Chemistry 5, Part III: Coordination chemistry

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Chimie, un accompagnement au quotidien Tout-en-Un, PC/PC*
Ribeyre Tristan, Matthieu, et al., De Boeck (2014)

Inorganic chemistry
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Cote Studium : 546 HOU

Inorganic chemistry
Miessler, Gary L
Upper Saddle River : Pearson Education
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Physico-Chimie Inorganique
Kettle, Schriver, Ed. De Boeck; 1999

Chimie Inorganique
Huheey, Keiter, Keiter, Ed. De Boeck; 1996

Chimie Inorganique
Schriver, Atkins, Ed. De Boeck; 2001

Les orbitales moléculaires dans les complexes
Jean, Yves, Ed. Ecole polytechnique, (2003)

Chimie PC/PC*, Parcours prépa
Emond, Matthieu, et al., Edisciences, Dunod (2022)

Chemistry 5, Part III:
Coordination chemistry

Prerequisites:

Molecular inorganic chemistry notions:

VSEPR, acid-base and redox reactions, electronic configuration,

periodic table of the elements, atomic orbitals,

covalent bond (Lewis model), ionic bond

basic visible, NMR and IR spectroscopies

Main objectives:

1) Determine the geometry of a coordination complex, know how to represent them and establish their reactivity .

2) Write down the reaction mechanisms of organometallic chemistry, observing the writing conventions.

3) Predict and explain the optical and magnetic properties of a complex using crystal field or ligand field theory.

Chemistry 5, Part III:
Coordination chemistry

<u>Menu:</u>

- Complexes of d-block metals
- Recognise the coordination site(s) of a ligand from a Lewis structure
- Establish the interaction diagram

between a d-block orbital and a σ-donor ligand orbital.

- Electron counting
- Recognise a π-donor or π-acceptor ligand from a Lewis structure or its frontier orbitals.
- optical and magnetic properties of a complex.
- Catalytic activity of complexes; catalytic cycles:
    - Recognise the nature of a step in a catalytic cycle,
    - Identify the orbital interactions between a metal and an alkene, dihydrogen and carbon monoxide.

Coordination complexes

Chemical formula :

ML_p with M **metal** (oxidation number = 0) or **metal ion** at the center of the structure

= Lewis Acid

L **ligand**, = molecule with a lone pair of electrons ('doublet non liant'), or a double bond (ex: C=C) or H_2

= Lewis base

Lewis Base:

A substance that can **supply** a pair of electrons to create a covalent bond, electron donor

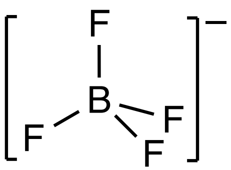
Lewis Acid:

A substance that can **receive** a pair of electrons from a base ('possède une lacune électronique')

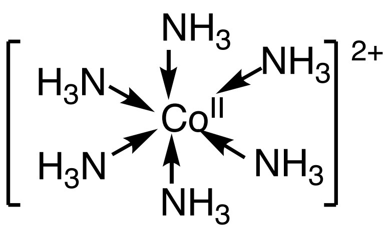
Electron acceptor

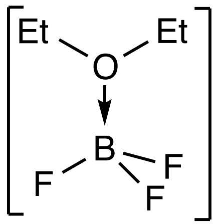
In a complex: Housecroft p237

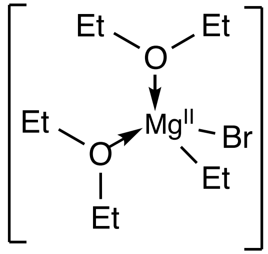
- A **line** denotes the interaction between an ***anionic*** ligand and the acceptor

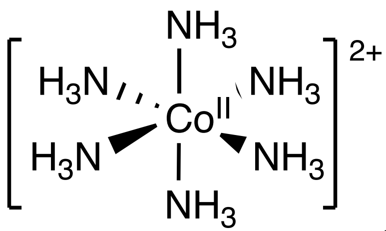


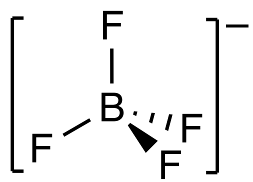
- An **arrow** shows the donation of an electron pair from a ***neutral*** ligand to an acceptor











convention often ignored

Nomenclature of coordination complexes

Major rules:[Missler Ed 1 p340]

1. The cation comes first, then the anion (the same for simple salts).
   It is the **reverse in French!**
2. The complex (coordination sphere) is enclosed in square brackets, the counter ions placed after.
   the ligands are named before the metal; in the formula the metal is written first.

Ex: diamminesilver(I)chloride $[Ag^{I}(NH_3)_2]Cl$ sodium chloride : NaCl)
Chlorure de diammineargent(I) chlorure de sodium

3. The oxidation number is put in parentheses as a Roman numeral after the metal name complex. It can be written as superscript at the left of the symbol of the metal in the formula.

4. If the complex is negative, add the suffix -ate.
   If no specified counter-ion, begin by ion.

Ex: hexachloroplatinate(IV) $[PtCl_6]^{2-}$ ion hexachloroplatinate(IV)

Nomenclature of coordination complexes

<u>Major rules:</u> Missler Ed 1 p340

5. Ligands are named in alphabetical order (regardless of their charge). The name of the ligand is considered, not the prefix.

6. Anionic ligands are given an –o suffix.
   Neutral ligands retain their names, coordinated water is called *aqua*.
   a**mm**ine (with 2 m) is used to distinguish NH_3 from alkyl amines.
   In the formula, begin by anionic ligand and the coordinated atom.

7. The number of ligands of one kind is given by simple prefixes di-, tri-, tetra-…. If the ligand name includes these prefixes or is complicated, prefixes bis, tris, tetrakis… are used.

Ex: **aqua**chloro**bis**(ethylenedia**m**ine)cobalt(III) $[CoCl(en)_2(OH_2)]^{2+}$
ion aquachloro**bis**(éthylène**dia**mine)cobalt(III)

8. Add prefixes *cis*– or *trans*–; *mer*– or *fac*– to distinguish geometrical isomers; Δ– or Λ– for optical stereoisomers.

9. Use the prefix μ– for bridging ligands.

Stability constants of coordination complexes

Stepwise stability constants: K_n Housecroft p239

('constantes partielles de formation')

In aqueous solution, metal ions are hydrated:

$[Co(OH_2)_6]^{2+}$

In presence of a (neutral) ligand (for ex. NH_3):

$$[Co(OH_2)_6]^{2+} + NH_{3(aq)} \leftrightarrows [Co(NH_3)(OH_2)_5]^{2+} + OH_{2(aq)} \qquad K_1 = \frac{a([Co(NH_3)(OH_2)_5]^{2+})}{a([Co(OH_2)_6]^{2+}).a(NH_3)}$$

$$[Co(NH_3)(OH_2)_5]^{2+} + NH_{3(aq)} \leftrightarrows [Co(NH_3)_2(OH_2)_4]^{2+} + OH_{2(aq)}$$

$$K_2 = \frac{a([Co(NH_3)_2(OH_2)_4]^{2+})}{a([Co(NH_3)(OH_2)_5]^{2+}).a(NH_3)}$$

....

$$[Co(NH_3)_n(OH_2)_{6-n}]^{2+} + NH_{3(aq)} \leftrightarrows [Co(NH_3)_{n+1}(OH_2)_{5-n}]^{2+} + OH_{2(aq)}$$

$$K_{n+1} = \frac{a([Co(NH_3)_{n+1}(OH_2)_{5-n}]^{2+})}{a([Co(NH_3)_n(OH_2)_{6-n}]^{2+}).a(NH_3)}$$

$$[Co(NH_3)_{p-1}(OH_2)_{5-p}]^{2+} + NH_{3(aq)} \leftrightarrows [Co(NH_3)_p]^{2+} + OH_{2(aq)}$$

$$K_p = \frac{a([Co(NH_3)_p]^{2+})}{a([Co(NH_3)_{p-1}(OH_2)_{5-p}]^{2+}).a(NH_3)}$$

Stability constants of coordination complex, denticity

Overall stability constants: β_p Housecroft p241

(‘constante globale de formation’)

$[Co(OH_2)_6]^{2+} + p\ NH_{3(aq)} \leftrightarrows [Co(NH_3)_p]^{2+} + p\ OH_{2(aq)}$

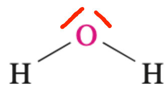
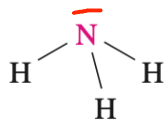
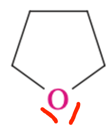
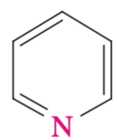
$$\beta_p = \frac{a([Co(NH_3)_p]^{2+})}{a([Co(OH_2)_6]^{2+}).a(NH_3)^p}$$

$$\beta_p = \prod_{n=1}^{p} K_n$$

Denticity: Housecroft p242 (or 183) (‘denticité’)

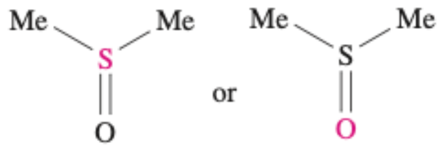
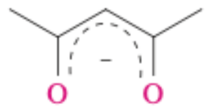
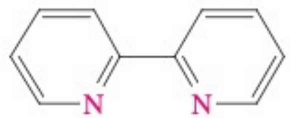
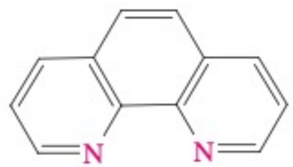
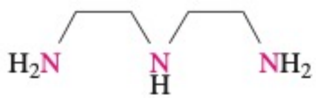
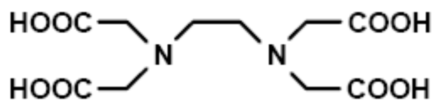
Number of donor atoms through which a ligand coordinates to a metal ion

Monodentate ligands
(‘monodente’)

Name of ligand	Abbreviation (if any)	Denticity	Structure with donor atoms marked in red
Water		Monodentate	
Ammonia		Monodentate	
Tetrahydrofuran	THF	Monodentate	
Pyridine	py	Monodentate	

Denticity, examples of ligands

Denticity: Housecroft p242 (or 183) ('denticité')

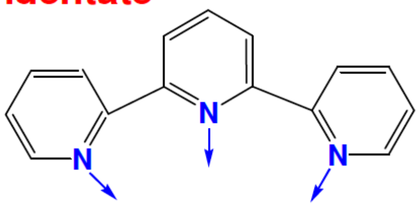
	Name of ligand	Abbreviation (if any)	Denticity	Structure with donor atoms marked in red
Monodentate ligands	Dimethylsulfoxide	DMSO	Monodentate	
Bidentate ligands ('bidente')	1,2-Ethanediamine[‡] ethylenediamine	en	Didentate	
	Acetylacetonate ion	$[acac]^-$	Didentate	
	2,2'-Bipyridine	bpy or bipy	Didentate	
	1,10-Phenanthroline	phen	Didentate	
tridentate ligands ('tridente')	1,4,7-Triazaheptane[‡] diethylenetriamine	dien	Tridentate	
	1,4,7,10-Tetraazadecane[‡] triethylenetetramine	trien	Tetradentate	
hexadentate ('hexadente')	*N,N,N',N'*-Ethylenediaminetetraacetate ion[*]	$[EDTA]^{4-}$	Hexadentate	

Denticity, examples of ligands

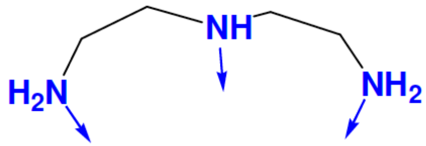
Denticity: Kettle beginning book, + Bulach V. ch 1 ('denticité') **Physico-Chimie Inorganique**
Kettle, Schriver, Ed. De Boeck; 1999

tridentate ligands

Tridentate

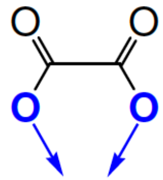


2,2',6',2''- Terpyridine (terpy)



dien

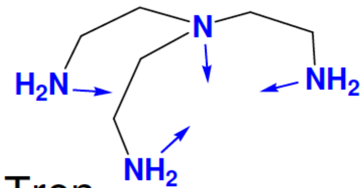
bidentate ligand



Oxalatato (ox)

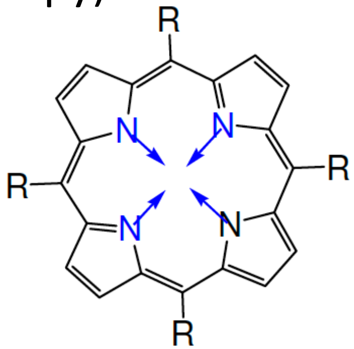
tetradentate ligands

Tétradentate

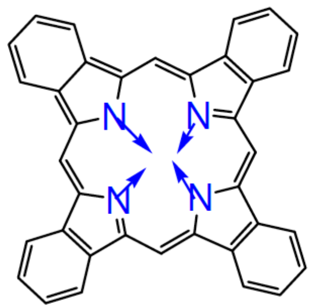


Tren

Tris(2-aminoethyl)amine (tren)



Porphyrin

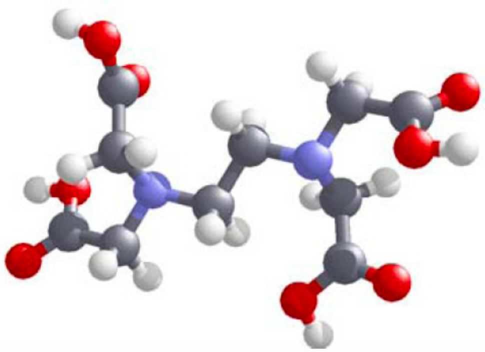


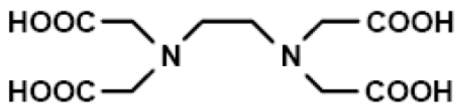
Phthalocyanin

hexadentate ligands

Hexadentate

EDTA



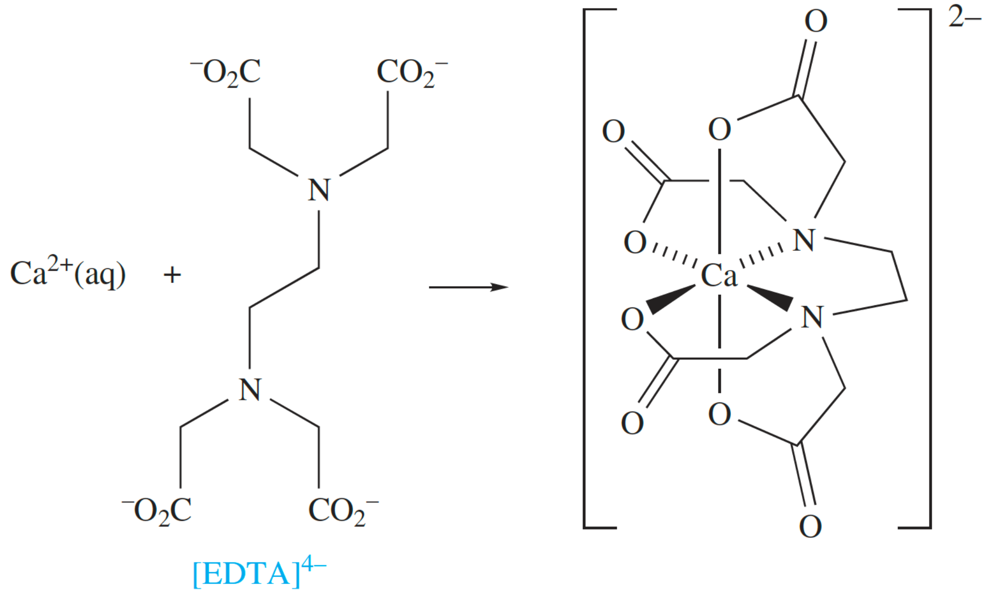


Chelate effect

Coordination of a polydentate ligand to an ion leads to the formation of a **chelate ring.** Housecroft p242 (or 183)

5 such rings can be seen in $[Ca(EDTA)]^{2-}$

Chelate is derived from the Greek for a crab's claw ('pince').



<u>Chelate effect:</u> Housecroft p241 (' effet chélate')

For a given metal ion:

Polydentate ligands form more stable complexes than monodentate ones

$[Ni(NH_3)_6]^{2+}{}_{(aq)} + 3\ en_{(aq)} \leftrightarrows [Ni(en)_3]^{2+} + 6\ NH_{3\ (aq)}$

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ \qquad \log K = 9.27 \qquad \Delta_r G^\circ = -52.9\ \mathrm{kJ\ mol^{-1}}$$

Chelate effect

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$\Delta rH° = -16.8\ kJ.mol^{-1}$ & $\Delta rS° = +161\ J.K^{-1}.mol^{-1}$ $T\Delta rS° = +36.1\ kJ.mol^{-1}$

Thus, both the negative ΔrH° and positive TΔrS° terms contribute to the overall <0 value of ΔrG°.

Enthalpic term:

- electrostatic repulsion ↘ from 2 NH_3 to en;

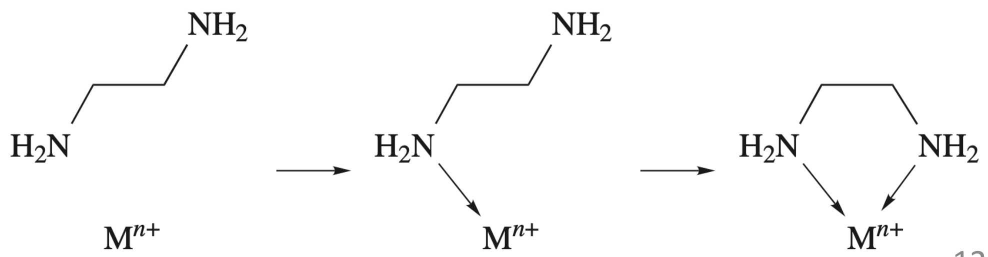
* desolvation effects :more H bonds formed with NH_3 compared to en;

* an inductive effect of the alkyl bridges which ↗ the donor strength of en versus NH_3.

Entropic term:

* 4 reactants and 7 products: the number of species in solution ↗ : ΔrS° >0

* high probability of M^{n+} to attach to the 2nd N because the ligand is already anchored to M^{n+}.

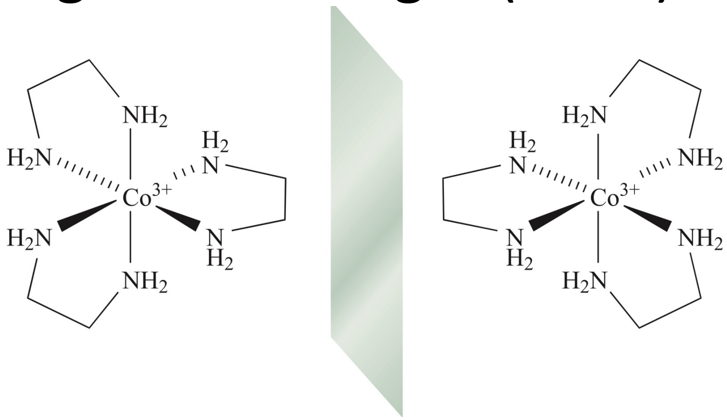


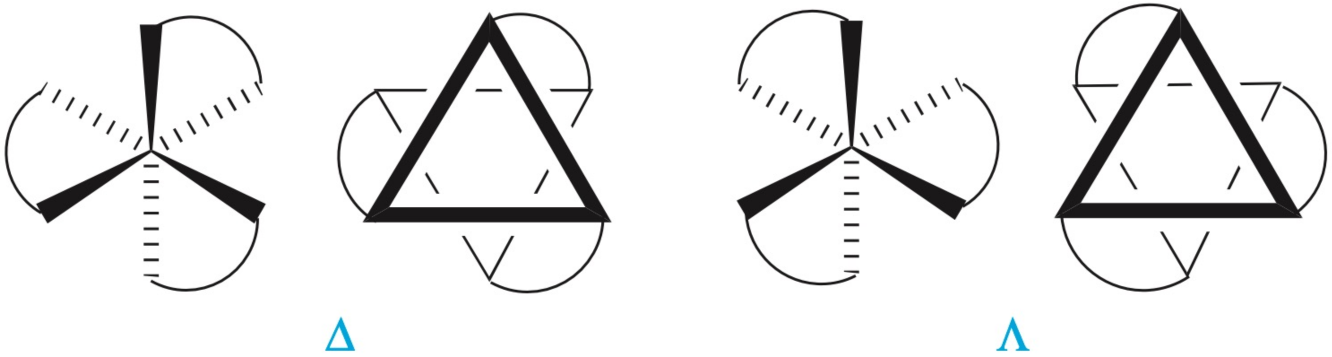
Optical isomers with bidentate ligands

<u>Optical isomers = enantiomers:</u> Housecroft p551-2

Octahedron complexes containing 2 or 3 bidentate ligands exit as enantiomers distinguished using Δ (delta) and Λ (lambda) prefixes.

Ex: $[Co(en)_3]^{3+}$



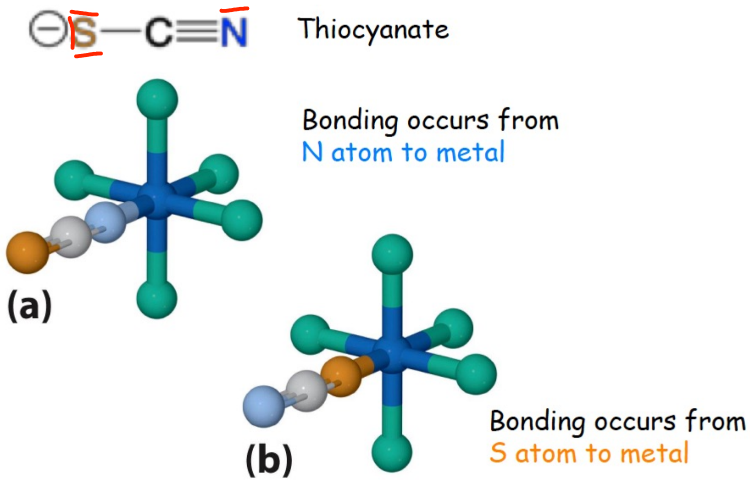


Octahedron viewed down a three-fold axis, and the chelates then define either a right- (Δ) or left-handed helix (Λ).

Starting from a donor atom at the front and going to the other at the back on the same ligand, if you turn right, it is Δ , otherwise Λ.

Ambidendate, bridging ligands, hapticity

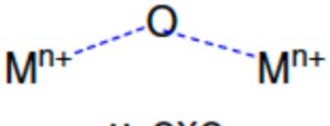
Ambidentates ligands: ('ambidente') Huheey pA73 + V. Bulach



Can bind by one or the other end

- SCN$^-$: thiocyanate or κ*S*-thiocyanate
- NCS$^-$: isothiocyanate or κ*N*-thiocyanate
- OCN$^-$: cyanate or κ*O*-cyanate
- NCO$^-$: isocyanate or κ*N*-cyanate

Bridging ligands ('pontant')

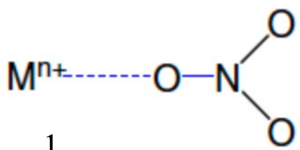


Hapticity: ('hapticité') https://en.wikipedia.org/wiki/Hapticity

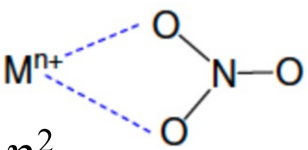
= coordination of a ligand to a metal center *via* an uninterrupted and contiguous series of atoms.

Ex: Nitrate

cyclopentadienyl in ferrocene [Fe(η^5-Cp)$_2$]

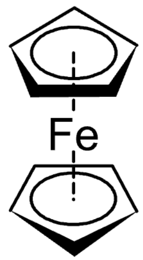


η^1-



η^2-

η^5-



Coordination number and geometry

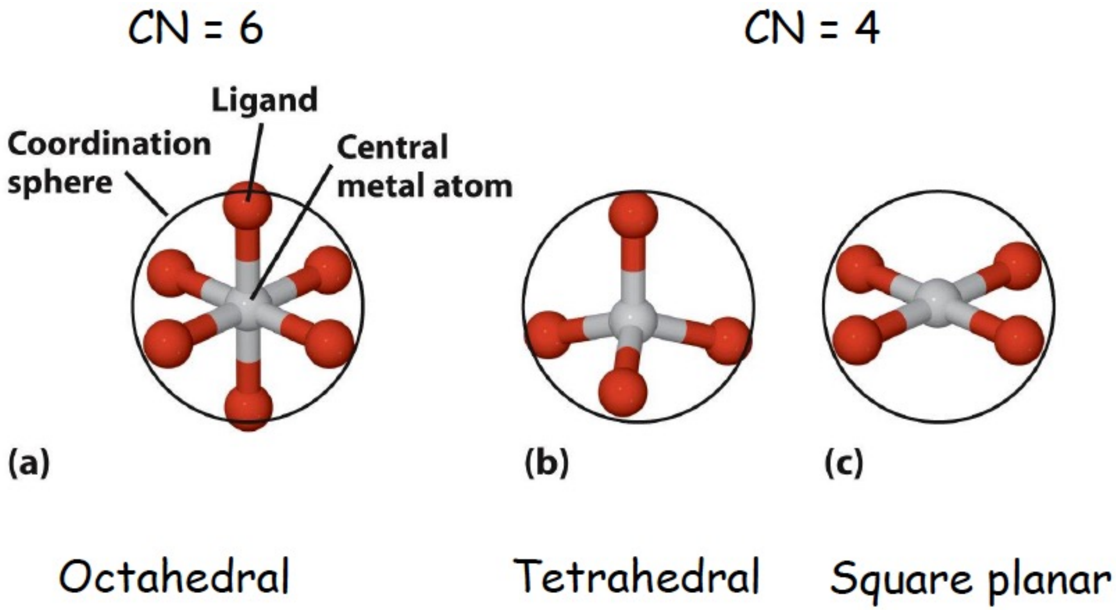
Coordination number (or ligancy): (‘coordinence’) of a central metal (ion) is the number of neighbours (atoms, molecules, ions) bound to it. Wikipedia

Geometry: depends on the coordination number (CN). Most often,

if CN = 6 octahedral geometry

If CN = 4 tetrahedral

or square planar geometry (especially if d^8 metal ion)



CN	Arrangement of donor atoms around metal centre
2	Linear
3	Trigonal planar
4	Tetrahedral; square planar
5	Trigonal bipyramidal; square-based pyramidal
6	Octahedral
7	Pentagonal bipyramidal
8	Dodecahedral; square antiprismatic; hexagonal bipyramidal
9	Tricapped trigonal prismatic

Housecroft p541 and V. Bulach

Electron counting ('décompte d'électrons') for a complex

consists of formally assigning a number of valence electrons to individual atoms in a molecule. of neighbours (atoms, molecules, ions) bound to it.

https://en.wikipedia.org/wiki/Electron_counting

Aids in predicting redox reactivity and catalytic cycles.

2 methods:

A. Ionic couting: ('modèle ionique')

1 Write the dissociation equilibrium of the complex (reverse of formation)

The more electronegative atom (the ligand) gains electron from the borken coordination bonds.

$$[Fe(NH_3)_6]^{2+} \leftrightarrows Fe^{2+} + 6\ NH_3$$

2. Deduce the oxidation number (on) by applying the electroneutrality rule. on(Fe) = +II

3. Determine the electronic configuration of the obtained metal ion: d^n.

Mind that external electrons are first removed (4s before 3d). $n = nb(e^-M) - on$

Fe on column 8 of the periodic table: $3d^6 4s^2$ Fe(II): $3d^6 4s^0$

4. Each donor atom donates 2 electrons (a lone pair). Assume L donors.

Then, the total number of electrons (ten) of the complex is

ten = n + 2 X L ten = 6 + 2 X 6 = 18 electrons

Electron counting (‘décompte d’électrons’) for a complex

B. Neutral couting: (‘modèle covalent’)

1. Dissociate the complex assuming each bond is equally split into neutral fragments: one e^- /bond is given to the metal, and one to the donor atom.

$[RuCl_2(bipy)_2] \leftrightarrows Ru + 2\ Cl^\bullet + 2\ bipy$

If the ligand becomes a radical, it is called a X ligand. $Cl^\bullet$ 1 X ligand

Such ligand are the ones that are anionic when dissociating according to the ionic method.

If the ligand is neutral (with closed-shell configuration, no unpaired electron), it is called a L ligand. Bipy counts as 2 L Ligands

2. The complex, charged q, can then be written: $[ML_lX_x]^q$, here $[ML_4X_2]^0$

Then, the total number of electrons (ten) of the complex is

$$ten = n_{COL}(M) + 2.l + 1.x - q$$

$$ten = 8 + 2 \times 4 + 1 \times 2 - 0 = 18 \text{ electrons}$$

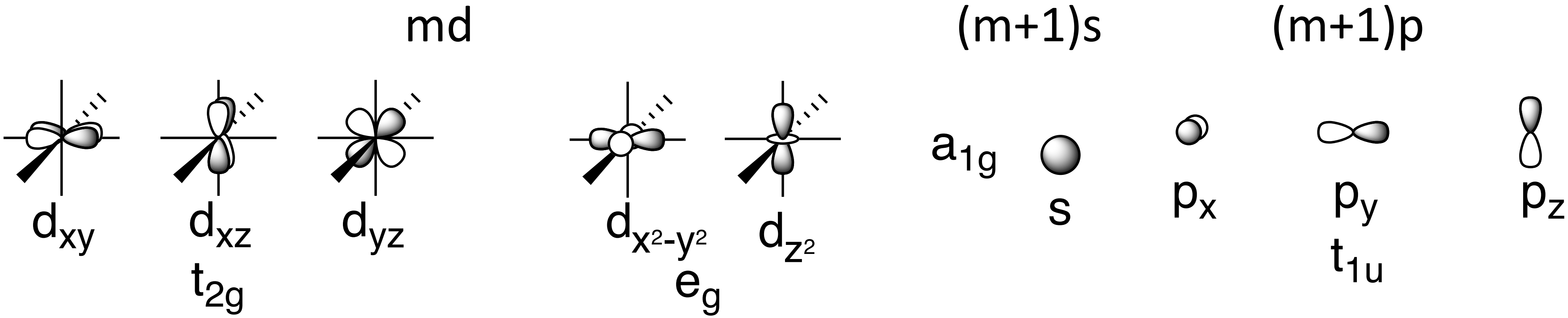
3. Deduce the oxidation number (on): on(Ru) = x + q = 2+0 = +II

4. Deduce the electronic configuration of the obtained metal ion: d^n.

$n = n_{COL}(M) – on$ $n = 8 – 2 = 6$ d^6

Orbitals and type of interaction/ligands

<u>Valence orbitals **of d block** metal:</u>



The coordination bond is a **covalent** bond, with a partial ionic character.

<u>Conditions of interaction:</u> between a metal orbital and a ligand orbital

2 orbitals interact if :

- they are close enough in energy
- they have the same symmetry (have a non-zero overlap *S*)

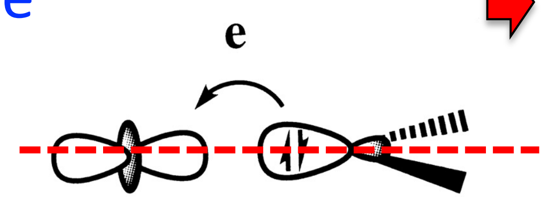
<u>Interaction σ with **σ-donor ligands**</u> Jean

Anions/molecules with a single lone pair of electrons on the donor atom

Ex: NH_3, H^-, ethylenediamine → axial overlap with M

The ligand donates electrons to M

Every ligand is σ-donor



Type of interaction/ligands

Jean, OM dans les complexes, Emond p 435

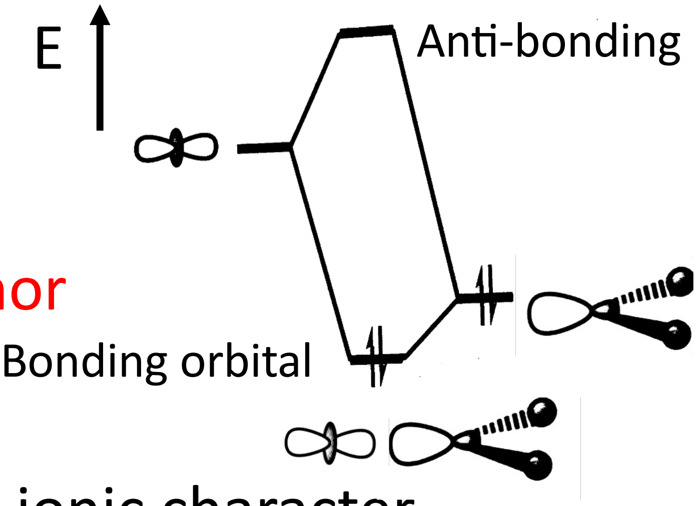
Interaction σ with **σ-donor ligands**

Anions/molecules with a single lone pair of electrons on the donor atom

(n_σ ) Ex: NH_3, H^-, ethylenediamine…

axial overlap with M

The ligand donates electrons to M



Every ligand is σ-donor

The bonding orbital is

- occupied by 2 e^- ➡ stability of the complex
- Is mainly developped on the ligand ➡ partial ionic character

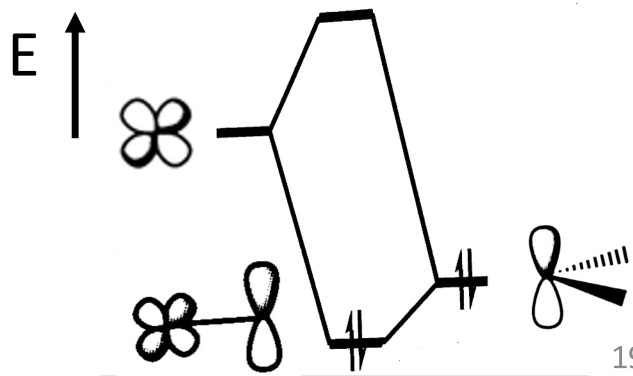
Interaction π with **π-donor ligands**

Anions/molecules with > 1 lone pair of electrons on the donor atom

Ex: OH_2, Cl^-, OH^-… n_p 

lateral overlap between the OM

of this 2nd lone pair and an OM d of M

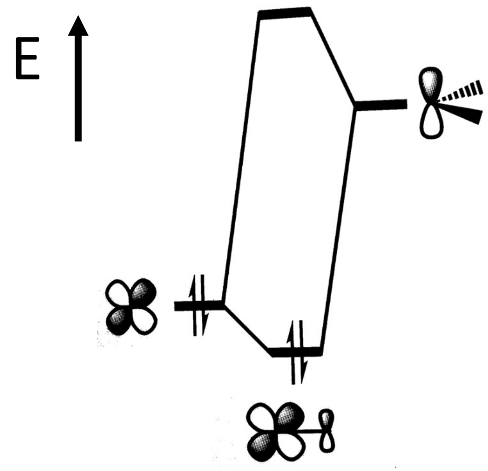


➡ Stabilization of high oxidation number of M

Type of interaction/ligands

Interaction π with **π-acceptor ligands** Jean, OM dans les complexes, Emond p 435

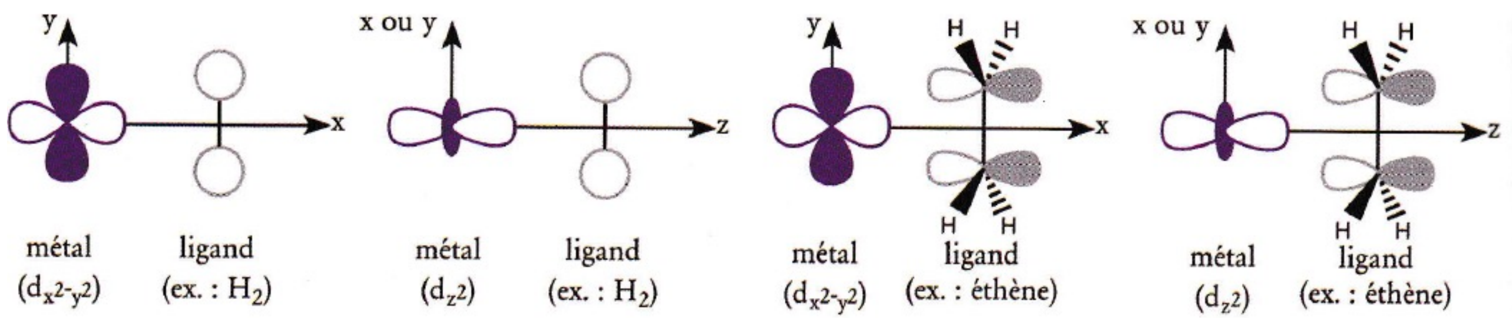
Anions/molecules whose donor atom is involved in a multiple bond ;
There is a vacant π* MO likely to accept electrons from the metal, with a lateral overlap.



➡ Stabilization of low oxidation number of M

Special case of PPh_3: lateral overlap between a d MO of M and a d-type MO based on P

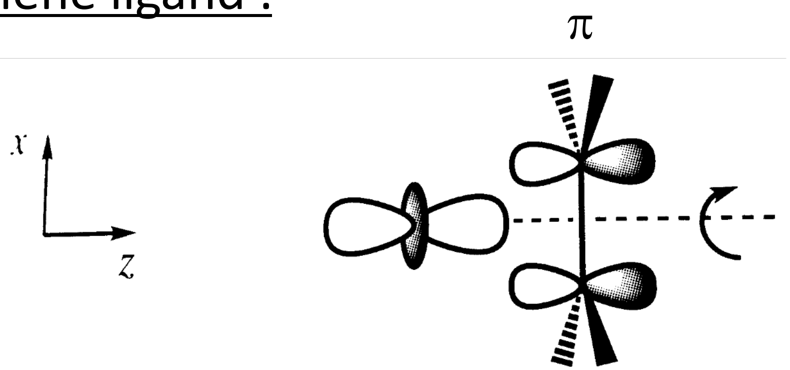
Special case of « special ligands »: H_2, alkene
σ-donor ligands with the 2 e^- coming from a bonding orbital
➡ weakens bond between atoms of the ligand



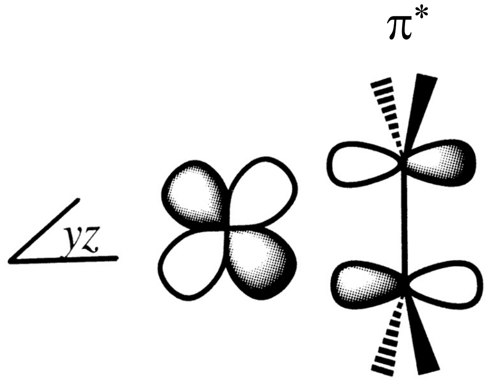
Chimie tout en un
PC 2ème année, p568
T. Ribeyre, Ed De Boeck

& σ or π-acceptor ligands, σ * or π* MO partially filled ➡ weakens bond

<u>Ethylene ligand :</u>

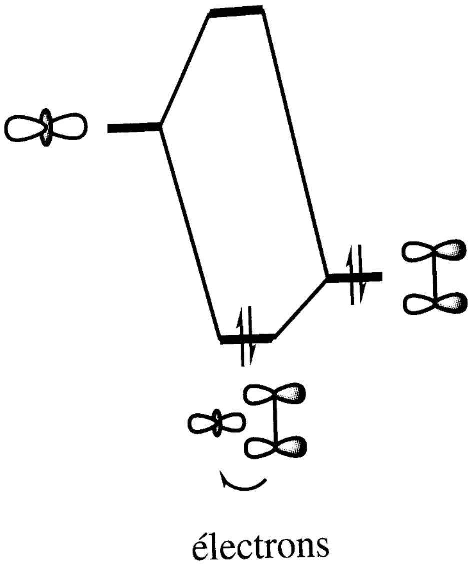


σ interaction
unchanged by rotation

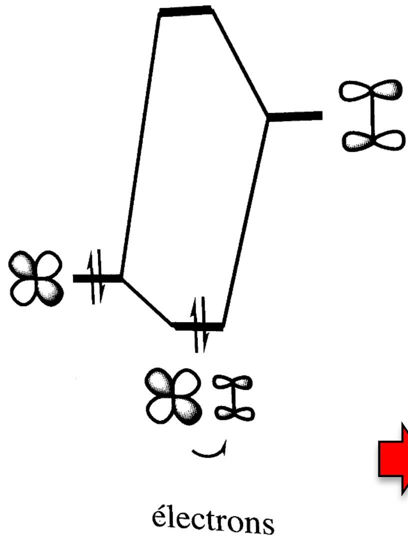


π interaction : nodal plane (yz)
rotation about z
decreases the overlap *S*

L ligand



σ–donation
σ–donor ligand



π-retrodonation
π–acceptor ligand

AND π-acceptor ligands,
π* MO partially occupied
➔ weakens C=C bond

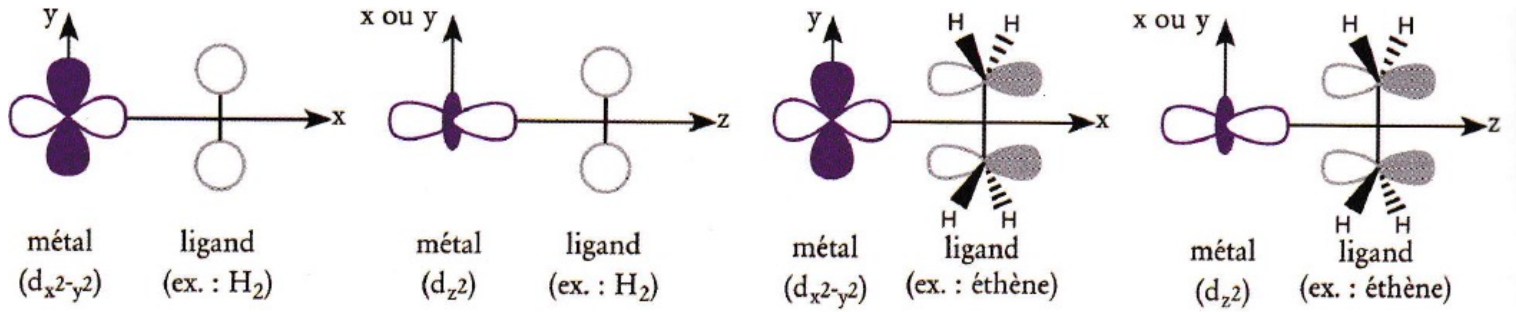
Les OM dans les complexes, Yves Jean, p174

Type of interaction/ligands

<u>Special case of « special ligands »</u>: H_2, alkene

Both **σ-donor ligands** with the 2 e^- coming from a bonding orbital

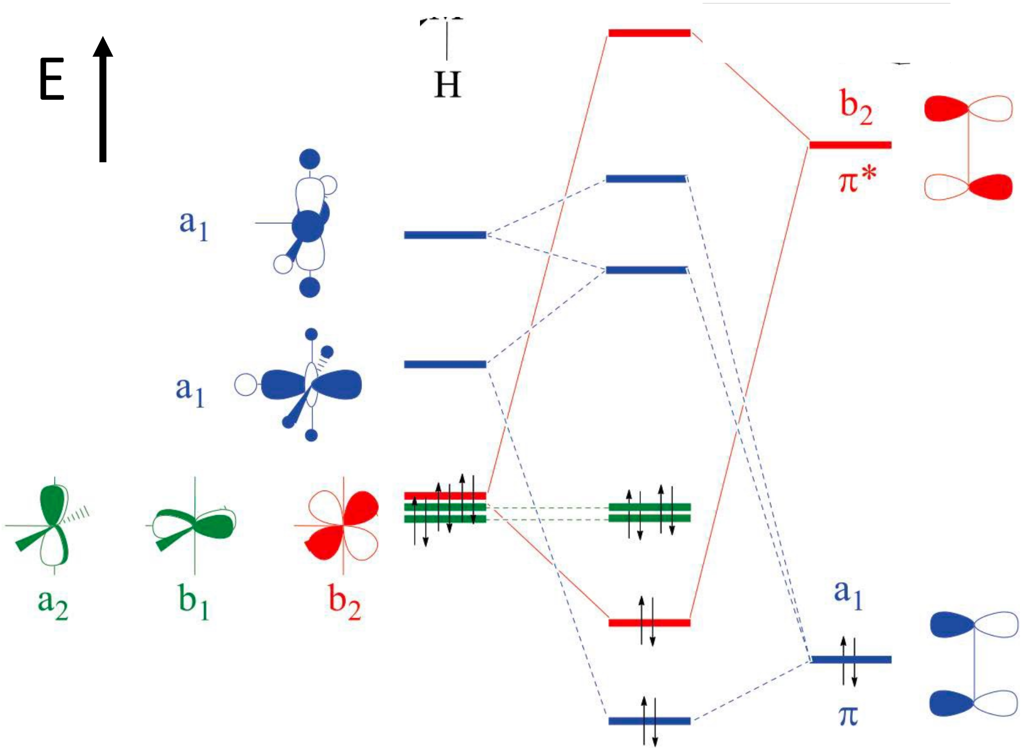
Chimie tout en un
PC 2ème année, p568
T. Ribeyre, Ed De Boeck



AND **π-acceptor ligands**, σ* or π* MO partially occupied

➡ weakens H-H or C=C bond

Volatron, F. Chaquin, P., *BUP* **2018**, *112*, 1051



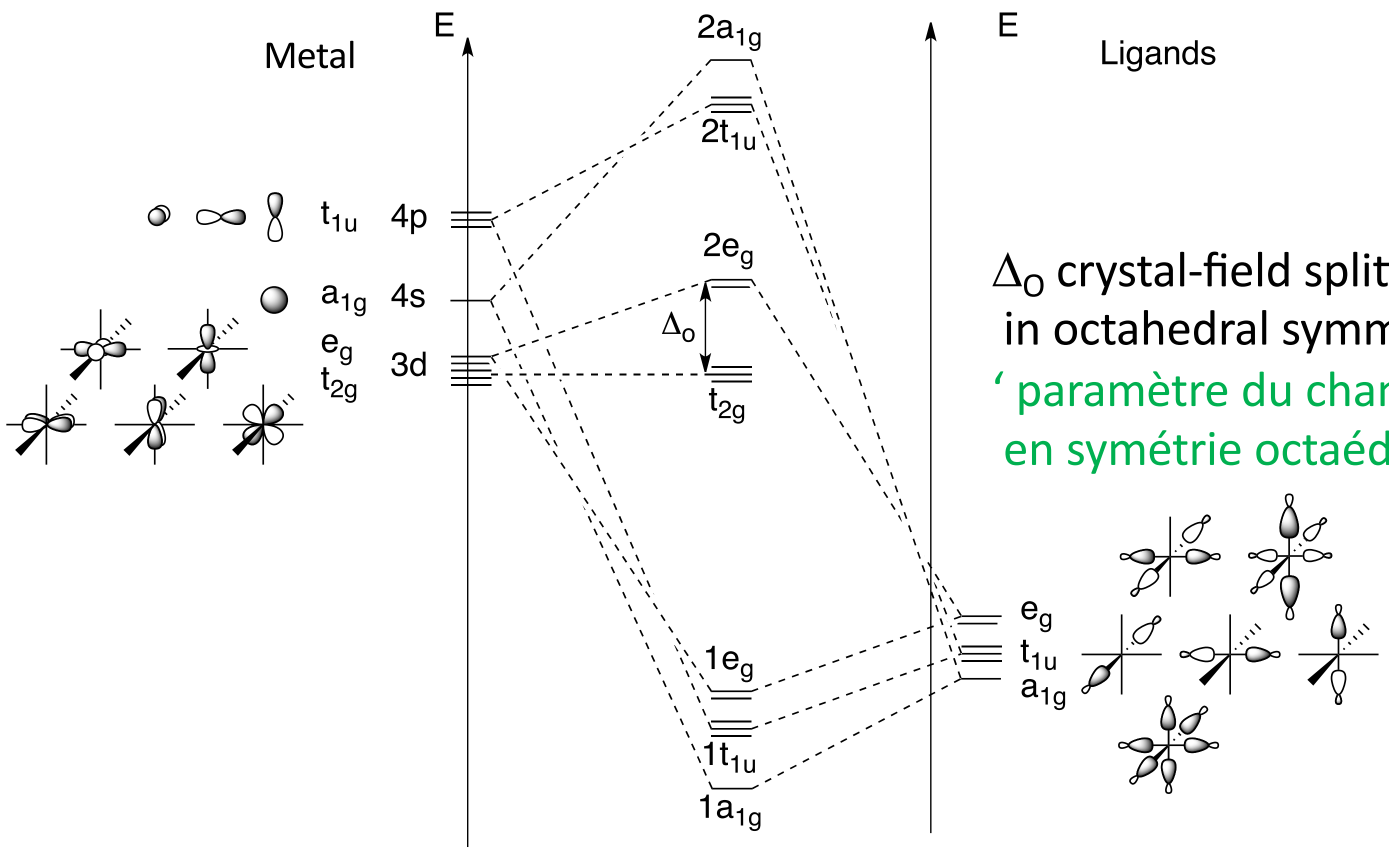
➡ Applications in catalysis

molecular orbital diagramm of an octaedric complex :

Conditions of interaction: between a metal AO and a ligand orbital, 2 orbitals interact if :

- they are close enough in energy
- they have the same symmetry (have a non-zero overlap *S*)

The s orbital of metal is entirely symmetric (sym/plane xy, sym/plane xz, sym/plane yz = SSS).
The fragment orbital of a_{1g} symmetry too, they interact and 1 bonding MO ($S>0$) and 1 antibonding MO ($S<0$) are obtained.
The fragment orbital of e_g symmetry (left) is antisymmetric versus the vertical plane bisecting the x and y axes, the d_{x2-y2} orbital also interacts.
On the other hand, the antisymmetric/yz fragment orbital t_{1u} (along x) has zero overlap with the d_{x2-y2} orbital (symmetric/yz).



Δ_O crystal-field splitting parameter in octahedral symmetry

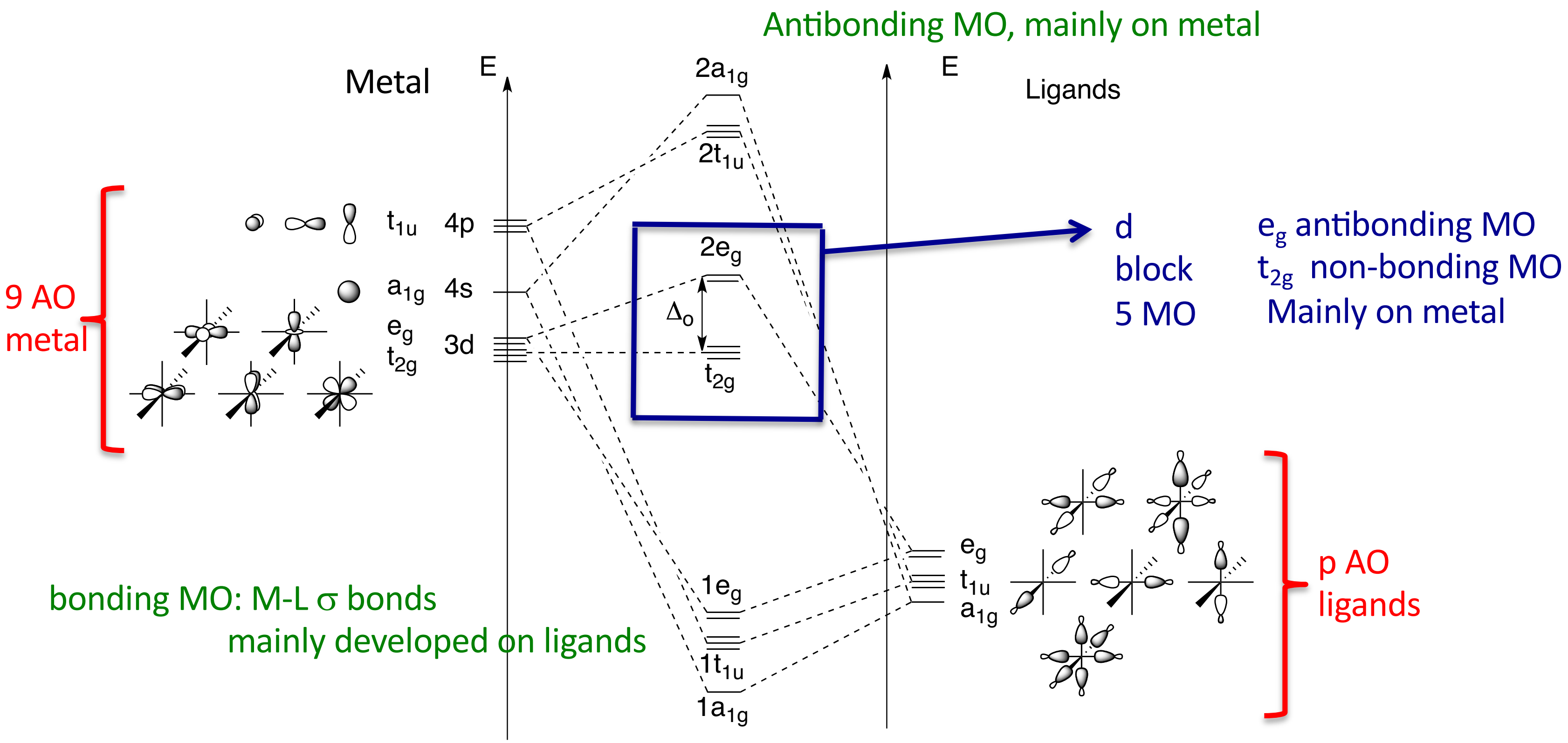
' paramètre du champ cristallin en symétrie octaédrique '

ELECTRONIC CONFIGURATION OF COMPLEXES

Electronic configuration:

The OM diagram is filled by (2 times the number of donor atoms of ligands + the number of electrons coming from the metal):

- In order of increasing energy
- Pauli's exclusion principle (2 e- cannot have all their quantum numbers identical)
- Hund's rule (maximum spin **S** when filling degenerate orbitals)

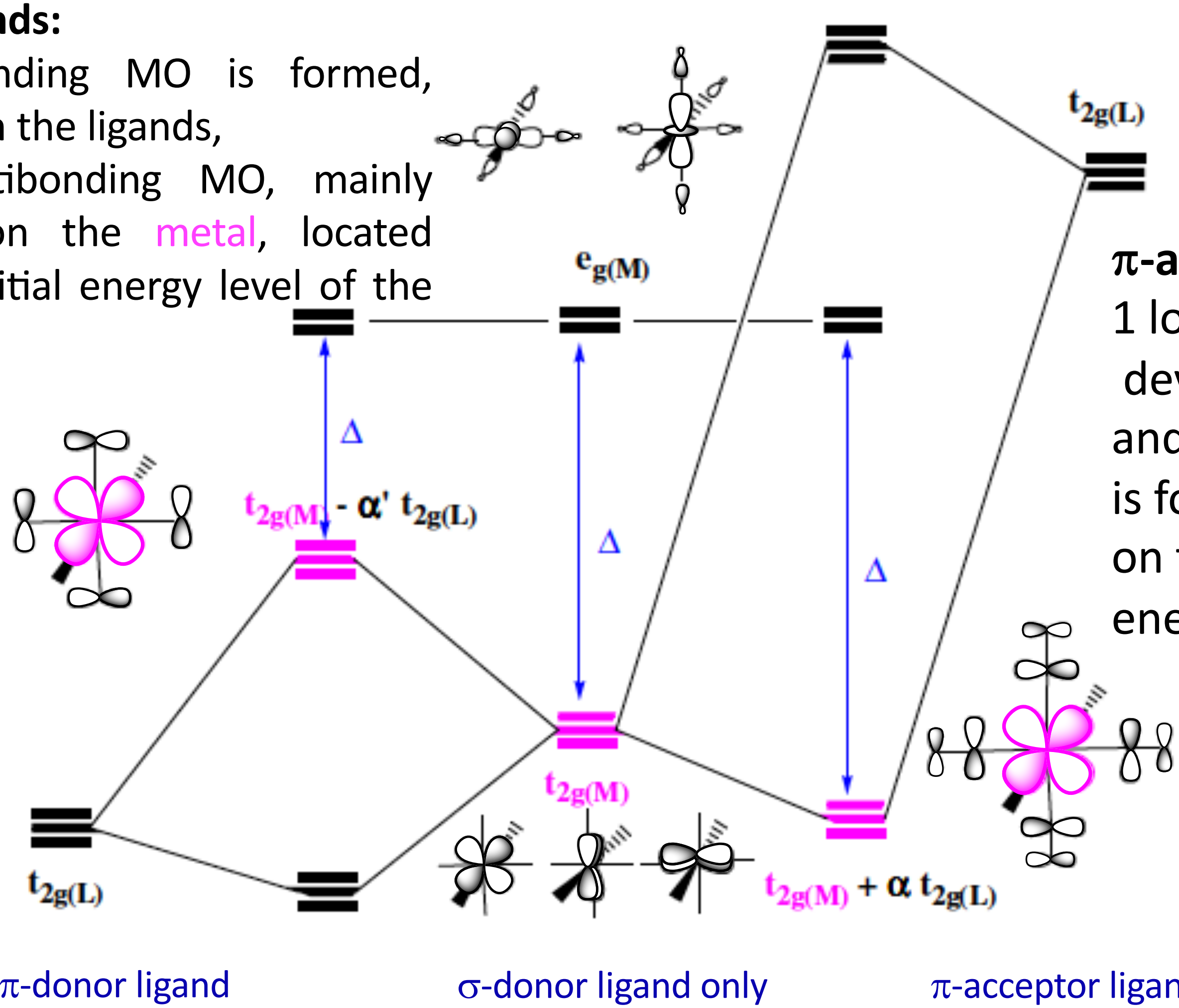


18-electron rule: A complex with 18 valence electrons is stabilised (has the configuration of the nearest rare gas, extension of the octet rule).

Influence of ligands on Δ_O

Possible **lateral overlap** between the t_{2g} MOs of the ligands and t_{2g} MOs of the metal

π-donor ligands:
1 lower binding MO is formed, developed on the ligands,
and an antibonding MO, mainly developed on the metal, located above the initial energy level of the t_{2g} of M



π-acceptor ligands:
1 lower binding MO is formed,
developed on the metal,
and an antibonding MO
is formed, mainly developed
on the ligands, of higher
energy than the OM π*
of the ligands.

Explains the spectrochemical series:

$$\Delta_O\ (\pi\text{-donor}) < \Delta_O\ (\sigma\text{-donor}) < \Delta_O\ (\pi\text{-acceptor})$$

Crystal field theory

Another way to determine electronic structure and explain bonds and properties of complexes

<u>Disadvantage:</u> covalency not taken into account ➡ MO theory better

also called Ligand field theory

<u>Advantages:</u>

- Simple
- symmetry is taken into account
- explains - breaking of degeneracy of e^- orbital states, d OA levels
  - stability
  - optical properties (colors)
  - magnetic properties

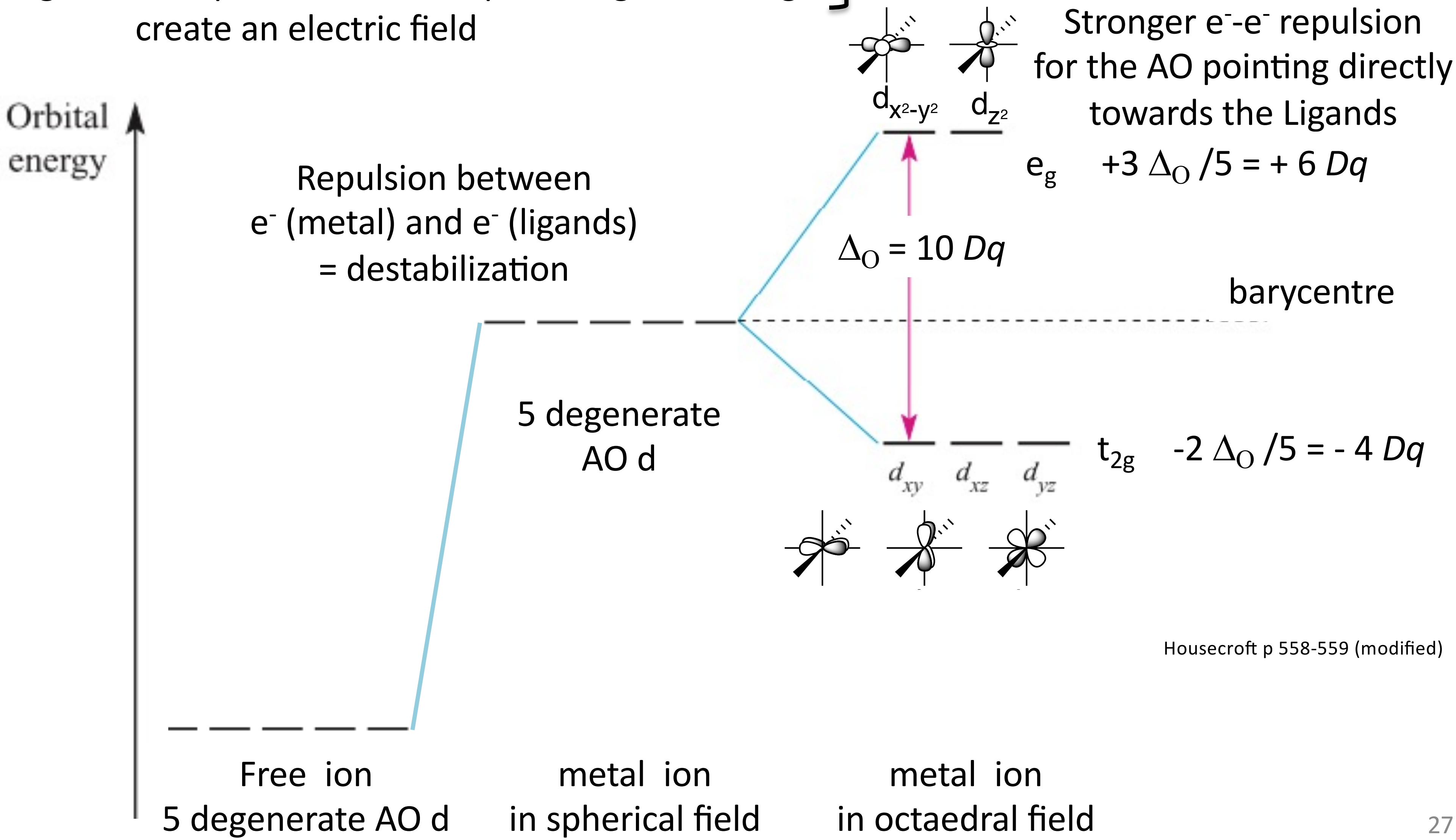
Crystal field theory

Electrostatic model (Hans BETHE, 1929)

- Metal ion modeled as point positive charge
- Ligands lone pairs modeled as point negative charges

  create an electric field

} Overall attraction & stabilization



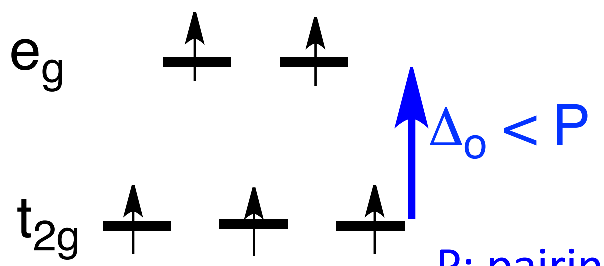
Housecroft p 558-559 (modified)

Crystal field theory

Electronic configuration:

The d block is filled by the number of valence e^- from the metal <u>only</u>, Pauli & Hund's rules
For a d^1 to d^3 metal ion and d^8 to d^{10}, the filling of the energy diagram is obvious.
For a d^4 to d^7 metal ion, however, 2 options (ex : d^5)

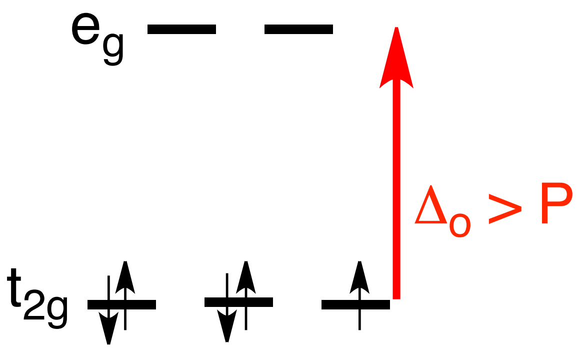
weak field



P: pairing energy
(' énergie d'appariement ')

High spin S = 5/2

strong field



low spin S = 1/2

Factors influencing Δ_o: Jørgensen's relation $\Delta_o = f.g$

<u>Nature of metal</u>: *g* parameter

$\Delta_o \nearrow$ - if the oxidation number of the metal $\nearrow$
- size of d orbital $\nearrow$ (overlap $S \nearrow$) : Δ_o (3d) < Δ_o (4d) < Δ_o (5d)

$Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Co^{3+} < Mn^{4+} < Mo^{3+} < Rh^{3+} < Ru^{3+} < Pd^{4+} < Ir^{3+} < Pt^{4+}$

<u>Nature of ligand</u>: *f* parameter   **spectrochemical series** (' série spectrochimique ')

$I^- < Br^- < S^{2-} < \underline{S}CN^- < Cl^- < N\underline{O}_3^-$ $N_3^- < F^- <$ urée, $HO^- <$ ox $< H_2O < \underline{N}CS^- < CH_3CN <$ Py $< NH_3 <$ en $<$ bipy $<$ phen $< \underline{N}O_2^- < PPh_3 < CN^- < CO$

(determined from absorption spectra)

Coordination number and geometry

Crystal field theory

Schriver Atkins p 228)

Ligand-field splitting parameters Δ_o of octaedral ML_6 complexes (cm^{-1})

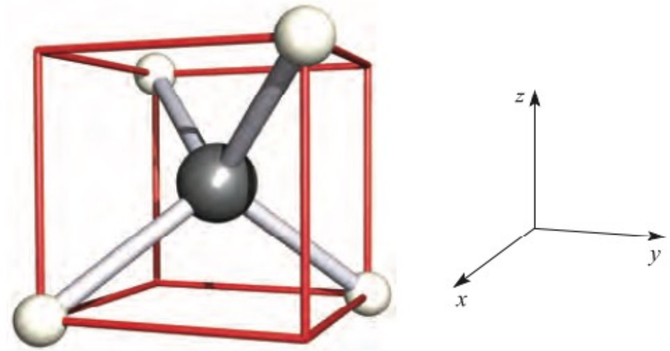
	Ions	Ligands				
		Cl^-	H_2O	NH_3	en	CN^-
d^3	Cr^{3+}	13700	17400	21500	21900	26600
d^5	Mn^{2+}	7500	8500		10100	30000
	Fe^{3+}	11000	14300			(35000)
d^6	Fe^{2+}		10400		10100	30000
	Co^{3+}		(20700)	(22900)	(23200)	(35000)
	Rh^{3+}	(20400)	(27000)	(34000)	(34600)	(45500)
d^8	Ni^{2+}	7500	8500	10800	11500	

(values in parentheses are for low-spin complexes)

Crystal field theory

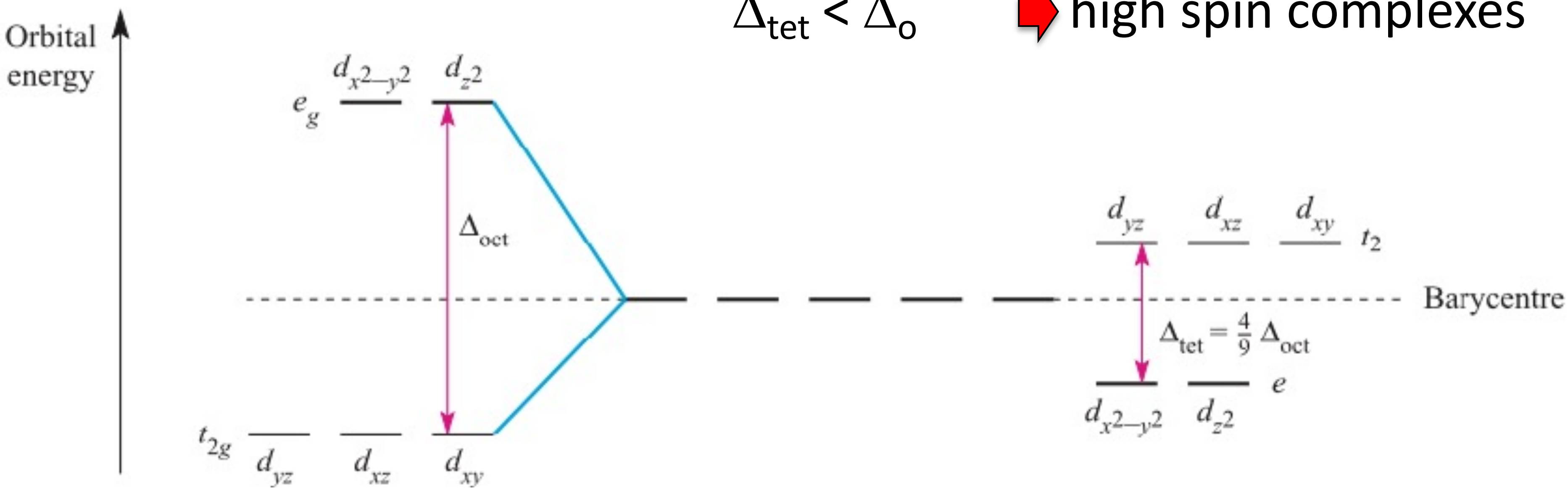
In other geometries:

Housecroft p 562-563



No ligand on the axes : weakest e^- - e^- interaction

$\Delta_{tet} < \Delta_o$ ➡ high spin complexes



metal ion
in octaedral field

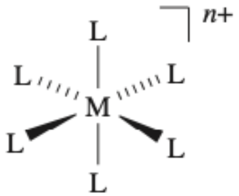
metal ion
in spherical field

metal ion
in tetraedral field

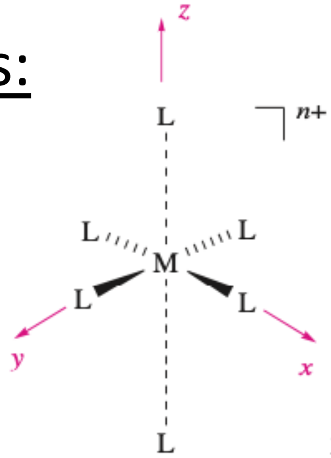
Crystal field theory

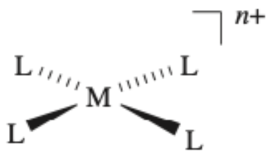
In other geometries:

Housecroft p 562-563

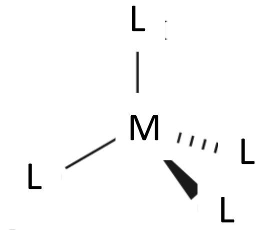


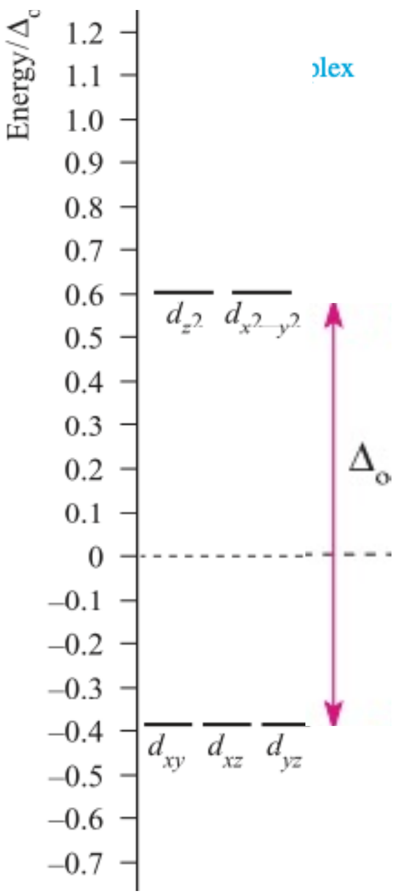
octaedral



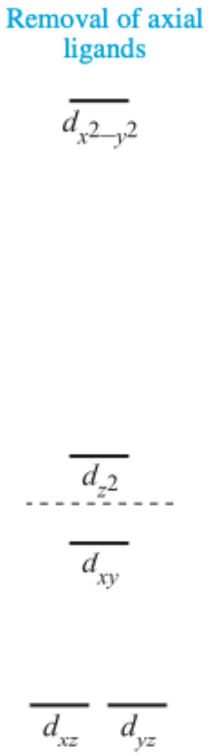


square planar

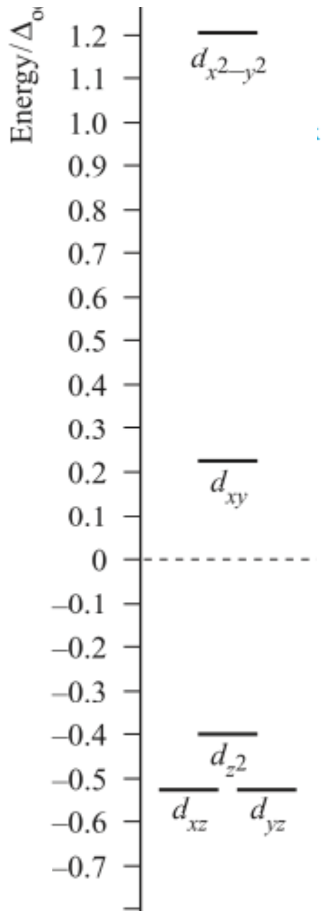




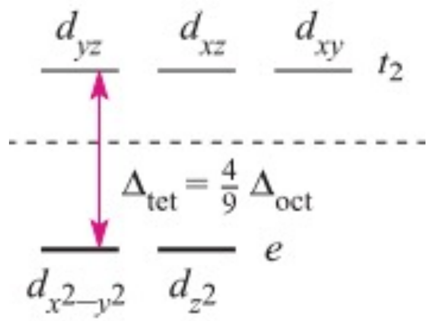
octaedral



Tetragonal
(Jahn-teller distortion)



square planar



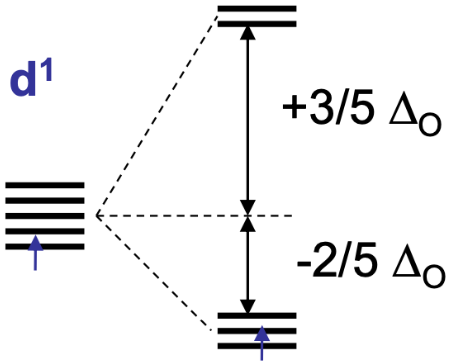
tetrahedral

Crystal field theory

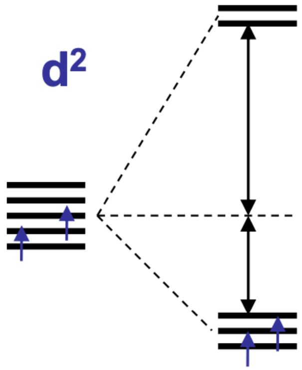
Housecroft p 560 + V. Bulach ch2 P 20

<u>Crystal field stabilization energy (CFSE)</u>: in octahedral geometry

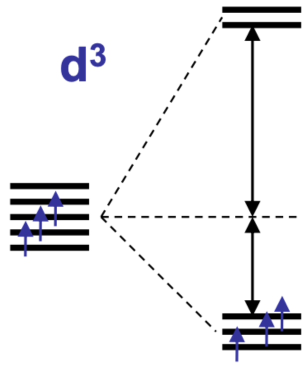
For a d^n configuration, the CFSE is the difference in energy between the d electrons in an octahedral crystal field and in a spherical crystal field.



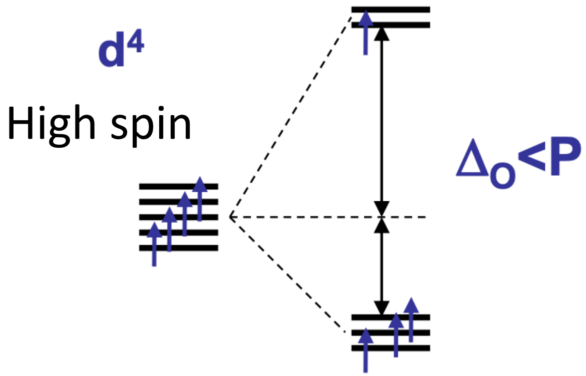
ESCC = $-2/5\ \Delta_O$



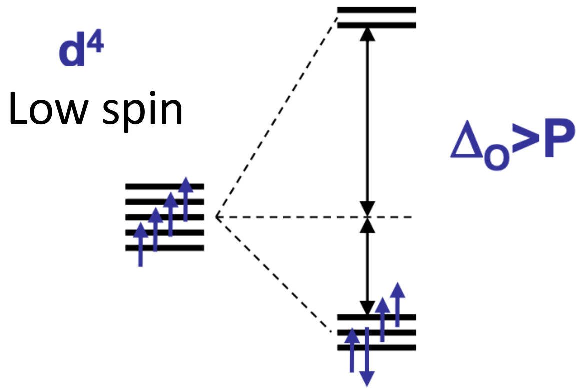
ESCC = $-4/5\ \Delta_O$



ESCC = $-6/5\ \Delta_O$



CFSE = $-3/5\ \Delta_O$



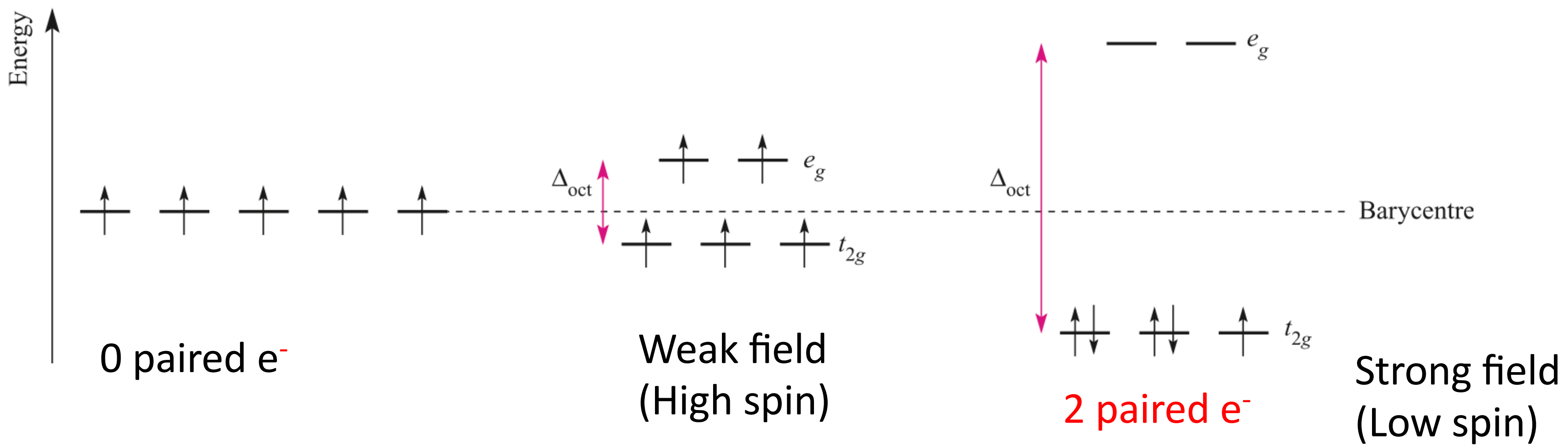
ESCC = $-8/5\ \Delta_O$

Crystal field theory

Housecroft p 560 + V. Bulach ch2 P 20

Crystal field stabilization energy (CFSE): in octahedral geometry

d^n	High-spin = weak field		Low-spin = strong field	
	Electronic configuration	CFSE	Electronic configuration	CFSE E_{tot} = CFSE + p.P
d^1	$t_{2g}{}^1 e_g{}^0$	$-0.4\Delta_{oct}$		
d^2	$t_{2g}{}^2 e_g{}^0$	$-0.8\Delta_{oct}$		
d^3	$t_{2g}{}^3 e_g{}^0$	$-1.2\Delta_{oct}$		
d^4	$t_{2g}{}^3 e_g{}^1$	$-0.6\Delta_{oct}$	$t_{2g}{}^4 e_g{}^0$	$-1.6\Delta_{oct}$ + P
d^5	$t_{2g}{}^3 e_g{}^2$	0	$t_{2g}{}^5 e_g{}^0$	$-2.0\Delta_{oct}$ + 2 P
d^6	$t_{2g}{}^4 e_g{}^2$	$-0.4\Delta_{oct}$	$t_{2g}{}^6 e_g{}^0$	$-2.4\Delta_{oct}$ + 2 P
d^7	$t_{2g}{}^5 e_g{}^2$	$-0.8\Delta_{oct}$	$t_{2g}{}^6 e_g{}^1$	$-1.8\Delta_{oct}$ + P
d^8	$t_{2g}{}^6 e_g{}^2$	$-1.2\Delta_{oct}$		
d^9	$t_{2g}{}^6 e_g{}^3$	$-0.6\Delta_{oct}$		
d^{10}	$t_{2g}{}^6 e_g{}^4$	0		



Magnetic properties

Housecroft p 570+ V. Bulach ch2 P 20

Paramagnetic species: has unpaired electrons, total spin $S \neq 0$

attracted by a magnetic field

Diamagnetic species: has no unpaired electron, total spin S = 0

repelled by a magnetic field

magnetic moment μ_{SO}: (spin-only) $$\mu(\text{spin-only}) = 2\sqrt{S(S+1)}$$

μ_{eff} obtained experimentally by measuring the molar magnetic susceptibility, χ_m
expressed in Bohr magnetons (μ_B)

Metal ion	d^n configuration	S	μ_{eff}(spin-only) / μ_B	Observed values of μ_{eff} / μ_B
Sc^{3+}, Ti^{4+}	d^0	0	0	0
Ti^{3+}	d^1	$^1/_2$	1.73	1.7–1.8
V^{3+}	d^2	1	2.83	2.8–3.1
V^{2+}, Cr^{3+}	d^3	$^3/_2$	3.87	3.7–3.9
Cr^{2+}, Mn^{3+}	d^4	2	4.90	4.8–4.9
Mn^{2+}, Fe^{3+}	d^5	$^5/_2$	5.92	5.7–6.0
Fe^{2+}, Co^{3+}	d^6	2	4.90	5.0–5.6
Co^{2+}	d^7	$^3/_2$	3.87	4.3–5.2
Ni^{2+}	d^8	1	2.83	2.9–3.9
Cu^{2+}	d^9	$^1/_2$	1.73	1.9–2.1
Zn^{2+}	d^{10}	0	0	0

OPTICAL PROPERTIES

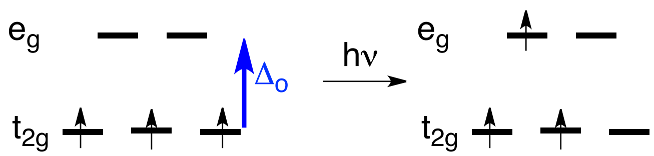
Colors :

selection rules

- Spin rule: $\Delta S = 0$ (unless there is spin-orbit coupling, if heavy atom present)
- Laporte rule: The parity of the arithmetic sum $\sum_i \ell_i$ changes.
  transitions between levels from the same electronic configuration are prohibited.
- Symmetry rule: only $g \rightarrow u$ and $u \rightarrow g$ transitions are allowed

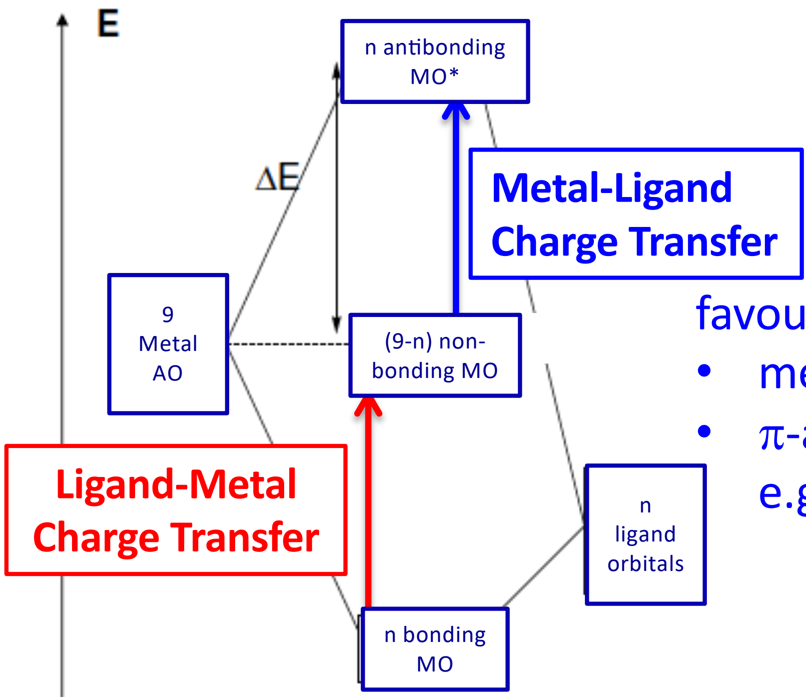
d-d transition

prohibited by the selection rules,
not very intense



Charge Transfer

authorised by the selection rules,
very intense



favoured by
high oxidation number of the metal

- π-donneurs ligands e.g. O^{2-}
  $[MnO_4]^-$, $[CrO_4]^{2-}$, Ce^{4+}

favoured by

- metal d^n ($n>0$)
- π-acceptor ligands
  e.g. CO, phen, bipy

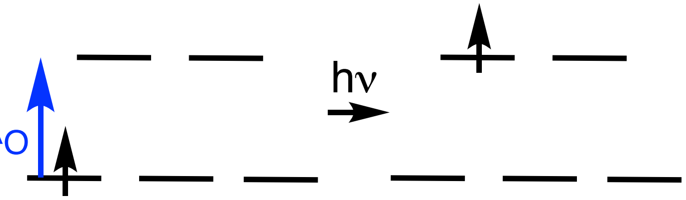
$[Fe(phen)_3]^{2+}$
$[Ru(bipy)_3]^{2+}$

OPTICAL PROPERTIES

Colors :

d-d transition

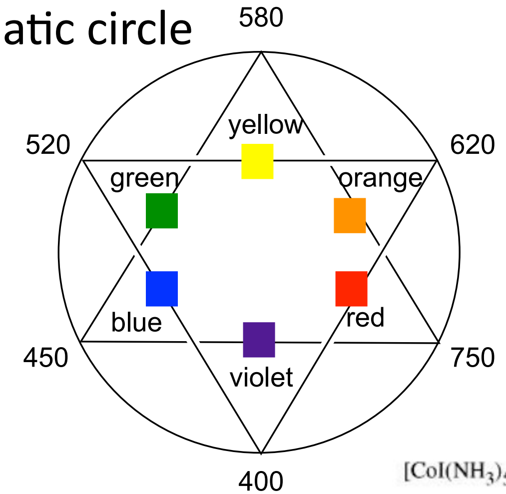
Absorbed energy hν proportional to Δ_O

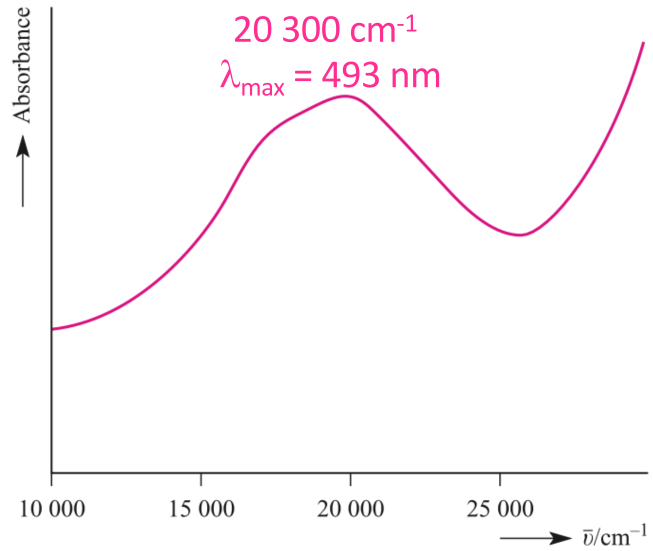


Housecroft p 559

If **only one band** in the visible region:
color can be deduced from the chromatic circle

$[Ti(OH_2)_6]^{3+}$
d^1
pourpre





Depends on Δ_O:

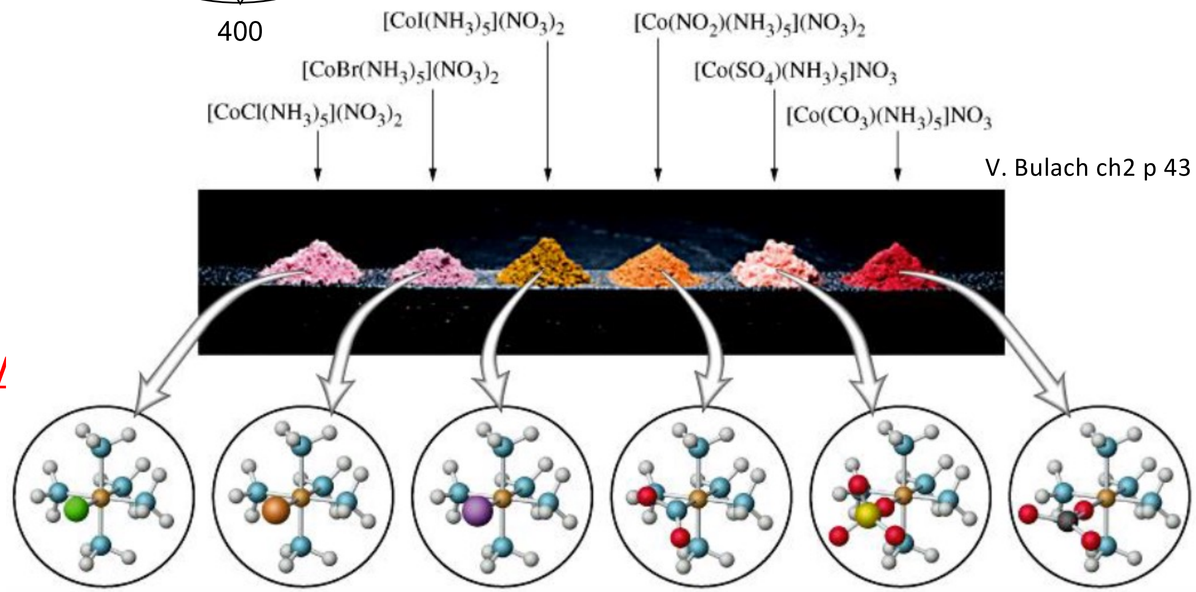
- Nature of metal:

  Δ_o ↗ - if oxidation number ↗
  - if size of d orbital ↗

- Nature of ligand:

- Coordination number and geometry

The **spectrochemical series** is deduced from UV-visible spectra



V. Bulach ch2 p 43

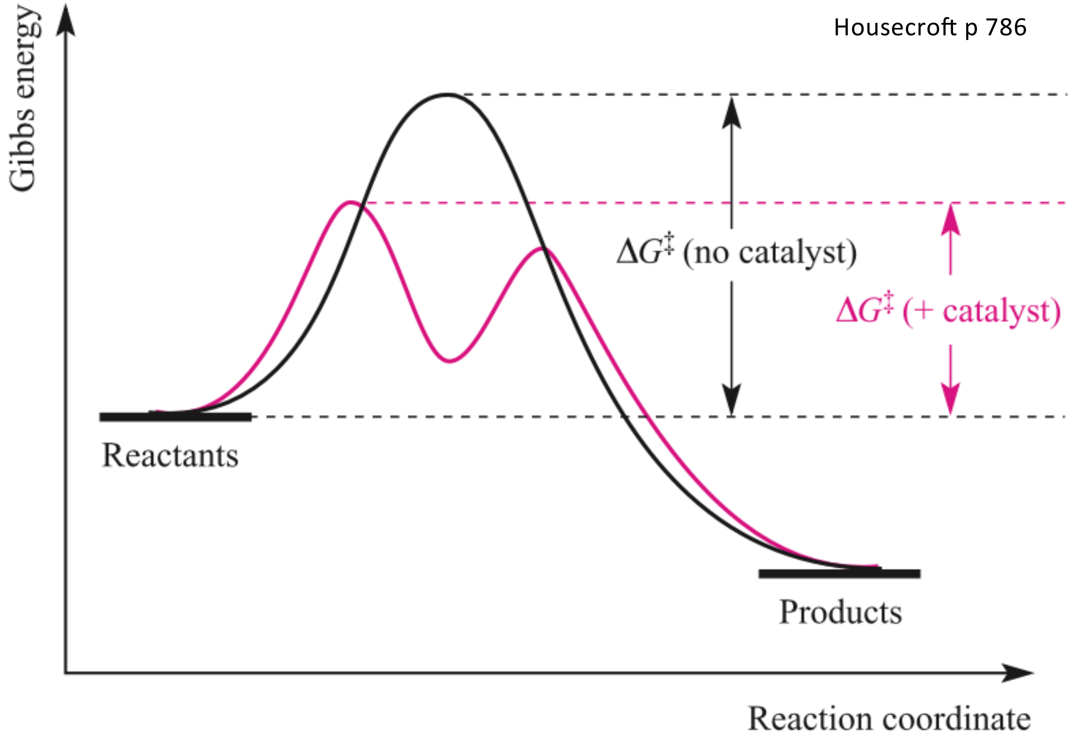
CATALYTIC PROPERTIES OF COMPLEXES

Principle of catalysis:

A catalyst:
- ↗ the rate of reaction
  by lowering the activation energy
- Does not appear in any of the products of that reaction;
- Is not consumed by the reaction
  is regenerated
  Only a small amount is necessary.

https://en.wikipedia.org/wiki/Catalysis

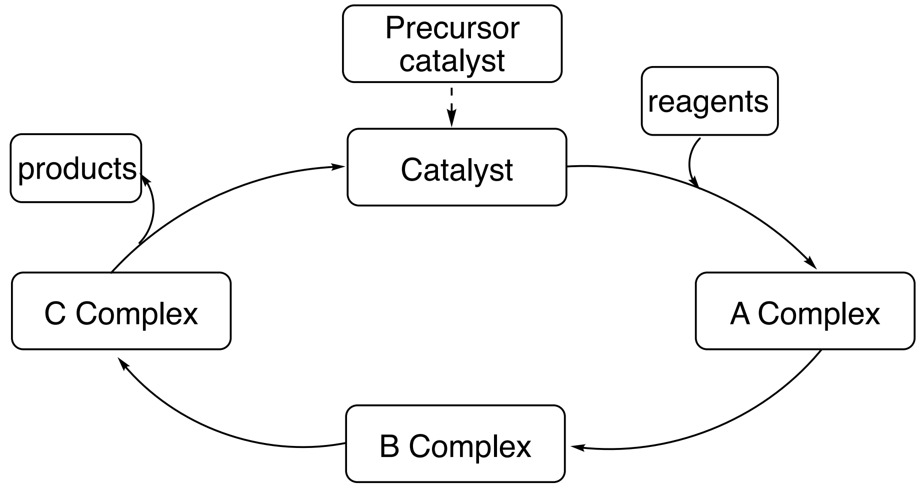
Housecroft p 786



Catalytic cycle:

Series of stoichiometric reactions (often reversible) that form a closed loop

Ribeyre p572



HOMOGENEOUS CATALYSIS BY METAL COMPLEXES

Catalytic steps:

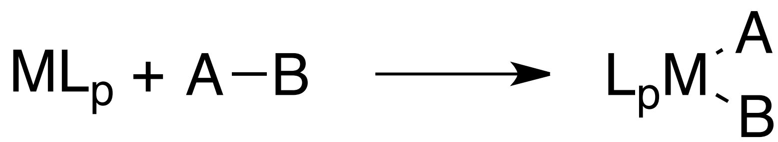
Ligand Coordination/ Ligand Dissociation (’ Coordination/décoordination ‘)

$$ML_p + L' \rightleftharpoons ML_pL'$$

Ligands exchange (‘ Echange de ligands ’)

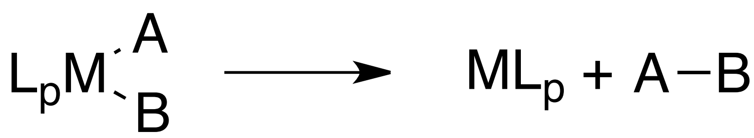
$$ML_p + X \longrightarrow ML_{p-1}X + L$$

Oxidative addition (‘ Addition oxydante ’)



oxidation number (metal) ↗ + 2, Coordination Number ↗ + 2, number of electrons (ten) ↗ + 2

Reductive elimination (‘ Elimination reductrice ’) (reverse of oxidative addition)



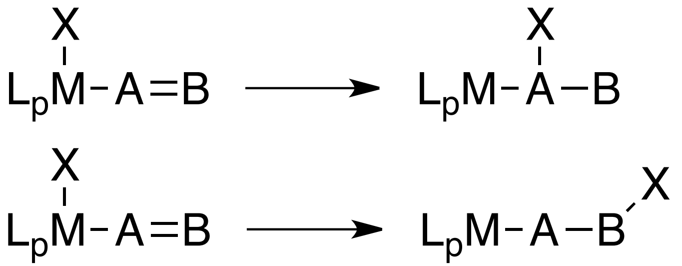
oxidation number (metal) ↘ - 2, Coordination Number ↘ - 2, number of electrons (ten) ↘ - 2

HOMOGENEOUS CATALYSIS BY METAL COMPLEXES

Catalytic steps:

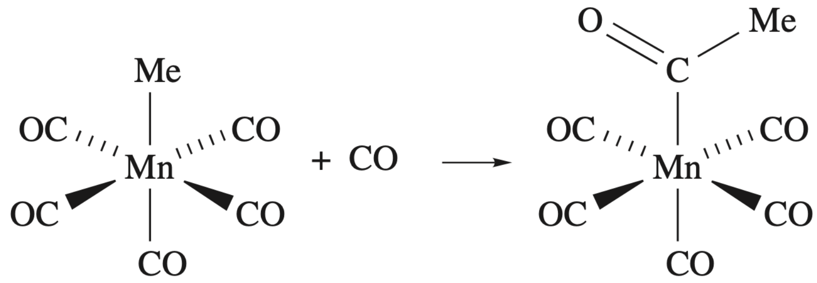
Housecroft p 720

Insertion need 2 ligands in cis (‘ insertion ’)

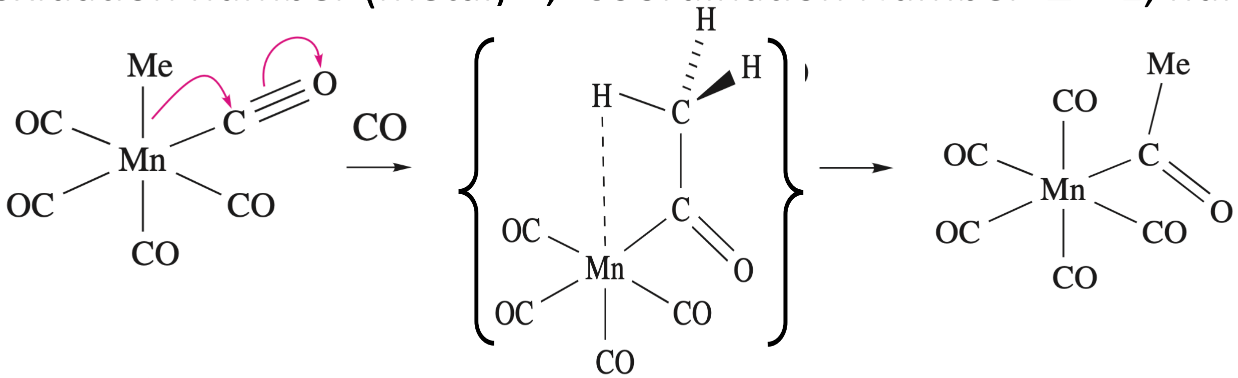


insertion 1,1

insertion 1,2

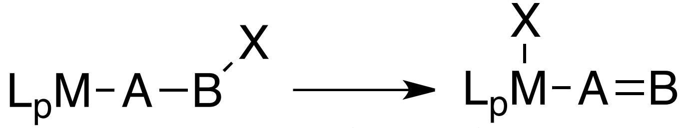


oxidation number (metal) =, Coordination Number ↘ - 1, number of electrons (ten) ↘ - 2



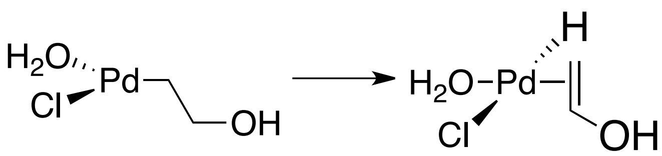
agostic M-H-C interaction is a 3-centre 2-e⁻ interaction between a metal centre, M, and a C-H bond in a ligand attached to M

α– or β–Elimination (‘ Désinsertion (extrusion, élimination) ’) (reverse of insertion)



oxidation number (metal) =, Coordination Number ↗ + 1, number of electrons (ten) ↗ + 2

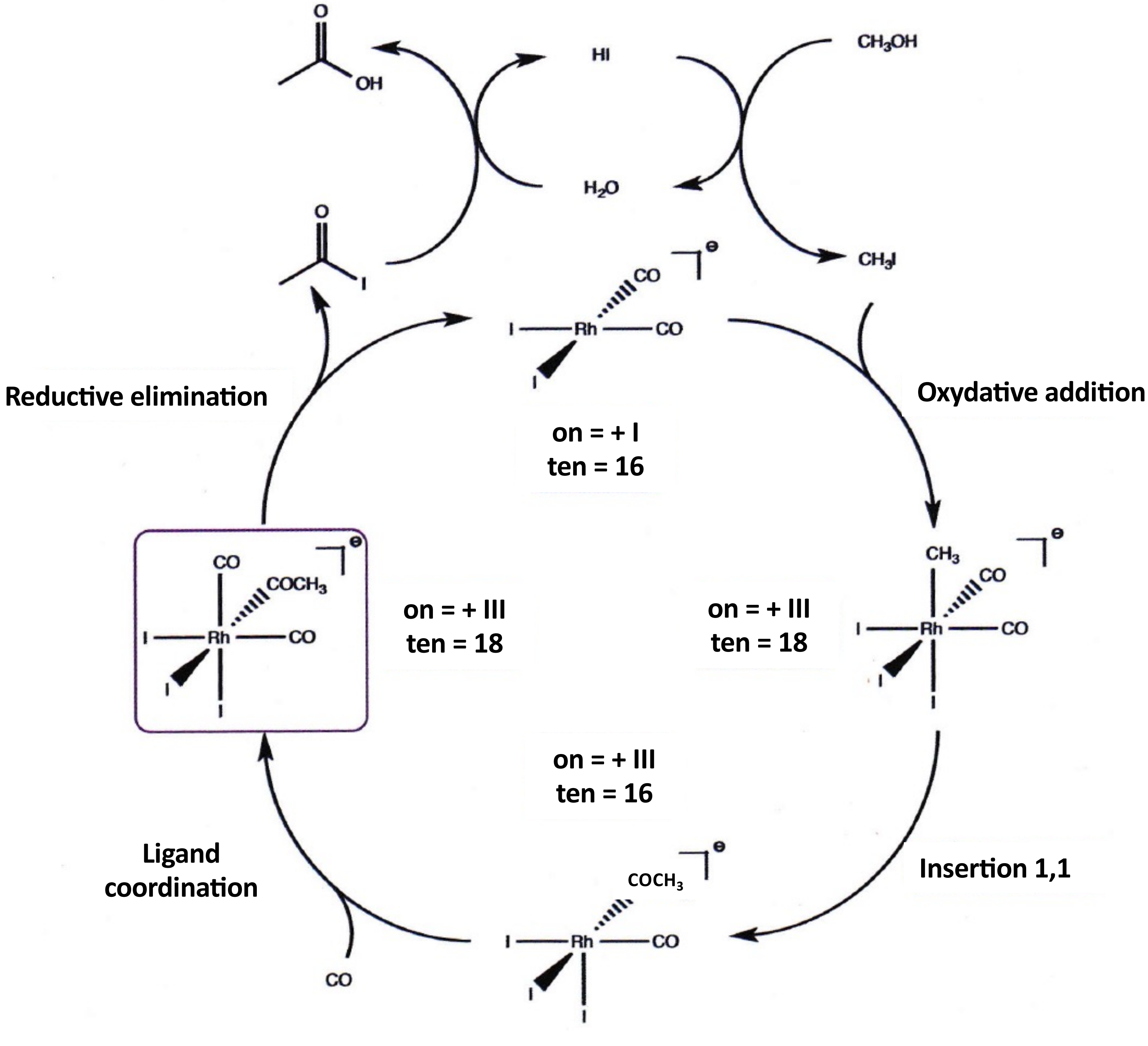
Ex : Wacker process (alkene oxidation)



HOMOGENEOUS CATALYSIS BY METAL COMPLEXES

Example :

Mosanto process



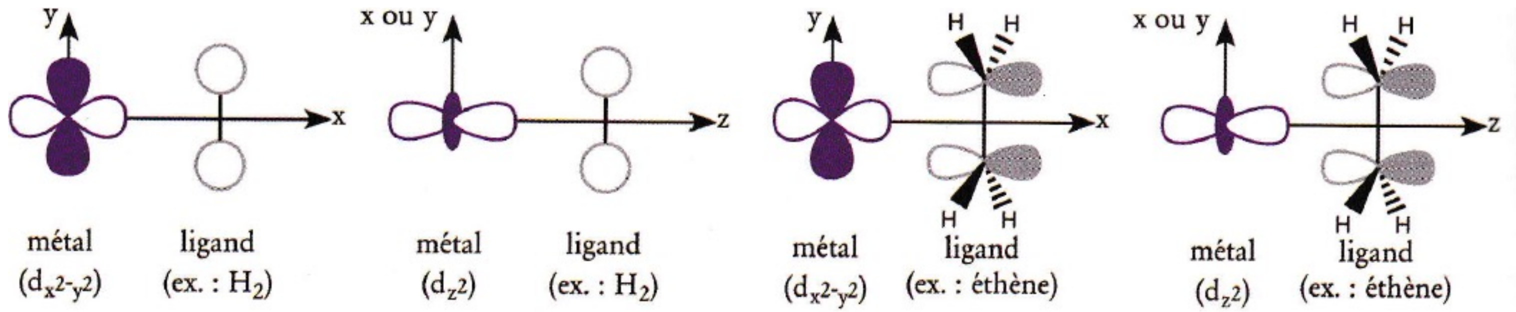
Chimie tout en un
PC 2ème année, p598
T. Ribeyre, Ed De Boeck

Type of interaction/ligands

<u>Special case of « special ligands »</u>: H_2, alkene

Both **σ-donor ligands** with the 2 e^- coming from a bonding orbital

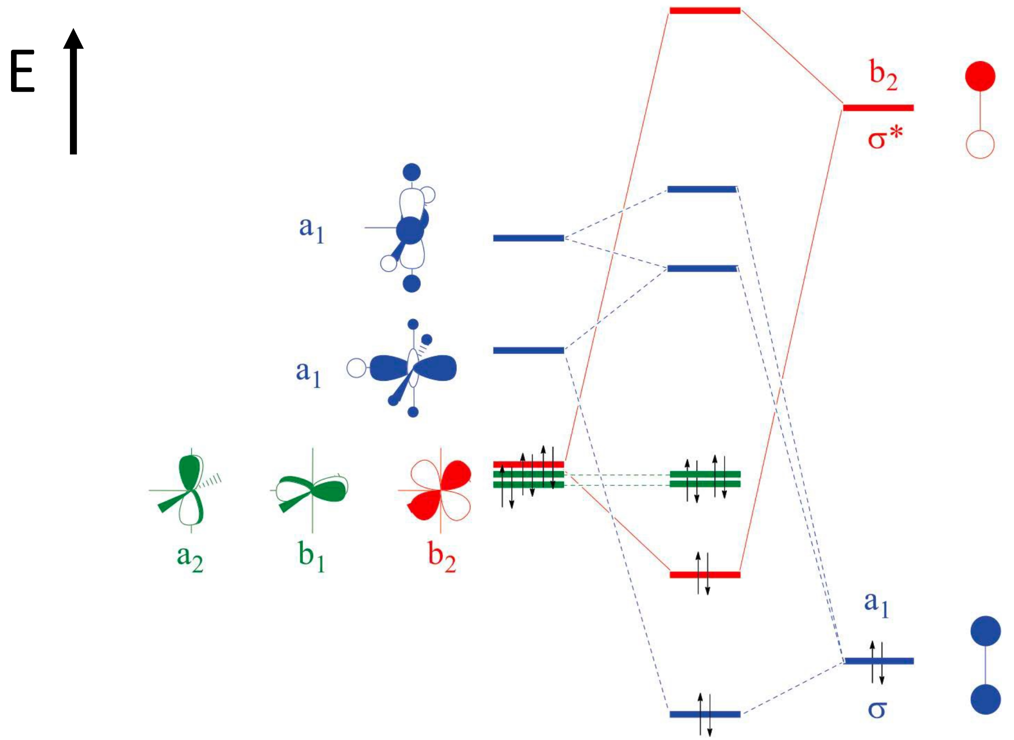
Chimie tout en un
PC 2ème année, p568
T. Ribeyre, Ed De Boeck



AND **π-acceptor ligands**, σ* or π* MO partially occupied

➡ weakens H-H or C=C bond

Volatron, F. Chaquin, P., *BUP* **2018**, *112*, 1051



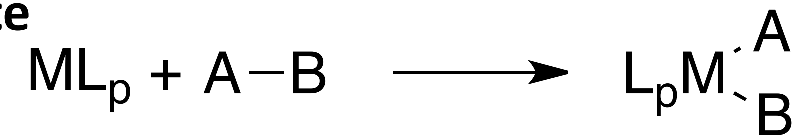
CATALYSE PAR LES COMPLEXES

Réactions élémentaires : **Coordination/décoordination** $ML_p + L' \rightleftharpoons ML_pL'$

Echange de ligands

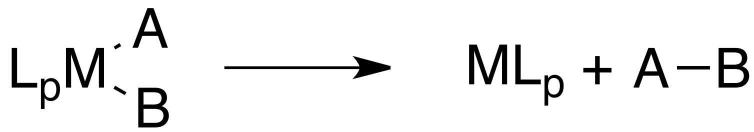
$$ML_p + X \longrightarrow ML_{p-1}X + L$$

Addition oxydante



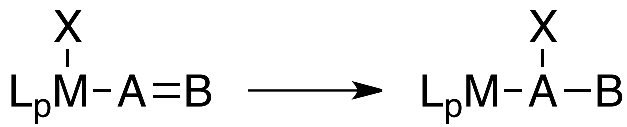
degré d'oxydation (métal) + 2, nombre (ligands) + 2, nombre d'e$^-$ valence +2

Elimination réductrice (inverse de la précédente)

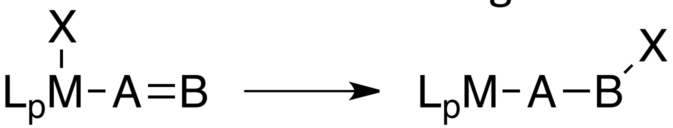


degré d'oxydation (métal) - 2, nombre (ligands) - 2, nombre d'e$^-$ valence -2

Insertion nécessite 2 ligands en cis



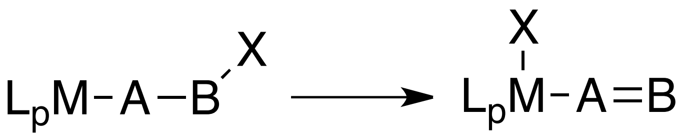
insertion 1,1



insertion 1,2

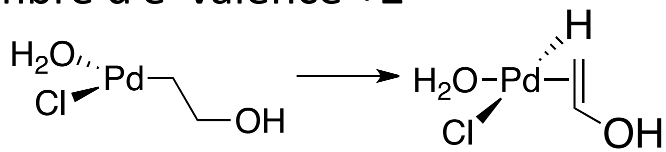
degré d'oxydation (métal) =, nombre (ligands) - 1, nombre d'e$^-$ valence -2

Désinsertion (extrusion, élimination) (inverse de la précédente)



degré d'oxydation (métal) =, nombre (ligands) + 1, nombre d'e$^-$ valence +2

Ex : procédé Wacker (oxydation des alcènes)

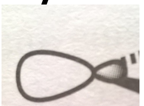


Type of interaction/ligands

Jean, OM dans les complexes, Emond p 435

<u>Interaction σ with **σ-donor ligands**</u>

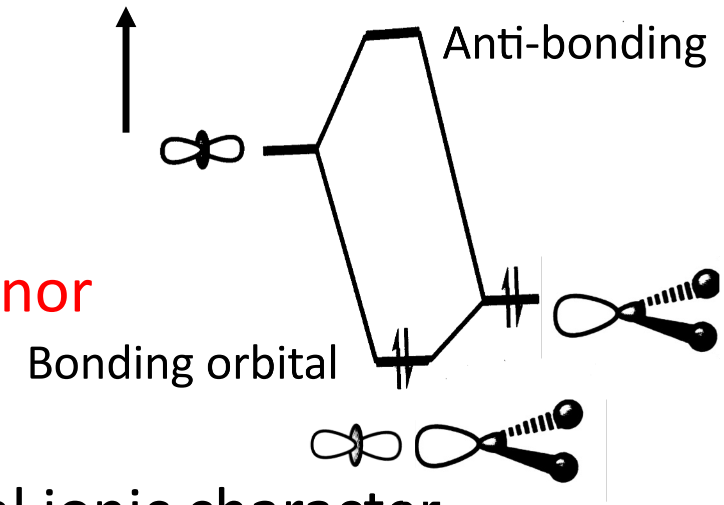
Anions/molecules with a single lone pair of electrons on the donor atom

(n_σ ) Ex: NH_3, H^-, ethylenediamine…

axial overlap with M

The ligand donates electrons to M

Every ligand is σ-donor



The bonding orbital is

- occupied by 2 e^- ➡ stability of the complex
- Is mainly developped on the ligand ➡ partial ionic character

<u>Interaction π with **π-donor ligands**</u>

Anions/molecules with > 1 lone pair of electrons on the donor atom

Ex: OH_2, Cl^-, OH^-…

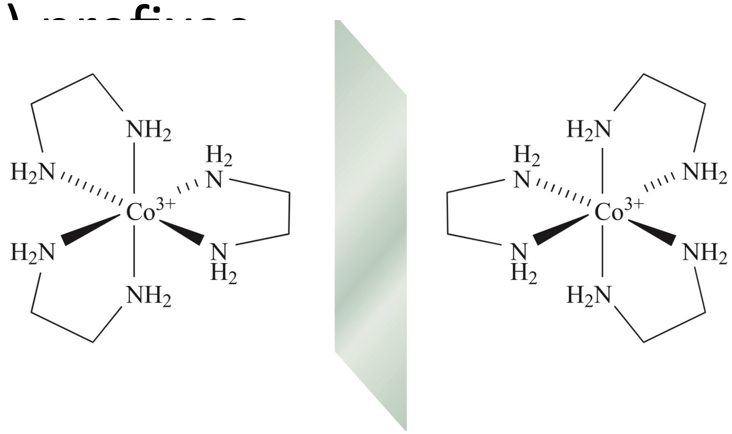
lateral overlap between the OM of this 2^{nd} lone pair and an OM d of M

Optical isomers delta/lamba Ambidendate

<u>Optical isomers with bidentate ligands:</u> Housecroft p552 and

Octahedron complexes containing bidentate ligands exit as enantiomers distinguished using Δ (delta) and Λ (lambda

Ex: $[Co(NH_3)_6]^{3+}$



The octahedron is viewed down a three-fold axis, and the chelates then define either a right- or left-handed helix. The enantiomer with right-handedness is labelled ⍰, and that with left-handedness is ⍰.

Coordination of a polydentate ligand to an ion leads to the formation of a

Optical isomers delta/lamba Ambidendate

Coordination of a polydentate ligand to an ion leads to the formation of a **chelate ring**. Housecroft p242 (or 183)

Ambidentates ligands (‘ambidente’)

Can bind by one or the other end

- SCN^-: thiocyanate or κ-S-thiocyanate
- NCS^-: isothiocyanate or κ-N-thiocyanate
- OCN^-: cyanate or κ-O-cyanate
- NCO^- : isocyanate or κ-N-cyanate

-

notation kappa, hapticité , bridging ligands

Coordination number (or ligancy): (‘coordinence’) of a central metal (ion) is the number of neighbours (atoms, molecules, ions) bound to it.

Geometry

PROPRIETES DES COMPLEXES

Différents types de ligands :

Ligands σ-donneurs : NH_3, H^-, éthylènediamine H_2N ⁀ NH_2 …

molécules possédant un seul doublet non liant (DNL) sur l'atome donneur ; ainsi, les électrons situés dans la Haute Occupée (DNL) peuvent faire une liaison σ avec l'ion métallique (recouvrement selon un axe de révolution).

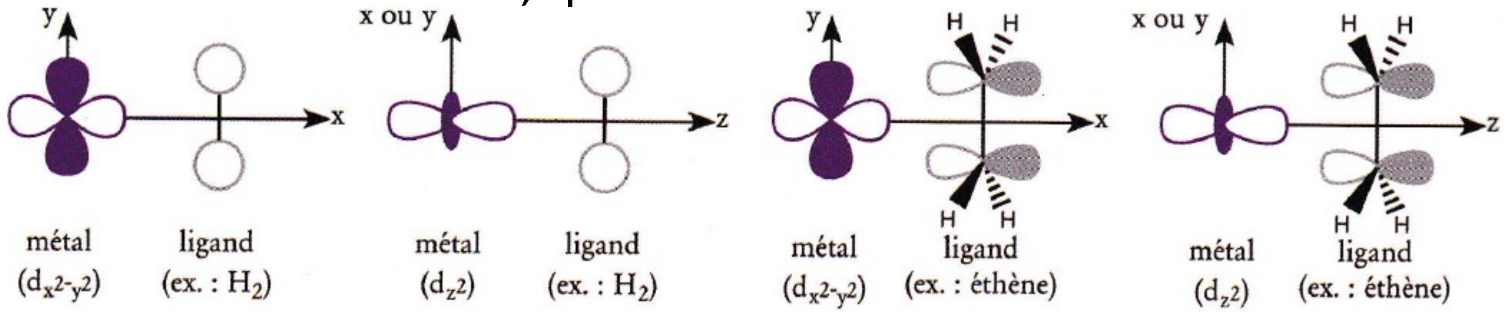
Ligands Π-donneurs : OH_2, Cl^-, OH^- …

molécules possédant plus d'un doublet non liant (DNL) sur l'atome donneur ;
Recouvrement latéral possible entre l'OM de ce 2ème DNL et une OM d du métal

Ligands Π-accepteurs : pyridine, phénanthroline, CO, CN^-, PPh_3 …

molécules dont l'atome donneur est impliqué dans une liaison multiple ;
alors il existe une OM π^* vacante susceptible d'accueillir des électrons du métal, avec un recouvrement latéral. Cas particulier PPh_3 : recouvrement latéral entre une OM d du métal et une OM de type d basée sur le P

Recouvrement avec des « ligands particuliers » : H_2, alcène,
les 2 e^- apportés sont ceux d'1 liaison, qui est affaiblie.

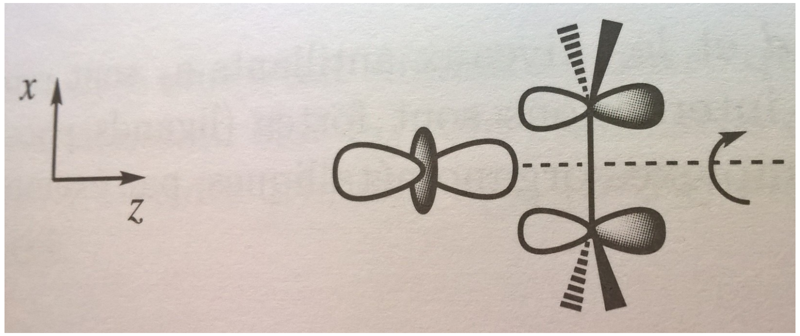


Chimie tout en un
PC 2ème année, p568
T. Ribeyre, Ed De Boeck

COMPLEXES π

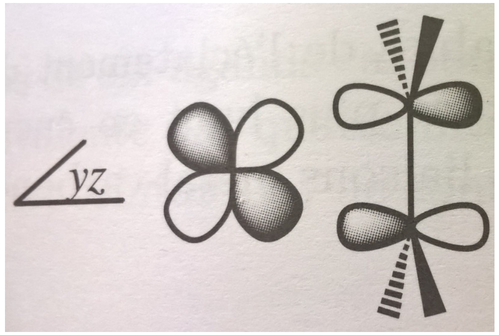
<u>Ligand éthylène :</u>

π



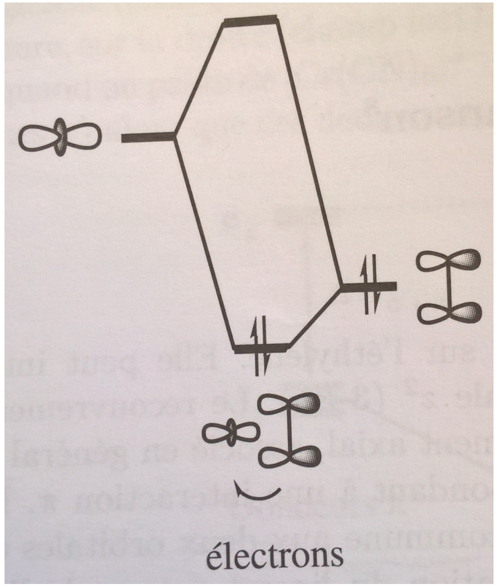
Interaction σ
Inchangé par rotation

π^*

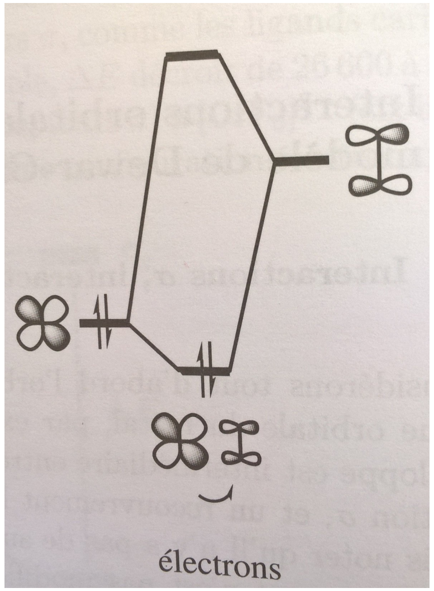


Interaction π : Plan nodal (yz)
La rotation autour de z
diminue le recouvrement S

Ligand L



Donation
Ligand σ–donneur



Rétrodonation
Ligand π–accepteur

Les OM dans les complexes, Yves Jean, p174

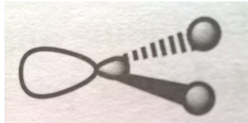
Ligand carbonyle

Les OM dans les complexes, Yves Jean, p149

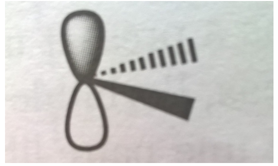
Ligand carbène : H_2C

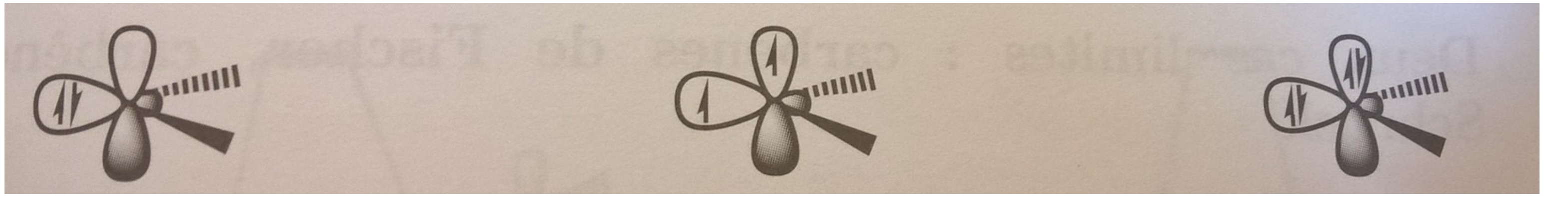
2 OM non liantes proches en énergie
à remplir par 2 électrons

n_σ



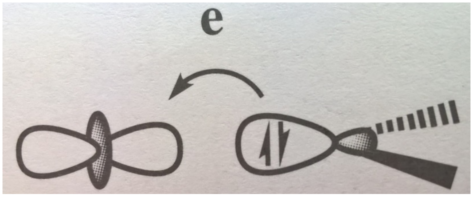
n_p



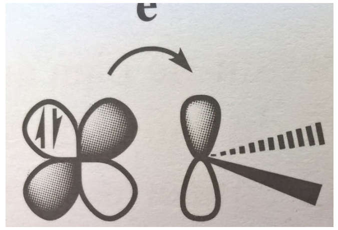


Ligand L | Ligand X_2 | Ligand dianionique

Donation
Ligand σ–donneur

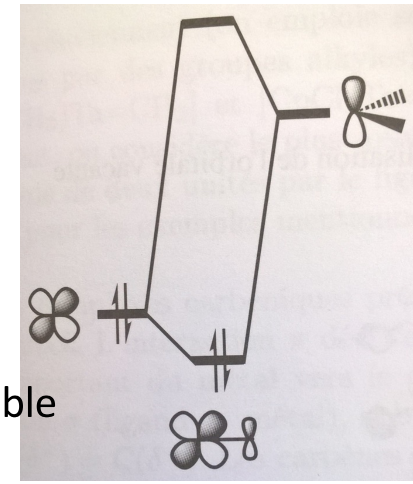


Rétrodonation
Ligand π–accepteur



Si $E(n_p) > E(d)$: carbène de **Fischer**

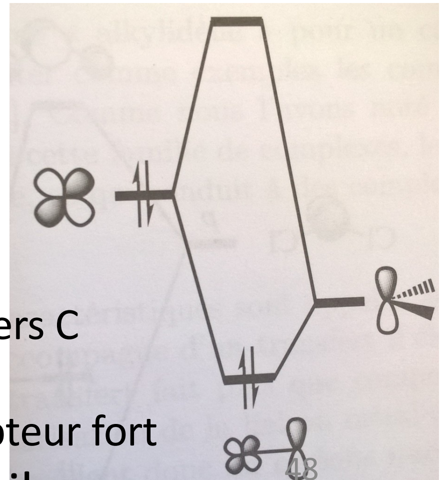
- groupes mésomères donneurs sur carbène
- métaux à droite
- ligands π–accepteurs



2e⁻ dans OM développée
sur métal, non oxydé,
Carbène ligand L π–accepteur faible
$C^{\delta+}$, carbone électrophile

Si $E(n_p) < E(d)$: carbène de **Schrock**

- **Pas** de gpes mésomères donneurs sur carbène
- métaux à gauche
- Ligands π–donneurs



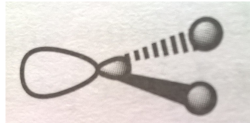
Transfert de $2e^-$ du métal vers C
Métal oxydé,
Carbène ligand X_2 π–accepteur fort
$C^{\delta-}$, carbone nucléophile

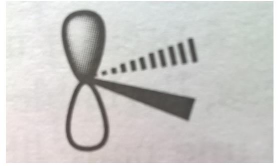
Ligands carbènes

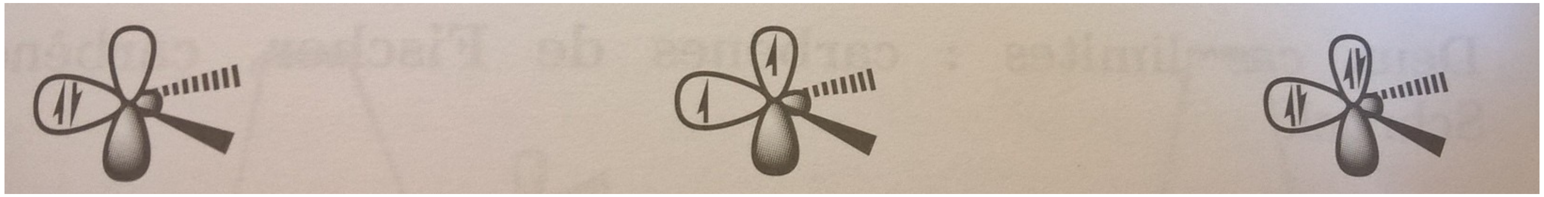
Les OM dans les complexes, Yves Jean, p226

Ligand carbène : H_2C

2 OM non liantes proches en énergie
à remplir par 2 électrons

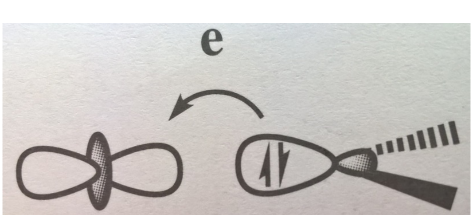
n_σ 

n_p 

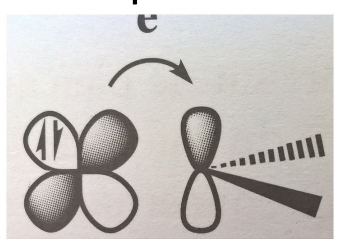


Ligand L | Ligand X_2 | Ligand dianionique

Donation
Ligand σ–donneur

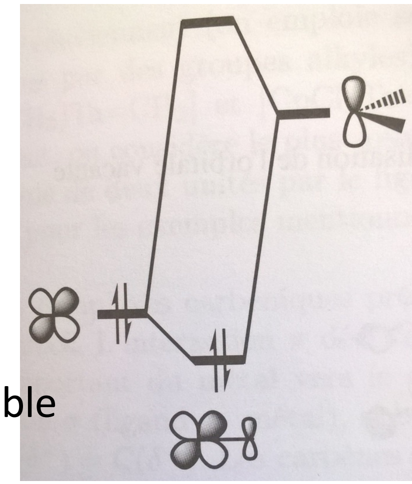


Rétrodonation
Ligand π–accepteur



Si $E(n_p) > E(d)$: carbène de **Fischer**

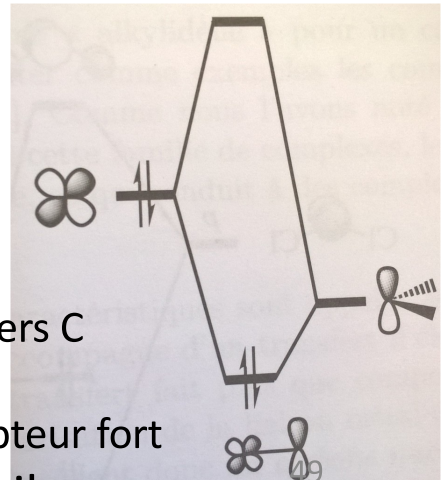
- groupes mésomères donneurs sur carbène
- métaux à droite
- ligands π–accepteurs



$2e^-$ dans OM développée
sur métal, non oxydé,
Carbène ligand L π–accepteur faible
$C^{\delta+}$, carbone électrophile

Si $E(n_p) < E(d)$: carbène de **Schrock**

- **Pas** de gpes mésomères donneurs sur carbène
- métaux à gauche
- Ligands π–donneurs



Transfert de $2e^-$ du métal vers C
Métal oxydé,
Carbène ligand X_2 π–accepteur fort
$C^{\delta-}$, carbone nucléophile

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Chimie inorganique, Housecroft, Ed De Boeck