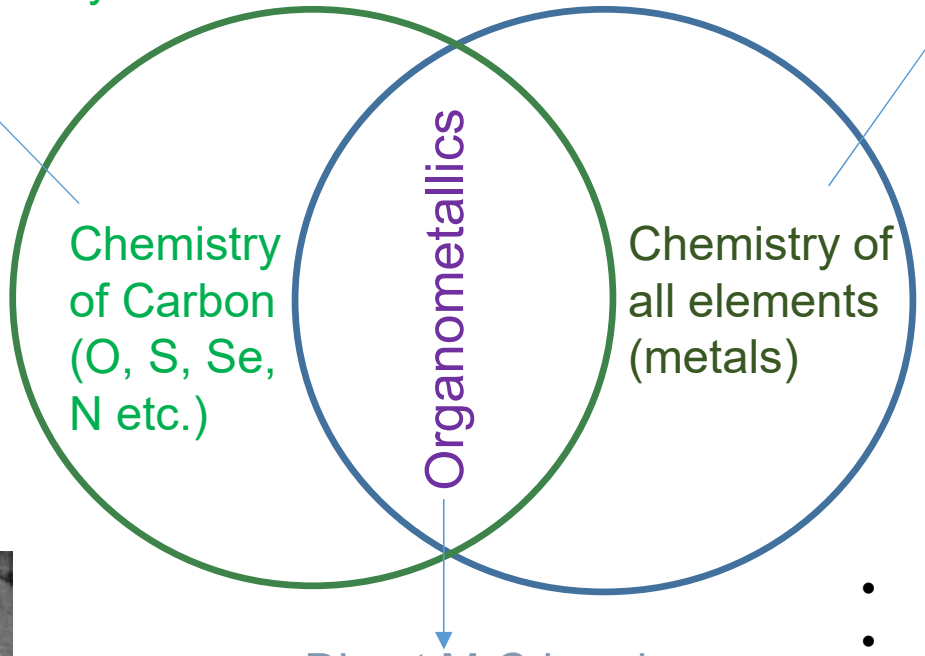
Organometallic Chemistry

Organic Chemistry

Inorganic Chemistry



- more or less covalent bonds
- rigid element environments
- fixed oxidation states

- primarily ionic M-X bonds, dative M-L bonds
- variable and often fluxional environments
- variable oxidation states

Edward Frankland

Direct M-C bond

- more covalent (less ionic)
- often less symmetric than coordination compounds

Importance

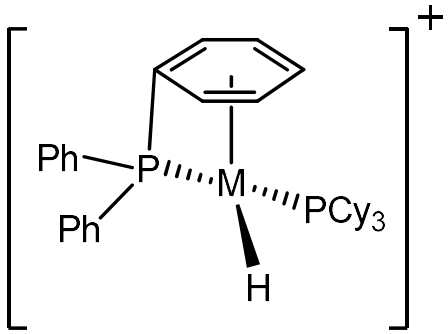
- Easy access to C-C bond
- Catalysis
- Small molecule activation
- New industry
- Around 2000 research article
- Six Nobel Prizes

Innocent Ligands: In a metal complex, if the ligands whose oxidation state is clearly known, **Eg:** O^{2-}, Cl^{-}

Non-innocent ligands: In a metal complex, if the ligands igands whose oxidation state is not known, **Eg:** NO

Exercises

The following organometallic compounds are stable and have a 2nd row transition metal at its centre. Find out the metal and its oxidation state



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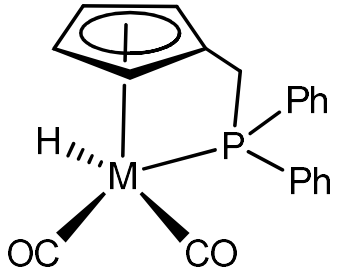

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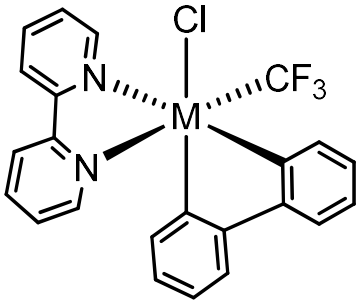

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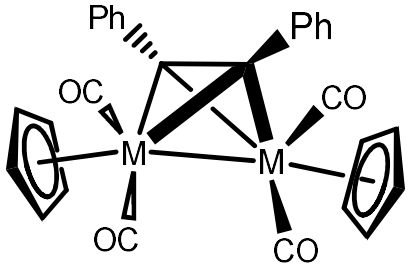
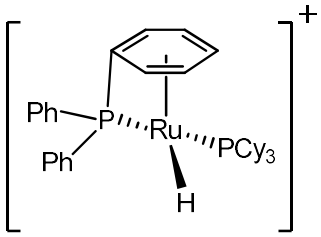


D

yttrium	zirconium	niobium	molybdenum	technetium	ruthenium	rhodium	palladium	silver	cadmium
39	40	41	42	43	44	45	46	47	48
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
88.906	91.224	92.906	95.94	[98]	101.07	102.91	106.42	107.87	112.41



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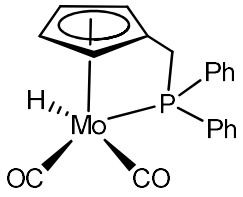

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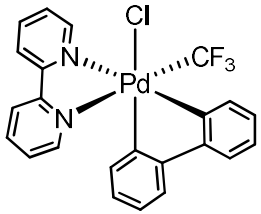

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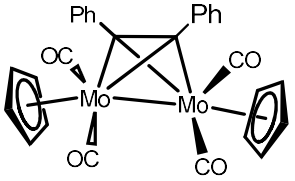
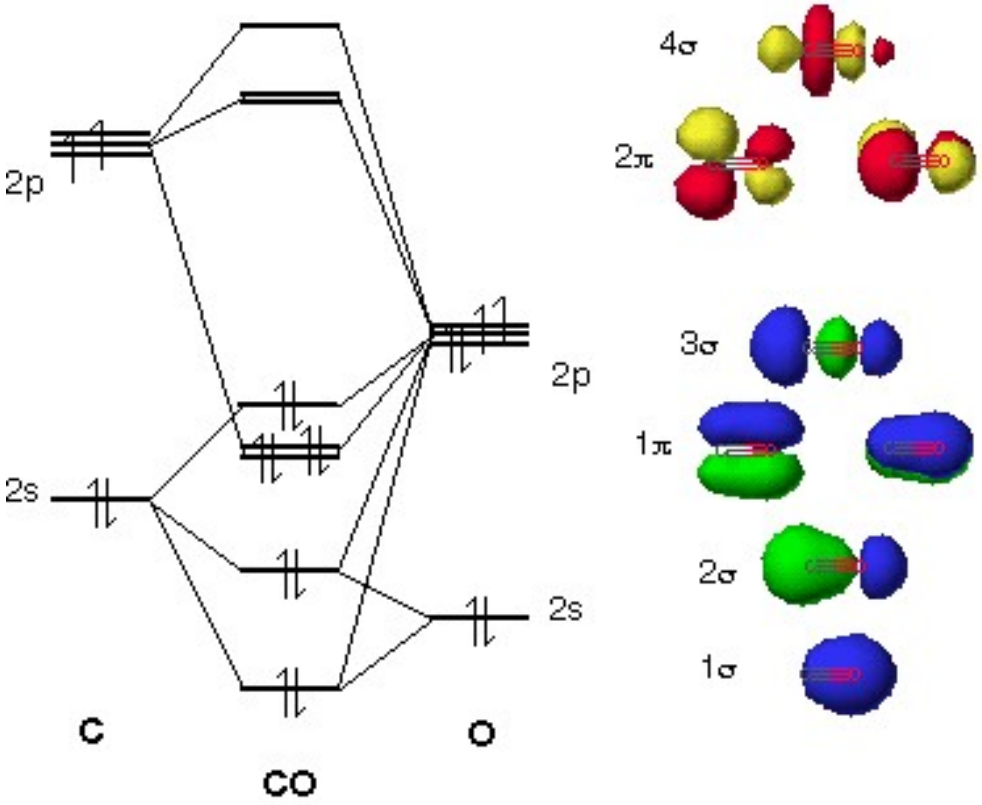


D

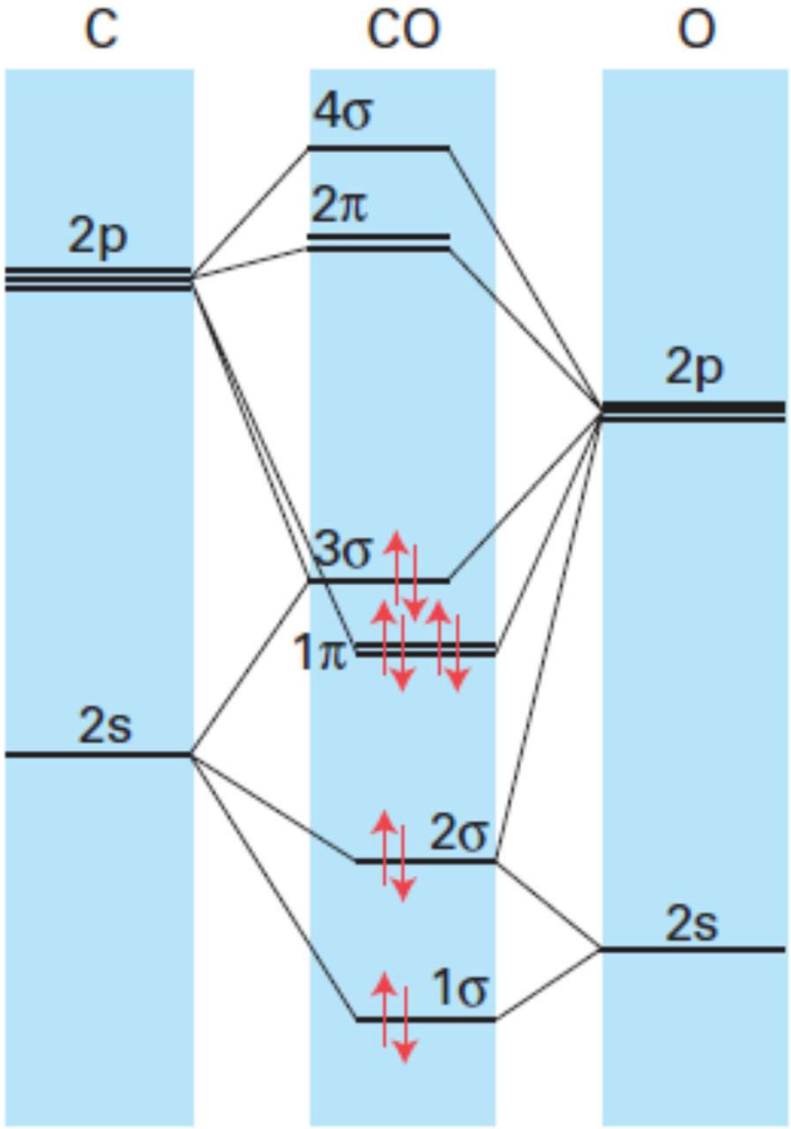
Exceptions to the 18 electron rule

- Square planar organometallic complexes of the late transition metals (16e).
- Some organometallic complexes of the early transition metals (e.g.Cp_2TiCl_2, WMe_6, Me_2NbCl_3, $CpWOCl_3$) [Possible reason: Some of the orbitals of these complexes are too high in energy for effective utilization in bonding or the ligands are mostly σ donors.]
- Some high valent d^0 complexes have a lower electron count than 18. [Eg:]
- Sterically demanding bulky ligands force complexes to have less than 18 electrons.
- The 18 electron rule fails when bonding of organometallic clusters of moderate to big sizes (6 Metal atoms and above) are considered.
- The rule is not applicable to organometallic compounds of main group metals as well as to those of lanthanide and actinide metals.

Molecular Orbital diagram of CO

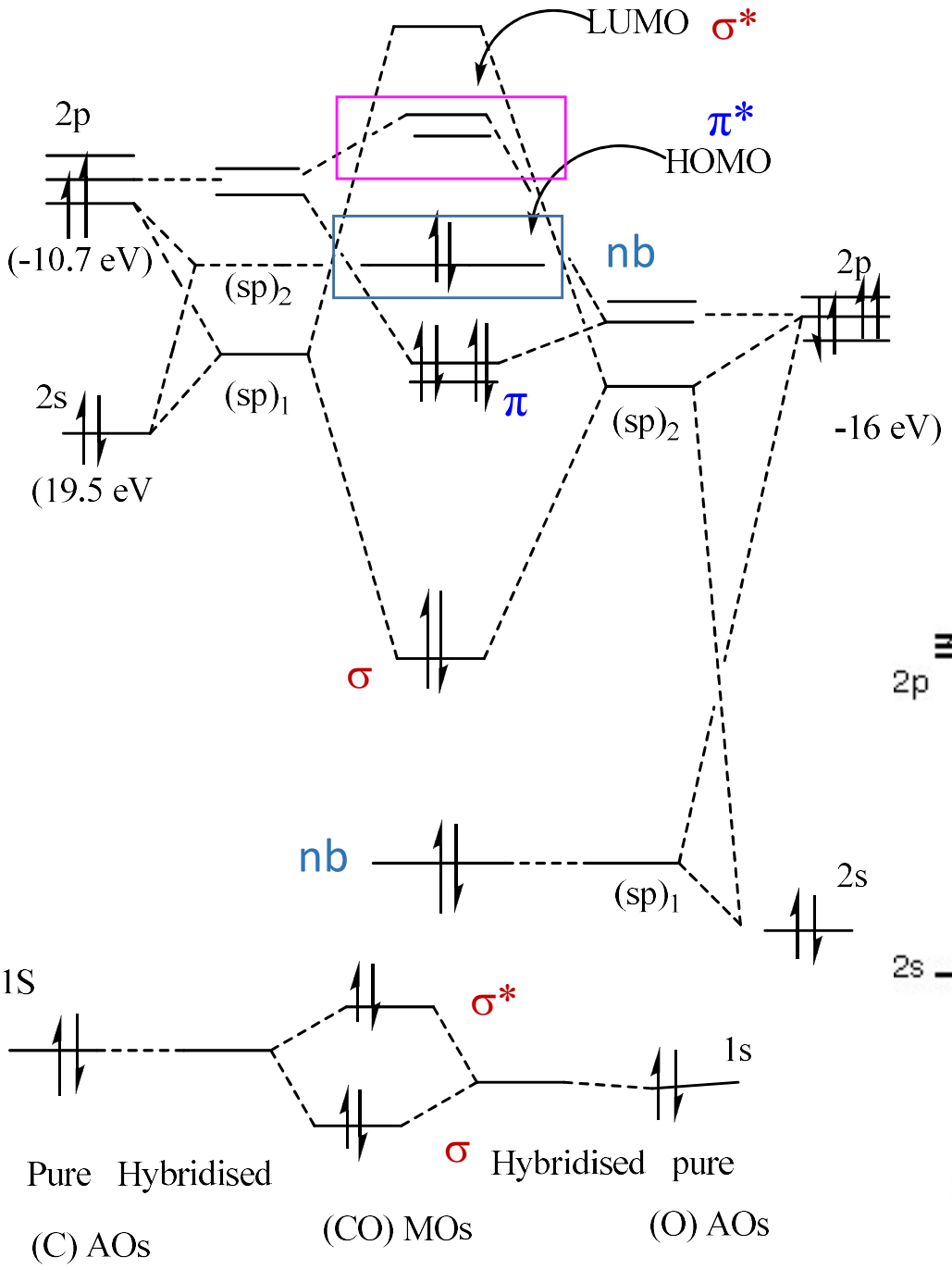


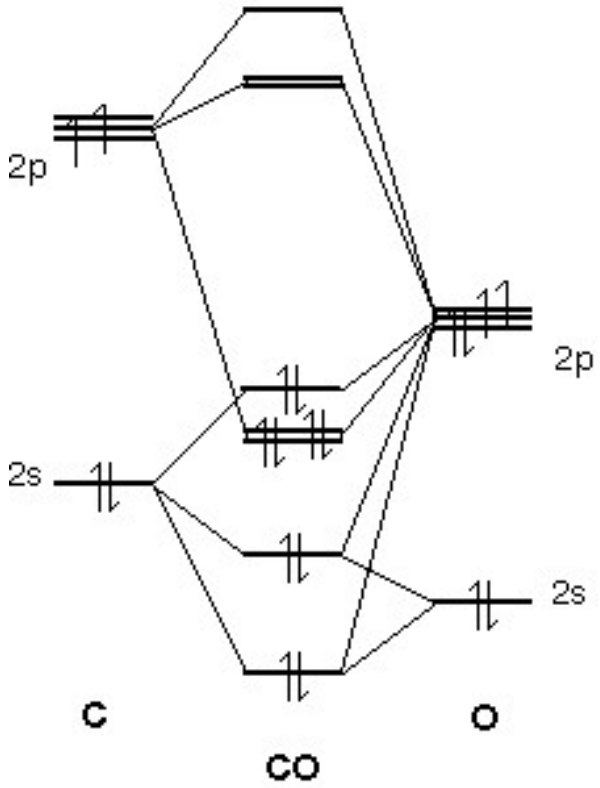
orbital (LUMO) is also of comparatively lower energy which makes it possible to interact with metal t_{2g} orbitals for π bonding. There exists a strong back bonding of metal electrons to the π* antibonding orbitals of CO

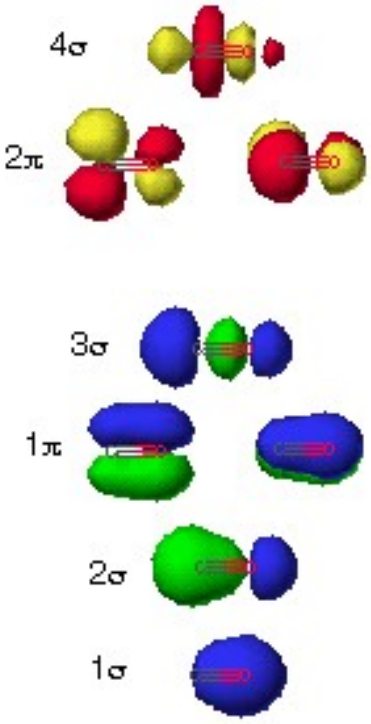


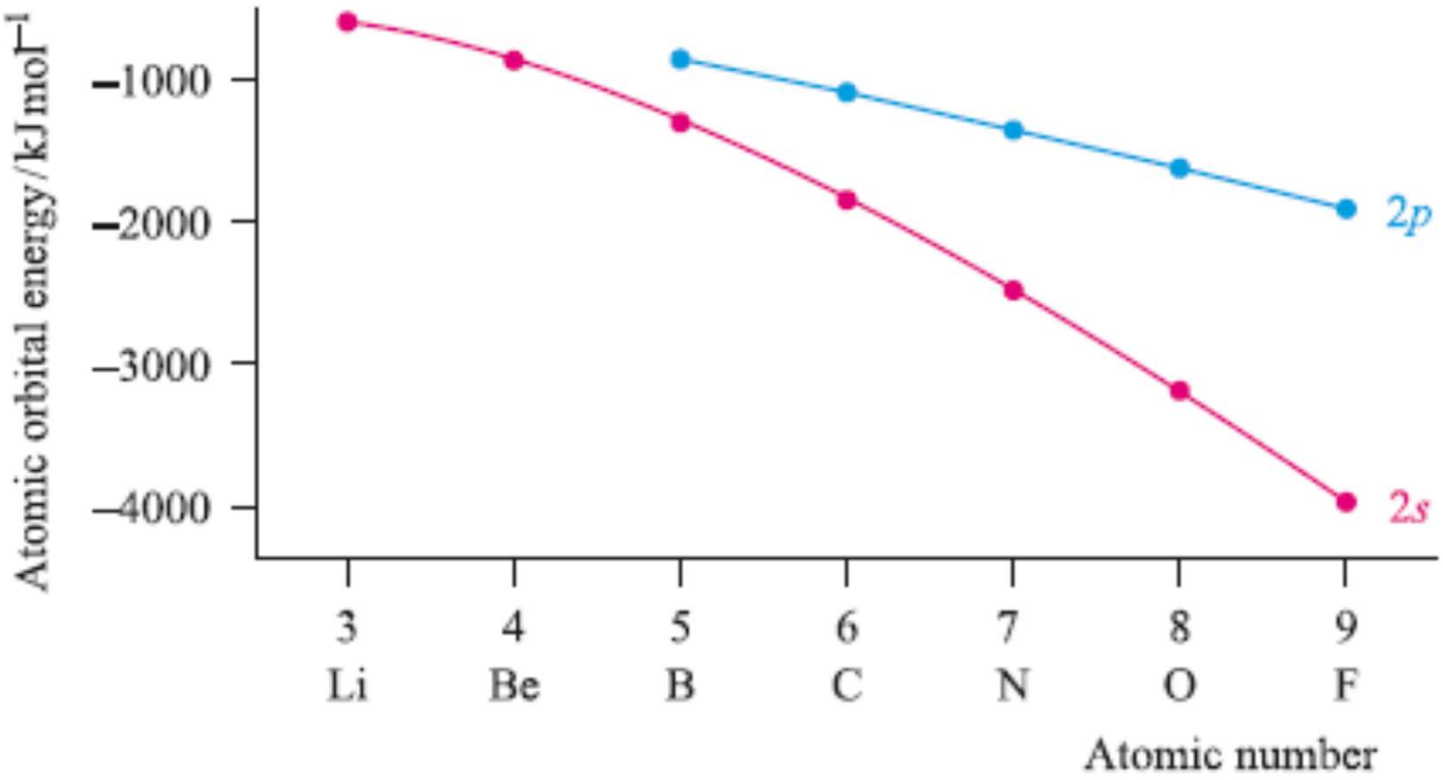
Source: ***Inorganic chemistry*** *by Shriver & Atkins, page 541*

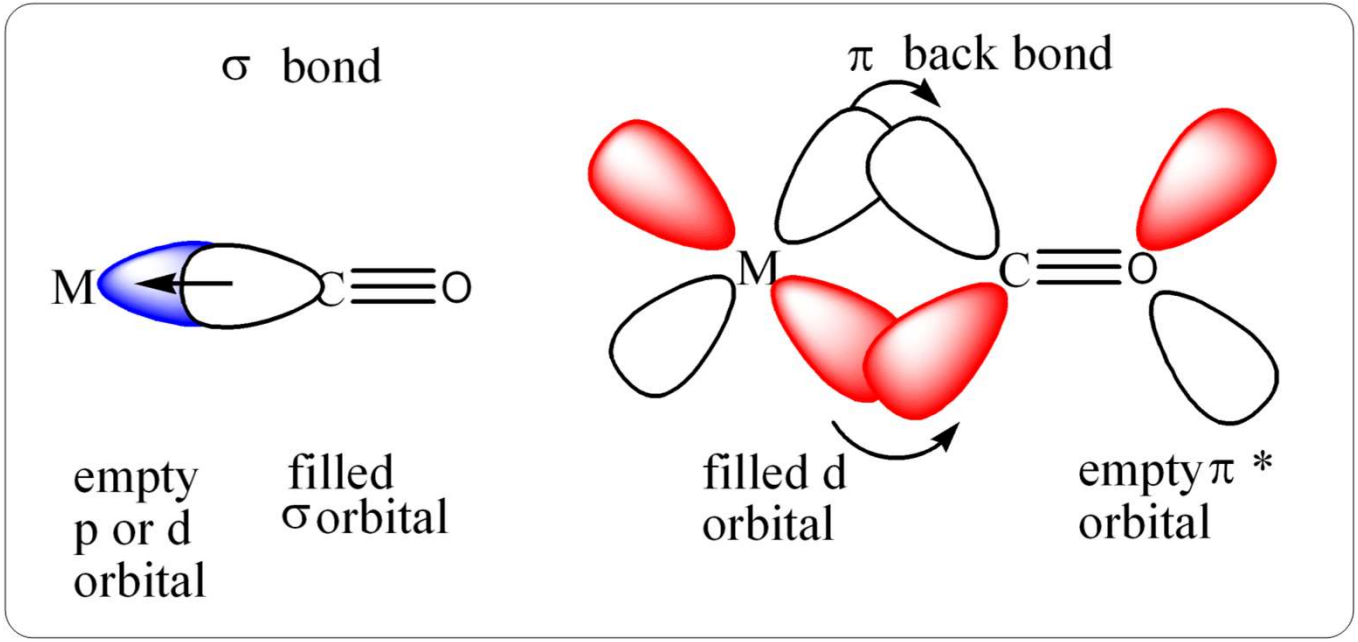
Stabilizing Low Oxidation State: CO Can Do the Job







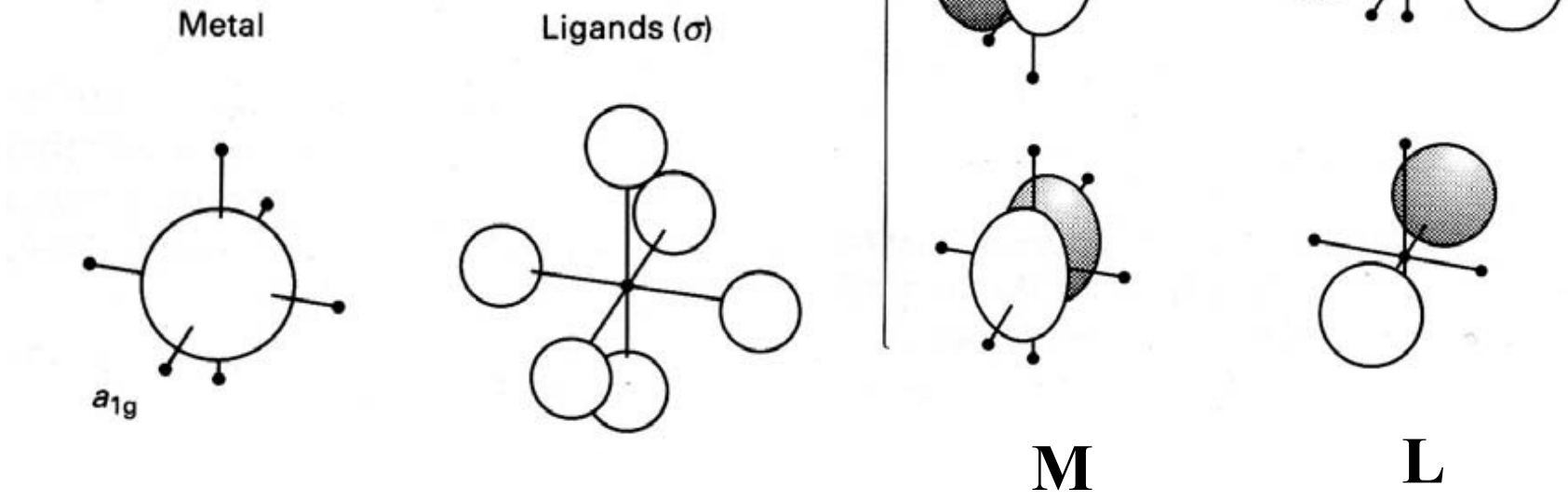

Atomic orbital energy/kJ mol⁻¹
−1000
−2000
−3000
−4000
2p
2s
3 Li
4 Be
5 B
6 C
7 N
8 O
9 F
Atomic number

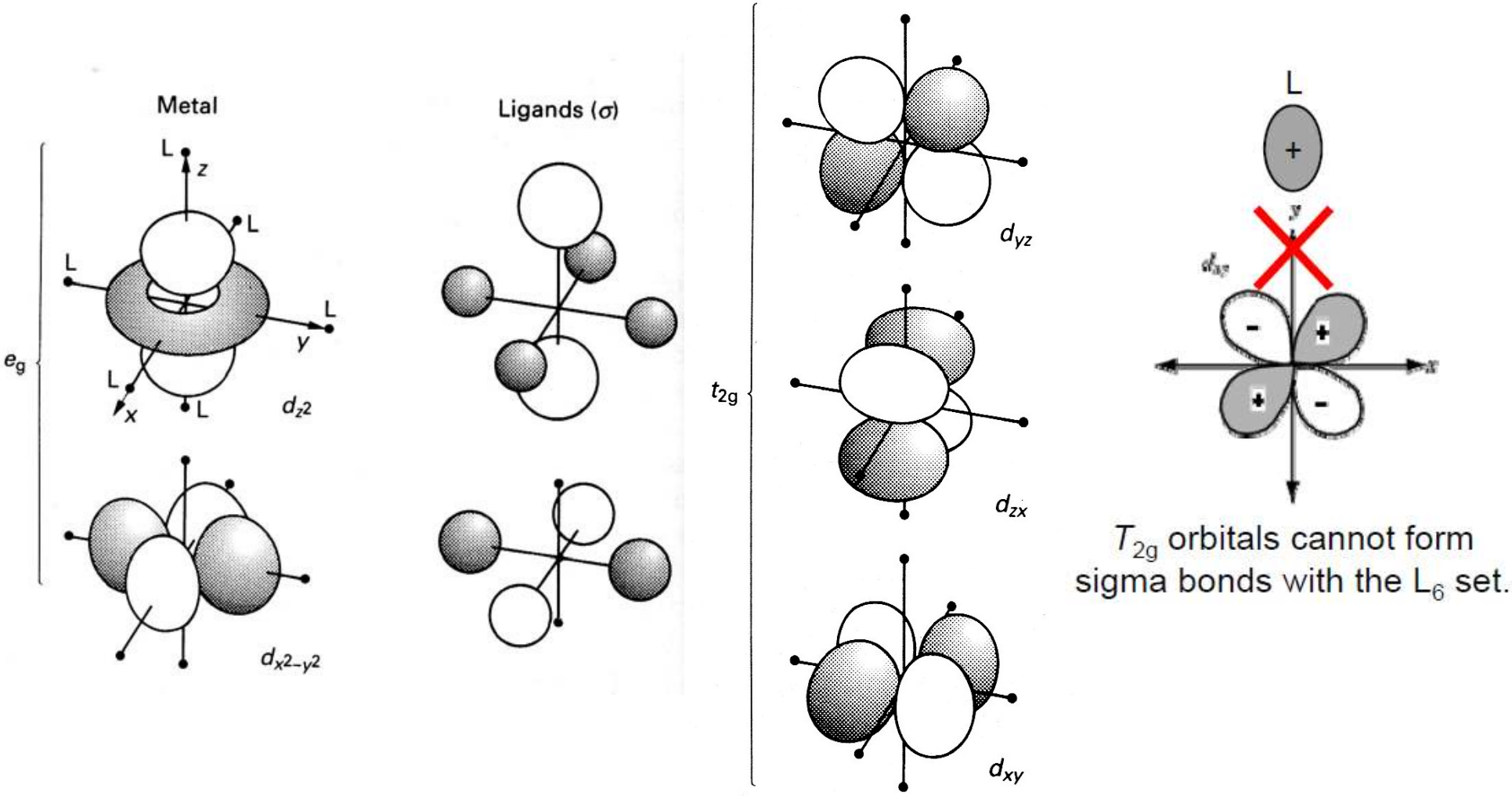

σ bond
π back bond
M
C
O
empty p or d orbital
filled σ orbital
filled d orbital
empty π * orbital

Why 18- electrons ?

Ligand Field Theory: Concepts

- Ligand Orbitals(LGO)are obtained by Linear Combination of Atomic Orbitals (LCAO)
- **LGO**s overlap with **symmetry related** Metal Orbitals





T_{2g} orbitals cannot form sigma bonds with the L_6 set.

MO diagram of an Octahedral complex

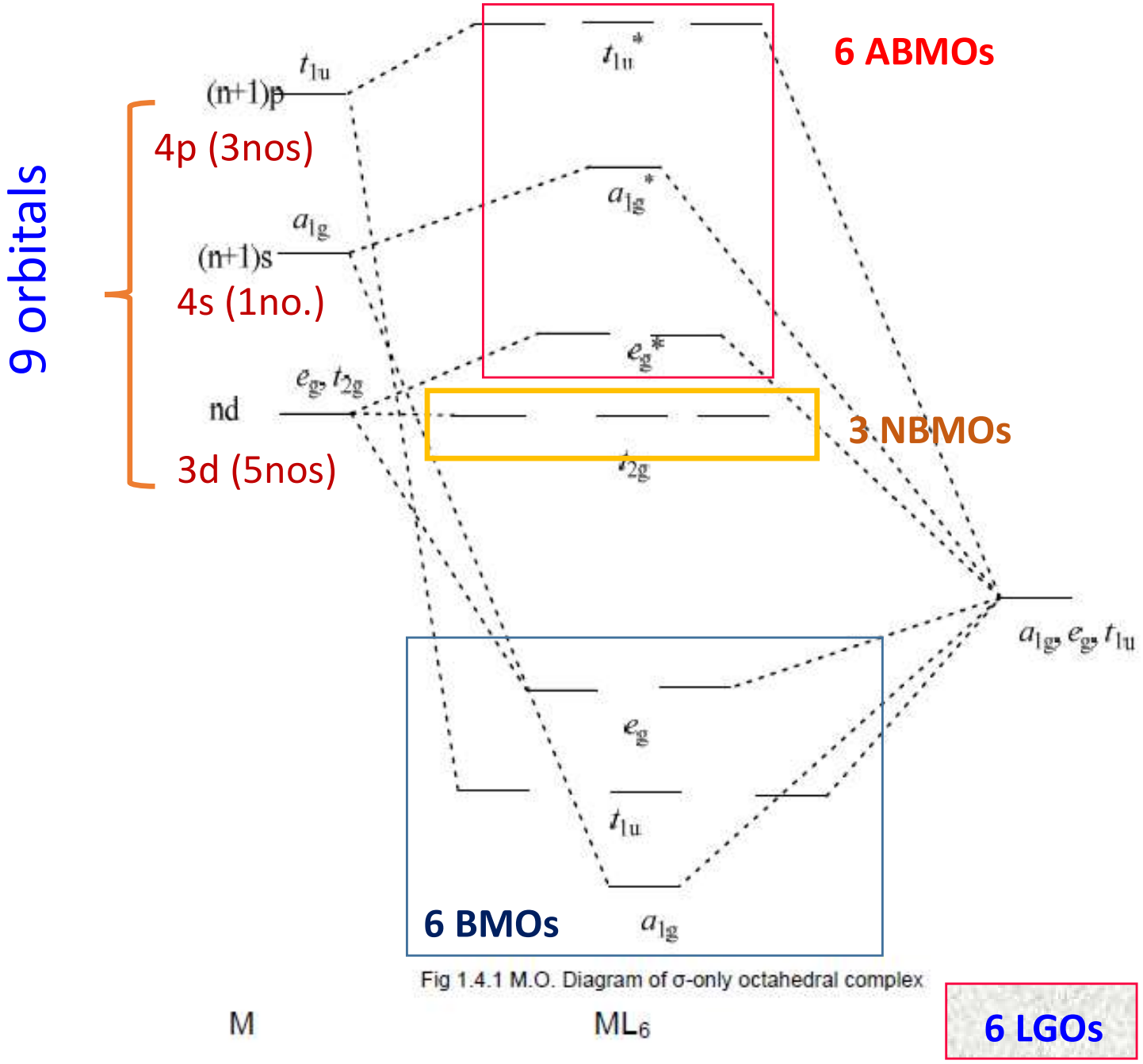
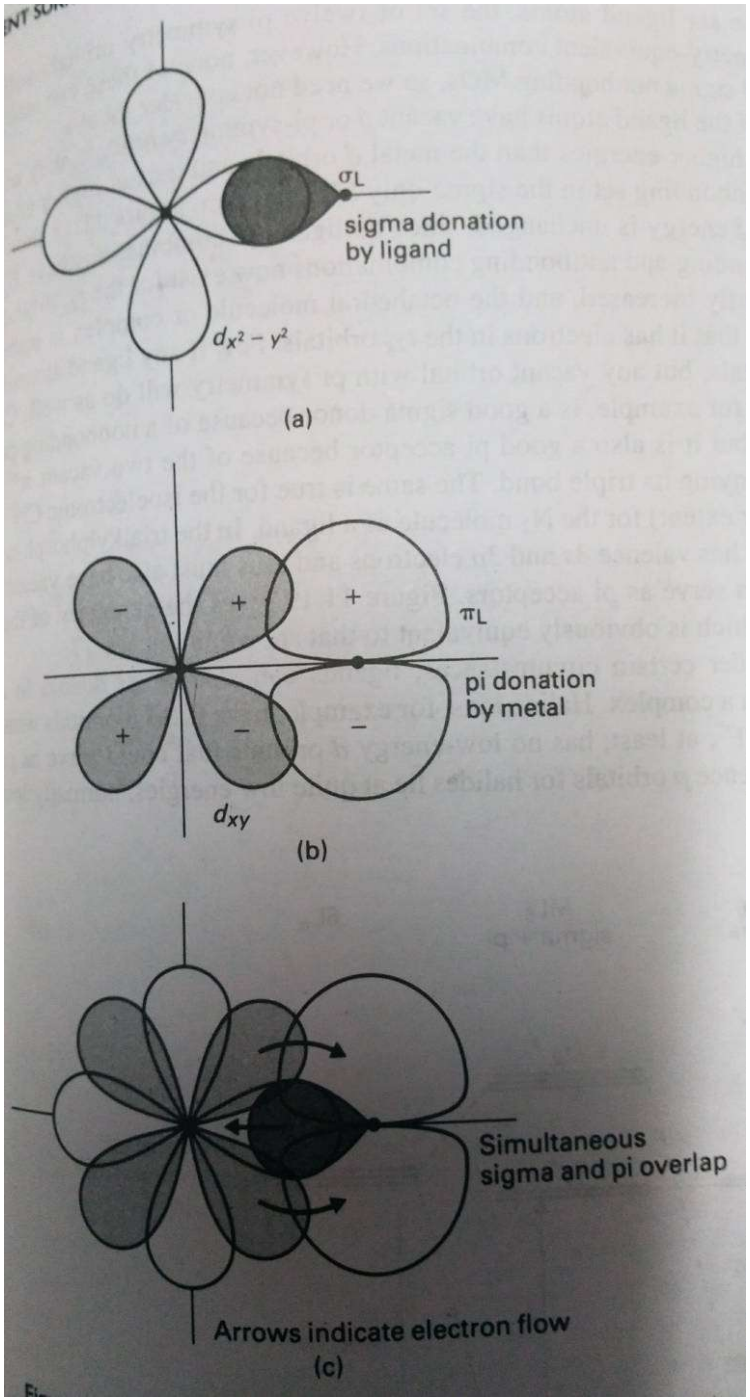
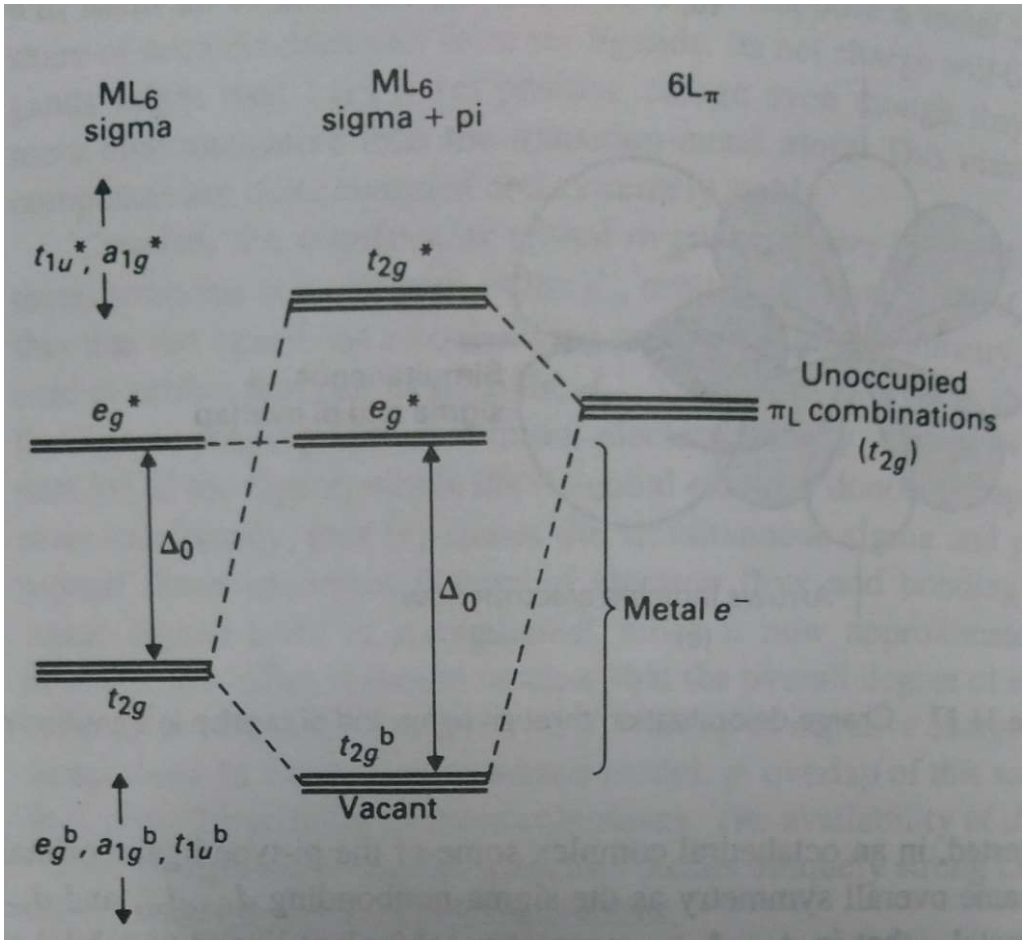


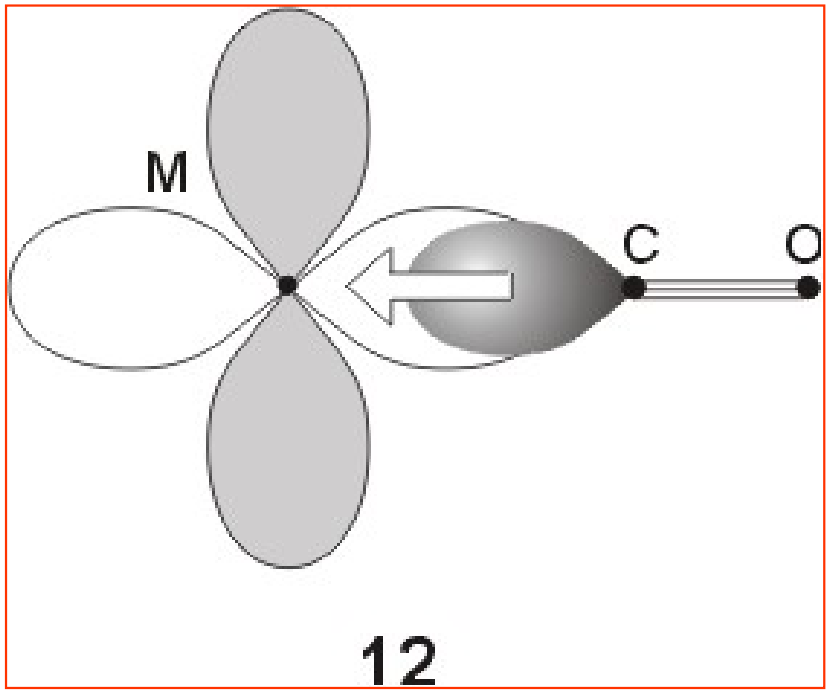
Fig 1.4.1 M.O. Diagram of σ-only octahedral complex

MO of π-complex





Stabilizing Low Oxidation State: CO Can Do the Job



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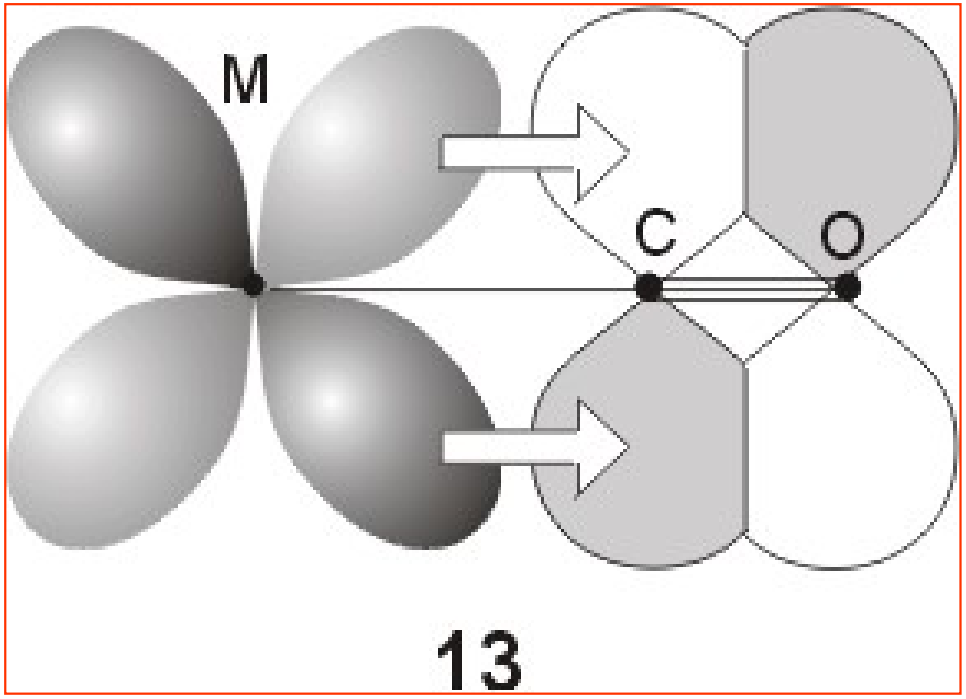


13

$Ni(CO)_4]$, $[Fe(CO)_5]$, $[Cr(CO)_6]$, $[Mn_2(CO)_{10}]$, $[Co_2(CO)_8]$, $Na_2[Fe(CO)_4]$, $Na[Mn(CO)_5]$

A σ MO diagram for a complex of O_h symmetry

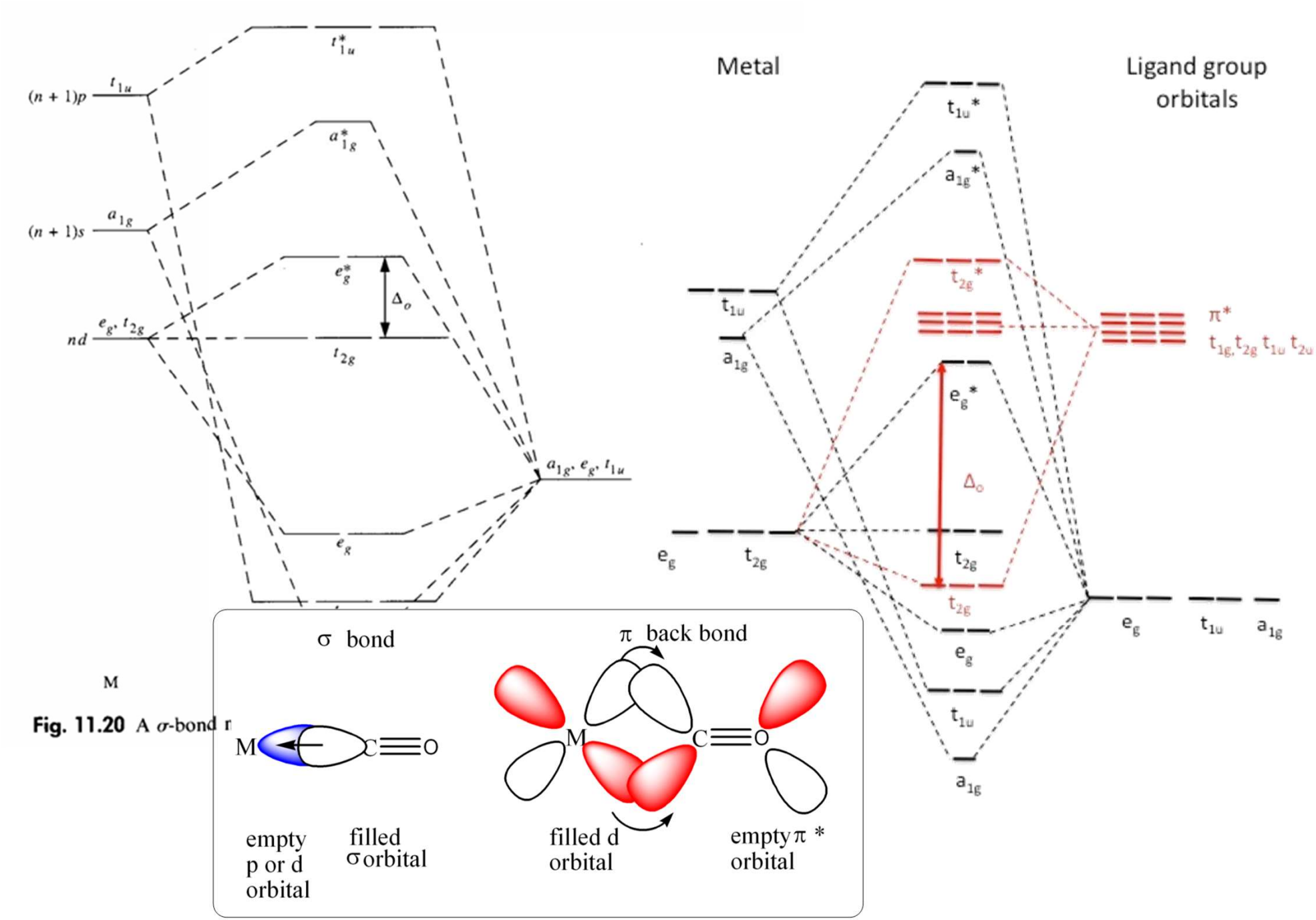
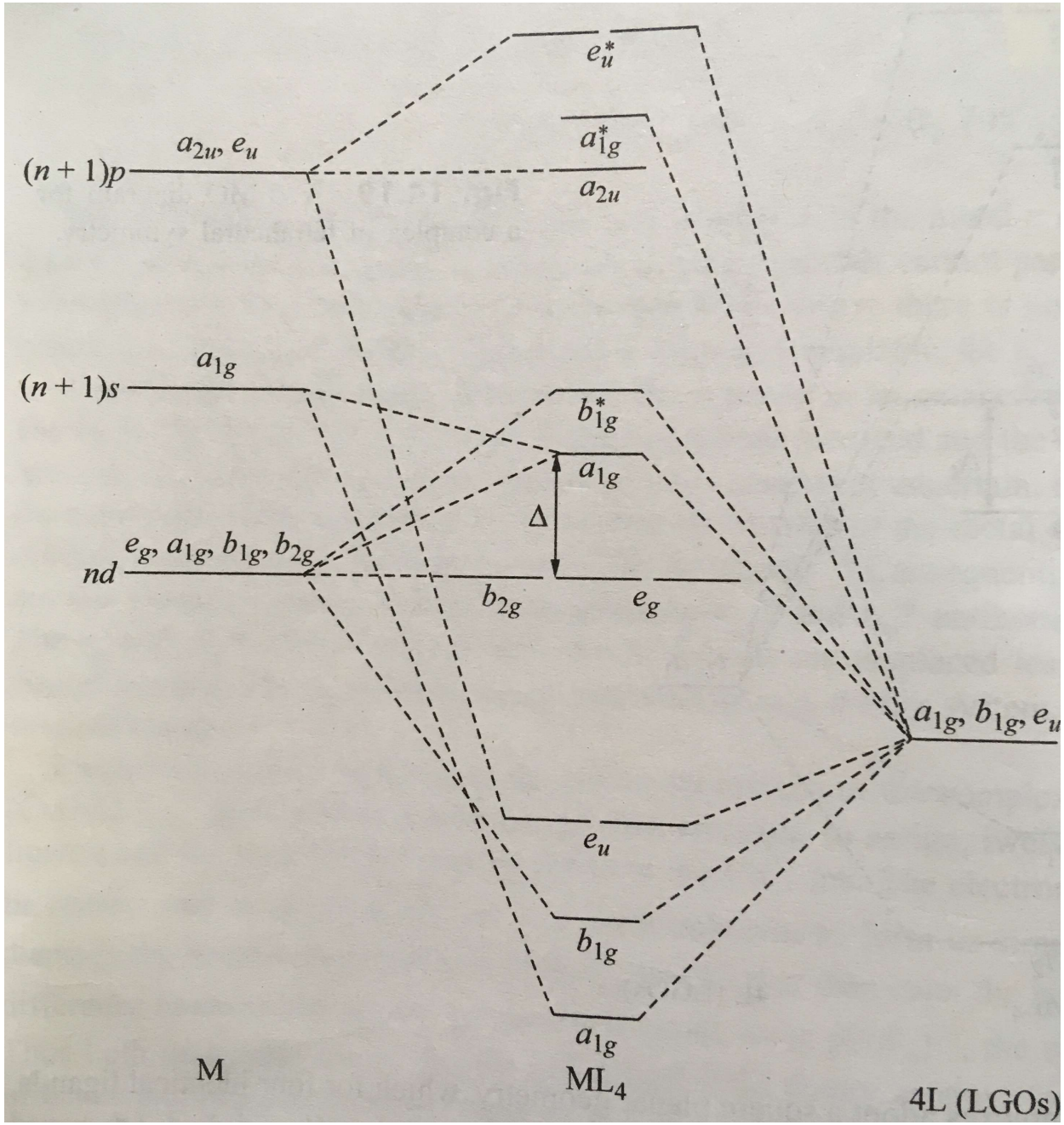


Fig. 11.20 A σ-bond r

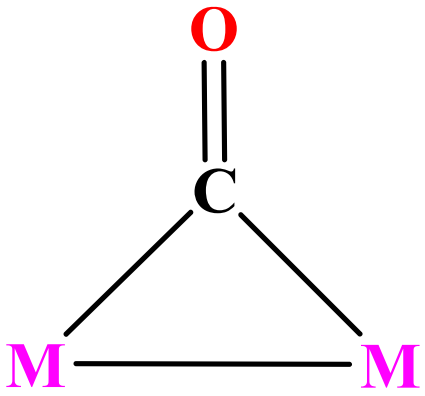
A σ MO diagram for a complex of sq. planar symmetry



Bonding modes of CO

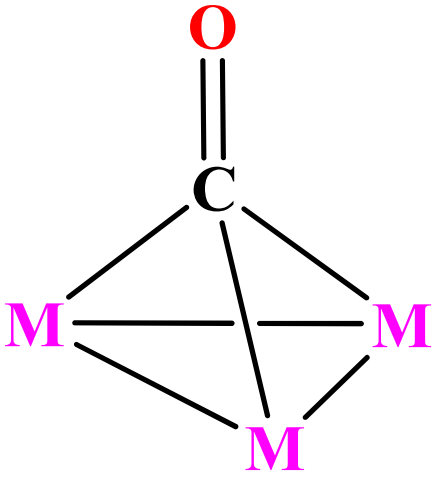
terminal

ν_{CO} = 2120-1850 cm^{-1}



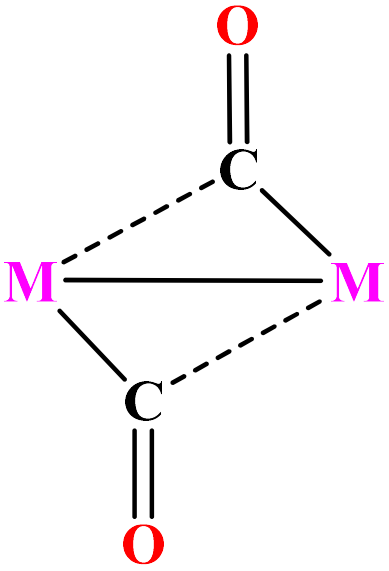
bridging μ_2

ν_{CO} = 1850-1700 cm^{-1}

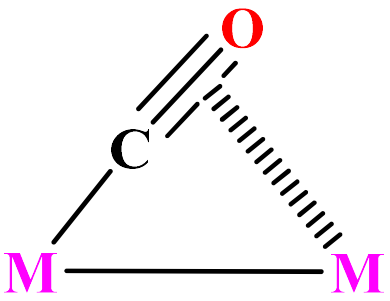


bridging μ_3

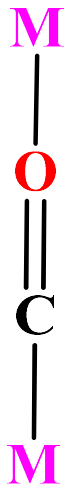
ν_{CO} = 1730-1620 cm^{-1}



Semi-bridging

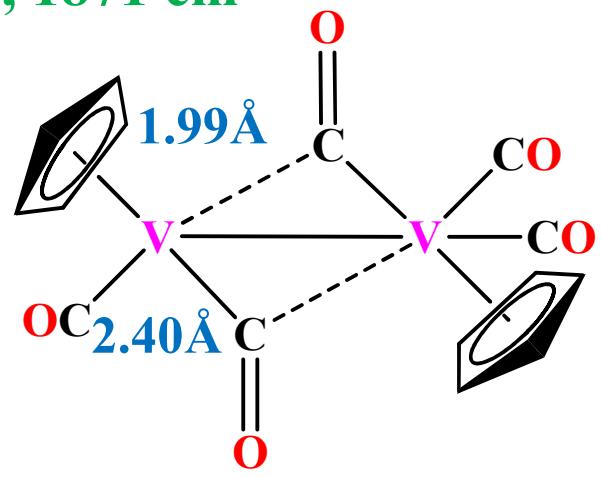


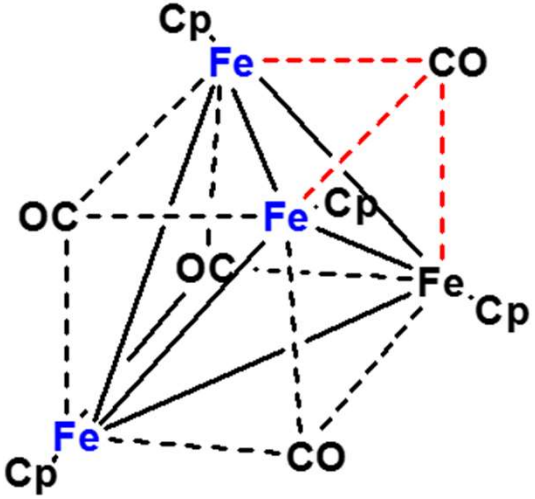
σ/π asymmetric bridge



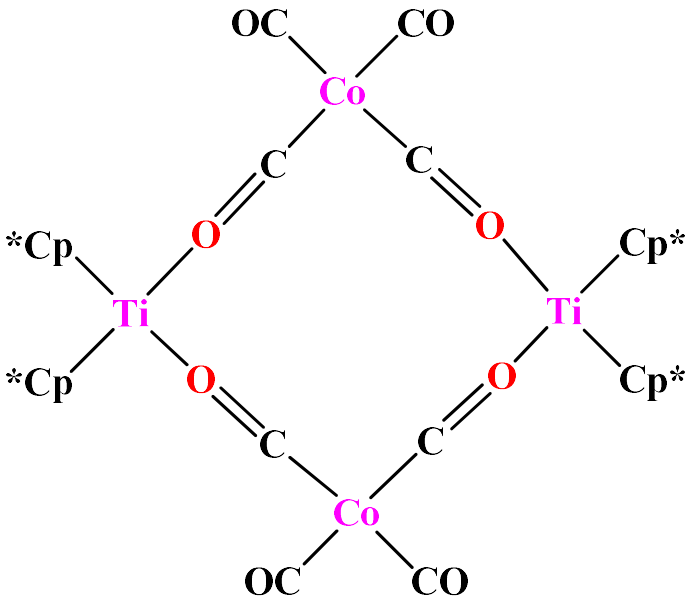
Iso-carbonyl coordination

ν_{CO} = 1832, 1871 cm^{-1}

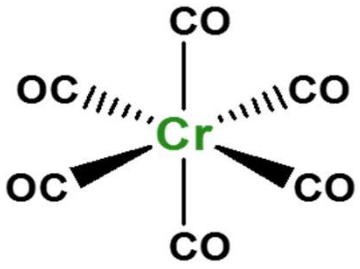




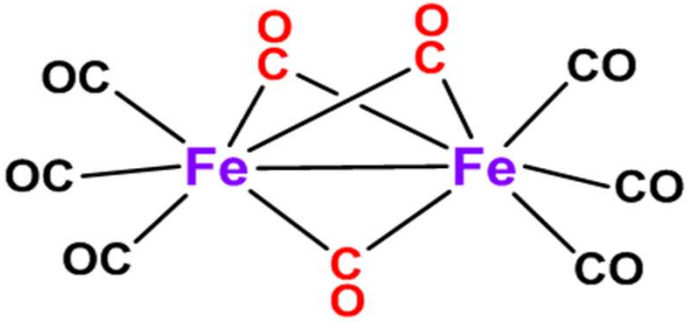
1620 cm-1



ν_{CO} = 1835 cm^{-1}

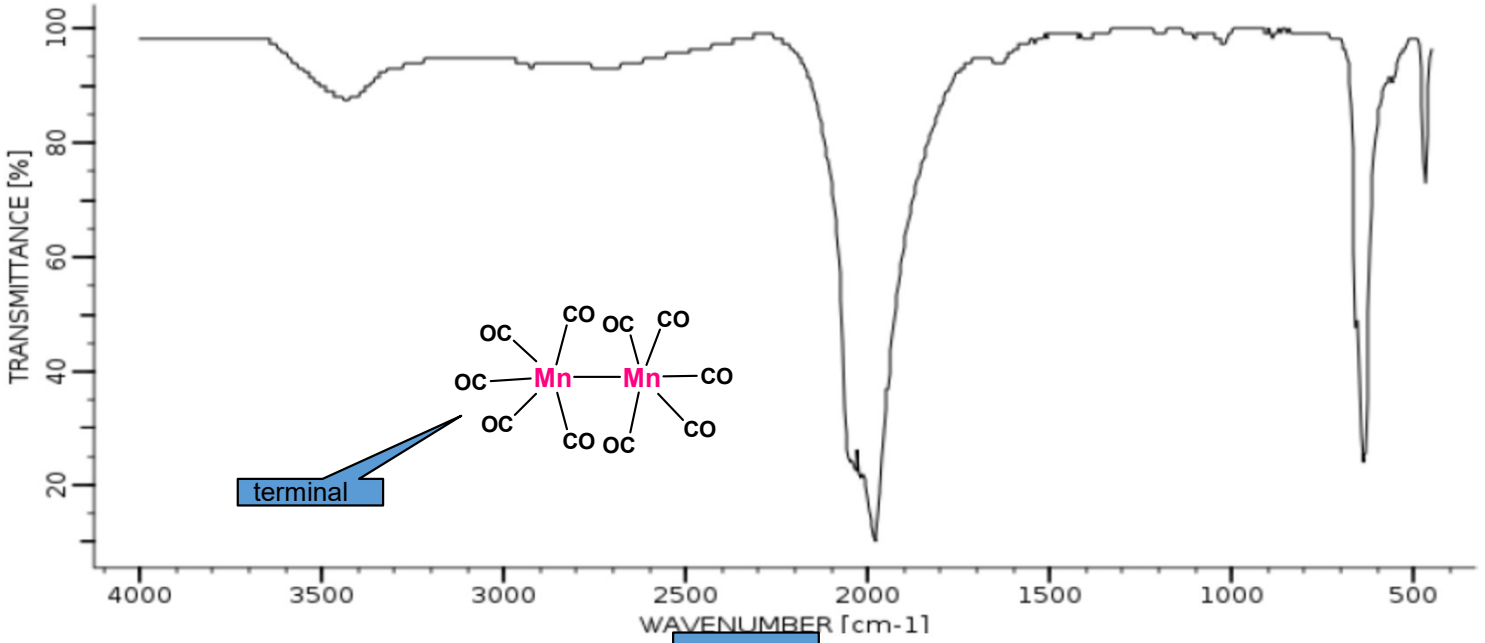


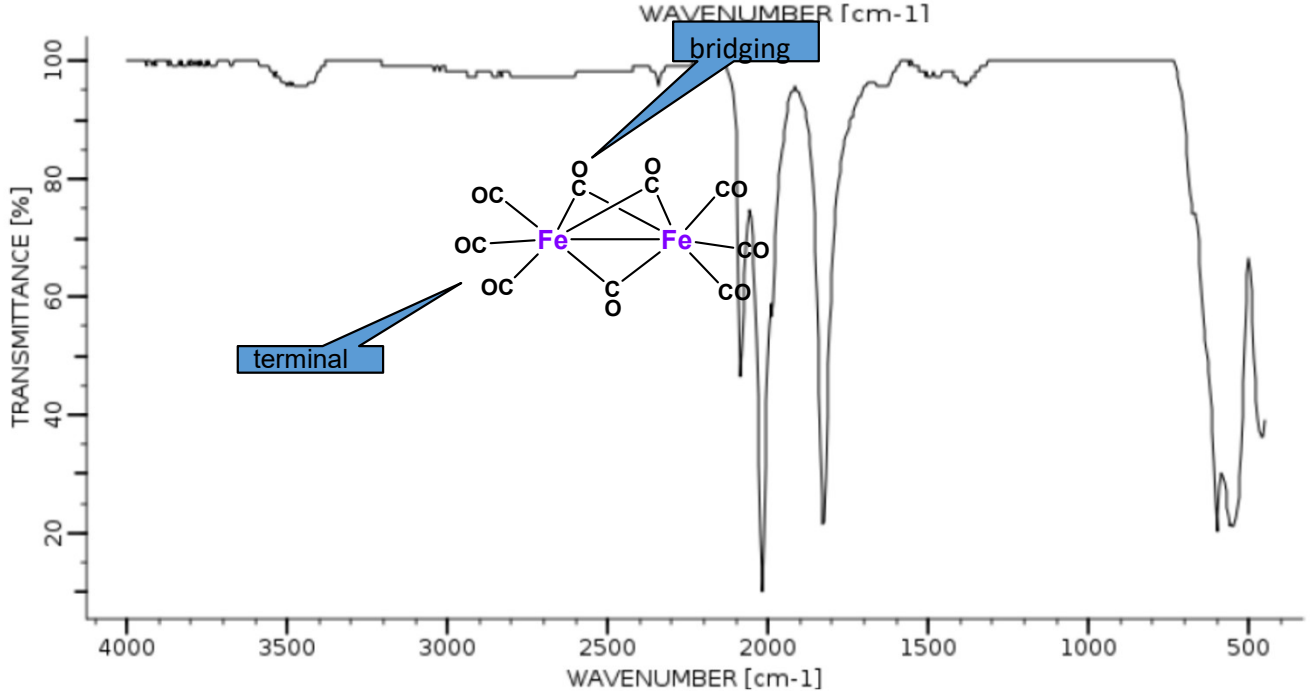
2000 cm-1



2018, 1826 cm-1

Infrared Spectroscopy- Spectra of Metal Carbonyls





- Bridging or terminal COs are identified from the **range** at which the band appears

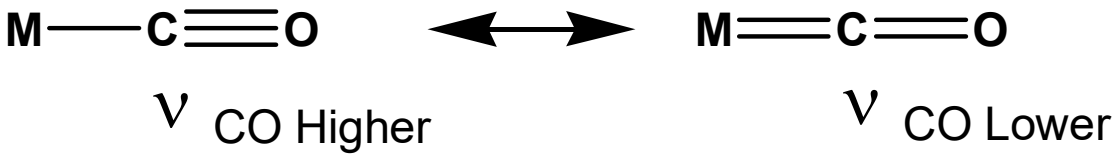
Factors which affect ν_{CO} stretching frequencies

Variation in ν_{CO} (cm^{-1}) of the first row transition metal carbonyls		
	free CO - 2143	
$Ni(CO)_4$ 2057		
$Co(CO)_4^-$ 1890		$Co_2(CO)_8$ 2044
$[Fe(CO)_4]^{2-}$ 1815	$Fe_2(CO)_9$ 2018, 1826	$Fe(CO)_5$ 2030
$[Mn(CO)_4]^{3-}$ 1600,1790	$Mn(CO)_6^+$ 2098	$Mn_2(CO)_{10}$ 2013
$[Cr(CO)_4]^{4-}$ 1462,1657		$Cr(CO)_6$ 2000
	$V(CO)_6^-$ 1860	$V(CO)_6$ 1976
	$Ti(CO)_6^{2-}$ 1747	

1. Charge on the metal
2. Effect of other ligands

- As the electron density on a metal centre increases, more π-backbonding to the **CO ligand(s)** takes place.
- This weakens the **C–O** bond further as more electron density is pumped into the **empty π* anti-bonding carbonyl orbital**.
- This increases the **M–C** bond order and reduces the **C-O** bond order.
- That is, the resonance structure M=C=O becomes more dominant.

More back bonding



ν CO Higher

ν CO Lower

Exercises

Q1: Account for the following observations

A) $V(CO)_6^-$ 1860 cm^{-1}, $V(CO)_6$1976 cm^{-1}

B) $[Mn(CO)_4]^{3-}$ 1600 cm^{-1}, 1790 cm^{-1}, $Mn(CO)_6^+$ 2098 cm^{-1}, $Mn_2(CO)_{10}$ 2013 cm^{-1}

C) $[Fe(CO)_4]^{2-}$ 1815 cm^{-1}, $Fe(CO)_5$ 2030 cm^{-1}

D) $Co_2(CO)_8$ 2044 cm^{-1}, $Co(CO)_4^-$ 1890 cm^{-1}

E) Free CO - 2143 cm^{-1}, $Ni(CO)_4$ 2057 cm^{-1}, $V(CO)_6$1976 cm^{-1}, $Fe(CO)_5$ 2030 cm^{-1}

F) $Mn_2(CO)_{10}$ 2013 cm^{-1}, $Co_2(CO)_8$ 2044 cm^{-1}

Q2: Predict the number of M-M bonds in the following

a) $(\mu\text{-}Cl)_2Rh_2(CO)_4$, b) Co_2CO_8,

Q3: What are the cases where the 18 electron rule is not valid?

Q4: Explain using Molecular Orbital Theory, how CN^-, CO and PPh_3 give rise to low spin complexes