Inorganic Mechanisms II

Core Module 7

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Synopsis

Lecture 1: Outer sphere electron transfer I

Lecture 2: Outer sphere electron transfer II

Lecture 3: Inner sphere electron transfer

Lecture 4: How catalysts work

Lecture 5: Isomerisation, hydrogenation and hydroformylation

Lecture 6: CO/alkene compolymerisation, dehydrogenation and borylation of alkanes

Workshop

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

i)   Understand distinction between outer sphere and inner sphere electron transfer.
ii)   Describe how rearrangement of solvent and internal atom coordinates affects the rate of outer sphere electron transfer.
iii)   Use the Marcus cross relation and discuss the relation ship between λ, $\Delta G^{\ddagger}$ and ΔG^{o}
iv)   Understand that a bridging group (atom or molecule) is required for inner sphere electron transfer.
v)   Distinguish factors that indicate if electron transfer occurs by an outer or inner sphere mechanism.
vi)   Understand what a catalyst is and the principal ways that a catalyst affects the rate of a chemical reaction.
vii)   Understand the concept of the catalytic cycle and the principle of microscopic reverse.
viii) Illustrate the basic mechanisms of some catalytic reactions incorporating alkenes.
ix)   Illustrate the basic mechanisms of some catalytic reaction incorporating alkanes.

Bibliography:

Electron transfer:

J. E. Huheey, E A Keiter and R. L. Keiter. *Inorganic Chemistry*, 4th Ed., 1993, p 547 – 576.
R. A. Henderson. The Mechanisms of Reactions at Transition Metal Sites, 1995
R. B. Jordan, *Reaction Mechanisms of Inorganic and Organometallic Systems*, 1991 Ch 3 and 6.
R. A. Marcus, Angew. Chem. Int. Ed. 1993, **32**, 1111.

Catalysis:

C. Elschenbroich and A Salzer. *Organometallics*, 2nd Ed.,1992, Ch 17
F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th Ed.
Chen, H *et al.* Science, 2000, **287**, p1995
R. B. Jordan, *Reaction Mechanisms of Inorganic and Organometallic Systems*, 1991 Ch 5.

Associated Core Courses

AKDK	Transition metal chemistry	1st year
JML	Transition metal organometallics	2nd year
SBD	Inorganic mechanisms I	2nd year
MCRC	Vibrational spectroscopy	2nd year
RED	Metal-ligand bonding	2nd year
JML	Main group clusters and organometallics	3rd year
AKDK	Bioinorganic chemistry	3rd year
PBK	Electrons in chemical reactions	3rd year
RNP	Photochemistry	3rd year

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.
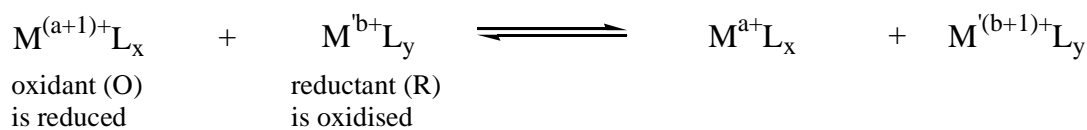
Recap

Substitution: Inert vs labile octahedral complexes

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

$$M^{(a+1)+}L_x \quad + \quad M'^{b+}L_y \quad \xrightarrow{K_{eq}} \quad \left\{ M^{(a+1)+}L_x^{\text{''''''}} M'^{b+}L_y \right\} \quad \text{Precursor complex}$$
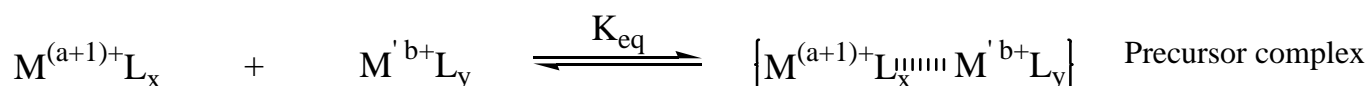
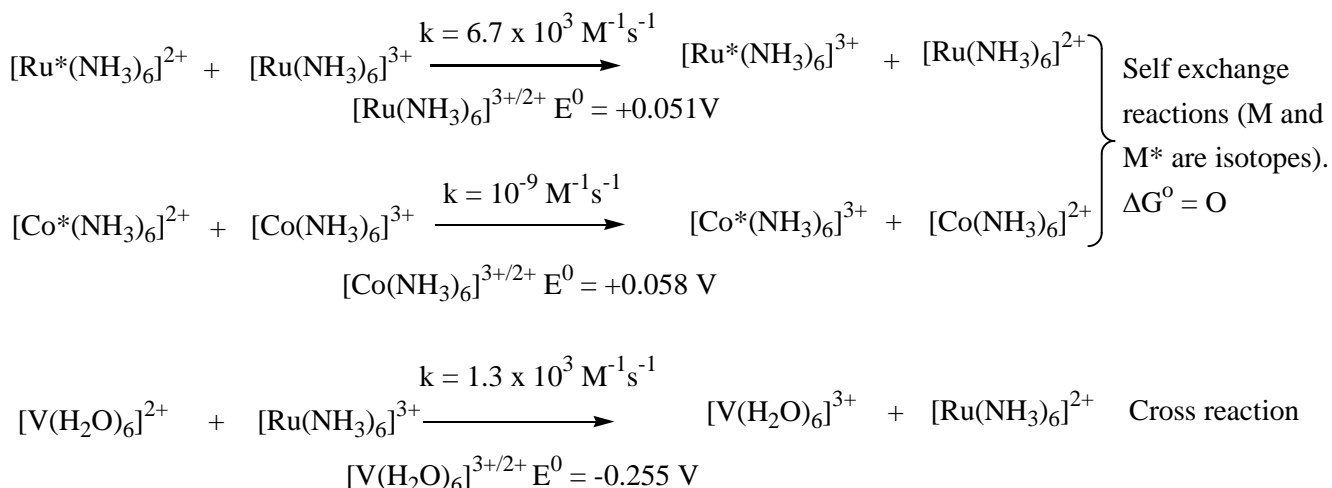### 2. Activation/reorganisation of precursor complex. Electron transfer. Relaxation to successor complex

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

3. Dissociation of successor complex

$$\left\{ M^{a+}L_x^{\text{''''''}} M'^{(b+1)+}L_y \right\} \quad \xrightarrow{k_{diss}} \quad M^{a+}L_x \quad + \quad M'^{(b+1)+}L_y$$
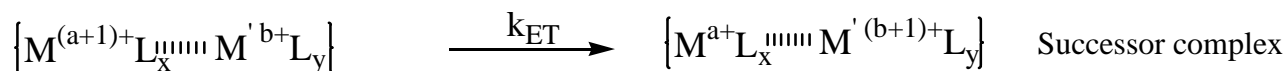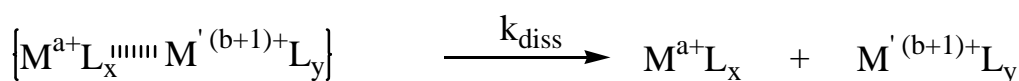
Formation of precursor complex and dissociation of successor complex are fast. Electron transfer slow
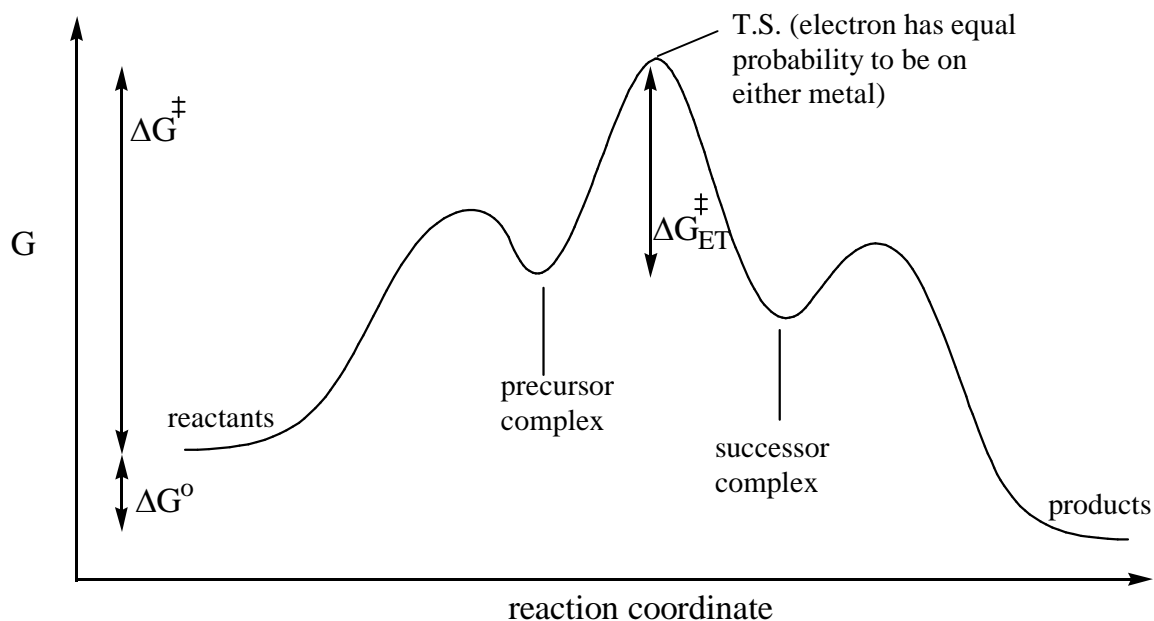
remember from thermodynamics, driving force $\Delta G^o = -nF\Delta E^0$
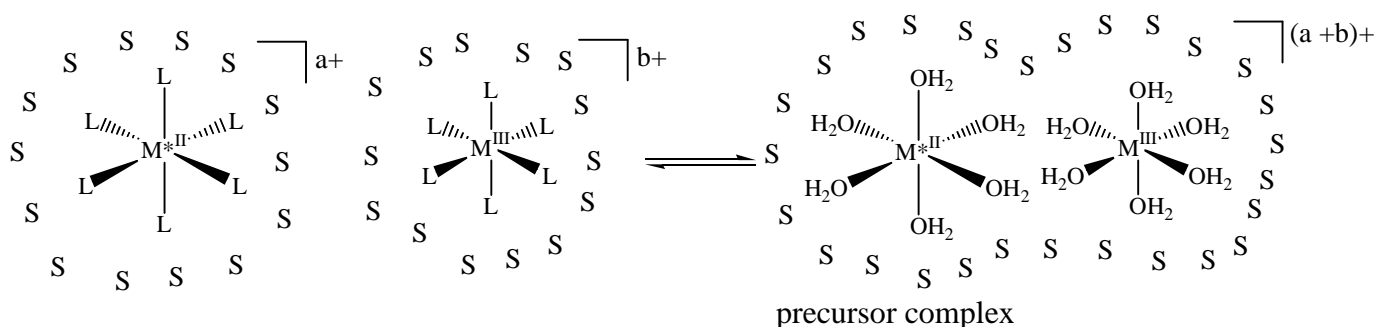
$$[Ru^*(NH_3)_6]^{2+} + [Ru(NH_3)_6]^{3+} \xrightarrow{k = 6.7 \times 10^3 \text{ M}^{-1}\text{s}^{-1}} [Ru^*(NH_3)_6]^{3+} + [Ru(NH_3)_6]^{2+}$$
$$[Ru(NH_3)_6]^{3+/2+} \; E^0 = +0.051\text{V}$$

$$[Co^*(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+} \xrightarrow{k = 10^{-9} \text{ M}^{-1}\text{s}^{-1}} [Co^*(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+}$$
$$[Co(NH_3)_6]^{3+/2+} \; E^0 = +0.058 \text{ V}$$

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

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

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

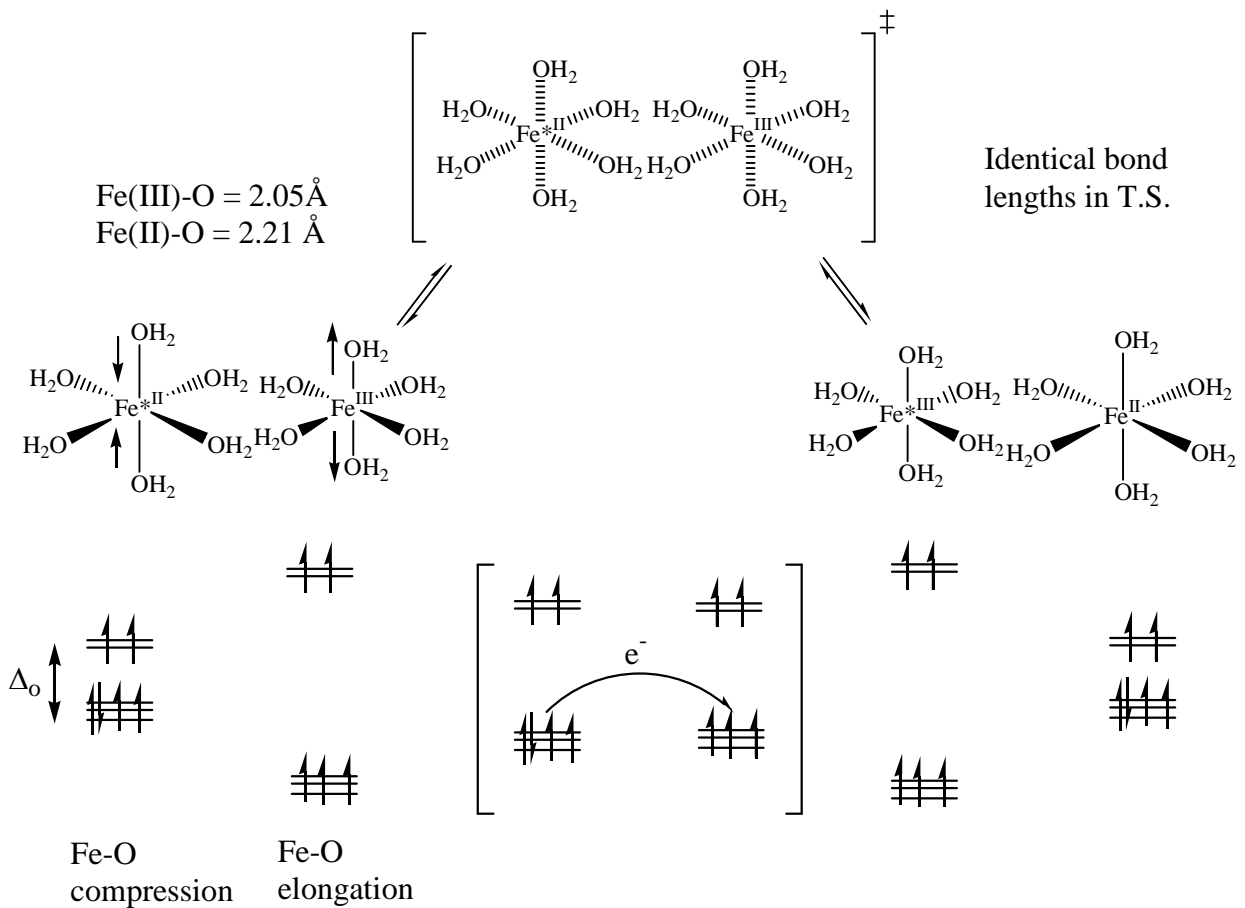| energy to bring reactants together (including overcoming coulombic repulsion) | energy needed for solvent reorganisation | energy required for reorganisation of bond lengthening/compression to make interacting orbitals the same energy |
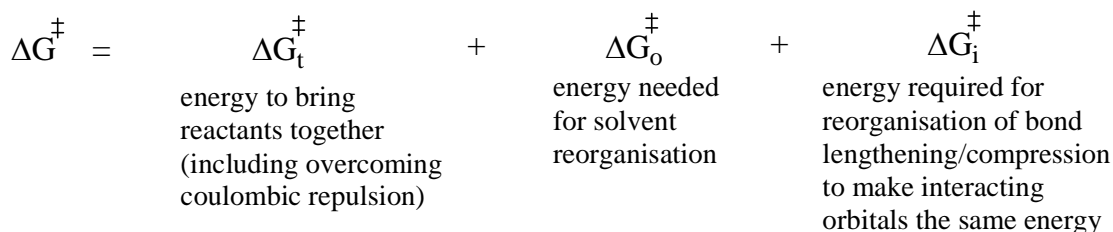
i) $\Delta G_o^{\ddagger}$. Energy is required to reorganise the solvent.

precursor complex

Solvents 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.

$$\begin{bmatrix} & OH_2 & & OH_2 \\ H_2O_{\prime\prime\prime\prime} & \underset{Fe^{*II}}{\vert} \cdots\prime\prime OH_2 \ H_2O_{\prime\prime\prime\prime} & \underset{Fe^{III}}{\vert} \cdots\prime\prime OH_2 \\ H_2O^{\prime\prime\prime\prime} & \prime\prime\prime OH_2 \ H_2O^{\prime\prime\prime\prime} & \prime\prime\prime OH_2 \\ & OH_2 & & OH_2 \end{bmatrix}^{\ddagger}$$

$$[Fe^{*II}][Fe^{III}] \rightleftharpoons$$ ... $$\rightleftharpoons [Fe^{*III}][Fe^{II}]$$

Fe-O
compression

Fe-O
elongation

Δ_o

e^-

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

Why not transfer electron then relax bonds?

Potential energy diagrams
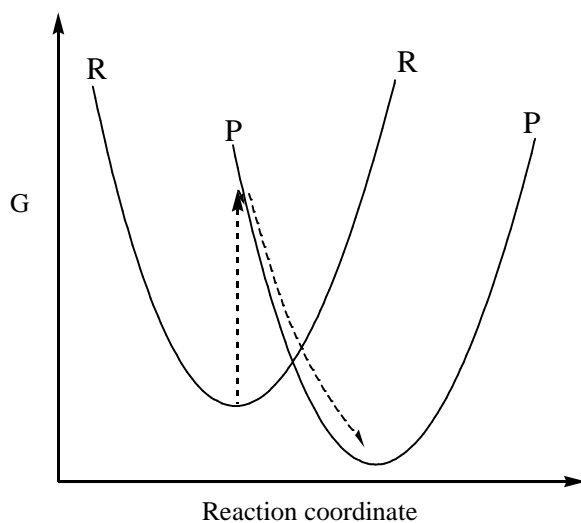
R = potential energy surface of reactants + environment
P =   "   products   "

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.

G

Reaction coordinate

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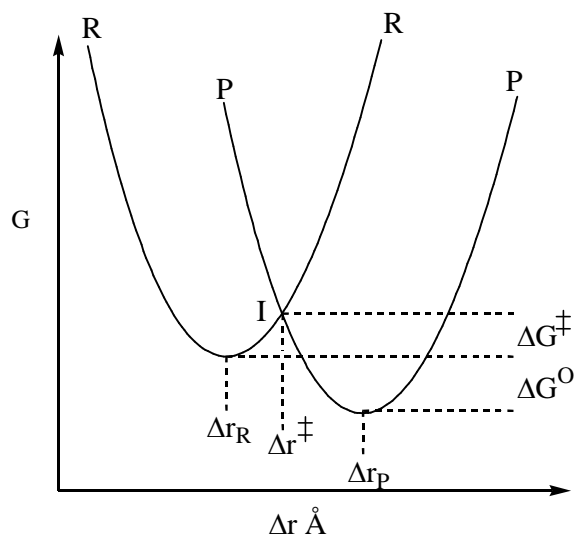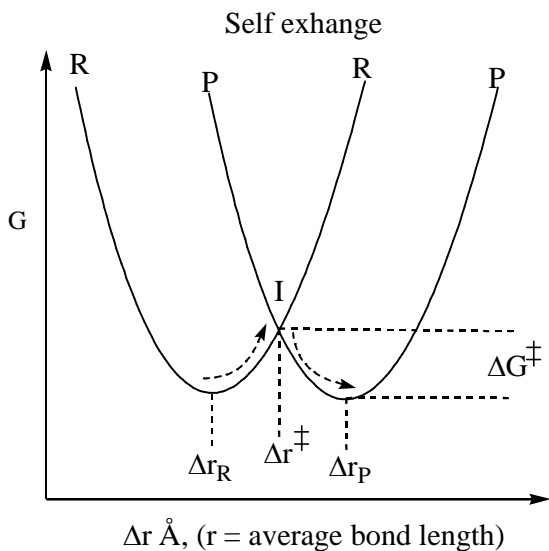
At I, the requirement of equal orbital energies is met allowing the possibility of electron transfer.

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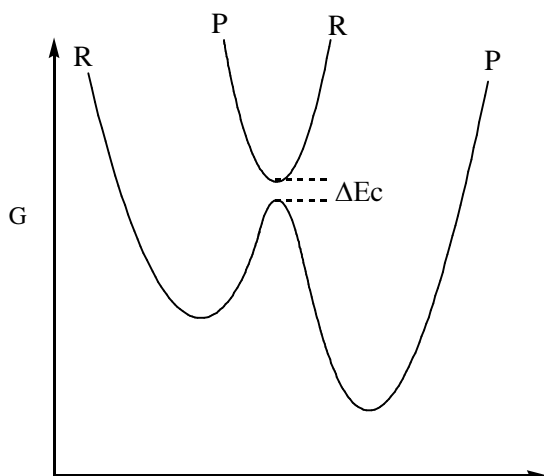
Wavefunction is reactant-like at the left of the well. When get to crossing point turn on mixing due to coupling. (only near the crossing point is this important). Large ΔEc means large probability of crossing to product-like well on right.

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

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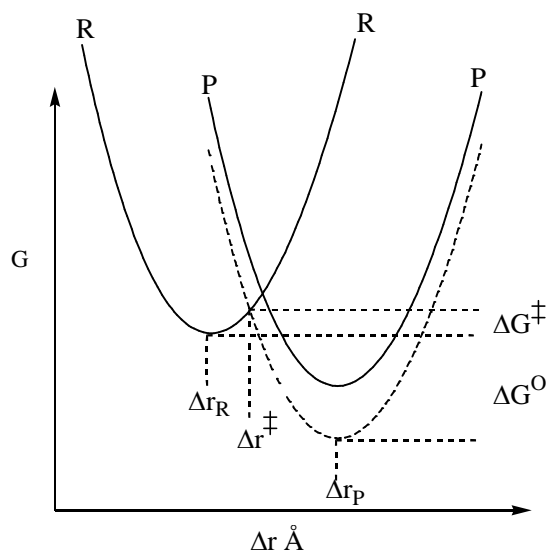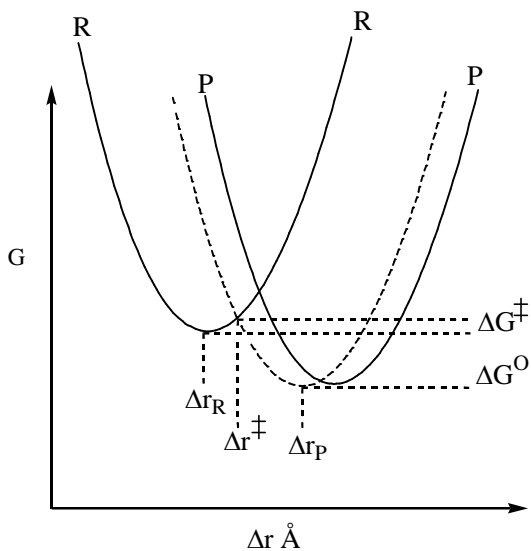
$$\Delta G^{\ddagger} \propto 1/(\Delta G^{o})^2 \quad (\text{ however see inverted Marcus region})$$

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

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

Electron transfer requires orbital overlap and occurs between orbitals of the same symmetry
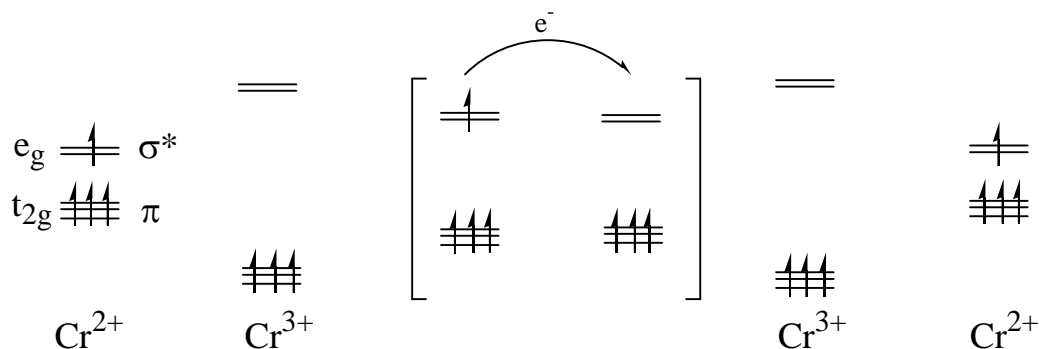
Orbital symmetry

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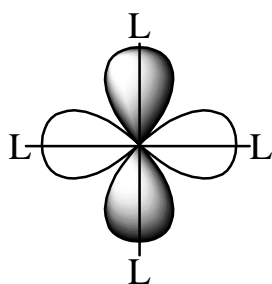
+ poor overlap (ligand sterics)

In O_h field t_{2g} is π/π^*: $t_{2g} \rightarrow t_{2g}$ transition = small change in bond length. 'Fast' electron transfer
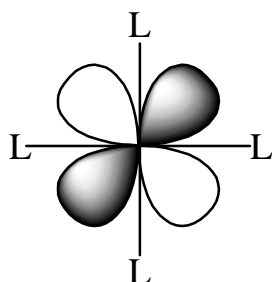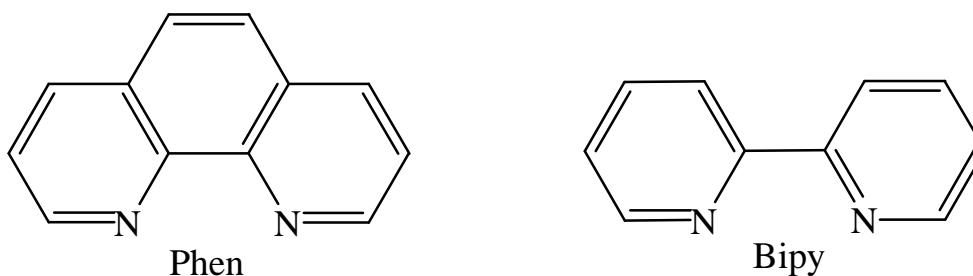

better overlap (depends on ligands)

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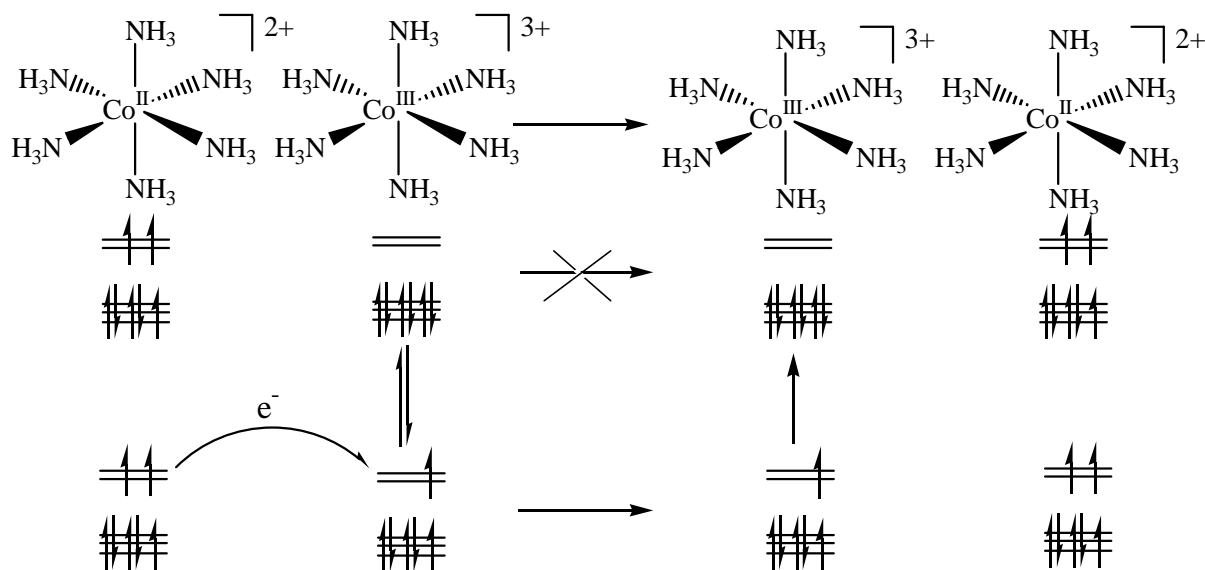
Ligands that have extended π-systems e.g. Phen, bipy etc can assist electron transfer.

Electronic Configuration

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.

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 same charge or if the reactants are effectively fixed in space such as in a protein w $\approx$ 0. Therefore

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

and for a self exchange reaction $\Delta G^o = 0$.

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

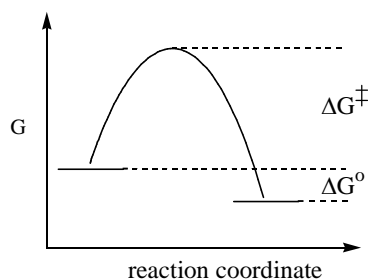Note that a thermodynamic parameter (ΔG^o_{AB}) is being used in a kinetic expression
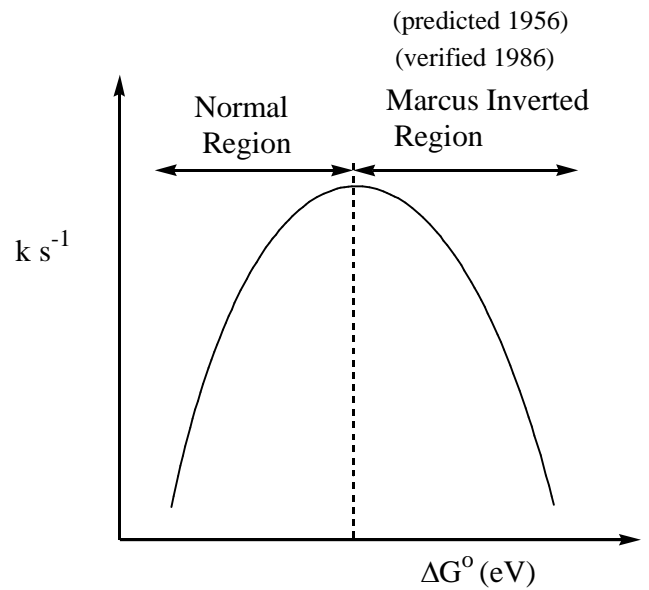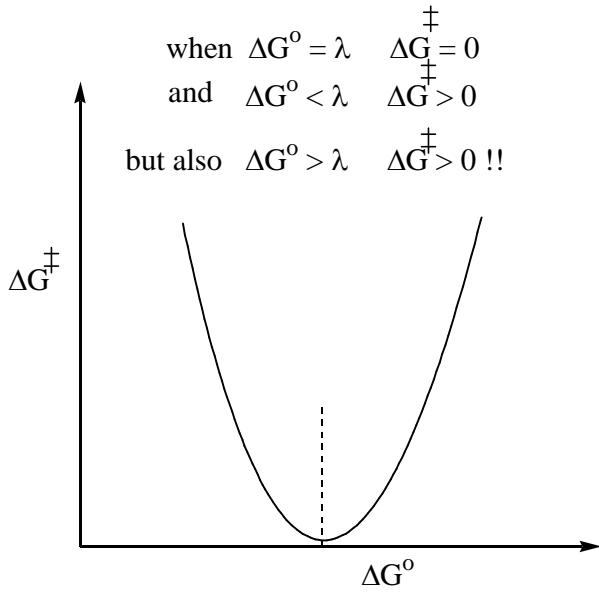

reaction coordinate
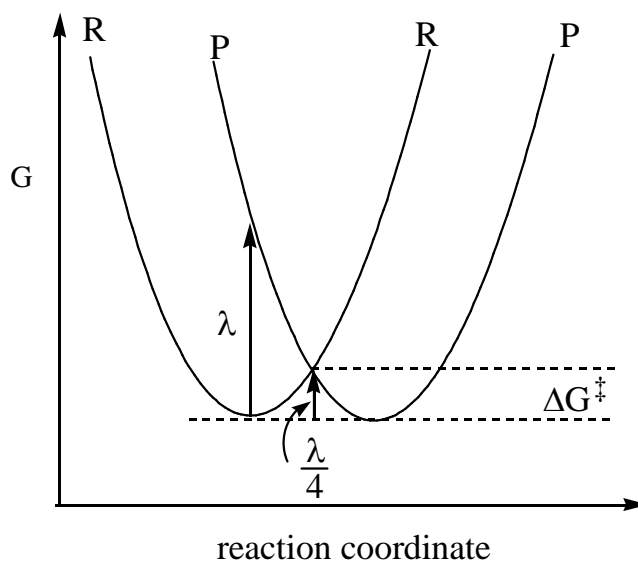
Recap

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

(predicted 1956)

(verified 1986)

In the inverted region the rate (k) decreases as the thermodynamic driving force increases!

This is most easily visualised using a potential energy diagram
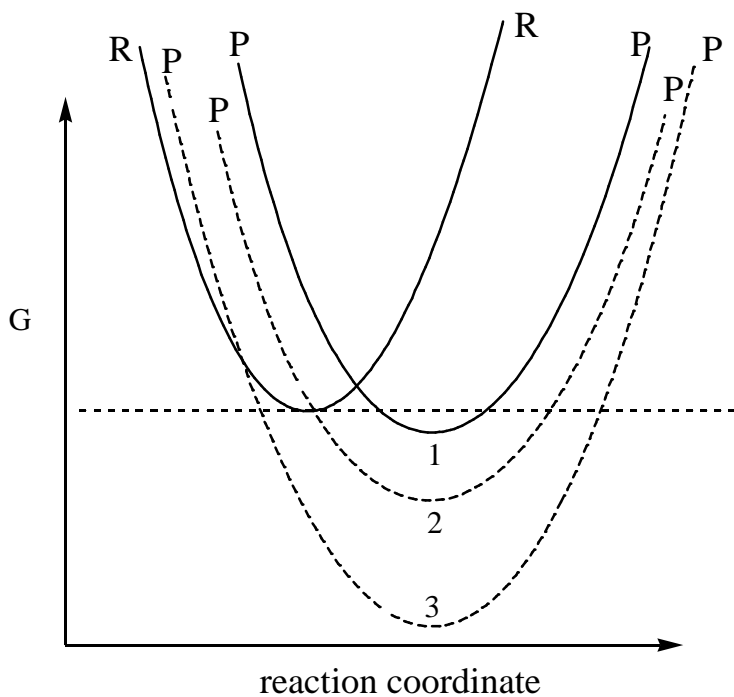
1. Normal Region $\Delta G^{\ddagger} > 0$

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

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

$\Delta G^o \; 3 > 2 > 1$

The Marcus inverted region is probably important in photosynthesis where wasteful back electron transfer reactions (which are highly exothermic) are prevented.

Marcus cross-relation

Self exchange reaction $\Delta G^o = 0$

cross reaction $\Delta G^o < 0$

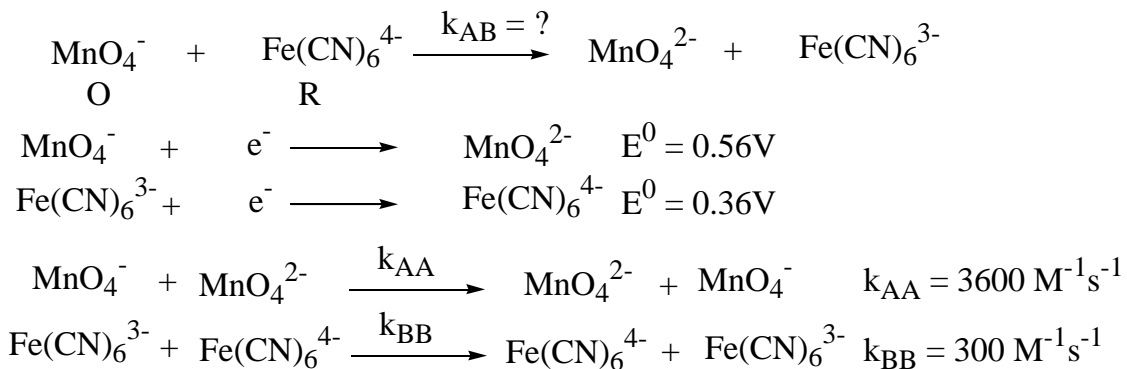Marcus related the cross reaction to the two self exchange reactions.

$$k_{AB} = (k_{AA}k_{BB}K_{AB}f_{AB})^{1/2} \quad f_{AB} = \frac{(\log K_{AB})^2}{4 \log \left(\dfrac{k_{AA}k_{BB}}{Z^2} \right)} \approx 1$$

k_{AB} = rate of cross reaction: k_{AA}, k_{BB} = self exchange rates: K_{AB} = equilibrium constant of reaction Z = collision frequency for hypothetical uncharged complex (10^{11}-10^{13} $M^{-1}s^{-1}$). Can calculate the rate of electron transfer cross reaction k_{12} if other parameters are known.

$$k_{AB} \approx (k_{AA}k_{BB}K_{AB})^{1/2}$$

$$\text{or} \quad \Delta G_{AB}^{\ddagger} \approx \frac{1}{2}\left(\Delta G_{AA}^{\ddagger} + \Delta G_{BB}^{\ddagger} + \Delta G_{AB}^{o} \right)$$

e.g.

$$MnO_4^- + Fe(CN)_6^{4-} \xrightarrow{k_{AB} = ?} MnO_4^{2-} + Fe(CN)_6^{3-}$$
$$ O \phantom{+ Fe(CN)_6^{4-}} R$$

$$MnO_4^- + e^- \longrightarrow MnO_4^{2-} \quad E^0 = 0.56V$$
$$Fe(CN)_6^{3-} + e^- \longrightarrow Fe(CN)_6^{4-} \quad E^0 = 0.36V$$

$$MnO_4^- + MnO_4^{2-} \xrightarrow{k_{AA}} MnO_4^{2-} + MnO_4^- \quad k_{AA} = 3600 \ M^{-1}s^{-1}$$
$$Fe(CN)_6^{3-} + Fe(CN)_6^{4-} \xrightarrow{k_{BB}} Fe(CN)_6^{4-} + Fe(CN)_6^{3-} \quad k_{BB} = 300 \ M^{-1}s^{-1}$$

Rem: $\Delta G^o = -RT\ln K$

and $\Delta G^o = -nF\Delta E^0$

therefore $-RT\ln K = -nF\Delta E^0 \quad K = e^{\left(\frac{nF\Delta E^0}{RT} \right)}$

$$(\ O \ - \ R \ )$$
$$K_{AB} = e^{(38.94(0.56 - 0.36))} = 2.4 \times 10^3$$

$$k_{AB} = (3600 \times 300 \times 2.4 \times 10^3)^{1/2} = 5.1 \times 10^4 \ M^{-1}s^{-1}$$

$$k_{exp} = 1.3 \times 10^4 \ M^{-1}s^{-1}$$

Reactants	k_{AB} calc ($M^{-1}s^{-1}$)	k_{AB} obsd ($M^{-1}s^{-1}$)
$[Co(Phen)_3]^{3+} + [Ru(NH_3)_6]^{2+}$	3.5×10^{-5}	1.5×10^{-4}
$[Co(en)_3]^{3+} + [V(H_2O)_6]^{2+}$	3.1×10^{-3}	5.8×10^{-4}
$[Ru(NH_3)_6]^{3+} + [V(H_2O)_6]^{2+}$	2.2×10^{3}	1.3×10^{3}
$[Fe(H_2O)_6]^{3+} + [V(H_2O)_6]^{2+}$	1.6×10^{6}	1.8×10^{4}
$[Fe(H_2O)_6]^{3+} + [Ru(NH_3)_6]^{2+}$	1.0×10^{8}	3.4×10^{5}

Reasons for k_{calc} vs k_{obsd} differences

1. Cross relation assumes that activation process of each reactant is independent of the other and that the activated species are the same in the self exchange and the cross reaction. But if the reactants have opposite charge they will attract each other and $Z_{AB} \gg Z_{AA}$ and Z_{BB} therefore $f_{AB} \gg 1$.

2. If ΔEc is small, transmission coefficient $\kappa < 1$. Not all transition states with $\Delta G > \Delta G^{\ddagger}$ go to products.

$$k = \frac{k_B T}{h} e^{-\Delta G^{\ddagger}/RT} \quad \text{vs} \quad k = \kappa_{el} \frac{k_B T}{h} e^{-\Delta G^{\ddagger}/RT}$$

$$\text{"adiabatic"} \qquad\qquad \text{"nonadiabatic"}$$
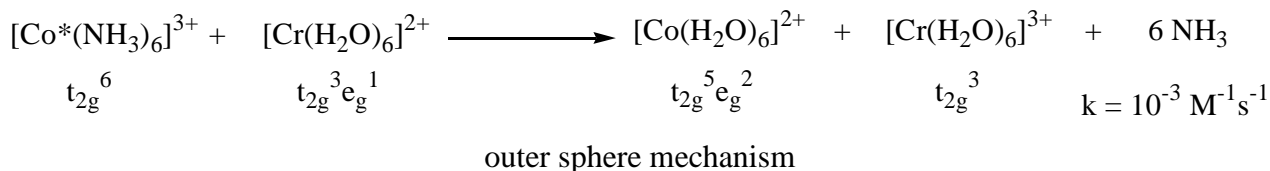
3. Not outer sphere (Inner sphere?)

Inner sphere electron transfer

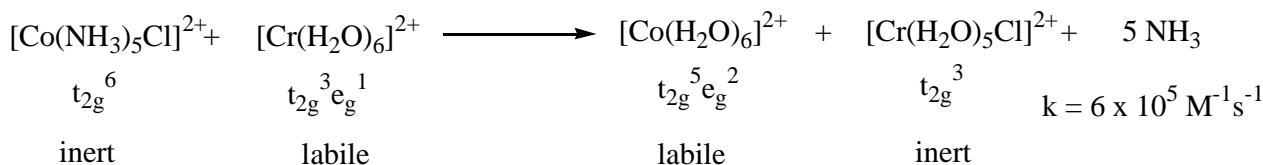Inner sphere electron transfer is mediated by a bridging ligand.

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

ii) On activation the electron is transferred between the metals.
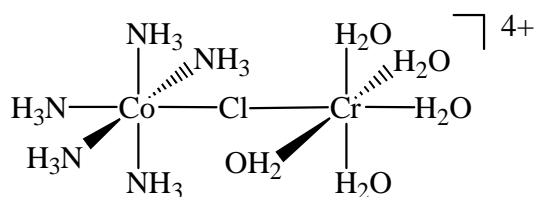
iii) The ligand **may** transfer between complexes.

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

$$\underset{O}{} \qquad \underset{R}{}$$

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

$$Y + \left\{L_5M^{II}-X-M'^{III}Y_5\right\} \; \xrightarrow{k_d} \; L_5M^{II}Y \;+\; XM'^{III}Y_5$$

$$\text{or} \quad Y + \left\{L_5M^{II}-X-M'^{III}Y_5\right\} \; \longrightarrow \; L_5M^{II}X \;+\; M'^{III}Y_6$$
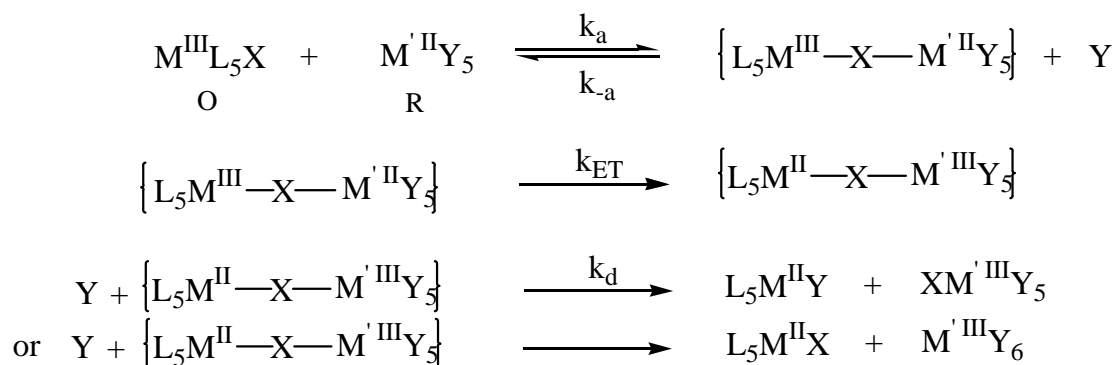
In O$_h$ complexes dissociation of a ligand is required to form bridge

$$[Co^*(NH_3)_6]^{3+} \;+\; [Cr(H_2O)_6]^{2+} \; \longrightarrow \; [Co(H_2O)_6]^{2+} \;+\; [Cr(H_2O)_6]^{3+} \;+\; 6\,NH_3$$

$$t_{2g}^6 \qquad\qquad t_{2g}^3 e_g^1 \qquad\qquad\qquad t_{2g}^5 e_g^2 \qquad\qquad t_{2g}^3 \qquad k = 10^{-3}\ M^{-1}s^{-1}$$

outer sphere mechanism

add Cl$^-$

$$[Co(NH_3)_5Cl]^{2+} \;+\; [Cr(H_2O)_6]^{2+} \; \longrightarrow \; [Co(H_2O)_6]^{2+} \;+\; [Cr(H_2O)_5Cl]^{2+} \;+\; 5\,NH_3$$

$$t_{2g}^6 \qquad\qquad t_{2g}^3 e_g^1 \qquad\qquad\qquad t_{2g}^5 e_g^2 \qquad\qquad t_{2g}^3 \qquad k = 6 \times 10^5\ M^{-1}s^{-1}$$

$$\text{inert} \qquad\qquad \text{labile} \qquad\qquad\qquad \text{labile} \qquad\qquad \text{inert}$$

inner sphere mechanism (Cl$^-$ transfer)

Conclusive proof of inner sphere mechanism
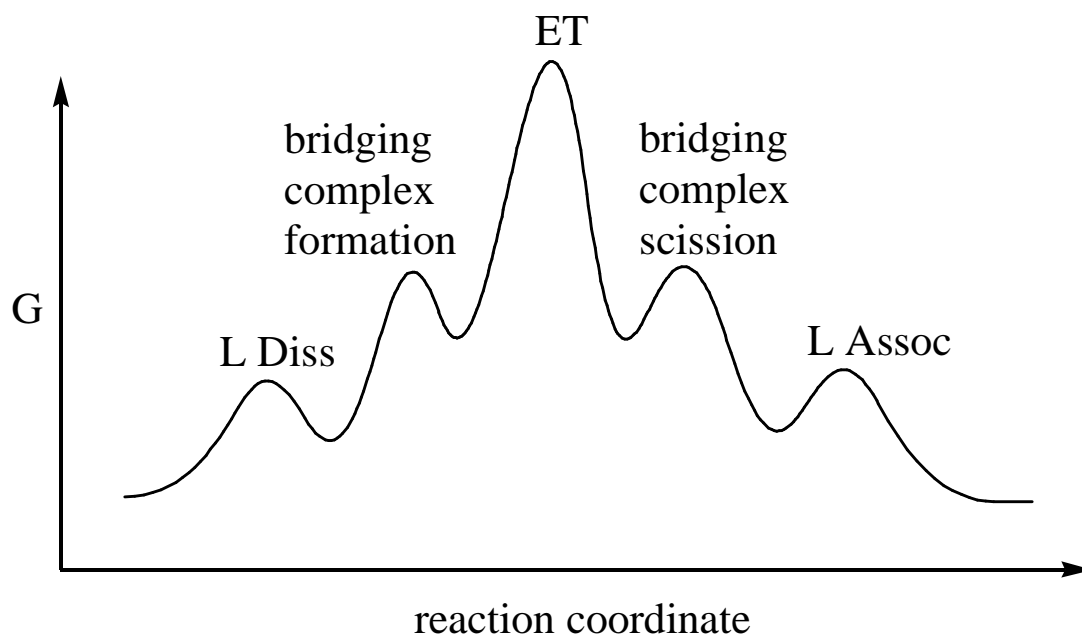
If we use [Co(NH$_3$)$_5$Cl]$^{2+}$ at start and add Cl^{*-}, Cl^{*-} is **not** in final product.

However ligand transfer is not a requirement of inner sphere mechanism

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

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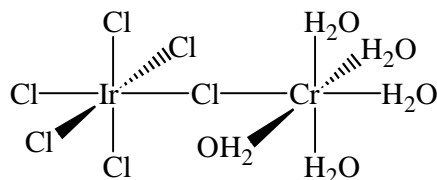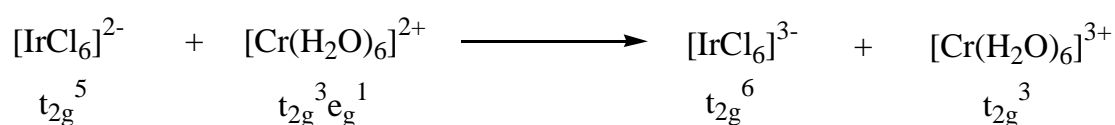
Transfer is determined by relevant bond strengths Ir-Cl + Ir-OH$_2$ vs Cr-Cl + Cr-OH$_2$

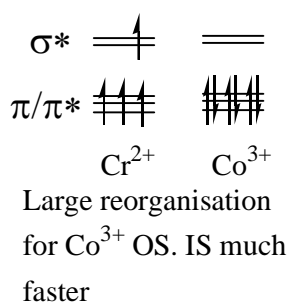**Factors that affect the rate of inner sphere electron transfer reactions**

ET

bridging complex formation

bridging complex scission

G

L Diss

L Assoc

reaction coordinate

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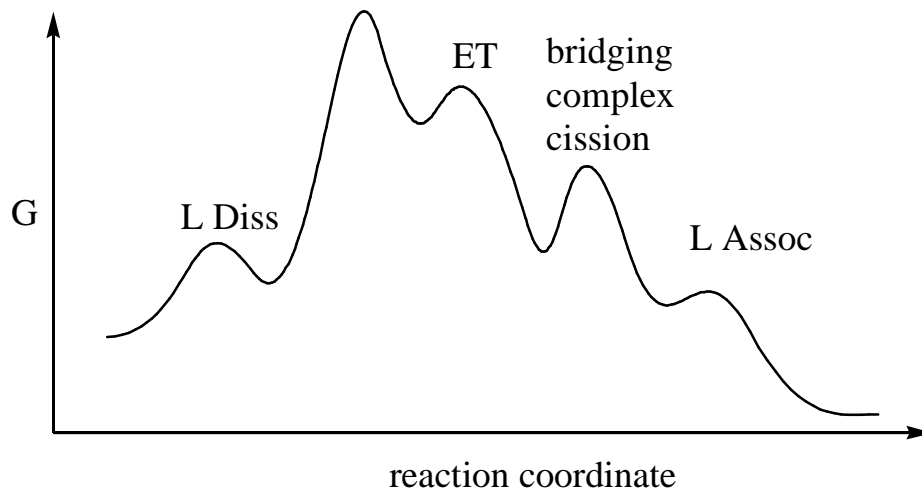
ii) Electronic configurations. σ^* ('e_g') orbitals interact strongly with bridging ligand. Orbital symmetries of metal σ^* and bridging ligands facilitate electron transfer. Massive acceleration in rates from outer to inner sphere can be achieved.

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.

$M(\sigma^*)$ $M(\sigma^*)$
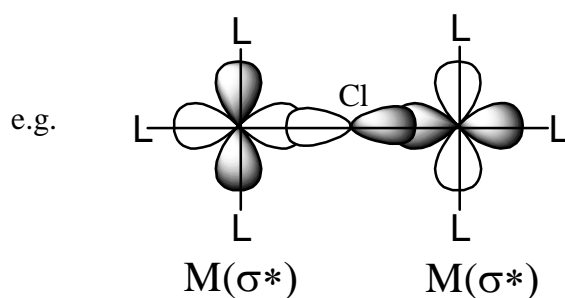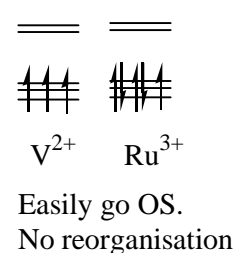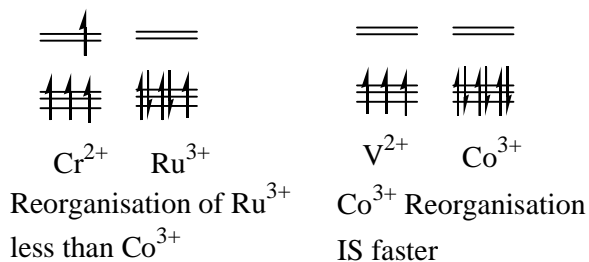
iii) Bridging ligand. Inner sphere electron transfer is very sensitive to bridging ligand.
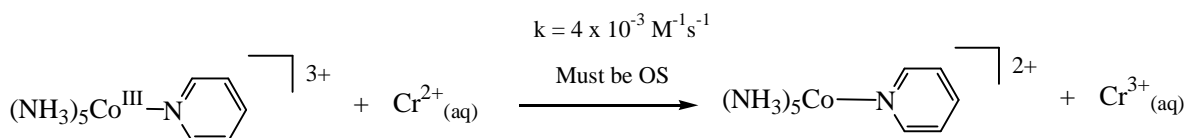
1) The bridge connects the two metals.
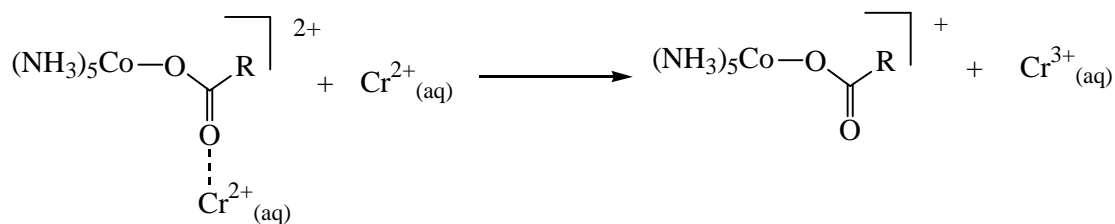
$$R = H \qquad Me \qquad Ph \qquad ^tBu$$

$$k\ M^{-1}s^{-1} \qquad 7.2 \qquad 0.35 \qquad 0.15 \qquad 9.6 \times 10^{-3}$$

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.

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

Must be OS

$$k = 17.4\ M^{-1}s^{-1}$$

Coordination of Cr^{2+}

IS
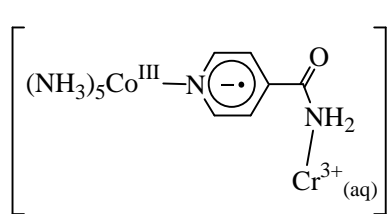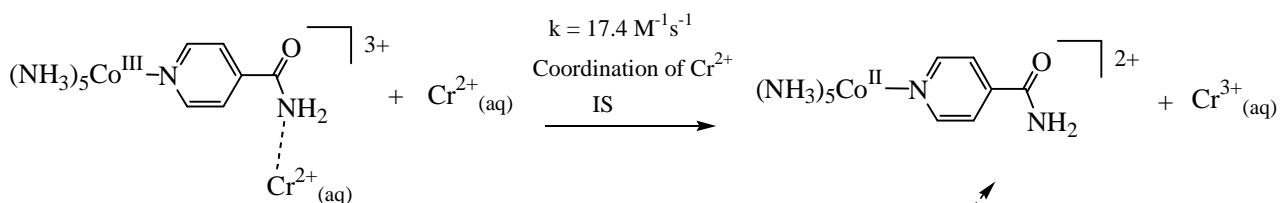
ligand mediates electron transfer

18

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   M-N=C=S-M

'faster' electron transfer   'slower' electron transfer

A.O. energies are more uniform   greater difference between A.O. energies
M.O. 'smoother'   M.O. 'rougher'

Catalysis

Catalysis is involved in the production of approximately 90% of the chemicals currently used in industry and forms the basis of technologies designed to remove or prevent noxious chemicals detrimental to the environment. Through the action of enzymes, catalysis also plays a central role in the life cycle.

Catalysis is a *kinetic* phenomenon. A catalyst increases the rate that a reaction reaches equilibrium but does not affect the position of the equilibrium. If a catalyst changed the position of equilibrium the second law of thermodynamics would be contravened.
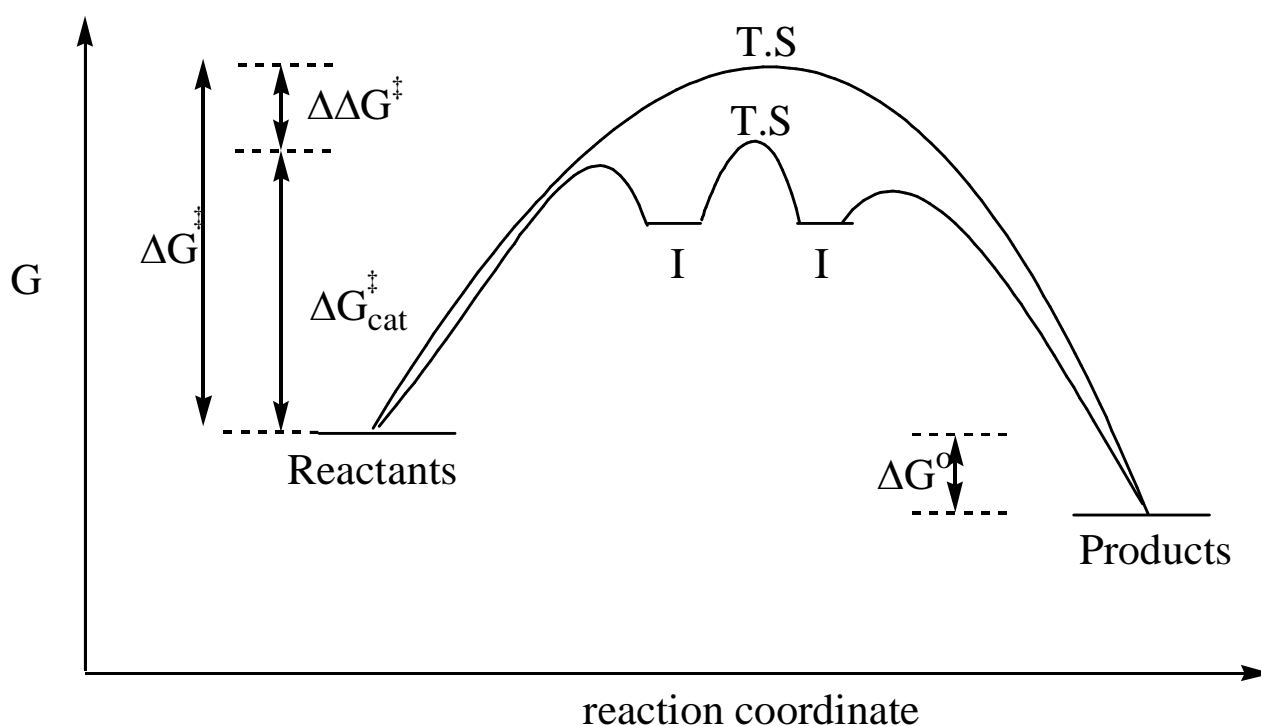
Amongst other properties, a good catalyst will give high yields of the desired product. i.e the catalyst affects the product distribution of a reaction. This is not because the catalyst has changed the position of equilibrium but because **most catalytic reactions are run under non-equilibrium conditions**.

In homogeneous catalysis $\Delta G^{\neq} \sim 90 - 140$ kJ mol^{-1} at RT possible.

But product distribution sensitive to differences in $\Delta G^{\neq}$ of < 4 kJ mol^{-1}

e.g. asymmetric catalysis. Product enantiomers have the same ground state energy but $\Delta G^{\neq}$'s are different.

Kinetics determines selectivity. No thermodynamic difference between the products

$$\Delta\Delta G^{\ddagger}$$

reactant

k_1 k_2

Enantiomer A $k_1 > k_2$ Enantiomer B
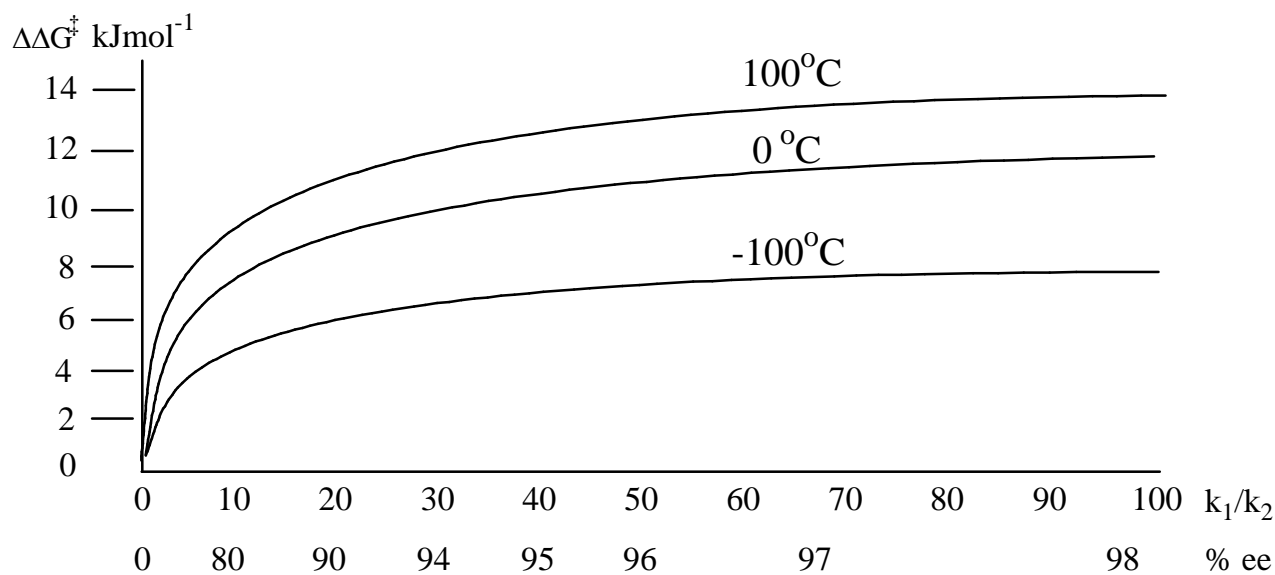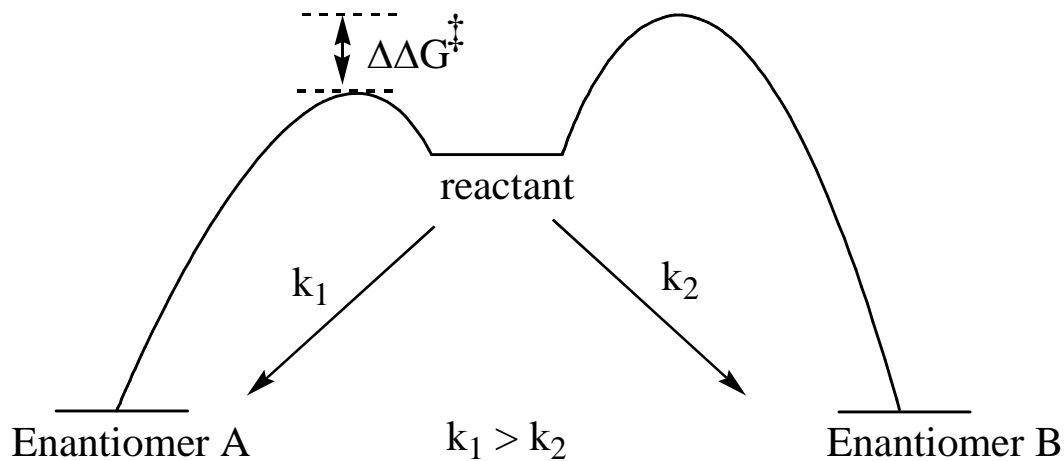
$\Delta\Delta G^{\ddagger}$ kJmol^{-1}

Product distribution sensitive to very small changes

e.g. at 0 ^{o}C 80% ee to 95% ee requires a $\Delta\Delta G^{\ddagger}$ of < 2 kJ mol^{-1}

c.f. ΔG difference between gauche and anti conformations of butane is 3.76 kJ mol^{-1}
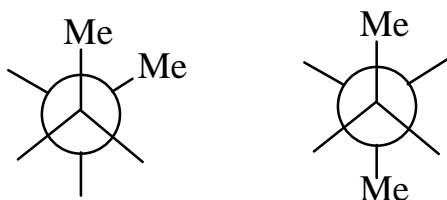
How does a catalyst work?

Bond breakage and formation are integral to all chemical reactions and are a consequence of the redistribution of valence electrons. MO theory provides a convenient way to understand the factors that effect bond breaking/forming processes.

1. Orbital overlap and directionality. Two atoms (molecules) must be physically within the same region of space if reaction is to occur.

A catalyst can act as a template increasing the probability and preferred directionality of orbital interactions.
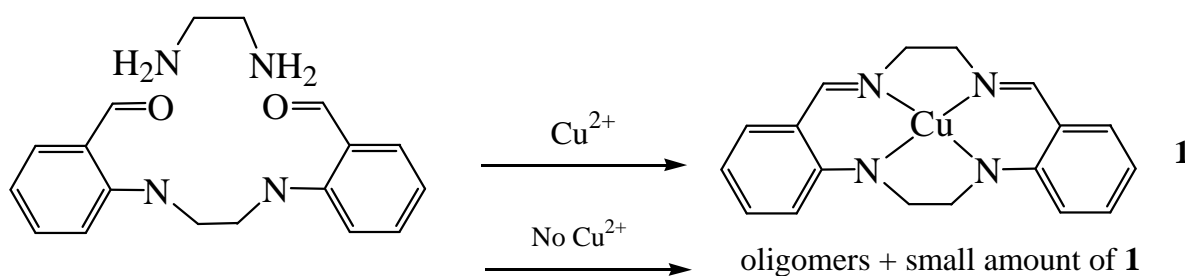
2. Orbital energy. Perturbation of the reactant orbital energies by interaction with a catalyst can change reaction rates.
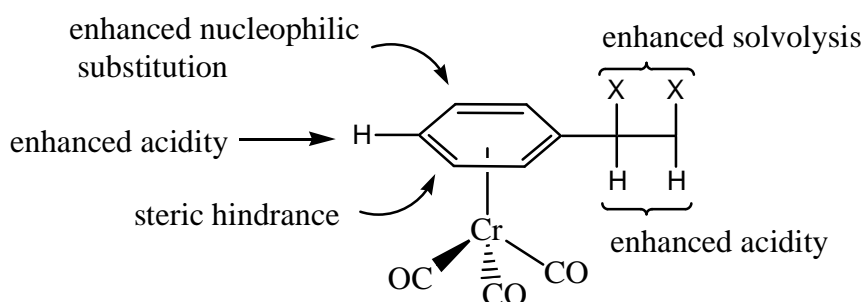
3. Orbital symmetry. A bond forming reaction requires interacting orbitals of the same symmetry. The frontier molecular orbitals and hence symmetry may change on interaction with a catalyst
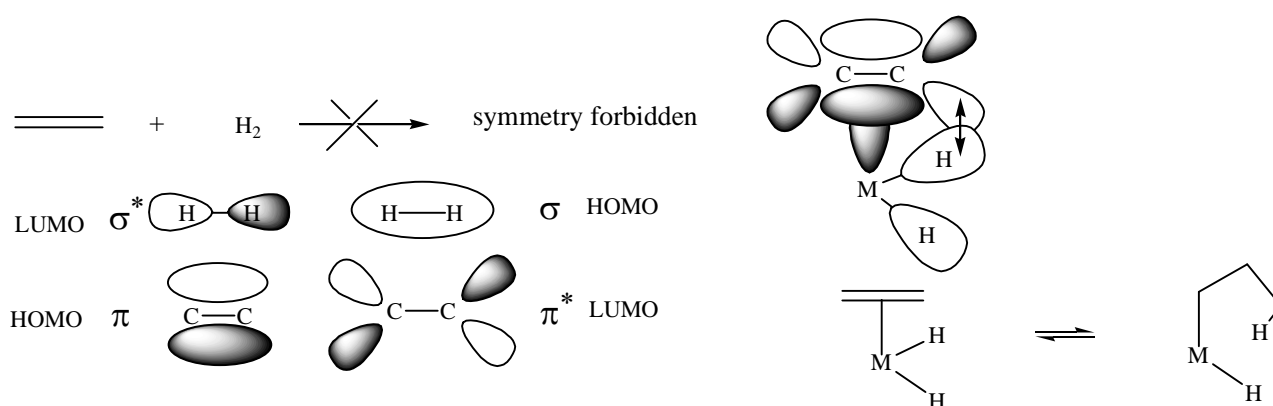
Some Terminology

Precatalyst: The transition metal complex that is added to a reaction. The true catalytic species usually results from a preliminary reaction or event (e.g. ligand dissociation) of the precatalyst before binding of the substrate and catalysis can occur.

(18 e)

no space for substrate
'closed shell' configuration

(16 e)

space for incoming substrate
electron 'deficient'
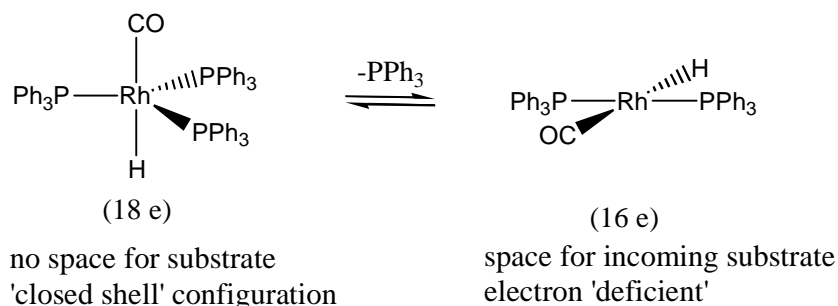
Turnover/Activity: Moles of product per second per mole of metal precatalyst.

Lifetime/Stability: Common catalyst decomposition reactions are hydrolysis, metal cluster formation and ligand degradation. Some decomposition products catalyse the formation of undesired products. The product may also poison a catalyst.

Resting state: The catalyst may be in equilibrium with another complex that does not catalyse the reaction but can act as a 'reservoir' for the catalyst.

catalyst

resting state
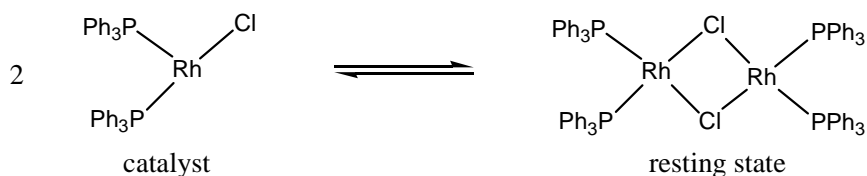
Fundamental Reactions

Dissociation/association, oxidative addition/reductive elimination and insertion/extrusion are the most common elementary steps that support a catalytic cycle and conform to the principle of microscopic reverse.

Principle of microscopic reversibility

The mechanism of a reverse reaction must be the same as the mechanism for the forward reaction *under the same conditions*. This results because the least energetic pathway in one direction must be the least energetic pathway in the other direction. i.e. The intermediates and transition state must be the same in either direction. *One consequence of this is that a catalyst for a forward reaction will be a catalyst for the reverse reaction.*

Homogeneous Transition Metal Mediated Catalysis

4	5	6	7	8	9	10
Ti	V	Cr	Mn	Fe	Co	Ni
Zr	Nb	Mo	Tc	Ru	Rh	Pd
Hf	Ta	W	Re	Os	Ir	Pt

fewer d-electrons high coordination numbers high oxidation states oxophilic prefer hard ligands	lower coordination numbers lower oxidation states strong bonds with π-acid and softer ligands (e.g. alkyls and H) undergo reductive elimination/oxidative addition

Reactivity of complexes $1^{st}, 2^{nd} > 3^{rd}$

Catalytic activity $1^{st}, 2^{nd} > 3rd$

M-H, M-C, M-M bond strengths $2^{nd}, 3^{rd} > 1^{st}$

Late metals are used in most catalytic reactions involving M-C and M-H bonds (notable exceptions are Ziegler Natta polymerisation (Ti, Cr) and alkene epoxidation (Ti, Mn)

Also M-H and M-C bonds of the later metals are less sensitive to water and oxygen

Some catalysis of unsaturated substrates

Isomerisation of alkenes

Alkene isomerisation is a useful reaction for the synthesis of certain steroids and using mixtures of alkene isomers as feedstock.
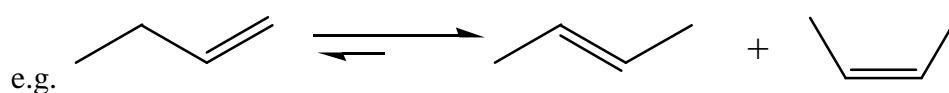
Two mechanisms have been recognised. Catalytic mechanisms are usually depicted as cycles.
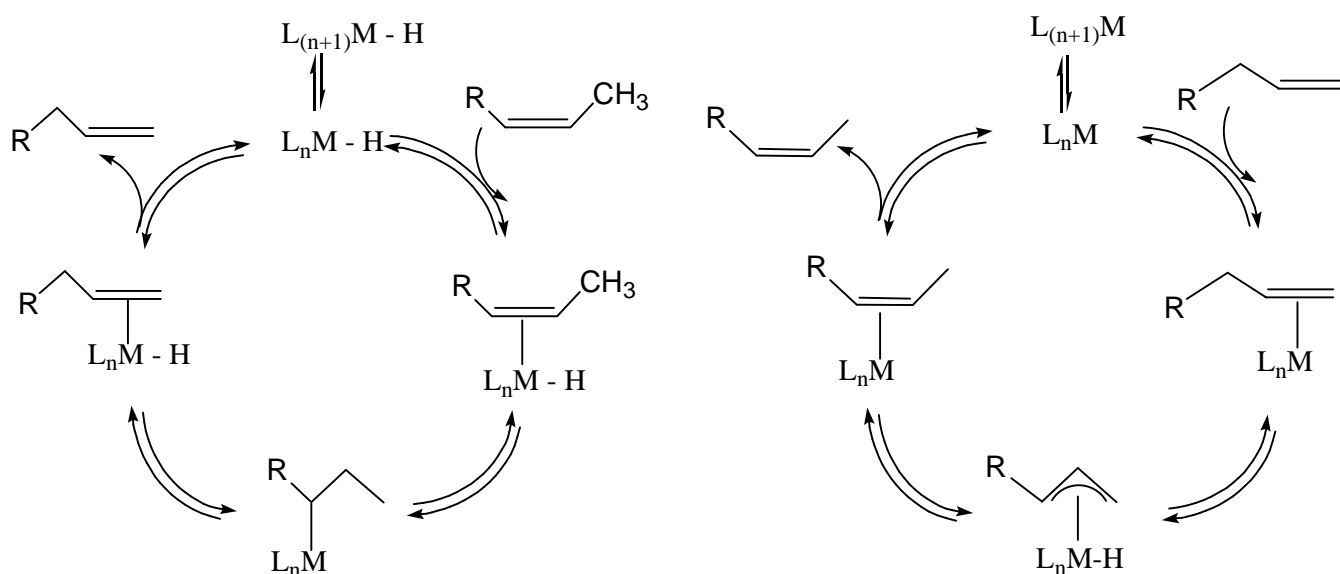
σ-alkyl/ β-hydride elimination (more common) route   π-allyl

Internal alkenes are thermodynamically more stable than terminal alkenes. Isomerisation gives mixtures of thermodynamic products.

e.g.

Many metal complexes are catalysts for isomerisation. Rhodium catalysts tend to be the most rapid.

Addition to alkenes: Hydrogenation and hydroformylation ('oxo' process)

Anti-Markovnikov addition

Hydrogenation

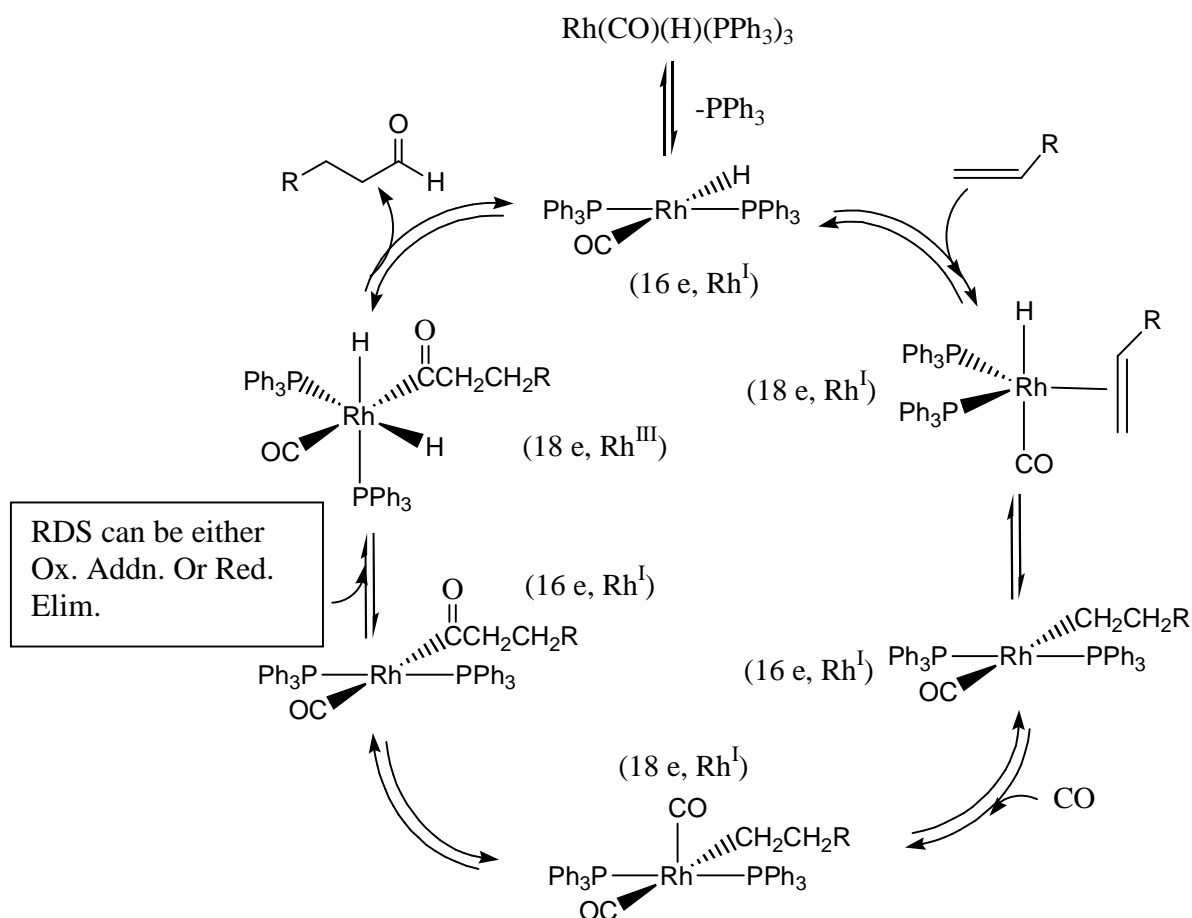

Oxidative addition
RDS (change in
Ox. St.)
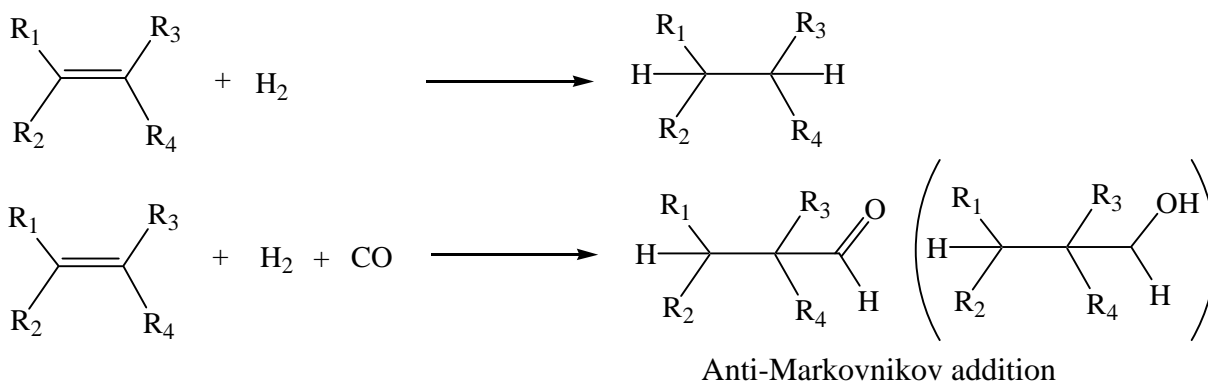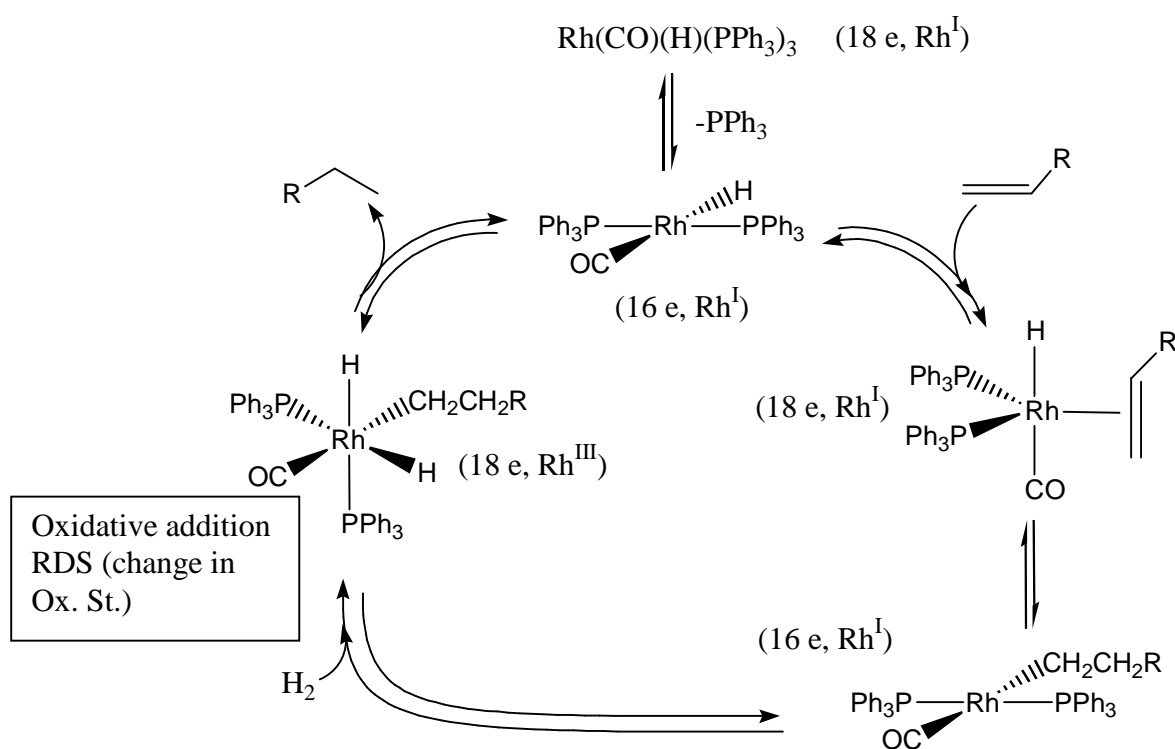
Mechanism can change dependent on if alkene or H_2 adds to metal first.

$Rh(CO)(H)(PPh_3)_3$ is selective for terminal alkenes. Isomerisation can compete with hydrogenation.
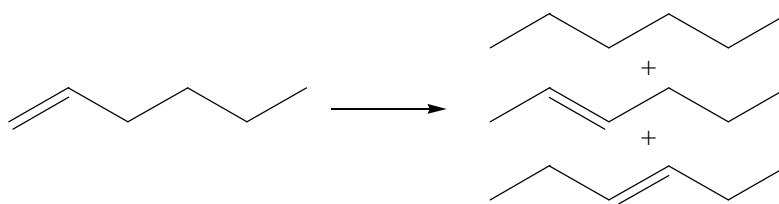

Other precatalysts include $RhH(PPh_3)_3$, (good for internal and terminal alkenes). Can do asymmetric.
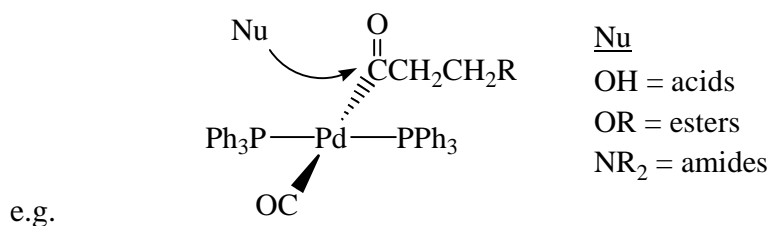
Hydroformylation

$Rh(CO)(H)(PPh_3)_3$

$-PPh_3$

(16 e, Rh^I)

$Ph_3P-Rh-PPh_3$ with H, OC

R (alkene)

(18 e, Rh^I)
$Ph_3P-Rh-CO$ with H, Ph_3P, alkene R

(16 e, Rh^I)
$Ph_3P-Rh-PPh_3$ with CH_2CH_2R, OC

CO

(18 e, Rh^I)
$Ph_3P-Rh-PPh_3$ with CO, CH_2CH_2R, OC

(16 e, Rh^I)
$Ph_3P-Rh-PPh_3$ with $\overset{O}{\overset{\|}{C}}CH_2CH_2R$, OC

(18 e, Rh^{III})
Rh with H, $\overset{O}{\overset{\|}{C}}CH_2CH_2R$, Ph_3P, OC, H, PPh_3

RDS can be either Ox. Addn. Or Red. Elim.

$R-CH_2CH_2-\overset{O}{\overset{\|}{C}}H$ (aldehyde product)

Other common precatalyst is $Co_2(CO)_8$ (Otto Roelen 1938 discovered hydroformylation using this precatalyst). Isomerisation and hydrogenation can be competitive. Can do asymmetric hydroformylation.

Isomerisation can be useful. Hydroformylation of terminal alkenes is much quicker than internal alkenes due to alkene/ligand sterics at metal.
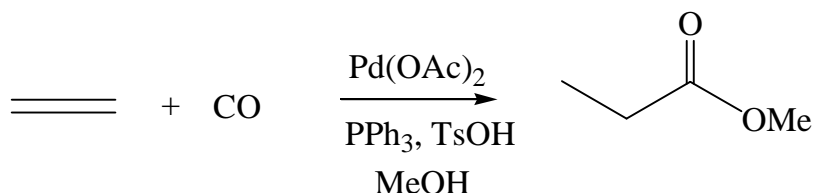
e.g.

(alkene) $\xrightarrow{H_2/CO}$ (linear aldehyde) (Linear aldehydes are desired)
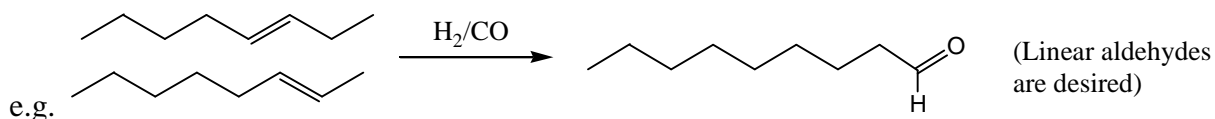
Other carbonylations proceed by similar mechanisms to give a range of products

e.g.

Nu attacks $\overset{O}{\overset{\|}{C}}CH_2CH_2R$ on $Ph_3P-Pd-PPh_3$ with OC
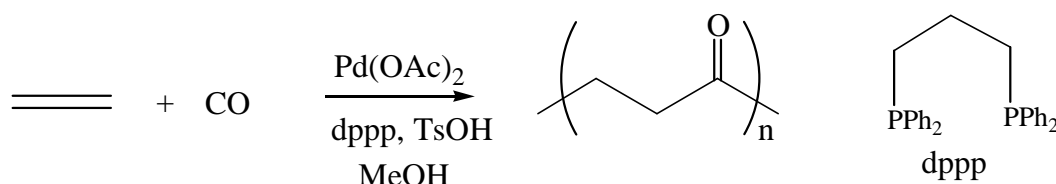
Nu
OH = acids
OR = esters
NR_2 = amides

Alkene/CO copolymerisation
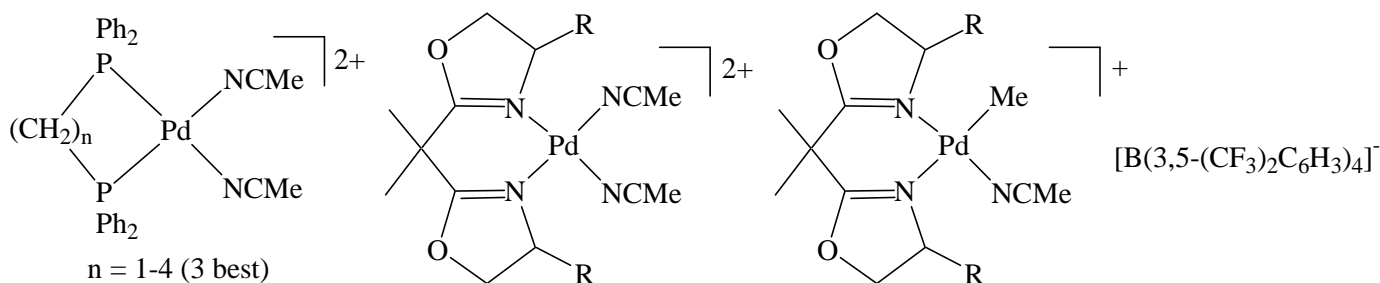
Copolymerisation of CO and Alkenes

In the early 1980's Shell were investigating the use of *cationic* palladium phosphine complexes as catalysts for the methoxycarbonylation of ethene (methyl propionate).

$$\text{CH}_2=\text{CH}_2 \ + \ \text{CO} \quad \xrightarrow[\substack{\text{PPh}_3,\ \text{TsOH} \\ \text{MeOH}}]{\text{Pd(OAc)}_2} \quad \text{CH}_3\text{CH}_2\text{C(O)OMe}$$

Using chelating bis-phosphines it was found a high molecular weight polyketone was formed.

$$\text{CH}_2=\text{CH}_2 \ + \ \text{CO} \quad \xrightarrow[\substack{\text{dppp, TsOH} \\ \text{MeOH}}]{\text{Pd(OAc)}_2} \quad \left(\!\!-\text{CH}_2\text{CH}_2\text{C(O)}-\!\!\right)_n$$

dppp

Pre-catalysts for CO/alkene copolymerisation

n = 1-4 (3 best)

$[B(3,5-(CF_3)_2C_6H_3)_4]^-$

Important features:

i) chelating bidentate ancillary ligands seem to be required

ii) weakly coordinating anions

iii) Electrophilic metal centre required to bind alkene but not too electrophilic or CO binds too strongly and inhibits copolymerisation.

Mechanism of CO/alkene Copolymerisation

Co-polymerisation is usually performed in protic solvents and mainly in methanol.

i) what is the catalytic species?

End group analysis shows esters and ketones. Catalyst can be hydride or methoxy complex.
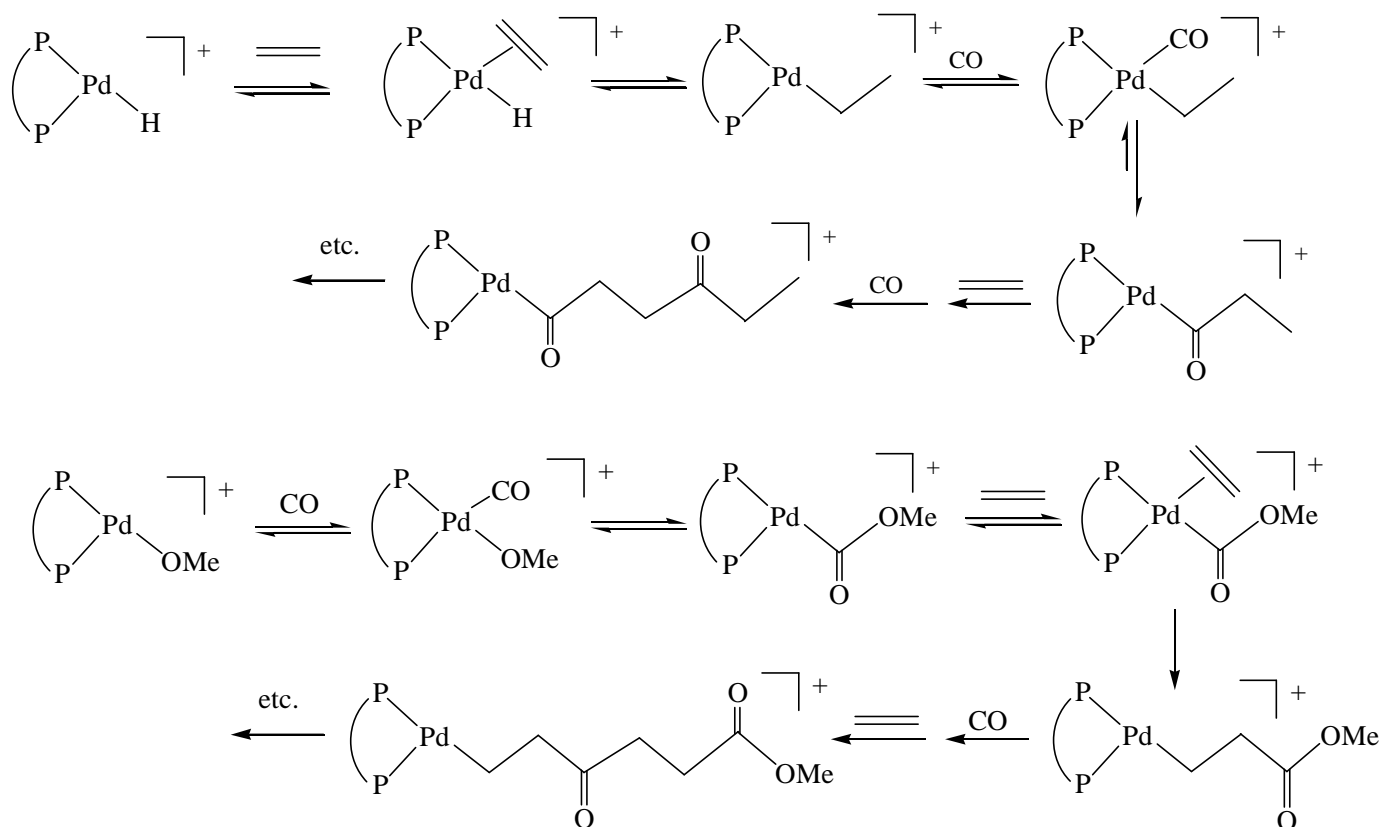
Propagation rate determines formation of polyketones or propionates. Chelating bidentate ligands enforce cis-coordination of the growing polymer chain and vacant coordination site. In mono-phosphine complexes cis/trans isomerisation prevents propagation.
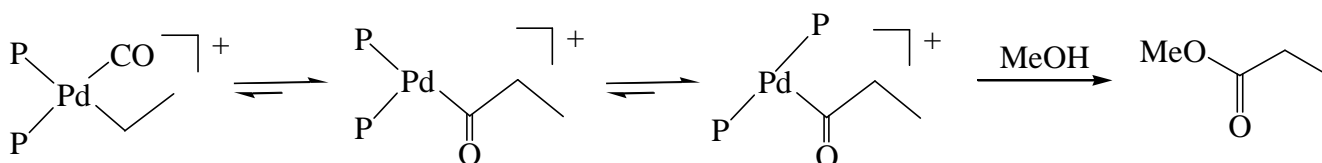
iii) Why is there strict alternation of CO and ethylene in the co-polymer? Double CO or double ethene defects are rarely observed.

Double CO insertion is thermodynamically unfavourable and will not occur.

Double ethene insertion is thermodynamically favourable by ~ 80 kJ mol^{-1}

An ethene/CO ratio of 10:1 still gives strict alternation until the CO has been consumed.

Explanation: The acyl intermediate coordinates via the carbonyl oxygen to Pd to give a metallocycle. Formation of the metallocycle has two consequences

1) Prevents double ethene insertion as the ethene is not a strong enough donor to displace the Pd-O bond and

2) Prevents β-H elimination
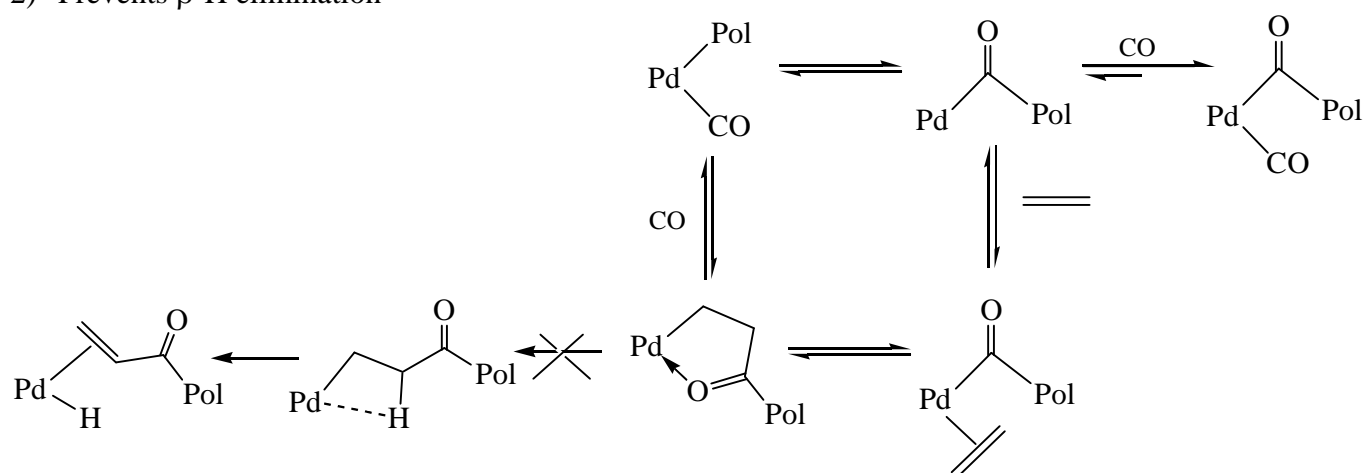
# Catalysis of saturated substrates

Dehydrogenation of alkanes

Essentially the reverse of hydrogenation of alkenes.
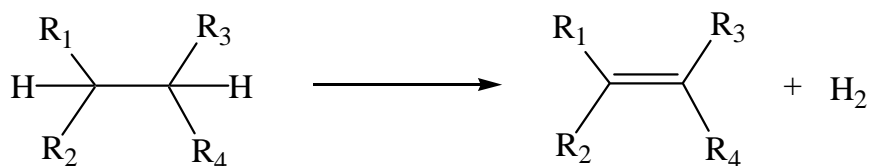
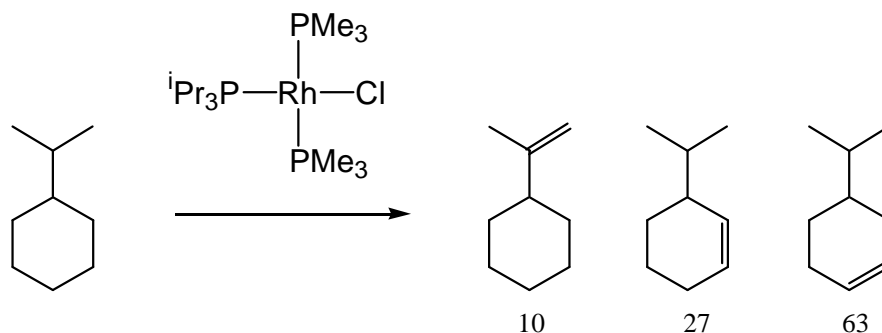| Bond	Dissociation bond energy (kJ mol^{-1})
C-H	400-415
H-H	432
C=C (π)	260-275

$$\Delta H_{rxn} = 2 \times 400 \text{ (C-H)} - [432 \text{ (H-H)} + 275 \text{ (C=C)}] = 93 \text{ kJ mol}^{-1} \text{ (endothermic)}$$

Very slow compared to hydrogenation. Lots of energy (heat) is required 150-200 $^{\circ}$C. The catalyst needs to be stable at high temperature. From the principle of microscopic reverse it should be expected that the same type of catalysts that hydrogenate alkenes also dehydrogenate alkanes.
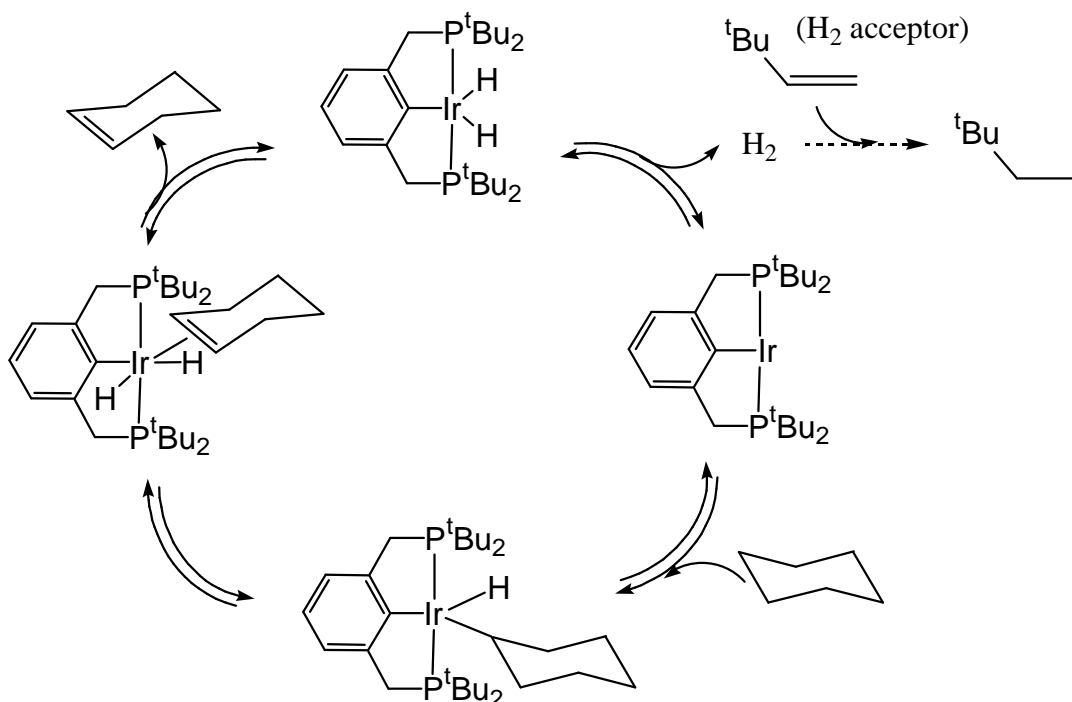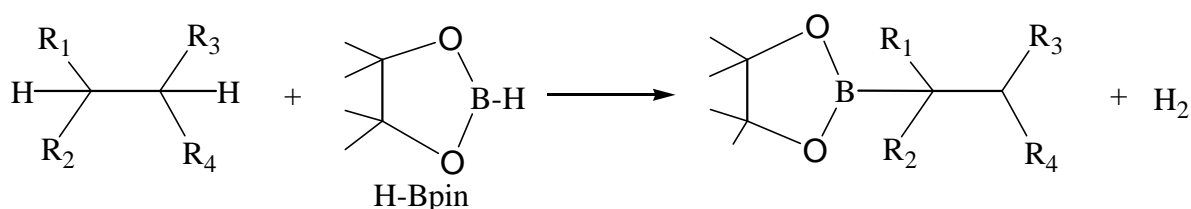

Addition of an H$_2$ acceptor helps to drive the reaction by removing H$_2$ and formation of 2 x C-H bonds ($\Delta H_{rxn} \approx 0$, thermoneutral reaction)

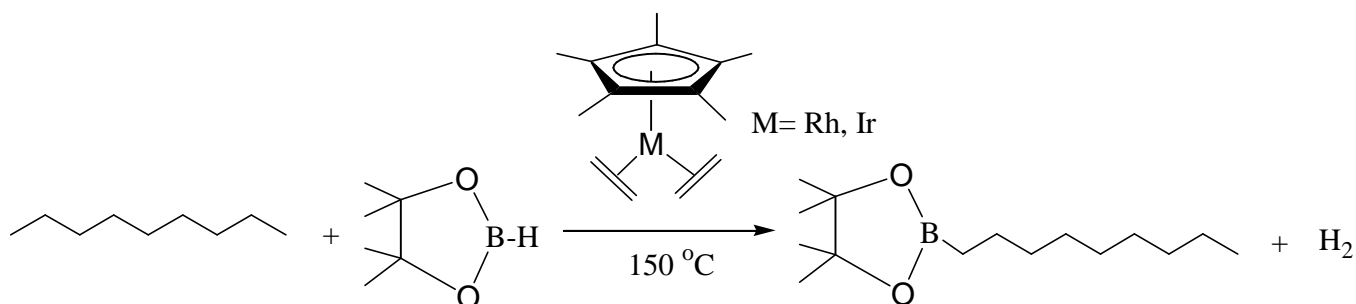Internal alkenes are more stable than terminal alkenes. Distribution of mainly thermodynamic products

| 10 | 27 | 63 |

Borylation of alkanes

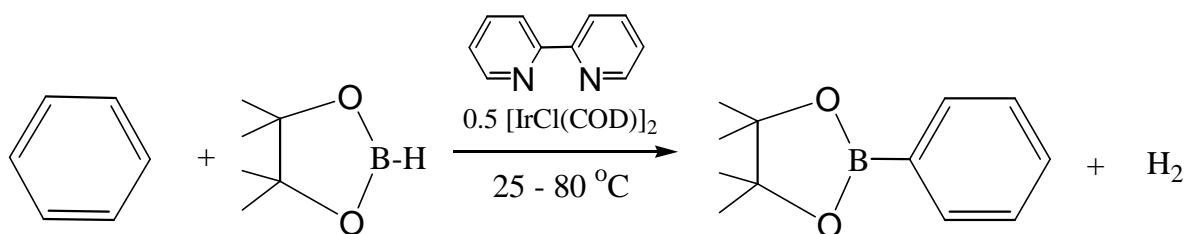Organoboranes are very useful intermediates for a large range of organic compounds.

Bond	Dissociation bond energy (kJ mol^{-1})
C-H	400-415
H-H	432
B-H	464
B-C	472

ΔH_{rxn} = [415 (C-H) + 464 (B-H)] – [432 (H-H) + 472 (B-C)] = -25 kJ mol^{-1} (exothermic)
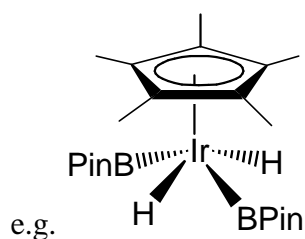

Regiospecific for terminal C-H bonds

More recently, functionalisation of arenes at room temperature has been achieved. Many functional groups on the arene can be tolerated.

Mechanism still unclear but probably involves metal boryl intermediates

e.g.

B-C bond formation could be via oxidative addition of C-H/reductive elimination of B-C or

σ-bond metathesis

oxidative addition/
reductive elimination
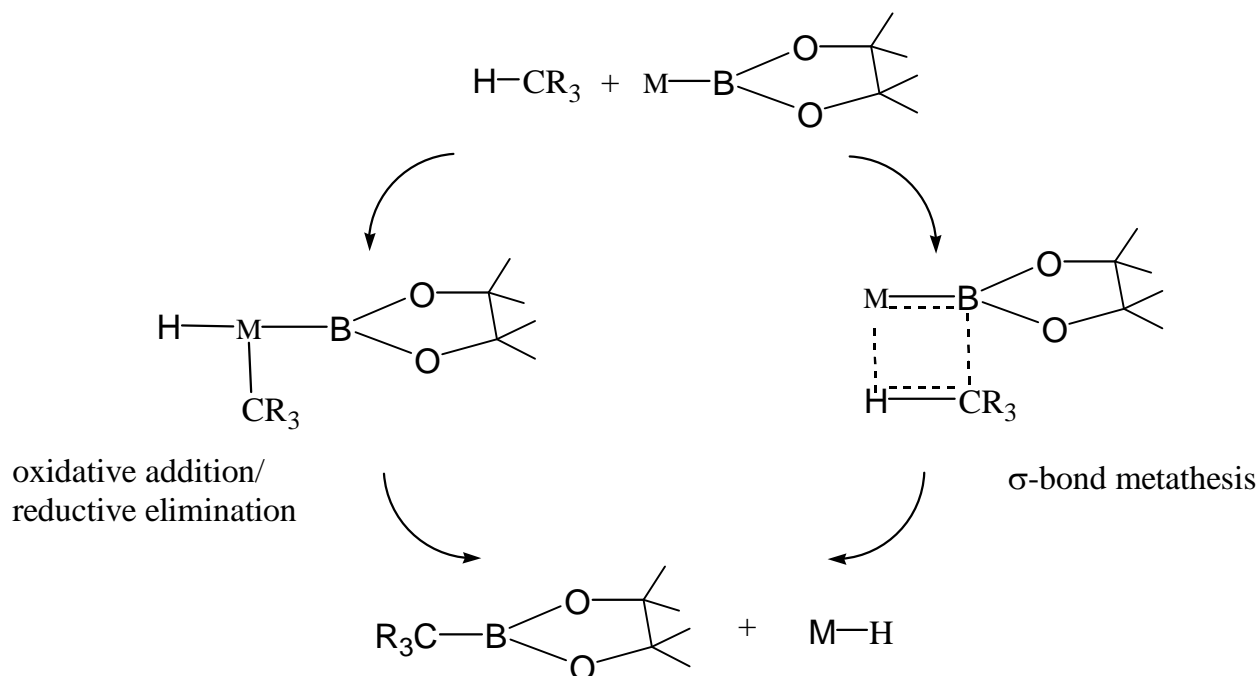
σ-bond metathesis

Theoretical evidence suggests σ-bond metathesis.