HOMOGENEOUS CATALYSIS: INDUSTRIAL APPLICATIONS AND PHOTOCATALYSIS

***LM Chimica @UniTS* – 6CFU**

ORGANOMETALLIC CHEMISTRY (2 CFU) *Prof.ssa Elisabetta Iengo*

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

Ligand classification/Bonding modes

Metal-Carbenes/Metal-carbonyls/Metallocenes

Reactivity/Fluxional Processes

HOMOGENEOUS CATALYSIS AND PHOTOCATALYSIS (4 CFU) *Prof.ssa Barbara Milani*

Basic Principles of Homogeneous Catalysis

Study of selected industrial processes based on Homogeneous Catalysis

Introduction to Homogeneous Photocatalysis

Visit to the Industrial Plant LyondellBaseli (Ferrara)

Final Exam: Oral examination on both modules.

ADVISED TEXTBOOKS

❖Homogeneous Catalysis: understanding the art
Autore: Piet W.N.M. van Leeuwen
Kluwer Academy Publisher
Springer: www.springer.com/chemistry

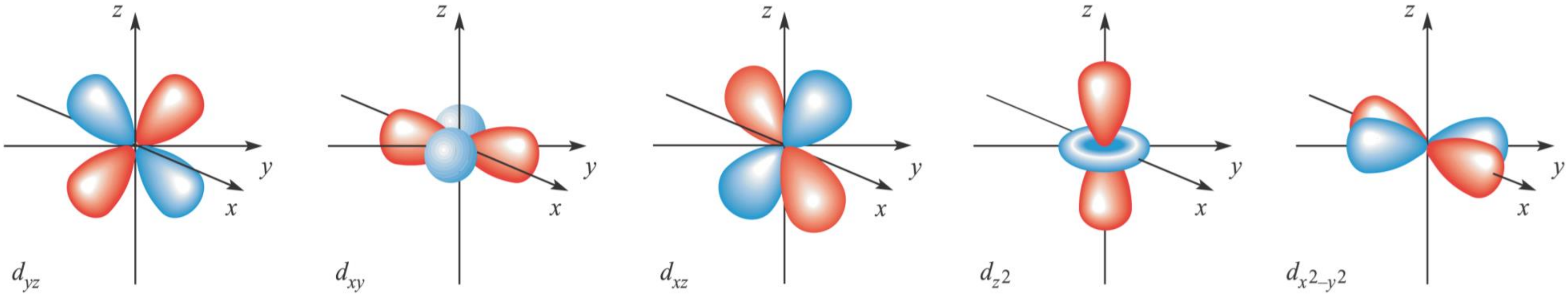
❖ Inorganic Chemistry - Fifth Edition
Catherine E. Housecroft and Alan G. Sharpe
Pearson Prentice Hall

❖ 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

d-block Organometallic Compounds



Coordination Compounds (Werner's type complexes)

- Typically simple ligands, σ-donor and π-donor
- Usually charged
- Variable number of *d*-electrons
- Typically soluble in water

Organometallic Compounds (at least one M–C bond)

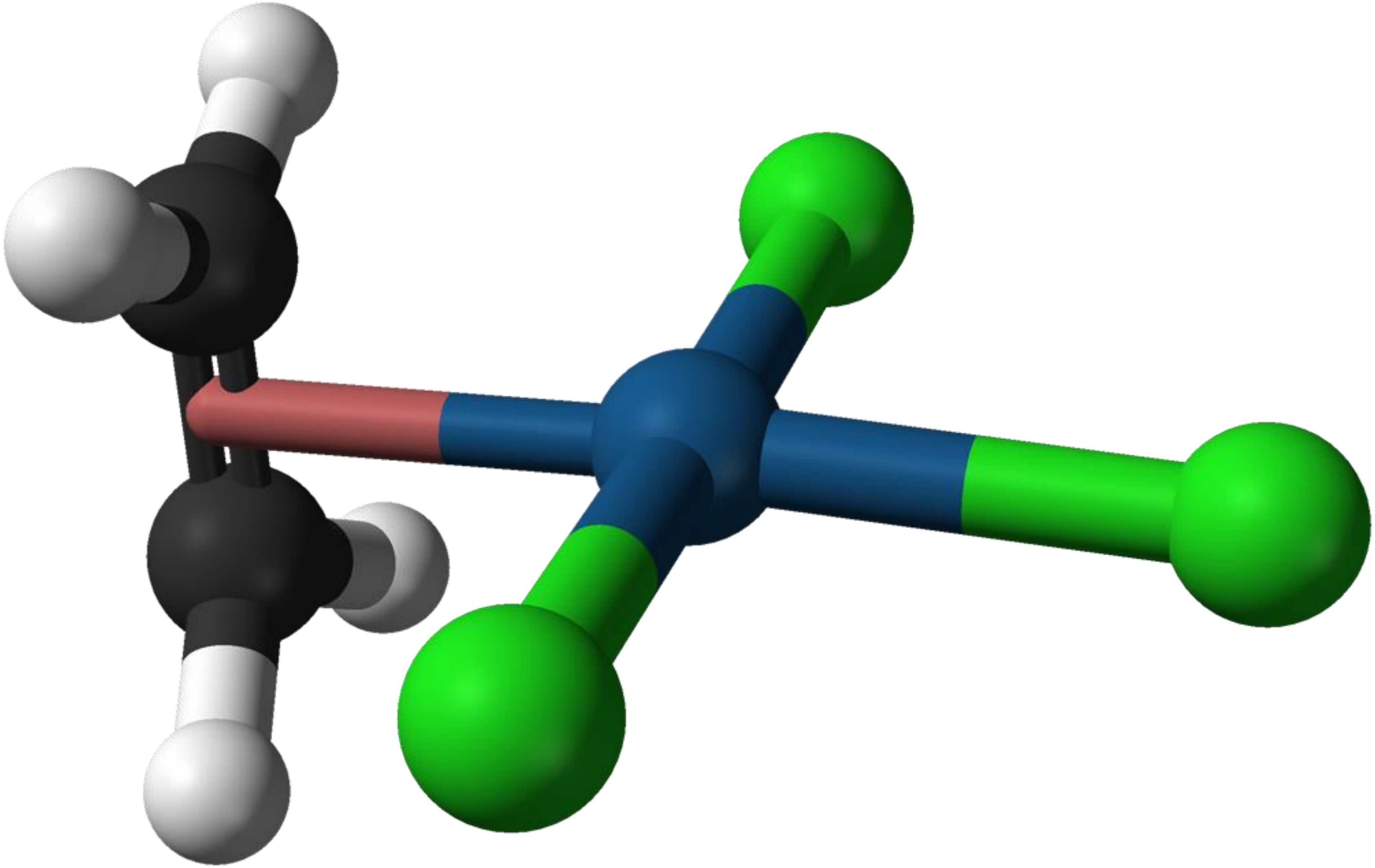
- Often neutral
- Fixed number of*d*-electrons (16 or 18 are the stable eletron configurations)
- Soluble in organic solvents (*e.g.* THF)
- Properties more similar to organic compounds than to inorganic salts (*e.g.* low melting points; some are even liquid at r.T.)

W C Zeise, Danish pharmacist, **I789- I847**

'The breakthrough, the isolation of a pure, crystalline compound came when Zeise added potassium chloride to a concentrated $PtCl_4$ /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°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

$$K_2PtCl_4 + C_2H_5OH \longrightarrow K[(C_2H_4)PtCl_3].\ H_2O + KCl$$



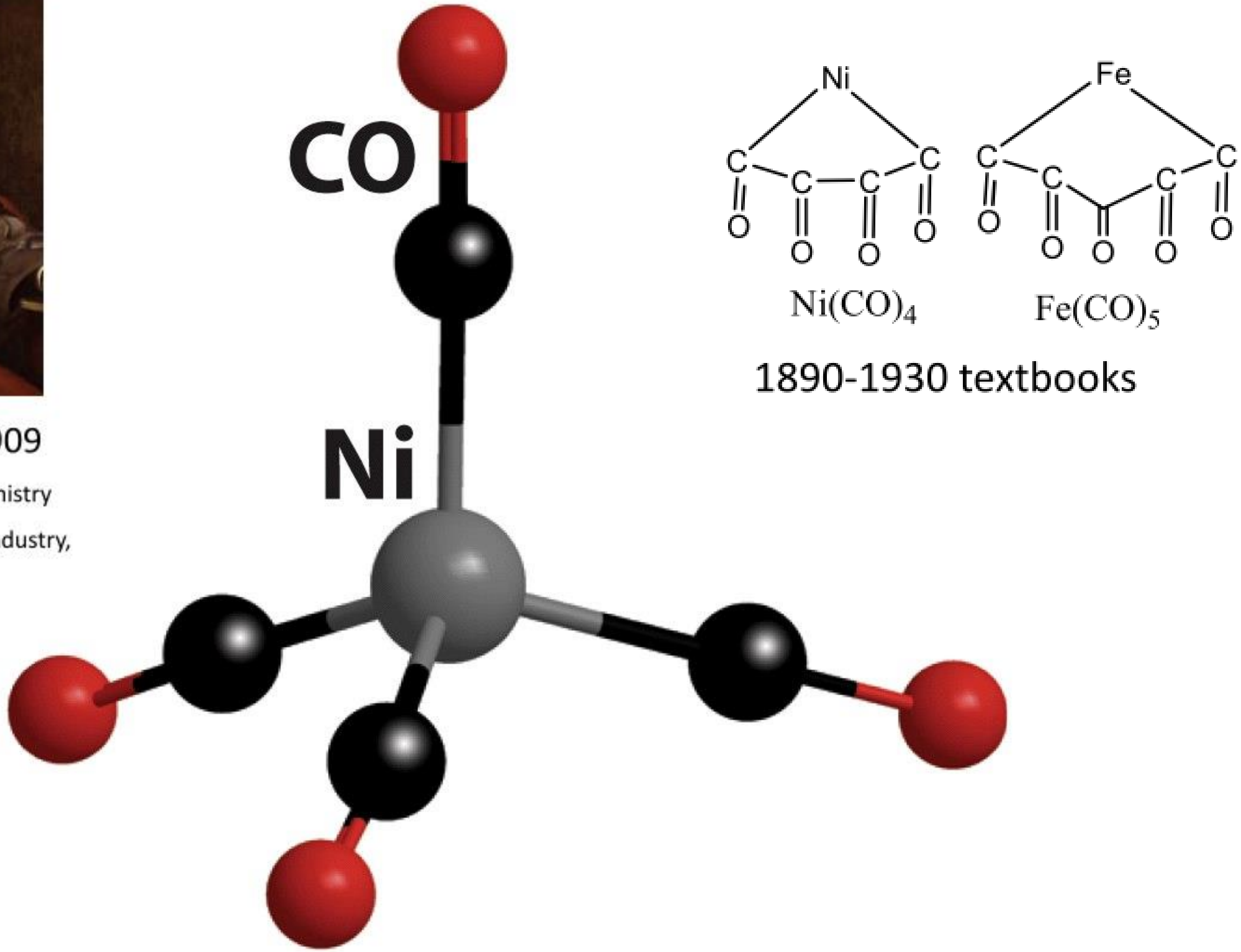
$[Pt(C_2H_4)Cl_3]^-$

Zeise Salt, 1827

Ludwig Mond 1839-1909

Father of Metal Carbonyl Chemistry

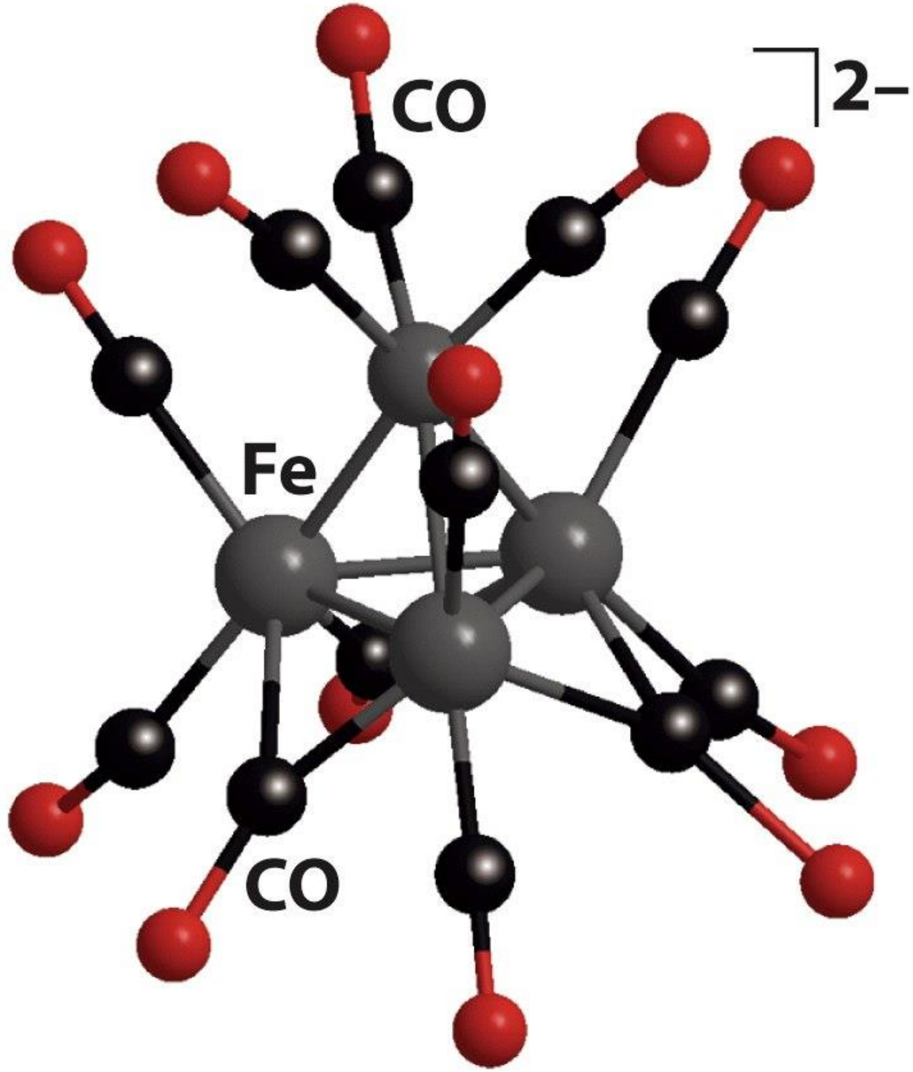
Founder of Imperial Chemical Industry, England



1890-1930 textbooks

$Ni(CO)_4$

Mond, Langer, Quinke, 1890



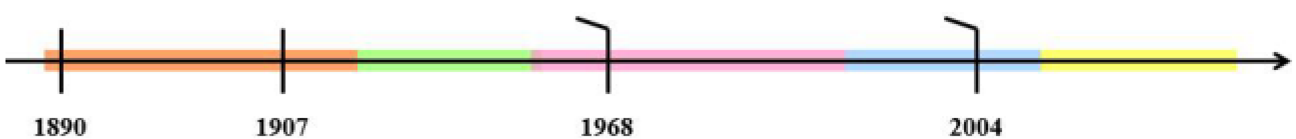
$[Fe_4(CO)_{13}]^{2-}$

Hieber, 1930-….

Walter Otto Hieber (1895-1876)
Technische Hochschule München

1868	$Pt(CO)_2Cl_2$	M.P. Schützenberger
1890	$Ni(CO)_4$	L. Mond et al.
1891	$Fe(CO)_5$	L. Mond, F. Quinke, M. Berthelot
1905	$Fe_2(CO)_9$	J. Dewar, H.O. Jones
1907	$[Fe_3(CO)_{12}]^*$	
1910	$Co_2(CO)_8$	L. Mond et al.
	$Co_4(CO)_{12}$	
1910	$Mo(CO)_6$	
1927/28	$Cr(CO)_6$	A. Job et al.
	$W(CO)_6$	

"... 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!"



Chemical Analysis Ir, Raman, NMR X-ray diffraction

Walter Otto Hieber (1895-1876)
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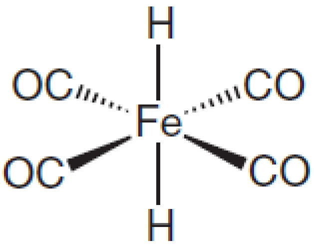
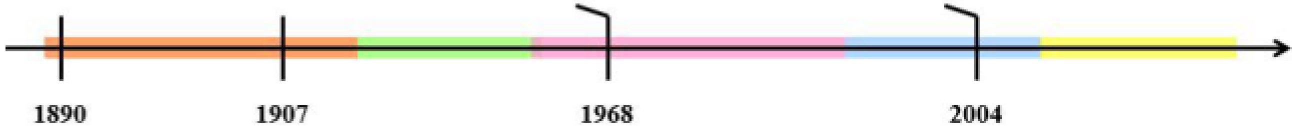
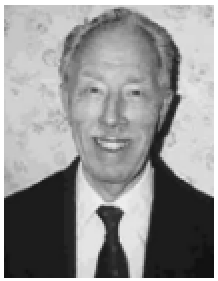


First metal-hydride complex
Hieber, 1931

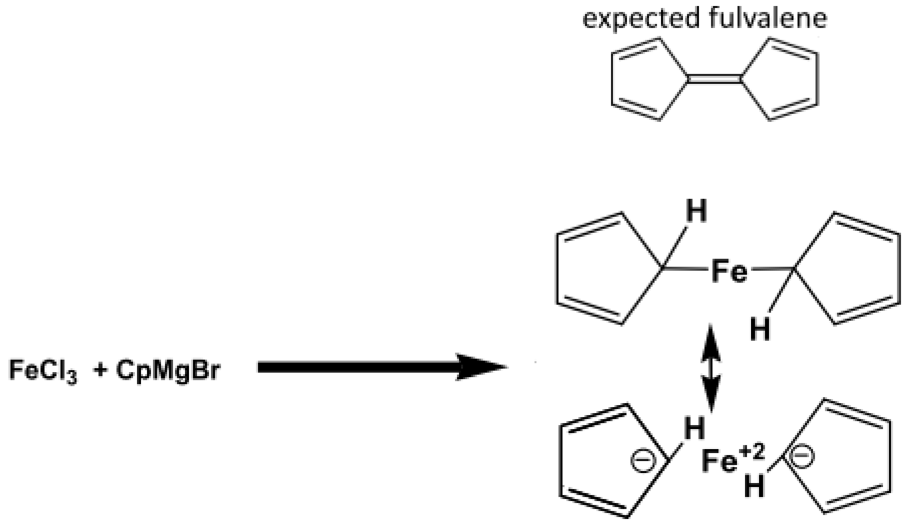


Chemical Analysis Ir, Raman, NMR X-ray diffraction

Pauson



Kealy

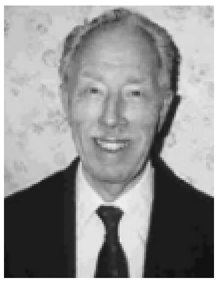


A New Type of Organo-Iron Compound

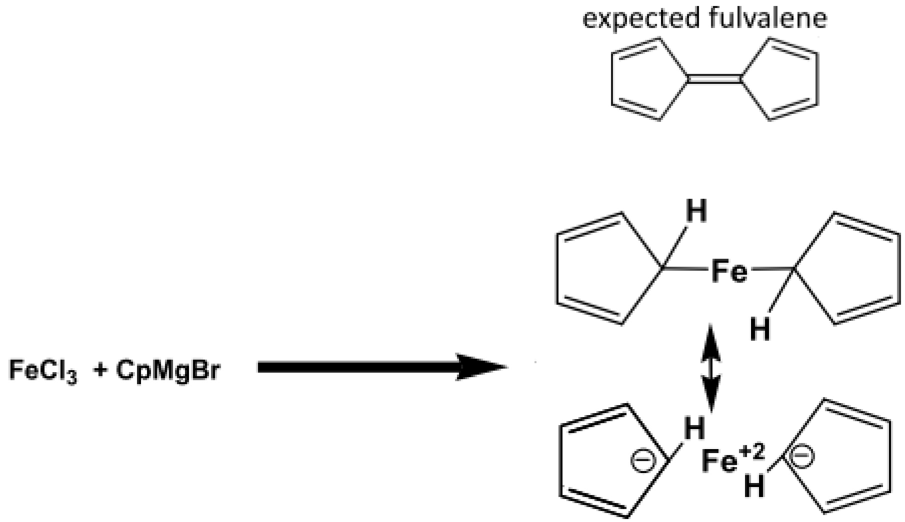
letters to nature

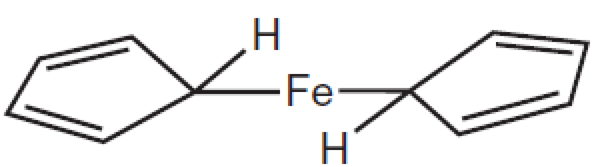
Nature **168**, 1039 - 1040 (15 December 1951); doi:10.1038/1681039b0

Pauson

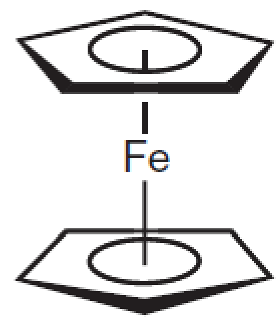


Kealy

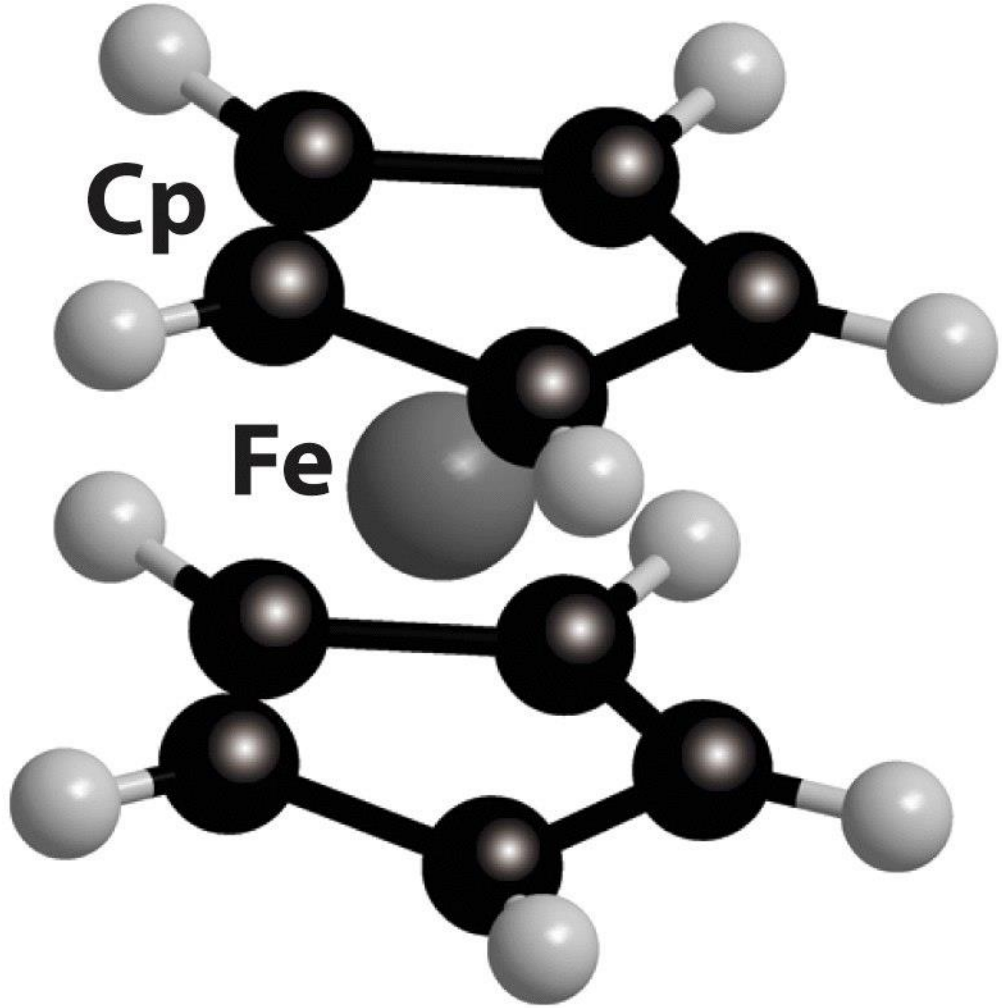




$FeCp_2$: erroneous σ structure
Pauson, 1951

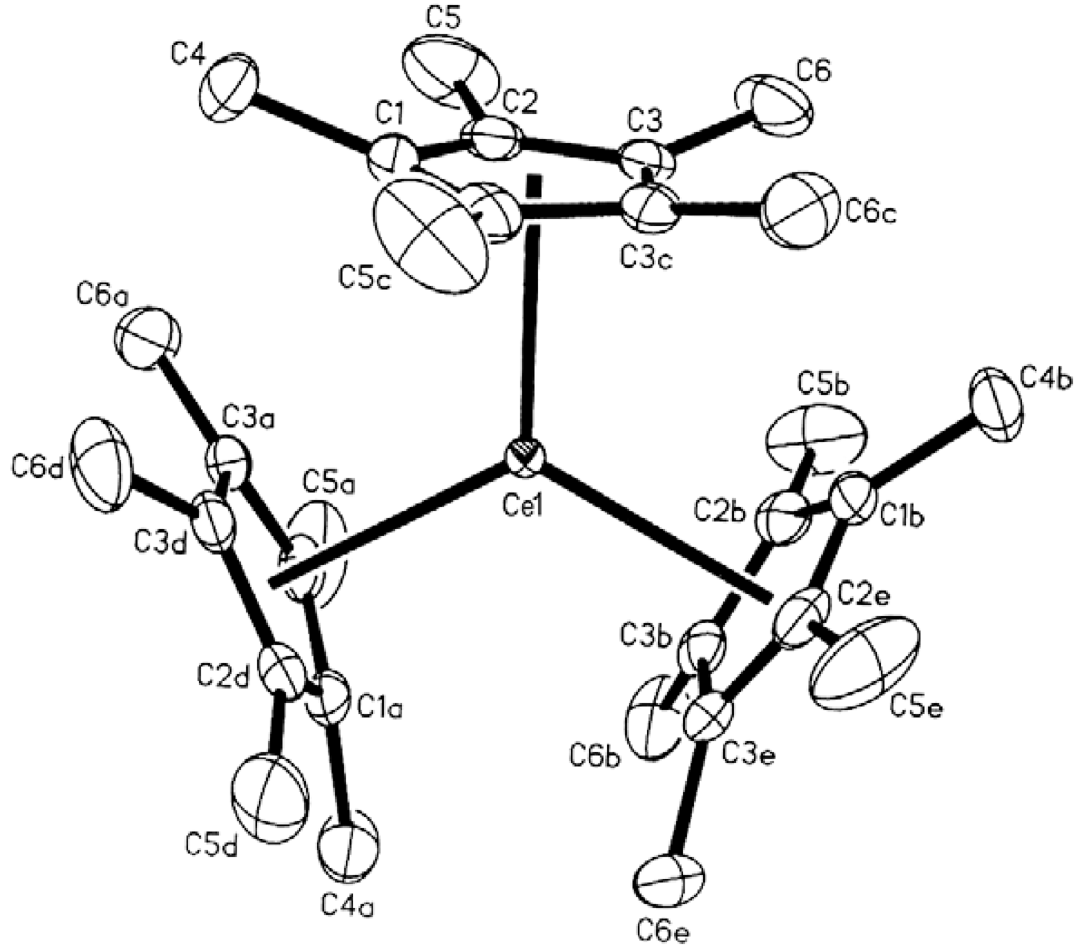


π-sandwich structure of ferrocene
Wilkinson and Fischer, 1952



$FeCp_2$ $Cp = C_5H_5^-$

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



1970 - … Ln-Cp* compounds

Cp* = $C_5Me_5^-$

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_3	2
Hydride	H^-	2
Dihydrogen	H_2	2
η^1-Alkyl, -alkenyl, -alkynyl, and -aryl groups	R^-	2
η^2-Alkene	$CH_2{=}CH_2$	2
η^2-Alkyne	$RCCR$	2
Dinitrogen	N_2	2
Butadiene	$CH_2{=}CH{-}CH{=}CH_2$	4
Benzene	C_6H_6	6
η^3-Allyl	$CH_2CHCH_2^-$	4
η^5-Cyclopentadienyl	$C_5H_5^-$	6

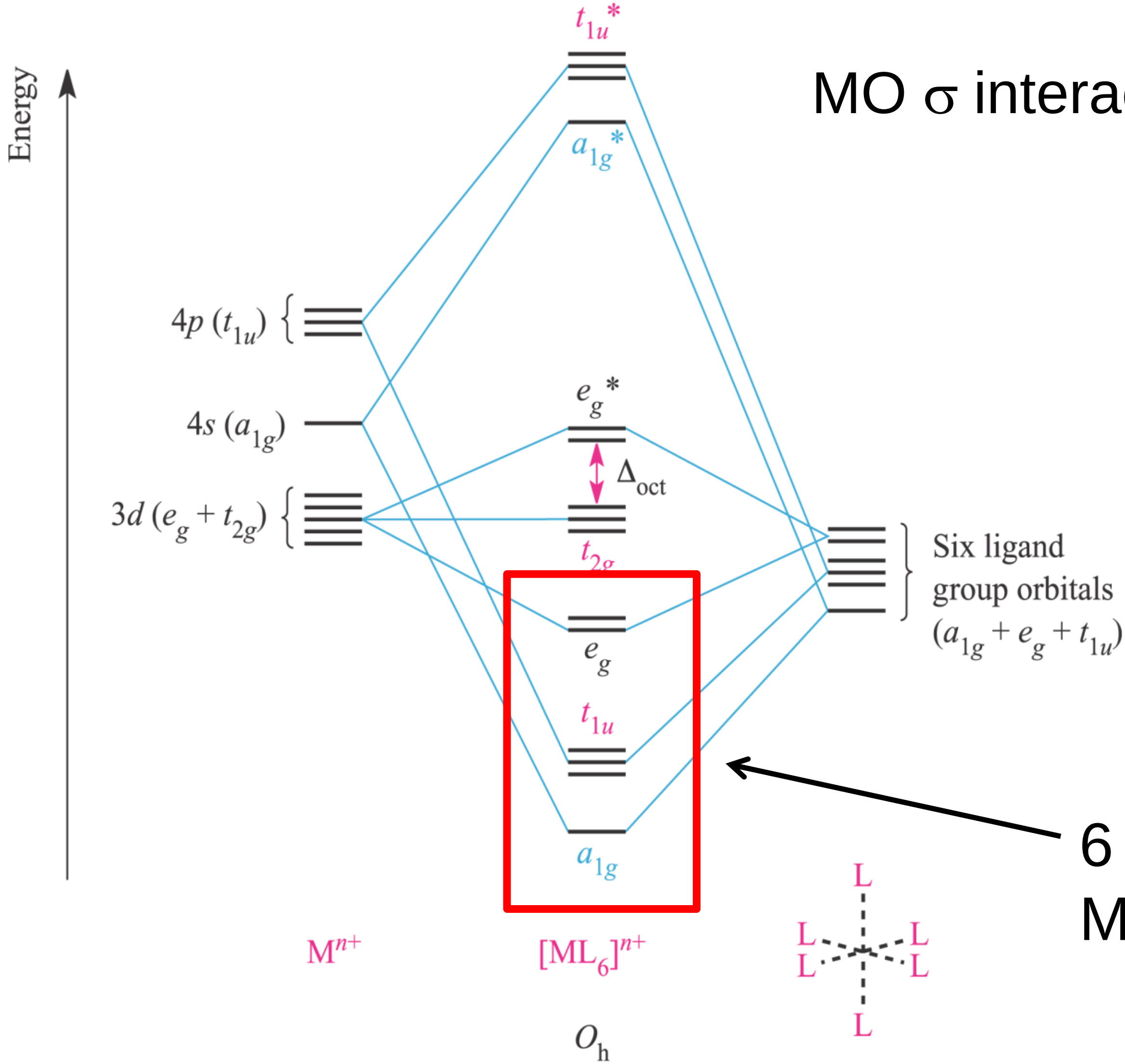
* We use this method throughout this book.

Electron Counting

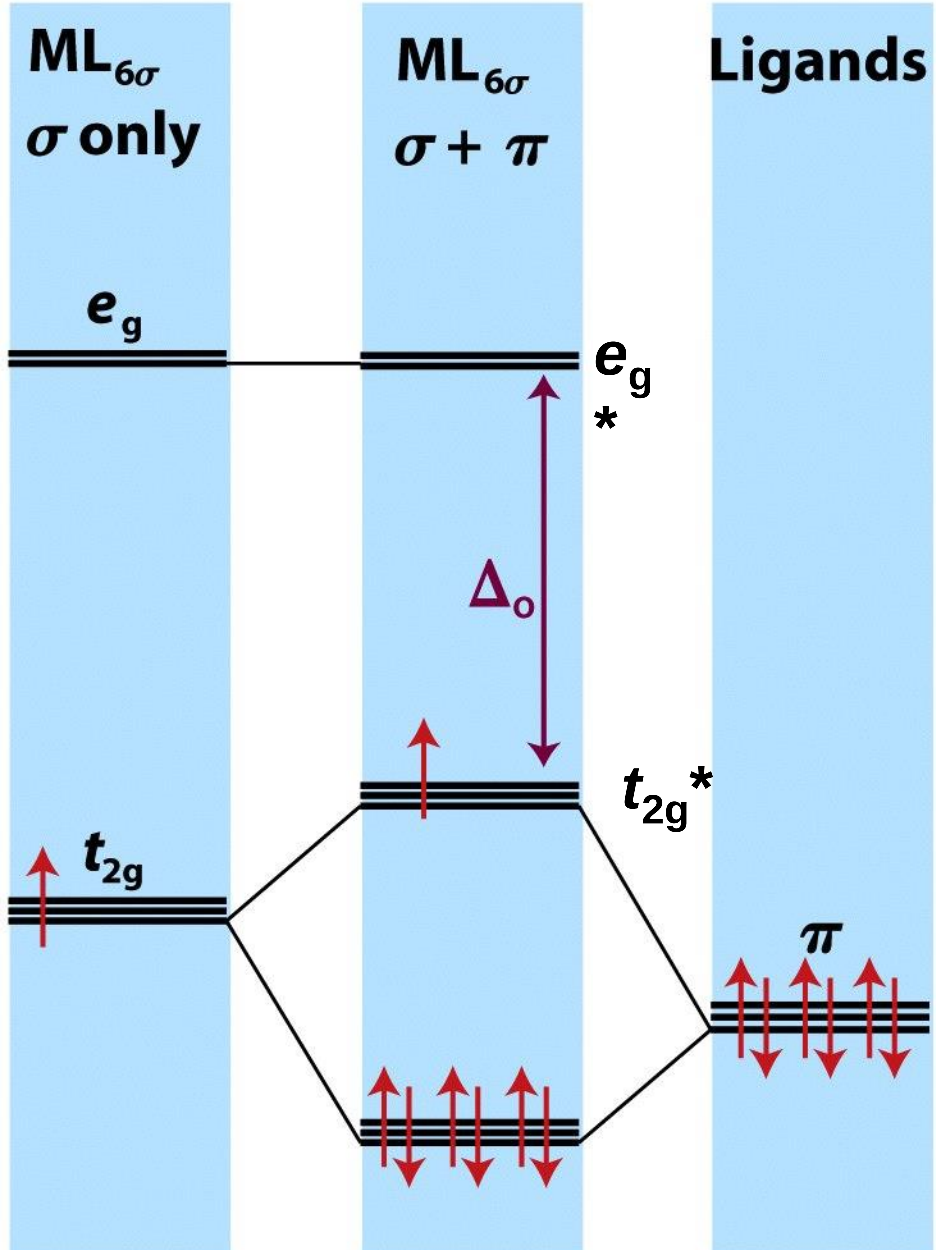
- The *oxidation state* of the metal atom is given by the difference between the compound total charge and the sum of the ligand charges.
- The *number of electrons* of the metal atom is identified by the difference of the metal Group number and the metal oxidation state.
- The *total number of electrons*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

(a) $[IrBr_2(CH_3)(CO)(PPh_3)_2]$
(b) $[Cr(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]$
(c) $[Pt(CH_2{=}CH_2)Cl_3]^-$
(d) $[Mn(CO)_5]^-$

MO σ interactions only

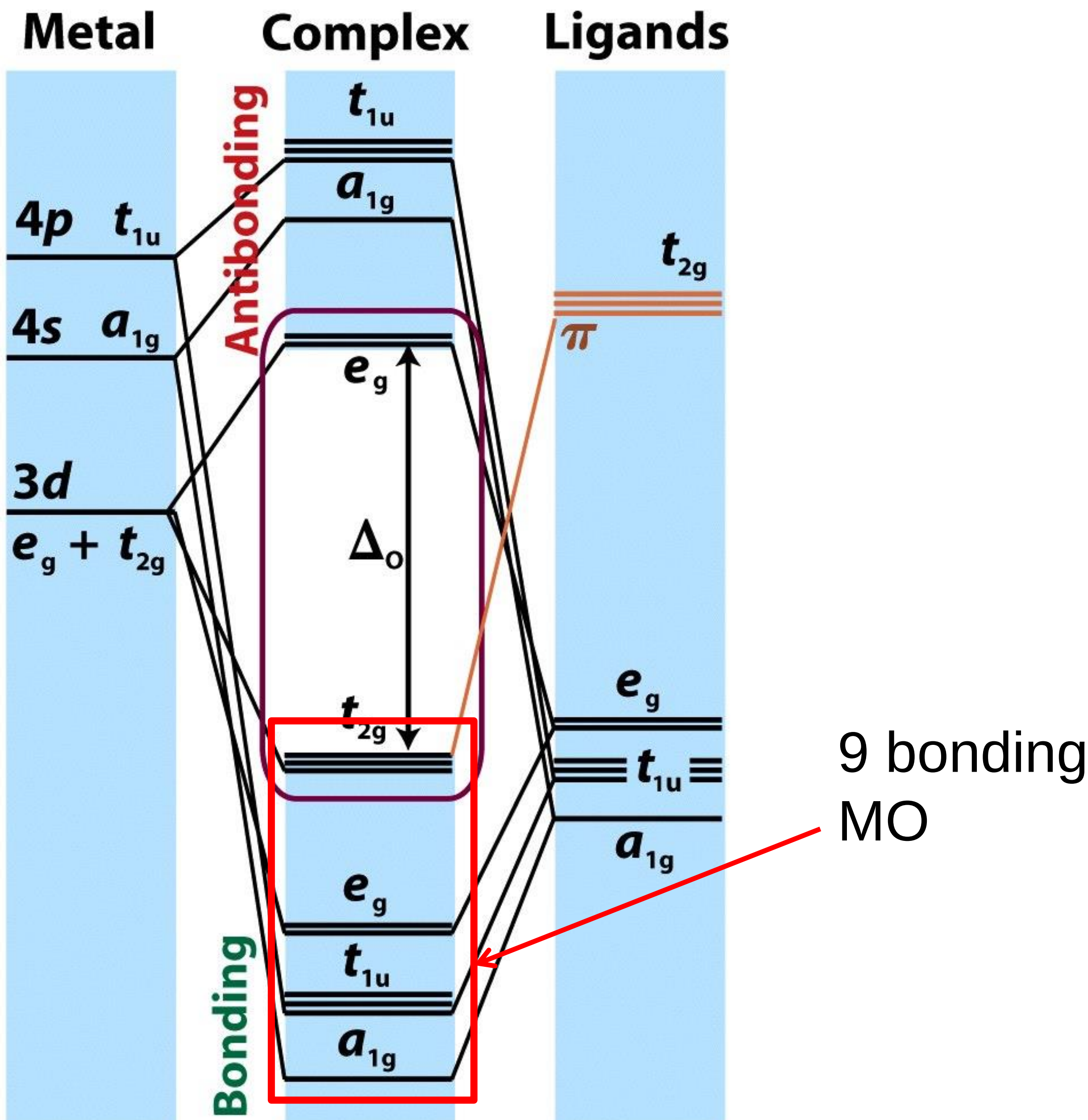


6 bonding MO

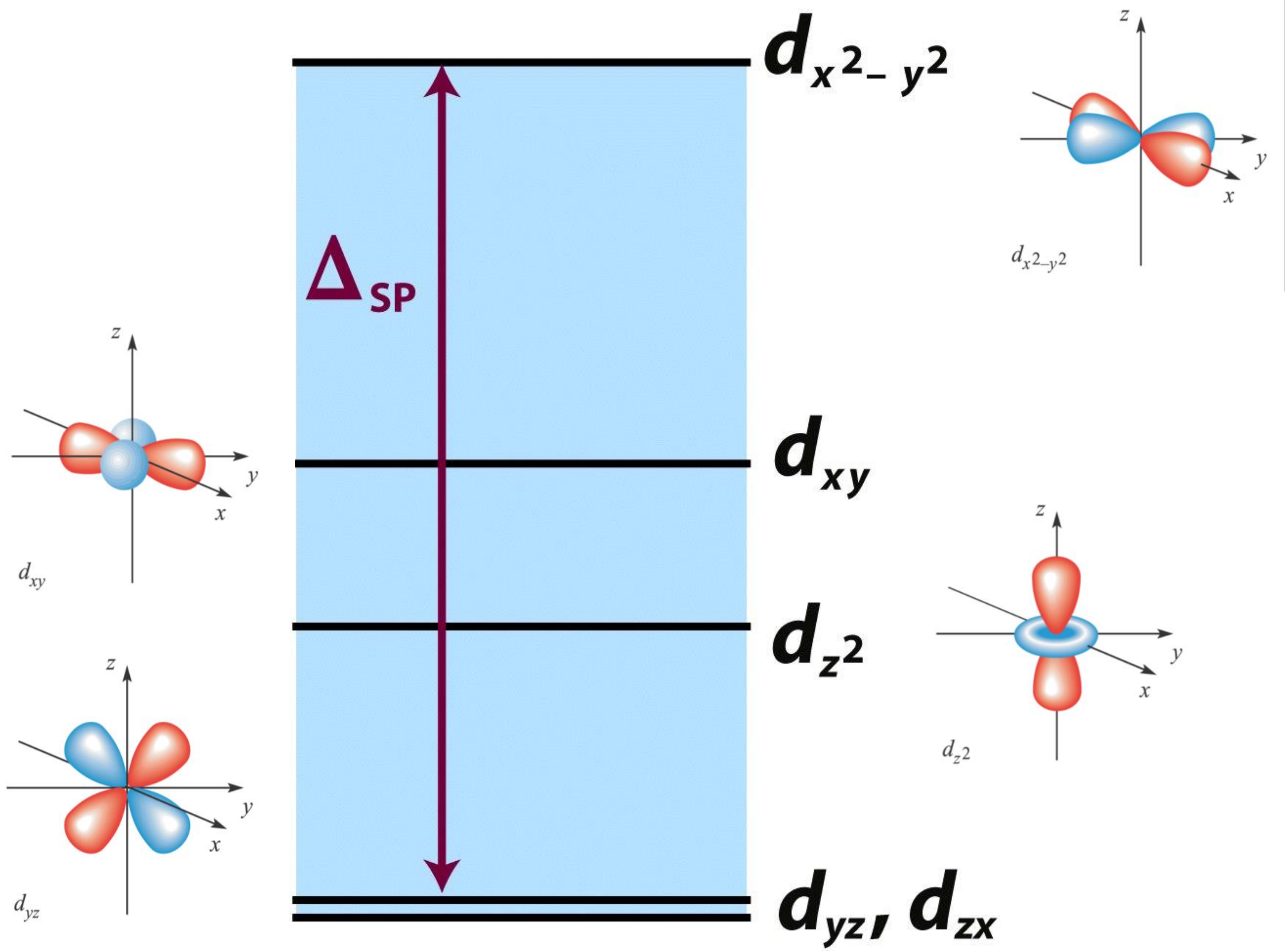


π-donors

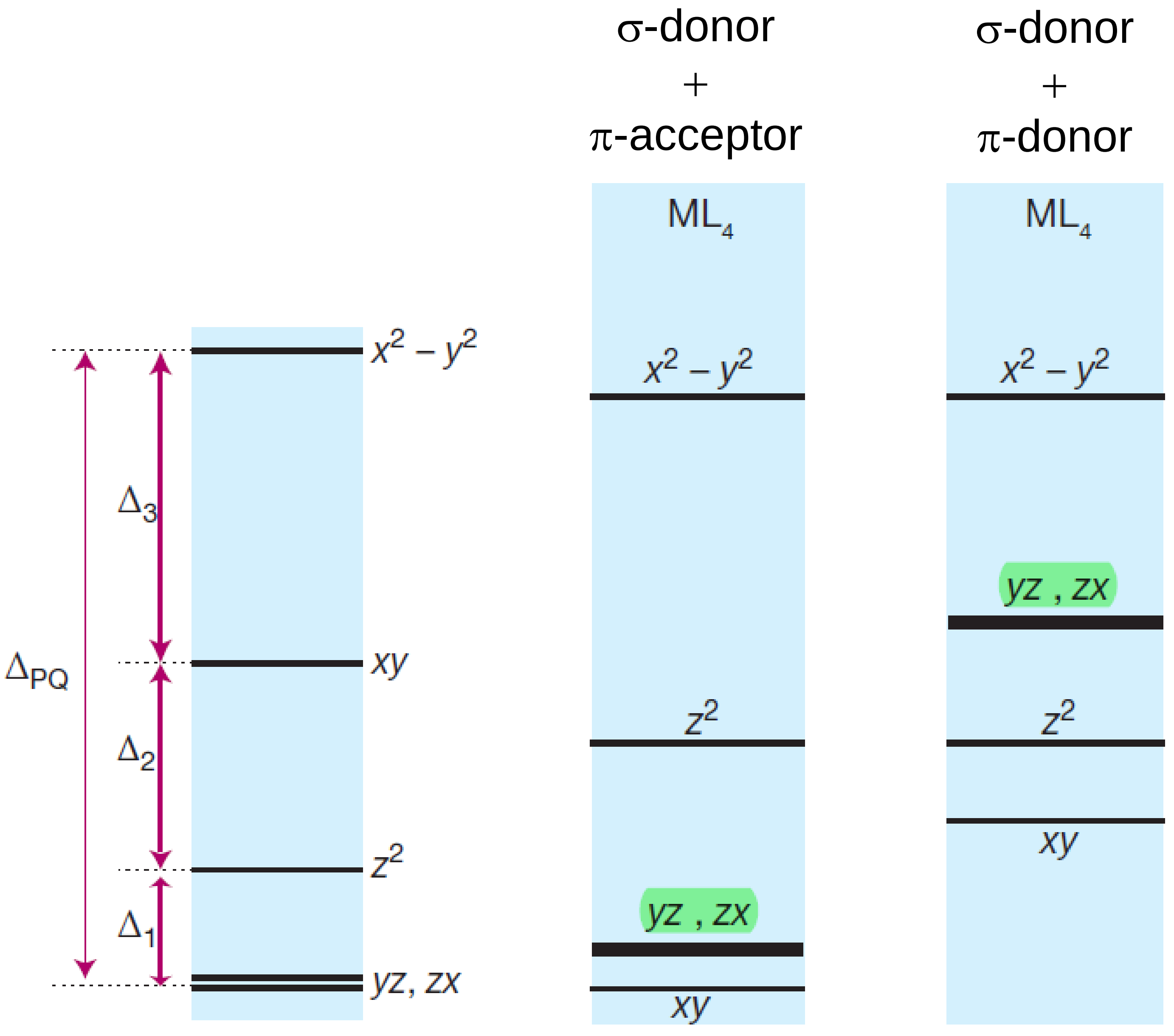
LGO t_{2g}



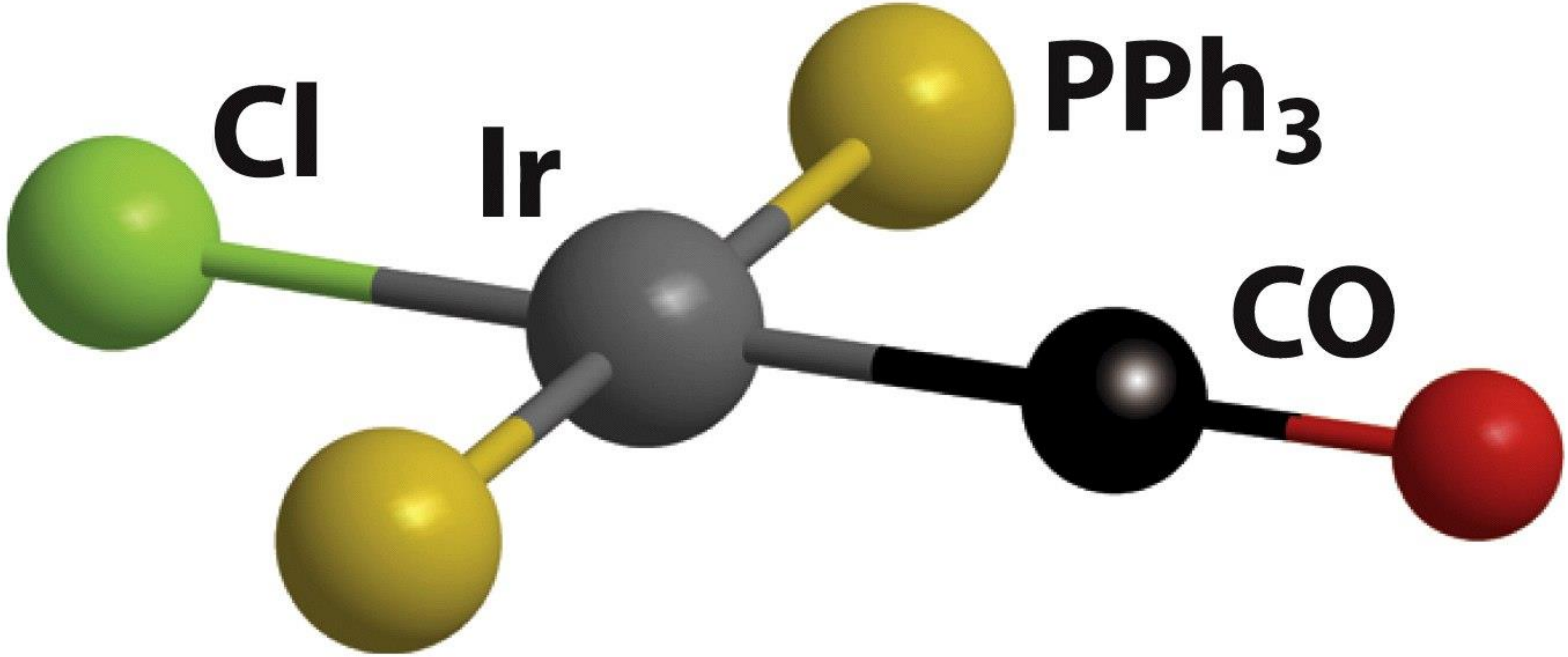
Energetic levels for the MO of a octahedral complex with strong field ligands (π acceptors)



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



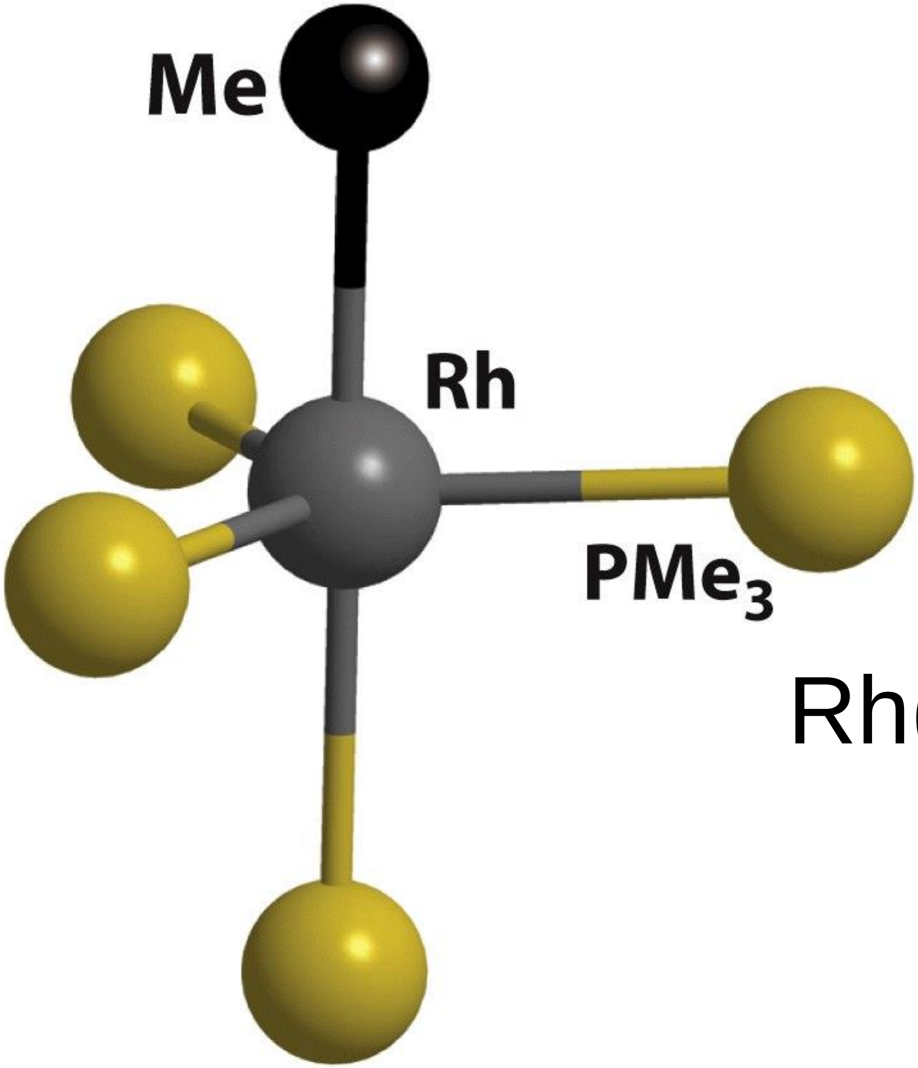
σ-donor
+
π-acceptor
σ-donor
+
π-donor
ML4
ML4
x2 – y2
Δ3
ΔPQ
xy
Δ2
z2
Δ1
yz, zx
x2 – y2
z2
yz , zx
xy
x2 – y2
yz , zx
z2
xy



trans-[IrCl(CO)$(PPh_3)_2$]

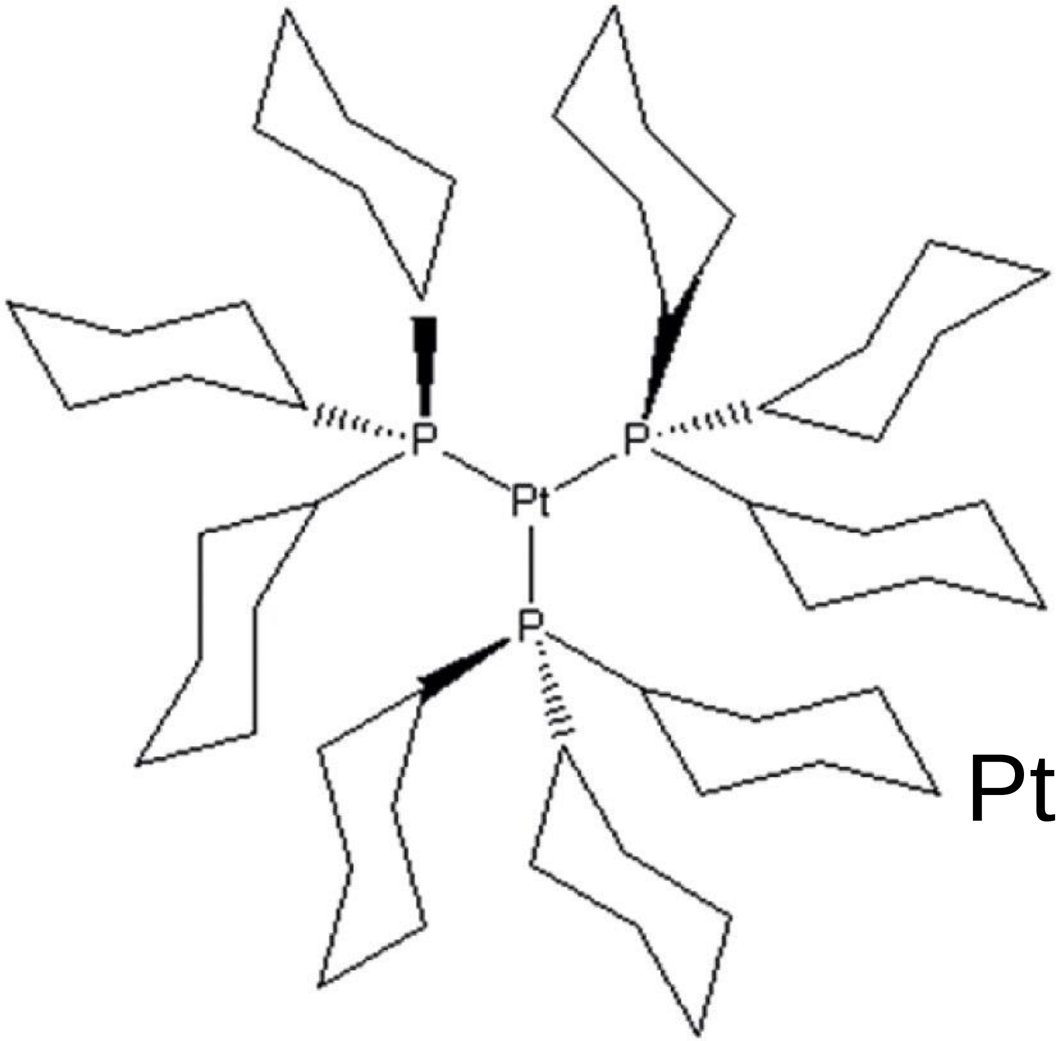
1962, The Vaska Complex (16e$^-$)

Exceptions to the 16-18 electron rule



Rh(I), 18e⁻

Exceptions to the 16-18 electron rule



Pt(0), 16e⁻

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 eletrons			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

$[V(CO)_6]$	17 electrons
$[W(CH_3)_6]$	12 electrons
$[Cr(\eta^5\text{-}Cp)(CO)_2(PPh_3)]$	17 electrons
$[Cr(\eta^5\text{-}Cp)(CO)_3]_2$	18 electrons

Cr–Cr (epta-coordination)

Nomenclature

(see also Supplemental Material on Moodle)

Extended Name

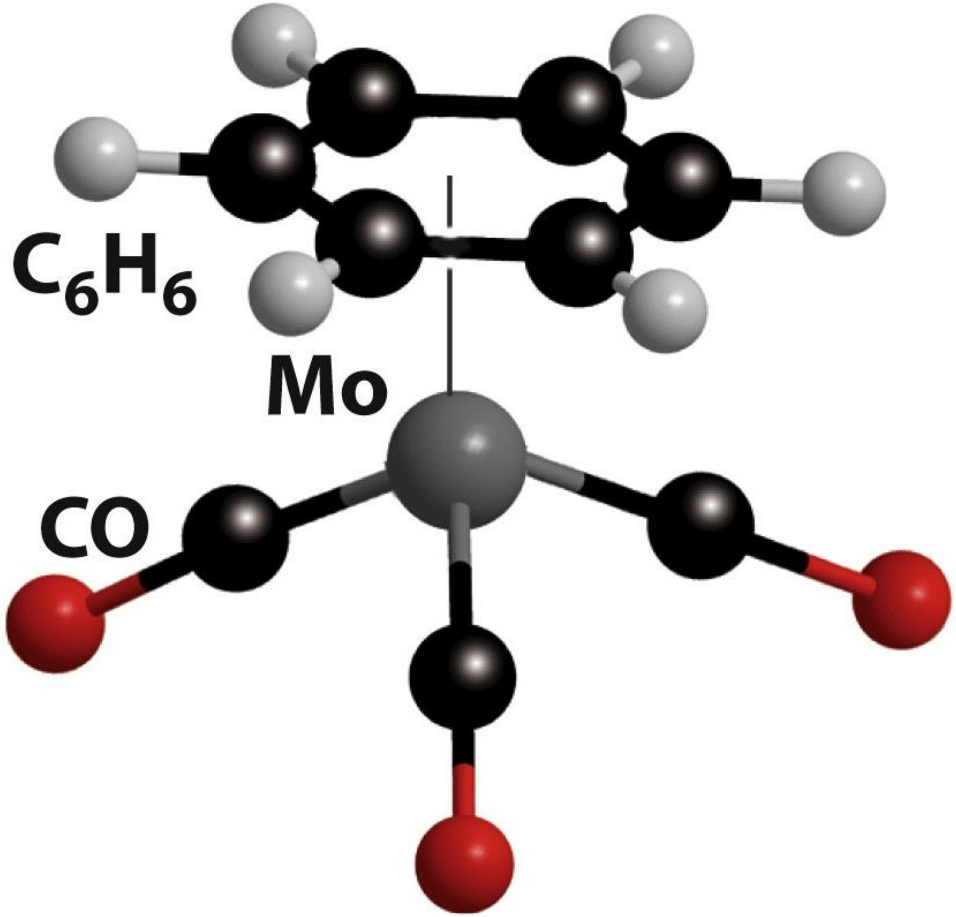
One single word:

- 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 [ ] brakets)

- 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

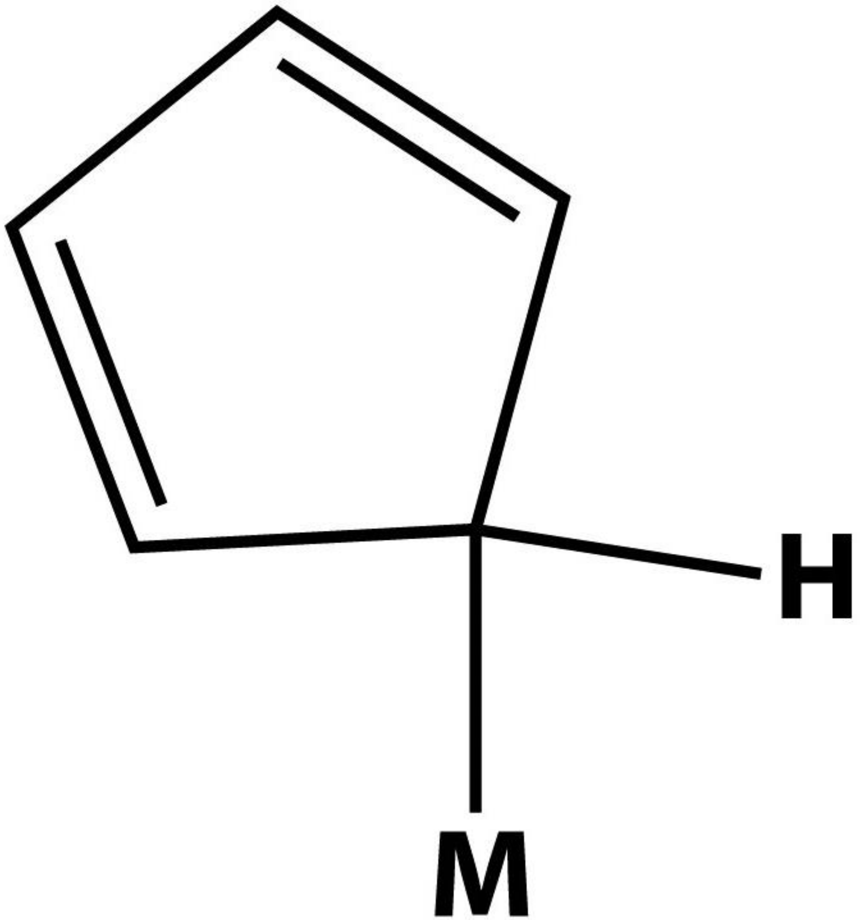


$[Mo(\eta^6\text{-}C_6H_6)(CO)_3]$

benzene(tricarbonyl)molybdenum(0)

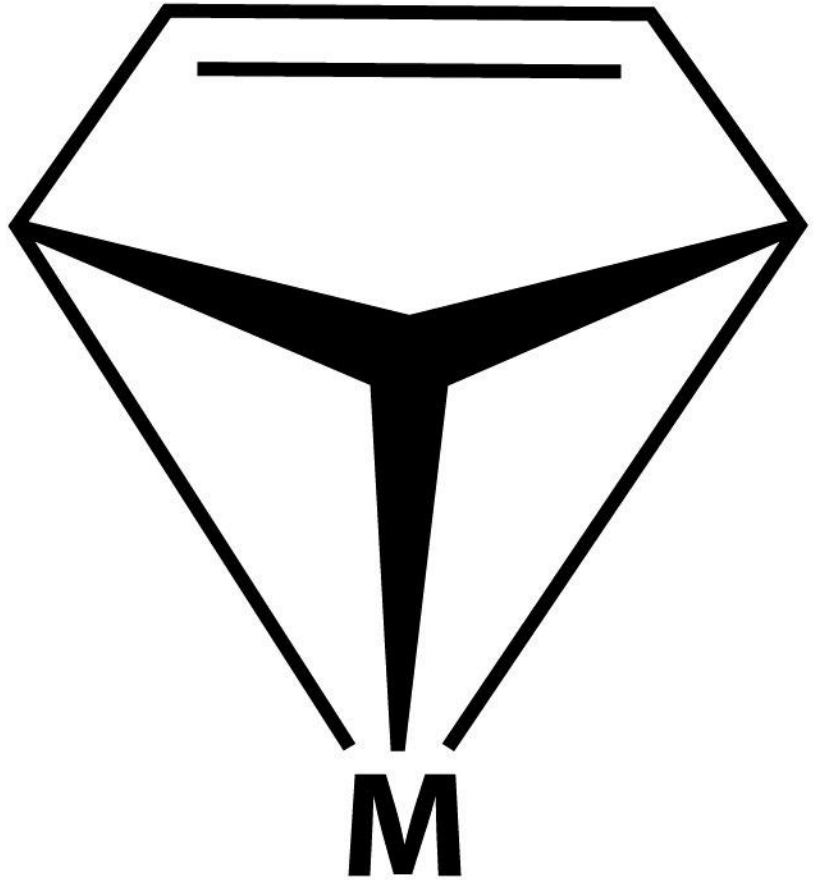
benzenemolybdenum-tricarbonyl

$[(\eta^6\text{-}C_6H_6)Mo(CO)_3]$



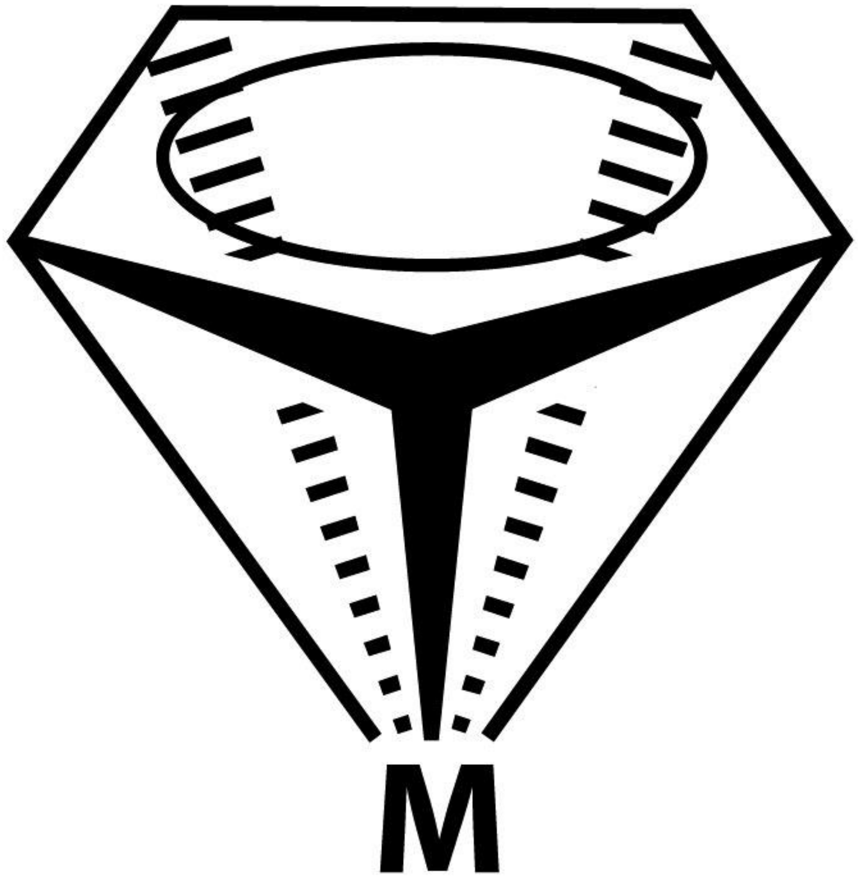
Apticity = number of ligand atoms that are formally directly bound to the metal – electron counting changes!

η^1-Cyclopentadienyl 2 electrons



η³-Cyclopentadienyl

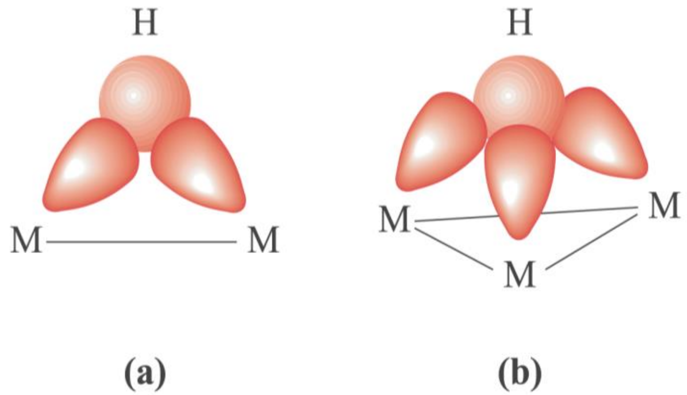
4 electrons



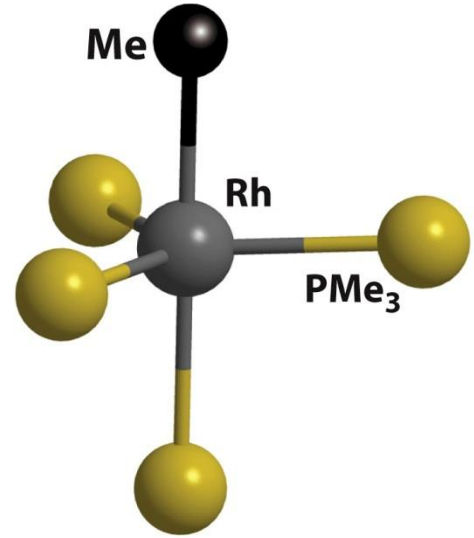
η^5-Cyclopentadienyl

6 electrons

Bridging Ligands

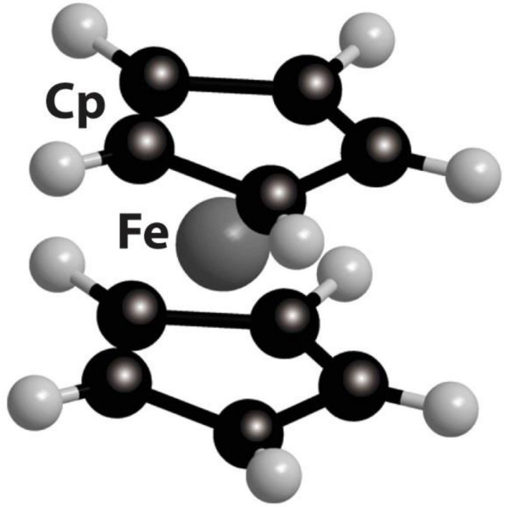


μ_2-H μ_3-H



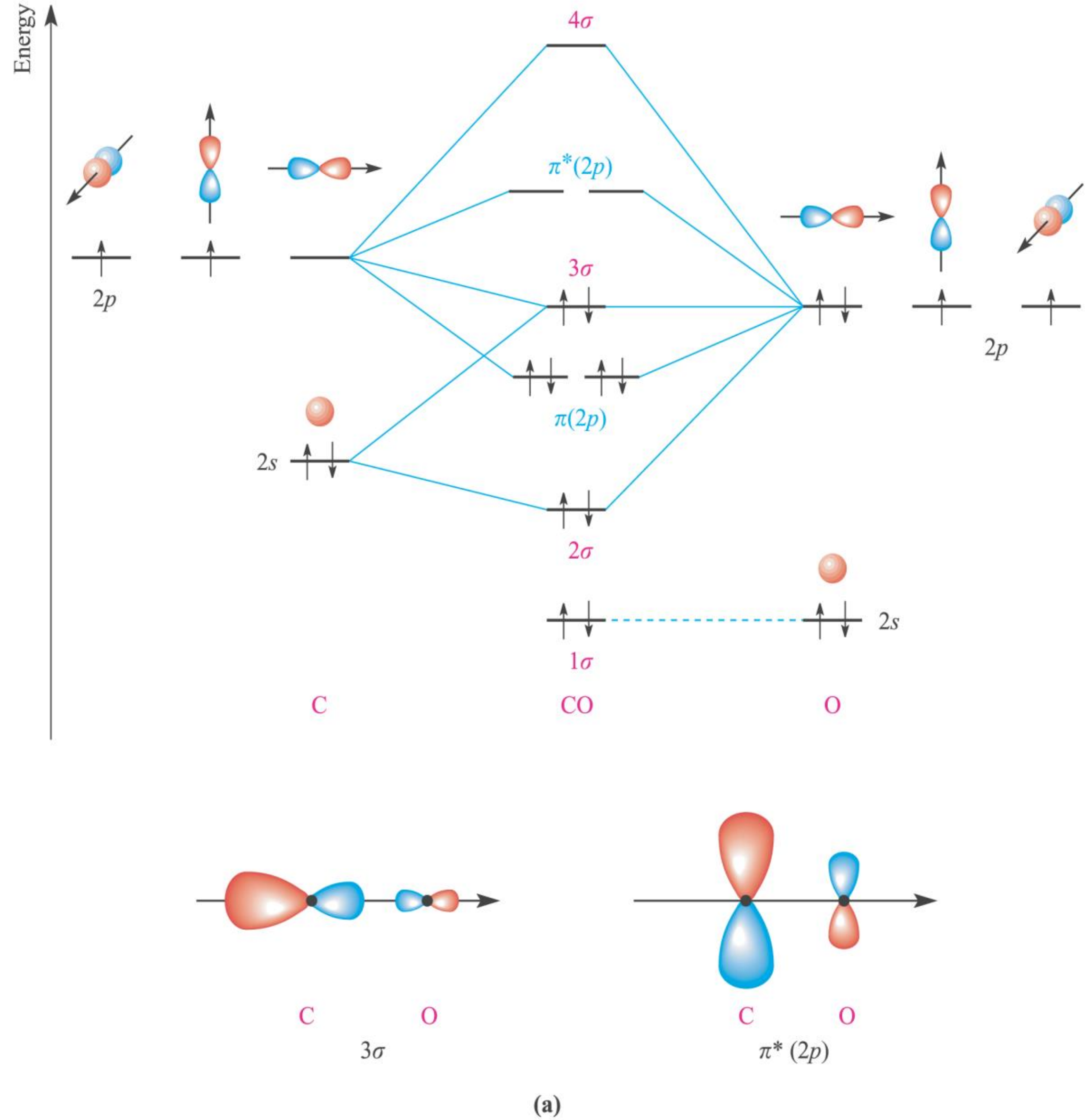
$[RhMe(PMe_3)_4]$

methyltetrakis(trimethylphosphine)rhodium(I)

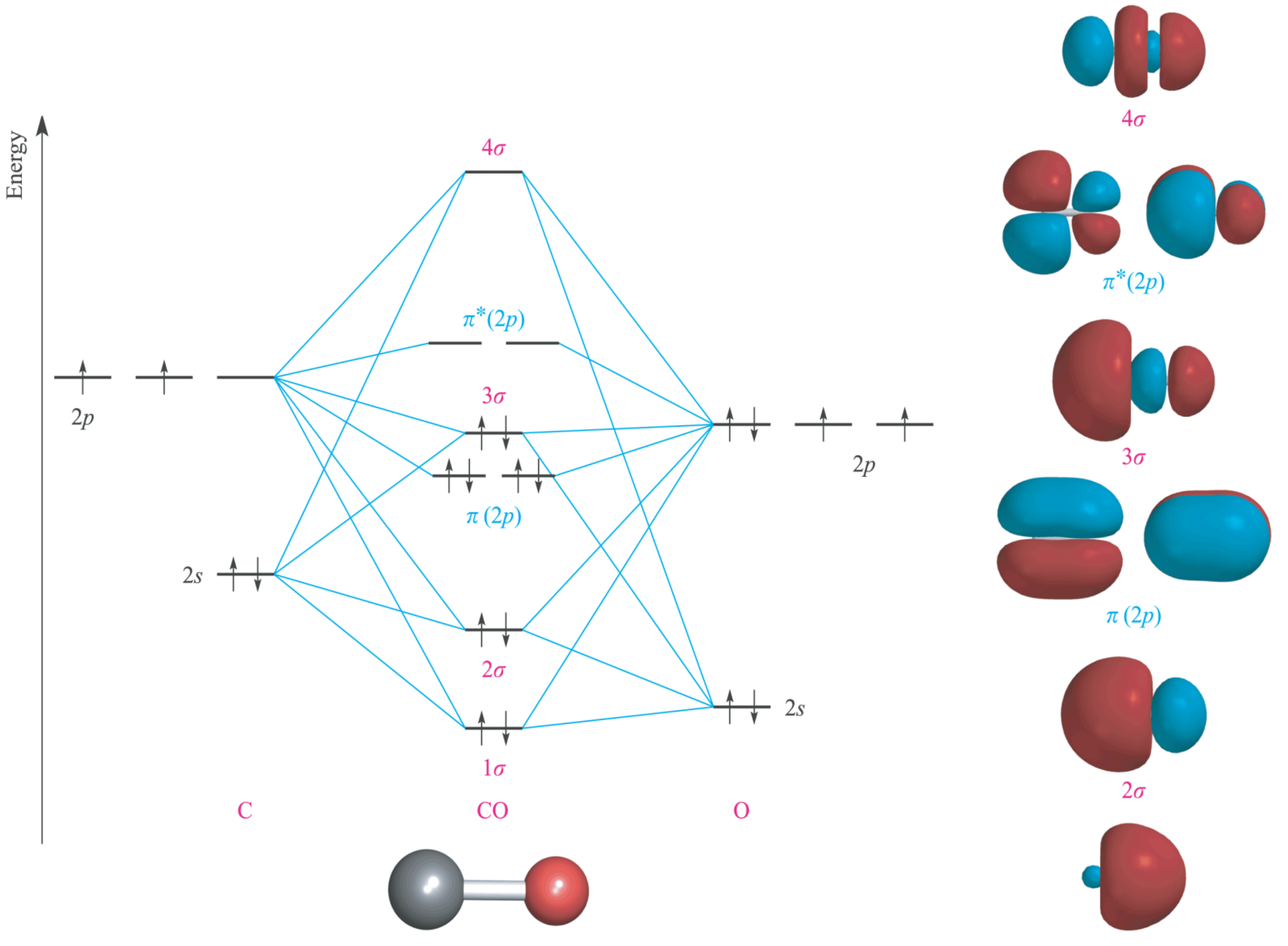


$[FeCp_2]$

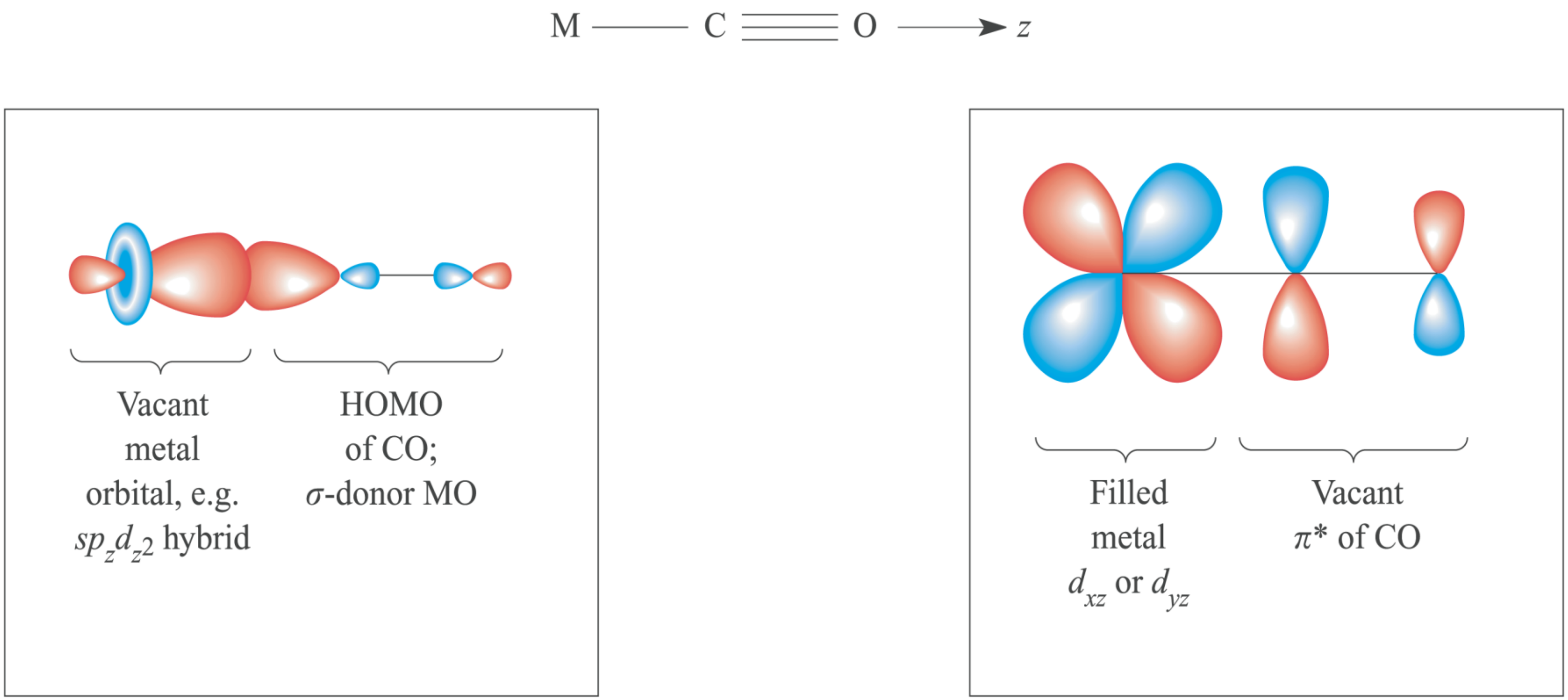
bis(η^5-cyclopentadienyl)iron(II)



Simplified MO diagram of CO

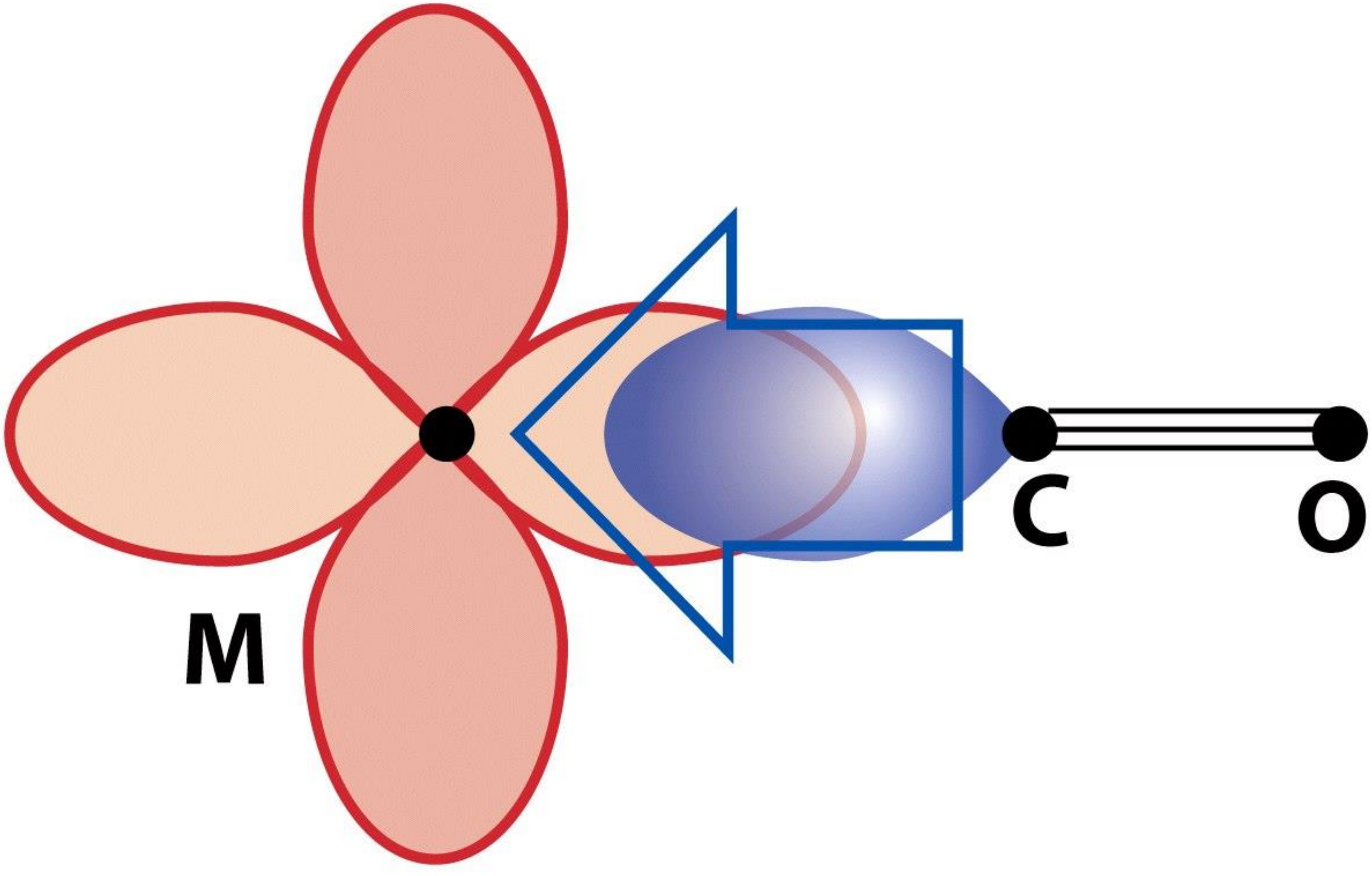


The MO level diagram of CO shows that the HOMO (3σ) has σ symmetry, this orbital is positioned mainly on the C, as a sprouting lobe; on the other hand the LUMO has a π symmetry.



CO-to-M donation
(a)

M-to-CO back-donation
(b)



C
O
M

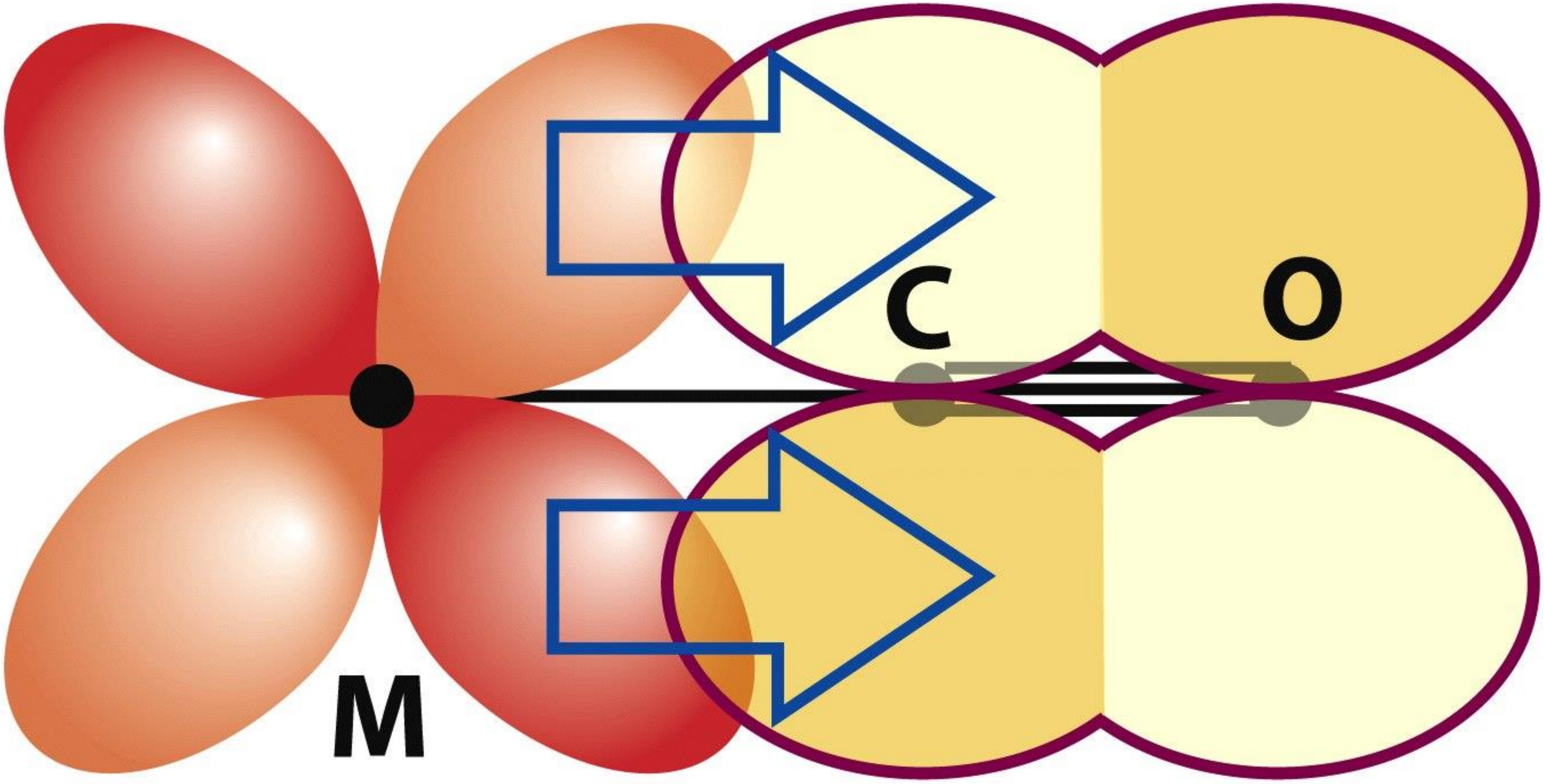
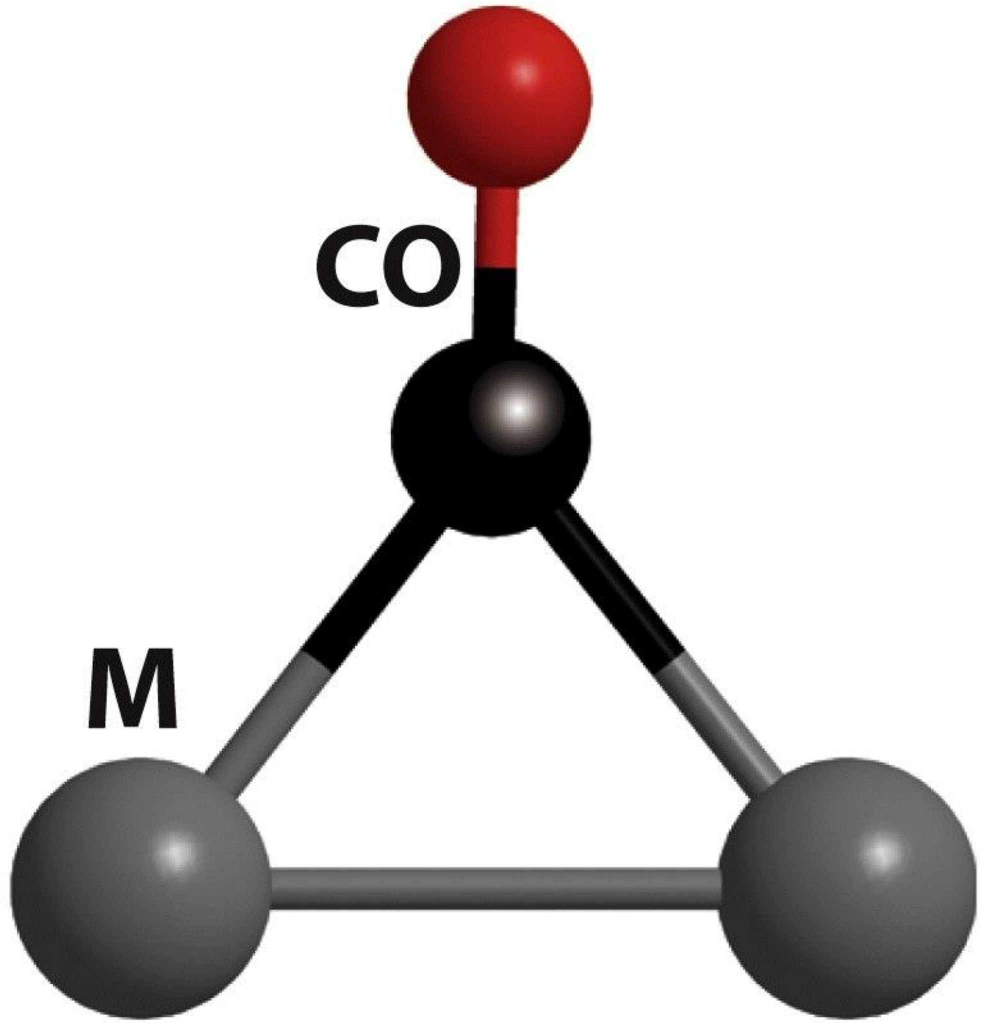
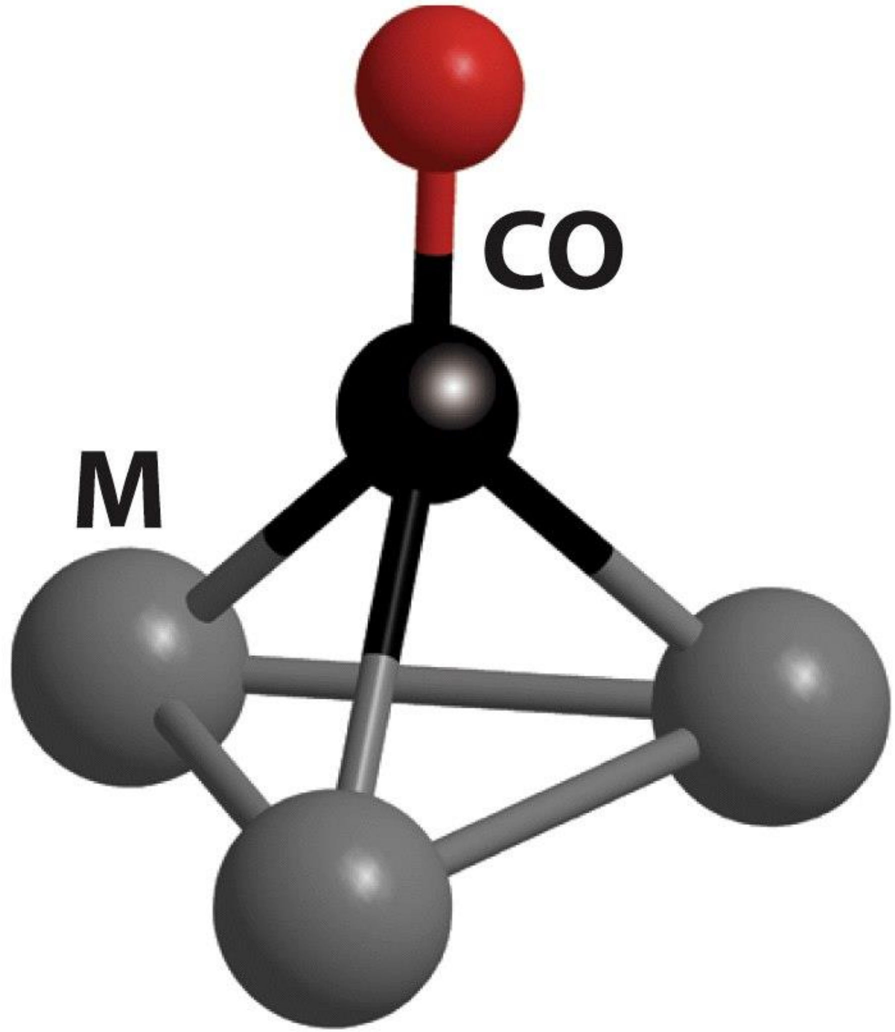

C
O
M

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

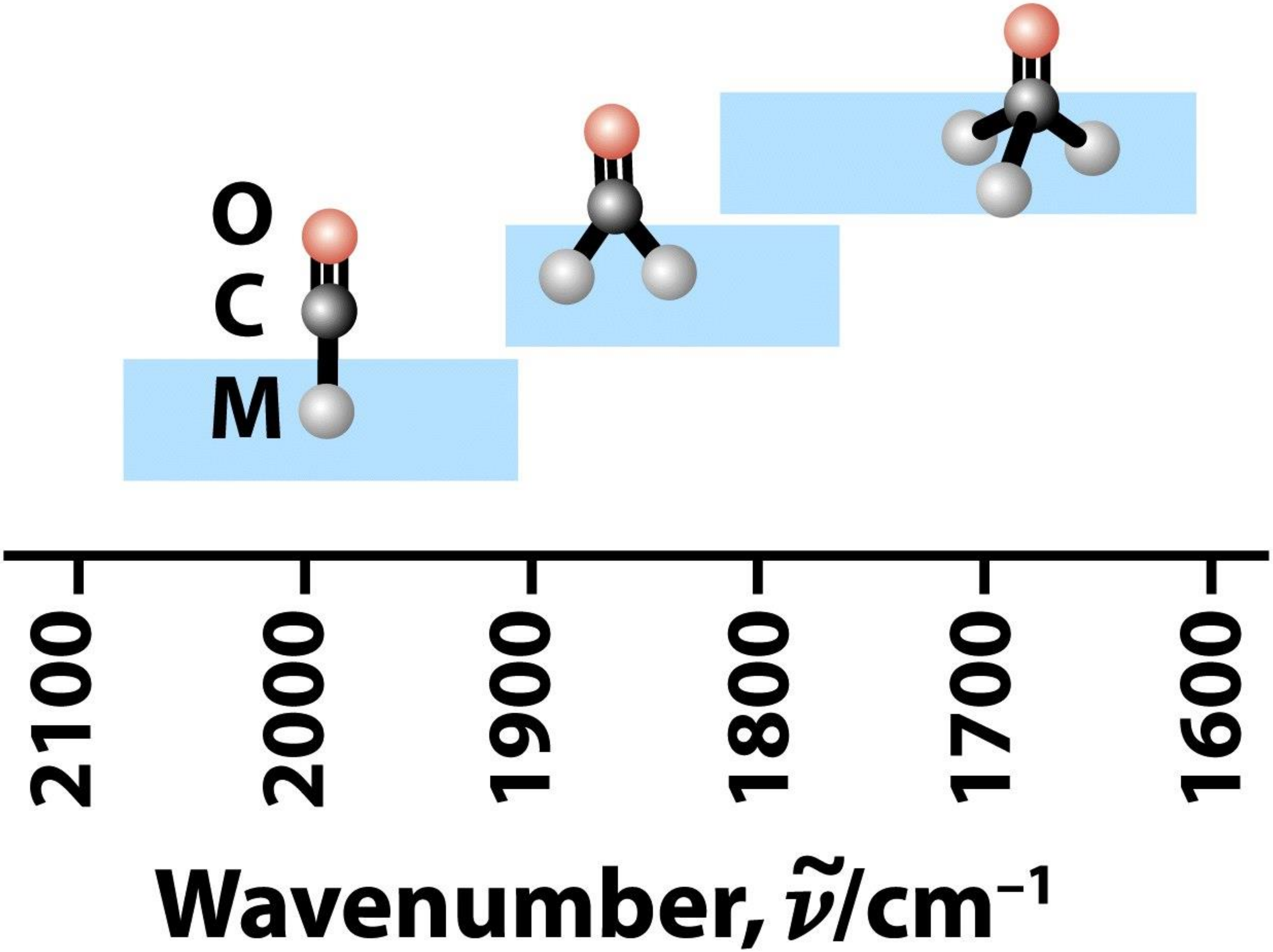
Compound	$\tilde{\nu}/\mathrm{cm}^{-1}$
CO	2143
$[Mn(CO)_6]^+$	2090
$Cr(CO)_6$	2000
$[V(CO)_6]^-$	1860
$[Ti(CO)_6]^{2-}$	1750



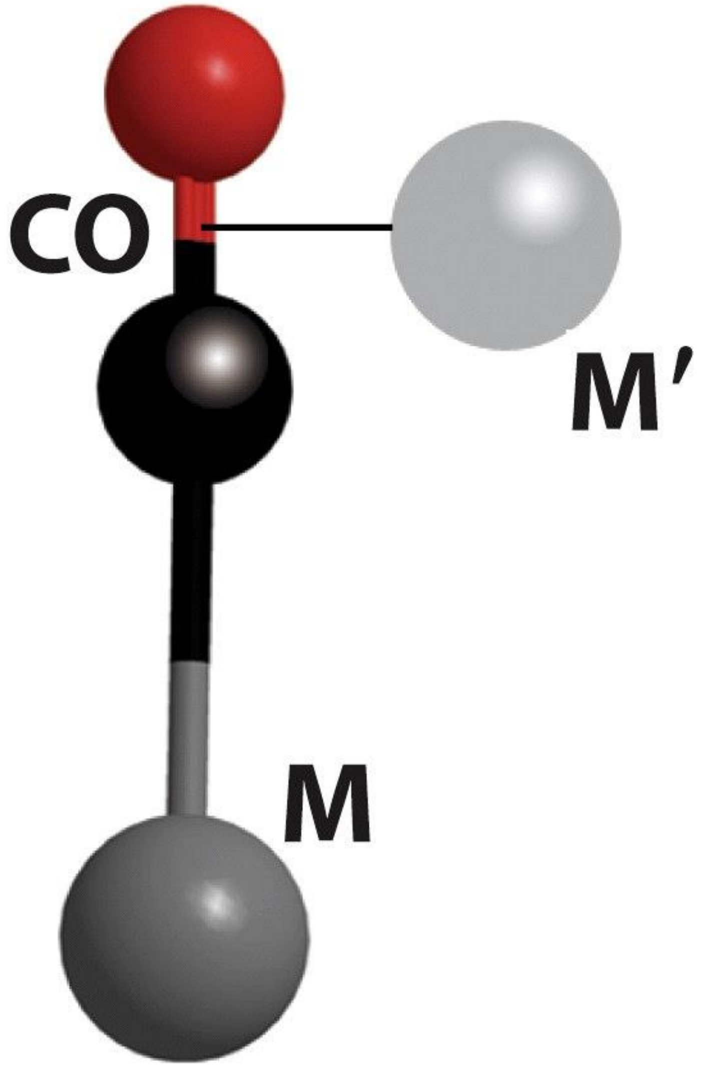
μ_2-CO



μ_3-CO



Reference CO vibrational bands ranges for neutral metal-carbonyls.



side-on