

# Inorganic Chemistry 6BA40

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students  
kids

### Teaching corner

Students TU/e : 6BA40 COLLEGE ANORGANISCHE CHEMIE SLIDES, STUDIEWIJZER EN OVERIGE INFO

- SLIDES
- STUDIEWIJZER & LEERDOELEN
- MEDEDELINGEN

**kids** *the lotuseffect* voor VWO-werkweek

Applications of the materials we make (the so called PO: (covering/paint, for example on a car or house). The inspi model, coatings were made that clean themselves: the l as a fakir on his bed with spikes.

Rain flushes away all dirt... Imagine nobody has to clean h



The sr the leaf of a lotus and to the right: a leaf through a micro glass), it really is like a bed with spikes!!

**6BA40:** [Dr. H.C.L. Abbenhuis, Helix STW 4.43](#)

SLIDES

[6 OKT](#)      [8 OKT](#)      [10 OKT](#)

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[20 OKT](#)      [22 OKT](#)      [24 OKT](#)

[27 OKT](#)      [29 OKT](#)      31 OKT

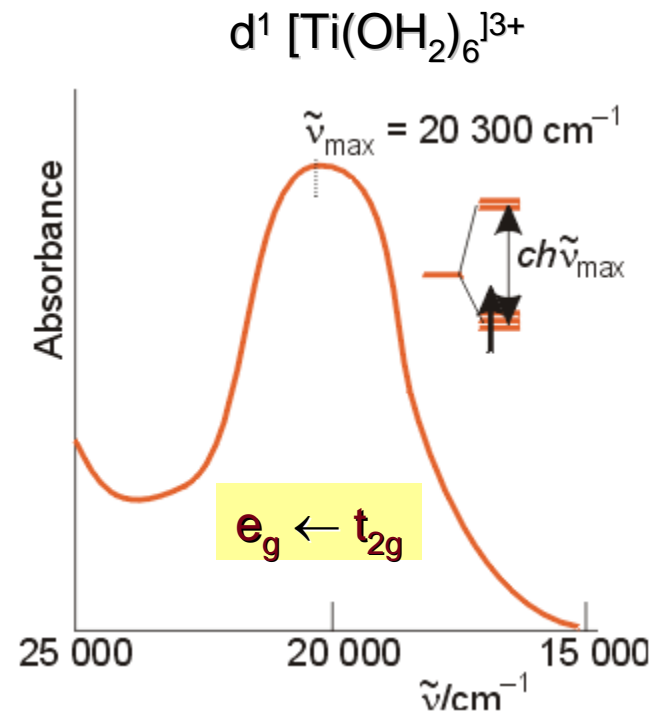
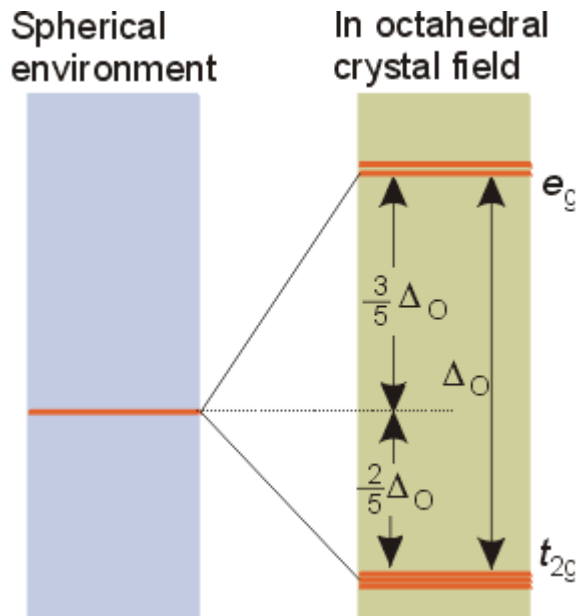
**STUDIEWIJZER & LEERDOELEN**

# Electronic Spectra of d-Metal Complexes

- Absorptions arise from transitions between electronic energy levels
  - transitions between metal-centered orbitals with d-character (*d-d transitions*)
  - transitions between metal- and ligand-centered MO's which transfer charge from metal-to-ligand or ligand-to-metal (Charge-Transfer transitions, CT)
- MLCT = metal-to-ligand charge transfer
- LMCT = ligand-to-metal charge transfer

# d-Metal Complexes

## *Ligand Field Splitting*



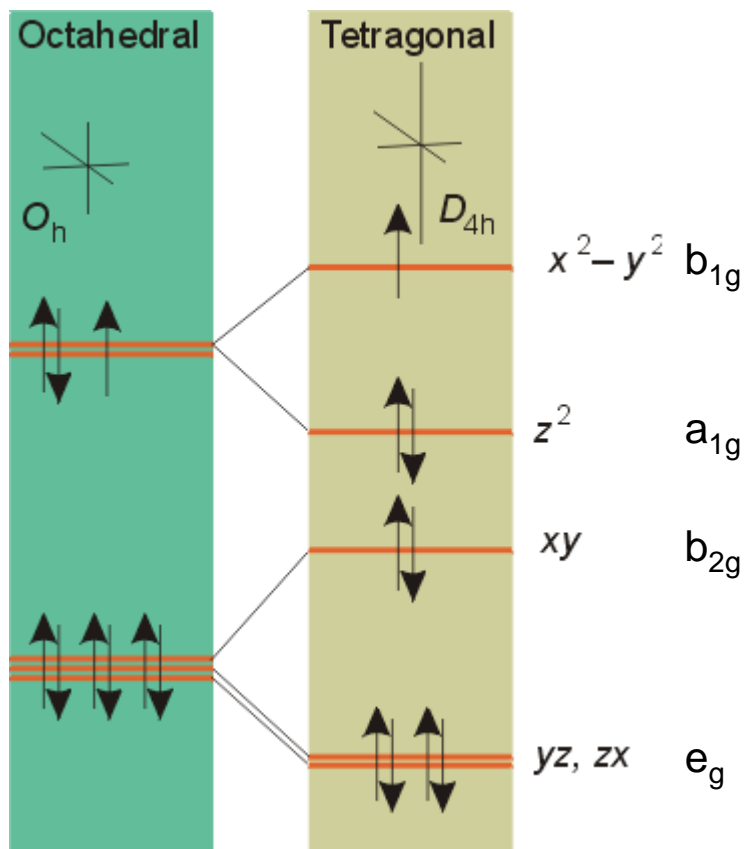
- The ligand field splitting  $\Delta_{\text{Oct}}$  is strongly dependent on the nature of the ligand

→ *Empirical findings!*

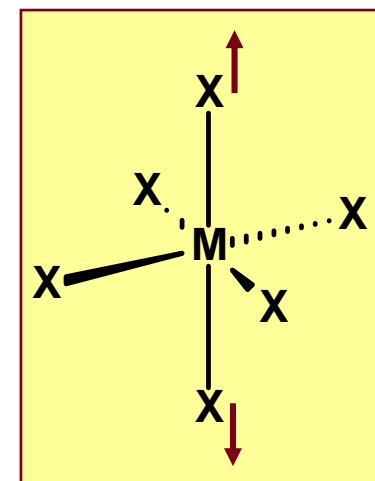
- For electron configurations other than  $d^1$ , this transition energy gives not only the difference in orbital energy, but is also dep. on electron repulsions.

# d-Metal Complexes

## *Tetragonal Ligand Field & Tetragonal Distortion*



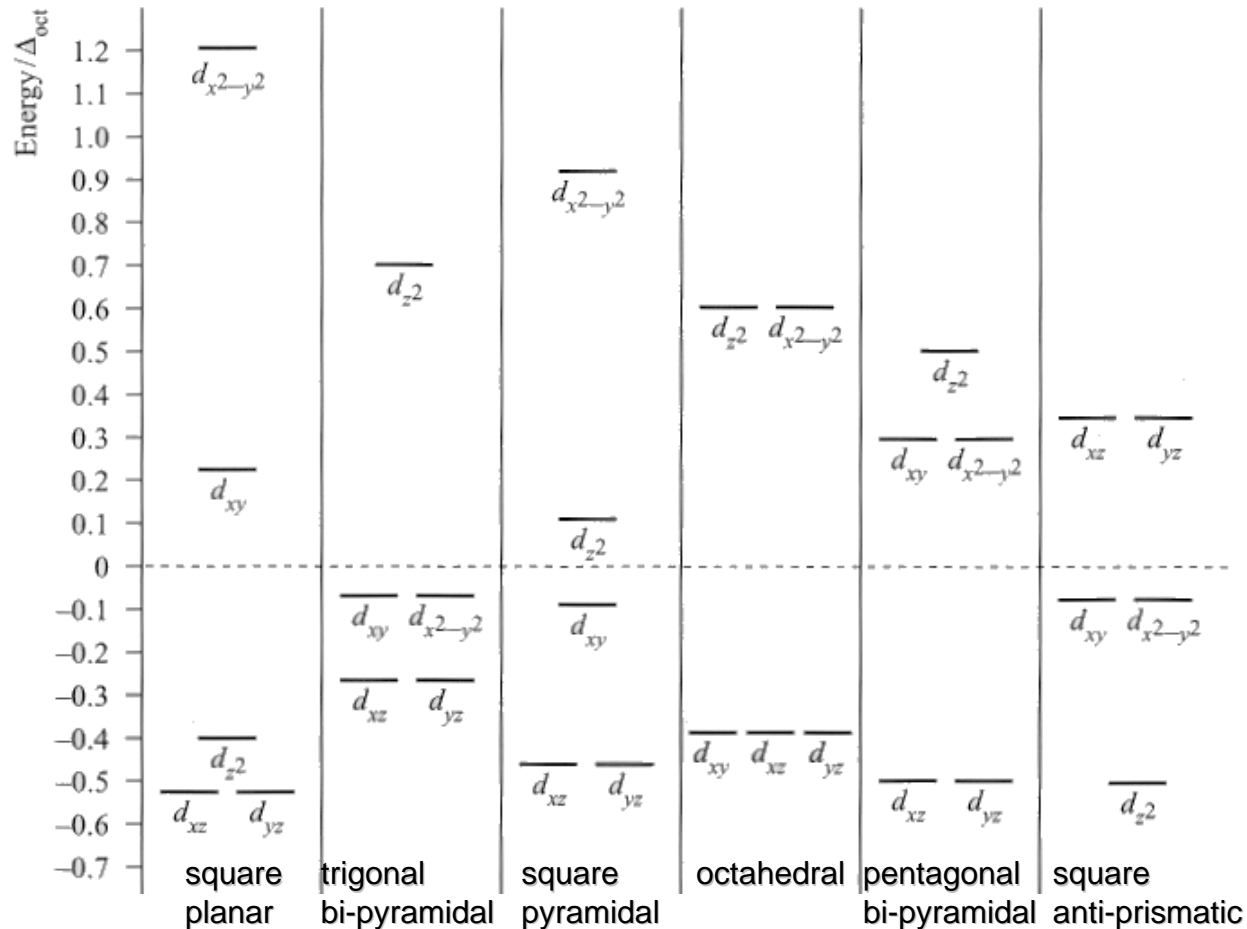
- typical for high spin  $d^4$  and  $d^9$   
 $Cu^{II}$  is a typical example



- *Jahn-Teller Effect*: If the ground state of a nonlinear complex is orbital degenerate, the complex will distort in order to lower energy by removing the degeneracy
- Orbitals with a  $z$  component are stabilized, others destabilized

# d-Metal Complexes

## Some Common Ligand Fields



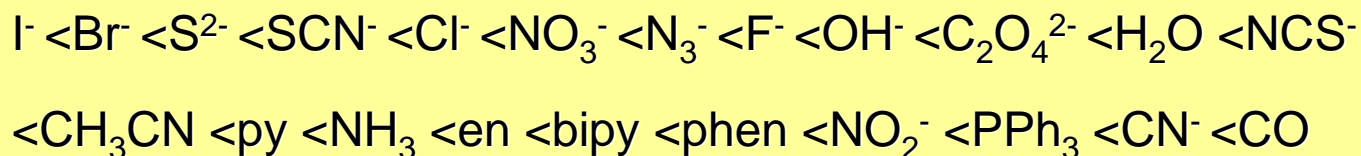
- Splitting diagrams referred to a common barycenter
- Splitting with respect to  $\Delta_{\text{O}}$

# d-Metal Complexes

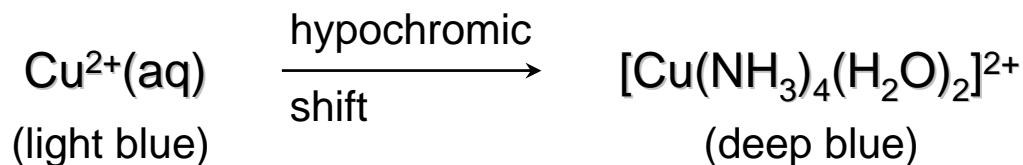
## *Spectrochemical Series*

- The ligand field splitting  $\Delta_o$  is strongly dependent on the nature of the ligand.

Independent from the central metal, ligands can be sorted by increasing  $\Delta_o$ .



- $\Delta_o$  is the larger, the more  $\pi$ -electrons the ligand has
- $\Delta_o$  is small in the presence of many lone-pairs ( $\text{Hal}^-$ )




# d-Metal Complexes

## *Spectrochemical Series*

- $\Delta_o$  increases slightly within a row of transition metals

e.g. for  $M^{2+}$  (3d series),  $\Delta_o \approx 7800 - 12000 \text{ cm}^{-1}$   
 (Mn<sup>2+</sup>) (Cr<sup>2+</sup>)

- $\Delta_o$  increases down a group 3d - 4d - 5d each by ca. 30%

$\Delta_o$		[Fe(CN) <sub>6</sub> ] <sup>4-</sup>	yellow
		[Ru(CN) <sub>6</sub> ] <sup>4-</sup>	pale color
		[Os(CN) <sub>6</sub> ] <sup>4-</sup>	colorless, (UV)

- $\Delta_o$  increases with increasing oxidation number

e.g. 3d series  $M^{2+}$   $\Delta_o \approx 10\,000 \text{ cm}^{-1}$  [Fe(CN)<sub>6</sub>]<sup>4-</sup> yellow

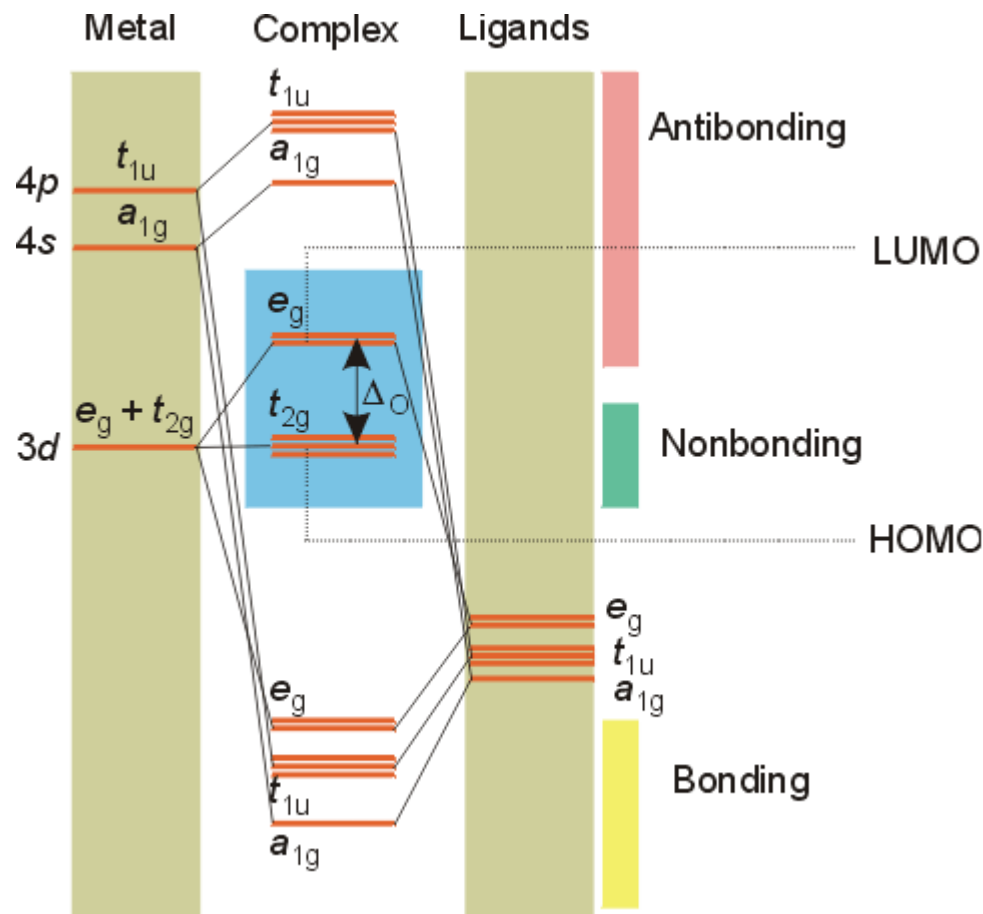
$M^{3+}$   $\Delta_o \approx 20\,000 \text{ cm}^{-1}$  [Co(CN)<sub>6</sub>]<sup>3-</sup> colorless, (UV)

# d-Metal Complexes

## MO Theory

$$\psi_{MO} = a \psi_M + b \psi_L$$

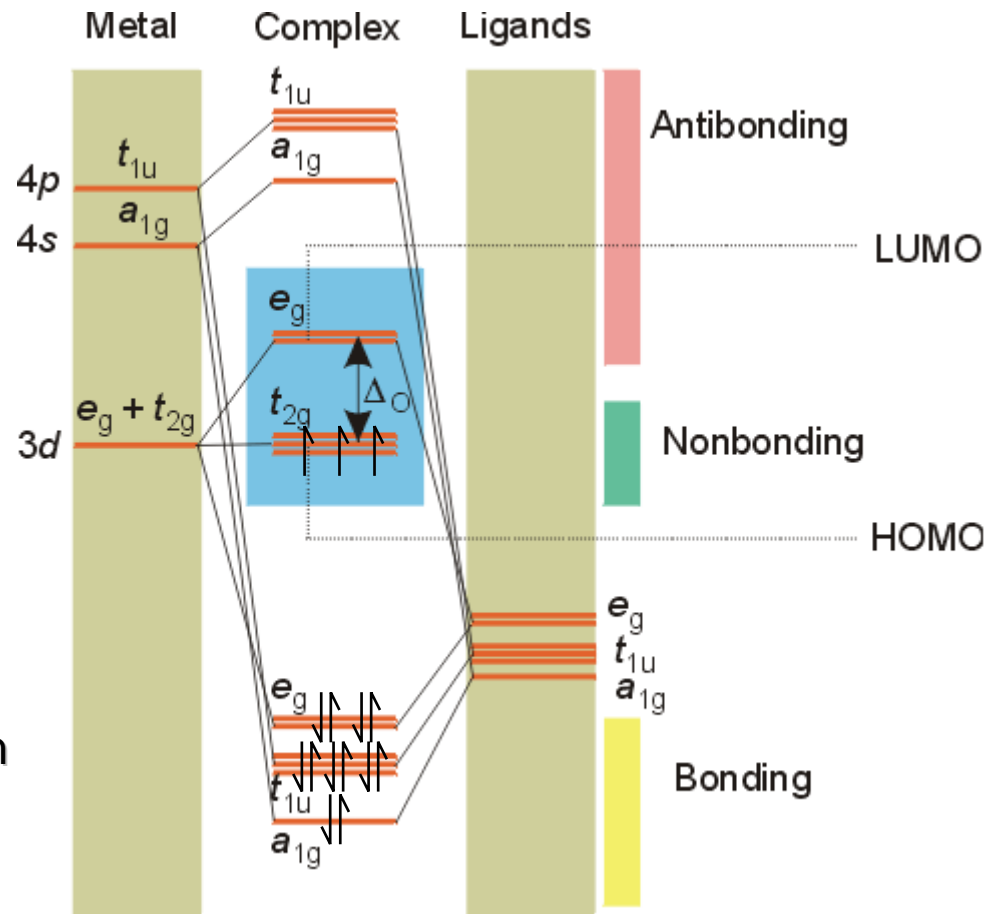
- The greatest contribution to MO's of lowest energy comes from atomic orbitals of lowest energy.
- Ligand  $\sigma$ -orbitals derived from atomic orbitals with energies well below the metal-d orbitals.
- ➔ Bonding  $\sigma$ -MO's of the complex are mainly of ligand-orbital character
- ➔  $t_{2g}$ -orbitals are confined to metal and  $e_g$  are also largely of metal character



# d-Metal Complexes

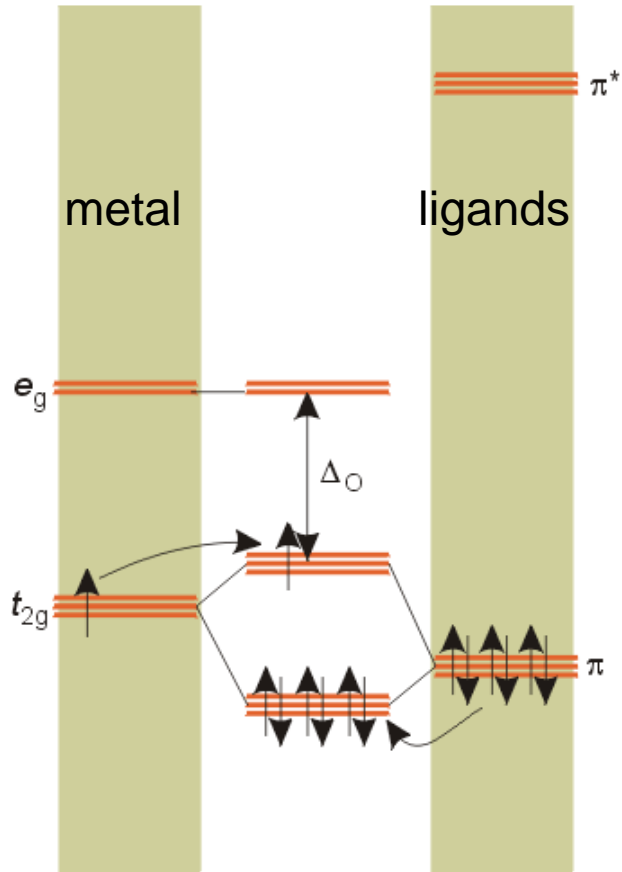
## *Ligand Field Theory*

- The 12 e<sup>-</sup> of the ligand lone-pairs fill the 6 bonding MO's.
- The n e<sup>-</sup> of a d<sup>n</sup> complex fill the nonbonding t<sub>2g</sub> and anti-bonding e<sub>g</sub> orbitals.
- Δ<sub>O</sub> is the HOMO-LUMO separation!
- In the example a d<sup>3</sup> complex is shown



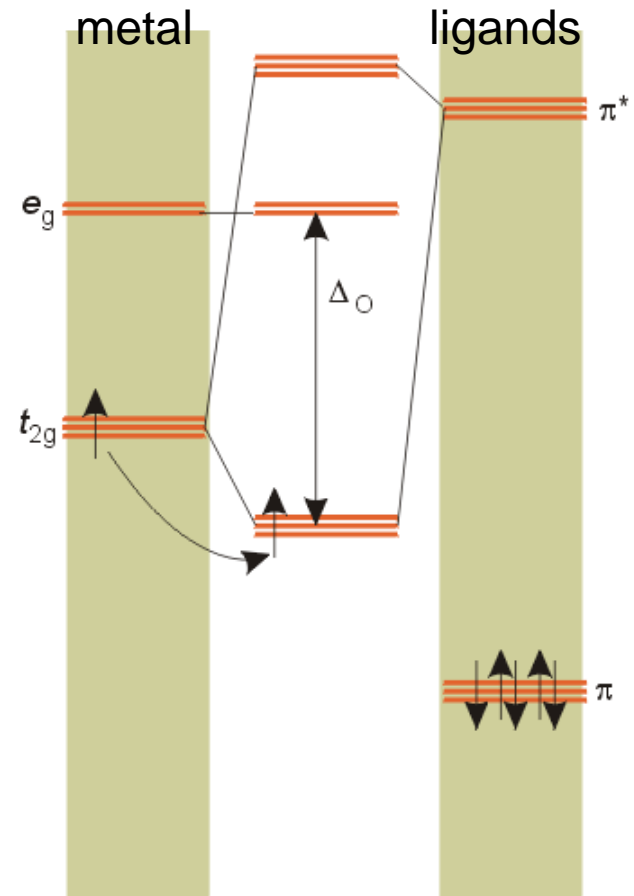
# d-Metal Complexes

## $\pi$ -Bonding, Donor & Acceptor Ligands



$\pi$ -donor ligands decrease  $\Delta_O$

$\pi$ -acceptor ligands increase  $\Delta_O$

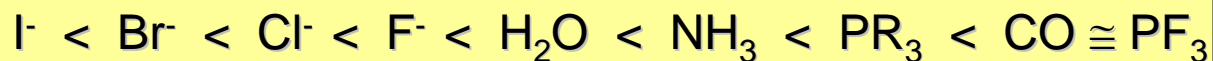


# d-Metal Complexes

## *$\pi$ -Bonding, Donor & Acceptor Ligands*

- $\pi$ -donor ligands decrease  $\Delta_O$  and
- $\pi$ -acceptor ligands increase  $\Delta_O$
- The spectrochemical series is largely a consequence of the effects of  $\pi$ -bonding, when this is feasible

increasing  $\Delta_O$



$\pi$ -donor < weak  $\pi$ -donor < no  $\pi$ -effects <  $\pi$ -acceptor

# Spectroscopic Terms

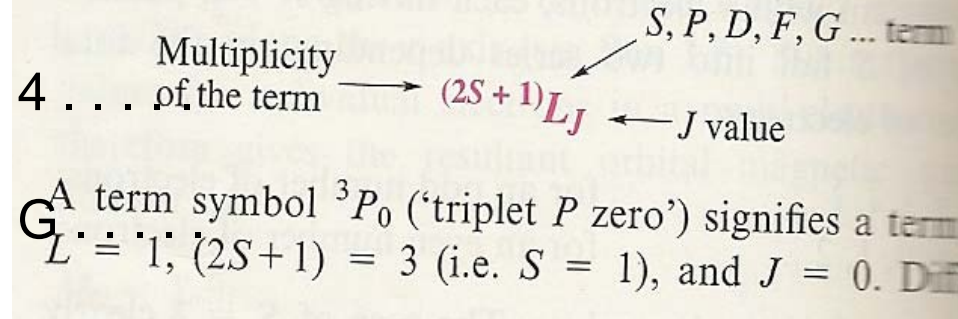
- Notification of the total quantum numbers

$$L = 0 \quad 1 \quad 2 \quad 3 \quad 4 \dots$$

S P D F  
alphabetical, omitting J

$$S = 0 \quad \frac{1}{2} \quad 1 \quad \frac{3}{2} \quad 2 \dots$$

$$2S + 1 = 1 \quad 2 \quad 3 \quad 4 \quad 5 \dots$$



The terms of atoms are specified by symbols in which L is indicated by one of the letters S, P, D, ... , and  $2S+1$  (multiplicity) is given as left superscript.

e.g.  $L = 1, S = 1 \Rightarrow {}^3P$

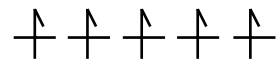
# The Energies of the Terms

- To just identify the ground term of an atom or ion:
  - Identify the microstate that has the highest value of  $M_S$ .
  - Identify the highest permitted value of  $M_L$  for that multiplicity.

*Example:*

*What is the ground term for the configuration  $3d^5$  of  $Mn^{2+}$  ?*

$$S = 5 \times 1/2 = 5/2 \Rightarrow \text{maximum multiplicity is } 2 \times 5/2 + 1 = 6$$



all  $e^-$  have the same  $m_s \Rightarrow$  they have to have different  $m_l$

$$m_l = +2, +1, 0, -1, -2 \Rightarrow M_L = 0 \Rightarrow L = 0$$

➔ The ground term is  ${}^6S$

# Electronic Spectra of d-Metal Complexes

## *The Spectroscopic Terms*

- The terms of an octahedral metal complex are labeled by the symmetry species of the overall orbital state; a superscript prefix shows the multiplicity of the term.

Atomic term	Number of states	Terms in $O_h$ symmetry
S	1	$A_{1g}$
P	3	$T_{1g}$
D	5	$T_{2g} + E_g$
F	7	$T_{1g} + T_{2g} + A_{2g}$
G	9	$A_{1g} + E_g + T_{1g} + T_{2g}$

- The free atom terms split in the ligand field of an octahedral complex and are then labeled by their symmetry species as given in the table.

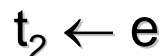
# Electronic Spectra of d-Metal Complexes

## Convention

The following notation is used for electronic transitions caused by absorption or emission of energy

- ⌋ Emission: (high E level) → (low E level)
- ⌋ Absorption: (high E level) ← (low E level)

e.g.: absorptive transitions from e to a  $t_2$  level in a tetrahedral complex:



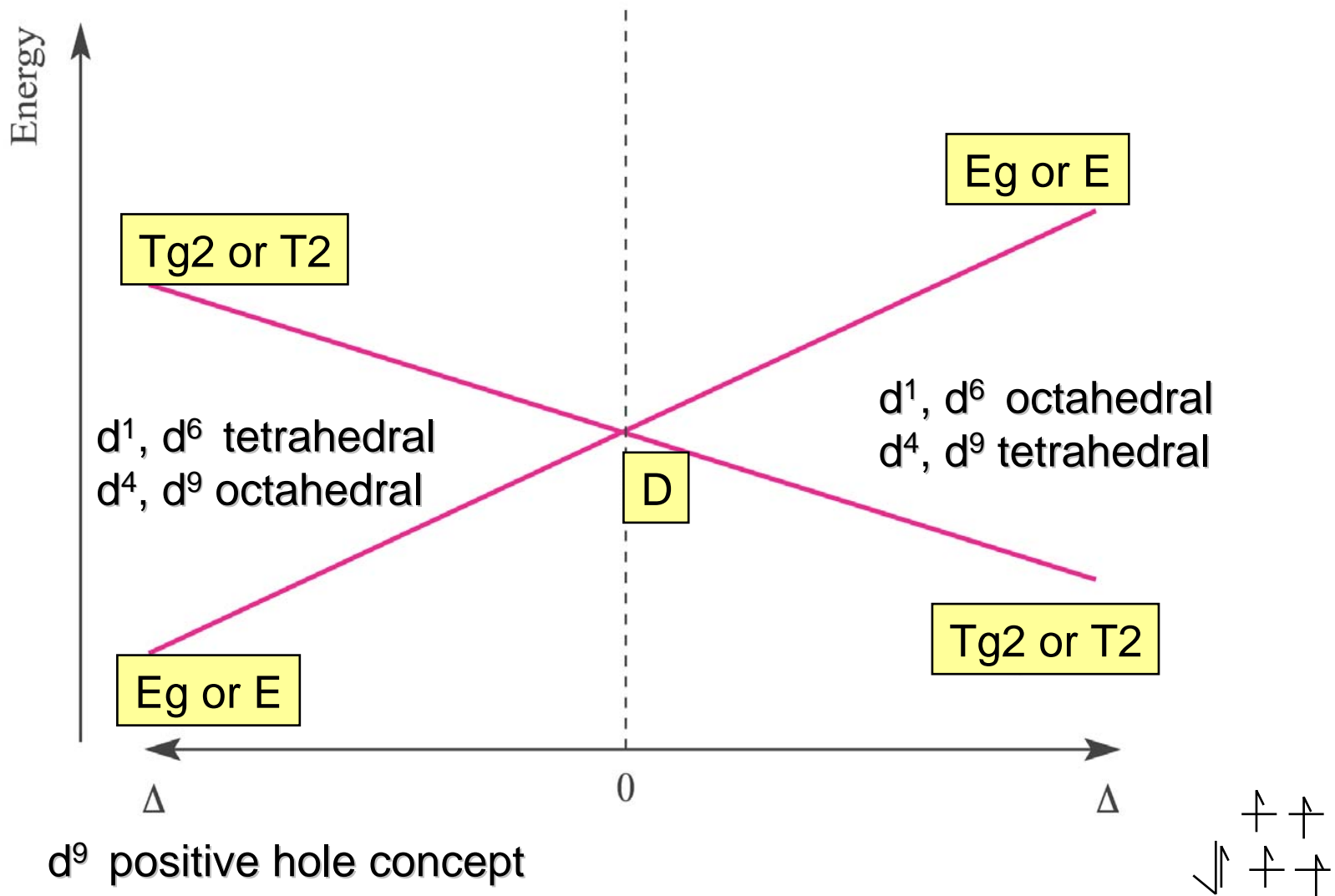
- ⌋  $d^1$ ,  $d^4$ ,  $d^6$ , and  $d^9$  complexes show one absorption
- ⌋  $d^2$ ,  $d^3$ ,  $d^7$ , and  $d^8$  complexes show three absorption
- ⌋  $d^5$  complexes show a series of very weak, relatively sharp absorptions

# Selection Rules

- Spin selection rule:  $\Delta S = 0$
- Transitions may occur from singlet to singlet, or triplet to triplet states and so on, but a change in spin multiplicity is forbidden.
- *The coupling of spin and orbital angular momentum can relax the spin selection rule. Spin-orbit coupling is stronger for heavy atoms:  
*heavy atom effect**
- Intensities of spin-forbidden transitions are greater for 4d or 5d metal complexes than for comparable 3d complexes.

# Term splitting in crystal fields

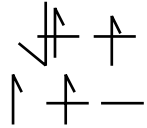
## *Orgel Diagram*



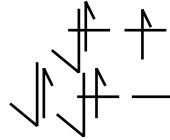
$d^6$   $^5D: L = 2, S = 4/2$

# Selection Rules Example

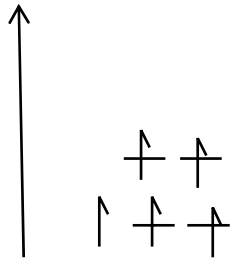
- *High spin  $d_5$  transition forbidden and high spin  $d_7$  transition allowed*



$^4S: L = 0, S = 3/2$

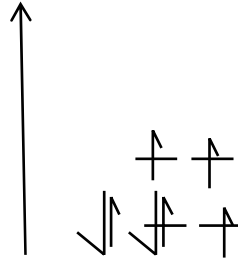


$^4D: L = 2, S = 3/2$



$^6S: L = 0, S = 5/2$

$\Delta S = 1$

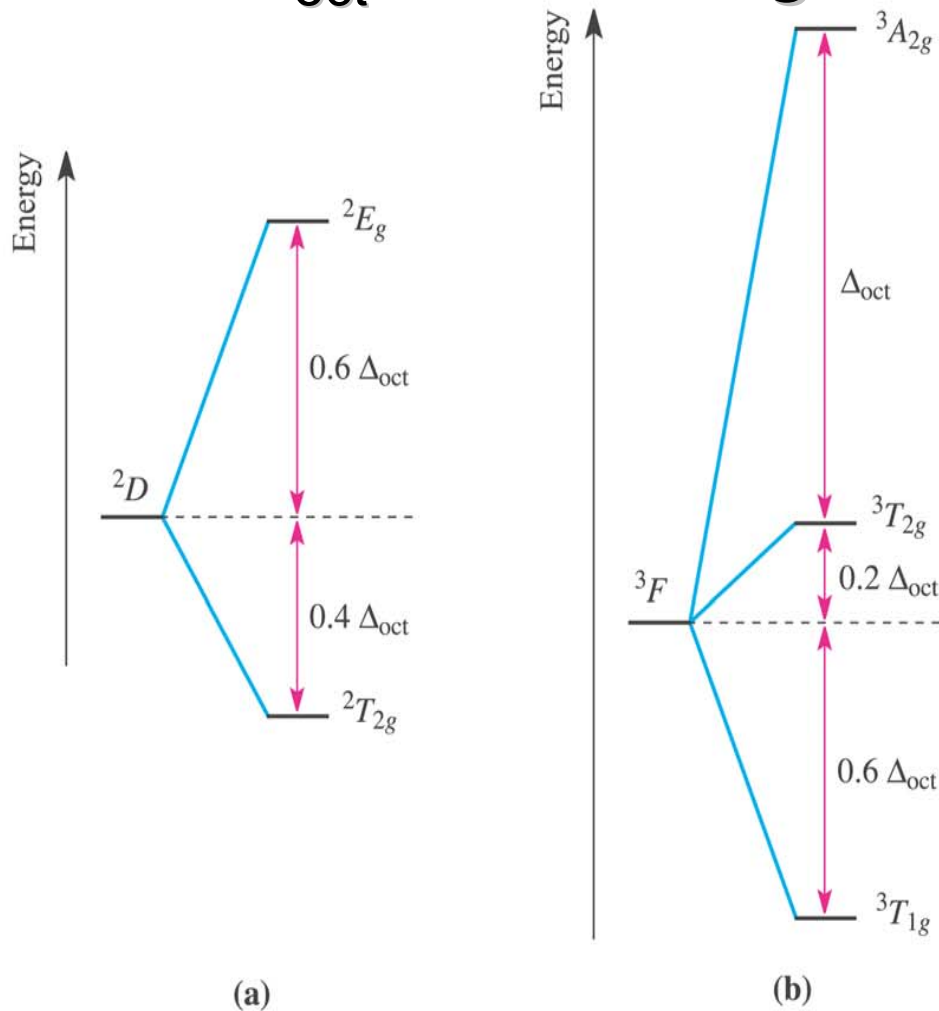


$^4F: L = 3, S = 3/2$

$\Delta S = 0$

• *Spin allowed*

# —How to find $\Delta_{\text{oct}}$ in $d^n$ configurations?



(a) Splitting in an octahedral field of the (a)  $^2D$  term arising from a  $d^1$  configuration, and (b)  $^3F$  term arising from a  $d^2$  configuration. The  $^3P$  term for the  $d^2$  configuration does not split. The diagram applies only to the weak field limit.

# Racah Parameters

- Due to electron repulsion, the terms of a configuration have different energies.
- The repulsion energies can be described by three combinations of integrals, that can be described by three empirical parameters **A**, **B**, and **C**, the **Racah parameters**.  
A, B, and C can be determined from gas-phase atomic spectra.

- For a  $d^2$  configuration:

$$E(^1S) = A + 14 B + 7 C$$

$$E(^1G) = A + 4 B + 2 C$$

$$E(^1D) = A - 3 B + 2 C$$

$$E(^3P) = A + 7 B$$

$$E(^3F) = A - 8 B$$

$$C \approx 4 B$$

$$\Delta E(P - F) = (A + 7 B) - (A - 8 B) = 15 B$$

- The Racah parameters summarize the effect of  $e^-e^-$  repulsion on the energies of the terms that arise from a single configuration. The parameters are the quantitative expression of the ideas underlying Hund's rules and account for deviations from them.

# Electronic Spectra of d-Metal Complexes

## *Weak and Strong Field Limits*

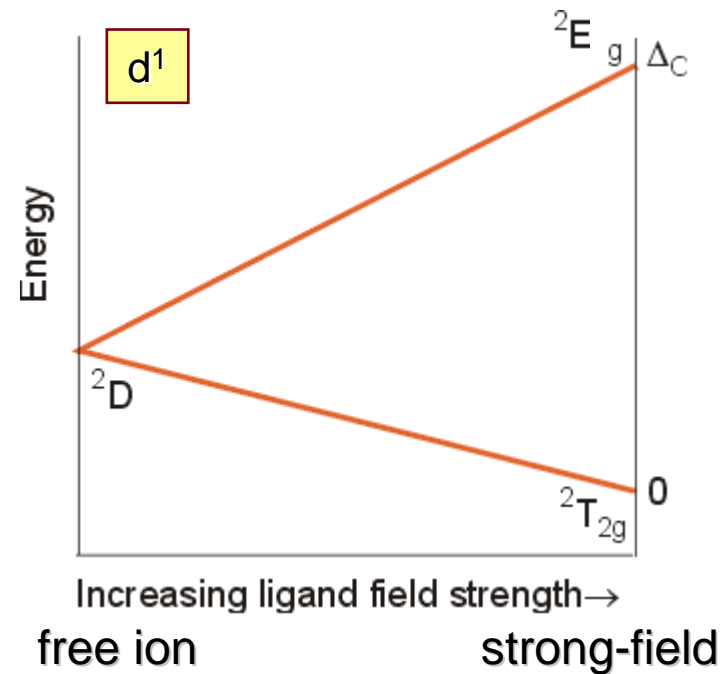
- Two extreme cases are taken into account in order to consider e-e- repulsions, which are difficult to quantify.
- Weak field limit**  $\Rightarrow$  e-e- repulsions are **important** and relative E can be expressed as combinations of **B** and **C**.
- Strong field limit**  $\Rightarrow$  e-e- repulsion can be ignored and E solely expressed in terms of  $\Delta_O$ .

- Intermediate cases are considered by drawing a correlation diagram between the two.

- Only term for a d<sup>1</sup> configuration in a free atom is <sup>2</sup>D

- $t_{2g}^1 \Rightarrow$  <sup>2</sup>T<sub>2g</sub> term, or

$e_g^1 \Rightarrow$  <sup>2</sup>E term



- $\rightarrow$  Because there is no e-e- repulsion, the separation is  $\Delta_O$ .

# Electronic Spectra of d-Metal Complexes

## *Weak and Strong Field Limits*

- For  $d^2$  configuration the triplet terms are  $^3F$  and  $^3P$  with the relative energies  $E(^3F)=0$  and  $E(^3P)=15B$ .

- A  $d^2$  ion has the configurations:

$$t_{2g}^2 < t_{2g}^1 e_g^1 < e_g^2$$

$$LFSE = (-0.4x + 0.6y) \Delta_O$$

$$E(t_{2g}^2, T_{1g}) = 2 (-2/5\Delta_O) = -0.8\Delta_O$$

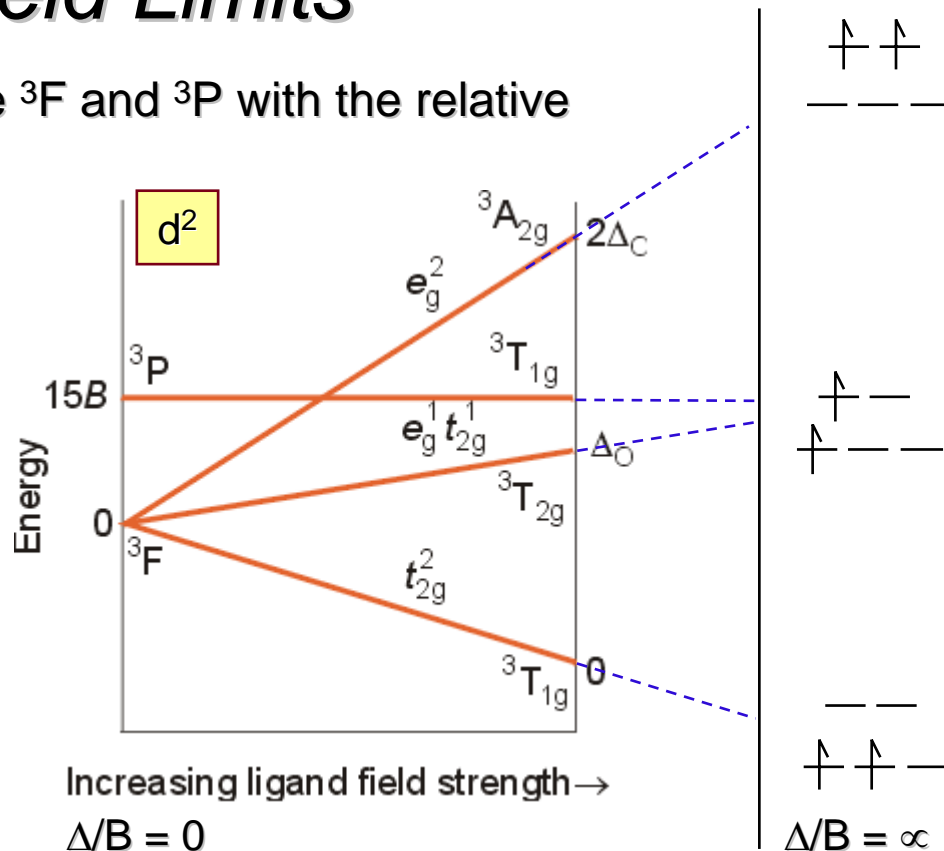
$$E(t_{2g}^1 e_g^1, T_{2g}) = (-2/5 + 3/5\Delta_O) = +0.2\Delta_O$$

$$E(e_g^2, A_{2g}) = 2 (3/5\Delta_O) = +1.2\Delta_O$$

- The relative E are:

$$E(t_{2g}^2, T_{1g}) = 0, E(t_{2g}^1 e_g^1, T_{2g}) = +\Delta_O, E(e_g^2, A_{2g}) = +2\Delta_O$$

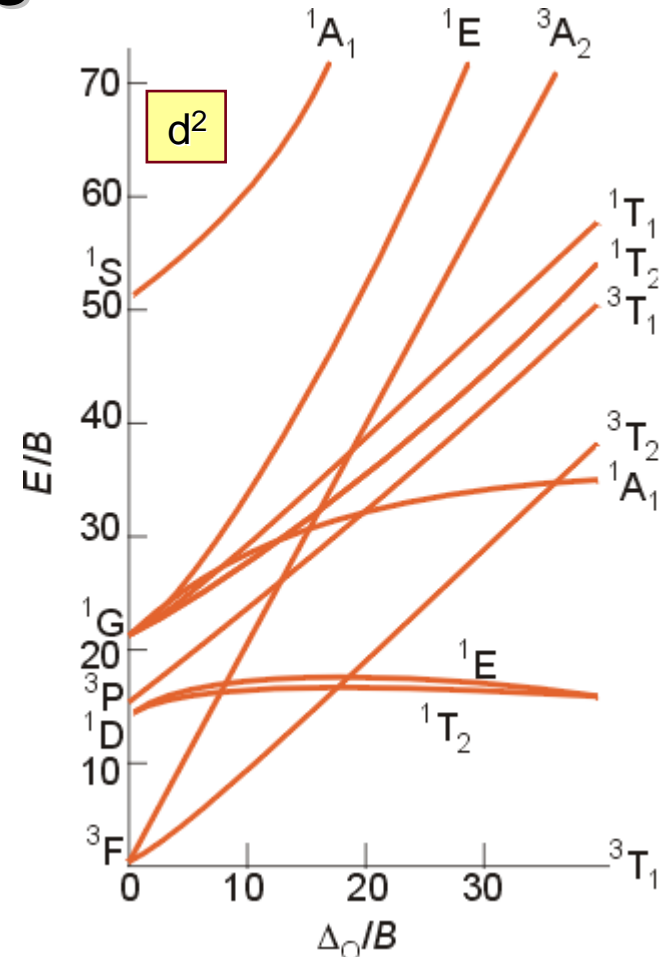
- For a given metal ion, the energies of the individual terms respond differently to ligands of increasing field strength and the correlation between free atom terms and terms of a complex can be displayed in an Orgel diagram.



# Electronic Spectra of d-Metal Complexes

## *Tanabe-Sugano Diagrams*

- Term energies expressed as  $E/B$  and plotted against  $\Delta_O/B$ .
- Because  $C \approx 4 B$ , terms that depend both on  $B$  and  $C$  can be plotted in the same diagram.
- Zero energy in a Tanabe Sugano diagram is always that of the lowest term.
- When there is a change in the identity of the ground term with the ligand field, the lines can have an abrupt change in slope.
- Tanabe Sugano diagrams are correlation diagrams that depict the energies of electronic states of complexes as a function of the strength of the ligand field.



# Electronic Spectra of d-Metal Complexes

## Example 13.4

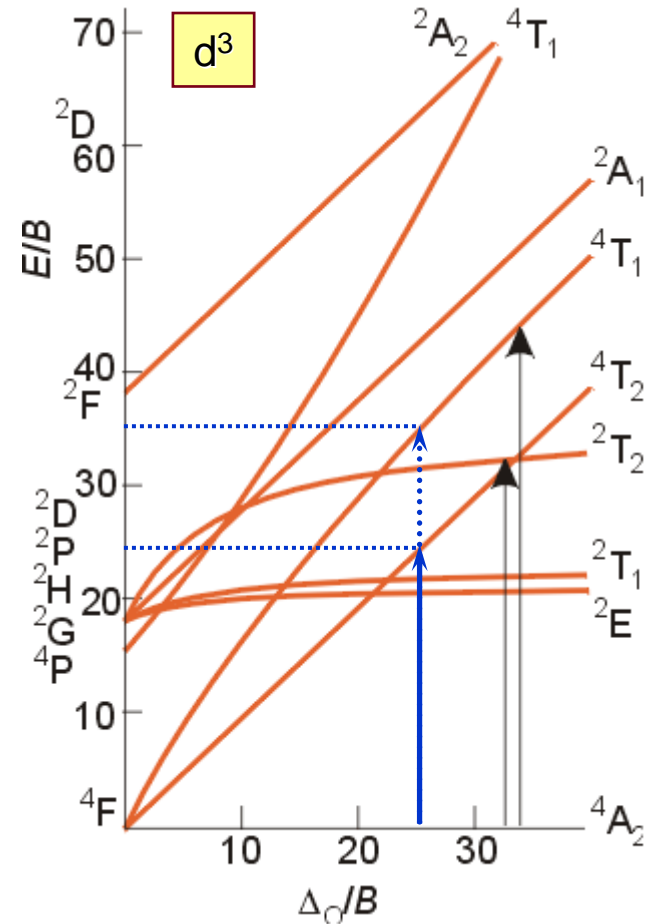
### Self-test 13.4

Use the Tanabe-Sugano diagram for  $d^3$  configuration to determine the first two spin-allowed quartet bands for  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

$$\Delta_{\text{O}} = 17\,600 \text{ cm}^{-1} ; B = 700 \text{ cm}^{-1}$$

$$\Rightarrow \frac{\Delta_{\text{O}}}{B} = 25.1$$

1. transition:  ${}^4\text{T}_{2\text{g}} \leftarrow {}^4\text{A}_{2\text{g}}$   
 $E/B = 24 \Rightarrow 16\,800 \text{ cm}^{-1}$
2. transition:  ${}^4\text{T}_{1\text{g}} \leftarrow {}^4\text{A}_{2\text{g}}$   
 $E/B = 35 \Rightarrow 24\,500 \text{ cm}^{-1}$



# Electronic Spectra of d-Metal Complexes

## Example 13.4

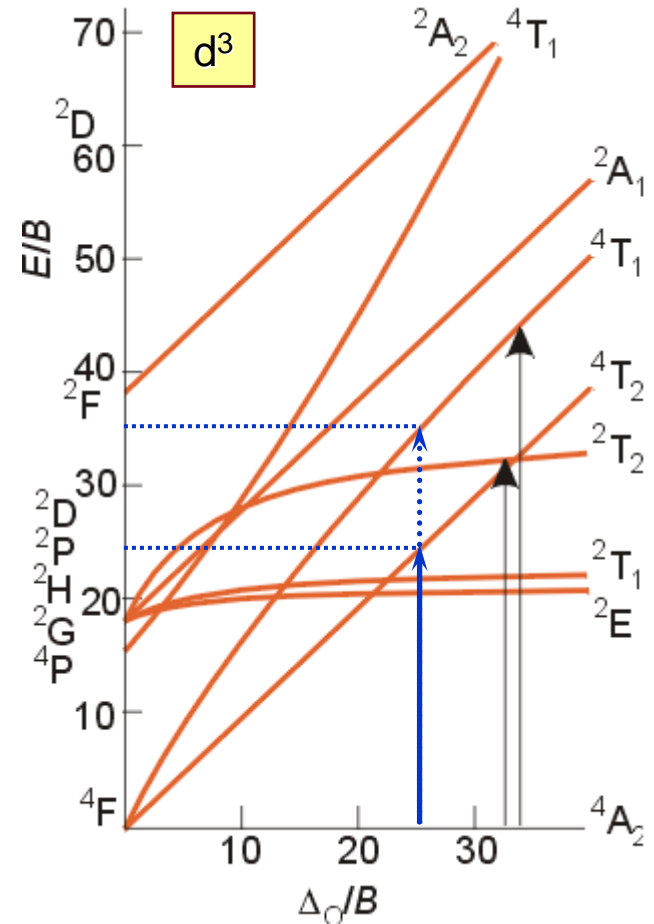
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$$\Delta_O = 17\,600\text{ cm}^{-1} ; B = 700\text{ cm}^{-1}$$

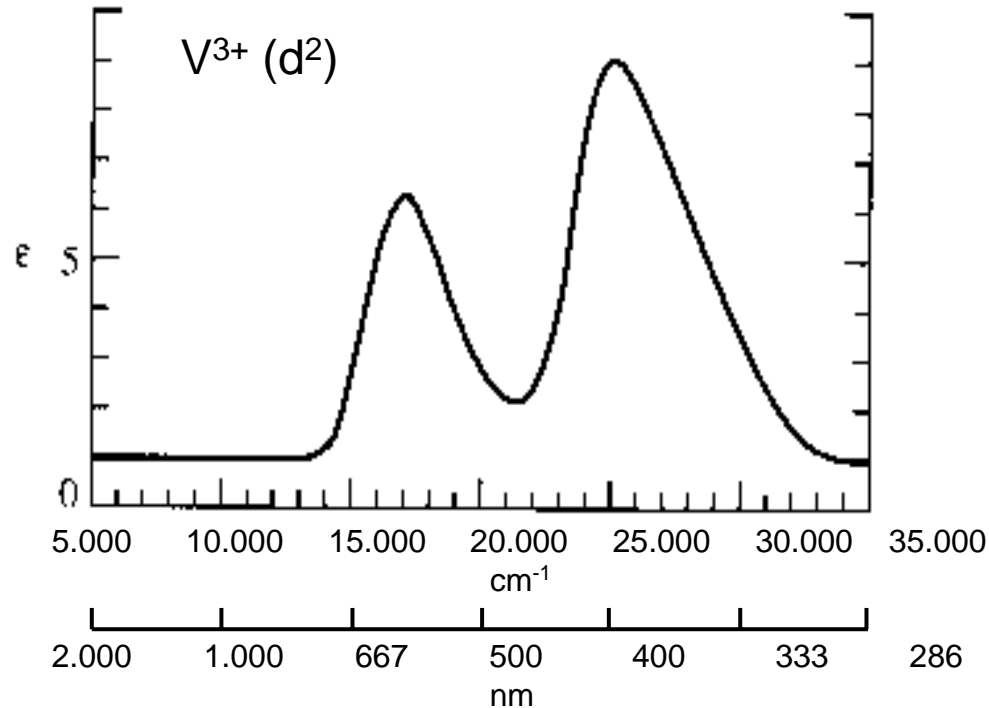
$$\Rightarrow \frac{\Delta_O}{B} = 25.1$$

1. transition:  ${}^4T_{2g} \leftarrow {}^4A_{2g}$   
 $E/B = 24 \Rightarrow 16\,800\text{ cm}^{-1}$
2. transition:  ${}^4T_{1g} \leftarrow {}^4A_{2g}$   
 $E/B = 35 \Rightarrow 24\,500\text{ cm}^{-1}$



# Application of Tanabe-Sugano Diagrams

- Given is the UV-vis spectrum of  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$



- Adsorption bands at  $17.800 \text{ cm}^{-1}$  and  $25.700 \text{ cm}^{-1}$ . Use the corresponding Tanabe-Sugano diagram to estimate the values of  $\Delta_0$  and B.

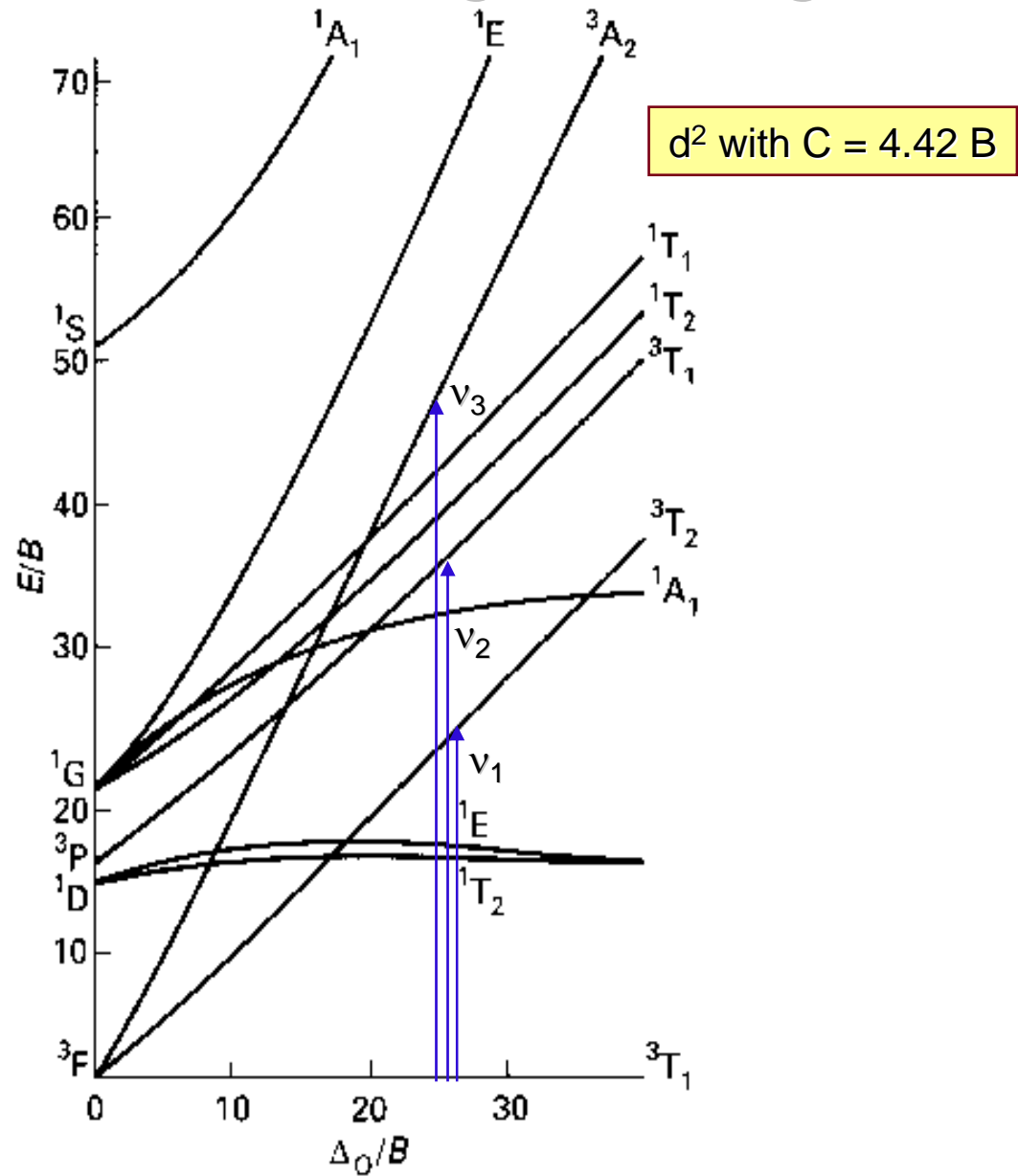
# Application of Tanabe-Sugano Diagrams

- spin allowed transitions

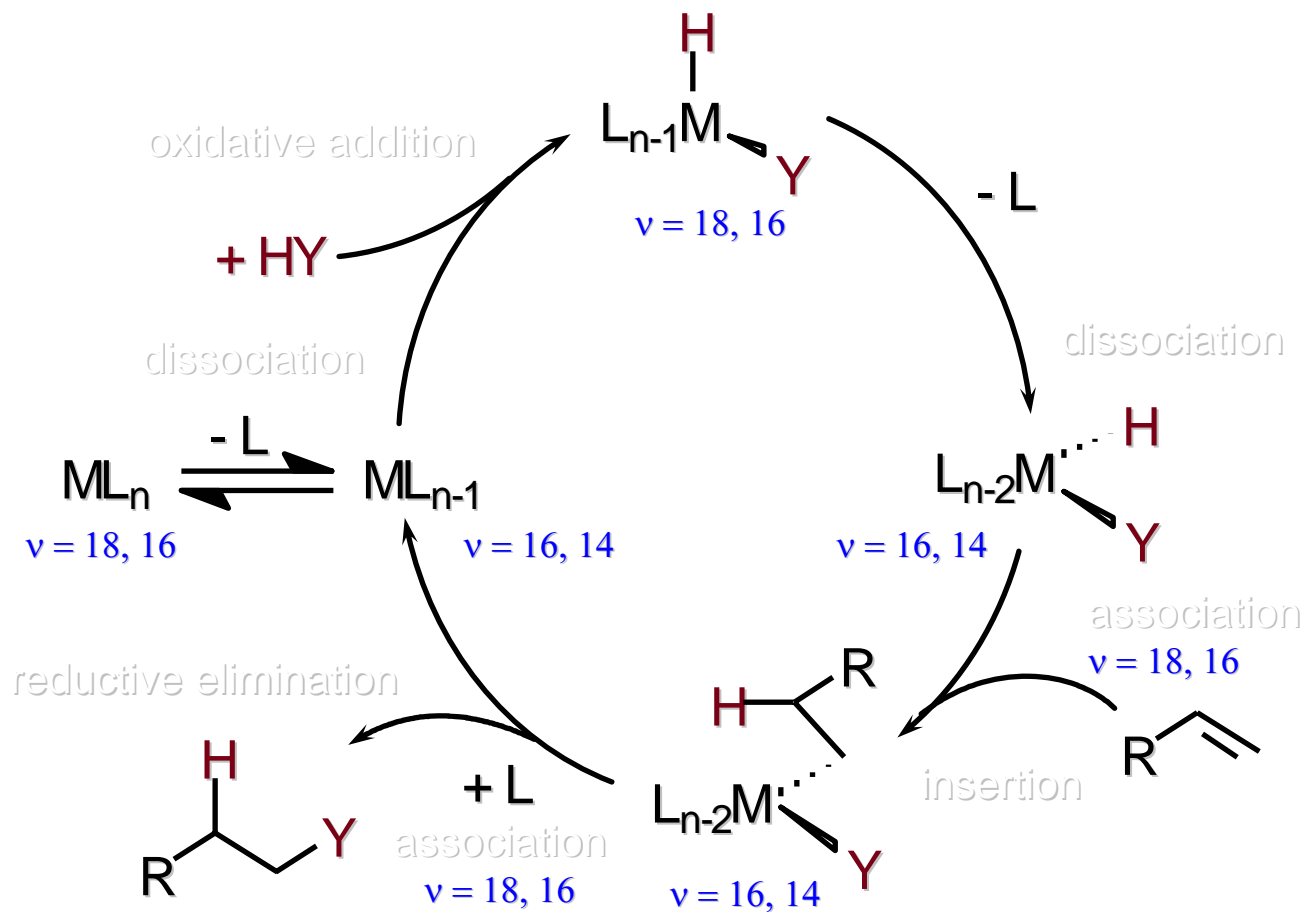
$v_1: {}^3T_2 \leftarrow {}^3T_1$  (lowest energy)

$v_2: {}^3T_1 \leftarrow {}^3T_1$

$v_3: {}^3A_2 \leftarrow {}^3T_1$



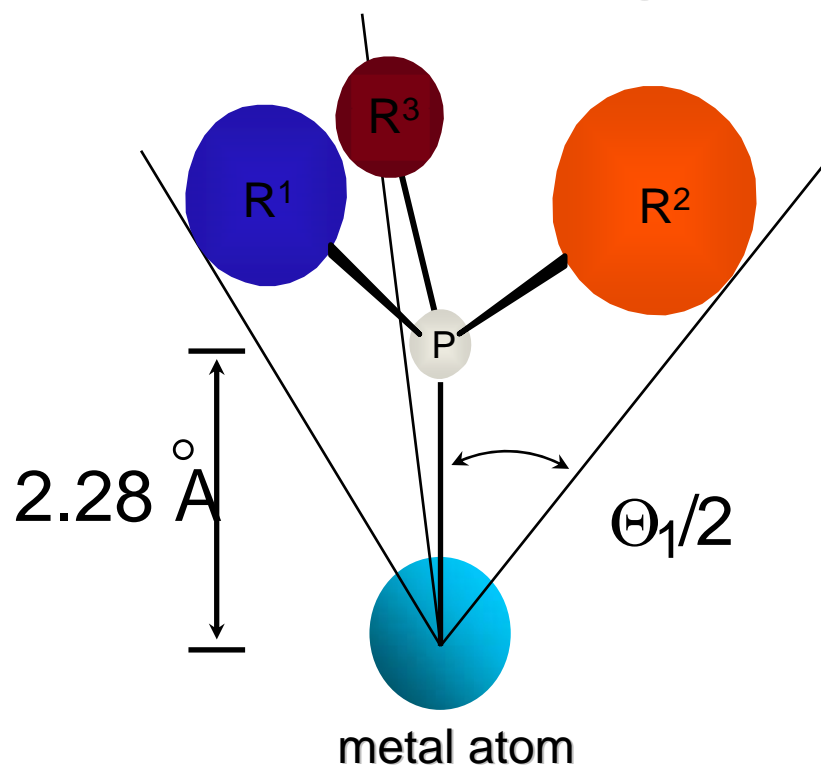
# Catalytic Cycle and Elementary Steps



# Activation of Octahedral Complexes

## *Steric Effects*

### *Tolman's Cone Angle*



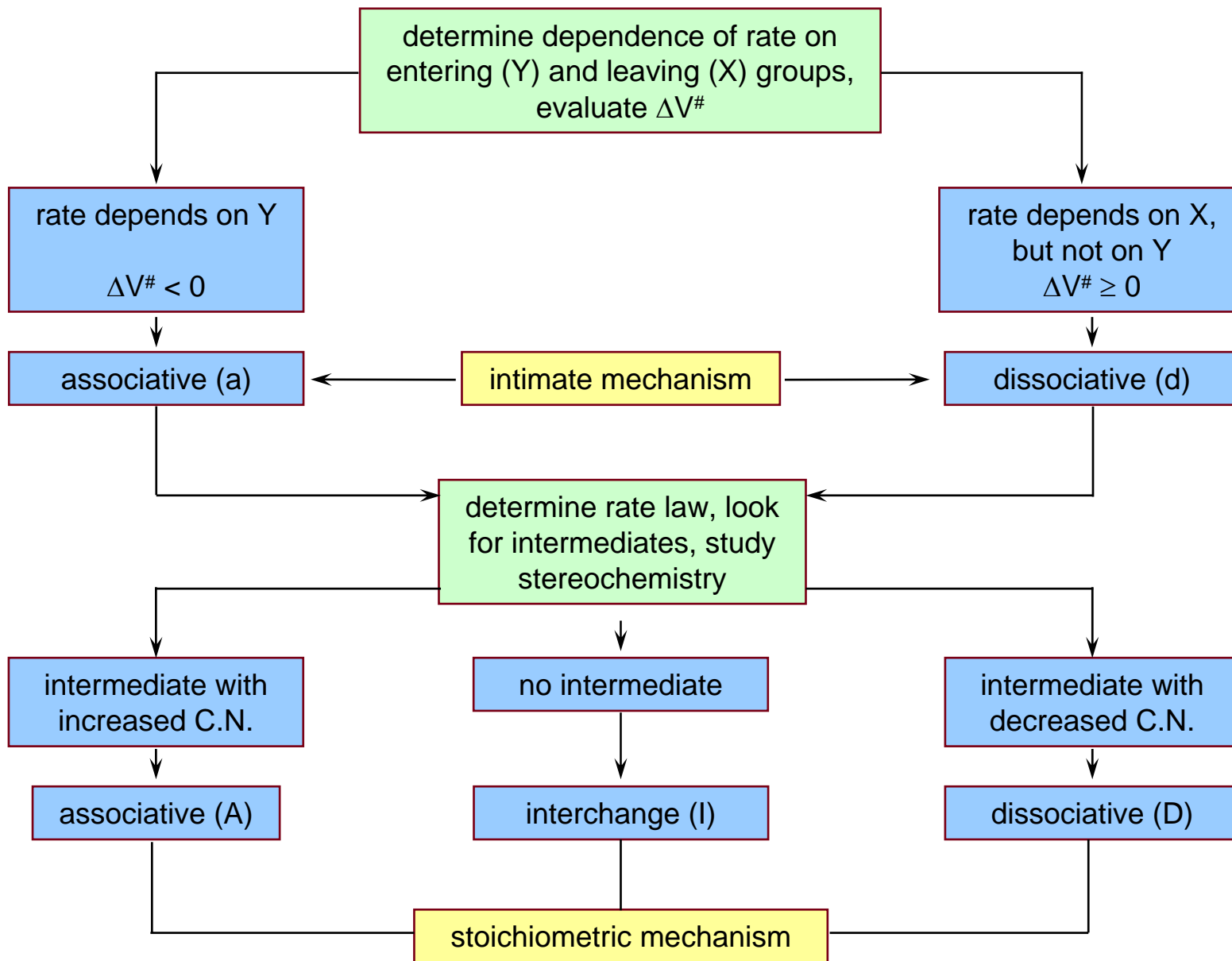
Chadwick A. Tolman

$$\Theta = 2/3 \sum_{i=1}^3 \Theta_i / 2$$

C. A. Tolman, *Chem. Rev.* 1977, 77, 313-348.

- Steric crowding favors dissociative activation because in this way the formation of the activated complex can relieve strain.

# Relations Between Substitution Mechanisms



# The *trans* Effect

- A strong  $\sigma$ -donor or  $\pi$ -acceptor ligand greatly accelerates the substitution of a ligand in *trans* position
- Substitutions on sqpl complexes proceed almost invariably via an associative rate-limiting stage.

## *trans-effect*

$\sigma$ -donor :  $\text{OH}^- < \text{NH}_3 < \text{Cl}^- < \text{Br}^- < \text{CN}^-$ ,  $\text{CO}$ ,  $\text{CH}_3^- < \text{I}^- < \text{SCN}^- < \text{PR}_3 < \text{H}^-$

$\pi$ -acceptor :  $\text{Br}^- < \text{I}^- < \text{NCS}^- < \text{NO}_2^- < \text{CN}^- < \text{CO}$ ,  $\text{C}_2\text{H}_4$

Effect of the *trans* ligand in substitutions of *trans*-[PtClL(PEt<sub>3</sub>)<sub>2</sub>]

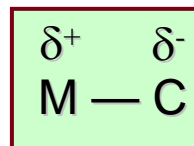
L	$k_1/\text{s}^{-1}$	$k_2/(\text{Lmol}^{-1}\text{s}^{-1})$
CH <sub>3</sub> <sup>-</sup>	$1.7 \cdot 10^{-4}$	$6.7 \cdot 10^{-2}$
C <sub>6</sub> H <sub>5</sub> <sup>-</sup>	$3.3 \cdot 10^{-5}$	$1.6 \cdot 10^{-2}$
Cl <sup>-</sup>	$1.0 \cdot 10^{-6}$	$4.0 \cdot 10^{-4}$
H <sup>-</sup>	$1.8 \cdot 10^{-2}$	4.2
PEt <sub>3</sub>	$1.7 \cdot 10^{-2}$	3.8

# Main-Group Organometallic Compounds

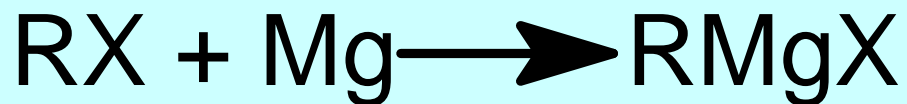
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- Electronegativity and ion-character

polarization of the metal-C bond



1901: Victor Grignard



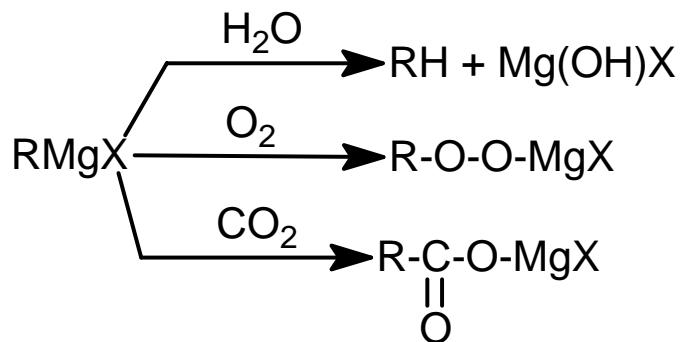
Solvent:

$\text{Et}_2\text{O}$ , THF

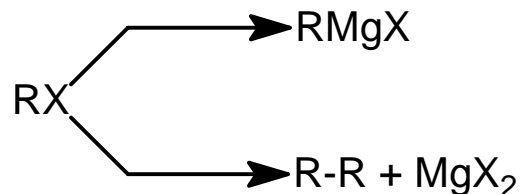
# Practical aspects

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- **Dry solvent is needed and an inert atmosphere**



- **RX should be added slowly, otherwise Wurtz coupling occurs**



# Types of M-C Bonds in the Periodic Table

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
<b>H</b> 1 1.00794(7)																	<b>He</b> 2 4.002602(2)	
<b>Li</b> 3 6.941(2)	<b>Be</b> 4 9.012182(2)											<b>B</b> 5 10.811(7)	<b>C</b> 6 12.0107(8)	<b>N</b> 7 14.00643(4)	<b>O</b> 8 15.999(4)	<b>F</b> 9 18.9984032(3)	<b>Ne</b> 10 20.1797(6)	
<b>Na</b> 11 22.98976928(2)	<b>Mg</b> 12 24.30506(1)											<b>Al</b> 13 26.9815385(2)	<b>Si</b> 14 28.0855(3)	<b>P</b> 15 30.97376199(4)	<b>S</b> 16 32.06(5)	<b>Cl</b> 17 35.453(6)	<b>Ar</b> 18 39.948(1)	
<b>K</b> 19 39.0983(1)	<b>Ca</b> 20 40.078(4)		<b>Sc</b> 21 44.95591(2)	<b>Ti</b> 22 47.867(1)	<b>V</b> 23 50.9415(1)	<b>Cr</b> 24 51.9961(6)	<b>Mn</b> 25 54.938044(1)	<b>Fe</b> 26 55.845(2)	<b>Co</b> 27 58.933194(5)	<b>Ni</b> 28 58.6934(4)	<b>Cu</b> 29 63.546(3)	<b>Zn</b> 30 65.39(2)	<b>Ga</b> 31 69.723(1)	<b>Ge</b> 32 72.61(2)	<b>As</b> 33 74.92160(2)	<b>Se</b> 34 78.96(3)	<b>Br</b> 35 79.904(1)	<b>Kr</b> 36 83.80(1)
<b>Rb</b> 37 85.4678(3)	<b>Sr</b> 38 87.62(1)		<b>Y</b> 39 88.90584(2)	<b>Zr</b> 40 91.224(2)	<b>Nb</b> 41 92.90638(2)	<b>Mo</b> 42 95.94(1)	<b>Tc</b> 43 98.9062(1)	<b>Ru</b> 44 101.07(2)	<b>Rh</b> 45 102.90550(2)	<b>Pd</b> 46 106.42(1)	<b>Ag</b> 47 107.8682(1)	<b>Cd</b> 48 112.411(8)	<b>In</b> 49 114.818(3)	<b>Sn</b> 50 118.710(7)	<b>Sb</b> 51 121.760(1)	<b>Te</b> 52 127.60(3)	<b>I</b> 53 126.90545(3)	<b>Xe</b> 54 131.29(4)
<b>Cs</b> 55 132.9054519(2)	<b>Ba</b> 56 137.327(7)	57-70 *	<b>Lu</b> 71 174.967(1)	<b>Hf</b> 72 178.49(2)	<b>Ta</b> 73 180.94788(2)	<b>W</b> 74 183.84(1)	<b>Re</b> 75 186.207(1)	<b>Os</b> 76 190.23(2)	<b>Ir</b> 77 192.222(1)	<b>Pt</b> 78 195.084(1)	<b>Au</b> 79 196.966569(4)	<b>Hg</b> 80 200.59(2)	<b>Tl</b> 81 204.3833(2)	<b>Pb</b> 82 207.2(1)	<b>Bi</b> 83 208.980388(2)	<b>Po</b> 84 [209]	<b>At</b> 85 [210]	<b>Rn</b> 86 [222]
<b>Fr</b> 87 [223]	<b>Ra</b> 88 [226]	89-102 **	<b>Lr</b> 103 [260]	<b>Rf</b> 104 [261]	<b>Db</b> 105 [262]	<b>Sg</b> 106 [263]	<b>Bh</b> 107 [264]	<b>Hs</b> 108 [265]	<b>Mt</b> 109 [266]	<b>Uun</b> 110 [267]	<b>Uuu</b> 111 [268]	<b>Uub</b> 112 [277]		<b>Uuq</b> 114 [289]		<b>Uuh</b> 116 [289]		<b>Uuo</b> 118 [289]

Key:  
 element name  
 atomic number  
 symbol  
 1997 atomic weight (mean relative mass)

\*lanthanoids

\*\*actinoids

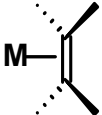

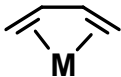
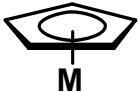
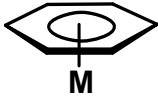
<b>La</b> 57 138.90547(7)	<b>Ce</b> 58 140.12(1)	<b>Pr</b> 59 140.90765(2)	<b>Nd</b> 60 144.24(1)	<b>Pm</b> 61 [145]	<b>Sm</b> 62 150.36(2)	<b>Eu</b> 63 151.964(1)	<b>Gd</b> 64 157.25(1)	<b>Tb</b> 65 158.92534(2)	<b>Dy</b> 66 162.50(1)	<b>Ho</b> 67 164.93032(2)	<b>Er</b> 68 167.259(1)	<b>Tm</b> 69 168.93032(2)	<b>Yb</b> 70 173.054(1)
<b>Ac</b> 89 [227]	<b>Th</b> 90 232.0377(1)	<b>Pa</b> 91 231.036888(2)	<b>U</b> 92 238.02891(3)	<b>Np</b> 93 [237]	<b>Pu</b> 94 [244]	<b>Am</b> 95 [243]	<b>Cm</b> 96 [247]	<b>Bk</b> 97 [247]	<b>Cf</b> 98 [251]	<b>Es</b> 99 [252]	<b>Fm</b> 100 [257]	<b>Md</b> 101 [258]	<b>No</b> 102 [259]

- electron deficiency compounds
- ionic compounds
- d-metals, M-C  $\sigma$ -bonding and  $\pi$ -bonding


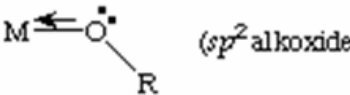
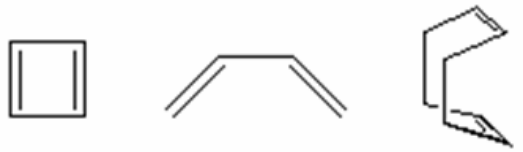
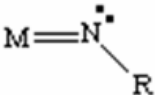
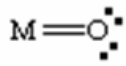
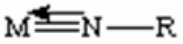

- covalent M-C  $\sigma$ -bonding
- metalloids
- non-metals

# Counting Electrons

- Metal atoms and ligands are treated as neutral
- Count all valence e<sup>-</sup> of the metal & all e<sup>-</sup> donated by the ligands
- Correct for charges of the complex

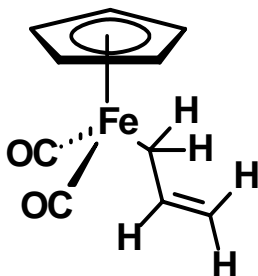
e <sup>-</sup> available	hapticity	Ligand	Metal-ligand structure
1	$\eta^1$	H	M-H
1	$\eta^1$	Cl, Br, I	M-X
1	$\eta^1$	OH	M-OH
1	$\eta^1$	CN	M-C $\equiv$ N
1	$\eta^1$	CH <sub>3</sub> , alkyl	M-CH <sub>3</sub> , M-R
2	$\eta^1$	CO, PR <sub>3</sub>	M-C $\equiv$ O, M-PR <sub>3</sub>
2	$\eta^1$	NH <sub>3</sub> , H <sub>2</sub> O	M-NH <sub>3</sub> , M-OH <sub>2</sub>
2	$\eta^1$	alkylidene	M=CR <sub>2</sub>
2	$\eta^2$	alkene	
2	$\eta^1$	=O, =S	M=O, M=S
3	$\eta^1$	NO(linear)	M-N $\equiv$ O
3	$\eta^3$	C <sub>3</sub> H <sub>5</sub> , allyl	
3	$\eta^1$	alkylidyne	M $\equiv$ C-R
4	$\eta^4$	1,3-diene, C <sub>4</sub> H <sub>6</sub>	
5	$\eta^5$	cyclopentadienyl, C <sub>5</sub> H <sub>5</sub>	
6	$\eta^6$	arene, C <sub>6</sub> H <sub>6</sub>	

# Counting electrons (special ligands)

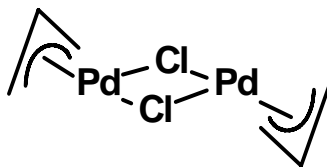
	Neutral/Covalent
R (H, Me, Et, Pr, H) -CN, OH, Cl, OR ( $sp^3$ ), acyl, NO (bent)	1
PR <sub>3</sub> , amines, ethers, NH <sub>3</sub> , R <sub>2</sub> S, CO, RCN, RNC, olefins, acetylenes (sometimes), ketones	2
 (allyl)	3
 ( $sp^2$ alkoxide)	3
NO (linear)	3
 (1,5-COD) Acetylenes (sometimes)	4
 (bent imido)  (oxo)	2
 (linear imido)  (oxo)	4

# Metal Allyl Bonds

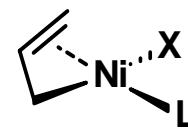
## *Bonding Modes*



$\eta^1$ - coordination

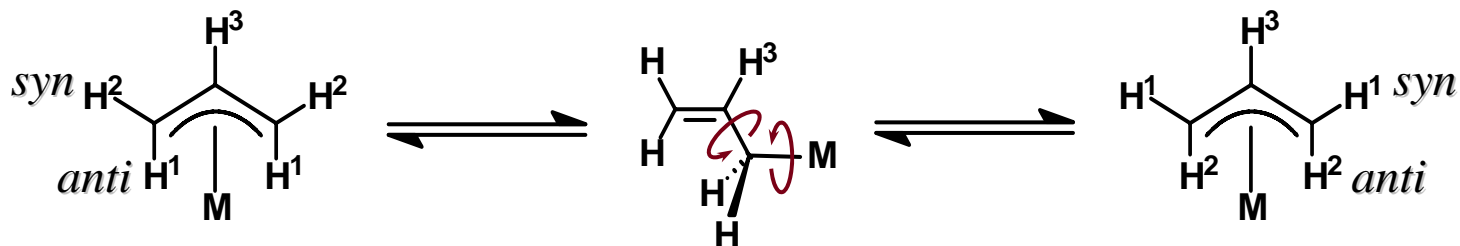


$\eta^3$ - coordination



$\eta^1$ -  $\eta^2$ - coordination

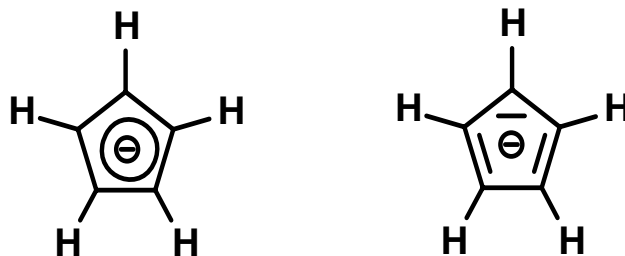
- *Syn* and *anti* protons can be distinguished in  $^1\text{H}$ -NMR spectrum
- *Dynamic behaviour (isomerization) on the NMR time-scale often leads to averaged signals*



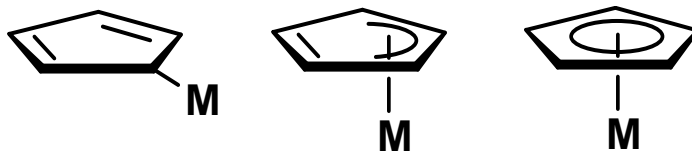
- Allyl metal complexes are important intermediates and metal-precursors in catalytic reactions

# Cyclopentadienyl Metal Complexes

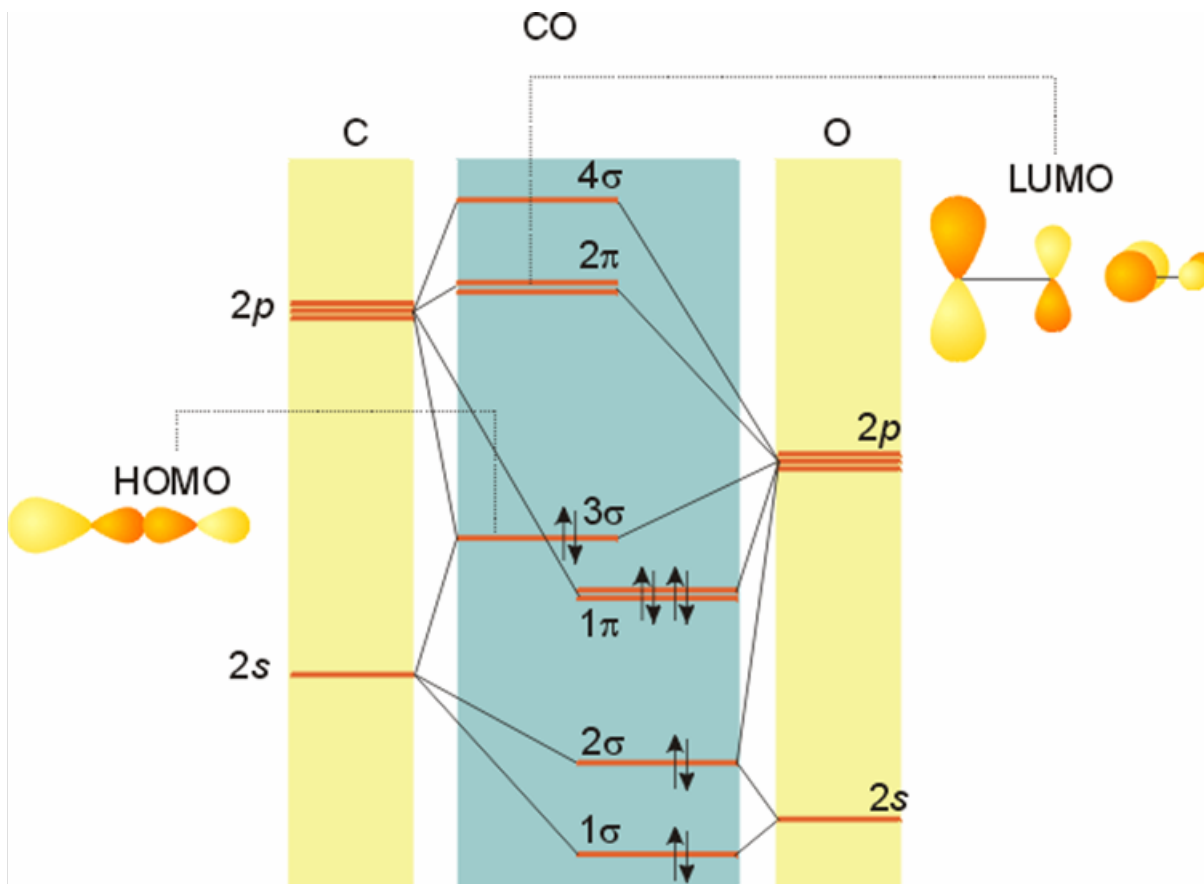
## *Metallocenes*



- Important Ligand in Organometallic Chemistry
- Frequently used Ligand in Organometallic Chemistry: 1990: ~80% of Organometallic compounds contain the Cp Ligand
- Electron-Buffer Ligand:  $\eta^1$ ;  $\eta^3$ ;  $\eta^5$  coordination common



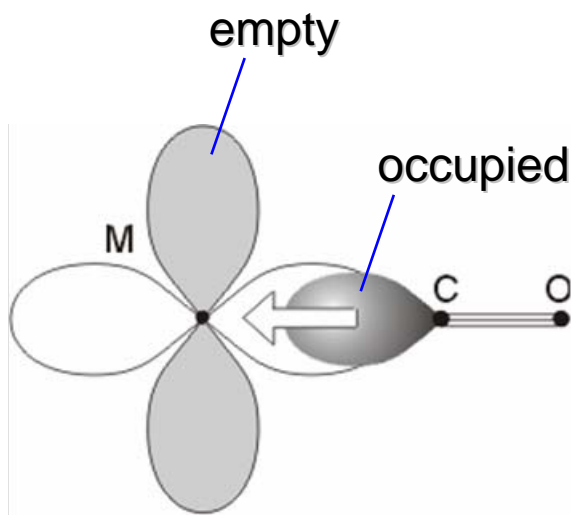
# MO's of Carbon Monoxide



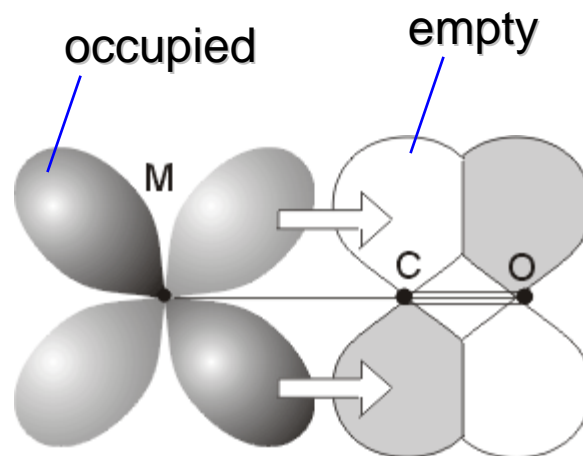
- HOMO has  $\sigma$  symmetry and point away from C in the CO-axis  
=> forms  $\sigma$ -donor bonds with the metal
- LUMO's are  $\pi^*$  orbitals which play a crucial role in overlap with  $t_{2g}$  metal orbitals  
=> CO acts as strong  $\pi$ -acceptor

# *MO's of Carbonyl Complexes*

## *Bond Characteristics*



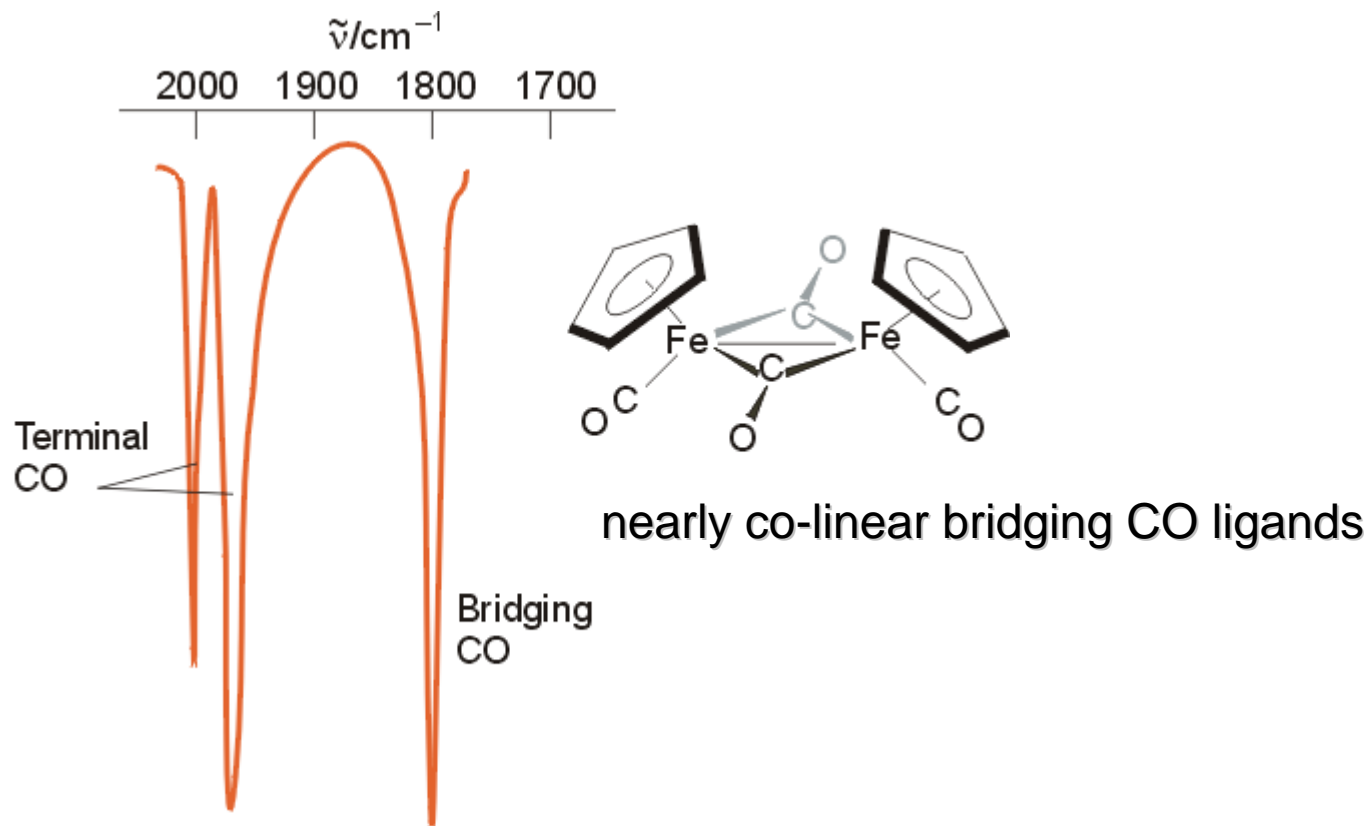
$\sigma$ -donor



$\pi$ -acceptor

# Structure

- If the positions of the CO ligands are more symmetrical arranged than the point group of the whole compound suggests, fewer  $\nu_{\text{CO}}$  will be observed!  
(see slide Organomet\_25)

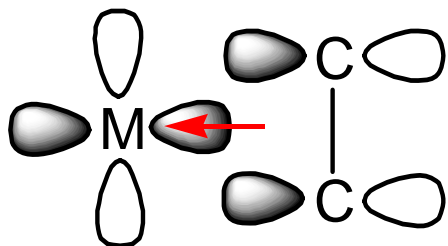


# Transition Metal - Alkene Complexes

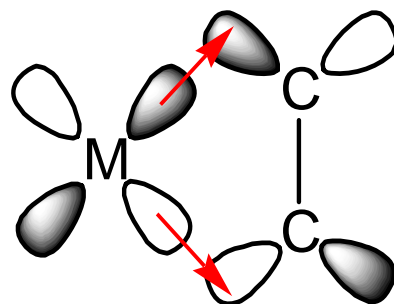
## *Bonding Situation*

## Dewar-Chatt-Duncanson Model

$\sigma$ -bond



$\pi$ -backbond

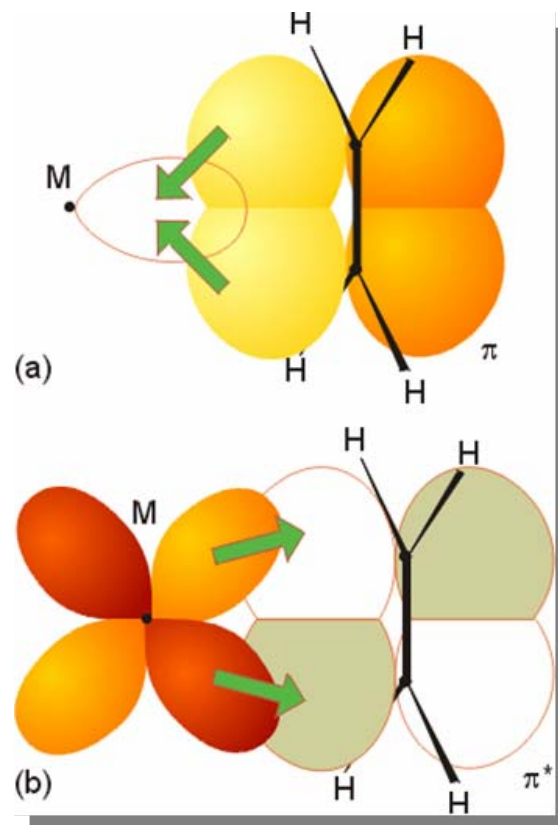


empty  
d-orbital

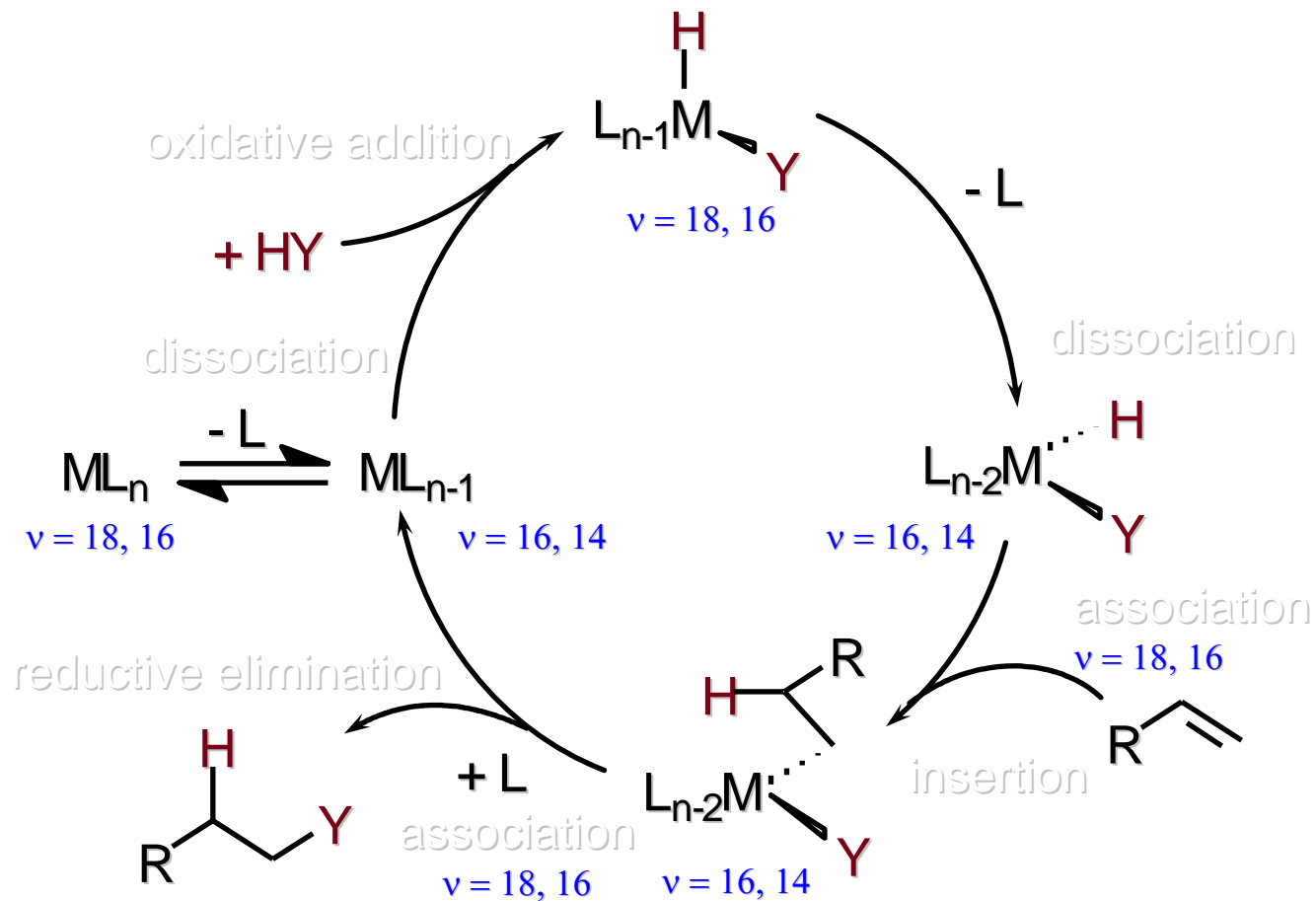
filled  
ethylene  
 $\pi$ -orbital

filled  
d-orbital

empty  
ethylene  
 $\pi^*$  orbital



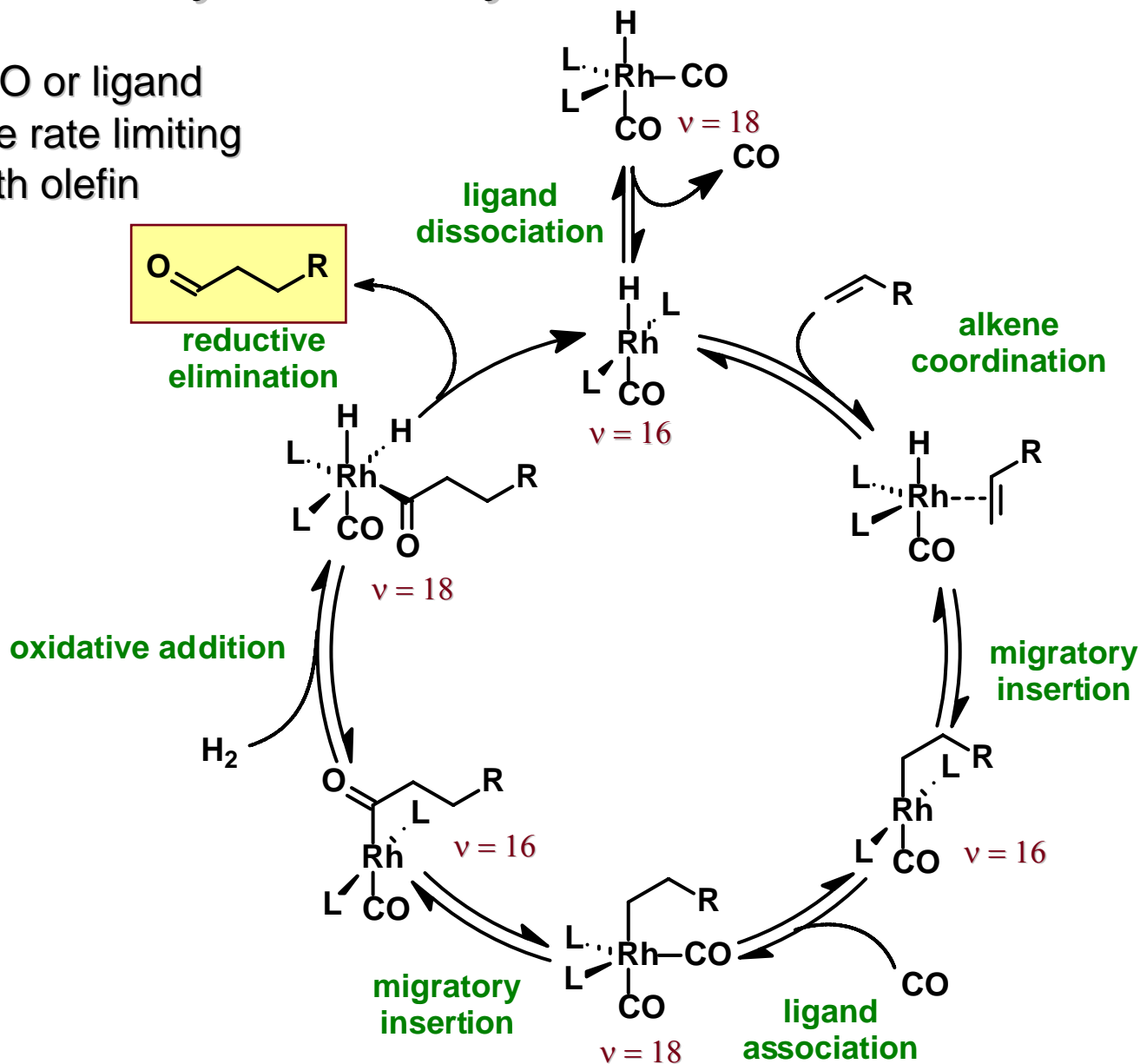
# Catalytic Cycle and Elementary Steps



- Most elementary steps have been discussed in chapter 24 (reaction mechanisms)

# Hydroformylation

- In most cases CO or ligand dissociation is the rate limiting step, together with olefin coordination.

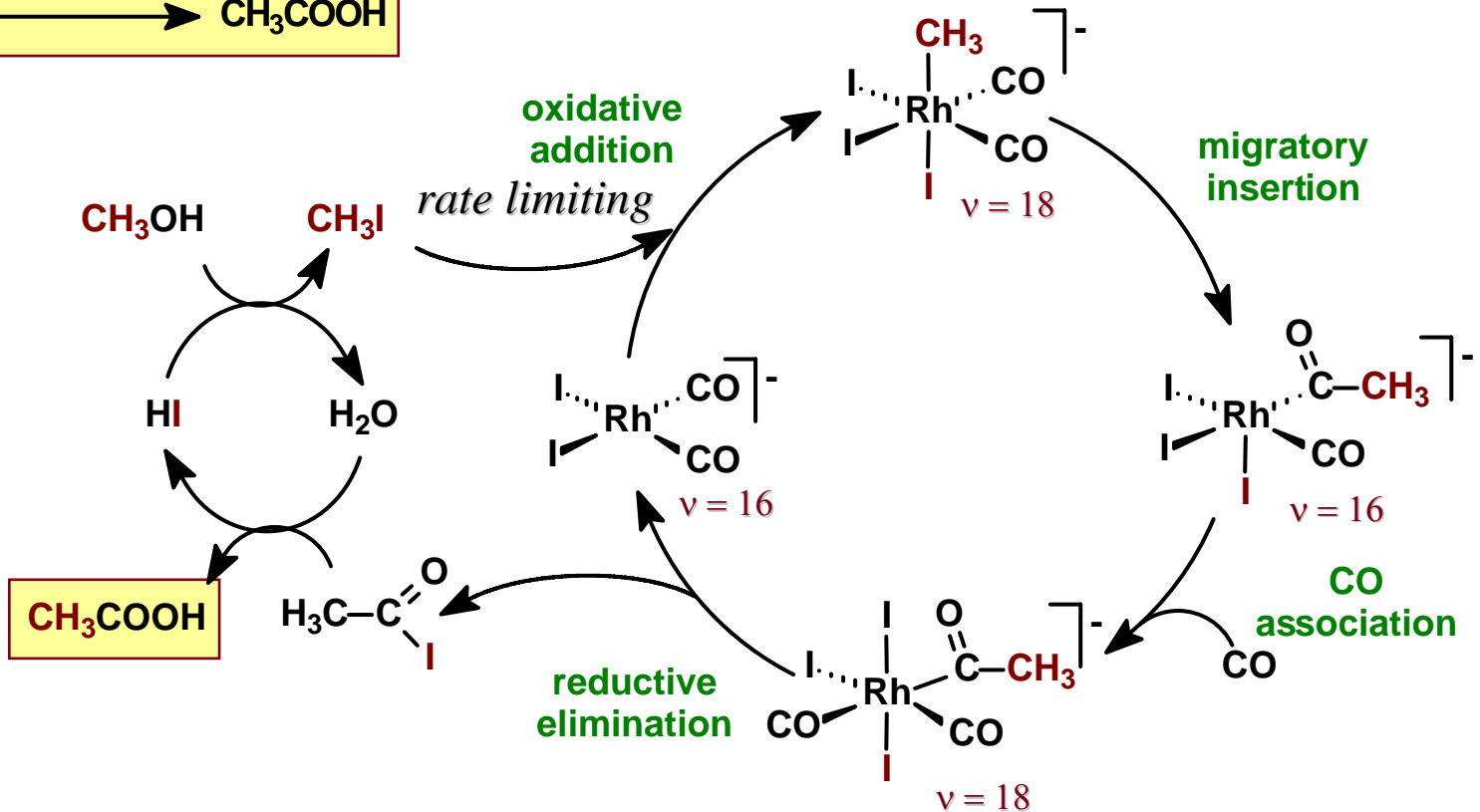
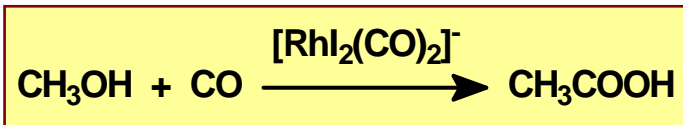


Type I rate law:

$$r = \frac{A[\text{alkene}][\text{Rh}]}{B + [L]}$$

# Monsanto Acetic Acid Process

## *Carbonylation of Methanol*



- Currently ~ 3.5 Mt/a produced worldwide, 60% of all acetyl compounds based on this process.
- New BP process uses  $[\text{IrI}_2(\text{CO})_2]^-$  with  $\text{Ru}_2(\text{CO})_6\text{I}_2(\mu\text{-I})_2$  as cocatalyst

# Good Luck !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!

<http://www.hybridcatalysis.com/teachingcorner.htm>



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- Research process
- Equipment

### Catalysts

- POSS® Nanotechnology
- Catalyst features

### Teaching corner

students  
kids

## Teaching corner

Students TU/e : 6BA40 COLLEGE ANORGANISCHE CHEMIE SLIDES, STUDIEWIJZER EN OVERIGE INFO

- SLIDES
- STUDIEWIJZER & LEERDOELEN
- MEDEDELINGEN

**kids** *the lotuseffect* voor VWO-werkweek

Applications of the materials we make (the so called PO: (covering/paint, for example on a car or house). The inspi model, coatings were made that clean themselves: the l as a fakir on his bed with spikes.

Rain flushes away all dirt... Imagine nobody has to clean h



The sr the leaf of a lotus and to the right: a leaf through a micro glass), it really is like a bed with spikes!!

**6BA40:** [Dr. H.C.L. Abbenhuis, Helix STW 4.43](#)

SLIDES

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[27 OKT](#)      [29 OKT](#)      31 OKT

STUDIEWIJZER & LEERDOELEN