

# HOMOGENEOUS CATALYSIS: INDUSTRIAL APPLICATIONS AND PHOTOCATALYSIS

*LM Chemistry @UniTS – 6 CFU*

**ORGANOMETALLIC CHEMISTRY - 2 CFU** *Prof.ssa Elisabetta Iengo eiengo@units.it*

**d-block organometallic compounds – Historical notes/Electron counting/Nomenclature**

**Ligand classification and their Bonding modes**

**Metal-Carbenes\*/Metal-carbonyls/Metallocenes**

**Reactivity/Fluxional Processes**

**HOMOGENEOUS CATALYSIS AND PHOTOCATALYSIS - 4 CFU** *Prof.ssa Barbara Milani milaniba@units.it*

**Basic Principles of Homogeneous Catalysis**

**Study of selected industrial processes based on Homogeneous Catalysis**

**Introduction to Homogeneous Photocatalysis**

**\*4hours on the 12 and 14 of may - Prof. Martin Albrecht, Visiting Professor from the University of Bern, Switzerland.**

**Visit to the Industrial Plant LyondellBasell - Ferrara**

**Final Exam: Oral examination on both modules.**

❖ **Homogeneous Catalysis: understanding the art**

Autore: Piet W.N.M. van Leeuwen

Kluwer Academy Publisher

Springer: [www.springer.com/chemistry](http://www.springer.com/chemistry)

❖ **Inorganic Chemistry - Fifth Edition**

Catherine E. Housecroft and Alan G. Sharpe

Pearson Prentice Hall

❖ **Inorganic Chemistry - Seventh Edition**

Weller, Overton, Rourke, Armstrong

Oxford University Press

❖ **Fundamentals of Organometallic Catalysis**

Dirk Steinborn

Wiley-VCH (2012)

❖ **Organometallics and Catalysis: an Introduction**

Manfred Bochmann

Oxford University Press 2015



## ORGANOMETALLIC CHEMISTRY



Organometallic Chemistry PART 1



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Organometallic Chemistry PART 2



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Organometallic Chemistry PART 3



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Organometallic Chemistry PART 4



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Organometallic Chemistry PART 5



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Organometallic Chemistry PART 6



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Organometallic Chemistry EXERCISES



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Video Jove On preparation of Carbenes

**ADVISE!**

**Print the Slides from MOODLE to take Notes**



## LITERATURE MATERIAL



### ORGANOMETALLIC CHEMISTRY - Supplemental Material



 2017 Brief Guide to the Inorganic Nomenclature.pdf  Amanote

 Albrecht\_ChemSocRev2010 NHCs Carbenes.pdf  Amanote

 Astruc\_EurJIC2017 Ferrocene.pdf  Amanote

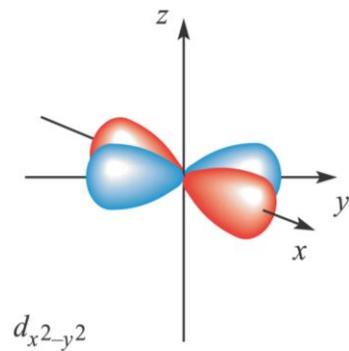
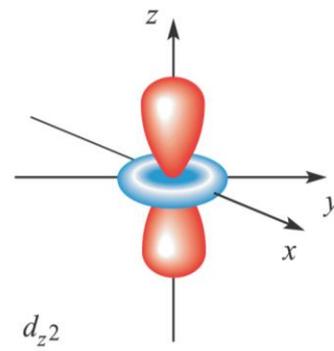
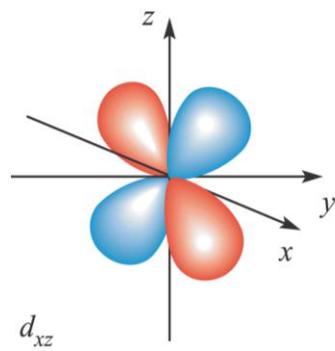
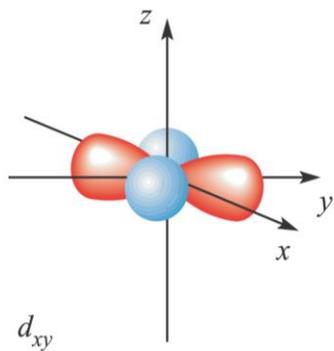
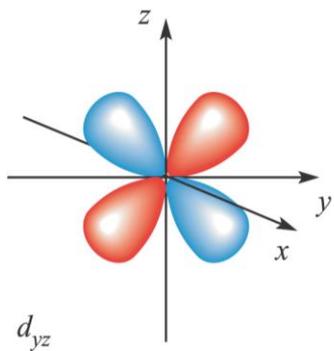
 Calderazzo\_JOrganometallicChem1967\_mechanism of migratory insertion.pdf  Amanote

 Nolan\_CoordChemRev2009 Carbenes.pdf  Amanote

 Red\_Book\_2005 iupac Inorganic Nomenclature.pdf  Amanote

 Tolman ChemRev1977 Phosphines.pdf  Amanote

# *d*-block Organometallic Compounds



## Coordination Compounds (Werner's type complexes)

- Typically simple ligands,  $\sigma$ -donor and  $\pi$ -donor
- Usually charged
- Variable number of  $d$ -electrons
- Typically soluble in water

## Organometallic Compounds (at least one M–C bond)

- Often neutral
- Fixed number of  $d$ -electrons (16 or 18 are the stable electron configurations)
- Soluble in organic solvents (*e.g.* THF)
- Properties more similar to organic compounds than to inorganic salts (*e.g.* low melting points; some are even liquid at r.T.)



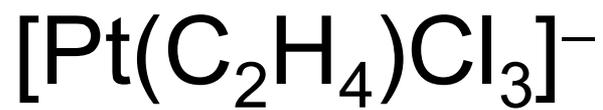
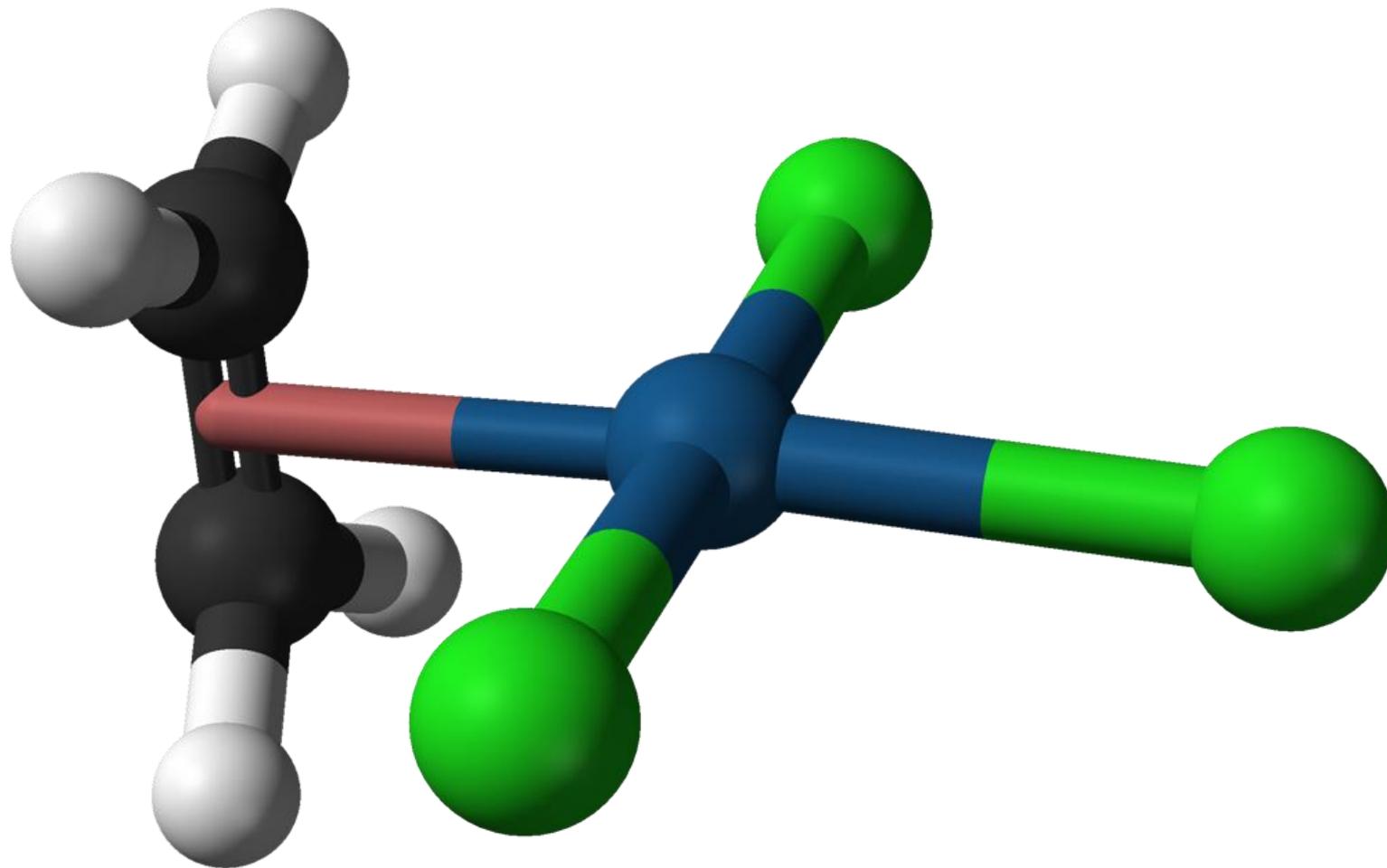
W C Zeise, Danish  
pharmacist, **1789- 1847**

*'The breakthrough, the isolation of a pure, crystalline compound came when Zeise added potassium chloride to a concentrated  $\text{PtCl}_4$  /ethyl alcohol reaction solution and evaporated the resulting solution. Beautiful lemon yellow crystals, often one half inch or more in length were isolated. On longer exposure to air and light, they gradually became covered with a black crust. They contained water of hydration, which was lost when they were kept over concentrated sulfuric acid in vacuo or when heated to around  $100^\circ\text{C}$ . Chemists in those days often reported how the compounds that they had prepared tasted. Zeise described the taste of this potassium salt as metallic, astringent and long lasting.'*

*Dietmar Seyferth, Organometallics, 2001, 20, 2*



**Zeise Salt, 1827**



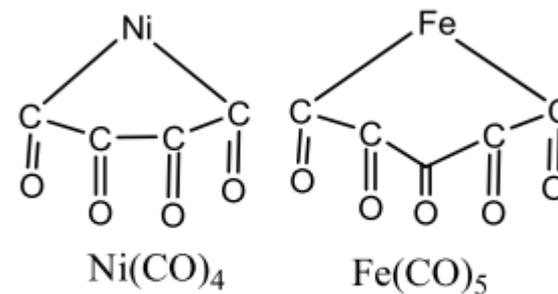
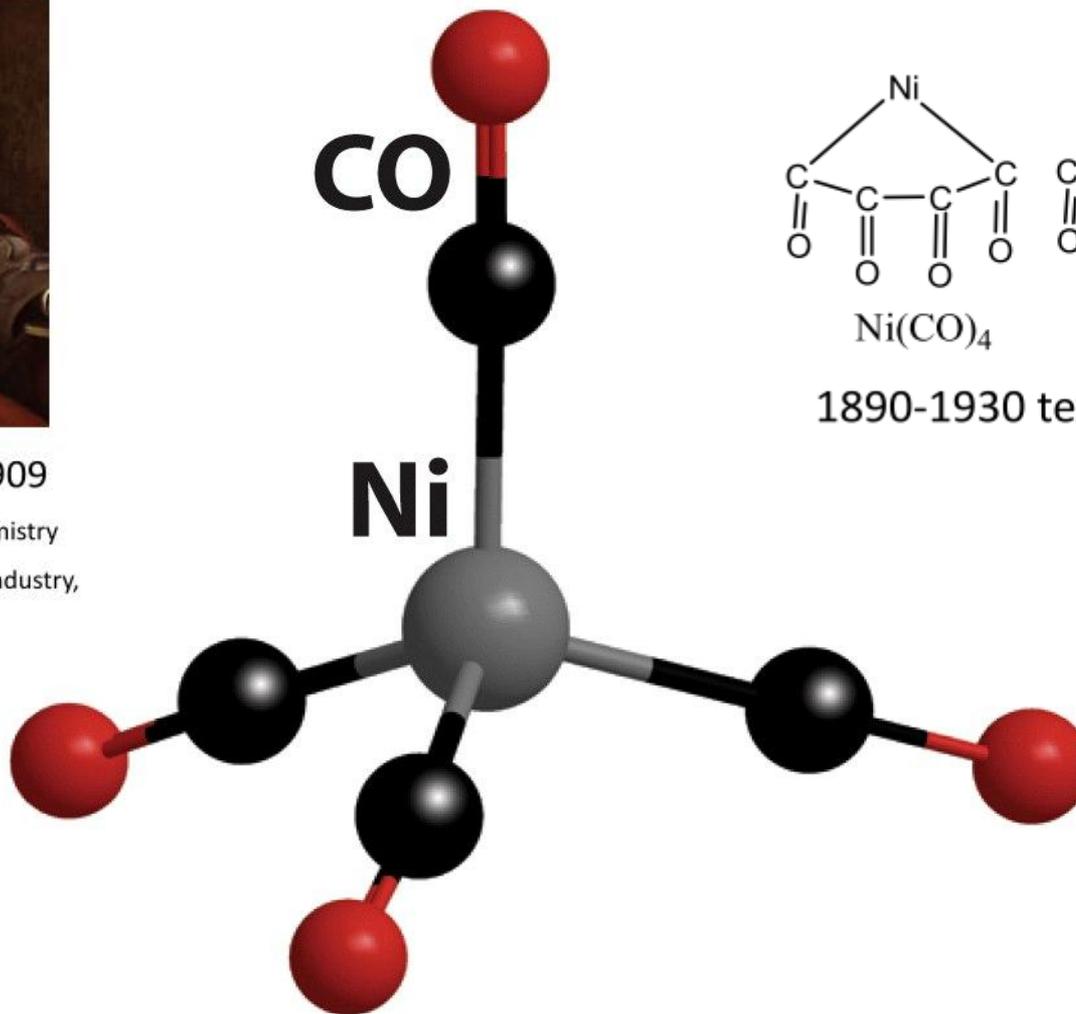
Zeise Salt, 1969



Ludwig Mond 1839-1909

Father of Metal Carbonyl Chemistry

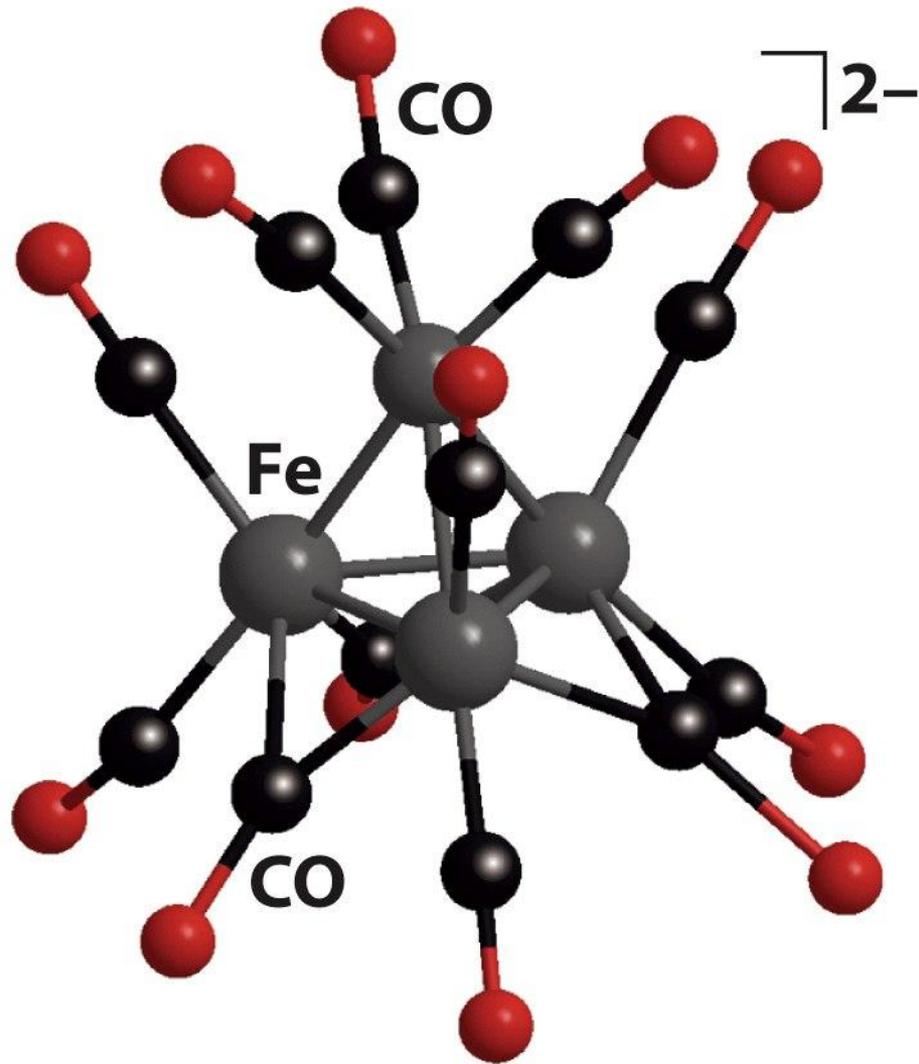
Founder of Imperial Chemical Industry,  
England



1890-1930 textbooks



Mond, Langer, Quinke, 1890



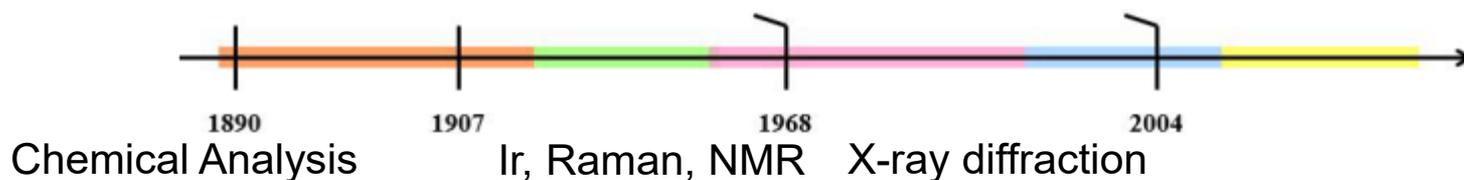
Hieber, 1930-....



1868	Pt(CO) <sub>2</sub> Cl <sub>2</sub>	M.P. Schützenberger
1890	Ni(CO) <sub>4</sub>	L. Mond et al.
1891	Fe(CO) <sub>5</sub>	L. Mond, F. Quinke, M. Berthelot
1905	Fe <sub>2</sub> (CO) <sub>9</sub>	J. Dewar, H.O. Jones
1907	[Fe <sub>3</sub> (CO) <sub>12</sub> ]*	
1910	Co <sub>2</sub> (CO) <sub>8</sub>	L. Mond et al.
	Co <sub>4</sub> (CO) <sub>12</sub>	
1910	Mo(CO) <sub>6</sub>	
1927/28	Cr(CO) <sub>6</sub>	A. Job et al.
	W(CO) <sub>6</sub>	

Walter Otto Hieber (1895-1976)  
Technische Hochschule München

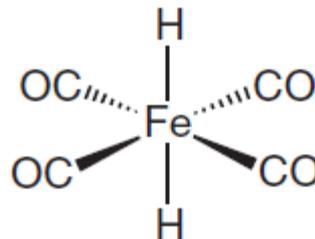
*"... it was only in the autumn of 1927 at the Institute of Chemistry of the University of Heidelberg that I took up research experiments with iron pentacarbonyl, which was kindly provided by Dr. A. Mittasch of BASF ... On the basis of his own experience with nickel carbonyl he warned me emphatically of the danger inherent in the use of these highly toxic substance, coupling his warning with the comment that in this field one could only expect a great deal of trouble and results of little scientific value!"*



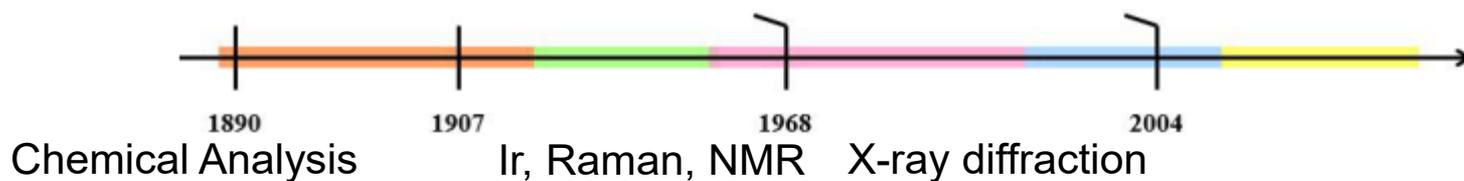


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Technische Hochschule München



**First metal-hydride complex**  
Hieber, 1931

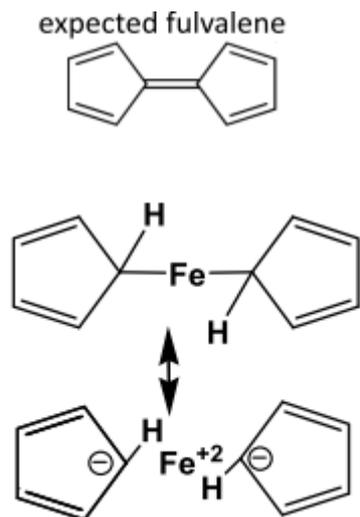
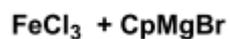




Pauson



Kealy



## A New Type of Organo-Iron Compound

letters to nature

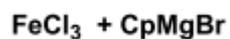
*Nature* **168**, 1039 - 1040 (15 December 1951); doi:10.1038/1681039b0



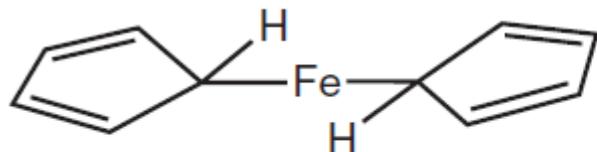
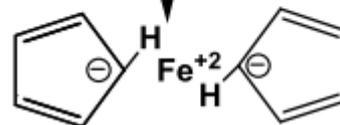
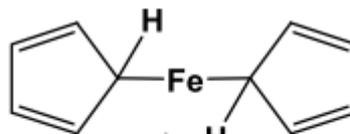
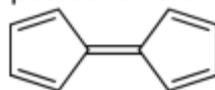
Pauson



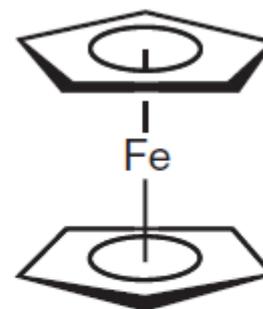
Kealy



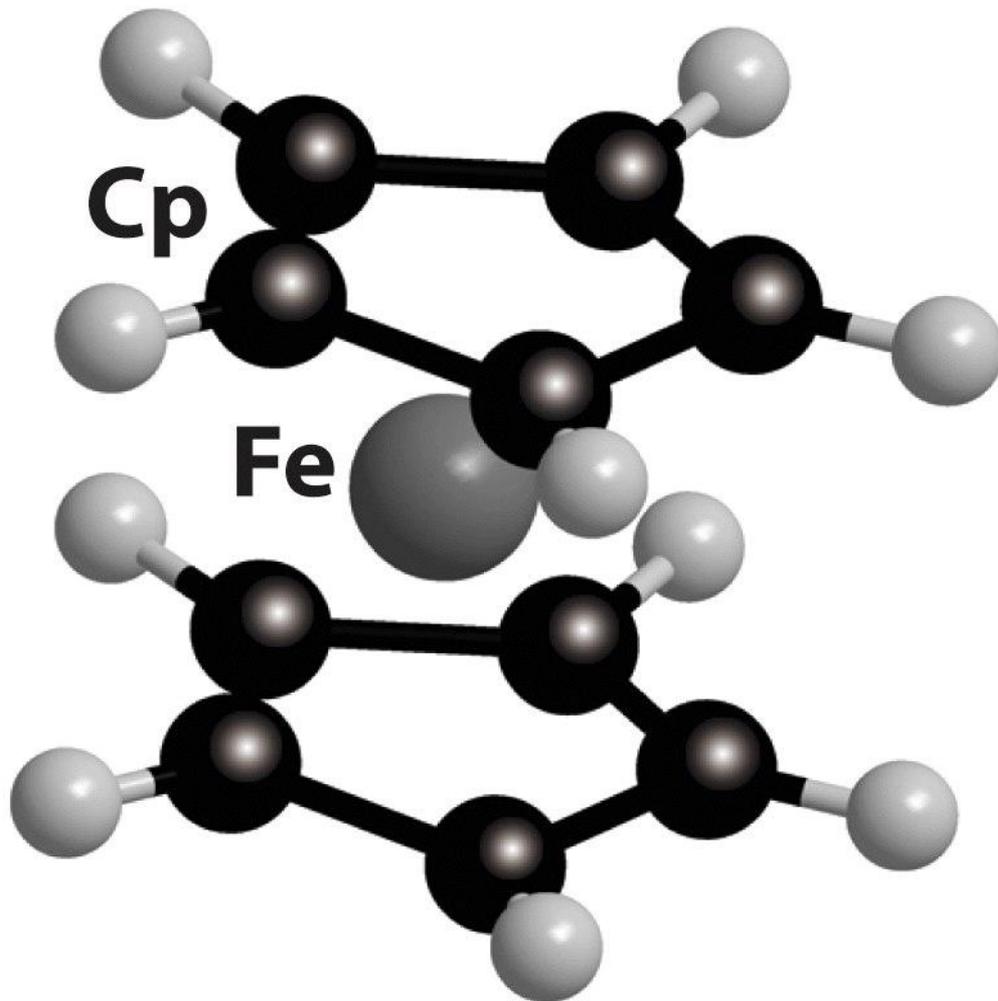
expected fulvalene



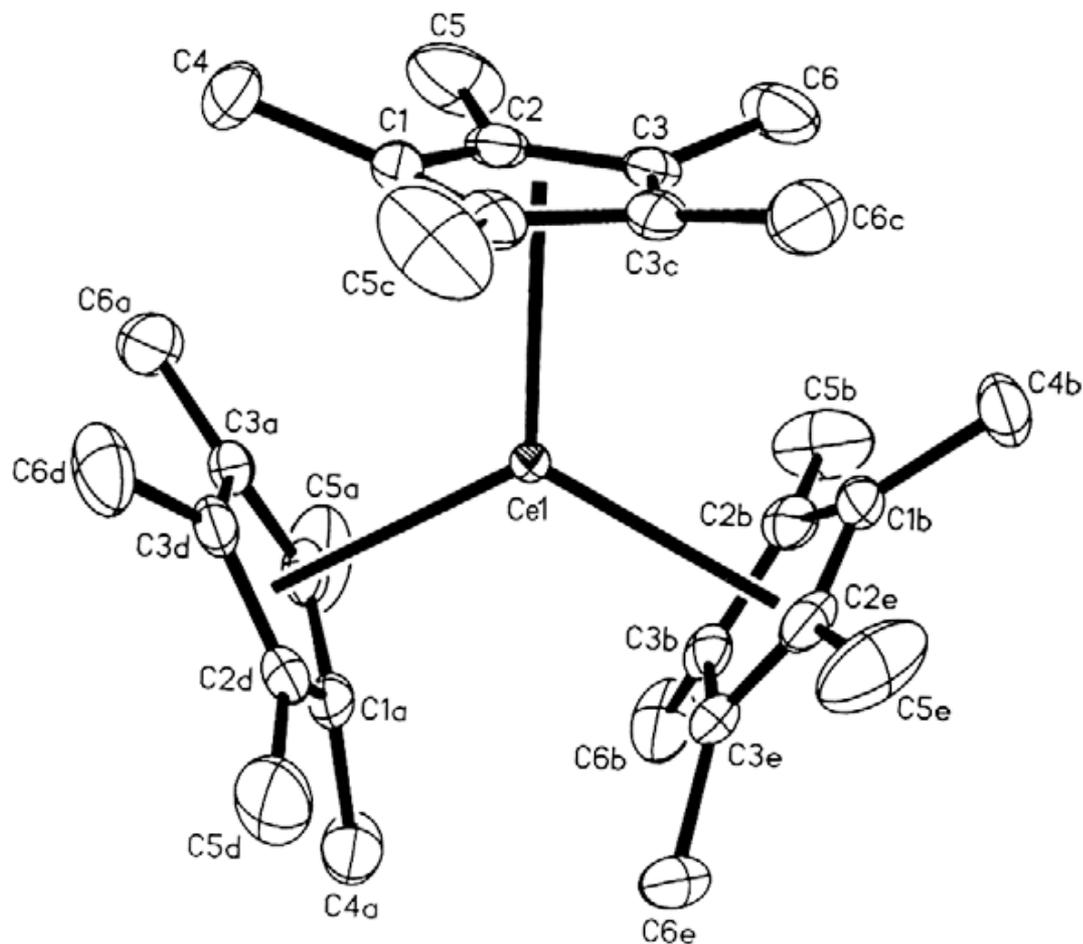
**FeCp<sub>2</sub> : erroneous  $\sigma$  structure**  
Pauson, 1951



**$\pi$ -sandwich structure of ferrocene**  
Wilkinson and Fischer, 1952



Ferrocene, 1951 (IR, X-ray, NMR)



1970 - ... Ln-Cp\* compounds





Photo from the Nobel Foundation archive.

**Ernst Otto Fischer**

Prize share: 1/2



Photo from the Nobel Foundation archive.

**Geoffrey Wilkinson**

Prize share: 1/2

# **1973 – Nobel Prize** for Organometallic Chemistry of the *d-block* elements

Ernst-Otto Fisher (Munich)  
&  
Geoffrey Wilkinson (London)

# Electron Counting

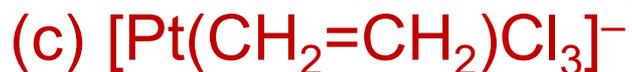
## Donor-pair method

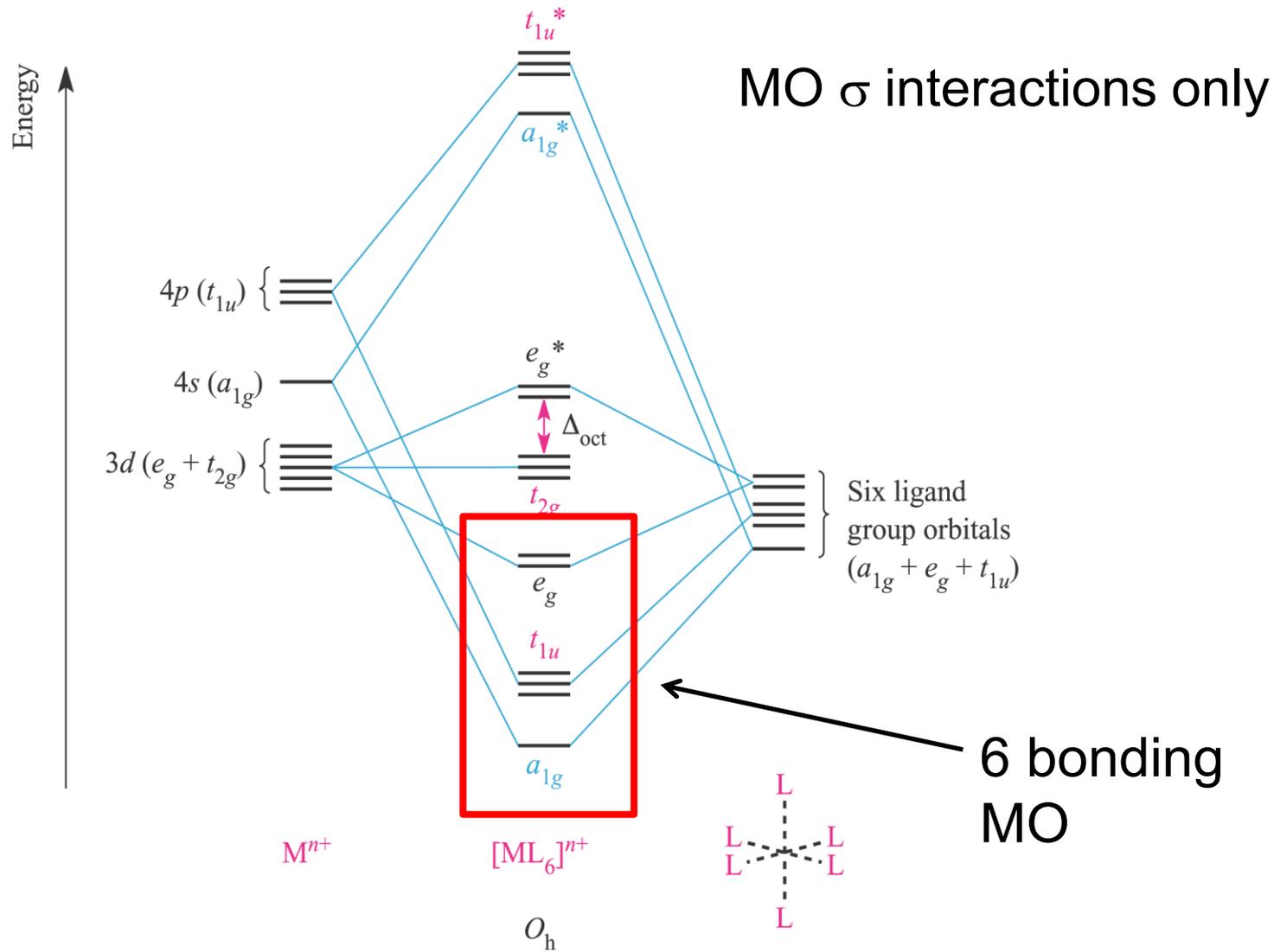
Ligand	Formula	Electrons donated
Carbonyl	CO	2
Phosphine	PR <sub>3</sub>	2
Hydride	H <sup>-</sup>	2
Dihydrogen	H <sub>2</sub>	2
η <sup>1</sup> -Alkyl, -alkenyl, -alkynyl, and -aryl groups	R <sup>-</sup>	2
η <sup>2</sup> -Alkene	CH <sub>2</sub> =CH <sub>2</sub>	2
η <sup>2</sup> -Alkyne	RCCR	2
Dinitrogen	N <sub>2</sub>	2
Butadiene	CH <sub>2</sub> =CH—CH=CH <sub>2</sub>	4
Benzene	C <sub>6</sub> H <sub>6</sub>	6
η <sup>3</sup> -Allyl	CH <sub>2</sub> CHCH <sub>2</sub> <sup>-</sup>	4
η <sup>5</sup> -Cyclopentadienyl	C <sub>5</sub> H <sub>5</sub> <sup>-</sup>	6

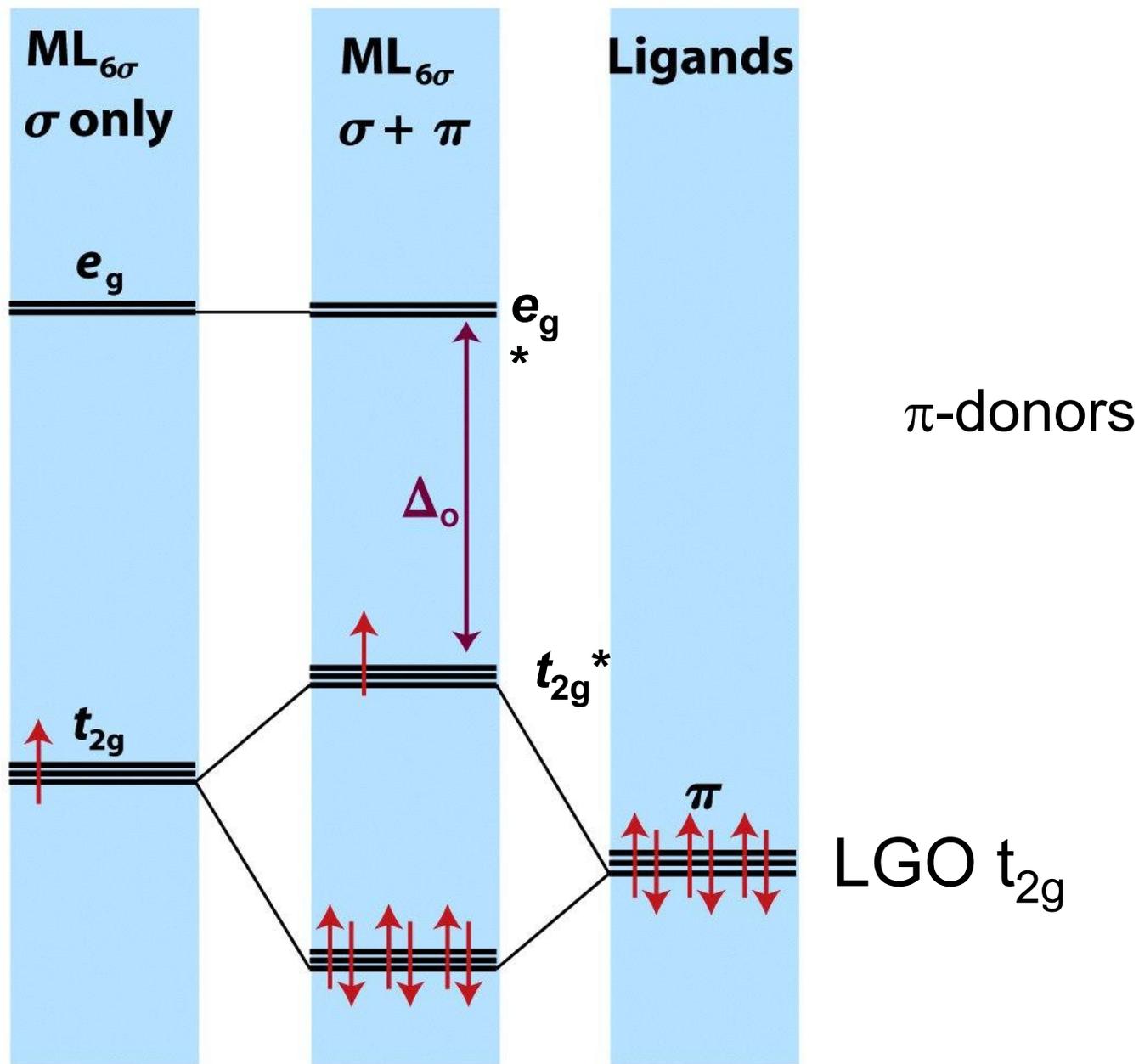
\* We use this method throughout this book.

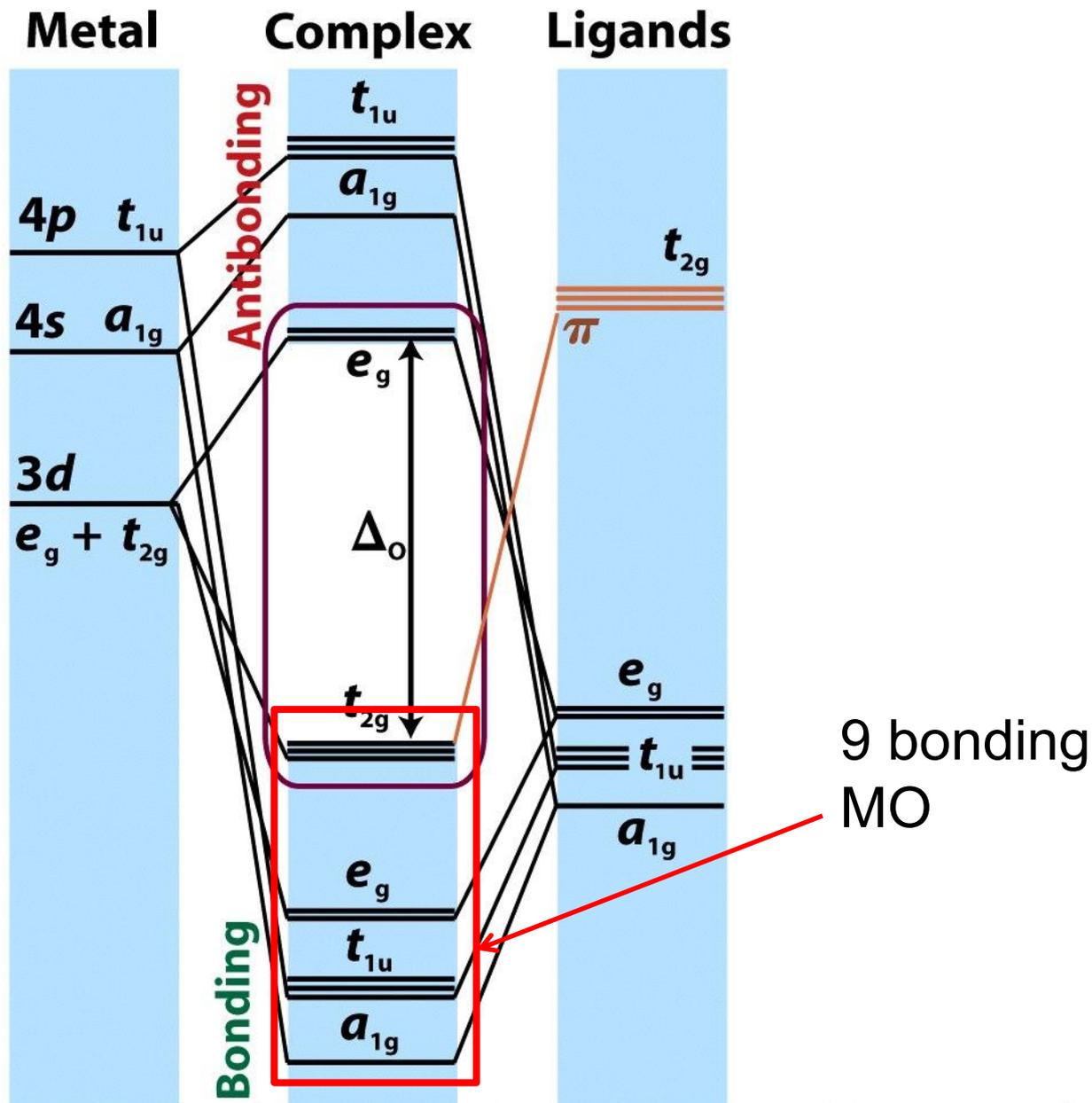
# Electron Counting

- The *oxidation state* of the metal atom is given by the difference between the compound total charge and the sum of the ligand charges.
- The *number of electrons* of the metal atom is identified by the difference of the metal Group number and the metal oxidation state.
- The *total number of electrons* is given by the sum of the electrons of the metal atom and those of the ligands.

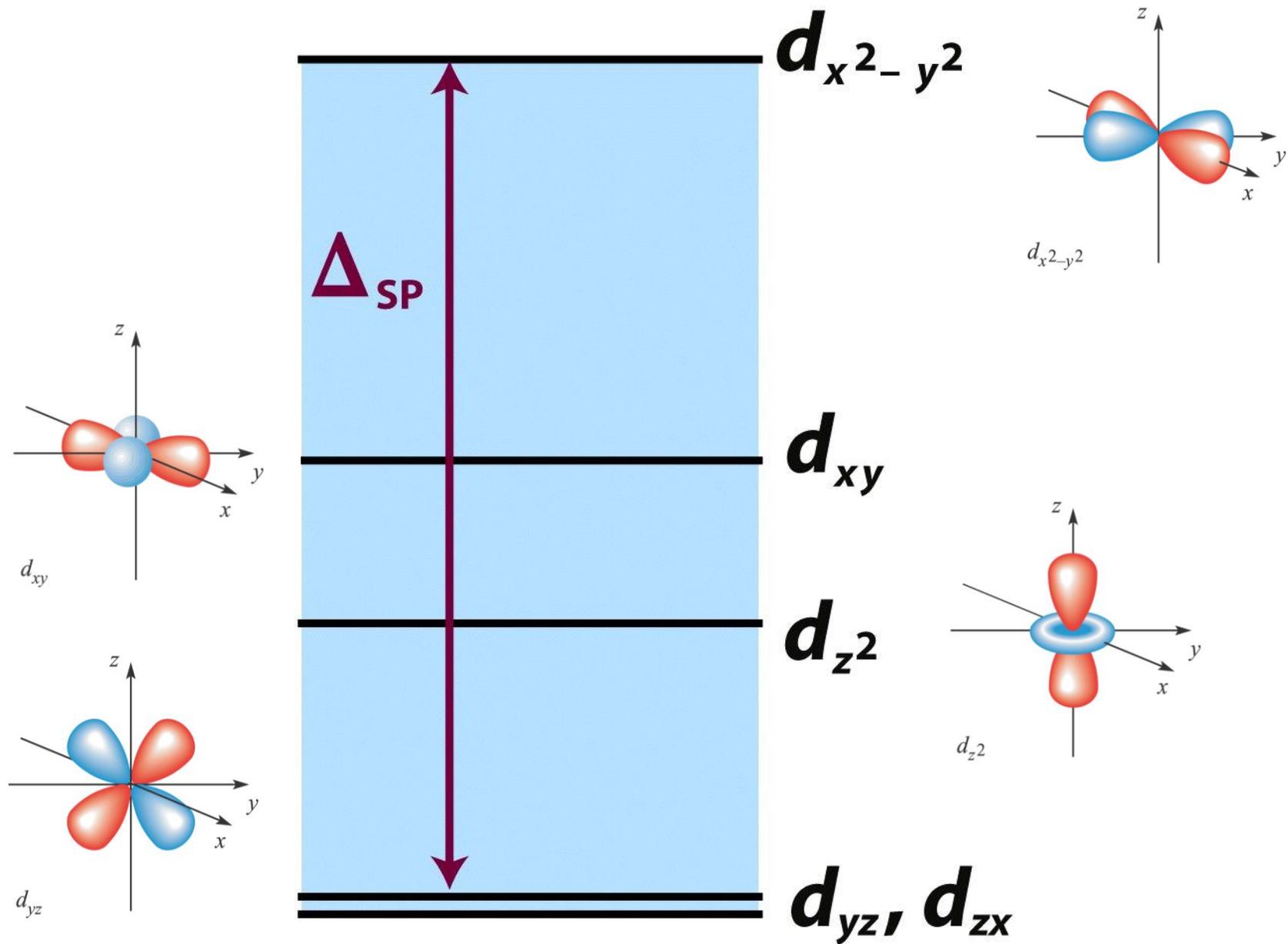








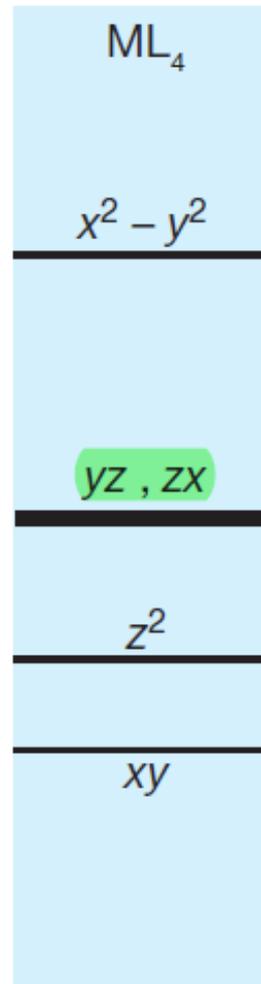
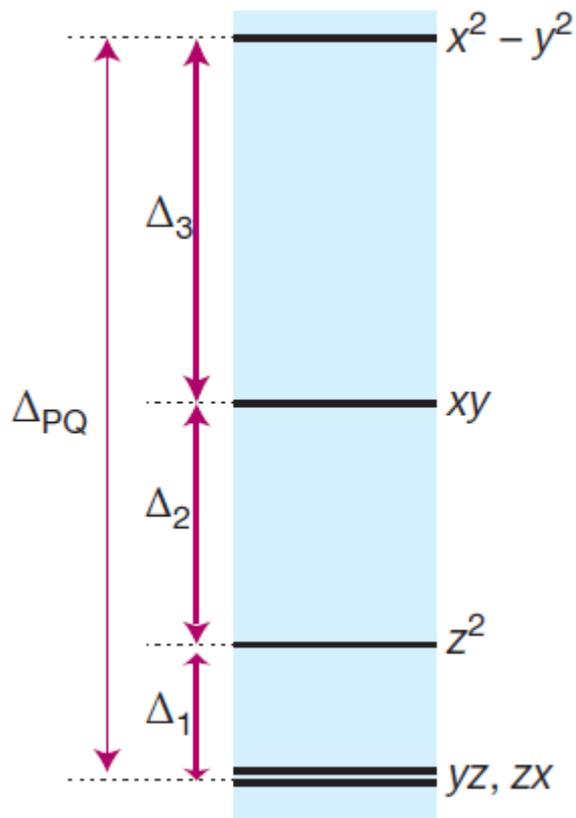
Energetic levels for the MO of a octahedral complex with strong field ligands ( $\pi$  acceptors)

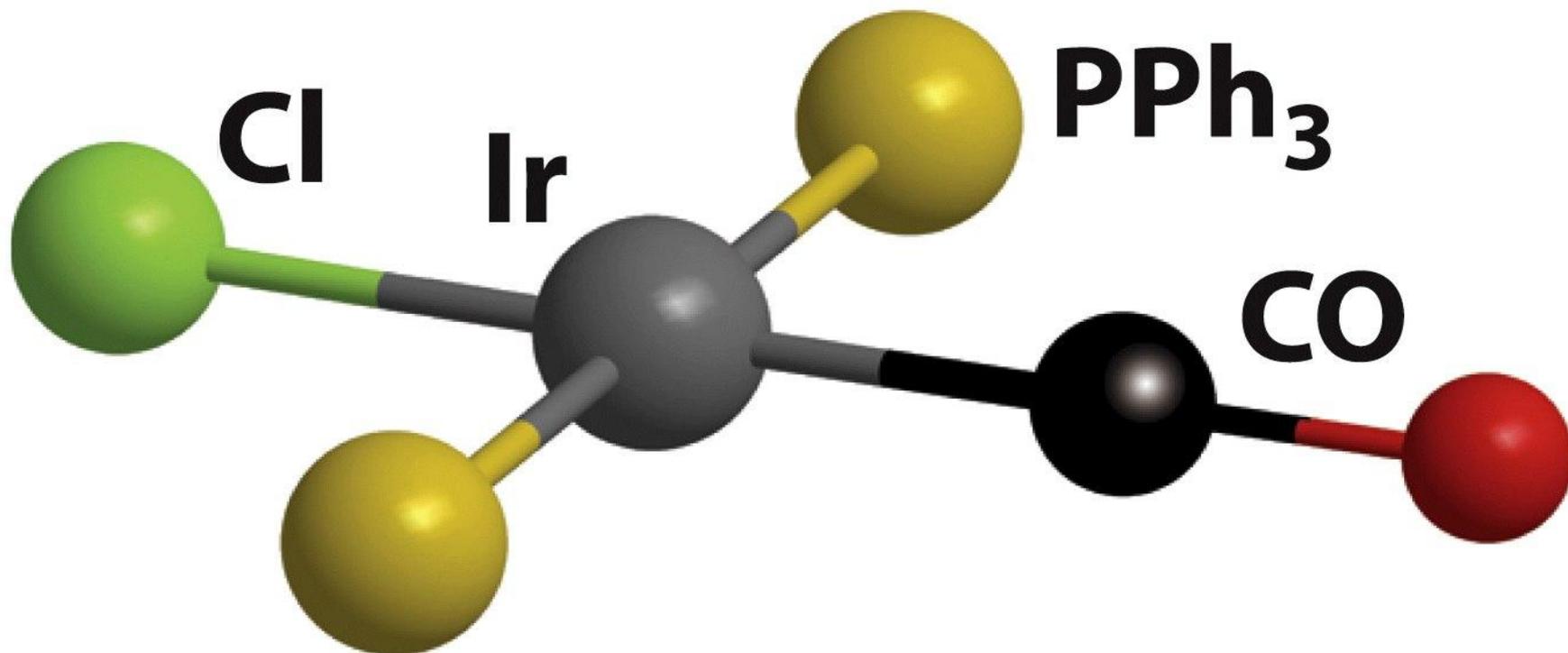


Energetic levels for the MO of a square planar complex with strong field ligands

$\sigma$ -donatore  
+  
 $\pi$ -donatore

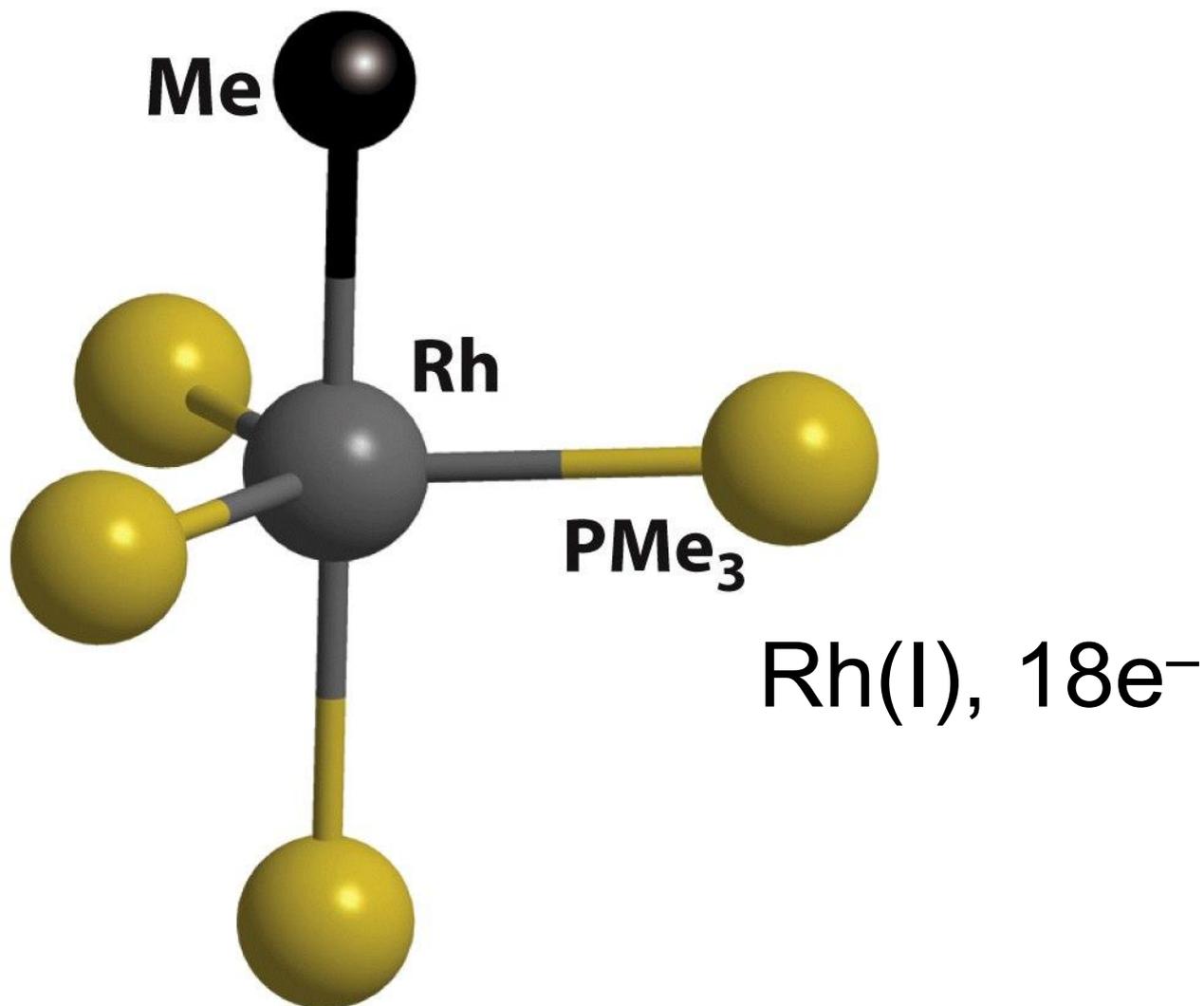
$\sigma$ -donatore  
+  
 $\pi$ -accettore



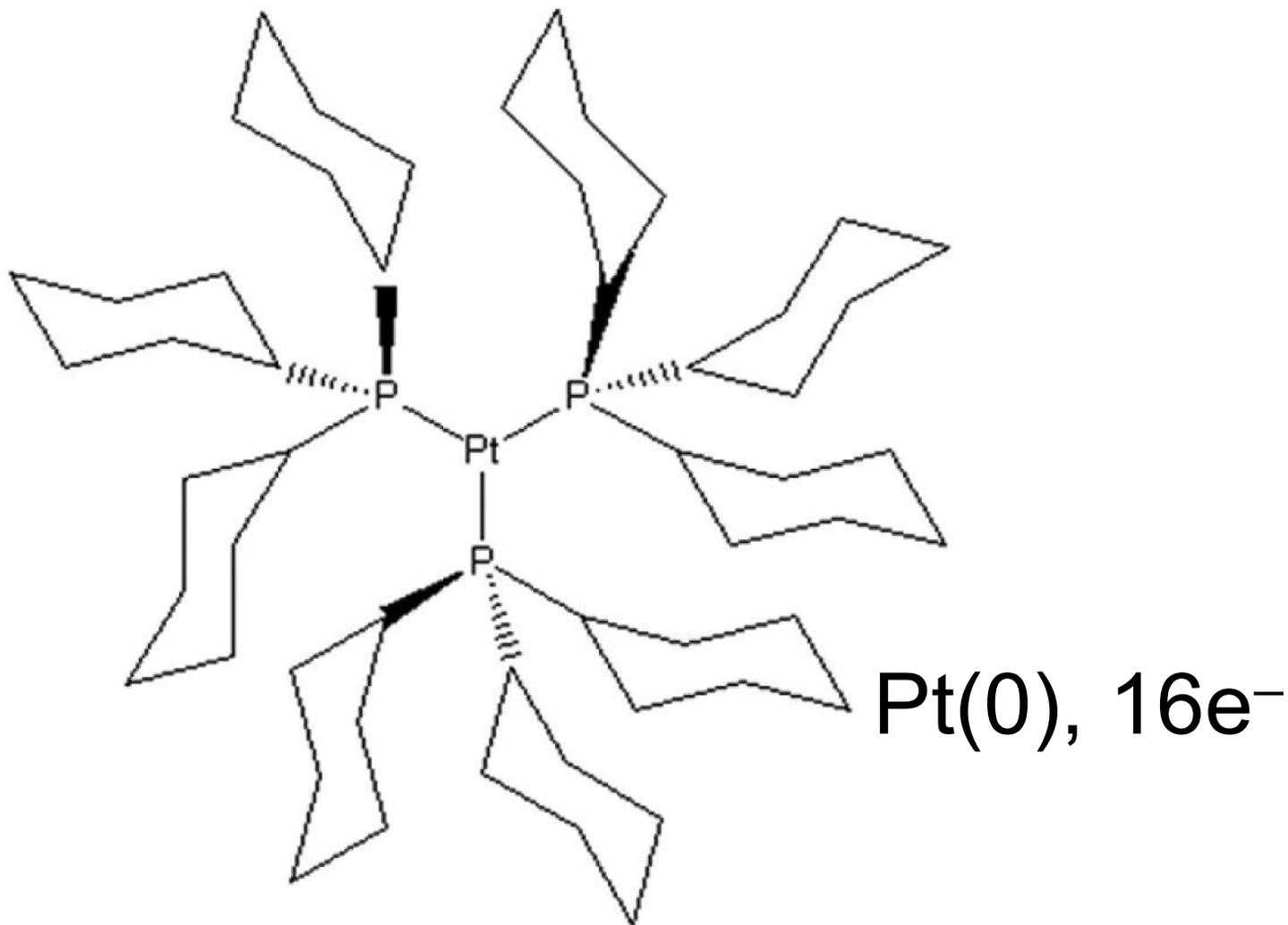


1962, The Vaska Complex (16e<sup>-</sup>)

# Exceptions to the 16-18 electron rule



# Exceptions to the 16-18 electron rule



# Exceptions to the 16-18 electron rule

**Table 21.1** Validity of the 16/18-electron rule for *d*-metal organometallic compounds

Usually less than 18 electrons			Usually 18 electrons			16 or 18 electrons	
Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
La	Hf	Ta	W	Re	Os	Ir	Pt

# Exceptions to the 16-18 electron rule

$[\text{V}(\text{CO})_6]$	17 electrons
$[\text{W}(\text{CH}_3)_6]$	12 electrons
$[\text{Cr}(\eta^5\text{-Cp})(\text{CO})_2(\text{PPh}_3)]$	17 electrons

$[\text{Cr}(\eta^5\text{-Cp})(\text{CO})_3]_2$  18 electrons



Cr–Cr (epta-coordination)

# Nomenclature

(see also Supplemental Material on Moodle)

## Extended Name

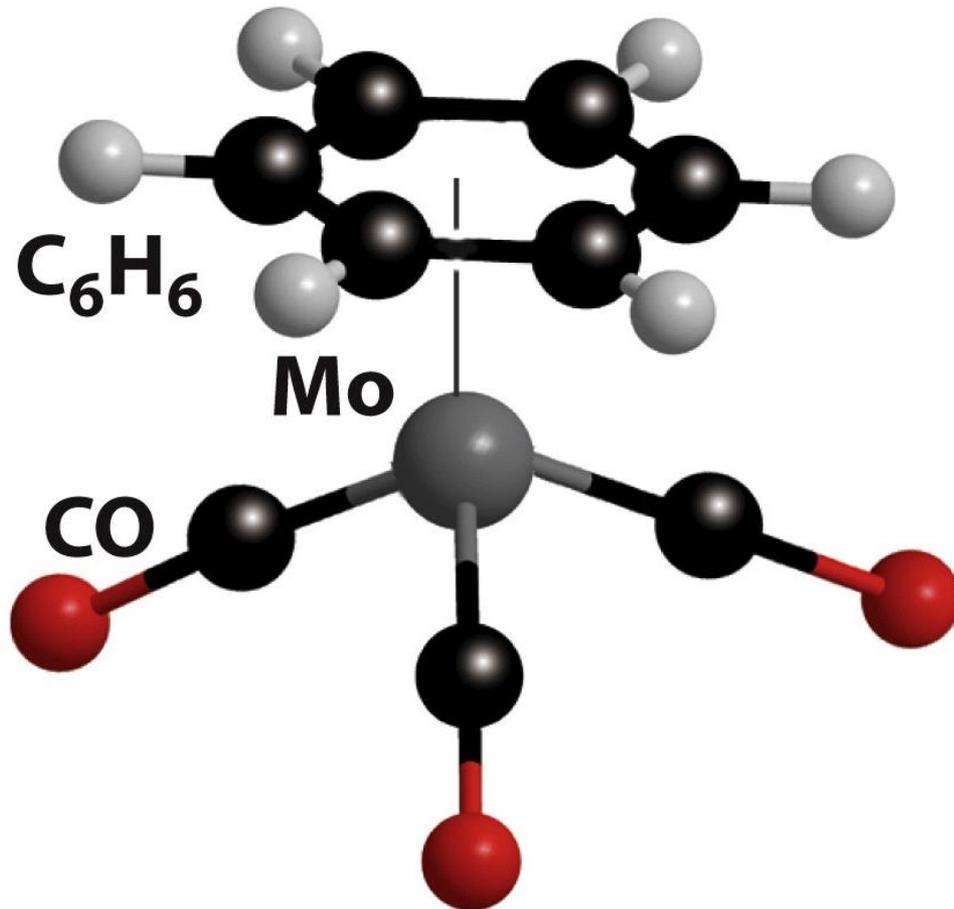
One single word:

- Ligands in alphabetical order – plus possible coefficients (bis, tris, tetrakis,..)
- Followed by the metal name,
- Followed by the metal oxidation state in parenthesis.

## Formula (in [ ] brackets)

- Metal symbol,
- Followed by the ligands in alphabetical order (based on their chemical symbols)

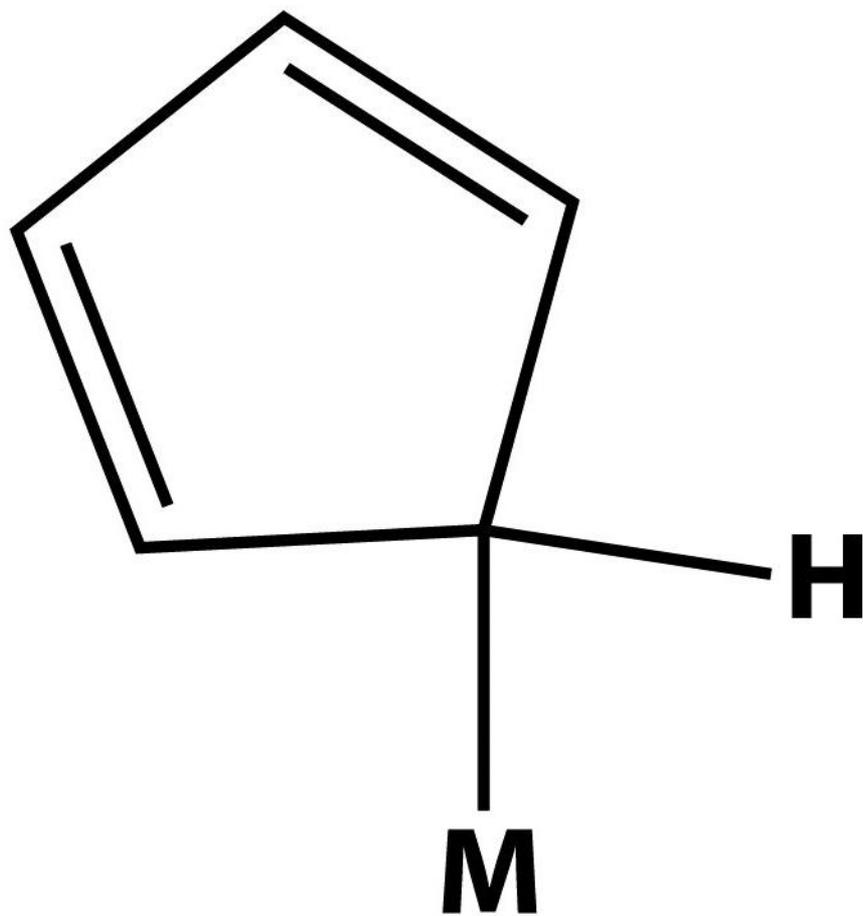
Not always the ligands order is the same  
for the two cases



benzene(tricarbonyl)molybdenum(0)

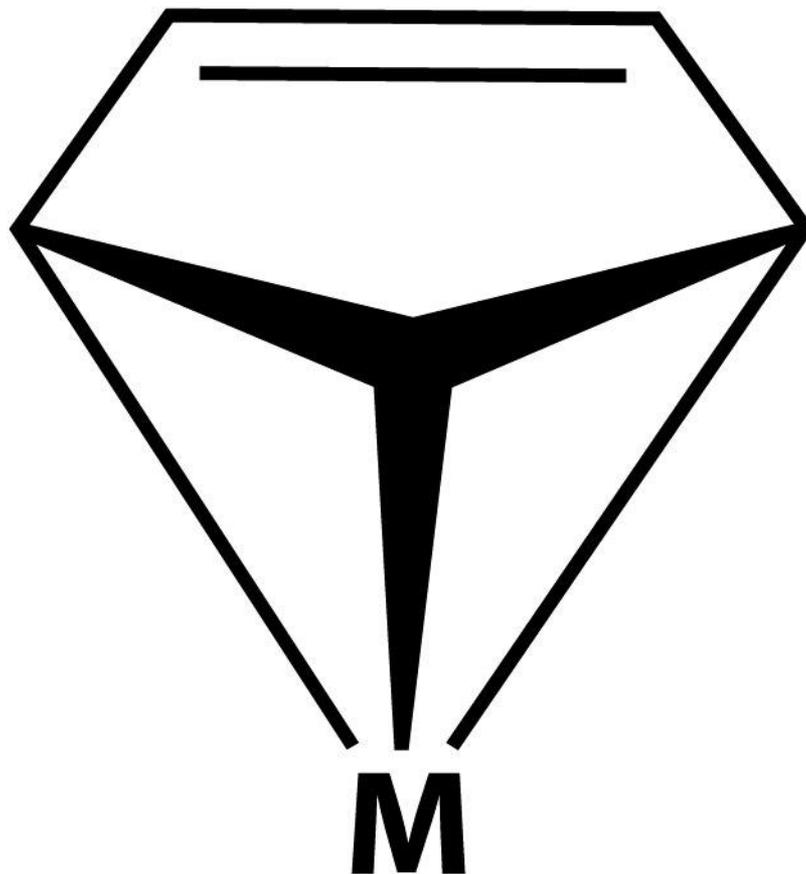
*benzenemolybdenum-tricarbonyl*





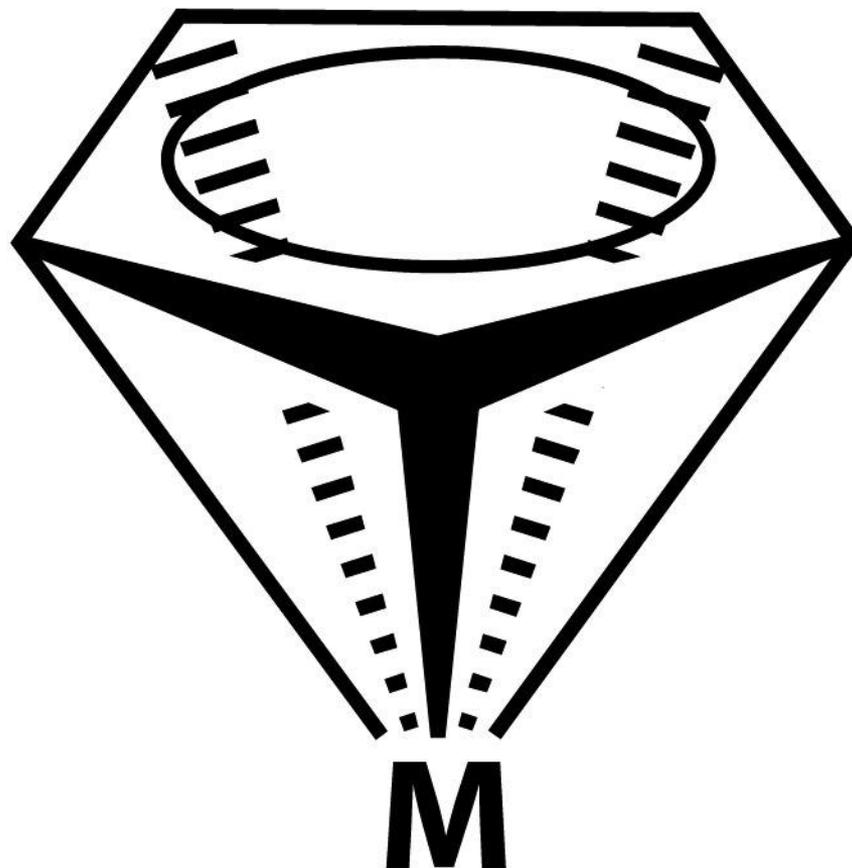
**Apticity** = number of ligand atoms that are formally directly bound to the metal – electron counting changes!

**$\eta^1$ -Cyclopentadienyl**      2 electrons



**$\eta^3$ -Cyclopentadienyl**

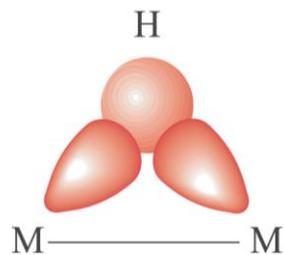
4 electrons



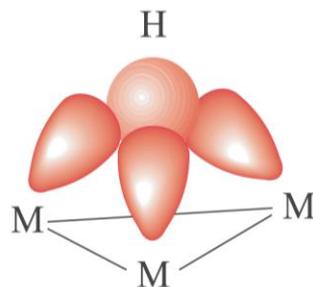
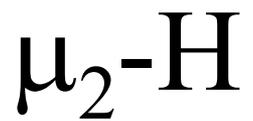
**$\eta^5$ -Cyclopentadienyl**

6 electrons

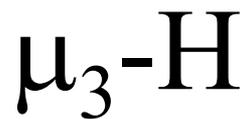
# Bridging Ligands

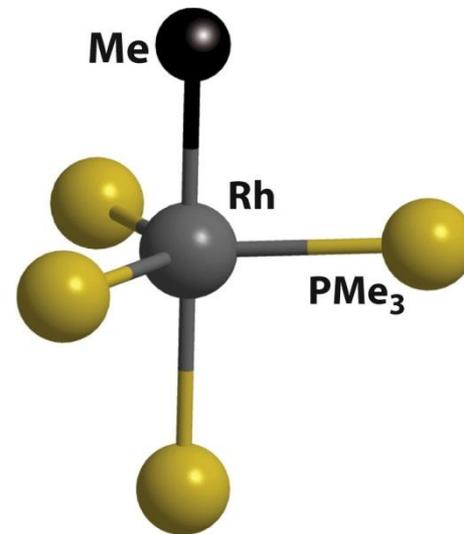


(a)

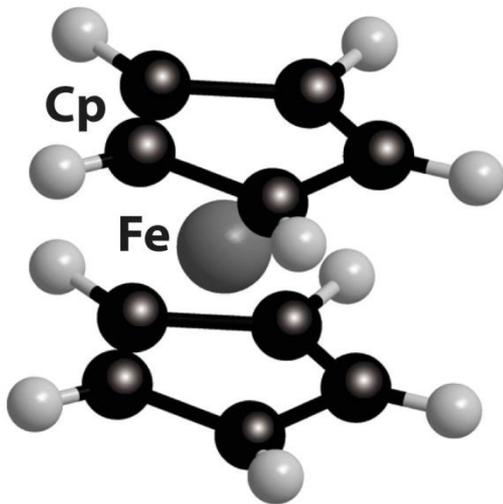


(b)

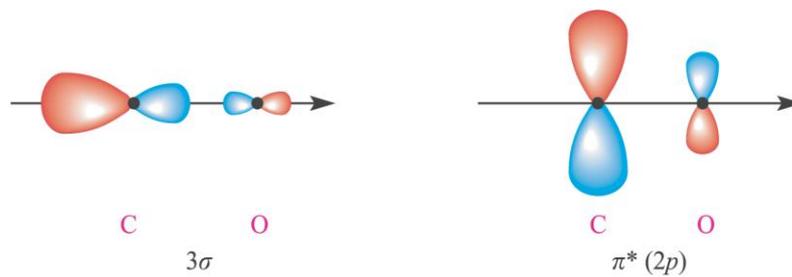
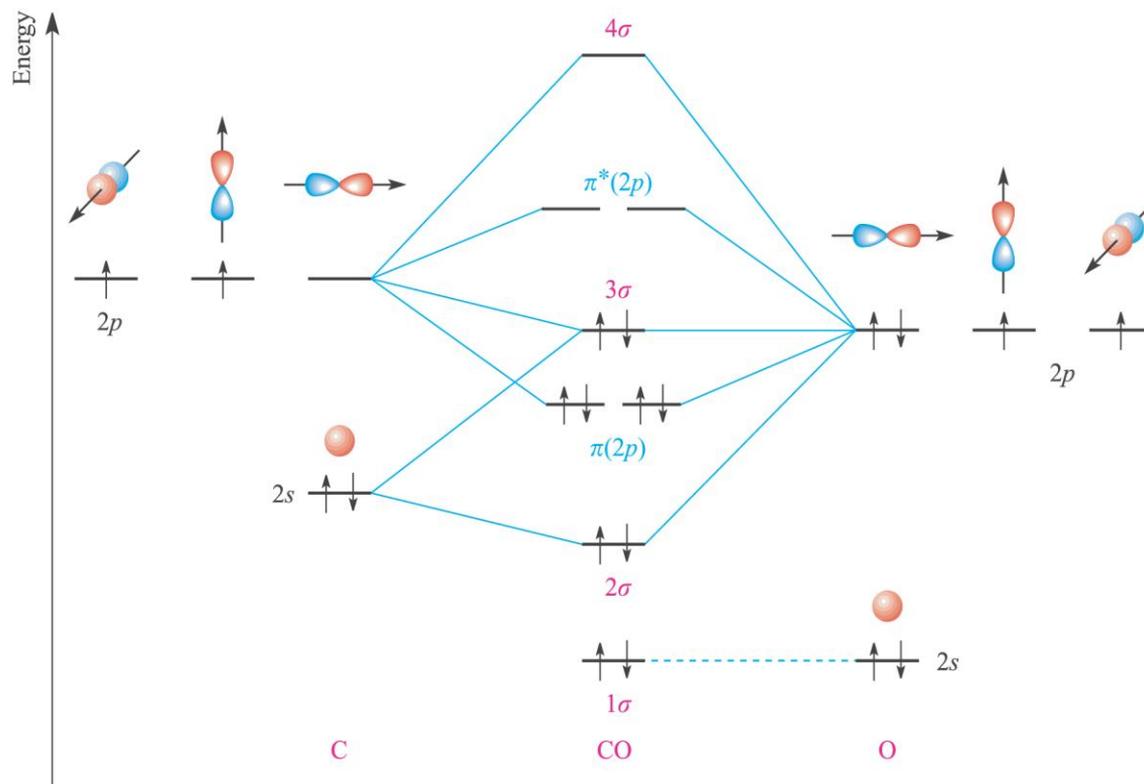




methyltetrakis(trimethylphosphine)rhodium(I)

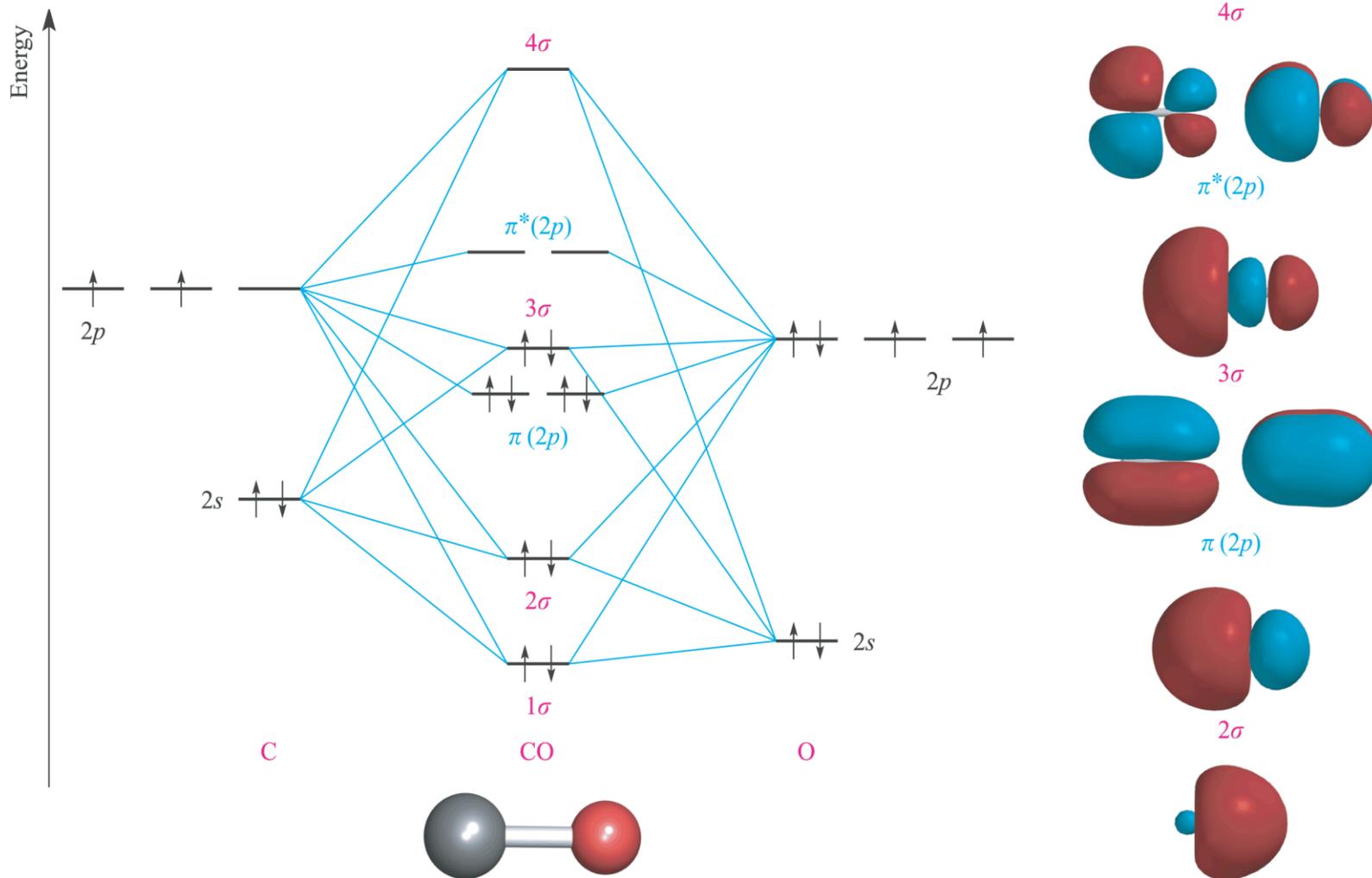


bis(η<sup>5</sup>-cyclopentadienyl)iron(II)

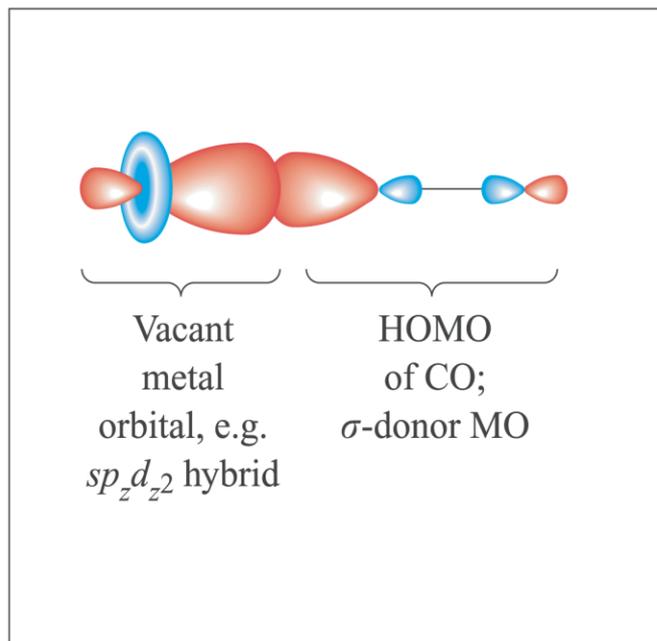
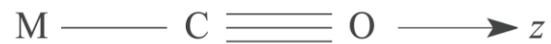


(a)

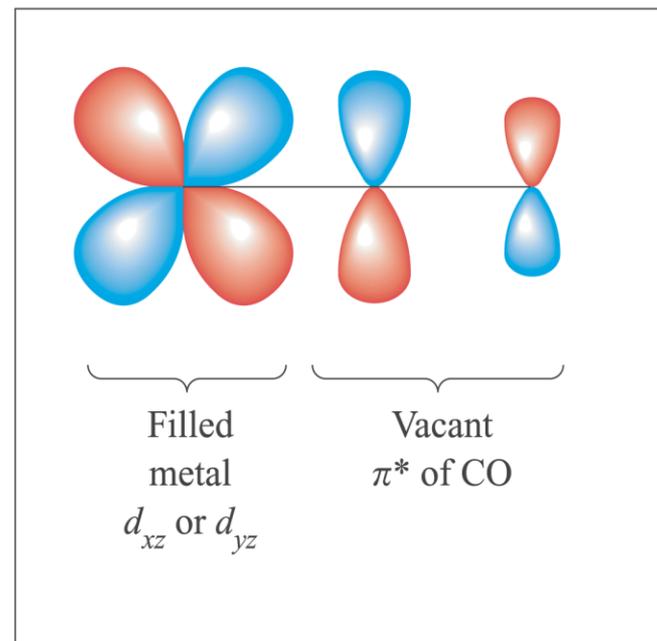
## Simplified MO diagram of CO



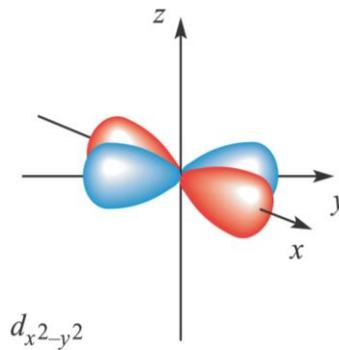
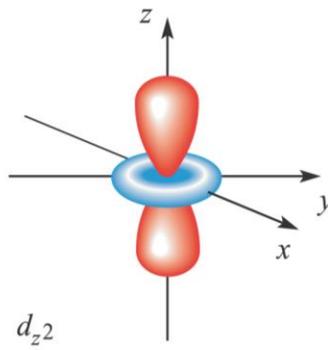
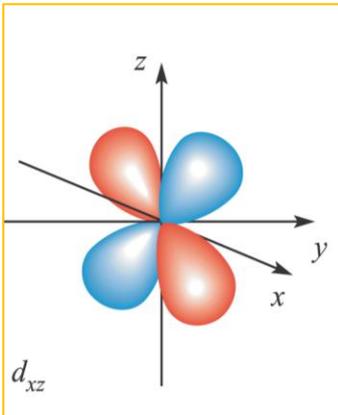
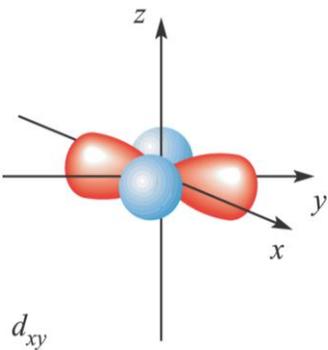
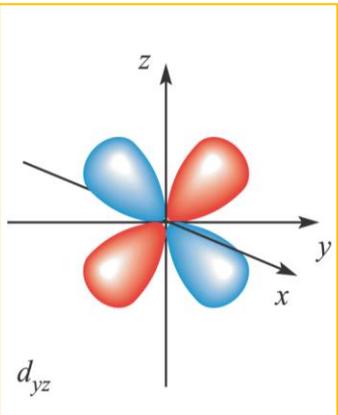
The MO level diagram of CO shows that the HOMO ( $3\sigma$ ) has  $\sigma$  symmetry, this orbital is positioned mainly on the C, as a sprouting lobe; on the other hand the LUMO has a  $\pi$  symmetry.

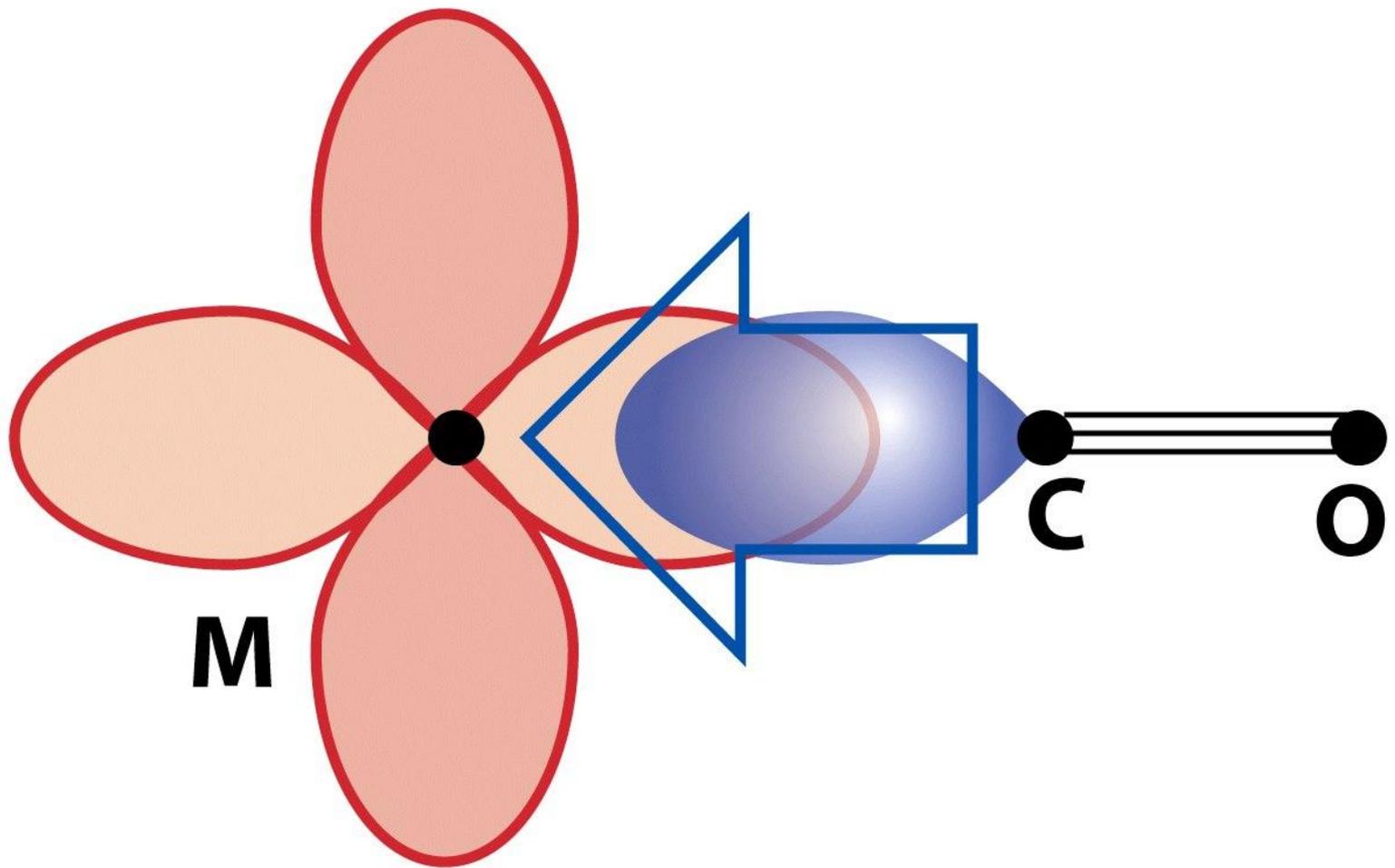


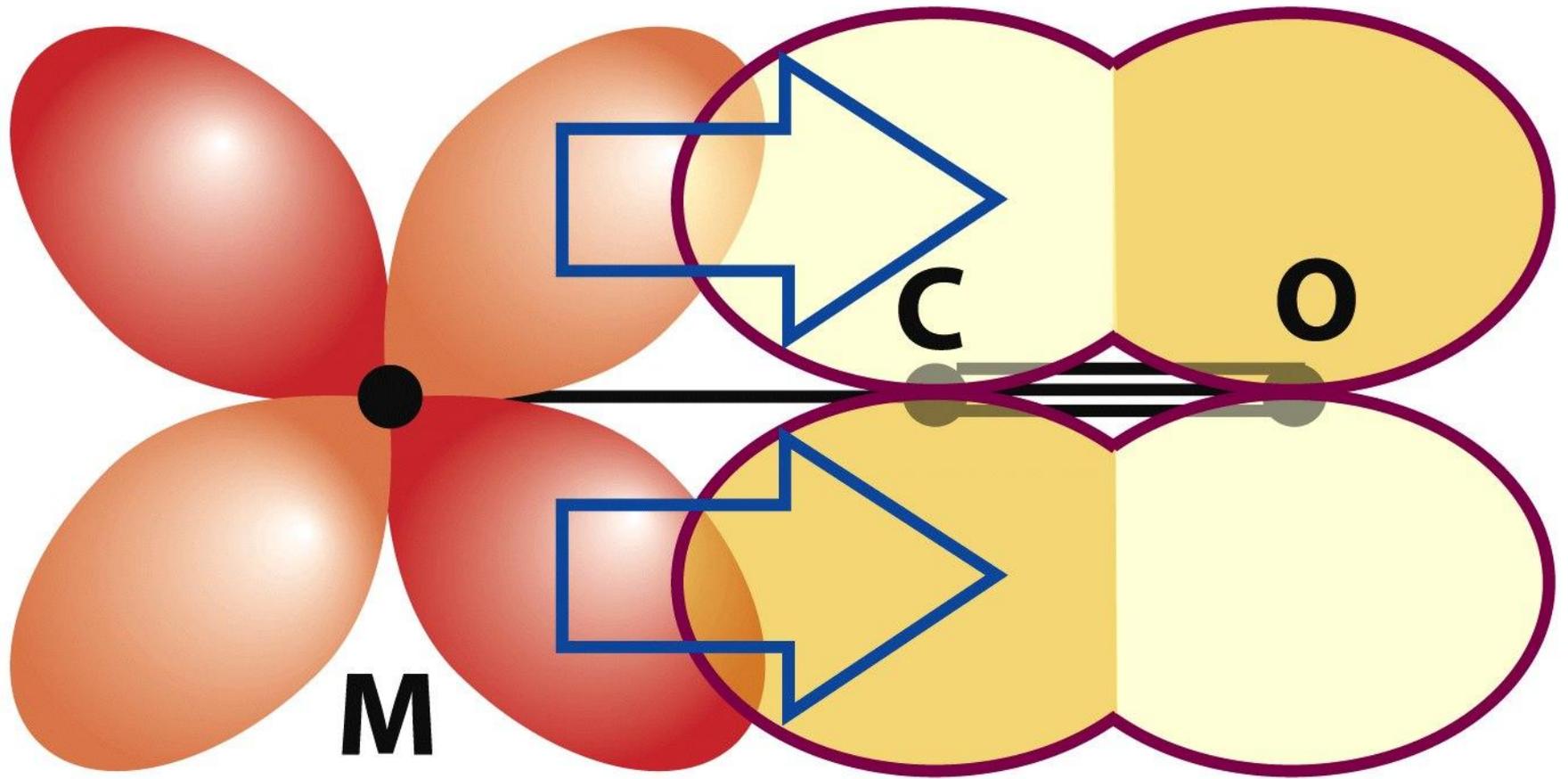
CO-to-M donation  
(a)

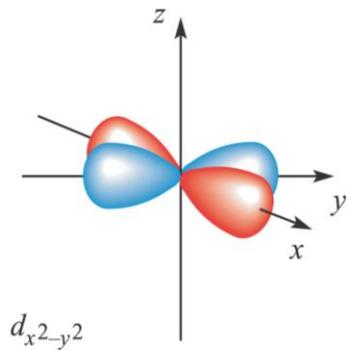
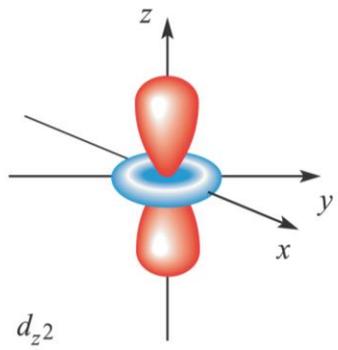
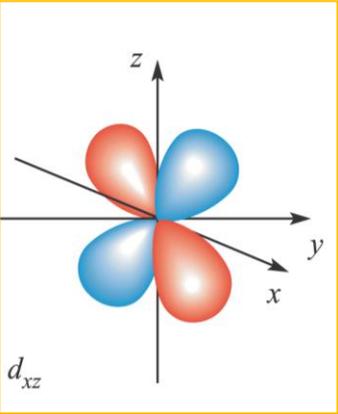
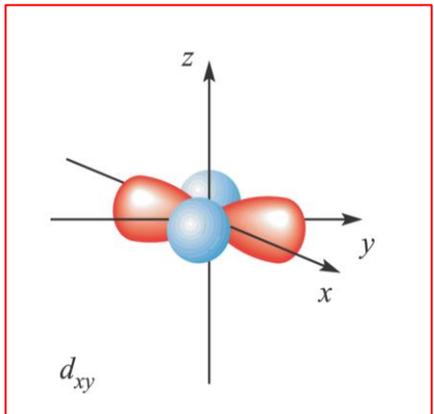
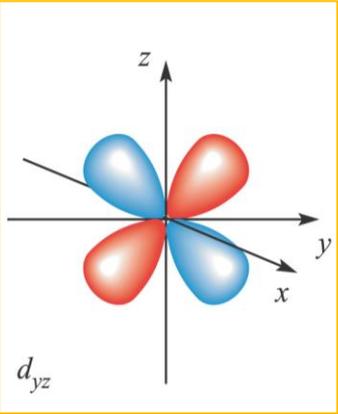


M-to-CO back-donation  
(b)



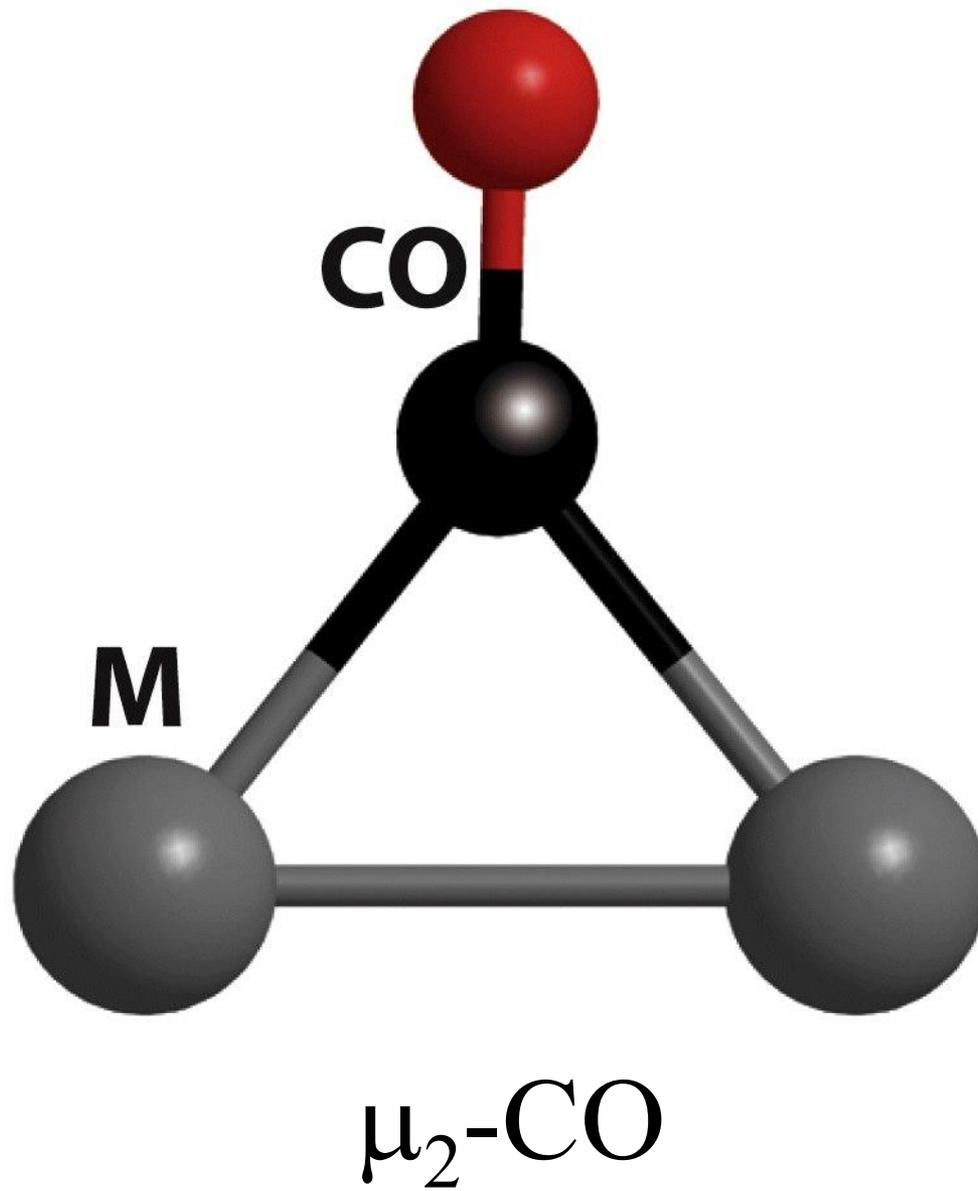


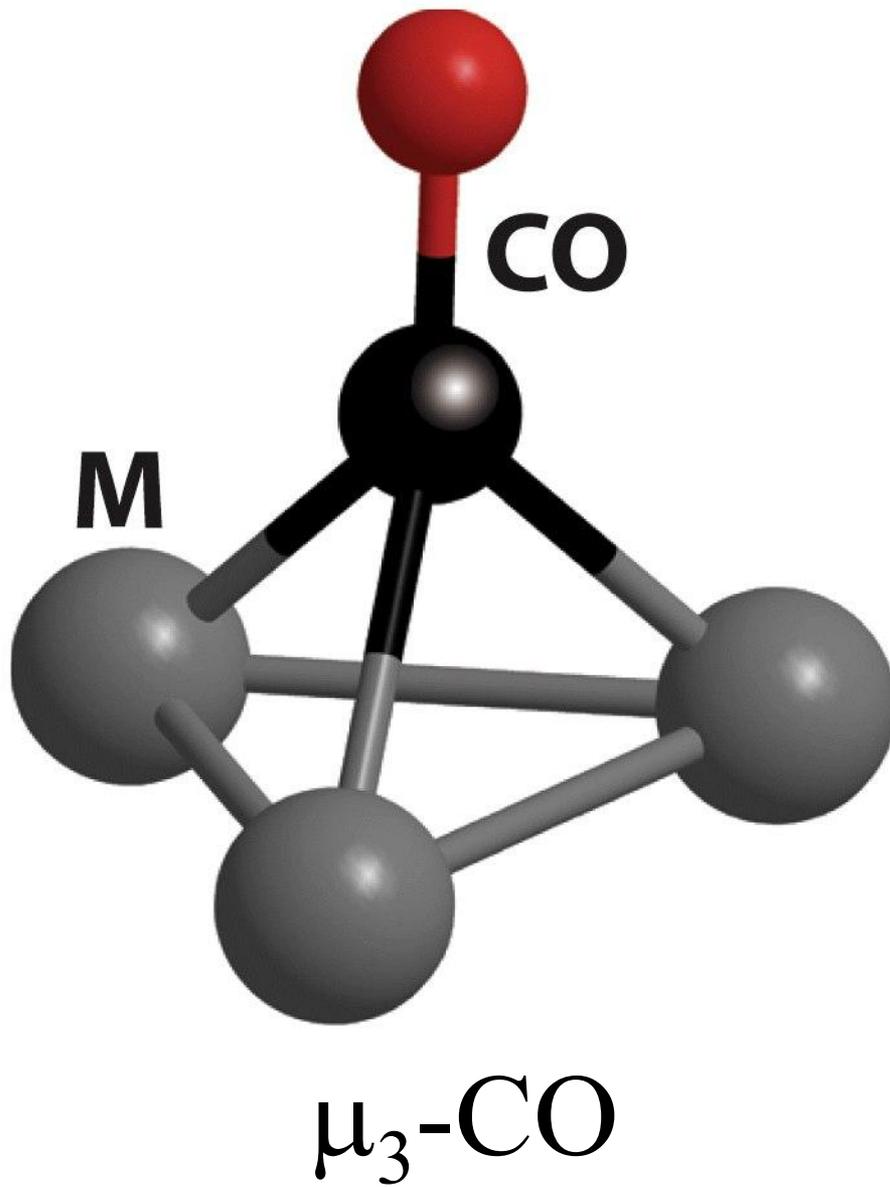


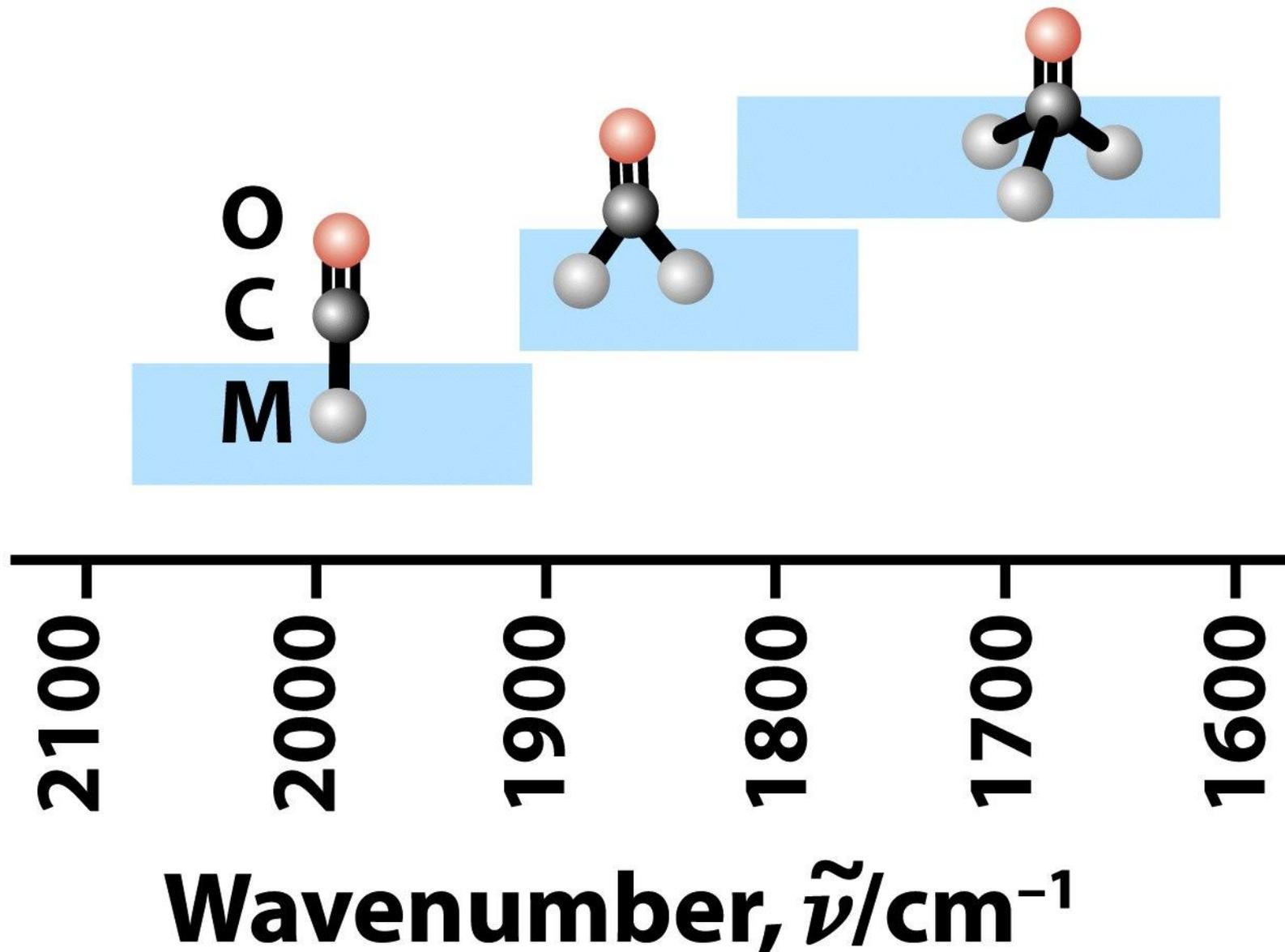


**Table 21.3** The influence of coordination and charge on CO stretching wavenumbers

Compound	$\tilde{\nu}/\text{cm}^{-1}$
CO	2143
$[\text{Mn}(\text{CO})_6]^+$	2090
$\text{Cr}(\text{CO})_6$	2000
$[\text{V}(\text{CO})_6]^-$	1860
$[\text{Ti}(\text{CO})_6]^{2-}$	1750







Reference CO vibrational bands ranges for neutral metal-carbonyls.

