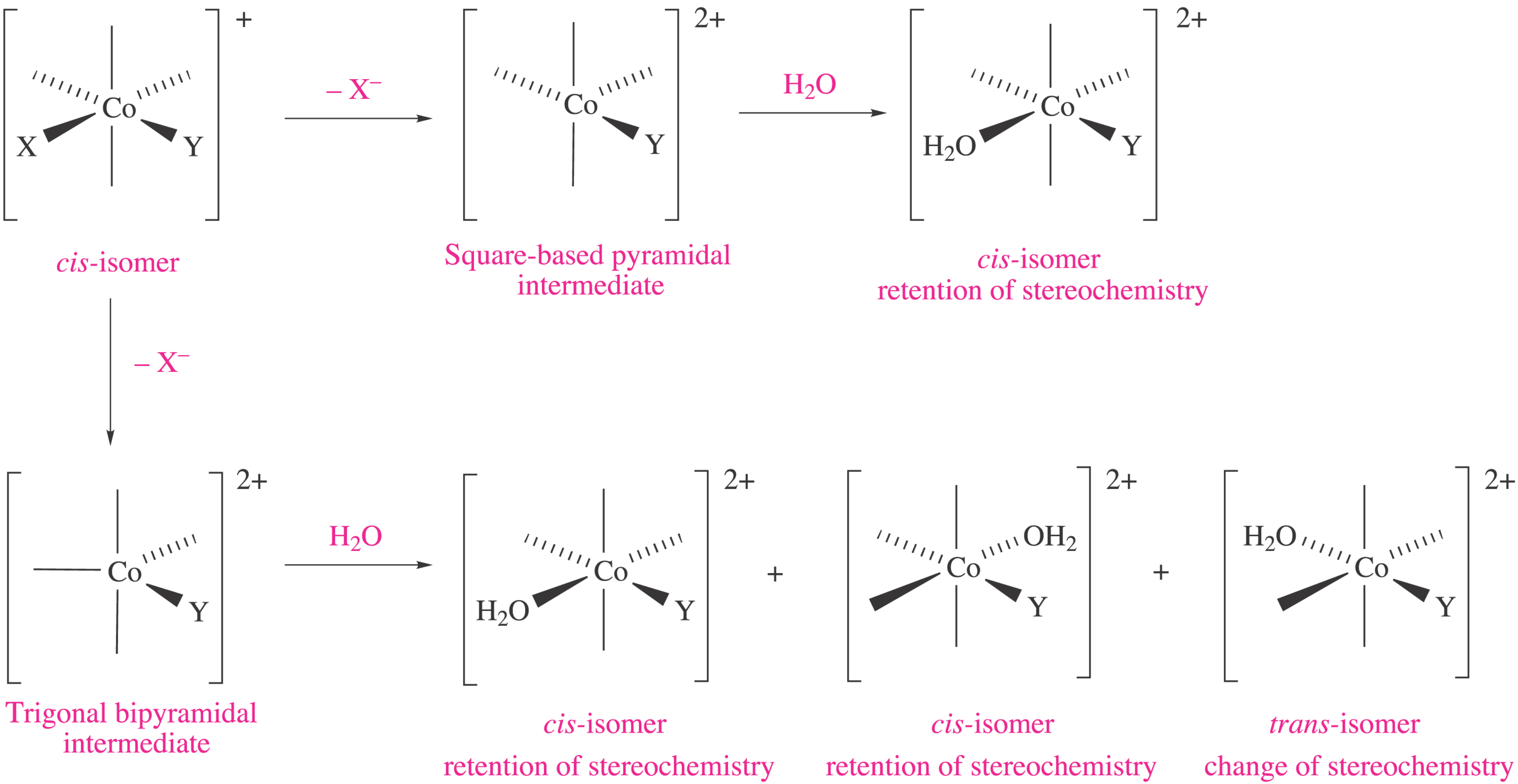
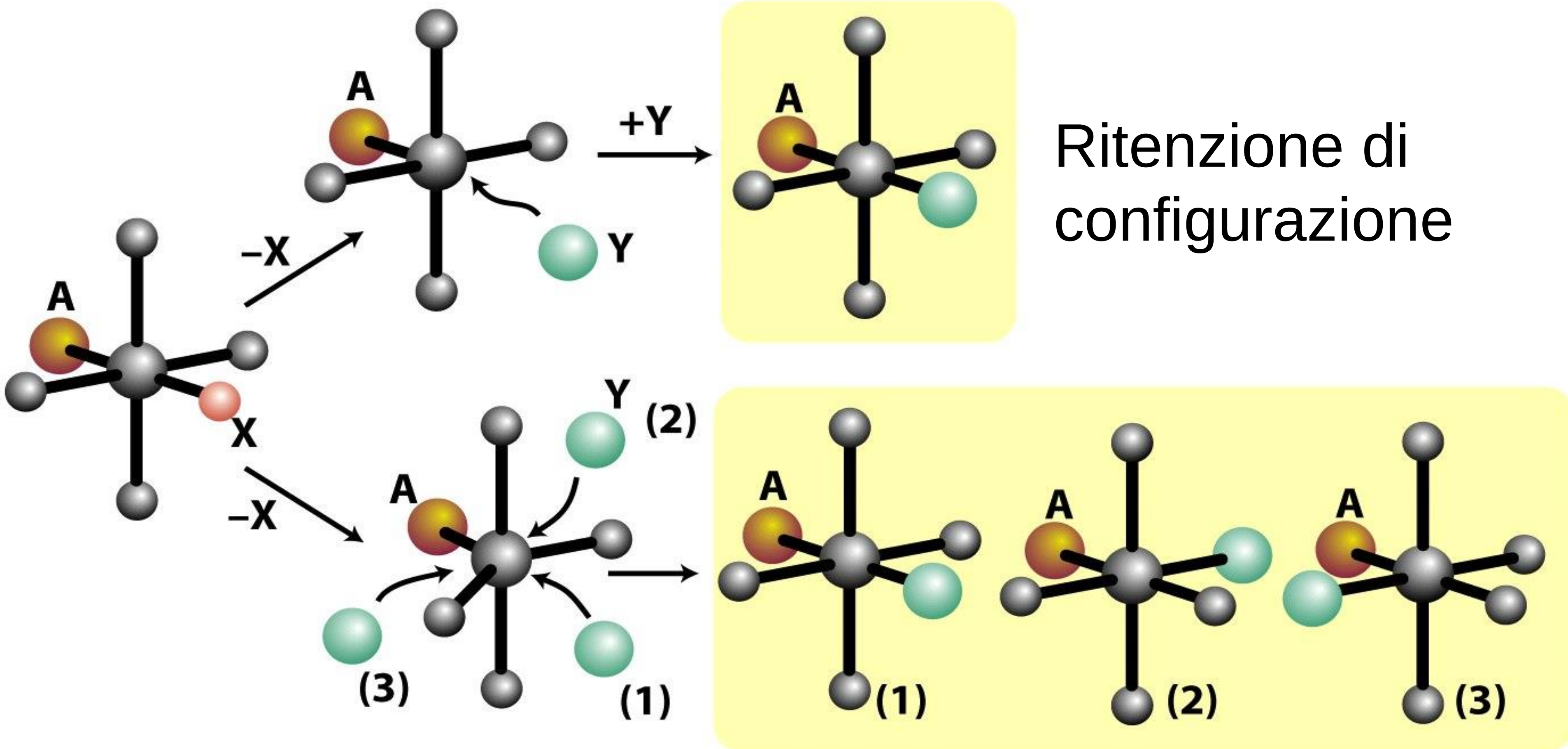
Stereochimica delle sostituzioni nei complessi ottaedrici





Ritenzione di configurazione

cis/*trans* = 2:1

Distribuzione degli isomeri *cis* e *trans*

$$[CoX(en)_2Y]^+ + H_2O \rightarrow [Co(OH_2)(en)_2Y]^{2+} + X^-$$

cis-$[CoX(en)_2Y]^+ + H_2O \rightarrow [Co(OH_2)(en)_2Y]^{2+} + X^-$			*trans*-$[CoX(en)_2Y]^+ + H_2O \rightarrow [Co(OH_2)(en)_2Y]^{2+} + X^-$		
Y^-	X^-	% of *cis*-product†	Y^-	X^-	% of *trans*-product‡
$[OH]^-$	Cl^-	84	$[OH]^-$	Cl^-	30
$[OH]^-$	Br^-	85	$[OH]^-$	Br^-	29
Cl^-	Cl^-	75	Cl^-	Cl^-	74
Br^-	Br^-	73.5	Br^-	Br^-	84.5
$[N_3]^-$	Cl^-	86	$[N_3]^-$	Cl^-	91
$[N_3]^-$	Br^-	85	$[N_3]^-$	Br^-	91
$[NO_2]^-$	Cl^-	100	$[NO_2]^-$	Cl^-	100
$[NO_2]^-$	Br^-	100	$[NO_2]^-$	Br^-	100
$[NCS]^-$	Cl^-	100	$[NCS]^-$	Cl^-	58.5
$[NCS]^-$	Br^-	100	$[NCS]^-$	Br^-	57

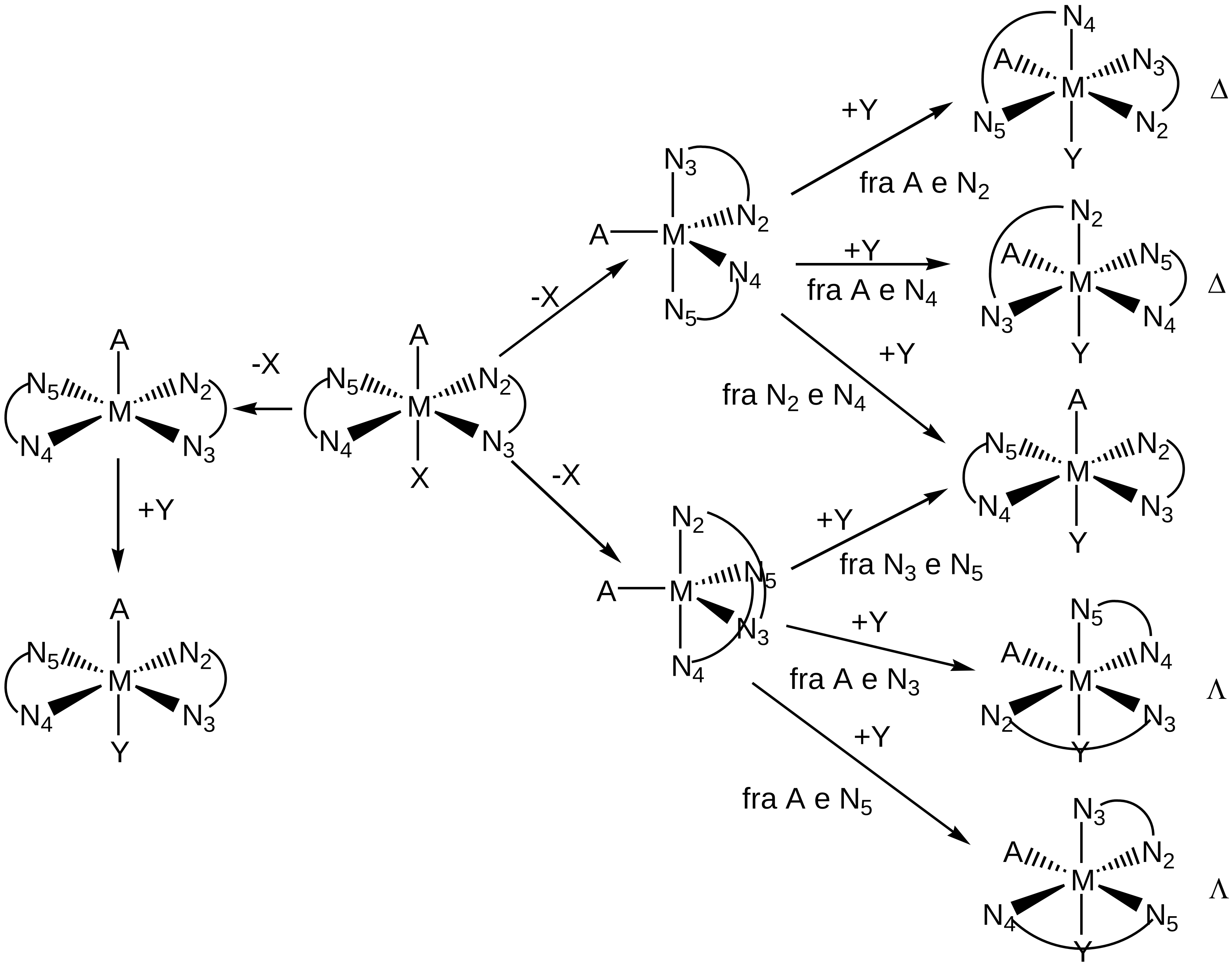
† Remaining % is *trans*-product.
‡ Remaining % is *cis*-product.

$Y = NO_2^- < Cl^- < NCS^- < OH^-$

π-donazione →

La stereochimica del processo **non dipende dal gruppo uscente**

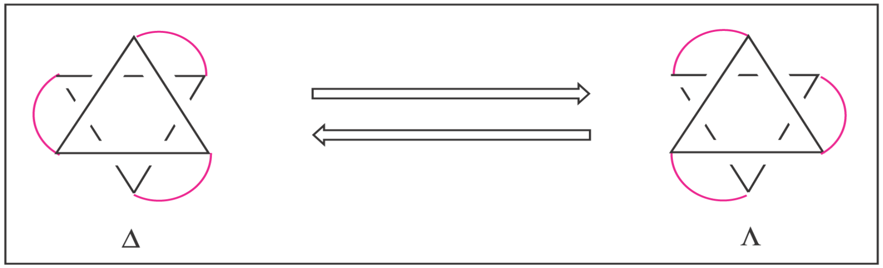
I complessi *cis* tendono a dare ritenzione della geometria

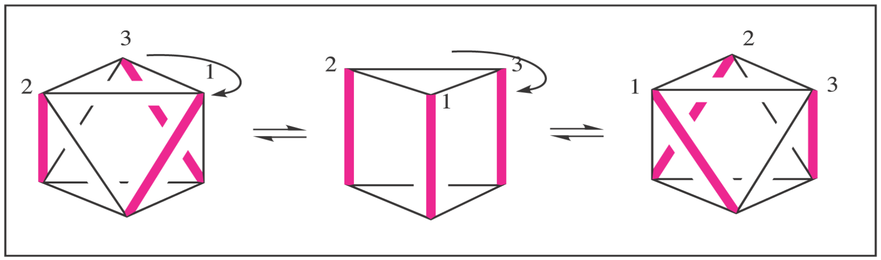


-X
+Y
fra A e N2
fra A e N4
fra N2 e N4
fra N3 e N5
fra A e N3
fra A e N5
Δ
Δ
Λ
Λ

isomerizzazione e racemizzazione in complessi ottaedrici

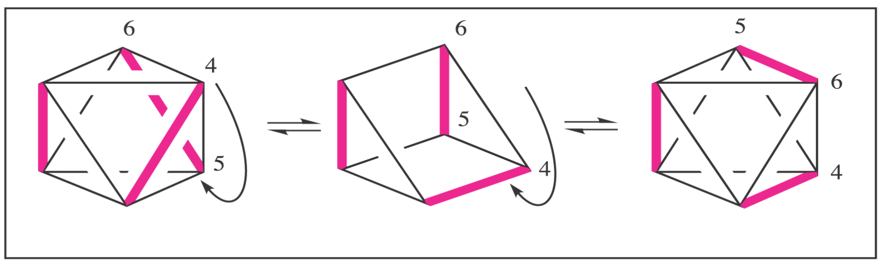
Meccanismi torsionali per l'interconversione di enantiomeri Λ e Δ di $[M(chel)_3]$





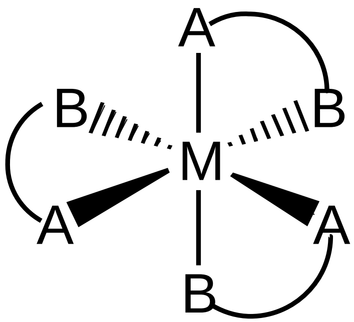
(a)

Bailar twist

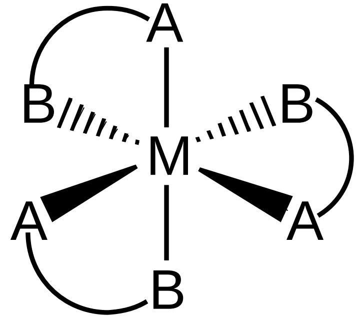


(b)

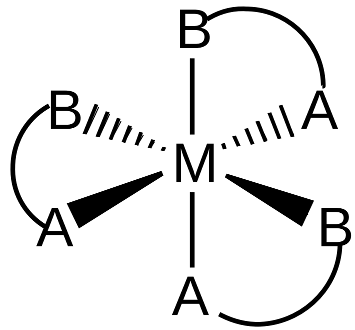
Ray-Dutt twist



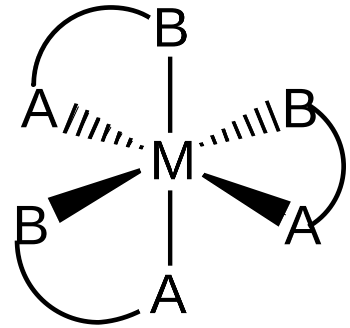
*fac*Δ



*fac*Λ



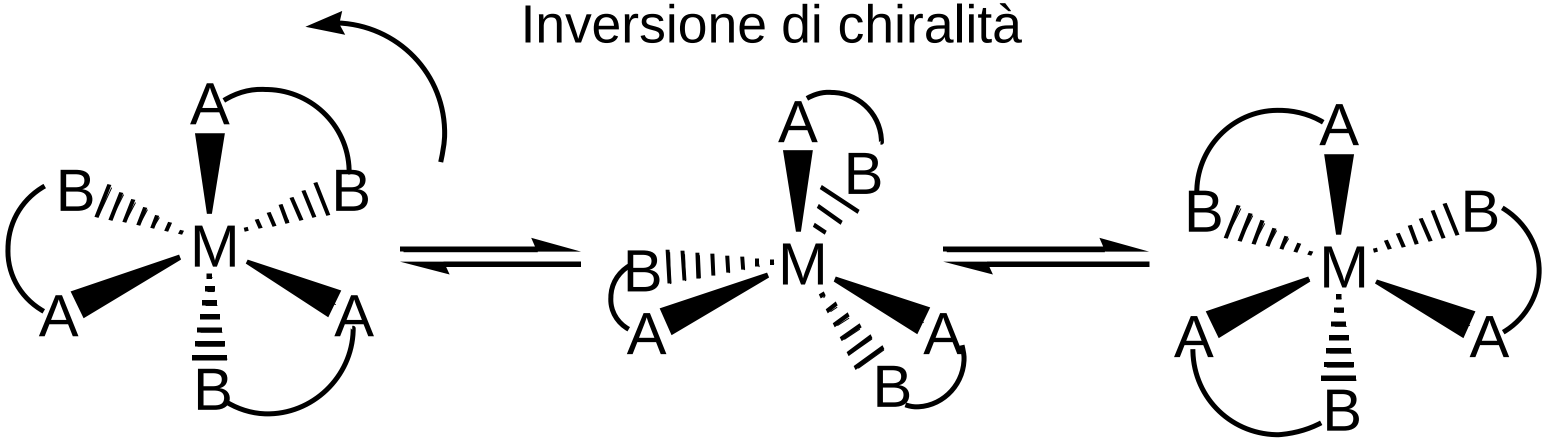
*mer*Δ



*mer*Λ

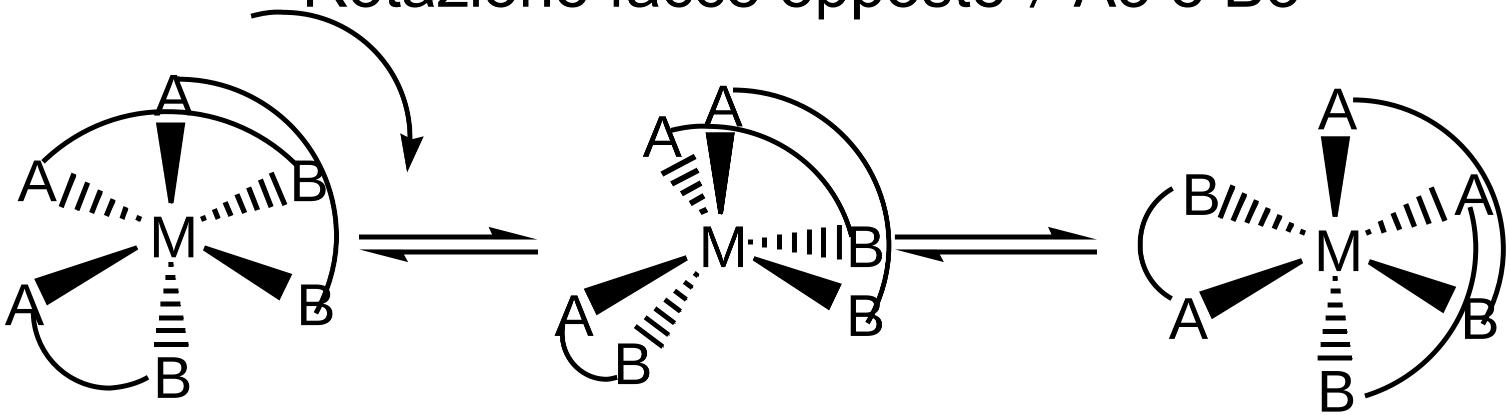
Rotazione facce opposte A3 e B3

Inversione di chiralità



*fac*Δ *fac*Λ

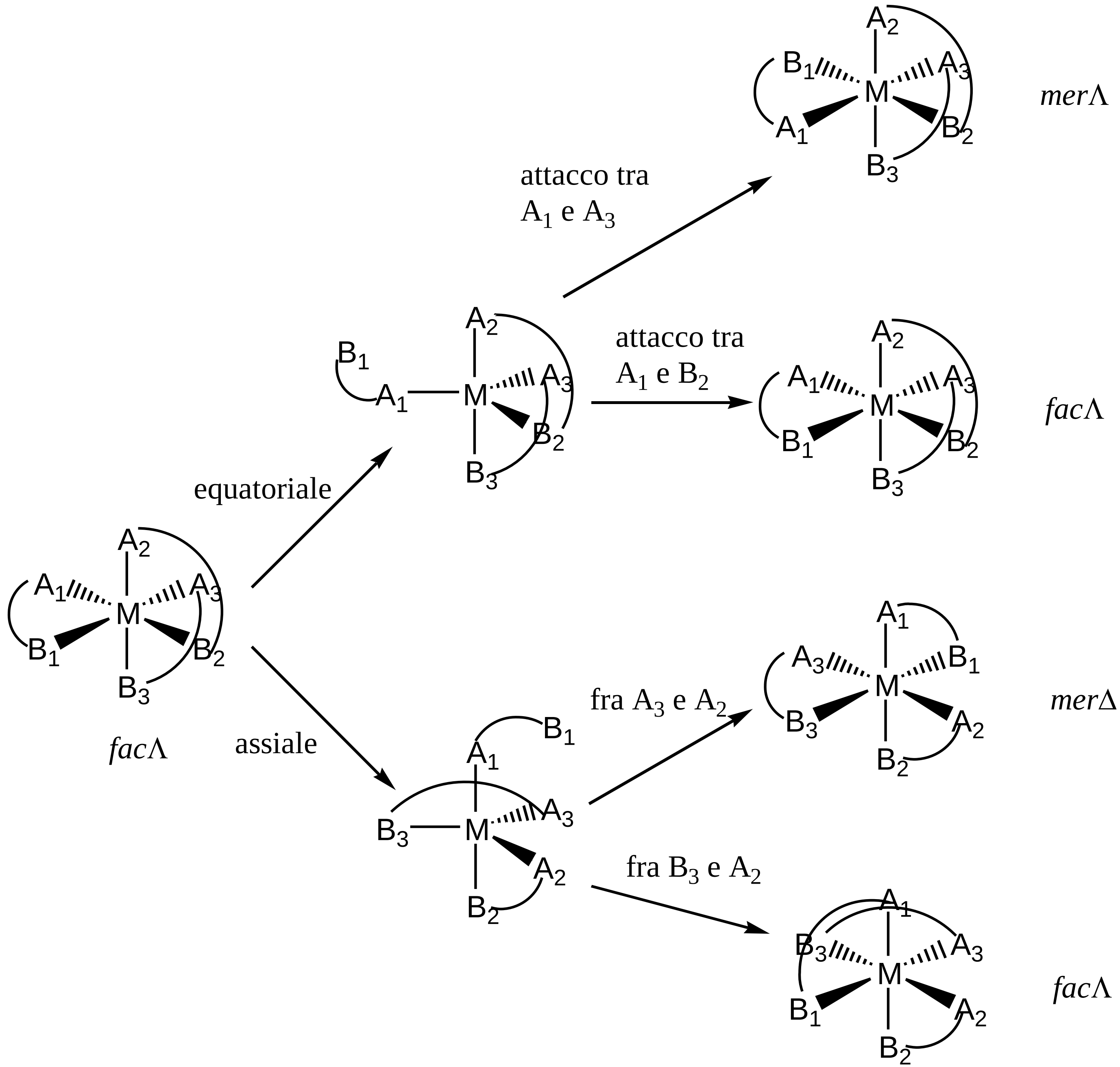
Rotazione facce opposte ≠ A3 e B3



*fac*Δ *mer*Λ

Inversione di chiralità + isomerizzazione

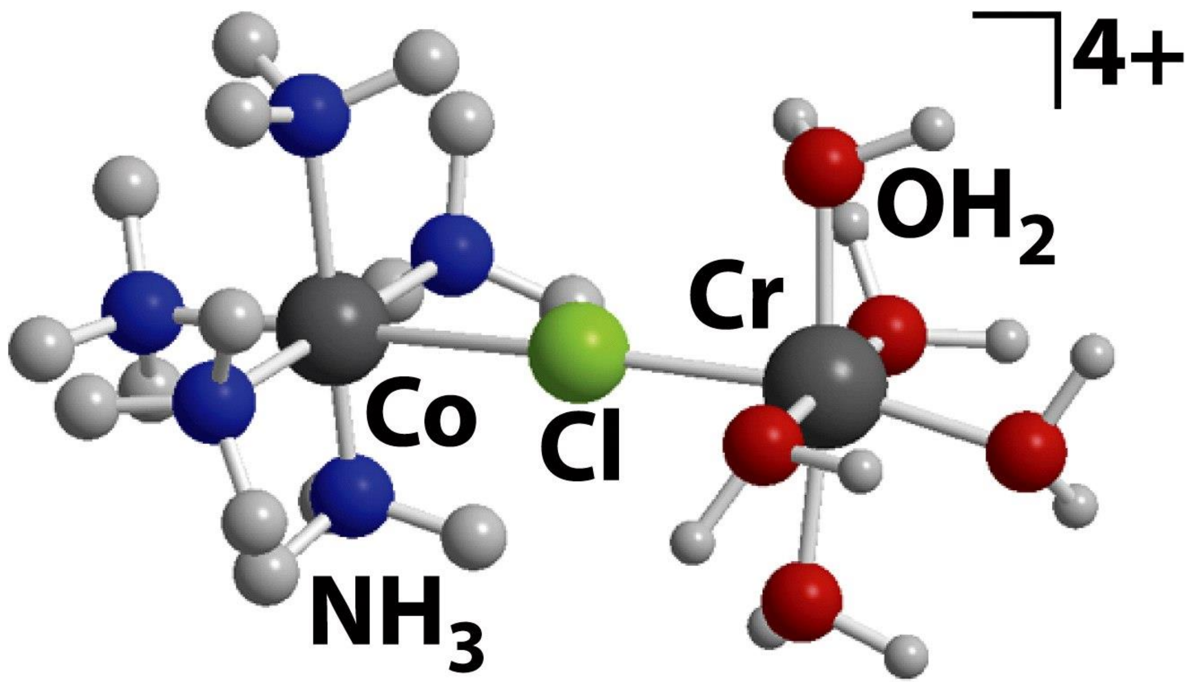
meccanismo con apertura di un chelante



Processi redox a sfera interna

$$[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} + 5H_3O^+ \rightarrow$$

$$[Co(OH_2)_6]^{2+} + [Cr(H_2O)_5Cl]^{2+} + 5NH_4^+$$



Processo redox senza trasferimento del legante a ponte

$$[Fe(CN)_6]^{3-} + [Co(CN)_5]^{3-} \rightarrow$$

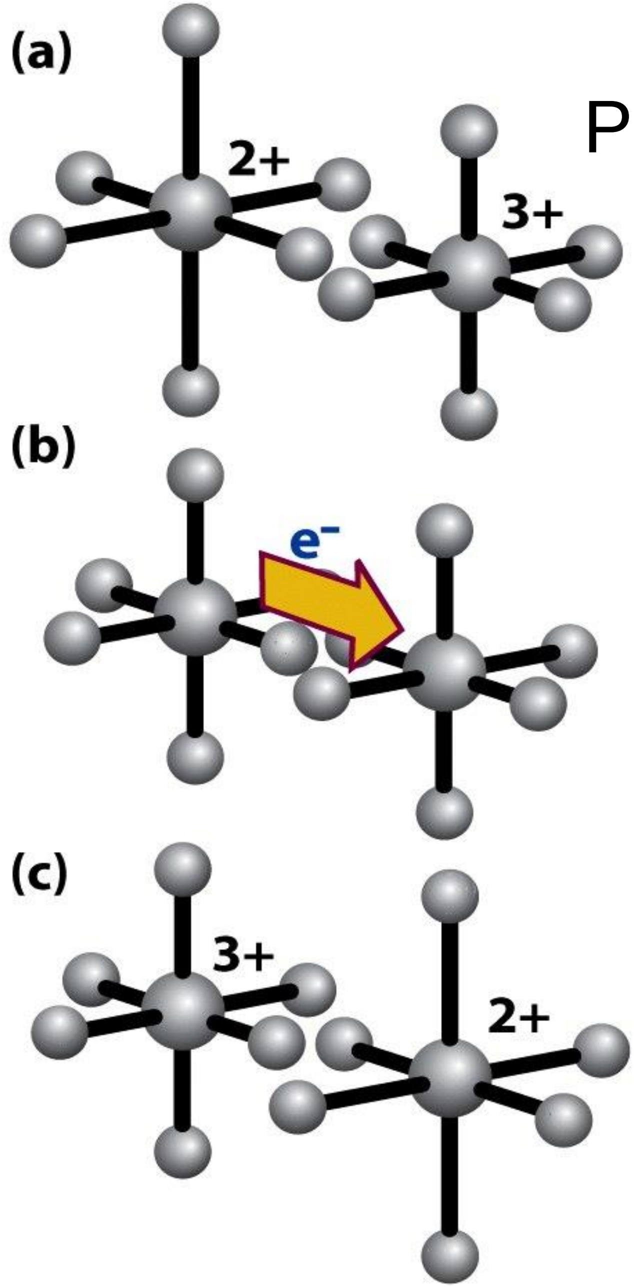
$$[Fe(CN)_5(\mu\text{-}CN)Co(CN)_5]^{6-} \rightarrow$$

$$[Fe(CN)_6]^{4-} + [Co(CN)_5(OH_2)]^{2-}$$

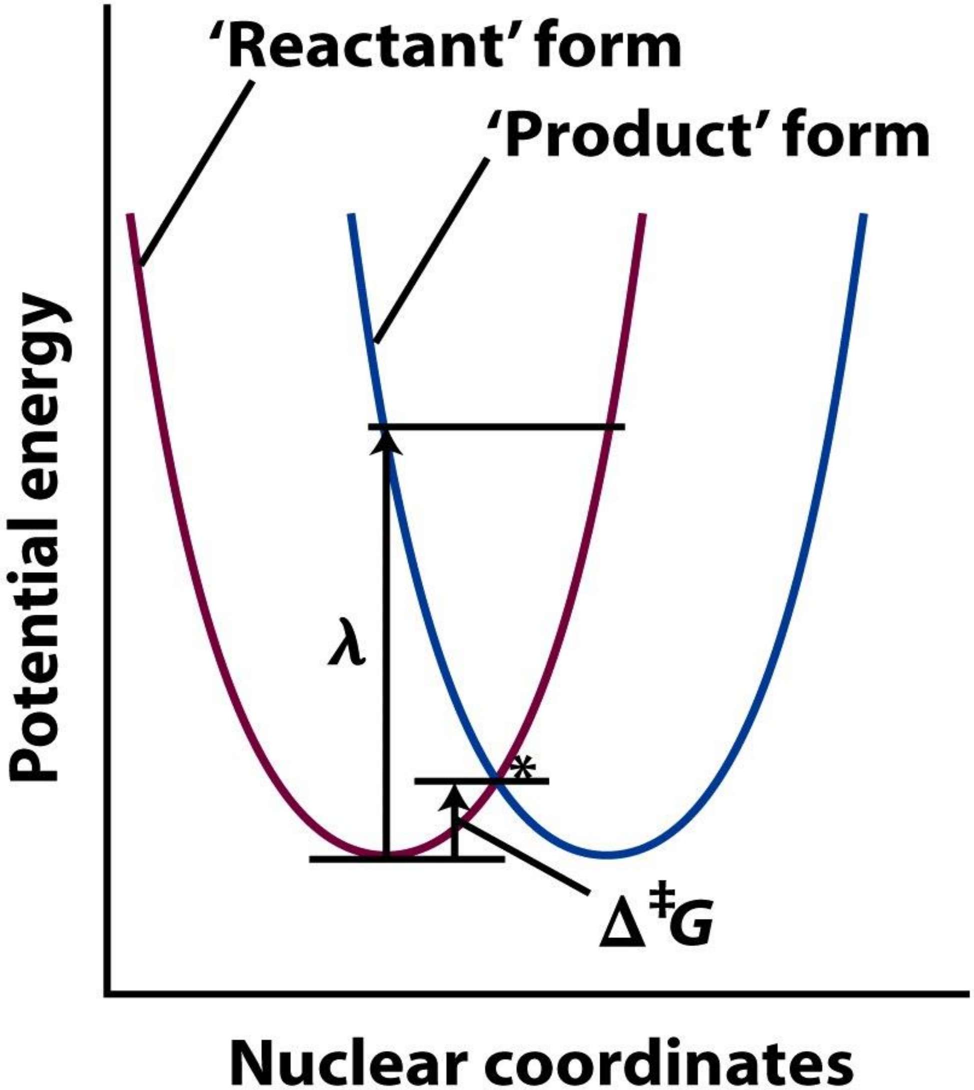
Processi redox a sfera esterna

	Reaction	k / dm^3 mol^{-1} s^{-1}
No net chemical reaction (self-exchange)	$[Fe(bpy)_3]^{2+} + [Fe(bpy)_3]^{3+} \longrightarrow [Fe(bpy)_3]^{3+} + [Fe(bpy)_3]^{2+}$	$>10^6$
	$[Os(bpy)_3]^{2+} + [Os(bpy)_3]^{3+} \longrightarrow [Os(bpy)_3]^{3+} + [Os(bpy)_3]^{2+}$	$>10^6$
	$[Co(phen)_3]^{2+} + [Co(phen)_3]^{3+} \longrightarrow [Co(phen)_3]^{3+} + [Co(phen)_3]^{2+}$	40
	$[Fe(OH_2)_6]^{2+} + [Fe(OH_2)_6]^{3+} \longrightarrow [Fe(OH_2)_6]^{3+} + [Fe(OH_2)_6]^{2+}$	3
	$[Co(en)_3]^{2+} + [Co(en)_3]^{3+} \longrightarrow [Co(en)_3]^{3+} + [Co(en)_3]^{2+}$	10^{-4}
	$[Co(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+} \longrightarrow [Co(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+}$	10^{-6}
Net chemical reaction	$[Os(bpy)_3]^{2+} + [Mo(CN)_8]^{3-} \longrightarrow [Os(bpy)_3]^{3+} + [Mo(CN)_8]^{4-}$	2×10^9
	$[Fe(CN)_6]^{4-} + [Fe(phen)_3]^{3+} \longrightarrow [Fe(CN)_6]^{3-} + [Fe(phen)_3]^{2+}$	10^8
	$[Fe(CN)_6]^{4-} + [IrCl_6]^{2-} \longrightarrow [Fe(CN)_6]^{3-} + [IrCl_6]^{3-}$	4×10^5

Principio di Frank – Condon



Complesso di incontro



'Reactant' form
'Product' form
Potential energy
λ
*
Δ‡G
Nuclear coordinates

Velocità di trasferimento elettronico

$k_{ET} = \nu_N \kappa_e e^{-\Delta G^{\neq}/RT}$ Equazione di Marcus

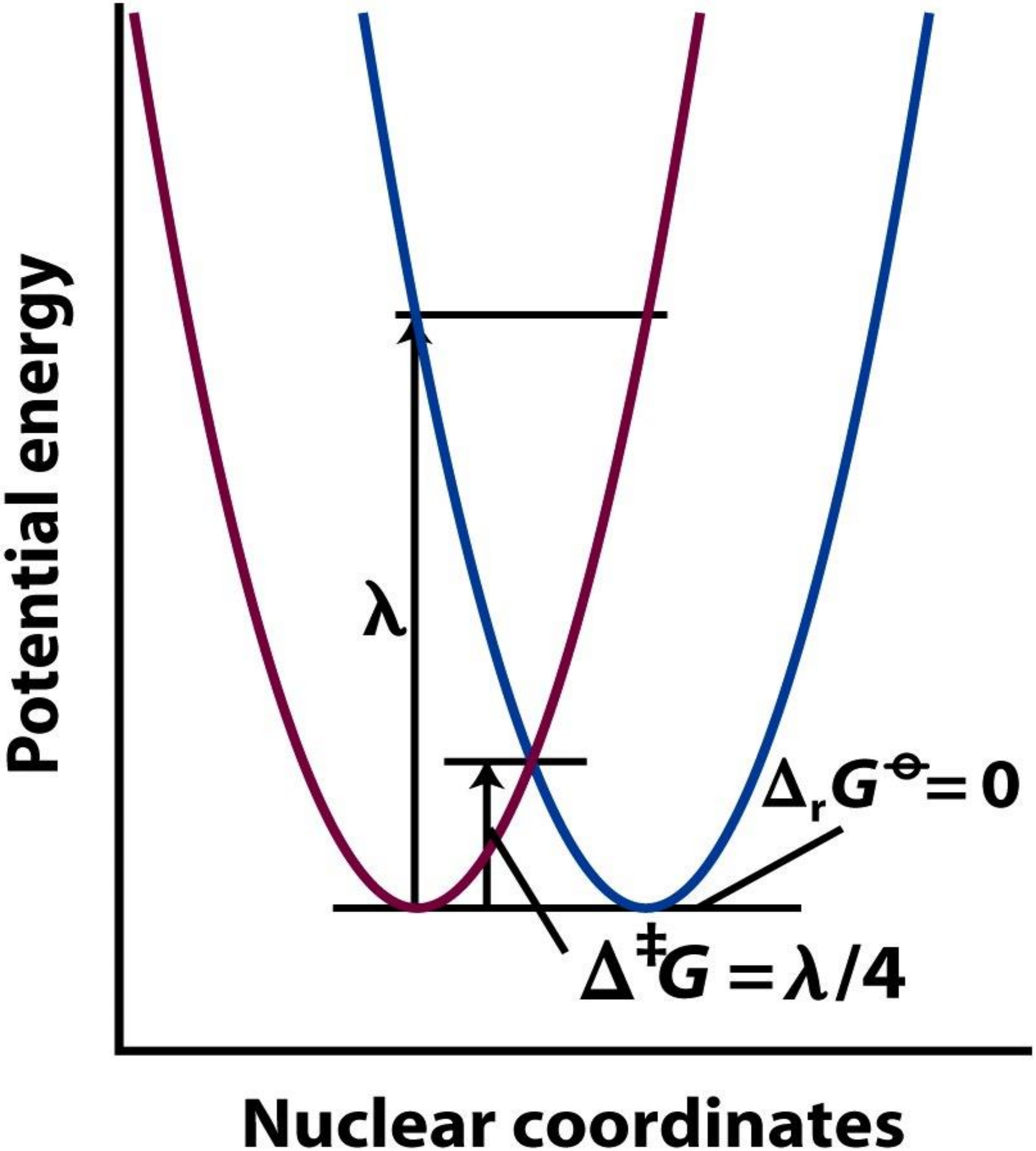
ν_N = fattore di frequenza nucleare

κ_e = fattore elettronico (0 ÷ 1)

$$\Delta G^{\neq} = \frac{\lambda}{4} \times \left(1 + \frac{\Delta G^{\circ}}{\lambda}\right)^2$$

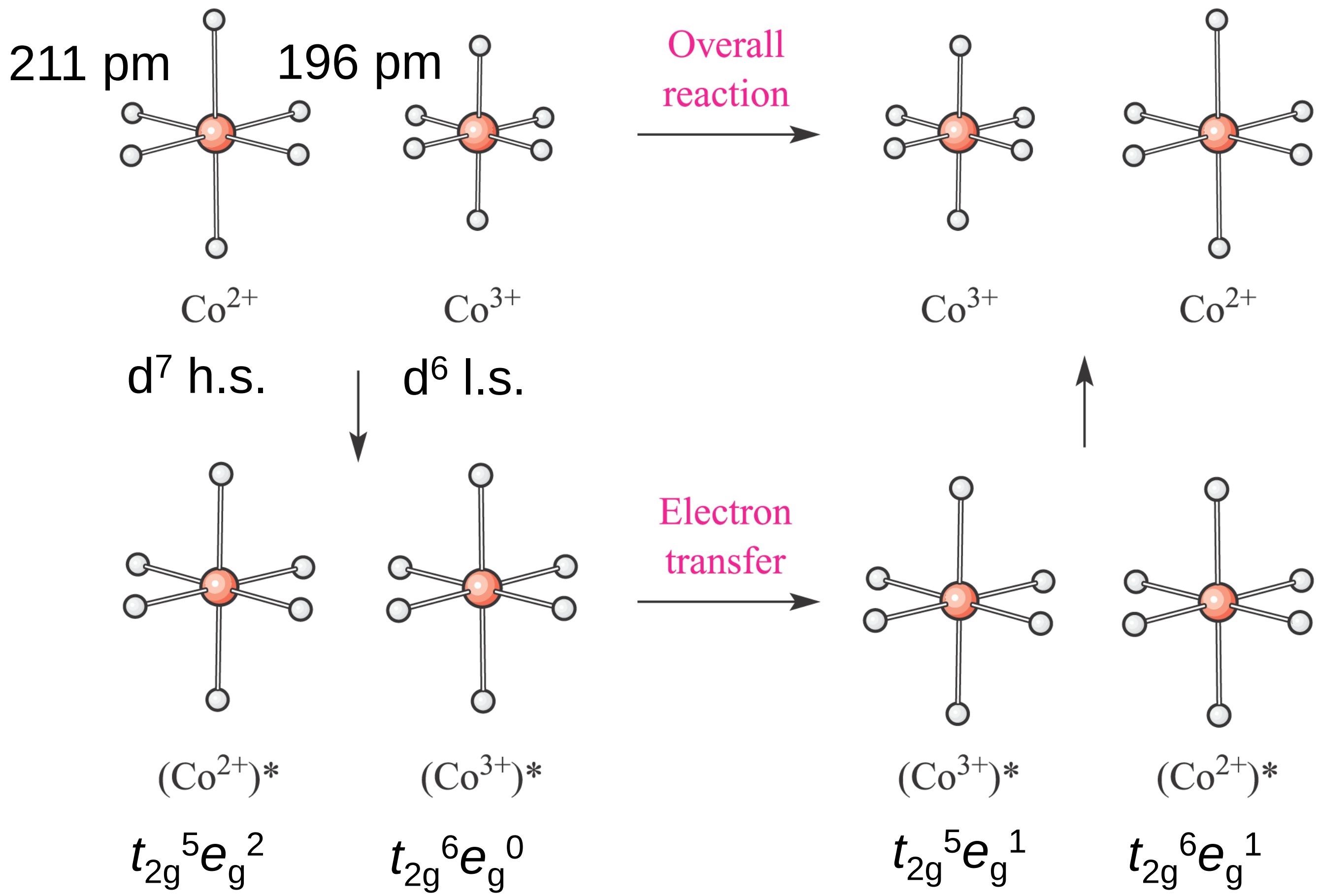
λ = **energia di riorganizzazione**

$\Delta G^{\neq} = \frac{\lambda}{4}$ per self-exchange



tipicamente $\lambda > 1$ eV

Elevata energia di riorganizzazione λ



stati vibrazionali eccitati

$k_{ET} = \nu_N \kappa_e e^{-\Delta G^{\neq}/RT}$ Equazione di Marcus

$$\Delta G^{\neq} = \frac{\lambda}{4} \times \left(1 + \frac{\Delta G^\circ}{\lambda}\right)^2$$

se $|\Delta G^\circ| \ll |\lambda|$

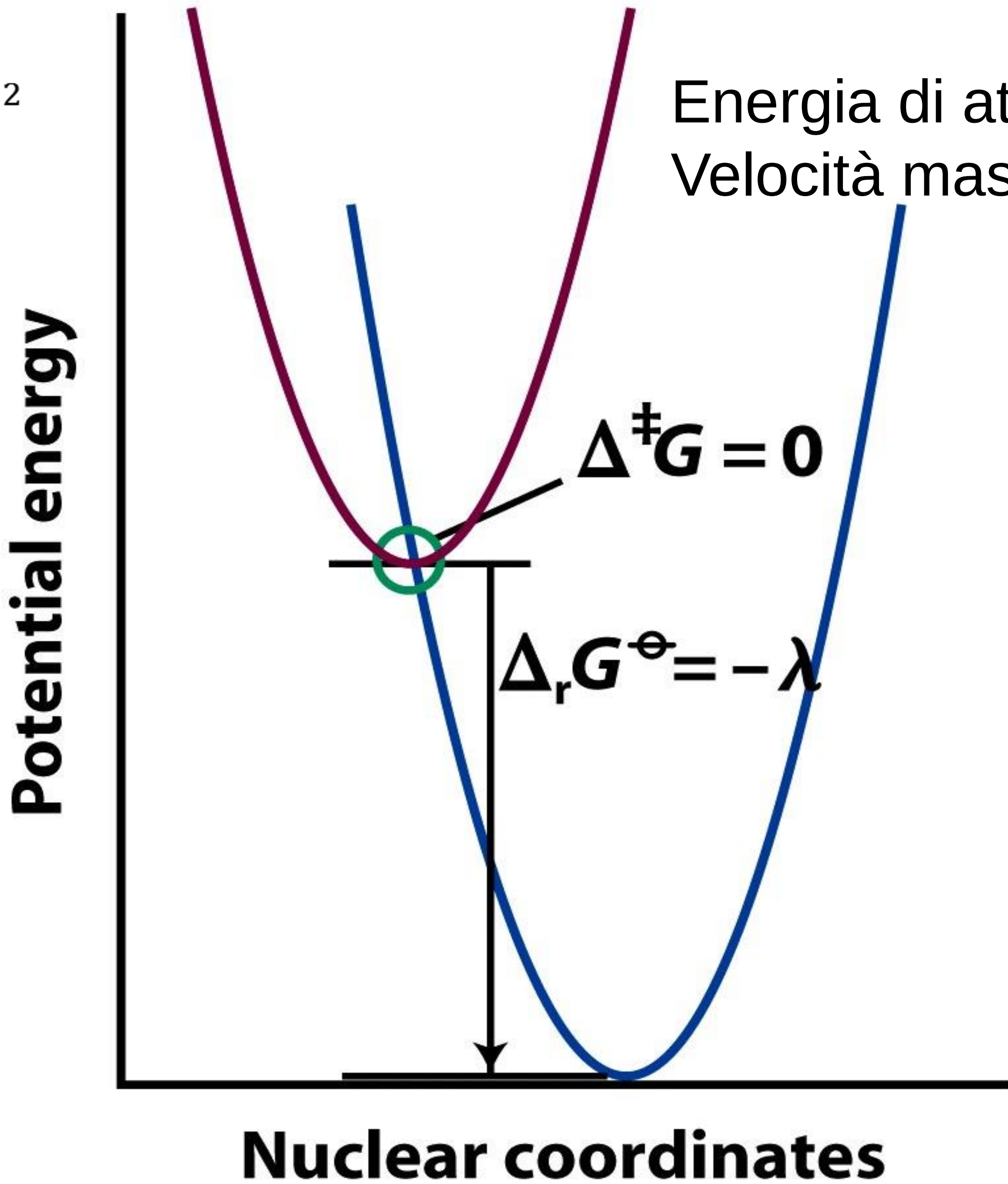
$$\Delta G^{\#} \approx 1/4 \times (\lambda + 2\Delta G^\circ)$$

$$k_{ET} \approx \nu_N \kappa_e e^{-(\lambda + 2\Delta G^\circ)/4RT}$$

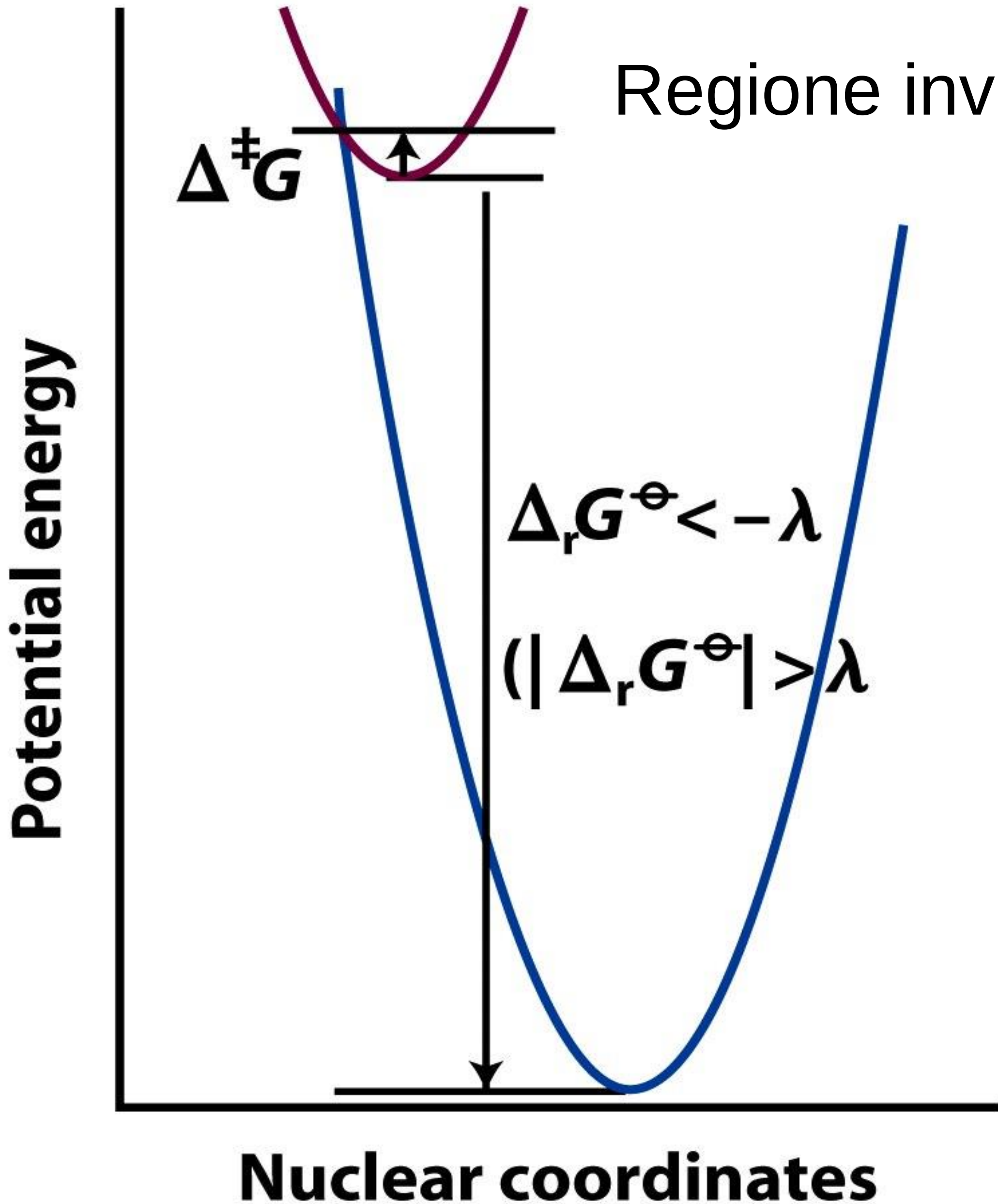
$\lambda + 2\Delta G^\circ > 0$

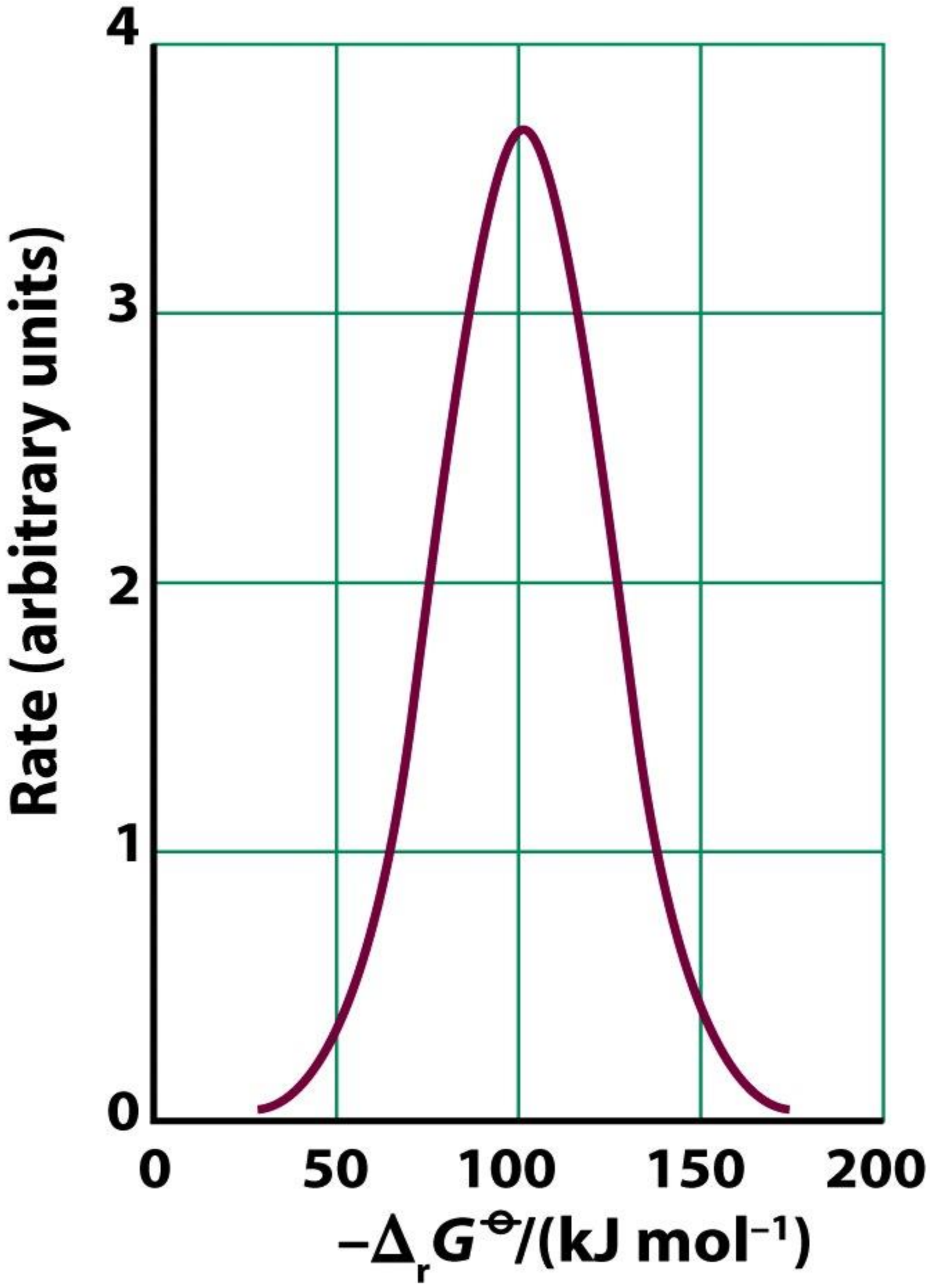
$$\Delta G^{\neq} = \frac{\lambda}{4} \times \left(1 + \frac{\Delta G^{\circ}}{\lambda}\right)^2$$

Energia di attivazione nulla
Velocità massima

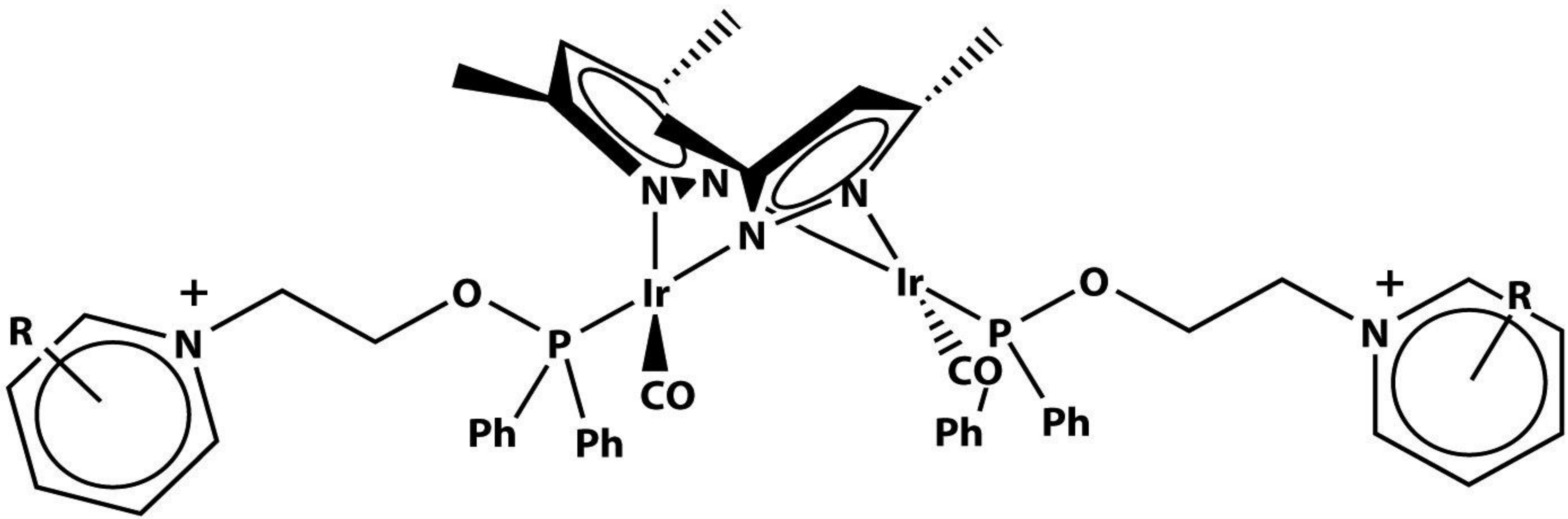


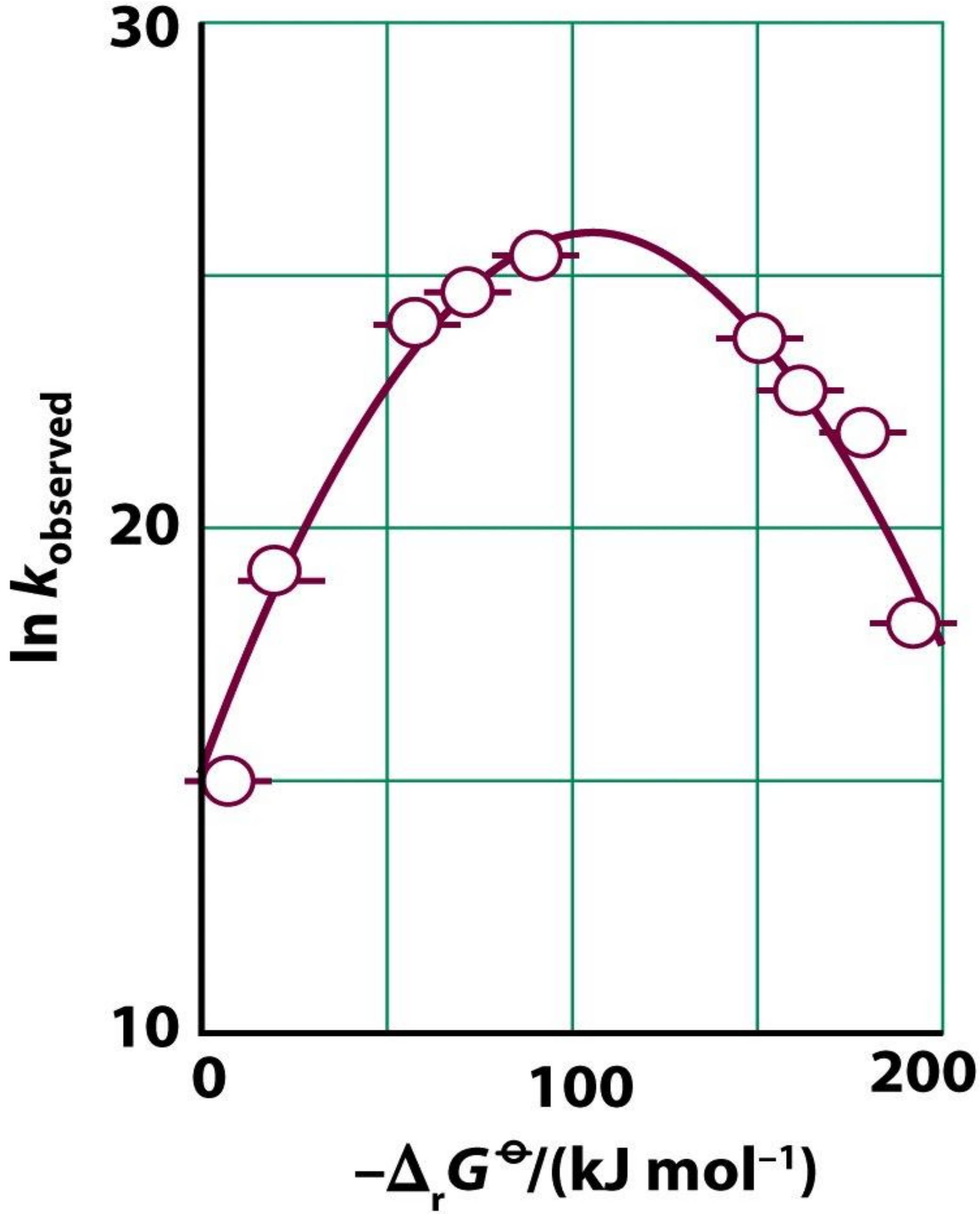
Regione inversa di Marcus





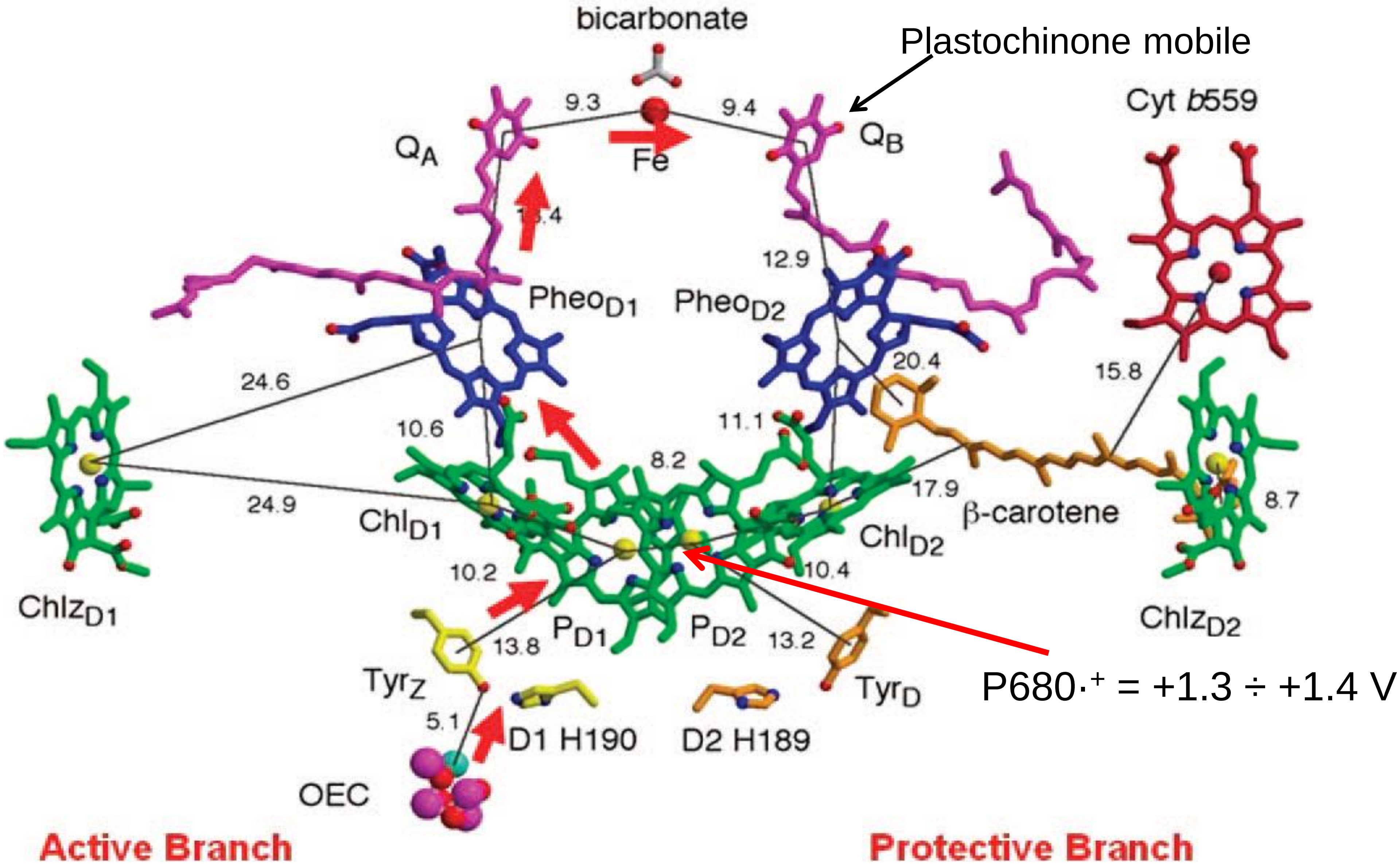
Rate (arbitrary units)
0
1
2
3
4
0
50
100
150
200
$-\Delta_r G^{\ominus}/(\text{kJ mol}^{-1})$


R
N
+
O
P
Ph
Ph
Ir
CO
N
N
N
N
Ir
CO
P
Ph
Ph
O
N
+
R



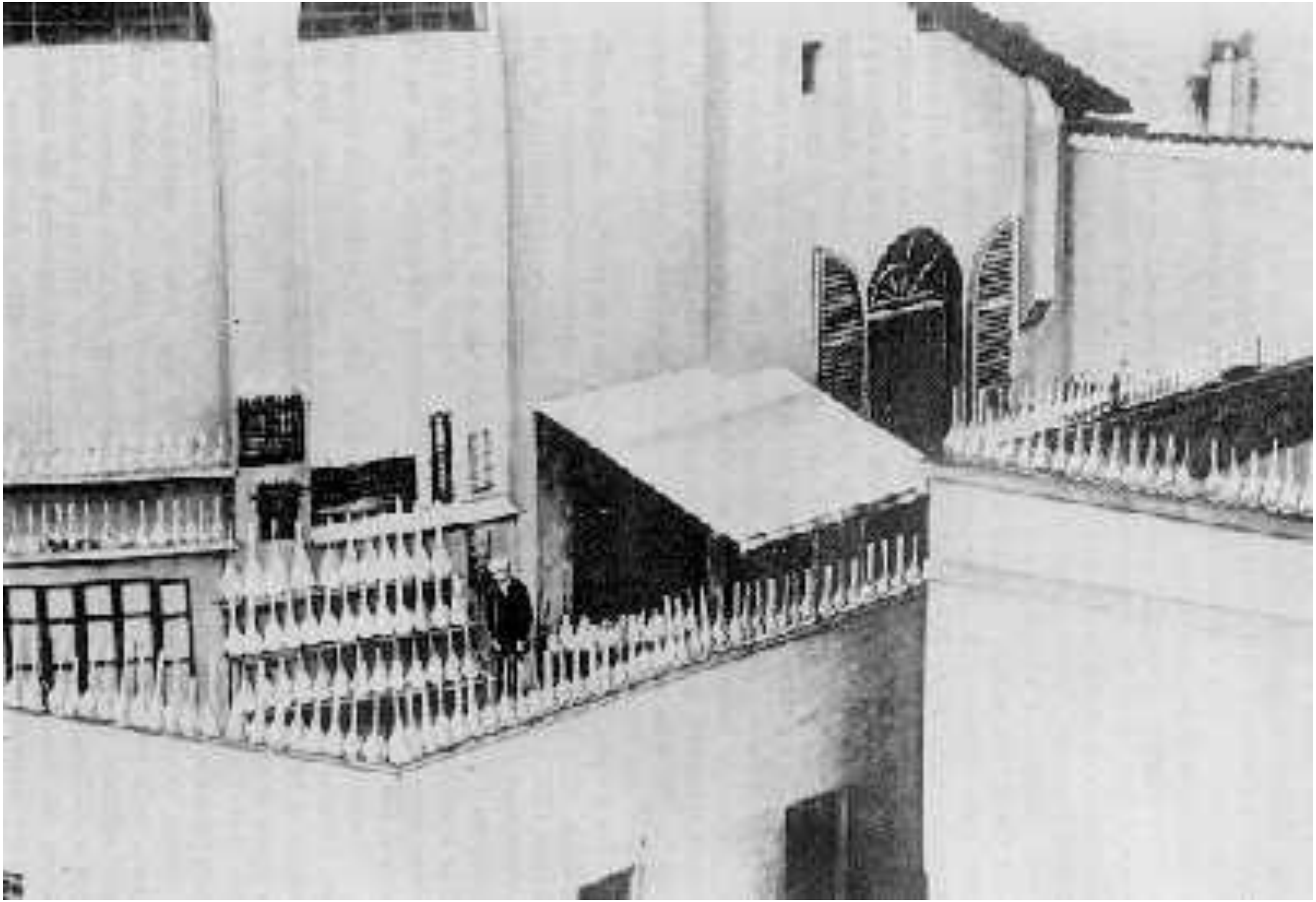
30
20
10
0
100
200
ln $k_{observed}$
$-\Delta_r G^{\ominus}$/(kJ mol^{-1})

Electron transport cofactors



Giacomo Luigi Ciamician

Trieste, 1857 – Bologna, 1922



SCIENCE

Friday, September 27, 1912

CONTENTS

MSS. intended for publication and books, etc., intended for review should be sent to the Editor of Science, Garrison-on-Hudson, N. Y.

THE PHOTOCHEMISTRY OF THE FUTURE[1]

Modern civilization is the daughter of coal, for this offers to mankind the solar energy in its most concentrated form; that is, in a form in which it has been accumulated in a long series of centuries. Modern man uses it with increasing eagerness and thoughtless prodigality for the conquest of the world and, like the mythical gold of the Rhine, coal is to-day the greatest source of energy and wealth.

The earth still holds enormous quantities of it, but coal is not inexhaustible. The problem of the future begins to interest us, and a proof of this may be seen in the fact that the subject was treated last year almost at the same time by Sir William Ramsay before the British Association for the Advancement of Science at Portsmouth and by Professor Carl Engler before the Versammlung deutscher Naturforscher und Aerzte at Karlsruhe. According to the calculations of Professor Engler Europe possesses to-day about 700 billion tons of coal and America about as much; to this must be added the coal of the unknown parts of Asia. The supply is enormous but, with increasing consumption, the mining of coal becomes more expensive on account of the greater depth to which it is necessary to go. It must therefore be remembered that in some regions the deposits of coal may become practically useless long before their exhaustion.

Is *fossil* solar energy the only one that may be used in modern life and civilization? That is the question.

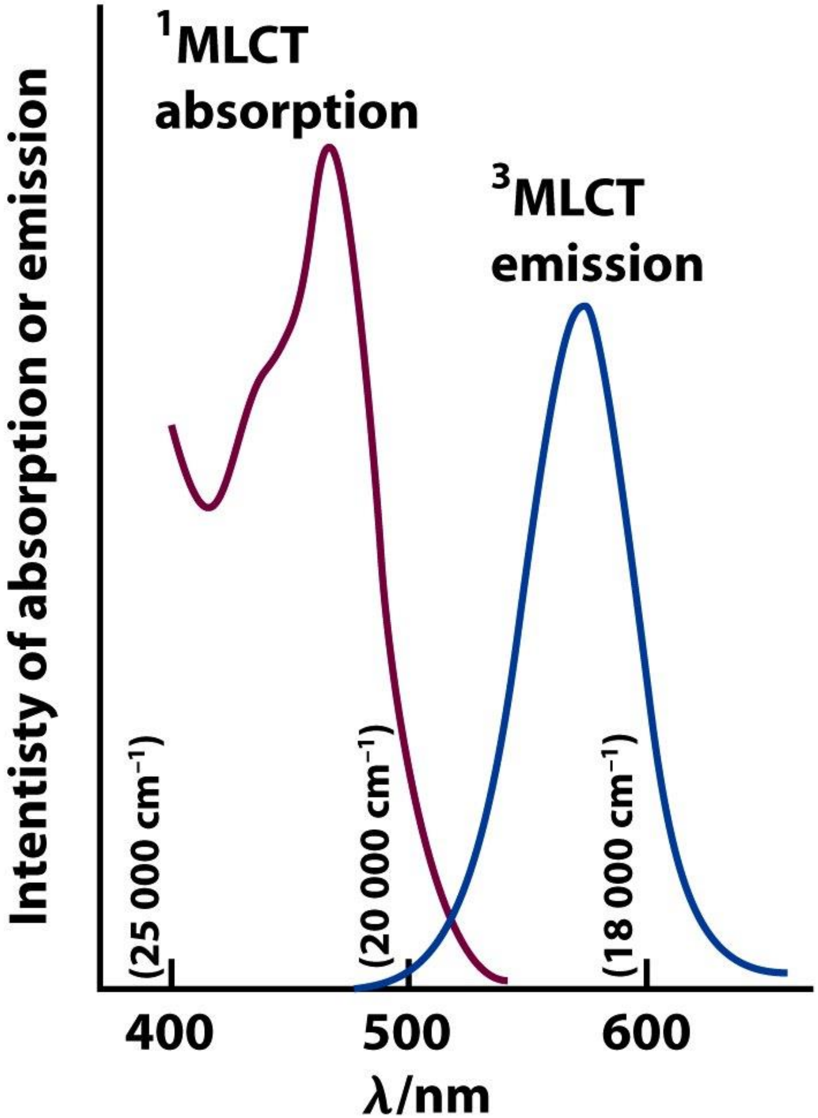
[1] General lecture before the International Congress of Applied Chemistry, New York, September 11, 1912.

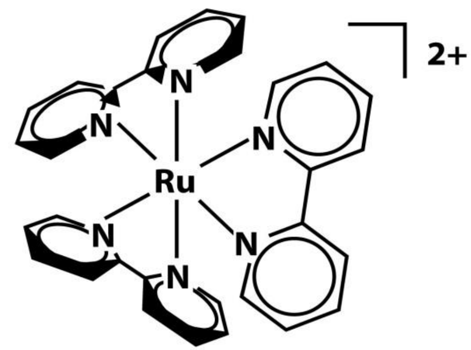
THE PHOTOCHEMISTRY OF THE FUTURE (1912)
GIACOMO CIAMICIAN (1857-1922)
(Translation supplied by the author)

Modern civilization is the daughter of coal for this offers to mankind the solar energy in its most concentrated form: that is in a form in which it has been accumulated in a long series of centuries.

And if in a distant future the supply of coal becomes completely exhausted, civilization will not be checked by that, for life and civilization will continue as long as the sun shines! If our black and nervous civilization, based on coal, shall be followed by a quieter civilization based on the utilization of solar energy, that will not be harmful to progress and to human happiness.

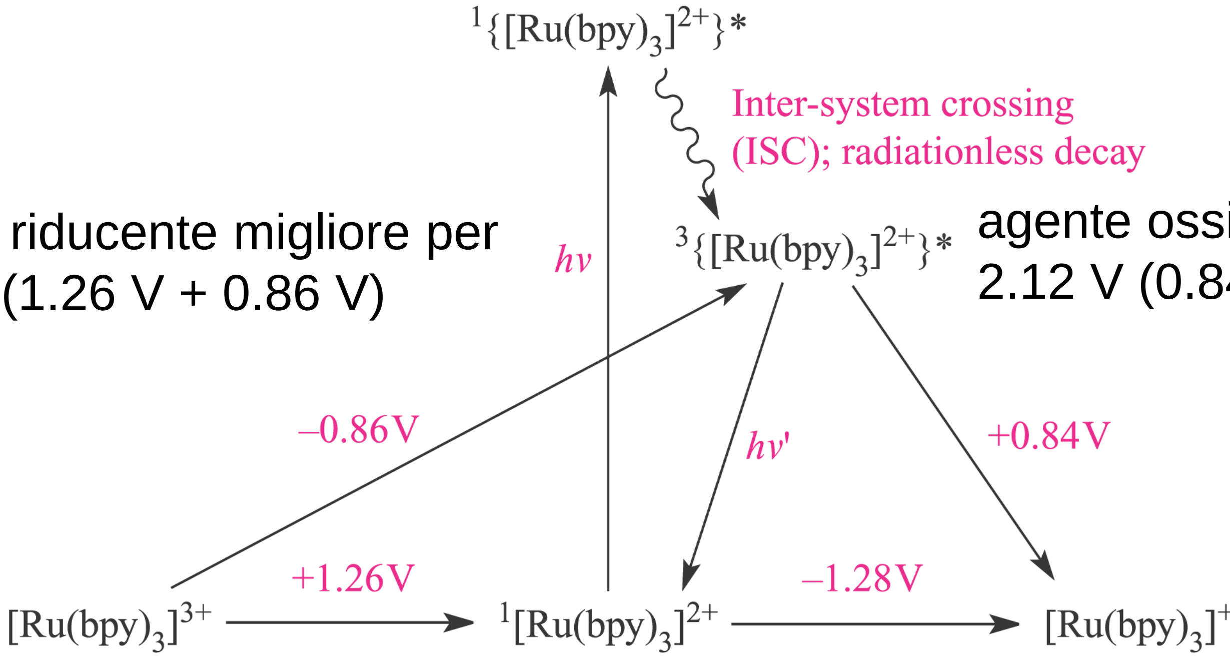
The photochemistry of the future should not however be postponed to such distant times; I believe that industry will do well in using from this very day all the energies that nature puts at its disposal. So far, human civilization has made use almost exclusively of fossil solar energy. Would it not be advantageous to make better use of radiant energy?





Le transizioni MLCT possono dare origine a reazioni redox

agente riducente migliore per
2.12 V (1.26 V + 0.86 V)



agente ossidante migliore per
2.12 V (0.84 V + 1.28 V)