# Chapter 13 Organometallic Chemistry

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>13-1</td>
<td>Historical Background</td>
</tr>
<tr>
<td>13-2</td>
<td>Organic Ligands and Nomenclature</td>
</tr>
<tr>
<td>13-3</td>
<td>The 18-Electron Rule</td>
</tr>
<tr>
<td>13-4</td>
<td>Ligands in Organometallic Chemistry</td>
</tr>
<tr>
<td>13-5</td>
<td>Bonding Between Metal Atoms and Organic $\pi$ Systems</td>
</tr>
<tr>
<td>13-6</td>
<td>Complexes Containing M-C, M=C, and M≡C Bonds</td>
</tr>
<tr>
<td>13-7</td>
<td>Spectral Analysis and Characterization of Organometallic Complexes</td>
</tr>
</tbody>
</table>

http://en.wikipedia.org/wiki/Expedia
13-1 Historical Background

Sandwich compounds

Cluster compounds

그림 13-2 동체화합물의 예.
Other examples of organometallic compounds
Organometallic chemistry is the study of chemical compounds containing bonds between carbon and a metal.

Organometallic chemistry combines aspects of inorganic chemistry and organic chemistry.

Organometallic compounds find practical use in stoichiometric and catalytically active compounds.

Electron counting is key in understanding organometallic chemistry. The 18-electron rule is helpful in predicting the stabilities of organometallic compounds. Organometallic compounds which have 18 electrons (filled s, p, and d orbitals) are relatively stable. This suggests the compound is isolable, but it can result in the compound being inert.
In attempt to synthesize fulvalene

Produced an orange solid (ferrocene)

\[ \text{cyclo-C}_5\text{H}_5\text{MgBr} + \text{FeCl}_3 \rightarrow (\text{C}_5\text{H}_5)_2\text{Fe} \]

Discovery of ferrocene began the era of modern organometallic chemistry.
Write hydrocarbon ligands before the metal.

\[ \eta \]
superscript

Bridging ligand - \( \mu \)
Subscript indicating the number of metal atoms bridged.

**FIGURE 13-7** Common Organic Ligands.
## 13-2 Organic Ligands and Nomenclature

<table>
<thead>
<tr>
<th>Number of Bonding Positions</th>
<th>Formula</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\eta^1$-C$_5$H$_5$</td>
<td>monohaptocyclopentadienyl</td>
</tr>
<tr>
<td>3</td>
<td>$\eta^3$-C$_5$H$_5$</td>
<td>trihaptocyclopentadienyl</td>
</tr>
<tr>
<td>5</td>
<td>$\eta^5$-C$_5$H$_5$</td>
<td>pentahaptocyclopentadienyl</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Number of Atoms Bridged</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (terminal)</td>
<td>CO</td>
</tr>
<tr>
<td>2</td>
<td>$\mu_2$-CO</td>
</tr>
<tr>
<td>3</td>
<td>$\mu_3$-CO</td>
</tr>
</tbody>
</table>
13-3 The 18-Electron Rule; counting electrons

In main group chemistry, the octet rule

\[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{Cl} \]

Donor Pair method

<table>
<thead>
<tr>
<th>Species</th>
<th>Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(II)</td>
<td>6</td>
</tr>
<tr>
<td>(\eta^5\text{-C}_5\text{H}_5^-)</td>
<td>6</td>
</tr>
<tr>
<td>2 (CO)</td>
<td>4</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>2</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>18</strong></td>
</tr>
</tbody>
</table>

Neutral Ligand method

<table>
<thead>
<tr>
<th>Species</th>
<th>Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe atom</td>
<td>8</td>
</tr>
<tr>
<td>(\eta^5\text{-C}_5\text{H}_5)</td>
<td>5</td>
</tr>
<tr>
<td>2 (CO)</td>
<td>4</td>
</tr>
<tr>
<td>Cl</td>
<td>1</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>18</strong></td>
</tr>
</tbody>
</table>
13-3 The 18-Electron Rule

; counting electrons

M-M single bond counts as one electron per metal

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Method A</th>
<th>Method B</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>2 (H(^+))</td>
<td>1</td>
</tr>
<tr>
<td>Cl, Br, I</td>
<td>2 (X(^-))</td>
<td>1</td>
</tr>
<tr>
<td>OH(^-), OR(^-)</td>
<td>2 (OH(^-), OR(^-))</td>
<td>1</td>
</tr>
<tr>
<td>CN</td>
<td>2 (CN(^-))</td>
<td>1</td>
</tr>
<tr>
<td>CH(_3), CR(_3)</td>
<td>2 (CH(_3), CR(_3))</td>
<td>1</td>
</tr>
<tr>
<td>NO (bent M—N—O)</td>
<td>2 (NO(^-))</td>
<td>1</td>
</tr>
<tr>
<td>NO (linear M—N—O)</td>
<td>2 (NO(^+))</td>
<td>3</td>
</tr>
<tr>
<td>CO, PR(_3)</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>NH(_3), H(_2)O</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>C(_2)R(_2)' (carbene)</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>H(_2)C═CH(_2) (ethylene)</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>CNR</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>O, N</td>
<td>4 (O(^2-), S(^2-))</td>
<td>2</td>
</tr>
<tr>
<td>(\eta^3)-C(_3)H(_5) ((\pi)-allyl))</td>
<td>2 (C(_3)H(_5^+))</td>
<td>3</td>
</tr>
<tr>
<td>CR (carbene)</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>(\eta^3)-N</td>
<td>6 (N(^3-))</td>
<td>3</td>
</tr>
<tr>
<td>Ethylenediamine (en)</td>
<td>4 (2 per nitrogen)</td>
<td>4</td>
</tr>
<tr>
<td>Bipyridine (bipy)</td>
<td>4 (2 per nitrogen)</td>
<td>4</td>
</tr>
<tr>
<td>Butadiene</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>(\eta^3)-C(_3)H(_5) (cyclopentadienyl)</td>
<td>6 (C(_3)H(_5^-))</td>
<td>5</td>
</tr>
<tr>
<td>(\eta^5)-C(_6)H(_6) (benzene)</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>(\eta^7)-C(_7)H(_7) (cyclopeptatrienyl)</td>
<td>6 (C(_7)H(_7^+))</td>
<td>7</td>
</tr>
</tbody>
</table>
13-3 The 18-Electron Rule

Why 18 electrons?

$s^2p^6$ vs $s^2p^6d^{10}$

Have to consider types of ligand

Strong $\sigma$–donor ability of CO

Strong $\pi$–acceptor ability of CO

Good for 18-electron rule
13-3 The 18-Electron Rule

Why 18 electrons?

$[\text{Zn}(\text{en})_3]^{2+}$; ?? Electron species

- good $\sigma$-donor not as strong as CO
- $e_g$ orbitals are not sufficiently antibonding

$\text{TiF}_6^{2-}$; ?? Electron species

- $\sigma$-donor
- $\pi$-donor

What happens?
**Ligand field theory; Pi-Bonding**

**Metal-to-ligand π bonding** or π back-bonding:
- Increase stability
- Low-spin configuration
- Result of transfer of negative charge away from the metal ion

**Ligand-to-metal π bonding**
- Decrease stability
- High-spin configuration
13-3 The 18-Electron Rule; square-planar complexes

16 electron complexes might be stable

Square-planar complexes have important catalytic behavior

Why?
13-4 Ligands in Organometallic Chemistry; carbonyl (CO) complexes
13-4 Ligands in Organometallic Chemistry; carbonyl (CO) complexes

그림 13-12 CO와 N_2에 대한 분자 궤도함수의 일부분.

그림 13-13 CO와 금속 원자 간의 σ 및 π 상호 작용.
13-4 Ligands in Organometallic Chemistry
; carbonyl (CO) complexes

Experimental evidence

**Free CO vs M-CO**

Infrared spectroscopy and X-ray crystallography

Free CO has a C-O stretch at 2143 cm\(^{-1}\)
Cr(CO)\(_6\) has a C-O stretch at 2000 cm\(^{-1}\)

C-O distance 112.8 pm
Metal complexes 115 pm
In general, the more negative the charge on the organometallic species, the greater the tendency of the metal to donate electrons to the $\pi^*$ orbitals of CO and the lower the energy of the C-O stretching vibrations.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$v$(CO), cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[Ti(CO)_6]^2^-$</td>
<td>1748</td>
</tr>
<tr>
<td>$[V(CO)_6]^-$</td>
<td>1859</td>
</tr>
<tr>
<td>Cr(CO)$_6$</td>
<td>2000</td>
</tr>
<tr>
<td>$[Mn(CO)_6]^+$</td>
<td>2100</td>
</tr>
<tr>
<td>$[Fe(CO)_6]^{2+}$</td>
<td>2204</td>
</tr>
</tbody>
</table>

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.
13-4 Ligands in Organometallic Chemistry; bridging modes of CO

**TABLE 13-2**
Bridging Modes of CO

<table>
<thead>
<tr>
<th>Type of CO</th>
<th>Approximate Range for $\nu$ (CO) in Neutral Complexes (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free CO</td>
<td>2143</td>
</tr>
<tr>
<td>Terminal M$\rightarrow$CO</td>
<td>1850–2120</td>
</tr>
<tr>
<td>Symmetric$^a$ $\mu_2$–CO</td>
<td>1700–1860</td>
</tr>
<tr>
<td>Symmetric$^a$ $\mu_3$–CO</td>
<td>1600–1700</td>
</tr>
</tbody>
</table>

**NOTE:**$^a$ Asymmetrically bridging $\mu_2$- and $\mu_3$-CO are also known.

![Diagram of bridging modes of CO](image)

- $\sigma$ Donor
- $\pi$ Acceptor

$\nu_{CO} = 2082, 2019$ cm$^{-1}$

$\nu_{CO} = 1829$ cm$^{-1}$
Terminal and bridging carbonyl ligands can be considered 2-electron donors.
13-4 Ligands in Organometallic Chemistry; bridging modes of CO

\[ \Delta 
\]

\[
[(\eta^5-C_5H_5)Mo(CO)_3]_2 \leftrightarrow [(\eta^5-C_5H_5)Mo(CO)_2]^2 + 2 CO
\]

1960, 1915 cm\(^{-1}\)

1889, 1859 cm\(^{-1}\)
13-4 Ligands in Organometallic Chemistry; binary carbonyl complexes

Binary carbonyl complexes

More detail analysis is necessary
13-4 Ligands in Organometallic Chemistry; binary carbonyl complexes

Synthesis of binary carbonyl complexes

1. Direct reaction of a transition metal and CO; high T & P

\[ \text{Ni} + 4 \text{CO} \rightarrow \text{Ni(CO)}_4 \]

2. Reductive carbonylations

\[ \text{CrCl}_3 + 6 \text{CO} + \text{Al} \rightarrow \text{Cr(CO)}_6 + \text{AlCl}_3 \]
\[ \text{Re}_2\text{O}_7 + 17 \text{CO} \rightarrow \text{Re}_2(\text{CO})_{10} + 7 \text{CO}_2 \]

3. Thermal or photochemical reaction

\[ 2 \text{Fe(CO)}_5 \xrightarrow{h\nu} \text{Fe}_2(\text{CO})_9 + \text{CO} \]
\[ 3 \text{Fe(CO)}_5 \xrightarrow{\Delta} \text{Fe}_3(\text{CO})_{12} + 3 \text{CO} \]

Exchange reaction

\[ \text{Cr(CO)}_6 + \text{PPh}_3 \xrightarrow{\Delta \text{or } h\nu} \text{Cr(CO)}_5(\text{PPh}_3) + \text{CO} \]
\[ \text{Re(CO)}_5\text{Br} + \text{en} \xrightarrow{\Delta} \text{fac-Re(CO)}_3(\text{en})\text{Br} + 2 \text{CO} \]
13-4 Ligands in Organometallic Chemistry; oxygen-bonded cabonyls

(a) 

(b) 

\( \text{H}_3\text{C} \rightarrow \text{Zr} \rightarrow \text{O} \rightarrow \text{C} \rightarrow \text{Mo} \rightarrow \text{C} \rightarrow \text{O} \)

\( \text{O} \rightarrow \text{W} \rightarrow \text{C} \rightarrow \text{O} \rightarrow \text{Al(C}_6\text{H}_5)_3 \)
13-4 Ligands in Organometallic Chemistry

; ligands similar to CO

CS, CSe
Similar to CO in their bonding modes
In terminal or bridging
CS usually functions as a stronger $\sigma$ donor and $\pi$ acceptor than CO

isoelectronic; CN$^-$ and N$_2$
CN$^-$ is a stronger $\sigma$ donor and a somewhat $\pi$ weaker acceptor than CO
CN$^-$ bonds readily to metals having higher oxidation states

N$_2$ is a weaker donor and acceptor than CO
Nitrogen fixation
13-4 Ligands in Organometallic Chemistry

; ligands similar to CO; NO complexes

<table>
<thead>
<tr>
<th>Linear</th>
<th>Bent</th>
<th>Bridging</th>
<th>NS complex</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Linear Ligand" /></td>
<td><img src="image2" alt="Bent Ligand" /></td>
<td><img src="image3" alt="Bridging Ligand" /></td>
<td><img src="image4" alt="NS Complex" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Linear</th>
<th>Bent</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image5" alt="Linear NO" /></td>
<td><img src="image6" alt="Bent NO" /></td>
</tr>
</tbody>
</table>

- $\text{M—N—O angle}$: $165^\circ - 180^\circ$ for $\text{M—N—O in neutral molecules}$, $119^\circ - 140^\circ$ for $\text{M—N—O in NO complexes}$
- $\nu (\text{N—O})$ in neutral molecules: $1610 - 1830 \text{ cm}^{-1}$ for linear, $1520 - 1720 \text{ cm}^{-1}$ for bent
- Electron donor count: 2 (as $\text{NO}^+$) for linear, 1 (as $\text{NO}^-$) for bent
Hydride complexes

Organic synthesis, catalytic reaction

\[
\text{Co}_2(\text{CO})_8 + \text{H}_2 \rightarrow 2 \text{HCo(CO)}_4
\]

\[
\text{trans-Ir(CO)Cl(PEt}_3)_2 + \text{H}_2 \rightarrow \text{Ir(CO)Cl(H)}_2(\text{PEt}_3)_2
\]

\[
\text{Co}_2(\text{CO})_8 + 2 \text{Na} \rightarrow 2 \text{Na}^+[\text{Co(CO)}_4]^{-}
\]

\[
[\text{Co(CO)}_4]^{-} + \text{H}^+ \rightarrow \text{HCo(CO)}_4
\]
Distance of H-H
the metal is electron rich and donate strongly to the $\pi^*$ of $H_2 \rightarrow ???$
with CO and NO $\rightarrow ???$
13-4 Ligands in Organometallic Chemistry

ligands having extended π systems

π bonding within the ligands themselves-linear systems

\[
\begin{align*}
H_2C=CH_2 & \quad p \text{ orbitals interacting} & \quad \text{Relative energy} \\
\text{[Diagram] } & \quad \pi^* \\
\text{[Diagram] } & \quad \pi \\
H_2C-CH-CH_2 & \quad p \text{ orbitals interacting} & \quad \text{Relative energy} \\
\text{[Diagram] } & \quad \pi^* \\
\text{[Diagram] } & \quad \pi_n \\
\text{[Diagram] } & \quad \pi
\end{align*}
\]
13-4 Ligands in Organometallic Chemistry; ligands having extended $\pi$ systems

$H_2C\equiv CH\equiv CH\equiv CH_2$

$\pi$ bonding within the ligands themselves-linear systems
13-4 Ligands in Organometallic Chemistry

\( \pi \) bonding within the ligands themselves - cyclic systems

\[
\text{cyclo-C}_3\text{H}_3
\]

\( p \) orbitals interacting

Relative energy

One 2-node \( \pi \) orbital

Two 1-node \( \pi \) orbitals

One 0-node \( \pi \) orbital

Relative energy
13-4 Ligands in Organometallic Chemistry; ligands having extended π systems

π bonding within the ligands themselves-cyclic systems
13-4 Bonding between Metal Atoms and Organic $\pi$ Systems; linear $\pi$ systems

Typically bent back away from the metal

$\pi$-bonding electron pair  the empty $\pi^*$-orbital

Free ethylene 133.7 pm, 1623 cm$^{-1}$
Coordinated ethylene 137.5 pm, 1516 cm$^{-1}$
13-4 Bonding between Metal Atoms and Organic $\pi$ Systems; linear $\pi$ systems

$\pi$-allyl complexes

$\eta^3$-C$_3$H$_5^-$

$\eta^1$-C$_3$H$_5^-$

Other metal orbitals of suitable symmetry

acceptor

Donor or acceptor

donor
13-4 Bonding between Metal Atoms and Organic $\pi$ Systems; linear $\pi$ systems

- $\pi$–allyl complexes
- Conversion between $\eta^1$ and $\eta^3$
- Catalytic reaction

\[
[Mn(CO)_5]^− + C_3H_5Cl \rightarrow (\eta^1-C_3H_5)Mn(CO)_5 + Cl^− \xrightarrow{\Delta \text{ or } h\nu} (\eta^3-C_3H_5)Mn(CO)_4 + CO
\]

Other linear $\pi$ systems
13-4 Bonding between Metal Atoms and Organic $\pi$ Systems; cyclic $\pi$ systems

Cyclopentadienyl (Cp) complexes

$n^1$, $n^3$ and $n^5$ $C_5(CH_3)_5$ Cp*

Gas phase and low-T

Most stable conformation
13-4 Bonding between Metal Atoms and Organic $\pi$ Systems; cyclic $\pi$ systems

Orbital lobes of like sign pointed toward each other

Orbital lobes of opposite sign pointed toward each other

Bonding 1

Antibonding 2

Actual shape of bonding orbital 1

2-Node group orbitals

1-Node group orbitals

0-Node group orbitals
Molecular orbital energy levels of Ferrocene
13-4 Bonding between Metal Atoms and Organic $\pi$ Systems; cyclic $\pi$ systems

**FIGURE 13-29** Molecular Orbitals of Ferrocene Having Greatest $d$ Character.
13-4 Bonding between Metal Atoms and Organic $\pi$ Systems; cyclic $\pi$ systems

Other metallocenes

$\#$ of electron $\rightarrow$ stability $\rightarrow$ reactivity

**TABLE 13-3**

Comparative Data for Selected Metallocenes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Electron Count</th>
<th>M–C Distance (pm)</th>
<th>$\Delta H$ for $M^{2+}$-$C_5H_5^-$ Dissociation (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\eta^5\text{-}C_5H_5)_2\text{Fe}$</td>
<td>18</td>
<td>206.4</td>
<td>1470</td>
</tr>
<tr>
<td>$(\eta^5\text{-}C_5H_5)_2\text{Co}$</td>
<td>19</td>
<td>211.9</td>
<td>1400</td>
</tr>
<tr>
<td>$(\eta^5\text{-}C_5H_5)_2\text{Ni}$</td>
<td>20</td>
<td>219.6</td>
<td>1320</td>
</tr>
</tbody>
</table>

$$2 \ (\eta^5\text{-}C_5H_5)_2\text{Co} + I_2 \rightarrow 2 \ [(\eta^5\text{-}C_5H_5)_2\text{Co}]^+ + 2 \ I^-$$

$19$ e$^-$

$18$ e$^-$

cobalticinium ion

$$(\eta^5\text{-}C_5H_5)_2\text{Ni} + 4\text{PF}_3 \rightarrow \text{Ni(PF}_3)_4 + \text{organic products}$$

$20$ e$^-$

$18$ e$^-$
13-4 Bonding between Metal Atoms and Organic $\pi$ Systems; cyclic $\pi$ systems

그림 13-30 코발티시늄과 수소화 이온의 반응.

그림 13-31 폐로센의 전전사성 야심 치환 반응.
13-4 Bonding between Metal Atoms and Organic $\pi$ Systems; cyclic $\pi$ systems

Complexes containing cyclopentadienyl and CO ligand
Half-sandwich

**FIGURE 13-33** Examples of Molecules Containing Cyclic $\pi$ Systems.

**FIGURE 13-32** Complexes Containing $C_3H_5$ and CO.
13-5 Fullerene Complexes

Types of fullerene complexes
1. Adducts to the oxygens
2. As a ligand
3. Encapsulated metals
4. Intercalation compounds of alkali metals

Adducts to the oxygens

FIGURE 13-34 Structure of $\text{C}_{60}(\text{OsO}_4)(4$-$t$-butylpyridine)$_2$. 
13-5 Fullerene Complexes

As ligands
Dihapto, pentahepto, hexahapto

Displacement reaction

\[ [(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Pt}(\eta^2-\text{C}_2\text{H}_4) + \text{C}_{60} \rightarrow [(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Pt}(\eta^2-\text{C}_{60}) \]

More than one metal

그림 13-36  \([(\text{C}_6\text{H}_5)_2\text{Pt}]_4\text{C}_{60}\)의 구조 (G. O. Spessard and G. L. Miessler, *Organometallic Chemistry*, Prentice Hall, Upper Saddle River, NJ, 1997, p. 511. Fig. 13-13에서 르락히에 계제).
13-5 Fullerene Complexes

\( \eta^2-C_{70} \)Ir(CO)(PPh3)2의 입체모양


\( n_2-n_2-n_2 \) and \( n_5 \)

그림 13-37

\( \text{(a) Ru}_4(\text{CO})_8(\eta^2-n_5, \eta^2, \eta^2-C_{70}) \). (b) 및 (c) Fe(\( \eta^2-C_{70} \)H(\( \eta^2-C_{70} \)CH3))의 ORTEP 및 공간체 모형 (H. F. Hsu and J. R. Shapley, *J. Am. Chem. Soc.*, 1996, 118, 9192, and from M. Sawamura, Y. Kunitoh, M. Toginoh, Y. Matuo, M. Yamanaka, and E. Nakamura, *J. Am. Chem. Soc.*, 2002, 124, 9354. © 1996 American Chemical Society에서 허락하여 게재됨).
13-5 Fullerene Complexes

Encapsulated metals

By laser-induced vapor phase reactions between carbon and the metal

\[
\text{U@C}_{60} \quad \text{contains U surrounded by C}_{60} \\
\text{Sc}_{3}@\text{C}_{82} \quad \text{contains three atoms of Sc surrounded by C}_{82}^{53} \\
\text{La@C}_{82}; \text{La}^{3+}, \text{C}_{82}^{3-}
\]
### TABLE 13-4
Complexes Containing M—C, M=C, and M≡C Bonds

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Formula</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkyl</td>
<td>=CR₃</td>
<td>W(CH₃)₆</td>
</tr>
<tr>
<td>Carbene (alkylidene)</td>
<td>=CR₂</td>
<td>(OC)₅Cr≡C</td>
</tr>
<tr>
<td>Carbyne (alkylidyne)</td>
<td>=CR</td>
<td>X—Cr≡C—C₆H₅</td>
</tr>
<tr>
<td>Cumulene</td>
<td>=C(=C)ₙRR’</td>
<td>Cl—Ir≡C≡C≡C≡C≡C₆H₅</td>
</tr>
</tbody>
</table>
13-6 Complexes Containing M-C, M=C and M≡C Bonds; alkyl and related complexes

Synthetic route

1. Reaction of a transition metal halide with organolithium, organomagnesium, or organoaluminum reagent.
   **Example:** \( \text{ZrCl}_4 + 4 \text{PhCH}_2\text{MgCl} \rightarrow \text{Zr(CH}_2\text{Ph})_4 (\text{Ph} = \text{phenyl}) \)

2. Reaction of a metal carbonyl anion with alkyl halide.
   **Example:** \( \text{Na[Mn(CO)}_5]^- + \text{CH}_3\text{I} \rightarrow \text{CH}_3\text{Mn(CO)}_5 + \text{NaI} \)

Relatively rare: kinetically unstable and difficult to isolate
Enhancing the stability; By blocking pathways to decomposition

mtallacycle

Proposed as intermediates in a variety catalytic processes
### TABLE 13-5
Other Ligands Forming σ Bonds to Metals

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Formula</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aryl</td>
<td><img src="image" alt="Aryl" /></td>
<td><img src="image" alt="Aryl" /></td>
</tr>
<tr>
<td>Alkenyl (vinyl)</td>
<td><img src="image" alt="Alkenyl" /></td>
<td><img src="image" alt="Alkenyl" /></td>
</tr>
<tr>
<td>Alkynyl</td>
<td><img src="image" alt="Alkynyl" /></td>
<td><img src="image" alt="Alkynyl" /></td>
</tr>
</tbody>
</table>
13-6 Complexes Containing M-C, M=C and M≡C Bonds; carbene complexes

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

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Fischer-type Carbene Complex</th>
<th>Schrock-type Carbene Complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical metal [oxidation state]</td>
<td>Middle to late transition metal [Fe(0), Mo(0), Cr(0)]</td>
<td>Early transition metal [Ti(IV), Ta(V)]</td>
</tr>
<tr>
<td>Substituents attached to C&lt;sub&gt;carbene&lt;/sub&gt;</td>
<td>At least one highly electronegative heteroatom (such as O, N, or S)</td>
<td>H or alkyl</td>
</tr>
<tr>
<td>Typical other ligands in complex</td>
<td>Good π acceptors</td>
<td>Good σ or π donors</td>
</tr>
<tr>
<td>Electron count</td>
<td>18</td>
<td>10–18</td>
</tr>
</tbody>
</table>

그림 13-40 카벤 측물과 알켄의 결합 비교.

![Diagram of bonding between d orbital and p orbital](image)
Highly electronegative atom can participate in the $\pi$ bonding $\rightarrow$ stabilize
13-6 Complexes Containing M-C, M=C and M≡C Bonds; carbene complexes

Olefin metathesis

\[
\text{Li}^+ : \text{C}_6\text{H}_5^- + \text{O}≡\text{C} \rightarrow \text{Cr(CO)}_5 \rightarrow \text{C}_6\text{H}_5^- \text{C} \rightarrow \text{Cr(CO)}_5 \leftarrow \text{C}_6\text{H}_5^- \text{C}≡\text{Cr(CO)}_5 + \text{Li}^+
\]

Highly nucleophilic reagent

\[
\text{OCH}_3
\]

\[
\text{O}
\]

\[
\text{C}_6\text{H}_5^- \text{C} \rightarrow \text{Cr(CO)}_5 + [(\text{CH}_3)_3\text{O}][\text{BF}_4] \rightarrow \text{C}_6\text{H}_5^- \text{C}≡\text{Cr(CO)}_5 + \text{BF}_4^- + (\text{CH}_3)_2\text{O}
\]

X-ray; Cr-C, C-O
NMR; RT (one signal), low T (two peak)
Why?

C-O 143 pm
C=O 116pm

Highly electronegative atom can participate in the \( \pi \) bonding \( \rightarrow \) stabilize
13-6 Complexes Containing M-C, M=C and M≡C Bonds; carbyne (alkylidyne) complexes

\[
\begin{align*}
(CO)_5Cr&\equiv C\xrightarrow{\text{Lewis acid}} \ [((CO)_5Cr\equiv C\equiv C_6H_5]^+X^- \\
&\quad + X_2BOCH_3
\end{align*}
\]

\[\sigma \text{ donor} \quad \pi \text{ acceptor}\]

**FIGURE 13-43** Bonding in Carbyne Complexes.
13-6 Spectral Analysis and Characterization of Organometallic Complexes; IR spectra

X-ray, Mass spectrometry, elemental analysis, conductivity measurement etc.

# of bands

Provide clues to the geometry or symmetry

**Symmetric Stretch**

\[ O \leftarrow C \rightarrow M \rightarrow C \rightarrow O \]

- No change in dipole moment; IR inactive
- Change in dipole moment; IR active

**Antisymmetric Stretch**

\[ O \leftarrow C \rightarrow M \leftarrow C \leftarrow O \]

- Change in dipole moment; IR active
- Change in dipole moment; IR active
<table>
<thead>
<tr>
<th>CO ligand number</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR peak</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>IR peak</td>
<td>3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>IR peak</td>
<td>4</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>IR peak</td>
<td>3</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

13-6 Spectral Analysis and Characterization of Organometallic Complexes; IR spectra
In general, the more negative the charge on the organometallic species, the greater the tendency of the metal to donate electrons to the $\pi^*$ orbitals of CO and the lower the energy of the C-O stretching vibrations.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$v$(CO), cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ti(CO)$_6$]$^{2-}$</td>
<td>1748</td>
</tr>
<tr>
<td>[V(CO)$<em>6$]$^-</em>{}$</td>
<td>1859</td>
</tr>
<tr>
<td>Cr(CO)$_6$</td>
<td>2000</td>
</tr>
<tr>
<td>[Mn(CO)$_6$]$^{+}$</td>
<td>2100</td>
</tr>
<tr>
<td>[Fe(CO)$_6$]$^{2+}$</td>
<td>2204</td>
</tr>
</tbody>
</table>

Provide clues to the electronic environment on the metal
The greater the electronic density on the metal $\rightarrow$ ???
terminal CO $>$ doubly bridging CO $>$ triply bridging CO

**TABLE 13-8**

Examples of Carbonyl Stretching Bands: Molybdenum Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$v$ (CO), cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$fac$-$Mo$(CO)$_3$(PF$_3$)$_3$</td>
<td>2090, 2055</td>
</tr>
<tr>
<td>$fac$-$Mo$(CO)$_3$(PCl$_3$)$_3$</td>
<td>2040, 1991</td>
</tr>
<tr>
<td>$fac$-$Mo$(CO)$_3$(PClPh$_2$)$_3$</td>
<td>1977, 1885</td>
</tr>
<tr>
<td>$fac$-$Mo$(CO)$_3$(PMe$_3$)$_3$</td>
<td>1945, 1854</td>
</tr>
</tbody>
</table>


What do you get from this data?

Other ligands also have similar correlation. (NO...)
13-6 Spectral Analysis and Characterization of Organometallic Complexes; NMR spectra

$^1$H, $^{13}$C, $^{19}$F, $^{31}$P, metal nuclei etc.
Chemical shifts, splitting patterns, coupling constants

$^{13}$C NMR

**TABLE 13-9**

$^{13}$C Chemical Shifts for Organometallic Compounds

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$^{13}$C Chemical Shift (Range)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M\rightarrow$CH$_3$</td>
<td>-28.9 to 23.5</td>
</tr>
<tr>
<td>$M\equiv$C</td>
<td>190 to 400</td>
</tr>
<tr>
<td>$M\equiv$C$^-$</td>
<td>235 to 401</td>
</tr>
<tr>
<td>$M\rightarrow$CO</td>
<td>177 to 275</td>
</tr>
<tr>
<td>Neutral binary CO</td>
<td>183 to 223</td>
</tr>
<tr>
<td>$M\rightarrow$(η$^5$-C$_5$H$_5$)</td>
<td>-790 to 1430</td>
</tr>
<tr>
<td>Fe(η$^5$-C$_5$H$_5$)$_2$</td>
<td>69.2</td>
</tr>
<tr>
<td>$M\rightarrow$(η$^3$-C$_3$H$_5$)</td>
<td>( \frac{C_2}{91 \text{ to } 129} )</td>
</tr>
<tr>
<td>$M\rightarrow$C$_6$H$_5$</td>
<td>( \frac{M\rightarrow C}{130 \text{ to } 193} )</td>
</tr>
<tr>
<td>&amp;</td>
<td>( \frac{ortho}{132 \text{ to } 141} )</td>
</tr>
<tr>
<td>&amp;</td>
<td>( \frac{meta}{127 \text{ to } 130} )</td>
</tr>
<tr>
<td>&amp;</td>
<td>( \frac{para}{121 \text{ to } 131} )</td>
</tr>
</tbody>
</table>

Note: $^a$Parts per million (ppm) relative to Si(CH$_3$)$_4$. 

Chemical shift
### TABLE 13-10
Examples of $^1$H Chemical Shifts for Organometallic Compounds

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^1$H Chemical Shift$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(CO)$_5$H</td>
<td>-7.5</td>
</tr>
<tr>
<td>W(CH$_3$)$_6$</td>
<td>1.80</td>
</tr>
<tr>
<td>Ni($^2$-C$_2$H$_4$)$_3$</td>
<td>3.06</td>
</tr>
<tr>
<td>($^5$-C$_5$H$_5$)$_2$Fe</td>
<td>4.04</td>
</tr>
<tr>
<td>($^6$-C$_6$H$_6$)$_2$Cr</td>
<td>4.12</td>
</tr>
<tr>
<td>($^5$-C$_5$H$_5$)$_2$Ta(CH$_3$)(==CH$_2$)</td>
<td>10.22</td>
</tr>
</tbody>
</table>

*NOTE: $^a$ Parts per million relative to Si(CH$_3$)$_4$.*

integration
13-6 Spectral Analysis and Characterization of Organometallic Complexes; NMR spectra

Molecular rearrangement processes

At RT; 2 singlets
At low T

Ring whizzer
Exercise 13-1~13-12

Problem 1, 2, 4, 6, 13, 20, 33.