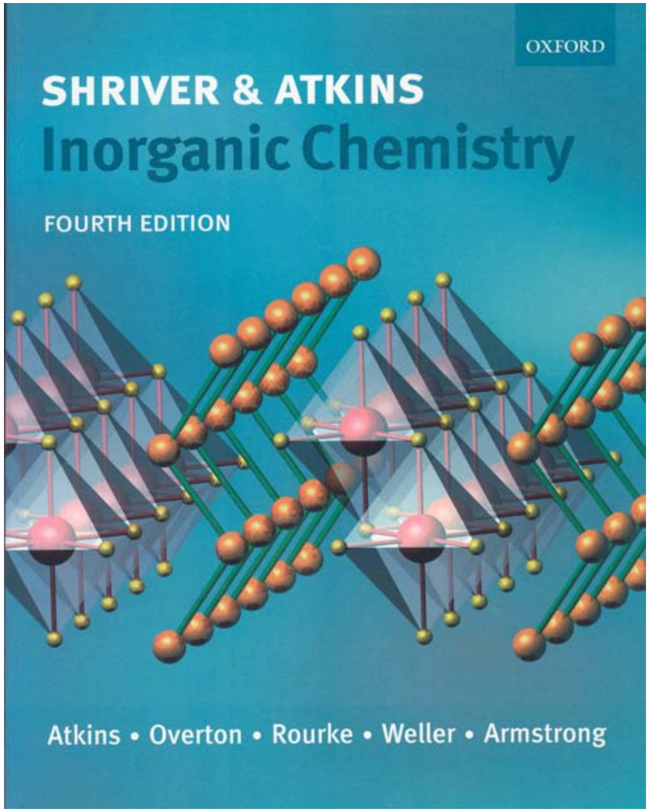
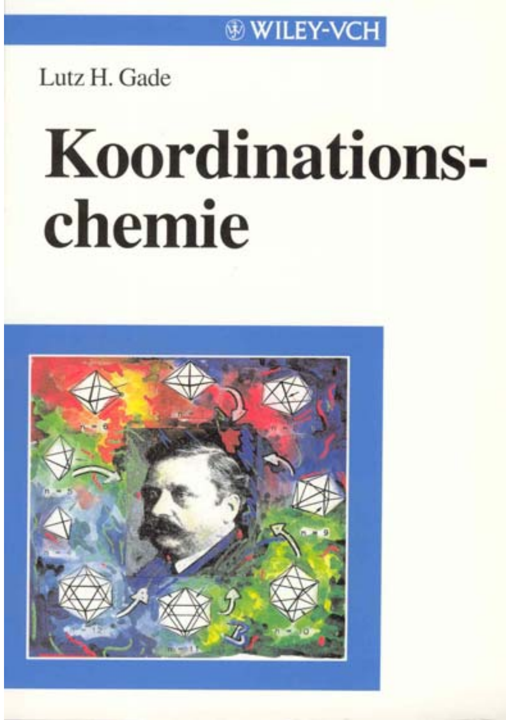
Coordination and Special Materials Chemistry

Elective I or II or IV: WS 2007/8 (Lecture)

H.J. Deiseroth

Coordination and special materials Chemistry
Recommended Textbooks





How did the study of coordination compounds start?

The coordination chemistry was pioneered by Nobel Prize winner Alfred Werner (1866-1919). He received the Nobel Prize in 1913 for his coordination theory of transition metal-amine complexes.

Werner studied the metal-ammine complexes such as $[Co(NH_3)_6Cl_3]$ and recognized the existence of several forms of „cobalt-ammonia chloride“. These compounds have different colour and other characteristics. The chemical formula has three chloride ions per mole, but the number of chloride ions that precipitate with Ag^+ ions per formula is not always three. He thought only **ionised chloride ions** will form a precipitate with silver ions. In the following table, the number below the **ionised Cl-** is the number of ionised chloride ions per formula. To distinguish ionised chloride from the coordinated chloride, Werner formulated the **Complex formula** and explained the structure of the cobalt complexes.

How did the study of coordination compounds start? Proposed Structures of Cobalt Ammine Complexes from the Number of Ionized Chloride ions

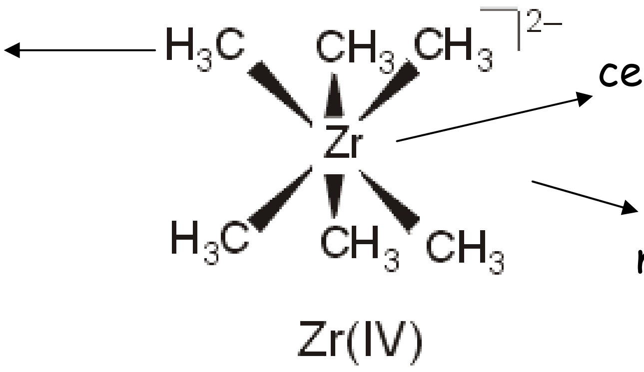
$CoCl_3$ $6NH_3$:Yellow $[Co(NH_3)_6]Cl_3$
$CoCl_3$ $5NH_3$ Purple$[Co(NH_3)_5Cl]Cl_2$
$CoCl_3$ $4NH_3$ Green *trans*-$[Co(NH_3)_4Cl_2]Cl$
$CoCl_3$ $4NH_3$ Violet *cis*-$[Co(NH_3)_4Cl_2]Cl$

The structures of the complexes were proposed based on a coordination sphere of 6. The 6 ligands can be ammonia molecules or chloride ions. Two different structures were proposed for the last two compounds, the *trans* compound has two chloride ions on opposite vertices of an octahedron, whereas the two chloride ions are adjacent to each other in the *cis* compound. The *cis* and *trans* compounds are known as geometric isomers. Isomerism is a very common feature of coordination compounds and will be discussed in more detail later.

Coordination and special materials Chemistry

Coordination chemistry is the chemistry of compounds formed between metal atoms/ions and other neutral or negatively charged molecules

complex compounds ⇔ **coordination compounds**.



ligand (donor group)

central atom

coordination number (CN = 6)

Hexa-methyl-zirconate (IV)
$(CH_3)^-$ (!)

Isomers: Compounds with the same chemical formula but different structures.

Different types of isomerism: linkage isomerism, hydrate isomerism, cis-trans isomerism, coordination isomerism etc. (**see seminar talk**)

Naming of coordination compounds

- The names of complexes **start** with the **ligands (in alphabetical order)**, the **anionic ones first** , followed by **neutral ligands**, the **central atom** and the **oxidation state (**Roman numerals).
- If the complex is negative, the name ends with "**ate**".
- names of anionic ligands end with **„o“ : chloro-**, **oxo-**, **fluoro-, cyano.**
- neutral ones **without** specific ending: (exception: H_2O: **aqua**, NH_3: **ammine**) C_5H_5N, **pyridine**, $NH_2CH_2CH_2NH_2$, **ethylenediamine**, $C_5H_4N\text{-}C_5H_4N$, **dipyridyl**, $P(C_6H_5)_3$: **triphenylphosphine**, CO: **carbonyl,** CS: **thiocarbonyl,**

$[Co(NH_3)_5Cl]Cl_2$: Chloro-penta-ammine-cobalt(III)chloride
$[Cr(H_2O)_4Cl_2]Cl$: Dichloro-tetra-aqua-chromium(III)chloride
$K[PtCl_3NH_3]$: Potassium-tri-chloro-ammine-platinate(II)
$PtCl_2(NH_3)_2$: Di-chloro-diammine-platinum(II)
$[Co(en)_3]Cl_3$: Tris(ethylenediamine)-cobalt(III)chloride
$Ni(PF_3)_4$: Tetrakis(phosphorus(III)fluoride)-nickel(0)
or Tetrakis(phosphorus-tri-fluoride)-nickel(0)

simple ligands: di- tri-, tetra-, penta-, hexa- ...
complex ligands: bis-, tris-, tetrakis- ...

Symmetry Elements, Symmetry Operations, Point Groups

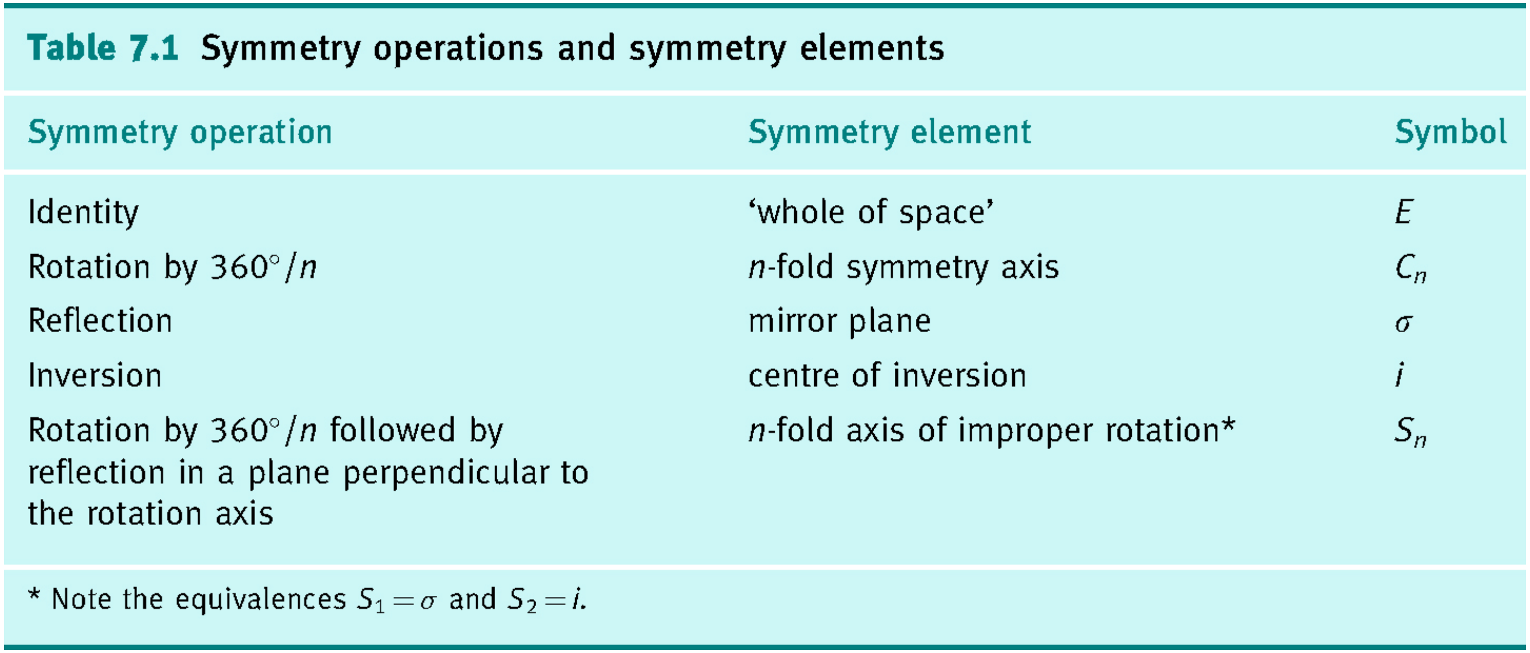


Table 7.1 Symmetry operations and symmetry elements

Symmetry operation	Symmetry element	Symbol
Identity	'whole of space'	E
Rotation by 360°/n	n-fold symmetry axis	C_n
Reflection	mirror plane	σ
Inversion	centre of inversion	i
Rotation by 360°/n followed by reflection in a plane perpendicular to the rotation axis	n-fold axis of improper rotation*	S_n

* Note the equivalences $S_1 = \sigma$ and $S_2 = i$.

Coordination compounds with CN = 2 (linear)

CN = 2 is very common for complex ions and molecules of Cu(I), Au(I), Ag(I) and Hg(II)

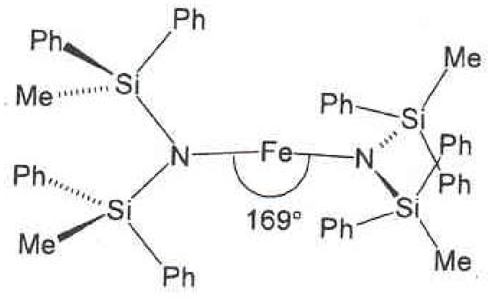
Cu(I) $[\mathrm{X-Cu-X}]^-$

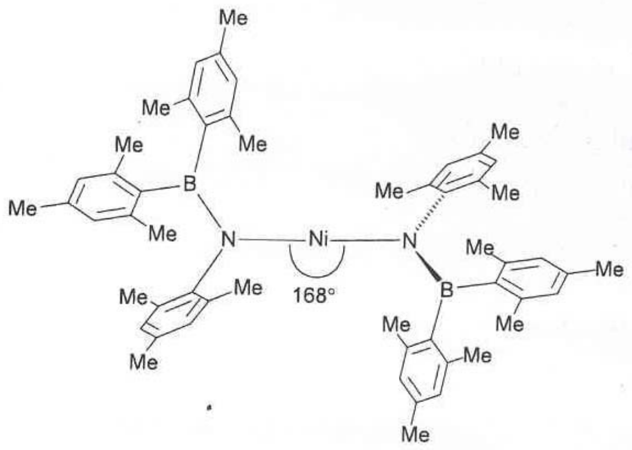
$\mathrm{X = Cl, Br}$

Ag(I) $[\mathrm{H_3N-Ag-NH_3}]^+$

Au(I) $[\mathrm{R_3P-Au-PR_3}]^+$

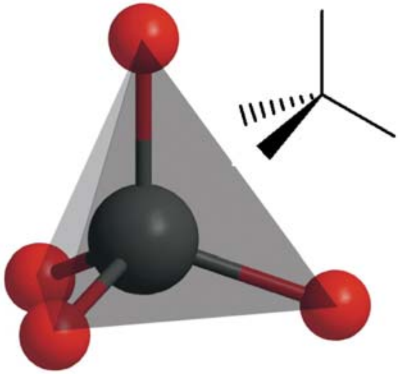
$\mathrm{H_3C-Hg-CH_3}$





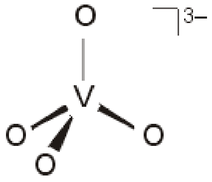
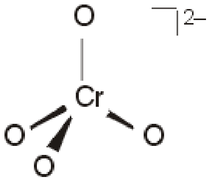
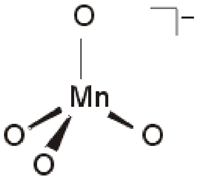
CN = 3 is very rare among normal coordination compounds of d-metals

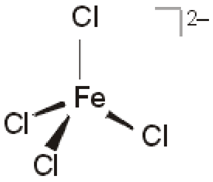
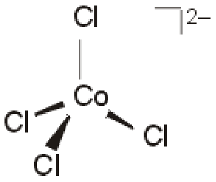
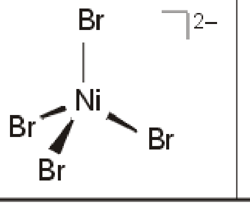
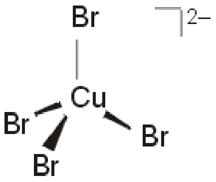
Coordination compounds with CN = 4 (tetrahedral)



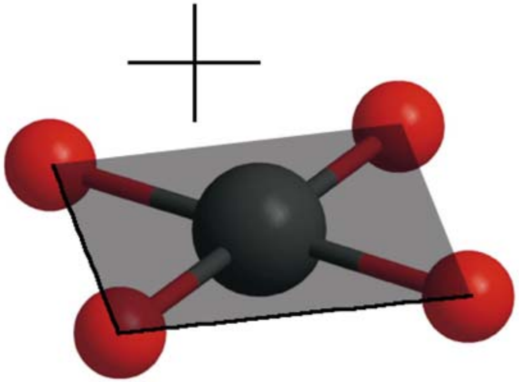
5 Tetrahedral complex, T_d

Structure 8-5
Shriver & Atkins Inorganic Chemistry, Fourth Edition
© 2006 by D.F. Shriver, P.W. Atkins, T.L. Overton, J.P. Rourke, M.T. Weller, and F.A. Armstrong

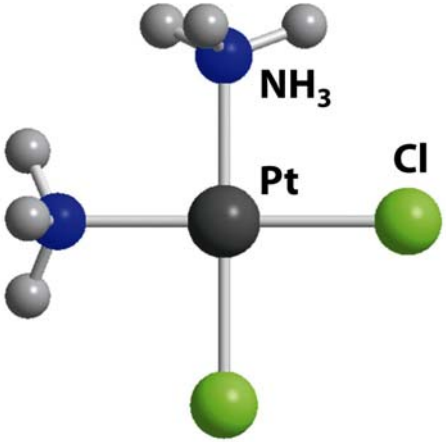
5	6	7
		

8	9	10	11
			

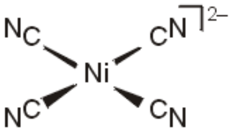
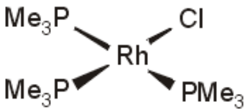
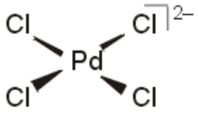
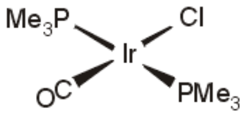
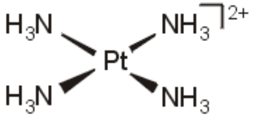
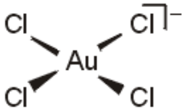
Coordination compounds with CN = 4 (square planar)



8 Square-planar complex, D_{4h}

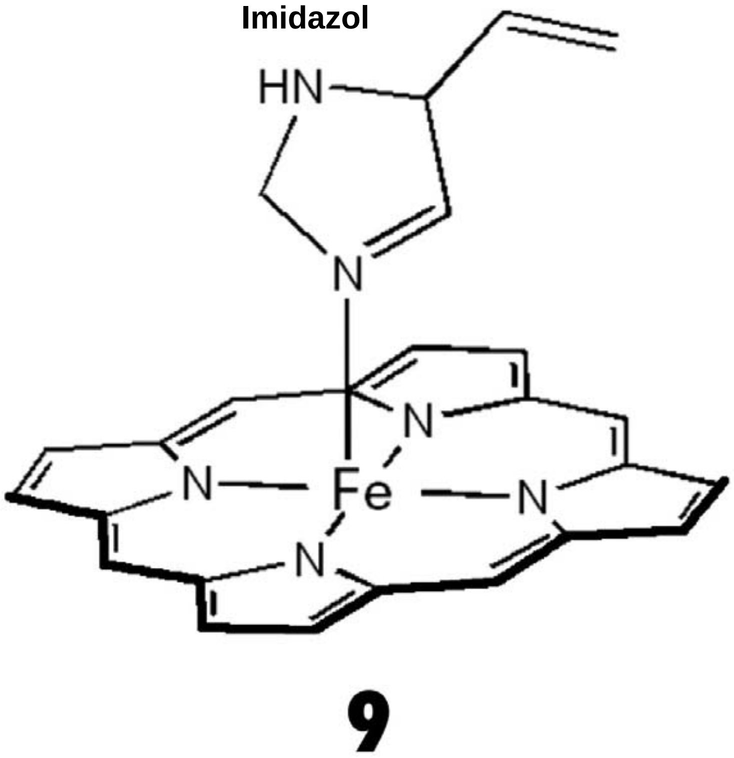


6 *cis*-[Pt(Cl)$_2$(NH$_3$)$_2$]

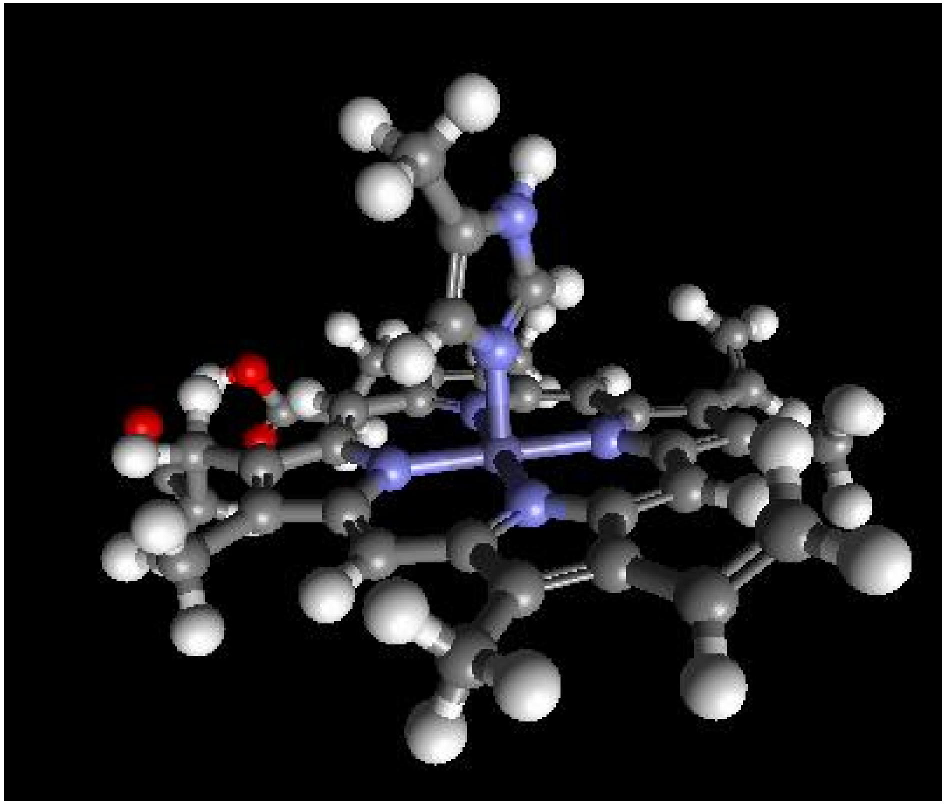
9	10	11
	 Ni(II)*	
 Rh(I)	 Pd(II)	
 Ir(I)	 Pt(II)	 Au(III)

Preferred coordination of d^8 central atoms !!

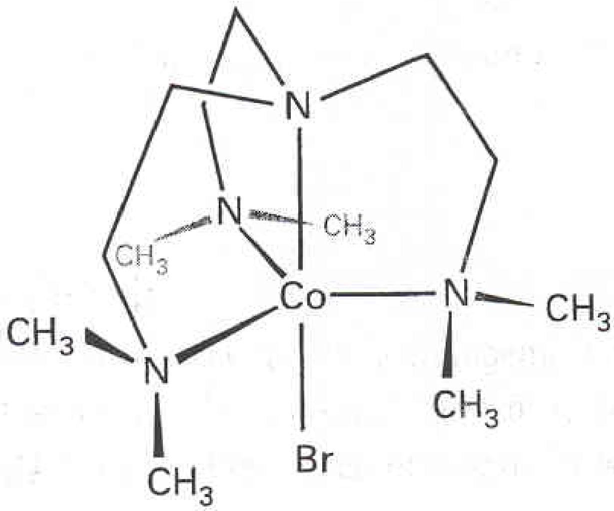
Coordination compounds with CN = 5 (Square pyramidal)
(e.g. active center of myoglobin and haemoglobin)



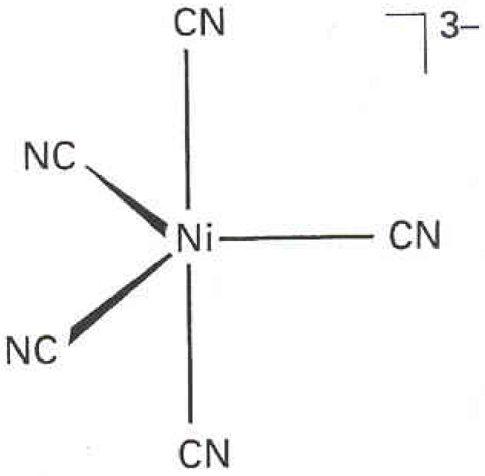
Structure 8-9
Shriver & Atkins Inorganic Chemistry, Fourth Edition



Coordination compounds with CN = 5 (trigonal bipyramidal)

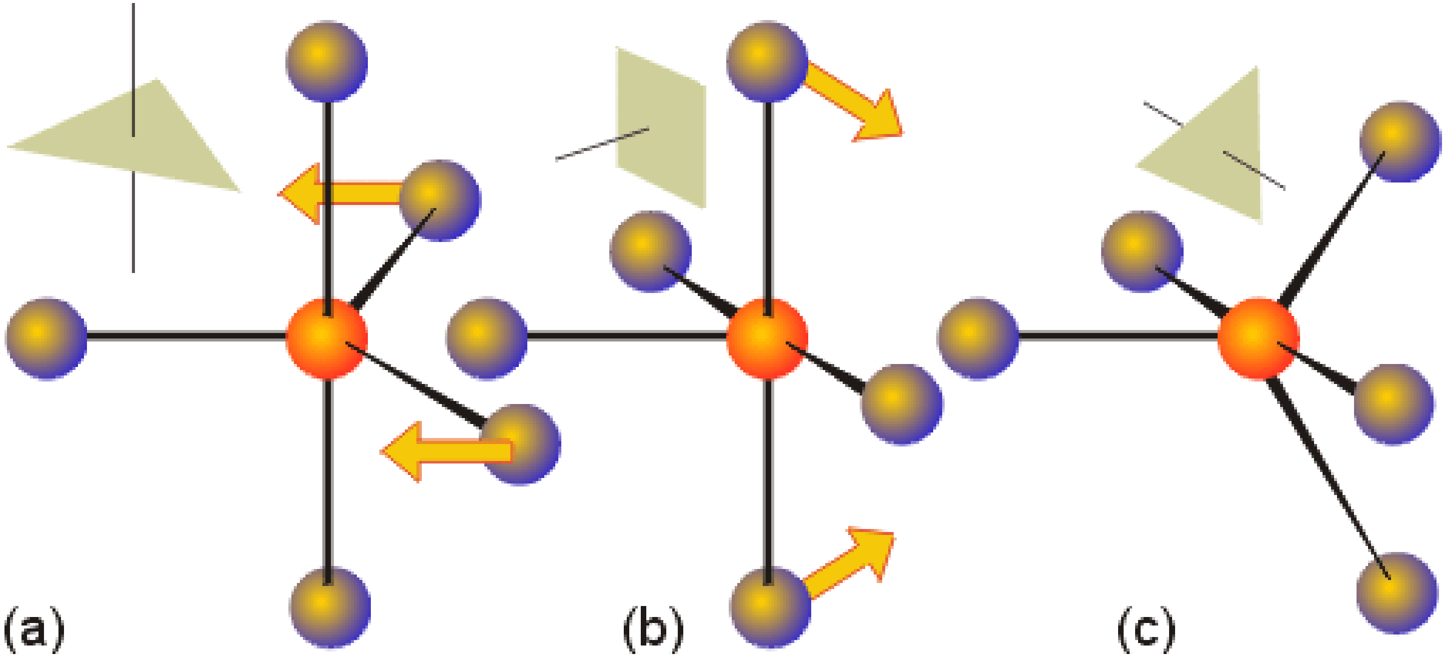


8

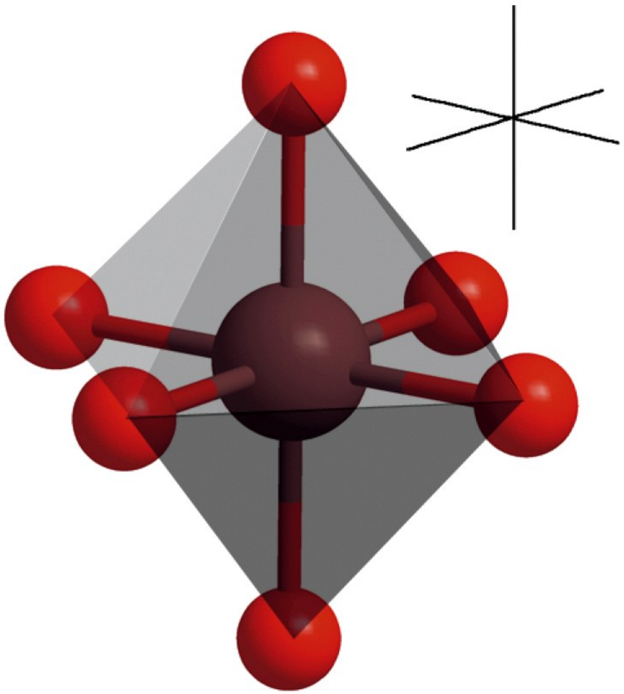


9b $[Ni(CN)_5]^{3-}$ (trigonal-bipyramidal conformation)

Pseudorotation (CN = 5): square pyramidal ↔ trigonal pyramidal



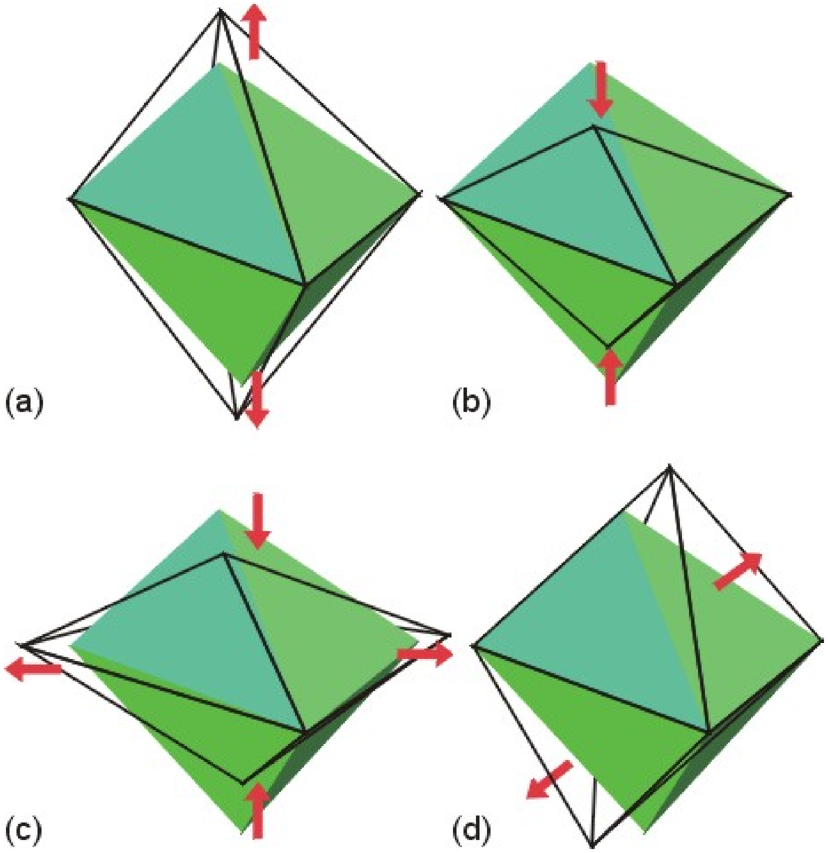
Coordination compounds with CN = 6 (octahedralal)



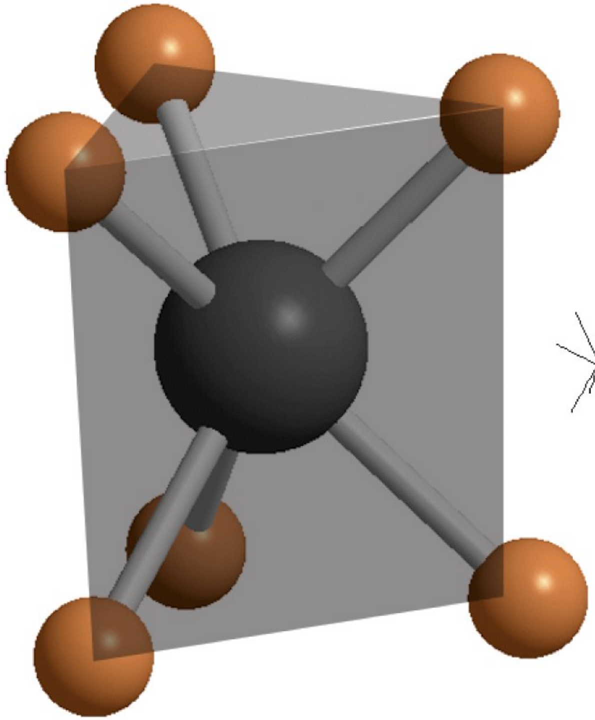
13 Octahedral complex, O_h

Structure 8-13
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Types of distortions of octahedra



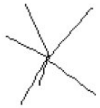
Coordination compounds with CN = 6 (trigonal prismatic)

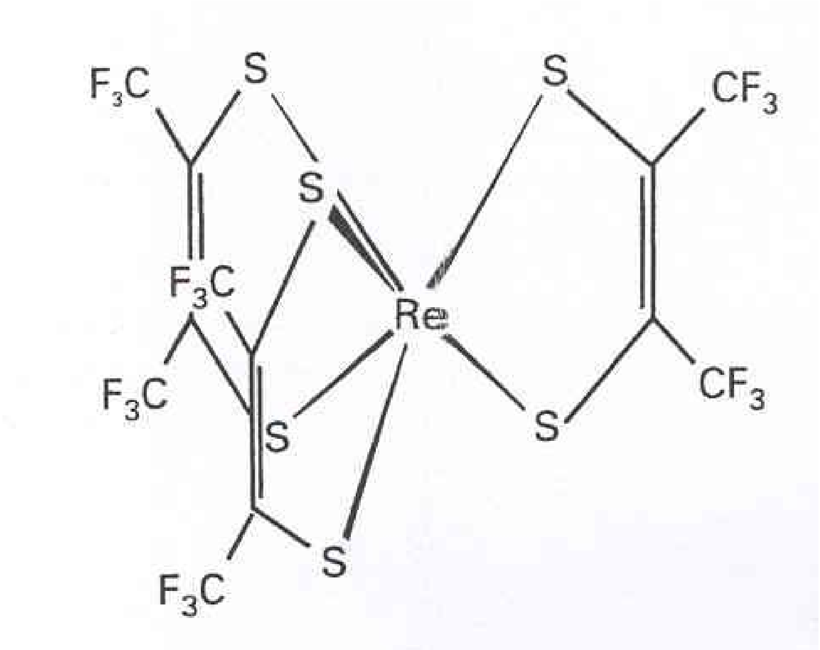


14 Trigonal prism, D_{3h}

Structure 8-14

Shriver & Atkins Inorganic Chemistry, Fourth Edition





Constitution and Coordination Number, higher CN's

The most important factors that determine the constitution and coordination number of a complex are:

- **size of the central atom**
- **steric interactions between ligands**
- **electronic interactions**

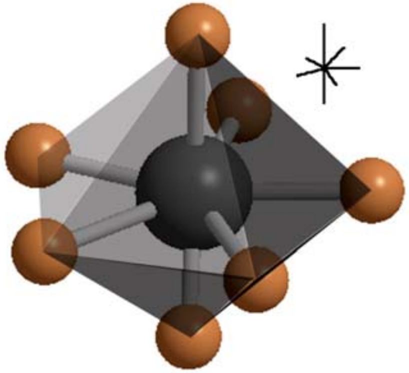
Higher coordination numbers (CN's) are favoured:

- in complexes with atoms (and ions) of the **periods 5 and 6**
- on the **left of a row of the d-block** where atoms are relatively large and have a small number of d-electrons
- for central atoms with a high oxidation number and thus a mall number of remaining d-electrons (e.g. $[Mo(CN)_8]^{4-}$

Coordination compounds with CN = 7 („capped“)

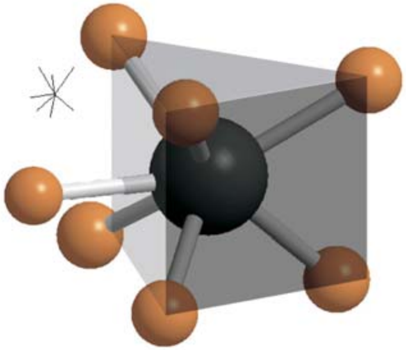
- rare with 3d elements but more common with 4d and 5d metals

CN = 7: pentagonal bipyramid, (mono-) capped trigonal prism, capped octahedron
e.g. $[ZrF_7]^{3-}$, $[ReOCl_6]^{2-}$, $[UO_2(OH_2)_5]^{2+}$ ...



16 Pentagonal bipyramid, D_{5h}

Structure 8-16
Shriver & Atkins Inorganic Chemistry, Fourth Edition



18 Capped trigonal prism

Structure 8-18
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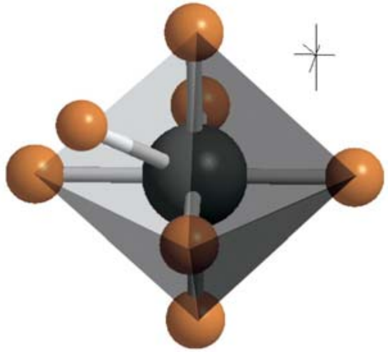


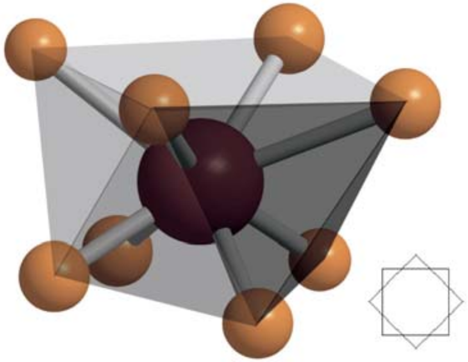
17 Capped octahedron

Structure 8-17
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Coordination compounds with CN = 8

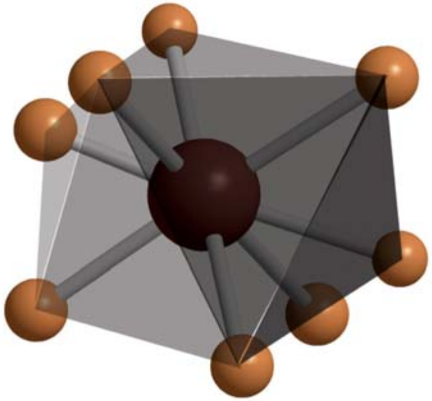
CN = 8:

square antiprism („archimedian“ antiprism), trigonal dodecahedron, **cube**



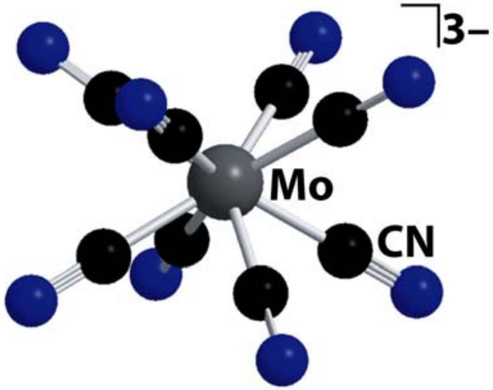
20 Square antiprism, D_4

Structure 8-20
Shriver & Atkins Inorganic Chemistry, Fourth Edition



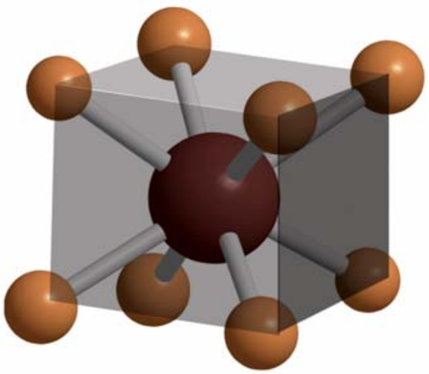
21 Dodecahedron

Structure 8-21
Shriver & Atkins Inorganic Chemistry, Fourth Edition



22 $[Mo(CN)_8]^{3-}$

Structure 8-22
Shriver & Atkins Inorganic Chemistry, Fourth Edition



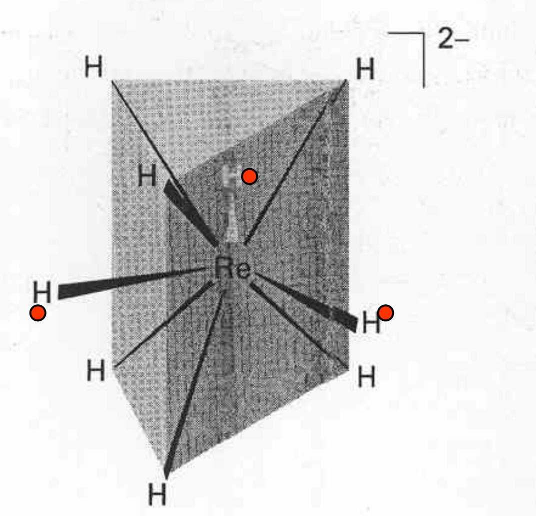
24 Cube

Structure 8-24
Shriver & Atkins Inorganic Chemistry, Fourth Edition

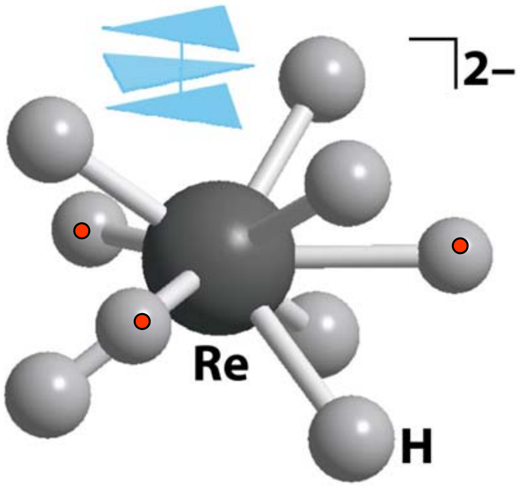
Coordination compounds with CN = 9 („capped trigonal prism")

CN = 9: common with Re (e.g. $[ReH_9]^{2-}$) and f-block elements (e.g. $[Nd(OH_2)_9]^{3+}$)

CN > 9: important only for complexes with heavy metal central atoms
(e.g. f-elements)



21 $[ReH_9]^{2-}$, D_{3h}



25 $[ReH_9]^{2-}$, D_{3h}

Structure 8-25
Shriver & Atkins Inorganic Chemistry, Fourth Edition
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Exercises

1 Preferably without using reference material, write out the 3d elements in their arrangement in the periodic table. Indicate the metal ions that commonly form tetrahedral complexes of formula $[MX_4]^{2-}$ where X is a halide ion.

2 (a) On a chart of the d-block elements in their periodic table arrangement, identify the elements and associated oxidation numbers that form square-planar complexes. (b) Give formulas for three examples of square-planar complexes.

3 (a) Sketch the two structures that describe most six-coordinate complexes. (b) Which one of these is rare? (c) Give formulas for three different d-metal complexes that have the more common six-coordinate structure.

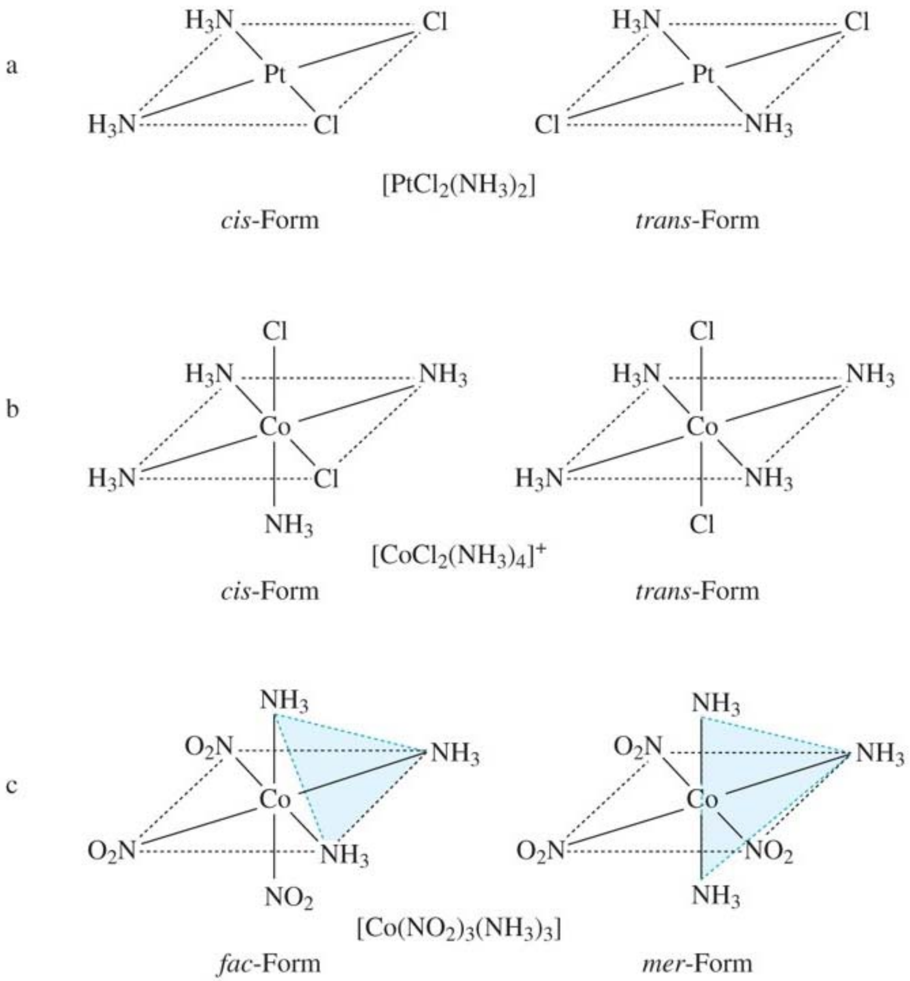
4 Name and draw structures of the following complexes: (a) $[Ni(CO)_4]$; (b) $[Ni(CN)_4)^{2-}$ (c) $[CoCl_4]^{2-}$ (d) $[Ni(NH_3)_6]^{2+}$.

5 Draw the structures of representative complexes that contain the ligands (a) en, (b) ox^{2-}, (c) phen, and (d) $edta^{4-}$

6 Draw the structure of (a) a typical square-planar four-coordinate complex; (b) a typical trigonal prismatic six-coordinate complex; (c) a typical complex of coordination number 2. Name each complex.

7 Give formulas for (a) pentaamminechlorocobalt(III) chloride, (b) hexaaquairon(3+) nitrate; (c) cis-dichlorobis(ethylenediamine)ruthenium(II); (d) μ-hydroxobis[pentaamminechromium(III)] chloride.

Isomerism: cis-trans isomerism

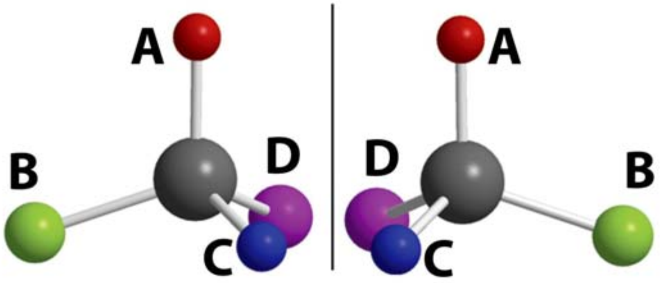


mer: meridional
fac: facial

Isomerism and Chirality (important terms)

- A **chiral** molecule is not superimposable on its own mirror image
- **Optical isomerism:** Rotation of the plane of polarized light shown by optical isomers
- **Enantiomeric pair ("racemate"):** Two mirror-image isomers in one sample
- **Diastereomers:** Molecules with **more** than **one** center of chirality (e.g. organic sugar molecules)

Criteria for **absence of** chirality: 1. mirror plane through central atom (S_1), 2. inversion centre (S_2), 3. no improper rotation



49 [MABCD] enantiomers

Structure 8-49
Shriver & Atkins Inorganic Chemistry, Fourth Edition
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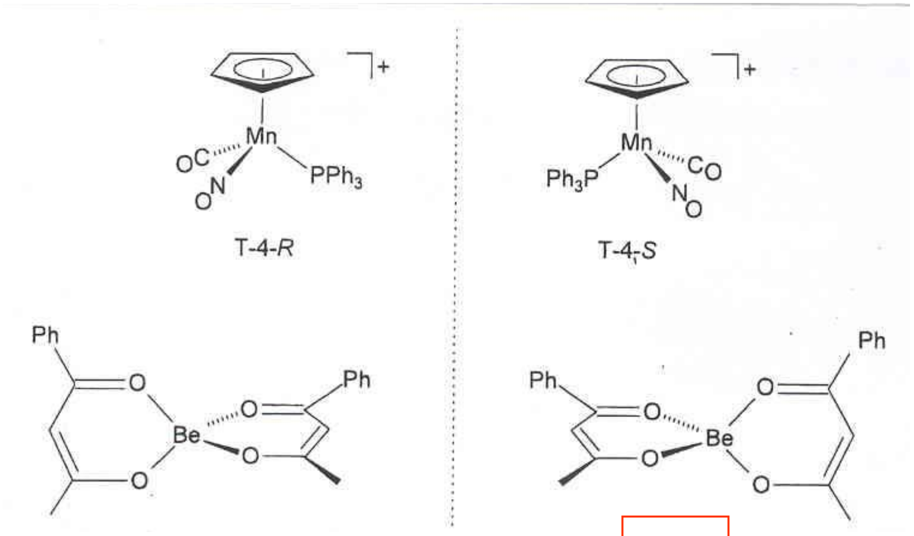
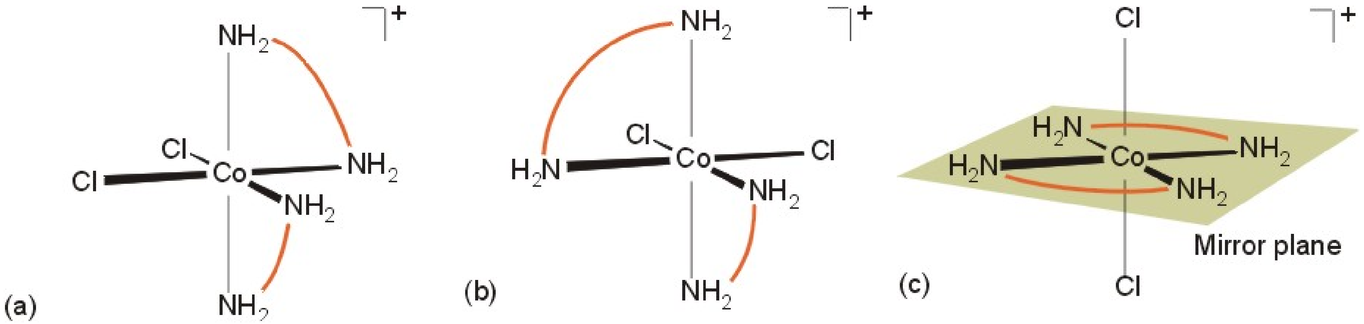
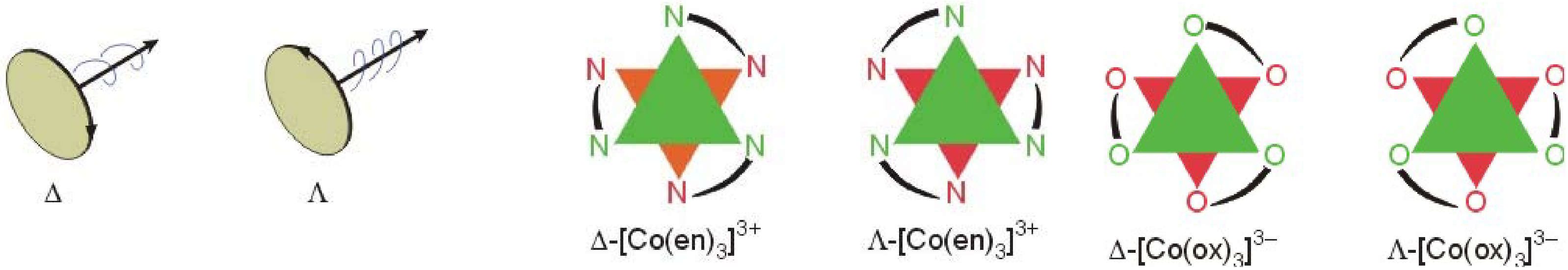


S_4

Isomerism and Chirality



7.6 (a) and (b) Enantiomers of *cis*-$[CoCl_2(en)_2]$ and (c) the achiral *trans* isomer. The curves represent the CH_2CH_2 bridges in the en ligands. The mirror plane for testing whether there is an S_1 axis is also shown.



Δ

Λ

Δ-$[Co(en)_3]^{3+}$

Λ-$[Co(en)_3]^{3+}$

Δ-$[Co(ox)_3]^{3-}$

Λ-$[Co(ox)_3]^{3-}$

7.7 Absolute configurations of $[M(L—L)_3]$ complexes; Δ is a right-hand screw and Λ is a left-hand screw, as is indicated in the diagrams at the top of the figure by the direction that a screw would turn when being driven in the direction shown.

Exercises

8 Name the octahedral complex ions (a) cis-$[CrCl_2(NH_3)_4]$+, (b) trans-$[Cr(NCS)_4(NH_3)_2]^-$, and (c) $[Co(C_2O_4)(en)_2)^+$. Is the oxalato complex cis or trans?

9 Draw all possible isomers of (a) octahedral $[RuCl_2(NH_3)_4]$, (b) square-planar $[IrH(CO)(PR_3)_2]$, (c) tetrahedral $[CoCl_3(OH_2)]$-, (d) octahedral $[IrCl_3(PEt_3)_3]$, and (c) octahedral $[CoCl_2(en)(NH_3)_2]^+$.

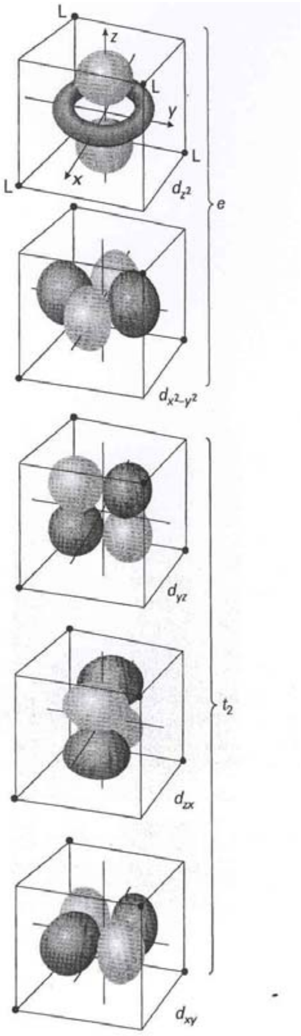
10 The compound Na_2IrCl_5 reacts with triphenylphosphine in diethylene glycol under an atmosphere of CO to give trans-$[IrCl(CO)(PPh_3)_2]$, known as Vaska's compound. Excess CO produces a five-coordinate species and treatment with $NaBH_4$ in ethanol gives $[IrH(CO)_2(PPh_3)_2]$. Draw and name the three complexes.

11 Which of the following complexes are chiral? (a) $[Cr(ox)_3]^{3-}$, (b) cis-$[PtCl_2(en)]$, (c} cis-$(RhCl_2(NH_3)_4]^+$, (d) $[Ru(bipy)_3]^{2+}$, (e) $[Co(edta)]^-$, (f) *fac*-$[Co(NO_2)_3(dien)]$, (g) *mer*-$[Co(NO_2)_3(dien)$. Draw the enantiomers of the complexes identified as chiral and identify the plane of symmetry in the structures of the achiral complexes.

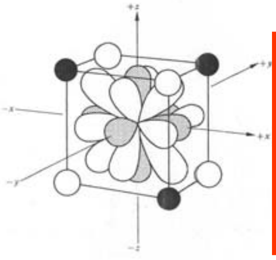
12 One pink solid has the formula $CoCl_3$ $5NH_3$ H_2O. A solution of this salt is also pink and rapidly gives 3 mol AgCI on titration with silver nitrate solution. When the pink solid is heated, it loses 1 mol H_2O to give a purple solid with the same ratio at NH_3:Cl:Co. The purple solid releases two of its chlorides rapidly; then, on dissolution and after titration with $AgNO_3$, releases one of its chlorides slowly. Deduce the structures of the two octahedral complexes and draw and name them.

13 The hydrated chromium chloride that is available commercially has the overall composition $CrCl_3$ $6H_2O$. On boiling a solution, it becomes violet and has a molar electrical conductivity similar to that of $[Co(NH_3)_6]Cl_3$. In contrast, $CrCl_3.5H_2O$ is green and has a lower molar conductivity in solution. If a dilute acidified solution of the green complex is allowed to stand for several hours, it turns violet Interpret these observations with structural diagrams.

Basic Crystal Field Theory: tetrahedral and octahedral field

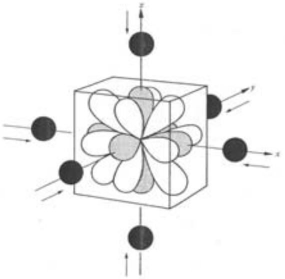


7.13 The effect of a tetrahedral crystal field on a set of *d* orbitals is to split them into two sets; the *e* pair (which point less directly at the ligands) lie lower in energy than the t_2 triplet.

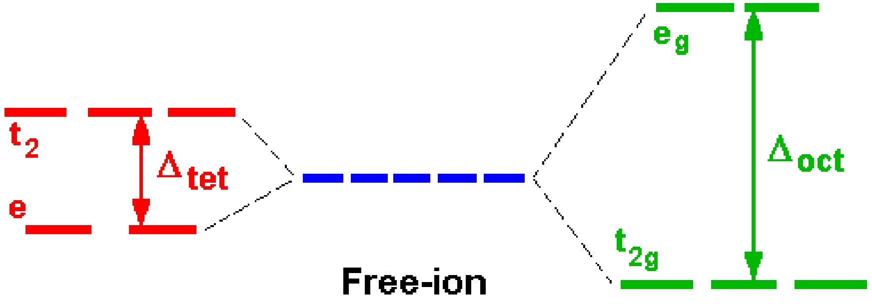


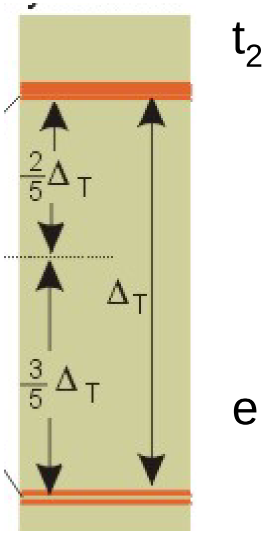
Tetrahedral

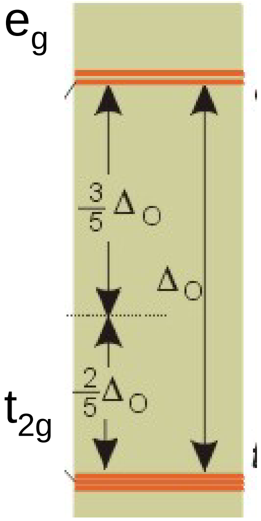
All atoms/molecules are treated as electrical point charges

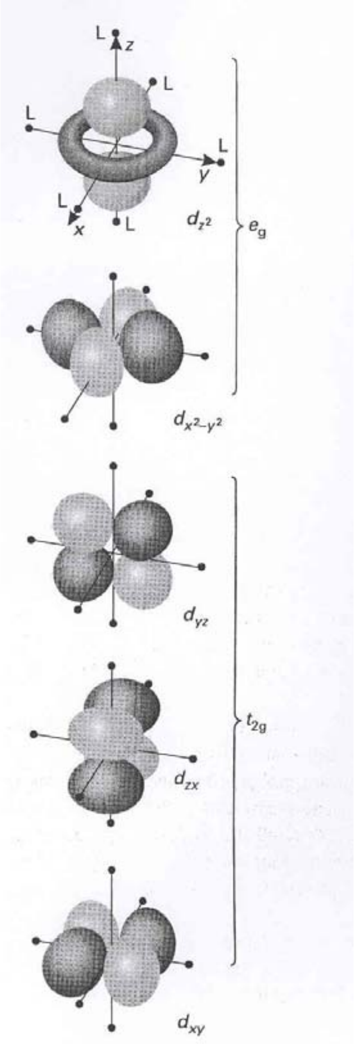


Octahedral





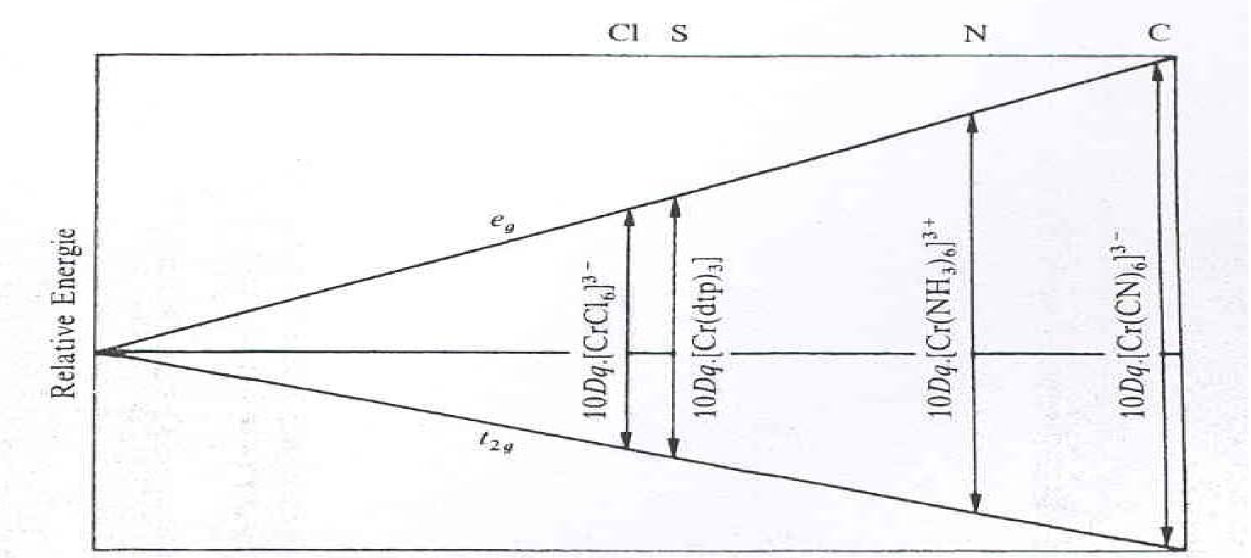




7.8 The orientation of the five *d* orbitals with respect to the ligands of an octahedral complex.

Basic Crystal Field Theory: splitting of energy levels (spectrochemical series)

The influence of **different ligands** on the **size** of $\Delta = 10Dq$



Increasing strength of the ligand field →

$I^- < S^{2-} < Cl^- < NO_3^- < F^- < H_2O < NH_3 <$ en $< NO_2^- < CN^- < CO$

The strength of the ligand field varies with:

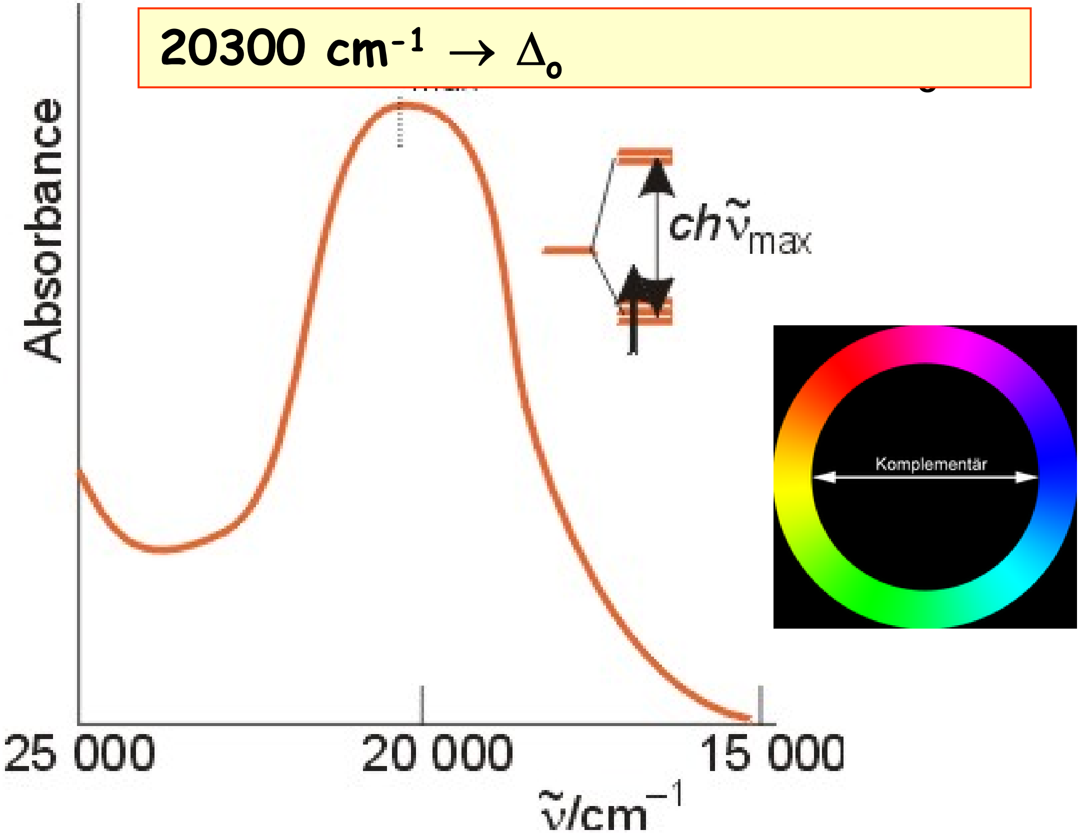
a) the **size and chemical properties** of the ligand (**no** simple relation !)

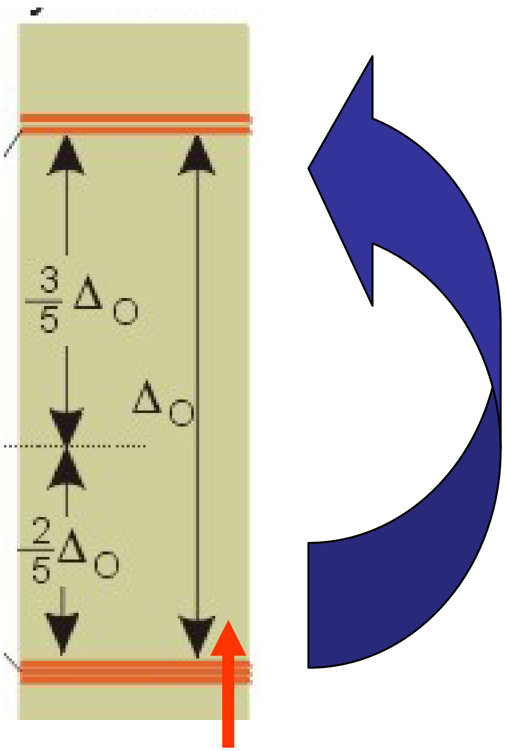
b) the **oxidation number of the central atom** (the higher the oxidation number the stronger the ligand field)

Basic Crystal Field Theory: optical spectrum and ligand field

≈ 500 nm (red) – absorption in the blue green region, complex has complementary color

20300 $cm^{-1} \rightarrow \Delta_o$





$[Ti(H_2O)_6]^{3+}$
Ti^{3+}: (Ar)d^1, octahedral complex

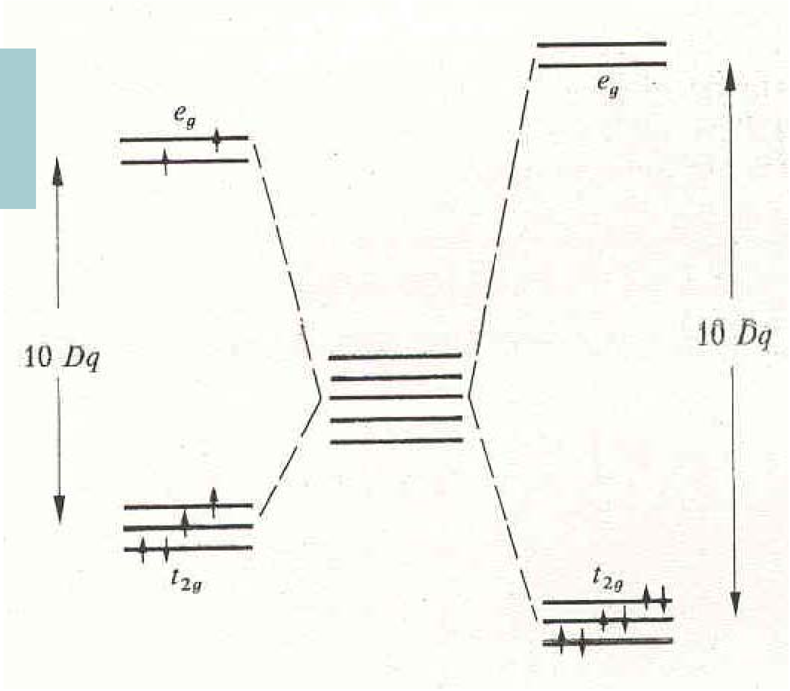
Basic Crystal Field Theory: Weak Field – Strong Field

Spin **pairing energy** versus **ligand field splitting**

octahedral complex

weak field **strong field**

d^6 high spin
(paramagnetism)



d^6 low spin
(diamagnetism)

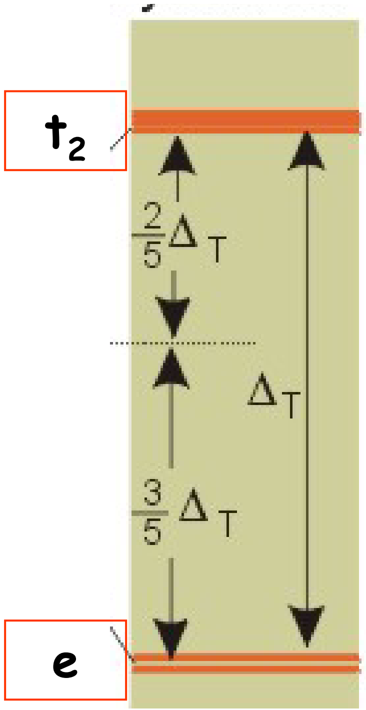
high spin: <u>maximum</u> number of unpaired electrons
low spin: <u>minimum</u> number of unpaired electrons

→ **tetrahedral**: high spin (preferably) **octahedral**: low spin (preferably)

Basic Crystal Field Theory: Ligand field stabilization energies (LFSE)

LFSE: Energetic stabilization **relative** to a field with **spherical** symmetry

Tetrahedral



Tetrahedral case:

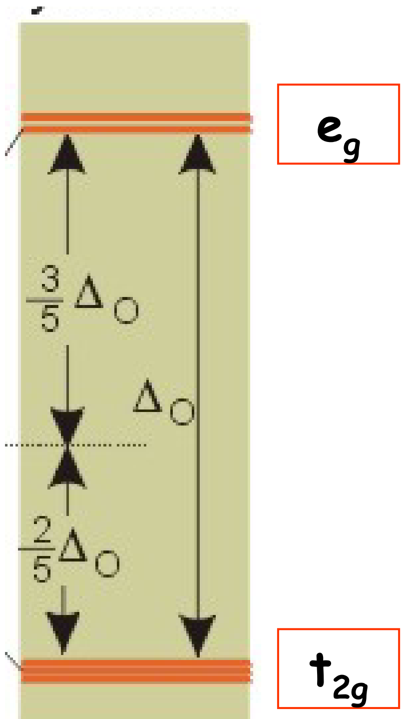
LFSE = $(-0.6 \times x(e) + 0.4 \times y(t_2)) \times \Delta_T$

Octahedral case:

LFSE = $(-0.4 \times x(t_{2g}) + 0.6 \times y(e_g)) \times \Delta_O$

x, y: number of electrons in the respective electronic states (e_g or t_{2g})

Octahedral



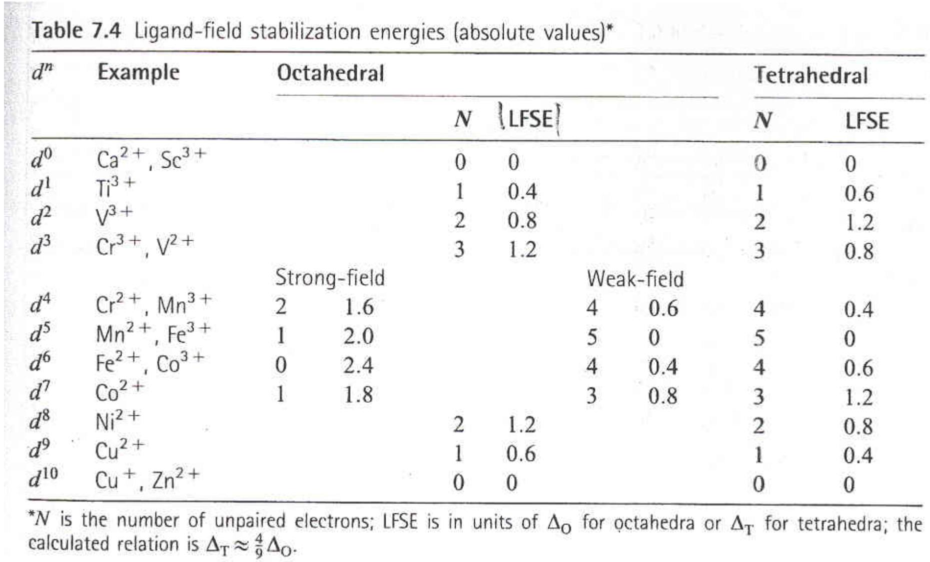


Table 7.4 Ligand-field stabilization energies (absolute values)*

d^n	Example	Octahedral						Tetrahedral	
				N	$\lvert \mathrm{LFSE} \rvert$			N	LFSE
d^0	Ca^{2+}, Sc^{3+}			0	0			0	0
d^1	Ti^{3+}			1	0.4			1	0.6
d^2	V^{3+}			2	0.8			2	1.2
d^3	Cr^{3+}, V^{2+}			3	1.2			3	0.8
		Strong-field				Weak-field			
d^4	Cr^{2+}, Mn^{3+}	2	1.6			4	0.6	4	0.4
d^5	Mn^{2+}, Fe^{3+}	1	2.0			5	0	5	0
d^6	Fe^{2+}, Co^{3+}	0	2.4			4	0.4	4	0.6
d^7	Co^{2+}	1	1.8			3	0.8	3	1.2
d^8	Ni^{2+}			2	1.2			2	0.8
d^9	Cu^{2+}			1	0.6			1	0.4
d^{10}	Cu^{+}, Zn^{2+}			0	0			0	0

*N is the number of unpaired electrons; LFSE is in units of Δ_O for octahedra or Δ_T for tetrahedra; the calculated relation is $\Delta_T \approx \frac{4}{9}\Delta_O$.

Basic Crystal Field Theory: Ligand field stabilization energies (LFSE)

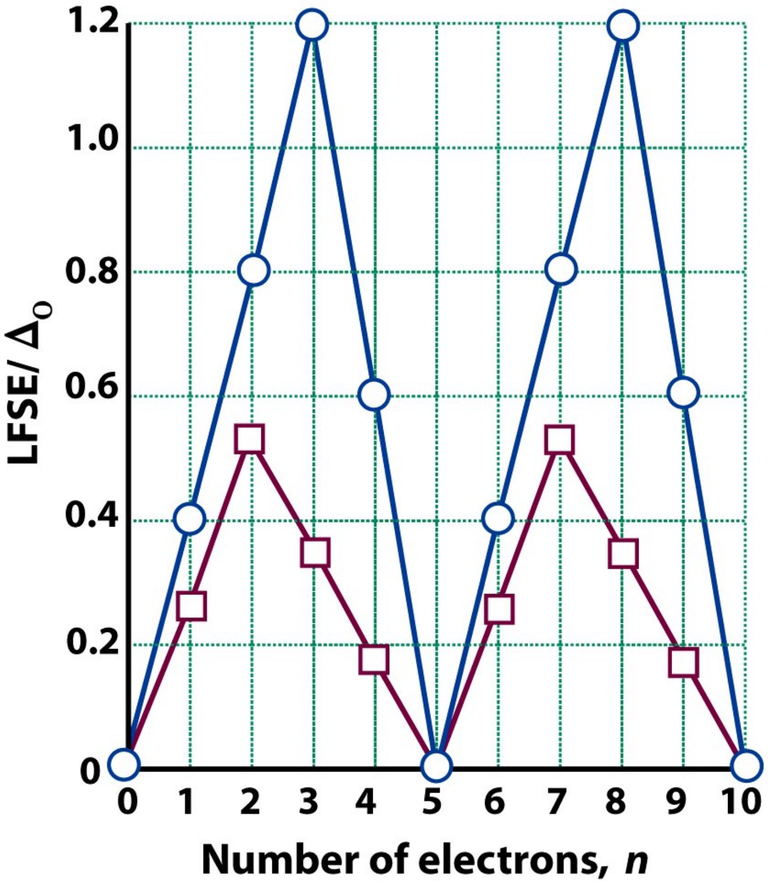


Figure 19-11
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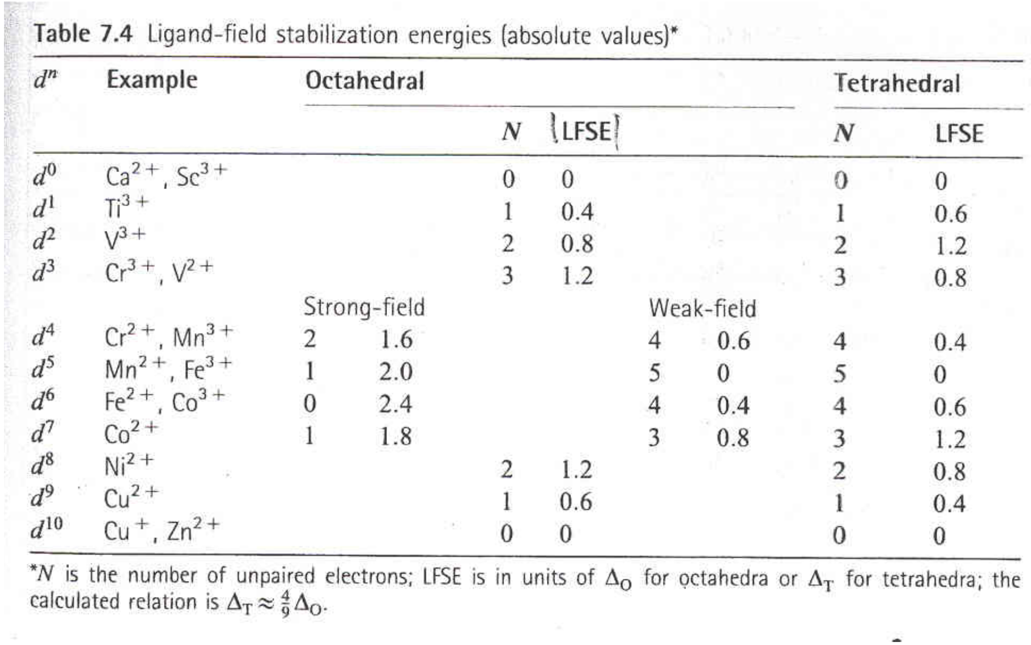


Table 7.4 Ligand-field stabilization energies (absolute values)*

d^n	Example	Octahedral						Tetrahedral	
				N	|LFSE|			*N*	LFSE
d^0	Ca^{2+}, Sc^{3+}			0	0			0	0
d^1	Ti^{3+}			1	0.4			1	0.6
d^2	V^{3+}			2	0.8			2	1.2
d^3	Cr^{3+}, V^{2+}			3	1.2			3	0.8
		Strong-field				Weak-field			
d^4	Cr^{2+}, Mn^{3+}	2	1.6			4	0.6	4	0.4
d^5	Mn^{2+}, Fe^{3+}	1	2.0			5	0	5	0
d^6	Fe^{2+}, Co^{3+}	0	2.4			4	0.4	4	0.6
d^7	Co^{2+}	1	1.8			3	0.8	3	1.2
d^8	Ni^{2+}			2	1.2			2	0.8
d^9	Cu^{2+}			1	0.6			1	0.4
d^{10}	Cu^{+}, Zn^{2+}			0	0			0	0

*N is the number of unpaired electrons; LFSE is in units of Δ_O for octahedra or Δ_T for tetrahedra; the calculated relation is $\Delta_T \approx \frac{4}{9}\Delta_O$.

Basic Crystal Field Theory: Ligand field stabilization energies (LFSE) – Ionic radii

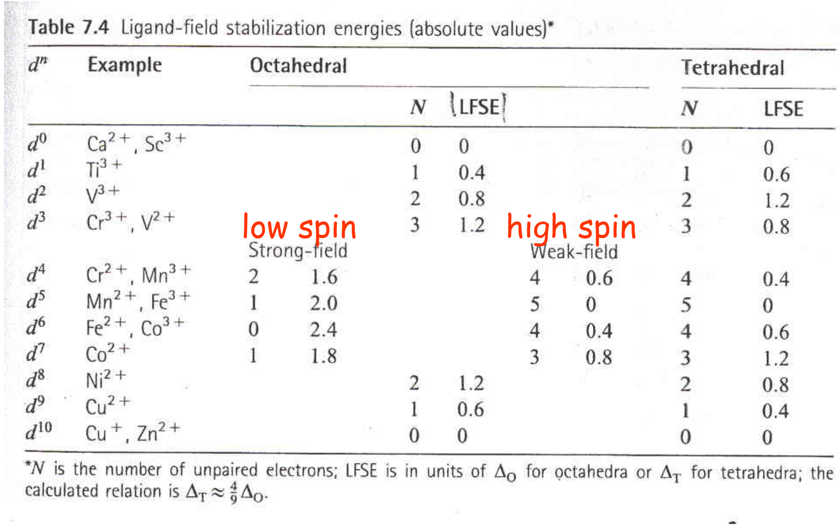
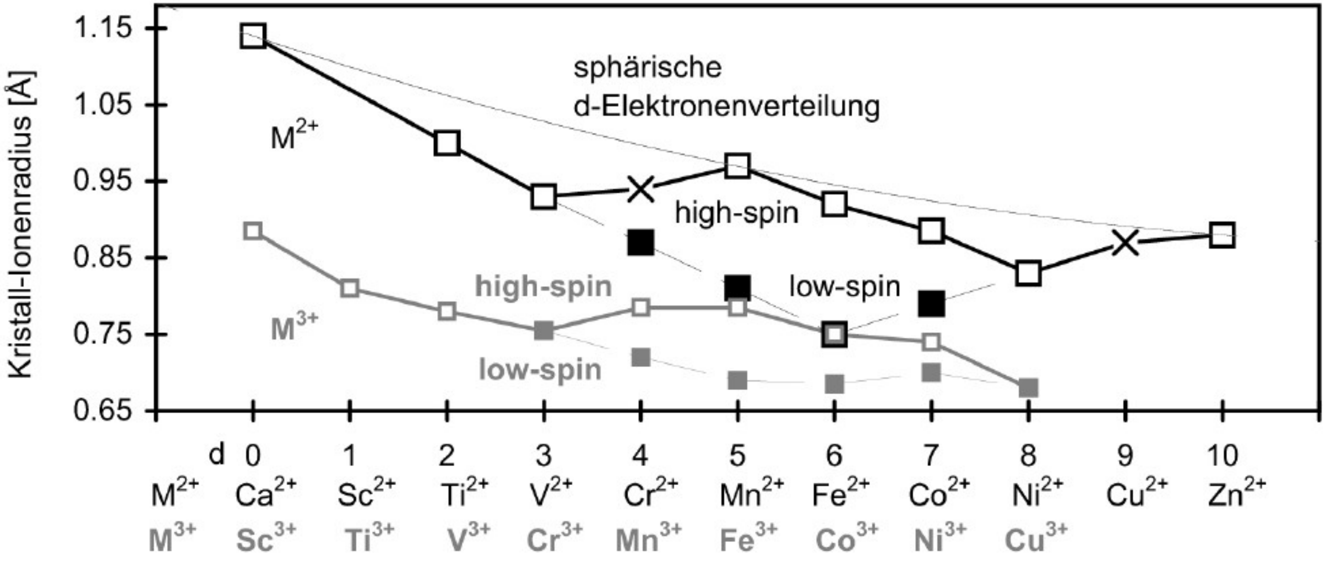


Table 7.4 Ligand-field stabilization energies (absolute values)*

d^n	Example	Octahedral						Tetrahedral	
		low spin Strong-field		N	$\lvert$LFSE$\rvert$	high spin Weak-field		N	LFSE
d^0	Ca^{2+}, Sc^{3+}			0	0			0	0
d^1	Ti^{3+}			1	0.4			1	0.6
d^2	V^{3+}			2	0.8			2	1.2
d^3	Cr^{3+}, V^{2+}			3	1.2			3	0.8
d^4	Cr^{2+}, Mn^{3+}	2	1.6			4	0.6	4	0.4
d^5	Mn^{2+}, Fe^{3+}	1	2.0			5	0	5	0
d^6	Fe^{2+}, Co^{3+}	0	2.4			4	0.4	4	0.6
d^7	Co^{2+}	1	1.8			3	0.8	3	1.2
d^8	Ni^{2+}			2	1.2			2	0.8
d^9	Cu^{2+}			1	0.6			1	0.4
d^{10}	Cu^{+}, Zn^{2+}			0	0			0	0

*N is the number of unpaired electrons; LFSE is in units of Δ_O for octahedra or Δ_T for tetrahedra; the calculated relation is $\Delta_T \approx \frac{4}{9}\Delta_O$.



Basic Crystal Field Theory: Ligand field stabilization energies (LFSE) – Hydration enthalpy of M^{2+} ions

Yellow points: after subtraction of LFSE from experimental value

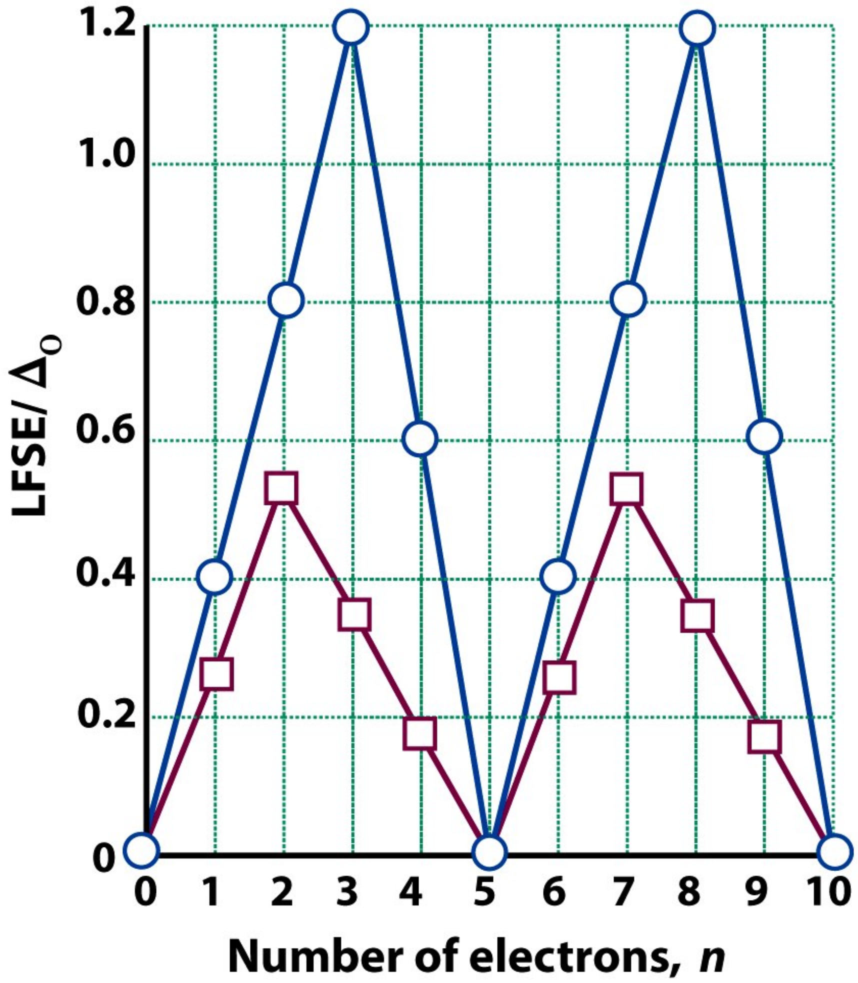


Figure 19-11
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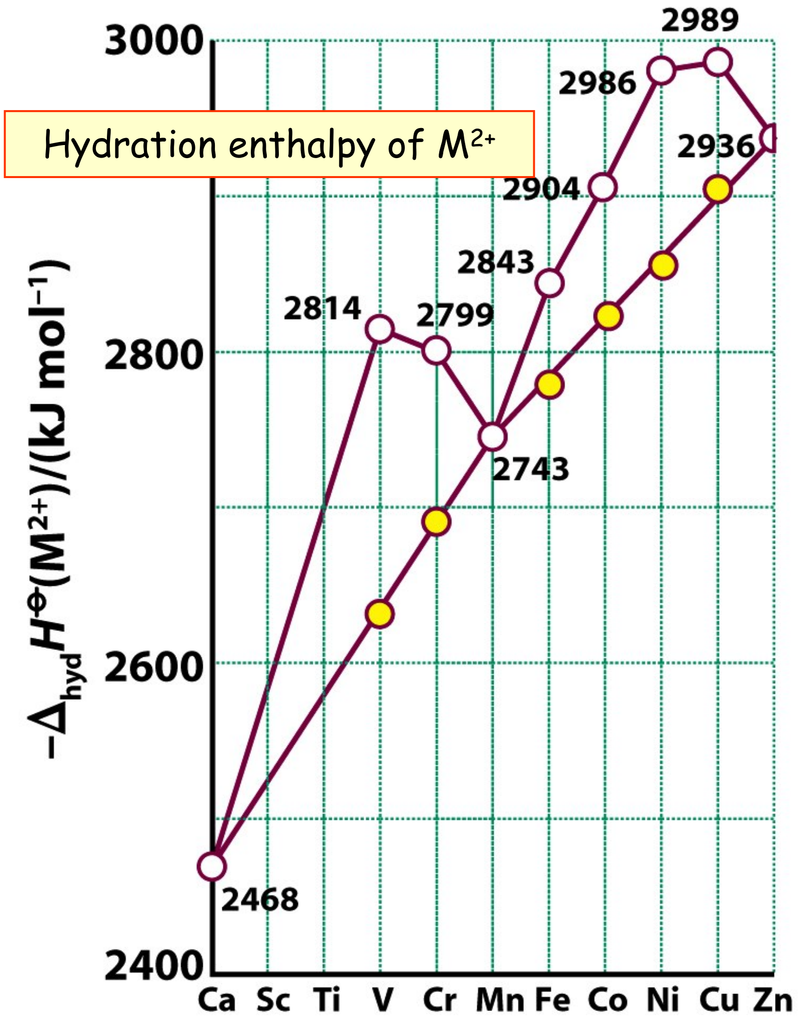
Hydration enthalpy of M^{2+}

Figure 19-6
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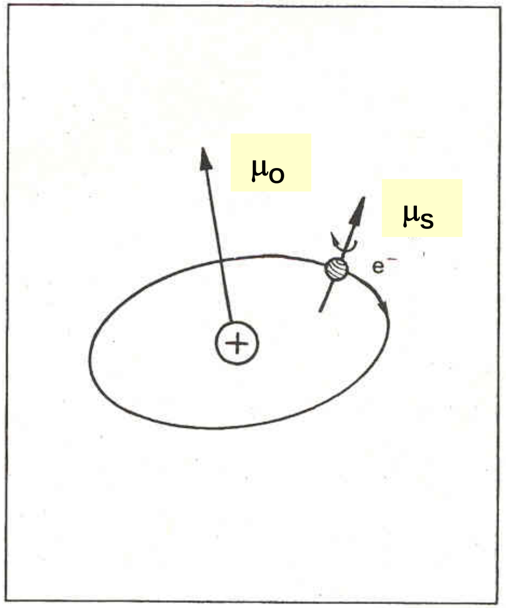
Magnetism of coordination compounds: magnetic (dipole) moments

In general there are **two components** of the resulting magnetic moment of an atom (ion):

⇒ **orbital angular momentum (μ_O)** ⇒ **spin momentum (μ_S)**

- In most coordination compounds with **3d elements** as central atoms the orbital angular momentum can be neglected (technical term: "**quenched**").
- typical for 3d complexes with **one** central atom: **spin only magnetism (μ_S)**



Definition of μ_S:

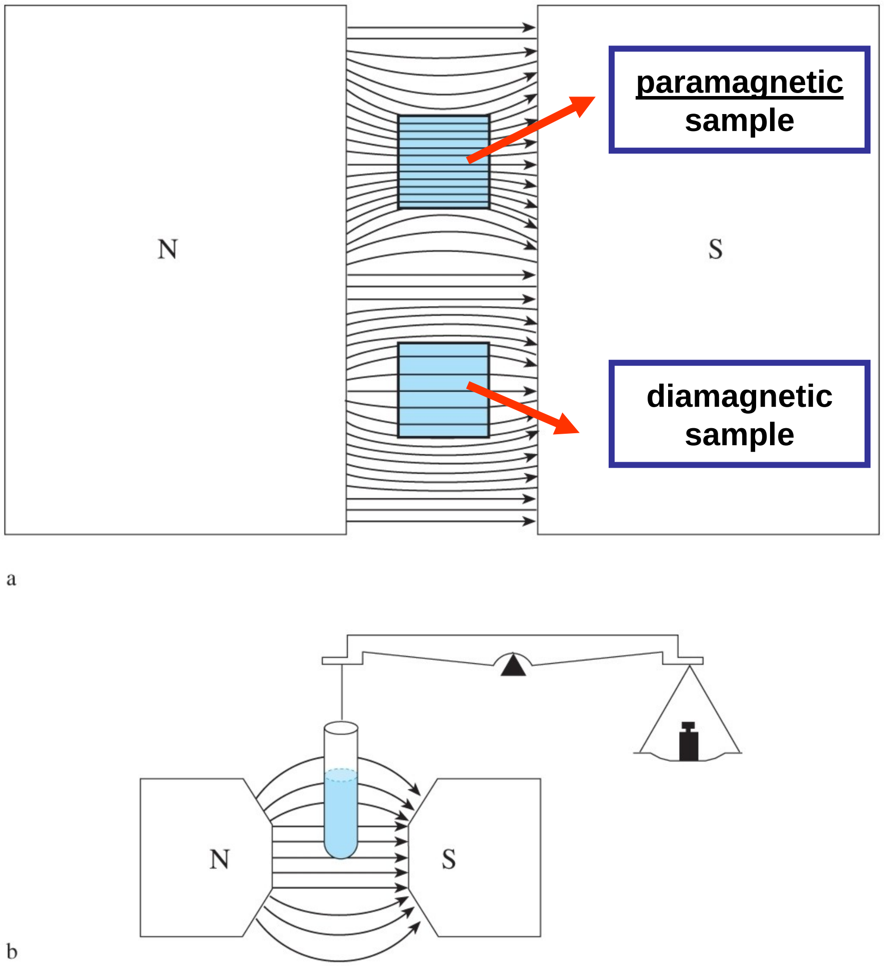
$\mu_S = \mu_B \times 2 \times (S(S+1))^{1/2}$

$\mu_B = 9{,}27 \times 10^{-24}$ Am² (Bohr magneton, smallest quantity of a magnetic moment)

$S = \frac{1}{2} \times n$ (Total spin quantum number
n: number of <u>unpaired electrons</u>)

n	1	2	3	4	5
μ_S	1,73	2,83	3,87	4,90	5,91

Magnetism of coordination compounds: Gouy-balance



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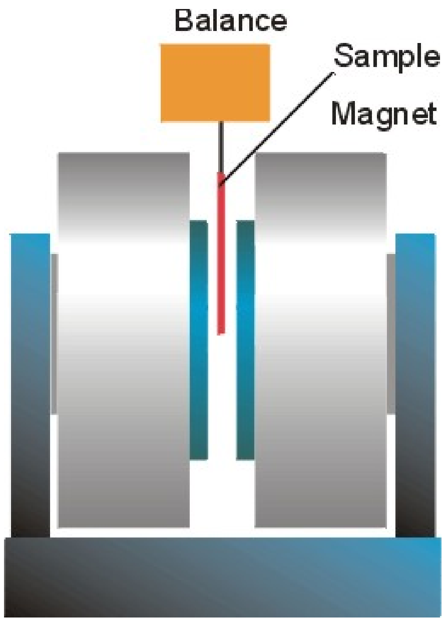
central atom with **unpaired valence electrons** ⇒ **paramagnetism**

central atom with **paired valence electrons only** ⇒ **diamagnetism**



Magnetism of coordination compounds: SQUID

SQUID: Superconducting Quantum Interference Device

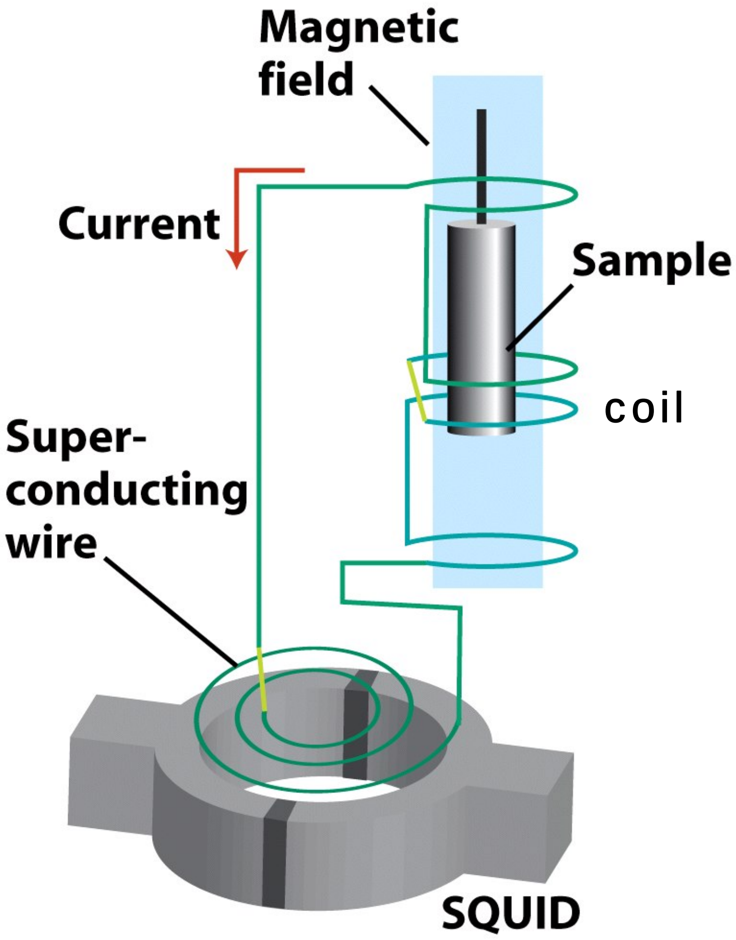
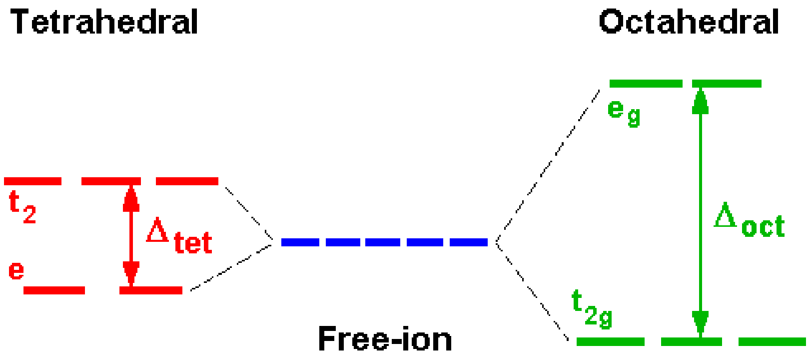


Figure 6-29
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Sophisticated physical background based on the **quantization of magnetic flux** (one or two weak links, „**Josephson contacts**") in a superconducting wire (loop) that allow the tunneling of „**Cooper pairs**".

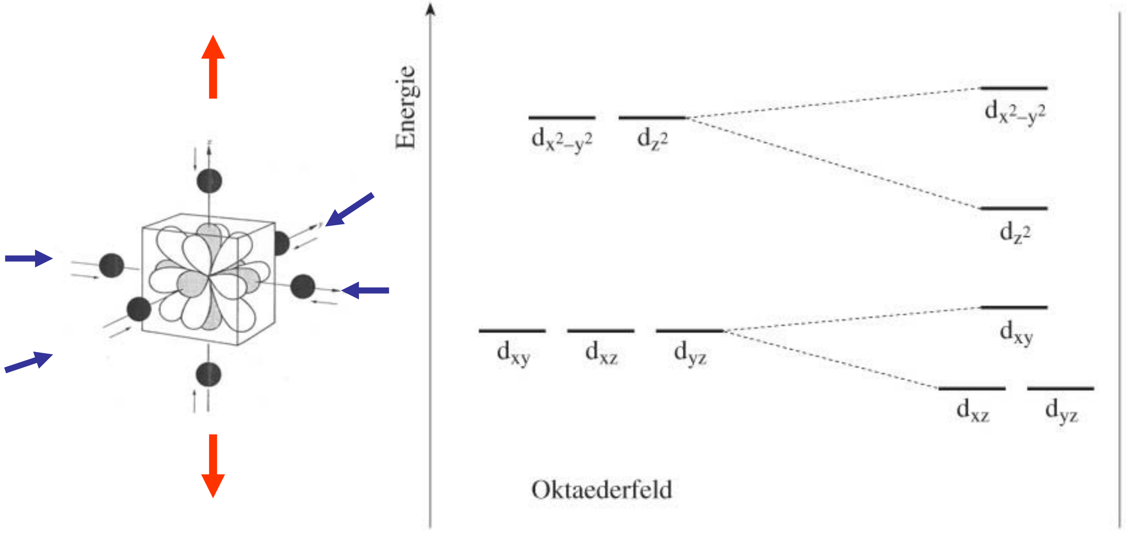
Special aspects of the electronic structure of complexes with CN 4

1. Tetrahedral coordination

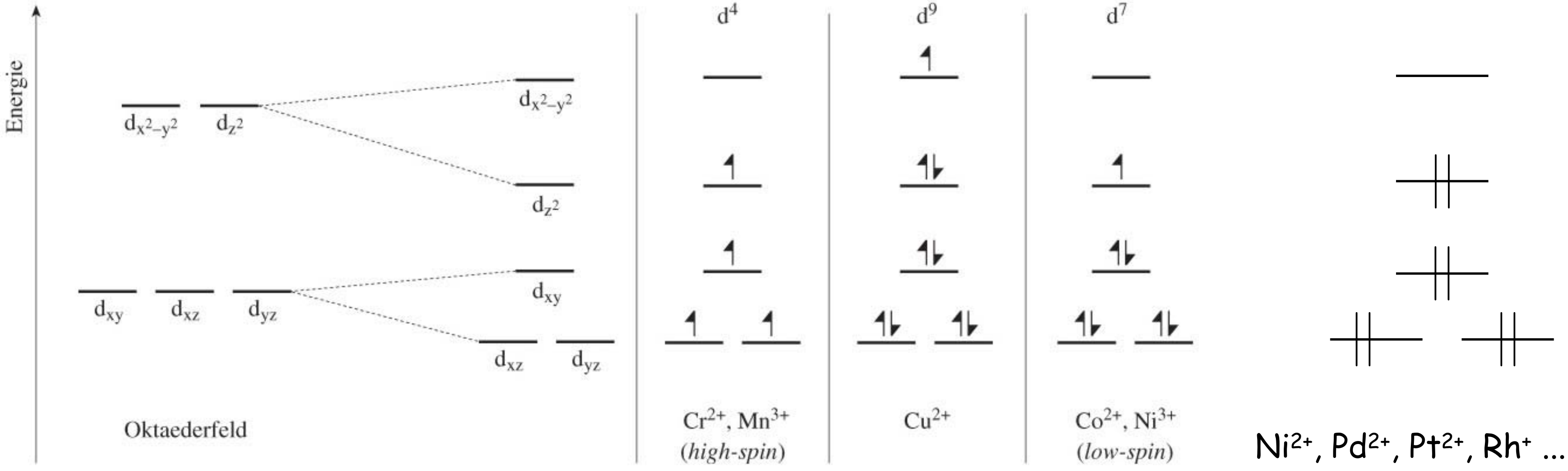


- inverse splitting (compared to octahedral case)
- only the weak field case is of importance (⇒ high spin magnetism)

2. Tetragonal and square planar coordination ⇒ (**Jahn-Teller-effect)**



Special aspects of the electronic structure of complexes with CN 4



d^4 **d^9** **d^7**

tetragonally elongated

d^8

square planar

dynamic Jahn-Teller effect
temperature driven intramolecular change of the elongation direction

Exercises

1. Determine the configuration (in the form $t_{2g}^x\ e_g^y$ or $e^x\ t^y$, as appropiate), the number of unpaired electrons and the ligand field stabilization energy (LFSE) as a multiple of Δ_{oct} or Δ_{tet} for each of the following complexes: $[Co(NH_3)_6]^{3+}$, $[Fe(H_2O)_6]^{2+}$, $[Fe(CN)_6]^{3-}$, $[W(CO)_6]$ and $[FeCl_4]^{2-}$. Estimate the spin only contribution to the magnetic moment in each complex.
2. Solutions of the complexes $[Co(NH_3)_6]^{2+}$, $[Co(H_2O)_6]^{2+}$ (both O_h) and $[CoCl_4]^{2-}$ (T_d) are colored. One is pink, another yellow and the third is blue. Considering the spectrochemical series and the relative magnitudes of Δ_{tet} and Δ_{oct} assign each color to one of the complexes.
3. For each of the following pairs of complexes identify the one that has the larger LFSE:

   $[Cr(H_2O)_6]^{2+}$ - $[Mn(H_2O)_6]^{2+}$
   $[Mn(H_2O)_6]^{2+}$ - $[Fe(H_2O)_6]^{3+}$
   $[Fe(H_2O)_6]^{3+}$ - $[Fe(CN)_6]^{3-}$

4. Estimate the spin only contribution to the magnet moments for each of the complexes in 1.

Ligand-field theory

Crystal field theory has problems to explain why the ligand field splitting for some uncharged molecules (e.g. CO) is unusually large and is moderate for others (e.g. NH_3). CFT is unable to explain spectra of more complex coordination compounds.

⇒ solution: the interaction between ligands and central atom has to be discussed in terms of **atomic and molecular** orbitals and **not only** in terms of **point charges** (as in crystal field theory)

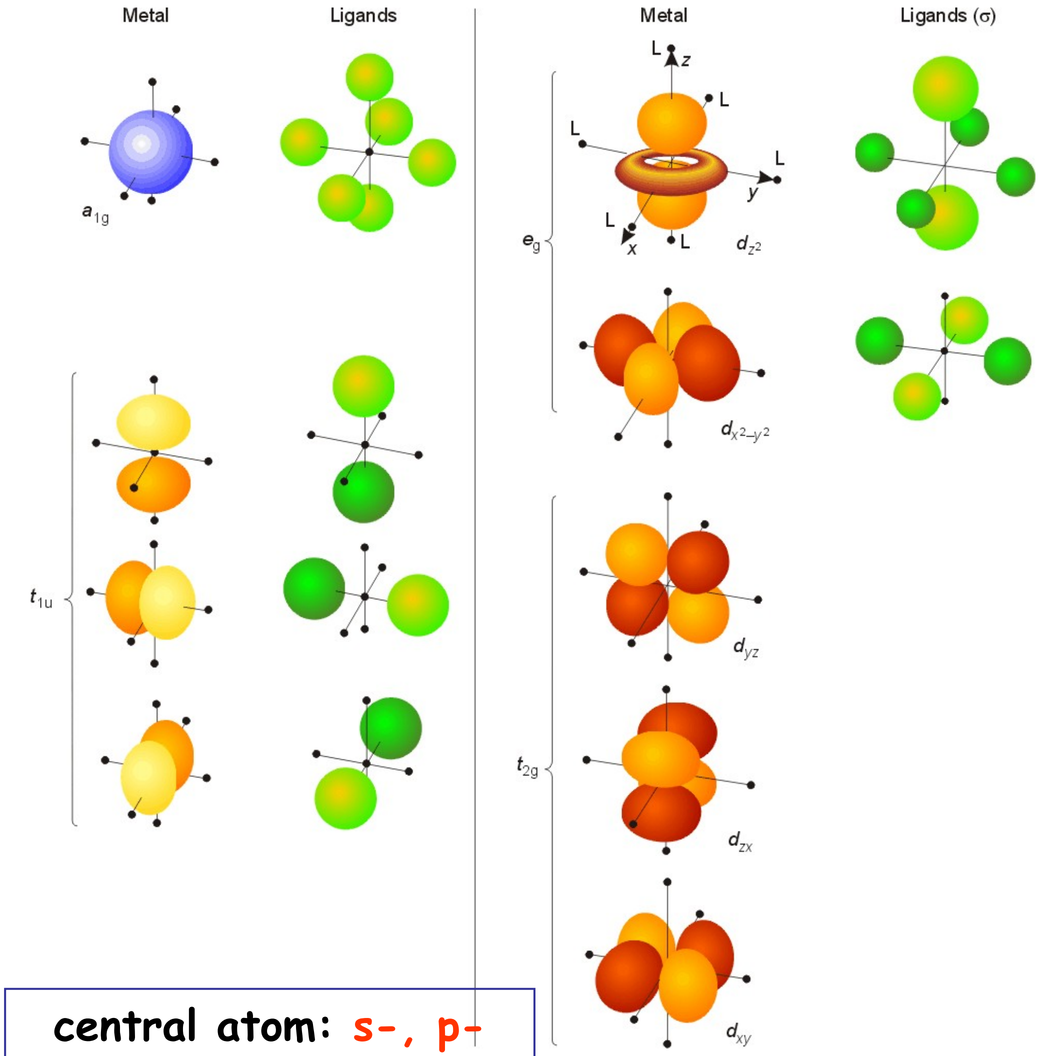
⇒ σ- and π-bonding contributions have to be analyzed separately

1. Analyze the symmetry properties of **groups** of atomic orbitals (**separate** for ligands and central atoms) ⇒ **symmetry adapted** orbitals

2. **Overlap** atomic orbitals of **similar** symmetry to form molecular orbitals (necessary: basic knowledge in **group theory** and basic **MO-theory**)

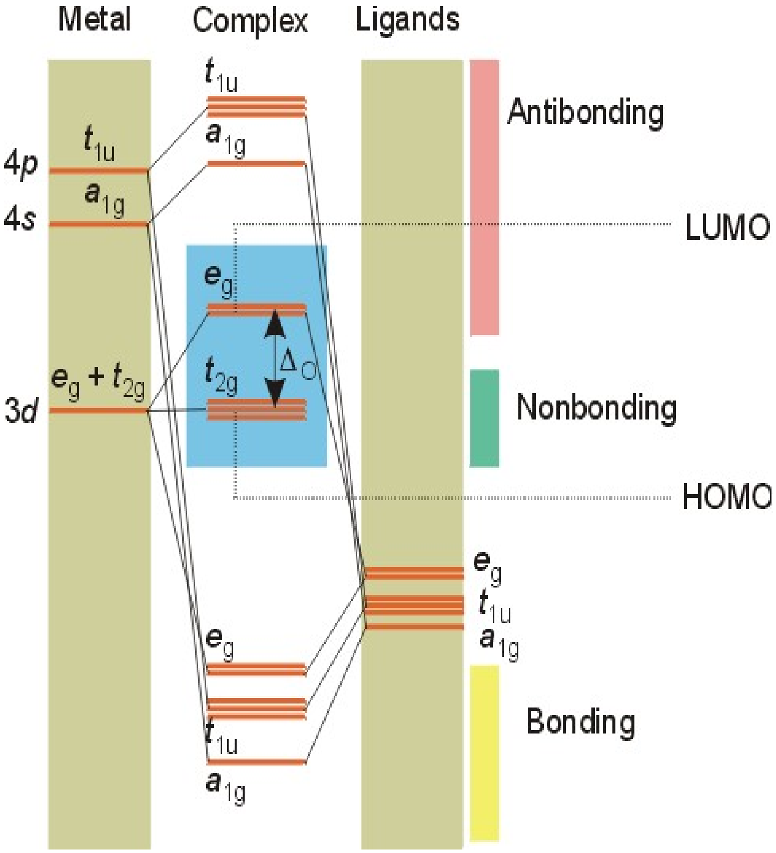
Central atom (3d-element) orbital	**symmetry label**	**Degeneracy**
s	a_{1g}	1
p_x, p_y, p_z	t_{1u}	3
d_{xy}, d_{xz}, d_{yz}	t_{2g}	3
$d_{x^2-y^2}$, d_{z^2}	e_g	2

Ligand-field theory: symmetry-adapted groups of orbitals: σ-bonding only

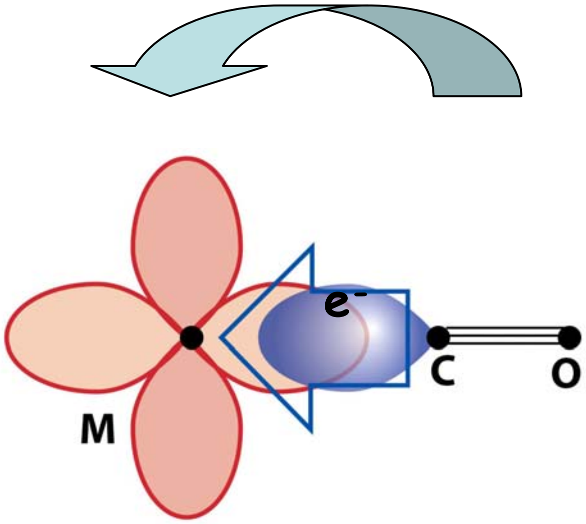


central atom: s-, p- and d-Orbitals are taken into account

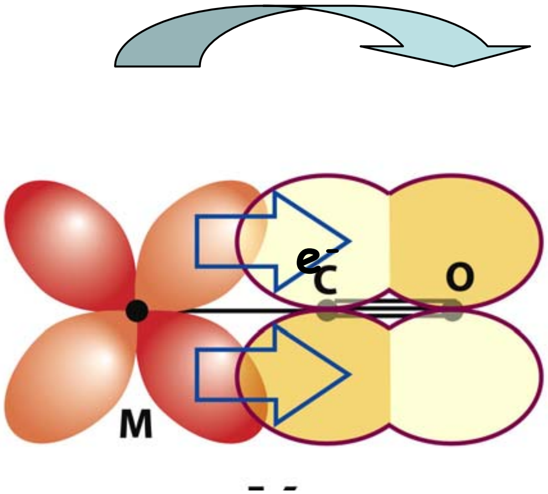
ligands: only s-orbitals but no p-orbitals are taken into account



Ligand-field theory: summary σ- and π- acceptor effects



σ-donor

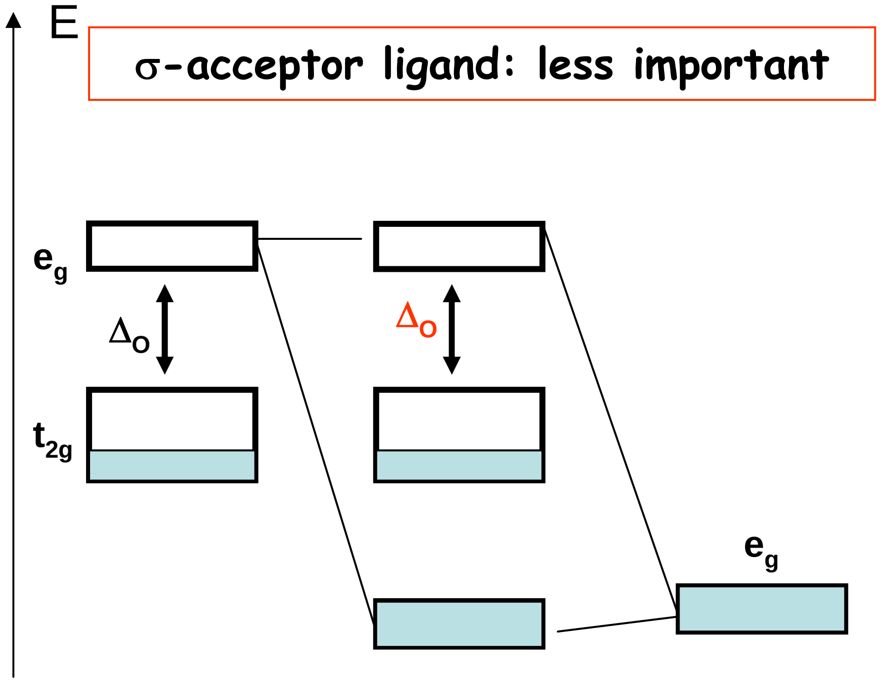


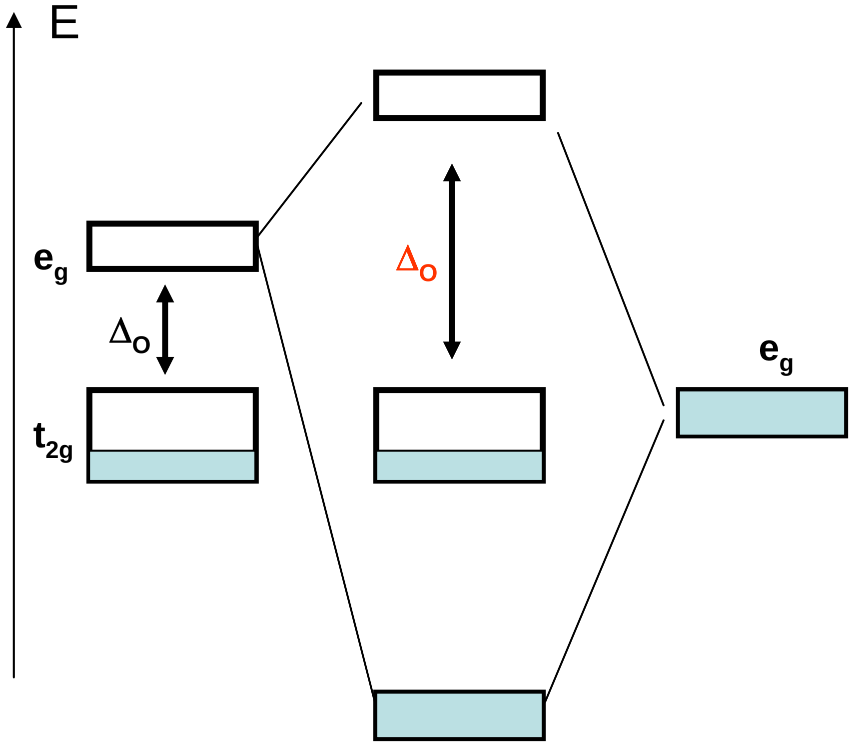
π-acceptor

participating orbitals:
d_{z^2} and $d_{x^2-y^2}$
e_g-symmetry orbitals

participating orbitals:
d_{xz}, d_{xy}, d_{yz}
t_{2g}-symmetry orbitals

Ligand-field theory: σ-donor ligands („Lewis basicity“)

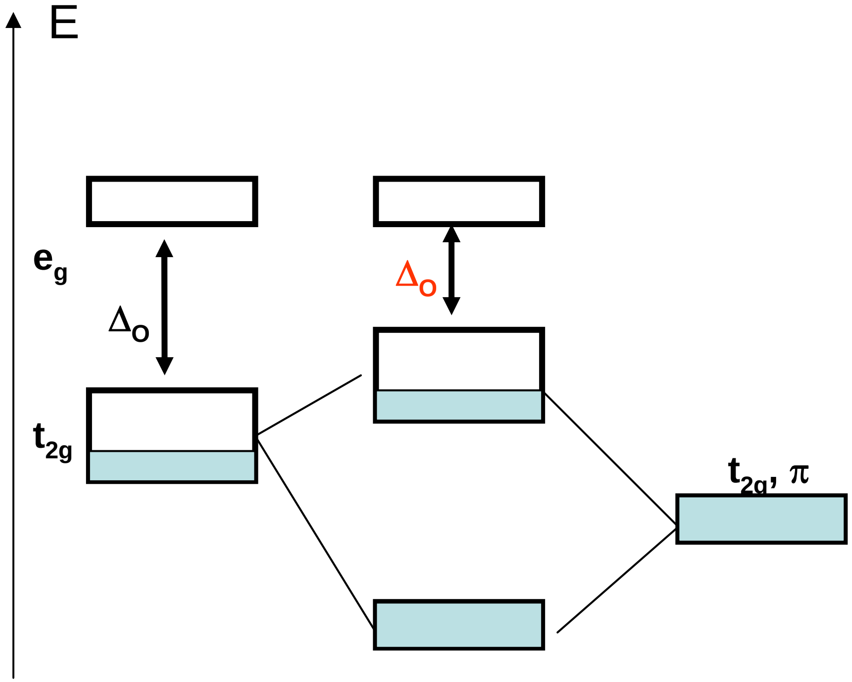


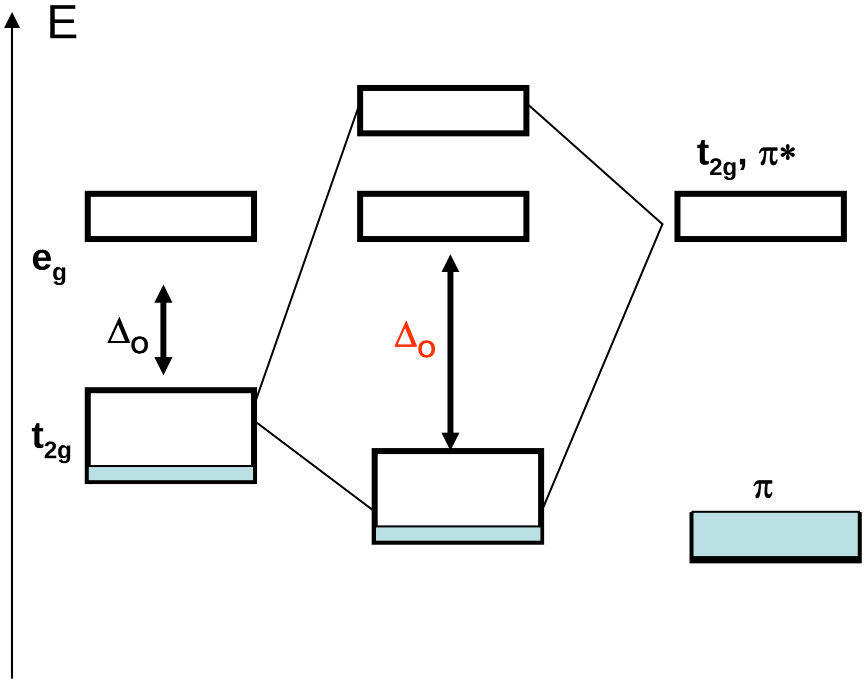


bad σ-donor:
- low energy donor orbitals (e_g), bad orbital overlap
- small inter-orbital exchange due to large size differences between M and L
- no change of Δ_o,

good σ-donor:
- high energy donor orbitals (e_g), good orbital overlap
- strong inter-orbital-exchange due to small size differences between M and L
- increase of Δo,

Ligand-field theory: π-donor/acceptor ligands





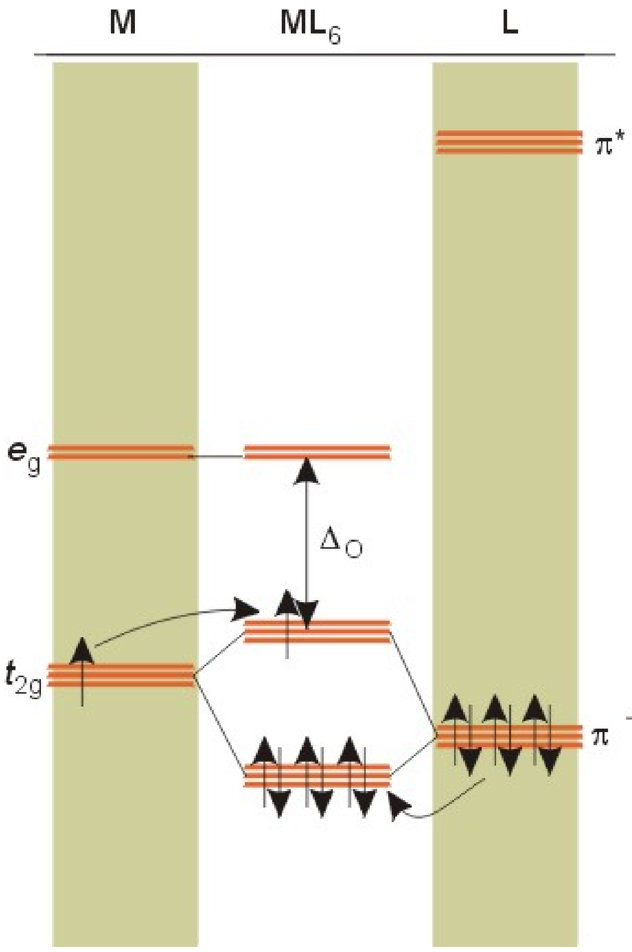
good π-donor:

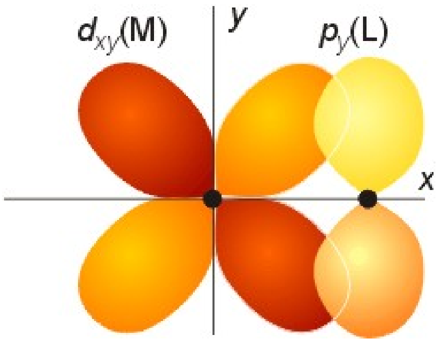
- decrease of Δ_o,

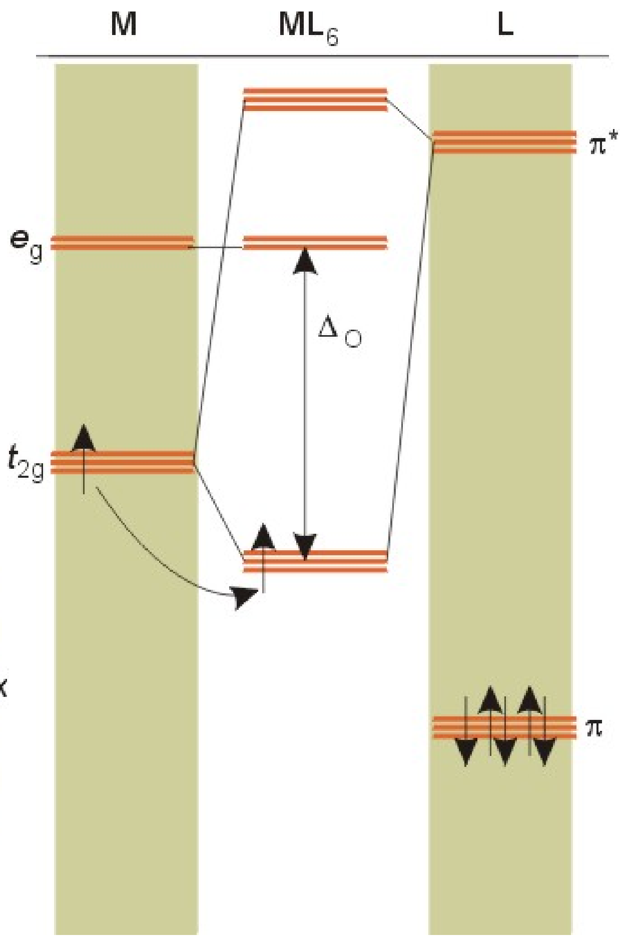
good π-acceptor:

- increase of Δ_o,

Ligand-field theory: π-donor and –acceptor effect





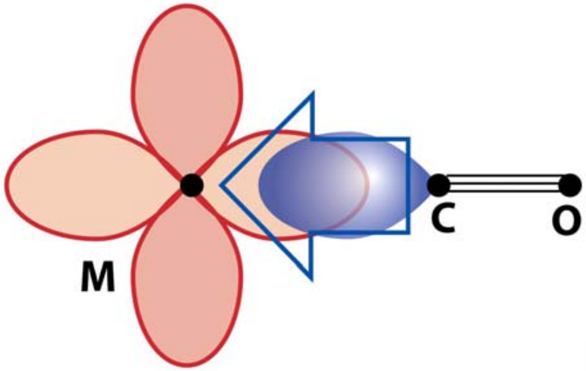


π -donor ligand: completely filled low-energy **π-orbitals**, t_{2g}-π-overlap preferred: Δ_o reduced

π -acceptor ligand: incompletely filled low-energy **π*-orbitals**, t_{2g}-π-overlap preferred: Δ_o increased

Ligand-field theory: carbonyl complexes

Synergistic bonding in carbonyl complexes with transition metals:
the CO-molecule is a σ-donor and a π-acceptor at the same time



15

Structure 21-15
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σ-donor

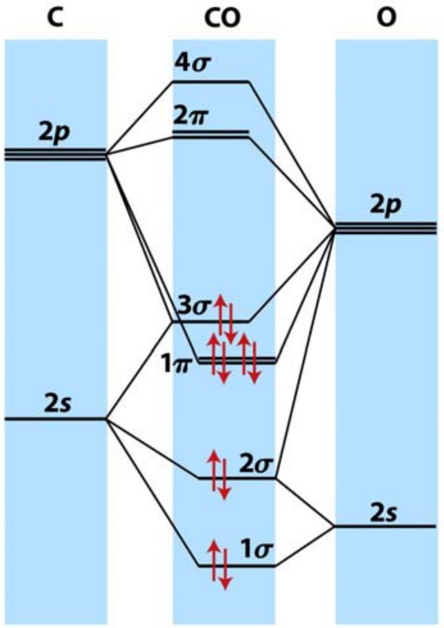

Figure 21-3
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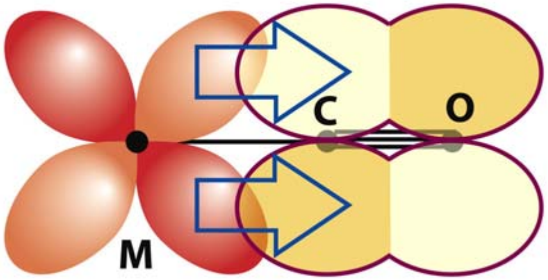

16

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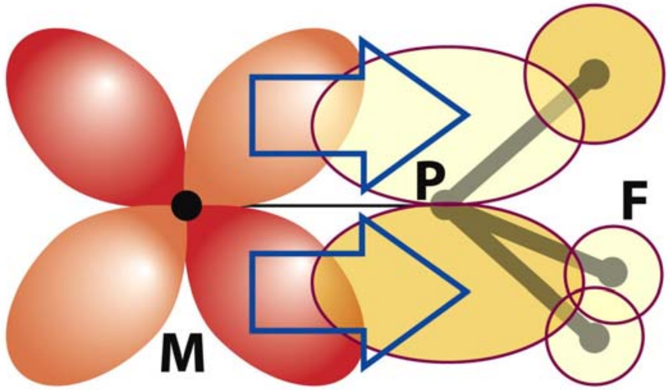
π-acceptor

Ligand-field theory: phosphines, σ-donors and π-acceptors

The bonding of phosphines PR_3 to transition metal atoms is basically similar to that of CO; dependent on the respective substituents σ-donor and π-acceptor-strength, however, are different

σ-donor-effect: lone pair at phosphorous atom

π-acceptor-effect: empty p- (and d-)orbitals at the P-atom



22

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electron rich phosphines are good σ-donors and bad π-acceptors whereas for electron poor ones the inverse statement holds.

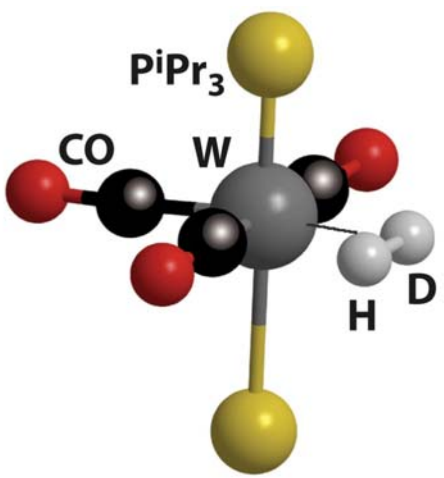
order of „Lewis basicity“:

e.g.: $PMe_3 > P(OMe)_3 > PF_3$

σ-/π-donor:	Lewis base
σ-/π-acceptor:	Lewis acid

Ligand-field theory: dihydrogen complexes

examples



26

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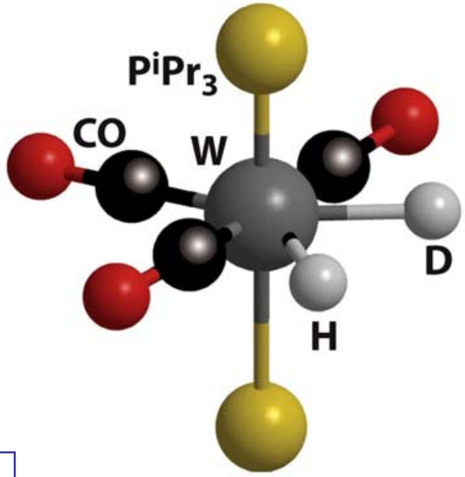

27

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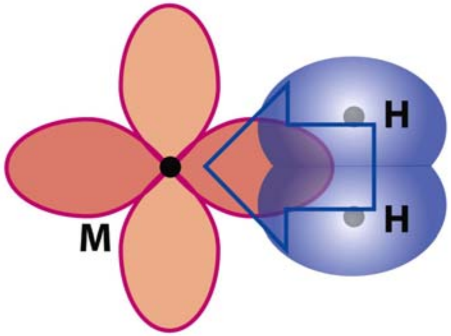
σ-donor and π-acceptor effect



24

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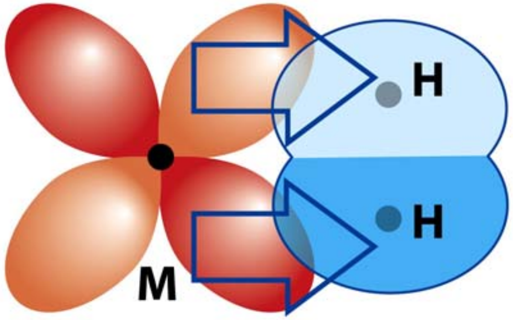

25

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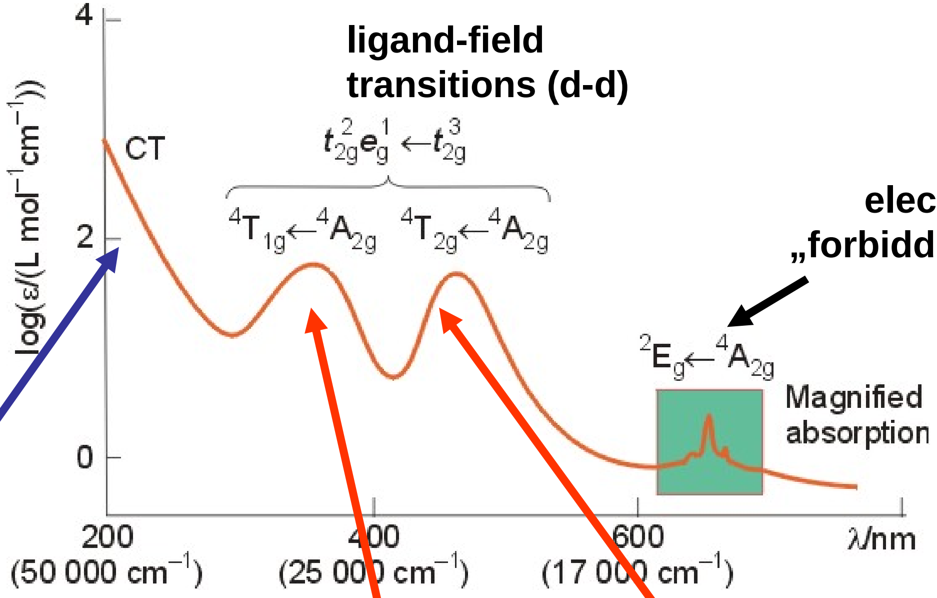
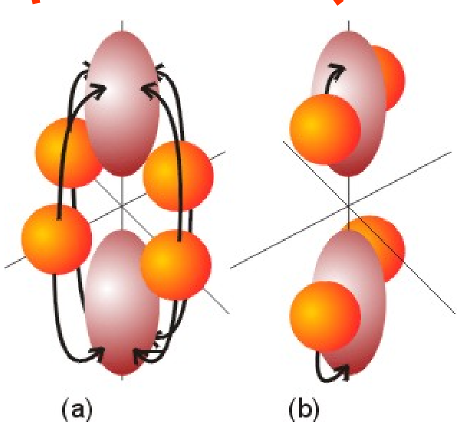
Electronic Spectra - Spectroscopy

Typical example: The spectrum of the d^3 complex $[Cr(NH_3)_6]^{3+}$



ligand-field transitions (d-d)

electronically „forbidden“ transition

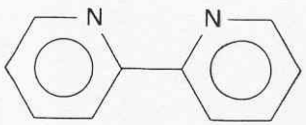


Charge Transfer transition (CT)
electronic transition from a metal π-Orbital to a ligand π*-Orbital or vice versa. (**high intensity**, strongly influenced by the type of solvent)

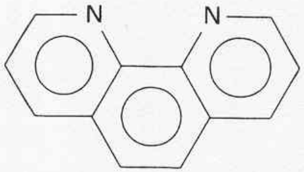
Charge-Transfer transitions

Charge-transfer-transitions (CT) show up in electronic spectra by strong transitions in the visible region and are characterized by intense colour (high extinction)

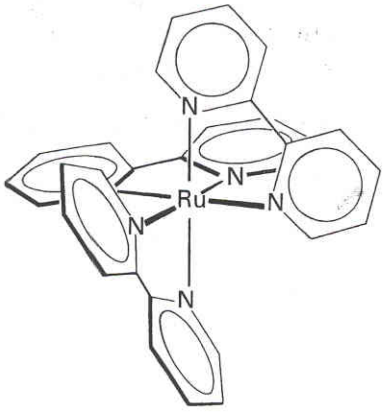
- **metal-to-ligand** transitions: from a metal d-Orbital to a ligand π*-orbital: preferably observed for **ligands with low-lying π*-orbitals** (e.g. aromatic ligands with donor N-atoms like 2,2‘ bipyridine or 1,10 phenanthroline) and metal atoms with **low oxidation number** thus relatively **high** valence states



4 2,2′–Bipyridine (bipy)



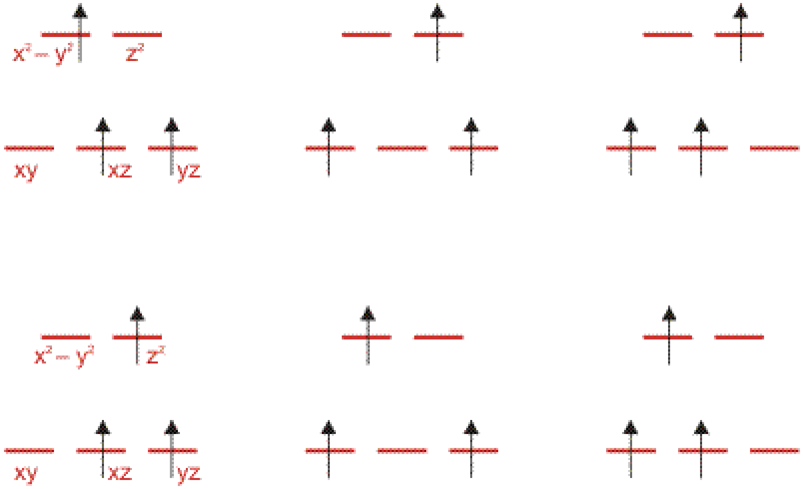
5 1,10–Phenthroline (phen)



tris(2,2‘-bipyridyl)ruthenium(II)

- **ligand-to-metal transitions**: from a **ligand π-orbital** (relatively high in energy: e.g. lone pairs of S^{2-}, O^{2-}) to an **empty and low lying d orbital** of the central metal atom (high oxidation number): e.g. MnO_4^{1-}, CrO_4^{2-}, VO_4^{3-} etc.

Coordination Chemistry: Spectroscopy - microstates



- Two sets of energetically different excited microstates for the excitation of one electron in $[Cr(H_2O)_6]^{3+}$ (d^3)
- each threefold degenerate
- electron-electron repulsion is responsible for different excitation energies

Multiplicity (M) of a microstate: $M = 2S + 1$ (S: total spin moment)

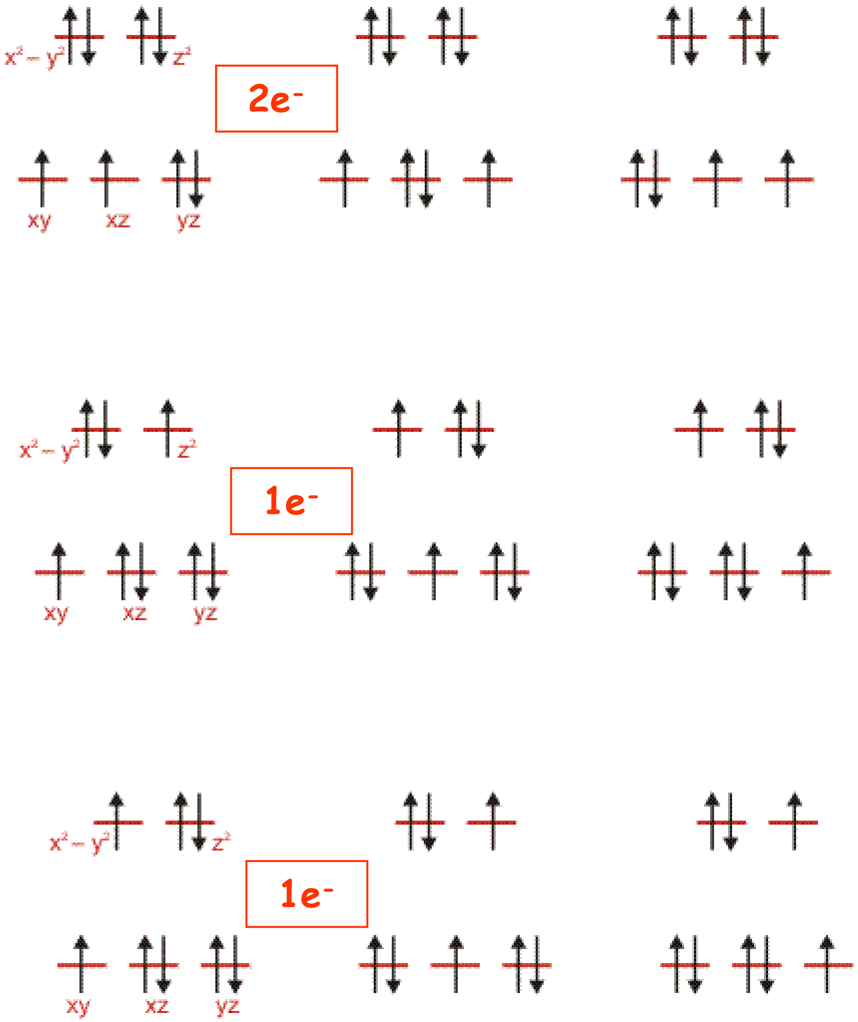
e.g. for above excitet states (and the ground state) holds:

$$S = 3 \times \frac{1}{2} = 3/2$$

$$M = 2x(3/2)+1 = 4$$ (Quartett-term)

Importance of Multiplicity: M of ground and excited state is similar → allowed (strong) excitations !

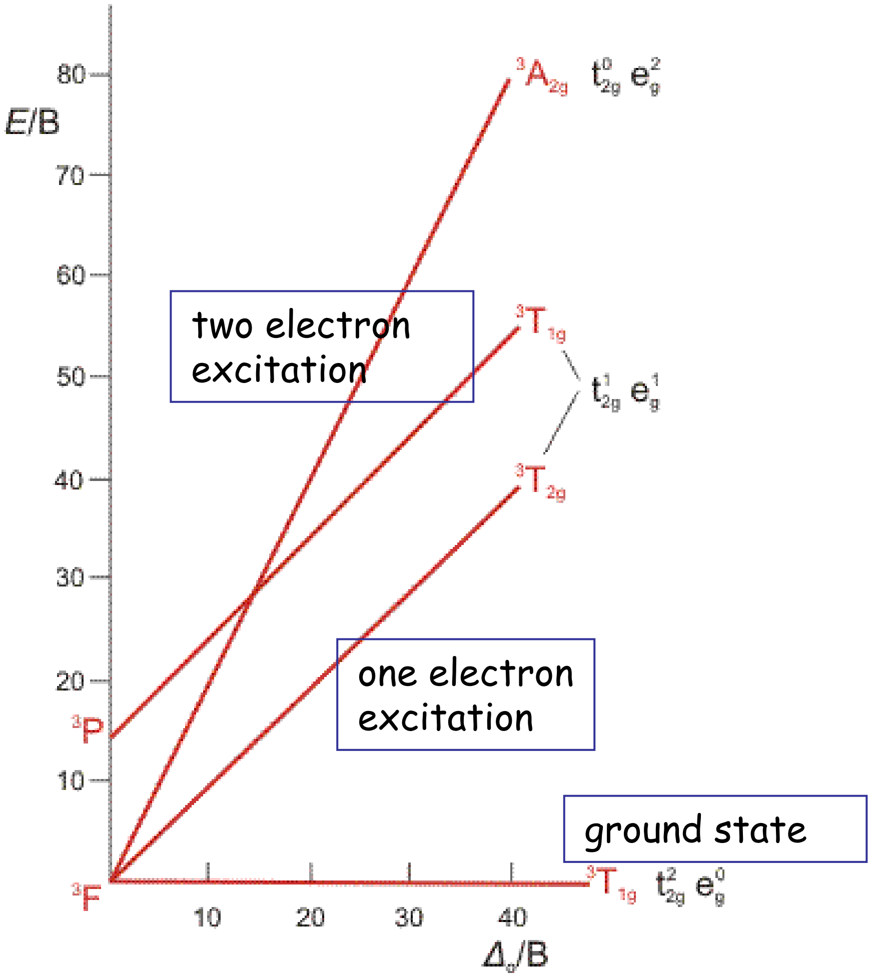
Coordination Chemistry: Spectroscopy - microstates



- Three sets of energetically different excited microstates for the excitation of one or two electrons in $[Ni(H_2O)_6]^{2+}$ (d^8)
- **each threefold degenerate**
- Triplett terms, multiplicity unchanged with respect to ground state
- **analysis of spectra in this way would be very time consuming**
- **Selection rules** distinguish between **allowed** and **forbidden** electronic transitions. They are based on the magnitude of the **transition dipole moment**, which is a measure for the coupling strength of the electronic system of the complex molecule to the external field (special case: **Laporte rules**, transitions between **even parity** states are forbidden).

Coordination Chemistry: Tanabe-Sugano-diagram

Tanabe-Sugano-diagram for a d^2 ground state



two electron excitation

one electron excitation

ground state

weak field

strong field

A complete T.S. diagram contains all possible electronic excitations (including the forbidden ones)

y-axis: Excitation energy in units of B (B. typical energy for an electron-electron repulsion = Racah-parameter ~ 1000 cm^{-1})

x-axis: crystal field splitting energy (Δ_o, Δ_T) in units of B

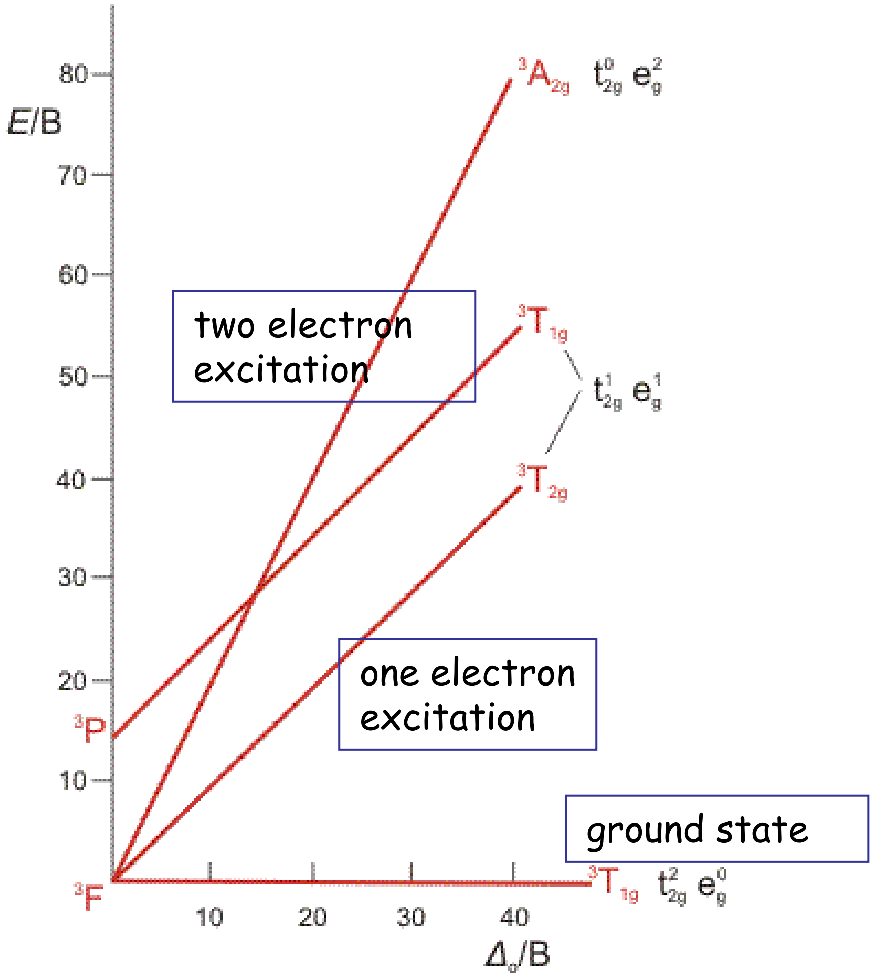
A, (E), T are symmetry symbols (group theory) that denote the degree of degeneration (**A**: non degenerate, **E**: twofold degenerate, **T**: threefold degenerate

(^{3}): multiplicity

($_g$): gerade symmetry information

Coordination Chemistry: Tanabe-Sugano-diagram

Tanabe-Sugano-diagram for a d² ground state



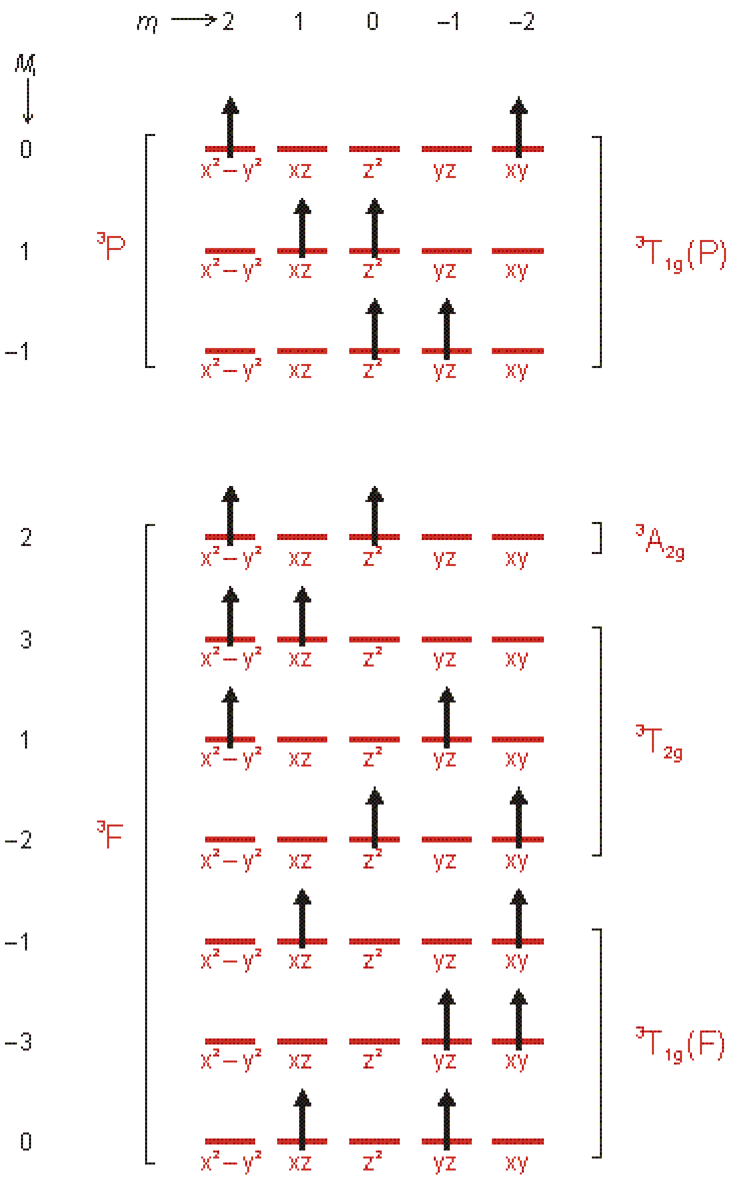
two electron excitation

one electron excitation

ground state

weak field

strong field



Coordination Chemistry: Russel-Saunders and jj-coupling

A more detailed treatment of the physical background is based on a sophisticated combined treatment of the **total orbital momentum** (L), **total spin momentum** (S), **total momentum** (J) and the **spin multiplicity** (M).

- definitions:

- $\mathbf{L = \Sigma\, l_n}$; $\mathbf{S = \Sigma\, s_n}$; $\mathbf{J = L + S}$, $\mathbf{M = 2S + 1}$

(special: L = 0→**S,** L = 1→**P** L = 2→**D** L = 3→**F)**

- Symbol: $\mathbf{{}^{M}L_{J}}$ (e.g. $^3P_2$, $^3F_4$)

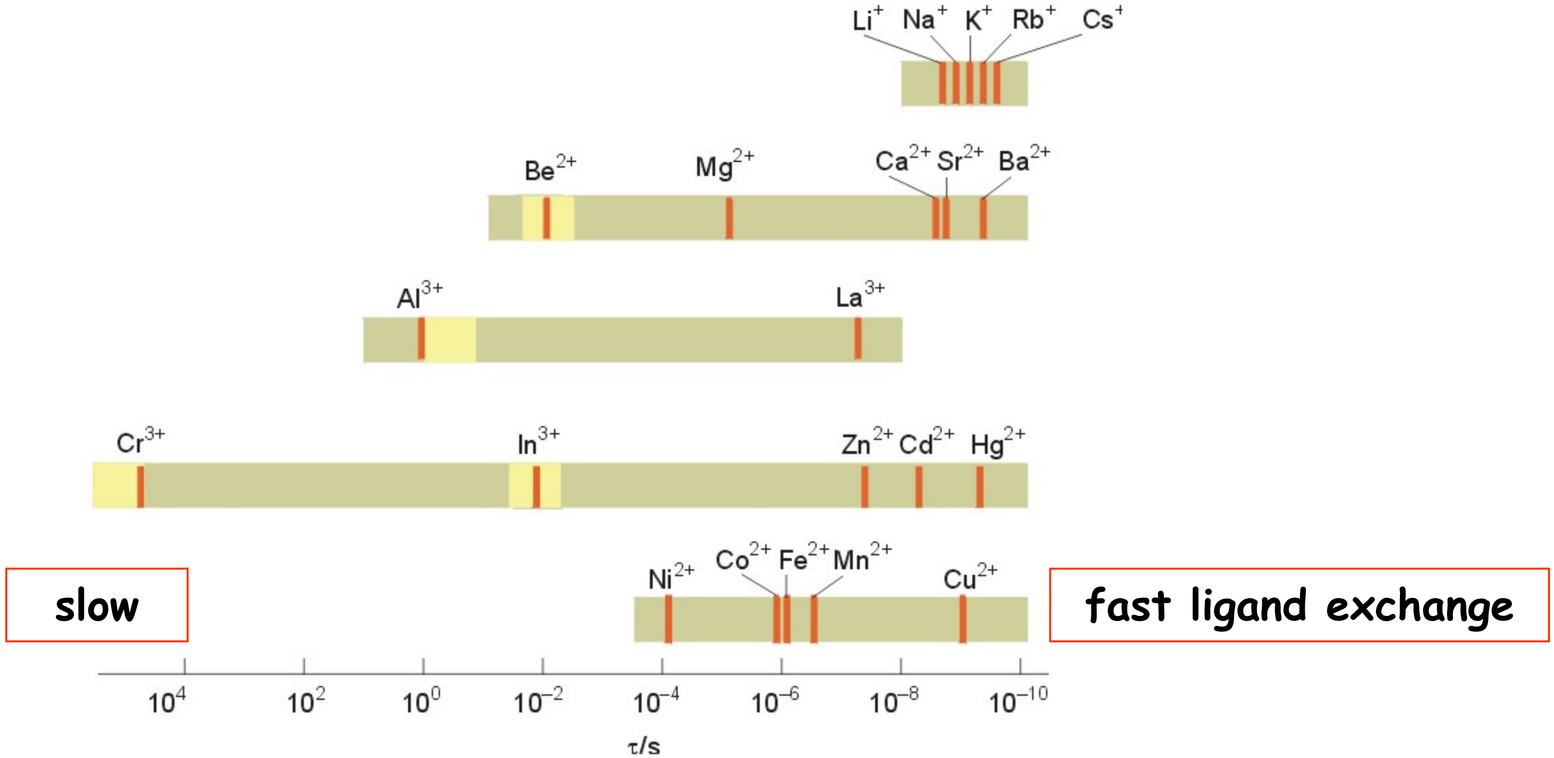
- $\mathbf{J = L + S}$ refers to a **Russel-Saunders-coupling** (coupling of the **total moments,** preferably 3d elements)

- the spectra of heavier elements must be treated on the basis of **jj-coupling** (coupling of the individual moments: $j_n = l_n + s_n \rightarrow J = \Sigma j_n$)

Coordination Chemistry: Basic aspects of reactivity in solutions

Inert Complexes: Kinetically stable (high activation energy); slow exchange of ligands.
- e.g. strong field d^3 and d^6 complexes of Cr^{3+} and Co^{3+}

Labile Complexes: Kinetically unstable (low activation energy) rapid exchange of ligands.
- e.g. most aquo complexes with s-block elements ($[Na(H_2O)_6]^+$ ..) except those ones with Be^{2+} or Mg^{2+}, complex molecules with low oxidation number d^{10} ions (Zn^{2+} ...)

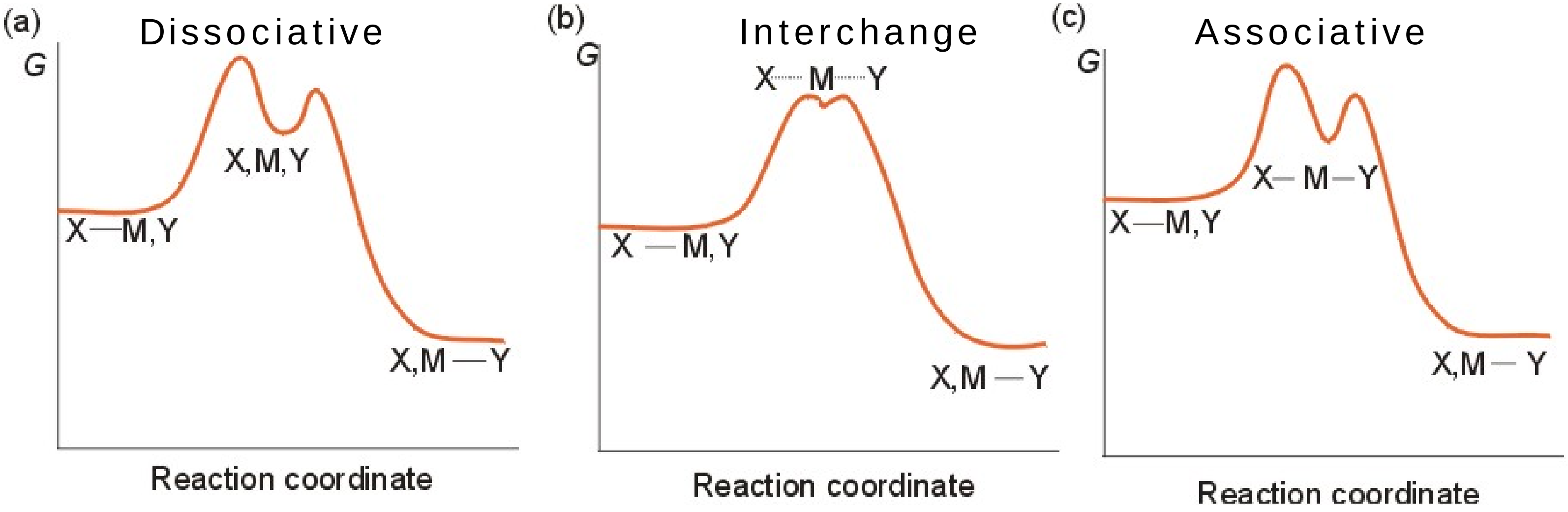


Coordination Chemistry: Basic aspects of reactivity

- **Reaction mechanism**: model for a sequence of reaction steps with special emphasis on the activated state (transition state) and the rate determining step
- **Rate law**: differential equation for the rate of the change of molar concentrations of reactands (educts) and products
- **Rate determining step:** slowest step in the sequence of reactions; determines in a first approximation the total reaction rate.

Different types of reaction mechanisms are distinguished by the activated state:

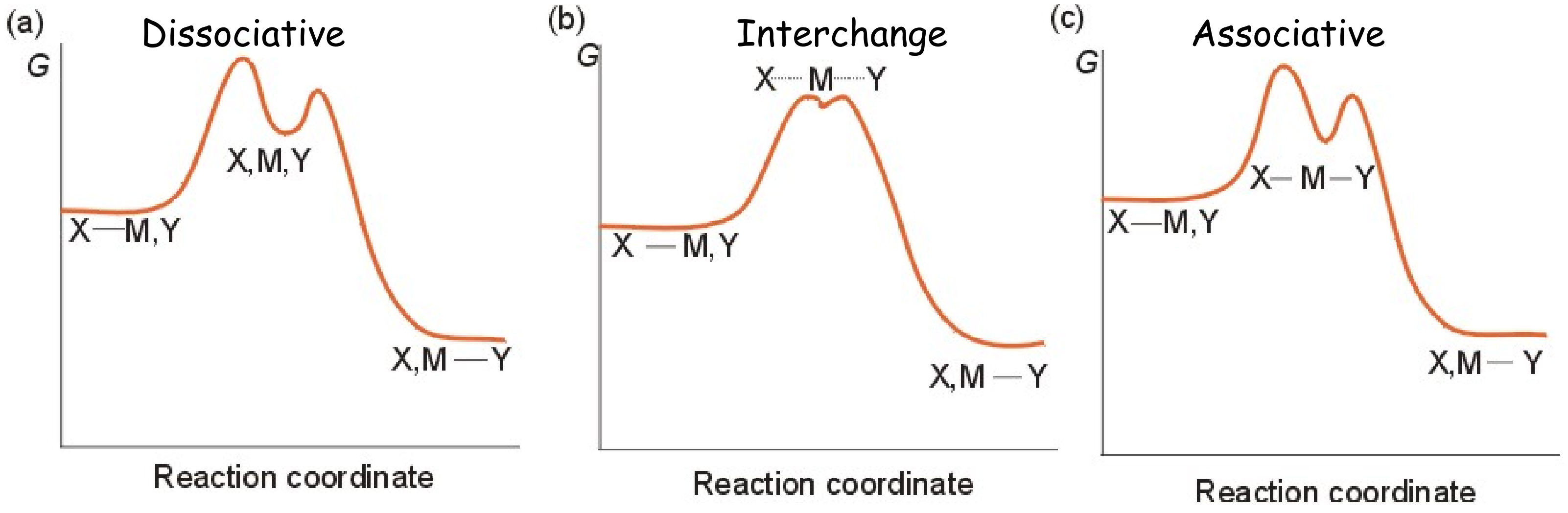
Dissociative: activated state has lower coordination number due to dissociation of the leaving group
Associative: activated state has a higher coordination number due to bonding of the incoming group



$W(CO)_6 + PPh_3 \rightarrow W(CO)_5\, PPh_3 + CO$

$[Ni(CN)_4]^{2-} + (^{14}CN)^- \rightarrow [Ni\,(^{14}CN)(CN)_3]^{2-} + CN^-$

Coordination Chemistry: Basic aspects of reactivity



Rate determining step: dissociation of X (outgoing group) is fast

$$\mathrm{X{-}M} + \mathrm{Y} \underset{\text{fast}}{\leftrightarrow} \mathrm{X,M,Y} \underset{\text{slow}}{\rightarrow} \mathrm{X} + \mathrm{MY}$$

long lifetime of the intermediate

Rate determining step: association of Y (incoming group) is slow

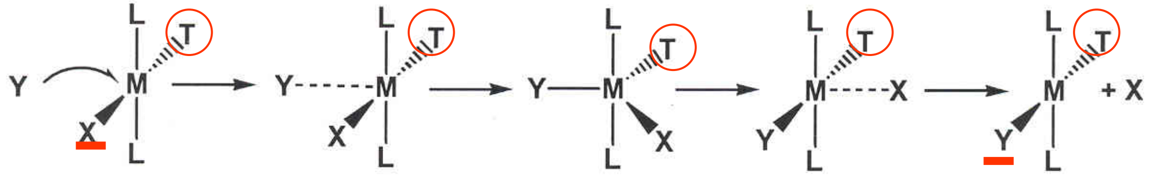
$$\mathrm{X{-}M} + \mathrm{Y} \underset{\text{slow}}{\leftrightarrow} \mathrm{X{-}\ M{-}Y} \underset{\text{fast}}{\rightarrow} \mathrm{X} + \mathrm{MY}$$

short lifetime of the intermediate

More detailed analyses require measurements of the „reaction order“(first, second etc.) and considerations about possible molecular mechanisms of the sequence of reactions.

Coordination Chemistry: square planar complexes - the „trans“ effect

Mechanism for the substitution of a ligand X by a nucleophilic reactand Y in a square planar complex

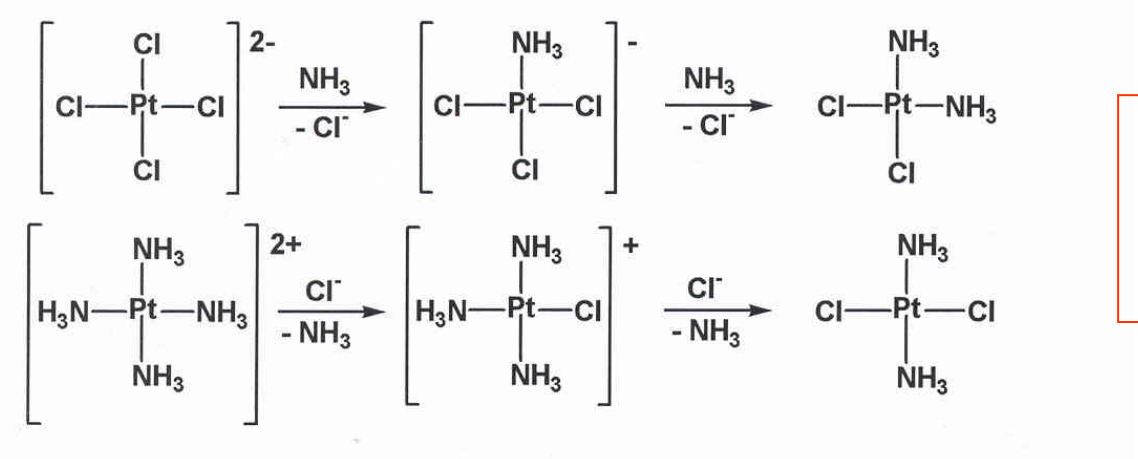


the transition state (activated complex) is approximately trigonal bipyramidal

A strong σ-**donor** or π-**acceptor** ligand (T) greatly influences the substitution of a ligand that lies in the trans-position by favouring its dissociation

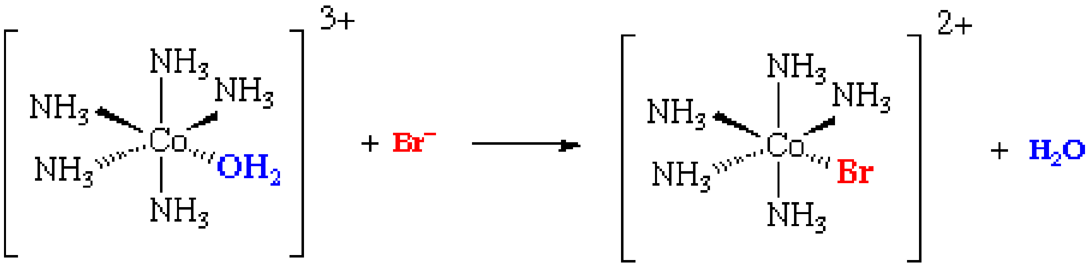
Tentative sequence of the trans-effect for different ions (molecules):

$\mathbf{CN^- > CO > PR_3 > H^- > SCN^- > I^- > Br^- > Cl^- > NH_3 > OH^- > H_2O}$



different synthetic routes to cis- or trans-$PtCl_2(NH_3)_2$ utilizing the trans-effect

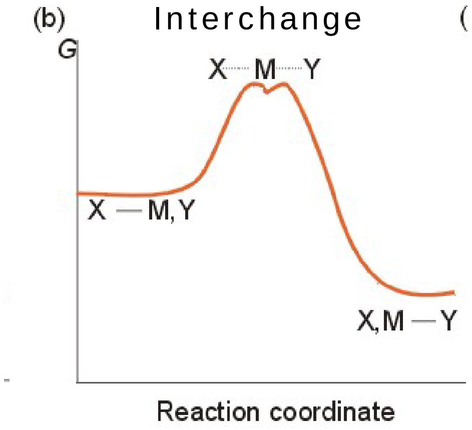
Coordination Chemistry: Substitution in octahedral complexes



$Co(NH_3)_5(H_2O),Br^-$

„encounter complex"

CN 7



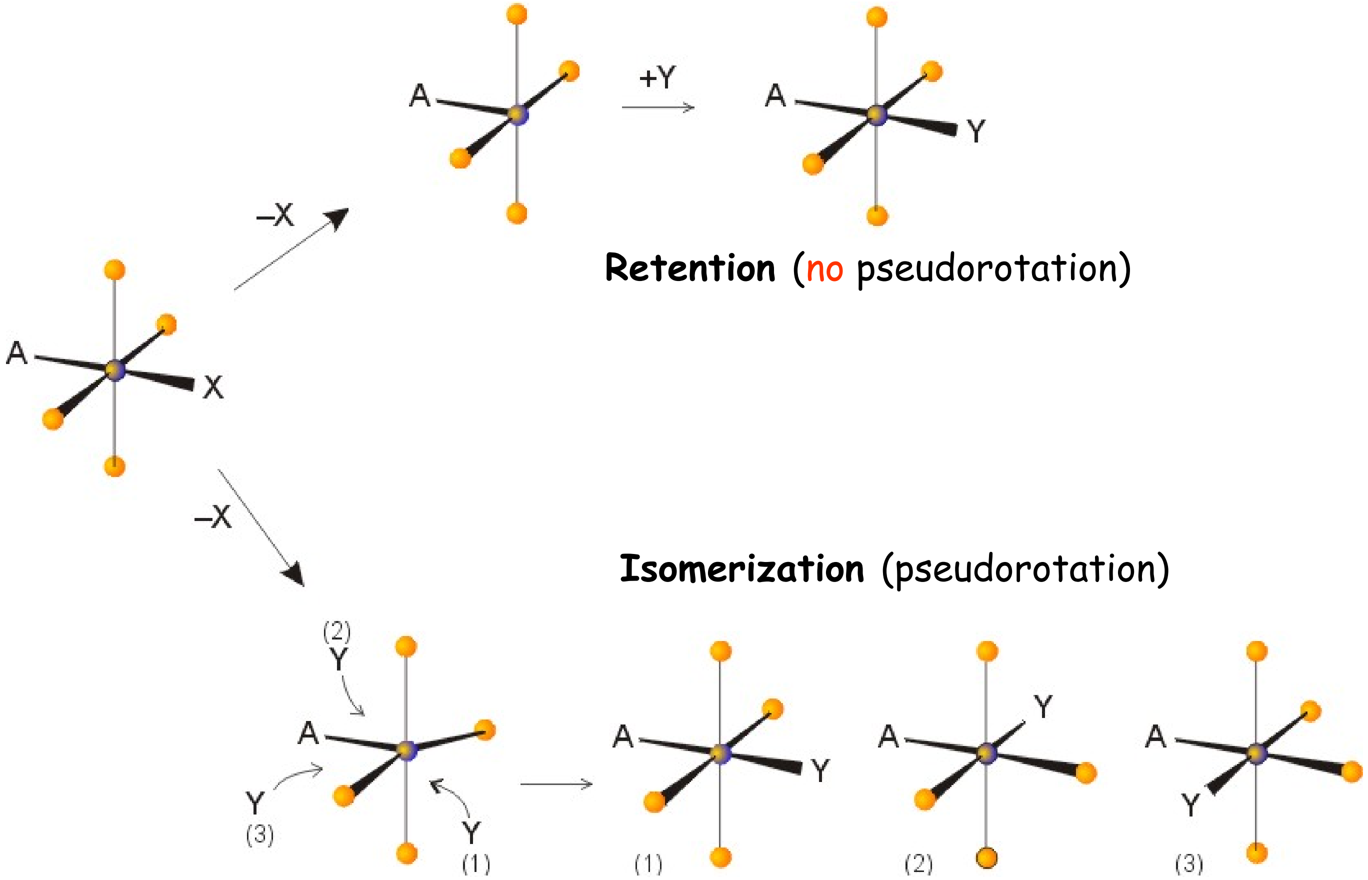
- several models for possible mechanisms: e.g. **Eigen-Wilkins** mechanism assuming the formation of an **„encounter complex" $(MX_6);Y$** in a pre-equilibrium step with products formed by subsequent rate determining steps

- reaction mechanism of type interchange

- incoming or leaving group determines whether interchange with an associative or dissociative rate determining step

- in general: analysis of **thermodynamic data** (e.g. activation-energy/entropy/volume) offers insight into possible reaction mechanisms

Substitution in octahedral complexes: retention and isomerization
(no encounter complex assumed)

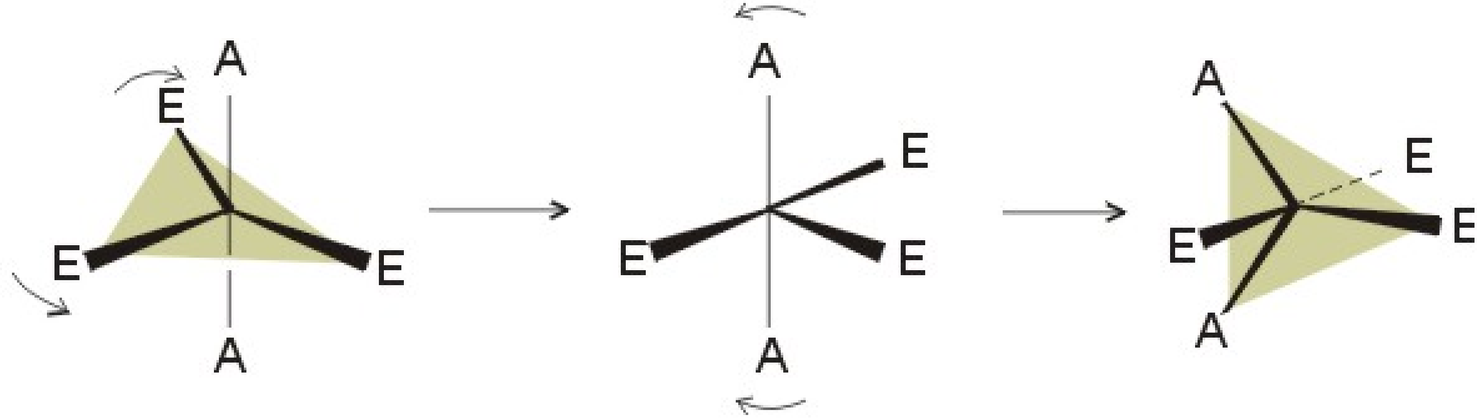


Retention (no pseudorotation)

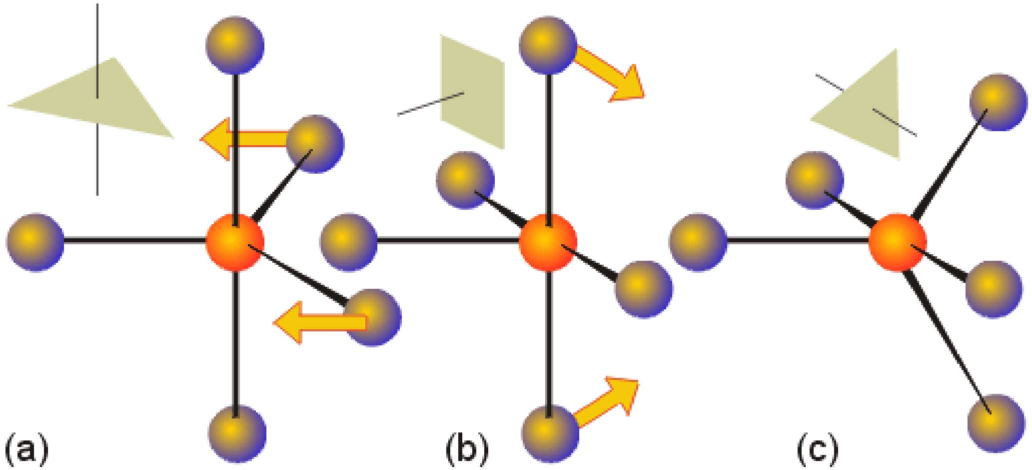
Isomerization (pseudorotation)

- reaction via a **square-pyramidal** complex results in **retention of the original geometry** (top)
- reaction via a **trigonal bipyramidal** complex can lead to **isomerization** (bottom)

Isomerization via trigonal bipyramidal activated complex
(things can be more complicated !)



Isomerization in the activated complex (change of axial and equatorial ligands) can occur by a „twist“ through a square pyramidal conformation (pseudorotation)



Inner and Outer sphere mechanism: redox reactions → electron transfer

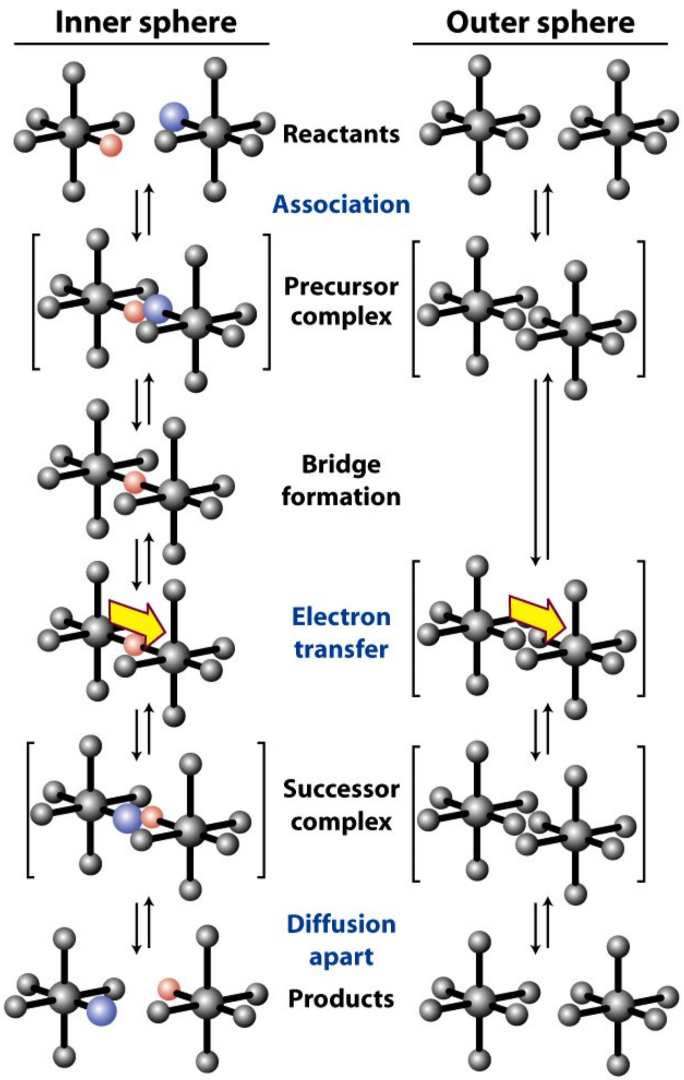
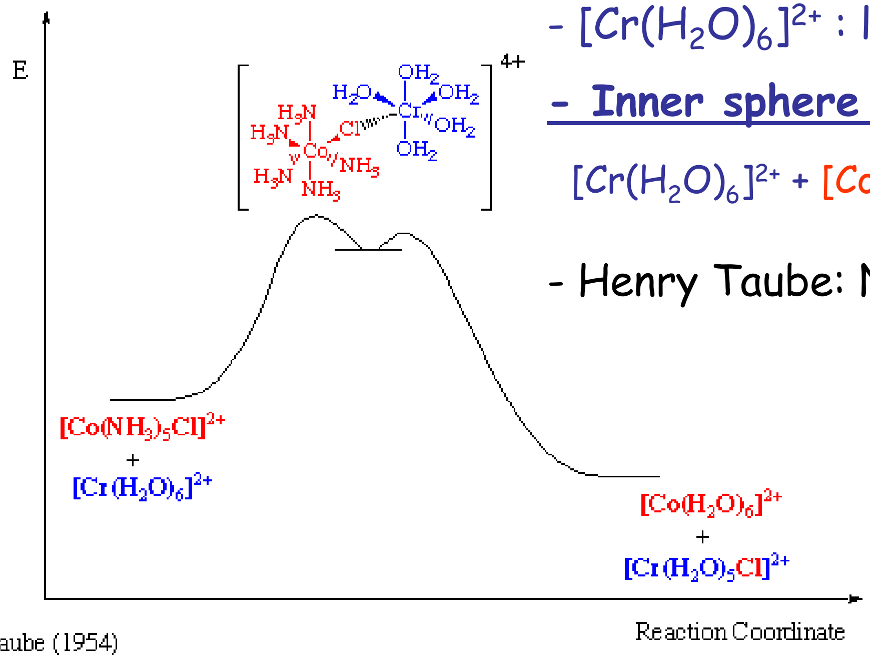


Figure 20-17
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Redox reactions - inner sphere mechanism

Inner sphere mechanism: Upon an electron transfer reaction occurring between two complex molecules an activated complex is formed in which the two participating molecules **share** a common ligand which serves as a bridge for the electron transfer.

$r(Cr^{2+})$ = 73 pm, $r(Co^{3+})$ = 61 pm, $r(Cr^{3+})$ = 61 pm, $r(Co^{2+})$ = 75 pm



Taube (1954)

- $[Cr(H_2O)_6]^{2+}$: labile against substitution

- **Inner sphere mechanism**,

$$[Cr(H_2O)_6]^{2+} + [Co(NH_3)_5Cl]^{2+} \rightarrow [Cr(H_2O)_5Cl]^{2+} + [Co(NH_3)_5(H_2O)]^{2+}$$

- Henry Taube: Nobel prize 1983

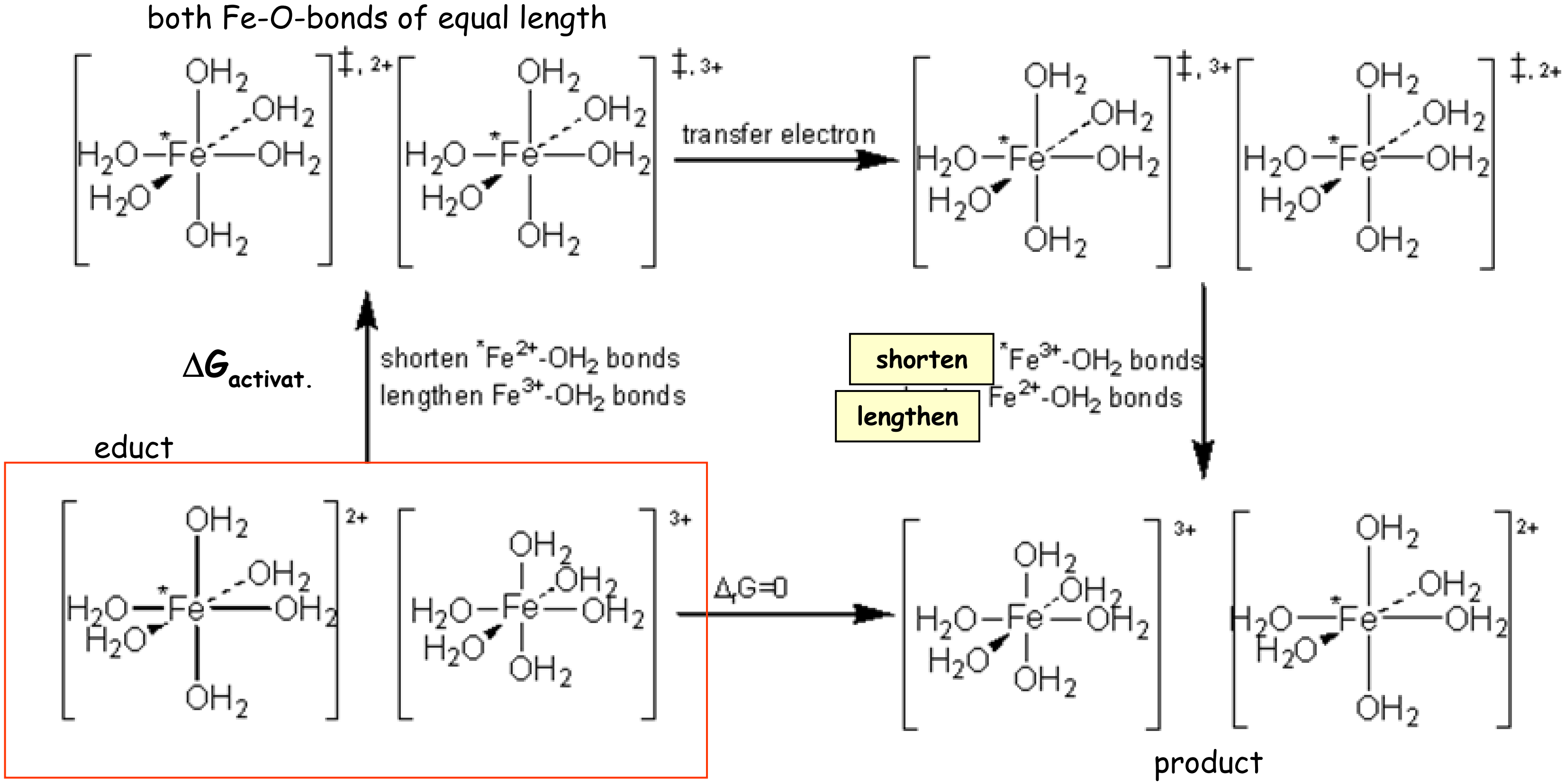
labile: „rapid“ exchange of ligands
inert: „very slow“ exchange of ligands (although the molecule may be thermodynamically instable)

Redox reactions - outer sphere mechanism

Outer sphere mechanism: The electron transfer is achieved via a **cascade of subsequent reactions without** sharing a common ligand; a strong change of interatomic distances between ligands and central atom is characteristic

$r(Fe^{2+})$ = 78 pm,
$r(Fe^{3+})$ = 65 pm

$$[Fe^{*}(H_2O)_6]^{2+} + [Fe(H_2O)_6]^{3+} \rightarrow [Fe^{*}(H_2O)_6]^{3+} + [Fe(H_2O)_6]^{2+}$$


both Fe-O-bonds of equal length

$\Delta G_{activat.}$

educt

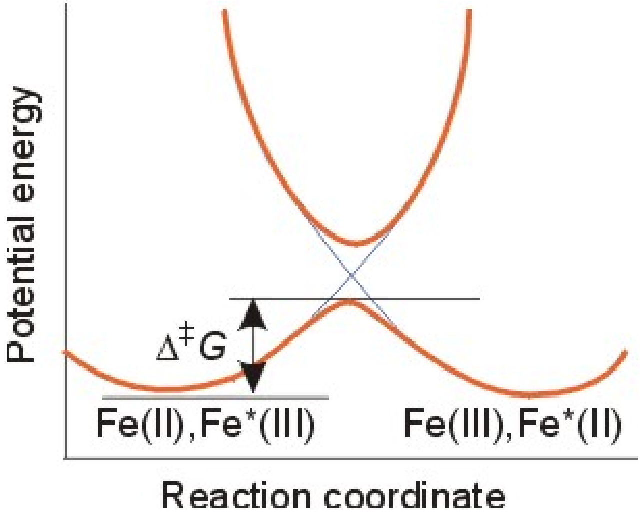
shorten

lengthen

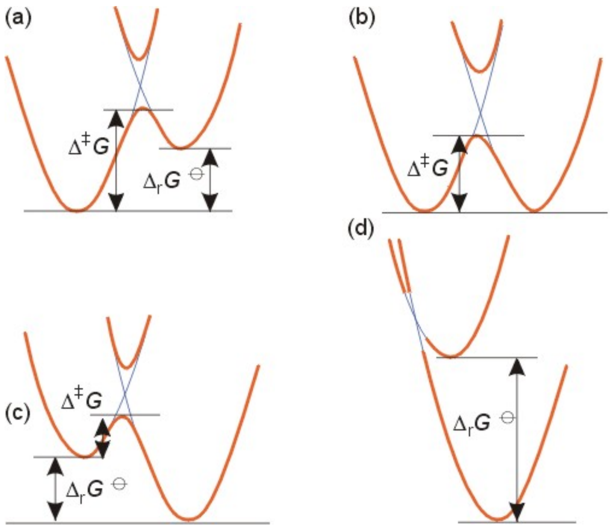
product

Redox reactions – Marcus equation

Special case: similar central atoms



General case: different central atoms



According to Marcus' ideas at least **two factors** determine the rate of electron transfer in an outer sphere mechanism:

a) the **shape of the potential curves** of the reactands

b) the **magnitude of the standard reaction Gibbs free energy** for the total reaction (the more negative it is the lower the activation energy of the reaction)

Marcus Equation for the rate constant k of the overall reaction:

$$k^2 \sim k_1 k_2 K$$

k_1 and k_2 are the two **rate constants** for the exchange reactions and K is the **equilibrium constant** for the overall reaction

e.g. $L_nFe^{2+} + L_mIr^{4+} \Leftrightarrow L_nFe^{3+} + L_mIr^{3+}$ **(k, K)**

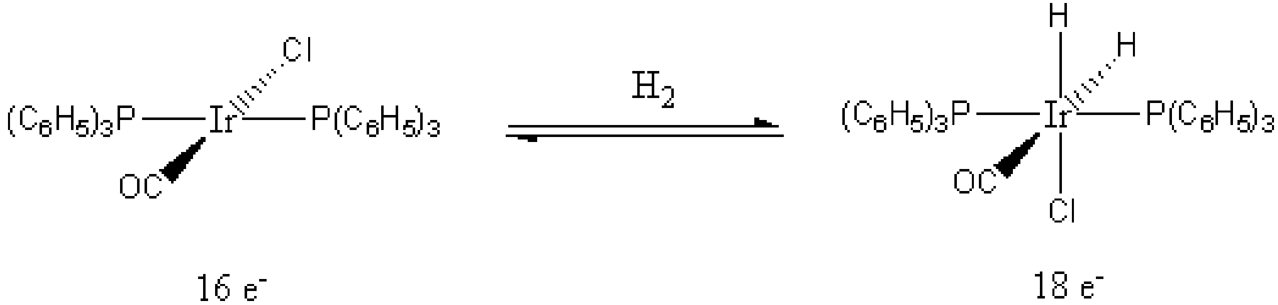
$L_nFe^{2+} + L_nFe^{*3+} \Leftrightarrow L_nFe^{3+} + L_nFe^{*2+}$ (k_1)

$L_mIr^{4+} + L_mIr^{*3+} \Leftrightarrow L_mIr^{3+} + L_mIr^{*4+}$ (k_2)

„Marcus-Cross-Relation" R.A. Marcus: NP 1992

Oxidative addition and reductive elimination

- An example of oxidative addition is the reaction of Vaska's complex, *trans*-$IrCl(CO)[P(C_6H_5)_3]_2$, with hydrogen.



- In this transformation, the metal oxidation state changes from Ir(I) to Ir(III) because the product is described as Ir^{3+} bound to three anions: Cl-, and two hydride, H-, ligands.

- The metal complex initially has 16 valence electrons and a coordination number of four. After the addition of hydrogen, the complex has 18 electrons and a coordination number of six.

Oxidative addition and reductive elimination

Oxidative addition and **reductive elimination** are two important classes of reactions in organometallic chemistry. Their relationship is shown below where y represents the number of ligands on the metal and n is the oxidation state of the metal.

$$XY + \underset{\mathbf{1}}{L_yM^n} \underset{\text{reductive elimination}}{\overset{\text{oxidative addition}}{\rightleftharpoons}} \underset{\mathbf{2}}{L_yM^{n+2}XY}$$

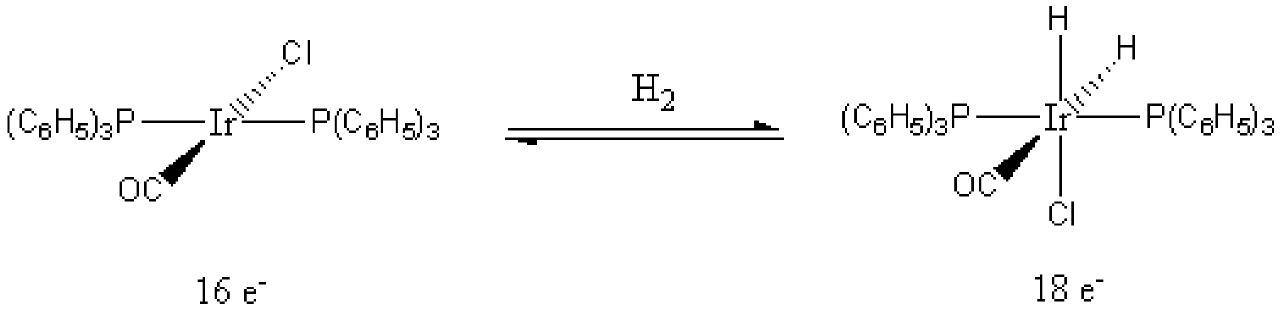
- In oxidative addition, a metal complex with vacant coordination sites and a relatively low oxidation state is oxidized by the insertion of the metal into a covalent bond (X-Y).

- Both the **formal oxidation state of the metal**, n, and the **electron count of the complex** increase by two.

- Oxidative additions are most commonly seen with H-H and carbon(sp^3)-halogen bonds.

Oxidative addition and reductive elimination

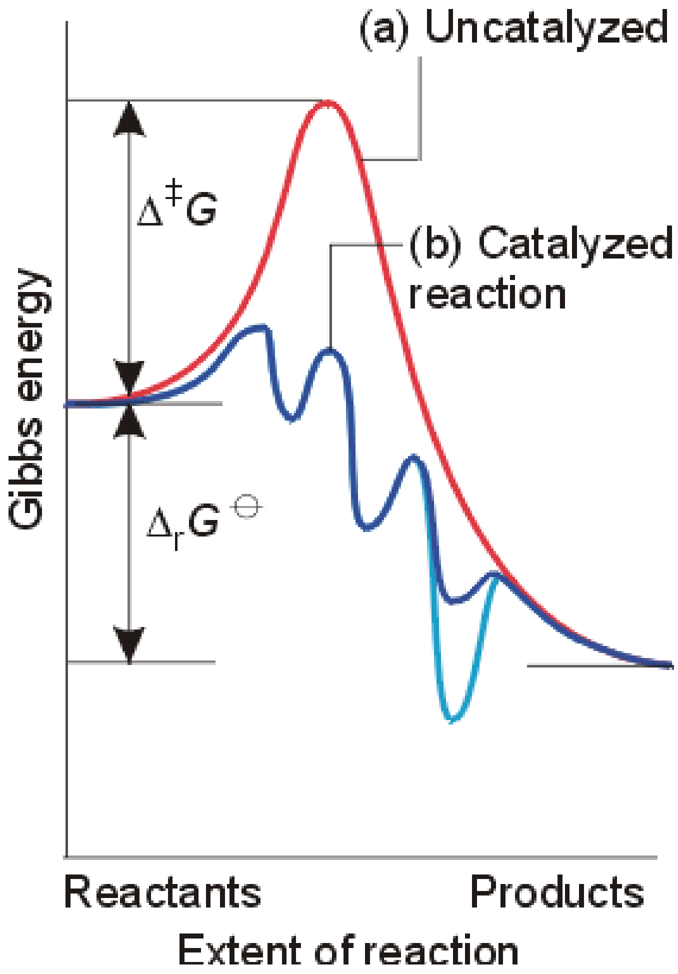
- The reverse of oxidative addition is **reductive elimination**. In this case hydrogen gas is lost and the metal complex is reduced.



- Reductive elimination is favored when the newly formed X-Y (H-H) bond of the outgoing group is strong.

- For reductive elimination to occur the two groups (X and Y) should be adjacent to each other in the metal's coordination sphere.

Catalysis and Catalysts: General aspects

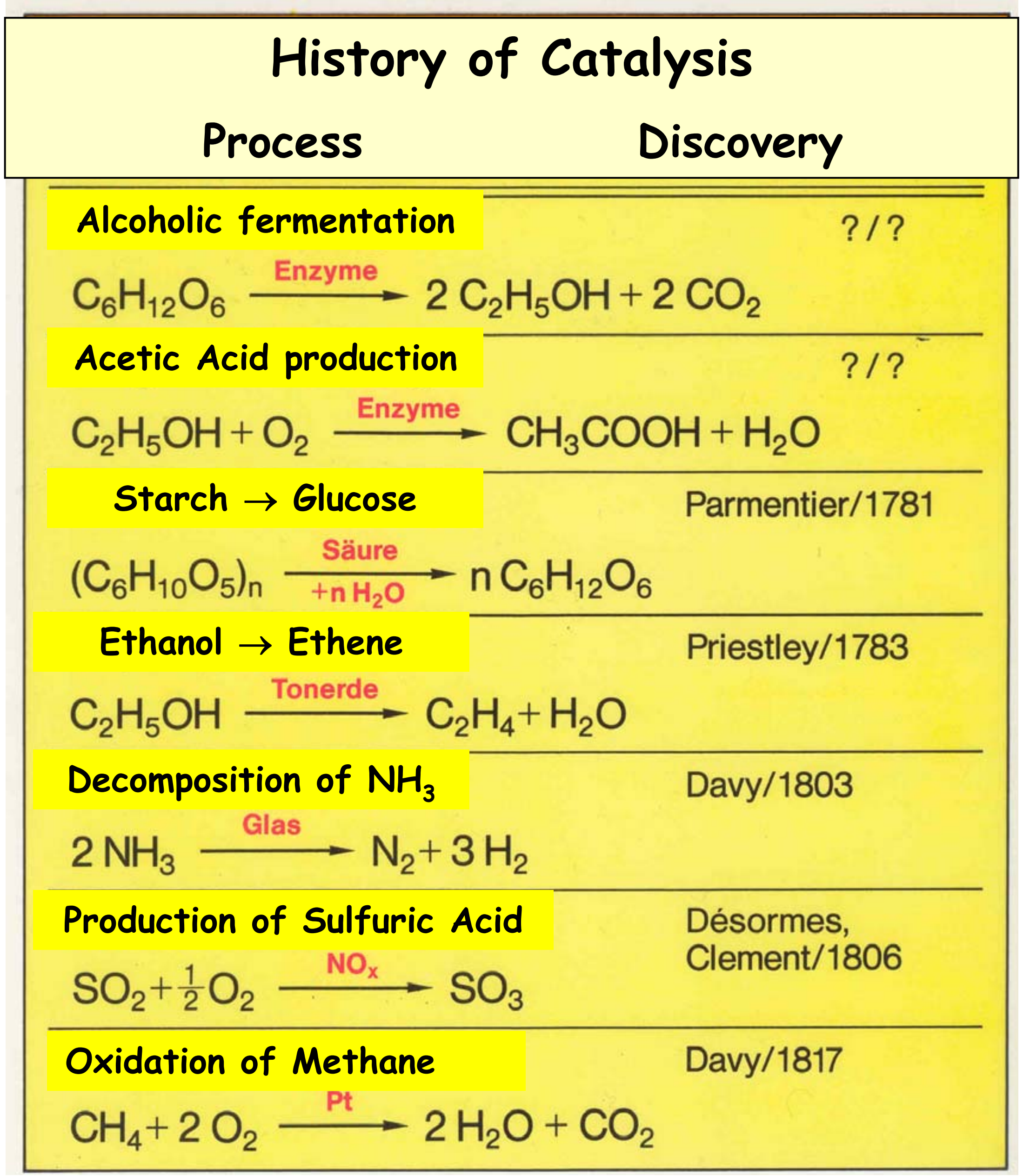


A catalyst increases the rate of a chemical process by offering new pathways with lower Gibbs energies of activation

Homogeneous catalysis: The catalyst is present in the **same phase** as the reactants

Heterogeneous catalysis: Catalyst and reactants belong to **different phases.**

Catalysis and Catalysts: General aspects



History of Catalysis

Process	Discovery
Alcoholic fermentation $C_6H_{12}O_6 \xrightarrow{\text{Enzyme}} 2\,C_2H_5OH + 2\,CO_2$	? / ?
Acetic Acid production $C_2H_5OH + O_2 \xrightarrow{\text{Enzyme}} CH_3COOH + H_2O$	? / ?
Starch → Glucose $(C_6H_{10}O_5)_n \xrightarrow[+n\,H_2O]{\text{Säure}} n\,C_6H_{12}O_6$	Parmentier/1781
Ethanol → Ethene $C_2H_5OH \xrightarrow{\text{Tonerde}} C_2H_4 + H_2O$	Priestley/1783
Decomposition of NH_3 $2\,NH_3 \xrightarrow{\text{Glas}} N_2 + 3\,H_2$	Davy/1803
Production of Sulfuric Acid $SO_2 + \frac{1}{2}O_2 \xrightarrow{NO_x} SO_3$	Désormes, Clement/1806
Oxidation of Methane $CH_4 + 2\,O_2 \xrightarrow{\text{Pt}} 2\,H_2O + CO_2$	Davy/1817

Catalysis and Catalysts: General aspects

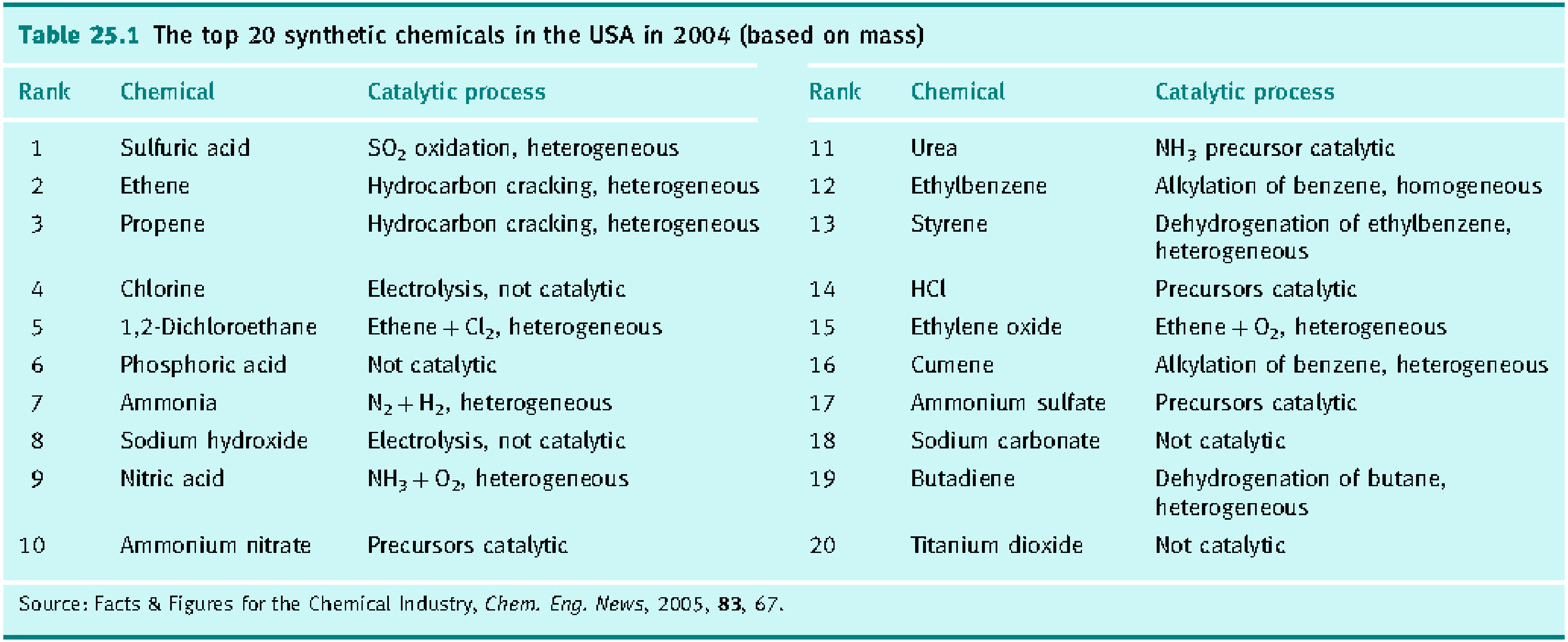


Table 25.1 The top 20 synthetic chemicals in the USA in 2004 (based on mass)

Rank	Chemical	Catalytic process
1	Sulfuric acid	SO_2 oxidation, heterogeneous
2	Ethene	Hydrocarbon cracking, heterogeneous
3	Propene	Hydrocarbon cracking, heterogeneous
4	Chlorine	Electrolysis, not catalytic
5	1,2-Dichloroethane	Ethene + Cl_2, heterogeneous
6	Phosphoric acid	Not catalytic
7	Ammonia	$N_2 + H_2$, heterogeneous
8	Sodium hydroxide	Electrolysis, not catalytic
9	Nitric acid	$NH_3 + O_2$, heterogeneous
10	Ammonium nitrate	Precursors catalytic
11	Urea	NH_3 precursor catalytic
12	Ethylbenzene	Alkylation of benzene, homogeneous
13	Styrene	Dehydrogenation of ethylbenzene, heterogeneous
14	HCl	Precursors catalytic
15	Ethylene oxide	Ethene + O_2, heterogeneous
16	Cumene	Alkylation of benzene, heterogeneous
17	Ammonium sulfate	Precursors catalytic
18	Sodium carbonate	Not catalytic
19	Butadiene	Dehydrogenation of butane, heterogeneous
20	Titanium dioxide	Not catalytic

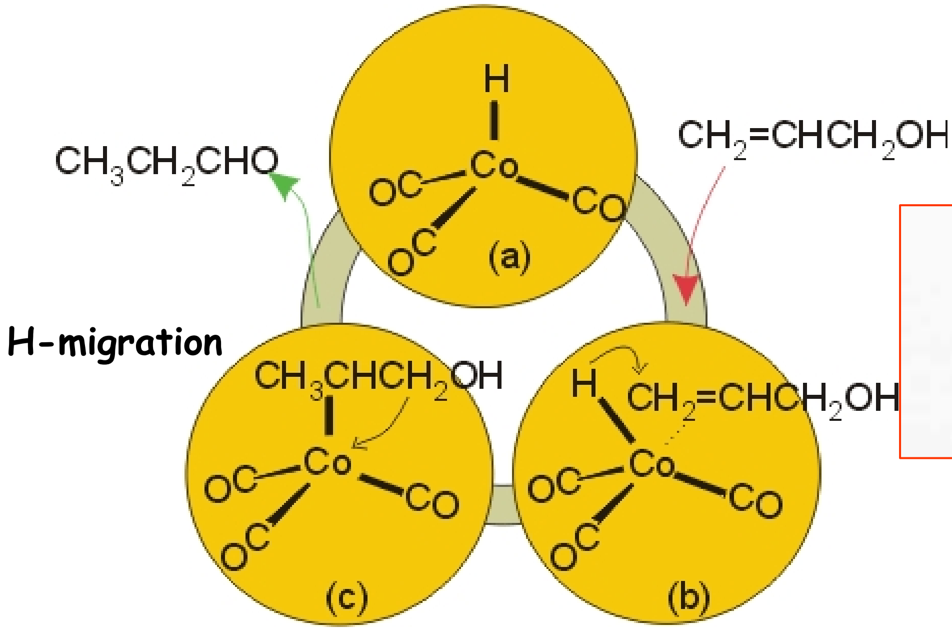
Source: Facts & Figures for the Chemical Industry, *Chem. Eng. News*, 2005, **83**, 67.

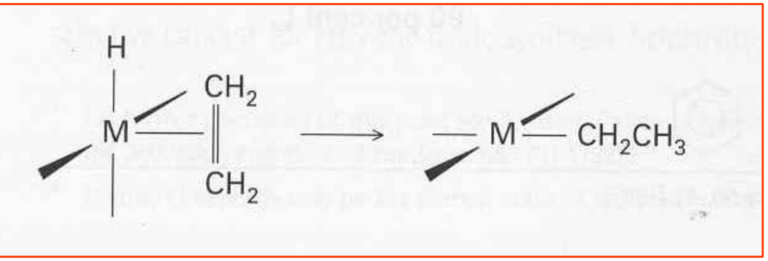
Catalytic cycle based on a cobalt-carbonyl-complex

Homogeneous catalysis: the oxidation of allylalcohol to propionaldehyde:

$CH_2{=}CH{-}CH_2OH \rightarrow CH_3{-}CH_2{-}CHO$

catalyst assisted migration of two H-atoms





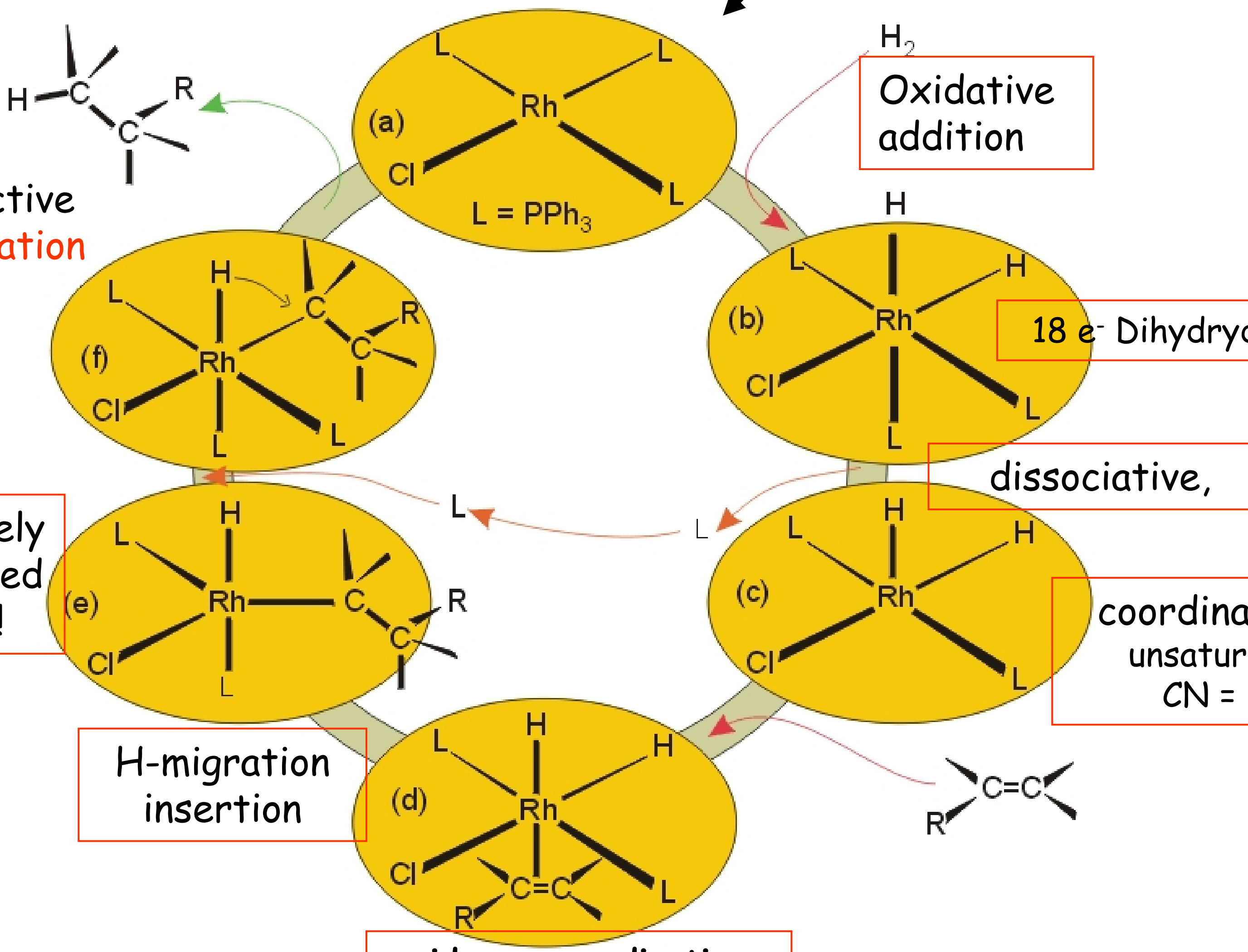
- Insertion

Hydrogenation of alkenes: with Wilkinson's catalyt

$H_2C{=}CHR + H_2 \rightarrow H_3C{-}CH_2R$

$\Delta G \sim -100\ kJ\ mol^{-1}$

(very slow without catalyst)



Wilkinson's catalyst, L = PPh_3

16 e^-

Oxidative addition

18 e^- Dihydrydo complex

dissociative,

coordinatively unsaturated CN = 5 !

side-on coordination

H-migration insertion

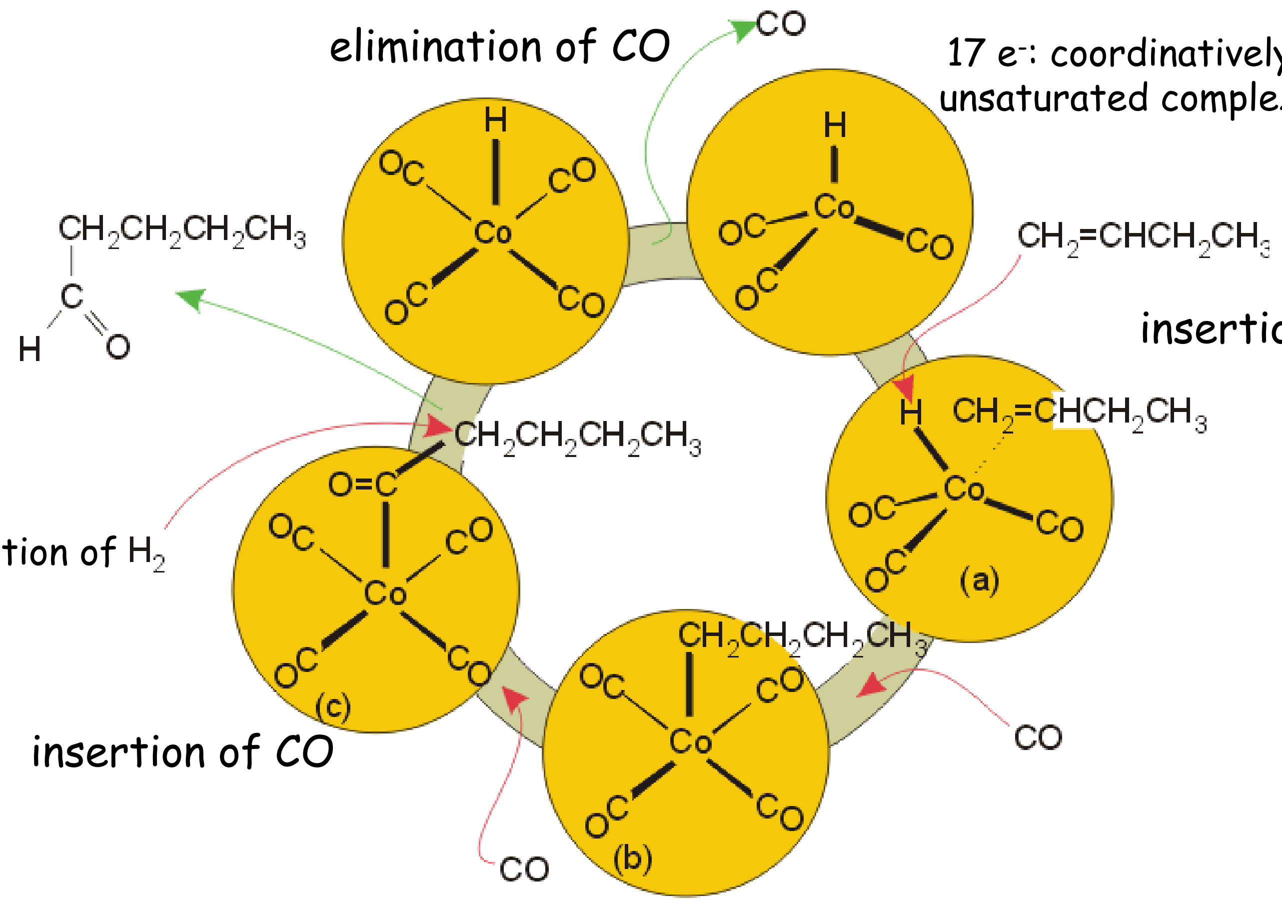
coordatively unsaturated CN = 5 !

reductive elimination

Hydrocarbonylation (-formylation)

alkene → aldehyde with one additional C:

$CH_3\text{-}CH\text{-}CH{=}CH_2 + CO + H_2 \rightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CHO$



elimination of CO

17 e⁻: coordinatively unsaturated complex

insertion - migration

insertion of H_2

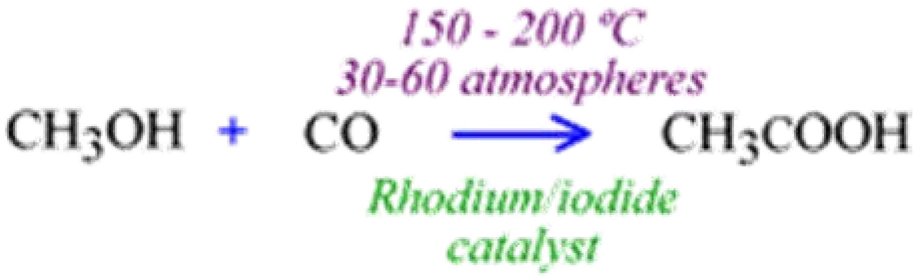
insertion of CO

coordinatively unsaturated complex

Coordination Chemistry: Monsanto process

Just as a metal oxidatively inserts itself into a H-H bond, it can also oxidatively add to C-H bonds. This process is called C-H bond activation and is an active research area because of its potential value in converting petroleum-derived hydrocarbons into more complex products. Oxidative addition and reductive elimination are seen in many catalytic cycles such as the monsanto process and alkene hydrogenation using Wilkinson's catalyst.

„Monsanto"-process: formation of acetic acid from methanol using a Rh-iodide complex



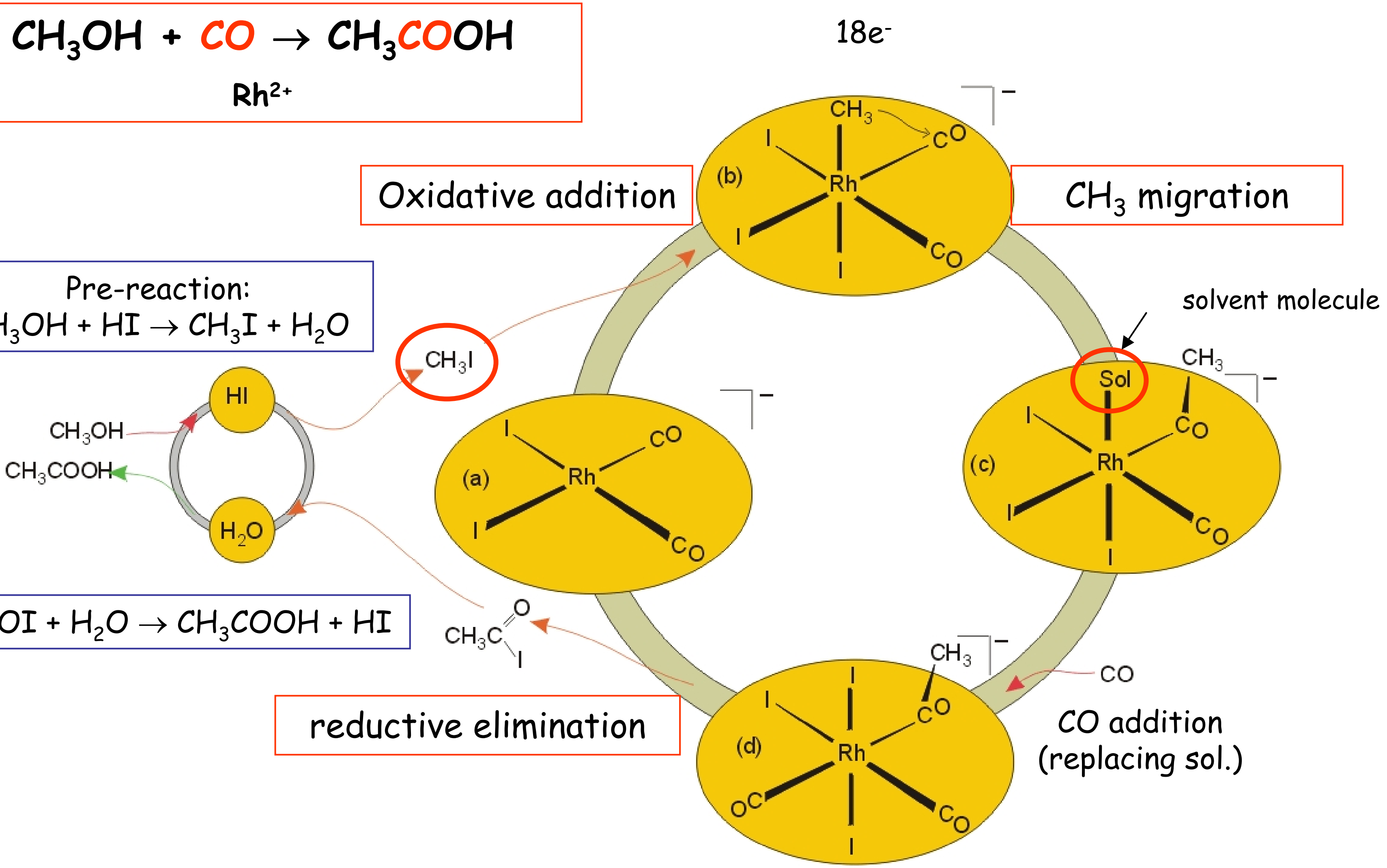
$$CH_3OH + CO \xrightarrow[\text{Rhodium/iodide catalyst}]{\text{150 - 200 °C, 30-60 atmospheres}} CH_3COOH$$

Monsanto process

$CH_3OH + CO \rightarrow CH_3COOH$

Rh^{2+}

$18e^-$



Oxidative addition

CH_3 migration

solvent molecule

Pre-reaction:
$CH_3OH + HI \rightarrow CH_3I + H_2O$

CO addition
(replacing sol.)

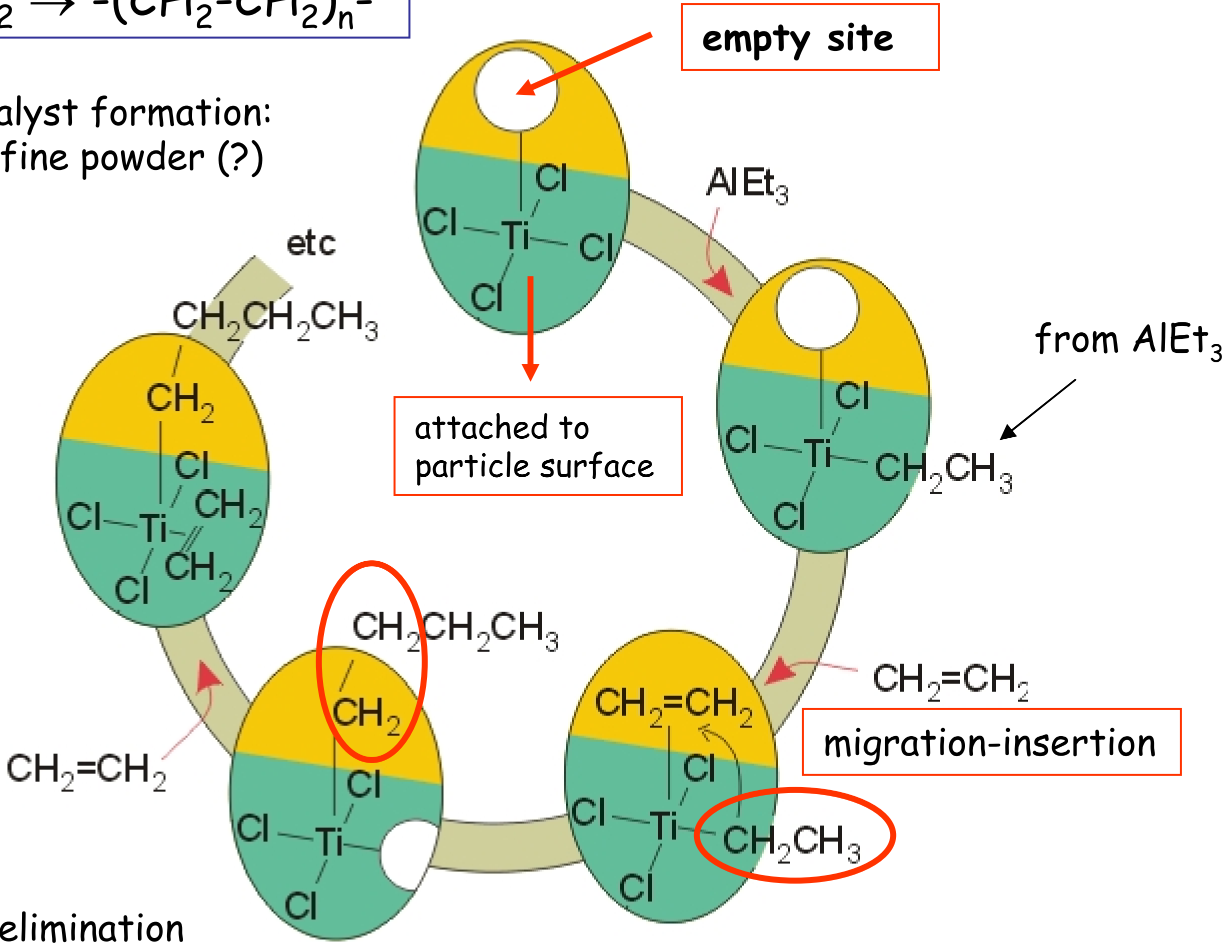
reductive elimination

$CH_3COI + H_2O \rightarrow CH_3COOH + HI$

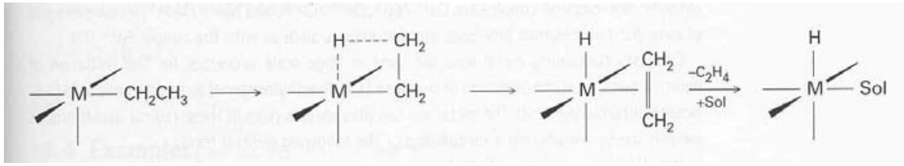
Alkene polymerisation (Ziegler-Natta-process)

$n\ CH_2{=}CH_2 \rightarrow -(CH_2\text{-}CH_2)_n-$

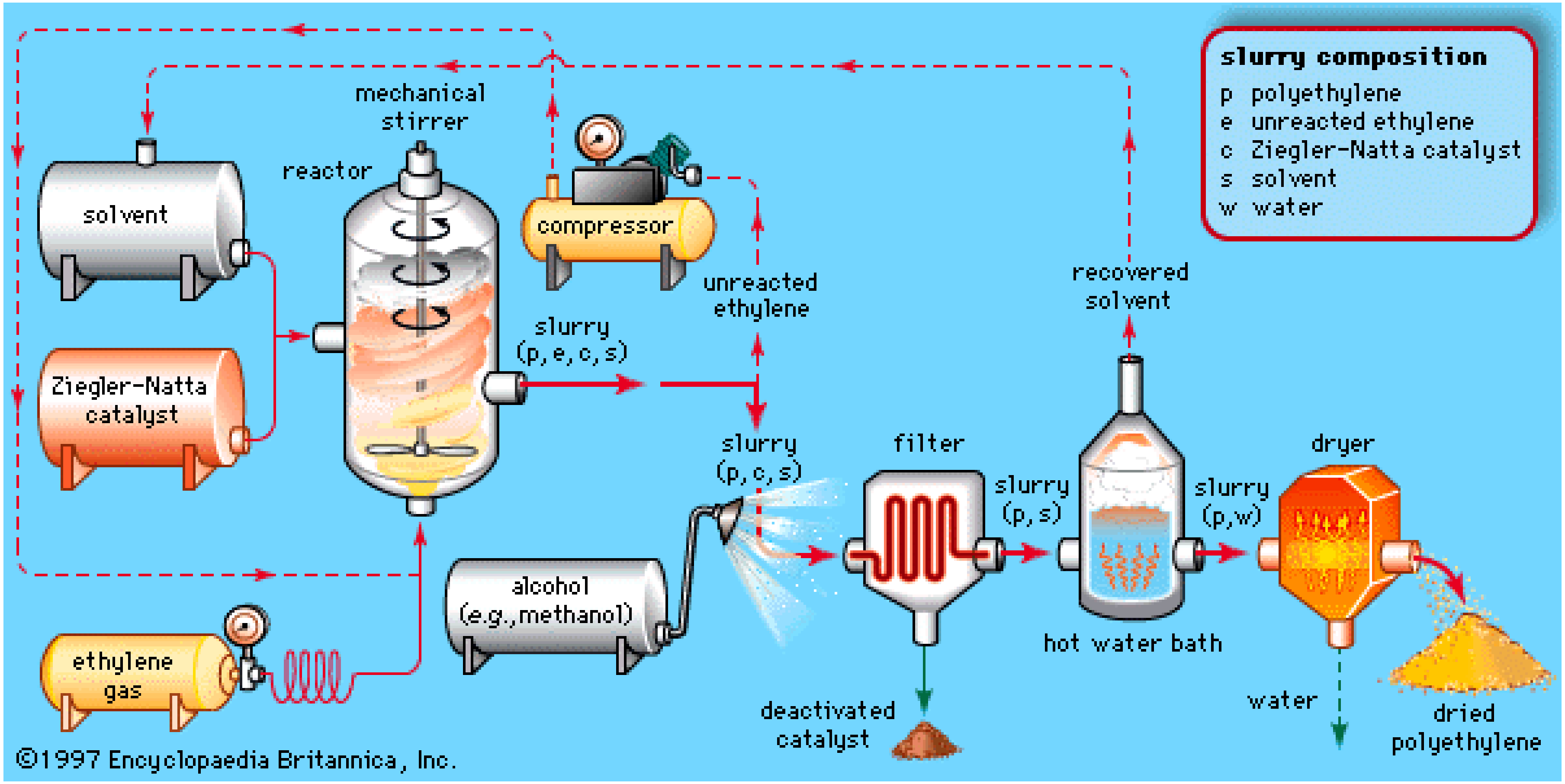
Prereaction: catalyst formation:
$TiCl_4 + AlEt_3 \rightarrow$ fine powder (?)



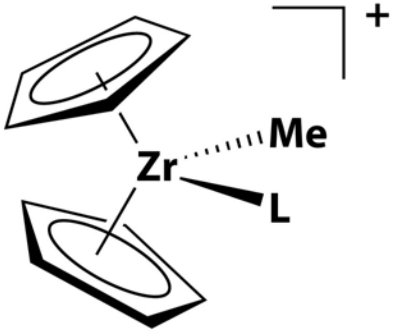
chain termination: β-elimination



Alkene polymerisation (Ziegler-Natta-process) (technical realization)

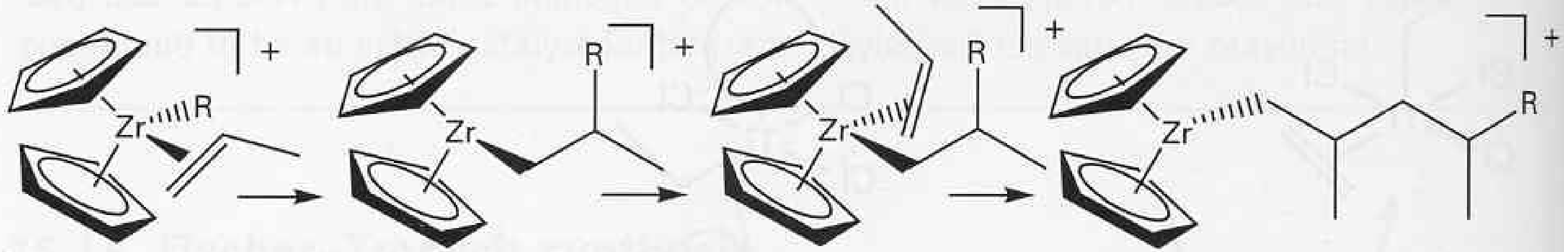


Alkene polymerisation: current and future catalysts replacing Ziegler-Natta



12 $[Zr(\eta^5\text{-}Cp)_2(CH_3)L]^+$

Structure 25-12
Shriver & Atkins Inorganic Chemistry, Fourth Edition



Special aspects of coordination compounds

16 e and 18 e complexes tend to be more stable than others.

But: how to count electrons in coordination compounds ?

a) Assume a reasonable charge for the central atom and for the ligands (Lewis formula !) → external charge of the complex molecule.
b) Consider how many electrons each ligand will donate and add this number to the number of electrons at the (charged?) central atom
→ number of valence electrons at the central atom.

e.g.
1.) $[Fe(CN)_6]^{4-}$: Fe^{2+} (6e), CN^- (2e-donor), 6e + 6x2e = 18e

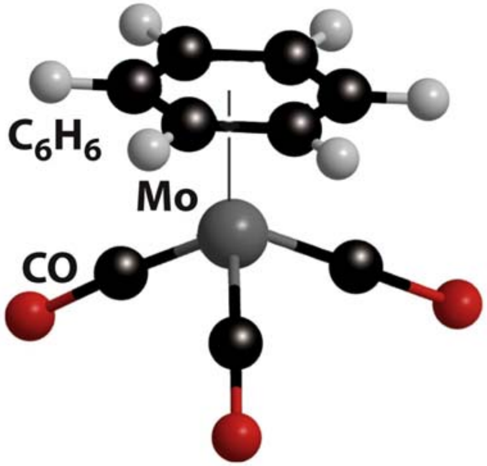
2.) $[Fe(CN)_6]^{3-}$: Fe^{3+} (5e), CN^- 2e-donor, 5e + 6x2e = 17e

3.) $[IrBr_2(CH_3)(CO)(PPh_3)_2]$: Ir^{3+} (6e), Br^-, CH_3^-, CO, PPh_3 (all 2e-donors), 6e + 6x2 = 18e

4.) $[Cr(\eta^5C_5H_5)(\eta^6C_6H_6)]$: Cp^{1-}(6e-donor), C_6H_6 (6e-donor), Cr^{1+} (5e): 5e + 2x6e = 17e

5.) $[Mn(CO)_5]^-$: Mn(7e), CO: neutral 2e-donor, 7e + 5x2e + 1e = 18e

Some additional nomenclature



11 $[Mo(\eta^6\text{-}C_6H_6)(CO)_3]$

Structure 21-11
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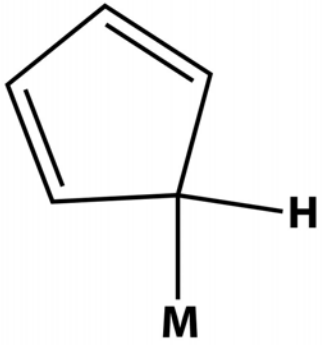

η^1-Cyclopentadienyl

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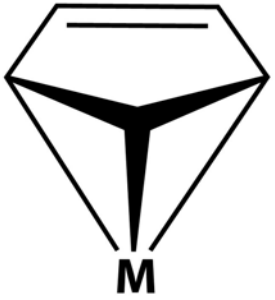

η^3-Cyclopentadienyl

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η^5-Cyclopentadienyl

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Typical ligands and their electron counts

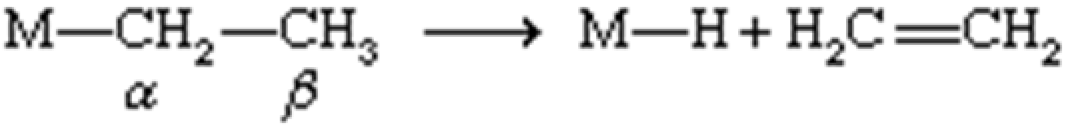
Ligand	Formula	Electrons donated
Carbonyl	CO	2
Phosphine	PR_3	2
Hydride	H^-	2
Dihydrogen	H_2	2
η^1-Alkyl, -alkenyl, -alkynyl, and -aryl groups	R^-	2
η^2-Alkene	$CH_2{=}CH_2$	2
η^2-Alkyne	$RCCR$	2
Dinitrogen	N_2	2
Butadiene	$CH_2{=}CH{-}CH{=}CH_2$	4
Benzene	C_6H_6	6
η^3-Allyl	$CH_2CHCH_2^-$	4 ?
η^5-Cyclopentadienyl	C_5H_5	6

Important ligands and their bonding types

-CO, Phosphines and H_2 have already been discussed

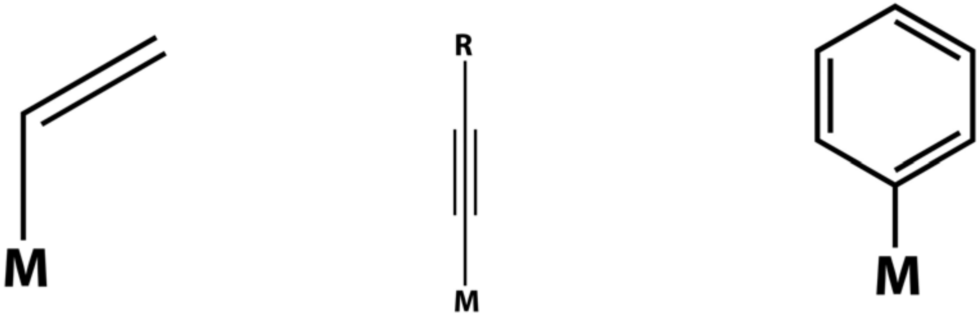
- alkyl groups show in most cases σ-interactions (donor or acceptor); in case of an H-atom at the β-C a β-elimination can occur

β-elimination:



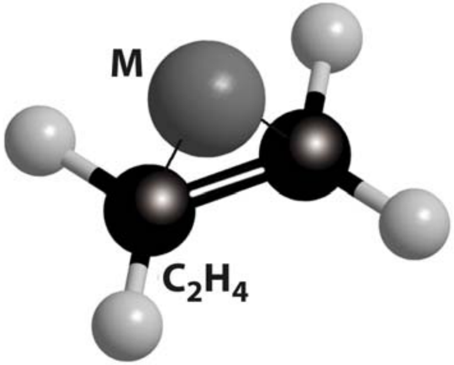
$$\underset{}{M}-\underset{\alpha}{CH_2}-\underset{\beta}{CH_3} \longrightarrow M-H + H_2C{=}CH_2$$

-alkenyl, alkynyl and aryl groups may bond to M atoms in a similar fashion (η^1: monohapto)



Important ligands and their bonding types
(direct bonding of M to a multiple CC-bond)

- best described as σ-bond from the CC-bond to the M-atom and a π-backbonding from the metal d-orbitals to the π* orbitals of the CC-bond



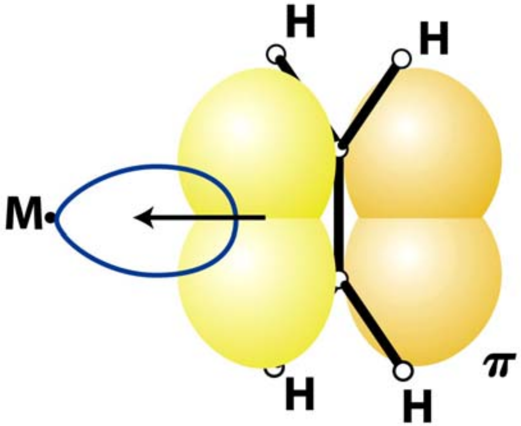


Figure 21-5a
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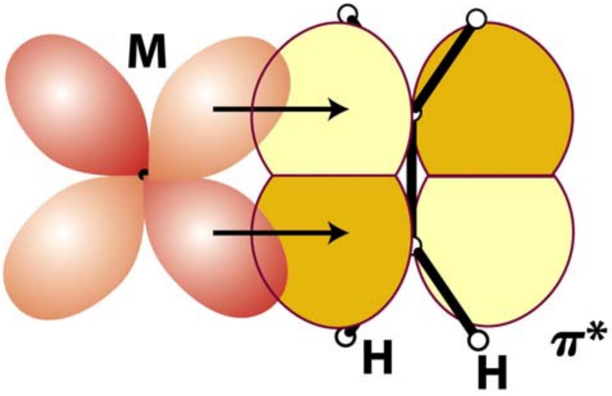

Figure 21-5b
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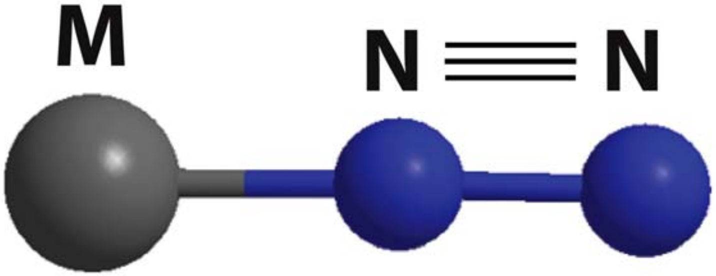
η^2: **dihapto**

max. $2e^-$ donation from double bond (alkene)

degree of donation and backdonation depends strongly on the type of ligands

Important ligands and their bonding types

(Nitrogen N_2 as ligand)



35

Structure 21-35
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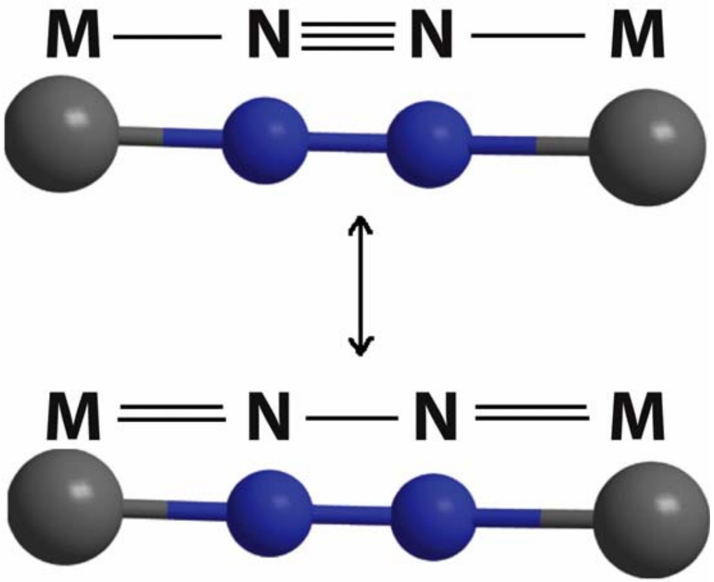

36

37

Structure 21-37
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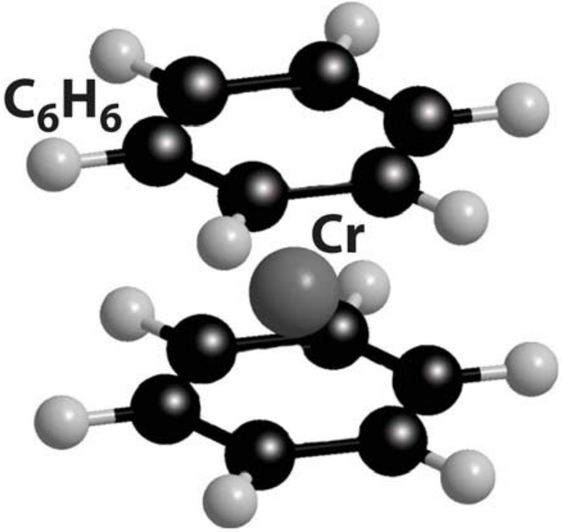
- bonding basically similar to isoelectronic CO, but N_2 is a weaker σ-donor and a weaker π-acceptor ligand
- dinitrogen complexes are important as precursors for N_2 fixation from air to replace the Haber-Bosch process in the future

Important ligands and their bonding types
(benzene)

- assuming **three CC-double bonds** for a benzene molecule each one can act as a ligand and the molecule can be regarded as a **tridentate η^6 ligand**

dibenzene-chromium



46

Structure 21-46
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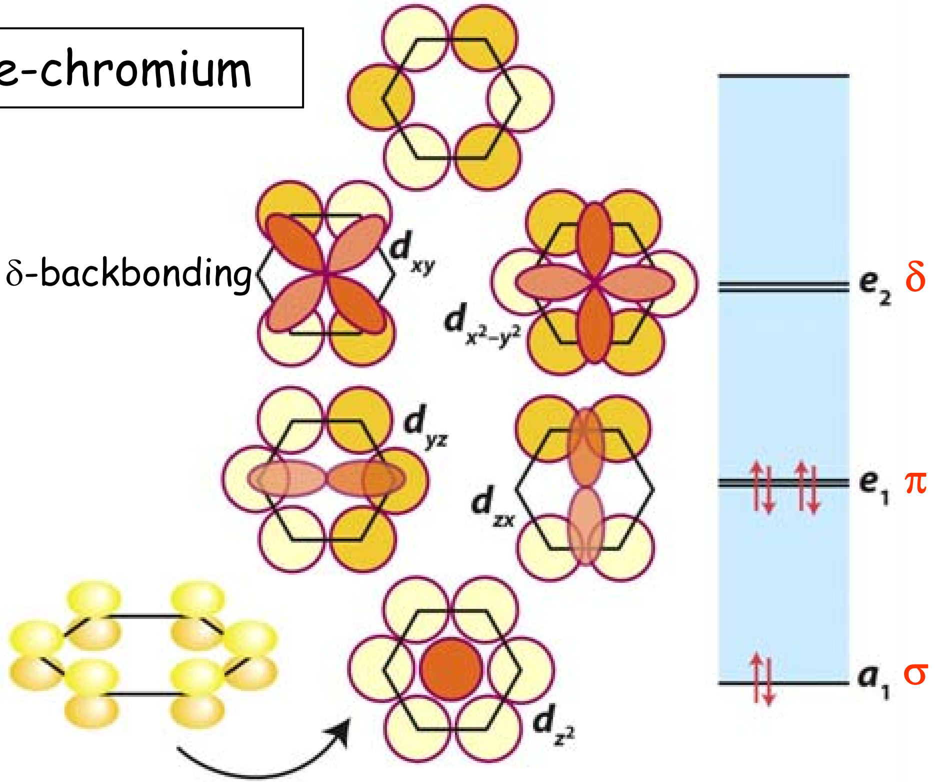
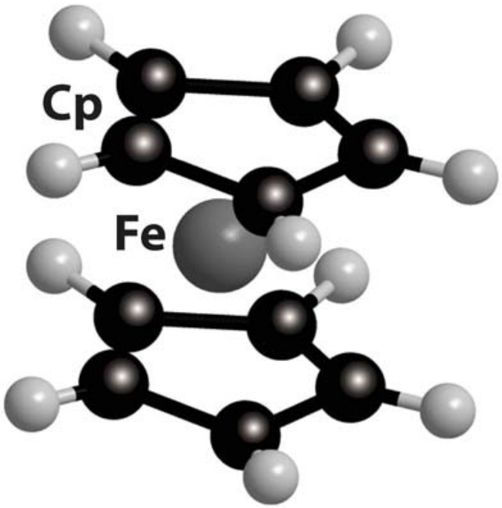

δ-backbonding

Figure 21-8
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Important ligands and their bonding types

(the cyclopentadienyl ligand: sandwich or metallocene compounds)

- the bonding of the Cp ligand to the metal atom can interpreted as a mixture of σ- and π-donation combined with δ-backbonding components



4 $FeCp_2, Cp{=}C_5H_5$

Structure 21-4
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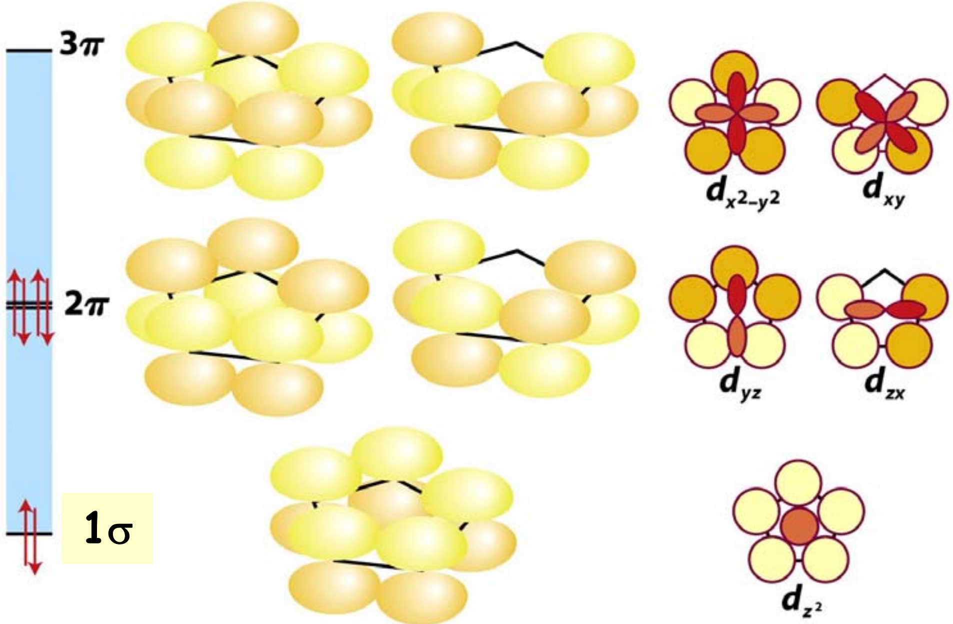

Figure 21-10
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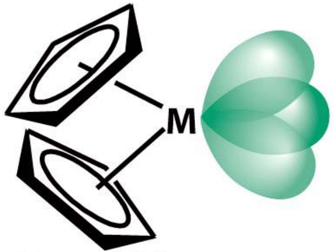
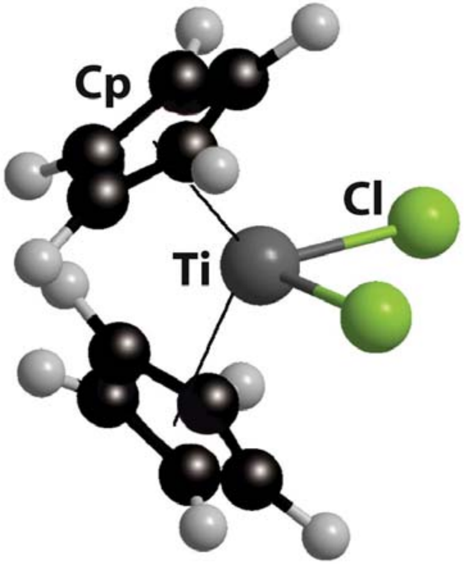
Important ligands and their bonding types
(the variety of metallocene: bent and multi decker)



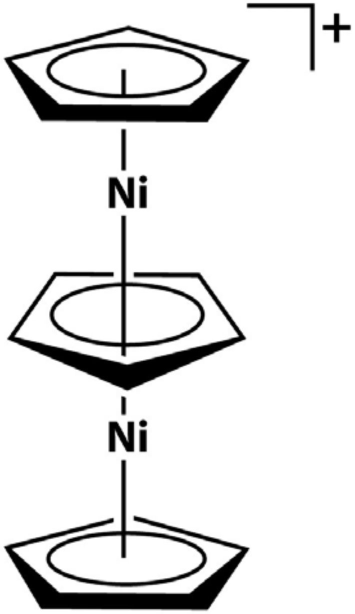
General form

bent sandwich



72

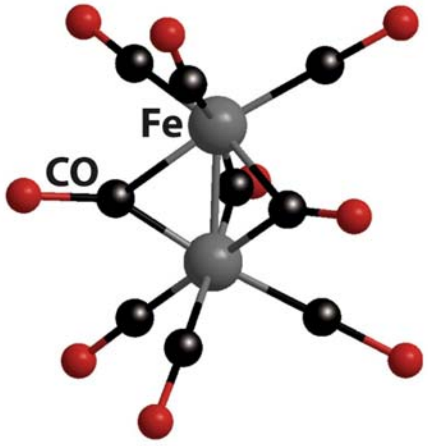
„triple decker“



74 $[Ni_2(Cp)_3]^+$

Structure 21-74
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Important ligands and their bonding types
(the variety of metallocene: clusters and carbonyls)



77 $[Fe_2(CO)_9]$

Structure 21-77
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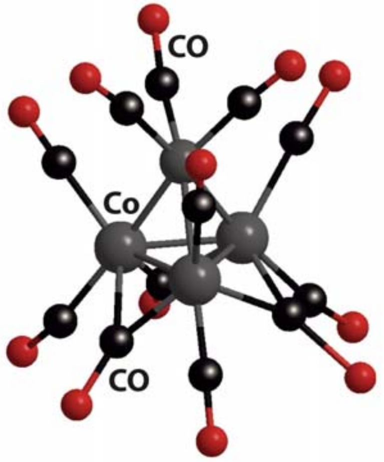

76 $[Co_4(CO)_{12}]$

Structure 21-76
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Table 21.5 Formulas and electron count for some 3*d*-series carbonyls

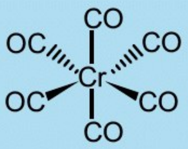
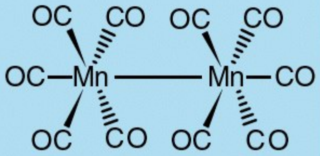
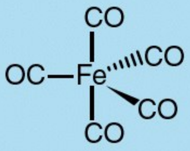
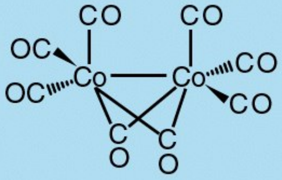
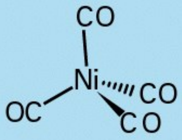
Group	Formula	Valence electrons		Structure
6	$Cr(CO)_6$	Cr 6(CO)	6 12 18	
7	$Mn_2(CO)_{10}$	Mn 5(CO) M—M	7 10 1 18	
8	$Fe(CO)_5$	Fe 5(CO)	8 10 18	
9	$Co_2(CO)_8$	Co 4(CO) M—M	9 8 1 18	
8	$Ni(CO)_4$	Ni 4(CO)	10 8 18	

Table 21-5
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Important ligands and their bonding types

(isolobal analogies as helpful tool for the interpretation of chemical bonding)

isolobal analogies allow correlations between seemingly unrelated fragments

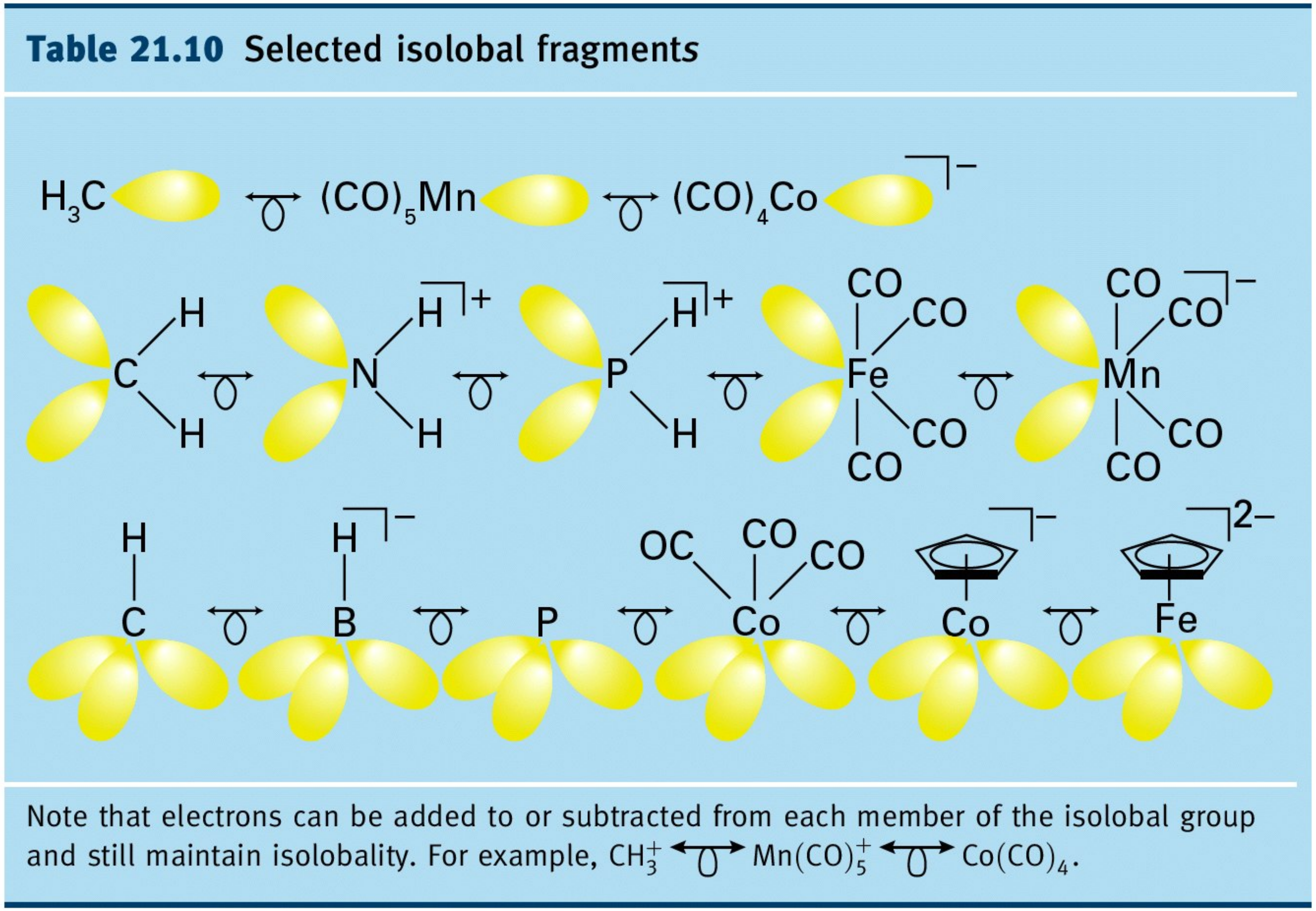

Table 21.10 Selected isolobal fragments

Note that electrons can be added to or subtracted from each member of the isolobal group and still maintain isolobality. For example, $CH_3^+ \underset{\circ}{\longleftrightarrow} Mn(CO)_5^+ \underset{\circ}{\longleftrightarrow} Co(CO)_4$.

Table 21-10
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