

# Lecture Subset TM Complexes

Ligands and Bonding and Electron Counting in Organo-Transition Metal Compounds

Stable electronic configurations: MO Energy Level Diagrams Reviewed  
Electron count preference  
Electron count and Oxidation States

- ◆ Stable electronic configurations: MO Energy Level Diagrams Reviewed
- ◆ Electron count preference
- ◆ Electron count and Oxidation States
- ◆ Ligands
  - Carbon Monoxide
  - Phosphines
  - Cyclopentadienide and arenes
  - Hydrides and dihydrogen

# Classification of Ligands: II

## The L, X, Z approach

Malcolm Green : The CBC Method for Covalent Bond Classification used extensively in organometallic chemistry.

- L** ligands are derived from charge-neutral precursors:  $\text{NH}_3$ , amines, N-heterocycles such as pyridine,  $\text{PR}_3$ , CO, alkenes etc.
- X** ligands are derived from anionic precursors: halides, hydroxide, alkoxide alkyls—species that are one-electron neutral ligands, but two electron donors as anionic ligands. [EDTA](#)<sup>4-</sup> is classified as an  $\text{L}_2\text{X}_4$  ligand, features four anions and two neutral donor sites.  $\text{C}_5\text{H}_5$  is classified an  $\text{L}_2\text{X}$  ligand.
- Z** ligands are RARE. They accept two electrons **from** the metal center. They donate none. The “ligand” is a Lewis Acid that accepts electrons rather than the Lewis Bases of the X and L ligands that donate electrons.

## Electron Counts

*Electron counting and the 18-electron "Rule" (Guide is better. It is the "octet" rule for transition metals—but not as rigorously obeyed.)*

*2 Approaches => Same answer:*

**Ionic** (method A on next slide):

*# of electrons on Metal its oxidation state +  
# of electrons from donated pairs (X<sup>-</sup> is 2; L is 2)*

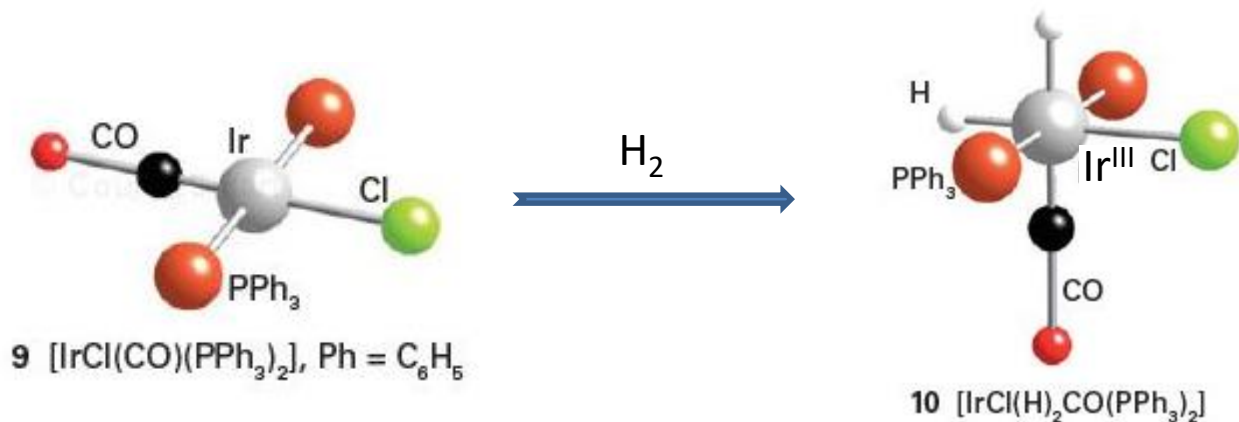
**Neutral:**

*# of electrons on Metal in ox. State of 0 +  
# of electrons from ligands (X is 1; L is 2)*

**Table 3-1** Electron Counting Schemes for Common Ligands

	<b>Ligand</b>	<b>Method A</b>	<b>Method B</b>
	H	2 (:H <sup>-</sup> )	1
	F, Cl, Br, I	2 (:X <sup>-</sup> )	1
Table listings of no. of electrons Donated by ligands.	OH	2 (:OH <sup>-</sup> )	1
	CN	2 (:C≡N: <sup>-</sup> )	1
	CH <sub>3</sub>	2 (:CH <sub>3</sub> <sup>-</sup> )	1
Advantage of Method A (the “ionic” method)	NO (bent M–N–O)	2 (:N=O: <sup>-</sup> )	1
Oxidation state of metal Automatically obtained)	<u>CO, PR<sub>3</sub></u>	2	2
	NH <sub>3</sub> , H <sub>2</sub> O	2	2
	=CRR' (carbene)	2	2
	H <sub>2</sub> C = CH <sub>2</sub>	2	2
	= O, = S	4 (:O <sup>2-</sup> , :S <sup>2-</sup> )	2
	NO (linear M–N–O)	2 (:N≡O: <sup>+</sup> )	3
	η <sup>3</sup> -C <sub>3</sub> H <sub>5</sub> (allyl)	2 (C <sub>3</sub> H <sub>5</sub> <sup>+</sup> )	3
	≡CR (carbyne)	3	3
	≡N	6 (N <sup>3-</sup> )	3
	η <sup>4</sup> -C <sub>4</sub> H <sub>6</sub> (butadiene)	4	4
Illustration from page 57	<u>η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub></u> (cyclopentadienyl)	6 (C <sub>5</sub> H <sub>5</sub> <sup>-</sup> )	5
	η <sup>6</sup> -C <sub>6</sub> H <sub>6</sub> (benzene)	6	6
	η <sup>7</sup> -C <sub>7</sub> H <sub>7</sub> (tropylium ion)	6 (C <sub>7</sub> H <sub>7</sub> <sup>+</sup> )	7

Oxidative addition of  $\text{H}_2$  to chloro carbonyl bis triphenylphosphine Iridium(I) yields Chloro-dihydrido-carbonyl bis-triphenylphosphine Iridium(III). Note the neutral precursor,  $\text{H}_2$ , becomes two  $\text{X}^-$  ligands once added to Ir.



An  $\text{ML}_3\text{X}$  complex

An  $\text{ML}_3\text{X}_3$  complex

### Electron counting: Ionic method

Electron count: 16 e

$\text{Ir(I)} \text{ d}^8 = 8 \text{ e}$

L ligands:  $2 \times (2) + 2 = 6$

$\text{X}^-$  ligand: 2

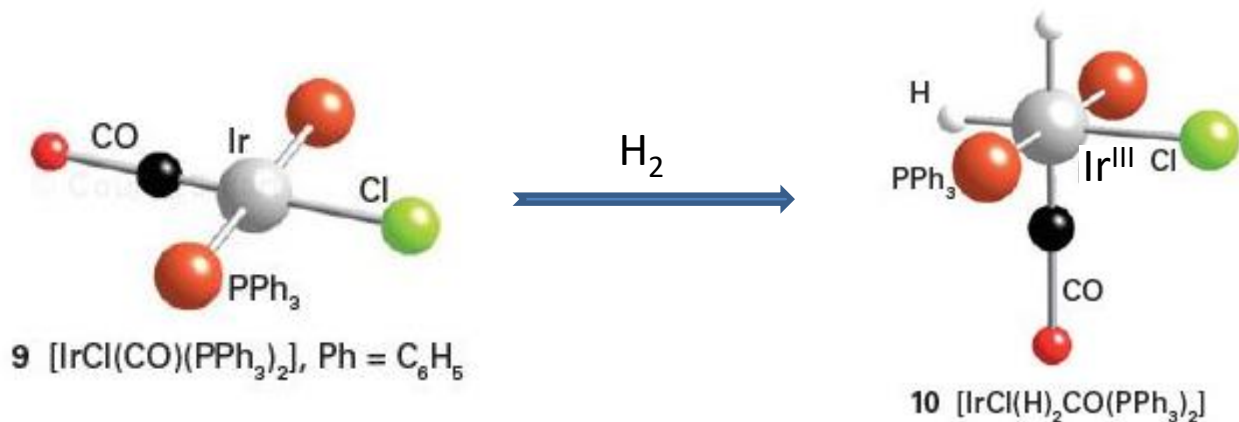
18 e

$\text{Ir(III)} \text{ d}^6 = 6 \text{ e}$

3 L ligands:  $3 \times 2 = 6$

3  $\text{X}^-$  ligands:  $3 \times 2 = 6$

Oxidative addition of  $\text{H}_2$  to chloro carbonyl bis triphenylphosphine Iridium(I) yields Chloro-dihydrido-carbonyl bis-triphenylphosphine Iridium(III). Note the neutral precursor,  $\text{H}_2$ , becomes two  $\text{X}^-$  ligands once added to Ir.



An  $\text{ML}_3\text{X}$  complex

An  $\text{ML}_3\text{X}_3$  complex

## Electron counting: Neutral method

Electron count: 16 e

$\text{Ir}(0) d^9 = 9 e$

L ligands:  $2 \times (2) + 2 = 6$

X ligand: 1

18 e

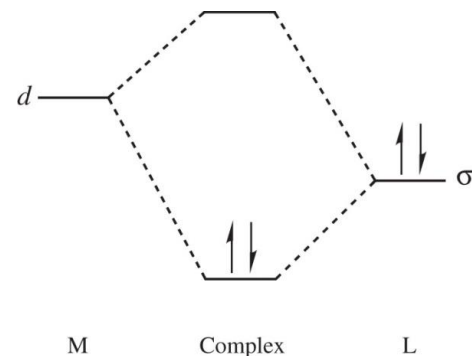
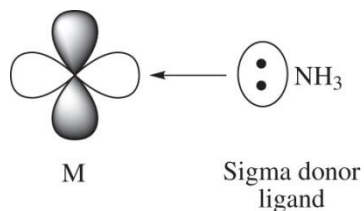
$\text{Ir}(0) d^9 = 9 e$

3 L ligands:  $3 \times 2 = 6$

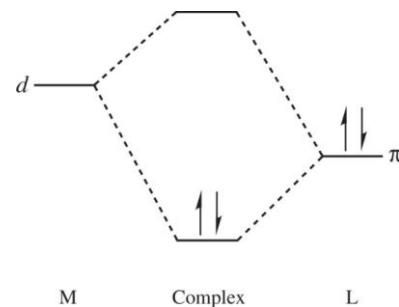
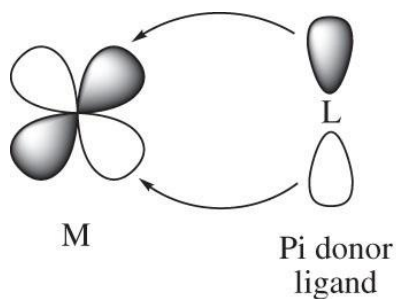
3 X ligands:  $3 \times 1 = 3$

# Types of ligands: $\sigma$ -donor, $\pi$ -donating and $\pi$ -accepting

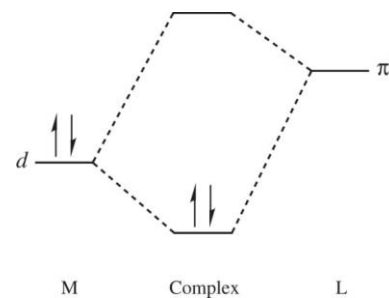
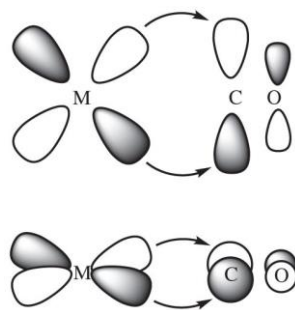
$\sigma$ -donor



$\pi$ -donor



$\pi$ -accepting



**Table 3-2** Examples of Donor and Acceptor Ligands.

$\sigma$ Donor	$\pi$ Donor <sup>a</sup>	$\pi$ Acceptor <sup>a</sup>
NH <sub>3</sub>	OH <sup>-</sup>	CO
H <sub>2</sub> O	Cl <sup>-</sup>	CN <sup>-</sup>
H <sup>-</sup>	RCO <sub>2</sub> <sup>-</sup>	PR <sub>3</sub>

<sup>a</sup>These ligands also act as  $\sigma$  donors.

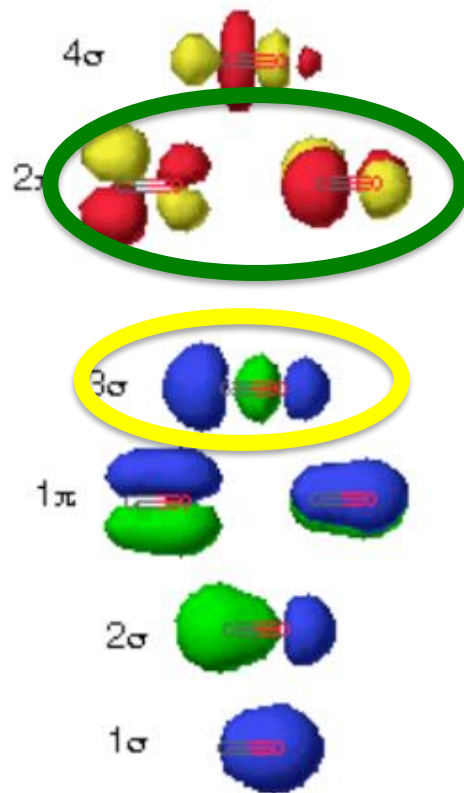
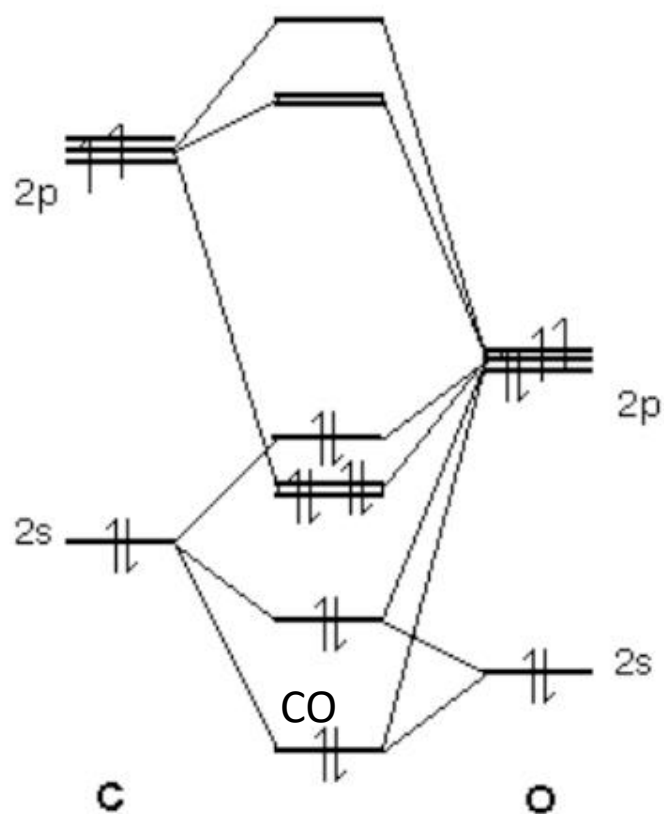
***Other  $\pi$  acceptors: olefins, NO<sup>+</sup>  
and H<sub>2</sub> !!!***

Are cyanide complexes  
Considered to be  
organometallics?

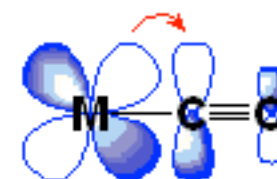


The importance of CO—could be a full lecture/course!

Empty pi-accepting orbitals as on CO: Pi back-bonding!



electron donation  
 $\sigma$  bond

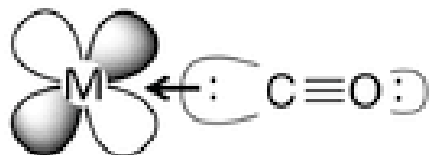


electron donation  
 $\pi$  backbonding

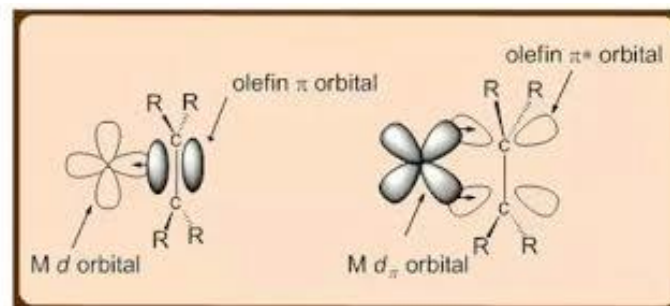
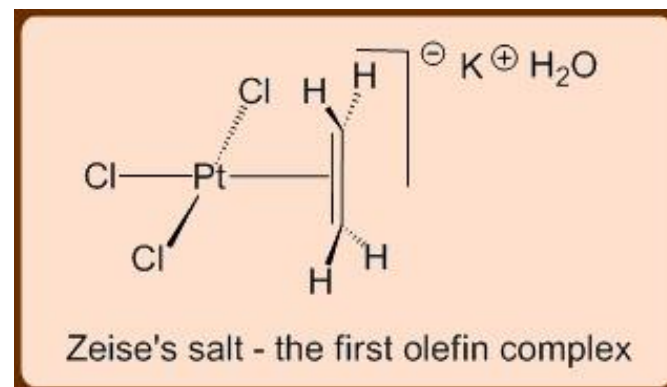
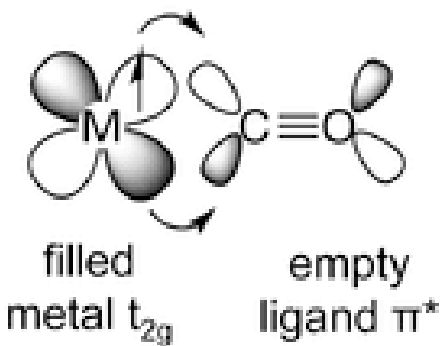
$\nu(\text{CO})$  is IR diagnostic of amount of pi-backbonding



$\sigma$ -bonding:



$\pi$ -bonding:



Examples:  $\text{V}(\text{CO})_6$     $\text{Cr}(\text{CO})_6$     $\text{Fe}(\text{CO})_5$     $\text{Ni}(\text{CO})_4$

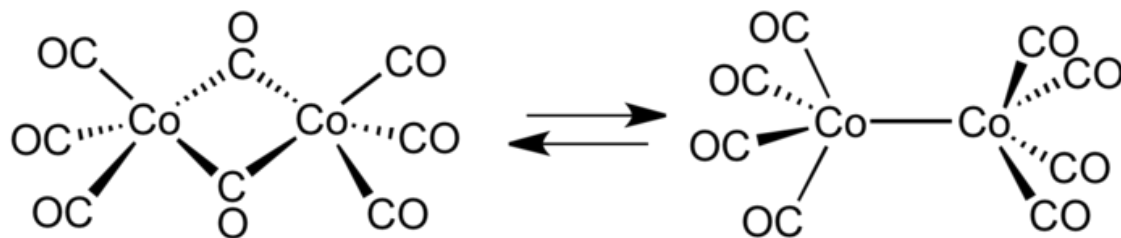
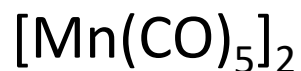
Electron counting:   17      18      18      18

$\text{PtCl}_3(\text{C}_2\text{H}_4)^-$

# Other 18-electron Metal Carbonyls

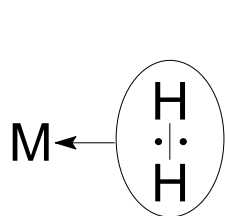
- $\text{V}(\text{CO})_6^-$
- $\text{Mn}(\text{CO})_6^+$
- $\text{Mn}(\text{CO})_6^-$
- $\text{Cr}(\text{CO})_6$
- $\text{Fe}(\text{CO})_5$
- $\text{Co}(\text{CO})_4^-$
- $\text{Ni}(\text{CO})_4$

Neutral forms with M-M bonds

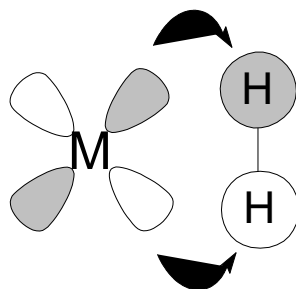


# The $\eta^2\text{-H}_2$ Complexes:

- Typically  $d^6$ , Oh structures of  $\text{Cr}^0$ ,  $\text{Mo}^0$ ,  $\text{W}^0$ ,  $\text{Fe}^{\text{II}}$ ,  $\text{Ru}^{\text{II}}$ ,  $\text{Ir}^{\text{III}}$ .
- Bonding: Delicate Balance Required for Stability



$\sigma$  - donor



$\sigma^*$  acceptor



$\text{M}^{2+}(\text{H}^-)_2$



Kubas, LANL

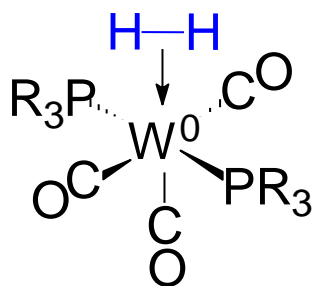


Morris, U. Toronto

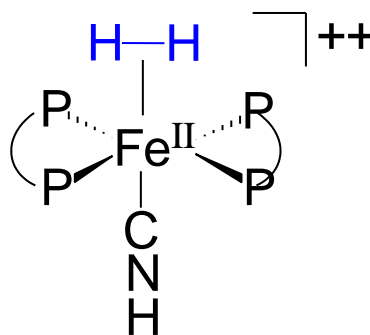


Crabtree, Yale

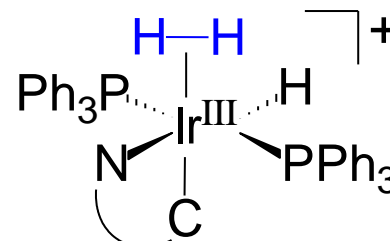
- Examples of  $\eta^2\text{-H}_2$  complexes



Kubas

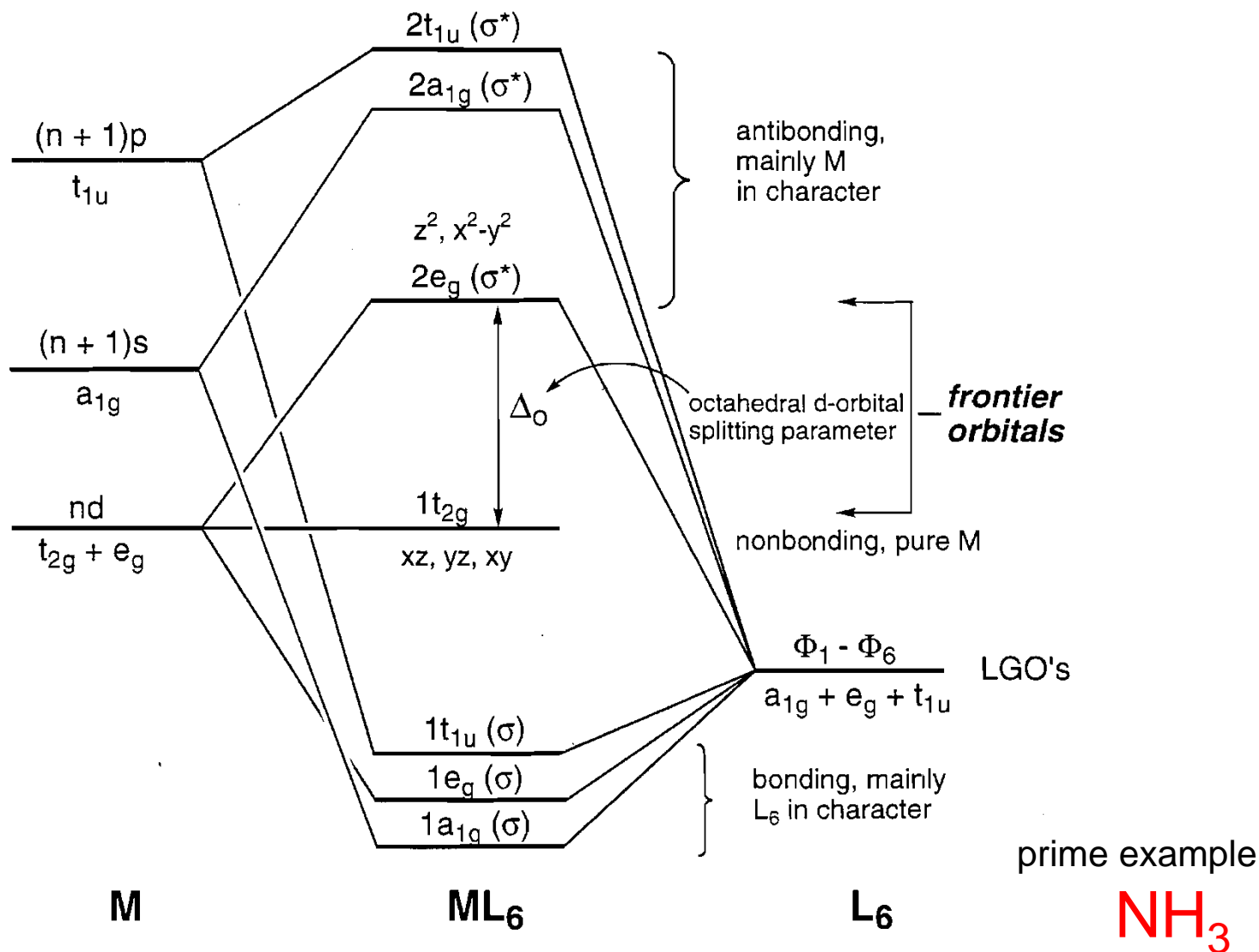


Morris



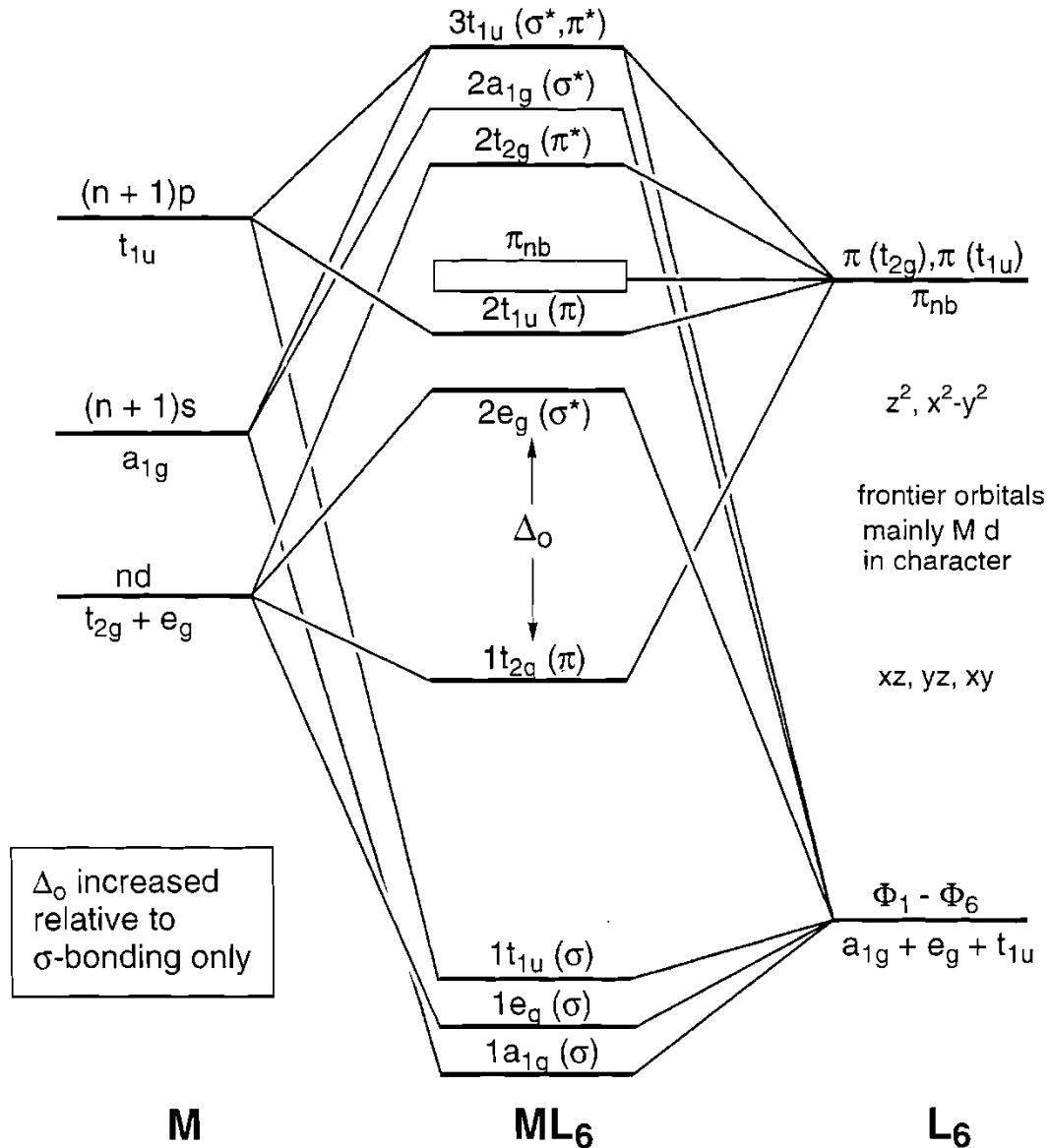
Crabtree

To explain magnetism and colors, need electronic configuration of the Transition Metal Complex: MO diagram for  $\sigma$ -donor ligands in octahedral complex



Case 2.  $L\pi$  orbitals vacant and less stable than  $d\pi$  orbitals  
(L is a  $\pi$ -acceptor)

A more accurate MO energy level diagram for  $\text{Cr}(\text{CO})_6$ .



Simplified MO energy level diagram for  $\text{Cr}(\text{CO})_6$ . Note the empty  $\pi^*$  orbitals. Only three are involved in overlap with metal d orbitals.

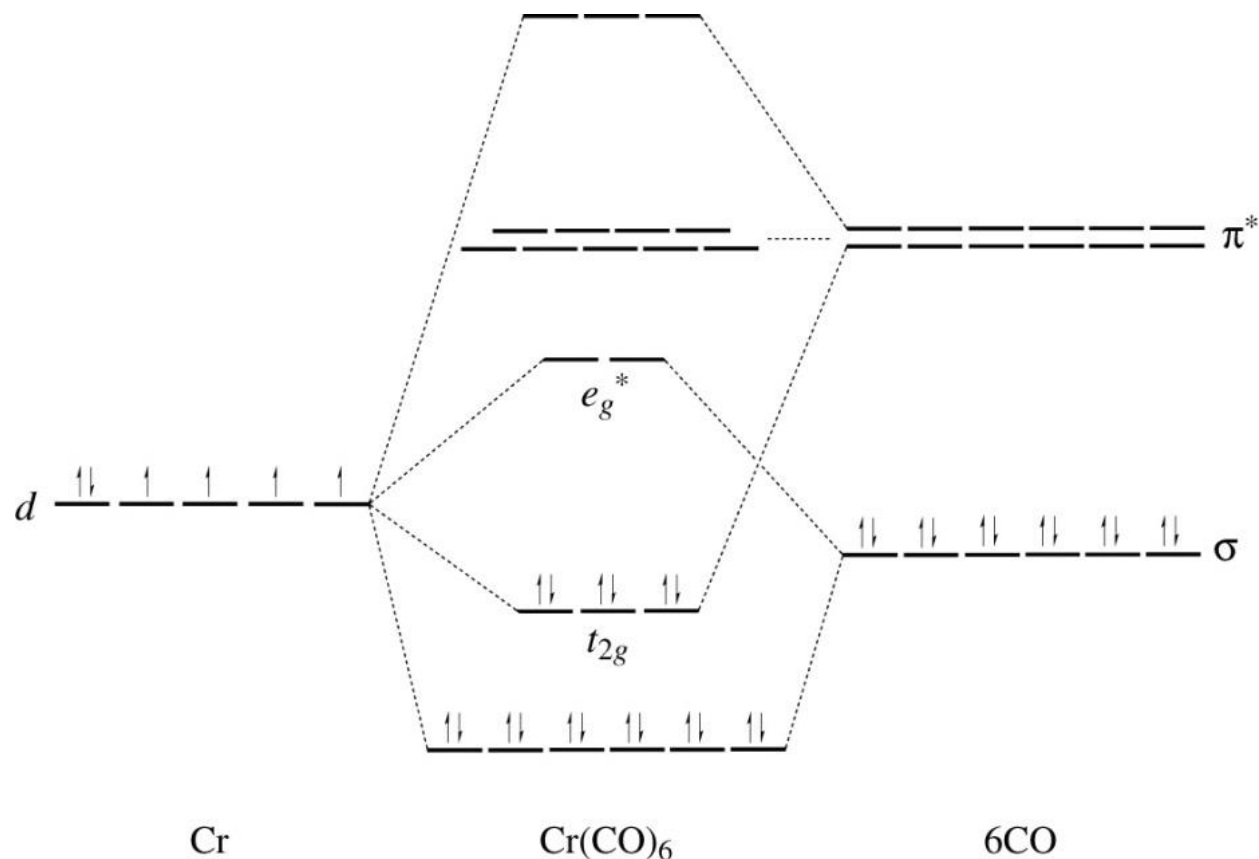
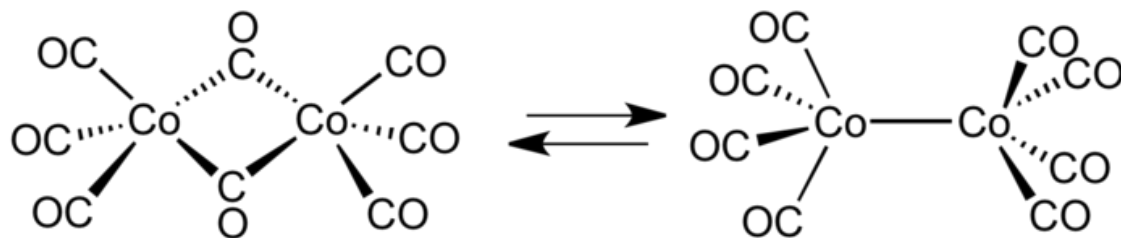
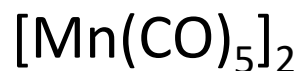


Figure 3-1 Molecular orbitals of  $\text{Cr}(\text{CO})_6$  (Only interactions between Ligand ( $\sigma$ - and  $\pi^*$ ) orbitals and metal d-orbitals are shown.)

# Other 18-electron Metal Carbonyls

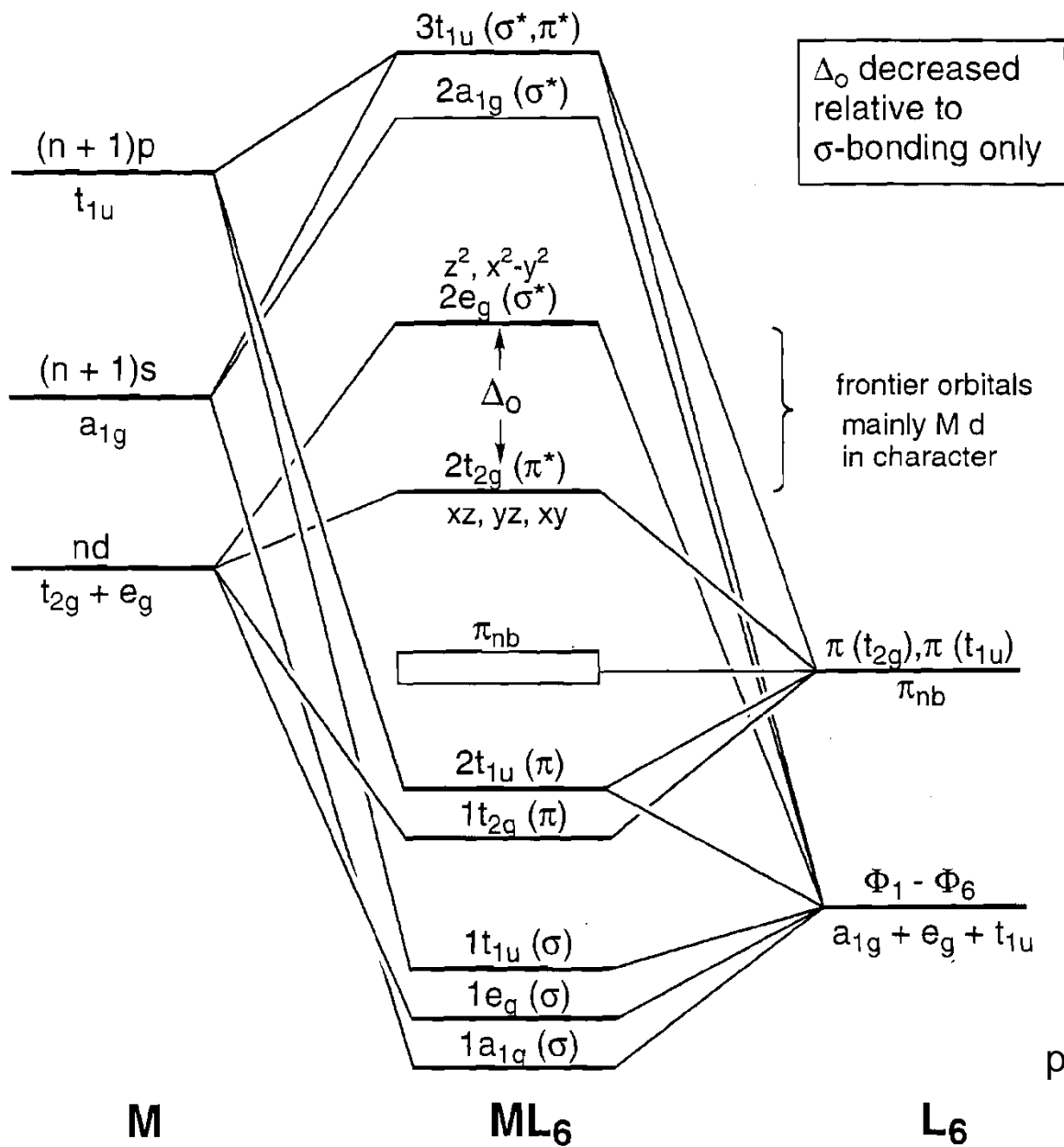
- $\text{V}(\text{CO})_6^-$
- $\text{Mn}(\text{CO})_6^+$
- $\text{Mn}(\text{CO})_6^-$
- $\text{Cr}(\text{CO})_6$
- $\text{Fe}(\text{CO})_5$
- $\text{Co}(\text{CO})_4^-$
- $\text{Ni}(\text{CO})_4$

Neutral forms with M-M bonds





## Modification for $\pi$ -Donor Ligands



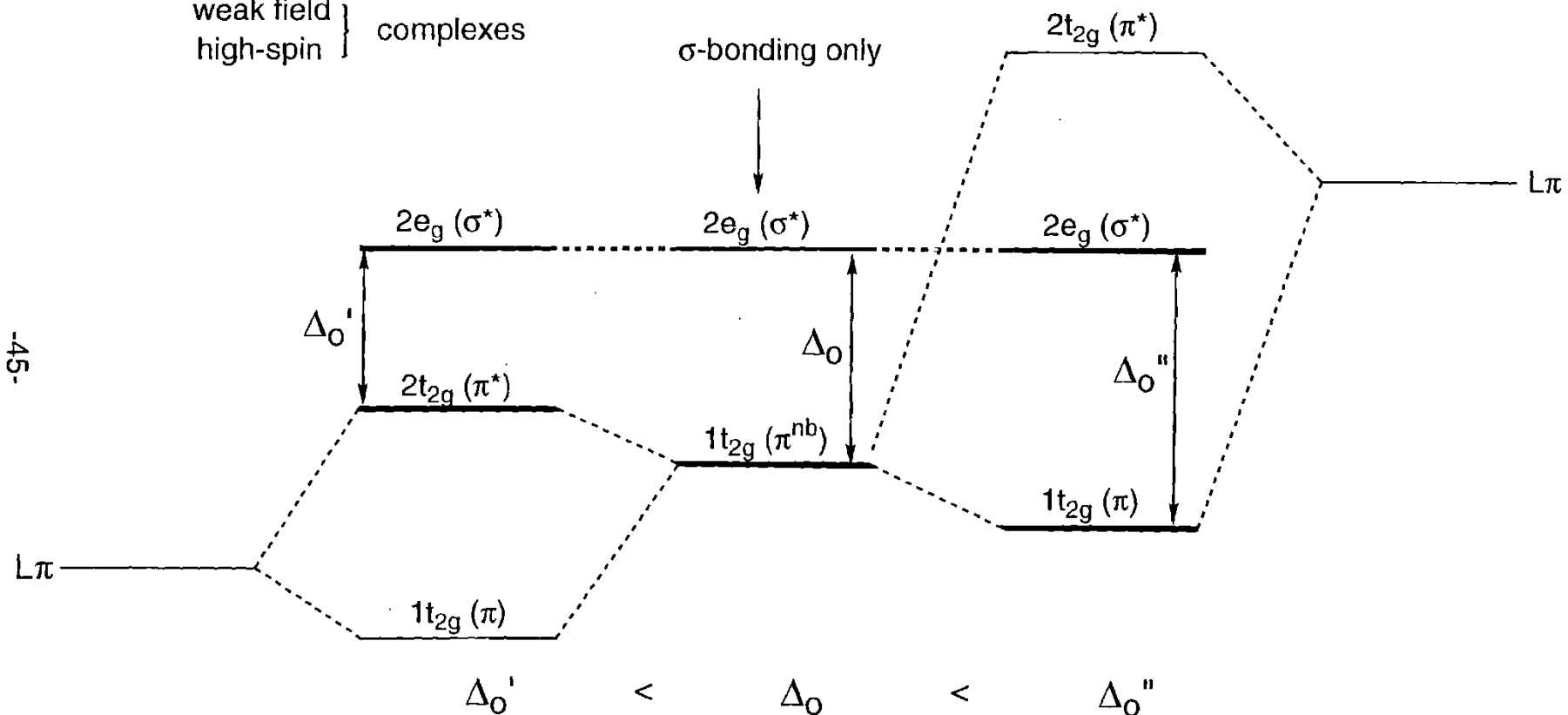
# Important Cases of d-Orbital Splittings in Octahedral Complexes

Case 1.  $L\pi$  orbitals filled and more stable than  $d\pi$  orbitals. L are  $\pi$ -donors.

— mainly M orbitals  
 — mainly L orbitals

Case 2.  $L\pi$  orbitals vacant and less stable than  $d\pi$  orbitals. L are  $\pi$ -acceptors.

weak field } complexes  
 high-spin }



$L_{\pi\text{-donor}} = F^-, Cl^-, Br^-, I^-, H_2O, OH^-,$   
 $RS^-, S^{2-}, NCS^-, NCO^-, \dots$

(virtually any ligand which, after forming  
 M-L  $\sigma$ -bonds, has lone pairs)

$L_{\sigma} = NR_3$

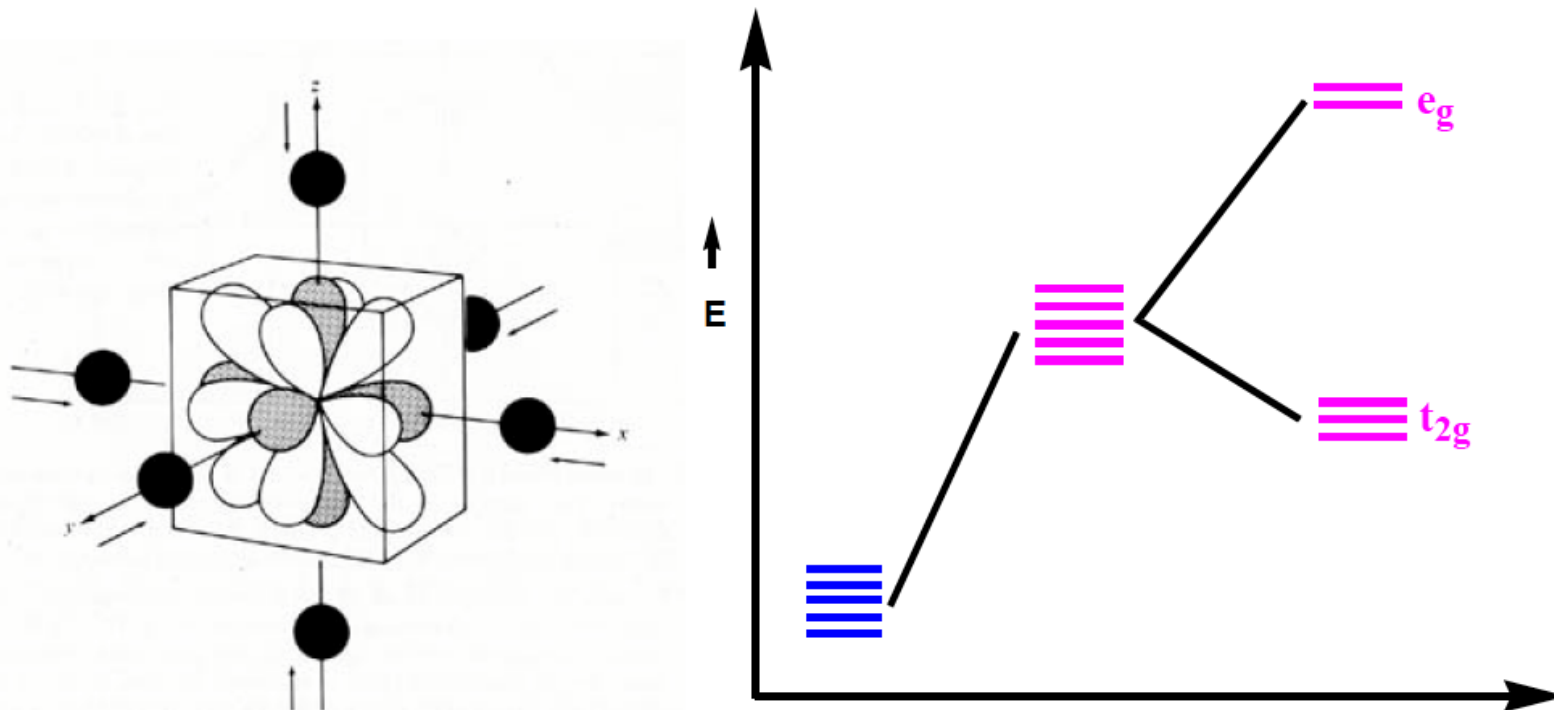
$PR_3$

$L_{\pi\text{-acceptor}} = CO, NO, CN^-, N_2, \text{bipy}, \text{phen},$   
 $RNC, C_5H_5^-, \text{>C=C<}, \text{—C≡C—}$

(virtually any ligand with vacant  
 $\pi^*$  MO's)

# Octahedral Field

• If rather than a spherical field, discrete point charges (ligands) are allowed to interact with the metal, the degeneracy of the d orbitals is removed (or, better said, lifted). The splitting of d orbital energies and its consequences are at the heart of crystal field theory.

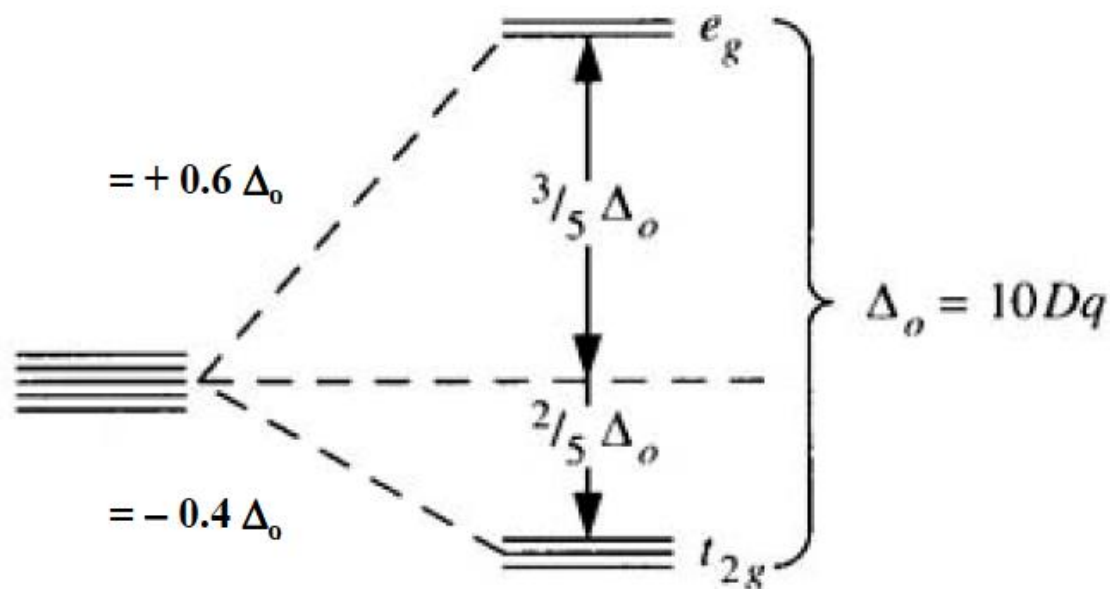


• Not all d orbitals will interact to the same extent with the six point charges located on the  $+x$ ,  $-x$ ,  $+y$ ,  $-y$ ,  $+z$  and  $-z$  axes respectively.

• The orbitals which lie along these axes (i.e.  $x^2-y^2$ ,  $z^2$ ) will be destabilized more than the orbitals which lie in-between the axes (i.e.  $xy$ ,  $xz$ ,  $yz$ ).

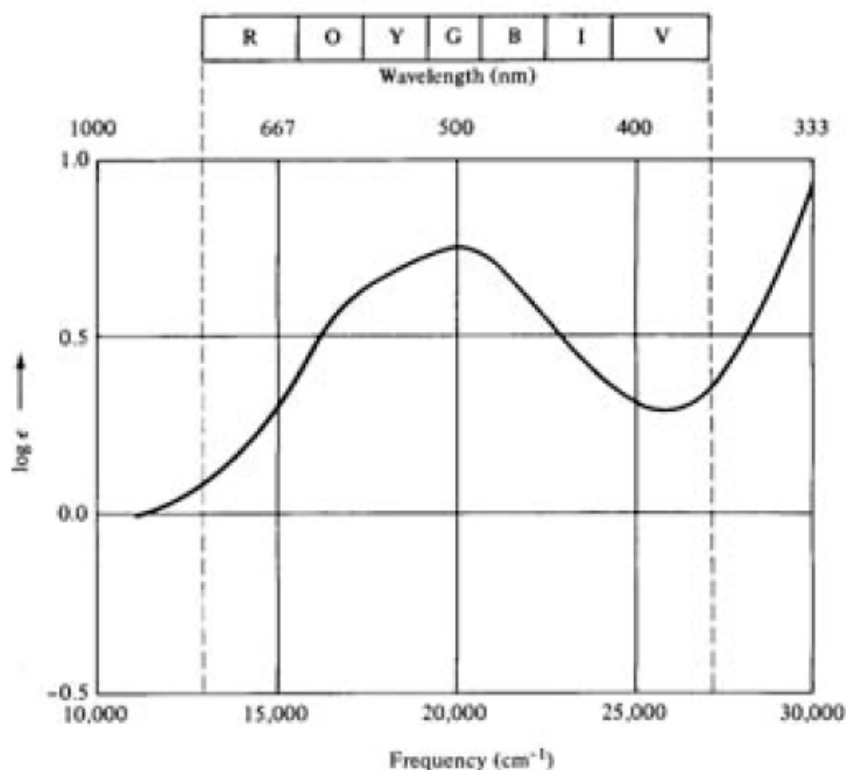
# CFT-Octahedral Complexes

- For the  $O_h$  point group, the  $x^2-y^2$ ,  $z^2$  orbitals belong to the  $E_g$  irreducible representation and  $xy$ ,  $xz$ ,  $yz$  belong to the  $T_{2g}$  representation.
- The extent to which these two sets of orbitals are split is denoted by  $\Delta_o$  or alternatively  $10Dq$ . As the **baricenter** must be conserved on going from a spherical field to an octahedral field, the  $t_{2g}$  set must be stabilized as much as the  $e_g$  set is destabilized.



# Illustration of CFSE

$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  : a  $d^1$  complex and the  $e^-$  occupies the lowest energy orbital, i.e. one of the three degenerate  $t_{2g}$  orbitals. The **purple colour** is a result of the absorption of light which results in the promotion of this  $t_{2g}$  electron into the  $e_g$  level.  $t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$

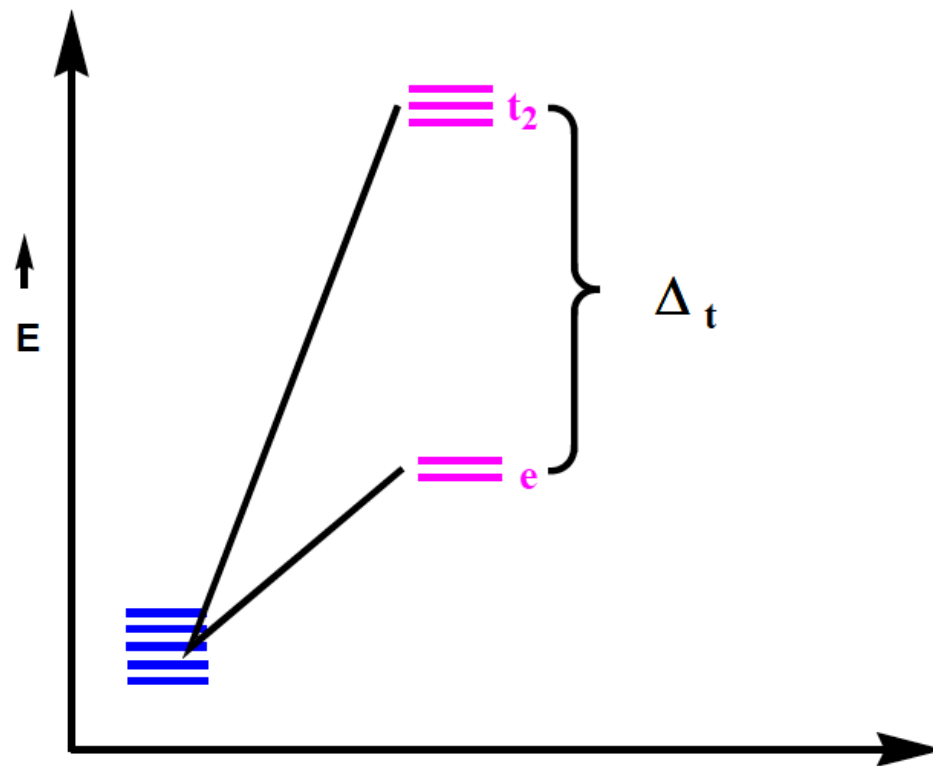
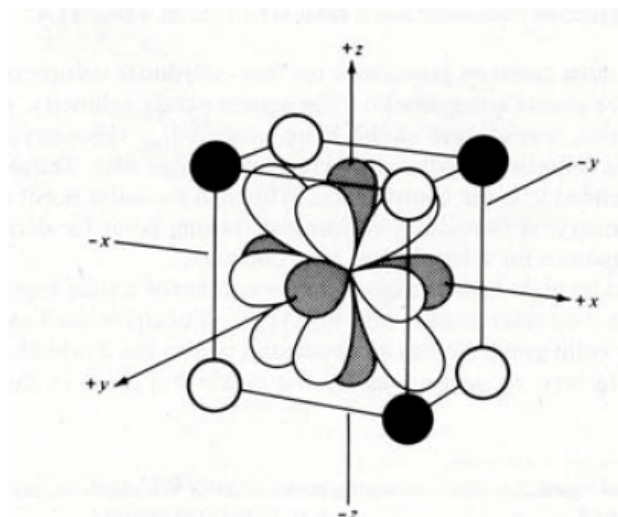


The UV-Vis absorption spectrum reveals that this transition occurs with a maximum at  $20300 \text{ cm}^{-1}$  which corresponds to  $\Delta_o$  243 kJ/mol.

( $1000 \text{ cm}^{-1} = 11.96 \text{ kJ/mol}$  or  
 $2.86 \text{ kcal/mol}$  or  
 $0.124 \text{ eV.}$ )

Typical  $\Delta_o$  values are of the same order of magnitude as the energy of a chemical bond.

# Tetrahedral Field



$$\Delta_t < \Delta_o$$

Other frontier molecular orbitals can be expected from Crystal Field splitting

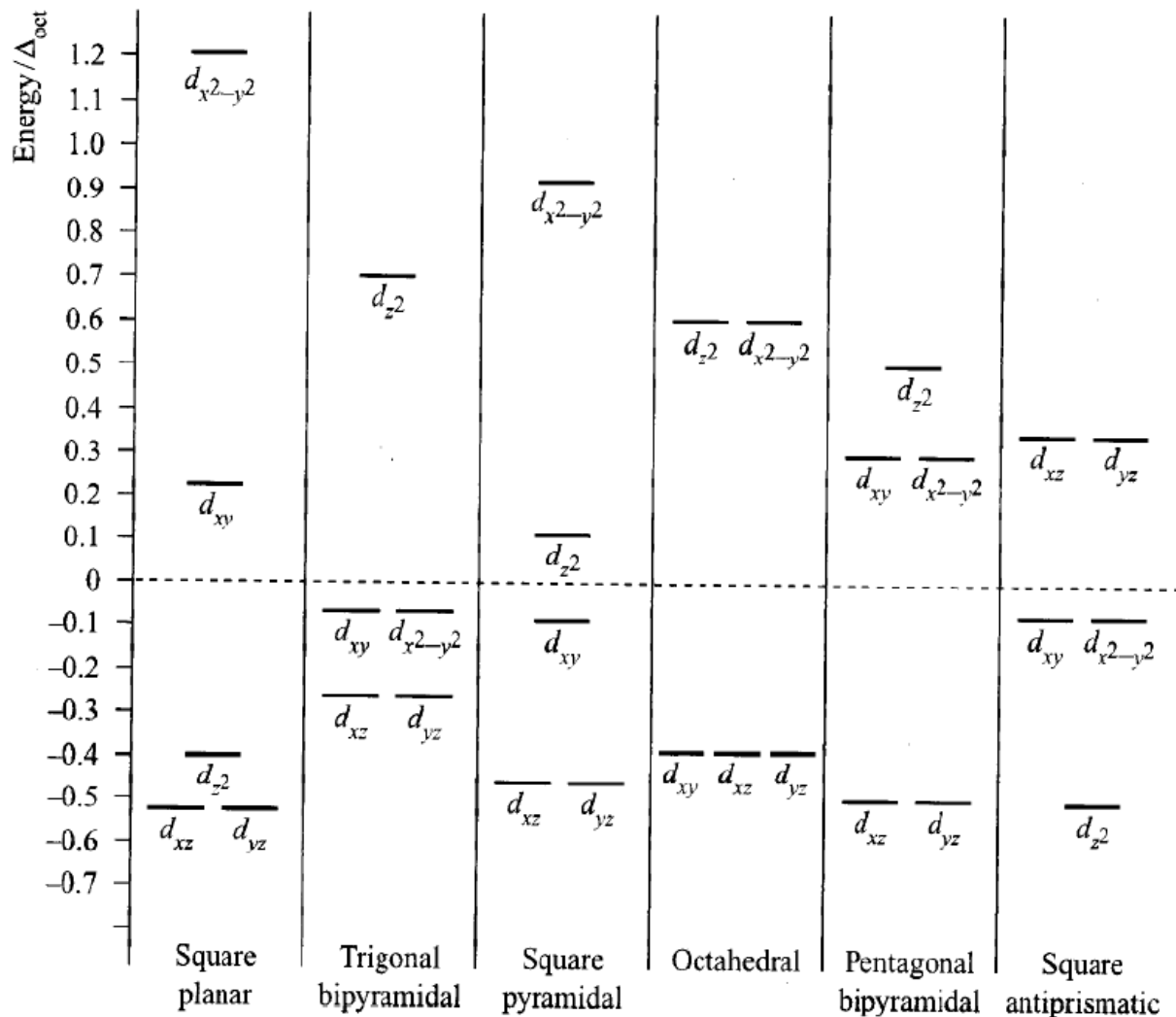
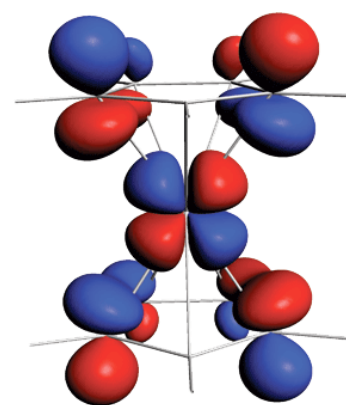
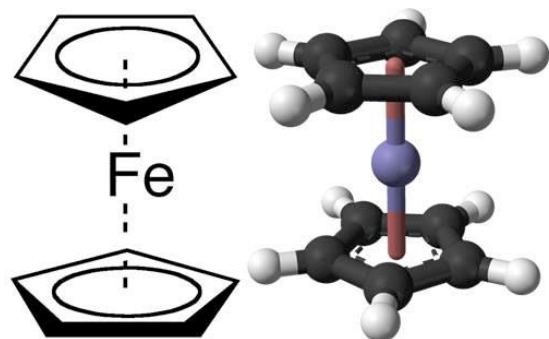


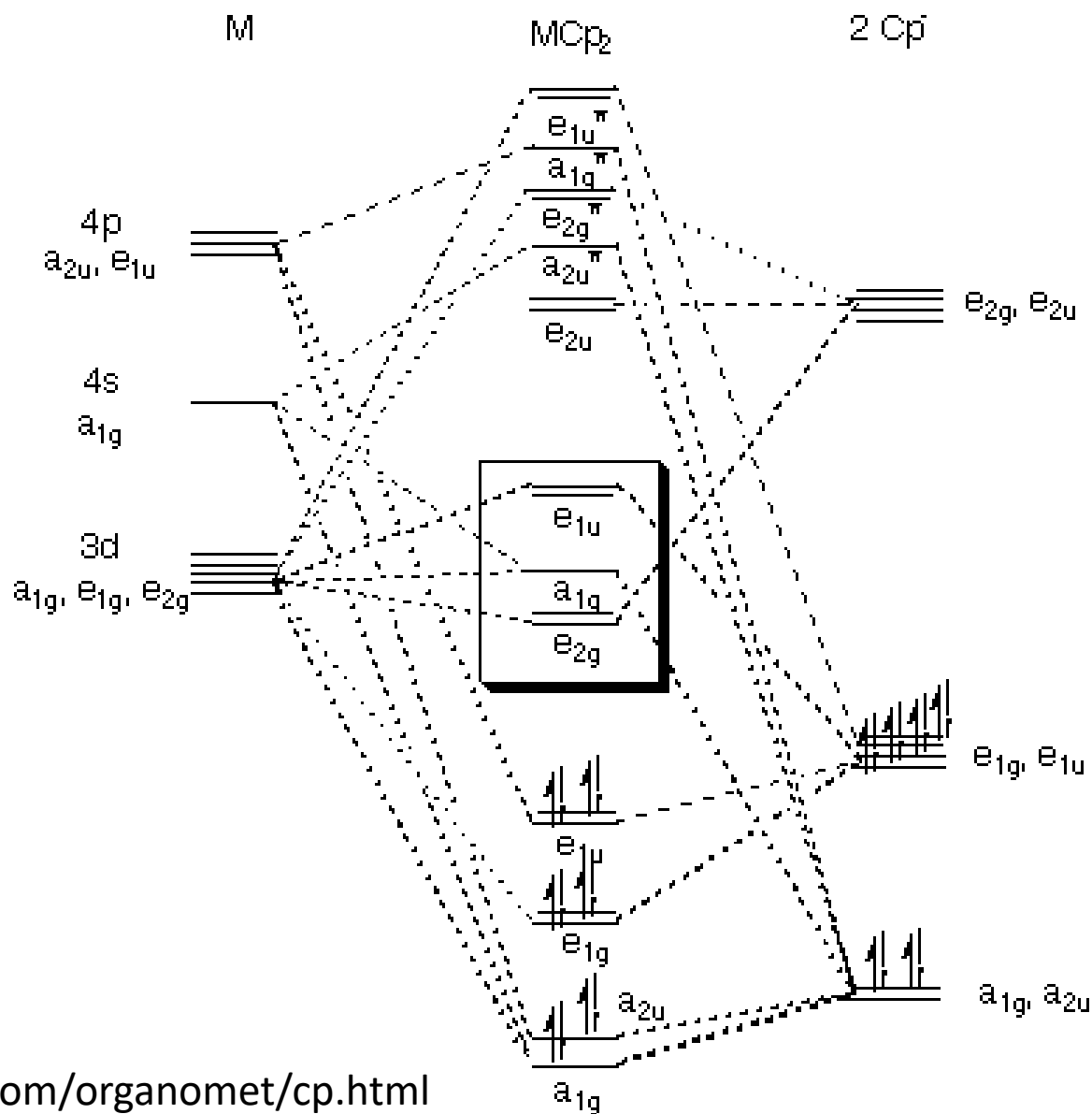
Figure 2 Crystal field splittings of d orbitals



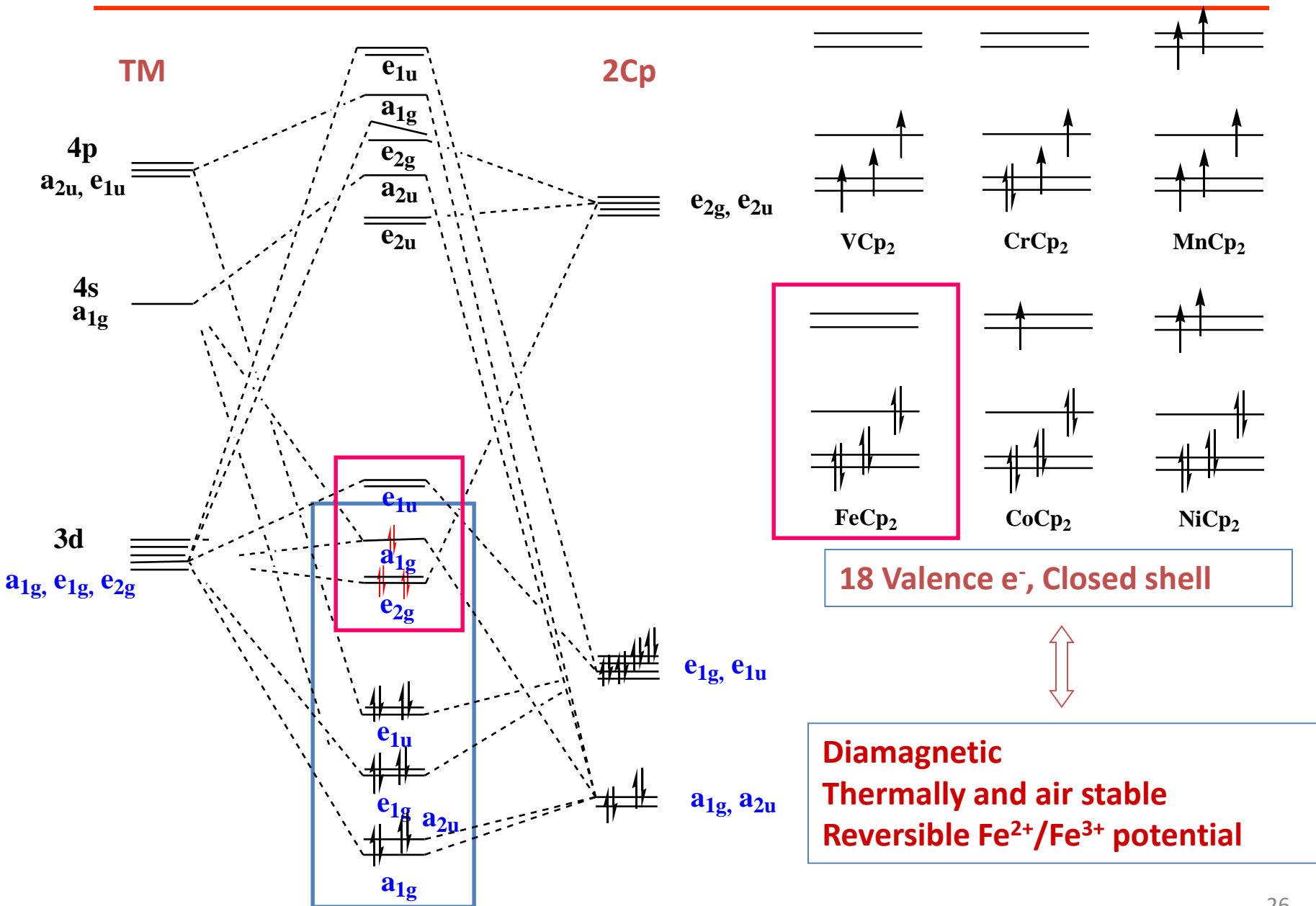
Questions/classwork

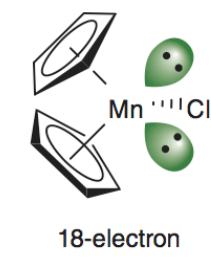
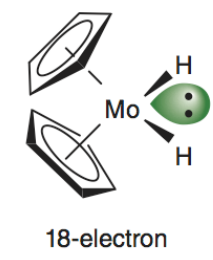
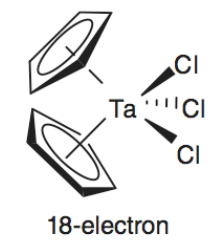
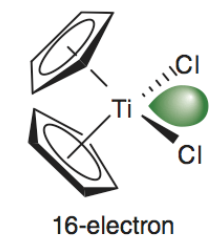
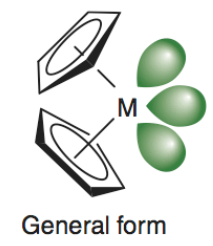
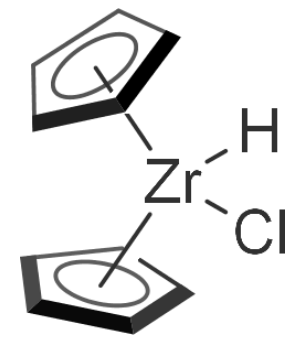
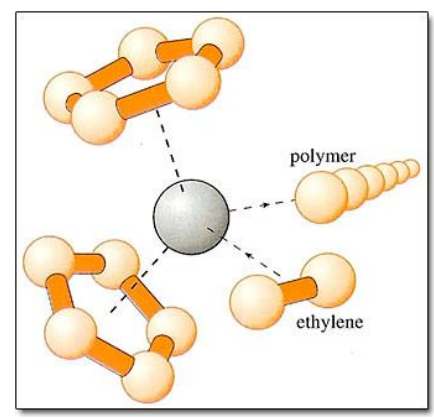
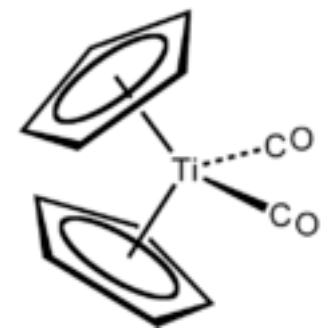
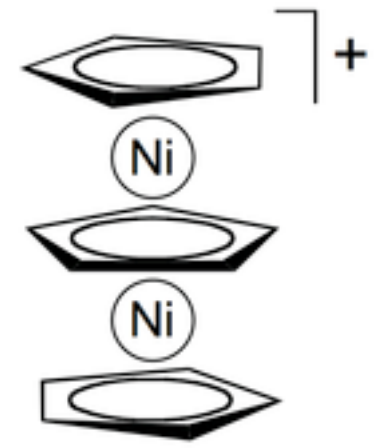
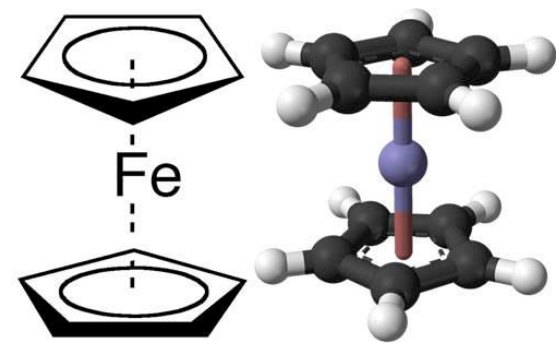
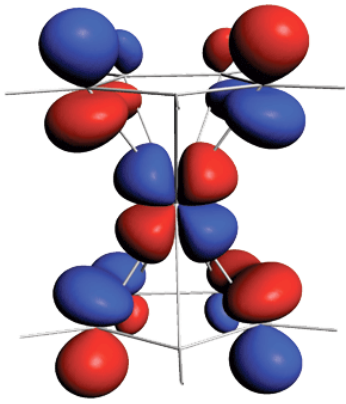


# MO Energy Level Diagram for ferrocene and related metallocenes



# Electronic structure and properties

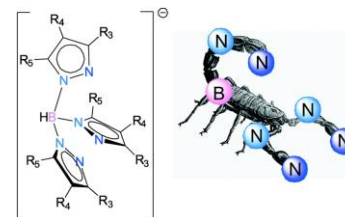
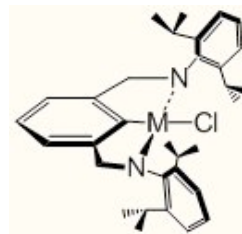
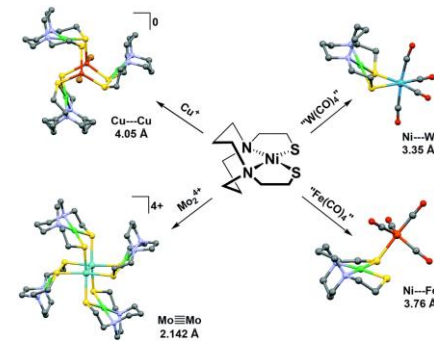




# Classification of Ligands: III

## Terminology and description of properties

- ❑ Strong Field/Weak Field Ligands
- ❑ Chelating Ligands and Denticity
  - ❖ Polydentate: bi-, tri-, tetra, penta-
  - ❖ Hexadentate, etc.
- ❑ Bridging Ligands
  - ❖ 4-electron bridge; 3 center, 4 electrons
  - ❖ 2-electron bridge; 3-center, 2 electrons
- ❑ Ambidentate Ligands
- ❑ Bulky Ligands
- ❑ Chiral Ligands
- ❑ Hemi-labile Ligands
- ❑ Non-innocent Ligands
- ❑ Spectator Ligands
- ❑ Designer Ligands
  - ◆ Pincer
  - ◆ Scorpionate
  - ◆ Metallodithiolates



So, how do we mix and match these ligands and metals with their various oxidation states to get stable molecules?

1. Hard/Soft Acid Base approach to stability

2. Knowledge of preferred coordination numbers and geometries

The Chemical Bond:

- a) The sharing of an electron pair between two atoms.
- b) A mixture of electrostatic and covalent interactions.

*Together these interactions lead to stable molecules.*

*Now, How about those colors and the magnetism in Werner type complexes?*

*Where are the electrons? Show me the electrons!!*

**Color:** *Electronic transitions due to energy levels whose gaps are in the visible range of the electromagnetic spectrum.*

**Magnetism:** *partially filled orbitals, unpaired electrons.*

*high spin: maximum no. of d electrons*

*unpaired*

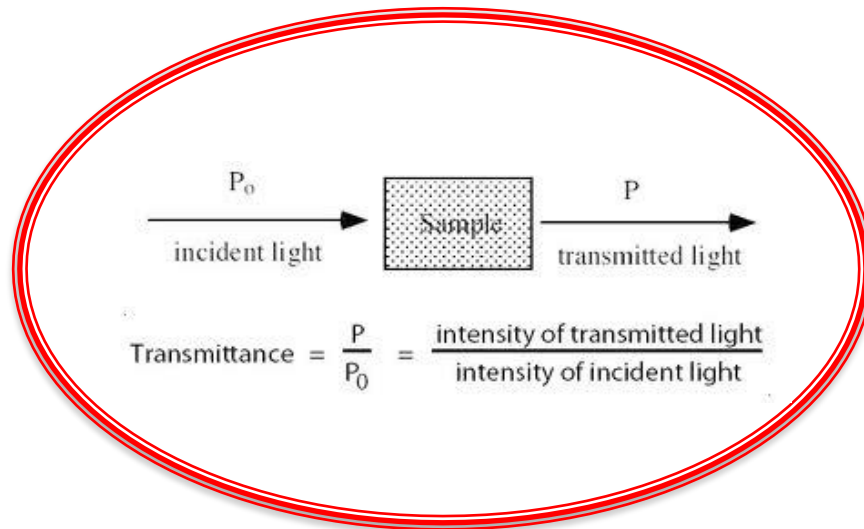
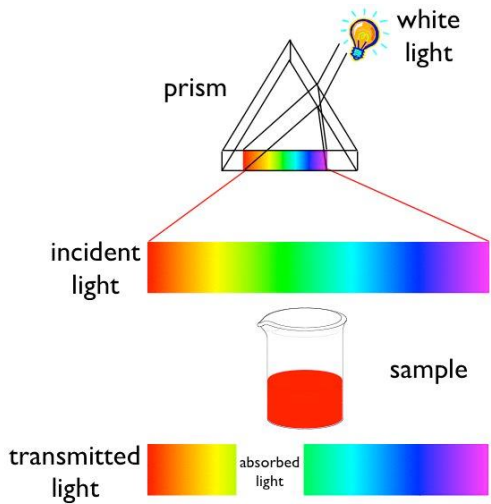
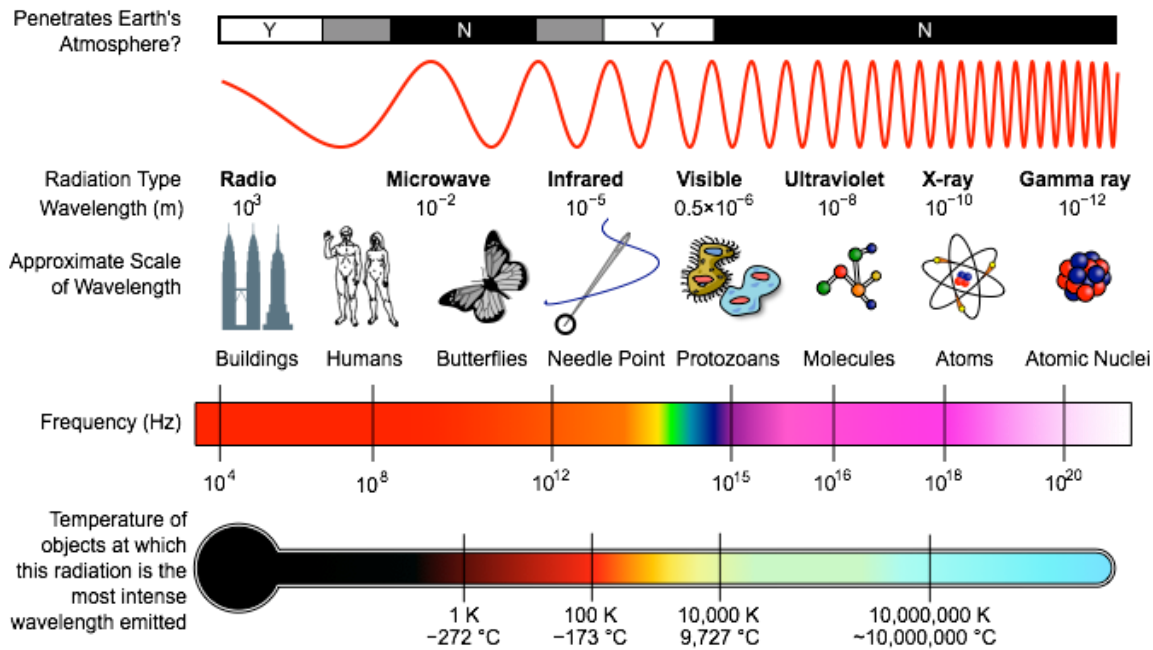
*low spin: electrons paired up in d orbitals. WHY??*

**Bonding models:**

Valence bond (coordinate covalent bond needs empty orbitals on metal)

Crystal Field Theory (originally from ionic crystals; influence of ligand lone pair repulsion on d-orbitals)

Molecular Orbital Theory (all orbitals defined)



- What happens for more than 1 electron in d orbitals?
- The electron-electron interactions must be taken into account.
- For **d<sup>1</sup>-d<sup>3</sup> systems**: Hund's rule predicts that the electrons will not pair and occupy the  $t_{2g}$  set.
- For **d<sup>4</sup>-d<sup>7</sup> systems** ( there are two possibilities): Either put the electrons in the  $t_{2g}$  set and therefore pair the electrons (**low spin case** or **strong field situation**. Or put the electrons in the  $e_g$  set, which lies higher in energy, but the electrons do not pair (**high spin case** or **weak field situation**).
- Therefore, there are two important parameters to consider: **The Pairing energy (P)**, and **the  $e_g - t_{2g}$  Splitting (referred to as  $\Delta_0$ ,  $10Dq$  or CFSE)**
- For both the high spin (h.s.) and low spin (l.s.) situations, it is possible to compute the **CFSE**.



# For an octahedral complex, CFSE

$$= -0.4 \times n(t_{2g}) + 0.6 \times n(e_g) \Delta_o$$

Where,  $n(t_{2g})$  and  $n(e_g)$  are the no. of electrons occupying the respective levels

If CFSE is very large, pairing occurs (i.e.  $CFSE > P$ )

If CFSE is rather small, no pairing occurs (i.e.  $P > CFSE$ )

## $d^5$ system



Case I results in LS complex

Case II results in HS complex

## $\Delta_o$ is dependent on:

- *Nature of the ligands*
- *The charge on the metal ion*
- *Whether the metal is a 3d, 4d, or 5d element*

Ligands which cause a small splitting are *Weak field ligands* (CFSE in the range 7000 - 30000  $\text{cm}^{-1}$ ) and those cause a large splitting are *Strong field ligands* (CFSE typically  $> 30000 \text{ cm}^{-1}$ )

### *Spectrochemical Series*

$\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{Cl}^- < \text{N}_3^-, \text{F}^- < \text{urea}, \text{OH}^- < \text{ox}, \text{O}^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{py}, \text{NH}_3 < \text{en} < \text{bpy}, \text{phen} < \text{NO}_2^- < \text{CH}_3^-, \text{C}_6\text{H}_5^- < \text{CN}^- < \text{CO}.$

$[\text{CrCl}_6]^{3-}$	13640 $\text{cm}^{-1}$	163 kJ/mol
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	17830	213
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	21680	314
$[\text{Cr}(\text{CN})_6]^{3-}$	26280	314

$[\text{Co}(\text{NH}_3)_6]^{3+}$	24800 $\text{cm}^{-1}$	163 kJ/mol
$[\text{Rh}(\text{NH}_3)_6]^{3+}$	34000	213
$[\text{Ir}(\text{NH}_3)_6]^{3+}$	41000	314

# Tetrahedral Field- Considerations

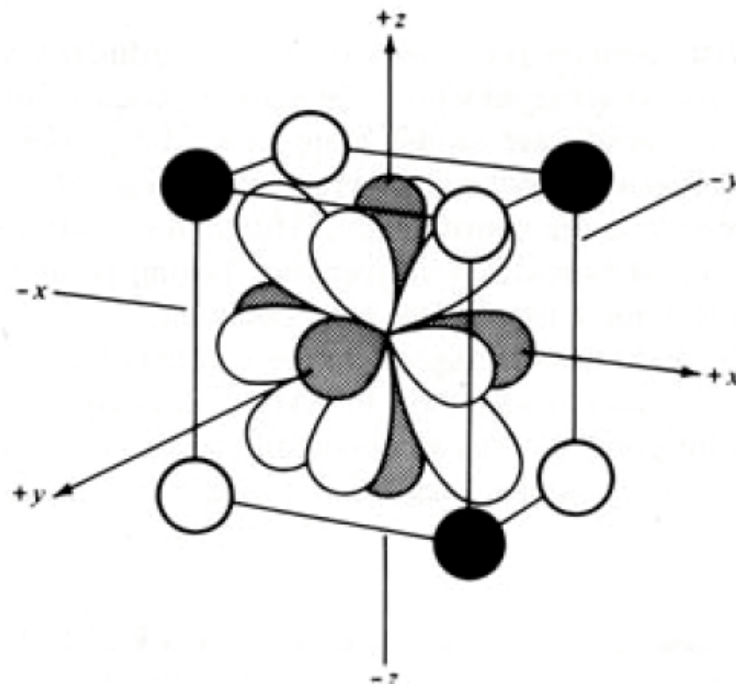
Imagine a tetrahedral molecule inside a cube with metal ions in the center of the cube. The ligands occupy the four alternate corners of the cube leaving the rest four corners empty.

The two 'e' orbitals point to the center of the face of the cube while the three 't<sub>2</sub>' orbitals point to the center of the edges of the cube.

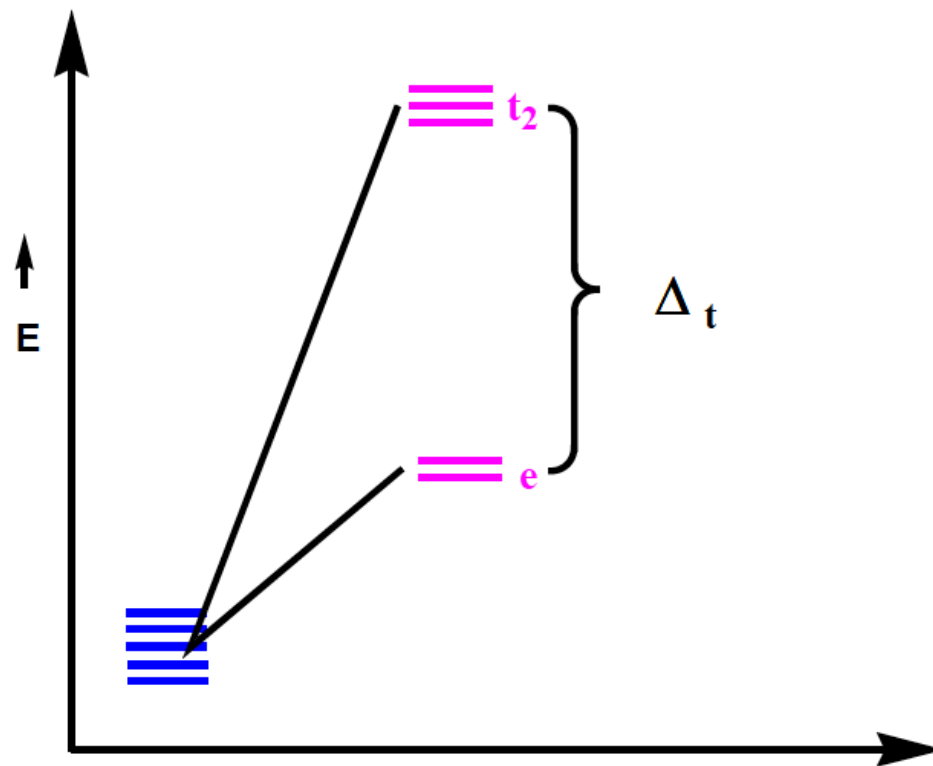
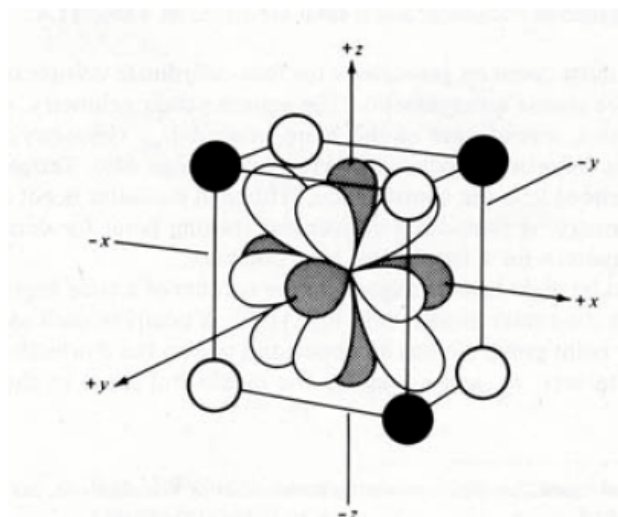
Therefore, the angle between the e-orbitals, metal and ligand is one-half of the tetrahedral angle, i.e.  $109^{\circ}28' / 2 = 54^{\circ}44'$ . But the angle between the t<sub>2</sub>-orbitals, metal and ligand is one-third of the tetrahedral angle, i.e.  $109^{\circ}28' / 3 = 35^{\circ}16'$ .

Thus the t<sub>2</sub> orbitals are nearer to the direction of approach of the ligands than the e orbitals.

Hence, t<sub>2</sub> orbitals have higher energy compared to e-orbitals



# Tetrahedral Field



$$\Delta_t < \Delta_o$$

$$\Delta_t = 4/9 \Delta_o$$

There are only 4 ligands in the tetrahedral complex, and hence the ligand field is roughly 2/3 of the octahedral field.

The direction of ligand approach in tetrahedral complex does not coincide with the d-orbitals. This reduces the field by a factor of 2/3. Therefore  $\Delta_t$  is roughly  $2/3 \times 2/3 = 4/9$  of  $\Delta_o$ .

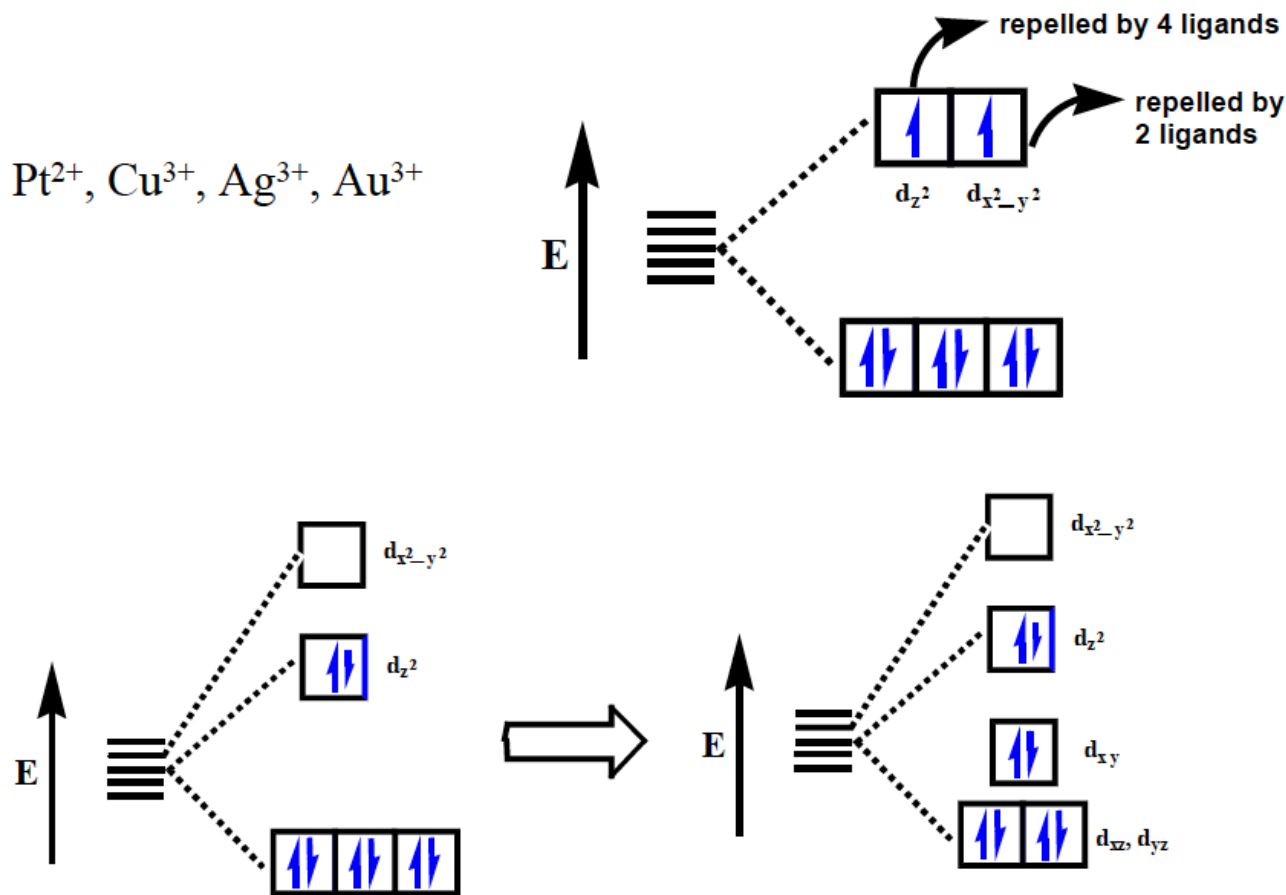
As a result, **all tetrahedral complexes are high-spin** since the CFSE is normally smaller than the pairing energy.

Hence low spin configurations are rarely observed. Usually, if a very strong field ligand is present, the square planar geometry will be favored.

# Special case of $d^8$ Octahedral

Examples:

$Ni^{2+}$ ,  $Pd^{2+}$ ,  $Pt^{2+}$ ,  $Cu^{3+}$ ,  $Ag^{3+}$ ,  $Au^{3+}$



Square-planar complex is formed ; attempts to form octahedral complexes become impossible

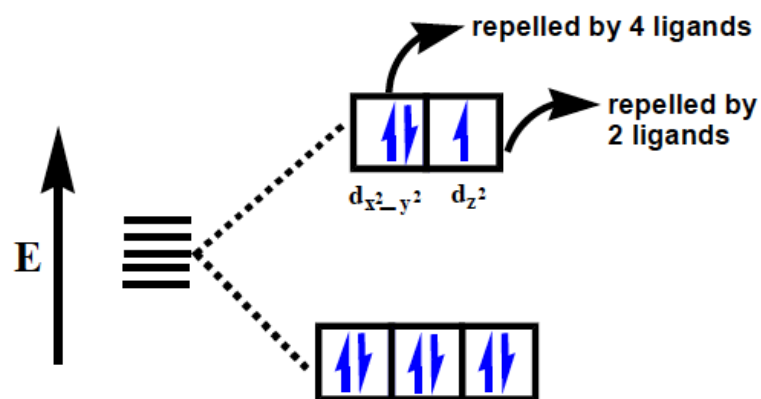
## Special case II

# Jahn-Teller Distortion

If both the  $e_g$  orbitals are symmetrically filled - all ligands are repelled equally.

**Result:** regular octahedron

If **asymmetrically** filled - some ligands are repelled more than the other. **Result:** Distorted octahedron



Consider  $e_g$  configuration:  $(d_{z^2})^1 d_{x^2-y^2})^2$

Ligands along x, -x, y, -y will be repelled more and bonds elongated. i.e. the octahedron will be compressed along the z axis.

Consider  $e_g$  configuration:  $(d_{z^2})^2 d_{x^2-y^2})^1$

Ligands along z, -z will be repelled more and bonds elongated. i.e. the octahedron will be elongated along the z axis.



The Jahn-Teller Theorem was published in 1937 and states:

"any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy thereby removing the degeneracy"

The  $e_g$  point along bond axes. The effect of JT distortions is best documented for Cu(II) complexes (with 3e in  $e_g$ ) where the result is that most complexes are found to have elongation along the z-axis.

