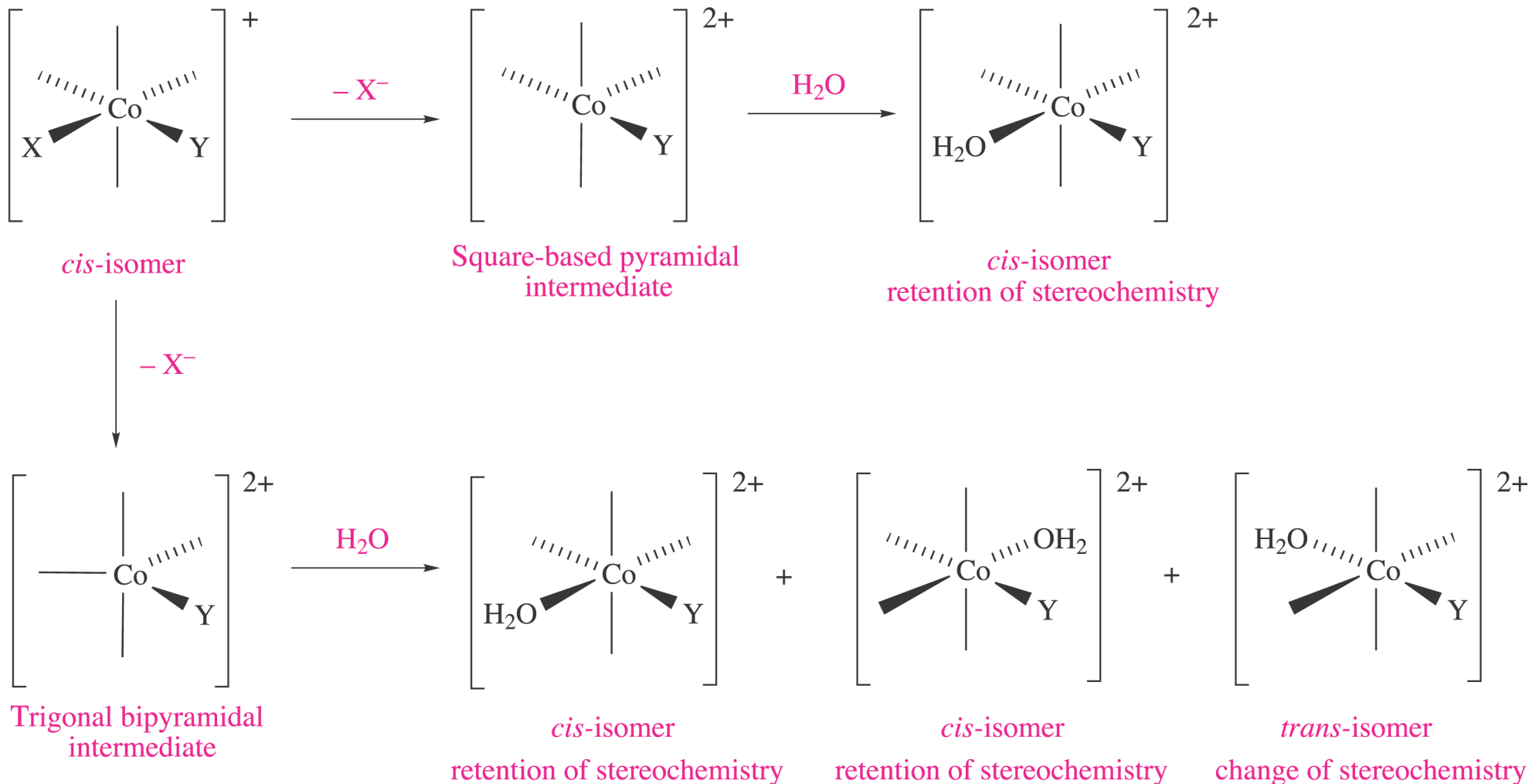
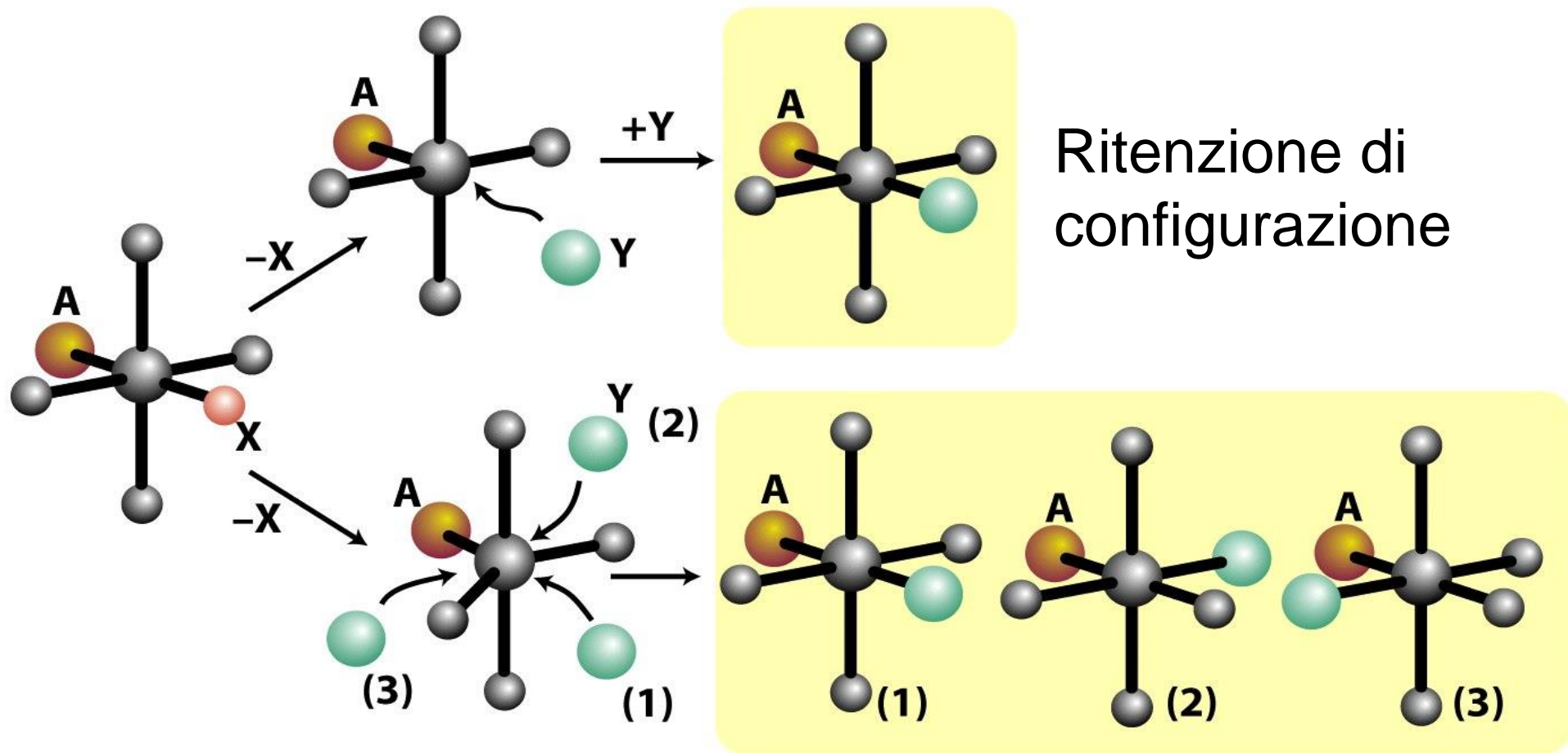
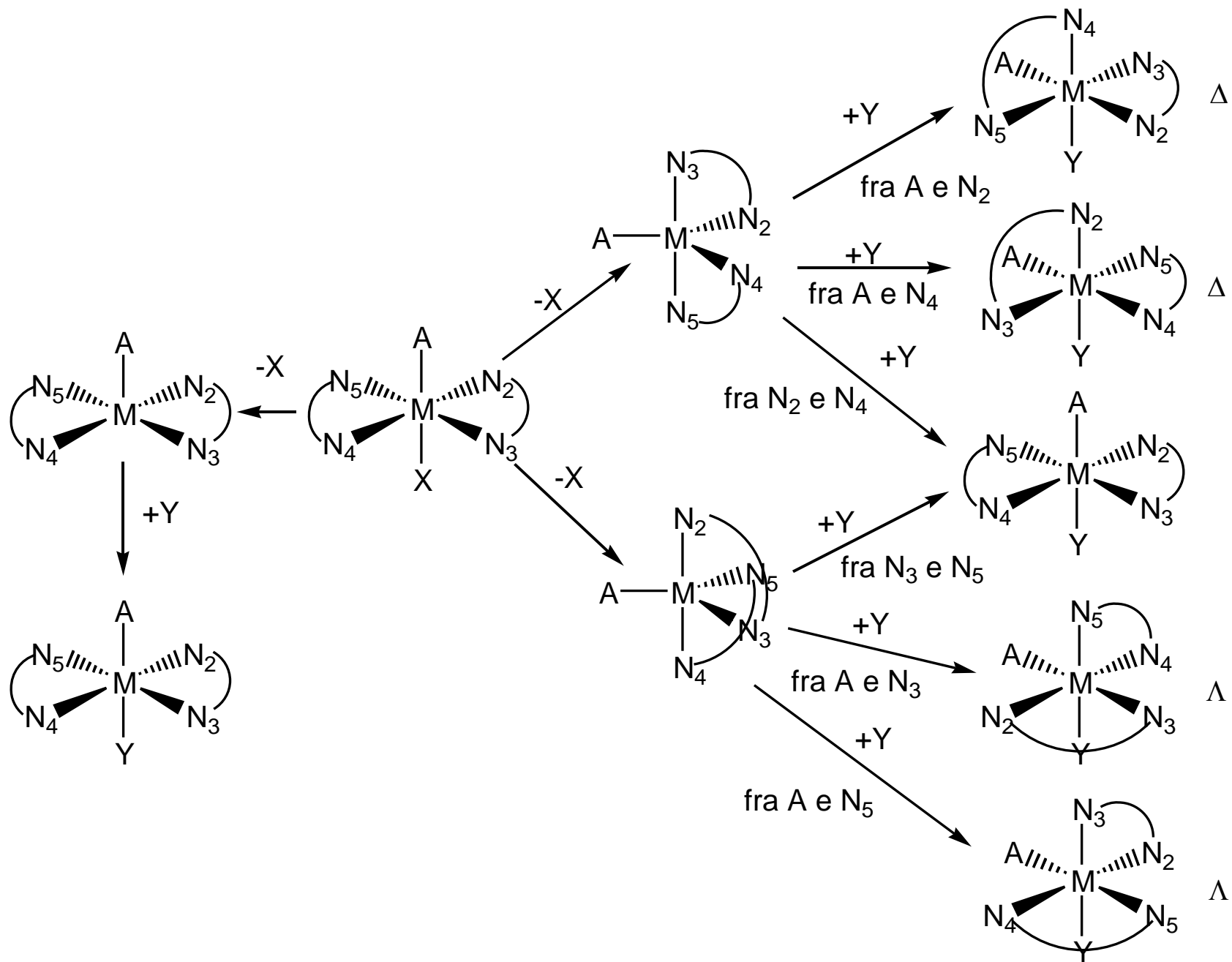


Stereochimica delle sostituzioni nei complessi ottaedrici



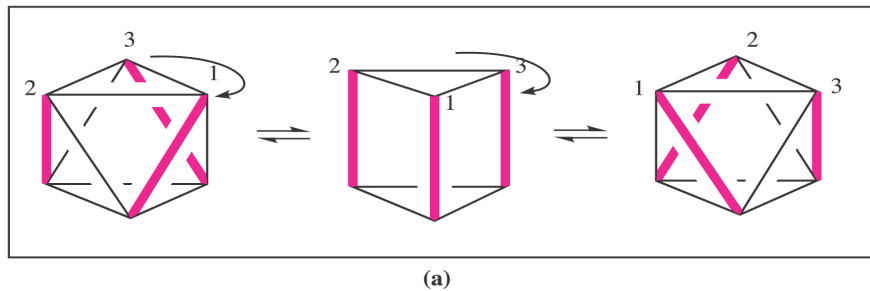
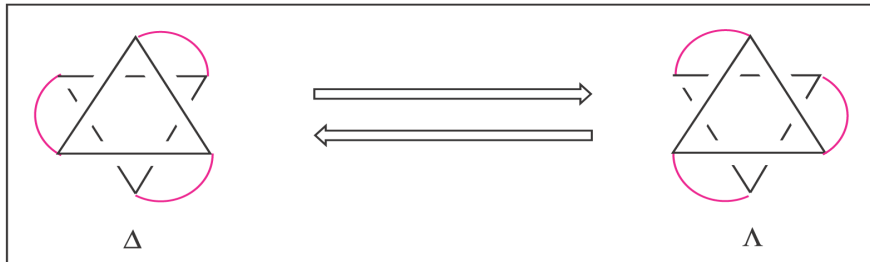


$cis/trans = 2:1$

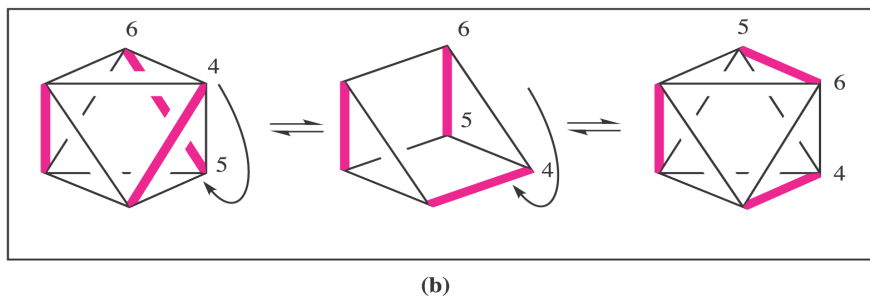


isomerizzazione e racemizzazione in complessi ottaedrici

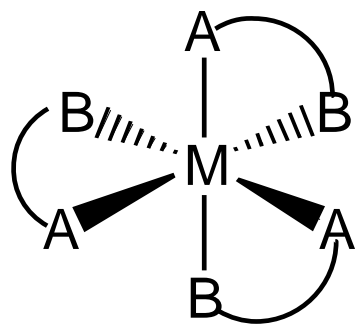
Meccanismi torsionali per l'interconversione di enantiomeri Λ e Δ di $[M(\text{chel})_3]$



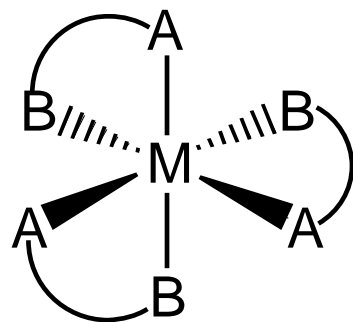
Bailar twist



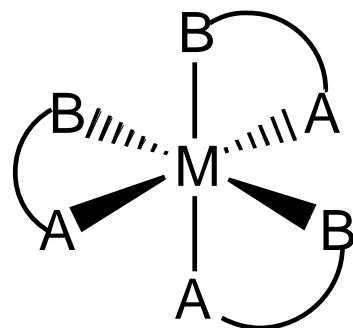
Ray-Dutt
twist



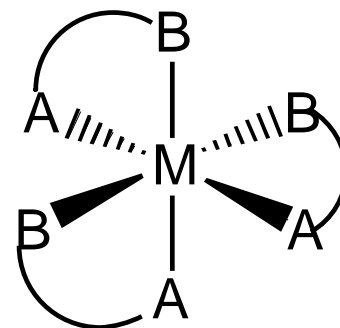
*fac*Δ



*fac*Δ



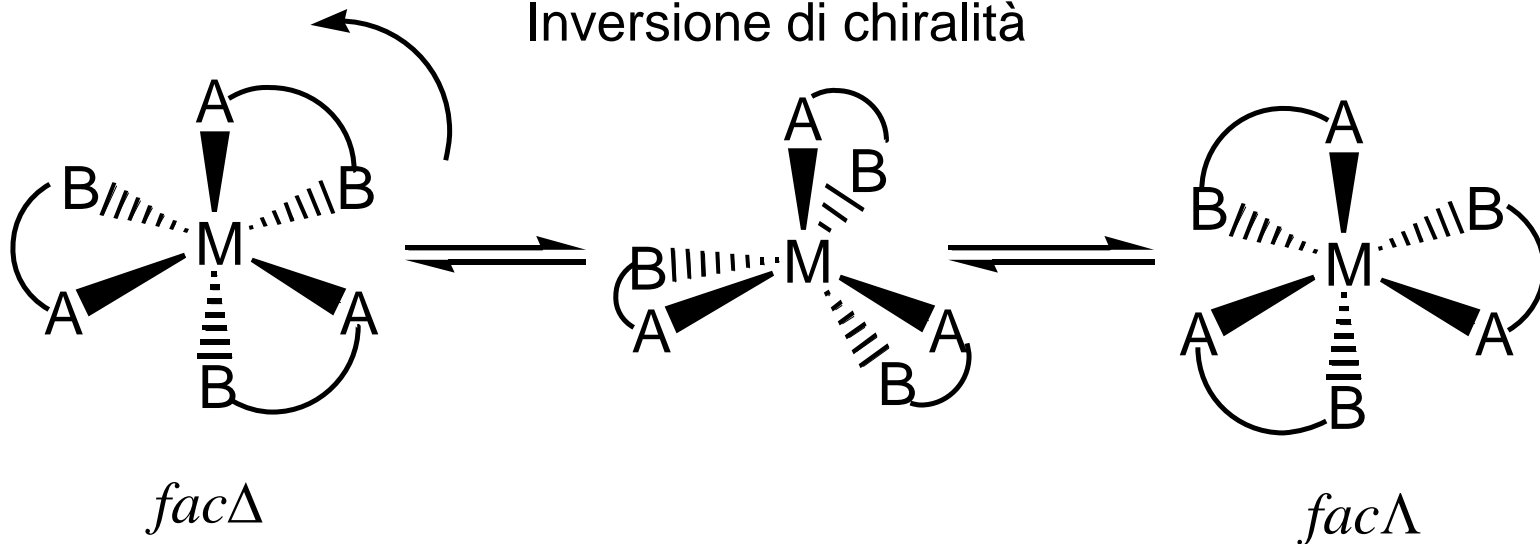
*mer*Δ



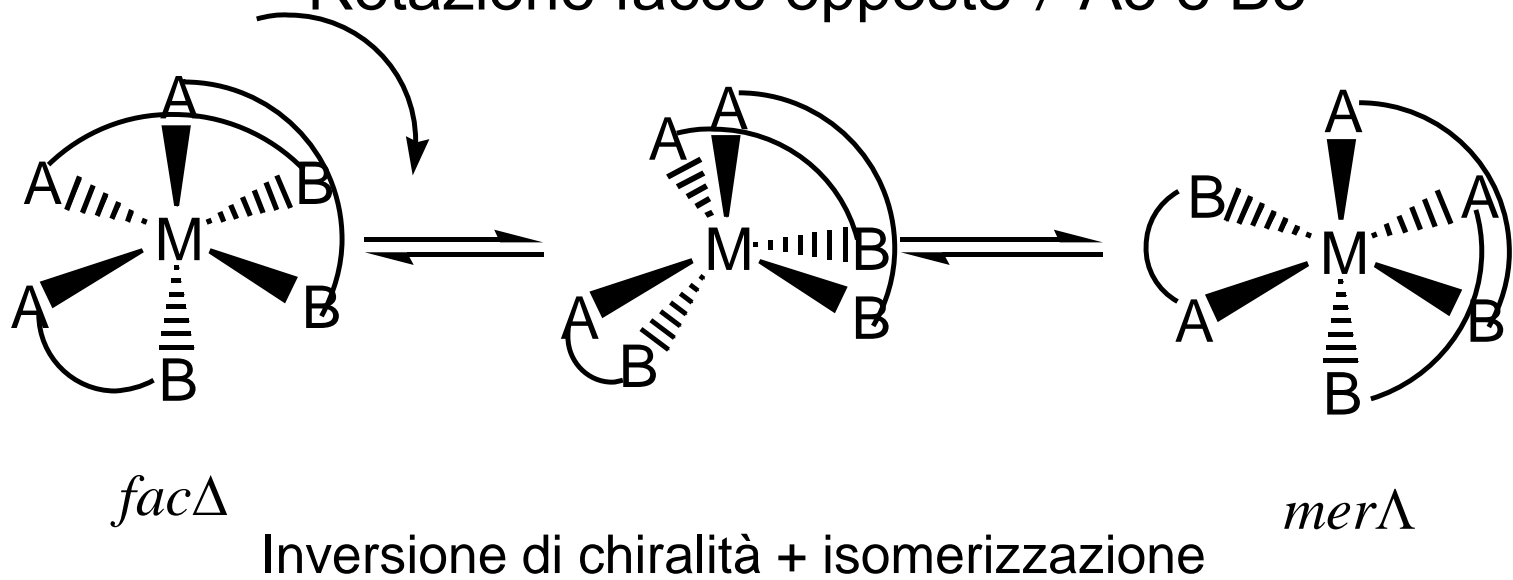
*mer*Δ

Rotazione facce opposte A3 e B3

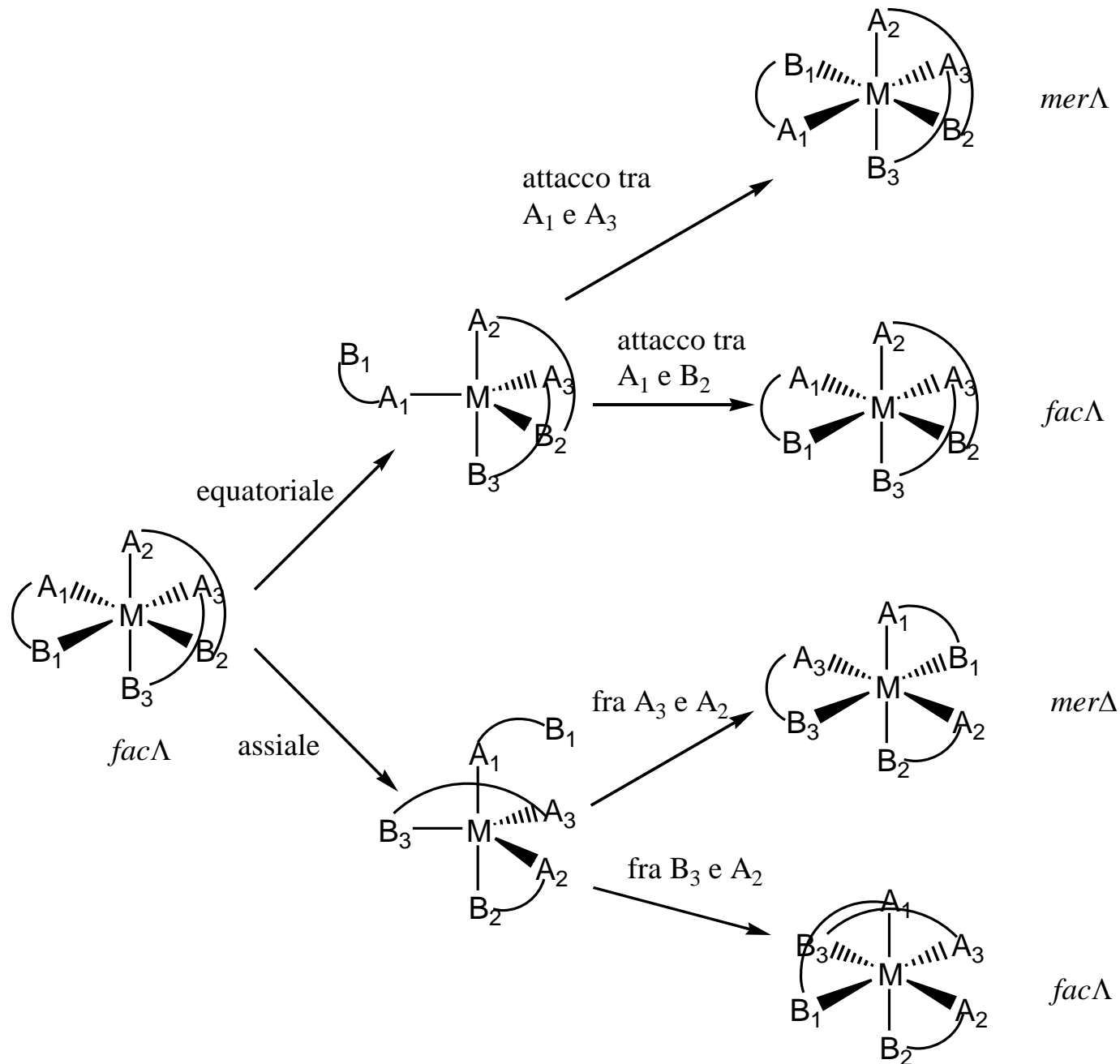
Inversione di chiralità



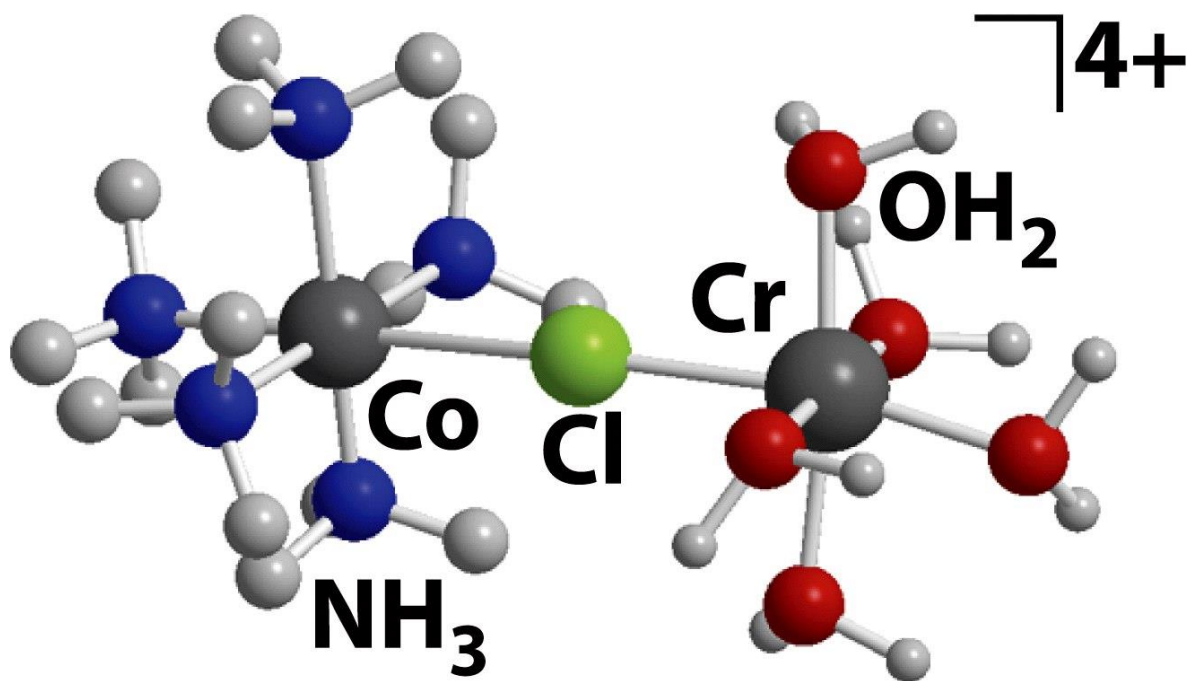
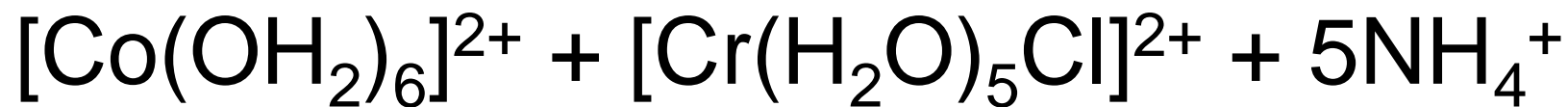
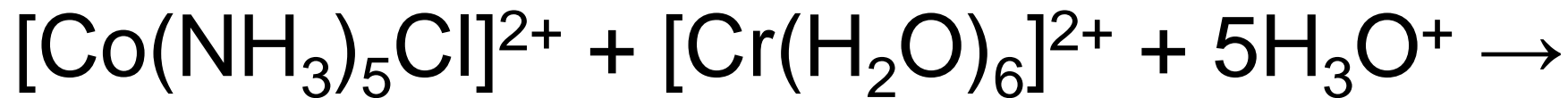
Rotazione facce opposte ≠ A3 e B3



meccanismo con apertura di un chelante



Processi redox a sfera interna

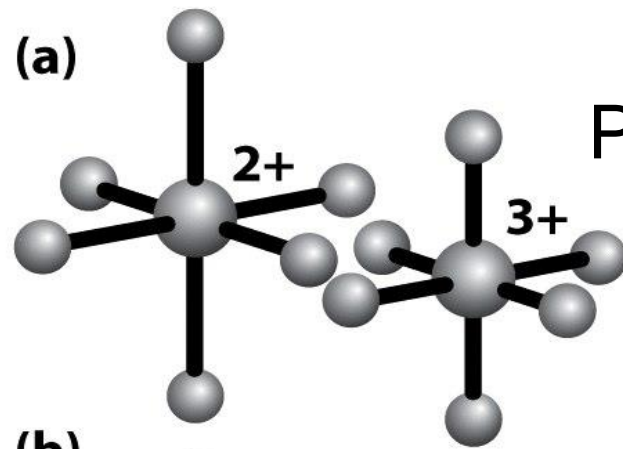


Processo redox senza trasferimento del legante a ponte



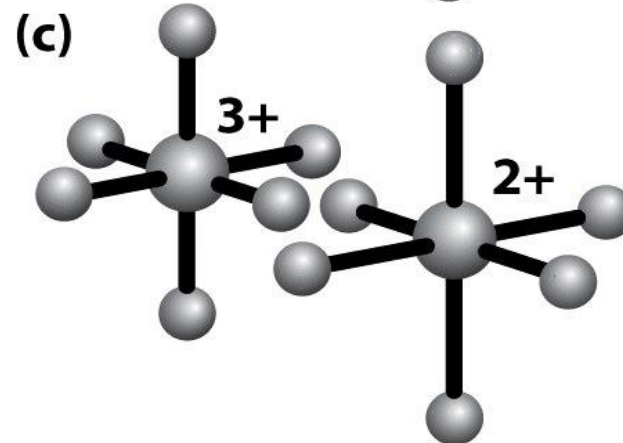
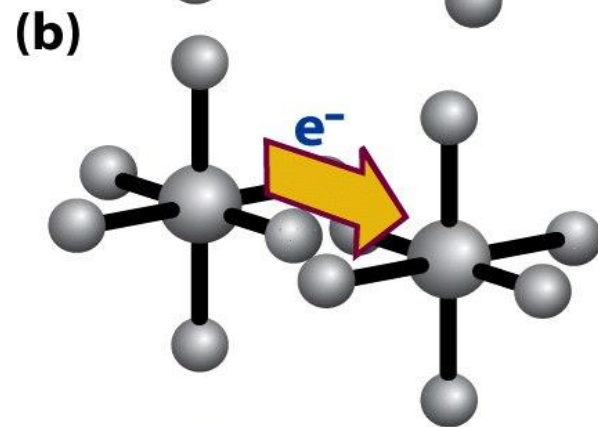
Processi redox a sfera esterna

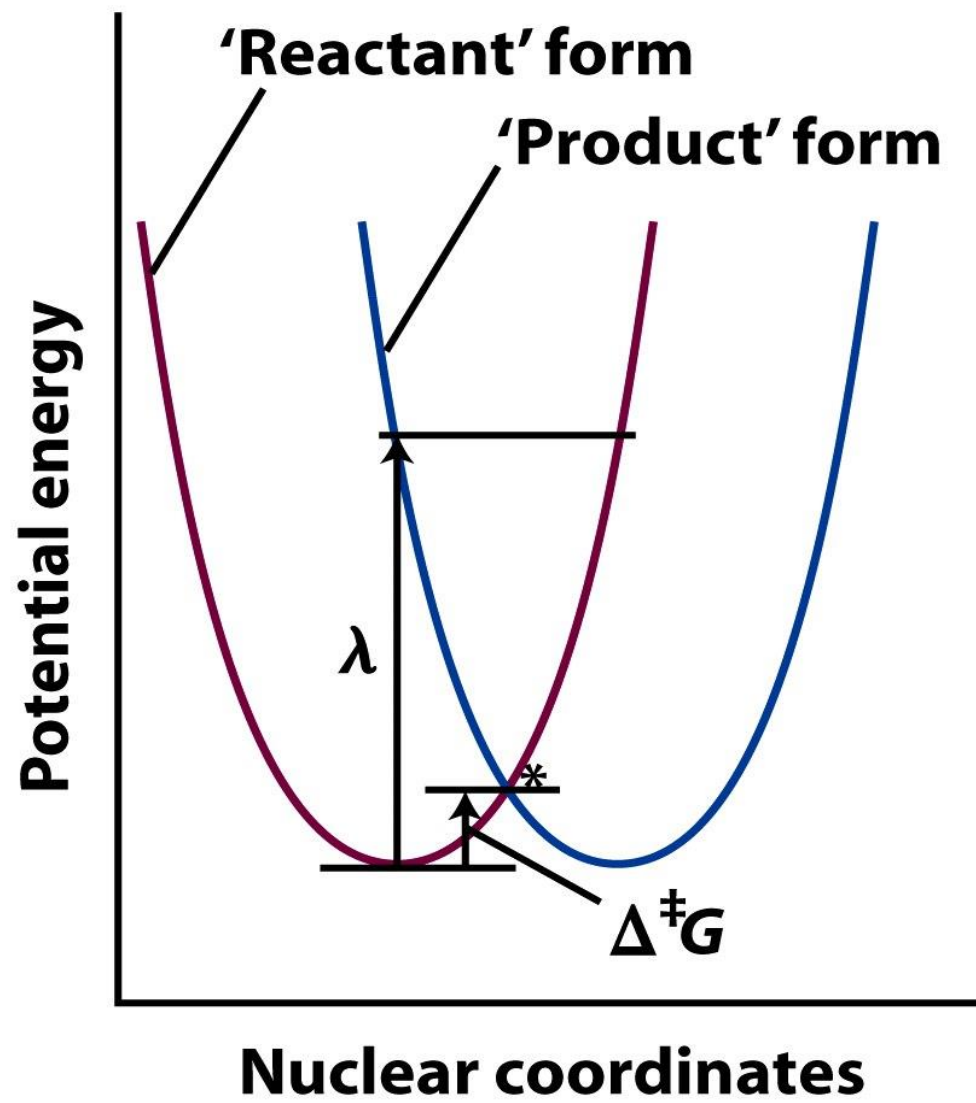
| | Reaction | $k / \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ |
|---|---|---|
| No net chemical reaction (self-exchange) | $[\text{Fe}(\text{bpy})_3]^{2+} + [\text{Fe}(\text{bpy})_3]^{3+} \rightarrow [\text{Fe}(\text{bpy})_3]^{3+} + [\text{Fe}(\text{bpy})_3]^{2+}$ | $>10^6$ |
| | $[\text{Os}(\text{bpy})_3]^{2+} + [\text{Os}(\text{bpy})_3]^{3+} \rightarrow [\text{Os}(\text{bpy})_3]^{3+} + [\text{Os}(\text{bpy})_3]^{2+}$ | $>10^6$ |
| | $[\text{Co}(\text{phen})_3]^{2+} + [\text{Co}(\text{phen})_3]^{3+} \rightarrow [\text{Co}(\text{phen})_3]^{3+} + [\text{Co}(\text{phen})_3]^{2+}$ | 40 |
| | $[\text{Fe}(\text{OH}_2)_6]^{2+} + [\text{Fe}(\text{OH}_2)_6]^{3+} \rightarrow [\text{Fe}(\text{OH}_2)_6]^{3+} + [\text{Fe}(\text{OH}_2)_6]^{2+}$ | 3 |
| | $[\text{Co}(\text{en})_3]^{2+} + [\text{Co}(\text{en})_3]^{3+} \rightarrow [\text{Co}(\text{en})_3]^{3+} + [\text{Co}(\text{en})_3]^{2+}$ | 10^{-4} |
| | $[\text{Co}(\text{NH}_3)_6]^{2+} + [\text{Co}(\text{NH}_3)_6]^{3+} \rightarrow [\text{Co}(\text{NH}_3)_6]^{3+} + [\text{Co}(\text{NH}_3)_6]^{2+}$ | 10^{-6} |
| Net chemical reaction | $[\text{Os}(\text{bpy})_3]^{2+} + [\text{Mo}(\text{CN})_8]^{3-} \rightarrow [\text{Os}(\text{bpy})_3]^{3+} + [\text{Mo}(\text{CN})_8]^{4-}$ | 2×10^9 |
| | $[\text{Fe}(\text{CN})_6]^{4-} + [\text{Fe}(\text{phen})_3]^{3+} \rightarrow [\text{Fe}(\text{CN})_6]^{3-} + [\text{Fe}(\text{phen})_3]^{2+}$ | 10^8 |
| | $[\text{Fe}(\text{CN})_6]^{4-} + [\text{IrCl}_6]^{2-} \rightarrow [\text{Fe}(\text{CN})_6]^{3-} + [\text{IrCl}_6]^{3-}$ | 4×10^5 |



Principio di Frank – Condon

Complesso di incontro





Velocità di trasferimento elettronico

$$k_{\text{ET}} = v_{\text{N}} \kappa_{\text{e}} e^{-\Delta G^{\ddagger}/RT} \quad \text{Equazione di Marcus}$$

v_{N} = fattore di frequenza nucleare^a

κ_{e} = fattore elettronico (0 ÷ 1)^b

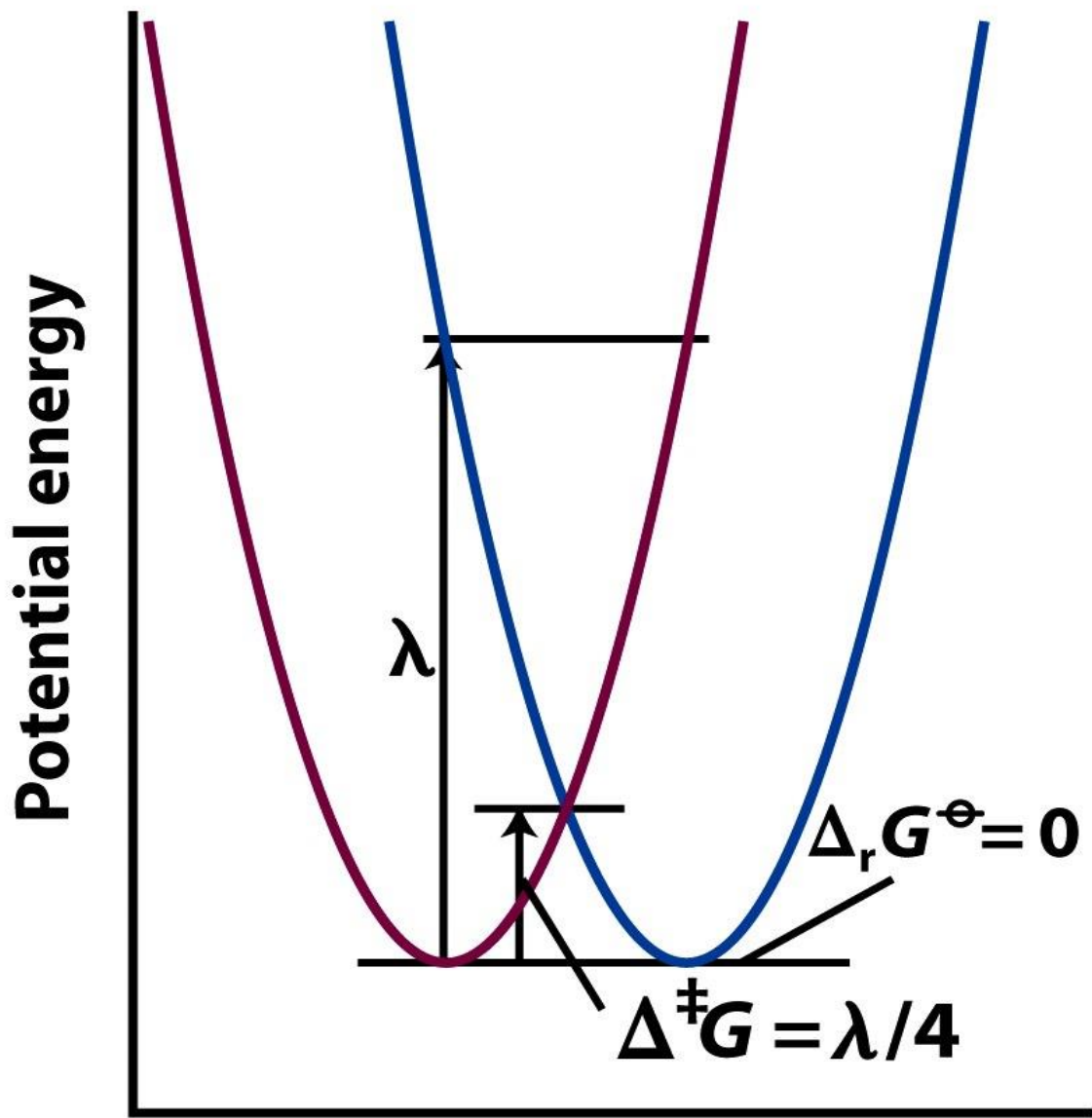
$$\Delta G^{\ddagger} = \frac{\lambda}{4} \times \left(1 + \frac{\Delta G^{\circ}}{\lambda}\right)^2$$

λ = **energia di riorganizzazione**

$$\Delta G^{\ddagger} = \frac{\lambda}{4} \quad \text{per self-exchange}$$

^a frequenza alla quale i due complessi, dopo aver formato il complesso di incontro in soluzione, raggiungono lo stato di transizione.

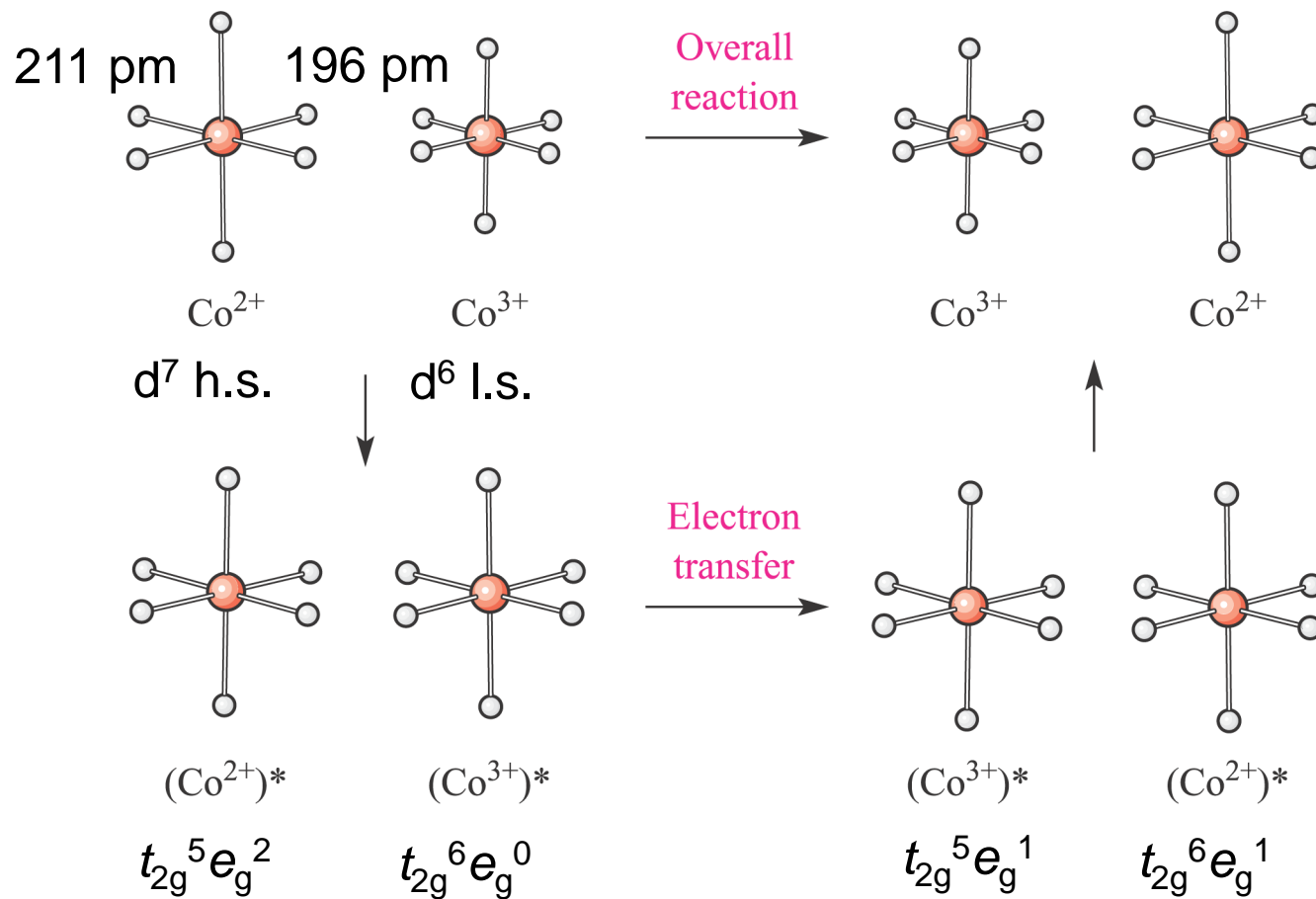
^b probabilità, in una scala da 0 a 1, che avvenga il trasferimento di un elettrone quando sia stato raggiunto lo stato di transizione.



Nuclear coordinates

tipicamente $\lambda > 1$ eV

Elevata energia di riorganizzazione λ



stati vibrazionali eccitati

$$k_{\text{ET}} = \nu_{\text{N}} \kappa_{\text{e}} e^{-\Delta G^{\ddagger}/RT} \quad \text{Equazione di Marcus}$$

$$\Delta G^{\ddagger} = \frac{\lambda}{4} \times \left(1 + \frac{\Delta G^{\circ}}{\lambda}\right)^2 \quad \underline{\text{se}} \quad |\Delta G^{\circ}| \ll |\lambda|$$

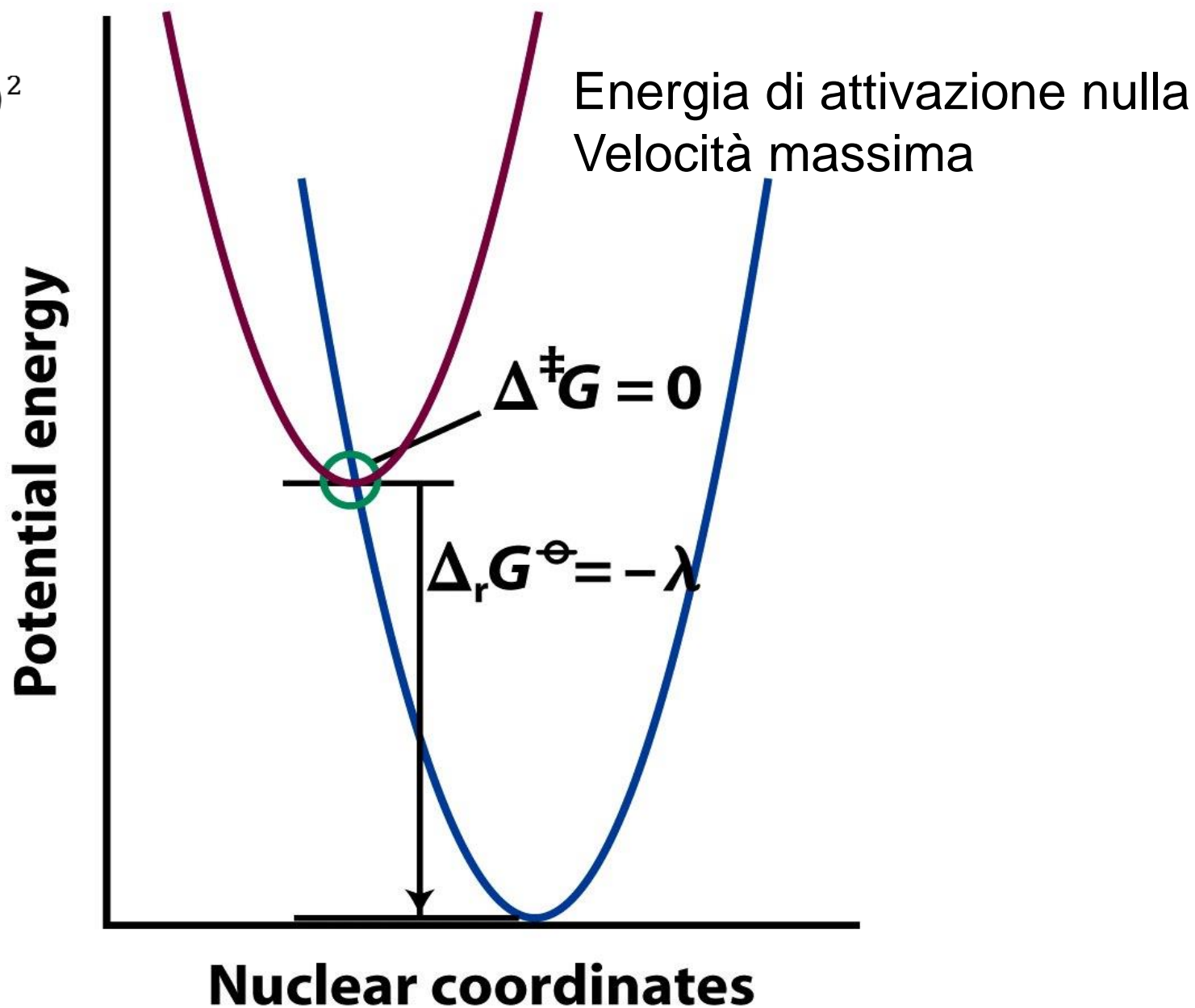
$$\Delta G^{\ddagger} \approx 1/4 \times (\lambda + 2\Delta G^{\circ})$$

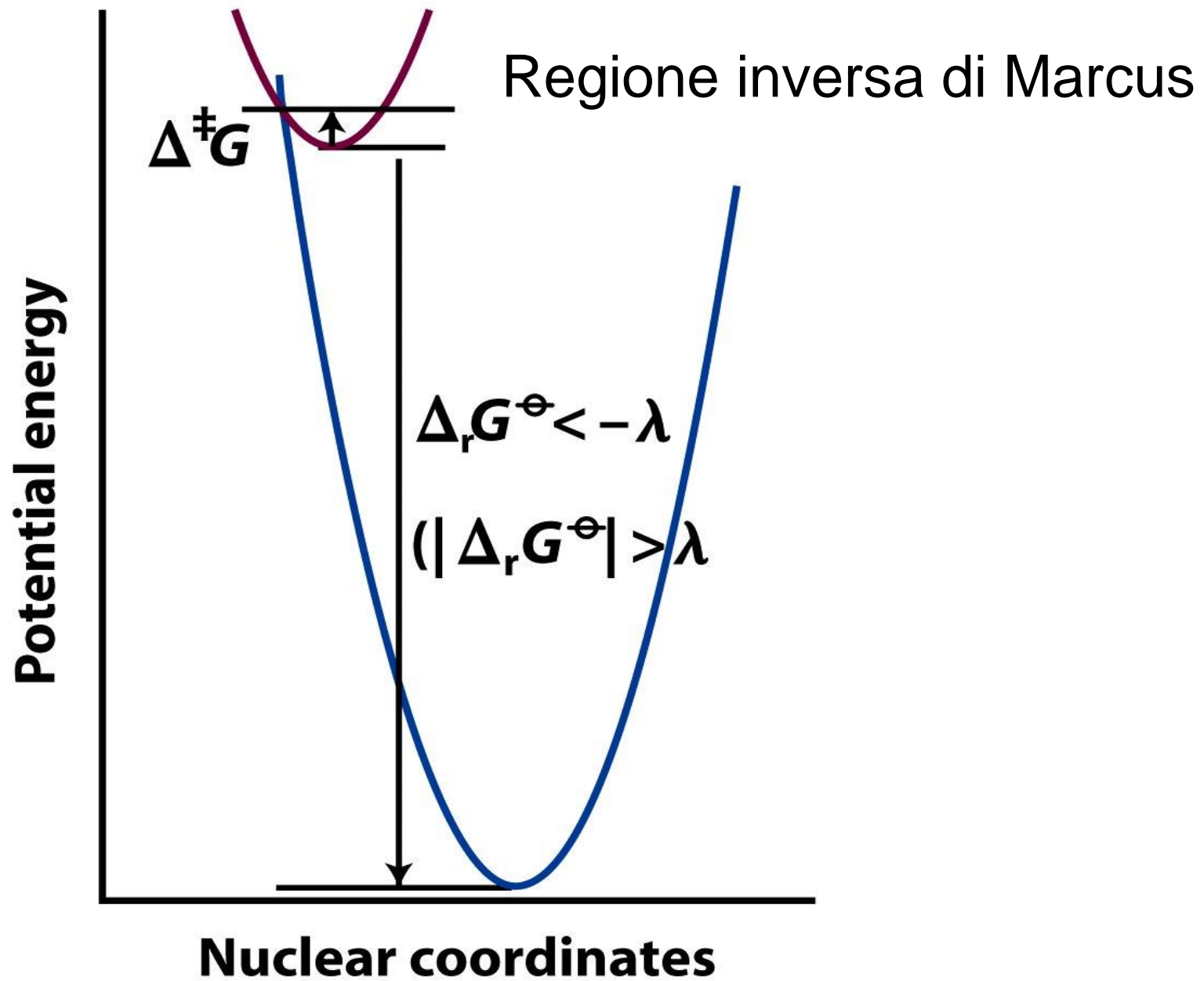
$$k_{\text{ET}} \approx \nu_{\text{N}} \kappa_{\text{e}} e^{-(\lambda + 2\Delta G^{\circ})/4RT}$$

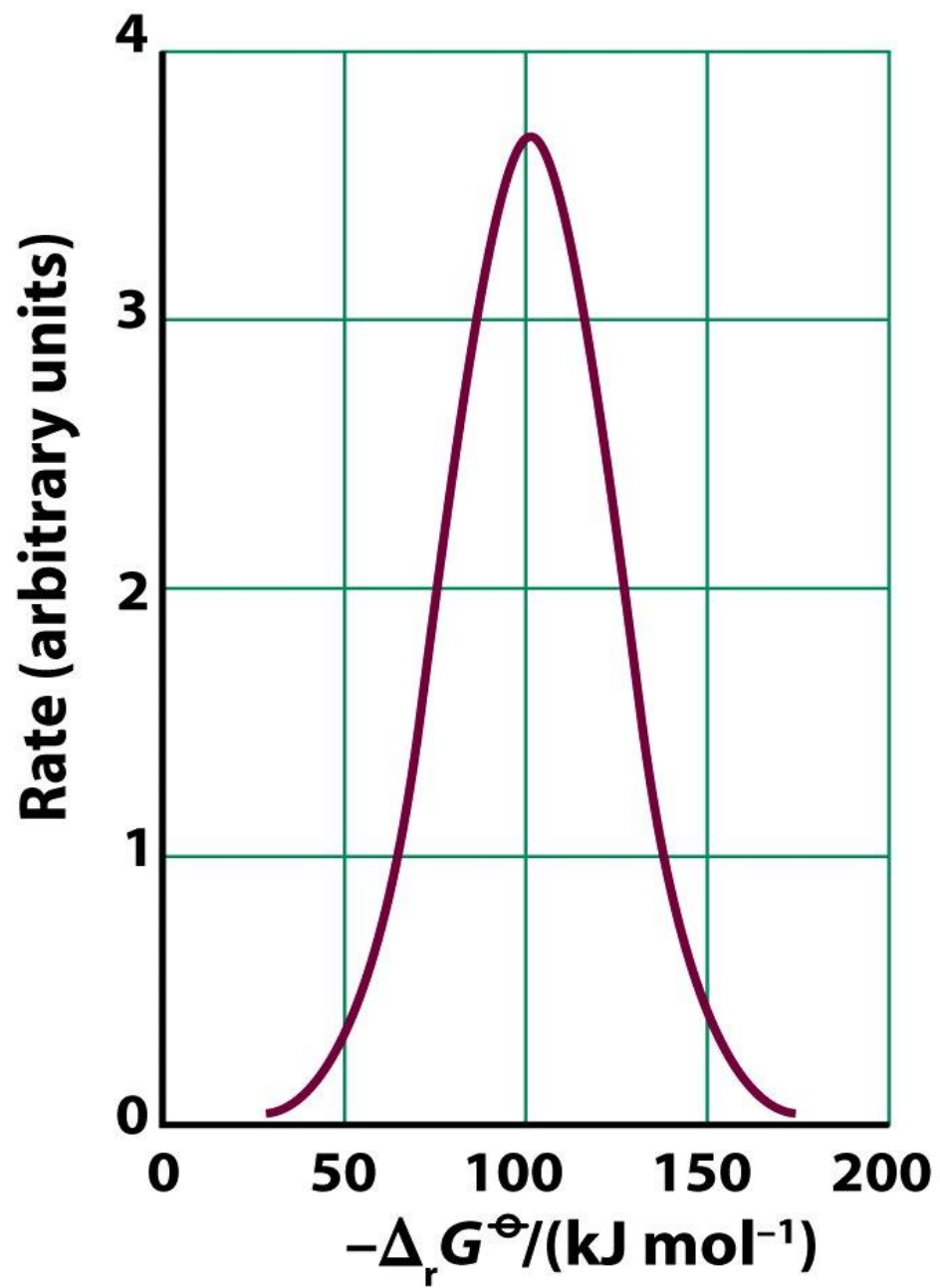
$$\lambda + 2\Delta G^{\circ} > 0$$

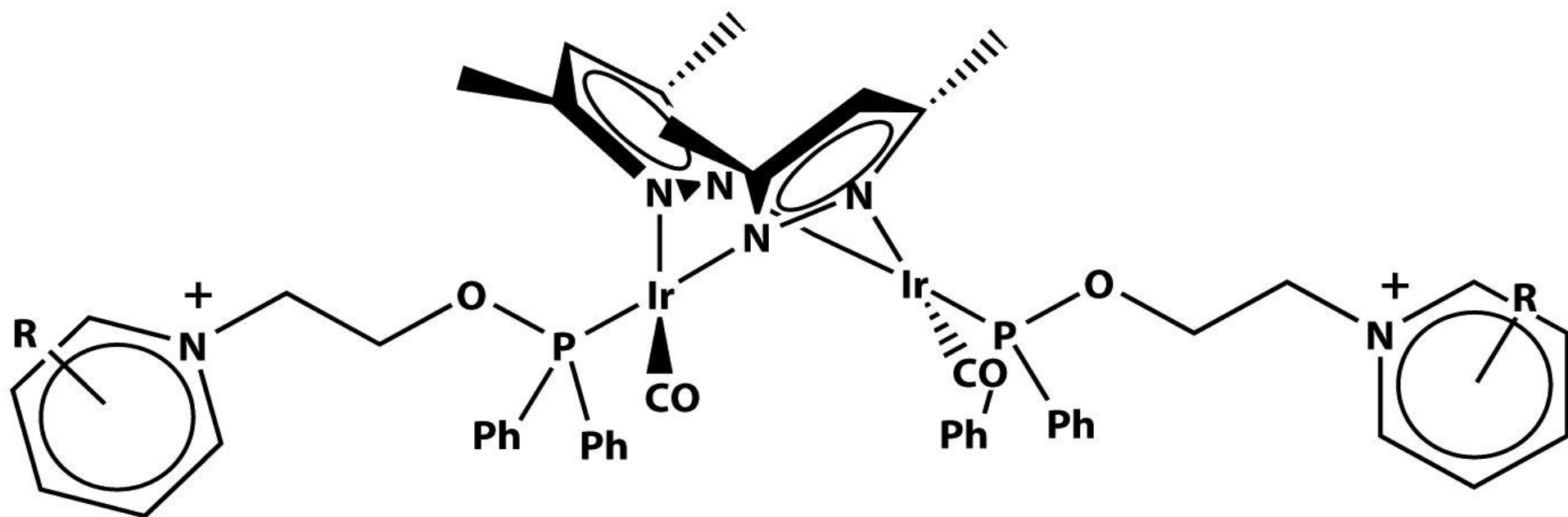
tanto più negativo è ΔG° e tanto più piccolo è ΔG^{\ddagger}

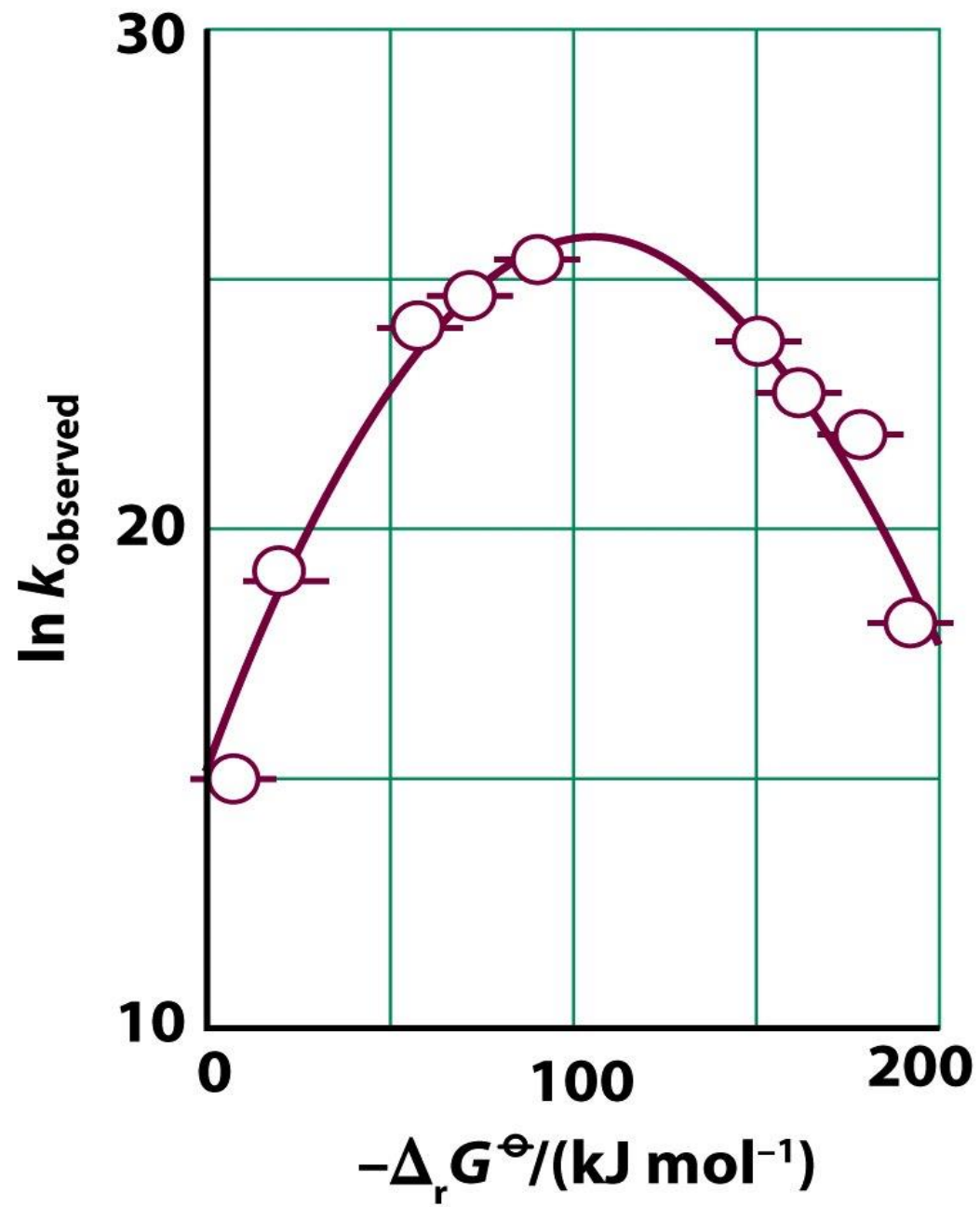
$$\Delta G^\ddagger = \frac{\lambda}{4} \times \left(1 + \frac{\Delta G^\ominus}{\lambda}\right)^2$$



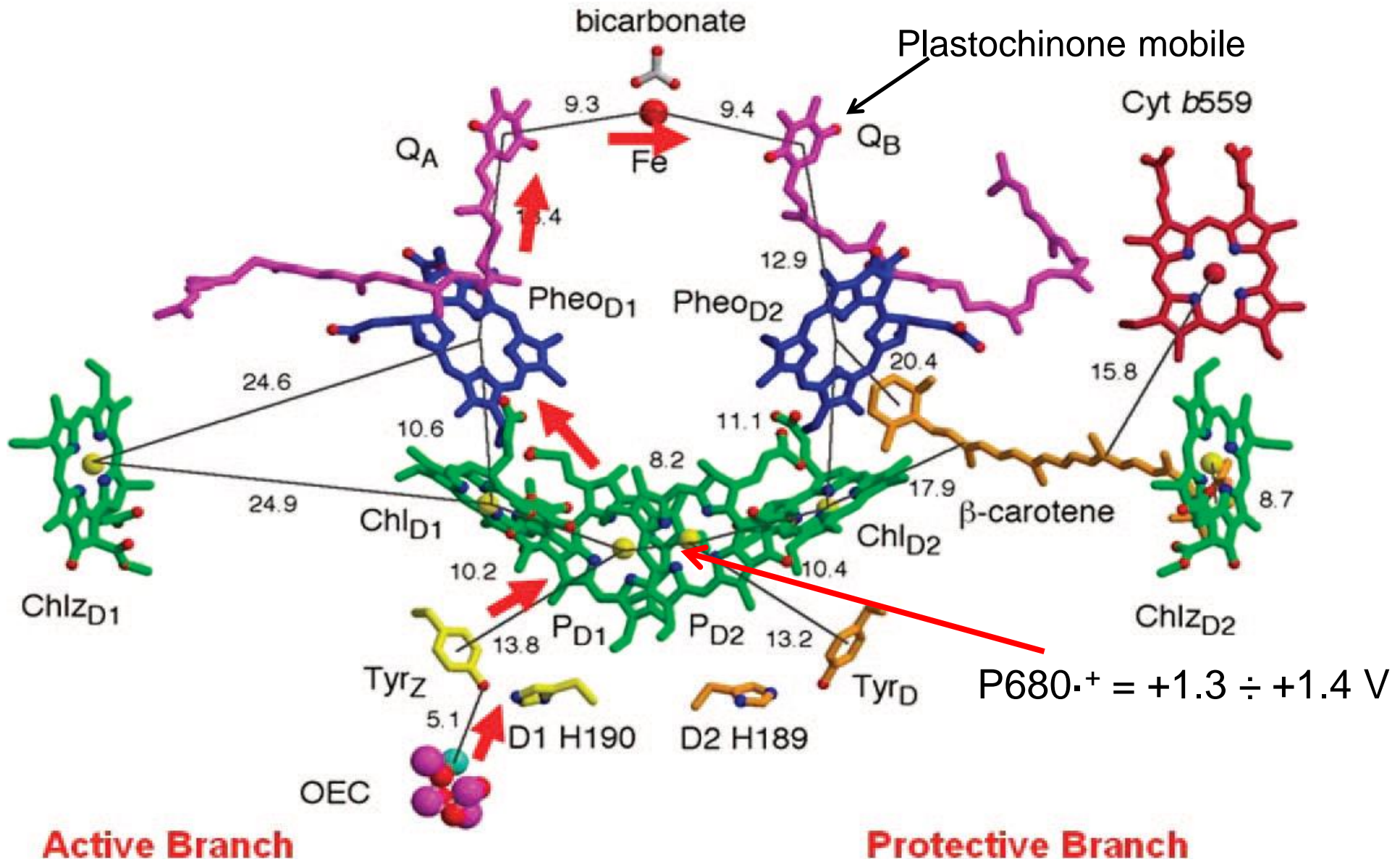








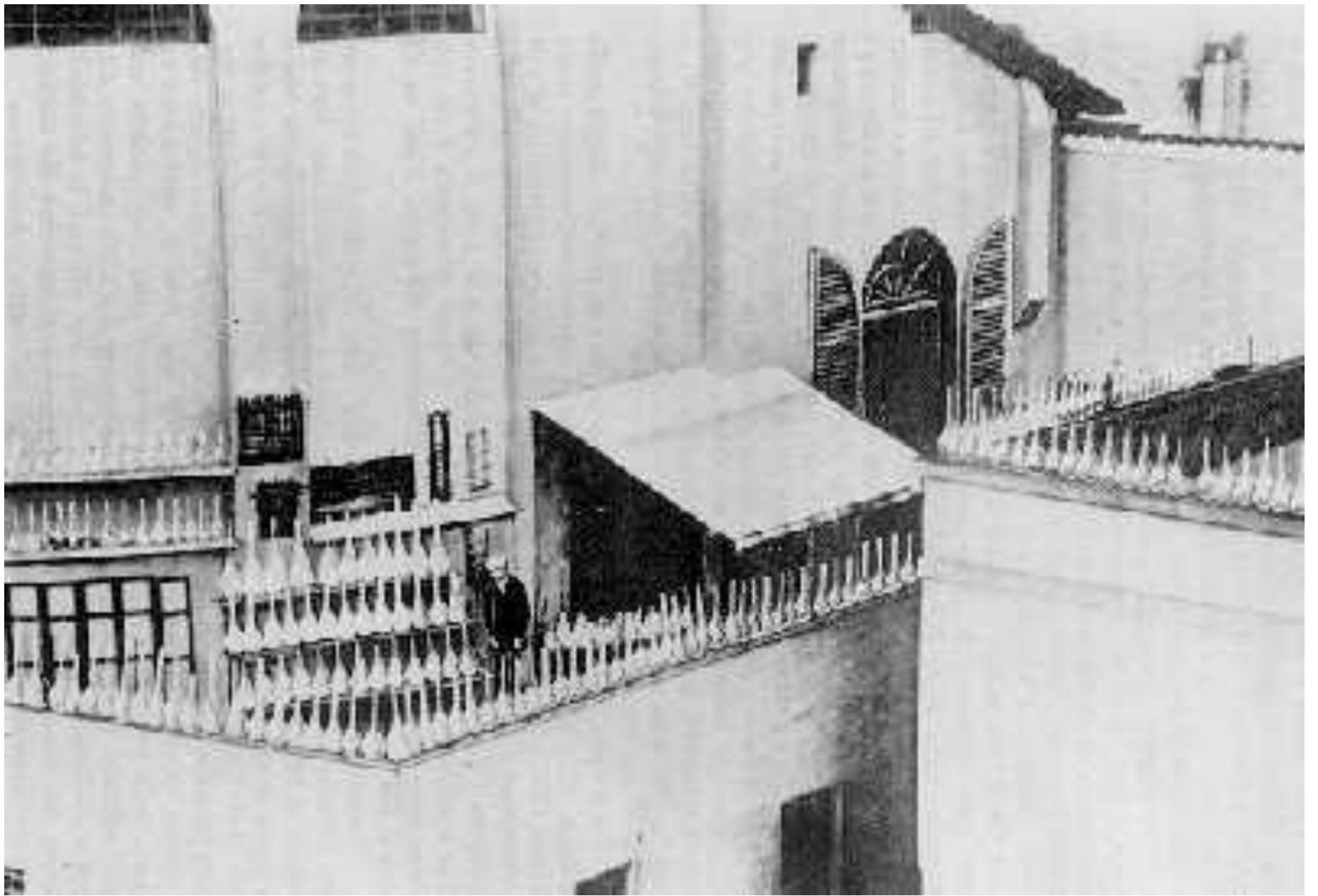
Electron transport cofactors



Giacomo Luigi Ciamician
Trieste, 1857 – Bologna, 1922



G. Ciamician



SCIENCE

FRIDAY, SEPTEMBER 27, 1912

CONTENTS

| | |
|---|-----|
| <i>The Photochemistry of the Future: PROFESSOR GIACOMO CIAMICIAN</i> | 385 |
| <i>The First International Eugenics Congress: PROFESSOR RAYMOND PEARL</i> | 395 |
| <i>Industrial Education in the Philippines</i> | 396 |
| <i>Graduates from American Colleges and Universities</i> | 397 |
| <i>The Harpswell Laboratory</i> | 397 |
| <i>Scientific Notes and News</i> | 398 |
| <i>University and Educational News</i> | 400 |
| <i>Discussion and Correspondence:—</i> | |
| <i>The Policy of the Geological Survey: DR. GEO. OTIS SMITH. School Grades—to What Type of Distribution shall they conform? DR. A. P. WEISS</i> | 401 |
| <i>Scientific Books:—</i> | |
| <i>Colman on Nature's Harmonic Unity: PROFESSOR ARNOLD EMCH. Case's Revision of the Amphibia and Pisces of the Permian of North America: DR. MAURICE G. MEHL</i> | 407 |
| <i>Notes on Infectious Abortion in Cattle: DR. FRANK M. SURFACE</i> | 409 |
| <i>Special Articles:—</i> | |
| <i>The Effects of Alkaloids on the Development of Fish (Fundulus) Embryos: DR. J. F. MCCLENDON. On the Relationship between the Bilateral Asymmetry of the Unilocular Fruit and the Weight of the Seed which it produces: DR. J. ARTHUR HARRIS. Heat Conductivity of Crystals: DR. R. W. CLARK. Some Curious Cases of Selective Reflection in Ultra-violet Light: GUSTAVE MICHAUD</i> | 412 |

MSB. 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 FUTURE¹

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)

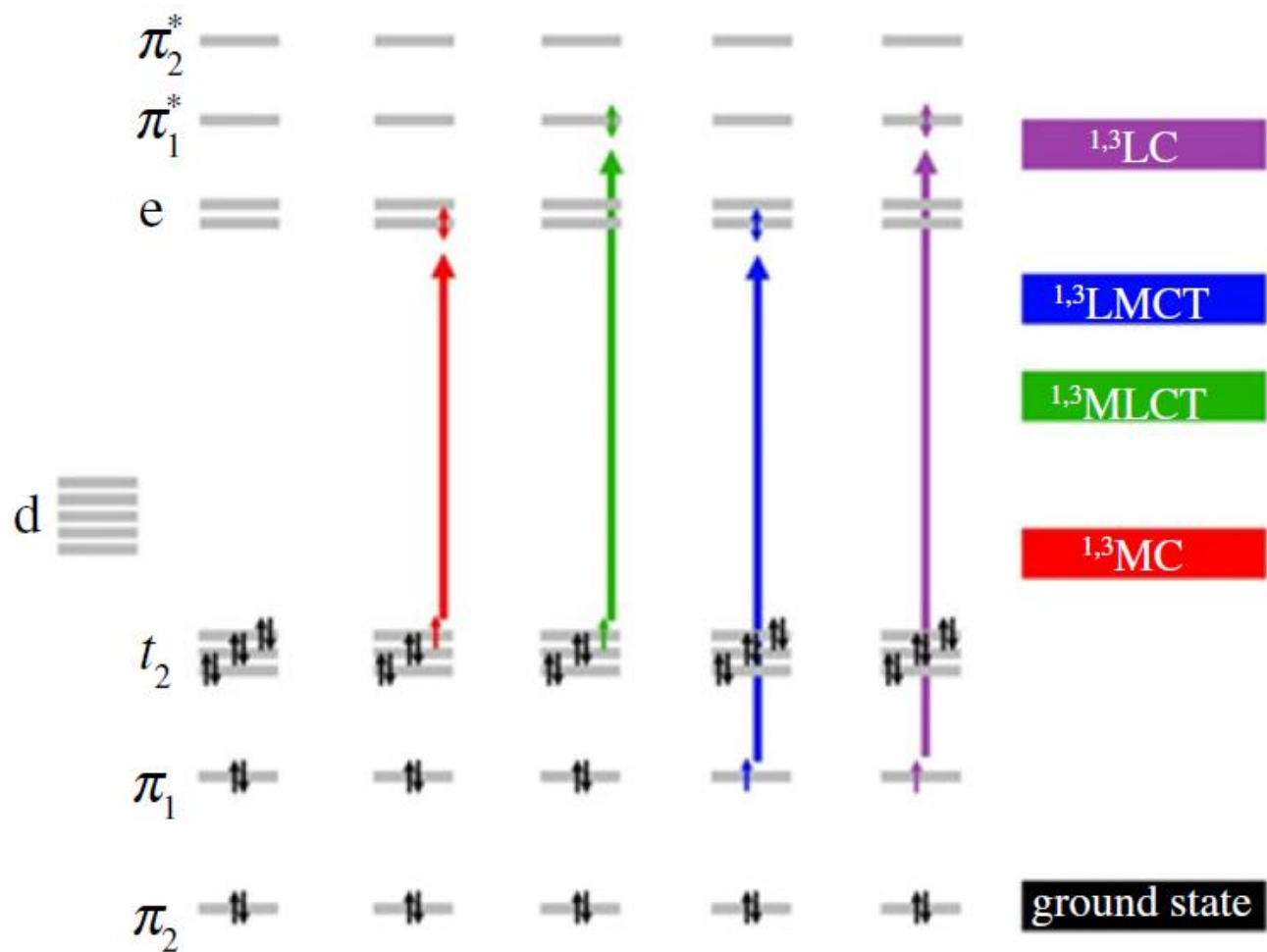
GIACOMO CIAMICIAN (1857-1922)

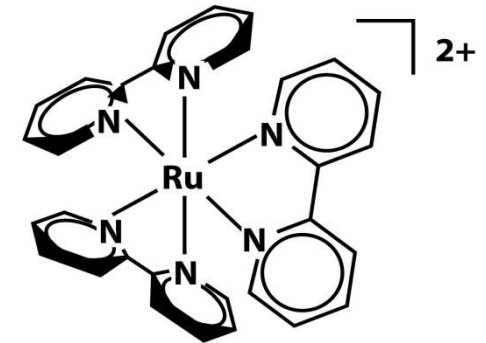
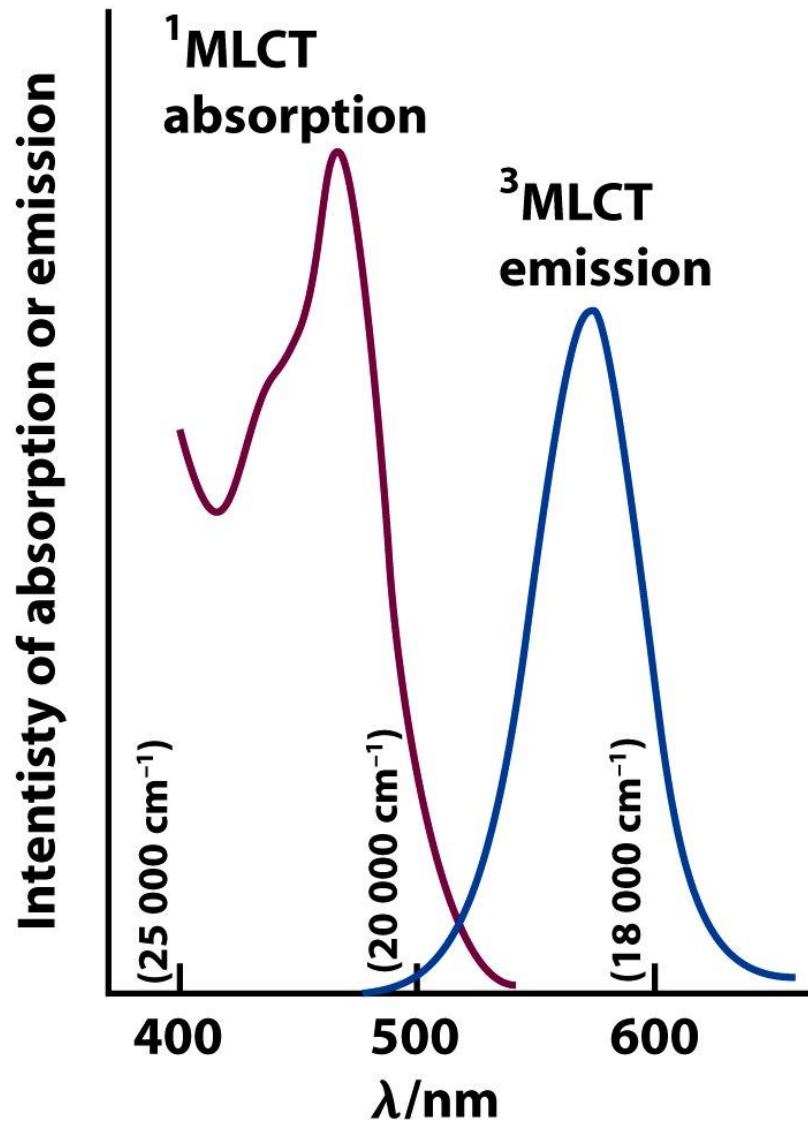
(Translation supplied by the author)

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

