Reattività dei composti di coordinazione

- **Reazioni di sostituzione**

- **Reazioni di trasferimento elettronico (redox)**

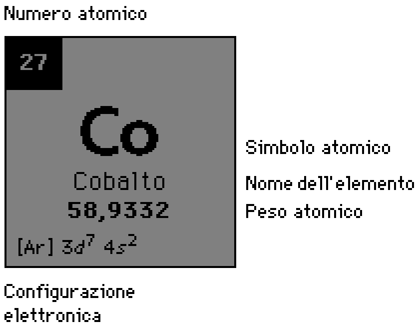
Substitution Reactions

$$\mathrm{MX + Y \rightleftharpoons MY + X}$$

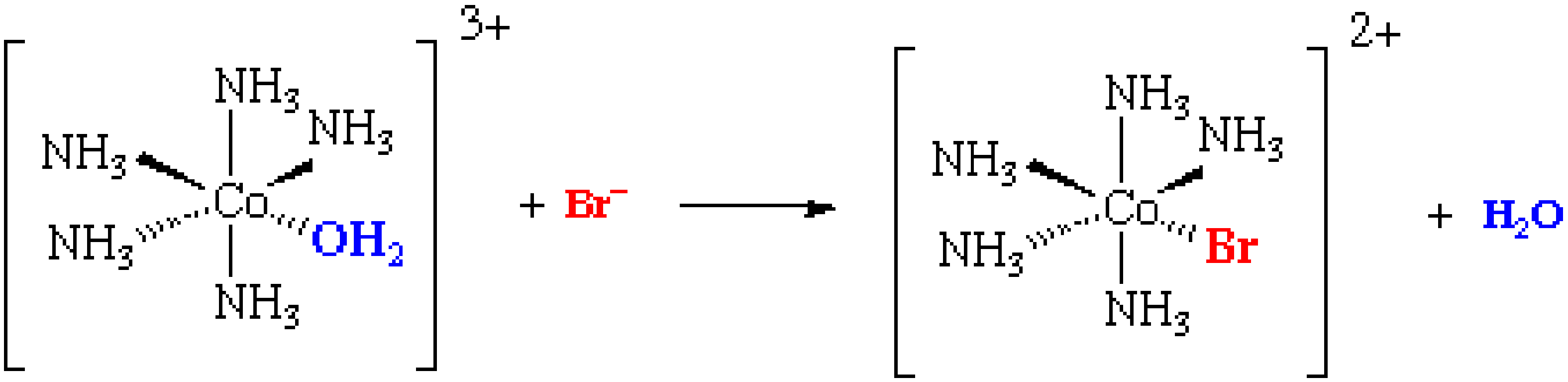
- X is leaving group and Y is entering group
- One example is the competition of a ligand, L for a coordination site with a solvent molecule such as H_2O

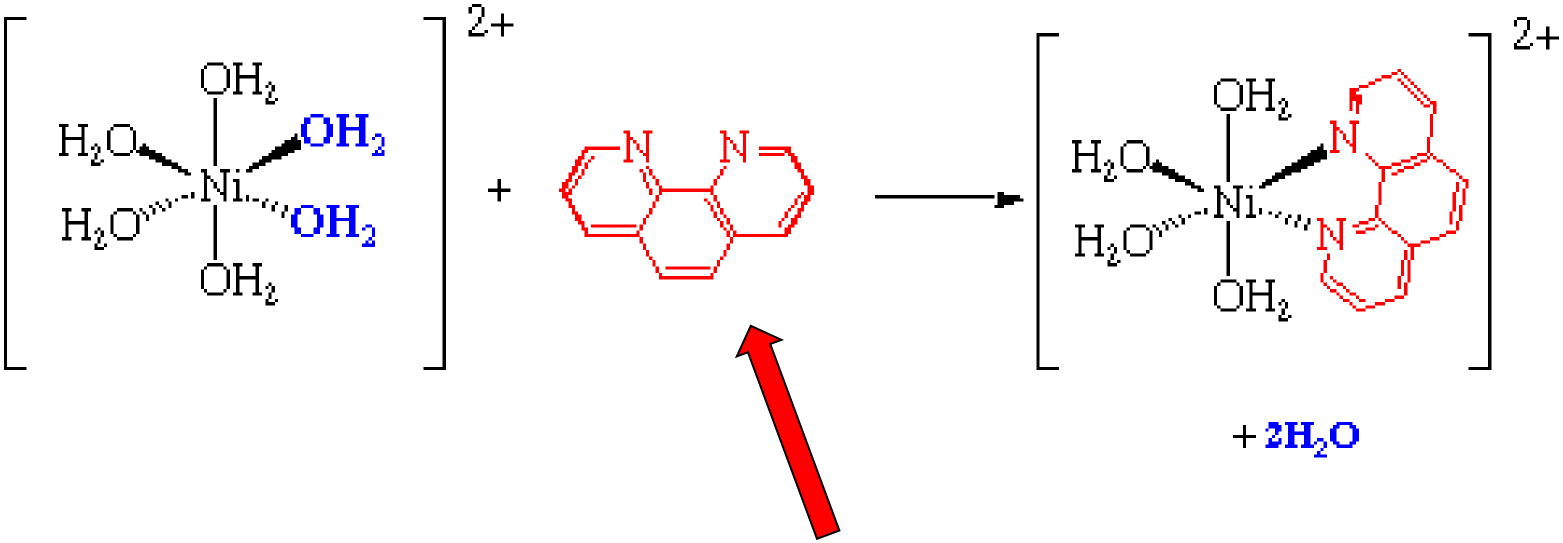
$$\mathrm{[Co(OH_2)_6]^{2+} + Cl^- \longrightarrow [Co(OH_2)_5Cl]^+ + H_2O}$$

- Three types of ligands can be important:
  - Entering Ligand: Y
  - Leaving Ligand: X
  - Spectator Ligand
    - Species that neither enters nor leaves



Some other example



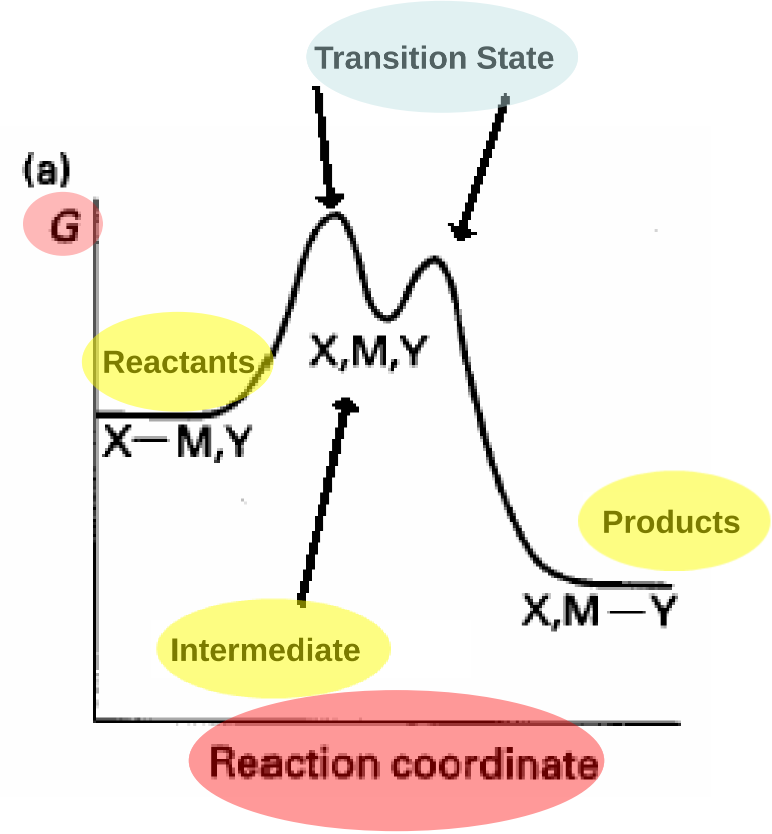


fenantrolina

Reaction mechanisms for substitution reactions

Free energy diagrams are often used to illustrate the course of a reaction. They show the relative energies of the reactants, products, intermediates and transition states as a function of the reaction coordinate

- The reaction coordinate is some variable that changes continuously during the reaction
  - It is used as a measure of how far the reaction between two species has progressed
  - It could be a real quantity like distance between two atoms, but very often its physical nature is not specified and it should be viewed as just an indicator of how far the reaction has progressed

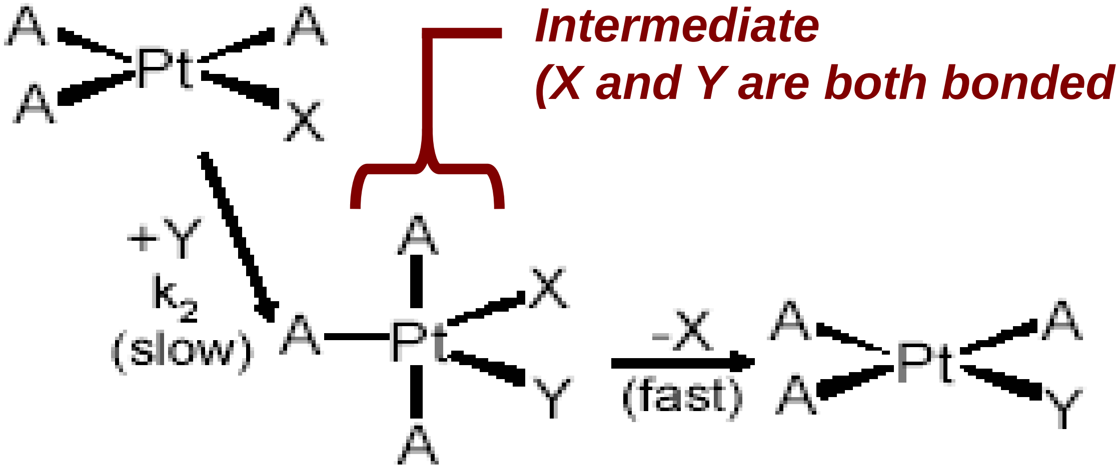


Reaction mechanisms for substitution reactions

- **Associative**
- **Dissociative**
- **Interchange**

Associative - A (2 steps)

$$ML_nX + Y \longrightarrow ML_nXY \longrightarrow ML_nY + X$$



Intermediate
(X and Y are both bonded to the metal)

S_N2

Stadio lento
bimolecolare

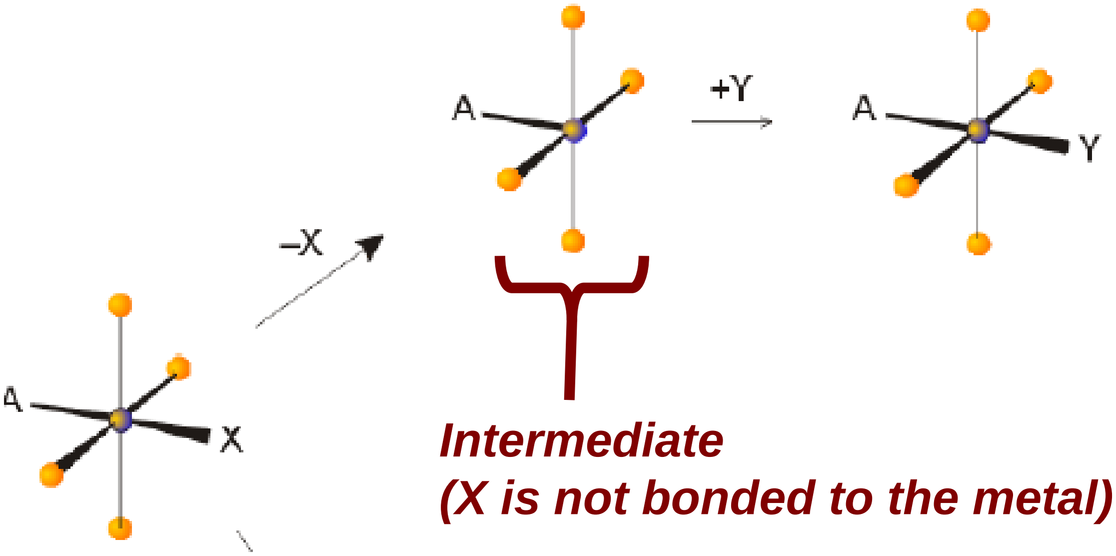
- Bond formation is of primary importance in transition state
- Sensitivity of rate to entering group
- Coordination number increases in the intermediate

Substitution of Square Planar Complexes

- substitution of square planar complexes is almost always A mechanisms
  - rate depends on the entering group
  - rate determining step is the M-Y bond formation

- Dissociative - D (2 steps)

$$ML_nX + Y \longrightarrow ML_n + X + Y \longrightarrow ML_nY + X$$

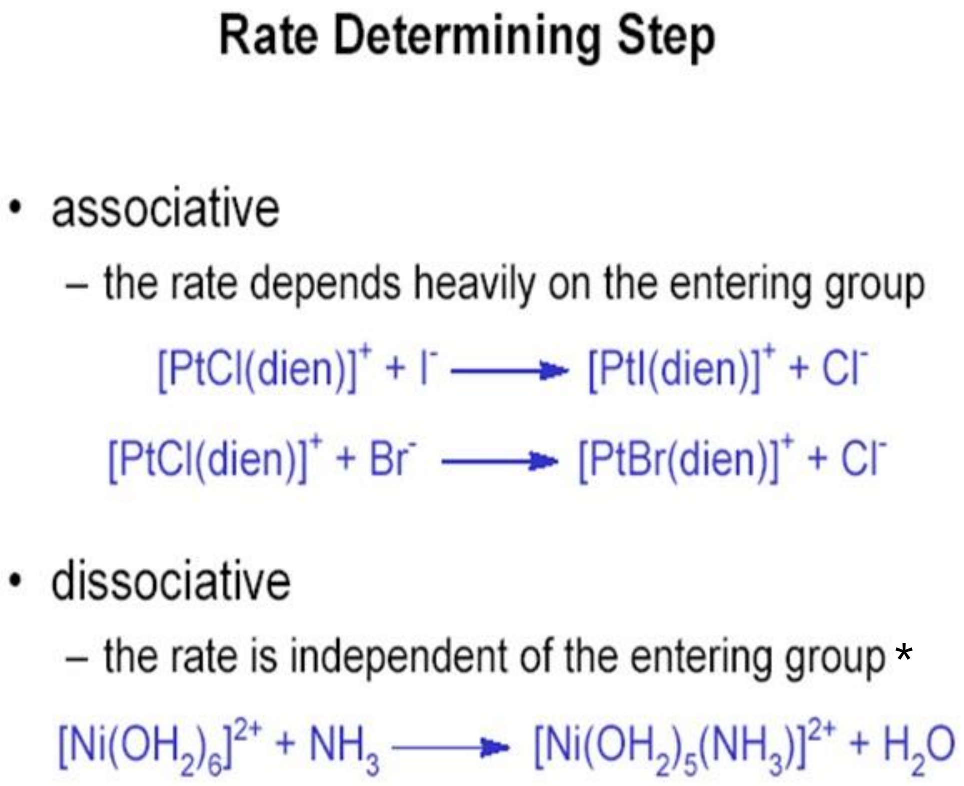


Intermediate
(X is not bonded to the metal)

S_N1

Stadio lento
monomolecolare

- Bond breaking important in transition state
- Sensitivity of rate to leaving group
- Coordination number *decreases* in intermediate



Rate Determining Step

- associative
  - the rate depends heavily on the entering group

$$[PtCl(dien)]^+ + I^- \longrightarrow [PtI(dien)]^+ + Cl^-$$

$$[PtCl(dien)]^+ + Br^- \longrightarrow [PtBr(dien)]^+ + Cl^-$$

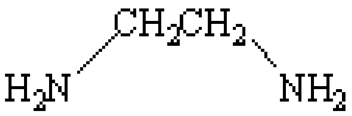
- dissociative
  - the rate is independent of the entering group *

$$[Ni(OH_2)_6]^{2+} + NH_3 \longrightarrow [Ni(OH_2)_5(NH_3)]^{2+} + H_2O$$

* But depends on the leaving group

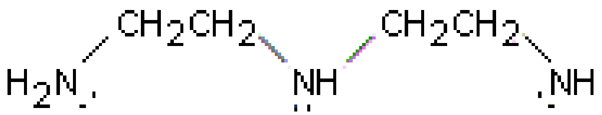
dien = diethylenetriamine

Bidentate Ligand:



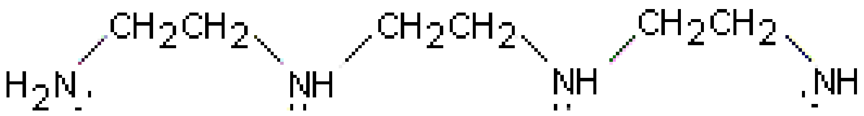
ethylenediamine (en)

Tridentate Ligand:



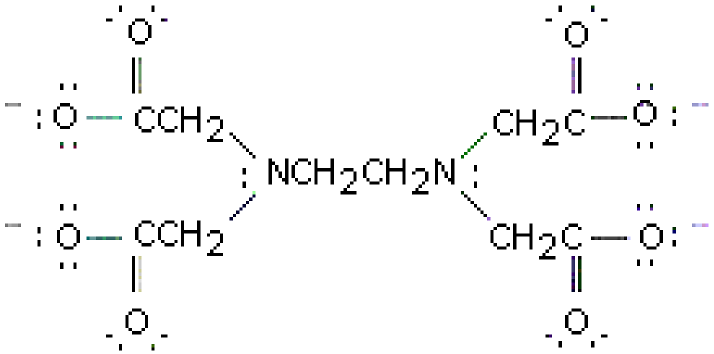
diethylenetriamine (dien)

Tetradentate Ligand:



triethylenetetraamine (trien)

Hexadentate Ligand:



ethylenediaminetetraacetate (EDTA)

I is the most important reaction mechanism for substitution of O_h complexes

Octahedral complexes (Point Group O_h)

- Interchange (1 continuous process)

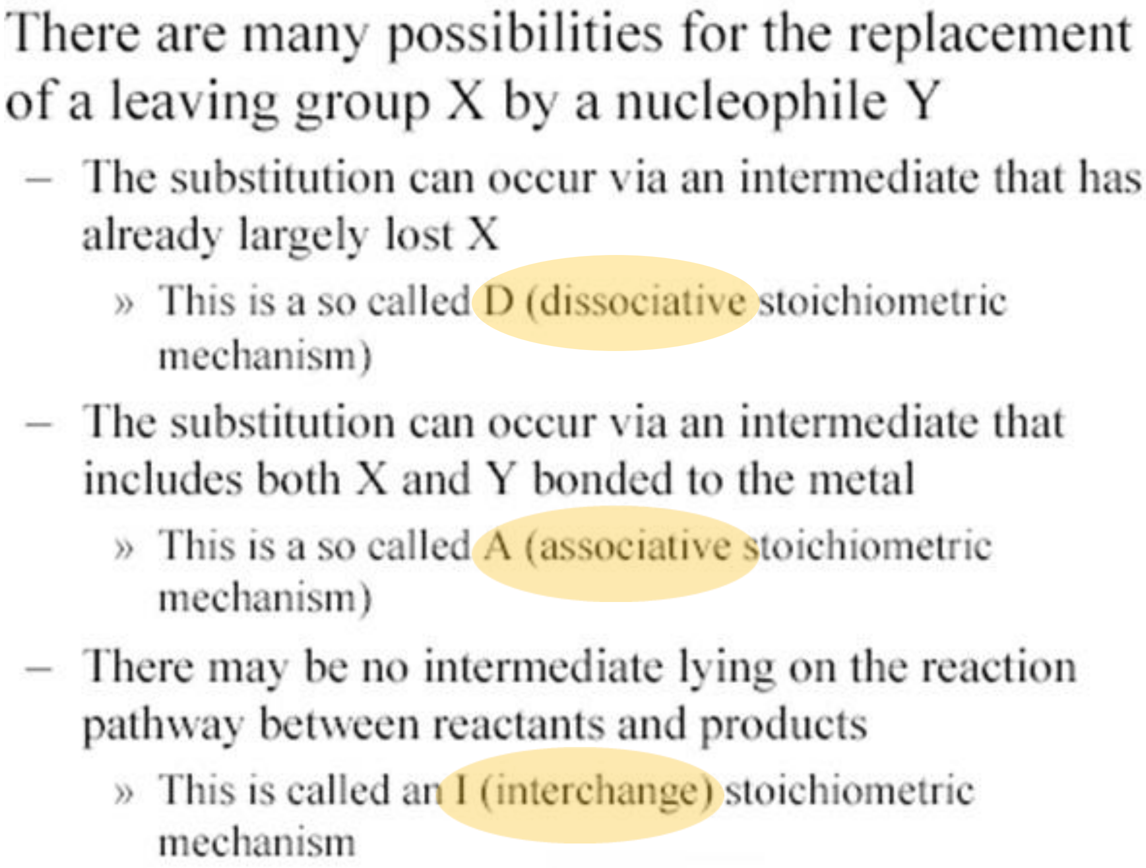
$$ML_nX + Y \longrightarrow Y\text{--}ML_n\text{--}X \longrightarrow ML_nY + X$$

I_a : Interscambio associativo (interazione M - - L più avanzata)

I_d : interscambio dissociativo (interazione M - - L poco pronunciata, legame molto allungato)

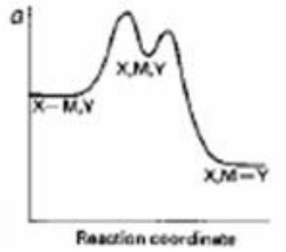
Non si osservano intermedi di reazione ben definiti

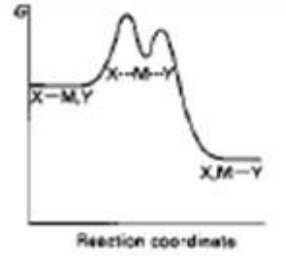
Summary

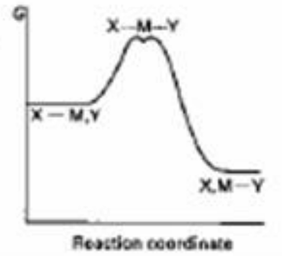


There are many possibilities for the replacement of a leaving group X by a nucleophile Y

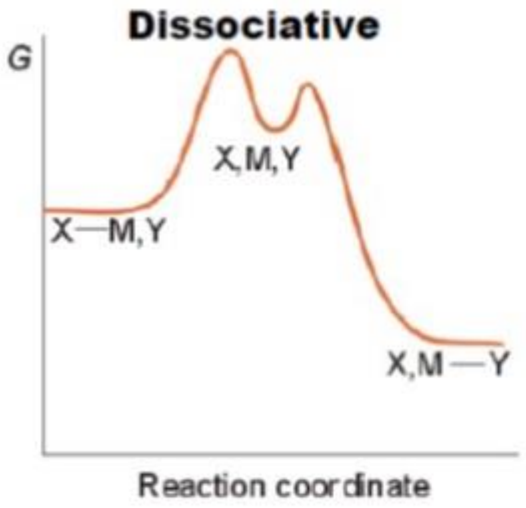
- The substitution can occur via an intermediate that has already largely lost X
  - This is a so called D (dissociative stoichiometric mechanism)
- The substitution can occur via an intermediate that includes both X and Y bonded to the metal
  - This is a so called A (associative stoichiometric mechanism)
- There may be no intermediate lying on the reaction pathway between reactants and products
  - This is called an I (interchange) stoichiometric mechanism

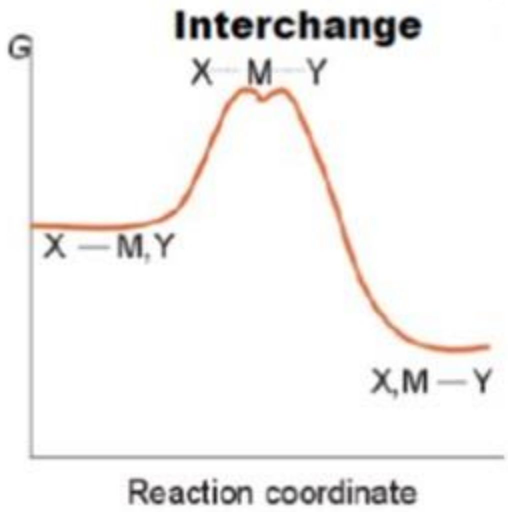


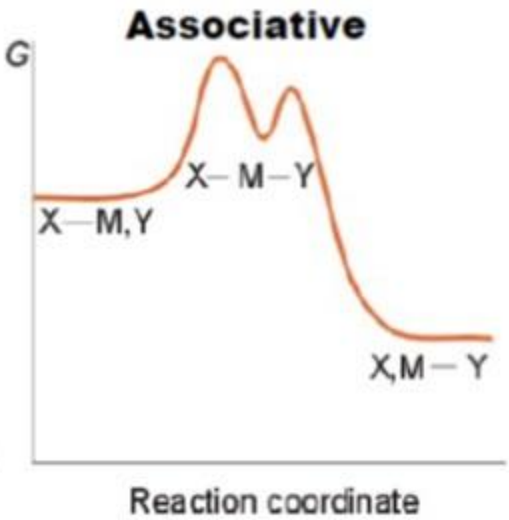




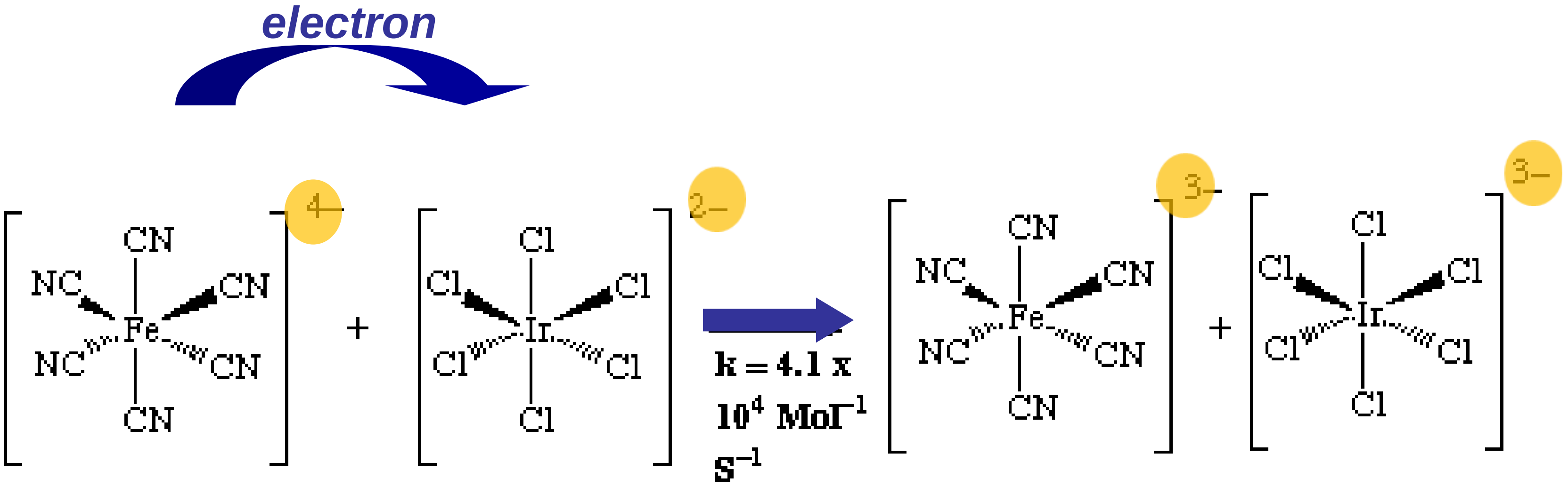
Dissociative: activated state has lower coordination number due to dissociation of the leaving group
Associative: activated state has a higher coordination number due to bonding of the incoming group


Dissociative


Interchange


Associative

Redox Reactions



Two reaction mechanism

- **Inner sphere***

- **Outer sphere***

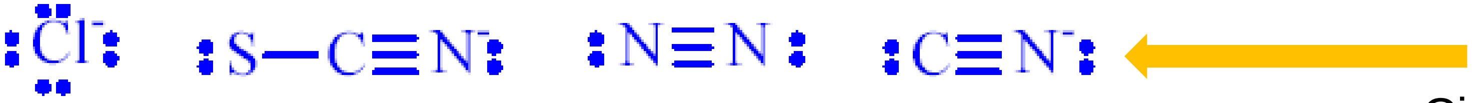
*** coordination sphere**

Inner sphere reaction mechanism

Prerequisites

***1. One reactant (usually the oxidant) possesses at least one ligand capable of binding simultaneously to two metal ions*.**

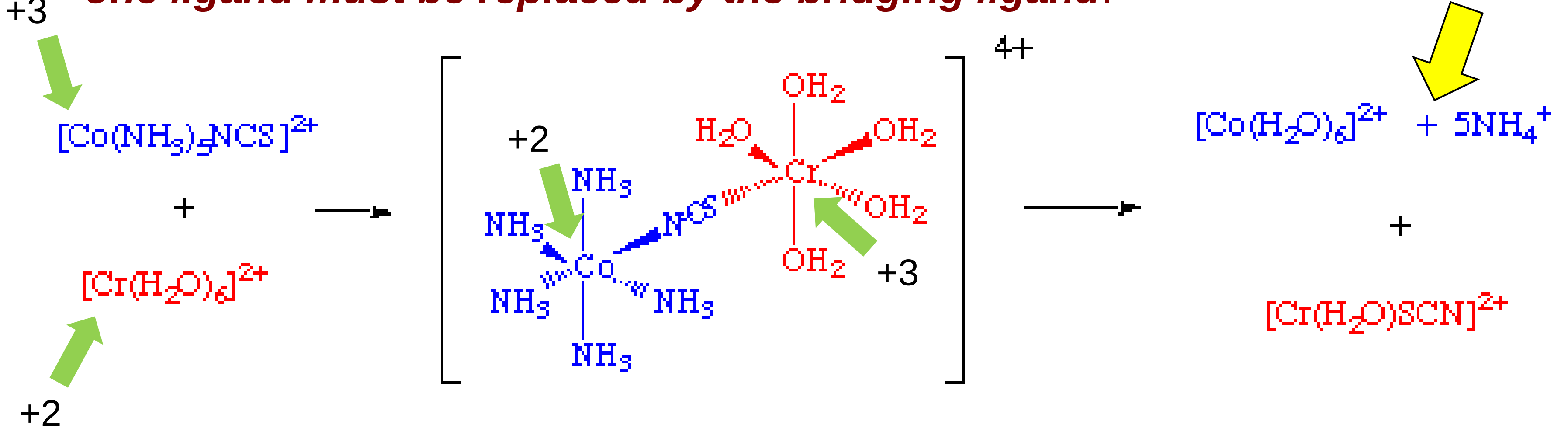
- Ligands with multiple pairs of electrons to donate



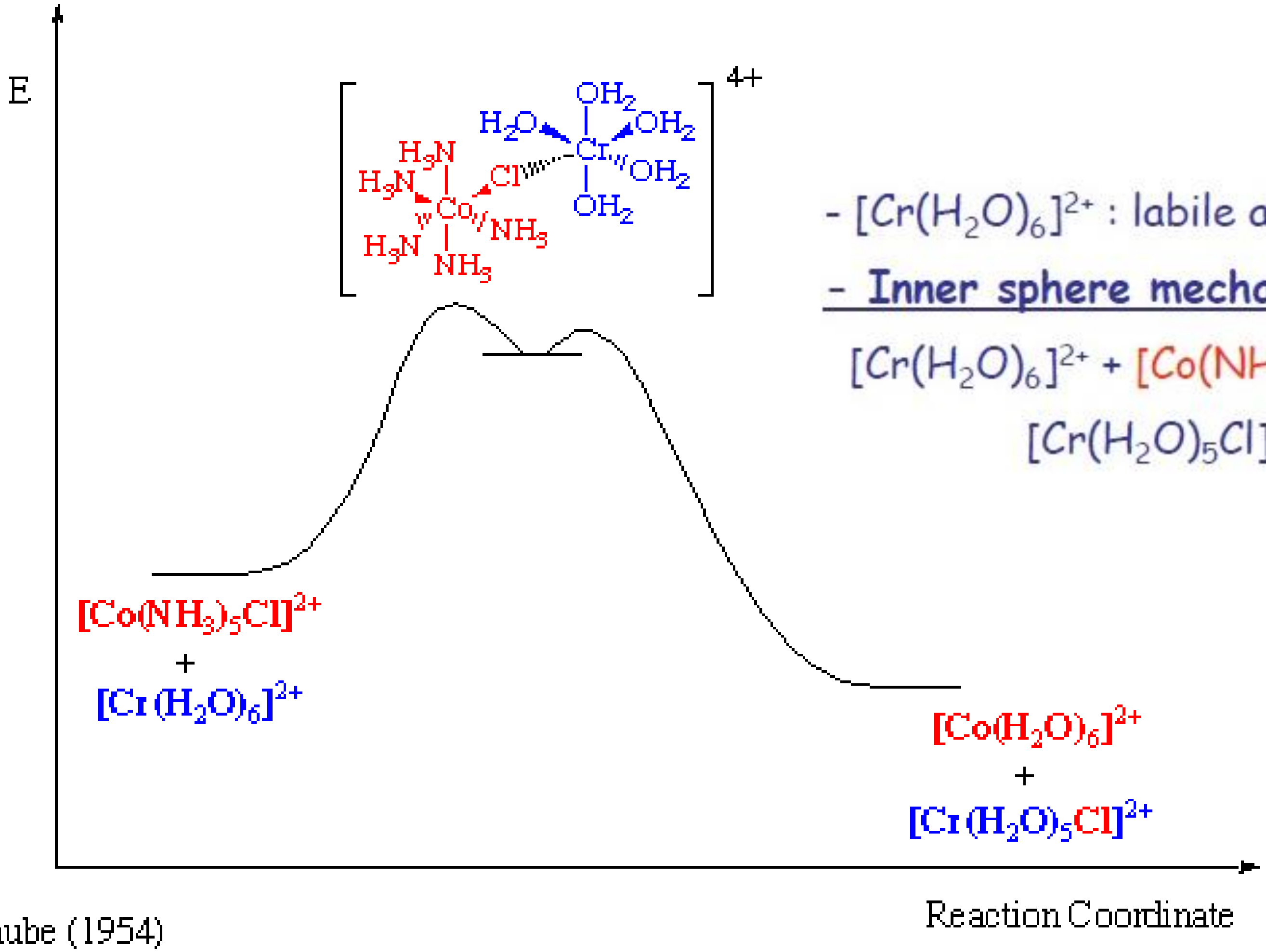
Nitrile
Ciano-
Cianuri (inorg.)

***2. The other reactant is substitutionally labile: one ligand must be replaced by the bridging ligand*.**

Aquation (idrolisi)



The reductant and the oxidant share a ligand in their primary coordination sphere, the electron being transferred “across” a bridging group.



Taube (1954)

- $[Cr(H_2O)_6]^{2+}$: labile against substitution

- <u>Inner sphere mechanism</u>,

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

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

Inner Sphere Reaction Steps

- Formation of Bridged Complex

$$M^{II}L_6 + XM^{III}L_5' \longrightarrow L_5M^{II}{-}XM^{III}L_5' + L$$

- Electron Transfer

$$L_5M^{II}{-}XM^{III}L_5' \longrightarrow L_5M^{III}{-}XM^{II}L_5'$$

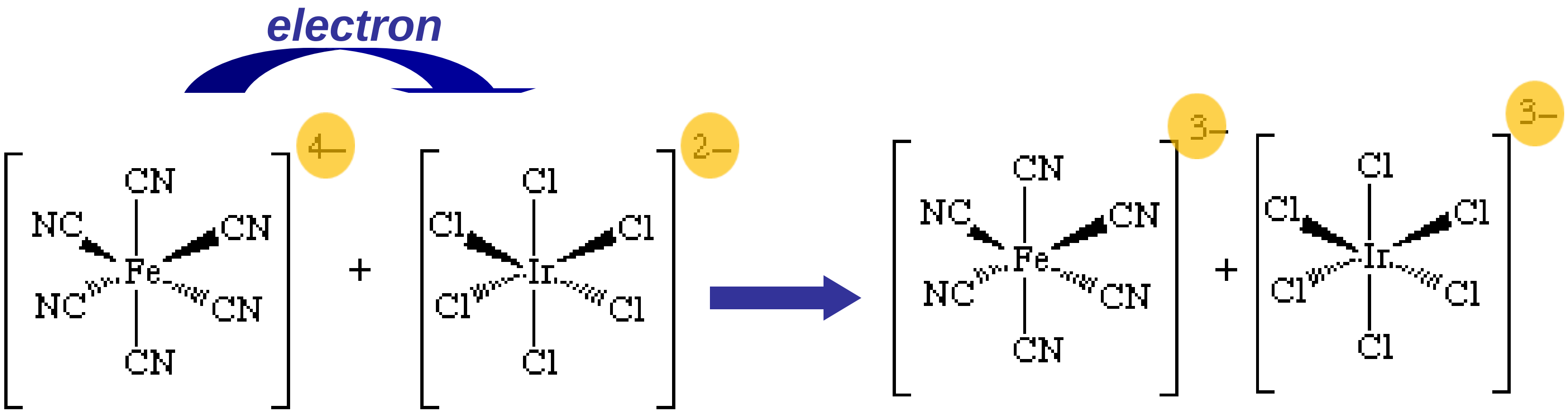
- Decomposition into Final Products

$$L_5M^{III}{-}XM^{II}L_5' \longrightarrow \text{products} \quad L_5M^{III}{-}X + M^{II}L_5'$$

Outher sphere reaction mechanism

- Readily identified when no ligand transfer occurs between the species
- Easier to identify when complexes are inert with respect to ligand substitution

No new bonds are broken or formed



1. Formation of precursor complex

$$M^{(a+1)+}L_x + M'^{\,b+}L_y \overset{K_{eq}}{\rightleftharpoons} \{M^{(a+1)+}L_x \cdots M'^{\,b+}L_y\}$$

Precursor complex

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

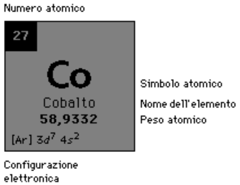
$$\{M^{(a+1)+}L_x \cdots M'^{\,b+}L_y\} \xrightarrow{k_{ET}} \{M^{a+}L_x \cdots M'^{\,(b+1)+}L_y\}$$

Successor complex

3. Dissociation of successor complex

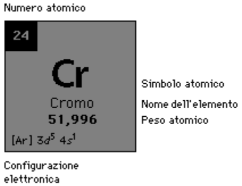
$$\{M^{a+}L_x \cdots M'^{\,(b+1)+}L_y\} \xrightarrow{k_{diss}} M^{a+}L_x + M'^{\,(b+1)+}L_y$$

Formation of precursor complex and dissociation of successor complex are fast. Electron transfer slow



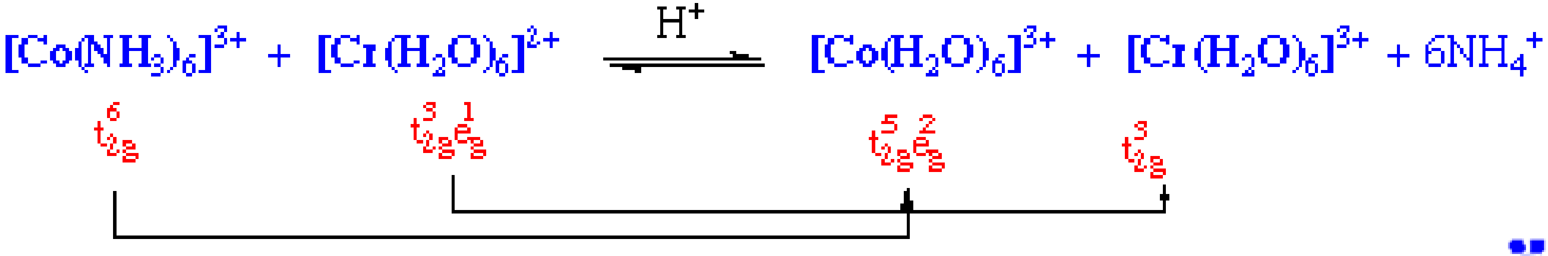
s^2d^7

A comparison of the reaction rate between the two mechanisms



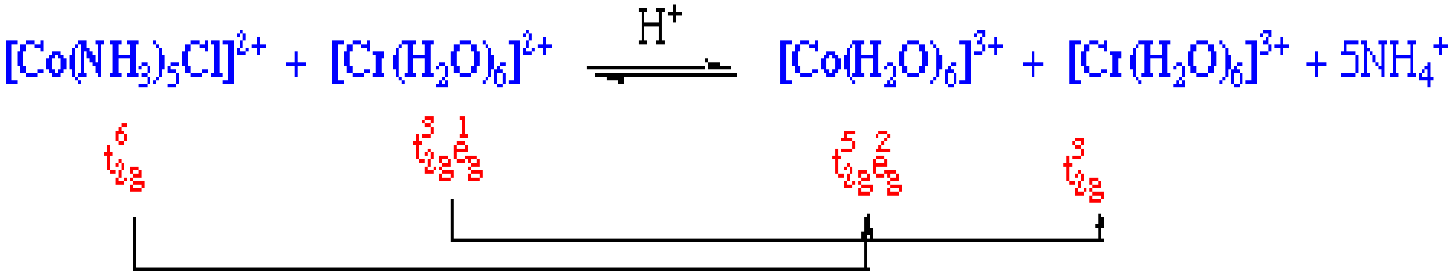
s^1d^5

The reduction of hexaamminecobalt(III) by hexaaquochromium(II) occurs slowly (k = 10^{-3} $M^{-1}sec^{-1}$) by an outer sphere mechanism.



$$[Co(NH_3)_6]^{3+} + [Cr(H_2O)_6]^{2+} \xrightarrow{H^+} [Co(H_2O)_6]^{3+} + [Cr(H_2O)_6]^{3+} + 6NH_4^+$$

However, if one ammonia ligand on Co(III) is substituted by Cl^- (inner-like ligand), reaction now occurs with a substantially greater rate (k = 6 x 10^5 M^{-1} sec^{-1}).



$$[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} \xrightarrow{H^+} [Co(H_2O)_6]^{3+} + [Cr(H_2O)_6]^{3+} + 5NH_4^+$$