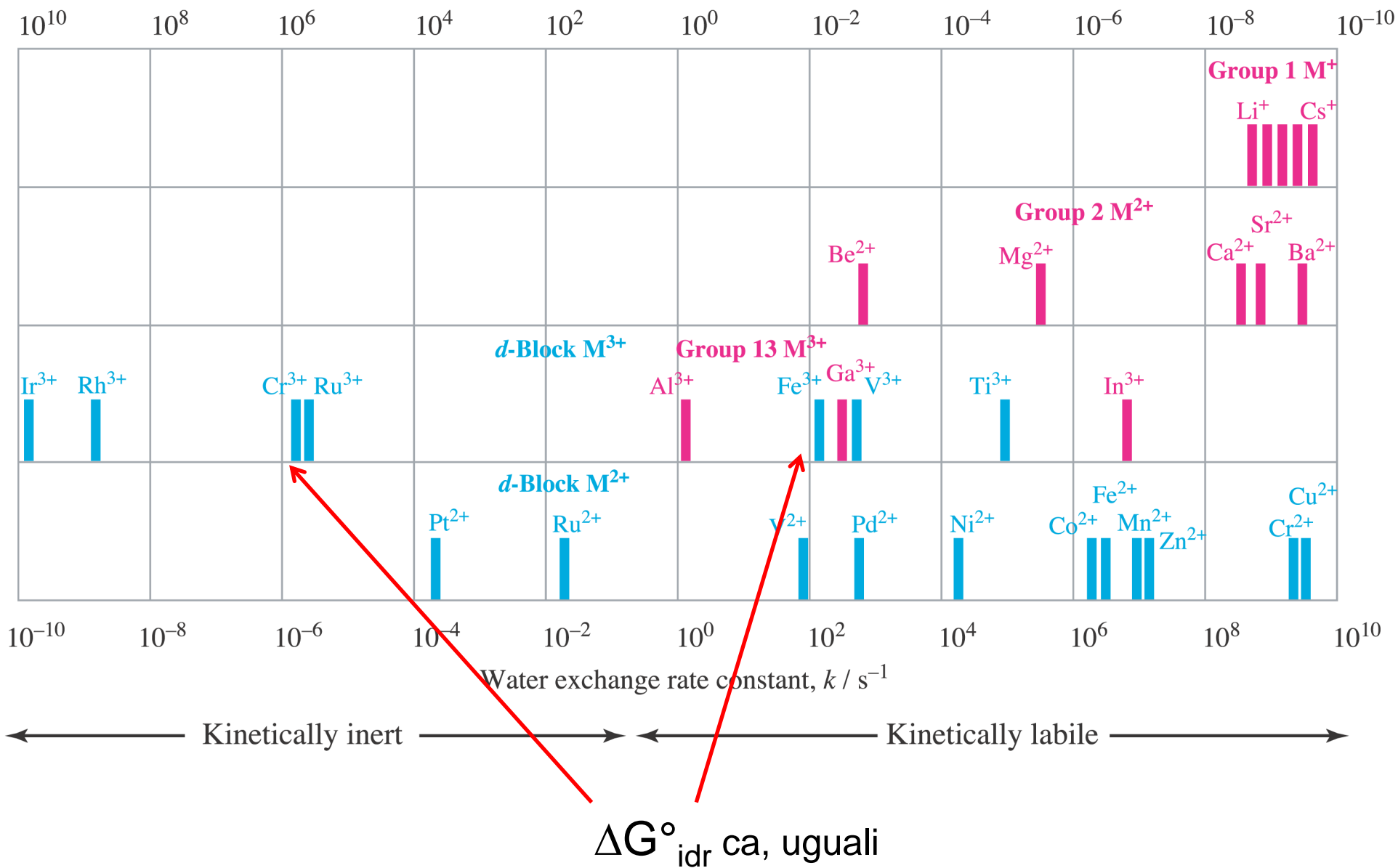
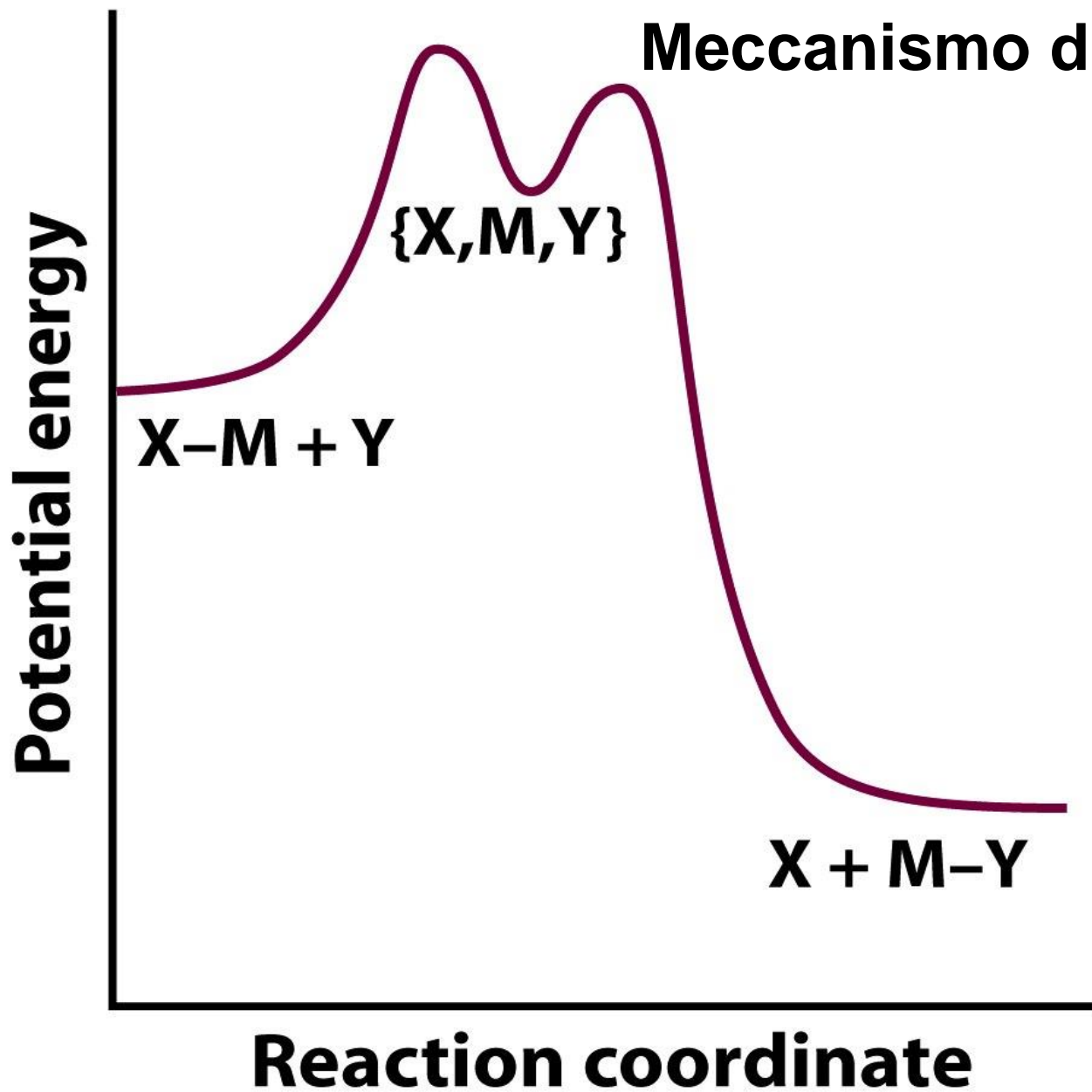
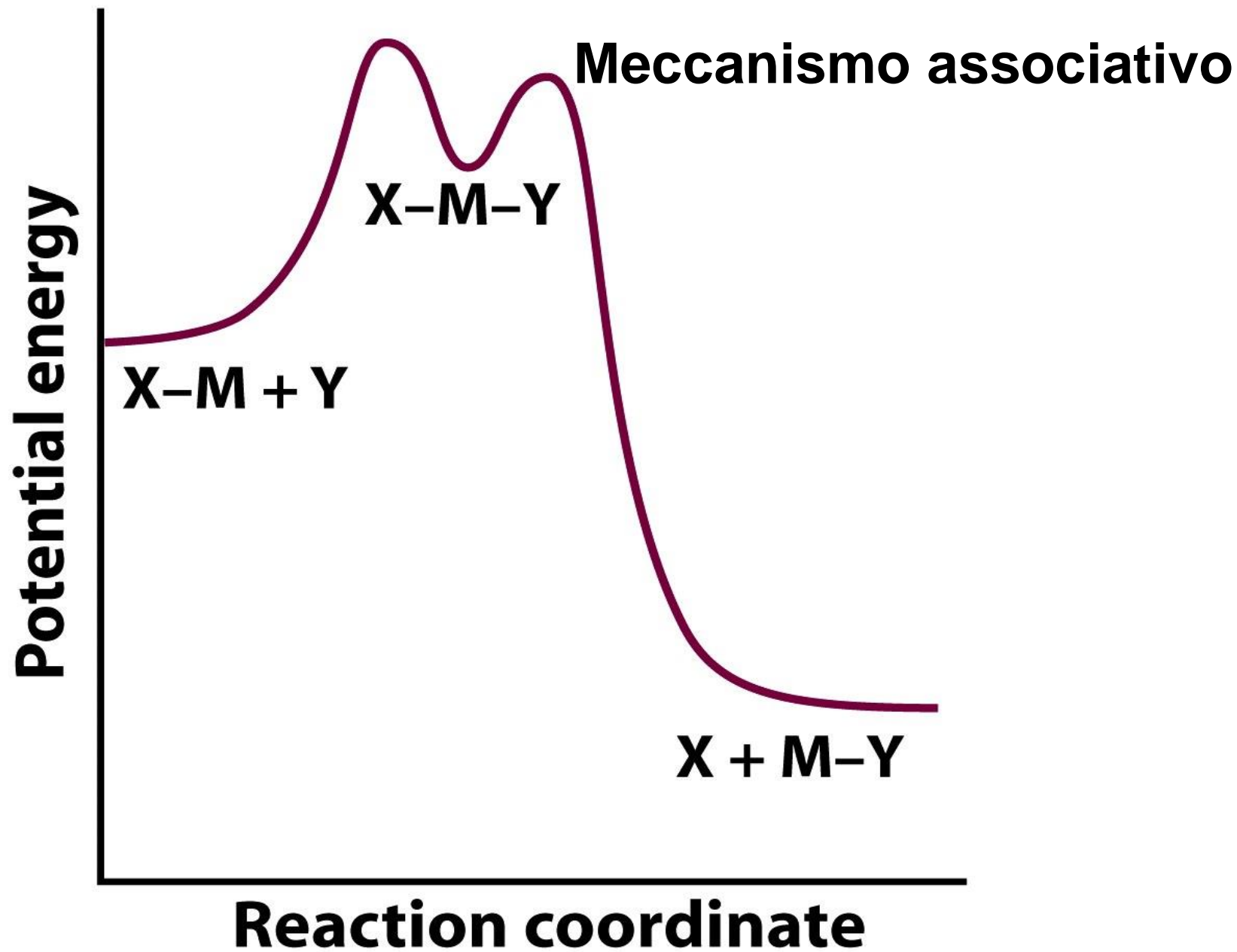


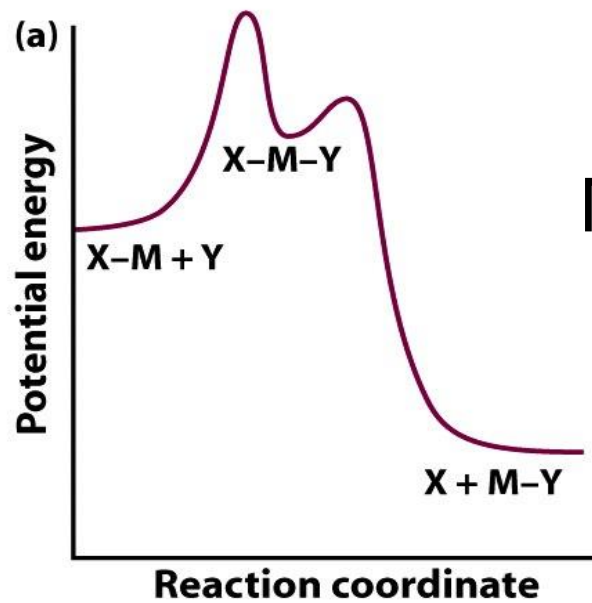
Average residence time for H₂O molecule in first hydration shell / s



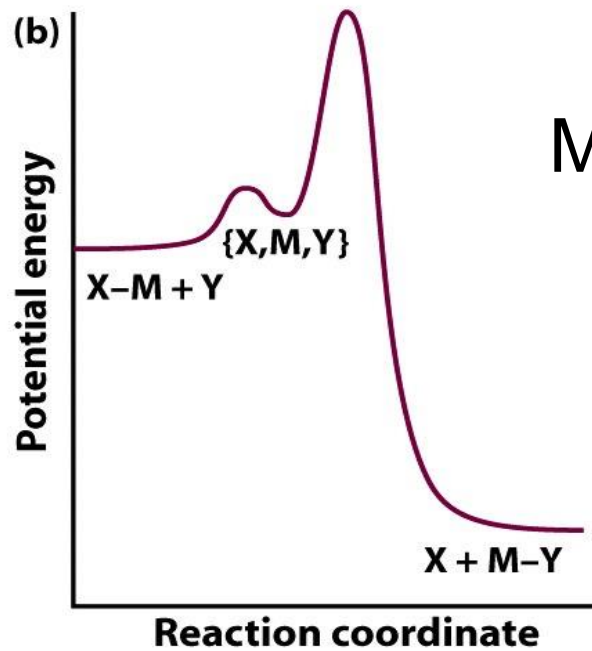
Meccanismo dissociativo



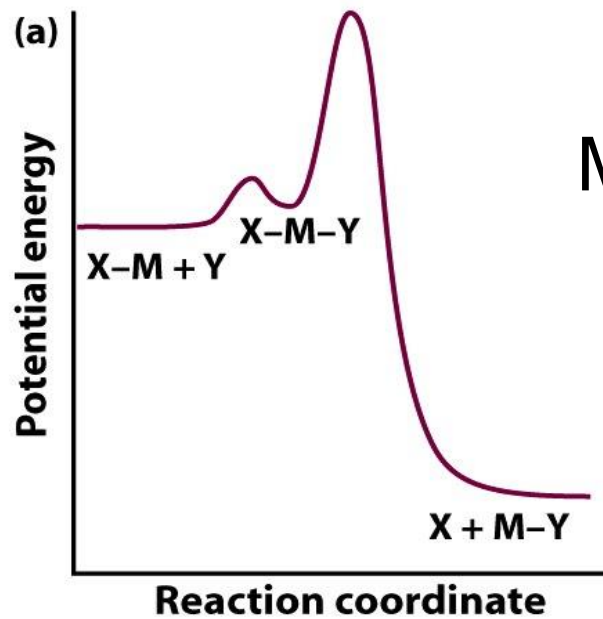




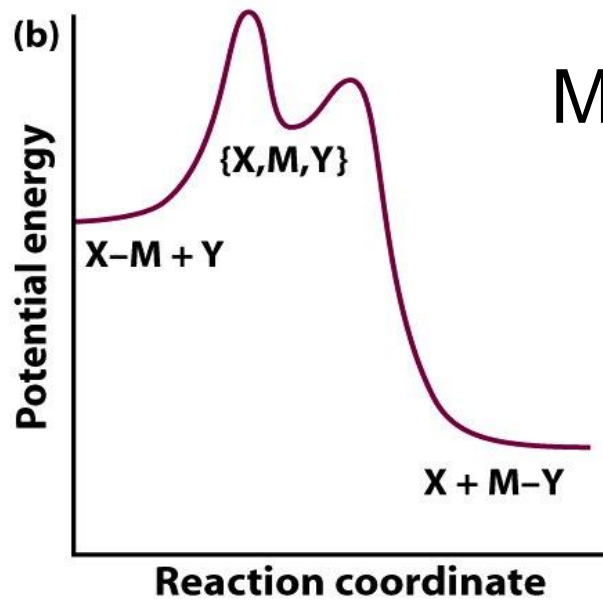
Meccanismo associativo
stadio lento associativo



Meccanismo dissociativo
stadio lento associativo



Meccanismo associativo
stadio lento dissociativo



Meccanismo dissociativo
stadio lento dissociativo

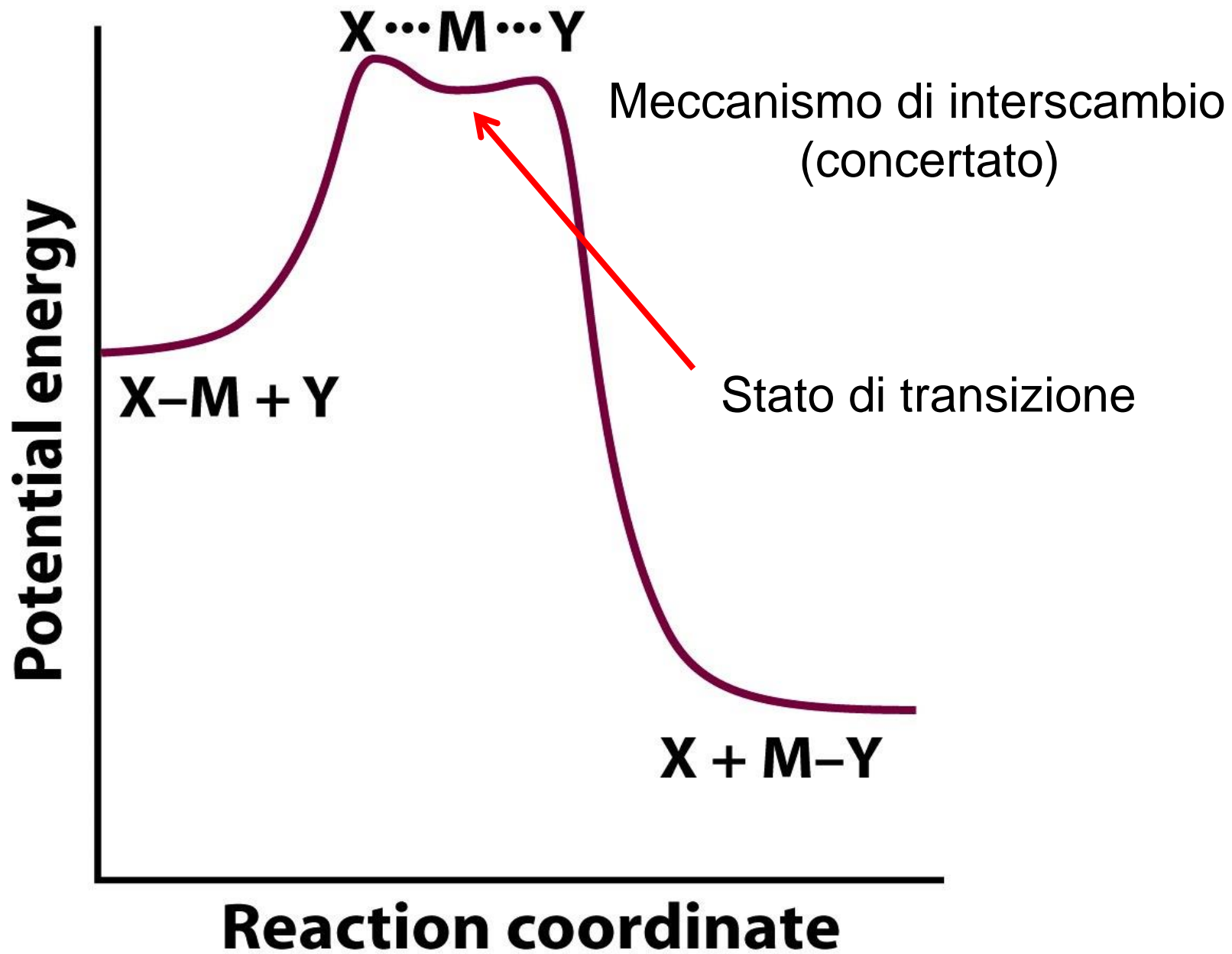
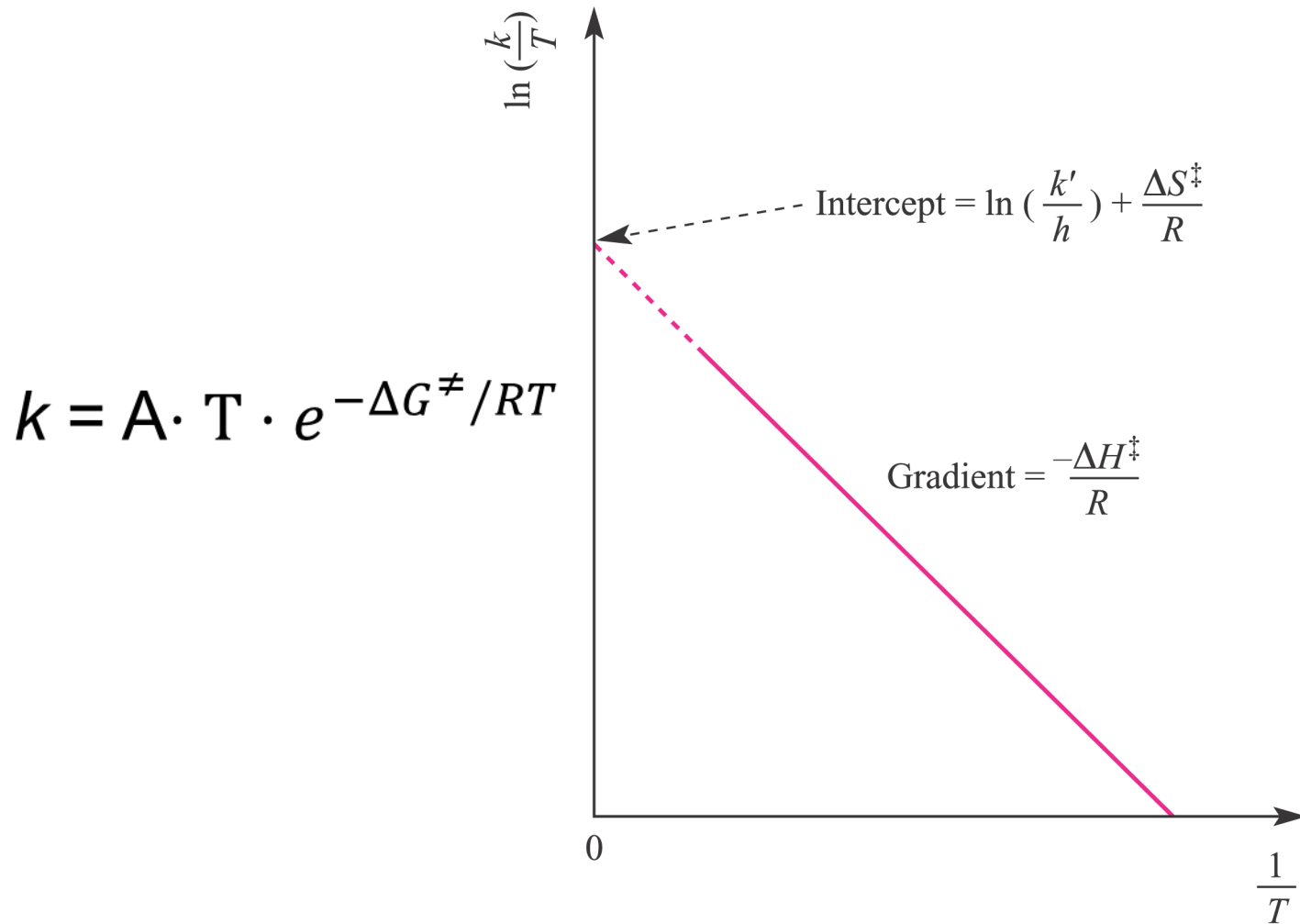


Diagramma di Eyring e parametri di attivazione



$$k = A \cdot T \cdot e^{-\Delta G^\ddagger / RT}$$

$$\ln(k/T) = \ln A - \Delta H^\ddagger / RT + \Delta S^\ddagger / R$$

Se ΔS^\ddagger è ampiamente negativo \rightarrow
meccanismo associativo

$$\frac{d(\ln k)/dP}{\Delta V^\ddagger} = - \Delta V^\ddagger / RT$$

ΔV^\ddagger = volume di attivazione

$\Delta V^\ddagger \ll 0 \rightarrow$ meccanismo associativo

$\Delta V^\ddagger \gg 0 \rightarrow$ meccanismo dissociativo

Sostituzioni su complessi planari quadrati

Reactants	$\Delta H^\ddagger / \text{kJ mol}^{-1}$	$\Delta S^\ddagger / \text{J K}^{-1} \text{mol}^{-1}$	$\Delta V^\ddagger / \text{cm}^3 \text{mol}^{-1}$
$[\text{Pt}(\text{dien})\text{Cl}]^+ + \text{H}_2\text{O}$	+84	-63	-10
$[\text{Pt}(\text{dien})\text{Cl}]^+ + [\text{N}_3]^-$	+65	-71	-8.5
<i>trans</i> - $[\text{PtCl}_2(\text{PEt}_3)_2] + \text{py}$	+14	-25	-14
<i>trans</i> - $[\text{PtCl}(\text{NO}_2)(\text{py})_2] + \text{py}$	+12	-24	-9

Meccanismo di tipo A o I_a

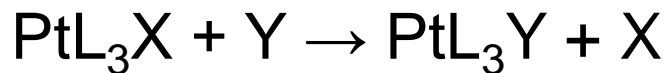
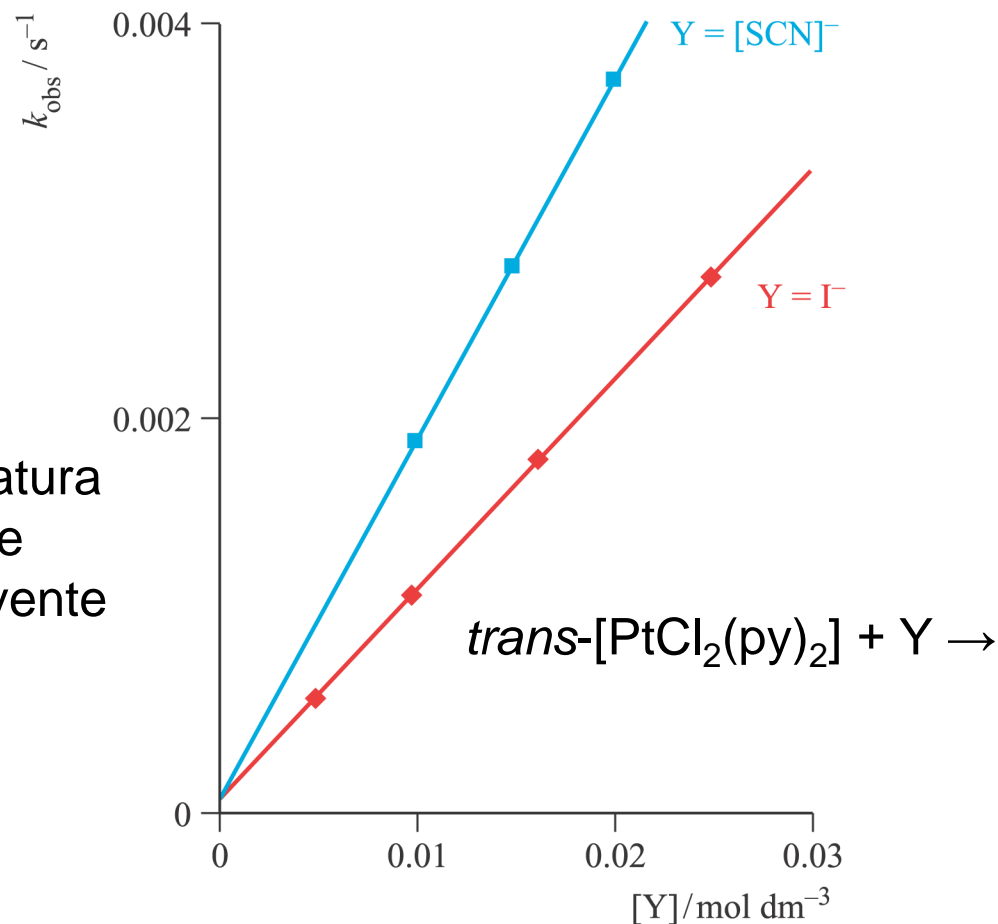
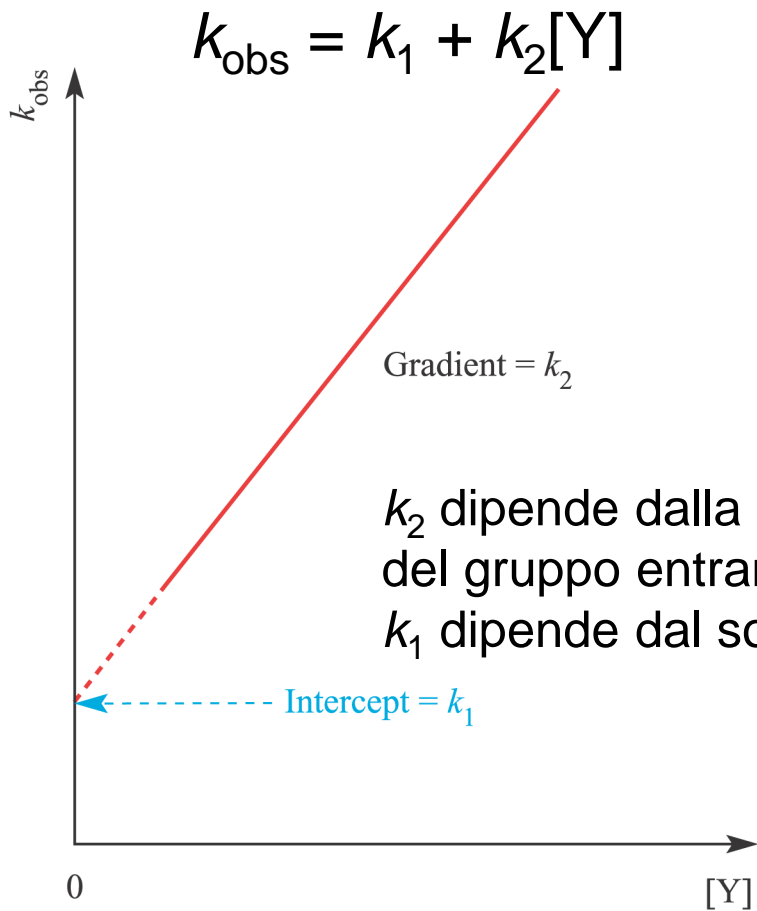
Le costanti cinetiche per la sostituzione di Cl^- con H_2O in



sono tutte molto simili



Meccanismo di tipo associativo



equazione cinetica sperimentale

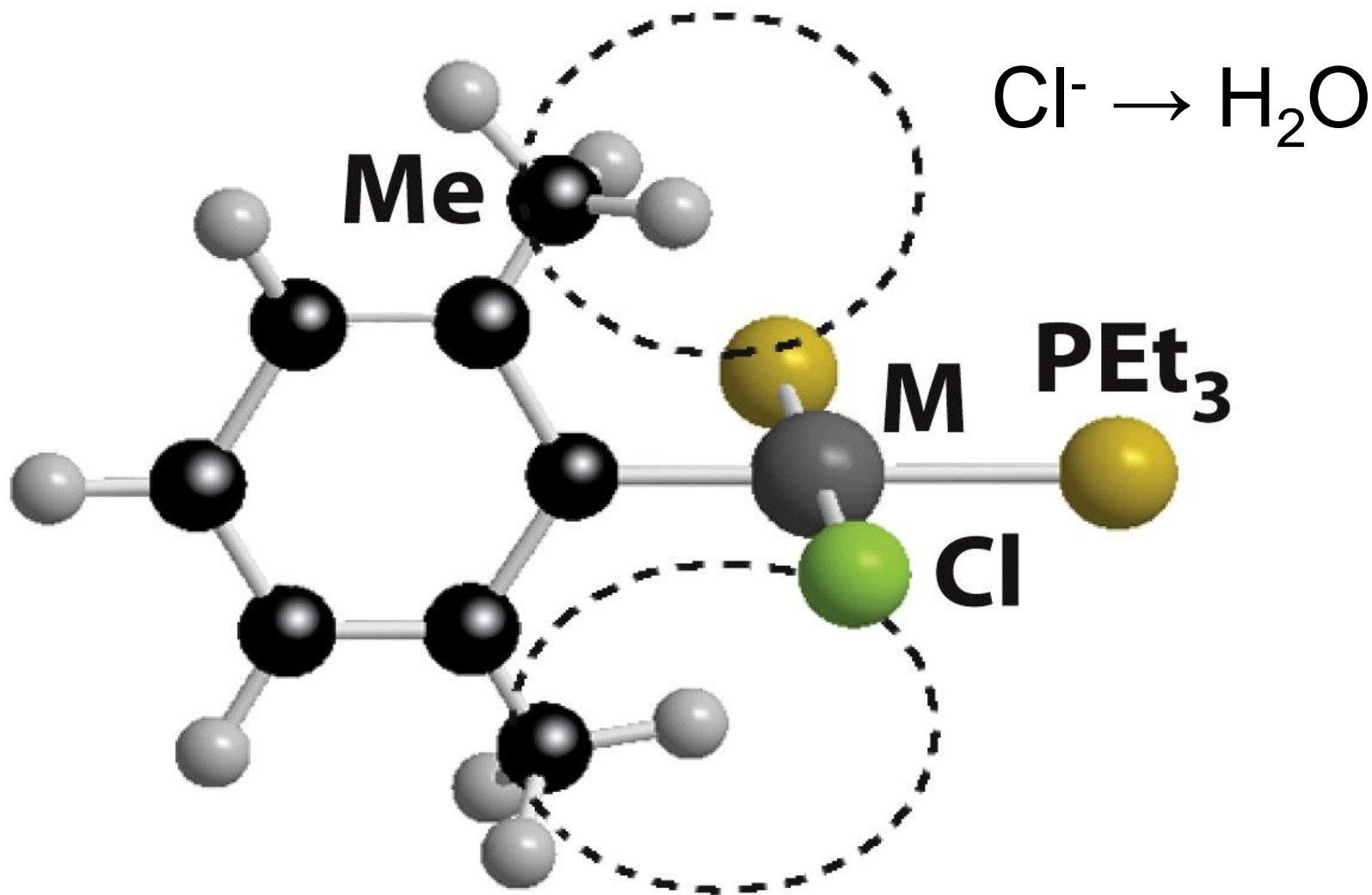
$$v = -\frac{d[\text{PtL}_3\text{X}]}{dt} = k_1[\text{PtL}_3\text{X}] + k_2[\text{PtL}_3\text{X}][\text{Y}] = k_{\text{obs}}[\text{PtL}_3\text{X}]$$

(in condizioni di pseudo primo ordine)

$$v = -d[\text{PtL}_3\text{X}]/dt = k_3[\text{PtL}_3\text{X}][\text{S}] + k_2[\text{PtL}_3\text{X}][\text{Y}]$$

$$k_1 = k_3[\text{S}]$$

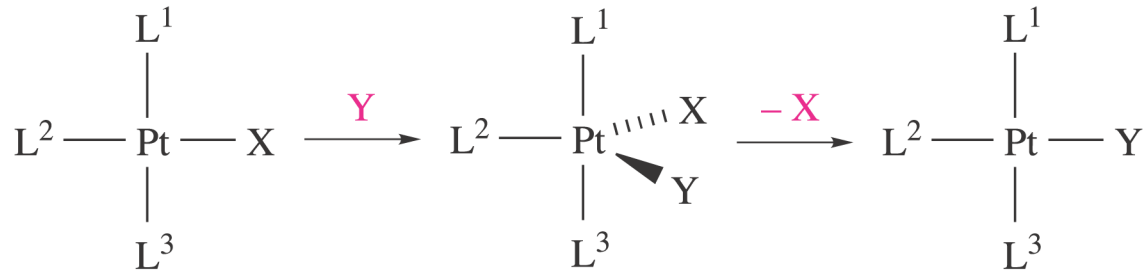
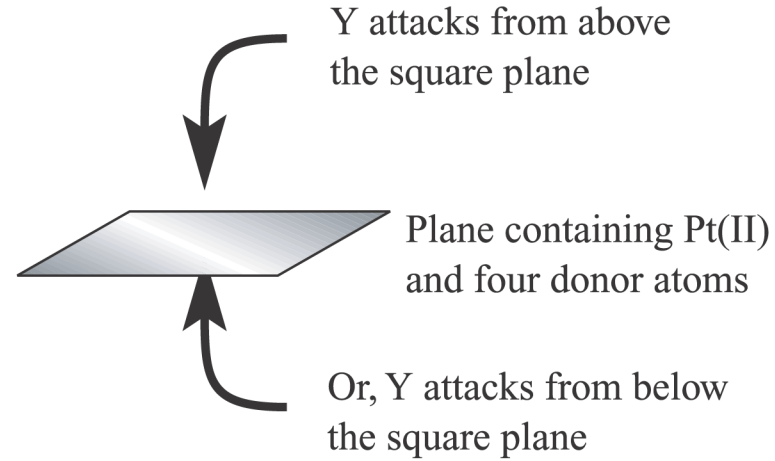
k_1 e k_2 diminuiscono al crescere dell'ingombro sterico sia di Y che di L



$k = 8 \times 10^{-2} \text{ s}^{-1}$ per L = py

$k = 1.0 \times 10^{-6} \text{ s}^{-1}$ per L = 2,6-dimetilpiridina

Ritenzione di configurazione



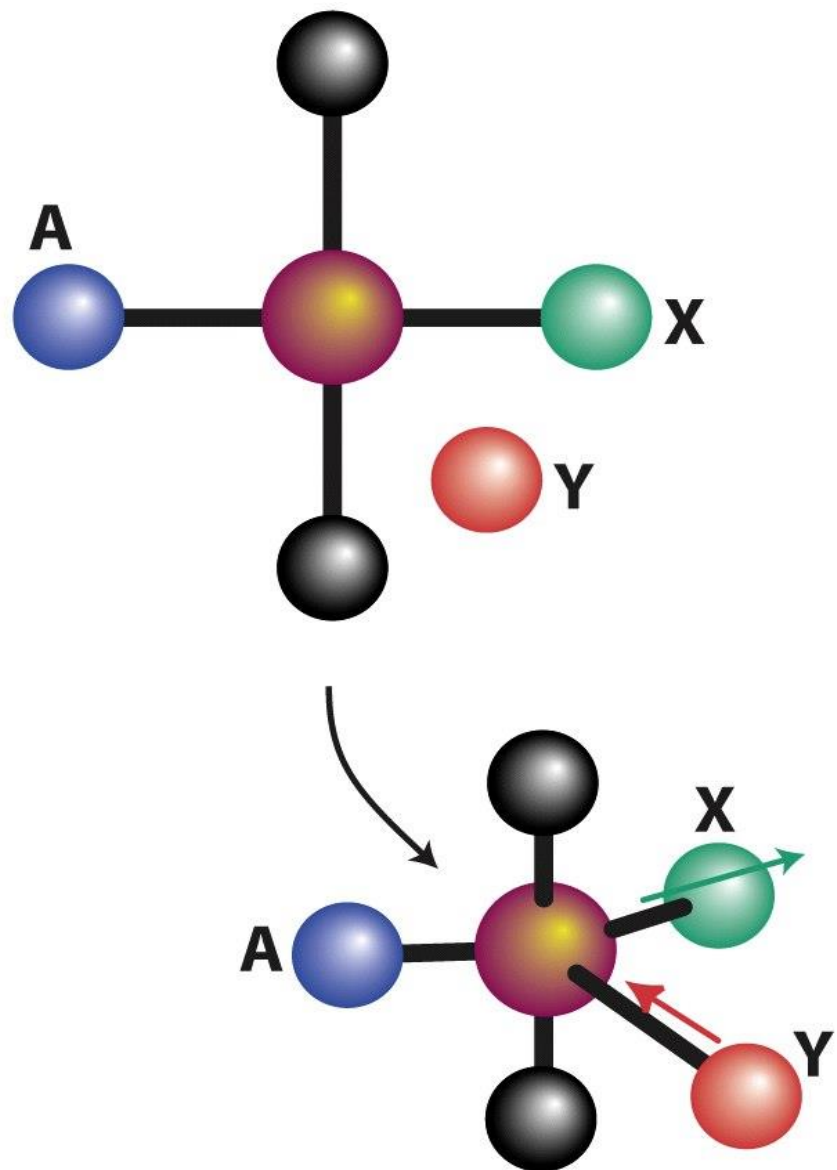
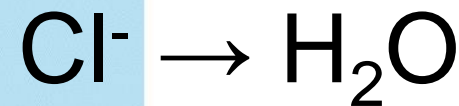


Table 20.6 The effect of the *trans* ligand in reactions of *trans*-[PtCl(PEt₃)₂L]

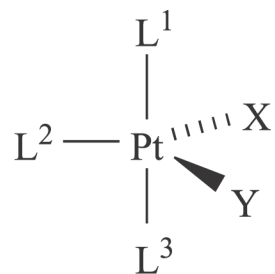


L	k_1/s^{-1}	$k_2/(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$
CH ₃ ⁻	1.7×10^{-4}	6.7×10^{-2}
C ₆ H ₅ ⁻	3.3×10^{-5}	1.6×10^{-2}
Cl ⁻	1.0×10^{-6}	4.0×10^{-4}
H ⁻	1.8×10^{-2}	4.2
PEt ₃	1.7×10^{-2}	3.8

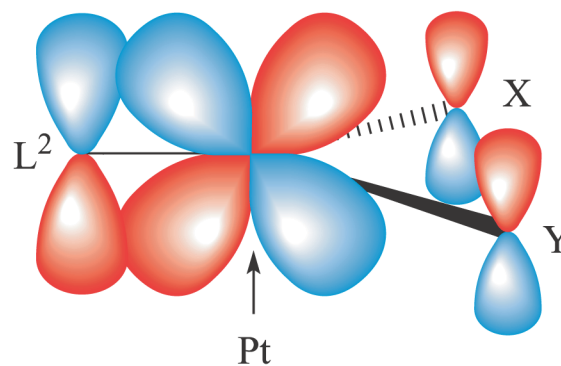
H₂O ≈ OH⁻ ≈ NH₃ ≈ py < Cl⁻ < Br⁻ < I⁻ ≈ NO₂⁻ < Ph⁻ < Me⁻ < PR₃ ≈ H⁻ « CO ≈ CN⁻

Sequenza di effetto trans

Effetto-*trans*: contributo cinetico

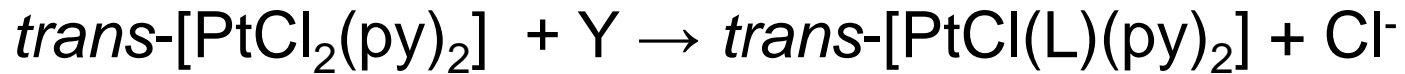


Trigonal bipyramidal
transition state or
intermediate



π -Bonding in the trigonal plane

Sequenza di nucleofilicità del gruppo entrante

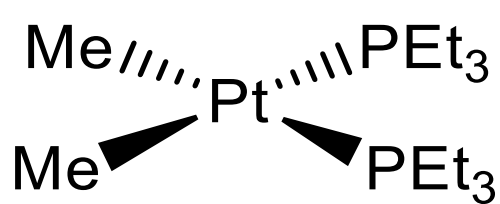


Nucleophile	Donor atom	n_{Pt}
Cl^-	Cl	3.04
I^-	I	5.42
CN^-	C	7.00
CH_3OH	O	0
$\text{C}_6\text{H}_5\text{SH}$	S	4.15
NH_3	N	3.06
$(\text{C}_6\text{H}_5)_3\text{P}$	P	8.79

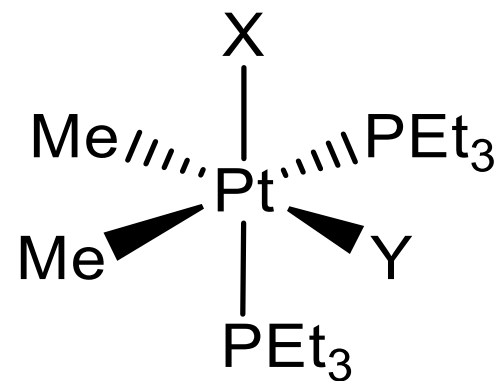
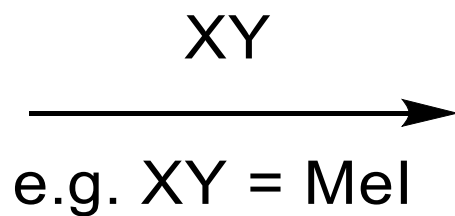
parametro di nucleofilicità: $n_{\text{Pt}} = \log k_2/k'_2(\text{MeOH})$

n_{Pt} non correla con la basicità di Brønsted di Y

Addizione ossidativa

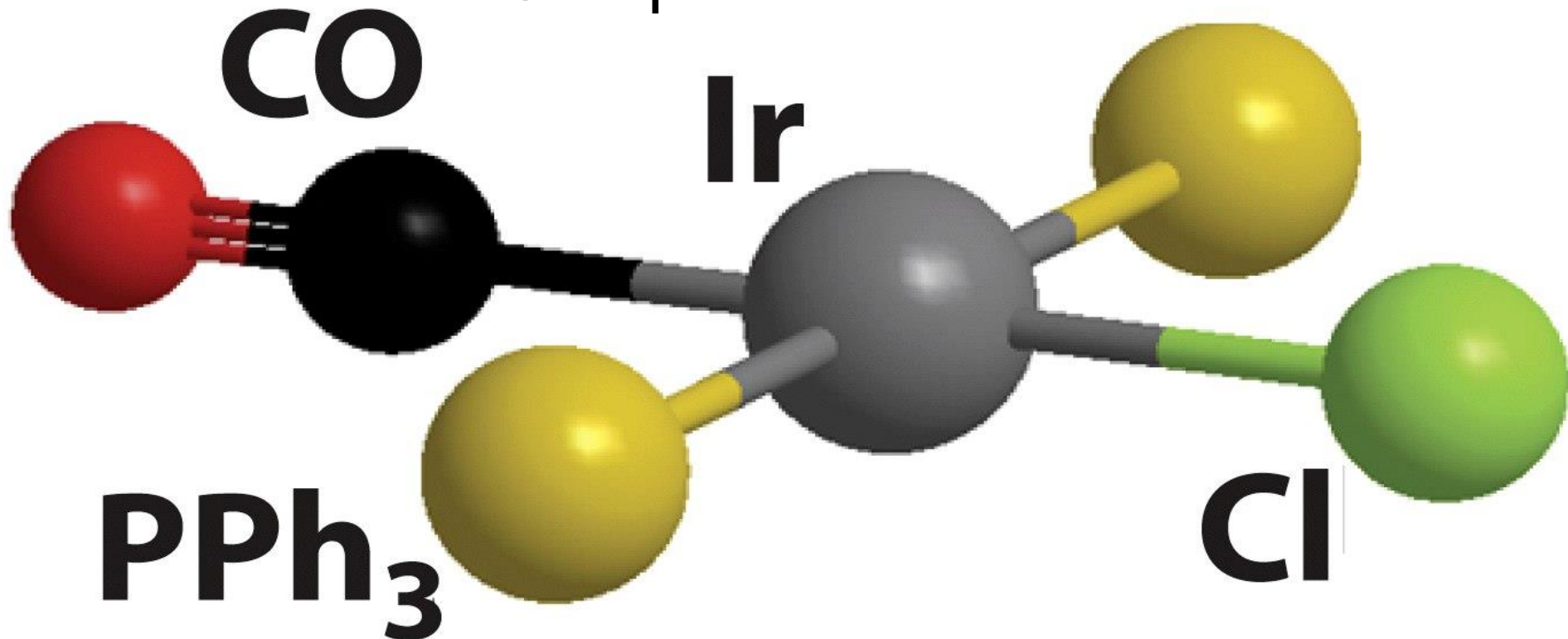


16e Pt(II)

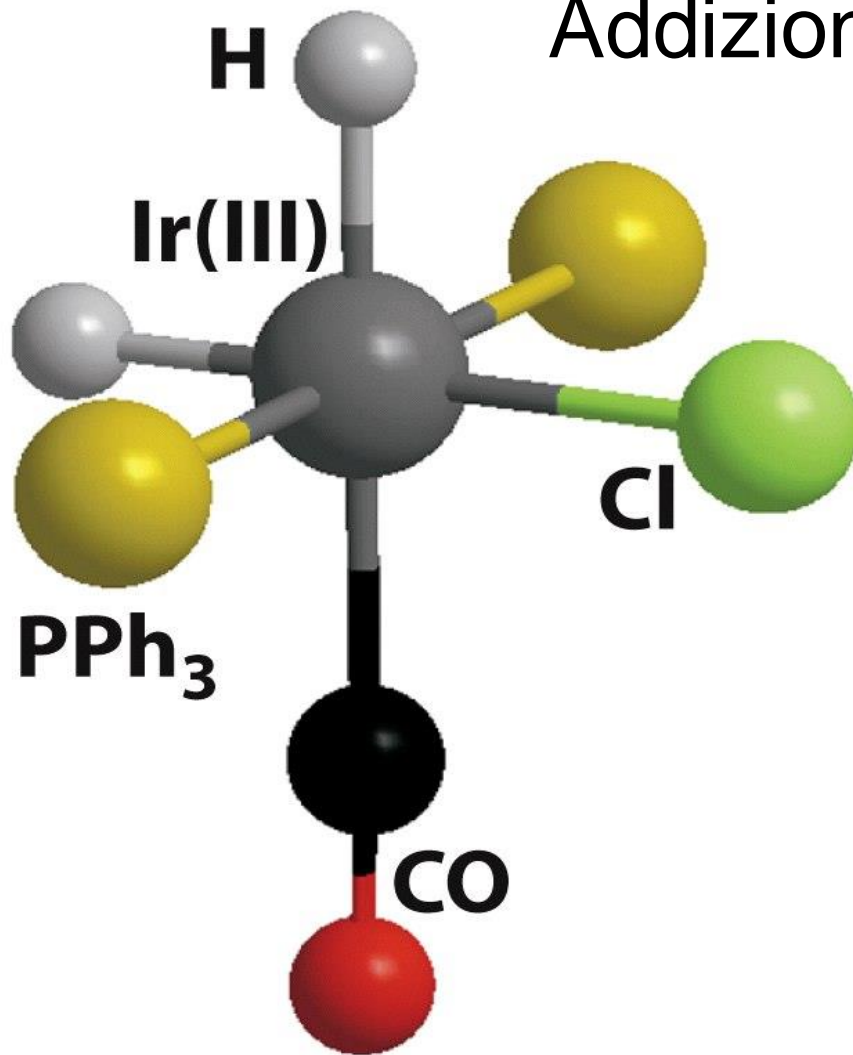


18e Pt(IV)

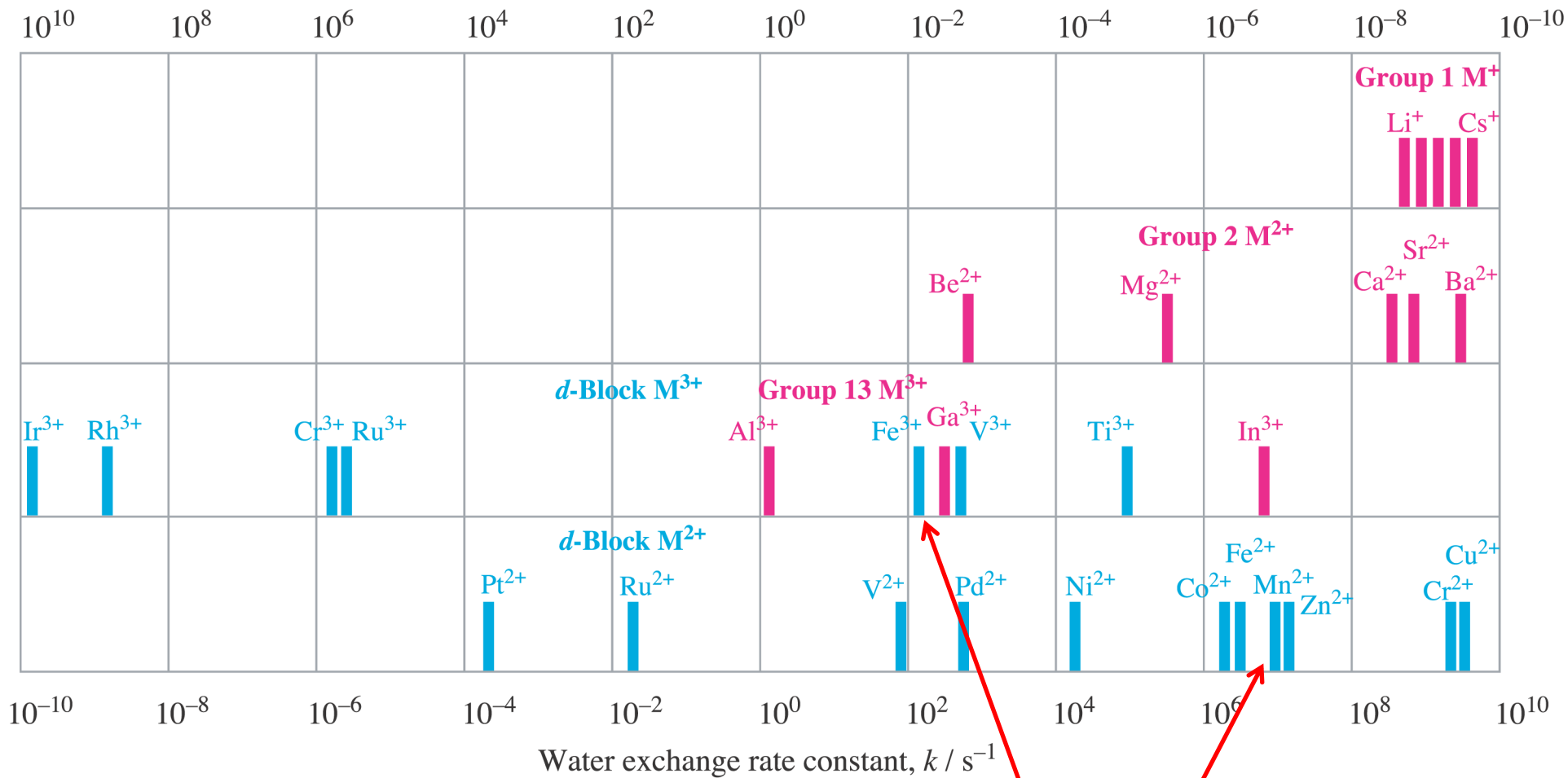
Complesso di Vaska



Addizione ossidativa



Average residence time for H₂O molecule in first hydration shell / s

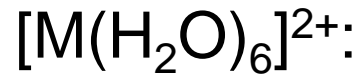


Kinetically inert

Kinetically labile

d⁵ h.s.

Ordine di velocità osservato per lo scambio di H₂O in



Variazioni di LFSE nel passaggio da ottaedro allo stato di transizione

Metal ion (high-spin)	d^n	$\Delta CFSE / \Delta_{oct}$	
		Square-based pyramidal	Pentagonal bipyramidal
Sc ²⁺	d^1	+0.06	+0.13
Ti ²⁺	d^2	+0.11	+0.26
V ²⁺	d^3	-0.20	-0.43
Cr ²⁺	d^4	+0.31	-0.11
Mn ²⁺	d^5	0	0

Metal ion (high-spin)	d^n	$\Delta CFSE / \Delta_{oct}$	
		Square-based pyramidal	Pentagonal bipyramidal
Fe ²⁺	d^6	+0.06	+0.13
Co ²⁺	d^7	+0.11	+0.26
Ni ²⁺	d^8	-0.20	-0.43
Cu ²⁺	d^9	+0.31	-0.11
Zn ²⁺	d^{10}	0	0

Un Δ negativo implica una diminuzione di velocità

Meccanismo di Eigen - Wilkins

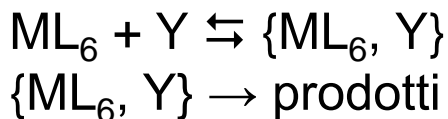
Table 20.8 Complex formation by the $[\text{Ni}(\text{OH}_2)_6]^{2+}$ ion $\text{ML}_6 + \text{Y} \rightarrow$ prodotti

Ligand	$k_{\text{obs}}/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	$K_E/(\text{dm}^3 \text{ mol}^{-1})$	$(k_{\text{obs}}/K_E)/\text{s}^{-1}$
CH_3CO_2^-	1×10^5	3	3×10^4
F^-	8×10^3	1	8×10^3
HF	3×10^3	0.15	2×10^4
H_2O^*			3×10^3
NH_3	5×10^3	0.15	3×10^4
$[\text{NH}_2(\text{CH}_2)_2\text{NH}_3]^+$	4×10^2	0.02	2×10^4
SCN^-	6×10^3	1	6×10^3

meccanismo associativo

meccanismo dissociativo

* The solvent is always in encounter with the ion so that K_E is undefined and all rates are inherently first-order.



pre-equilibrio veloce, **complesso di incontro**
r.d.s.

$$v = kK_E \frac{[\text{Y}][\text{M}]_{\text{tot}}}{1 + K_E[\text{Y}]}$$

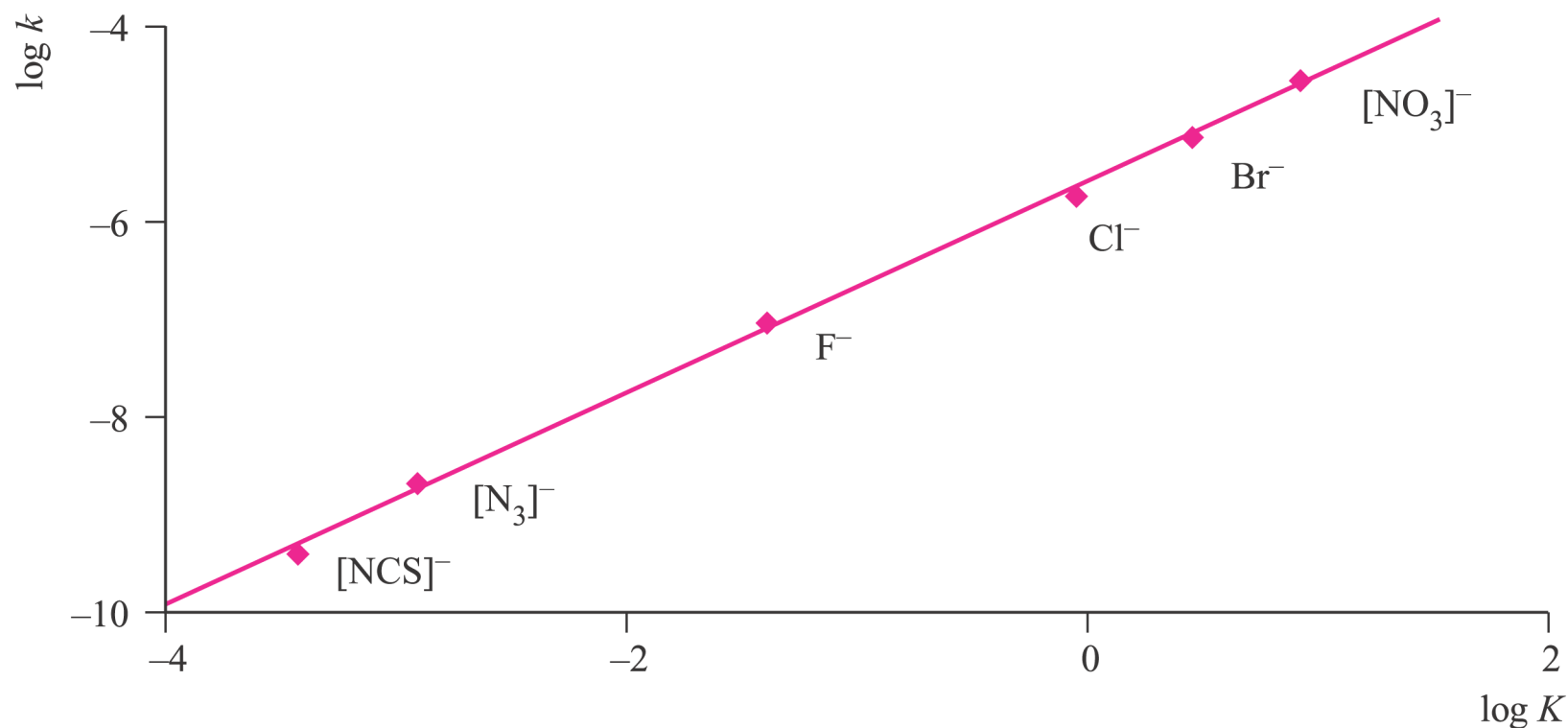
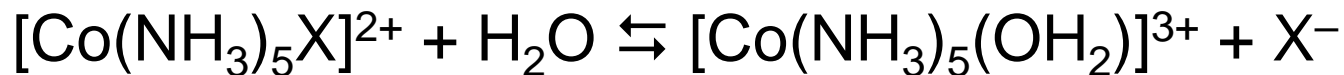
$$k_{\text{obs}} = kK_E$$



Entering ligand, Y	NH_3	py	$[\text{MeCO}_2]^-$	F^-	$[\text{SCN}]^-$
$k \times 10^{-4} / \text{s}^{-1}$	3	3	3	0.8	0.6

La velocità non dipende dalla natura del gruppo entrante → *meccanismo dissociativo*

Dipendenza della velocità di sostituzione dalla natura del **gruppo uscente**

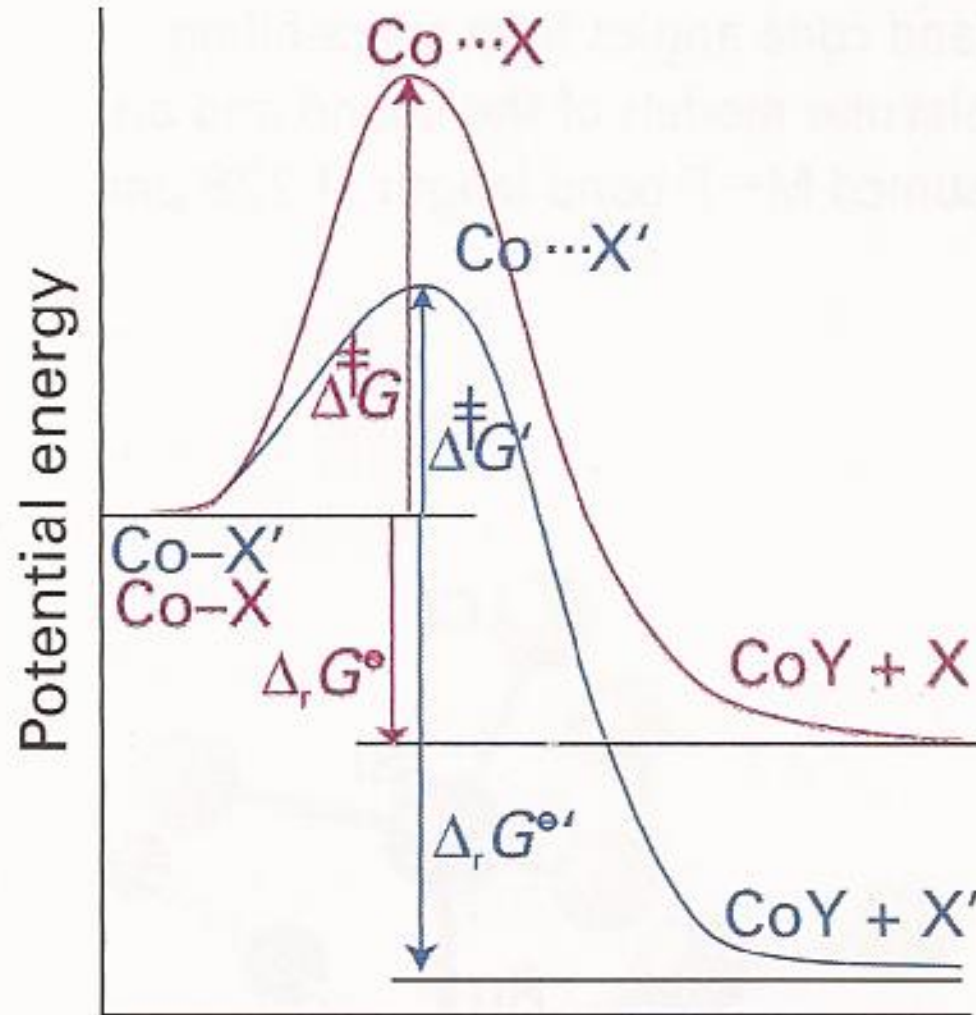


LFER: *Linear Free Energy Relation* (fra ΔG^\ddagger e ΔG°)

più il legame M-X è debole (cioè la K è grande) e più la sostituzione è veloce

LFER: *Linear Free Energy Relation*

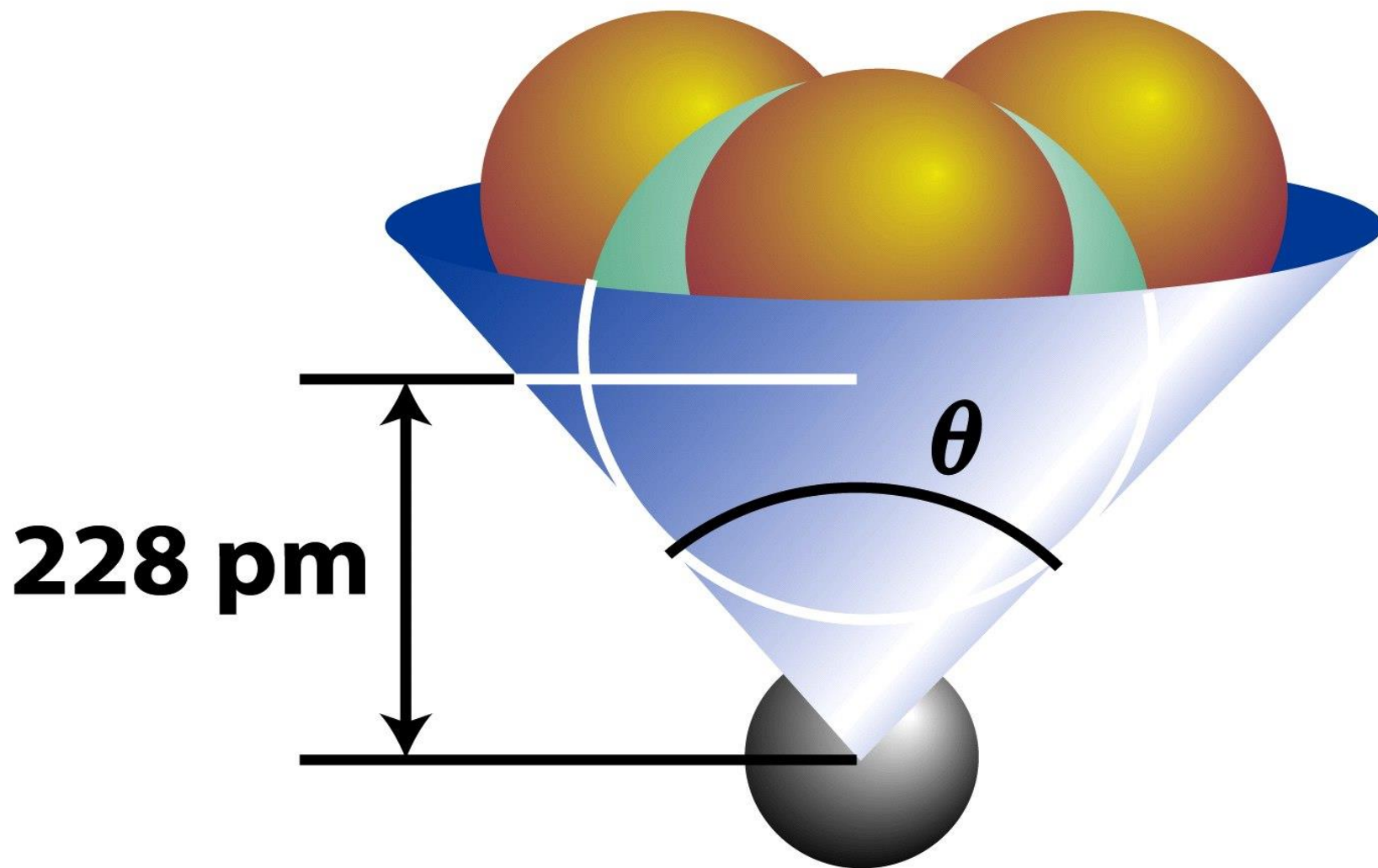
relazione lineare fra ΔG^\ddagger e ΔG° con pendenza praticamente unitaria



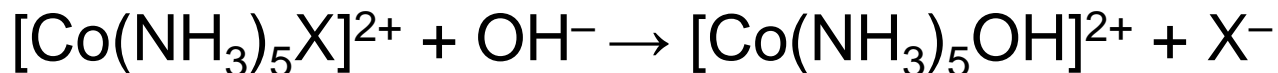
Reaction coordinate

lo stato di transizione è molto simile al prodotto

Angolo di cono di Tolman



Idrolisi catalizzata da base (S_N1cb)



$$v = k_{\text{obs}}[\text{Co}(\text{NH}_3)_5\text{X}^{2+}][\text{OH}^-]$$

Legge cinetica apparentemente di tipo associativo

