbital. The net effect weakens and lengthens the C—C bond in the C_2H_4 ligand. In addition, vibrational frequencies of coordinated ethylene are at lower energy than in free ethylene; for example, the C=C stretch in the anion of Zeise's salt is at 1516 cm^{-1} in comparison with 1623 cm^{-1} in free ethylene.

π-Allyl complexes

The allyl group most commonly functions as a trihapto ligand, using delocalized π orbitals as described previously, or as a monohapto ligand, primarily σ bonded to a metal. Examples of these types of coordination are shown in Figure 13-24.

Bonding between η^3-C_3H_5 and a metal atom is shown schematically in Figure 13-25. The lowest energy π orbital can donate electron density in a σ fashion to a suitable orbital on the metal. The next orbital, nonbonding in free allyl, can act as a donor or acceptor, depending on the electron distribution between the metal and the ligand. The highest energy π orbital acts as an acceptor; thus, there can be synergistic σ and π interactions between allyl and the metal. The C—C—C angle within the ligand is generally near 120°, consistent with sp^2 hybridization.

Allyl complexes (or complexes of substituted allyls) are intermediates in many reactions, some of which take advantage of the capability of this ligand to function in

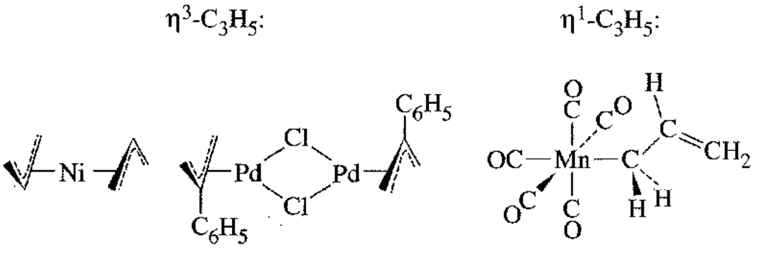


FIGURE 13-24 Examples of Allyl Complexes.

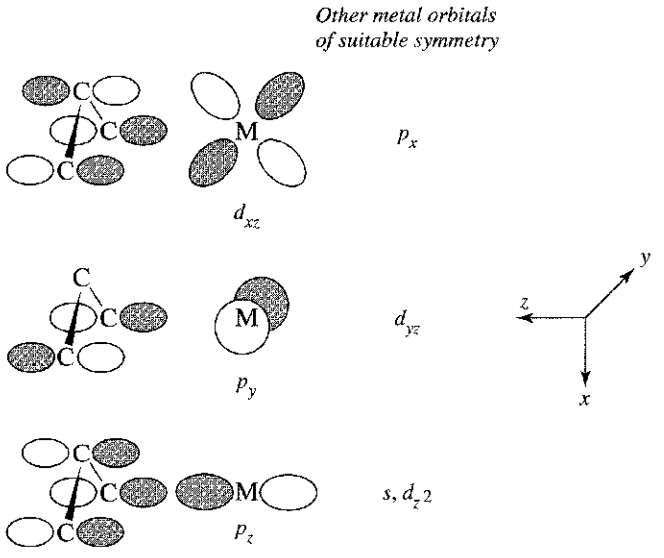
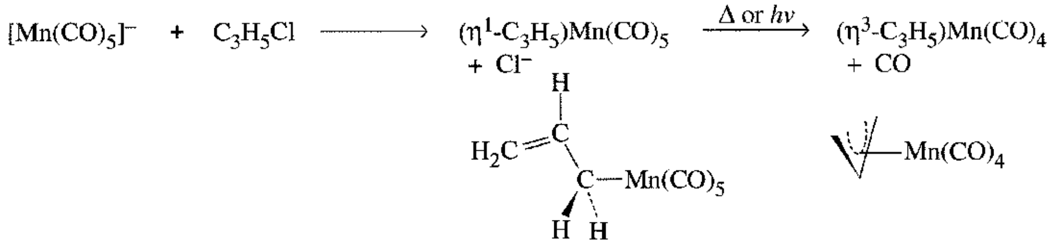


FIGURE 13-25 Bonding in η^3-Allyl Complexes.

both a η^3 and η^1 fashion. Loss of CO from carbonyl complexes containing η^1-allyl ligands often results in conversion of η^1- to η^3-allyl. For example,



$$[Mn(CO)_5]^- + C_3H_5Cl \longrightarrow \begin{matrix}(\eta^1\text{-}C_3H_5)Mn(CO)_5 \\ + Cl^-\end{matrix} \xrightarrow{\Delta \text{ or } h\nu} \begin{matrix}(\eta^3\text{-}C_3H_5)Mn(CO)_4 \\ + CO\end{matrix}$$

The $[Mn(CO)_5]^-$ ion displaces Cl^- from allyl chloride to give an 18-electron product containing η^1-C_3H_5. The allyl ligand switches to trihapto when a CO is lost, preserving the 18-electron count.

Other linear π systems

Many other such systems are known; several examples of organic ligands having longer π systems are shown in Figure 13-26. Butadiene and longer conjugated π systems have the possibility of isomeric ligand forms (*cis* and *trans* for butadiene). Larger cyclic ligands may have a π system extending through part of the ring. An example is cyclooctadiene (COD);

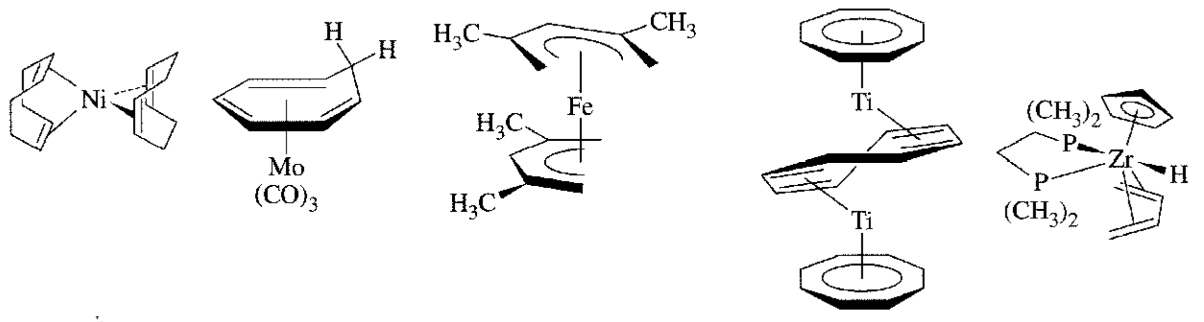


FIGURE 13-26 Examples of Molecules Containing Linear π Systems.

the 1,3-isomer has a 4-atom π system comparable to butadiene; 1,5-cyclooctadiene has two isolated double bonds, one or both of which may interact with a metal in a manner similar to ethylene.

EXERCISE 13-8

Identify the transition metal in the following 18-electron complexes:

a. $(\eta^5\text{-}C_5H_5)(cis\text{-}\eta^4\text{-}C_4H_6)M(PMe_3)_2(H)$ (M = second-row transition metal)

b. $(\eta^5\text{-}C_5H_5)M(C_2H_4)_2$ (M = first row-transition metal)

13-5-2 CYCLIC π SYSTEMS

Cyclopentadienyl (Cp) complexes

The cyclopentadienyl group, C_5H_5, may bond to metals in a variety of ways, with many examples known of the η^1-, η^3-, and η^5-bonding modes. As described previously in this chapter, the discovery of the first cyclopentadienyl complex, ferrocene, was a landmark in the development of organometallic chemistry and stimulated the search for other compounds containing π-bonded organic ligands. Substituted cyclopentadienyl ligands are also known, such as $C_5(CH_3)_5$ (often abbreviated Cp*) and C_5(benzyl)$_5$.

Ferrocene and other cyclopentadienyl complexes can be prepared by reacting metal salts with $C_5H_5^-$.[36]

$$FeCl_2 + 2\,NaC_5H_5 \longrightarrow (\eta^5\text{-}C_5H_5)_2Fe + 2\,NaCl$$

Ferrocene, $(\eta^5\text{-}C_5H_5)_2Fe$. Ferrocene is the prototype of a series of sandwich compounds, the metallocenes, with the formula $(C_5H_5)_2M$. Electron counting in ferrocene can be viewed in two ways. One possibility is to consider it an iron(II) complex with two 6-electron cyclopentadienide ($C_5H_5^-$) ions, another to view it as iron(0) coordinated by two neutral, 5-electron C_5H_5 ligands. The actual bonding situation in ferrocene is much more complicated and requires an analysis of the various metal-ligand interactions in this molecule. As usual, we expect orbitals on the central Fe and on the two C_5H_5 rings to interact if they have appropriate symmetry; furthermore, we expect interactions to be strongest if they are between orbitals of similar energy.

For the purposes of our analysis of this molecule, it will be useful to refer to Figure 13-22 for diagrams of the π molecular orbitals of a C_5H_5 ring. Two of these rings are arranged in a parallel fashion in ferrocene to "sandwich in" the metal atom. Our discussion will be based on the eclipsed D_{5h} conformation of ferrocene, the conformation consistent with gas phase and low-temperature data on this molecule.[37, 38] The same approach using the staggered conformation would yield a similar molecular orbital picture. Descriptions of the bonding in ferrocene based on D_{5d} symmetry are common in the chemical literature, because this was once believed to be the molecule's most stable conformation.[39]

In developing the group orbitals for a pair of C_5H_5 rings, we pair up molecular orbitals of the same energy and same number of nodes; for example, we pair the zero-

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[36] Solutions of NaC_5H_5 in tetrahydrofuran are available commercially. Alternatively, NaC_5H_5 can be prepared in the laboratory by cracking of dicyclopentadiene, followed by reduction:

$$C_{10}H_{12}(\text{dicyclopentadiene}) \longrightarrow 2\,C_5H_6(\text{cyclopentadiene})$$

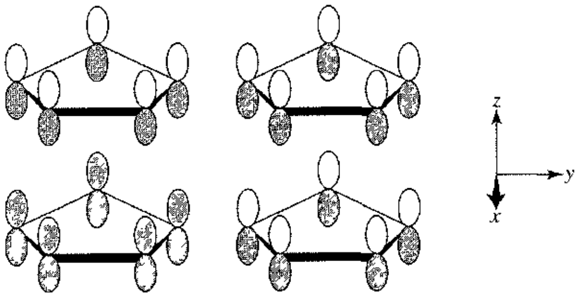
$$2\,Na + 2\,C_5H_6 \longrightarrow 2\,NaC_5H_5 + H_2$$

[37] A. Haaland and J. E. Nilsson, *Acta Chem. Scand.*, **1968**, *22*, 2653; A. Haaland, *Acc. Chem. Res.*, **1979**, *12*, 415.

[38] P. Seiler and J. Dunitz, *Acta Crystallogr., Sect. B*, **1982**, *38*, 1741.

[39] The $C_5(CH_3)_5$ and C_5(benzyl)$_5$ analogues of ferrocene do have staggered D_{5d} symmetry, as do several other metallocenes. See M.D. Rausch, W-M. Tsai, J. W. Chambers, R. D. Rogers, and H. G. Alt, *Organometallics*, **1989**, *8*, 816.

node orbital of one ring with the zero-node orbital of the other.[40] We also must pair up the molecular orbitals in such a way that the nodal planes are coincident. Furthermore, in each pairing there are two possible orientations of the ring molecular orbitals: one in which lobes of like sign are pointed toward each other, and one in which lobes of opposite sign are pointed toward each other. For example, the zero-node orbitals of the C_5H_5 rings may be paired in the following two ways:



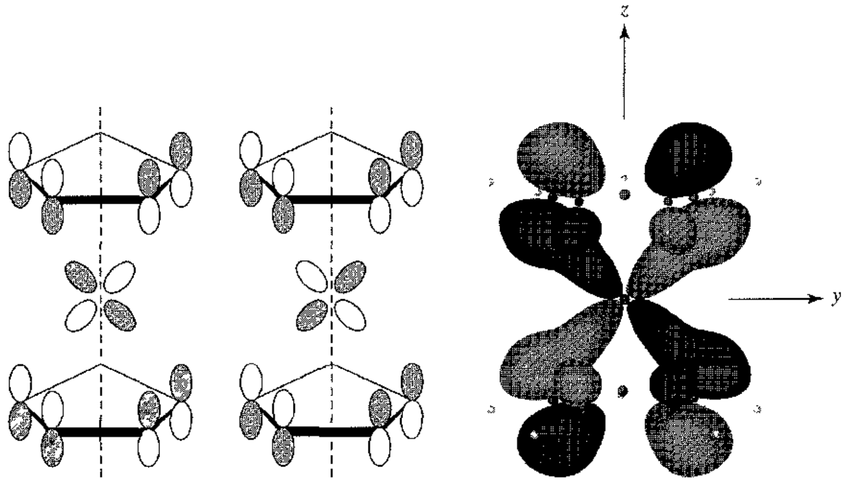
Orbital lobes of like sign pointed toward each other

Orbital lobes of opposite sign pointed toward each other

The ten group orbitals arising from the C_5H_5 ligands are shown in Figure 13-27.

The process of developing the molecular orbital picture of ferrocene now becomes one of matching the group orbitals with the *s*, *p*, and *d* orbitals of appropriate symmetry on Fe.

We will illustrate one of these interactions, between the d_{yz} orbital of Fe and its appropriate group orbital (one of the 1-node group orbitals shown in Figure 13-27). This interaction can occur in a bonding and an antibonding fashion:



Bonding
1

Antibonding
2

Actual shape of bonding orbital 1

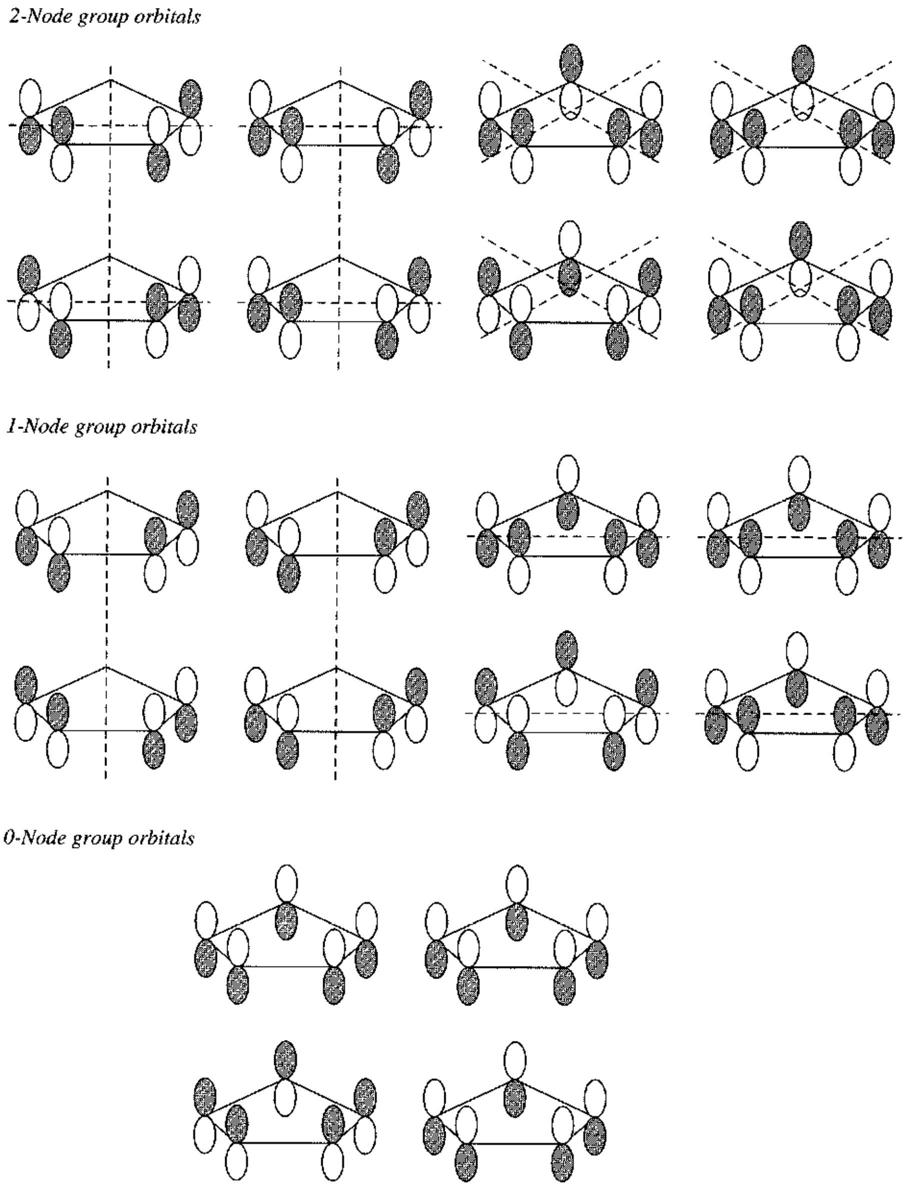
(Adapted with permission from G. O. Spessard and G. L. Miessler, *Organometallic Chemistry*, Prentice Hall, Upper Saddle River, NJ, 1997, p. 93, Fig. 5-7.)

EXERCISE 13-9

Determine which orbitals on Fe are appropriate for interaction with each of the remaining group orbitals in Figure 13-27.

---

[40] Not counting the nodal planes that are coplanar with the C_5H_5 rings.



2-Node group orbitals

1-Node group orbitals

0-Node group orbitals

FIGURE 13-27 Group Orbitals for C_5H_5 Ligands of Ferrocene.

The complete energy level diagram for the molecular orbitals of ferrocene is shown in Figure 13-28. The molecular orbital resulting from the d_{yz} bonding interaction, labeled **1** in the MO diagram, contains a pair of electrons. Its antibonding counterpart, **2**, is empty. It is a useful exercise to match the other group orbitals from Figure 13-27 with the molecular orbitals in Figure 13-28 to verify the types of metal-ligand interactions that occur.

The orbitals of ferrocene that are of most interest are those having the greatest *d*-orbital character; these are also the highest occupied and lowest unoccupied orbitals (HOMO and LUMO). These orbitals are highlighted in the box in Figure 13-28. Two of these orbitals, having largely d_{xy} and $d_{x^2-y^2}$ character, are weakly bonding and are occupied by electron pairs; one, having largely d_{z^2} character, is essentially nonbonding and is also occupied by an electron pair; and two,

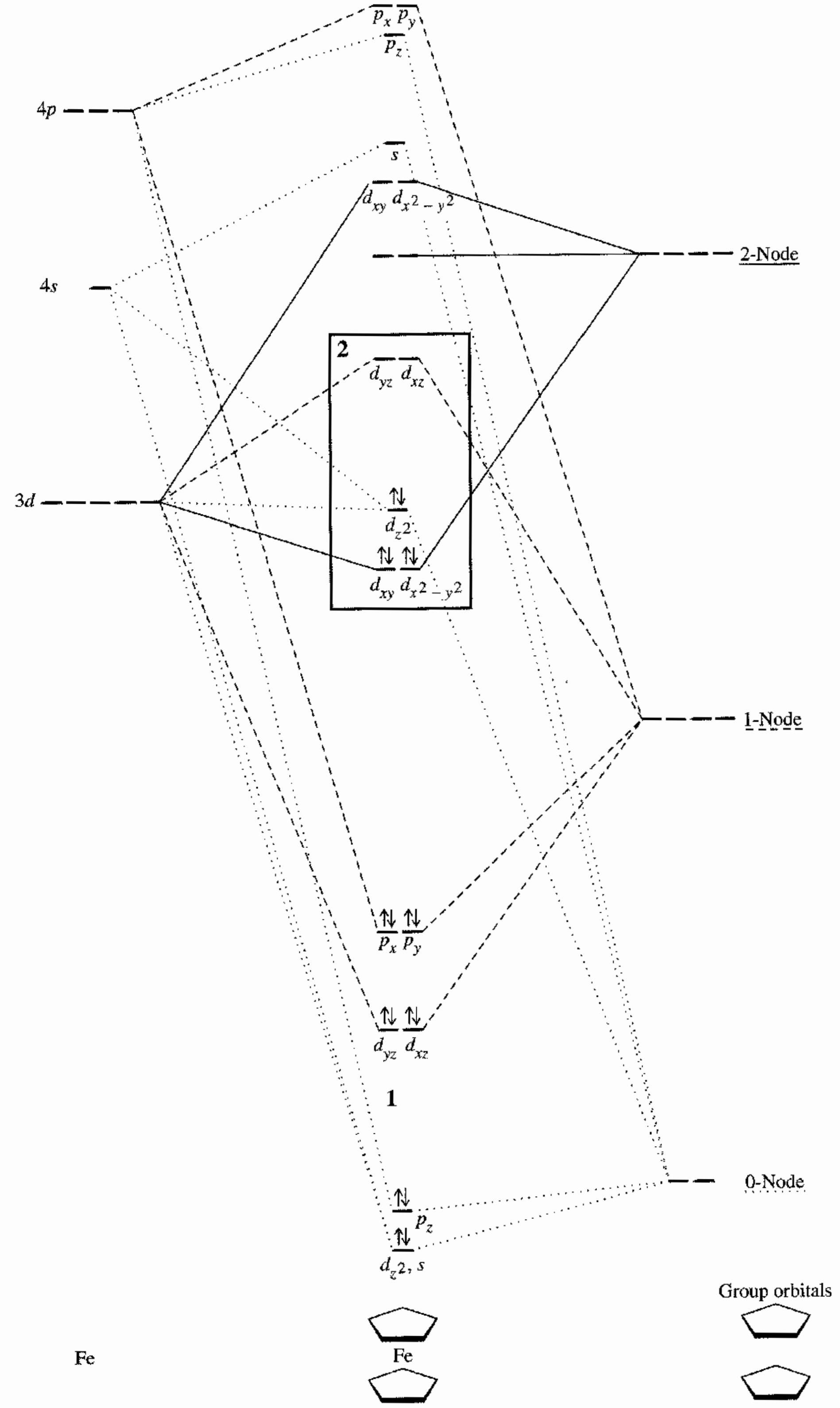


FIGURE 13-28 Molecular Orbital Energy Levels of Ferrocene.

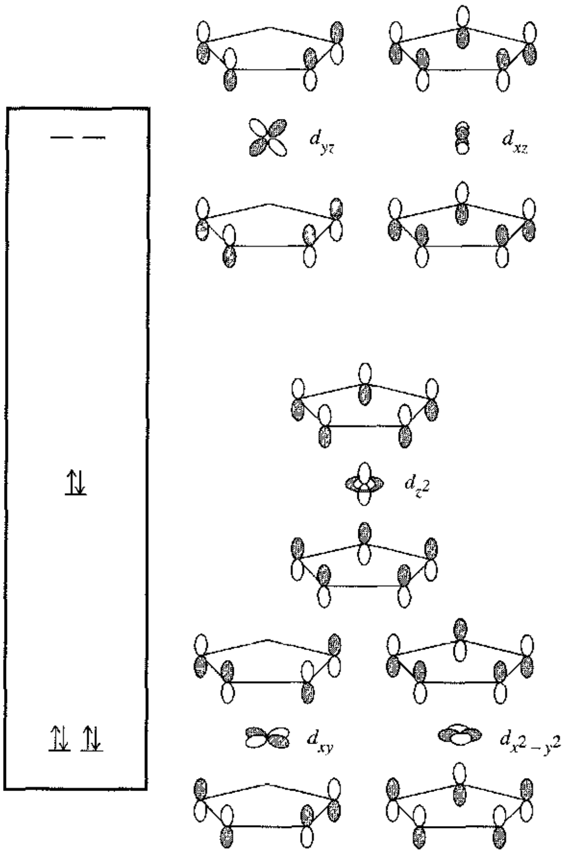


FIGURE 13-29 Molecular Orbitals of Ferrocene Having Greatest *d* Character.

having primarily d_{xz} and d_{yz} character, are empty. The relative energies of these orbitals and their *d*-orbital–group-orbital interactions are shown in Figure 13-29.[41, 42]

The overall bonding in ferrocene can now be summarized. The occupied orbitals of the η^5-C_5H_5 ligands are stabilized by their interactions with iron. Note especially the stabilization in energy of 0-node and 1-node group orbitals that have bonding interactions with the metal, forming molecular orbitals that are primarily ligand in nature (these are the orbitals labeled, from lowest to highest energy, d_{z^2}, s, p_z, d_{yz}, d_{xz}, p_x, and p_y).

The orbitals next highest in energy are largely derived from iron *d* orbitals; they are populated by 6 electrons as we would expect from iron (II), a d^6 metal ion. These molecular orbitals also have some ligand character, with the exception of the molecular orbital derived from d_{z^2}. The molecular orbital derived from d_{z^2} has almost no ligand character, because its cone-shaped nodal surface points almost directly toward the lobes of the matching group orbital, making overlap slight and giving an essentially nonbonding orbital localized on the iron. The molecular orbital description of ferrocene fits the 18-electron rule.

Other metallocenes have similar structures but do not necessarily obey the rule. For example, cobaltocene and nickelocene are structurally similar 19- and 20-electron species.

[41] The relative energies of the lowest three orbitals shown in Figure 13-29 have been a matter of controversy. UV photoelectron spectroscopy indicates that the order is as shown, with the orbital having largely d_{z^2} character slightly higher in energy than the degenerate pair having substantial d_{xy} and $d_{x^2-y^2}$ character. This order may be reversed for some metallocenes. See A. Haaland, *Acc. Chem. Res.*, **1979**, *12*, 415.

[42] J. C. Giordan, J. H. Moore, and J. A. Tossell, *Acc. Chem. Res.*, **1986**, *19*, 281; E. Rühl and A. P. Hitchcock, *J. Am. Chem. Soc.*, **1989**, *111*, 5069.

The extra electrons have important chemical and physical consequences, as can be seen from comparative data in Table 13-3. Electrons 19 and 20 of the metallocenes occupy slightly antibonding orbitals (largely d_{yz} and d_{xz} in character); as a consequence, the metal-ligand distance increases, and ΔH for metal-ligand dissociation decreases. Ferrocene itself shows much more chemical stability than cobaltocene and nickelocene; many of the chemical reactions of the latter are characterized by a tendency to yield 18-electron products. For example, ferrocene is unreactive toward iodine and rarely participates in reactions in which other ligands substitute for the cyclopentadienyl ligand. However, cobaltocene and nickelocene undergo the following reactions to give 18-electron products:

$$\underset{19\,e^-}{2\,(\eta^5\text{-}C_5H_5)_2Co} + I_2 \longrightarrow \underset{\substack{18\,e^-\\ \text{cobalticinium ion}}}{2\,[(\eta^5\text{-}C_5H_5)_2Co]^+} + 2\,I^-$$

$$\underset{20\,e^-}{(\eta^5\text{-}C_5H_5)_2Ni} + 4\,PF_3 \longrightarrow \underset{18\,e^-}{Ni(PF_3)_4} + \text{organic products}$$

TABLE 13-3
Comparative Data for Selected Metallocenes

Complex	*Electron Count*	M—C *Distance (pm)*	ΔH *for* M^{2+}-$C_5H_5^-$ *Dissociation (kJ/mol)*
$(\eta^5\text{-}C_5H_5)_2Fe$	18	206.4	1470
$(\eta^5\text{-}C_5H_5)_2Co$	19	211.9	1400
$(\eta^5\text{-}C_5H_5)_2Ni$	20	219.6	1320

Cobalticinium reacts with hydride to give a neutral, 18-electron sandwich compound in which one cyclopentadienyl ligand has been modified into η^4-C_5H_6, as shown in Figure 13-30.

Ferrocene, however, is by no means chemically inert. It undergoes a variety of reactions, including many on the cyclopentadienyl rings. A good example is that of electrophilic acyl substitution (Figure 13-31), a reaction paralleling that of benzene and its derivatives. In general, electrophilic aromatic substitution reactions are much more rapid for ferrocene than for benzene, an indication of greater concentration of electron density in the rings of the sandwich compound.

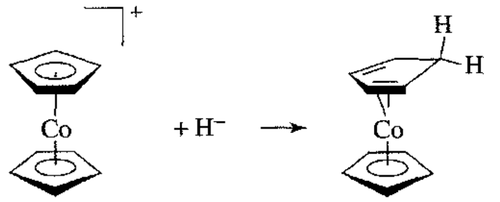


FIGURE 13-30 Reaction of Cobalticinium with Hydride.

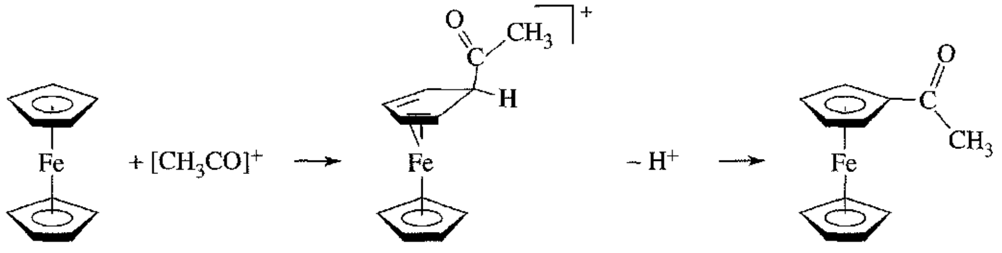


FIGURE 13-31 Electrophilic Acyl Substitution in Ferrocene.

Complexes containing cyclopentadienyl and CO ligands

Not surprisingly, many complexes are known containing both Cp and CO ligands. These include "half-sandwich" compounds such as (η^5-C_5H_5)Mn(CO)$_3$ and dimeric and larger cluster molecules. Examples are shown in Figure 13-32. As for the binary CO complexes, complexes of the second- and third-row transition metals show a decreasing tendency of CO to act as a bridging ligand.

Many other linear and cyclic π ligands are known. Examples of complexes containing some of these ligands are shown in Figure 13-33. Depending on the ligand and the electron requirements of the metal (or metals), these ligands may be capable of

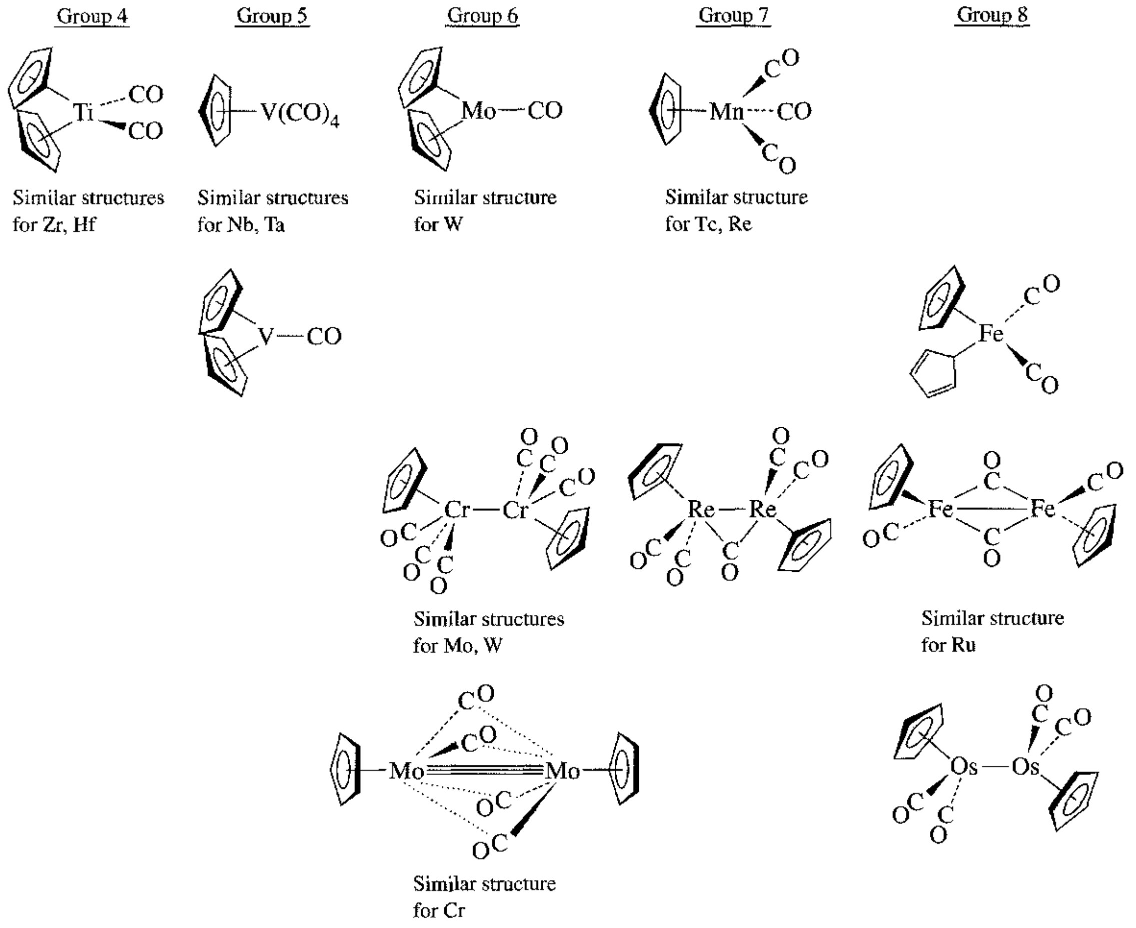


FIGURE 13-32 Complexes Containing C_5H_5 and CO.

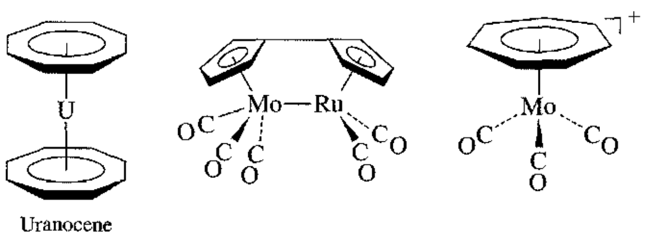


FIGURE 13-33 Examples of Molecules Containing Cyclic π Systems.

bonding in a monohapto or polyhapto fashion, and they may bridge two or more metals. Particularly interesting are the cases in which cyclic ligands can bridge metals to give "triple-decker" and higher order sandwich compounds. (See Figure 13-1.)

13-5-3 FULLERENE COMPLEXES

As immense π systems, fullerenes were early recognized as candidates to serve as ligands to transition metals. Fullerene-metal compounds[43] have now been prepared for a variety of metals. These compounds fall into several structural types:

- Adducts to the oxygens of osmium tetroxide.[44]
  Example: $C_{60}(OsO_4)(4\text{-}t\text{-butylpyridine})_2$
- Complexes in which the fullerene itself behaves as a ligand.[45]
  Examples: $Fe(CO)_4(\eta^2\text{-}C_{60})$, $Mo(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}C_{60})$, $[(C_6H_5)_3P]_2Pt(\eta^2\text{-}C_{60})$
- Compounds containing encapsulated metals. These may contain one, two, or three metals inside the fullerene sphere.[46]
  Examples: UC_{60}, LaC_{82}, Sc_2C_{74}, Sc_3C_{82}
- Intercalation compounds of alkali metals.[47] These contain alkali metal ions occupying interstitial sites between fullerene clusters.
  Examples: NaC_{60}, RbC_{60}, KC_{70}, K_3C_{60}

These are conductive, in some cases superconductive materials (such as K_3C_{60} and Rb_3C_{60}) and are of great interest in the field of materials science. These are principally ionic, rather than covalent compounds. The interested reader is encouraged to consult the reference below[48] for additional information about these compounds.

Adducts to oxygens of osmium tetroxide[49]

The first pure fullerene derivative to be prepared was $C_{60}(OsO_4)(4\text{-}t\text{-butylpyridine})_2$. The X-ray crystal structure of this compound provided the first direct evidence that the proposed structure for C_{60} was, in fact, correct. Osmium tetroxide, a powerful oxidizing agent, can add across the double bonds of many compounds, including polycyclic aromatic hydrocarbons. When OsO_4 was reacted with C_{60} and 4-*tert*-butylpyridine, 1:1 and 2:1 adducts were formed, products parallel to those anticipated in classic organic chemistry. The 1:1 adduct has been characterized by X-ray crystallography; its structure is shown in Figure 13-34.

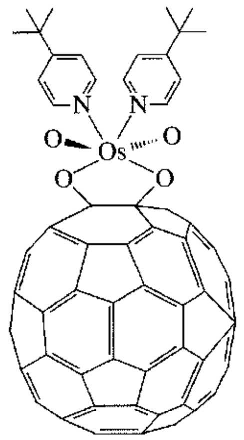


FIGURE 13-34 Structure of $C_{60}(OsO_4)(4\text{-}t\text{-butylpyridine})_2$.

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[43] For a review of metal complexes of C_{60} through 1991, see P. J. Fagan, J. C. Calabrese, and B. Malone, *Acc. Chem. Res.*, **1992**, *25*, 134.

[44] J. M. Hawkins, A. Meyer, T. A. Lewis, S. D. Loren, and F. J. Hollander, *Science*, **1991**, *252*, 312.

[45] P. J. Fagan, J. C. Calabrese, and B. Malone, "The Chemical Nature of C_{60} as Revealed by the Synthesis of Metal Complexes," in G. S. Hammond and V. J. Kuck, eds., *Fullerenes*, ACS Symposium Series 481, American Chemical Society, Washington, DC, 1992, pp. 177–186; R. E. Douthwaite, M. L. H. Green, A. H. H. Stephens, and J. F. C. Turner, *Chem. Commun. (Cambridge)*, **1993**, 1522; P. J. Fagan, J. C. Calabrese, and B. Malone, *Science*, **1991**, *252*, 1160.

[46] J. R. Heath, S. C. O'Brien, Q. Zhang, Y. Liu, R. F. Curl, H. W. Kroto, and R. E. Smalley, *J. Am. Chem. Soc.*, **1985**, *107*, 7779; H. Shinohara, H. Yamaguchi, N. Hayashi, H. Sato, M. Ohkohchi, Y. Ando, and Y. Saito, *J. Phys. Chem.*, **1993**, *97*, 4259.

[47] R. C. Haddon, A. F. Hebard, M. J. Rosseinsky, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, S. J. Duclos, R. M. Fleming, T. Siegrist, and R. Tycko, "Conductivity and Superconductivity in Alkali Metal Doped C_{60}," in Hammond and Kuck, *Fullerenes*, pp. 71–89.

[48] R. C. Haddon, *Acc. Chem. Res.*, **1992**, *25*, 127.

[49] J. M. Hawkins, *Acc. Chem. Res.*, **1992**, *25*, 150, and references therein.

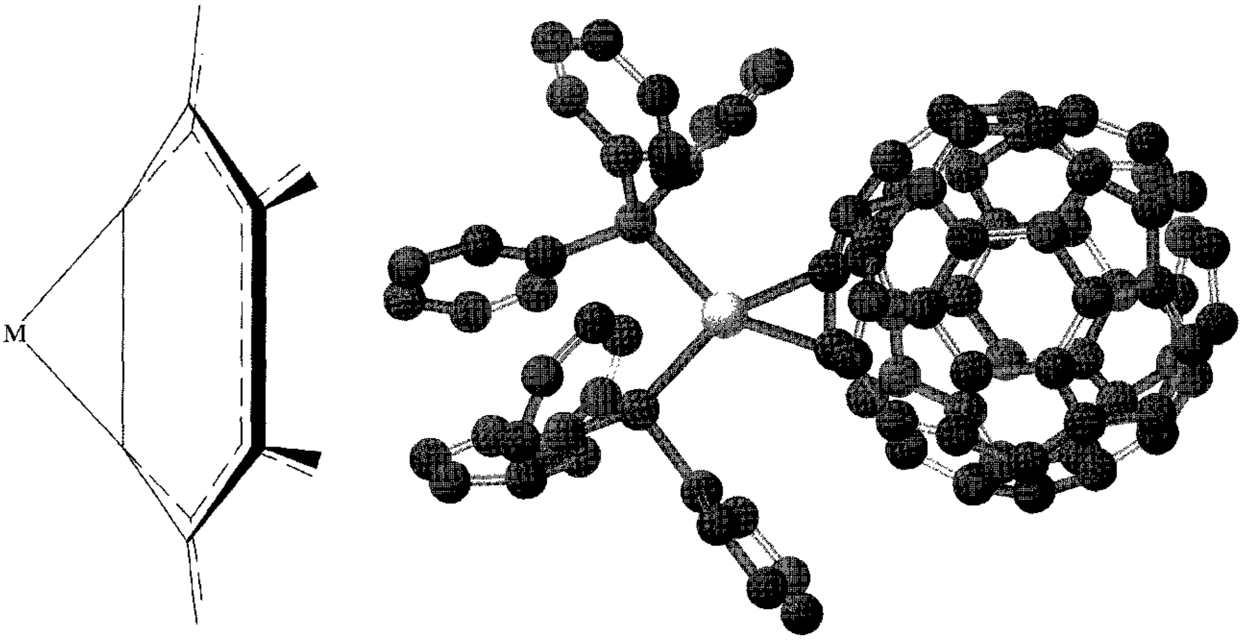

FIGURE 13-35 Bonding of C_{60} to Metal. (Adapted with permission from G. O. Spessard and G. L. Miessler, *Organometallic Chemistry*, Prentice Hall, Upper Saddle River, NJ, 1997, p. 509, Fig. 13-11.)

Fullerenes as ligands[50]

As a ligand, C_{60} behaves primarily as an electron-deficient alkene (or arene) and bonds to metals in a dihapto fashion through a C — C bond at the fusion of two 6-membered rings, as shown in Figure 13-35. However, there are also instances in which C_{60} bonds in a pentahapto or hexahapto fashion.

Dihapto bonding was observed in the first complex to be synthesized in which C_{60} acts as a ligand toward a metal, $[(C_6H_5)_3P]_2Pt(\eta^2\text{-}C_{60})$,[51] also shown in Figure 13-35.

A common route to the synthesis of complexes involving fullerenes as ligands is by displacement of other ligands, typically those weakly coordinated to metals. For example, the platinum complex shown in Figure 13-35 can be formed by the displacement of ethylene:

$$[(C_6H_5)_3P]_2Pt(\eta^2\text{-}C_2H_4) + C_{60} \longrightarrow [(C_6H_5)_3P]_2Pt(\eta^2\text{-}C_{60})$$

The *d* electron density of the metal can donate to an empty antibonding orbital of a fullerene. This pulls the two carbons involved slightly away from the C_{60} surface. In addition, the distance between these carbons is elongated slightly as a consequence of this interaction, which populates an orbital that is antibonding with respect to the C — C bond. This increase in C — C bond distance is analogous to the elongation that occurs when ethylene and other alkenes bond to metals, as discussed in Section 13-5-1.

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[50] P. J. Fagan, J. C. Calabrese, and B. Malone, *Acc. Chem. Res.*, **1992**, *25*, 134.

[51] P. J. Fagan, J. C. Calabrese, and B. Malone, *Science*, **1991**, *252*, 1160.

In some cases, more than one metal can become attached to a fullerene surface. A spectacular example is $[(Et_3P)_2Pt]_6C_{60}$,[52] shown in Figure 13-36. In this structure, the six $(Et_3P)_2Pt$ units are arranged octahedrally around the C_{60}.

Although complexes of C_{60} have been studied most extensively, some complexes of other fullerenes have also been prepared. An example is $(\eta^2\text{-}C_{70})Ir(CO)Cl(PPh_3)_2$, shown in Figure 13-37. As in the case of the known C_{60} complexes, bonding to the metal occurs at the fusion of two 6-membered rings.

C_{60} bonds to transition metals primarily in a *dihapto fashion*, but at least one example of a hexahapto structure has been reported. The coordination mode of the C_{60} in the triruthenium cluster in Figure 13-38(a) is perhaps best described as η^2, η^2, $\eta^2\text{-}C_{60}$, rather than $\eta^6\text{-}C_{60}$, because the C—C bonds bridged by the ruthenium atoms are slightly shorter than the other C—C bonds in the 6-membered ring.

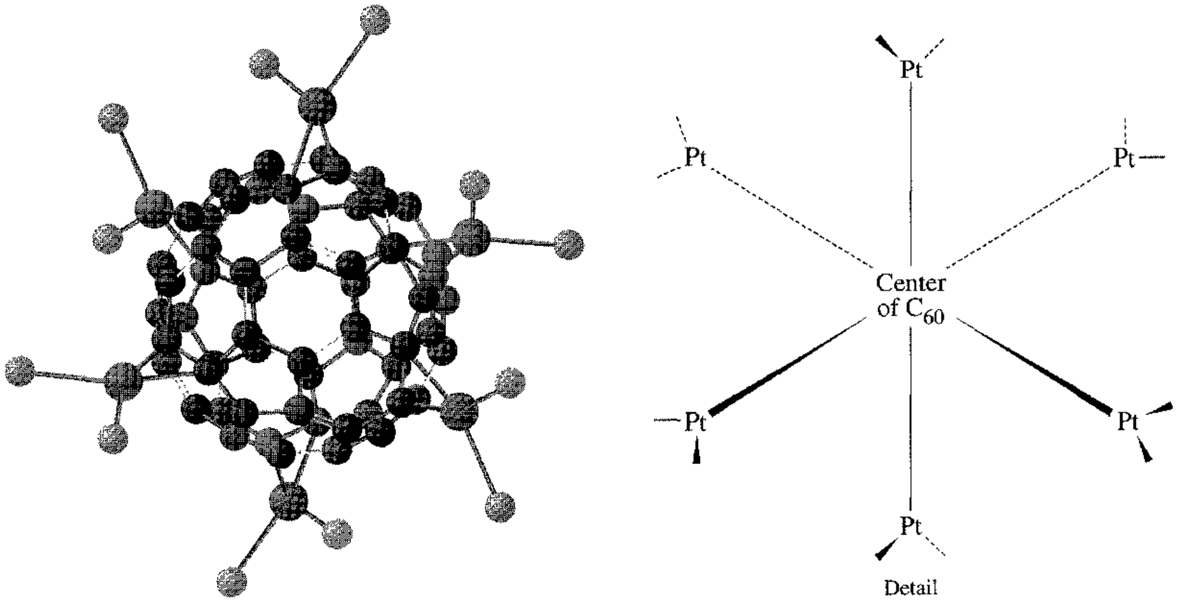

FIGURE 13-36 Structure of $[(Et_3P)_2Pt]_6C_{60}$. (Adapted with permission from G. O. Spessard and G. L. Miessler, *Organometallic Chemistry*, Prentice Hall, Upper Saddle River, NJ, 1997, p. 511, Fig. 13-13).

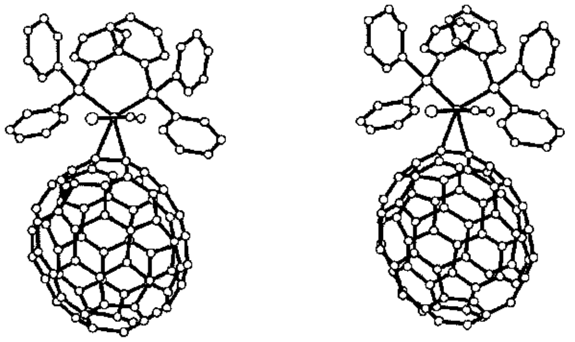

FIGURE 13-37 Stereoscopic View of $(\eta^2\text{-}C_{70})Ir(CO)Cl(PPh_3)_2$. (Reproduced with permission from A. L. Balch, V. J. Catalano, J. W. Lee, M. M. Olmstead, and S. R. Parkin, *J. Am. Chem. Soc.*, **1991**, *113*, 8953, © 1991 American Chemical Society.)

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[52] P. J. Fagan, J. C. Calabrese, and B. Malone, *J. Am. Chem. Soc.*, **1991**, *113*, 9408. See also P. V. Broadhurst, *Polyhedron*, **1985**, *4*, 1801.

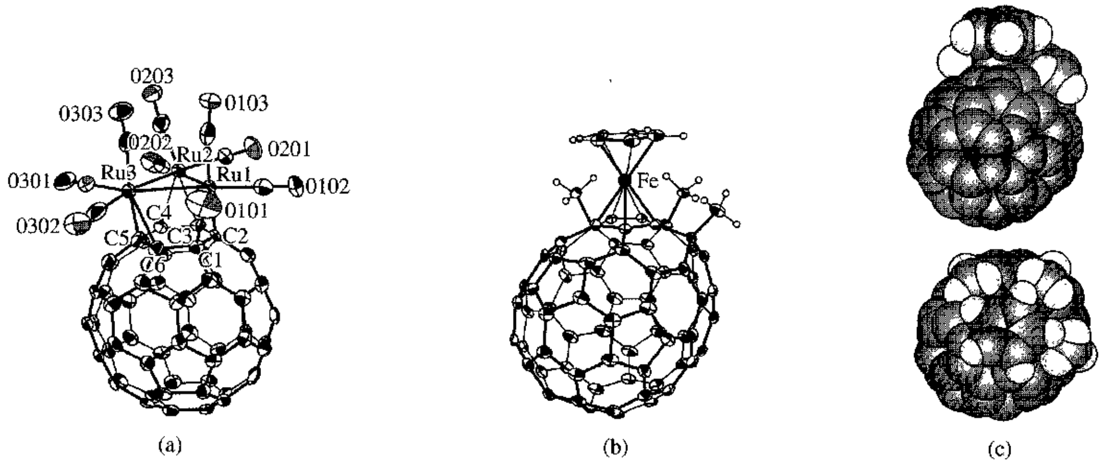

FIGURE 13-38 (a) $Ru_3(CO)_9(\mu_3\text{-}\eta^2, \eta^2, \eta^2\text{-}C_{60})$. (b) and (c) $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_{70}(CH_3)_3)$ in Ortep and space-filling formats. (Reproduced with permission from H.-F. Hsu and J. R. Shapley, *J. Am. Chem. Soc.*, **1996**, *118*, 9192, and from M. Sawamura, Y. Kuninobu, M. Toganoh, Y. Matsuo, M. Yamanaka, and E. Nakamura, *J. Am. Chem. Soc.*, **2002**, *124*, 9354. © 1996 American Chemical Society.)

Recently, hybrids of a fullerene and a ferrocene have been reported in which an ion is sandwiched between a $\eta^5\text{-}C_5H_5$ ring and a η^5-fullerene, shown in Figure 13-38(b). The fullerenes used, $C_{60}(CH_3)_5$, and $C_{70}(CH_3)_3$, have methyl groups that apparently help stabilize these compounds. The methyl groups are bonded to carbons adjacent to the 5-membered ring to which the iron bonds.

Complexes with encapsulated metals

These complexes are structural examples of "cage" organometallic complexes in which the metal is completely surrounded by the fullerene. Typically, complexes containing encapsulated metals are prepared by laser-induced vapor phase reactions between carbon and the metals. These compounds contain central metal cations surrounded by a fulleride, a fullerene that has been reduced.

Chemical formulas of fullerene compounds containing encapsulated metals are written with the @ symbol to designate encapsulation: Examples are

$U@C_{60}$	contains U surrounded by C_{60}
$Sc_3@C_{82}$	contains three atoms of Sc surrounded by C_{82}[53]

This designation indicates structure only and does not include charges on ions that may occur. For example, $La@C_{82}$ is believed to contain La^{3+} surrounded by the $C_{82}{}^{3-}$. Small molecules and ions can also be encapsulated in fullerenes. An example is $Sc_3N@C_{78}$, which contains a triangular Sc_3N inside the C_{78} cage, shown in Figure 13-39.

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[53] H. Shinohara, H. Yamaguchi, N. Mayashi, H. Sato, M. Ohkohchi, Y. Ando, and Y. Saito, *J. Phys. Chem.*, **1993**, *97*, 4259.

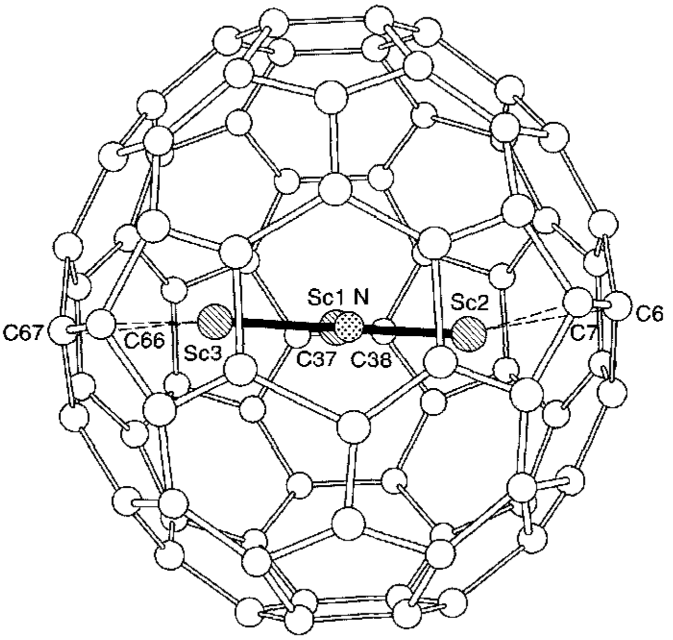


FIGURE 13-39 $Sc_3N@C_{80}$. At the low temperature used for the X-ray study, the Sc_3N is planar, with angles of 130.3°, 113.8°, and 115.9°, and each Sc bonds loosely to a C—C bond that is part of two six-membered rings; however, at higher temperatures, the Sc_3N cluster moves freely inside the cage. (Reproduced with permission from M. M. Olmstead, A. de Bettencort-Dias, J. C. Duchamp, S. Stevenson, D. Marciu, H. C. Dorn, and A. L. Balch, *Angew. Chem., Int. Ed.*, **2001**, *40*, 1223.)

13-6

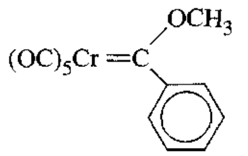
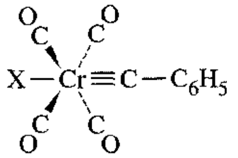
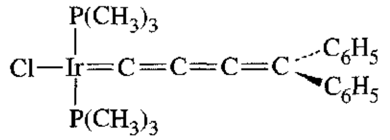
COMPLEXES CONTAINING M—C, M=C, AND M≡C BONDS

Complexes containing direct metal-carbon single, double, and triple bonds have been studied extensively. Table 13-4 gives examples of the most important types of ligands in these complexes.

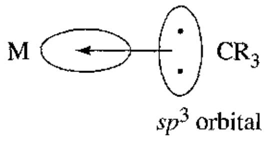
13-6-1 ALKYL AND RELATED COMPLEXES

Some of the earliest known organometallic complexes were those having σ bonds between main group metal atoms and alkyl groups. Examples include Grignard reagents, having magnesium-alkyl bonds (Figure 8-10), and alkyl complexes with alkali metals, such as methyllithium.

TABLE 13-4
Complexes Containing M—C, M=C, and M≡C Bonds

Ligand	*Formula*	*Example*
Alkyl	$-CR_3$	$W(CH_3)_6$
Carbene (alkylidene)	$=CR_2$	 $(OC)_5Cr=C(OCH_3)(C_6H_5)$
Carbyne (alkylidyne)	$\equiv CR$	 $X-Cr(CO)_4\equiv C-C_6H_5$
Cumulene	$=C(=C)_nRR'$	 $Cl-Ir(P(CH_3)_3)_2=C=C=C=C(C_6H_5)_2$

The first stable transition metal alkyls were synthesized in the first decade of the twentieth century; many such complexes are now known. The metal-ligand bonding in these complexes may be viewed as primarily involving covalent sharing of electrons between the metal and the carbon in a σ fashion, as shown here:



(R = H, alkyl, aryl)

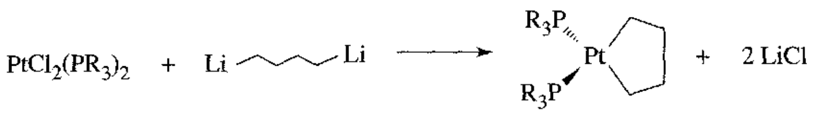
In terms of electron counting, the alkyl ligand may be considered a 2-electron donor $:CR_3^-$ (method A) or a 1-electron donor $\cdot CR_3$ (method B). Significant ionic contribution to the bonding may occur in complexes of highly electropositive elements, such as the alkali metals and alkaline earths.

Many synthetic routes to transition metal alkyl complexes have been developed. Two of the most important of these methods are as follows:

1. Reaction of a transition metal halide with organolithium, organomagnesium, or organoaluminum reagent.
   Example: $ZrCl_4 + 4\ PhCH_2MgCl \longrightarrow Zr(CH_2Ph)_4$ (Ph = phenyl)
2. Reaction of a metal carbonyl anion with alkyl halide.
   Example: $Na[Mn(CO)_5]^- + CH_3I \longrightarrow CH_3Mn(CO)_5 + NaI$

Although many complexes contain alkyl ligands, transition metal complexes containing alkyl groups as the only ligands are relatively rare. Examples include $Ti(CH_3)_4$, $W(CH_3)_6$, and $Cr[CH_2Si(CH_3)_3]_4$. Alkyl complexes have a tendency to be kinetically unstable and difficult to isolate;[54] their stability is enhanced by structural crowding, which protects the coordination sites of the metal by blocking pathways to decomposition. For example, the 6-coordinate $W(CH_3)_6$ can be melted at 30° C without decomposition, whereas the 4-coordinate $Ti(CH_3)_4$ is subject to decomposition at approximately −40° C.[55] In an interesting and unusual use of alkyls, diethylzinc has been used to treat books and documents (neutralizing the acid in the paper) for their long-term preservation. Many alkyl complexes are important in catalytic processes; examples of reactions of these complexes will be considered in Chapter 14.

Several other important ligands have direct metal-carbon σ bonds. Examples are given in Table 13-5. In addition, there are many examples of metallacycles, complexes containing metals incorporated into organic rings. The following reaction provides an example of a metallacycle synthesis:



Metallacyclopentane

In addition to being interesting in their own right, metallacycles are proposed as intermediates in a variety of catalytic processes.

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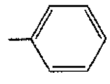
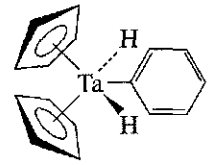
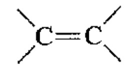
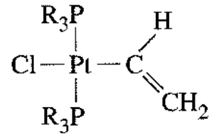
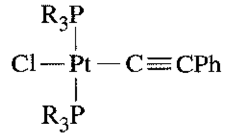
[54] An interesting historical perspective on alkyl complexes is in G. Wilkinson, *Science*, **1974**, *185*, 109.

[55] A. J. Shortland and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, **1973**, 872.

TABLE 13-5
Other Ligands Forming σ Bonds to Metals

Ligand	*Formula*	*Example*
Aryl		
Alkenyl (vinyl)		
Alkynyl	$—C{\equiv}C—$	 $Cl—Pt(PR_3)_2—C{\equiv}CPh$

13-6-2 CARBENE COMPLEXES

Carbene complexes contain metal-carbon double bonds.[56] First synthesized in 1964 by Fischer,[57] carbene complexes are now known for the majority of transition metals and for a wide range of ligands, including the prototype carbene, $:CH_2$. The majority of such complexes, including those first synthesized by Fischer, contain one or two highly electronegative heteroatoms such as O, N, or S directly attached to the carbene carbon. These are commonly designated as Fischer-type carbene complexes and have been studied extensively. Other carbene complexes contain only carbon and/or hydrogen attached to the carbene carbon. First synthesized several years after the initial Fischer carbene complexes,[58] these have been studied extensively by Schrock's research group and several others. They are sometimes designated as Schrock-type carbene complexes, commonly referred to as alkylidenes. The distinctions between Fischer- and Schrock-type carbene complexes are summarized in Table 13-6. In this text, we will focus primarily on Fischer-type carbene complexes.

TABLE 13-6
Fischer- and Schrock-type Carbene Complexes

Characteristic	*Fischer-type Carbene Complex*	*Schrock-type Carbene Complex*
Typical metal [oxidation state]	Middle to late transition metal [Fe(0), Mo(0), Cr(0)]	Early transition metal [Ti(IV), Ta(V)]
Substituents attached to $C_{carbene}$	At least one highly electronegative heteroatom (such as O, N, or S)	H or alkyl
Typical other ligands in complex	Good π acceptors	Good σ or π donors
Electron count	18	10–18

---

[56] IUPAC has recommended that the term "alkylidene" be used to describe all complexes containing metal-carbon double bonds and that "carbene" be restricted to free $:CR_2$. For a detailed description of the distinction between these two terms (and between "carbyne" and "alkylidyne," discussed later in this chapter), see W. A. Nugent and J. M. Mayer, *Metal-Ligand Multiple Bonds*, Wiley-Interscience, New York, 1988, pp. 11–16.

[57] E. O. Fischer and A. Maasbol, *Angew. Chem., Int. Ed.*, **1964**, *3*, 580.

[58] R. R. Schrock, *J. Am. Chem. Soc.*, **1974**, *96*, 6796.

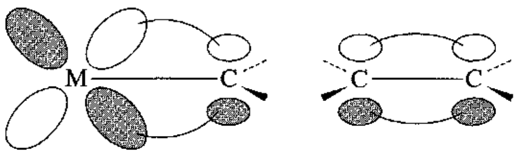
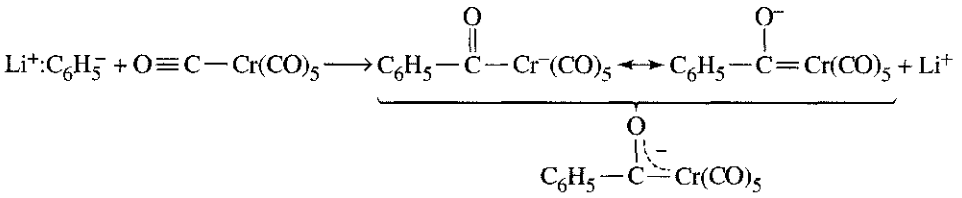


FIGURE 13-40 Bonding in Carbene Complexes and in Alkenes.

The formal double bond in carbene complexes may be compared with the double bond in alkenes. In the case of a carbene complex, the metal must use a *d* orbital (rather than a *p* orbital) to form the π bond with carbon, as illustrated in Figure 13-40.

Another aspect of bonding of importance to carbene complexes is that complexes having a highly electronegative atom such as O, N, or S attached to the carbene carbon tend to be more stable than complexes lacking such an atom. For example, $Cr(CO)_5[C(OCH_3)C_6H_5]$, with an oxygen on the carbene carbon, is much more stable than $Cr(CO)_5[C(H)C_6H_5]$. The stability of the complex is enhanced if the highly electronegative atom can participate in the π bonding, with the result a delocalized, 3-atom π system involving a *d* orbital on the metal and *p* orbitals on carbon and on the electronegative atom. Such a delocalized 3-atom system provides more stability to the bonding π electron pair than would a simple metal-to-carbon π bond. An example of such a π system is shown in Figure 13-41.

The methoxycarbene complex $Cr(CO)_5[C(OCH_3)C_6H_5]$ illustrates the bonding just described and some important related chemistry.[59] To synthesize this complex, we can begin with the hexacarbonyl, $Cr(CO)_6$. As in organic chemistry, highly nucleophilic reagents can attack the carbonyl carbon. For example, phenyllithium can react with $Cr(CO)_6$ to give the anion $[C_6H_5C(O)Cr(CO)_5]^-$, which has two important resonance structures, as shown here:



$$Li^+{:}C_6H_5^- + O\equiv C-Cr(CO)_5 \longrightarrow \underbrace{C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-Cr^-(CO)_5 \longleftrightarrow C_6H_5-\overset{\overset{\displaystyle O^-}{|}}{C}=Cr(CO)_5}_{C_6H_5-\overset{\overset{\displaystyle O}{|\text{-}}}{C}\text{=}Cr(CO)_5} + Li^+$$

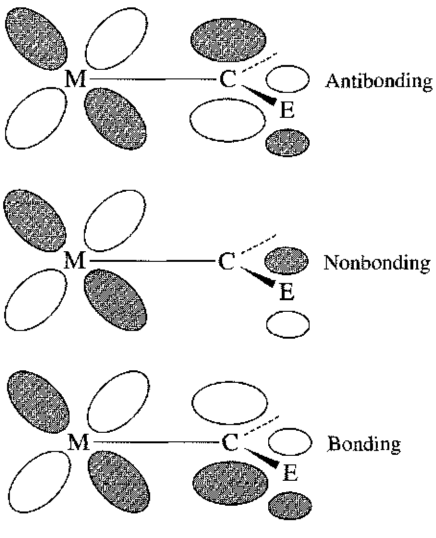


FIGURE 13-41 Delocalized π Bonding in Carbene Complexes. E designates a highly electronegative heteroatom such as O, N, or S.

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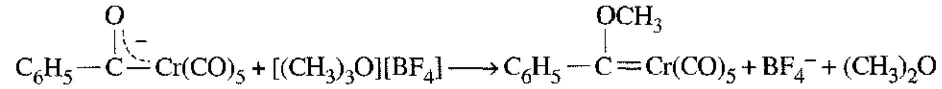
[59] E. O. Fischer, *Adv. Organomet. Chem.*, **1976**, *14*, 1.

Alkylation by a source of CH_3^+ such as $[(CH_3)_3O][BF_4]$ or CH_3I gives the methoxycarbene complex:



$$C_6H_5-\overset{O}{\overset{|}{C}}=Cr(CO)_5 + [(CH_3)_3O][BF_4] \longrightarrow C_6H_5-\overset{OCH_3}{\overset{|}{C}}=Cr(CO)_5 + BF_4^- + (CH_3)_2O$$

Evidence for double bonding between chromium and carbon is provided by X-ray crystallography, which measures this distance at 204 pm, compared with a typical Cr — C single bond distance of approximately 220 pm.

One very interesting aspect of this complex is that it exhibits a proton NMR spectrum that is temperature dependent. At room temperature, a single resonance is found for the methyl protons; however, as the temperature is lowered, this peak first broadens and then splits into two peaks. How can this behavior be explained?

A single proton resonance, corresponding to a single magnetic environment, is expected for the carbene complex as illustrated, with a double bond between chromium and carbon, and a single bond (permitting rapid rotation about the bond) between carbon and oxygen. The room-temperature NMR is therefore as expected. However, the splitting of this peak at lower temperature into two peaks suggests two different proton environments.[60] Two environments are possible if rotation is hindered about the C — O bond. A resonance structure for the complex can be drawn showing the possibility of some double bonding between C and O; were such double bonding significant, *cis* and *trans* isomers, as shown in Figure 13-42, might be observable at low temperatures.

Evidence for double-bond character in the C — O bond is also provided by crystal structure data, which show a C — O bond distance of 133 pm, compared with a typical C — O single bond distance of 143 pm.[61] The double bonding between C and O, although weak (typical C = O bonds are much shorter, approximately 116 pm), is sufficient to slow down rotation about the bond so that, at low temperatures, proton NMR detects the *cis* and *trans* methyl protons separately. At higher temperature, there is sufficient energy to cause rapid rotation about the C — O bond so that the NMR sees only an average signal, which is observed as a single peak.

X-ray crystallographic data, as mentioned, show double-bond character in both the Cr — C and C — O bonds. This supports the statement made at the beginning of this section that π bonding in complexes of this type (containing a highly electronegative atom, in this case oxygen) may be considered delocalized over three atoms. Although not absolutely essential for all carbene complexes, the delocalization of π electron density over three (or more) atoms provides an additional measure of stability to many of these complexes.[62]

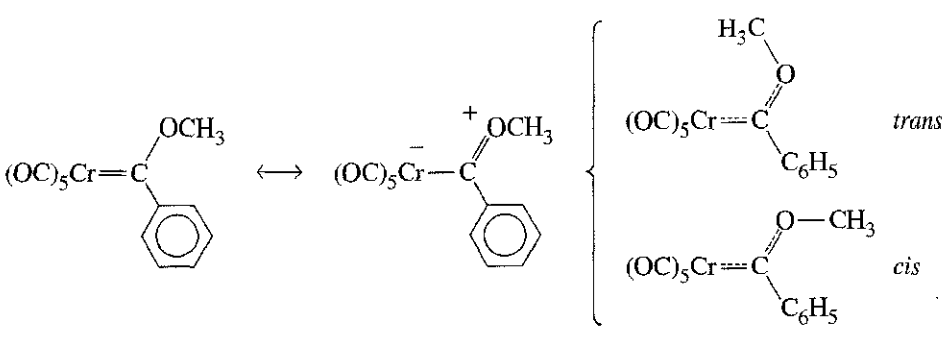


FIGURE 13-42 Resonance Structures and *cis* and *trans* Isomers for $Cr(CO)_5[C(OCH_3)C_6H_5]$.

[60] C. G. Kreiter and E. O. Fischer, *Angew. Chem., Int. Ed.*, **1969**, *8*, 761.

[61] O. S. Mills and A. D. Redhouse, *J. Chem. Soc. A*, **1968**, 642.

[62] K. H. Dötz, H. Fischer, P. Hofmann, F. R. Kreissl, D. Schubert, and K. Weiss, *Transition Metal Carbene Complexes*, Verlag Chemie, Weinheim, Germany, 1983, pp. 120–122.

Carbene complexes appear to be important intermediates in olefin metathesis reactions, which are of significant industrial interest; these reactions are discussed in Chapter 14.

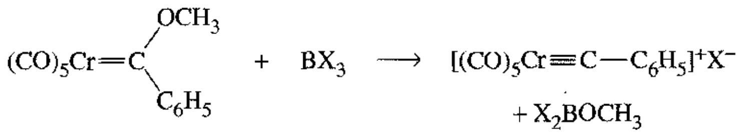
13-6-3 CARBYNE (ALKYLIDYNE) COMPLEXES

Carbyne complexes have metal-carbon triple bonds; they are formally analogous to alkynes.[63] Many carbyne complexes are now known; examples of carbyne ligands include the following:

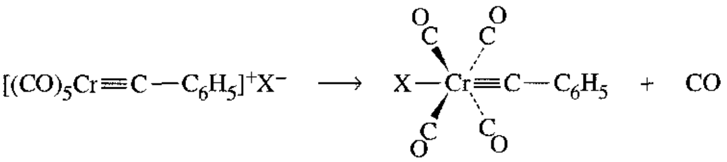
$$\mathrm{M{\equiv}C{-}R}$$

where R = aryl, alkyl, H, $\mathrm{SiMe_3}$, $\mathrm{NEt_2}$, $\mathrm{PMe_3}$, SPh, Cl. Carbyne complexes were first synthesized fortuitously in 1973 as products of the reactions of carbene complexes with Lewis acids.[64] For example, the methoxycarbene complex $\mathrm{Cr(CO)_5[C(OCH_3)C_6H_5]}$ was found to react with the Lewis acids $\mathrm{BX_3}$ (X = Cl, Br, or I):

First, the Lewis acid attacks the oxygen, the basic site on the carbene:



Subsequently, the intermediate loses CO, with the halogen coordinating in a position *trans* to the carbyne:



The best evidence for the carbyne nature of the complex is provided by X-ray crystallography, which gives a Cr—C bond distance of 168 pm (for X = Cl), considerably shorter than the 204 pm for the parent carbene complex. The Cr≡C—C angle is, as expected, 180° for this complex; however, slight deviations from linearity are observed for many complexes in crystalline form, in part a consequence of the manner of packing in the crystal.

Bonding in carbyne complexes may be viewed as a combination of a σ bond plus two π bonds, as illustrated in Figure 13-43.

The carbyne ligand has a lone pair of electrons in an *sp* hybrid on carbon; this lone pair can donate to a suitable orbital on Cr to form a σ bond. In addition, the carbon has two *p* orbitals that can accept electron density from *d* orbitals on Cr to form π bonds. Thus, the overall function of the carbyne ligand is as both a σ donor and π acceptor. (For electron counting purposes, a $:\mathrm{CR^+}$ ligand can be considered a 2-electron donor; it is usually more convenient to count neutral CR as a 3-electron donor.)

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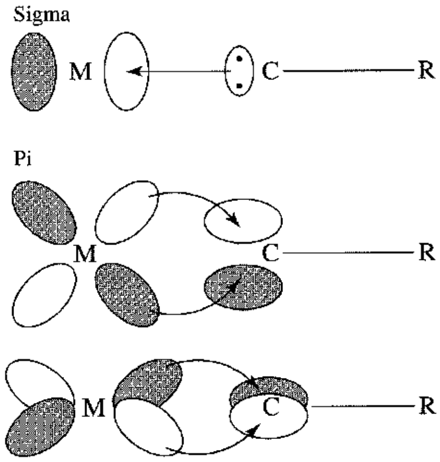
[63] IUPAC has recommended that "alkylidyne" be used to designate complexes containing metal-carbon triple bonds.

[64] E. O. Fischer, G. Kreis, C. G. Kreiter, J. Müller, G. Huttner, and H. Lorentz, *Angew. Chem., Int. Ed.*, **1973**, *12*, 564.



(May also involve *d* orbital or hybrid orbital on metal)

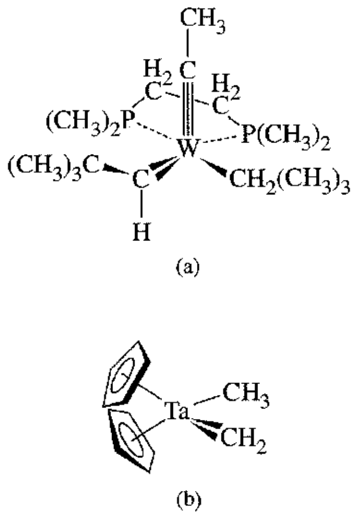
FIGURE 13-43 Bonding in Carbyne Complexes.

Carbyne complexes can be synthesized in a variety of ways in addition to Lewis acid attack on carbene complexes. Synthetic routes for carbyne complexes and the reactions of these complexes have been reviewed.[65]

In some cases, molecules have been synthesized containing two or three of the types of ligands discussed in this section (alkyl, carbene, and carbyne). Such molecules provide an opportunity to make direct comparisons of lengths of metal-carbon single, double, and triple bonds, as shown in Figure 13-44.

EXERCISE 13-10

Are the compounds shown in Figure 13-44 18-electron species?



W—C	225.8 pm
W=C	194.2 pm
W≡C	178.5 pm

Ta—C	224.6 pm
Ta=C	202.6 pm

FIGURE 13-44 Complexes containing Alkyl, Carbene, and Carbyne Ligands, (a) M. R. Churchill and W. J. Young, *Inorg. Chem.*, **1979**, *18*, 2454. (b) L. J. Guggenberger and R. R. Schrock, *J. Am. Chem. Soc.*, **1975**, *97*, 6578.

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[65] H. P. Kim and R. J. Angelici, "Transition Metal Complexes with Terminal Carbyne Ligands," in *Adv. Organomet. Chem.*, **1987**, *27*, 51; H. Fischer, P. Hoffmann, F. R. Kreissl, R. R. Schrock, U. Schubert, and K. Weiss, *Carbyne Complexes*, VCH, Weinheim, Germany, 1988.

13-7 SPECTRAL ANALYSIS AND CHARACTERIZATION OF ORGANOMETALLIC COMPLEXES

One of the most challenging (and sometimes most frustrating) aspects of organometallic research is the characterization of new reaction products. Assuming that specific products can be isolated (by chromatographic procedures, recrystallization, or other techniques), determining the structure can present an interesting challenge. Many complexes can be crystallized and characterized structurally by X-ray crystallography; however, not all organometallic complexes can be crystallized, and not all that crystallize lend themselves to structural solution by X-ray techniques. Furthermore, it is frequently desirable to be able to use more convenient techniques than X-ray crystallography (although, in some cases, an X-ray structural determination is the only way to identify a compound conclusively—and may therefore be the most rapid and inexpensive technique). Infrared spectroscopy and NMR spectrometry are often the most useful. In addition, mass spectrometry, elemental analysis, conductivity measurements, and other methods may be valuable in characterizing products of organometallic reactions. We will consider primarily IR and NMR as techniques used in the characterization of organometallic complexes.

13-7-1 INFRARED SPECTRA

IR can be useful in two respects. The number of IR bands, as discussed in Chapter 4, depends on molecular symmetry; consequently, by determining the number of such bands for a particular ligand (such as CO), we may be able to decide among several alternative geometries for a compound or at least reduce the number of possibilities. In addition, the position of the IR band can indicate the function of a ligand (e.g., terminal vs. bridging modes) and, in the case of π-acceptor ligands, can describe the electron environment of the metal.

Number of infrared bands

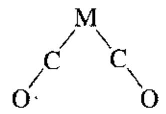
In Section 4-4-2, a method was described for using molecular symmetry to determine the number of IR-active stretching vibrations. The basis for this method is that vibrational modes, to be IR active, must result in a change in the dipole moment of the molecule. In symmetry terms, the equivalent statement is that IR-active vibrational modes must have irreducible representations of the same symmetry as the Cartesian coordinates x, y, or z (or a linear combination of these coordinates). The procedure developed in Chapter 4 is used in the following examples. It is suggested as an exercise that the reader verify some of these results using the method described in Chapter 4.

Our examples will be carbonyl complexes. Identical reasoning applies to other linear monodentate ligands (such as CN^- and NO). We will begin by considering several simple cases.

Monocarbonyl complexes. These complexes have a single possible C—O stretching mode and consequently show a single band in the IR.

Dicarbonyl complexes. Two geometries, linear and bent, must be considered:

O—C—M—C—O

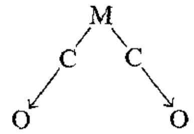


In the case of two CO ligands arranged linearly, only an antisymmetric vibration of the ligands is IR active; a symmetric vibrational mode produces no change in dipole moment and hence is inactive. However, if two CO ligands are oriented in a nonlinear fashion, both symmetric and antisymmetric vibrations result in changes in dipole moment, and both are IR active:

Symmetric Stretch

$$O \leftarrow C - M - C \rightarrow O$$

No change in dipole moment;
IR inactive

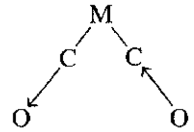


Change in dipole moment:
IR active

Antisymmetric Stretch

$$O \leftarrow C - M - C \leftarrow O$$

Change in dipole moment;
IR active



Change in dipole moment;
IR active

Therefore, an IR spectrum can be a convenient tool for determining structure for molecules known to have exactly two CO ligands: a single band indicates linear orientation of the CO ligands, and two bands indicate nonlinear orientation.

For molecules containing exactly two CO ligands on the same metal atom, the relative intensities of the IR bands can be used to determine approximately the angle between the COs, using the equation

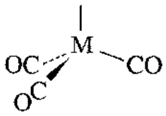
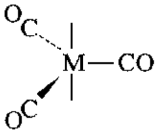
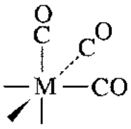
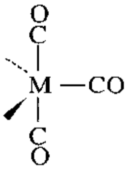
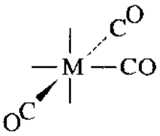
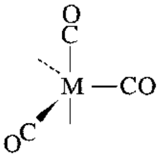
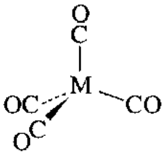
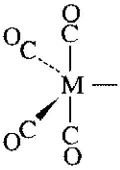
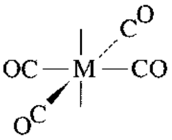
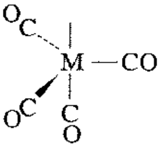
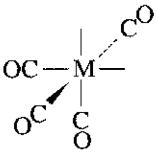
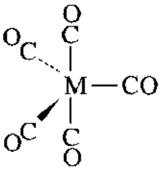
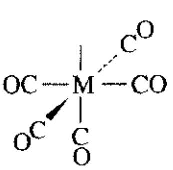
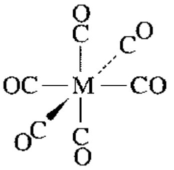
$$\frac{I_{\text{symmetric}}}{I_{\text{antisymmetric}}} = \text{cotan}^2\left(\frac{\phi}{2}\right)$$

where the angle between the ligands is ϕ. For example, for two CO ligands at 90°, $\text{cotan}^2(45°) = 1$. For this angle, two IR bands of equal intensity would be observed. For an angle $>90°$, the ratio is less than 1; the IR band due to symmetric stretching is less intense than the band due to antisymmetric stretching. If $\phi < 90°$, the IR band for symmetric stretching is the more intense. (For C—O stretching vibrations, the symmetric band occurs at higher energy than the corresponding antisymmetric band.) In general, this calculation is approximate and requires integrated values of intensities of absorption bands (rather than the more easily determined intensity at the wavelength of maximum absorption).

Complexes containing three or more carbonyls. Here, the predictions are not quite so simple. The exact number of carbonyl bands can be determined according to the symmetry approach of Chapter 4. For convenient reference, the numbers of bands expected for a variety of CO complexes are given in Table 13-7.

Several additional points relating to the number of IR bands are worth noting. First, although we can predict the number of IR-active bands by the methods of group theory, fewer bands may sometimes be observed. In some cases, bands may overlap to such a degree as to be indistinguishable; alternatively, one or more bands may be of very low intensity and not readily observed. In some cases, isomers may be present in the same sample, and it may be difficult to determine which IR absorptions belong to which compound.

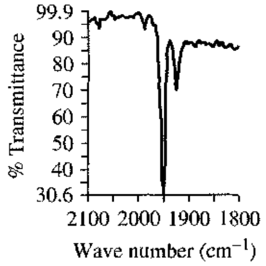
TABLE 13-7
Carbonyl Stretching Bands

		Coordination Number		
Number of CO Ligands			*4*	*5 6*
3				
	IR bands:	2	1	2
				
	IR bands:		3	3
				
	IR bands:		3	
4				
	IR bands:	1	4	1
				
	IR bands:		3	4
5				
	IR bands:		2	3
6				
	IR bands:			1

In carbonyl complexes, the number of C—O stretching bands cannot exceed the number of CO ligands. The alternative is possible in some cases (more CO groups than IR bands), when vibrational modes are not IR active (do not cause a change in dipole moment). Examples are given in Table 13-7. Because of their symmetry, carbonyl complexes of T_d and O_h symmetry have a single carbonyl band in the IR spectrum.

EXERCISE 13-11

The complex $Mo(CO)_3(NCC_2H_5)_3$ has the infrared spectrum shown here. Is this complex more likely the *fac* or *mer* isomer?



Positions of IR bands

We have already encountered in this chapter two examples in which the position of the carbonyl stretching band provides useful information. In the case of the isoelectronic species $[Mn(CO)_6]^+$, $Cr(CO)_6$, and $[V(CO)_6]^-$, an increase in negative charge on the complex causes a significant reduction in the energy of the C—O band as a consequence of additional π back-bonding from the metal to the ligands (Section 13-4-1). The bonding mode is also reflected in the infrared spectrum, with energy decreasing in the order

terminal CO > doubly bridging CO > triply bridging CO

The positions of infrared bands are also a function of other ligands present. For example, consider the data in Tables 13-7 and 13-8.

TABLE 13-8
Examples of Carbonyl Stretching Bands: Molybdenum Complexes

Complex	*ν (CO), cm⁻¹*
fac-$Mo(CO)_3(PF_3)_3$	2090, 2055
fac-$Mo(CO)_3(PCl_3)_3$	2040, 1991
fac-$Mo(CO)_3(PClPh_2)_3$	1977, 1885
fac-$Mo(CO)_3(PMe_3)_3$	1945, 1854

SOURCE: F. A. Cotton, *Inorg. Chem.*, **1964**, *3*, 702.

Going down the series in Table 13-8, the σ-donor ability of the phosphine ligands increases and the π-acceptor ability decreases. PF_3 is the weakest donor (as a consequence of the highly electronegative fluorines) and the strongest acceptor; conversely, PMe_3 is the strongest donor and the weakest acceptor. As a result, the molybdenum in $Mo(CO)_3(PMe_3)_3$ carries the greatest electron density; it is the most able to donate electron density to the π^* orbitals of the CO ligands. Consequently, the CO ligands in $Mo(CO)_3(PMe_3)_3$ have the weakest C—O bonds and the lowest energy stretching bands. Many comparable series are known.

The important point is that the position of the carbonyl bands can provide important clues to the electronic environment of the metal. The greater the electron density on the metal (and the greater the negative charge), the greater the back bonding to CO and the lower the energy of the carbonyl stretching vibrations. Similar correlations between the metal environment and IR spectra can be shown for a variety of other ligands, both organic and inorganic. NO, for example, has an IR spectrum that is strongly correlated with the environment in a manner similar to that of CO. In combination with information on the number of IR bands, the positions of such bands for CO and other ligands can therefore be extremely useful in characterizing organometallic compounds.

13-7-2 NMR SPECTRA

NMR is also a valuable tool in characterizing organometallic complexes. The advent of high-field NMR instruments using superconducting magnets has in many ways revolutionized the study of these compounds. Convenient NMR spectra can now be taken using many metal nuclei as well as the more traditional nuclei such as ^{1}H, ^{13}C, ^{19}F, and ^{31}P; the combined spectral data of several nuclei make it possible to identify many compounds by their NMR spectra alone.

As in organic chemistry, chemical shifts, splitting patterns, and coupling constants are useful in characterizing the environments of individual atoms in organometallic compounds. The reader may find it useful to review the basic theory of NMR as presented in an organic chemistry text. More advanced discussions of NMR, especially relating to ^{13}C, have been presented elsewhere.[66]

^{13}C NMR

Carbon-13 NMR has become increasingly useful with the advent of modern instrumentation. Although the isotope ^{13}C has a low natural abundance (approximately 1.1%) and low sensitivity for the NMR experiment (about 1.6% as sensitive as ^{1}H), Fourier transform techniques now make it possible to obtain useful ^{13}C spectra for most organometallic species of reasonable stability. Nevertheless, the time necessary to obtain a ^{13}C spectrum may still be an experimental difficulty for compounds present in very small amounts or of low solubility. Rapid reactions may also be inaccessible by this technique. Some useful features of ^{13}C spectra include the following:

1. An opportunity to observe organic ligands that do not contain hydrogen (such as CO and $F_3C—C{\equiv}C—CF_3$).
2. Direct observation of the carbon skeleton of organic ligands.
3. ^{13}C chemical shifts are more widely dispersed than ^{1}H shifts. This often makes it easy to distinguish between ligands in compounds containing several different organic ligands.

^{13}C NMR is also a valuable tool for observing rapid intramolecular rearrangement processes.[67]

Approximate ranges of chemical shifts for ^{13}C spectra of some categories of organometallic complexes are listed in Table 13-9. Several features of the data in this table are worth noting:

1. Terminal carbonyl peaks are frequently in the range δ 195 to 225 ppm, a range sufficiently distinctive that the CO groups are usually easy to distinguish from other ligands.

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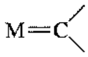
[66] B. E. Mann, "^{13}C NMR Chemical Shifts and Coupling Constants of Organometallic Compounds," in *Adv. Organomet. Chem.*, **1974**, *12*, 135; P. W. Jolly and R. Mynott, "The Application of ^{13}C NMR Spectroscopy to Organo-Transition Metal Complexes," in *Adv. Organomet. Chem.*, **1981**, *19*, 257; E. Breitmaier and W. Voelter, *Carbon 13 NMR Spectroscopy*, VCH, New York, 1987.

[67] Breitmaier and Voelter, *Carbon 13 NMR Spectroscopy*. pp. 127–133, 166–167, 172–178.

TABLE 13-9
^{13}C Chemical Shifts for Organometallic Compounds

Ligand	*^{13}C Chemical Shift (Range)*[a]			
$M-CH_3$	−28.9 to 23.5			
	190 to 400			
$M\equiv C-$	235 to 401			
$M-CO$	177 to 275			
Neutral binary CO	183 to 223			
$M-(\eta^5\text{-}C_5H_5)$	−790 to 1430			
$Fe(\eta^5\text{-}C_5H_5)_2$	69.2			
$M-(\eta^3\text{-}C_3H_5)$		C_2		C_1 and C_3
		91 to 129		46 to 79
$M-C_6H_5$	$M-C$	*ortho*	*meta*	*para*
	130 to 193	132 to 141	127 to 130	121 to 131

NOTE: [a] Parts per million (ppm) relative to $Si(CH_3)_4$.

2. The ^{13}C chemical shift is correlated with the strength of the $C-O$ bond; in general, the stronger the $C-O$ bond, the lower the chemical shift.[68]
3. Bridging carbonyls have slightly greater chemical shifts than terminal carbonyls and consequently may lend themselves to easy identification. (However, IR is usually a better tool than NMR for distinguishing between bridging and terminal carbonyls.)
4. Cyclopentadienyl ligands have a wide range of chemical shifts, with the value for ferrocene (68.2 ppm) near the low end for such values. Other organic ligands may also have fairly wide ranges in ^{13}C chemical shifts.[69]

^1H NMR

The ^1H spectra of organometallic compounds containing hydrogens can also provide useful structural information. For example, protons bonded directly to metals (in hydride complexes, discussed in Section 13-4-3) are very strongly shielded, with chemical shifts commonly in the approximate range −5 to −20 ppm relative to $Si(CH_3)_4$. Such protons are typically easy to detect, because few other protons commonly appear in this region.

Protons in methyl complexes ($M-CH_3$) typically have chemical shifts between 1 and 4 ppm, similar to their positions in organic molecules. Cyclic π ligands, such as $\eta^5\text{-}C_5H_5$ and $\eta^6\text{-}C_6H_6$, most commonly have ^1H chemical shifts between 4 and 7 ppm and, because of the relatively large number of protons involved, may lend themselves to easy identification.[70] Protons in other types of organic ligands also have characteristic chemical shifts; examples are given in Table 13-10.

As in organic chemistry, integration of NMR peaks of organometallic complexes can provide the ratio of atoms in different environments. For example, the area of a ^1H peak is usually proportional to the number of nuclei giving rise to that peak. However, for ^{13}C, this calculation is less reliable. Relaxation times of different carbon atoms in organometallic complexes vary widely; this may lead to inaccuracy in correlating peak

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[68] P. C. Lauterbur and R. B. King, *J. Am. Chem. Soc.*, **1965**, *87*, 3266.

[69] Extensive tables of chemical shifts and coupling constants can be found in B. E. Mann, "^{13}C NMR Chemical Shifts and Coupling Constants of Organometallic Compounds," in *Adv. Organomet. Chem.*, **1974**, *12*, 135.

[70] These are ranges for diamagnetic complexes. Paramagnetic complexes may have much larger chemical shifts, sometimes several hundred parts per million relative to tetramethylsilane.

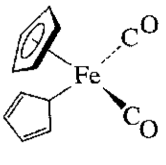
TABLE 13-10
Examples of ^{1}H Chemical Shifts for Organometallic Compounds

Complex	^{1}*H Chemical Shift*^{a}
$Mn(CO)_5\mathbf{H}$	−7.5
$W(C\mathbf{H}_3)_6$	1.80
$Ni(\eta^2\text{-}C_2\mathbf{H}_4)_3$	3.06
$(\eta^5\text{-}C_5\mathbf{H}_5)_2Fe$	4.04
$(\eta^6\text{-}C_6\mathbf{H}_6)_2Cr$	4.12
$(\eta^5\text{-}C_5H_5)_2Ta(CH_3)(=C\mathbf{H}_2)$	10.22

NOTE: ^{a} Parts per million relative to $Si(CH_3)_4$.

area with the number of atoms (the correlation between area and number of atoms is dependent on rapid relaxation). Adding paramagnetic reagents may speed up relaxation and thereby improve the validity of integration data. One paramagnetic compound often used is $Cr(acac)_3$ [acac = acetylacetonate = $H_3CC(O)CHC(O)CH_3^-$].[71]

Molecular rearrangement processes



The compound $(C_5H_5)_2Fe(CO)_2$ has interesting NMR behavior. This compound contains both η^1- and η^5-C_5H_5 ligands (and consequently obeys the 18-electron rule). The ^{1}H NMR spectrum at room temperature shows two singlets of equal area. A singlet would be expected for the five equivalent protons of the η^5-C_5H_5 ring but is surprising for the η^1-C_5H_5 ring, because the protons are not all equivalent. At lower temperatures, the peak at 4.5 ppm (η^5-C_5H_5) remains constant, but the other peak at 5.7 ppm spreads and then splits into new peaks near 3.5 and between 5.9 and 6.4 ppm—all consistent with a η^1-C_5H_5 ligand. A "ring whizzer" mechanism,[72] Figure 13-45, has been proposed by which the five ring positions of the monohapto ring interchange via 1,2-metal shifts so rapidly at 30° C that the NMR spectrometer can see only the average signal for the ring.[73] At lower temperatures, this process is slower and the different resonances for the protons of η^1-C_5H_5 become apparent, as also shown in Figure 13-45.

More detailed discussions of NMR spectra of organometallic compounds, including nuclei not mentioned here, have been given by Elschenbroich and Salzer.[74]

13-7-3 EXAMPLES OF CHARACTERIZATION

In this chapter, we have considered just a few types of reactions of organometallic compounds, principally the replacement of CO by other ligands and the reactions involved in syntheses of carbene and carbyne complexes. Additional types of reactions will be discussed in Chapter 14. We conclude this chapter with two examples of how spectral data may be used in the characterization of organometallic compounds. Further examples can be found in the problems at the end of this chapter and in Chapter 14.

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[71] For a discussion of the problems associated with integration in ^{13}C NMR, see J. K. M. Saunders and B. K. Hunter, *Modern NMR Spectroscopy*, W. B. Saunders, New York, 1992.

[72] C. H. Campbell and M. L. H. Green, *J. Chem. Soc., A*, **1970**, 1318.

[73] M. J. Bennett, Jr., F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Am. Chem. Soc.*, **1966**, *88*, 4371.

[74] C. Elschenbroich and A. Salzer, *Organometallics*, 2nd ed., VCH, New York, 1992.

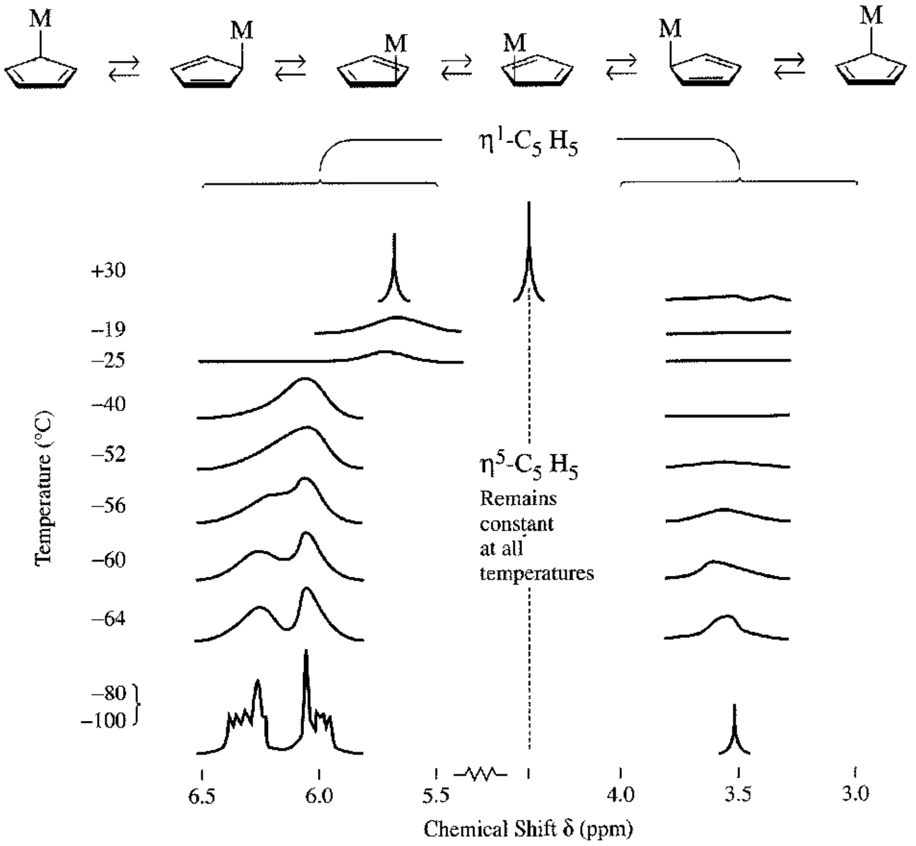
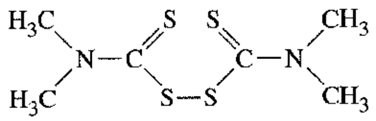


FIGURE 13-45 Ring Whizzer Mechanism and Variable Temperature NMR Spectra of $(C_5H_5)_2Fe(CO)_2$. The central peak at 4.5 ppm, due to the η^5-C_5H_5 ligand, remains constant throughout; it is not shown except in the highest temperature spectrum in order to simplify the figure. (NMR spectra reproduced with permission from M. H. Bennett, Jr., F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Am. Chem. Soc.*, **1966**, *88*, 4371. © 1966 American Chemical Society.)

EXAMPLE



tds

$[(C_5H_5)Mo(CO)_3]_2$ reacts with tetramethylthiuramdisulfide (tds) in refluxing toluene to give a molybdenum-containing product having the following characteristics:

^{1}H NMR: Two singlets, at δ 5.48 (relative area = 5) and δ 3.18 (relative area = 6). (For comparison, $[(C_5H_5)Mo(CO)_3]_2$ has a single ^{1}H NMR peak at δ 5.30.)

IR: Strong bands at 1950 and 1860 cm^{-1}.

Mass spectrum: A pattern similar to the Mo isotope pattern with the most intense peak at $m/e = 339$. (The most abundant Mo isotope is ^{98}Mo.)

What is the most likely identity of this product?

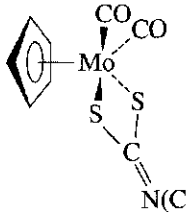
The ^{1}H NMR singlet at δ 5.48 suggests retention of the C_5H_5 ligand (the chemical shift is a close match for the starting material). The peak at δ 3.18 is most likely due to CH_3 groups originating from the tds. The 5:6 ratio of hydrogens suggests a 1:2 ratio of C_5H_5 ligands to CH_3 groups.

IR shows two bands in the carbonyl region, indicating at least two COs in the product.

The mass spectrum makes it possible to pin down the molecular formula. Subtracting the molecular fragments believed to be present from the total mass:

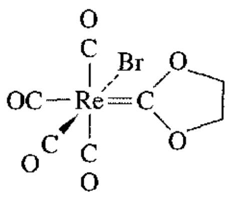
Total mass:	339
Mass of Mo (from mass spectrum pattern)	−98
Mass of C_5H_5	−65
Mass of two COs	−56
Remaining mass	120

120 is exactly half the mass of tds; it corresponds to the mass of $S_2CN(CH_3)_2$, the dimethyldithiocarbamate ligand, which we have encountered in previous chapters. Therefore, the likely formula of the product is $(C_5H_5)Mo(CO)_2[S_2CN(CH_3)_2]$. This formula has the necessary 5:6 ratio of protons in two magnetic environments and should give rise to two C—O stretching vibrations (because the carbonyls would not be expected to be oriented at 180° angles with respect to each other in such a molecule).



In practice, additional information is likely to be available to help characterize reaction products. For example, additional examination of the infrared spectrum in this case shows a moderately intense band at 1526 cm^{-1}, a common location for C—N stretching bands in dithiocarbamate complexes. Analysis of the fragmentation pattern of mass spectra may also provide useful information on molecular fragments.

EXAMPLE



I

When a toluene solution containing **I** and excess triphenylphosphine is heated to reflux, first compound **II** is formed, and then compound **III**. **II** has infrared bands at 2038, 1958, and 1906 cm^{-1}, and **III** at 1944 and 1860 cm^{-1}. ^1H and ^{13}C NMR data [δ values (relative area)] are as follows:

I	*II*	*III*
^1H: 4.83 singlet	7.62, 7.41 multiplets (15)	7.70, 7.32 multiplets (15)
	4.19 multiplet (4)	3.39 singlet (2)
^{13}C: 224.31	231.02	237.19
187.21	194.98	201.85
185.39	189.92	193.83
184.01	188.98	127.75–134.08 (several peaks)
73.33	129.03–134.71 (several peaks)	68.80
	72.26	

Additional useful information: the ^{13}C signal of **I** at δ 224.31 is similar to the chemical shift of carbene carbons in similar compounds; the peaks between δ 184 and 202 correspond to carbonyls; and the peak at δ 73.33 is typical of CH_2CH_2 bridges in dioxycarbene complexes.

Identify **II** and **III**.

This is a good example of the utility of ^{13}C NMR. Both **II** and **III** have peaks with similar chemical shifts to the peak at δ 224.31 for **I**, suggesting that the carbene ligand is retained in the reaction. Similarly, **II** and **III** have peaks near δ 73.33, a further indication that the carbene ligand remains intact.

The ^{13}C peaks in the range δ 184 to 202 can be assigned to carbonyl groups. **II** and **III** show new peaks in the range δ 129 to 135. The most likely explanation is that the chemical reaction involves replacement of carbonyls by triphenylphosphines and that the new peaks in the 129 to 135 range are due to the phenyl carbons of the phosphines.

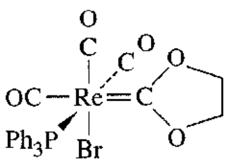
^1H NMR data are consistent with replacement of COs by phosphines. In both **II** and **III**, integration of the $—CH_2CH_2—$ peaks (δ 4.19 and 3.39, respectively) and the phenyl peaks (δ 7.32 to 7.70) give the expected ratios for replacement of one and two COs.

Finally, IR data are in agreement with these conclusions. In **II**, the three bands in the carbonyl region are consistent with the presence of three COs either in a *mer* or a *fac* arrangement.[75] In **III**, the two C—O stretches correspond to two carbonyls *cis* to each other.

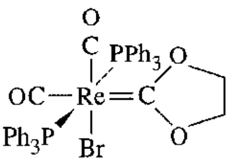
The chemical formulas of these products can now be written as follows:

II: $\mathrm{ReBr(CO)_3(\overline{COCH_2CH_2O})(PPh_3)}$

III: *cis*-$\mathrm{ReBr(CO)_2(\overline{COCH_2CH_2O})(PPh_3)_2}$



II



III

EXERCISE 13-12

Using ^{13}C NMR data, determine if **II** is more likely the *fac* or *mer* isomer.[76]

GENERAL REFERENCES

Much information on organometallic compounds is included in two general inorganic references, N.N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, 2nd ed., Butterworth Heinemann, Oxford, 1997, and F. A. Cotton, G. Wilkinson, C. A. Murillo, and M. Bochman, *Advanced Inorganic Chemistry*, 6th ed., Wiley-Interscience, New York, 1999. G. O. Spessard and G. L. Miessler, *Organometallic Chemistry*, Prentice Hall, Upper Saddle River, NJ, 1997, C. Elschenbroich and A. Salzer, *Organometallics*, 2nd ed., VCH, New York, 1992, and J. P. Collman, L. S. Hegedus, J. R. Norton, and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987, provide extensive discussion, with numerous references, of many additional types of organometallic compounds in addition to those discussed

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[75] In an octahedral complex of formula *fac*-$ML_3(CO)_3$ (having C_{3v} symmetry), only two carbonyl stretching bands are expected if all ligands L are identical. However, in this case, there are three different ligands in addition to CO, the point group is C_1, and three bands are expected.

[76] G. L. Miessler, S. Kim, R. A. Jacobson, and R. A. Angelici, *Inorg. Chem.*, **1987**, *26*, 1690.

in this chapter. The most comprehensive references on organometallic chemistry are the multiple-volume sets G. Wilkinson and F. G. A. Stone, eds. *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, 1982, and E. W. Abel, F. G. A. Stone, and G. Wilkinson, eds. *Comprehensive Organometallic Chemistry II*, Pergamon Press, Oxford, 1995. Each of these sets has an extensive listing of references on organometallic compounds that have been structurally characterized by X-ray, electron, or neutron diffraction. A useful reference to literature sources on the synthesis, properties, and reactions of specific organometallic compounds is J. Buckingham and J. E. Macintyre, eds., *Dictionary of Organometallic Compounds*, Chapman and Hall, London, 1984, to which supplementary volumes have also been published. The series *Advances in Organometallic Chemistry*, Academic Press, San Diego, provides valuable review articles on a variety of organometallic topics.

PROBLEMS

13-1 Which of the following obey the 18-electron rule?

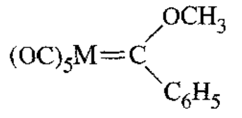
a. $Fe(CO)_5$
b. $[Rh(bipy)_2Cl]^+$
c. $(\eta^5\text{-}Cp^*)Re(=O)_3$ ($Cp^* = C_5(CH_3)_5$)
d. $Re(PPh_3)_2Cl_2N$
e. $Os(CO)(\equiv CPh)(PPh_3)_2Cl$

13-2 Which of the following square-planar complexes have 16-electron valence configurations?

a. $Ir(CO)Cl(PPh_3)_2$
b. $RhCl(PPh_3)_3$
c. $[Ni(CN)_4]^{2-}$
d. *cis*-$PtCl_2(NH_3)_2$

13-3 On the basis of the 18-electron rule, identify the first-row transition metal for each of the following:

a. $[M(CO)_7]^+$
b. $H_3CM(CO)_5$
c. $M(CO)_2(CS)(PPh_3)Br$
d. $[(\eta^3\text{-}C_3H_3)(\eta^5\text{-}C_5H_5)M(CO)]^-$
e.



$(OC)_5M{=}C(OCH_3)(C_6H_5)$

f. $[(\eta^4\text{-}C_4H_4)(\eta^5\text{-}C_5H_5)M]^+$
g. $(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)M(CH_3)(NO)$
h. $[M(CO)_4I(diphos)]^-$ (diphos = 1,2-bis(diphenylphosphino)ethane)

13-4 Determine the metal-metal bond order consistent with the 18-electron rule for the following:

a. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$
b. $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]^{2-}$

13-5 Identify the most likely second-row transition metal for each of the following:

a. $[M(CO)_3(NO)]^-$
b. $[M(PF_3)_2(NO)_2]^+$ (contains linear M—N—O)
c. $[M(CO)_4(\mu_2\text{-}H)]_3$
d. $M(CO)(PMe_3)_2Cl$ (square-planar complex)

13-6 On the basis of the 18-electron rule, determine the expected charge on the following:

a. $[Co(CO)_3]^z$
b. $[Ni(CO)_3(NO)]^z$ (contains linear M—N—O)
c. $[Ru(CO)_4(GeMe_3)]^z$
d. $[(\eta^3\text{-}C_3H_5)V(CNCH_3)_5]^z$
e. $[(\eta^5\text{-}C_5H_6)Fe(CO)_3]^z$
f. $[(\eta^5\text{-}C_5H_5)_3Ni_3(\mu_3\text{-}CO)_2]^z$