

Chapter 13 Organometallic Chemistry

13-1 Historical Background

13-2 Organic Ligands and Nomenclature

13-3 The 18-Electron Rule

13-4 Ligands in Organometallic Chemistry

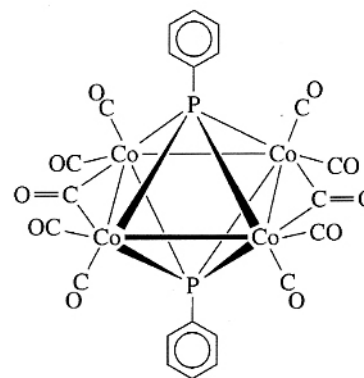
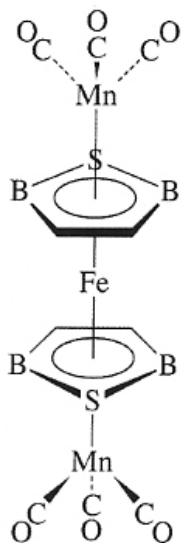
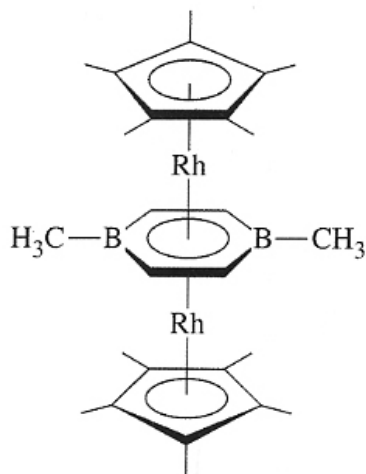
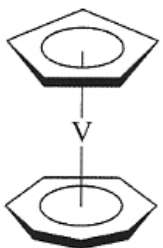
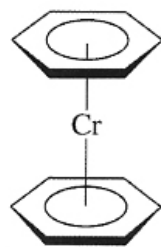
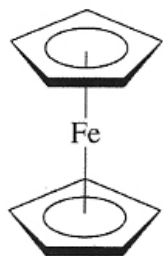
13-5 Bonding Between Metal Atoms and Organic π Systems

13-6 Complexes Containing M-C, M=C, and M \equiv C Bonds

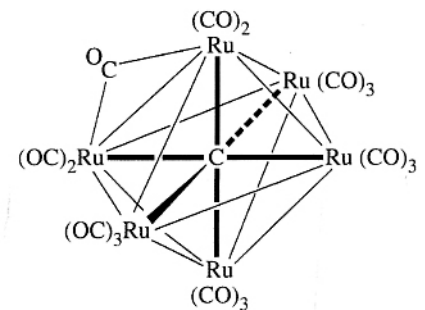
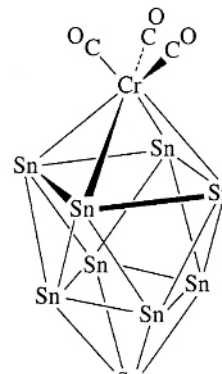
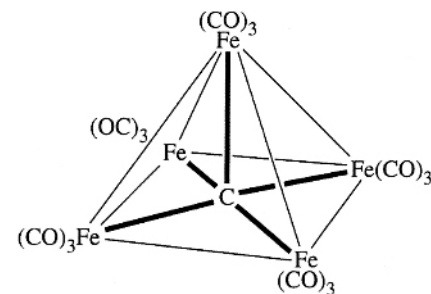
13-7 Spectral Analysis and Characterization of Organometallic Complexes

13-1 Historical Background

Sandwich compounds



Cluster compounds



13-1 Historical Background

Other examples of organometallic compounds

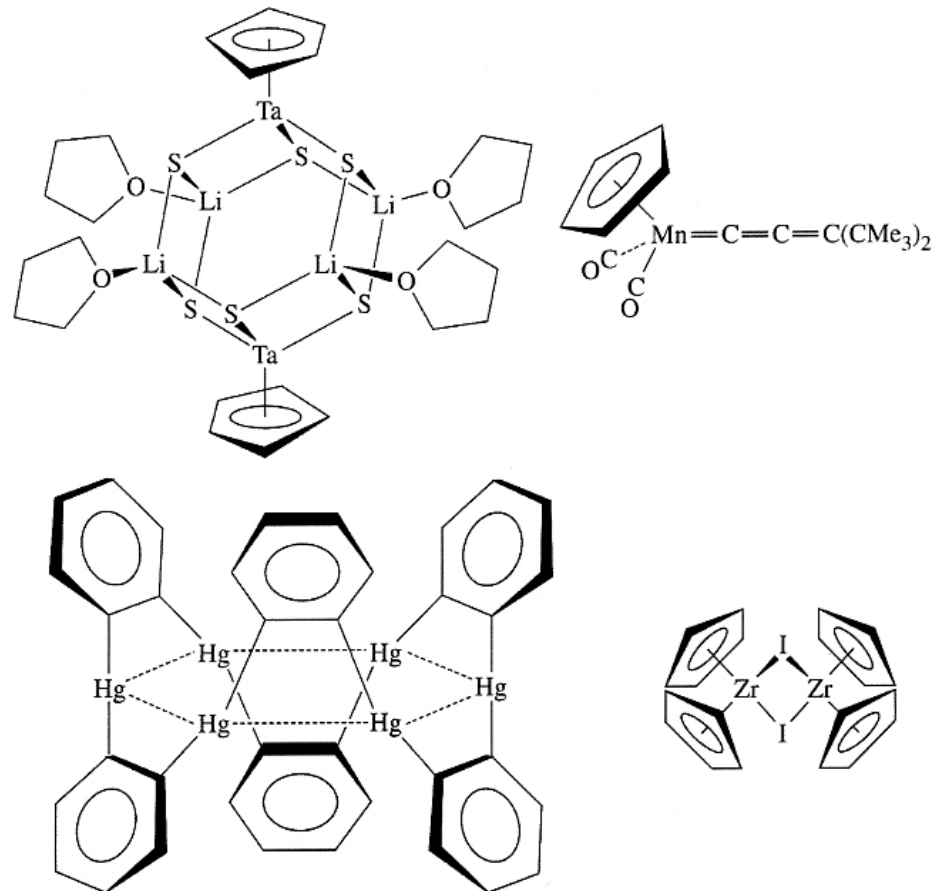


그림 13-3 유기금속 화합물의 다른 예.

13-1 Historical Background

Organometallic Compound

Organometallic chemistry is the study of chemical compounds containing bonds between carbon and a metal.

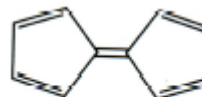
Organometallic chemistry combines aspects of inorganic chemistry and organic chemistry.

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.

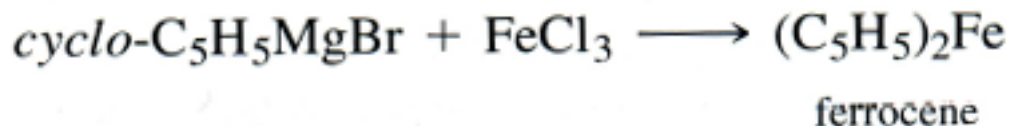
13-1 Historical Background

In attempt to synthesize fulvalene

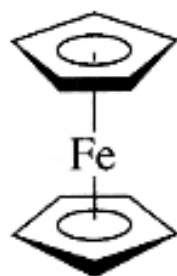


Fulvalene

Produced an orange solid (ferrocene)

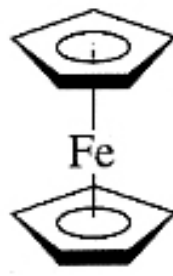


Discovery of ferrocene began the era of modern organometallic chemistry.



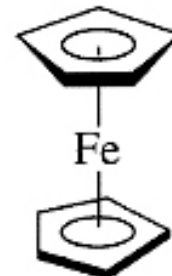
D_{5d}

Staggered rings



D_{5h}

Eclipsed rings



D_5

Skew rings

13-2 Organic Ligands and Nomenclature

Write hydrocarbon ligands before the metal.

η
superscript

Bridging ligand - μ

Subscript indicating the number of metal atoms bridged.







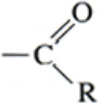
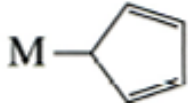
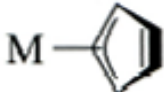

Ligand	Name	Ligand	Name
CO	Carbonyl		Benzene
$=\text{C}$	Carbene (alkylidene)		1,5-cyclooctadiene (1,5-COD) (1,3-cyclooctadiene complexes are also known)
$\equiv\text{C}-$	Carbyne (alkylidyne)	$\text{H}_2\text{C}=\text{CH}_2$	Ethylene
	Cyclopropenyl (<i>cyclo</i> - C_3H_3)	$\text{HC}\equiv\text{CH}$	Acetylene
	Cyclobutadiene (<i>cyclo</i> - C_4H_4)		π -Allyl (C_3H_5)
	Cyclopentadienyl (<i>cyclo</i> - C_5H_5)(Cp)	$-\text{CR}_3$	Alkyl
			Acyl

FIGURE 13-7 Common Organic Ligands.

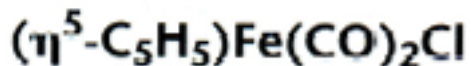
13-2 Organic Ligands and Nomenclature

<i>Number of Bonding Positions</i>	<i>Formula</i>	<i>Name</i>	
1	$\eta^1\text{-C}_5\text{H}_5$	monohaptocyclopentadienyl	M 
3	$\eta^3\text{-C}_5\text{H}_5$	trihaptocyclopentadienyl	M 
5	$\eta^5\text{-C}_5\text{H}_5$	pentahaptocyclopentadienyl	M 

<i>Number of Atoms Bridged</i>	<i>Formula</i>
None (terminal)	CO
2	$\mu_2\text{-CO}$
3	$\mu_3\text{-CO}$

13-3 The 18-Electron Rule ; counting electrons

In main group chemistry, the octet rule



Donor Pair method

Fe(II)	6 electrons
$\eta^5\text{-C}_5\text{H}_5^-$	6 electrons
2 (CO)	4 electrons
Cl^-	<u>2 electrons</u>
Total =	18 electrons

Neutral Ligand method

Fe atom	8 electrons
$\eta^5\text{-C}_5\text{H}_5$	5 electrons
2 (CO)	4 electrons
Cl	<u>1 electron</u>
Total =	18 electrons

13-3 The 18-Electron Rule ; counting electrons

M-M single bond counts as one electron per metal

TABLE 13-1
Electron Counting Schemes for Common Ligands

<i>Ligand</i>	<i>Method A</i>	<i>Method B</i>
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
$=\text{CRR}'$ (carbene)	2	2
$\text{H}_2\text{C}=\text{CH}_2$ (ethylene)	2	2
CNR	2	2
$=\text{O}$, $=\text{S}$	4 (O^{2-} , S^{2-})	2
$\eta^3\text{-C}_3\text{H}_5$ (π -allyl)	2 (C_3H_5^+)	3
$\equiv\text{CR}$ (carbyne)	3	3
$\equiv\text{N}$	6 (N^{3-})	3
Ethylenediamine (en)	4 (2 per nitrogen)	4
Bipyridine (bipy)	4 (2 per nitrogen)	4
Butadiene	4	4
$\eta^5\text{-C}_5\text{H}_5$ (cyclopentadienyl)	6 (C_5H_5^-)	5
$\eta^6\text{-C}_6\text{H}_6$ (benzene)	6	6
$\eta^7\text{-C}_7\text{H}_7$ (cycloheptatrienyl)	6 (C_7H_7^+)	7

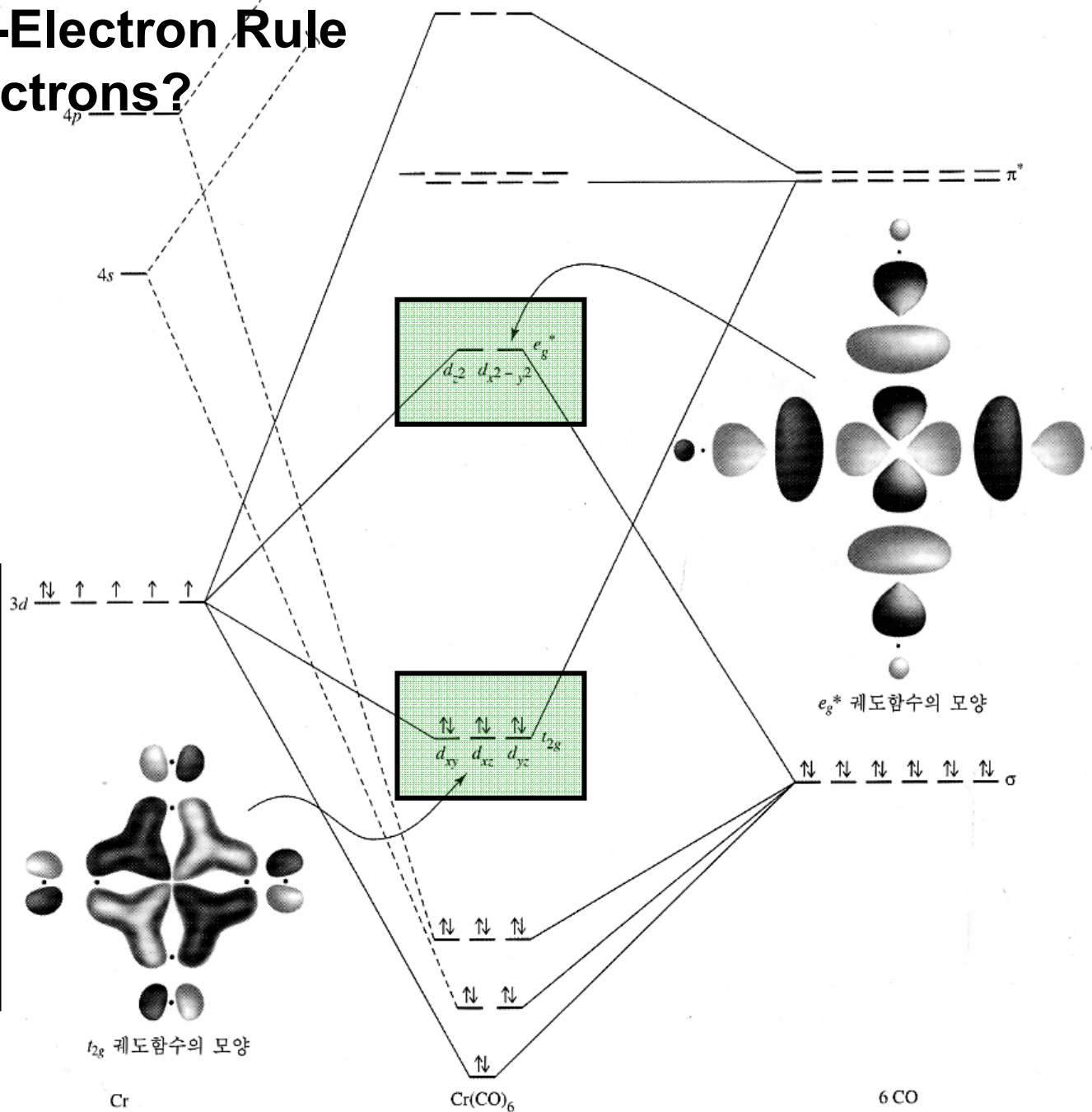
13-3 The 18-Electron Rule ; why 18 electrons?

s^2p^6 vs $s^2p^6d^{10}$
 Have to consider types of ligand

Strong σ -donor ability of CO

Strong π -acceptor ability of CO

Good for 18-electron rule

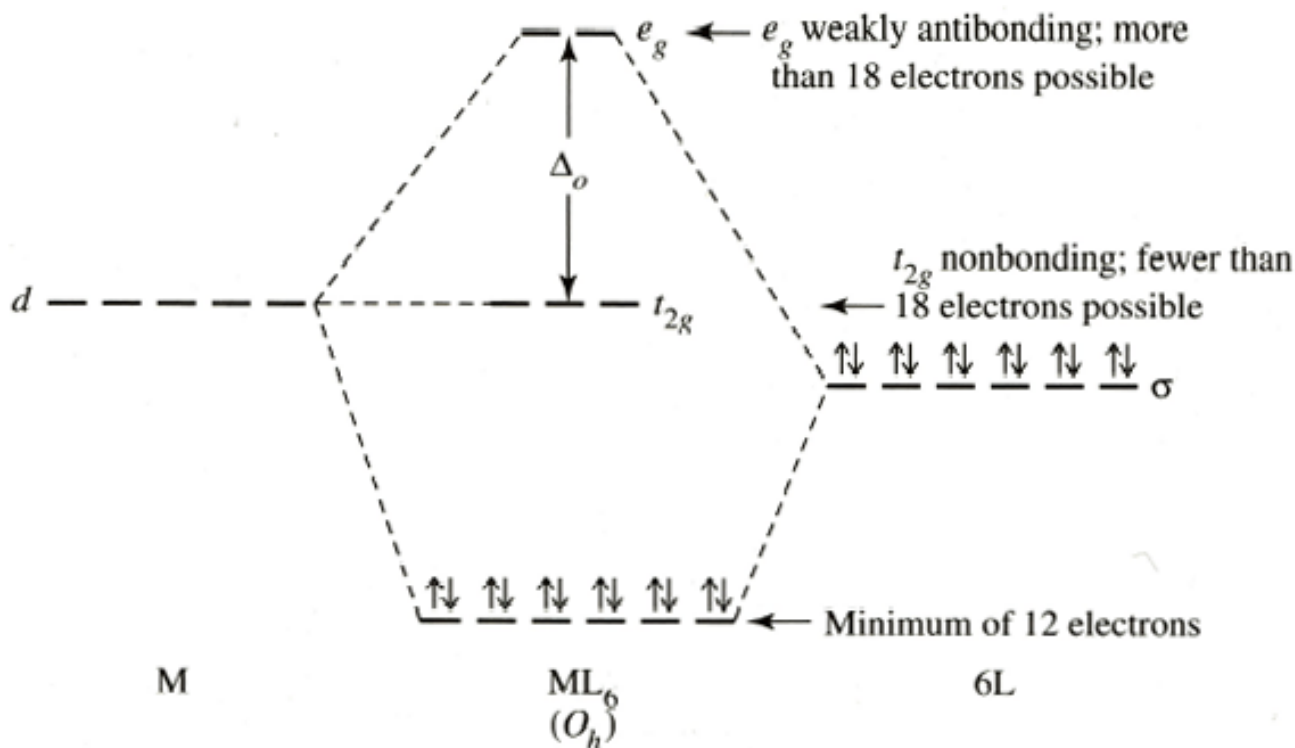


13-3 The 18-Electron Rule

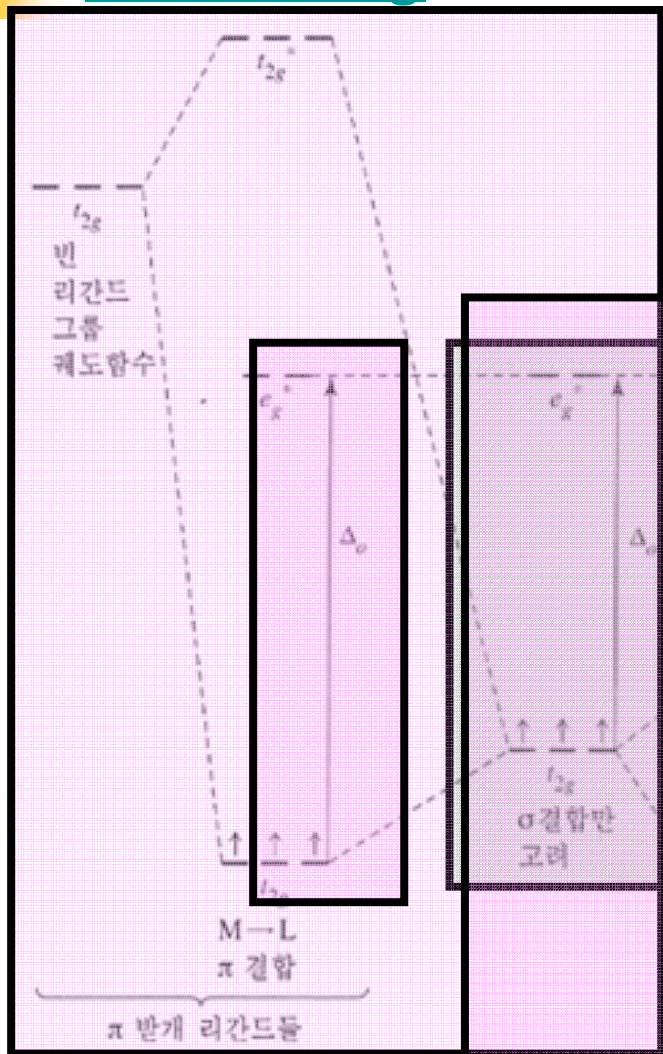
Why 18 electrons?

$[\text{Zn}(\text{en})_3]^{2+}$; ?? Electron species
good σ -donor not as strong as CO
 e_g orbitals are not sufficiently
antibonding

TiF_6^{2-} ; ?? Electron species
 σ -donor
 π -donor
What happen?



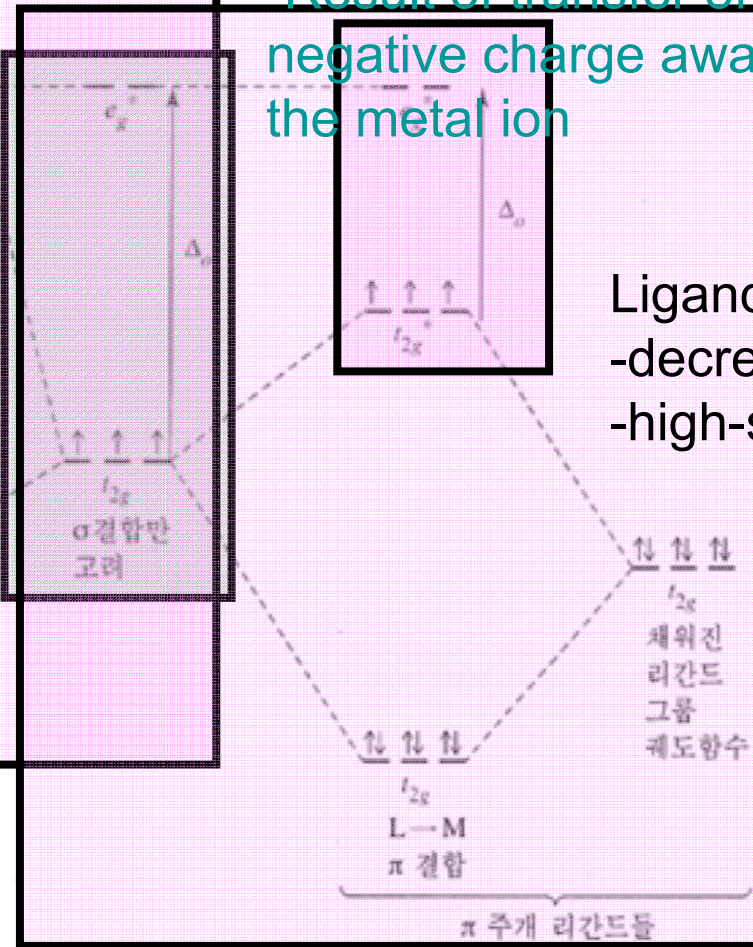
Ligand field theory; Pi-Bonding



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



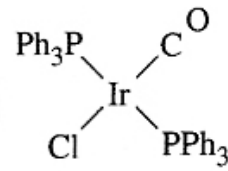
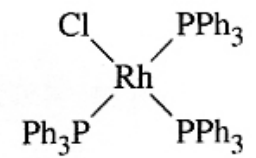
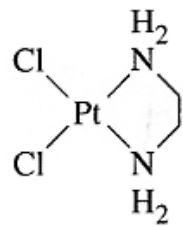
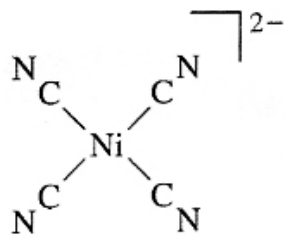
- Ligand-to metal π bonding
- decrease stability
 - high-spin configuration

그림 10-11 π 결합에 의한 Δ_o 의
변화(d^3 이온을 예로 설명함).

13-3 The 18-Electron Rule ; square-planar complexes

16 electron complexes might be stable

Square-planar complexes have important catalytic behavior
Why?



윌킨슨의 착물

바스카의 착물

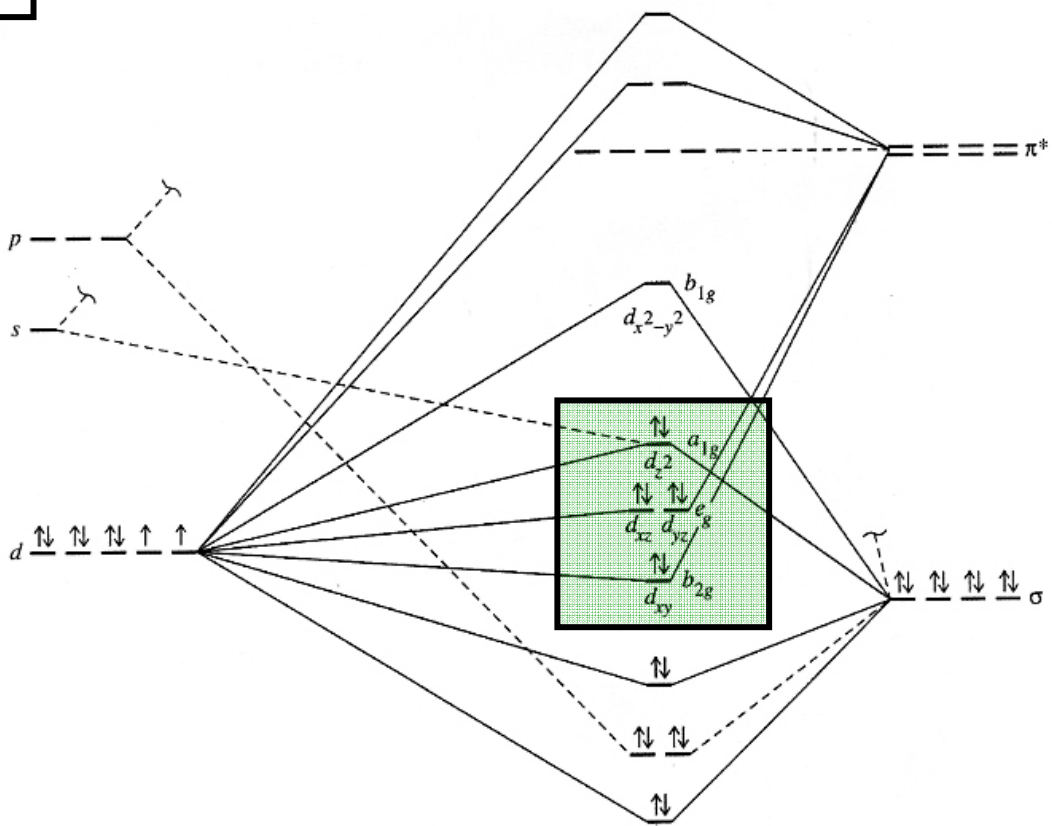


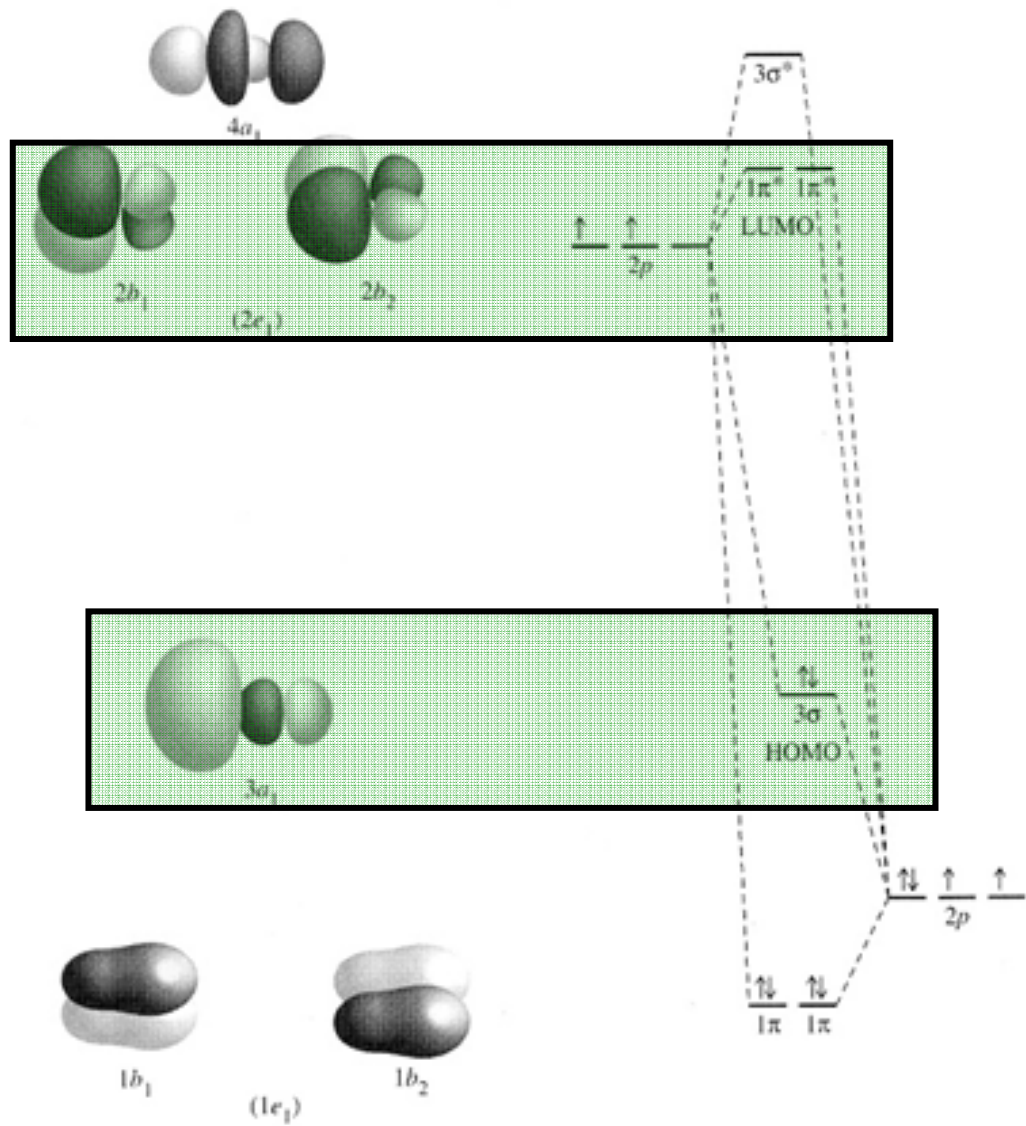
그림 13-11 평면사각형 착물의 분자 궤도함수 에너지 준위.

M

$ML_4(D_{4h})$

4L

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



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

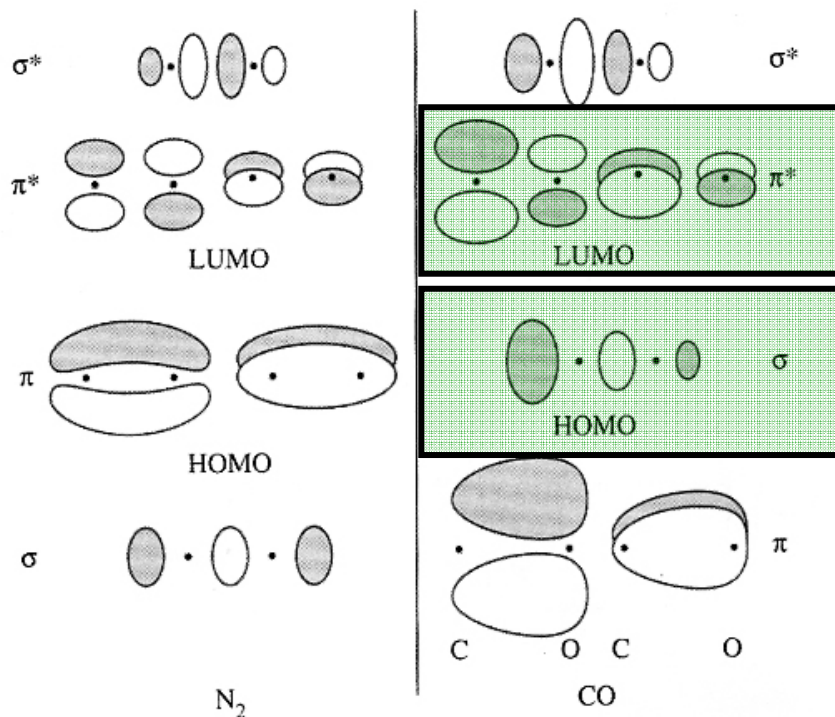


그림 13-12 CO 와 N_2 에 대한 분자 궤도함수의 일부분.

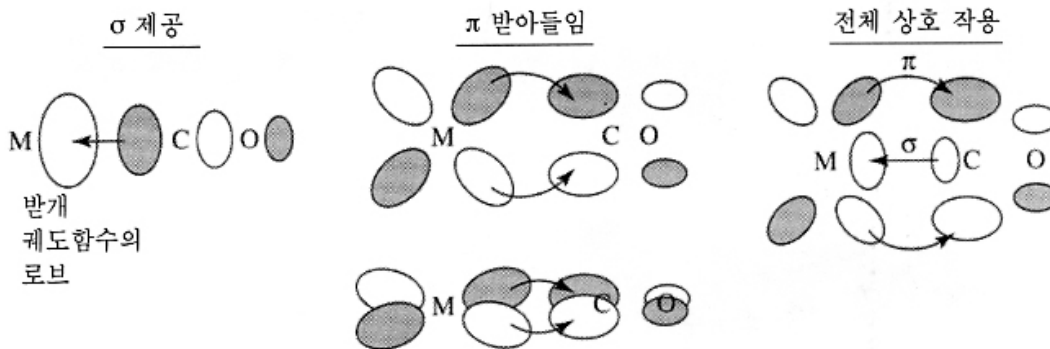


그림 13-13 CO 와 금속 원자 간의 σ 및 π 상호 작용.

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}

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

C-O distance 112.8 pm

Metal complexes 115 pm

13-4 Ligands in Organometallic Chemistry

; carbonyl (CO) complexes

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.**

<i>Complex</i>	$\nu(\text{CO}), \text{cm}^{-1}$
$[\text{Ti}(\text{CO})_6]^{2-}$	1748
$[\text{V}(\text{CO})_6]^-$	1859
$\text{Cr}(\text{CO})_6$	2000
$[\text{Mn}(\text{CO})_6]^+$	2100
$[\text{Fe}(\text{CO})_6]^{2+}$	2204

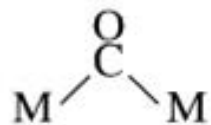
$\delta+ \delta-$	$\delta+ \delta-$
$\text{C}=\text{O}$	$\text{M}^{n+} \leftarrow \text{C}\equiv\text{O}$

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.

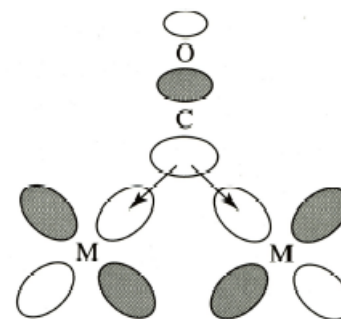
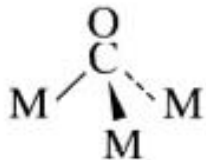
13-4 Ligands in Organometallic Chemistry ; bridging modes of CO

TABLE 13-2
Bridging Modes of CO

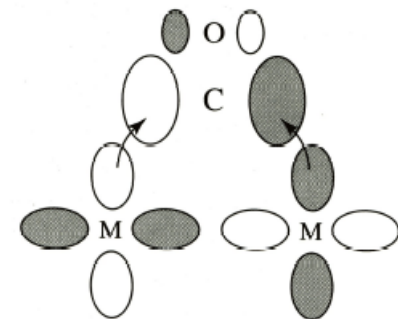
Type of CO	Approximate Range for ν (CO) in Neutral Complexes (cm^{-1})
Free CO	2143
Terminal M—CO	1850–2120
Symmetric ^a μ_2 —CO	1700–1860
Symmetric ^a μ_3 —CO	1600–1700



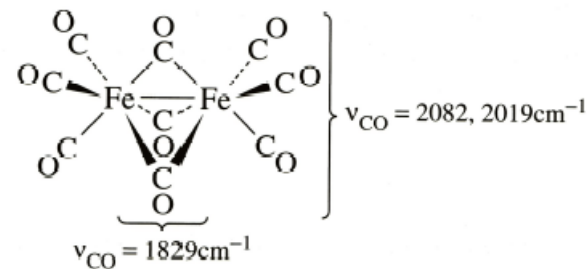
Symmetric^a μ_3 —CO



σ Donor



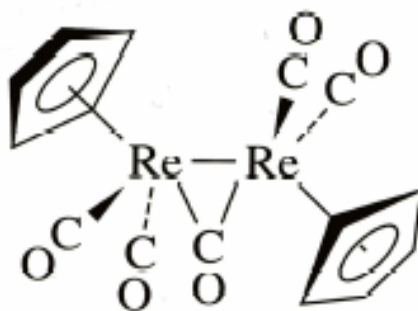
π Acceptor



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

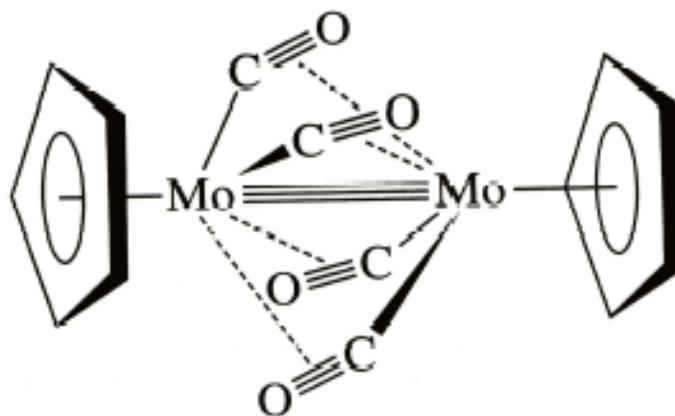
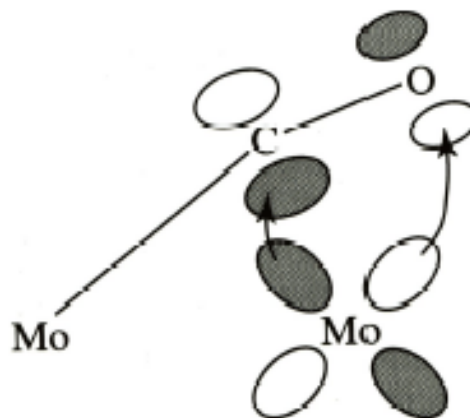
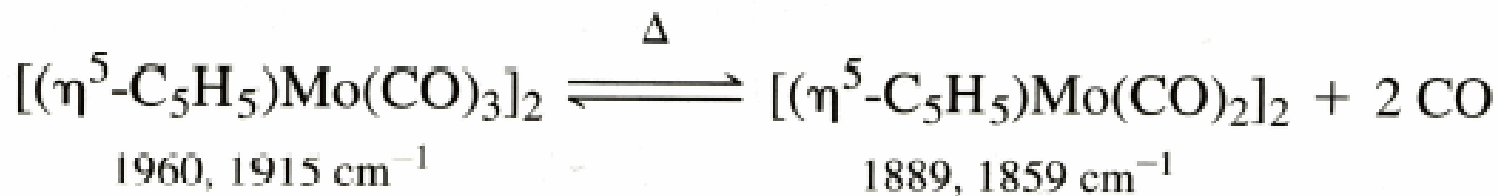
13-4 Ligands in Organometallic Chemistry ; bridging modes of CO

Terminal and bridging carbonyl ligands can be considered 2-electron donors.



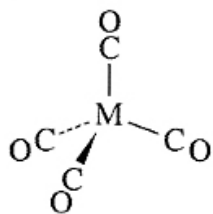
Re	$7 e^-$
$\eta^5\text{-C}_5\text{H}_5$	$5 e^-$
2 CO (terminal)	$4 e^-$
$\frac{1}{2}(\mu_2\text{-CO})$	$1 e^-$
M—M bond	$1 e^-$
Total =	$\underline{18 e^-}$

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

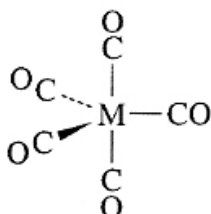


13-4 Ligands in Organometallic Chemistry ; binary carbonyl complexes

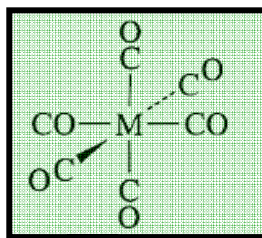
단핵 $[M(CO)_n]$



M = Ni, Pd

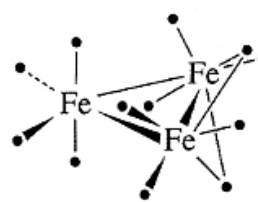


M = Fe, Ru, Os

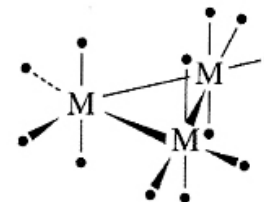


M = V, Cr, Mo, W

다핵 [CO를 간략하게 • 으로 표시함]

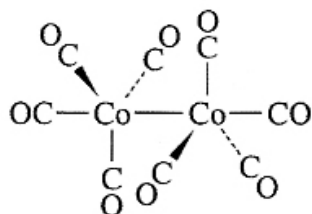


$Fe_3(CO)_{12}$

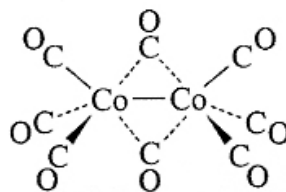


$M_3(CO)_{12}$
M = Ru, Os

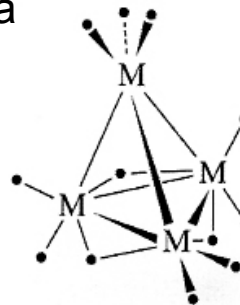
이핵 $[M_2(CO)_n]$



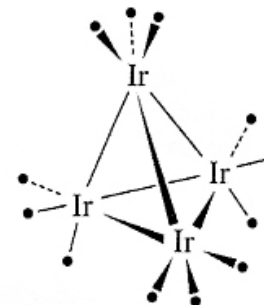
$Co_2(CO)_8$ (용액)



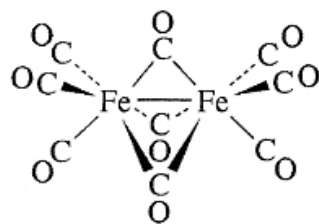
$Co_2(CO)_8$ (고체)



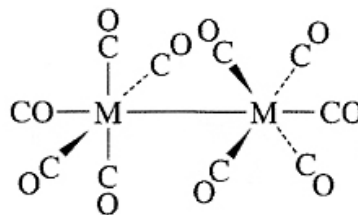
$M_3(CO)_{12}$
M = Co, Rh



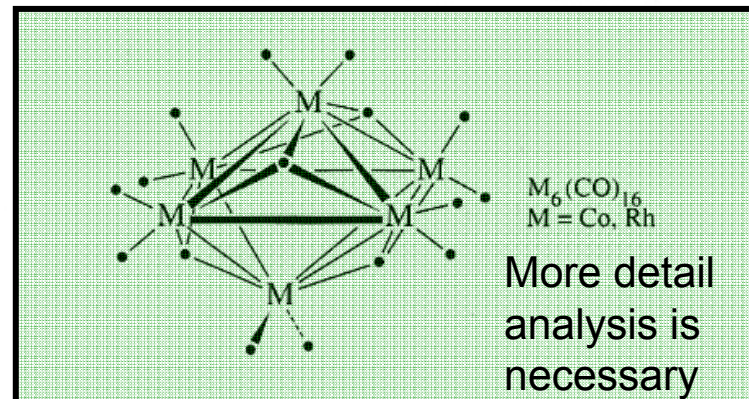
$Ir_4(CO)_{12}$



$Fe_2(CO)_9$



$M_2(CO)_{10}$
M = Mn, Tc, Re



$M_6(CO)_{16}$
M = Co, Rh

More detail
analysis is
necessary

Binary carbonyl complexes

13-4 Ligands in Organometallic Chemistry

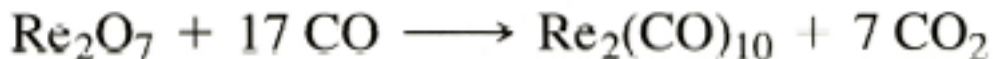
; binary carbonyl complexes

Synthesis of binary carbonyl complexes

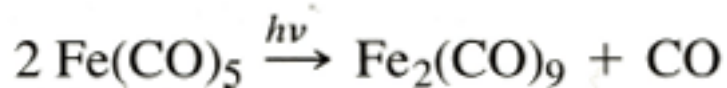
1. Direct reaction of a transition metal and CO; high T & P



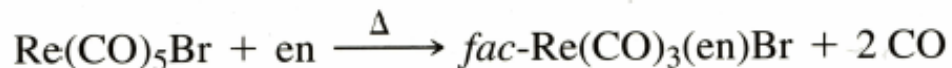
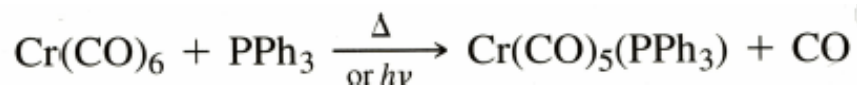
2. Reductive carbonylations



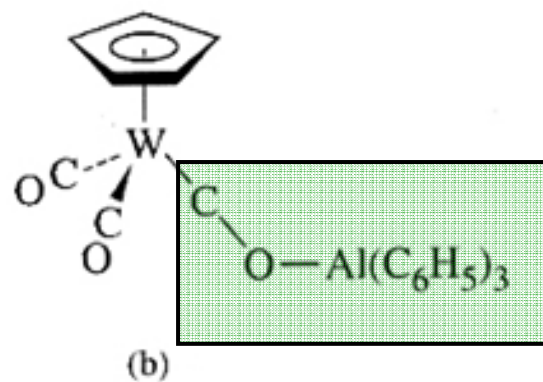
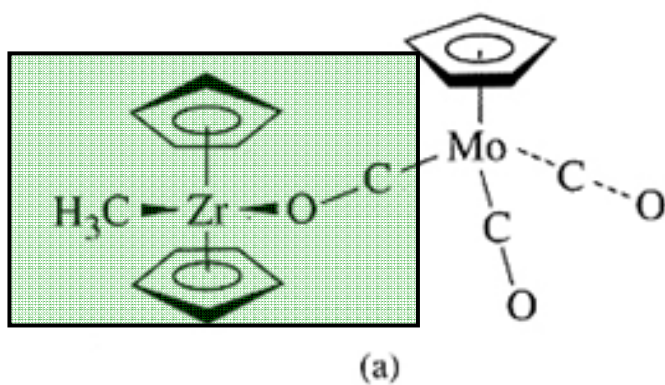
3. Thermal or photochemical reaction



Exchange reaction



13-4 Ligands in Organometallic Chemistry ; oxygen-bonded carbonyls



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 σ donor and π acceptor than CO

isoelectronic; CN^- and N_2

CN^- is a stronger σ donor and a somewhat π weaker acceptor than CO

CN^- bonds readily to metals having higher oxidation states

N_2 is a weaker donor and acceptor than CO

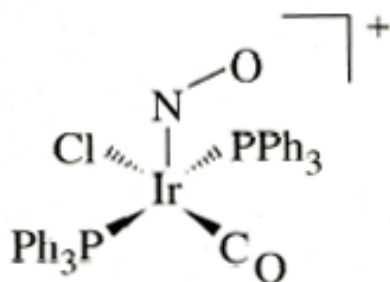
Nitrogen fixation

13-4 Ligands in Organometallic Chemistry

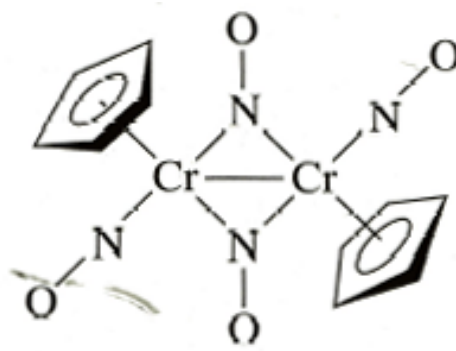
; ligands similar to CO; NO complexes



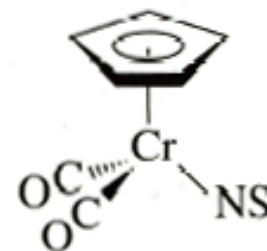
Linear



Bent



Bridging



NS complex

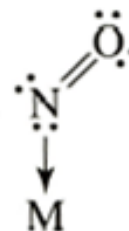
Linear



M—N—O angle
 ν (N-O) in neutral molecules
 Electron donor count

$165^\circ - 180^\circ$
 $1610 - 1830 \text{ cm}^{-1}$
 2 (as NO^+)
 3 (as neutral NO)

Bent

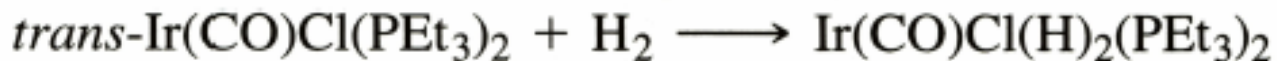


$119^\circ - 140^\circ$
 $1520 - 1720 \text{ cm}^{-1}$
 2 (as NO^-)
 1 (as neutral NO)

13-4 Ligands in Organometallic Chemistry ; hydride and dihydrogen complexes

Hydride complexes

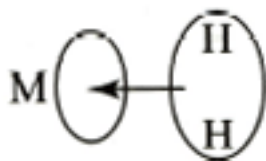
Organic synthesis,
catalytic reaction



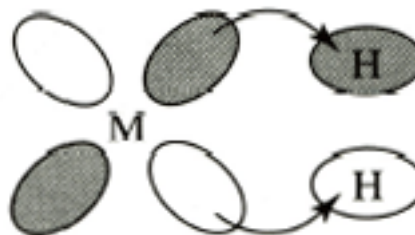
13-4 Ligands in Organometallic Chemistry ; hydride and dihydrogen complexes

Dihydrogen complexes

Organic synthesis,
catalytic reaction



σ donation

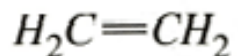


π acceptance

Distance of H-H
the metal is electron rich and donate
strongly to the π^* of $H_2 \rightarrow ???$
with CO and NO $\rightarrow ???$

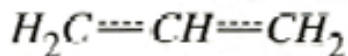
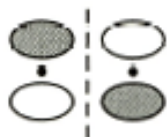
13-4 Ligands in Organometallic Chemistry ; ligands having extended π systems

π bonding within the ligands themselves-
linear systems



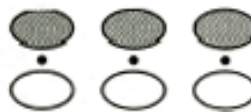
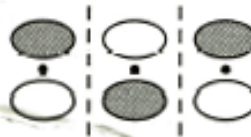
p orbitals interacting

Relative energy

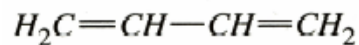


p orbitals interacting

Relative energy

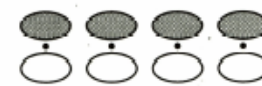
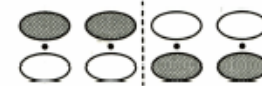
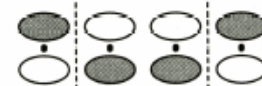
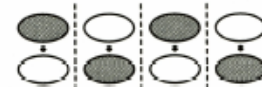


13-4 Ligands in Organometallic Chemistry ; ligands having extended π systems



p orbitals interacting

Relative energy

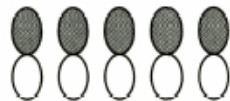
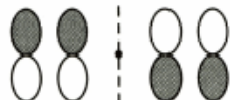
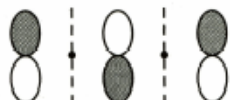
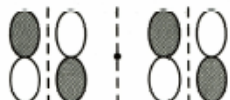


π bonding within the ligands themselves-
linear systems

p orbitals interacting

Relative energy

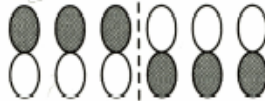
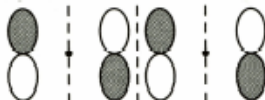
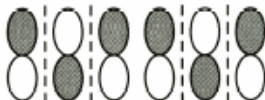
C_5H_7



p orbitals interacting

Relative energy

C_6H_8

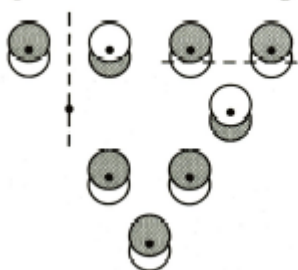


13-4 Ligands in Organometallic Chemistry ; ligands having extended π systems

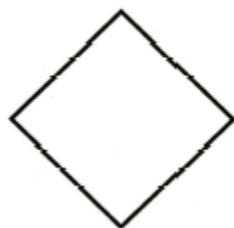
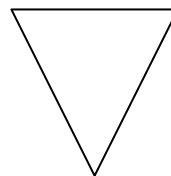
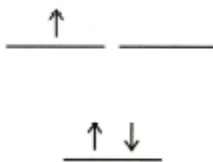
π bonding within the ligands themselves-
cyclic systems

cyclo- C_3H_3

p orbitals interacting



Relative energy



Relative energy

One 2-node π orbital



Two 1-node π orbitals

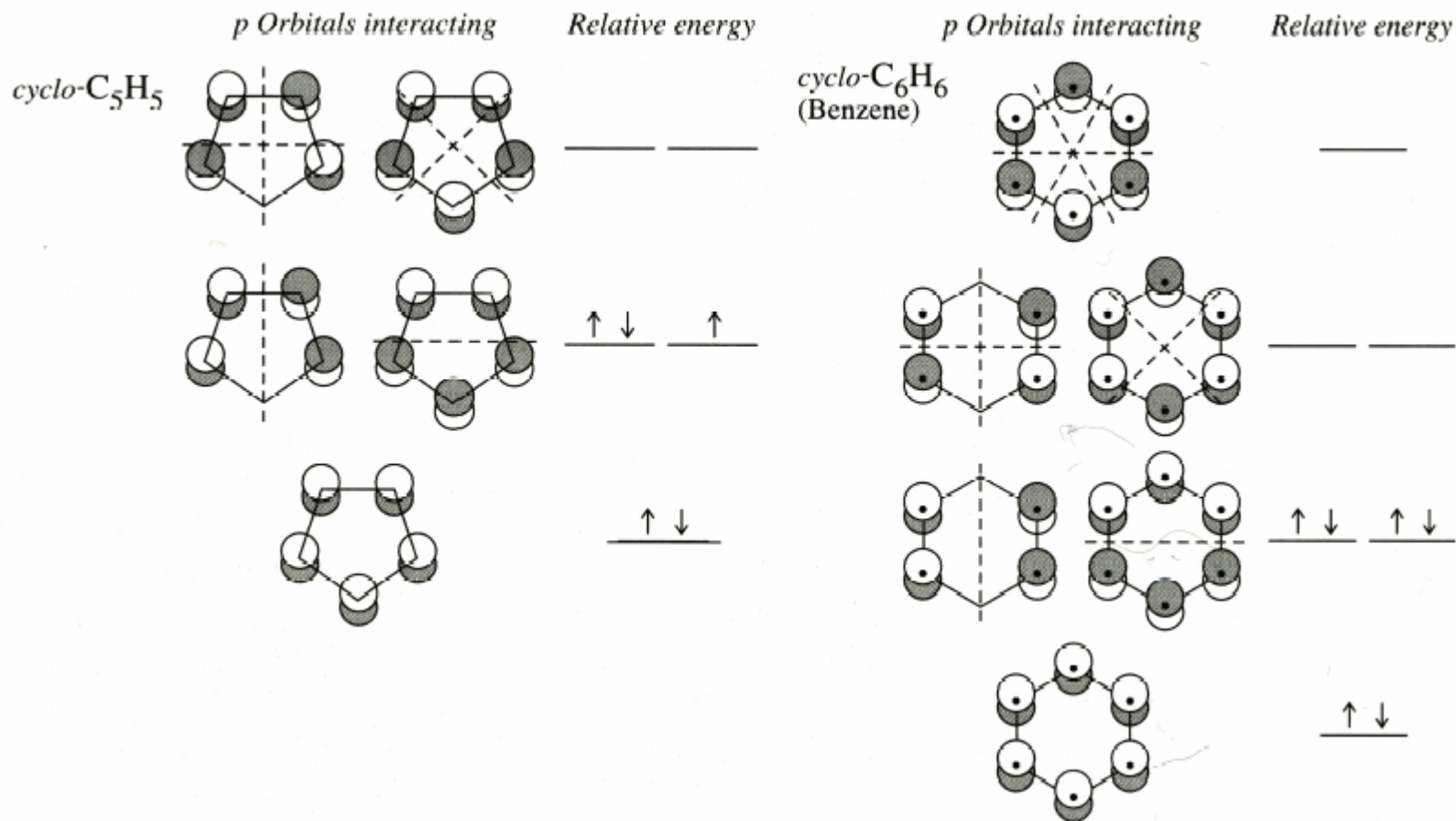


One 0-node π orbital



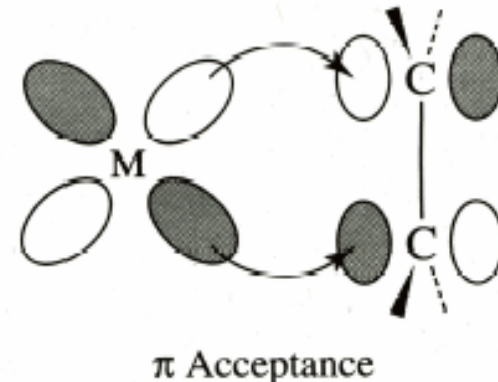
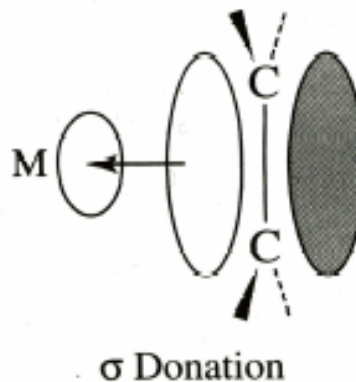
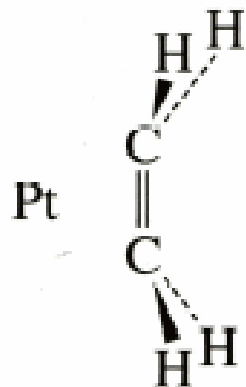
13-4 Ligands in Organometallic Chemistry ; ligands having extended π systems

π bonding within the ligands themselves-
cyclic systems



13-4 Bonding between Metal Atoms and Organic π Systems; linear π systems

π -ethylene complexes



Typically bent back
away from the metal

π -bonding electron pair

the empty π^* -orbital

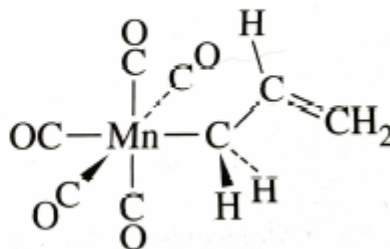
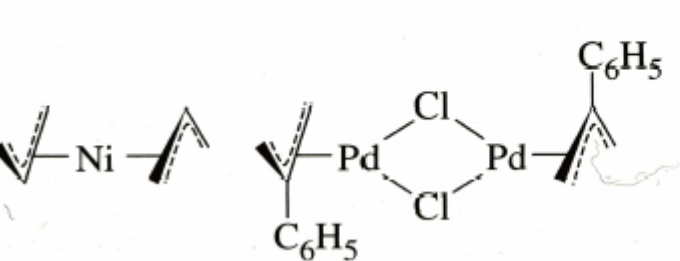
Free ethylene	133.7 pm, 1623 cm^{-1}
Coordinated ethylene	137.5 pm, 1516 cm^{-1}

13-4 Bonding between Metal Atoms and Organic π Systems; linear π systems

π -allyl complexes

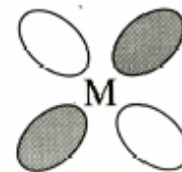
$\eta^3\text{-C}_3\text{H}_5$

$\eta^1\text{-C}_3\text{H}_5$



Other metal orbitals of suitable symmetry

acceptor



p_x

d_{xz}

Donor or acceptor



d_{yz}

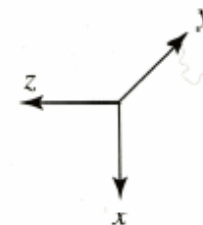
p_y

donor



s, d_{z^2}

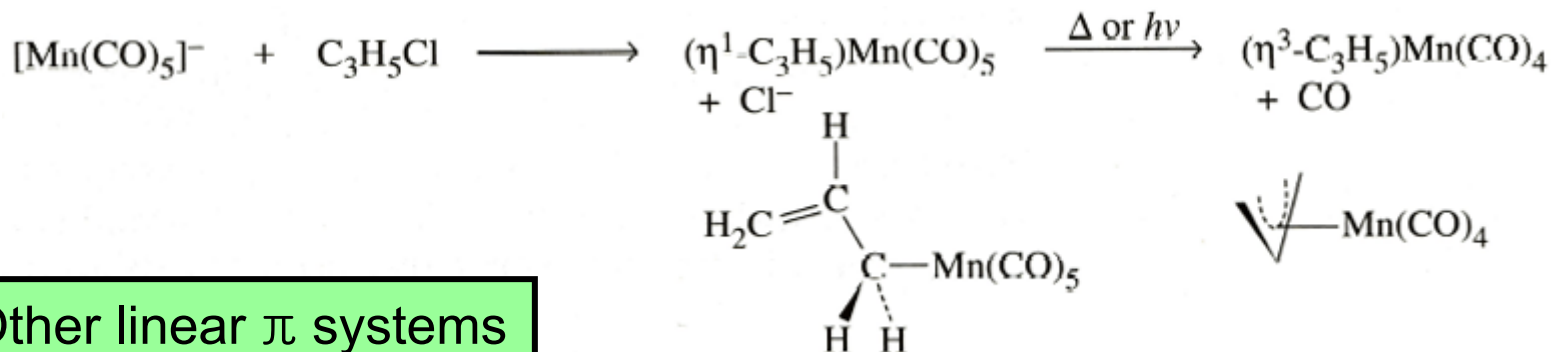
p_z



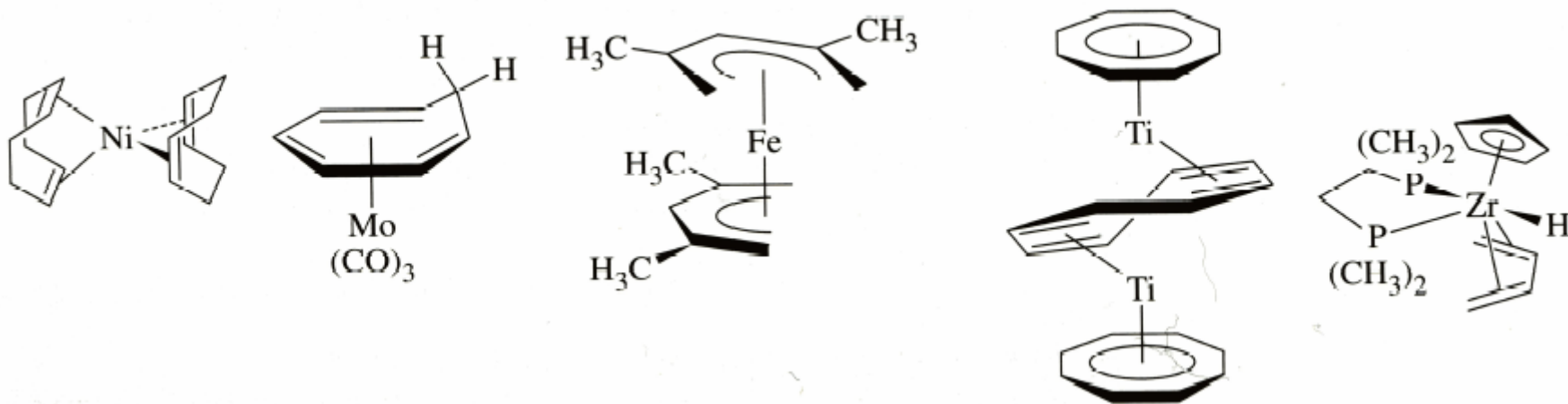
13-4 Bonding between Metal Atoms and Organic π Systems; linear π systems

π -allyl complexes

Conversion between η^1 and η^3
Catalytic reaction



Other linear π systems

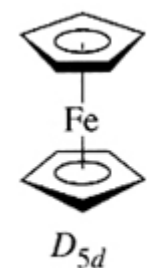


13-4 Bonding between Metal Atoms and Organic π Systems; cyclic π systems

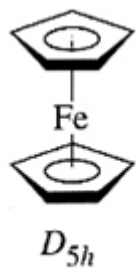
Cyclopentadienyl (Cp) complexes

η^1 , η^3 and η^5
 $C_5(CH_3)_5$ Cp*

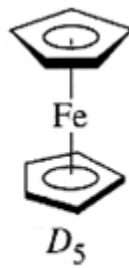
Gas phase and low-T



엇갈린 고리

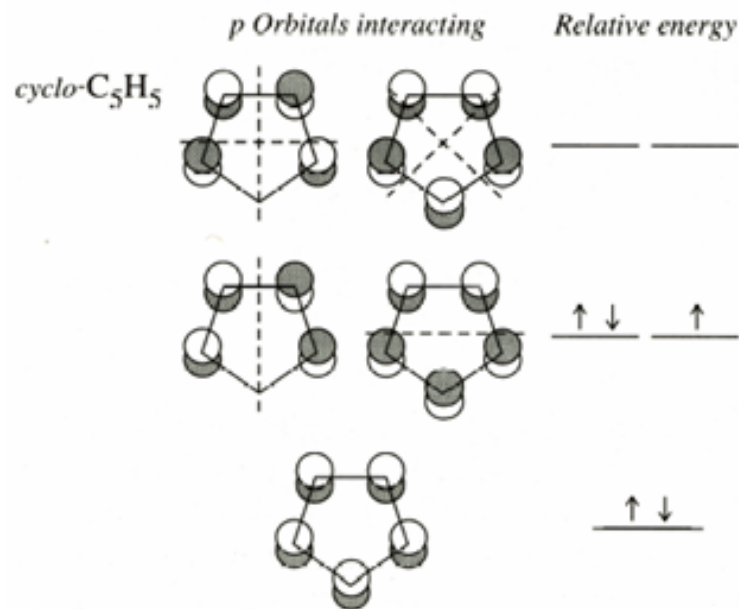


가리움 고리

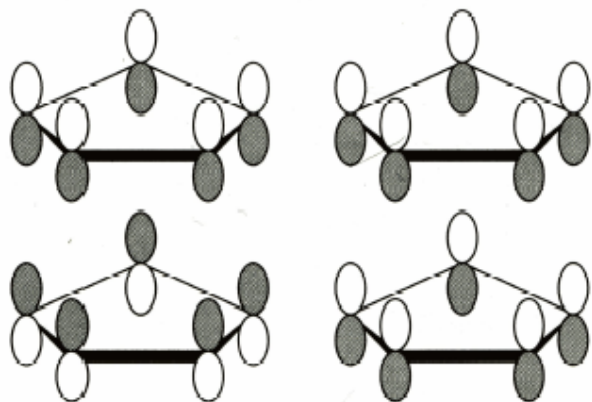


비틀린 고리

Most stable conformation

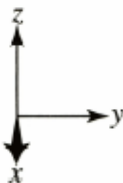


13-4 Bonding between Metal Atoms and Organic π Systems; cyclic π systems

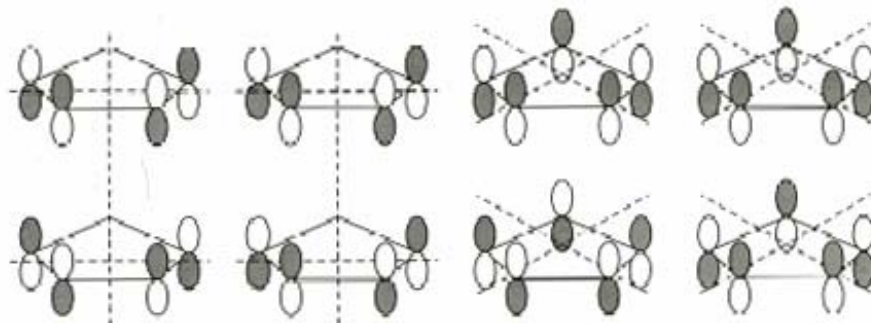


Orbital lobes of like sign pointed toward each other

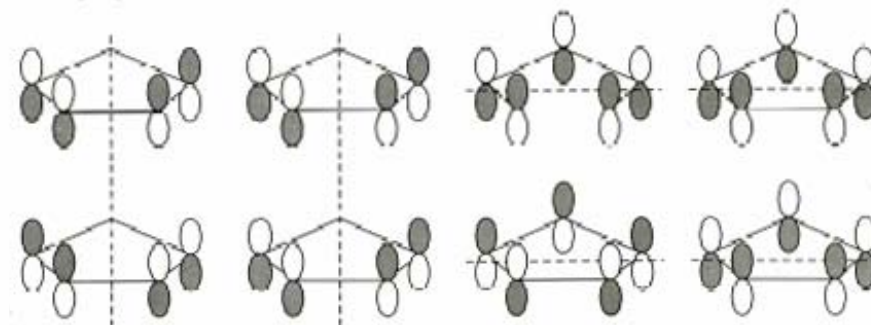
Orbital lobes of opposite sign pointed toward each other



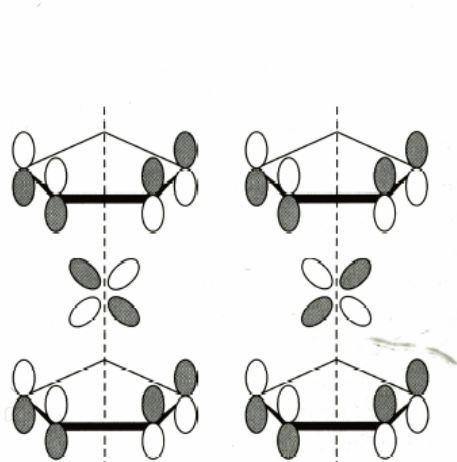
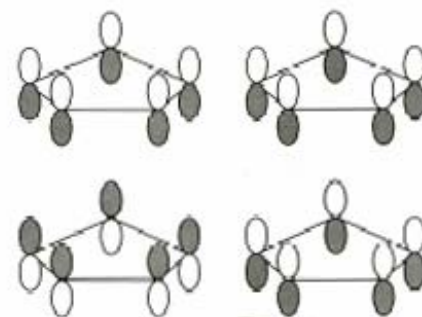
2-Node group orbitals



1-Node group orbitals

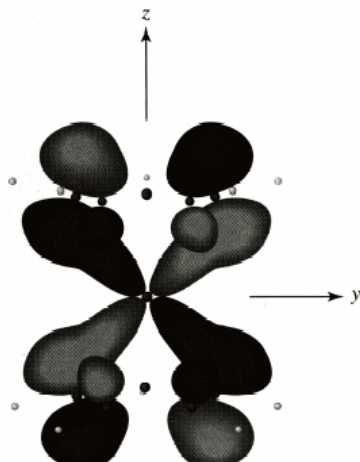


0 Node group orbitals



Bonding
1

Antibonding
2



Actual shape of bonding orbital 1

13-4 Bonding between Metal Atoms and Organic π Systems; cyclic π systems

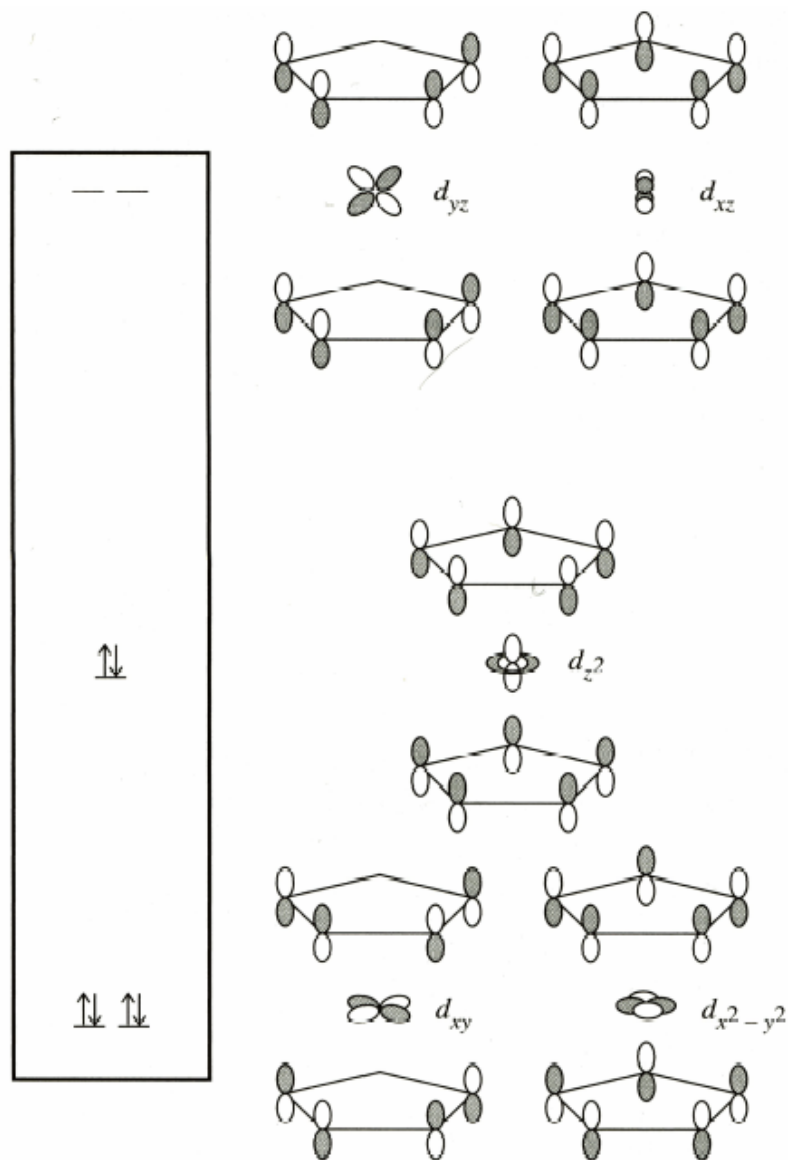


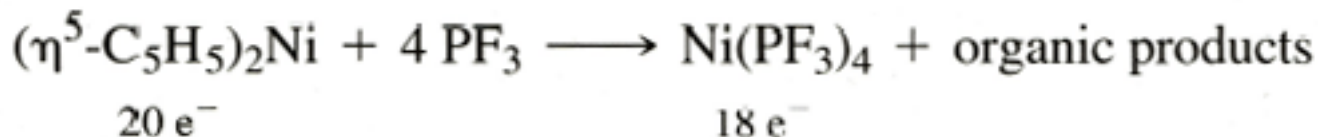
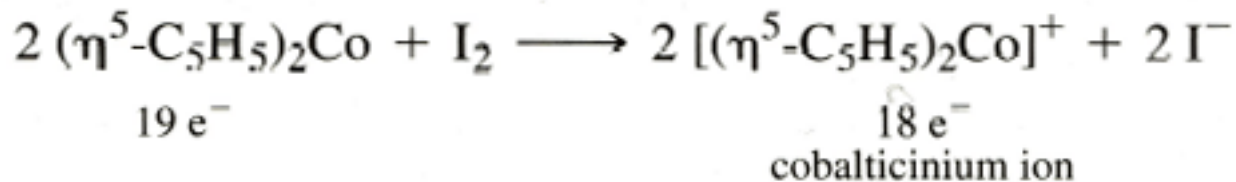
FIGURE 13-29 Molecular Orbitals of Ferrocene Having Greatest d Character.

13-4 Bonding between Metal Atoms and Organic π Systems; cyclic π systems

Other metallocenes
 # of electron \rightarrow stability \rightarrow reactivity

TABLE 13-3
Comparative Data for Selected Metallocenes

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



13-4 Bonding between Metal Atoms and Organic π Systems; cyclic π systems

그림 13-30 코발티시늄과 수소화 이온의 반응.

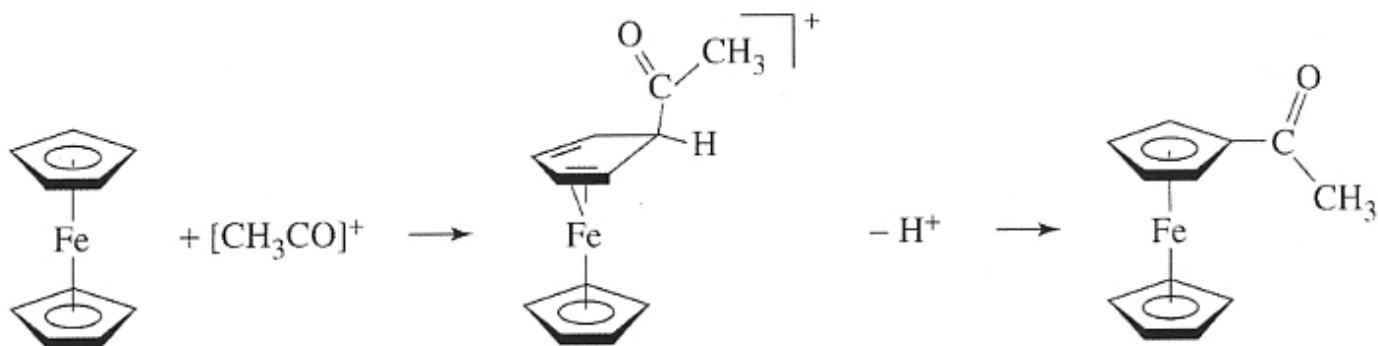
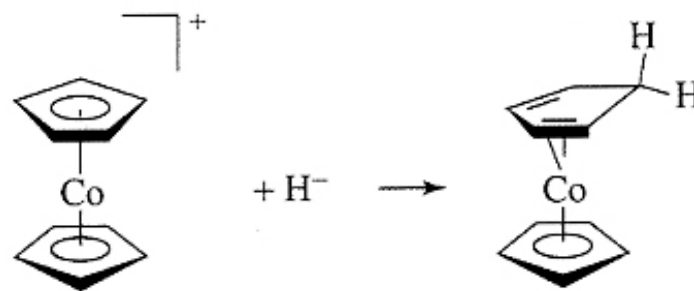


그림 13-31 페로센의 친전자성 아실 치환 반응.

13-4 Bonding between Metal Atoms and Organic π Systems; cyclic π systems

Complexes containing cyclopentadienyl and CO ligand
Half-sandwich

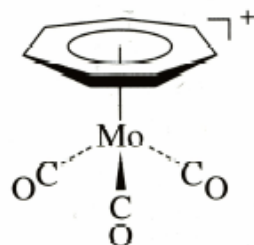
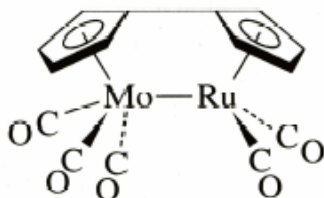
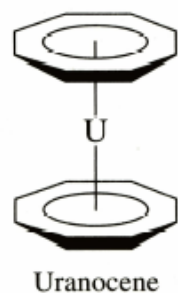


FIGURE 13-33 Examples of Molecules Containing Cyclic π Systems.

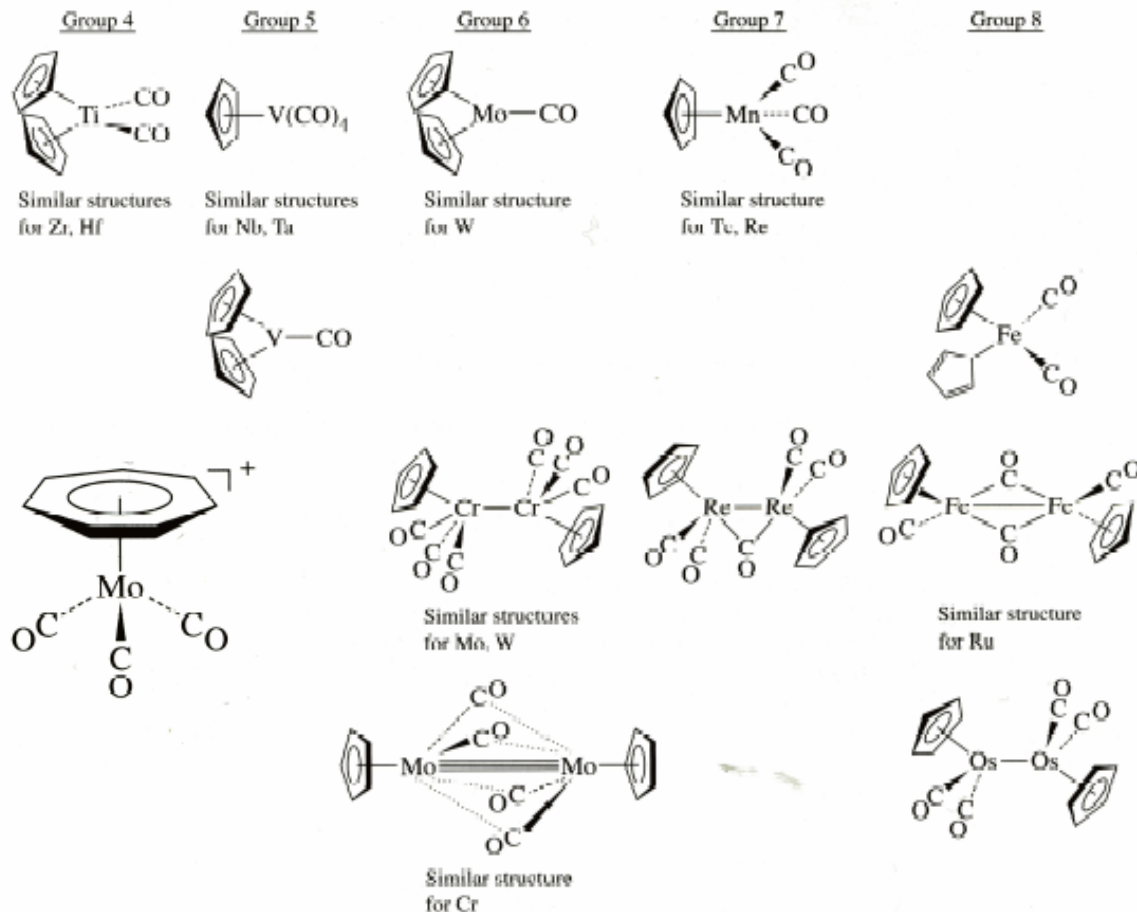


FIGURE 13-32 Complexes Containing C_5H_5 and CO.

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

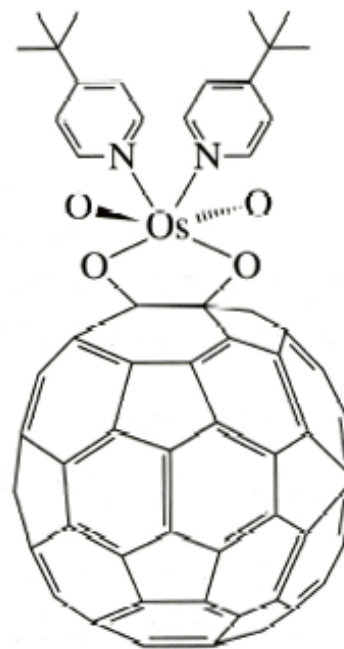
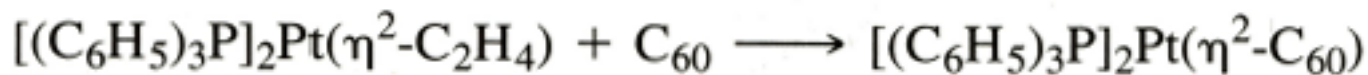


FIGURE 13-34 Structure of $C_{60}(OsO_4)(4-t\text{-butylpyridine})_2$.

13-5 Fullerene Complexes

As ligands
Dihapto, pentahepto, hexahapto

Displacement reaction



More than one metal

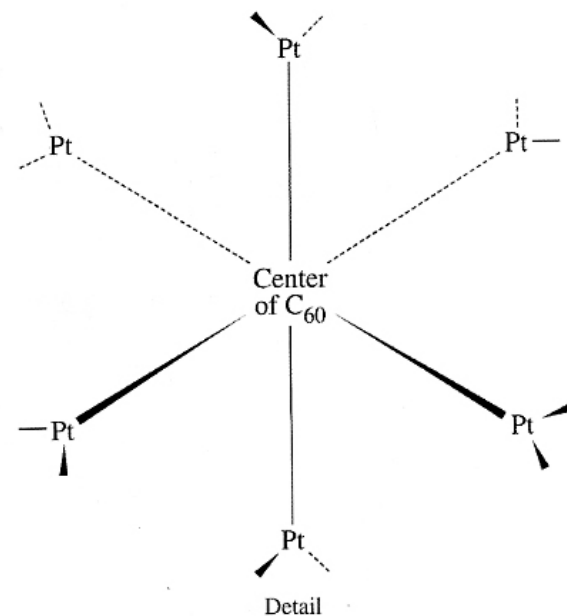
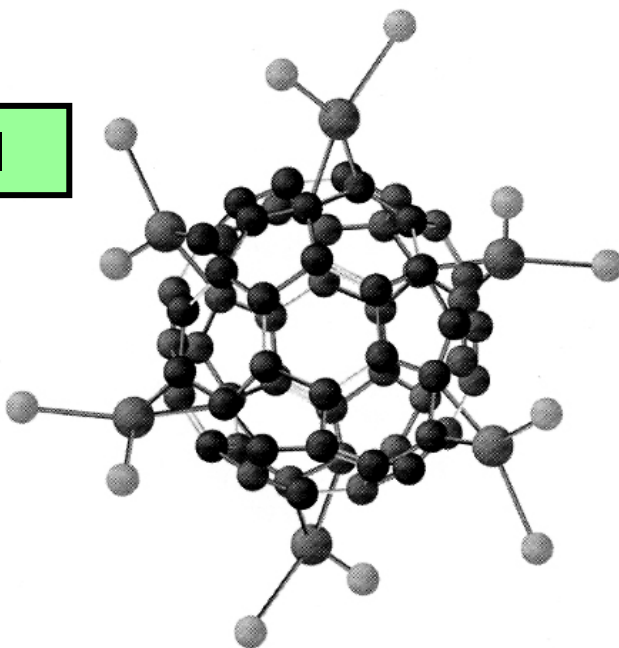


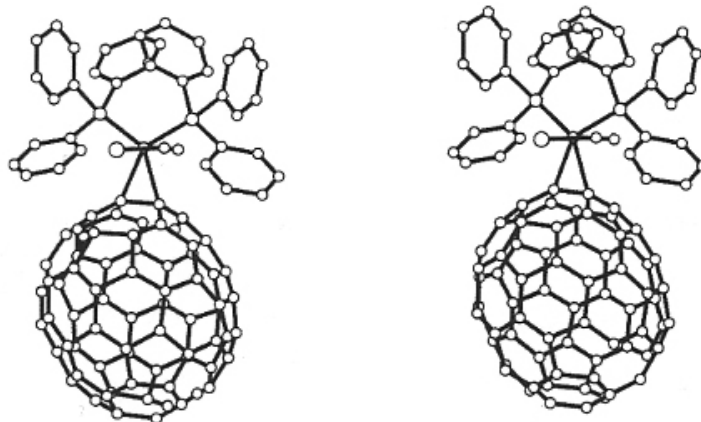
그림 13-36 $[(Et_3P)_2Pt]_6C_{60}$ 의 구조(G. O. Spessard and G. L. Miessler, *Organometallic Chemistry*, Prentice Hall, Upper Saddle River, NJ, 1997, p. 511. Fig. 13-13에서 허락하에 게재).

13-5 Fullerene Complexes

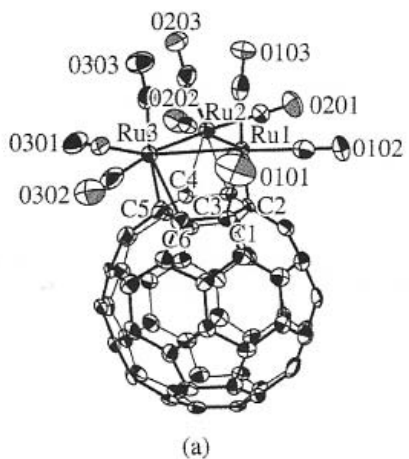
C₇₀

그림 13-37

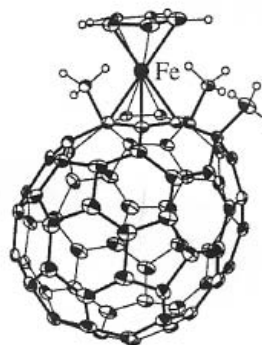
(η^2 -C₇₀)Ir(CO)Cl(PPh₃)₂의 입체도
(A. L. Balch, V. J. Catalano, J. W. Lee, M. M. Olmstead, and S. R. Parkin, *J. Am. Chem. Soc.*, 1991, 113, 8953, © 1991 American Chemical Society에서 허락하에 게재함).



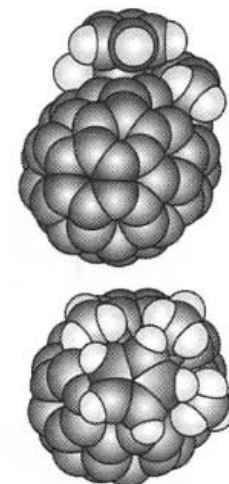
η_2 - η_2 - η_2 and η_5



(a)



(b)



(c)

그림 13-38 (a) Ru₃(CO)₉(μ^3 - η^2 , η^2 , η^2 -C₆₀). (b) 및 (c) Fe(η^5 -C₅H₅)(η^5 -C₇₀(CH₃)₃)의 ORTEP 및 공간채우기 모형 (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 Society에서 허락하에 게재).

13-5 Fullerene Complexes

Encapsulated metals

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

$U@C_{60}$ contains U surrounded by C_{60}

$Sc_3@C_{82}$ contains three atoms of Sc surrounded by C_{82}^{53}

$La@C_{82}$; La^{3+} , C_{82}^{3-}

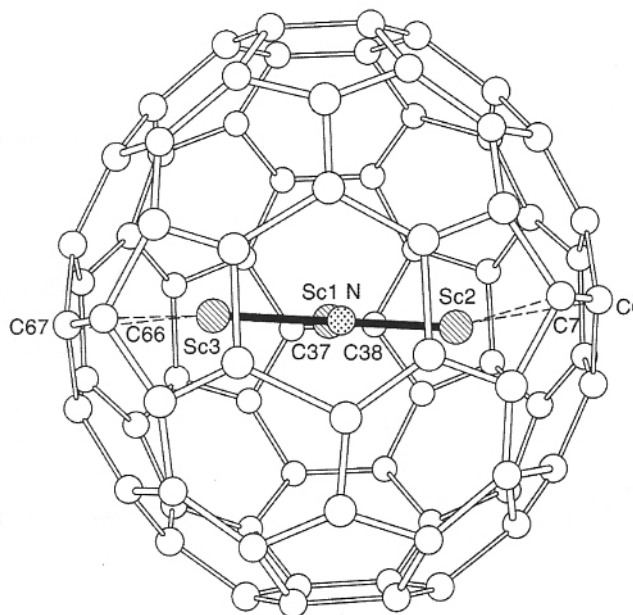
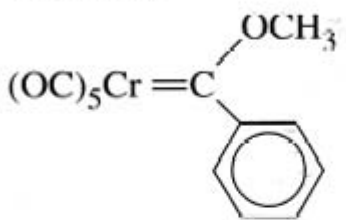
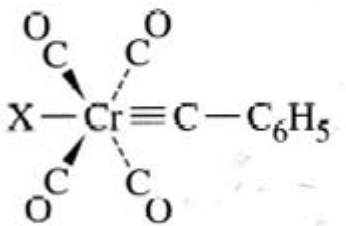
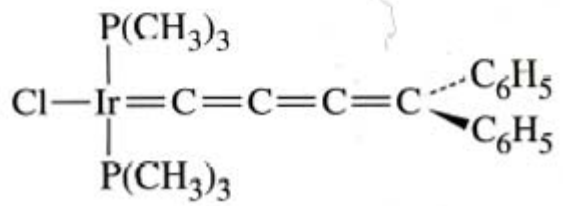


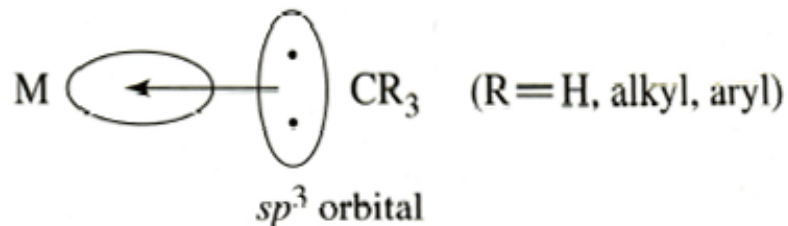
그림 13-39 $Sc_3N@C_{80}$. 저온에서 연구된 X-선 구조 결정에 의하면, Sc_3N 은 130.3° , 113.8° 및 115.9° 의 결합각을 지닌 평면형이며, 각각의 Sc은 두 개의 6-원소 고리를 이루는 C—C 결합 부분과 약하게 결합되어 있다. 그러나, 높은 온도에서는 Sc_3N 문치 화합물이 바구니 안에서 자유로이 움직인다.

13-6 Complexes Containing M-C, M=C and M≡C Bonds

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

<i>Ligand</i>	<i>Formula</i>	<i>Example</i>
Alkyl	$-\text{CR}_3$	$\text{W}(\text{CH}_3)_6$
Carbene (alkylidene)	$=\text{CR}_2$	$(\text{OC})_5\text{Cr}=\text{C}$ 
Carbyne (alkylidyne)	$\equiv\text{CR}$	
Cumulene	$=\text{C}(=\text{C})_n\text{RR}'$	

13-6 Complexes Containing M-C, M=C and M≡C Bonds; alkyl and related complexes

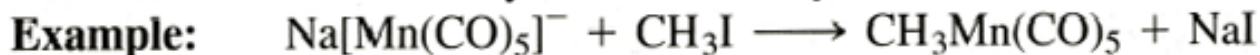


Synthetic route

1. Reaction of a transition metal halide with organolithium, organomagnesium, or organoaluminum reagent.

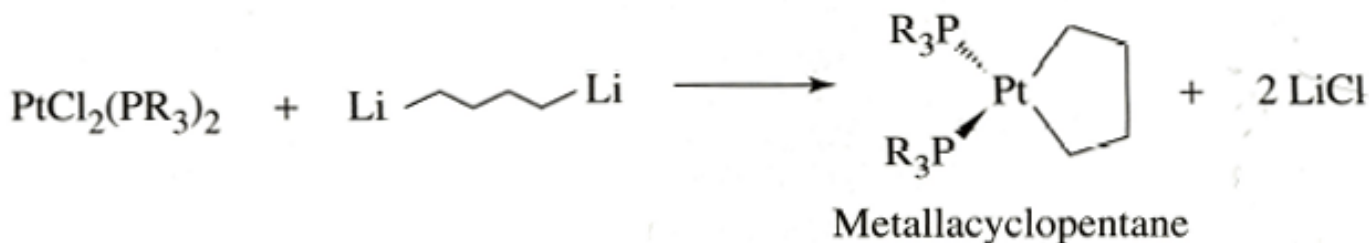


2. Reaction of a metal carbonyl anion with alkyl halide.



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

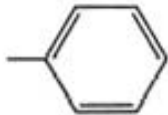
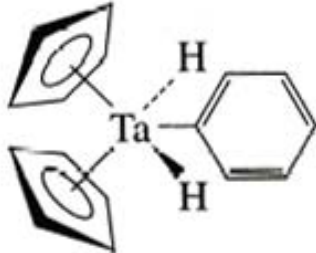
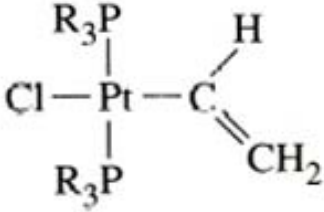
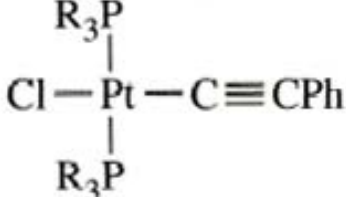
metallacycle



Proposed as intermediates in a variety catalytic processes

13-6 Complexes Containing M-C, M=C and M≡C Bonds ; alkyl and related complexes

TABLE 13-5
Other Ligands Forming σ Bonds to Metals

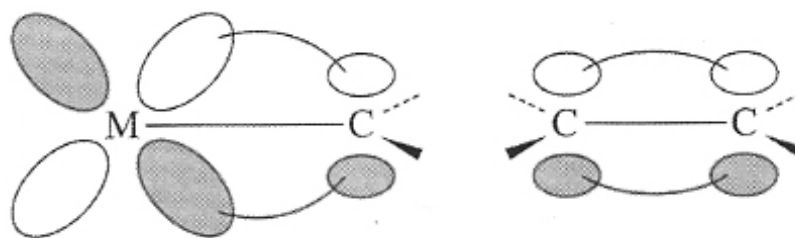
<i>Ligand</i>	<i>Formula</i>	<i>Example</i>
Aryl		
Alkenyl (vinyl)	>C=C<	
Alkynyl	$\text{—C}\equiv\text{C—}$	

13-6 Complexes Containing M-C, M=C and M≡C Bonds ; carbene complexes

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

<i>Characteristic</i>	<i>Fischer-type Carbene Complex</i>	<i>Schrock-type Carbene Complex</i>
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

그림 13-40 카벤 착물과 알켄의 결합 비교.



d orbital p orbital

13-6 Complexes Containing M-C, M=C and M≡C Bonds ; carbene complexes

2-electron donor

Highly electronegative atom can participate in the π bonding \rightarrow stabilize

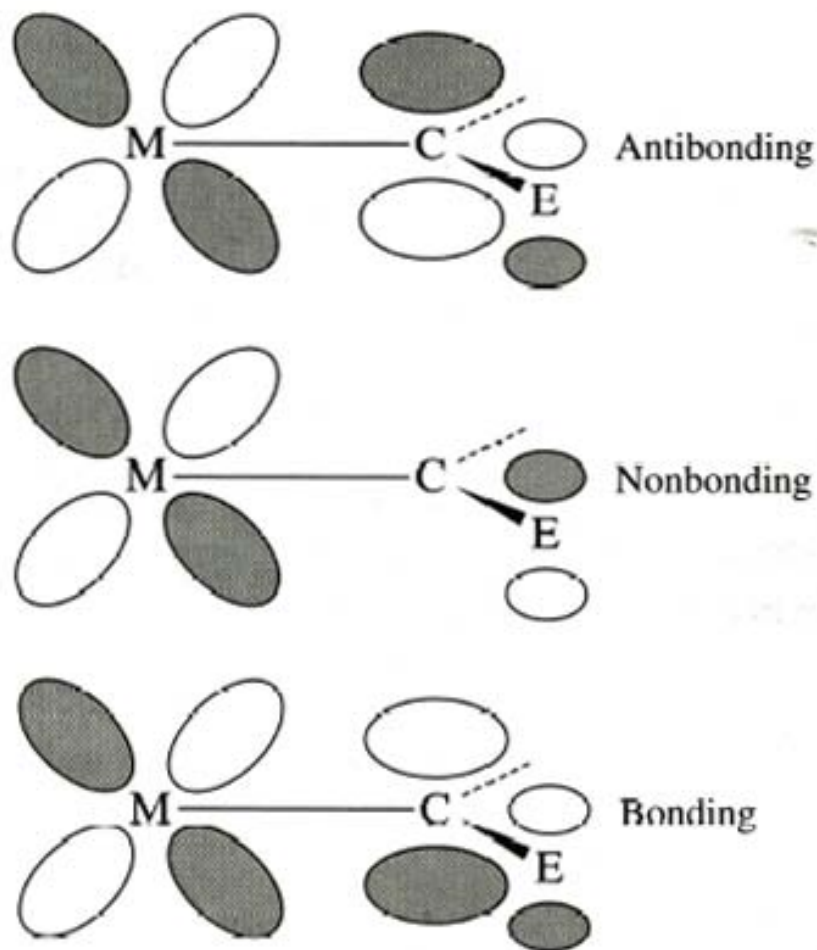
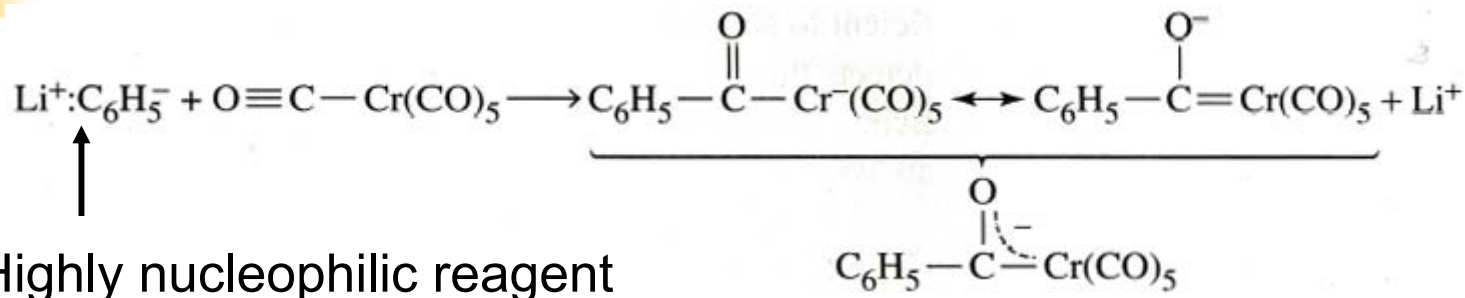


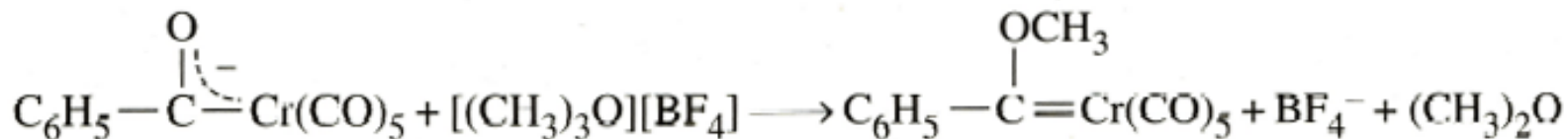
FIGURE 13-41 Delocalized π Bonding in Carbene Complexes. E designates a highly electronegative heteroatom such as O, N, or S.

13-6 Complexes Containing M-C, M=C and M≡C Bonds ; carbene complexes

Olefin metathesis



Highly nucleophilic reagent



X-ray; Cr-C, C-O

NMR; RT (one signal), low T (two peak)

Why?

C-O 143 pm

C=O 116pm

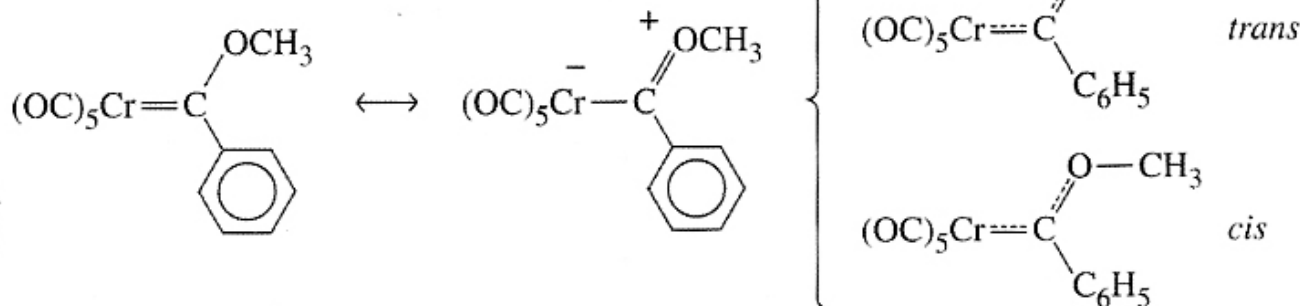


그림 13-42

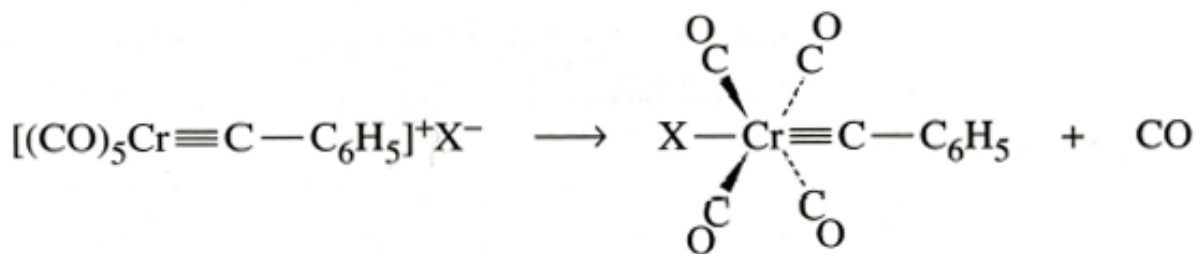
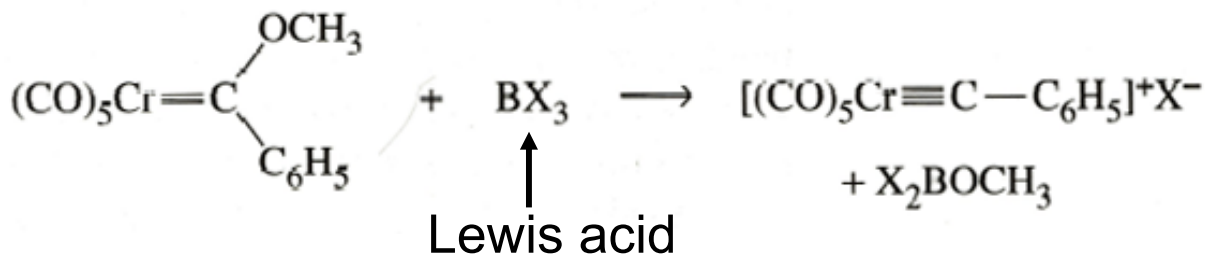
Cr(CO)₅[C(OCH₃)C₆H₅]에 대한 공명 구조와 시스 및 트랜스 이성질체.

Highly electronegative atom can participate in the π bonding → stabilize

13-6 Complexes Containing M-C, M=C and M≡C Bonds

; carbyne (alkylidyne) complexes

3-electron donor



σ donor
π acceptor

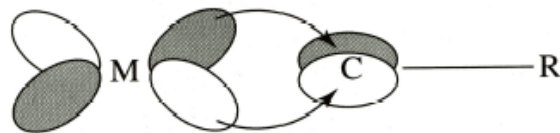
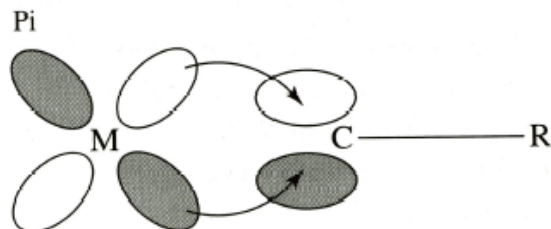


FIGURE 13-43 Bonding in Carbyne Complexes.

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

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

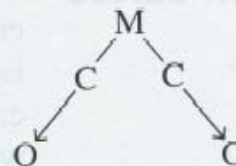
of bands

Provide clues to the geometry or symmetry

Symmetric Stretch



No change in dipole moment;
IR inactive

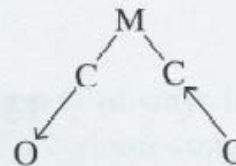


Change in dipole moment;
IR active

Antisymmetric Stretch

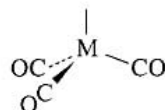
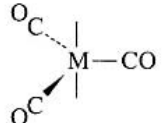
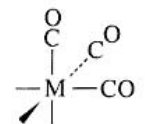
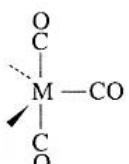
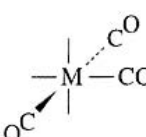
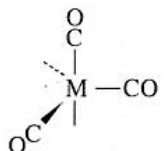
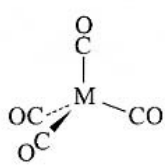
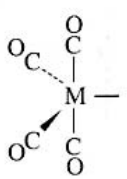
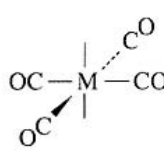
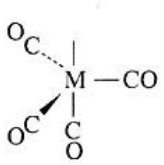
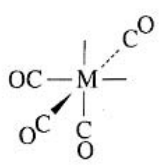


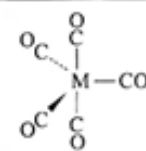
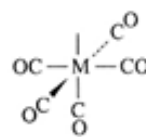
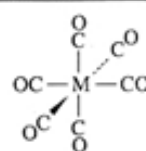
Change in dipole moment;
IR active



Change in dipole moment;
IR active

IR Characterization of Complexes; IR spectra

CO 리간드의 수	배위수		
	4	5	6
3	 IR 띠: 2	 IR 띠: 1	 IR 띠: 2
		 IR 띠: 3	 IR 띠: 3
		 IR 띠: 3	
4	 IR 띠: 1	 IR 띠: 4	 IR 띠: 1
		 IR 띠: 3	 IR 띠: 4

5	 IR 띠: 2	 IR 띠: 3
6		 IR 띠: 1

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

positions of bands

Provide clues to the electronic environment on the metal
The greater the electronic density on the metal \rightarrow ???

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.**

<i>Complex</i>	$\nu(\text{CO}), \text{cm}^{-1}$
$[\text{Ti}(\text{CO})_6]^{2-}$	1748
$[\text{V}(\text{CO})_6]^-$	1859
$\text{Cr}(\text{CO})_6$	2000
$[\text{Mn}(\text{CO})_6]^+$	2100
$[\text{Fe}(\text{CO})_6]^{2+}$	2204

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

terminal CO > doubly bridging CO > triply bridging CO

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

<i>Complex</i>	ν (CO), cm^{-1}
<i>fac</i> -Mo(CO) ₃ (PF ₃) ₃	2090, 2055
<i>fac</i> -Mo(CO) ₃ (PCl ₃) ₃	2040, 1991
<i>fac</i> -Mo(CO) ₃ (PClPh ₂) ₃	1977, 1885
<i>fac</i> -Mo(CO) ₃ (PMe ₃) ₃	1945, 1854

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

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

^1H , ^{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

Ligand	^{13}C Chemical Shift (Range) ^a			
M—CH ₃	-28.9 to 23.5			
M=C	190 to 400			
M≡C—	235 to 401			
M—CO	177 to 275			
Neutral binary CO	183 to 223			
M—(η^5 -C ₅ H ₅)	-790 to 1430			
Fe(η^5 -C ₅ H ₅) ₂	69.2			
M—(η^3 -C ₃ H ₅)	$\frac{\text{C}_2}{91 \text{ to } 129}$		$\frac{\text{C}_1 \text{ and } \text{C}_3}{46 \text{ to } 79}$	
M—C ₆ H ₅	$\frac{\text{M—C}}{130 \text{ to } 193}$	$\frac{\textit{ortho}}{132 \text{ to } 141}$	$\frac{\textit{meta}}{127 \text{ to } 130}$	$\frac{\textit{para}}{121 \text{ to } 131}$

NOTE: ^a Parts per million (ppm) relative to Si(CH₃)₄.

Chemical shift

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

^1H NMR

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

<i>Complex</i>	^1H Chemical Shift ^a
$\text{Mn}(\text{CO})_5\text{H}$	-7.5
$\text{W}(\text{CH}_3)_6$	1.80
$\text{Ni}(\eta^2\text{-C}_2\text{H}_4)_3$	3.06
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$	4.04
$(\eta^6\text{-C}_6\text{H}_6)_2\text{Cr}$	4.12
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Ta}(\text{CH}_3)(=\text{CH}_2)$	10.22

NOTE: ^a Parts per million relative to $\text{Si}(\text{CH}_3)_4$.

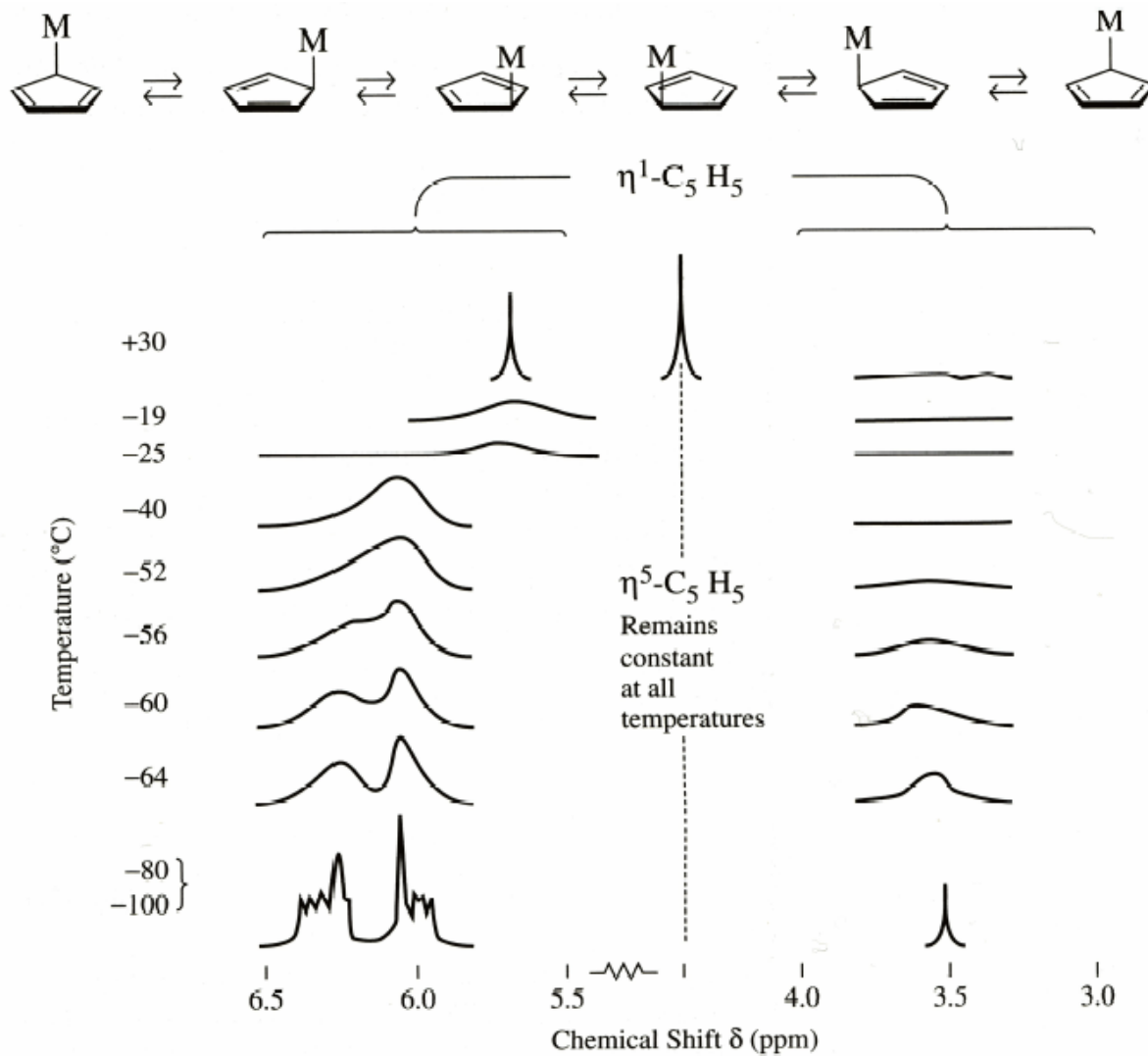
integration

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

Molecular rearrangement processes

At RT; 2 singlets
At low T

Ring whizzer





Homework

Exercise 13-1~13-12

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