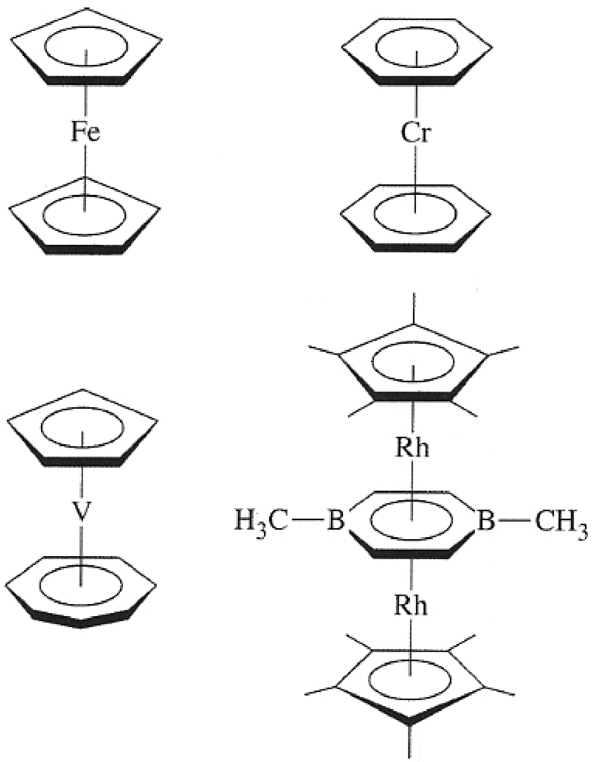
Chapter 13 Organometallic Chemistry

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 Btween Metal Atoms and Organic π Systems
13-6 Complexes Containing M-C, M=C, and M≡C Bonds
13-7 Spectral Analysis and Characterization of Organometallic Complexes

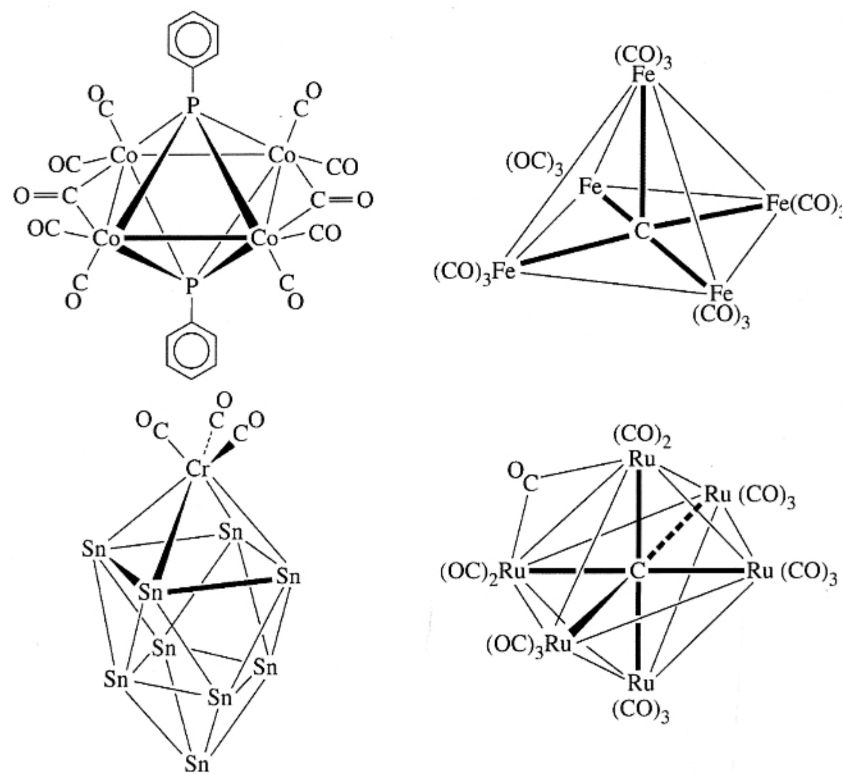
"Inorganic Chemistry" Third Ed. Gary L. Miessler, Donald A. Tarr, 2004, Pearson Prentice Hall
http://en.wikipedia.org/wiki/Expedia

13-1 Historical Background

Sandwich compounds



Cluster compounds



물의

그림 13-2 뭉치 화합물의 예.

13-1 Historical Background

Other examples of organometallic compounds

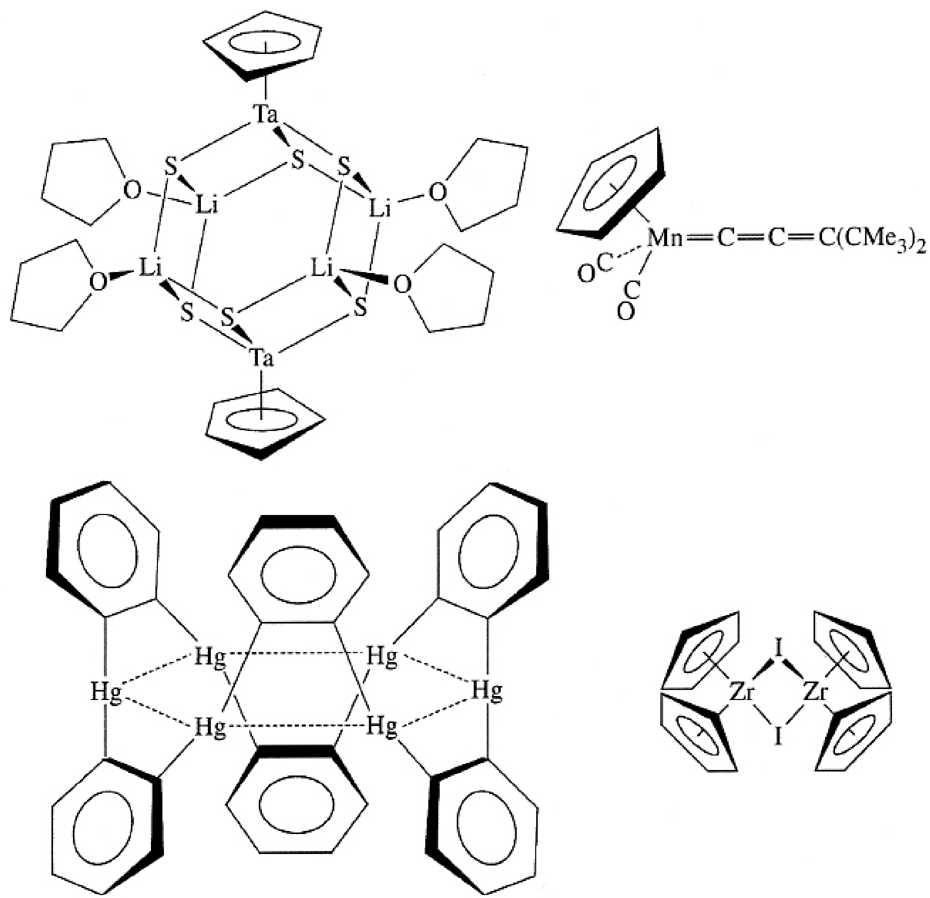


그림 13-3 유기금속 화합물의
다른 예.

Organometallic Compound

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

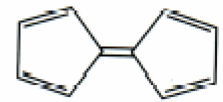
Organometallic chemistry combines aspects of inorganic chemistry and organic chemistry.

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

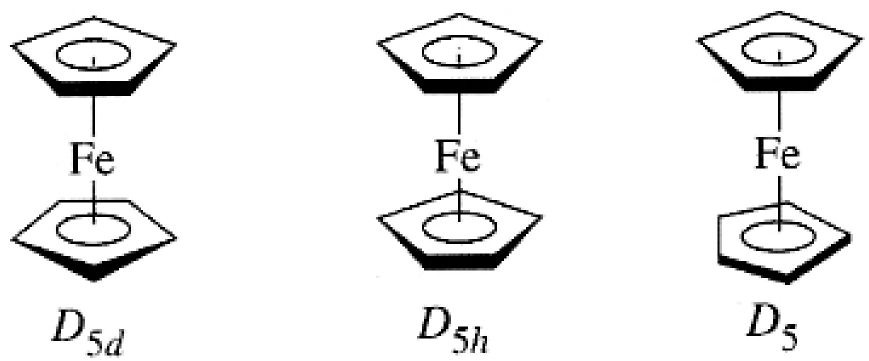


Fulvalene

Produced an orange solid (ferrocene)

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

Discovery of ferrocene began the era of modern organometallic chemistry.



Staggered rings Eclipsed rings 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.

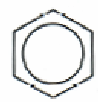
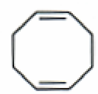
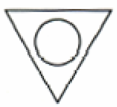
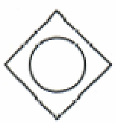
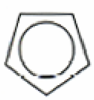
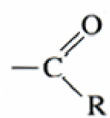
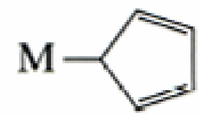
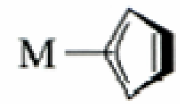
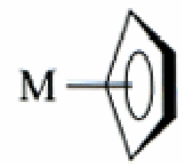
Ligand	*Name*	*Ligand*	*Name*
CO	Carbonyl		Benzene
$=C<$	Carbene (alkylidene)		1,5-cyclooctadiene (1,5-COD) (1,3-cyclooctadiene complexes are also known)
$\equiv C-$	Carbyne (alkylidyne)	$H_2C=CH_2$	Ethylene
	Cyclopropenyl (*cyclo*-C_3H_3)	$HC\equiv CH$	Acetylene
	Cyclobutadiene (*cyclo*-C_4H_4)		π-Allyl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

FIGURE 13-7 Common Organic Ligands.

13-2 Organic Ligands and Nomenclature

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	

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

13-3 The 18-Electron Rule
; counting electrons

In main group chemistry, the octet rule

$(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$

Donor Pair method

Fe(II)	6 electrons
$\eta^5\text{-}C_5H_5^-$	6 electrons
2 (CO)	4 electrons
Cl^-	2 electrons
Total =	18 electrons

Neutral Ligand method

Fe atom	8 electrons
$\eta^5\text{-}C_5H_5$	5 electrons
2 (CO)	4 electrons
Cl	1 electron
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

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

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

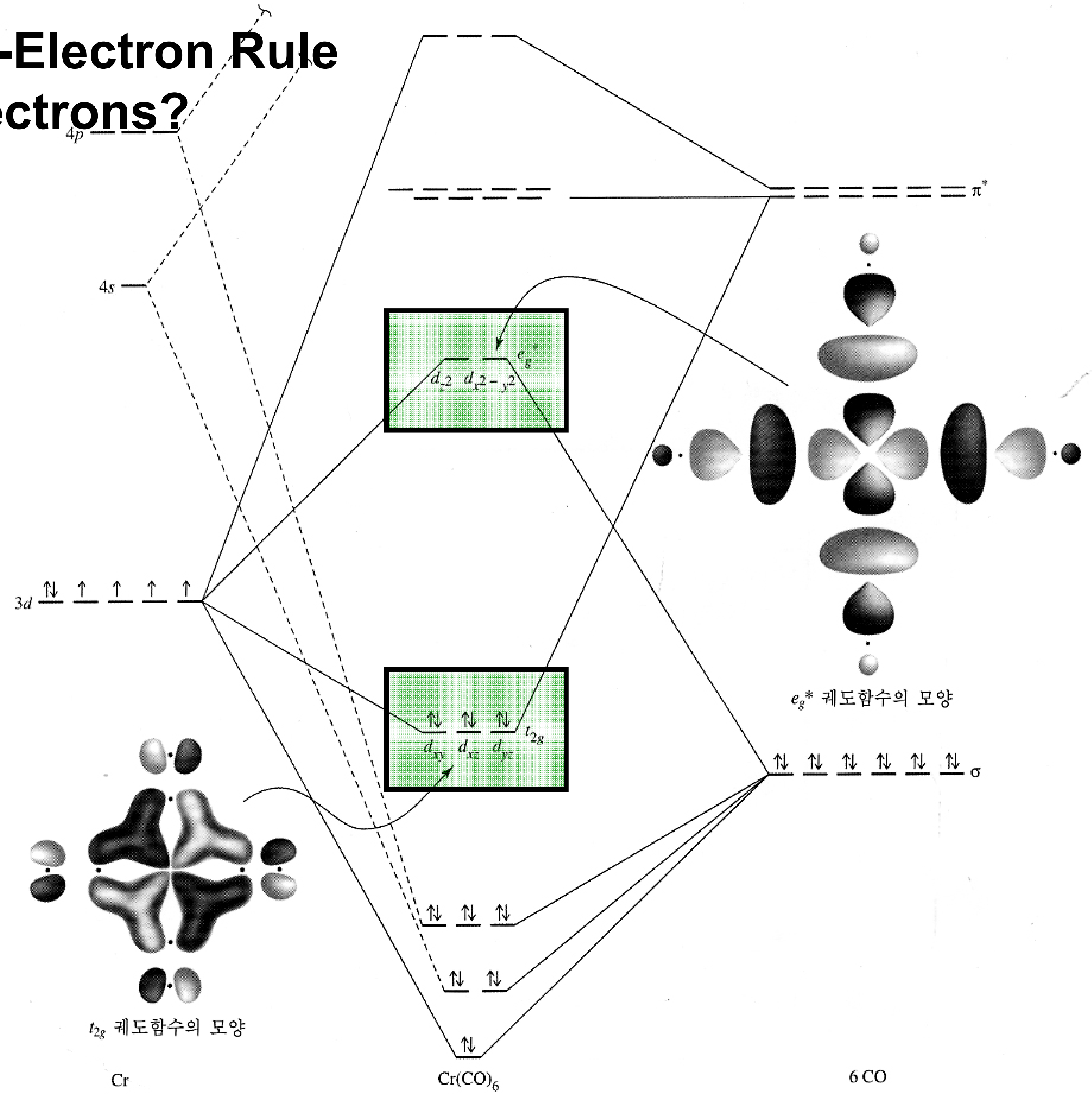
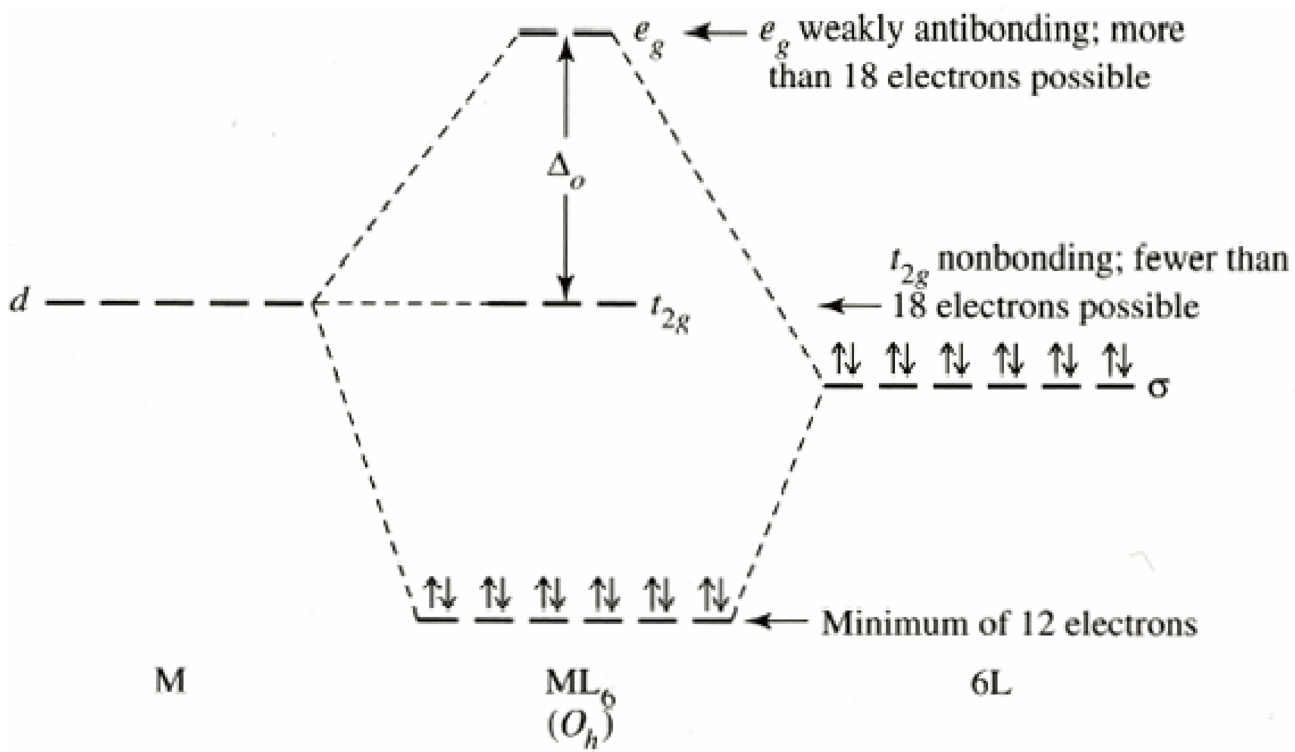


그림 13-8 $Cr(CO)_6$의 분자 궤도함수 에너지 준위 (G. O. Spessard and G. L. Miessler, *Organometallic*

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

$[Zn(en)_3]^{2+}$; ?? Electron species
good σ-donor
bad π-acceptor
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

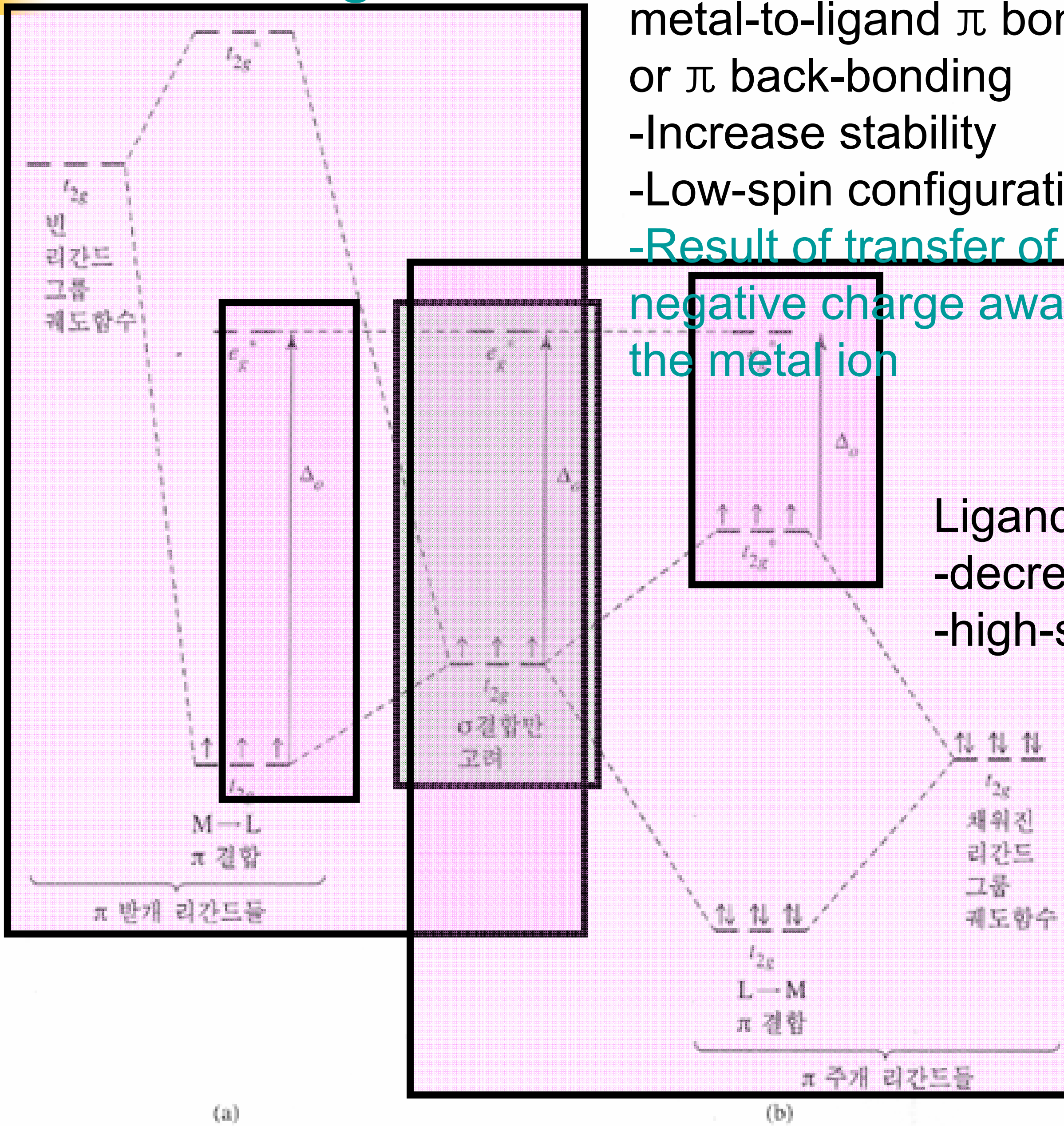
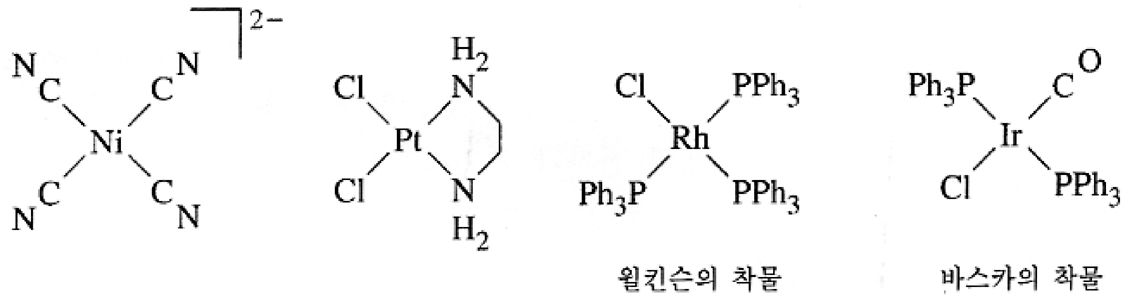


그림 10-11 π 결합에 의한 Δ_o의 변화(d^3 이온을 예로 설명함).

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

16 electron complexes might be stable

Square-planar complexes have important catalytic behavior



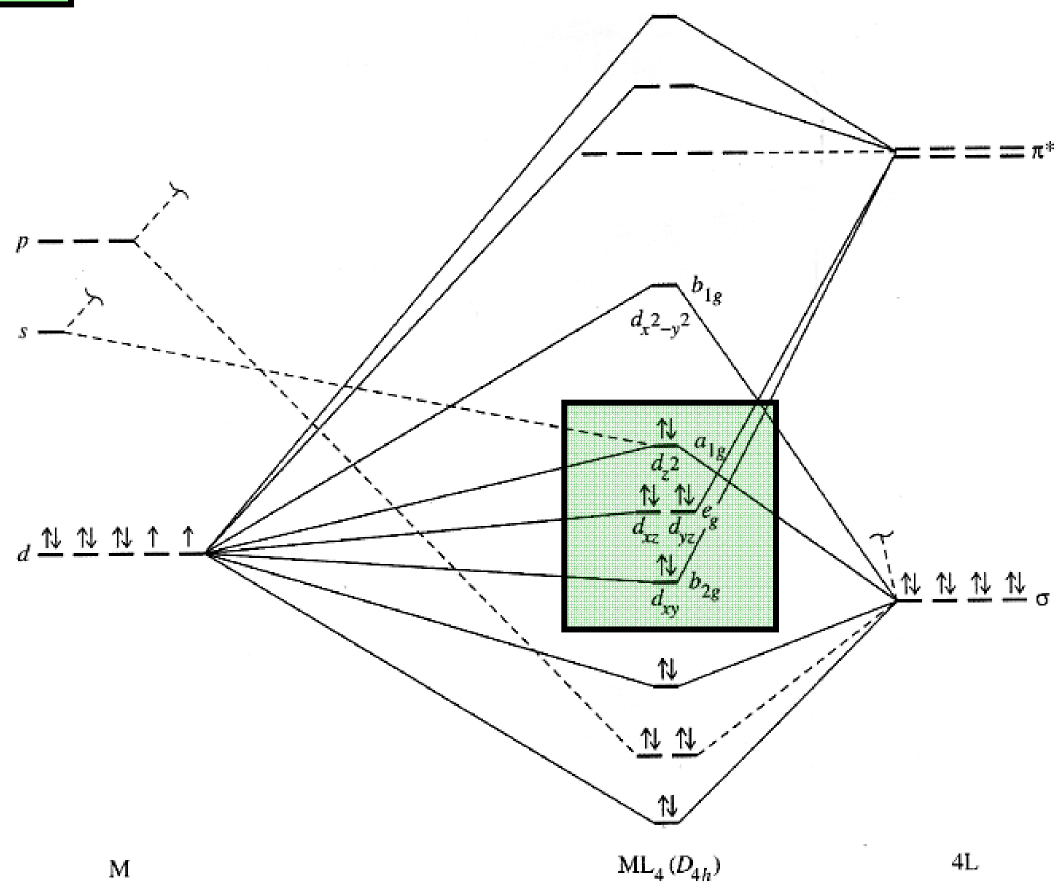
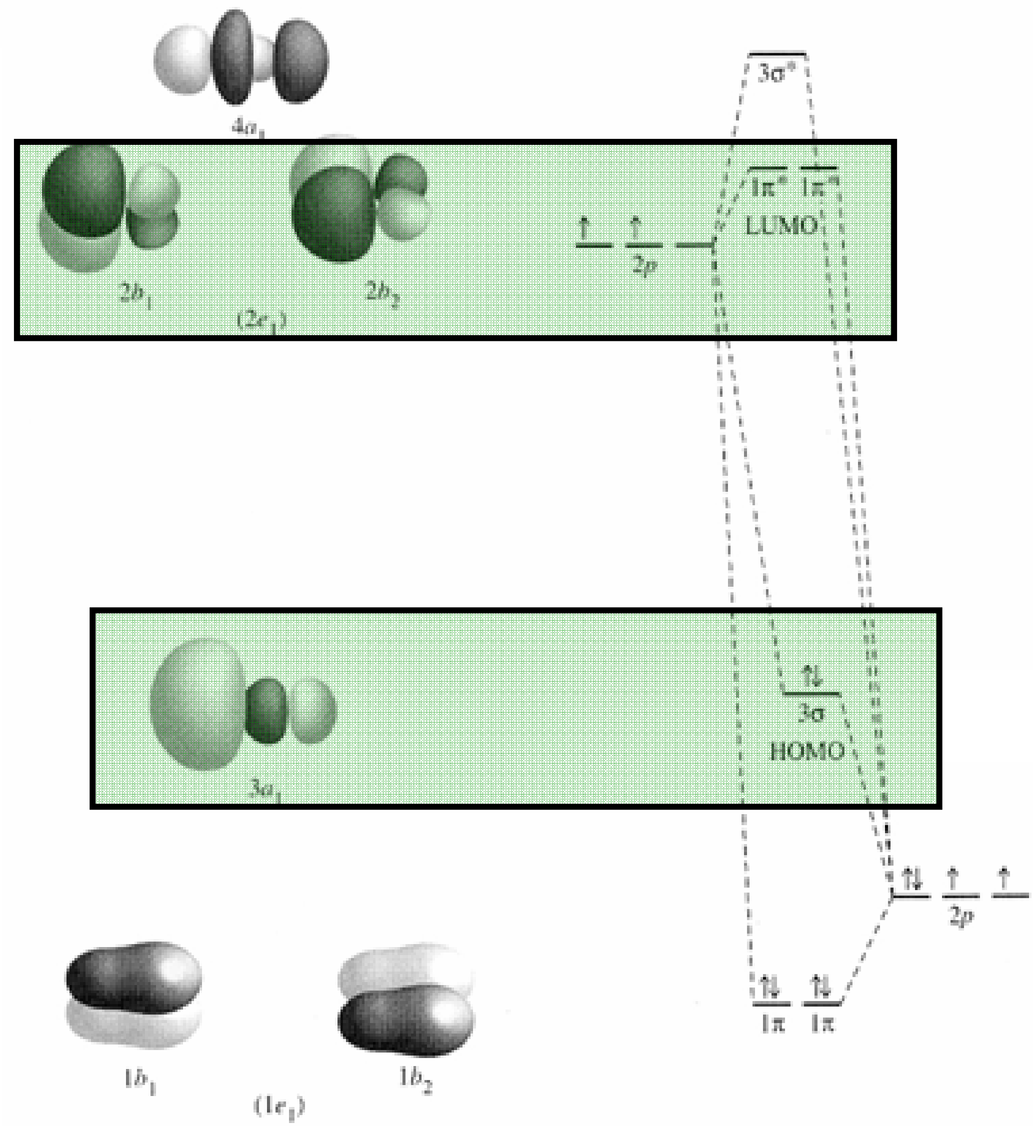


그림 13-11 평면사각형 착물의 분자 궤도함수 에너지 준위.

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



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

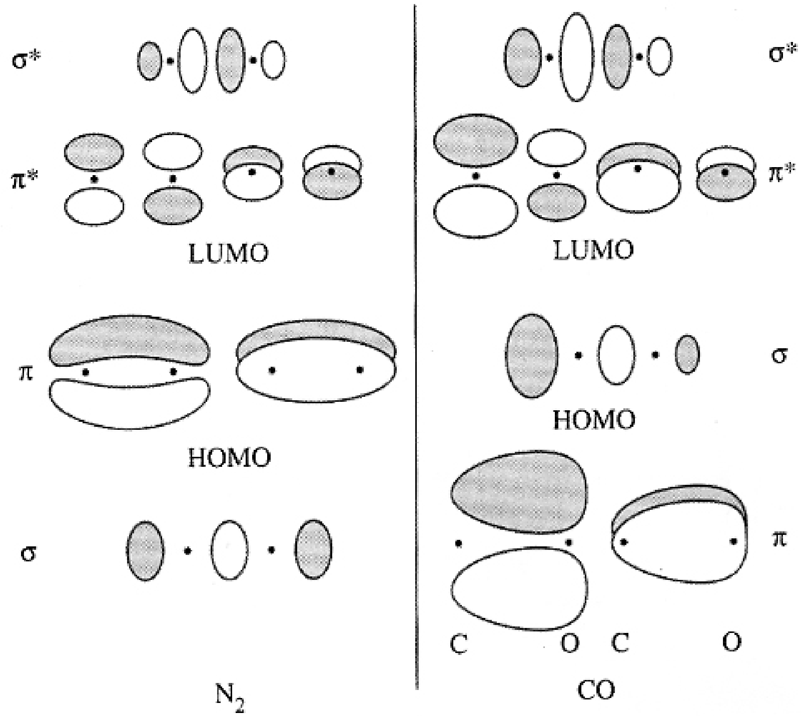


그림 13-12 CO와 N_2에 대한 분자 궤도함수의 일부분.

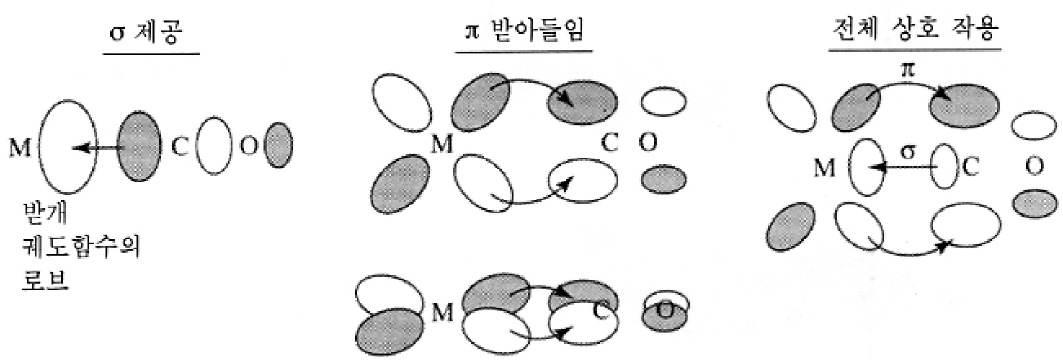


그림 13-13 CO와 금속 원자 간의 σ 및 π 상호 작용.

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

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.

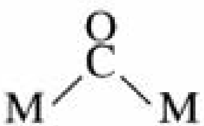
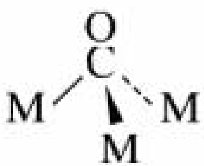
Complex	ν(CO), *cm*$^{-1}$
$[Ti(CO)_6]^{2-}$	1748
$[V(CO)_6]^-$	1859
$Cr(CO)_6$	2000
$[Mn(CO)_6]^+$	2100
$[Fe(CO)_6]^{2+}$	2204

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

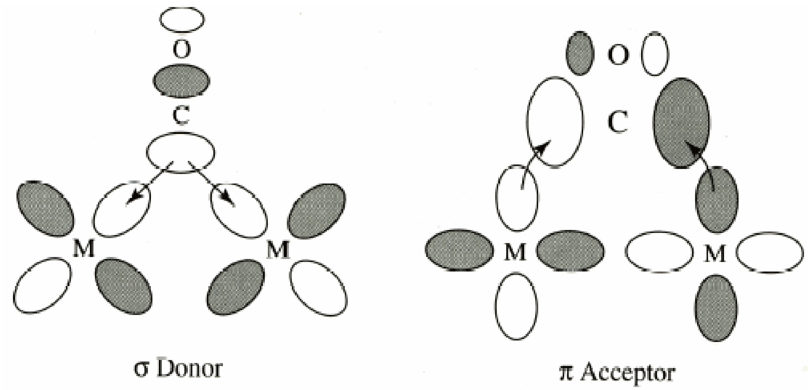
The consequence is that the electrons in the positively charged complex are more equally shared by the carbon and the oxygen, giving rise to a stronger bond and a higher energy C—O stretch.

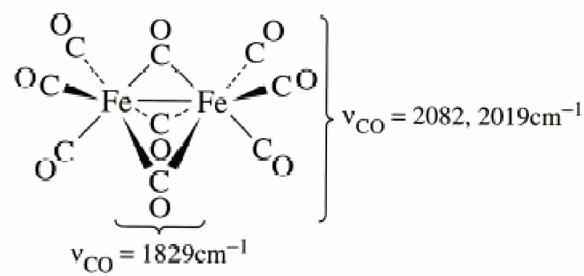
13-4 Ligands in Organometallic Chemistry ; bridging modes of CO

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

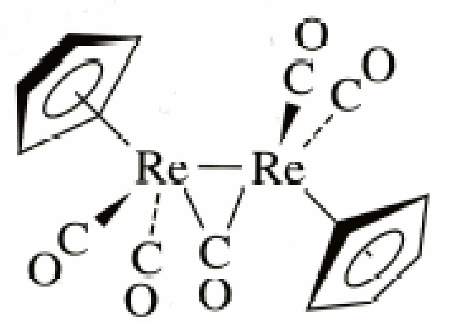
NOTE: [a] Asymmetrically bridging μ_2- and μ_3-CO are also known.





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

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

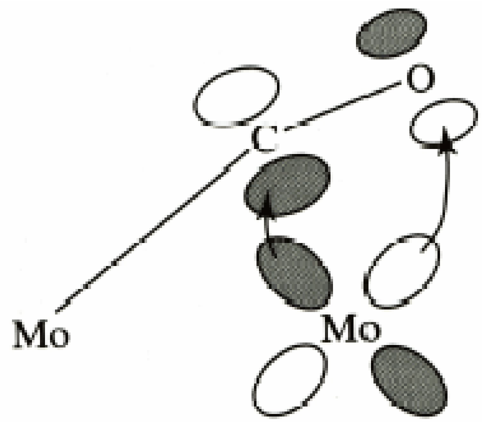


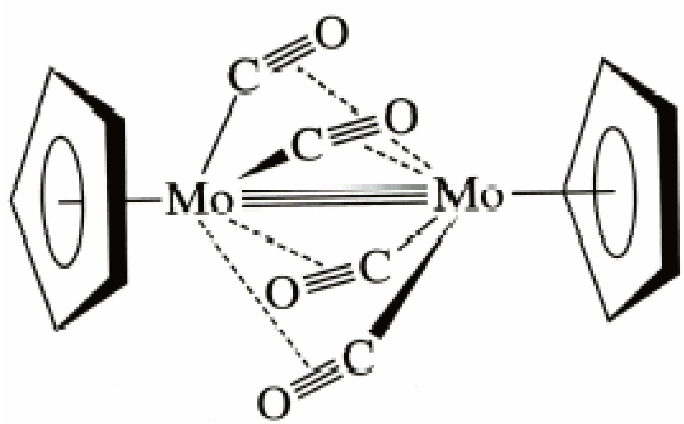
Re	7 e$^-$
η^5-C_5H_5	5 e$^-$
2 CO (terminal)	4 e$^-$
$^1/_2$(μ_2-CO)	1 e$^-$
M — M bond	1 e$^-$
Total =	18 e$^-$

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

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

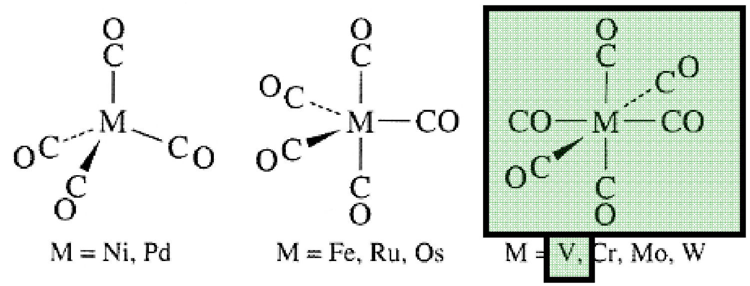
1960, 1915 cm^{-1} — 1889, 1859 cm^{-1}



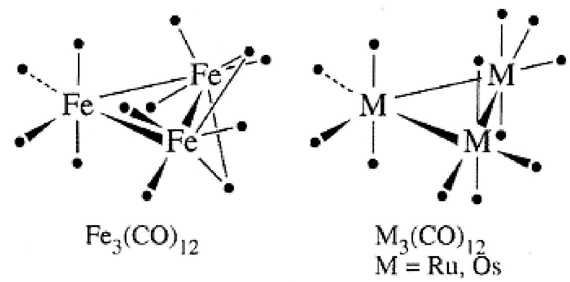


13-4 Ligands in Organometallic Chemistry
; binary carbonyl complexes

단핵 [M(CO)$_x$]

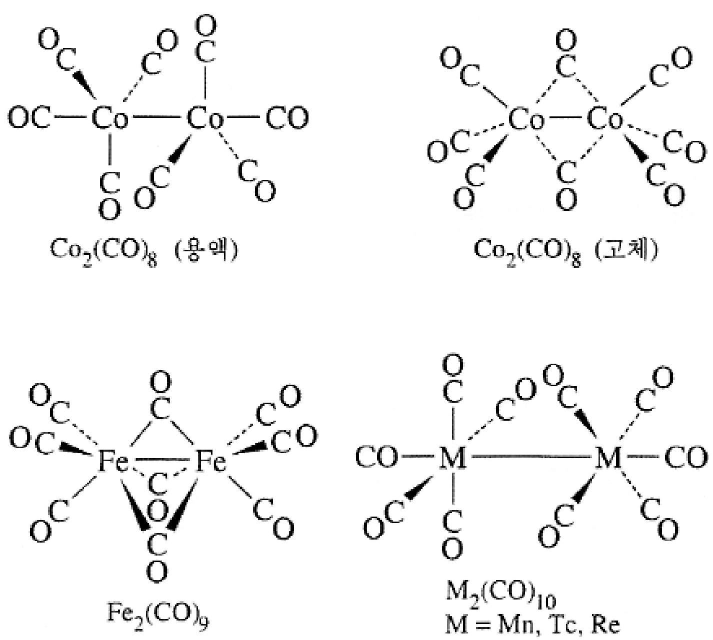


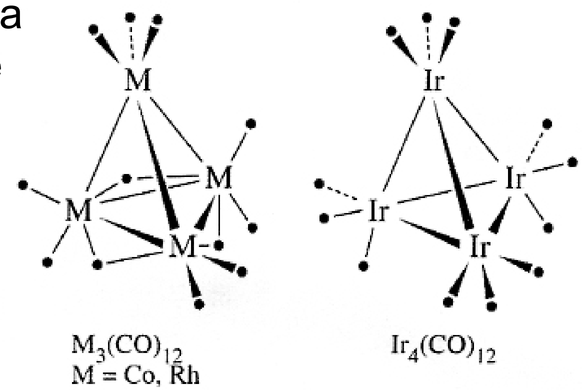
다핵 [CO를 간략하게 •으로 표시함)

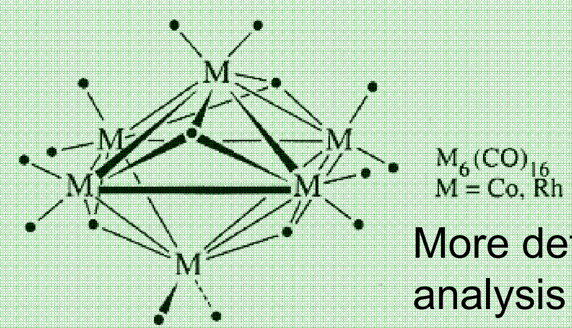


17-e$^-$ too small to permit a seventh coordination site

이핵 [M$_2$(CO)$_x$]







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

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

2. Reductive carbonylations

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

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

3. Thermal or photochemical reaction

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

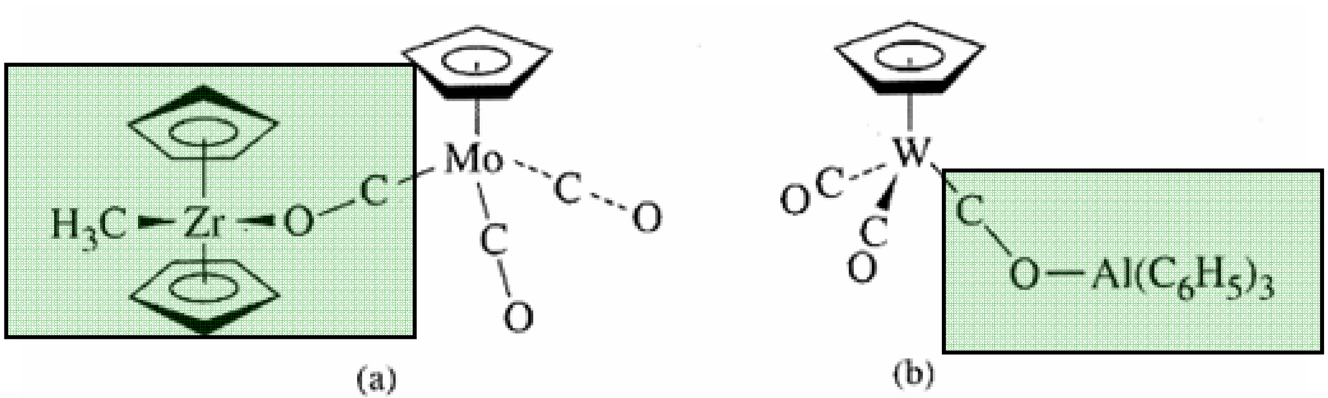
$$3\,Fe(CO)_5 \xrightarrow{\Delta} Fe_3(CO)_{12} + 3\,CO$$

Exchange reaction

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

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

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



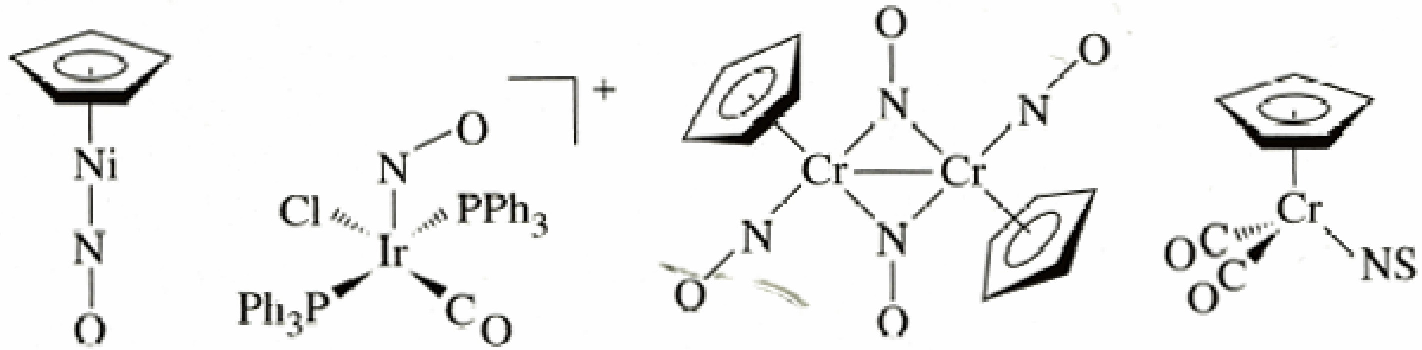
13-4 Ligands in Organometallic Chemistry ; ligands similar to CO

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

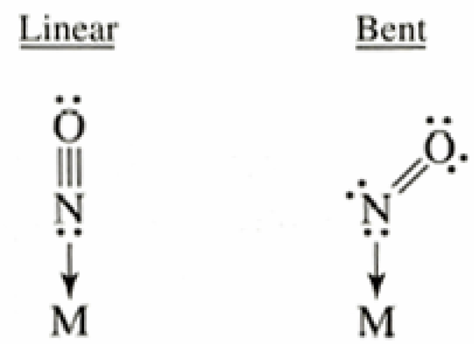
isoelectronic; CN^- and N_2
CN^- is a stronger σ donor and a somewhat π weaker acceptor than CO
CN^- bonds readily tp metals having higher oxidation states

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	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)

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

Hydride complexes

Organic synthesis, catalytic reaction

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

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

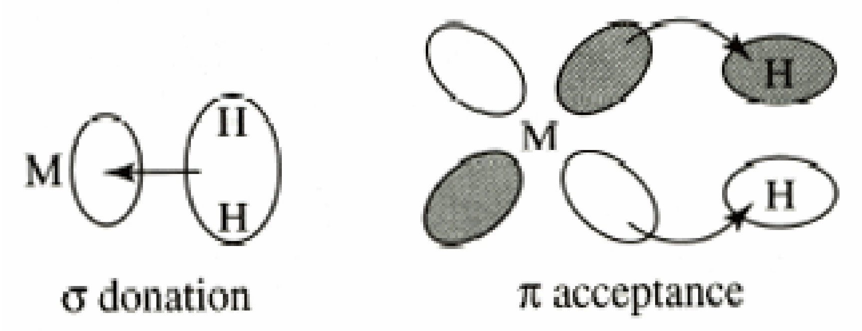
$$Co_2(CO)_8 + 2\,Na \longrightarrow 2\,Na^+[Co(CO)_4]^-$$

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

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

Dihydrogen complexes

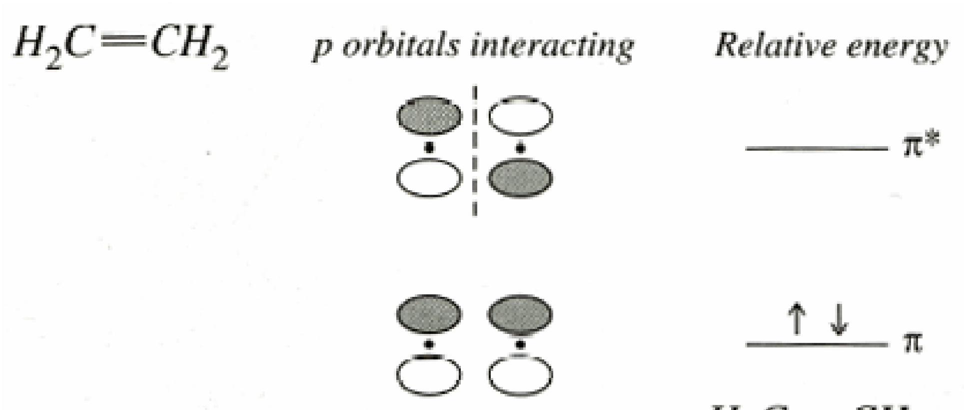
Organic synthesis, catalytic reaction

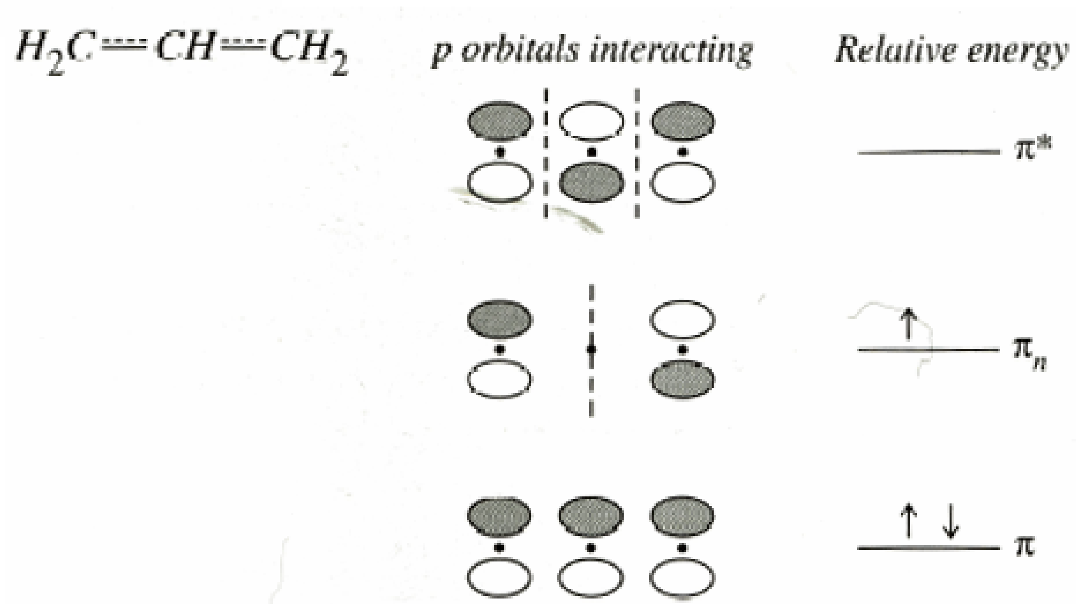


Distance of H-H
the metal is electron rich and donate strongly to the π* of H_2 → ???
with CO and NO → ???

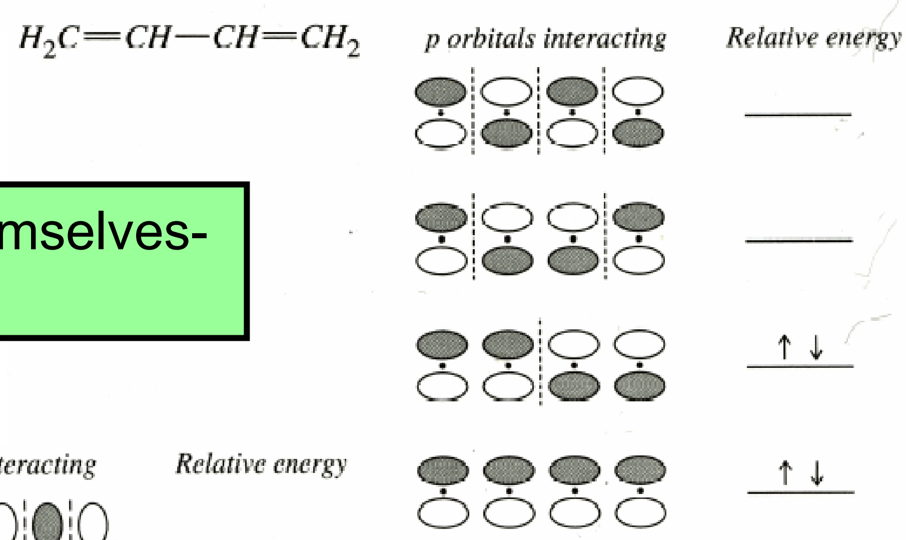
13-4 Ligands in Organometallic Chemistry ; ligands having extended π systems

π bonding within the ligands themselves-linear systems

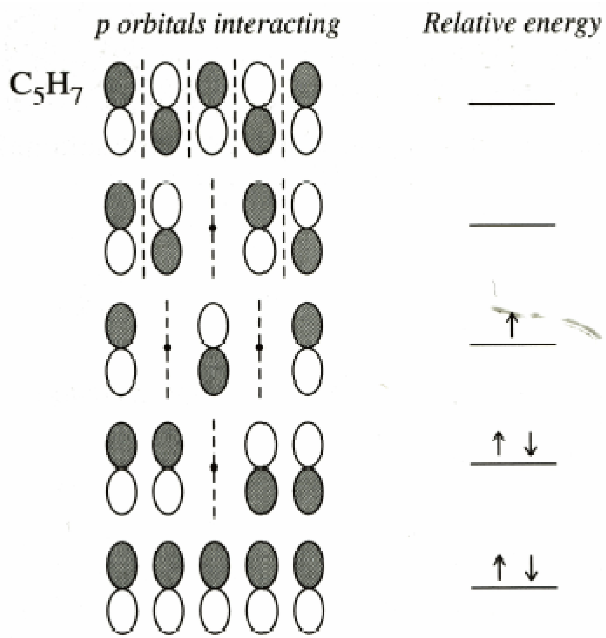


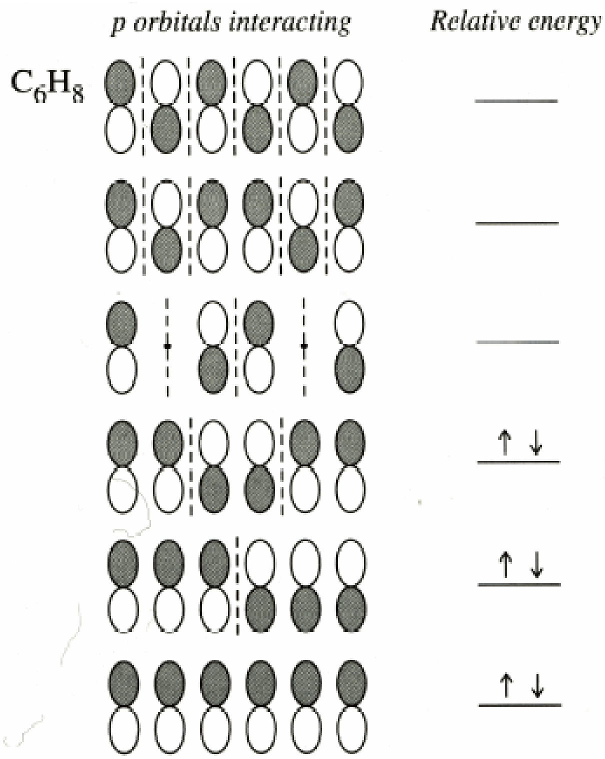


13-4 Ligands in Organometallic Chemistry
; ligands having extended π systems



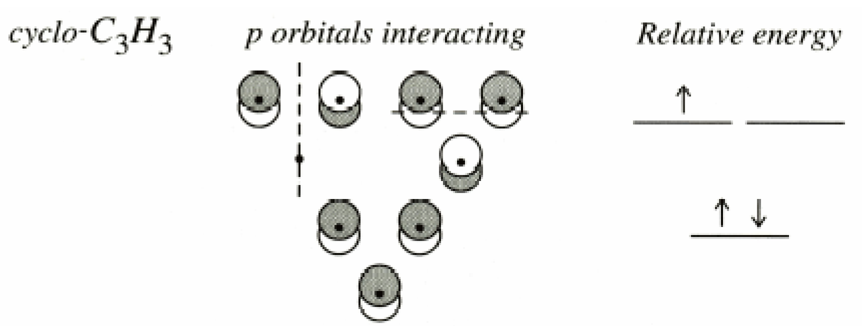
π bonding within the ligands themselves-
linear systems

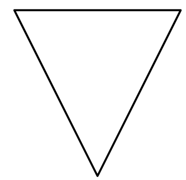


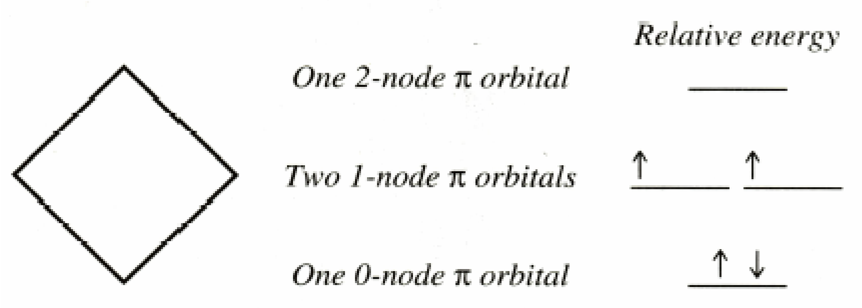


13-4 Ligands in Organometallic Chemistry
; ligands having extended π systems

π bonding within the ligands themselves-
cyclic systems







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

π bonding within the ligands themselves-
cyclic systems