# Metal-Ligand Bonding and
Inorganic Reaction Mechanisms
Year 2

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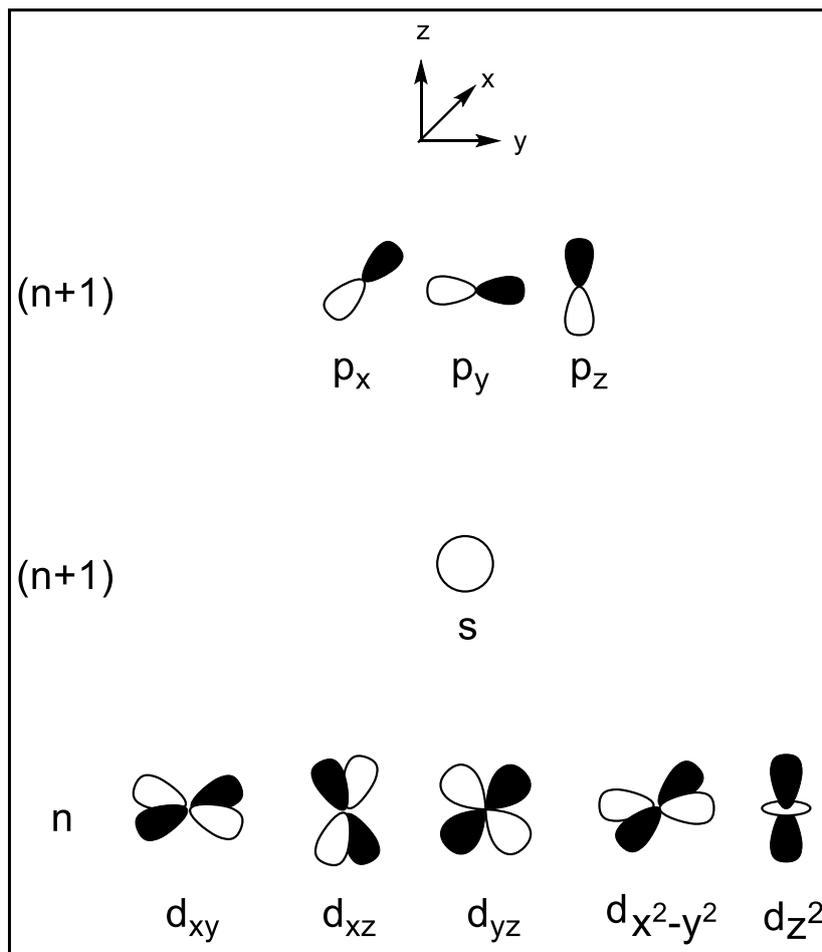
Metal-ligand and metal-metal bonding of the transition metal elements

Synopsis

Lecture 1:
Trends of the transition metal series. Ionic vs Covalent bonding. Nomenclature. Electron counting.

Lecture 2:
Thermodynamics of complex formation. Why complexes form. Recap of molecular orbital theory. 18-electron rule.

Lecture 3:
Ligand classes. σ-donor complexes. Octahedral ML_6 molecular orbital energy diagram.

Lecture 3:
$\pi-$acceptor ligands and synergic bonding. Binding of CO, CN^-, N_2, O_2 and NO.

Lecture 4:
Alkenes, $M(H_2)$ vs $M(H)_2$, $M_n(O_2)$ complexes, PR_3.

Lecture 5:
$\pi-$donor ligands, metal-ligand multiple bonds, O^{2-}, R_2N^-, RN^{2-}, N^{3-}.

Lecture 6:
ML_6 molecular orbital energy diagrams incorporating $\pi-$acceptor and $\pi-$donor ligands. Electron counting revisited and link to spectrochemical series.

Lecture 7:
Kinetics of complex formation. Substitution mechanisms of inorganic complexes. Isomerisation.

Lecture 8:
Ligand effects on substitution rates (trans-effect, trans-influence). Metal and geometry effects on substitution rates.

Lecture 9:
Outer sphere electron transfer.

Lecture 10:
Inner Sphere electron transfer. Bridging ligands.

Learning Objectives: by the end of the course you should be able to

i) Use common nomenclature in transition metal chemistry.
ii) Count valence electrons and determine metal oxidation state in transition metal complexes.
iii) Understand the physical basis of the 18-electron rule.
iv) Appreciate the synergic nature of bonding in metal carbonyl complexes.
v) Understand the relationship between CO, the 'classic' π-acceptor and related ligands such as NO, CN, N_2, and alkenes.
vi) Describe the nature of the interaction between η^2-bound diatomic molecules (H_2, O_2) and their relationship to π-acceptor ligands.
vii) Describe the difference between π-acceptor and π-donor ligands, and why exceptions to the 18-electron rule occur mainly for the latter.
viii) Qualitatively describe metal-ligand multiple bonding
ix) To be familiar with common reaction types, in particular ligand substitution reactions (square planar and octahedral complexes)
x) To appreciate the distinctions between associative, dissociative and interchange pathways
xi) To understand the trans-effect, the trans-influence and origin of the spectrochemical series.
xii) To understand the principles of outer-sphere and inner-sphere electron transfer
xiii) To be able to comment on factors that indicate if electron transfer occurs by an outer- or inner-sphere mechanism

Bibliography:

|	
Shriver and Atkins	"*Inorganic Chemistry*" Ch 8, 9, 19, 21.
Cotton, Wilkinson, Murillo and Bochmann	"*Advanced Inorganic Chemistry*"Ch 11, 16
Greenwood and Earnshaw	"*Chemistry of the Elements*" Ch 19, 20-28.
Owen and Brooker	"*A Guide to Modern Inorganic Chemistry*"
Mayer and Nugent	" Metal-Ligand Multiple Bonds"
R. A. Henderson	"*The Mechanisms of Reactions at Transition Metal Sites*, 1995."

Further reading

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Orbital Ordering	Keller, *J. Chem. Education.* 1962, **39**, 289; and Schwarz *ibid.* 2010, **87**, 444.
Electron Counting	Huheey, Keiter and Keiter, Inorganic Chemistry, 4th Ed pages 625-630.
Bonding	Murrell, Kettle and Tedder "*The Chemical Bond*" Tetrahedron, 1982, **38**, 1339.
Outer Sphere electron transfer	R. A. Marcus, *Angew. Chem. Int. Ed.* 1993, **32**, 1111.

Associated Courses

|		
AKDK	Transition metal chemistry	1st year
JML	Structure and bonding	1st year
CED	Atomic structure	1st year
JML	Main group chemistry	1st year
DWB	Group theory	2nd year
SBD	Organometallic chemistry	2nd year
DWB	Physical methods for structure determination	2nd year
AP	Dynamic Electrochemistry	2nd year
TJD	Processes at solid surfaces	3rd year
RNP	Photochemistry and UV spectra	3rd year
PHW	Bioinorganic chemistry	3rd year
RED	Inorganic materials chemistry	3rd year
PHW	f-block chemistry	3rd year
PAOB	Asymmetric synthesis	3rd year
IJSF	Metal mediated synthesis	3rd year
	Catalysis option	
	Bioinspired Chemistry option	
	Chemistry and Disease option	
	Reaction Intermediates and Pathways option	

Why is metal ligand bonding important?

Catalysts – e.g. polymers, pharmaceuticals, bulk chemicals, environmental

$[(\eta^5\text{-}C_5H_5)_2TiCl_2]$
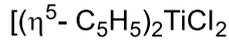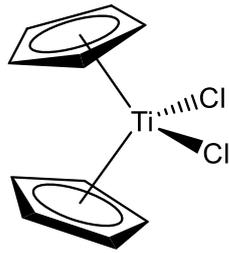
Alkene polymerisation precatalyst

$[Rh(H)(PPh_3)_3]$
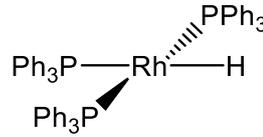
Hydrogenation precatalyst
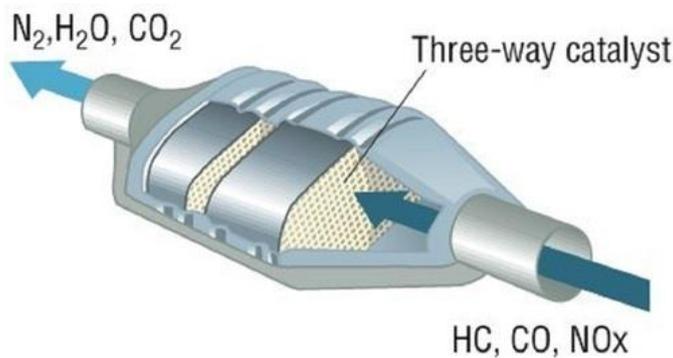

Catalytic converter for automobile

Biochemistry – e.g. oxygen transport, photosynthesis, enzymes, medicines, poisons

oxygen binding
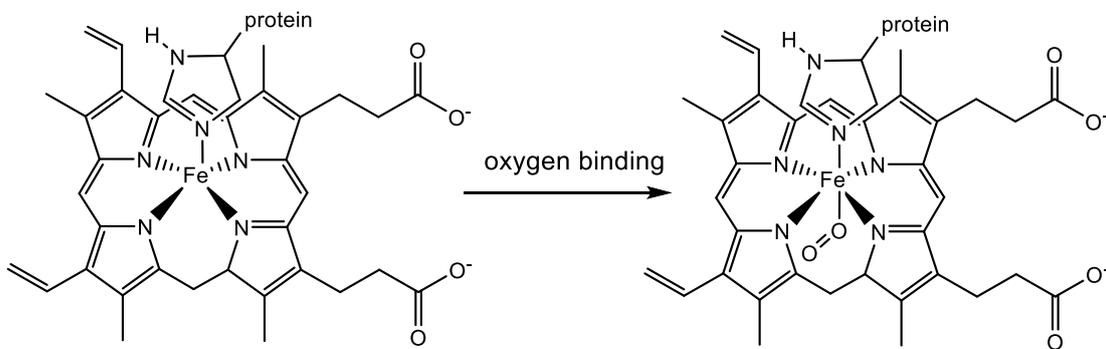
Haemoglobin and myoglobin
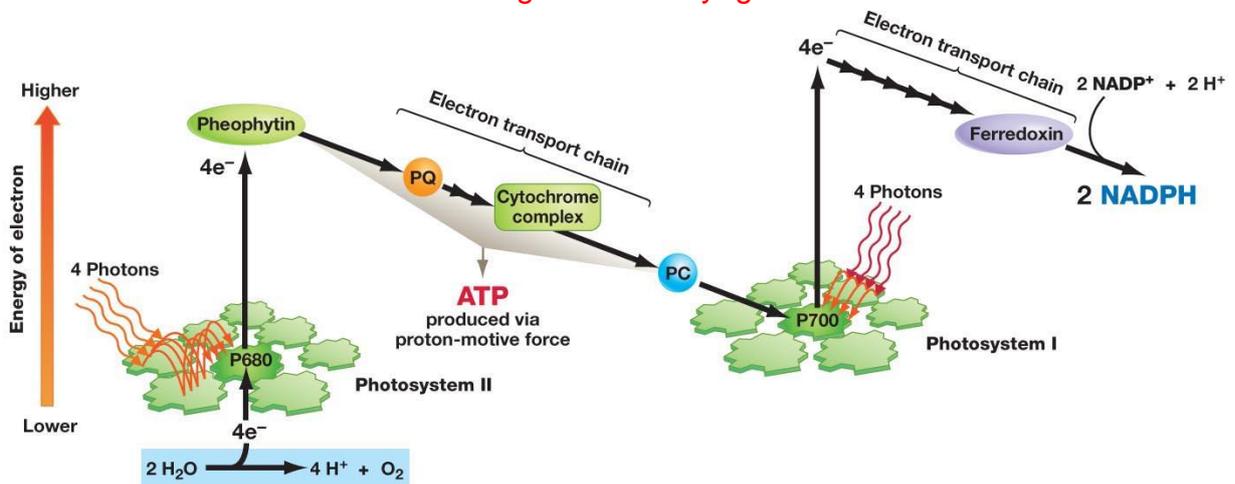
Photosynthesis

'Organic' chemistry methodology – e.g. $M(CO)_3$ arenes, Pd catalysed C-X (X = C, N, S, O) bond formation, metathesis.

enhanced nucleophilic substitution

enhanced solvolysis

enhanced acidity

enhanced acidity

steric hindrance
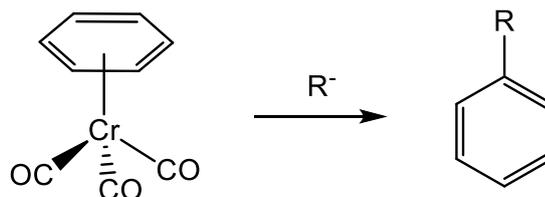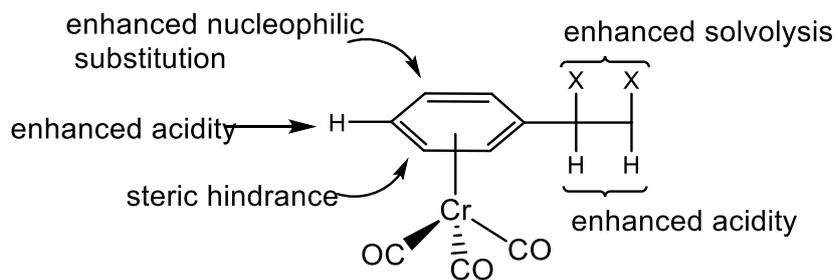
Inorganic Materials- e.g. magnets, batteries, dielectrics, lasers

$BaTiO_3$

Ba ⬤   Ti ⬤   O ◯

Dielectrics
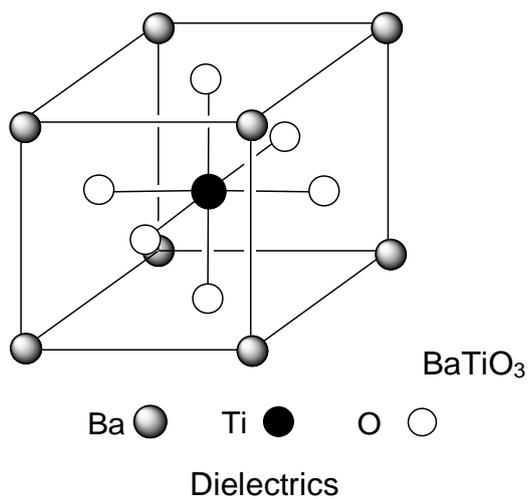
capacitors, microphones and thermal cameras

Smartphone technologies

This course is primarily concerned with the transition metals ('d-block' metals).

Recap
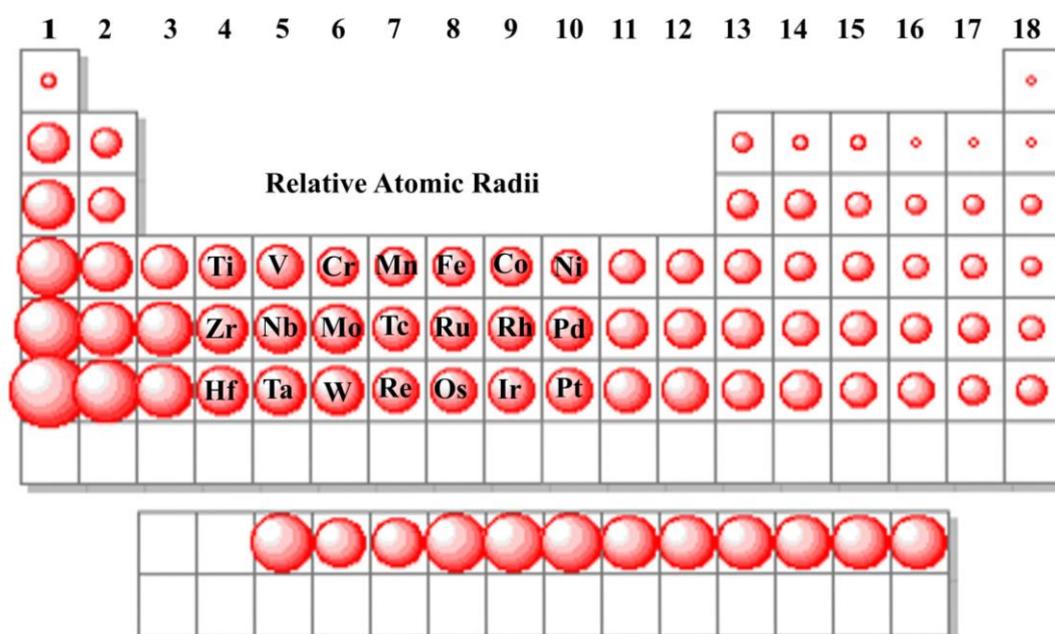
Important trends:

1. Radius (Covalent/ionic) :- Increases from right to left and down a group.

2. Electropositivity:- electropositive character increases from right to left and down a group.

The trends observed in 1 and 2 are a result of the effective nuclear charge (Z_{eff}) that is a consequence of *shielding* and *penetration*. $s > p > d > f$

The relatively very poor shielding of an electron in an *f*-orbital results in a steady decrease in the radii of the lanthanides (approximately 25%). This is known as the lanthanide contraction. With respect to the transition metals the result is that the radii of the 2nd and 3rd row transition metals are very similar. E.g. Co(III) (0.55), Rh(III) (0.67), Ir(III) (0.68). This has repercussions in metal-ligand bonding and hence chemical properties. In general when descending a group the 1st row transition metal is distinct in terms of its bonding and properties from the 2nd and 3rd row metals.

3. Variety in oxidation state:- earlier metals (group 4 to 7) exhibit the greatest variety in oxidation state. Higher oxidation states more commonly observed for 2nd and 3rd row metals.

e.g. Fe(III), Ru(VIII), Os (VIII).

4. Stronger bonds down a group (contrast to *p*-block)

Ionic vs covalent bonding

The $3d$ orbitals in the first row metals are not as diffuse as the 2nd and 3rd row $4d$ and $5d$ orbitals. This leads to a larger ionic component in the bonding of first row metal complexes. However in many cases the bonding in $3d$ metals can be described using covalent theories such as molecular orbital theory.

Compare this to the $4f$ orbitals of the lanthanides that are essentially core orbitals and cannot participate significantly in covalent bonding. The bonding in lanthanide complexes can be considered almost totally ionic and they are often considered to be more similar to the alkaline earth metals than the transition metals**.**

Nomenclature and electron counting

η **– hapticity** – the number of contiguous atoms of a ligand attached to a metal.

$\eta^1\text{-}O_2$ $\eta^2\text{-}O_2$ $\eta^6\text{-}C_6H_6$
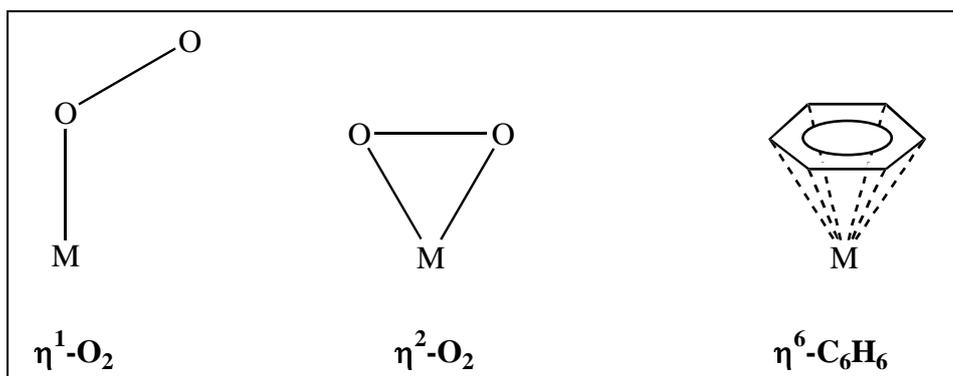
κ- **denticity**- the number of non-contiguous atoms coordinating from a ligand (often a chelating ligand)

κ^1-ethylene diamine κ^2-ethylene diammine
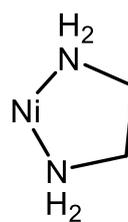
μ – The number of metal atoms bridged by a ligand

$\mu_2\text{-}CO$ $\mu_3\text{-}CO$
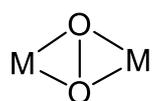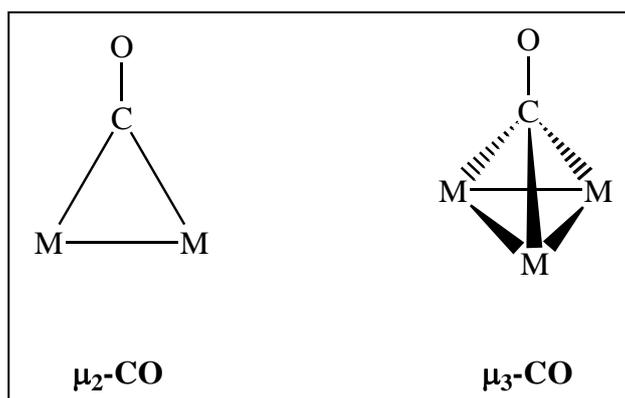
$\eta^2, \mu_2 \text{-} O_2$ $\mu_2 \text{-} O_2$
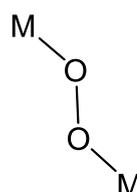
η^1 taken as default

Electron Counting

i) Metal oxidation state

$$\text{Oxidation state} = \frac{\text{Charge on the}}{\text{complex}} - \frac{\text{Sum of the charges}}{\text{of the ligands}}$$

Examples of formal charges on some ligands

+1 NO (linear)

0 CO, NR_3, PR_3, N_2, O_2, H_2, C_2H_4, H_2O, RCN, C_6H_6

-1 H, CH_3, F, Cl, Br, I, C_5H_5, CN, NO_2, NR_2, NO (bent)

-2 O, S, CO_3, NR, porphyrin

-3 N, P

e.g. $Ti(CH_3)_4$: $0 - (4 \times -1) = +4$ <u>Ti(IV)</u>

$[CoCl_6]^{3-}$: $-3 - (6 \times -1) = +3$ <u>Co(III)</u>

$[Co(NH_3)_6]^{3+}$: $+3 - (6 \times 0) = +3$ <u>Co(III)</u>

Ignoring NO the charge (n-) can be determined by adding H^+ until a neutral molecule is obtained

$$L^{n-} + n\,H^+ \longrightarrow H_nL$$

e.g. Cl^{n-} + $n\,H^+$ $\longrightarrow$ HCl n=1

CH_3^{n-} + $n\,H^+$ $\longrightarrow$ HCH_3 (CH_4) n=1

NR^{n-} + $n\,H^+$ $\longrightarrow$ H_2NR n=2

CO + $n\,H^+$ $\longrightarrow$ CO n=0

PPh_3^{n-} + $n\,H^+$ $\longrightarrow$ PPh_3 n=0

RC(O) + $n\,H^+$ $\longrightarrow$ RC(O)H n=1
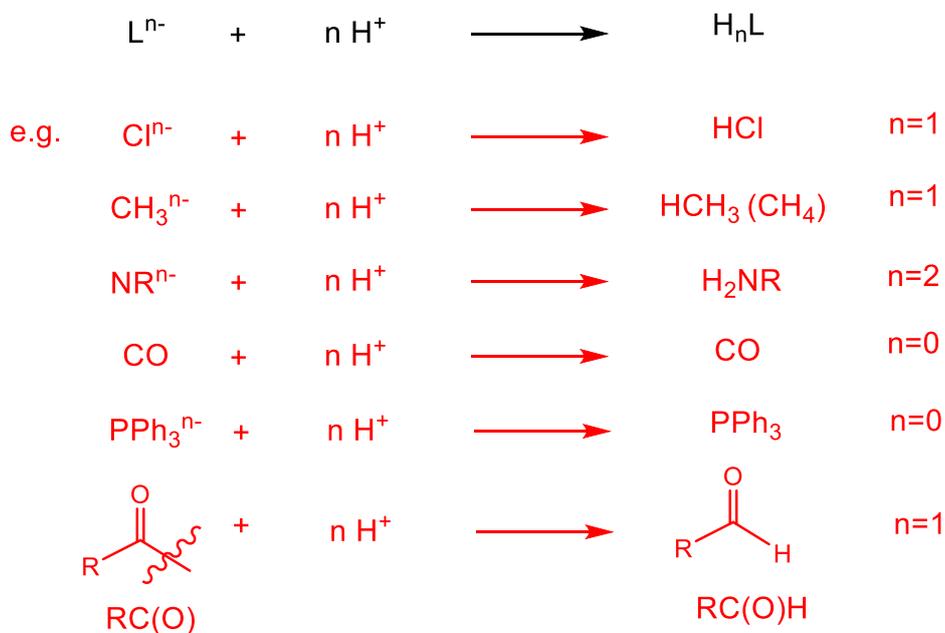
Electroneutrality principle

The electronic structure of substances is such to cause each atom to have essentially zero resultant charge. No atom will have an actual charge greater than ± 1. *i.e. the formal charge is not the actual charge distribution*.

e.g. Photoelectron spectroscopy (PES) is a technique that allows the experimental determination of orbital energies.

| Ir(V) | Ir(III) | Ir(I) |
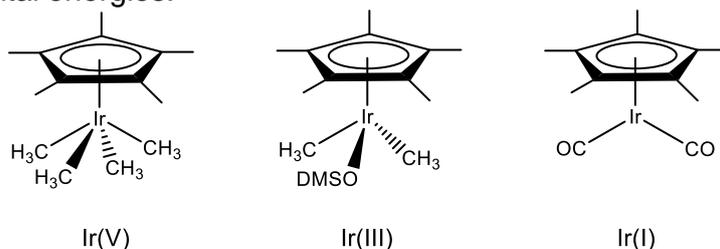
PES shows that all three iridium complexes have similar d-orbital energies indicating that the formal oxidation state is not the actual charge on the metal.

ii) metal d-electron count

$$\textbf{d-electron count} = \text{group number} - \text{oxidation state}$$

iii) Total valence electron count (TVEC) at the metal

$$\begin{array}{l}\textbf{Total Valence} \\ \textbf{Electron Count} \\ \textbf{(TVEC)}\end{array} = \begin{array}{l}\text{d-electron} \\ \text{count}\end{array} + \begin{array}{l}\text{electrons donated} \\ \text{by the ligands}\end{array} + \begin{array}{l}\text{number of} \\ \text{metal-metal bonds}\end{array}$$

(ignore overall charge on complex)

There are two methods that are commonly used and it is very important to avoid confusion.

M-L $\longrightarrow$ M· + L·   neutral (or radical) formalism

M-L $\longrightarrow$ M$^+$ + L$^-$ ionic formalism

To avoid confusion we will use the ionic formalism to determine the total number of valence electrons (electron count). However for some ligands O_2, NO and organometallics (carbenes, carbynes) the neutral formalism is more appropriate.

Number of electrons donated by each ligand (using ionic formalism)

2e CO, RCN, NR_3 (amines), PR_3 (phosphines), N_2, **O_2**, C_2R_4 (alkenes), H_2O, H^-, CH_3^- (or any alkyl or aryl group, R), F^-, Cl^-, Br^-, I^-, CN^-, NR_2^- (bent), $(\eta^1\text{-}C_5H_5)^-$

4e $R_2PCH_2CH_2PR_2$ (bis-phosphines), η^4-dienes, NR_2^-(linear), $(CH_3CO_2)^-$, NR^{2-}(bent), O^{2-} (double bond), S^{2-}

6e $(\eta^5\text{-}C_5H_5)^-$, $\eta^6\text{-}C_6H_6$, NR^{2-} (linear), O^{2-} (triple bond), N^{3-}, P^{3-}

Metal-metal bonds

Single bond counts 1 per metal

Double bond counts 2

Triple bond counts 3

Quadruple bond counts 4

Metal – metal bonding is more common for 2nd and 3rd row metals than for 1st row.

e.g.

$Cr(CO)_6$: 6 + (6 x 2) = 18 $[Co(NH_3)_6]^{3+}$: 6 + (6 x 2) = 18

$[CoCl_6]^{3-}$: 6 + (6 x 2) = 18 $PtBr_2(PPh_3)_2$: 8 + (2 x 2) + (2 x 2) = 16

c.f.   Cl————Cl
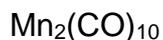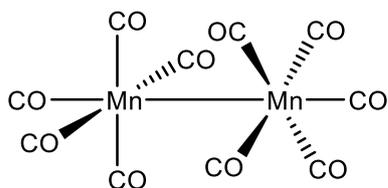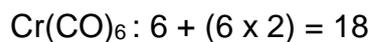
7 valence electrons each.
Electron sharing gives a count of 8 per Cl

$Mn_2(CO)_{10}$
per Mn: 7 + (5 x 2) + 1 = 18

	Coordination number	metal oxidation state	d-electron count	total valence electrons
$Cr(CO)_6$	6	0	6	18
$[Co(NH_3)_6]^{3+}$	6	III	6	18
$[CoCl_6]^{3-}$	6	III	6	18
$PtBr_2(PPh_3)_2$	4	II	8	16
$Rh(CO)(H)(PPh_3)_3$	5	I	8	18
$TiCl_4$	4	IV	0	8
$Cr(\eta^6\text{-}C_6H_6)_2$	6	0	6	18
$Fe(\eta^5\text{-}C_5H_5)_2$	6	II	6	18
$[ReOCl_5]^-$	6	VI	1	15 (17)

Why complexes form

$$\Delta G = \Delta H - T\Delta S = -RT \ln K_f \quad (K_f = \text{formation constant})$$

Enthalpic effects

1. The number and strength of metal-ligand bonds.

The greater the number of ligands, and the stronger the bonds, the greater the thermodynamic stability of the resulting complex. i.e. in general the more ligands the better. Larger metals can accommodate more ligands. In general coordination numbers are greater for the earlier transition metals (groups 4 – 7) compared to the later ones. Coordination numbers for lanthanide complexes are generally higher than for transition metals. d^8 square planar complexes are stable because 4 strong bonds are collectively stronger than 6 bonds that would be collectively weaker for this electron configuration.

2. Steric factors.

The number of ligands is limited by ligand – ligand repulsion. The size of metals and common ligands leads to transition metals generally accommodating a maximum of six ligands hence the vast number of 6 coordinate transition metal complexes. For similar reasons there are many 9 coordinate lanthanide complexes.

3. The charge on the complex.

Large positive and negative charges cannot easily be supported. Continually removing electrons from a complex will result in increasingly large ionisation energies, and increasing the number of electrons will lead to large electron-electron repulsive forces. (for $M^{2+} \sim$ -200 kJ mol^{-1}, for $M^{3+} \sim$ -350 kJ mol^{-1})

4. The electronic configuration.

Crystal field stabilisation energy, Jahn-Teller distortion.

i) electrostatic attraction
ii) destabilisation of core electrons
iii) destabilisation of valence electrons
iv) CFSE
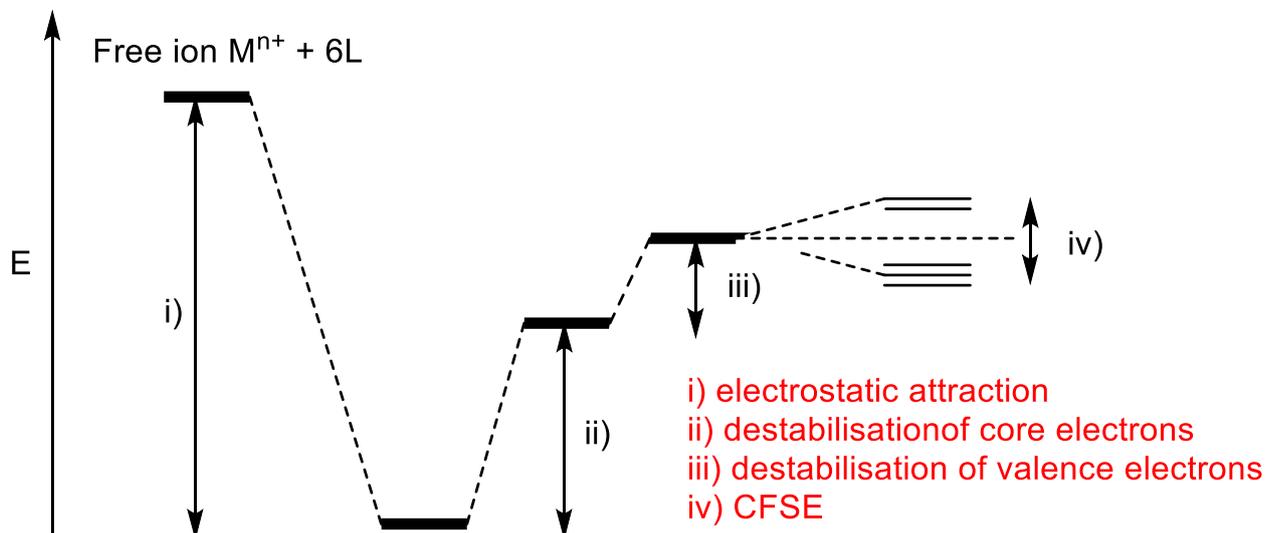
Note that crystal field stabilisation energy (CFSE) contributes only approximately 10% to the overall thermodynamic stability.

Entropic effects

1. number and size of any chelate rings

5 and 6 membered rings most stable (enthalpy due to least ring strain) and less likely to dissociate.

2. Solvation

Requirement for an ordered solvent cage lowers entropy. Solvent stabilises charge.

Molecular orbital description of metal-ligand bonding in a complex

Recap of molecular orbital theory

a) Orbitals must be of appropriate symmetry
b) Orbitals must overlap
c) Orbitals should be of similar energy
b) and c) determine the energy of the interaction. The interaction energy is stronger for orbitals that have good overlap and are close in energy.

When the MOs are made up of 2 component orbitals of different energies
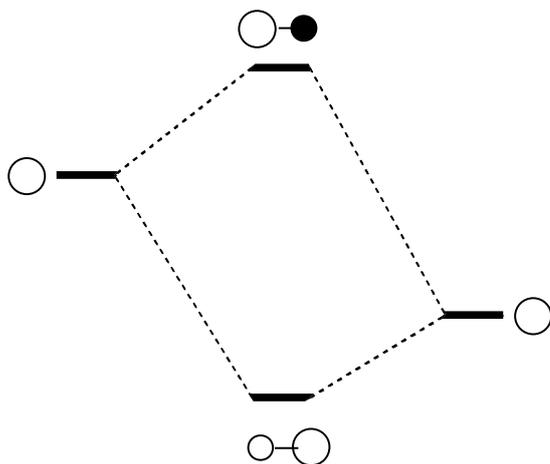
Rule of thumb

*The **bonding** orbital looks more like the **lower** energy component*

*The **antibonding** orbital looks more like the **higher** energy component*

Electronic configuration: Transition metal valence orbitals and the 18 electron rule

Valence shell of transition metals nd + $(n+1)s$ + $(n+1)p$ orbitals (where n = 3-5).
5 + 1 + 3 = 9 orbitals. Two electrons per orbital = **18 electrons**.
(Just a restatement of the Lewis octet rule with an extra 10 d-electrons)

Recap of Methane
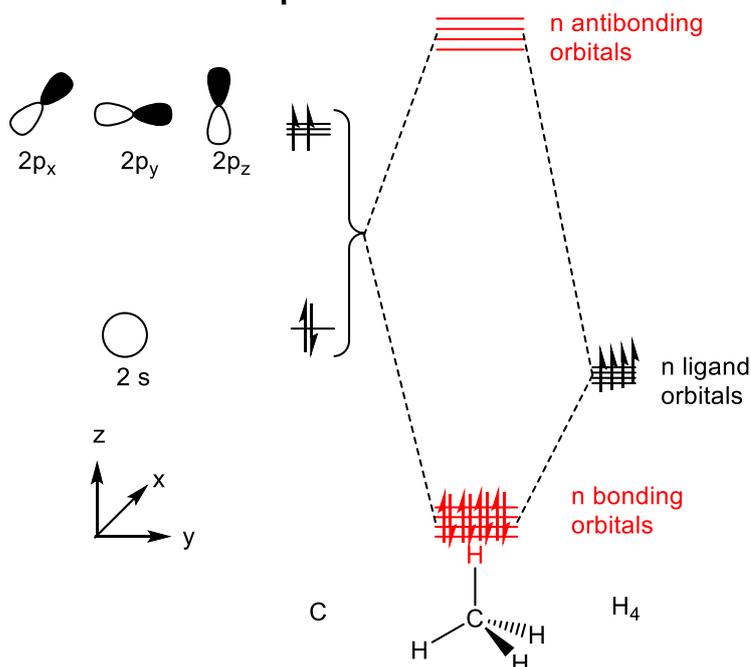
For an transition metal complex with n-ligands

e.g. an octahedral complex
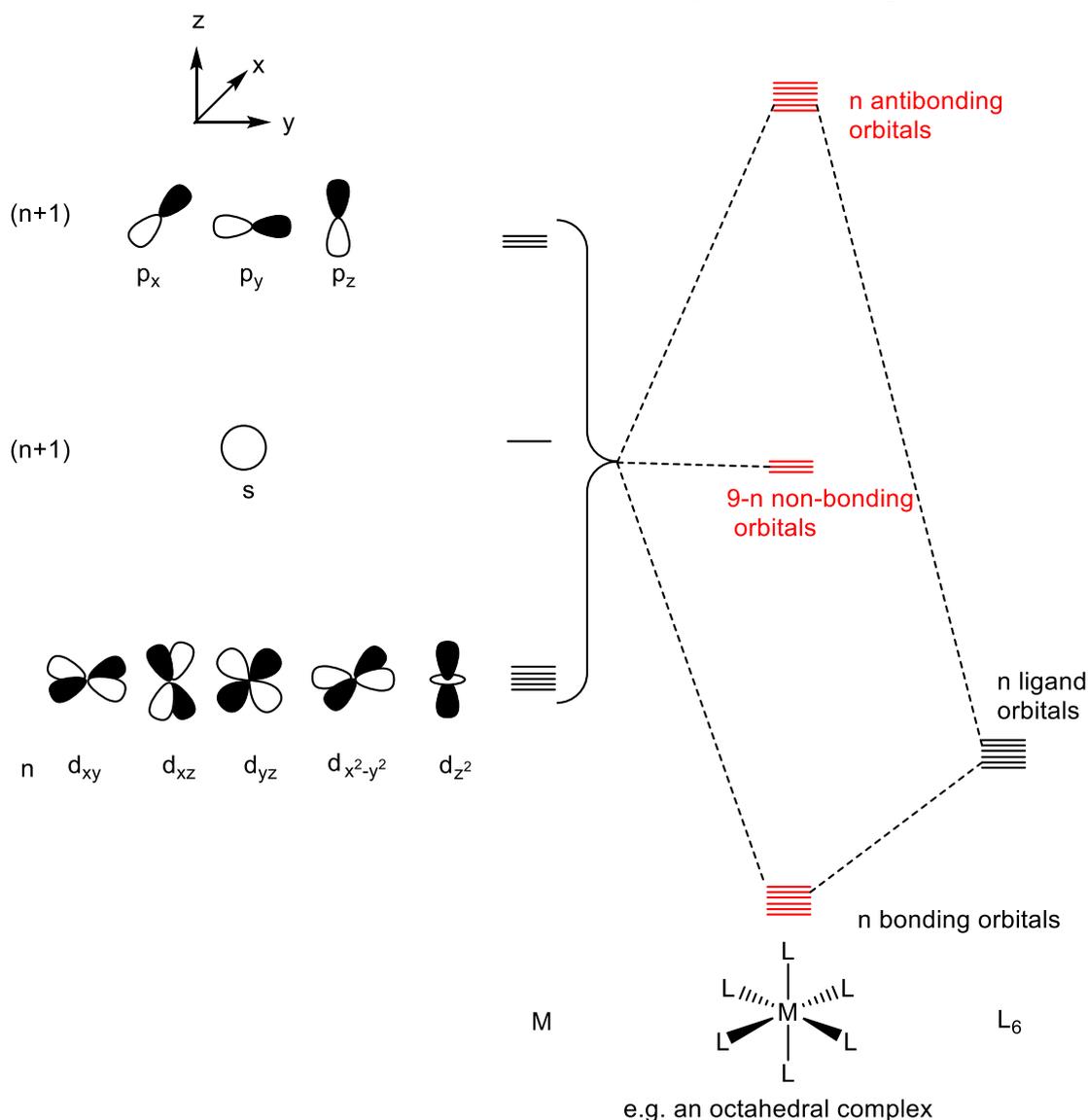
These diagrams not intended to represent degeneracy

For many complexes an electronic configuration of 18 valence electrons is the most thermodynamically stable, especially for diamagnetic organometallic complexes, however as noted earlier the electronic configuration is only one factor that contributes to the overall thermodynamic stability of a complex.

Can be highly predictive eg $Ni(CO)_4$, $Co(CO)_3NO$, $Fe(CO)_2(NO)_2$, $Mn(CO)(NO)_3$, $Cr(NO)_4$ isoelectronic 18e complexes but

There are many important exceptions to the 18 electron rule including:

- 1st row coordination complexes where the bonding is predominantly ionic. (see bioinorganic chemistry)
- square planar d^8 complexes (16 e⁻).
- early metal complexes with π-donor ligands.
- paramagnetic complexes with an odd number of electrons.

Ligand classification

Metal-ligand bonding can be divided into three basic classes

1. σ-donor

e.g. H, CH₃ (or any alkyl or aryl group, R), H₂O, NH₃, NR₂ (bent)

2. σ -donor, π-acceptor (sometimes referred to as 'π-acceptors' or 'π-acids')

e.g. CO, CN, NO, H₂, C₂H₄, N₂, O₂, PR₃, BR₂

3. σ -donor, π-donor (sometimes referred to as 'π-donors')

e.g. F, Cl, Br, I, O, OR, S, SR, N, NR₂(linear), NR (bent and linear), P, η³-C₃H₅, η⁵-C₅H₅, η⁶-C₆H₆

In terms of bond strength the σ-bond is much more important than π-bonding (donor or acceptor)

1. σ-donor

In these compounds the bond between the ligand and metal is a σ- bond. A good example of a σ-donor is hydride (H⁻). Some examples of transition metal hydrides are given below. Metal hydrides play a very important role in many catalytic reactions including hydrogenation and hydroformylation.
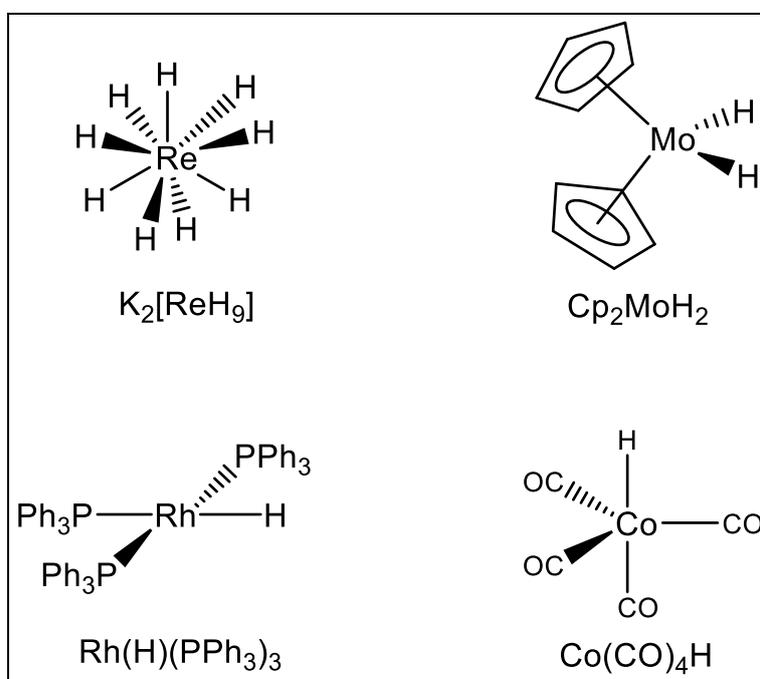
Characterisation of metal hydrides

IR: ν(M-H)~1750 cm⁻¹   NMR: Hydride resonance at high field (δ < 0ppm)
Neutron diffraction needed to locate hydrogen nuclei.

Molecular orbital diagram of a ML$_6$ complex (where L is a σ–donor ligand)

atomic orbitals

$\sigma*$ $2t_{1u}$

e.g. $[Co(NH_3)_6]^{3+}$

$(n+1)$ p_x p_y p_z t_{1u}

$\sigma*$ $2a_{1g}$

$(n+1)$ s a_{1g}

$\sigma*$ $\underline{2e_g}$

antibonding molecular orbital

a $2e_g$ orbital

$d_x{}^2$-y^2 $d_z{}^2$

n

e_g

atomic orbitals

d_{xy} d_{xz} d_{yz} t_{2g}

t_{2g}
nb π

e_g
t_{1u}
a_{1g}

bonding molecular orbital

σ $1e_g$

σ $1t_{1u}$

σ

e.g. 6 NH$_3$
lone pair
orbitals

a $1e_g$ orbital

$1a_{1g}$

metal in O$_h$ field

L—M—L ligands

ligands in O$_h$
arrangement
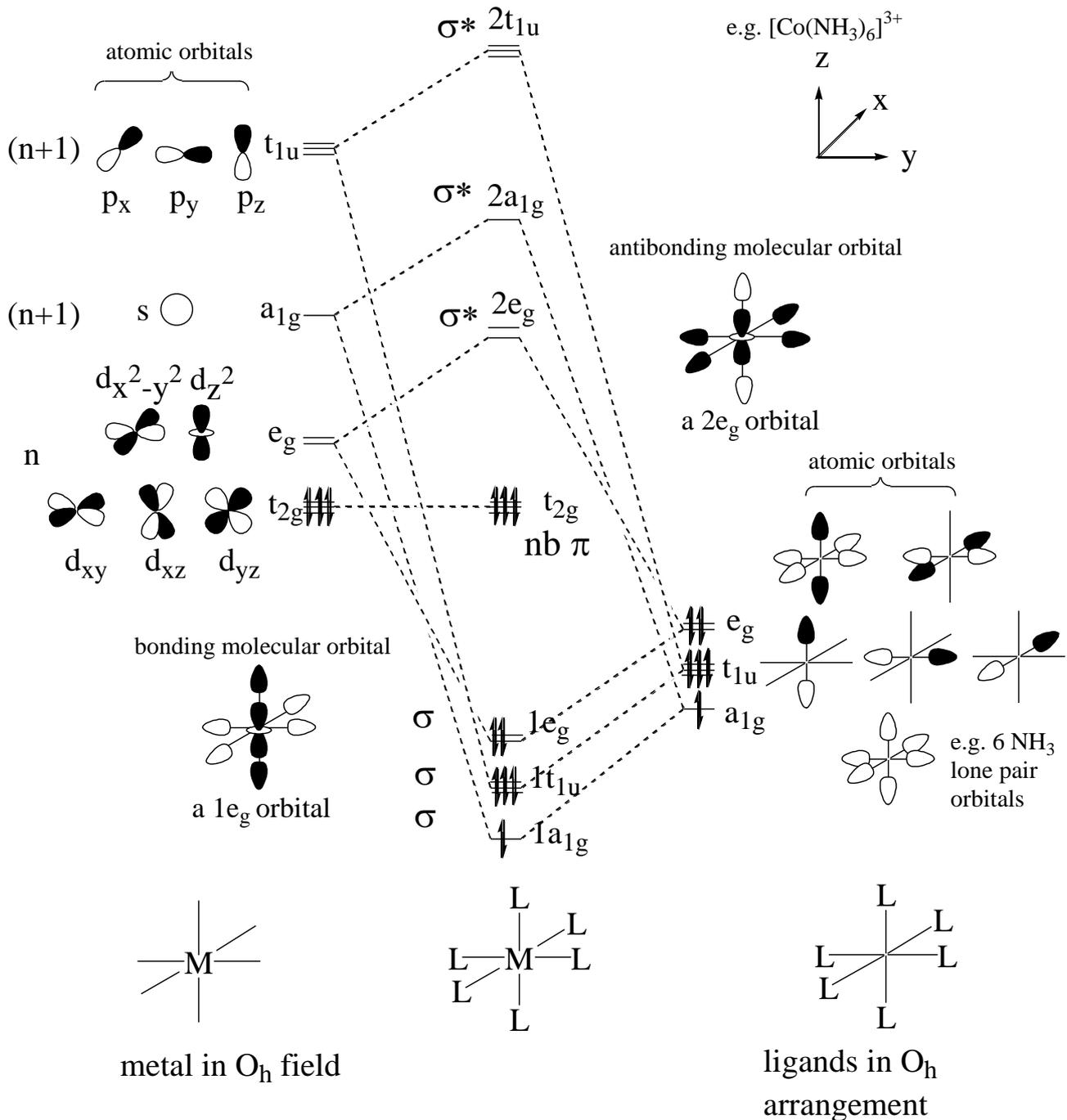
Note that there are no linear combinations of ligand orbitals that have t_{2g} symmetry. Therefore the t_{2g} orbitals are non-bonding, completely metal based and pure d-orbitals. The $2e_g$ orbitals are $\sigma*$ and have ligand character but are approximately 80% metal based. When we talk about splitting of metal 'd-orbitals' in crystal field theory we are ignoring the ligand character that is present in some of the 'd-orbitals', however it is still a good first approximation and the relative energies between d-orbitals are correct. We will see that when we include π-acceptors and π-donors that the t_{2g} orbitals are no longer pure metal orbitals but also contain some ligand character.

Notes on molecular orbital diagrams

1. The total number of molecular orbitals should be the sum of the number of precursor orbitals.

2. Only orbitals of the same symmetry can interact and the resulting molecular orbitals will have the same symmetry as the precursor orbitals

3. Where do the a_{1g}, e_g, t_{1u} linear combinations of atomic orbitals come from?
Using group theory it is possible to determine the symmetry of the orbitals involved.
i) determine the point group of the molecule (in this case O_h).
ii) treat the ligand orbitals (in this case σ) as a single entity and apply each symmetry element of the point group noting how many of the individual orbitals move under each operation. This is the *reducible representation*.
iii) determine which characters sum to the *reducible representation* thus obtaining the *irreducible representation*. (in this case for the octahedral array of σ-H orbitals it will be a_{1g} + e_g + t_{1u}).
iv) repeat for the 3 x *p* and 5 x *d* orbitals (the 1 x *s* can be read off directly as having a_{1g} symmetry) or alternatively look at the right hand portion of the group table and read off the orbital symmetries.
v) apply projection operators to determine the linear combinations of orbitals

4. The origin of symmetry labels nx_{yz}
Apart from being characters in group tables the labels can be used to describe the symmetry of orbitals.
n = orbitals of the same symmetry are numbered successively in order of increasing energy
x = a if singly degenerate and symmetrical to C_{2n} rotation about the principle rotation axis
x = b if singly degenerate and unsymmetrical to C_{2n} rotation about the principle rotation axis
x = e if doubly degenerate
x = t if triply degenerate
y = 1 if symmetrical to reflection through a reference mirror plane
y = 2 if unsymmetrical to reflection through a reference mirror plane
z = 'nothing' if there is no inversion centre
z = g if symmetrical to inversion
z = u if unsymmetrical to inversion

5. What group theory cannot tell us.
i) What the orbitals look like
i) The energy of the orbitals and the magnitude of the precursor orbital interactions

Comparison of Molecular Orbital and Crystal Field Theory

(From yr1 Transition Metal Chemistry) Crystal Field Theory compares the repulsive interactions between metal and ligand electrons to determine the ordering of metal d-orbitals. Crystal field theory is an electrostatic approach using pure metal d-orbitals.

$d_{x^2-y^2}$ d_{z^2} d_{xy} d_{xz} d_{yz}

$d_{x^2-y^2}$ ____

$d_{x^2-y^2}$ d_{z^2}

d_{xy} ——

Barycentre

d_{xy} d_{xz} d_{yz}

$d_{x^2-y^2}$ d_{z^2}

d_{xy} d_{xz} d_{yz}

d_{z^2} ____

d_{xz} d_{yz} ≡≡
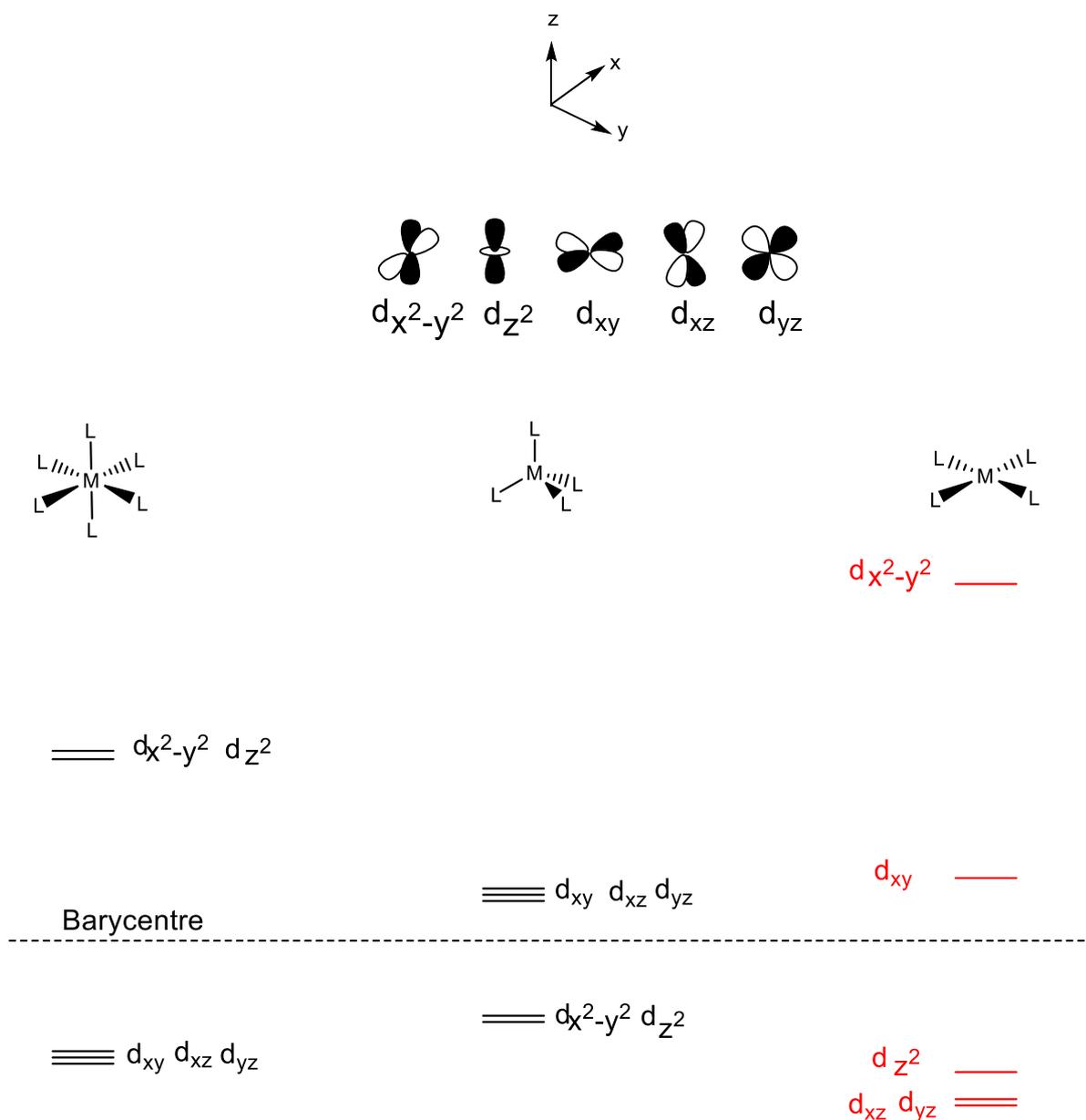
The ordering of the 'd-orbitals' is the same as the MO scheme but for CFT there is no knowledge of bonding or antibonding character and the absolute energies and Δ_O will differ. Can use CFT as a quick approximation to the metal 'd-orbital' ordering.

σ-donor, π-acceptor ('π-acceptors' or 'π-acids')

These include: CO, CN, NO(linear), H_2, C_2H_4, N_2, O_2, PR_3, CR_2

We can view the metal-ligand bonding as a σ-donor interaction (same as for H) with an additional π- interaction that arises from overlap between occupied metal-based orbitals and empty ligand orbitals that can *accept* electron density.

Metal complexes of CO are a good example.

e.g. Some of the binary metal carbonyls

Group5	6	7	8	9	10
$V(CO)_6$	$Cr(CO)_6$	$Mn_2(CO)_{10}$	$Fe(CO)_5$ $Fe_2(CO)_9$	$Co_2(CO)_8$	$Ni(CO)_4$
	$Mo(CO)_6$	$Tc_2(CO)_{10}$	$Ru(CO)_5$ $Ru_2(CO)_9$	$Rh_2(CO)_8$	
	$W(CO)_6$	$Re_2(CO)_{10}$	$Os(CO)_5$ $Os_2(CO)_9$	$Ir_2(CO)_8$	

Some structures
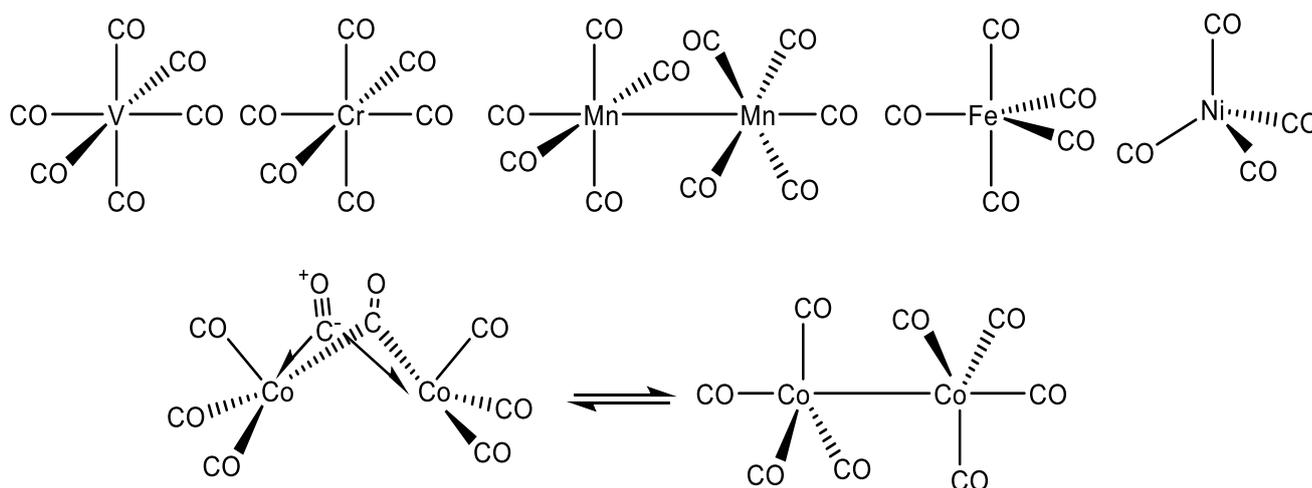
Note: Beware the formulation of complexes containing 3centre-2electron bonds such as those with bridging carbonyls. Many structures in text books and papers incorrectly include metal-metal bonds e.g. $Fe_2(CO)_9$ when none are present (see Chem. Commun., 2012, **48**, 11481).

MO diagram of CO
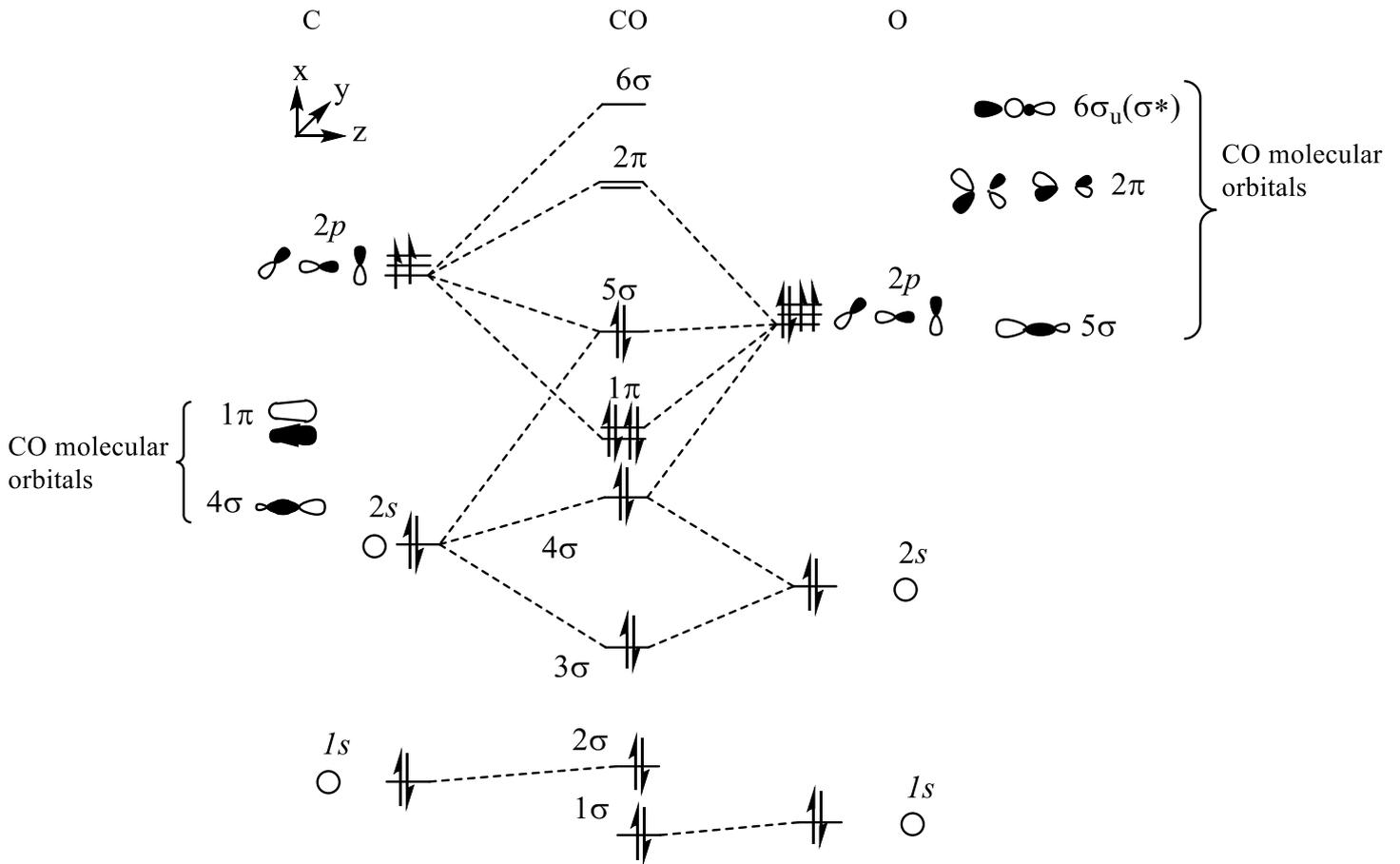
Frontier MO's often determine mode of bonding
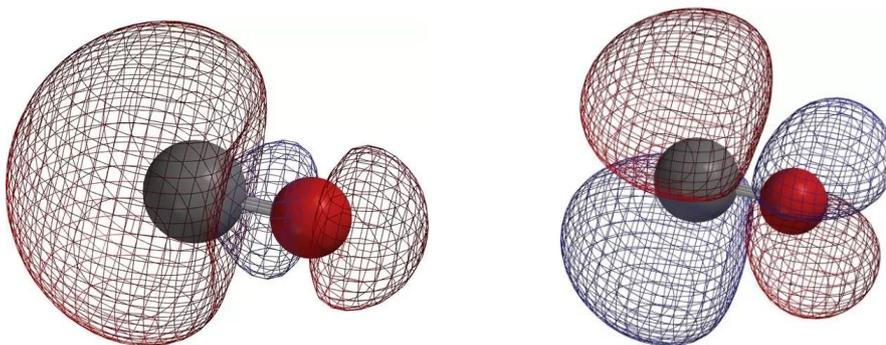
Electron density maps of 5σ and 2π orbitals

HOMO 5σ orbital is slightly bonding (or non-bonding) and has significant C 2*s* character. This is why CO bonds to a metal as a σ-donor through the C atom and not the O atom (better overlap).

In can be seen that the 2 x 2π LUMO orbitals (antibonding) are empty. It is these orbitals that can interact with metal d-orbitals accepting electron density.
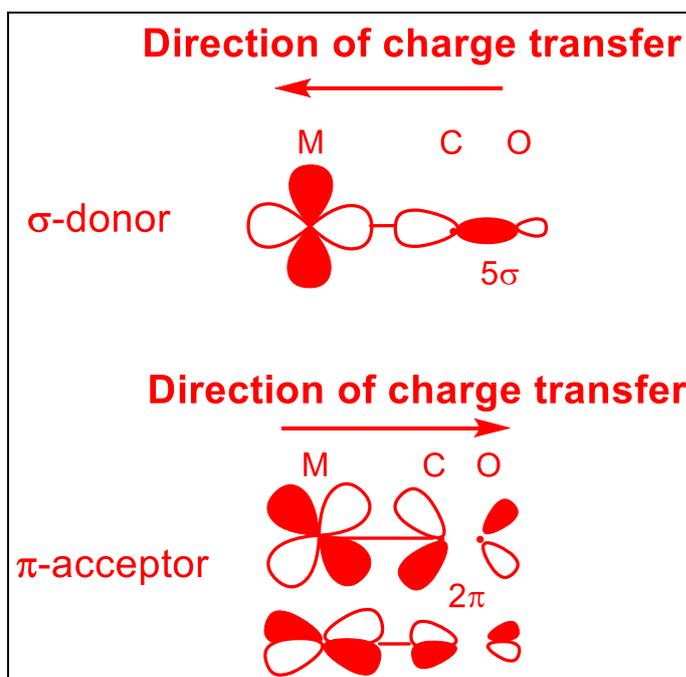
The σ-donor interaction increases the electron density on the metal and decreases the electron density on the CO ligand.

The π-acceptor interaction decreases the electron density on the metal and increases the electron density on the CO ligand.
Both effects 'reinforce' each other. Sometimes referred to as **synergic bonding**.

π -acceptor ligands such as CO can relieve negative charge build-up at a metal centre.
e.g. stabilise complexes with metals in a low formal oxidation state.

Experimental evidence for bonding model

IR and Raman spectroscopy and single crystal X-ray diffraction.

Characterisation of metal carbonyls

Typical covalent props: solubility, sublimation
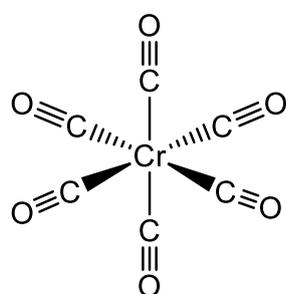
Cr-C = 195.5 pm
C-O = 114.0 pm
ν(C-O) = 1984 cm^{-1}
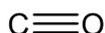
C-O = 112.8 pm
ν(C-O) = 2143 cm^{-1}

As ν(C-O) decreases C-O bonding decreases and M-C π-bonding increases

$$M-C\equiv O \implies M=C=O$$

Trends in ν(CO)

a) isoelectronic series	ν(CO) cm^{-1} (T_{1u})	b) as CO ligands are lost	ν(CO) cm^{-1}	c) as other ligands change	ν(CO) cm^{-1}
$Mn(CO)_6^+$	2094	$Mo(CO)_6$	1987	$Ni(CO)(PF_3)_3$	2073
$Cr(CO)_6$	1984	$Mo(CO)_5$	1966	$Ni(CO)(PCl_3)_3$	2059
$V(CO)_6^-$	1845	$Mo(CO)_4$	1944,1887	$Ni(CO)(PMe_3)_3$	1923
$Ti(CO)_6^{2-}$	1750	$Mo(CO)_3$	1862		

a) all d^6 but lower oxidation state implies greater electron density, therefore Ti(-II) exhibits the most back-donation, weakest CO bonds and lowest ν(CO).

b) All Mo(0) d^6. Fewer CO ligands share the metal electron density therefore $Mo(CO)_3$ exhibits weakest CO bonds and lowest ν(CO).

c) Electronegativity of F>Cl>Me. Back-donation of $PF_3 > PCl_3 > PMe_3$ which competes with CO back-donation for the metal electron density.

d) coordination mode

	Free	Terminal	μ_2-CO	μ_3-CO
ν_{CO} (cm^{-1})	2143	1850-2120	1750-1850	1620-1730

More metals = more electrons for back-donation and lower ν(CO)

Always think in terms of CO ligands competing for whatever electrons are available on the metal!

Non-classical carbonyls

	ν(CO)/cm^{-1}
$Pd(CO)_4^{2+}$	2248
$Pt(CO)_4^{2+}$	2244
$Ag(CO)_2^+$	2200
$Au(CO)_2^+$	2217
$Hg(CO)_2^{2+}$	2278

In these complexes electron density is not transferred from the metal to the ligand π-accepting orbitals. The major interaction is σ-donation from the CO 5σ orbital to the metal giving weak M-CO bonding. The CO stretching frequency is > free CO mainly due to electrostatic perturbation. (see JACS 1996, **118**, 12159)

Similar π–acceptor ligands

Other ligands that are expected to exhibit very similar bonding to CO are the isoelectronic ligands CN^- and NO^+. (We will see later that NO can also coordinate in an alternative terminal mode).

N_2 is also isoelectronic with CO.

MO diagram of N_2
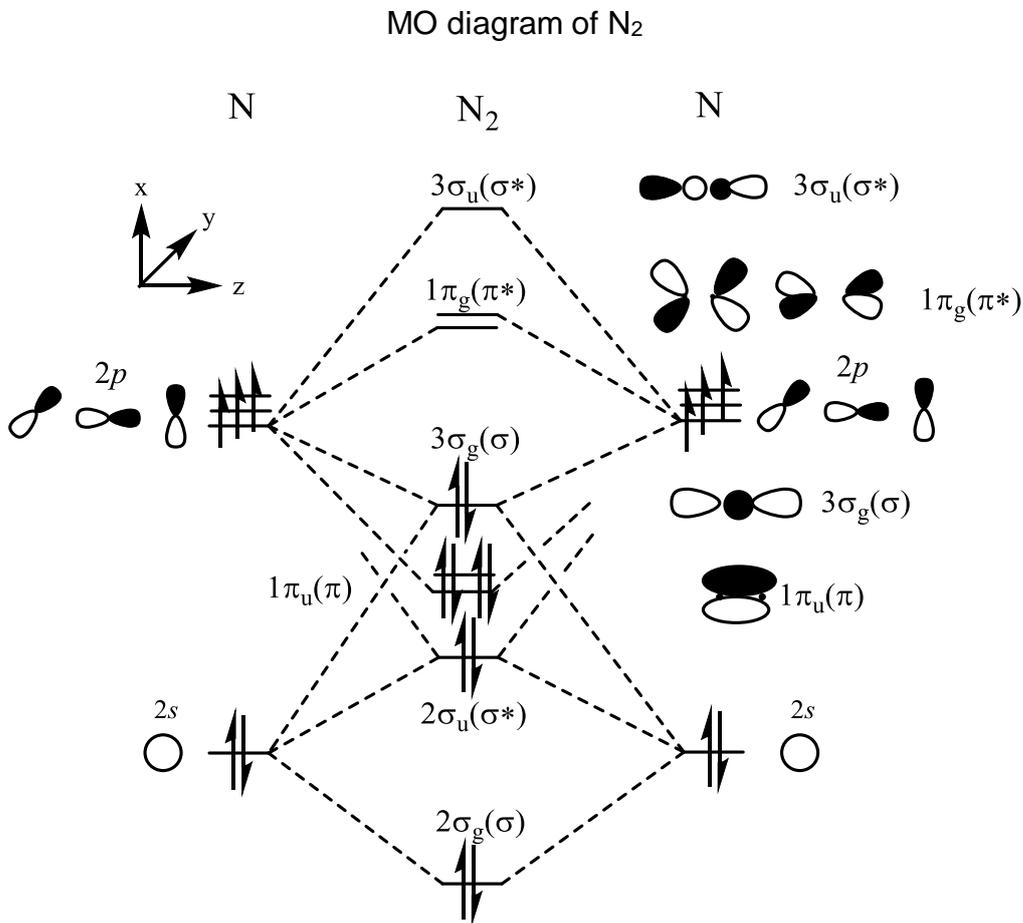
Compare HOMO 5σ (σ^*) of CO and HOMO $3\sigma_g$ (σ) of N_2.
Coordination of N_2 decreases N-N bond strength.
N_2 can act as a π-acceptor using LUMO $1\pi_g$ same as for CO.

Very few metal complexes of N_2 compared to CO and chemistry of N_2 is much less developed. The volume of the 3σ N_2 orbital used to bond to a metal is much less than that on the 5σ orbital on the carbon atom of CO.
The same argument also applies to the π-acceptor interactions.
Therefore the orbital overlap is less for the σ-donating and π-accepting interactions giving weaker bonding.

Other π–accepting ligands

Important examples include O_2, H_2, PR_3 and alkenes.

Complexes of dioxygen

haem

Ti(η^2-O$_2$)(porphyrin)

Cr(η^2-O$_2$)$_4$

haemocyanin
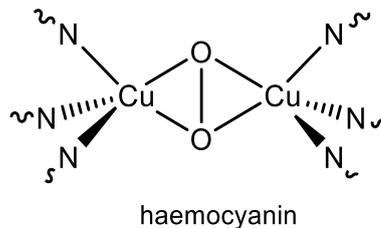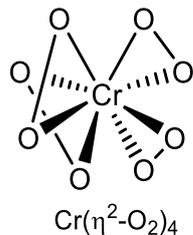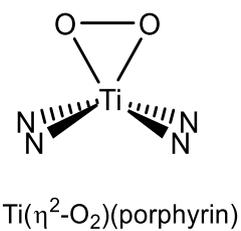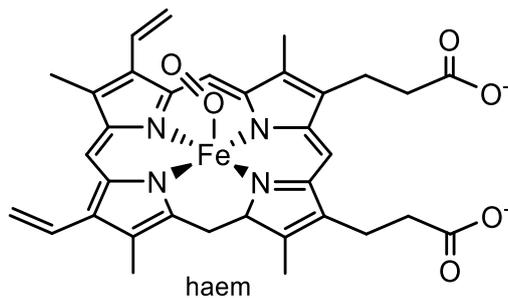
η^1 vs η^2 bonding in O₂ complexes

MO diagram of O₂

O   O₂   O

x
y
z

$3\sigma_u(\sigma*)$

$1\pi_g(\pi*)$

$2p$

$1\pi_u(\pi)$

$3\sigma_g(\sigma)$

$2\sigma_u(\sigma*)$

$2s$

$2\sigma_g(\sigma)$

$3\sigma_u(\sigma*)$

$1\pi_g(\pi*)$

$2p$

$1\pi_u(\pi)$

$3\sigma_g(\sigma)$

$2s$

HOMO and LUMO both in $\pi*$

η^1 - bonding

Direction of charge transfer

O
O
M
σ-donor
$1\pi_{gx}$

Direction of charge transfer

O
O
M
π-acceptor
$1\pi_{gy}$

η^2 - bonding (more difficult)

$M + O_2$ or $M^{2+} + O_2^{2-}$ Electron transfer first $1\pi_{gy}$ now full.

Direction of charge transfer   **Direction of charge transfer**

M
O
O
$1\pi_{gx}$

M
O
O
$1\pi_{gx}$

Direction of charge transfer

M
O
O
$1\pi_{gy}$

(no back-donation as 'accepting' orbitals are full)

O_2 is very oxidising. Think of as electron transfer followed by binding of O_2^{2-} to M^{2+}. Theory suggests this may be best option.

Characterisation – what is the oxidation state of O_2?

In any given complex, all we know for sure is that the O_2 molecule is bonded to the metal. Neutral dioxygen, superoxide (O_2^-) and peroxide (O_2^{2-}) are all well known forms of the 'O_2' unit, so any given complex could be {M-O_2}, {M^+-O_2^-} or {M^{2+}-O_2^{2-}}

$3\sigma_u(\sigma*)$

$1\pi_g(\pi*)$

$1\pi_u(\pi)$

$3\sigma_g(\sigma)$

O_2 O_2^- O_2^{2-}
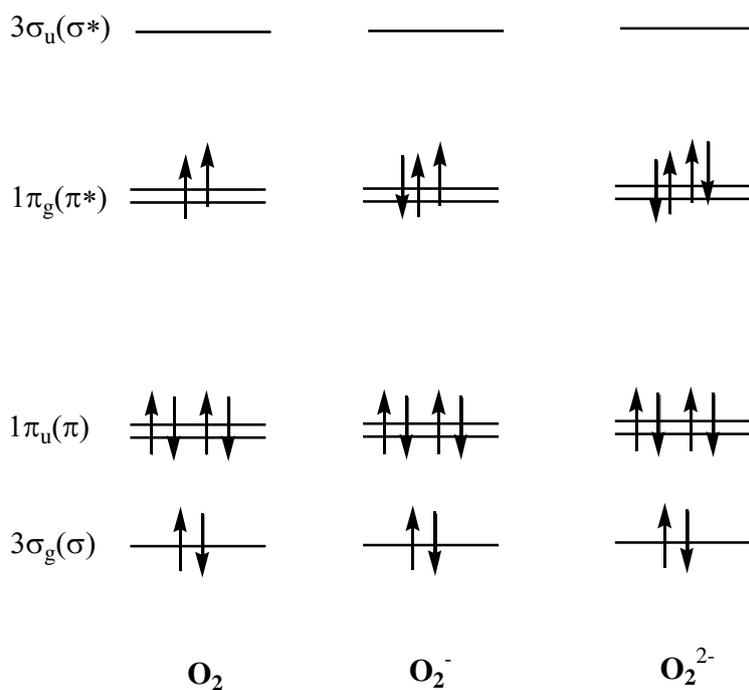
Comparison of MO diagrams of dioxygen, superoxide, and peroxide

Vibrational frequencies and O-O bond lengths

	r(O-O) / pm	ν(O-O) / cm^{-1}
$O_2^+(AsF_6^-)$	122	1858
O_2	121	1555
$O_2^-(K^+)$	133	1146
$O_2^{2-}(Na^+)_2$	149	842
η^1-O_2	115-130	1130-1195
η^2-O_2	130-152	800-930

As the electron density in the $\pi*$ orbitals increases the O-O distance increases and the vibrational frequency decreases

What happens if the $\sigma*$ ($3\sigma_u$) orbital becomes occupied?
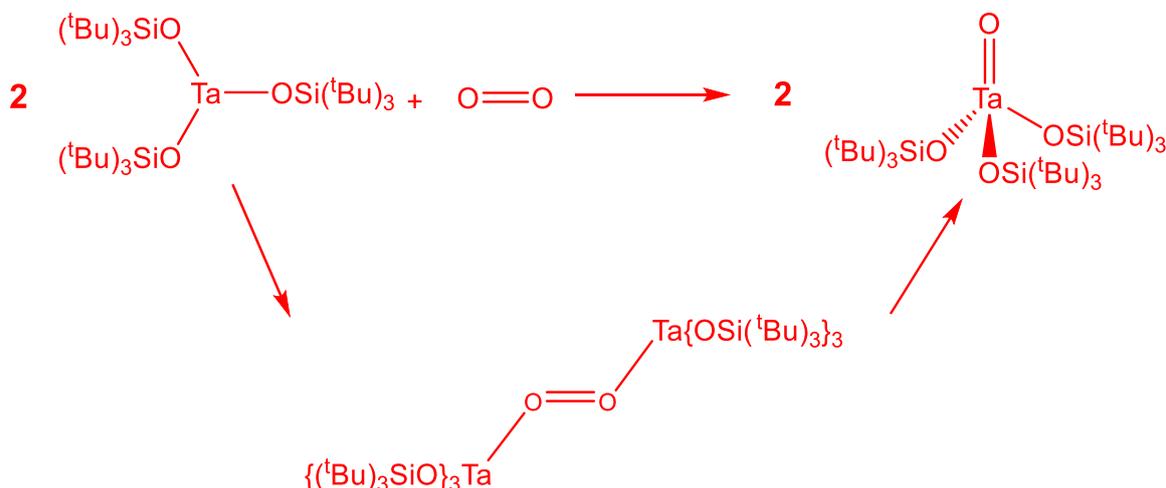
The Ta complex is reducing and has two electrons in a high-energy orbital HOMO. The Ta complexes have orbitals of the correct symmetry and can donate 4 electrons to a molecule of O_2 occupying $1\pi_g$ and $3\sigma_u$ of O_2 causing cleavage of the O_2 bond.

Why is η^1-O_2 bent when CO is linear?

Simply because O_2 has to accommodate an extra pair of electrons in the $1\pi_g$ ($\pi*$) orbital. These occupy $1\pi_{gx}$ (to form the σ-bond through one lobe of the $1\pi_{gx}$ orbital) leaving $1\pi_{gy}$ to form a π-acceptor interaction.

NO (a ligand that can change binding mode)

NO typically adopts one of two terminal coordination modes (bent and linear)

Cell signalling bound to Fe porphyrin (nobel prize), angina medication and viagra
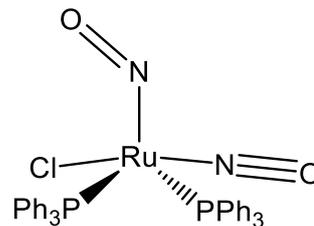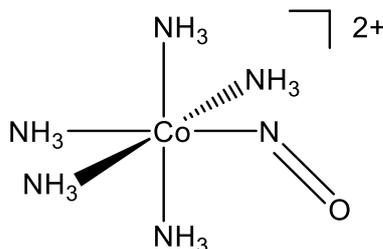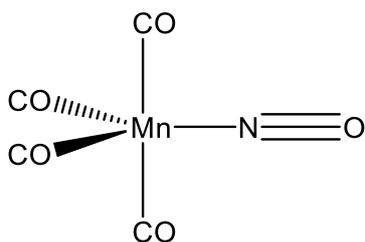
Characterisation

	M-N-O angle/ °	ν(N-O)/cm^{-1}
$Fe(CN)_5(NO)^{2-}$	178	1935
$Mn(CN)_5(NO)^{3-}$	174	1700
$Co(NH_3)_5(NO)^{2+}$	119	1610
$CoCl(en)_2(NO)^{+}$	124	1611

How many electrons does NO donate?

Linear:

i) 1 electron goes *from NO to the metal*, giving NO^+ + M^-.
ii) NO^+ is then isoelectronic with CO, and donates 2 electrons *from NO to metal*

2+1 = 3, so NO is a 3-electron donor.

Bent:

i) 1 electron goes *from metal to NO,* giving NO^- + M^+.
ii) NO^- is then isoelectronic with O_2, and donates 2 electrons *from NO to metal*

-1 + 2 = 1, so NO is a 1-electron donor

Strategy for determining bent or linear, electron count and oxidation state:
1) Remove NO (neutral) from complex and calculate electron count and oxidation state of remaining fragment.
2) Add 1 or 3 electrons per NO to increase electron count to 18 (or as close as possible without exceeding 18). You now have the total electron count at the metal and the M-NO geometry.
3) Determine the metal oxidation state of the complex including the NO ligand(s) and consider linear NO to be NO^+ and bent NO to be NO^-.

e.g.

	total valence electrons	metal oxidation state	d-electron count
$Mn(CO)_4(NO)$	18	-I	8
$Co(NH_3)_5(NO)^{2+}$	18	III	6
$RuCl(NO)_2(PPh_3)_2$	17	I	7

Dihydrogen (a reactive ligand)

Complexes of dihydrogen (H-H = 74.1 pm in H_2)

82 pm

H——H

P(Pr^i)$_3$—W—P(^{i}Pr)$_3$

CO, CO, CO

H

111 pm

H——H

P^{i}Pr$_3$—Ir—P^{i}Pr$_3$, Cl, H, Cl

H$_2$

160 pm

H--------H

PPh$_3$—Ir—PPh$_3$, CO, Cl

H

$1\sigma_u(\sigma^*)$

$1\sigma_u(\sigma^*)$

$1s$ $1s$

$1\sigma_g(\sigma)$

$1\sigma_g(\sigma)$

Direction of charge transfer

M

σ-donor   H, H $1\sigma_g(\sigma)$

Direction of charge transfer

M

π-acceptor   H, H $1\sigma_u(\sigma^*)$
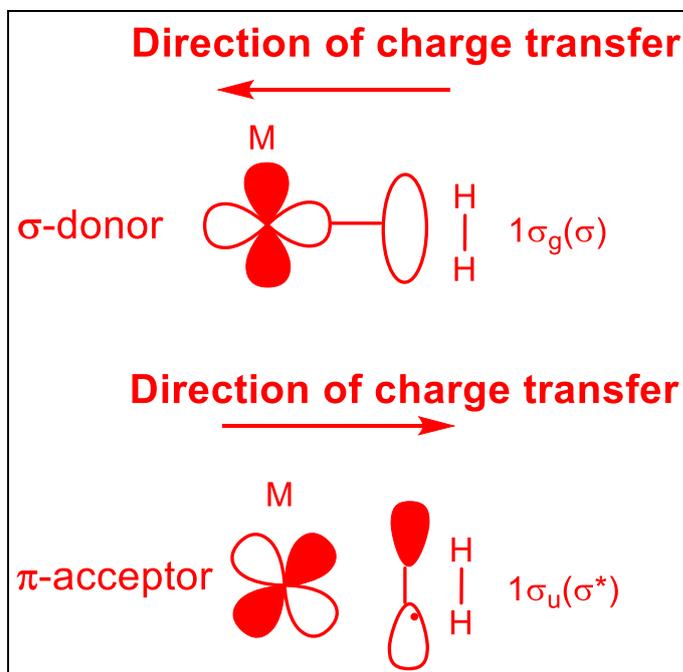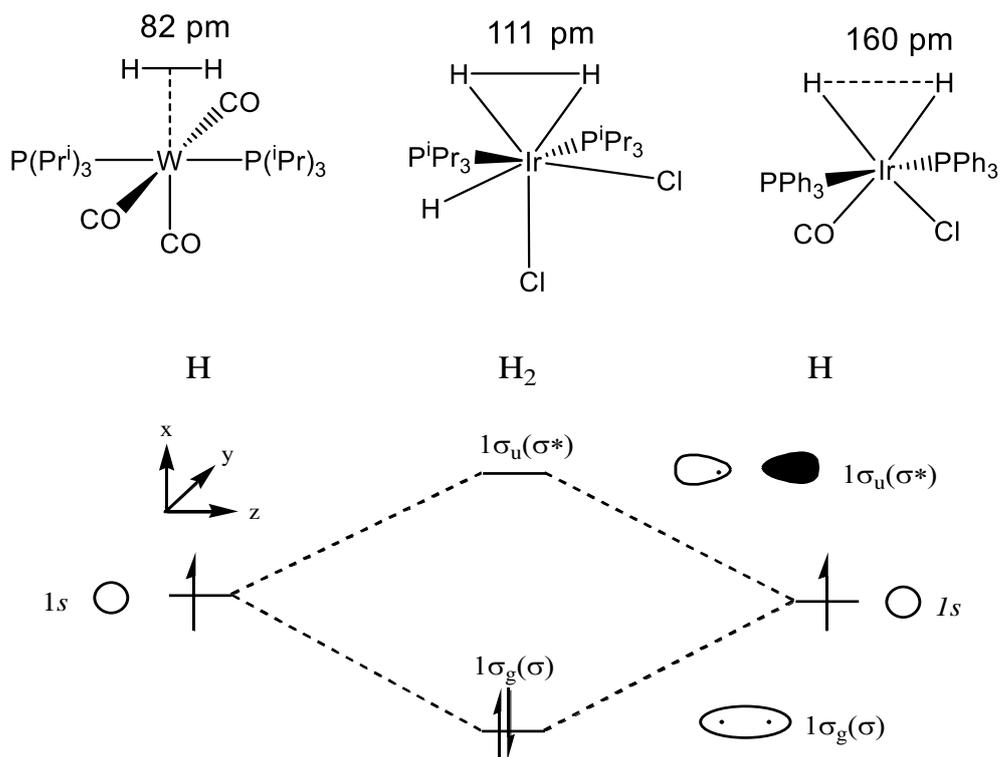
Note: the σ and σ* orbitals of H_2 perform the same roles as the σ and π* orbitals in CO.

The antibonding σ* H_2 orbital is of π-symmetry about an axis perpendicular to the H-H bond and can interact with a metal orbital of π-symmetry.

If sufficient electron density is transferred from the metal to the σ^* orbital of H_2 the H-H σ–bond will break and give two M-H (metal-hydride) σ–bonds (oxidative addition).

e.g.
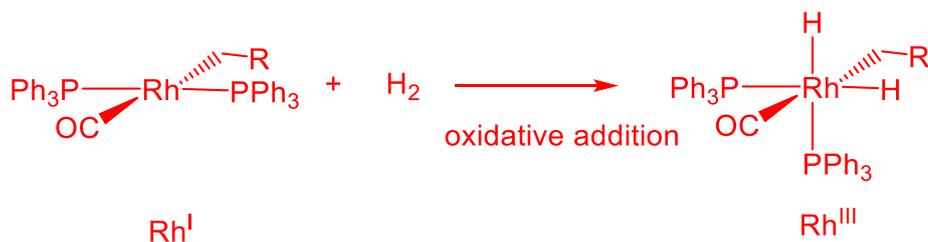
Characterisation – Dihydrogen M(H₂) or dihydride M(H)₂ complex ?

Technique	η^2 H-H	dihydride
Neutron diffraction	H-H~82 pm	H-H~160 pm
NMR	Low field, J_{HD}~30Hz	High field, J_{HD}~5Hz
IR	ν(H-H) ~ 3000 cm^{-1}	ν(M-H)~2150-1750 cm^{-1}
	ν(M-H) v. low	

Alkenes (a fluxional ligand)

π-acceptor ligands. Alkene complexes form basis of many catalytic reactions e.g. polymerisation, hydrogenation and metathesis.

Complexes of alkenes

σ-donor
Alkene π-orbital
Direction of charge transfer

π-acceptor
Alkene π*-orbital
Direction of charge transfer

sp^2

sp^3
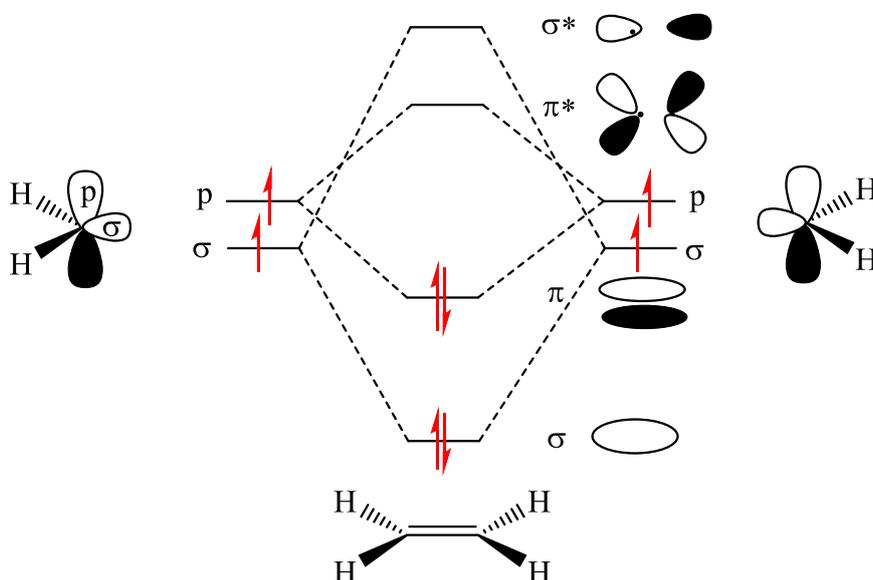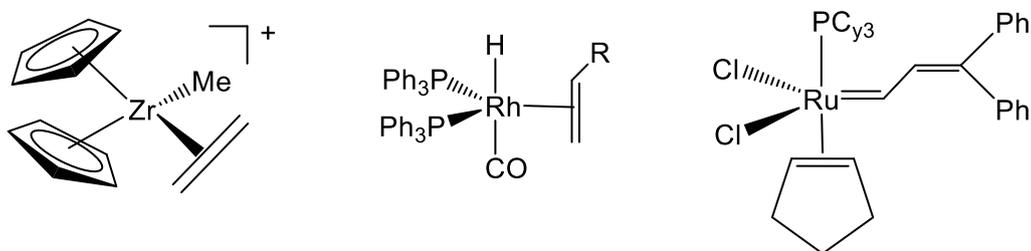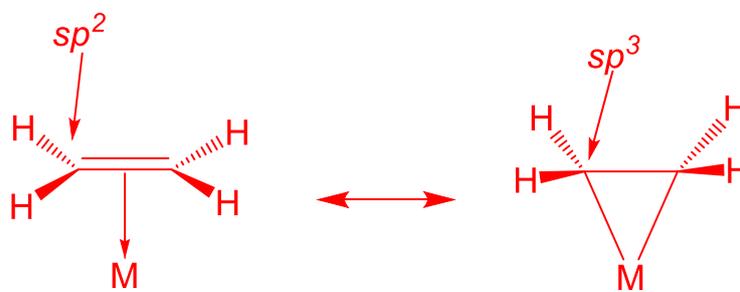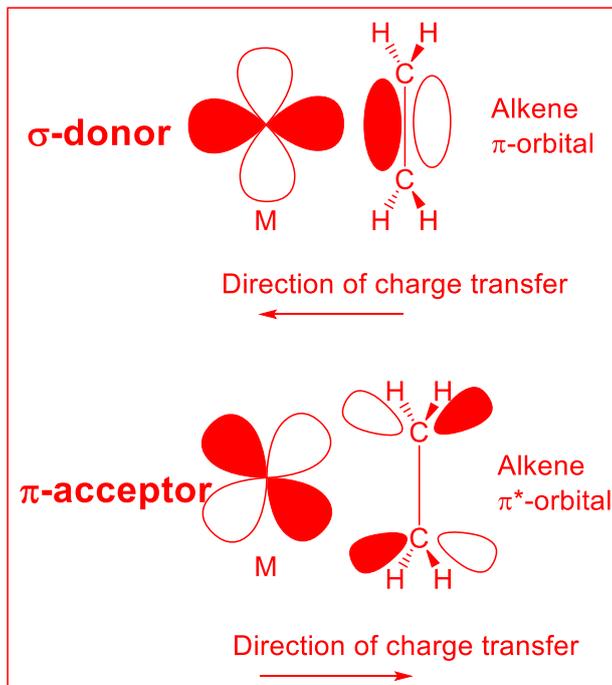
Dynamics in alkene complexes

373K

333K

313K

283K

233K

3   2   1ppm   0
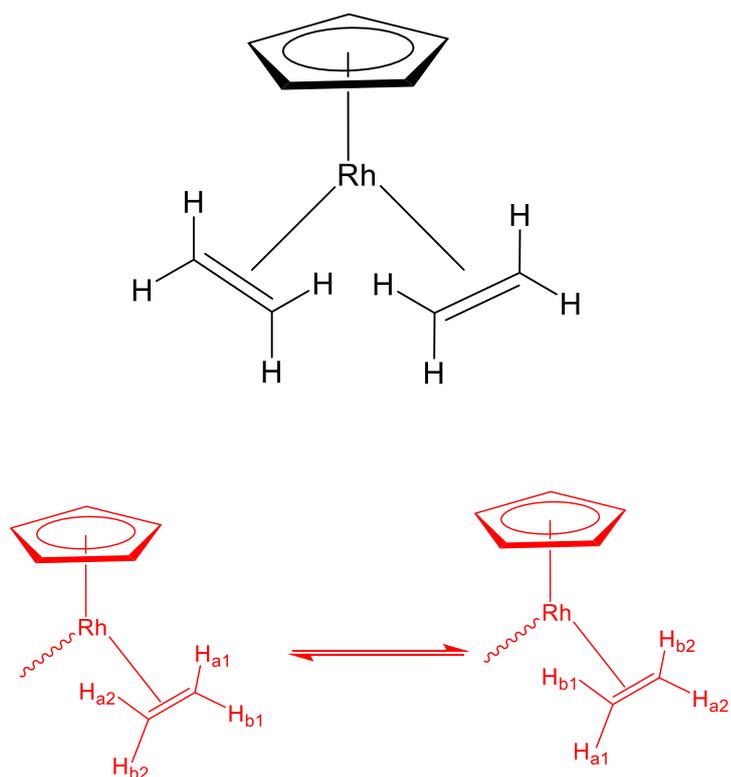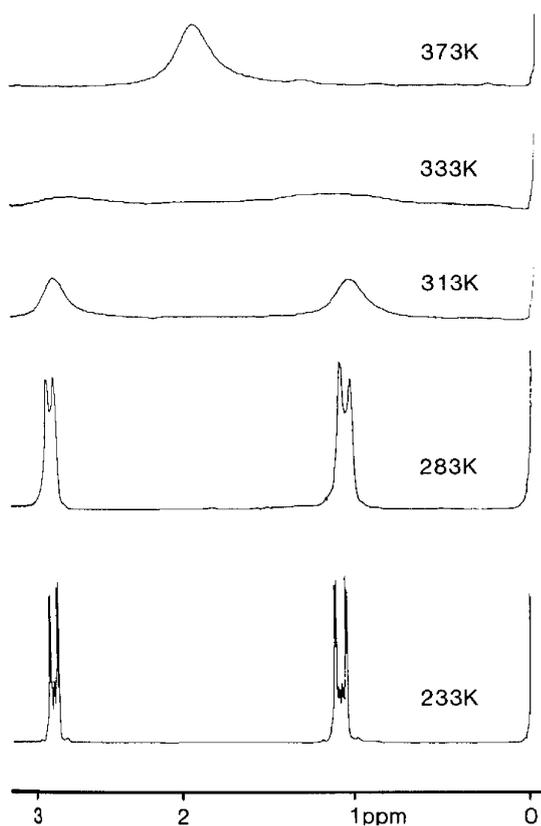
What determines energy barrier to rotation?

1. σ−bonding (dominant) interaction is not affected by rotation (no change in overlap)
2. π-bonding (minor) is broken, but other potential bonding orbitals at 90° to start point help lower activation energy.

PR₃ complexes

PR_3 can also act as π-acceptor ligands. In this case the orbitals are usually phosphorus σ* orbitals. Complexes of PR_3 ligands are very important catalysts for many reactions.

PR_3 ligands can stabilise low oxidation states by π-acceptor interactions and high oxidation states by strong σ-donation.

π-acceptor interaction

P σ* orbital

Direction of charge transfer
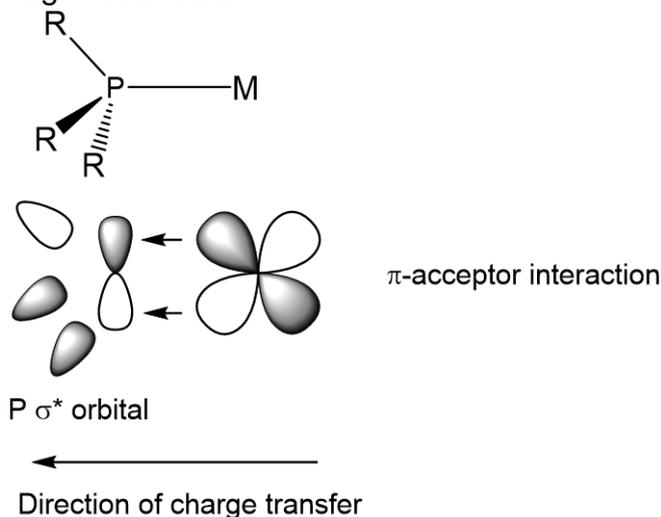
Π-Acceptor Ligand Effects in Action (Catalysis)

Enantioselective synthesis of S-DOPA

Solvent = MeOH
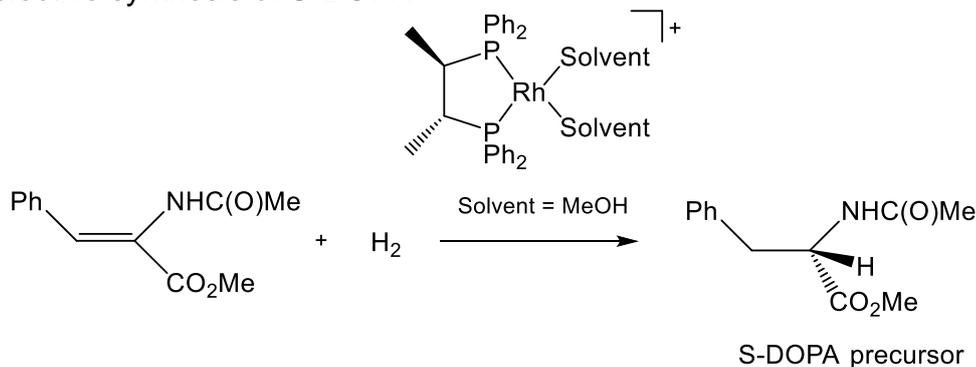
S-DOPA precursor
Treatment of Parkinson's Disease
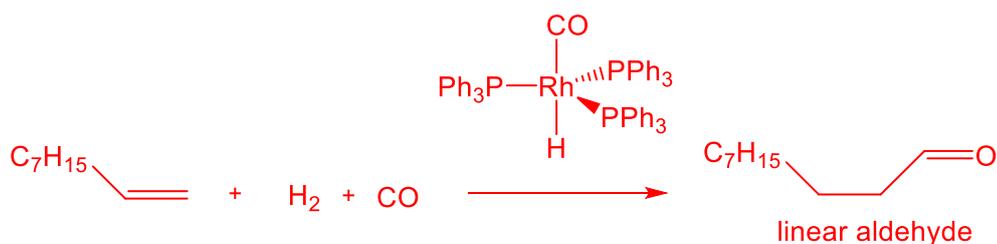
linear aldehyde
Lots of bulk chemical uses, e.g. Perfumes, agrochemicals

The Rh-L bonding of Rh-CO, Rh-H₂ (Rh-(H)₂), Rh-alkene, and Rh-PR₃ all play an integral role in this, and many other, catalytic reactions.

σ-donor, π-donor ('π-donors')

Ligands that fall into this category include: F, Cl, Br, I, O, OR, S, SR, N, NR$_2$(linear), NR (bent and linear), P.

We can view the metal-ligand bonding as a σ-donor interaction (same as for H) with an additional π- interaction that arises from overlap between metal-based orbitals and full orbitals on the ligand that can *donate* electron density.
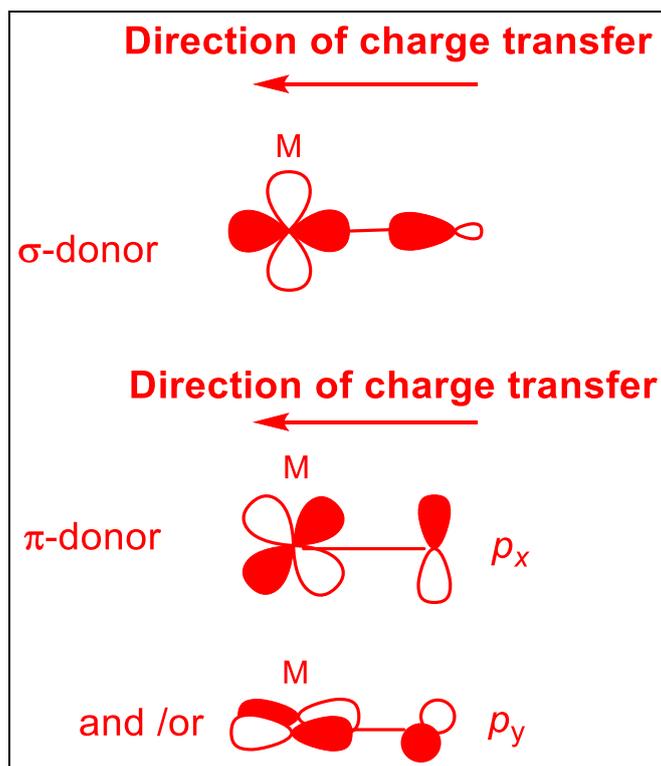
Note: there is no synergic bonding occurring here.

Metal - ligand multiple bonds

e.g.
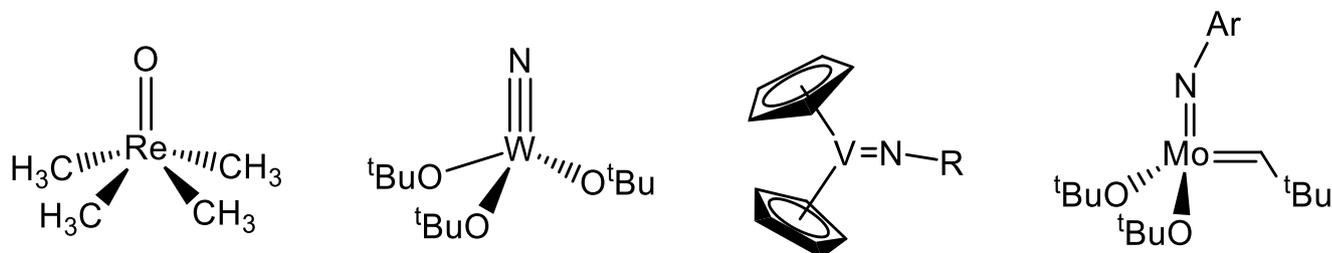
Metal-ligand multiple bonds contain a σ-bond and one or two π-bonds.
Complexes of O and N donor ligands usually have metals in high formal oxidation states with a low d-electron count.
For π-donation to occur there must be an empty metal d-orbital to accept the electrons.

A very important ligand that exhibits multiple bonding is the oxide ligand (O^{2-})

4 electron donor (O^{2-})	6 electron donor	6 electron donor
		Electrophilic O
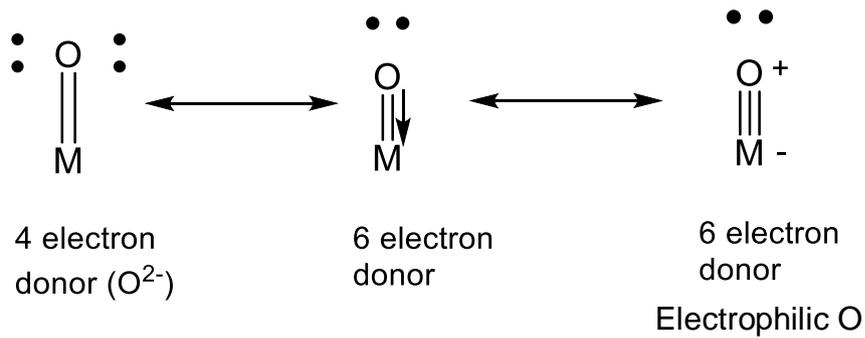
Look at M-O bond lengths to determine bonding

18 e⁻

double bond

16 e⁻

18 e⁻

X-ray shows very short W-O distance
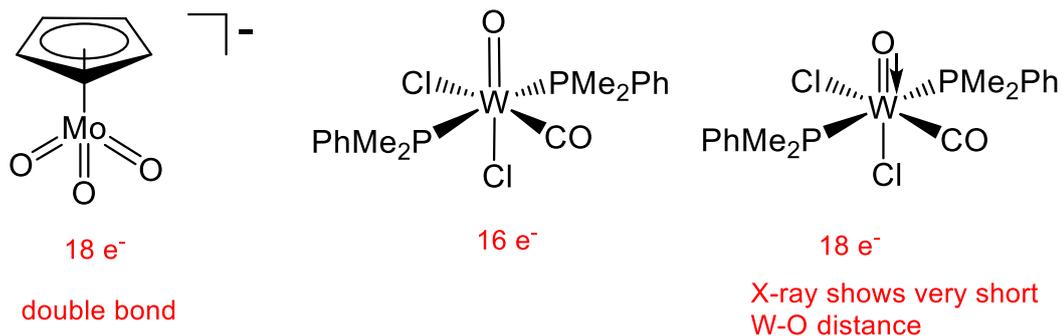
Metal oxides are used as source of oxygen for the oxidation of organic compounds

Stoichiometric dihydroxylation of alkenes
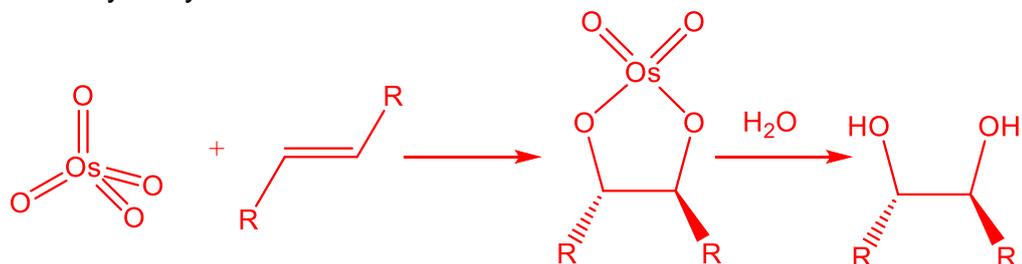
Catalytic epoxidation of alkenes.

NaOCl
(bleach)
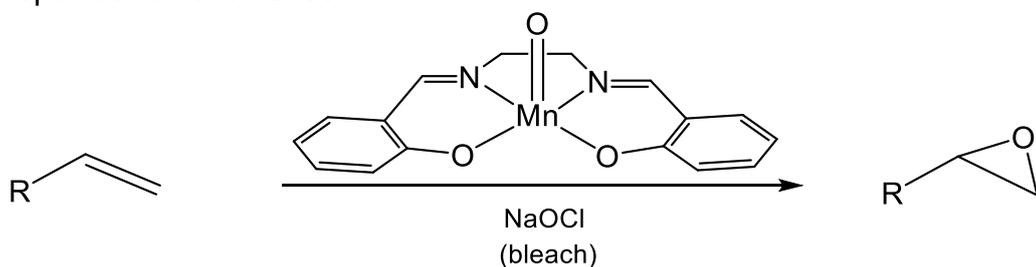
Protonation leads to hydroxides and aqua complexes (oxo chemistry is very pH sensitive) *cf* rust formation

Low pH ———————————————————→ High pH
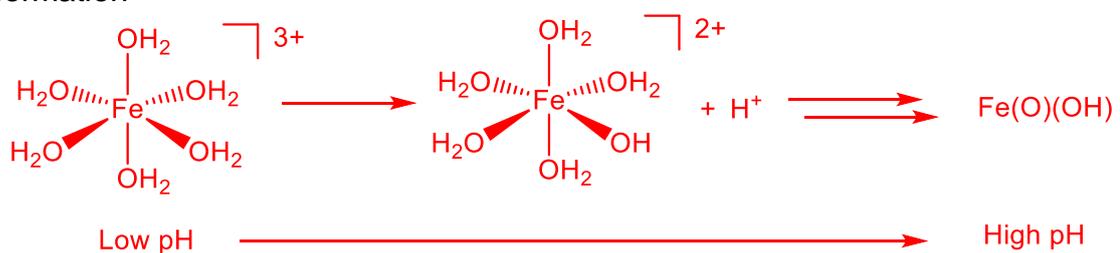
Other common multiple bonds are the amido (NR_2^-), imido (NR^{2-}) and nitrido (N^{3-}) ligands.

| 2 electron donor | 4 electron donor | 4 electron donor |

| 4 electron donor | 6 electron donor | 6 electron donor |
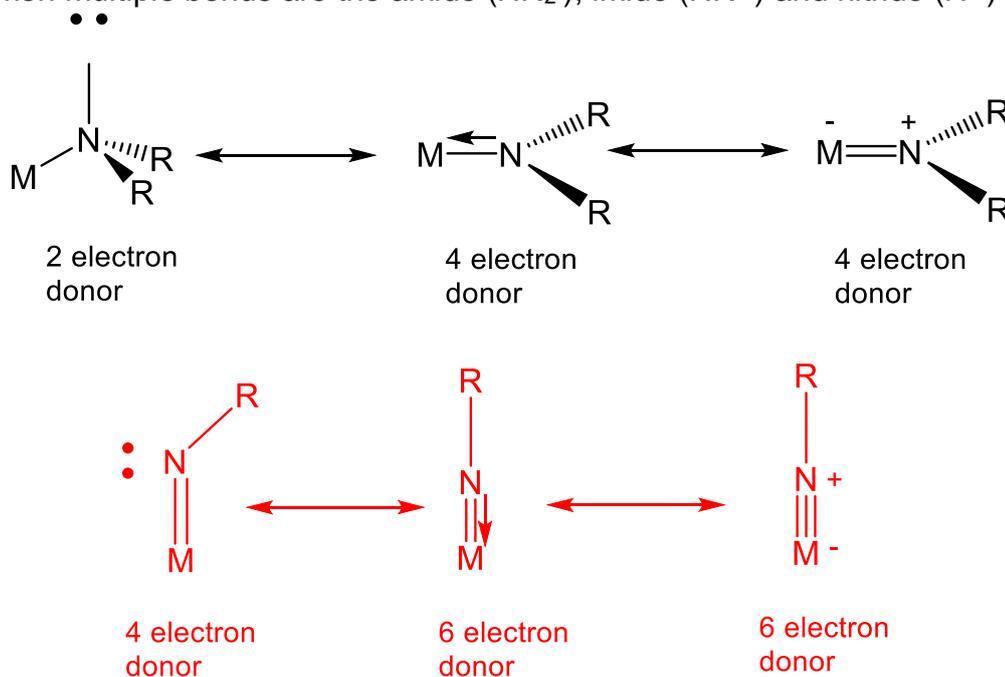
Can we use N_2 as a source of nitrogen in organic chemistry?
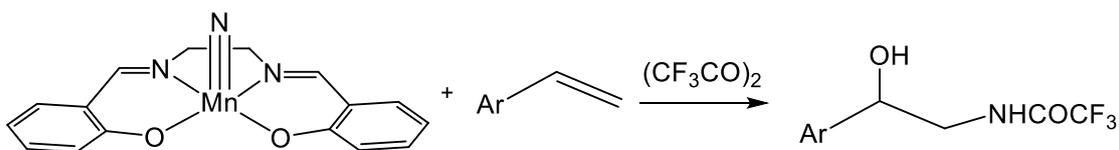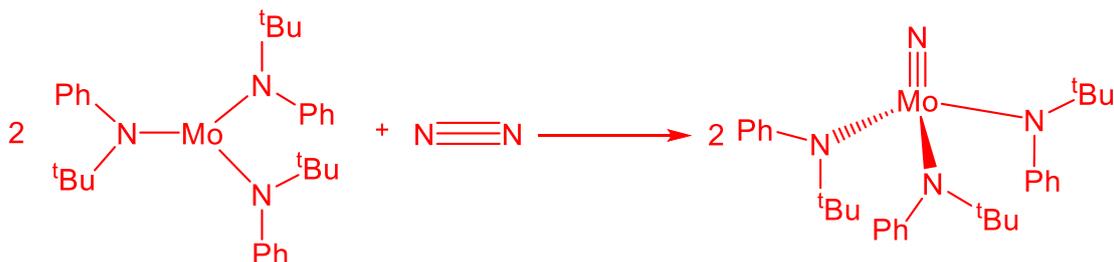
Electron counting of π-donor complexes can be difficult. As a rule of thumb invoke as many multiple bonds as possible to get as close to (but not over) 18.

	total valence electrons	metal oxidation state	d-electron count
$(^tBuO)_3WN$	12 (18)	VI	0
$(\eta-C_5H_5)_2V(NPh)$	17	IV	1
$ReMe_4(O)$	13(15)	VI	1

What effect do π-acceptors and π-donors have on the chemistry of metal complexes?

MO diagram of O_h complex with π-donor ligands

e.g. $[CoCl_6]^{3-}$

σ* $3t_{1u}$

t_{1u}

σ* $2a_{1g}$

ligand t_{2g}

a_{1g}

σ* $2e_g$

Δ_{oct}

e_g

π* t_{2g}

t_{2g}

σ* $2t_{1u}$

n.b. t_{1g}
n.b. t_{2u}

t_{1g}
t_{2u}
t_{1u}
t_{2g}
e_g
t_{1u}
a_{1g}

Mainly ligand in character. Ignored in electron counting of metal valence electrons. $[CoCl_6]^{3-}$ is considered 18 electron, even though 42 electrons in MO diagram.

π t_{2g}

σ $1e_g$

σ $1t_{1u}$

σ $1a_{1g}$

L
L—M—L
L

L

L

L

L—M—L

L

metal in O_h field

ligands in O_h arrangement
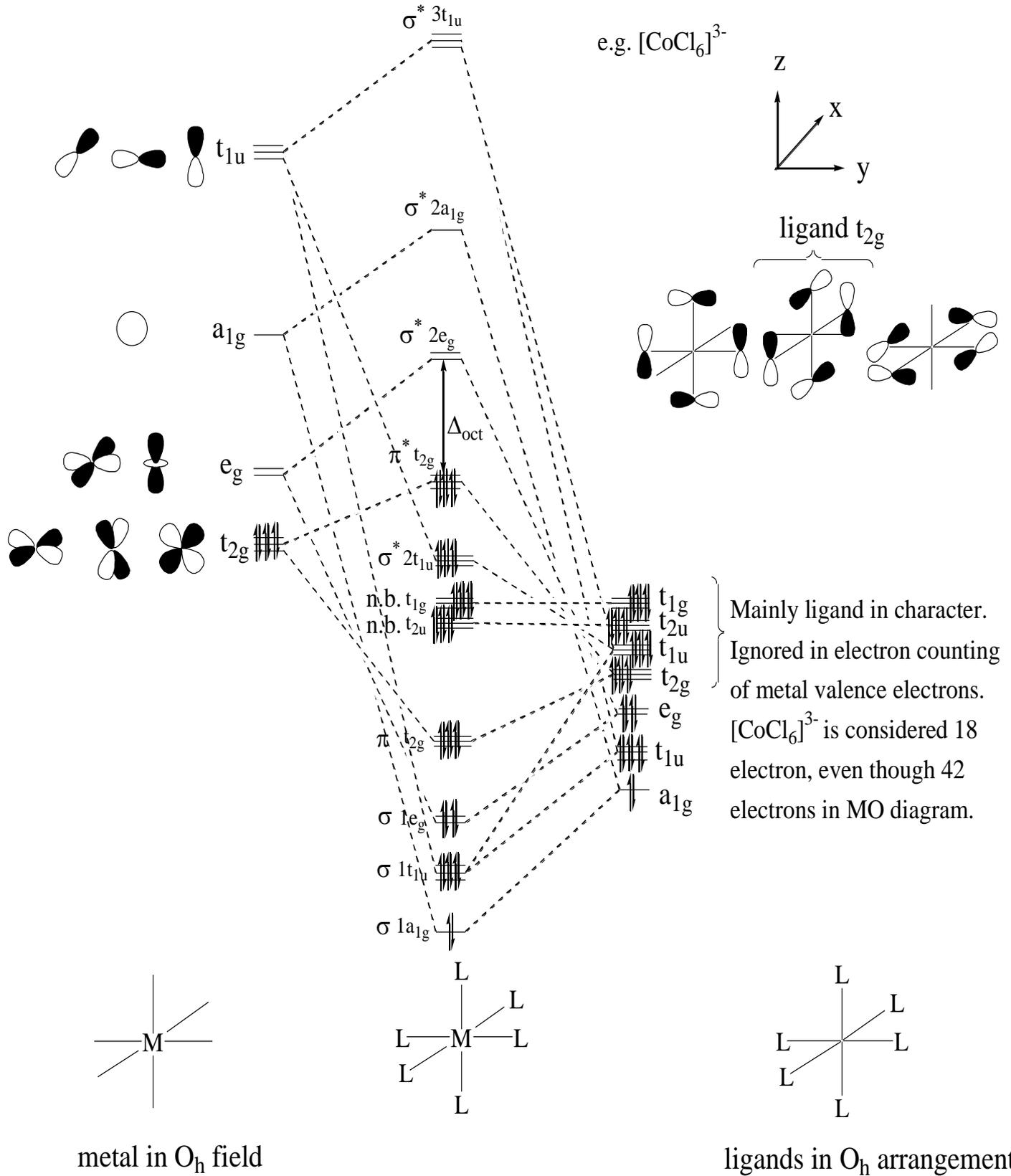
Note the effect on the t_{2g} d-orbitals in comparison to the σ-only case. These t_{2g} orbitals have risen in energy, closer to the e_g level, resulting in a reduction of Δ_{oct} (10 Dq).

MO diagram of O$_h$ complex with π-acceptor ligands

e.g. $[Co(CN)_6]^{3-}$

ligand t$_{2g}$

Δ_{oct}

metal in O$_h$ field

ligands in O$_h$ arrangement
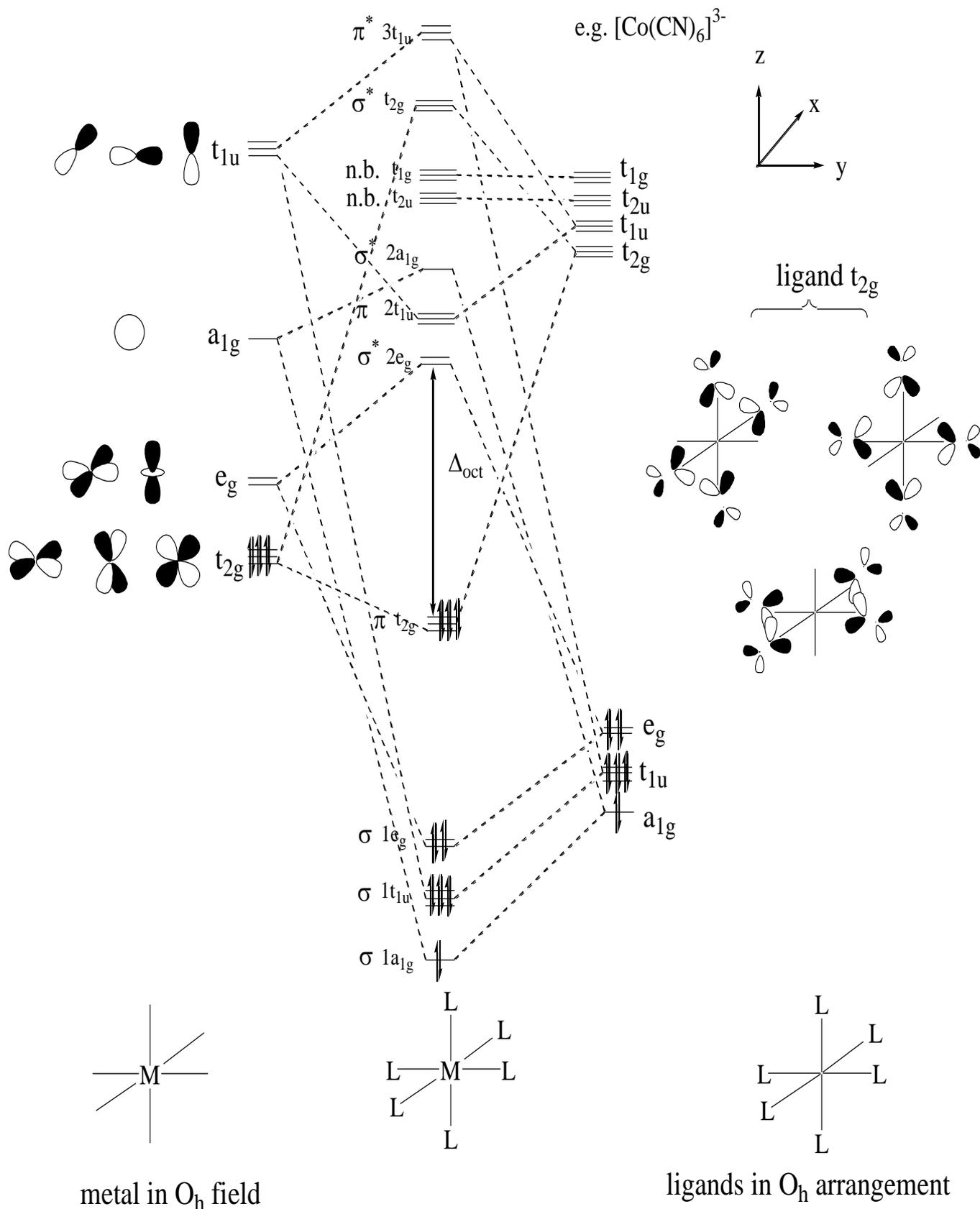
Note the effect on the t$_{2g}$ d-orbitals in comparison to the σ-only case. The t$_{2g}$ has been lowered in energy with respect to the e$_g$ level resulting in an increase in Δ_{oct} (10 Dq).

35

Summary

Δ_{oct} π-acceptor > σ-only > π-donor
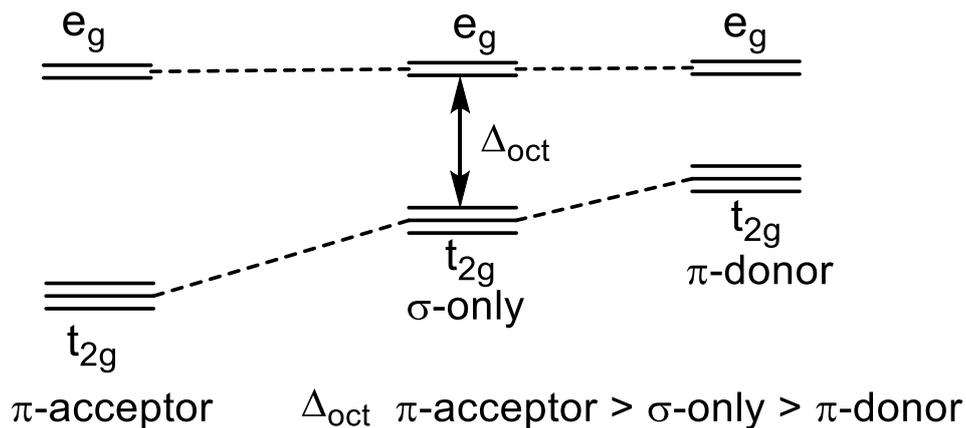
π-donors and the 18-electron rule

π-acceptor ligands usually obey the 18-electron rule, those with π-donors do not necessarily do so.

For π-donor ligands the metal t_{2g} orbitals are now slightly antibonding (π^*) therefore it is less energetically favourable to fill them.

e.g. $CrCl_6^{3-}$ with 15 total valence electrons is stable.

Spectrochemical series

The spectrochemical series is a list of ligands in order of increasing ligand field strength. Electrostatic model (Crystal Field Theory) cannot account for the order.

$$CO > CN^- > PPh_3 > NH_3 > H_2O > OH^- > F^- > Cl^- > S^{2-} > Br^- > I^-$$

| **π-acceptor** | **σ-only** | **π-donor** |

Increasing Δ_{oct}

$\longleftarrow$
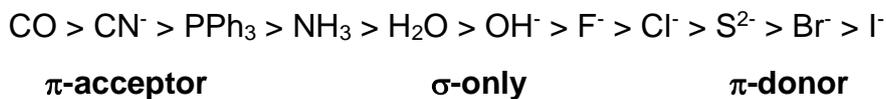
Δ_{oct} increases with increasing π-acidity of the ligands

e.g. Field strength determine spin state of metal complexes

$[CrCl_6]^{4-}$ $[Cr(CN)_6]^{4-}$
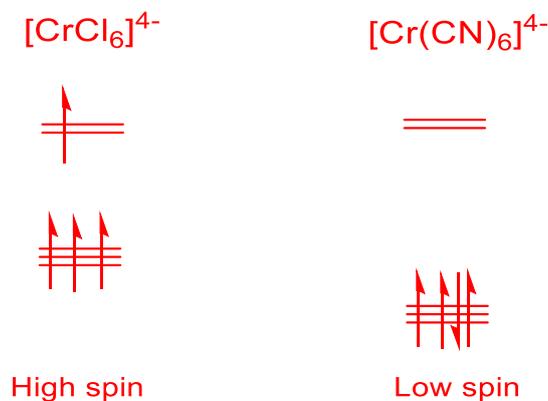
High spin   Low spin

The kinetics of ligand substitution is also affected. High spin complexes have electron density in antibonding M-L σ^* orbitals. Therefore the M-L bonding is weaker in comparison to low spin complexes. We will see the importance of this behaviour in REDOX electron transfer later.

Trans-effect and Trans-influence

The trans-effect and trans-influence help to rationalise the stability and substitution chemistry of transition metal complexes, particularly square planar Pd and Pt complexes. (see below in inorganic reaction mechanisms of square planar complexes)

The *trans effect* is a *kinetic* phenomenon and describes the influence of a non-labile group on the rate of substitution of a ligand *trans* to it.

$$CO, CN^- > PPh_3 > NO_2^- > I^- > Br^-, Cl^- > NH_3, OH^-, H_2O$$

| **π-acceptor** | **π-donor** | **σ-only** |

e.g.

$$PtCl_4^{2-} \xrightarrow{NH_3} \left[\begin{array}{c} Cl \\ | \\ Cl-Pt-NH_3 \\ | \\ Cl \end{array} \right]^- \xrightarrow{NO_2^-} \left[\begin{array}{c} NH_3 \\ | \\ Cl-Pt-NO_2 \\ | \\ Cl \end{array} \right]^- \xrightarrow{NH_3} \textbf{(1)}$$

$$PtCl_4^{2-} \xrightarrow{NO_2^-} \left[\begin{array}{c} Cl \\ | \\ Cl-Pt-NO_2 \\ | \\ Cl \end{array} \right]^{2-} \xrightarrow{NH_3} \left[\begin{array}{c} Cl \\ | \\ H_3N-Pt-NO_2 \\ | \\ Cl \end{array} \right]^- \xrightarrow{NH_3} \textbf{(2)}$$

<div style="color:red">

$$\begin{array}{c} NH_3 \\ | \\ Cl-Pt-NH_3 \\ | \\ Cl \end{array} \quad \textbf{(1)} \qquad\qquad \begin{array}{c} Cl \\ | \\ H_3N-Pt-NH_3 \\ | \\ Cl \end{array} \quad \textbf{(2)}$$
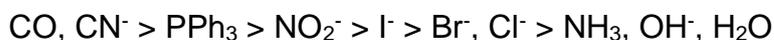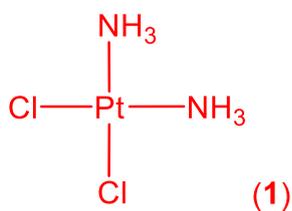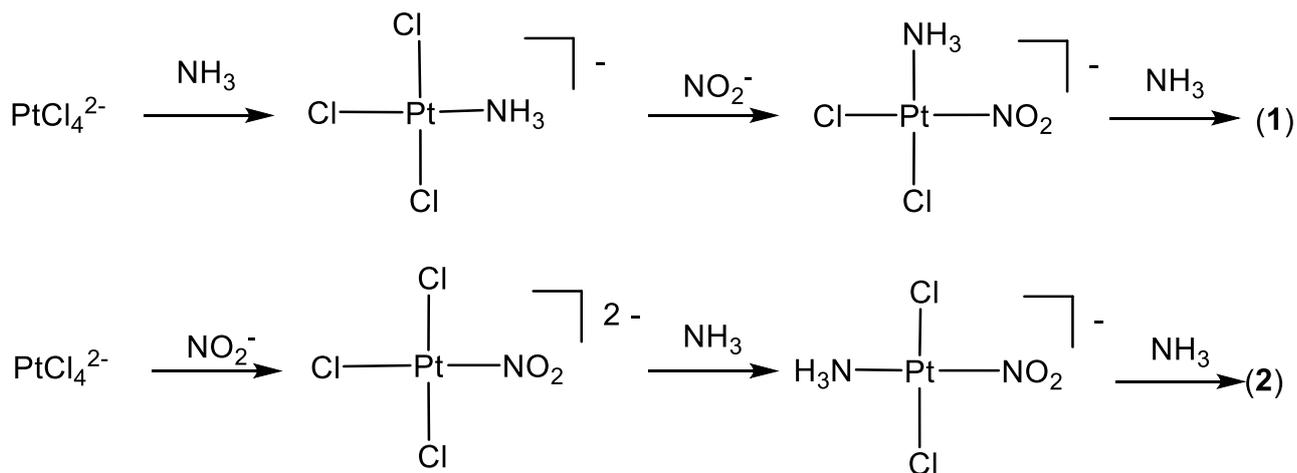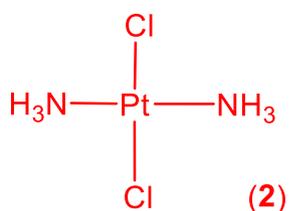
cis-platin   trans-platin

testicular cancer treatment

The order of ligand addition is important!

</div>

Inorganic Reaction Mechanisms

i) *Ligand substitution*
Most common reaction of coordination compounds
Substitution of one ligand in the coordination sphere for another

$$[Pt(NH_3)_4]^{2+} + Cl^- \longrightarrow [Pt(NH_3)_3Cl]^+ + NH_3$$
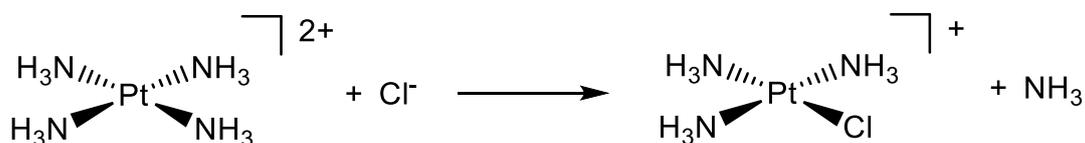
ii) Dissociation
Decreases the metal coordination number

$$Ph_3P{-}Pd(Ph)(PPh_3)(Ph) \longrightarrow Ph_3P{-}Pd{-}PPh_3 + Ph\text{-}Ph$$

4-coordinate → 2-coordinate
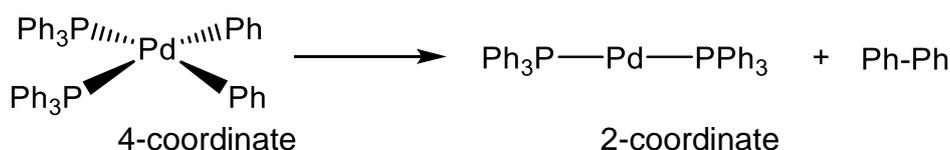
iii) Addition
Increases the metal coordination number

Cu(acac)$_2$ + Py → Cu(acac)$_2$(Py)

4-coordinate (square planar) → 5-coordinate(square pyramidal)
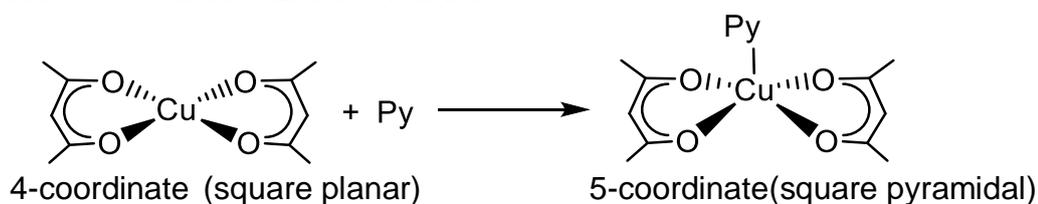
iv) *Redox reactions*
Oxidation, reduction, electron transfer

$$[Ru(NH_3)_6]^{3+} + [Cr(OH_2)_6]^{2+} \longrightarrow [Ru(NH_3)_6]^{2+} + [Cr(OH_2)_6]^{3+}$$

Ru(III) is reduced with Cr(II)
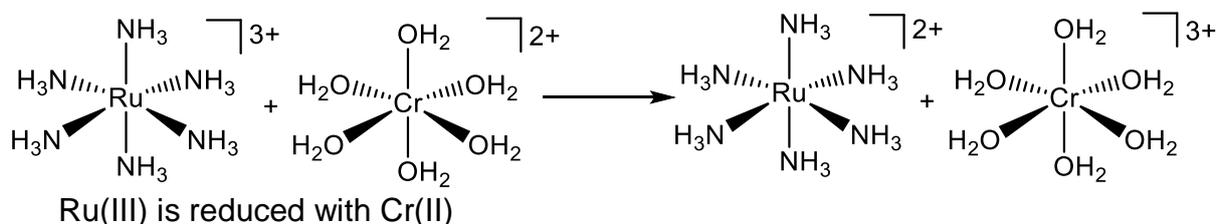
v) Reactions of coordinated ligands
Reactions of a ligand that take place without breaking the M-L bond

$$[Cr(OH_2)_6]^{3+} + OH^- \longrightarrow [Cr(OH_2)_5(OH)]^{2+} + H_2O$$
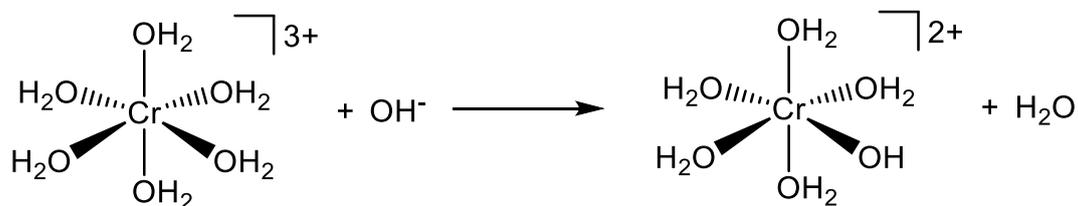
+ Lots of organometallic and organic chemistry using metal complexes

Ligand Substitutions Reactions

Organic Chemistry: S_N1, S_N2 etc

For inorganic

Dissociative (D) — intermediate. reduced coordination

Interchange (I) — intermediate. undetectable

Associative (A) — intermediate. greater coordination
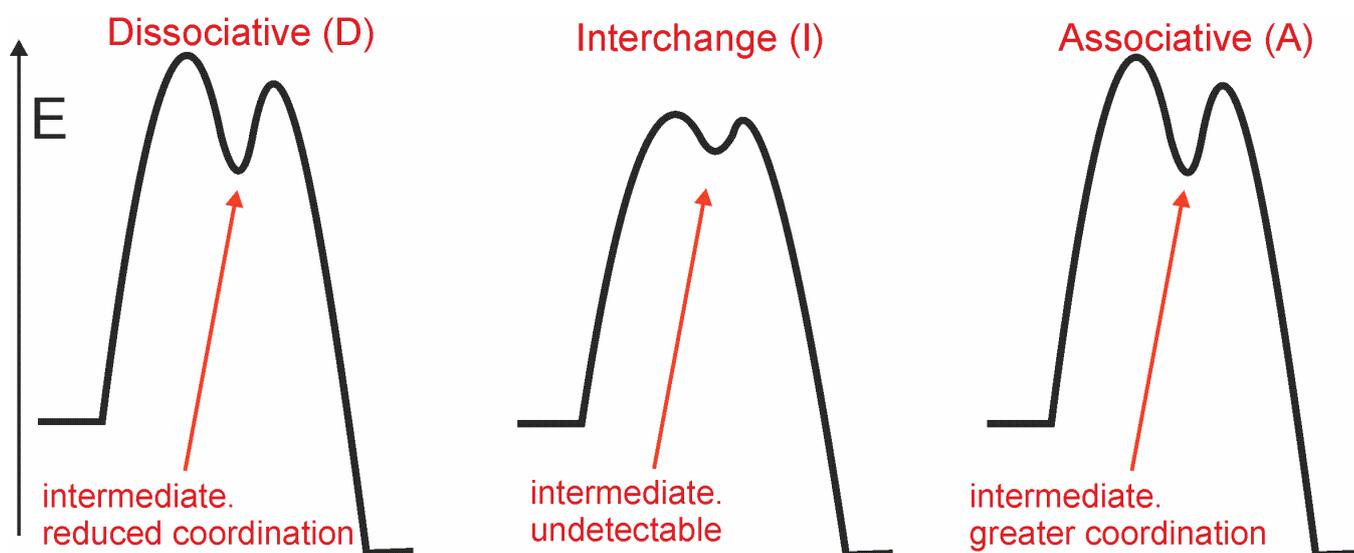
Stoichiometric Mechanism
Considers reactants, products and intermediates
Each step has a rate or equilibrium constant associated with it
Each species exists in a potential minimum along the reaction coordinate

Intimate Mechanism
Usually considers the transition state of the rate-determining step

Associative (a): M-L bond formation is well advanced at the transition state

Dissociative (d): M-L bond breaking is well advanced at the transition state

Recap:
Thermodynamically unstable complexes that survive for at least a minute are called inert
Complexes that equilibrate more quickly are called labile

Labile	Inert
complexes of d^{10} ions complexes of 3d M(II) ions (M(III) less labile)	d^3 and low-spin d^6 configurations 4d and 5d complexes due to high CFSE and better metal-ligand overlap Chelating ligands

Timescale: Process:
10^8 s   ligand exchange *(inert complex)*
1 ms   ligand exchange *(labile complex)*
1 μs   Intervalence charge transfer
1 ns   ligand exchange
10 ps   ligand association
1 ps   rotation time in liquid
1 fs   molecular vibration

Activation Parameters:
Reaction rate examined as a function of temperature:
Eyring equation yields the enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation.

The Eyring equation is obtained by applying activated complex theory to a reaction.

$$\ln\left(\frac{k_{rate}}{T}\right) = \ln\left(\frac{k_{Bolt}}{h}\right) - \frac{\Delta H^{\neq}}{RT} + \frac{\Delta S^{\neq}}{R}$$

A plot of reaction rate in the form of $\ln(k_{rate}/T)$ vs $1/T$ gives both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$

Measure the rate as a function of pressures. van't Hoff equation

$$\left(\frac{\partial \ln k_1}{\partial P}\right)_T = -\frac{\Delta V_1^{\neq}}{RT}$$

$\Delta V^{\ddagger}$ is the volume of activation, *volume differences between initial state and the transition state*
$\Delta H^{\ddagger}$ activation enthalpy, *bond strength differences between the initial and transition state*
$\Delta S^{\ddagger}$ activation entropy, *ordering effects between the initial and transition state*

We will consider square-planar and octahedral metal complex ligand substitutions

Square Planar Ligand substitutions

d^8 metal ions are the most common

Co$^+$ Ni^{2+} Cu^{3+}

Rh$^+$ Pd^{2+} Ag^{3+}

Ir$^+$ Pt^{2+} Au^{3+}
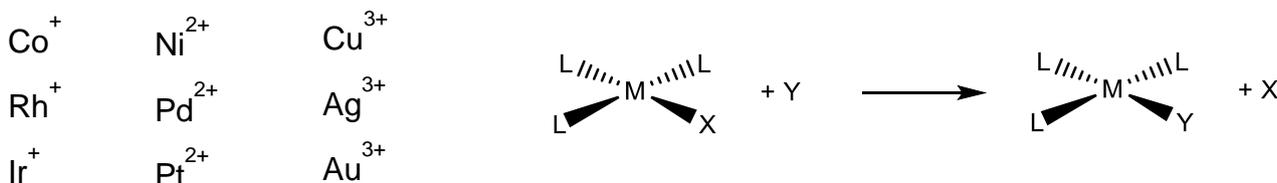
Square-planar Pt(II) complexes have been studied most extensively: suitable timescale
In an associative mechanism BOTH bond-breaking and bond-making can be important:
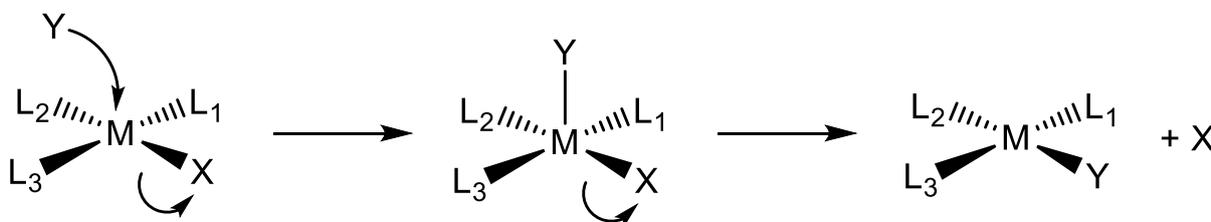
Mechanism and kinetics? What are the features that control which ligand is substituted and metal stereochemistry?

Study temperature and pressure dependence of the reaction rate

Activation parameters $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ are negative

A negative $\Delta S^{\ddagger}$ indicates transition state is more ordered than initial state.
A negative $\Delta V^{\ddagger}$ indicate transition state has smaller volume than initial state
Both indicate an associative mechanism (A):

The experimentally observed rate law for a square-planar substitution:

$$ML_3X + Y \rightarrow ML_3Y + X$$
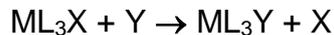
can be written as:

$$rate = k_1[ML_3X] + k_2[ML_3X][Y]$$

Where   X = leaving group
           Y = incoming group, nucleophile

Two pathways: *associative mechanism*

large H_2O conc. pseudo 1st order

$k_1 + H_2O$ → $ML_3X(H_2O)$

ML_3X (slow)   (fast) $-H_2O$ $+Y$

$k_2 + Y$ → ML_3Y

2nd order
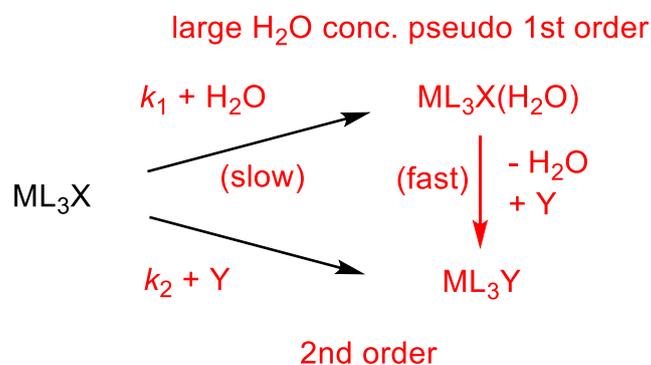
General Observations

In most cases, stereochemical retention of configuration is observed during substitution.
In some cases a 5-coordinated intermediate can be isolated.
Bulky groups decrease the rate of substitution.

Formation of a 5-coordinate trigonal bipyramidal intermediate:

41
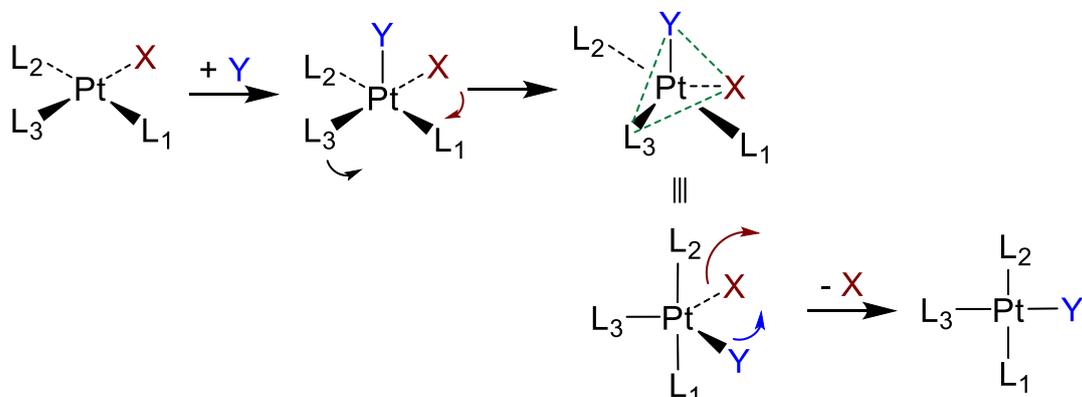
If the trigonal bipyramidal intermediate is sufficiently long-lived, isomerisation can be observed (via pseudorotation)

5-coordinate complexes are fluxional: *Berry pseudorotation*

Isomerisation *via* pseudorotation: Square based pyramid and trigonal prism geometries have very similar energy

L$_3$ and X *trans*

pseudorotation

L$_3$ and Y *cis*
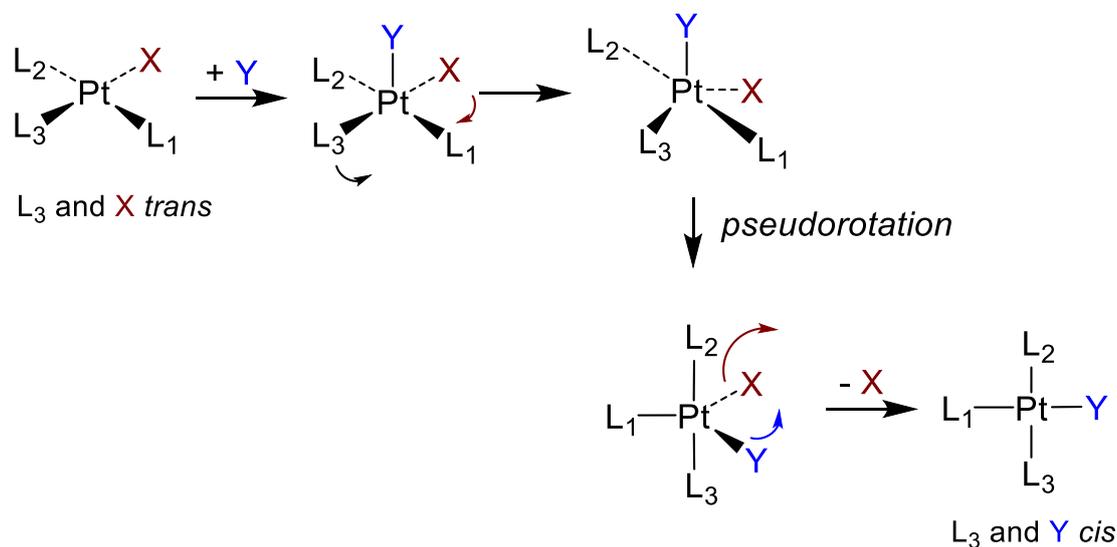
Factors affecting the rate of substitution

i) The entering group:
The rate of substitution is proportional to the nucleophilicity of entering group:
      i.e. for Pt(II), the rate increases in the order:

$$H_2O < NH_3 = py < Br^- < I^- < CN^- < PR_3$$
      hard   soft
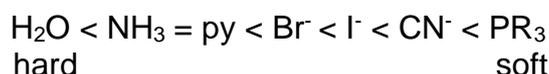
Element specific: the ordering is consistent with Pt(II) being a soft metal centre.

No correlation with other properties of the nucleophiles, such as basicity, redox potentials or pKa

The most important factor is polarisability or "softness":
I- > Br- > Cl-
PR$_3$ > AsR$_3$ > SbR$_3$ >> NR$_3$ (π-back bonding ability increases in the same order)

Exceptions: NO$_2$- and SeCN-, "biphilic", exhibit different reactivity depending on the charge on the complex.

ii) The leaving group:

The same principle applies: (but gives reverse order)

hard ligands, such as H$_2$O and Cl- leave quickly

soft ligands with considerable π-back bonding, such as NO$_2^-$ and CN$^-$ leave slowly

For the reaction:
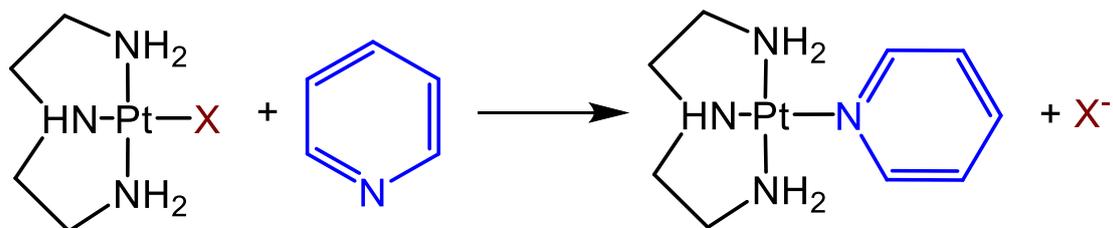
In water at 25 °C the sequence of lability of X^- is:

$$H_2O > Cl^- > Br^- > I^- > SCN^- > NO_2^- > CN^-$$
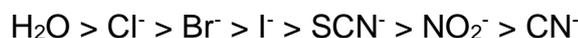
With a spread of over 10^6 in rate across series.
(The series mirrors the strength of the M-L bond strength)

iii) The nature of other ligands in the complex
The ***trans*-effect**:

> effect of a coordinated ligand on the rate of substitution of ligands opposite to it.

or

> *the ability of a ligand to direct the replacement of the ligand trans to it.*

Essentially arises from the competition between ligands for the same orbital.

The trans-effect for Pt(II):

$$CN^- \sim CO > NO_2^- > I^- \sim SCN^- > Br^- > Cl^- > py > NH_3 > H_2O$$

Examples:

Reaction1: $[Pt(NH_3)_4]^{2+}$ $\xrightarrow[- 2\ NH_3]{+\ 2\ Cl^-}$ $[PtCl_2(NH_3)_2]$
   trans

Reaction 2: $[Pt(Cl)_4]^{2-}$ $\xrightarrow[- 2\ Cl^-]{+\ 2\ NH_3}$ $[PtCl_2(NH_3)_2]$
   cis

Reaction 1:

directs next Cl⁻
trans to it
→ transplatin

Reaction 2:

less *trans*-directing
→ cisplatin
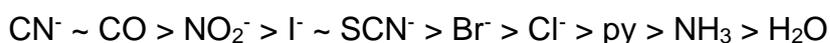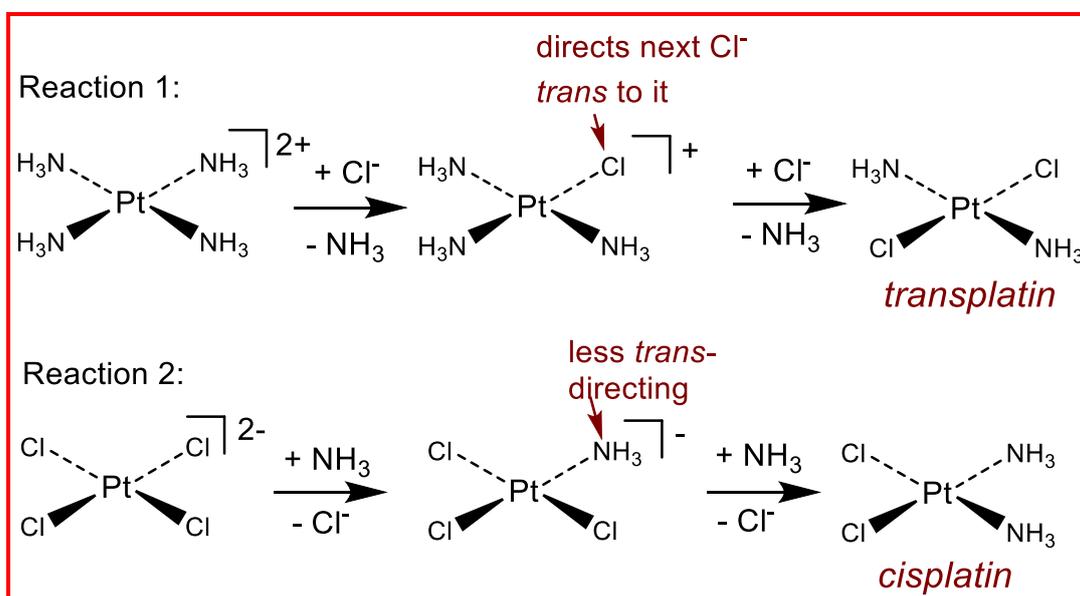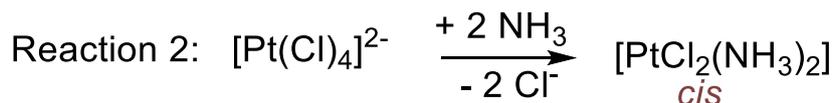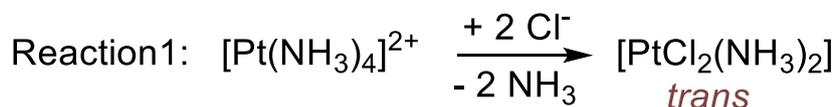
Conclusion:

Cl$^-$ has a greater trans-directing effect than NH_3.

The formed geometric isomer depends on the order in which the reagents are added

The free energy of activation ($\Delta G^{\ddagger}$) of ligand substitution is the difference between the reactant ground state and the first transition state. ($\Delta G^{\ddagger}$) can be decreased by:

1) destabilisation of the ground state
weakening of the bond in trans-position, σ-bonding effect

2) stabilisation of the transition state
lower energy of 5-coordinate transition state, π-bonding effect
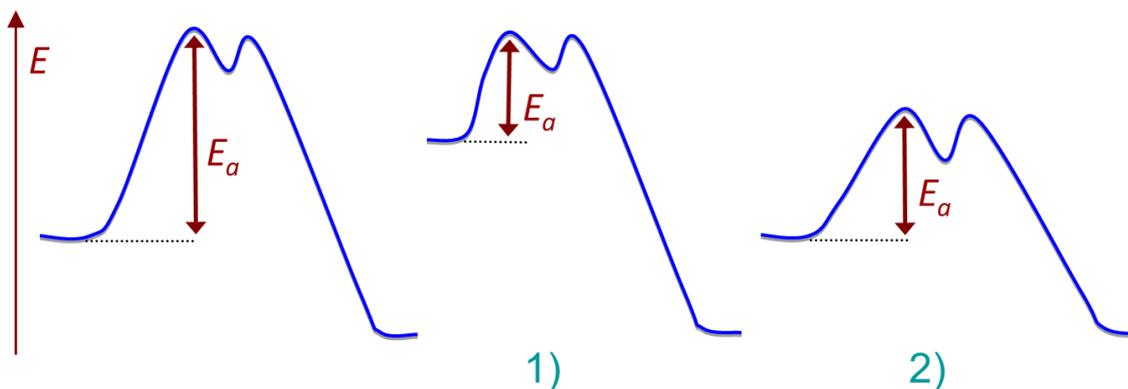
1) destabilisation of the ground state:
This is a thermodynamic effect. Some ligands weaken the M-L bond *trans* to them in *the ground state* and facilitate the substitution. (This is often also called ***trans*-influence)**

- e.g. strong σ-donors, such as H$^-$, I$^-$, Me$^-$, PR$_3$, *destabilise the M-L bond trans to themselves* (they repel electrons in the trans-ligand weakening the M-L bond)

2) stabilisation of the transition state:
In the trigonal plane of the 5-coordinate transition state or intermediate, π-back bonding can occur between a metal d-orbital and suitable orbitals of ligand T (the ligand *trans* to the leaving group) and Y (the entering nucleophile)
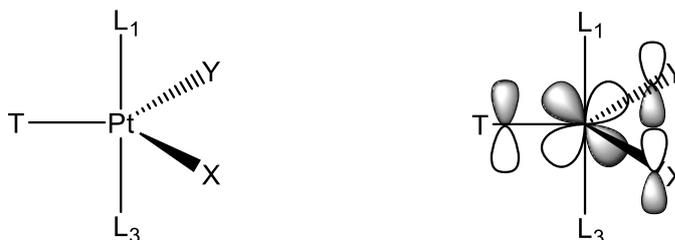
π-bonding in the trigonal plane

This is a kinetic effect.
strong π-acceptors, such as NO$^+$, C$_2$H$_4$, CO and CN$^-$ stabilise **the transition state** *by accepting electron density that the incoming nucleophile donates to the metal through π-interaction (*relieves charge build-up at the metal) a strong π-acceptor thus facilitates substitution at the site *trans* to it

Overall:
Ability of selected ligands to direct *trans*-substitution:

$CN^- \sim CO \sim NO^+ \sim C_2H_4 > PR_3, H^- > CH_3^- > Ph^-, NO_2^- > I^-, SCN^- > Br^- > Cl^- > py > NH_3 > H_2O$

       π-acceptors   *π-donors*   *σ-donors*
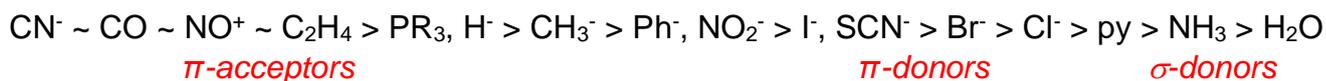
iv) The metal centre

The order of reactivity of the group 10 dications is;

Ni(II) > Pd(II) >> Pt(II)
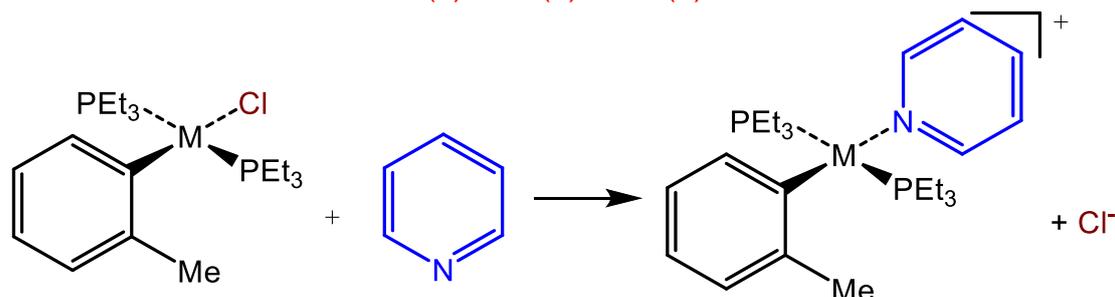
Ni(II): $k_2 = 33$ M^{-1} s^{-1}
Pd(II): $k_2 = 0.58$ M^{-1} s^{-1}
Pt(II): $k_2 = 6.7 \times 10^{-6}$ M^{-1} s^{-1}

reflects tendency to form 5-coordinate complexes/transition states

Square planar substitution reactions are generally slow due to loss of crystal field stabilisation energy (CFSE) during the formation of trigonal bipyramidal complex from square planar one.

The loss of CFSE increases down the group

Hence the square planar substitutions of 4d and 5d elements are slower

Or

M-L bonding stronger 5d > 4d > 3d (due to better M-L overlap). Within a series breaking stronger bonds requires more activation energy.

Octahedral ligand substitutions

Possible Mechanisms for:

$$ML_5X + Y \longrightarrow ML_5Y + X$$
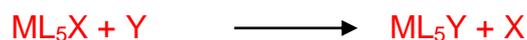
i)   Associative (A) *via 7-coordinate intermediate (rare)*

monocapped octahedron

or

pentagonal bipyramid
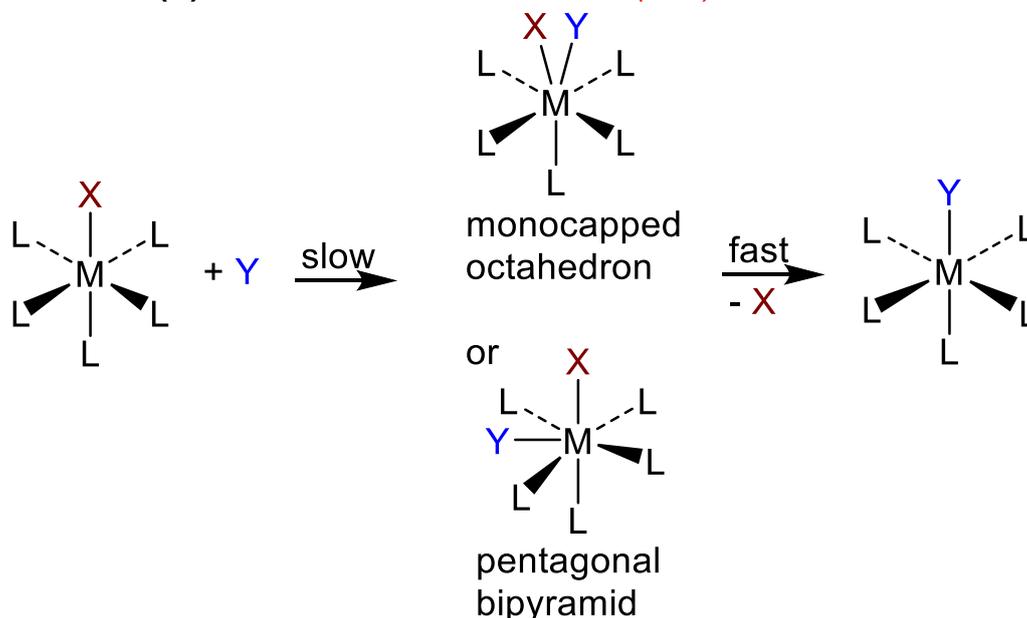
Rate determining step: formation of the **7-coordinate intermediate ML_5XY**
(mechanism: A_a since associatively activated)
The second faster step is dissociation of X *(intermediate cannot be detected)*

The rate of reaction depends on the concentration of ML_5X and Y

$$Rate = k_2[ML_5X][Y]$$

The activation parameters $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ are negative

ii) Dissociative (D) –= via a 5-coordinate intermediate *(organic S_N1)*

square pyramid
or

trigonal bipyramid
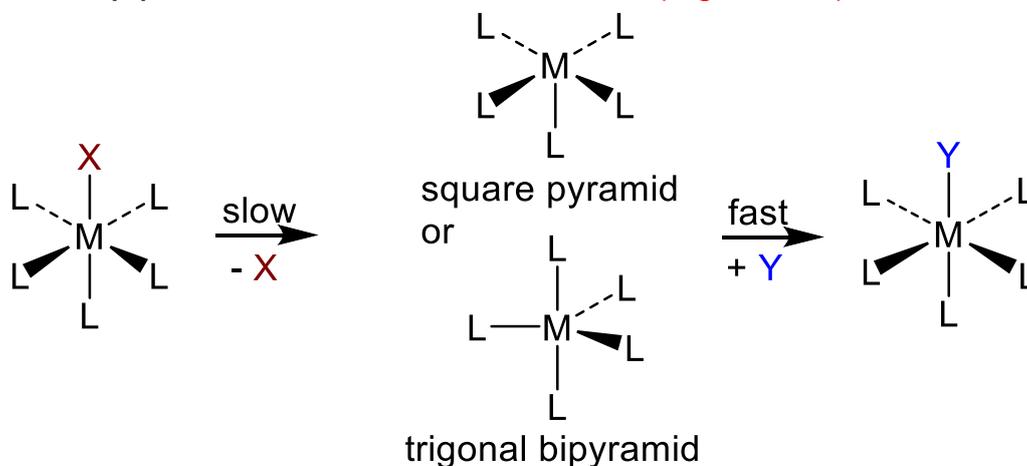
The rate of the substitution depends on $[ML_5X]$ and is independent of $[Y]$.
(mechanism: D_d since dissociatively activated)
Overall rate = $k_1[ML_5X]$
The activation parameters $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ are positive

iii) Interchange (I)
Most common mechanism in octahedral complexes

As Y begins to bond X begins to leave. i.e. the bond making to Y and bond breaking to X occur simultaneously *(organic S_N2)*
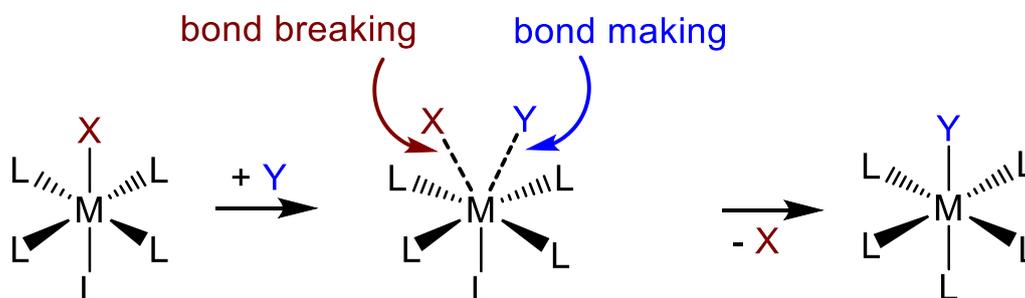
The designations I_d and I_a are used to differentiate associatively from dissociatively activated processes.

Complication:
There is masking of concentration dependence in aqueous solution.
    An associative mechanism is *usually first order in both reactant and incoming ligand.*

For example: $ML_5X + H_2O \longrightarrow ML_5(H_2O)$
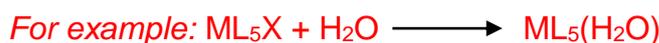
However: the concentration of H_2O in aqueous solution is so large it is very nearly constant.

    So it is combined with k_1 and the resulting rate law is **'pseudo' first order**
    Concentration dependence of the incoming ligand has been masked

In water and other coordinating solvents, such as dmso, the rate laws for the associative and dissociative mechanisms are identical:

$$\text{Rate} = k_1{}^{'} [ML_5X]$$

    So we cannot use the rate law to decide between the two mechanisms

Additional evidence for a dissociative rate-determining step in octahedral substitution reactions:

i) Entering group effect

$$[Ni(H_2O)_6]^{2+} + L \;=\; [Ni(H_2O)_5L]^{2+} + H_2O$$

vary L and compare the rate constants

range from $k = 3 \times 10^3 \, s^{-1}$ for L = NH_3 to $k = 30 \times 10^3 \, s^{-1}$ for L = CH_3COO^-

only a factor of 10 difference *(entering group has hardly any effect)*

rate constant

$$[CoX(NH_3)_5]^{2+} + H_2O \xrightarrow{k} [Co(NH_3)_5(OH_2)]^{3+} + X^-$$

formation constant

$$[Co(NH_3)_5(OH_2)]^{3+} + X^- \rightleftharpoons [CoX(NH_3)_5]^{2+} + H_2O$$
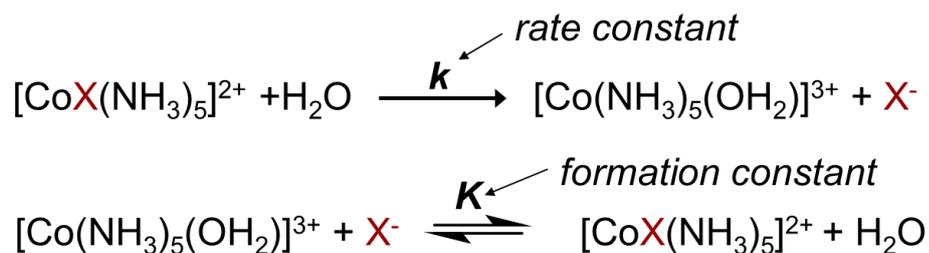
	X⁻	k, s⁻¹	K, M⁻¹ (log K)	
slow reaction ↑	F⁻	8.6 x 10⁻⁸	20 (1.3)	**strong Co-X bond**
	H₂PO₄⁻	2.6 x 10⁻⁷	7.4 (0.8)	
	Cl⁻	1.7 x 10⁻⁶	1.25 (0.1)	↑
	Br⁻	6.3 x 10⁻⁶	0.37 (-0.4)	
	I⁻	8.3 x 10⁻⁶	0.16 (-0.8)	
fast reaction	NO₃⁻	2.7 x 10⁻⁵	0.077 (-1.1)	**weak Co-X bond**

Basolo, Pearson: Mechanisms of Inorganic Reactions, Wiley, 1968.

Plot of log *K* (reflects bond strength) vs. log *k* (measure of the rate of aquation):
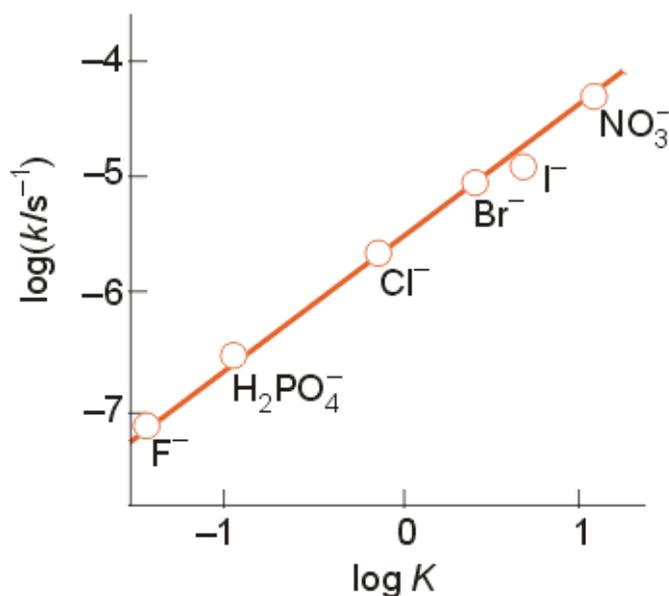
ln k ~ activation Gibbs energy
ln K ~ reaction Gibbs energy

Linear Free Energy Relationship: consistent with a rate determining step in which bonds of varying strength are broken. Or put anther way the thermodynamic bond strength determines the kinetic rate of reaction.

evidence for a dissociative rate-determining step

iii) Steric effects

In the dissociative mechanism, the coordination number is decreased in the transition state (TS)

if L is large, then the steric crowding is decreased in the TS so the rate increases

conversely, in an associative mechanism large L decrease the rate

Effect of the size of the spectator ligands on the aquation of $[Co(N-N)_2Cl_2]^+$ (N-N is a bidentate ligand):

N—N	rate constant / s^{-1}, 298 K
$NH_2CH_2CH_2NH_2$	3.2×10^{-5}
$NH_2CH_2CH(CH_3)NH_2$	6.2×10^{-5}
$NH_2CH(CH_3)CH(CH_3)NH_2$	1.5×10^{-4}
$NH_2CH_2C(CH_3)_2NH_2$	2.2×10^{-4}
$NH_2 C(CH_3)_2C(CH_3)_2NH_2$	immediate reaction

(source: R.G. Pearson, C.R. Boston and F. Basolo, *J. Am. ChemSoc*, **1953**, 75, 3089)

Increase in rate: dissociative rate-determining step

Increase in ligand size exerts chemical pressure on dissociating ligand

iv) Electron count *(for 18-electron reactants)*

dissociative mechanisms involving 16-electron intermediates are common

associative substitutions involving 20-electron intermediates are less common (unless accommodated by changes in e.g. hapticity)

Electron Transfer Reactions

One definition of chemistry could be 'The study and manipulation of valence electrons'. The transfer of electrons between molecular compounds is therefore an extremely important phenomenon.

We will be considering electron transfer between inorganic complexes. There are two mechanisms by which inorganic complexes transfer electrons. The **outer sphere mechanism** and the **inner sphere mechanism**. The outer sphere mechanism is important because of the analogy that can be drawn between electron transfer in metal complexes and electron transfer in metalloenzymes. The inner sphere mechanism is important because atom transfer (bond breaking/formation) can be concomitant with electron transfer. Both are important for photosynthesis.

Outer sphere electron transfer occurs between complexes that do not undergo substitution. No new bonds are broken or formed.

Inner sphere electron transfer occurs between complexes via a bridging ligand. At least one of the complexes needs to be labile to allow the bridge to form. Bonds are broken and formed.

Recap

Substitution: Inert vs labile octahedral complexes

From first year transition metals course

Electron configuration important (LS = low spin)

Inert	Labile
d^3, d^4 LS, d^5 LS, d^6	d^0, d^1, d^2, d^4 HS, d^5 HS, d^7 HS

Low spin complexes	High spin complexes
Strong field ligands CO, CN^-, PR_3	Weak field ligands H_2O, NH_3, Cl^-
All 2nd and 3rd row complexes	All 1st row H_2O complexes
Most Co(III)	Most Co(II)

Outer sphere electron transfer

$$M^{(a+1)+}L_x \quad + \quad M'^{b+}L_y \quad \rightleftharpoons \quad M^{a+}L_x \quad + \quad M'^{(b+1)+}L_y$$

oxidant (O)   reductant (R)
is reduced   is oxidised

Mechanism

1. Formation of precursor complex

$$M^{(a+1)+}L_x \quad + \quad M'^{\,b+}L_y \quad \overset{K_{eq}}{\rightleftharpoons} \quad \left\{M^{(a+1)+}L_x^{\text{''''''}}M'^{\,b+}L_y\right\}$$
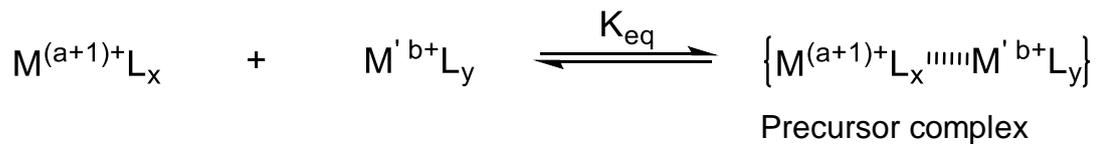
Precursor complex

2. Activation/reorganisation of precursor complex. Electron transfer. Relaxation to successor complex

$$\left\{M^{(a+1)+}L_x^{\text{''''''}} M'^{\,b+}L_y\right\} \quad \xrightarrow{k_{ET}} \quad \left\{M^{a+}L_x^{\text{''''''}} M'^{\,(b+1)+}L_y\right\}$$

Successor complex

3. Dissociation of successor complex

$$\left\{M^{a+}L_x^{\text{''''''}} M'^{\,(b+1)+}L_y\right\} \quad \xrightarrow{k_{diss}} \quad M^{a+}L_x \quad + \quad M'^{\,(b+1)+}L_y$$

Formation of precursor complex and dissociation of successor complex are fast. Electron transfer slow
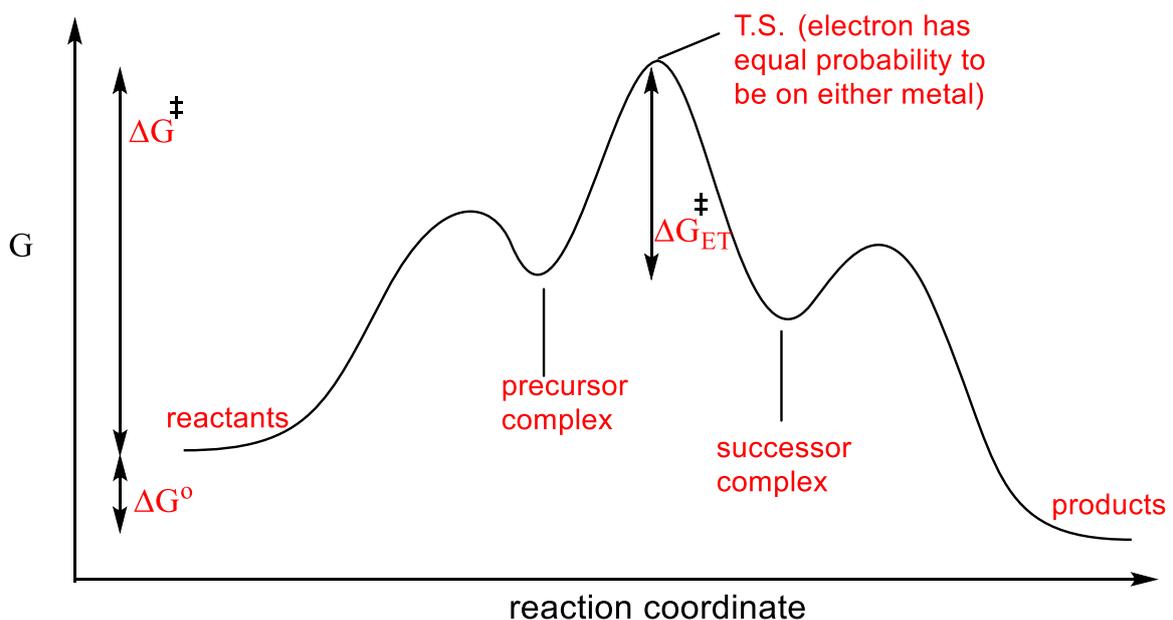
remember from thermodynamics, driving force $\Delta G^o = -nF\Delta E^0$

$$[Ru^*(NH_3)_6]^{2+} + [Ru(NH_3)_6]^{3+} \xrightarrow{k = 6.7 \times 10^3 \text{ M}^{-1}\text{s}^{-1}} [Ru^*(NH_3)_6]^{3+} + [Ru(NH_3)_6]^{2+}$$

$$[Ru(NH_3)_6]^{3+/2+} \; E^0 = +0.051\text{V}$$

$$[Co^*(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+} \xrightarrow{k = 10^{-9} \text{ M}^{-1}\text{s}^{-1}} [Co^*(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+}$$

$$[Co(NH_3)_6]^{3+/2+} \; E^0 = +0.058 \text{ V}$$

Self exchange reactions (M and M* are isotopes). $\Delta G^o = 0$

$$[V(H_2O)_6]^{2+} + [Ru(NH_3)_6]^{3+} \xrightarrow{k = 1.3 \times 10^3 \text{ M}^{-1}\text{s}^{-1}} [V(H_2O)_6]^{3+} + [Ru(NH_3)_6]^{2+}$$ Cross reaction

$$[V(H_2O)_6]^{3+/2+} \; E^0 = -0.255 \text{ V}$$

So why is there such a large range of rates?

Factors that affect the rate of outer sphere electron transfer

$$\Delta G^\ddagger = \Delta G_t^\ddagger + \Delta G_o^\ddagger + \Delta G_i^\ddagger$$

energy to bring reactants together (including overcoming coulombic repulsion)

energy needed for solvent reorganisation

energy required for reorganisation of bond lengthening/compression
to make interacting orbitals the same energy

i) $\Delta G_o^\ddagger$. Energy is required to reorganise the solvent.

precursor complex

Solvents allow two positively charged complexes to approach one another. Solvents that interact strongly with complexes (e.g. via hydrogen bonding) will reduce the rate of electron transfer

ii) $\Delta G_i^\ddagger$. Metal-ligand bond lengths will change when the oxidation state of the metal changes. The Frank-Condon principle states that because nuclei are much more massive than electrons, an electronic transition occurs much faster than the nuclei can respond. Complexes must adjust their M-L bond lengths before electron transfer.

Fe(III)-O = 2.05Å
Fe(II)-O = 2.21 Å

Identical bond lengths in T.S.

Fe-O compression   Fe-O elongation

Orbital energies must be of equal for electron transfer to occur (but not sole requirement)

Electron transfer requires orbital overlap and orbitals of the same symmetry

e_g — σ^*
t_{2g} — π

Cr^{2+} Cr^{3+} Cr^{3+} Cr^{2+}
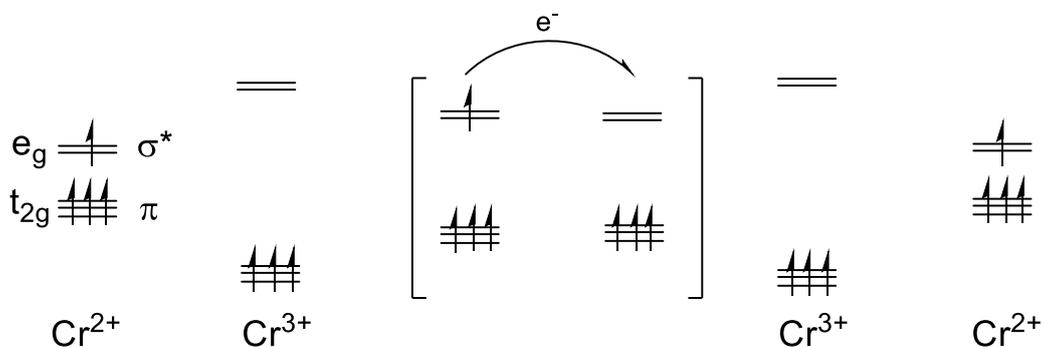
Orbital symmetry

In O_h field e_g is σ^*: $e_g \rightarrow e_g$ transition = large change in bond length. 'Slow' electron transfer
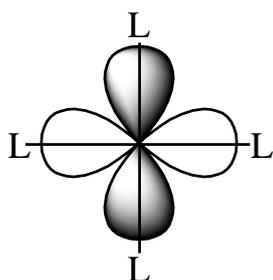
+ poor overlap (ligand sterics)

53
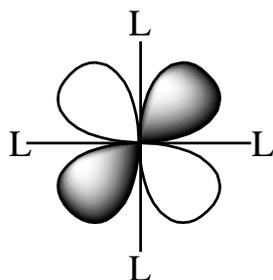
better overlap (depends on ligands)

Overlap

2nd and 3rd row metals generally faster that 1st row due to better overlap of 4d and 5d orbitals. (Also due to stronger ligand fields bond length distortions will be smaller).

Ligands that have extended π-systems e.g. Phen, bipy etc can assist electron transfer.

Phen

Bipy
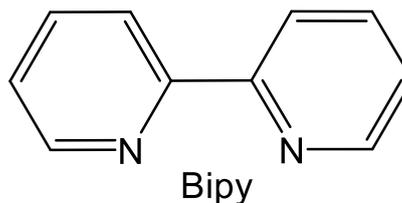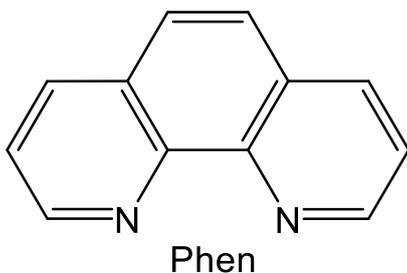
Electronic Configuration

Activation energy is required if a complex has to change electron configuration to allow electron transfer.

e.g.
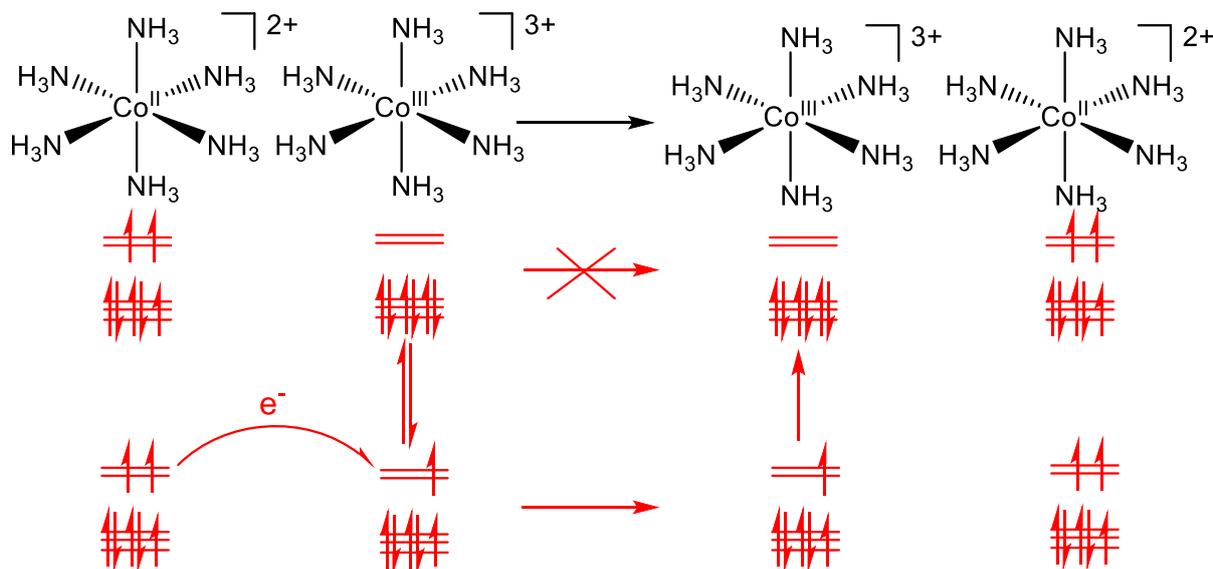
Think of electronic reorganisation being concomitant with bond elongation and compression.

Potential energy diagrams

Why not transfer electron then relax bonds?
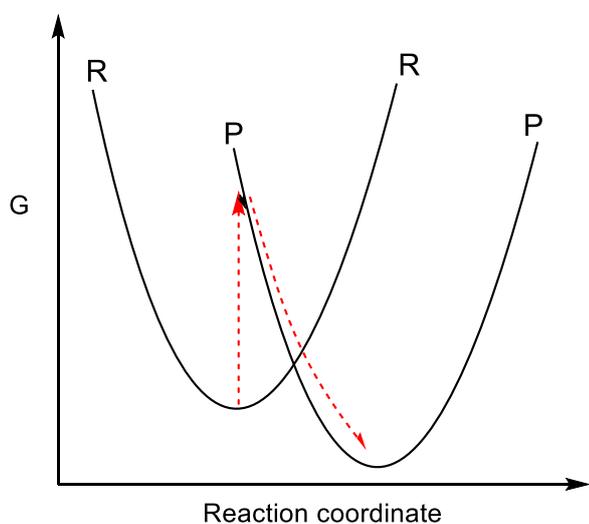
R = potential energy surface of reactants + environment
P =   "   products   "

1. Where did energy come from to 'activate' the electron ?

2. R $\xrightarrow{\text{ET}}$ P* $\xrightarrow{\text{relax}}$ P + heat

   (viloation of conservation of energy)

a photon could provide the required energy.

Self exhange

$\Delta G^{\ddagger}$

Δr_R $\Delta r^{\ddagger}$ Δr_P

Δr Å, (r = average bond length)

$\Delta G^{\ddagger}$

ΔG^{O}

Δr_R $\Delta r^{\ddagger}$

Δr_P

Δr Å

At
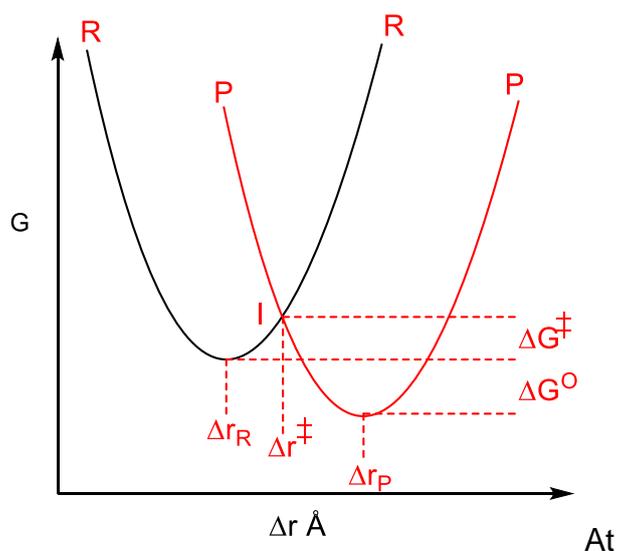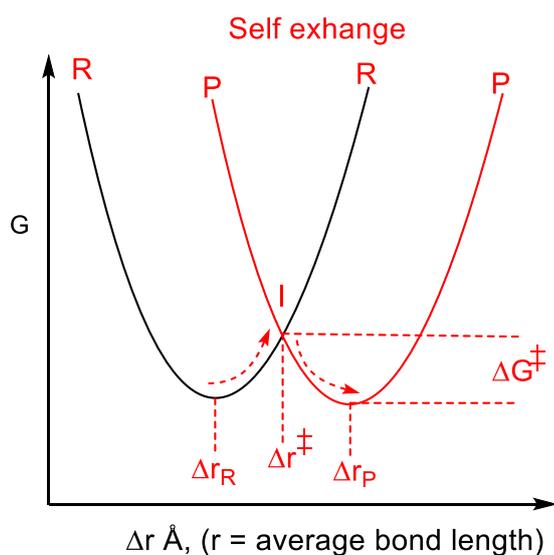
I, the requirement of equal orbital energies is met allowing the possibility of electron transfer.

How does electron move from reactant to product?

At I, electronic-vibrational coupling (ΔEc) determines the probability κ_{el} (transmission coefficient) that an electron will transfer. κ_{el} increases with increasing ΔEc.

Wavefunction is reactant-like at the left of the well. When get to crossing point turn on mixing due to coupling. (only near the crossing point is this important). Large ΔEc means large probability of crossing to product-like well on right.

What is the relationship between Δr, ΔG° and $\Delta G^\ddagger$?

$\Delta G^\ddagger \propto 1/(\Delta G^\circ)^2$ (however see inverted Marcus region)

$\Delta G^\ddagger \propto (\Delta r)^2$ (i.e. small changes in bond lengths = large changes in $\Delta G^\ddagger$)

Self Exchange Reaction	Configuration	k (M^{-1} s^{-1})	Δr Å
$[Cr(H_2O)_6]^{2+}$ / $[Cr(H_2O)_6]^{3+}$	$t_{2g}^3 e_g^1$ / $t_{2g}^3 e_g^0$	10^{-5}	0.3
$[V(H_2O)_6]^{2+}$ / $[V(H_2O)_6]^{3+}$	$t_{2g}^3 e_g^0$ / $t_{2g}^2 e_g^0$	10^{-2}	0.2
$[Fe(H_2O)_6]^{2+}$ / $[Fe(H_2O)_6]^{3+}$	$t_{2g}^4 e_g^2$ / $t_{2g}^3 e_g^2$	4	0.15
$[Ru(H_2O)_6]^{2+}$ / $[Ru(H_2O)_6]^{3+}$	$t_{2g}^6 e_g^0$ / $t_{2g}^5 e_g^0$	4×10^3	0.05
$[Fe(phen)_3]^{2+}$ / $[Fe(phen)_3]^{3+}$	$t_{2g}^6 e_g^0$ / $t_{2g}^5 e_g^0$	10^3	0.01

Reactions are fast if the reactants have similar bond distances

Quantitative interpretation of outer sphere electron transfer reaction rates

$$\Delta G^{\ddagger} = \frac{w}{2} + \frac{\lambda}{4}\left(1 + \frac{\Delta G^{o}}{\lambda}\right)^{2}$$

w = work term (energy required to bring two reactants together), λ = total reorganisation energy (includes solvent reorganisation and bond length changes of reactants)

For many reactions involving complexes of opposite charge or if the reactants are effectively fixed in space such as in a protein w ≈ 0. Therefore

$$\Delta G^{\ddagger} = \frac{\lambda}{4}\left(1 + \frac{\Delta G^{o}}{\lambda}\right)^{2}$$

and for a self exchange reaction ΔG^{o} = 0.

$$\Delta G^{\ddagger} = \frac{\lambda}{4}$$

Note that a thermodynamic parameter (ΔG^{o}_{AB}) is being used in a kinetic expression

reaction coordinate
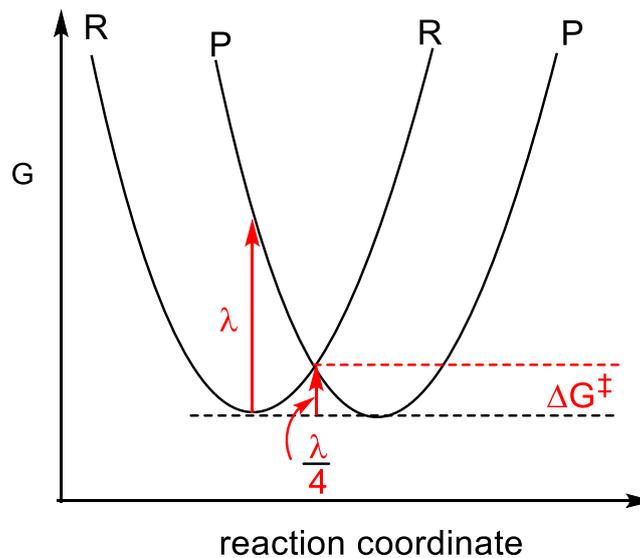
Recap

Eyring equation relates rate constants and free energy of activation

$$k = \frac{k_{B}T}{h}e^{-\Delta G^{\ddagger}/RT}$$

reaction coordinate
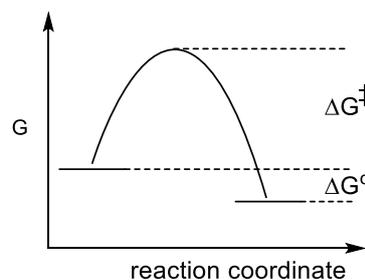
k = rate constant, k_{B} = Boltzmann constant, $\Delta G^{\ddagger}$ = free energy of activation (kinetic), ΔG^{o} = free energy of reaction (thermodynamic).

rem ΔG^o is negative for a spontaneous reaction

when $\Delta G^o = \lambda$ $\Delta G^{\ddagger} = 0$

and $\Delta G^o < \lambda$ $\Delta G^{\ddagger} > 0$

but also $\Delta G^o > \lambda$ $\Delta G^{\ddagger} > 0$!!

$\Delta G^{\ddagger}$

ΔG^o

(predicted 1956)
(verified 1986)

Normal Region   Marcus Inverted Region

$k\ s^{-1}$

ΔG^o (eV)
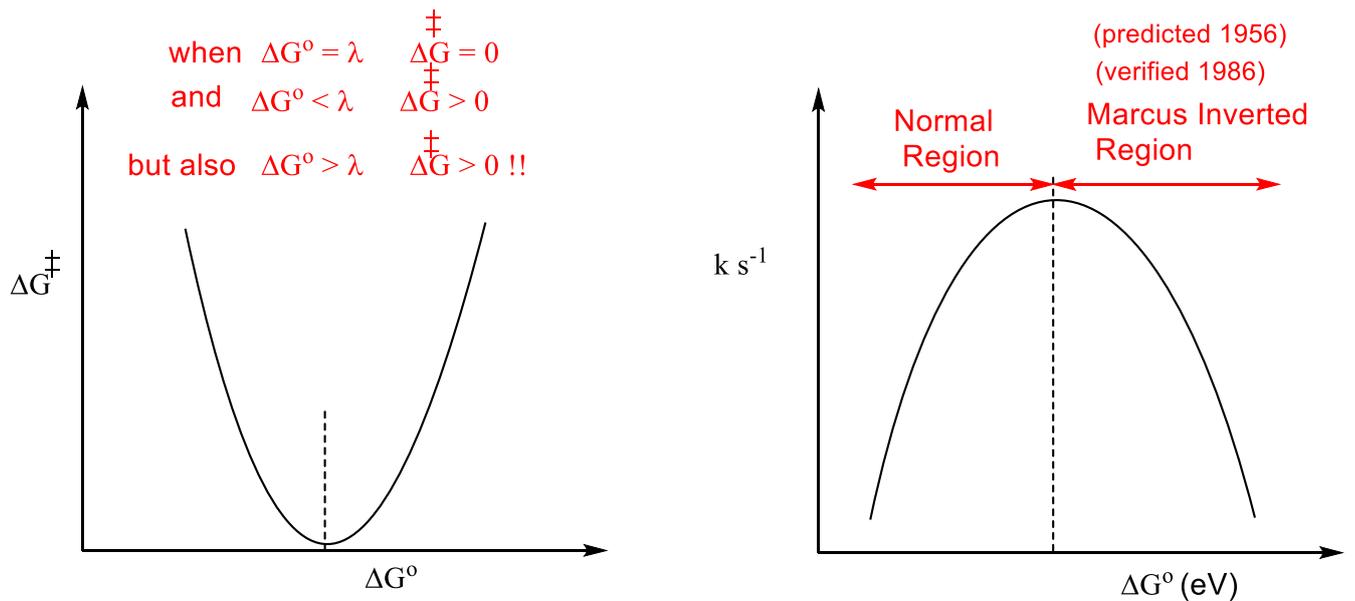
In the inverted region the rate (k) decreases as the thermodynamic driving force increases!

This is most easily visualised using a potential energy diagram

R P P R P P
P   P

G

1
2
3

reaction coordinate

1. Normal Region $\Delta G^{\ddagger} > 0$

2. $\Delta G^{\ddagger} = 0$

3. Marcus Inverted Region $\Delta G^{\ddagger} > 0$

ΔG^o 3 > 2 > 1
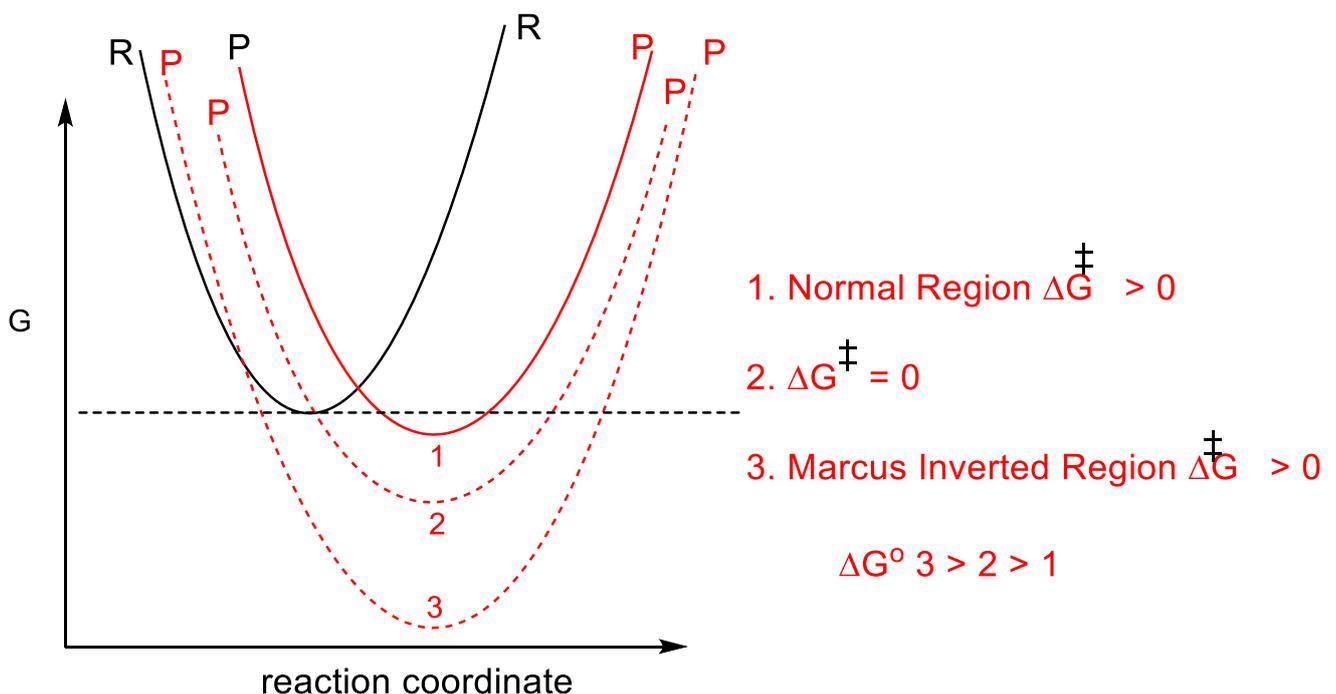
The Marcus inverted region is probably important in photosynthesis where wasteful back electron transfer reactions (which are highly exothermic) are prevented.

Chlorophyll absorbs the light.

The recombination of the photoelectron with the oxidised chlorophyll is retarded (to ~30 ns).

This allows electron transfer away from the reaction centre

Inner sphere electron transfer

Inner sphere electron transfer is mediated by a bridging ligand.

i) Reductant and oxidant share a ligand in the precursor and successor complex.

ii) On activation the electron is transferred between the metals.

iii) The ligand **may** transfer between complexes.

$$M^{III}L_5X \ + \ M'^{II}Y_5 \ \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \ \left\{L_5M^{III} \frown X - M'^{II}Y_5\right\} \ + \ Y$$
$$\quad\ \ O \qquad\qquad\ \ R$$

$$\left\{L_5M^{III} \frown X - M'^{II}Y_5\right\} \ \xrightarrow{k_{ET}} \ \left\{L_5M^{II} \frown X - M'^{III}Y_5\right\}$$

$$Y + \left\{L_5M^{II} \frown X - M'^{III}Y_5\right\} \ \xrightarrow{k_d} \ L_5M^{II}Y \ + \ XM'^{III}Y_5$$
$$\text{or} \ \ Y + \left\{L_5M^{II} \frown X - M'^{III}Y_5\right\} \ \longrightarrow \ L_5M^{II}X \ + \ M'^{III}Y_6$$
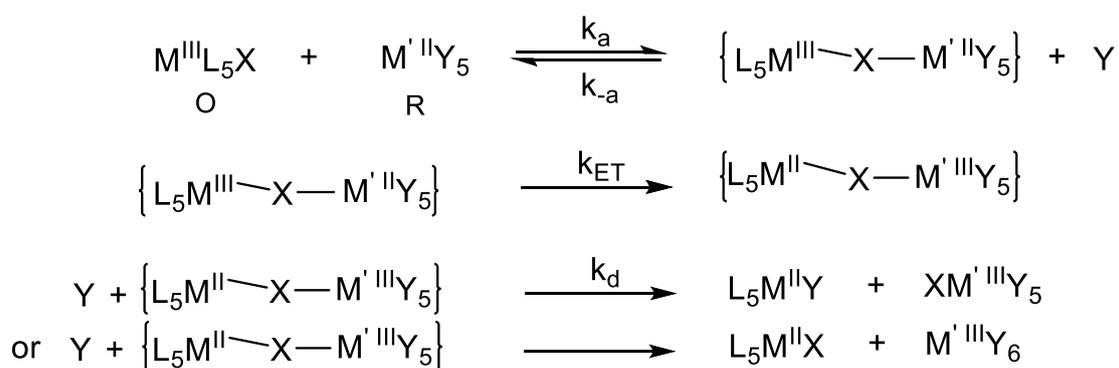
In O_h complexes dissociation of a ligand is required to form bridge

$$[Co^*(NH_3)_6]^{3+} + \ [Cr(H_2O)_6]^{2+} \longrightarrow [Co(H_2O)_6]^{2+} \ + \ [Cr(H_2O)_6]^{3+} \ + \ 6\ NH_3$$
$$t_{2g}^6 \qquad\qquad t_{2g}^3e_g^1 \qquad\qquad\quad t_{2g}^5e_g^2 \qquad\qquad t_{2g}^3 \qquad k = 10^{-3}\ M^{-1}s^{-1}$$

outer sphere mechanism

add Cl⁻

$$[Co(NH_3)_5Cl]^{2+} \ [Cr(H_2O)_6]^{2+} \longrightarrow [Co(H_2O)_6]^{2+} + \ [Cr(H_2O)_5Cl]^{2+} \ \ 5\ NH_3$$
$$t_{2g}^6 \qquad\quad t_{2g}^3e_g^1 \qquad\qquad\quad t_{2g}^5e_g^2 \qquad\quad t_{2g}^3 \qquad k = 6 \times 10^5$$
$$\text{inert} \qquad\quad \text{labile} \qquad\qquad\qquad \text{labile} \qquad\quad \text{inert} \qquad M^{-1}s^{-1}$$

inner sphere mechanism (Cl⁻ transfer)
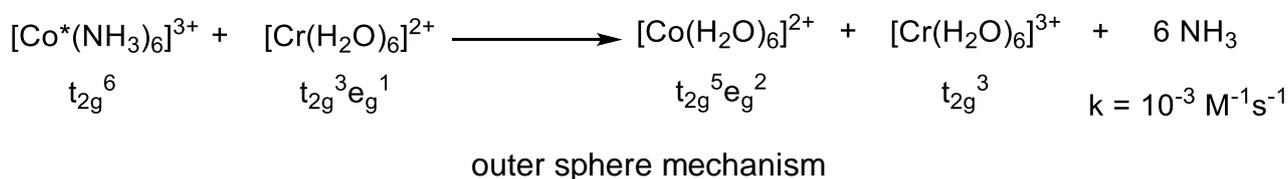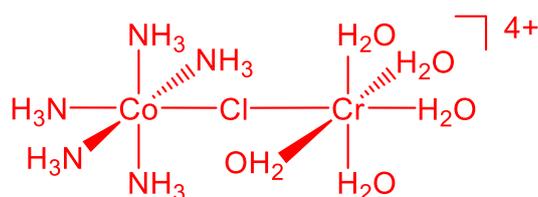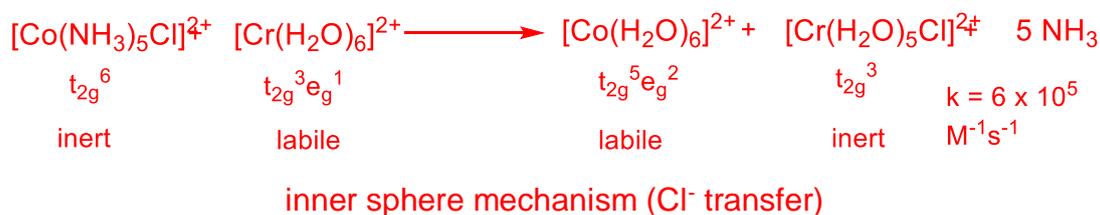
Conclusive proof of inner sphere mechanism

If we use $[Co(NH_3)_5Cl]^{2+}$ at start and add Cl^{*-}, Cl^{*-} is **not** in final product.

However ligand transfer is not a requirement of inner sphere mechanism

$$[IrCl_6]^{2-} \quad + \quad [Cr(H_2O)_6]^{2+} \quad \longrightarrow \quad [IrCl_6]^{3-} \quad + \quad [Cr(H_2O)_6]^{3+}$$

$$t_{2g}^5 \qquad\qquad t_{2g}^3 e_g^1 \qquad\qquad\qquad t_{2g}^6 \qquad\qquad t_{2g}^3$$
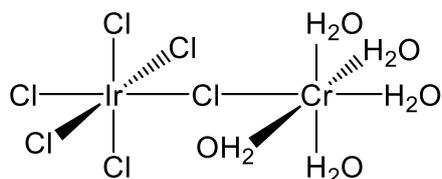
Transfer is determined by relevant bond strengths Ir-Cl + Ir-OH$_2$ vs Cr-Cl + Cr-OH$_2$

Factors that affect the rate of inner sphere electron transfer reactions

Self Exchange
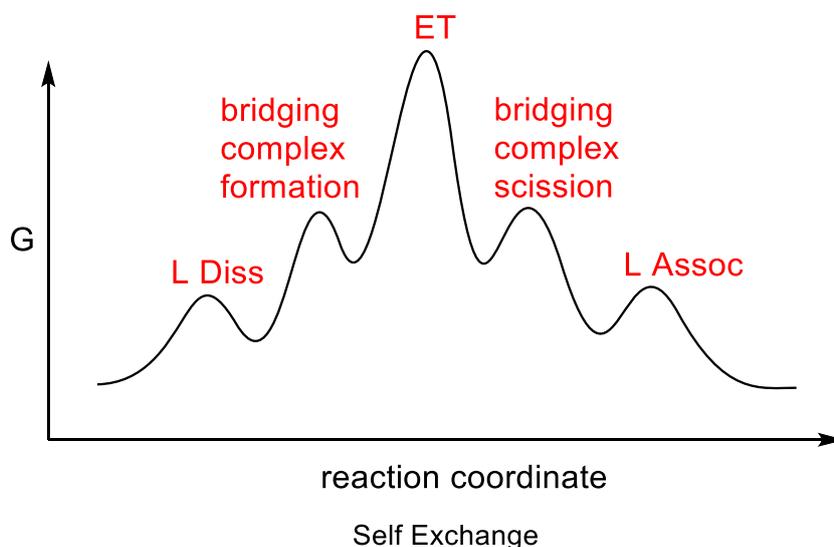
i) Formation of the bridging complex can be the rate limiting step (k_a). This will be dependent on how inert or labile the complexes are. (k_{ET} vs k_a). It is also possible that dissociation (k_d) is the rate limiting step.

Formation of bridging complex is rate determining scission
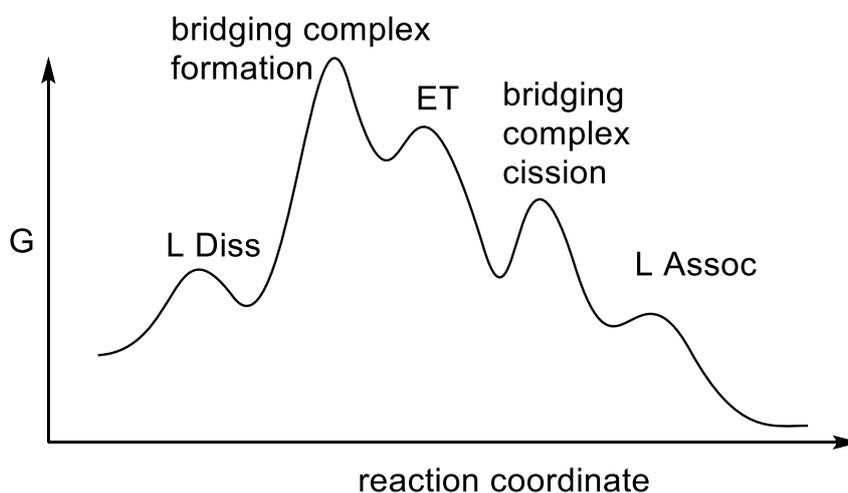
ii) Electronic configurations. σ^* ('e_g') orbitals interact strongly with bridging ligand. Orbital symmetries of metal σ^* and bridging ligands facilitate electron transfer. Massive acceleration in rates from outer to inner sphere can be achieved.

Reaction	HOMO	LUMO	Acceleration IS/OS
$Cr^{2+} + Co^{3+}$	σ^*	σ^*	$\sim 10^{10}$
$Cr^{2+} + Ru^{3+}$	σ^*	$\pi^* (\pi)$	$\sim 10^2$
$V^{2+} + Co^{3+}$	π^*	σ^*	$\sim 10^4$
$V^{2+} + Ru^{3+}$	π	π	All OS

σ^*

π/π^*

Cr^{2+} Co^{3+}
Large reorganisation for Co^{3+} OS. IS much faster

Cr^{2+} Ru^{3+}
Reorganisation of Ru^{3+} less than Co^{3+}

V^{2+} Co^{3+}
Co^{3+} Reorganisation IS faster

V^{2+} Ru^{3+}
Easily go OS. No reorganisation

e.g.

$M(\sigma^*)$ $M(\sigma^*)$
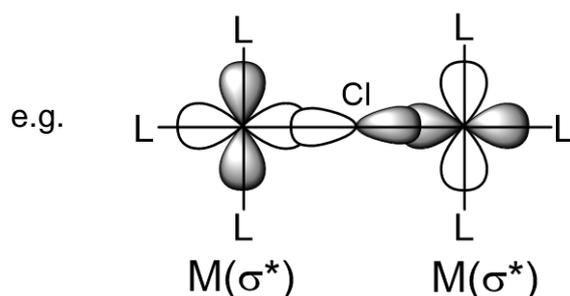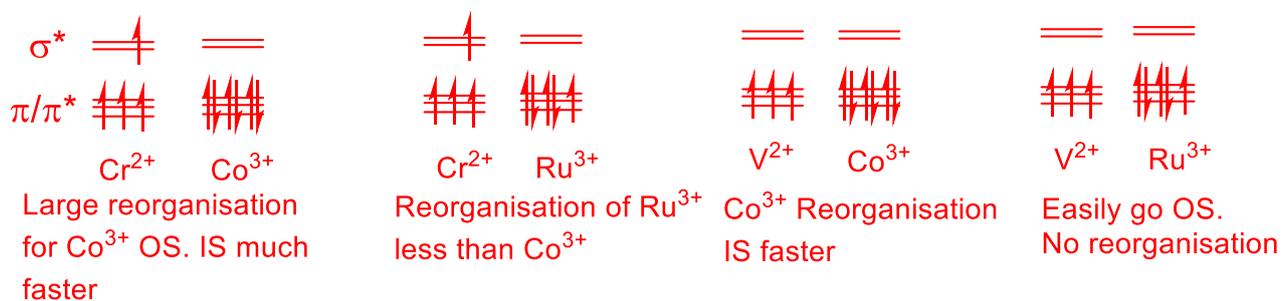
iii) Bridging ligand. Inner sphere electron transfer is very sensitive to bridging ligand.

1) The bridge connects the two metals.
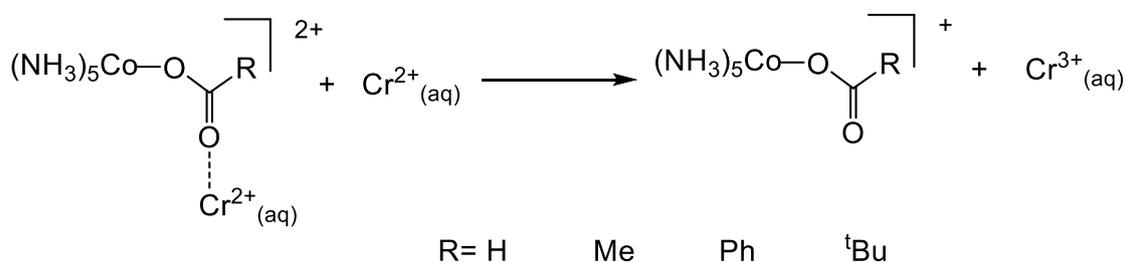
R=	H	Me	Ph	^tBu
k $M^{-1}s^{-1}$	7.2	0.35	0.15	9.6×10^{-3}

Increasing bulk of R slows binding of Cr^{2+} to bridge

2) Transfer can be a two step process from metal to ligand then ligand to metal. This circumvents the simultaneous reorganisation energy of both complexes that is required for outer sphere.

$$k = 4 \times 10^{-3} \ M^{-1}s^{-1}$$

$$[(NH_3)_5Co^{III}\!-\!N\text{(pyridine)}]^{3+} + Cr^{2+}{}_{(aq)} \xrightarrow{\text{Must be OS}} [(NH_3)_5Co\!-\!N\text{(pyridine)}]^{2+} + Cr^{3+}{}_{(aq)}$$

$$k = 17.4 \ M^{-1}s^{-1}$$
Coordination of Cr^{2+}
IS

$$[(NH_3)_5Co^{III}\!-\!N\text{(pyridine)}\text{C(O)NH}_2 \cdots Cr^{2+}{}_{(aq)}]^{3+} + Cr^{2+}{}_{(aq)} \longrightarrow [(NH_3)_5Co^{II}\!-\!N\text{(pyridine)}\text{C(O)NH}_2]^{2+} + Cr^{3+}{}_{(aq)}$$

$$[(NH_3)_5Co^{III}\!-\!N^{\bullet}\text{(pyridine)}\text{C(O)NH}_2\text{—}Cr^{3+}{}_{(aq)}]^{5+}$$

ligand mediates electron transfer

How do we distinguish if electron transfer is outer or inner sphere?

Is there a vacant coordination site?
Is there a substitutionally labile reactant?
Has ligand transfer occurred?
Are there large differences in rate on addition or substitution of potentially bridging ligand?

A good test is to compare electron transfer rates of N_3^- and NCS^- complexes.

$E_{1/2}$ (ΔG^o's) of N_3^- and NCS^- complexes are similar.

If $k_{N3-} / k_{NCS-} \sim 1$ (OS). If $k_{N3-} / k_{NCS-} \gg 1$ (IS). This is because N_3^- is symmetric.

O	R	k_{N3-} / k_{NCS-}	rxn type
$[(NH_3)_5CoX]^{2+}$	Cr^{2+}	10^4	IS
$[(NH_3)_5CoX]^{2+}$	V^{2+}	27	intermediate
$[(NH_3)_5CoX]^{2+}$	Fe^{2+}	$> 3 \times 10^3$	IS
$[(NH_3)_5CoX]^{2+}$	$Cr(bipy)_3^{2+}$	4	OS
$[(H_2O)_5CoX]^{2+}$	Cr^{2+}	4×10^4	IS

M-N=N=N-M
'faster' electron transfer
A.O. energies are more uniform
M.O. 'smoother'

M-N=C=S-M
'slower' electron transfer
greater difference between A.O. energies
M.O. 'rougher'