Substitution Reaction in Metal Complexes

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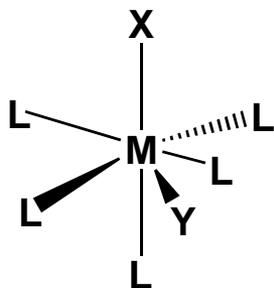
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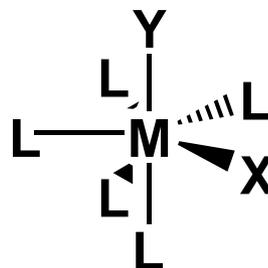
Associative Mechanism

$$ML_5X + Y \longrightarrow ML_5Y + X$$

Step 1. Collision of ML_5X with Y to yield a 7-coordinate intermediate. (slow)

$$ML_5X + Y \xrightarrow{K_1} ML_5XY \quad \text{(slow, rate determining)}$$

Capped Octahedron

Pentagonal Bipyramid

Step 2. Cleavage of the M-X bond. (fast)

$$ML_5XY \longrightarrow ML_5Y + X \qquad \text{(fast)}$$

rate law for this process is rate = $K_1[ML_5X][Y]$ (the units of K_1 are $sec^{-1}Mole^{-1}$)
 If we find a reaction follows this rate law we conclude it is associative.

Substitution reactions

$$ML_n + L' \rightleftharpoons ML_{n-1}L' + L$$

Labile complexes <==> Fast substitution reactions (< few min)
Inert complexes <==> Slow substitution reactions (>h)
a <u>kinetic</u> concept

Inert	Intermediate	Labile
d^3, low spin d^4-d^6 & d^8	d^8 (high spin)	d^1, d^2, low spin d^4-d^6 & d^7-d^{10}

Mechanisms of ligand exchange reactions in octahedral complexes

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

Dissociative (D)

$ML_nX \longrightarrow ML_nY$

$X \quad ML_n \quad Y$

Associative (A)

$ML_nX \longrightarrow ML_nY$

$Y \quad ML_nXY \quad X$

Interchange (I)

$ML_nX \longrightarrow ML_nY$

$Y \quad [ML_n]° \quad X$

$X \quad Y$
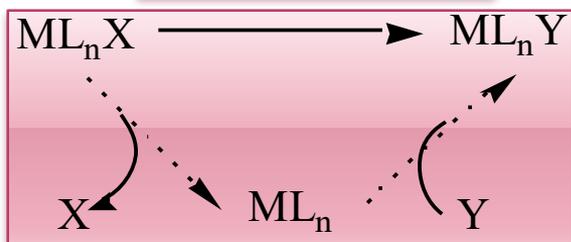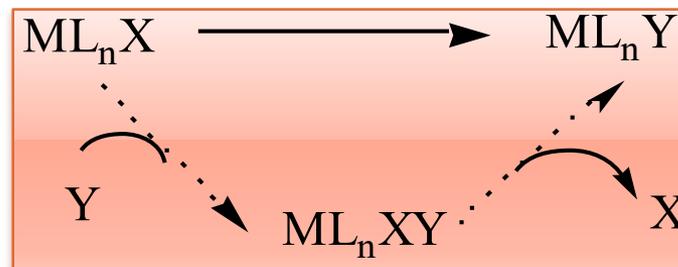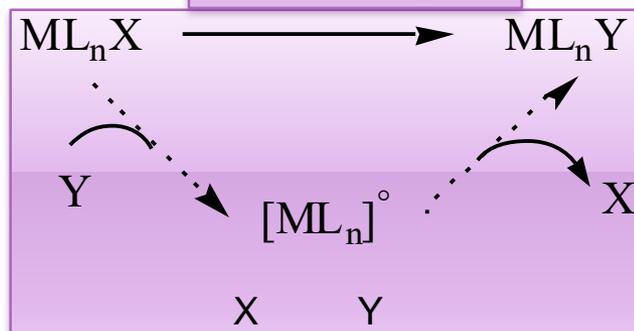
I_a *if association is more important*

I_d *if dissociation is more important*

***Kinetics
of dissociative reactions***

$$ML_5X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_5 + X$$

$$ML_5 + Y \xrightarrow{k_2} ML_5Y$$
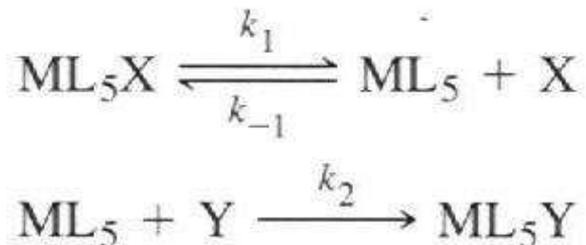
$$\frac{d[ML_5]}{dt} = k_1[ML_5X] - k_{-1}[ML_5][X] - k_2[ML_5][Y] = 0$$

Solving for $[ML_5]$,

$$[ML_5] = \frac{k_1[ML_5X]}{k_{-1}[X] + k_2[Y]}$$

and substituting into the rate law for formation of the product,

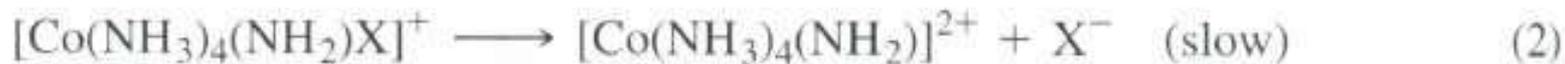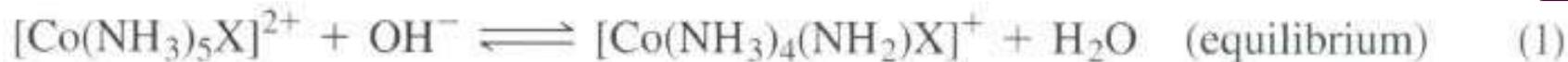$$\frac{d[ML_5Y]}{dt} = k_2[ML_5][Y]$$

leads to the rate law:

$$\frac{d[ML_5Y]}{dt} = \frac{k_2 k_1[ML_5X][Y]}{k_{-1}[X] + k_2[Y]}$$

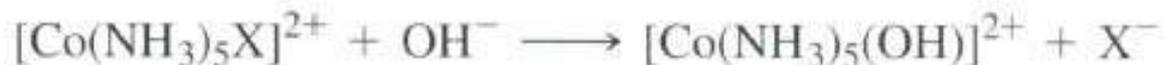**Experimental evidence in Octahedral substitution; Dissociation**

The evidence for dissociative mechanism

1. The rate of reaction changes **only slightly with changes in the incoming ligand. (rate constant of less than a factor of** 10)

2. Decreasing negative charge or increasing positive charge on the reactant compound **decreases the rate of substitution.**

3. Steric crowding on the reactant complex increases the rate of ligand dissociation.

4. The rate of reaction correlates with the metal-ligand bond strength of the leaving group, in a linear free energy relationship (LFER).

5. Activation energies and entropies are consistent with dissociation. (**volume of activation Δ Vact; positive or** negative?)

Experimental evidence in Octahedral substitution; The Conjugate Base Mechanism

$$[Co(NH_3)_5X]^{2+} + OH^- \rightleftharpoons [Co(NH_3)_4(NH_2)X]^+ + H_2O \quad \text{(equilibrium)} \quad (1)$$

$$[Co(NH_3)_4(NH_2)X]^+ \longrightarrow [Co(NH_3)_4(NH_2)]^{2+} + X^- \quad \text{(slow)} \quad (2)$$

$$[Co(NH_3)_4(NH_2)]^{2+} + H_2O \longrightarrow [Co(NH_3)_5(OH)]^{2+} \quad \text{(fast)} \quad (3)$$

Overall,

$$[Co(NH_3)_5X]^{2+} + OH^- \longrightarrow [Co(NH_3)_5(OH)]^{2+} + X^-$$

The ligand *trans to the amido or hydroxo group is frequently* the one lost

Additional evidence

1. Base catalyzed exchange of hydrogen from the amine groups takes place under the same conditions.
2. The *isotope ratio (18O/16O) in the product in 18O-enriched water is* the same as that in the water regardless of the leaving group. (no associative)
3. *RNH2 compounds react fast than NH3. (help to form 5-coordinate)*
4. A plot of *lnkOH versus lnKOH is linear.*
5. When *substituted amines used (no protons), the reaction is very* slow or nonexistent.
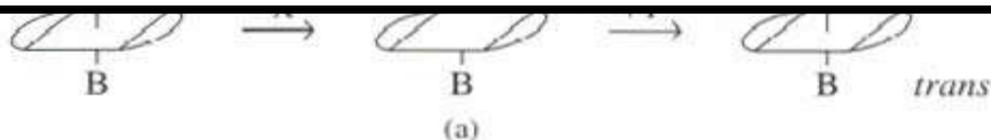
Stereochemistry of Reactions; Substitution in *trans complexes*

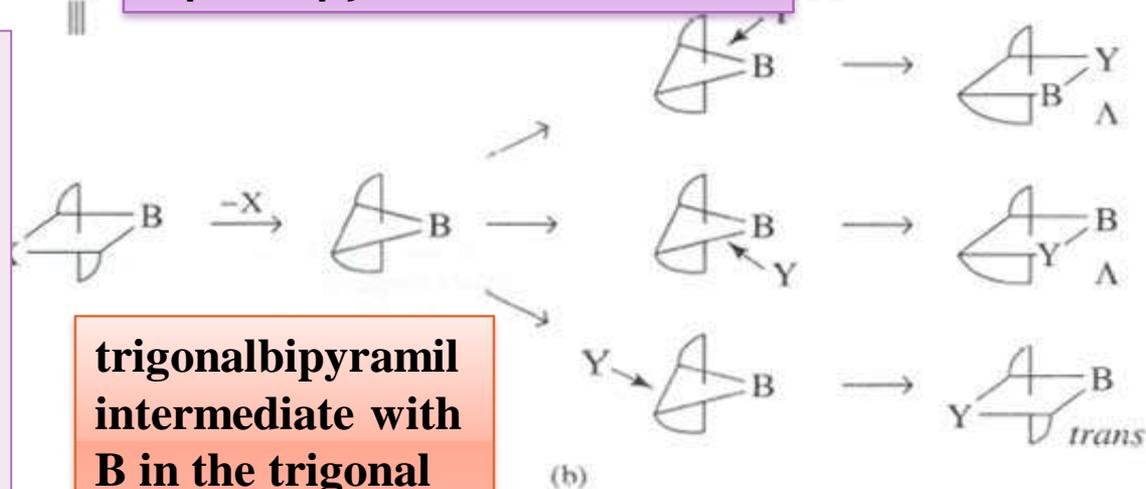Dissociation mechanism and stereochemical change; three different pathways

Axial B requires *more arrangement of the ligands* and *larger stretch for the LL ring in the equatorial* plane
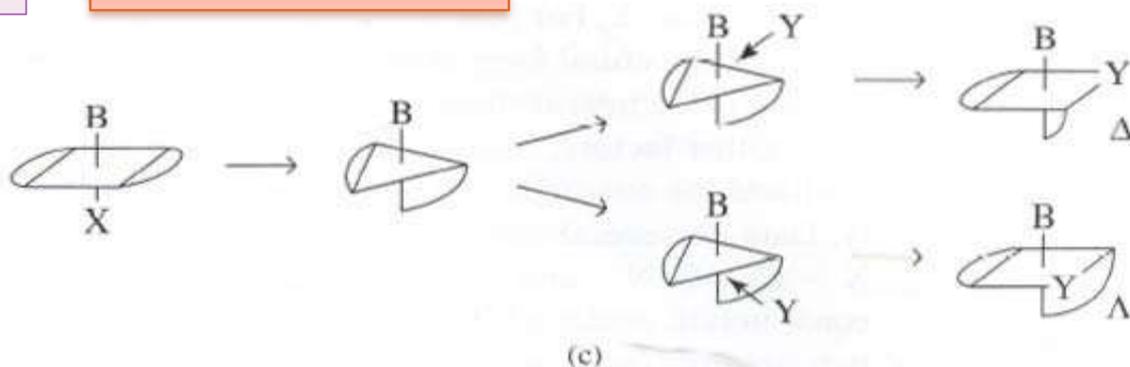A change from *trans to cis is* two thirds for a trigonalbipyramidal intermediate.

Square-pyramidal intermediate

**trigonalbipyramil intermediate with B in the trigonal plane**

trigonalbipyramidal intermediate with B in the axial position

(a)

(b)

(c)

three different pathways

As a general rule, *cis* reactants retain their *cis* configuration, but *trans* reactants are more likely to give a mixture of *cis and trans products*.

trigonalbipyramidal intermediate with B in the axial position

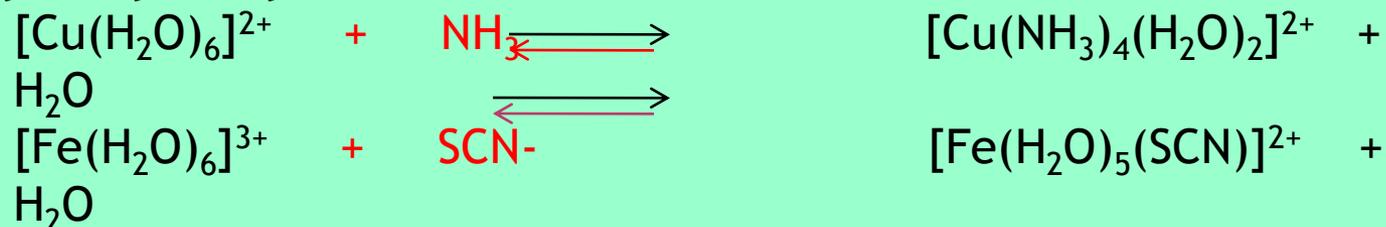**trigonalbipyramidal intermediate with B in the axial position**
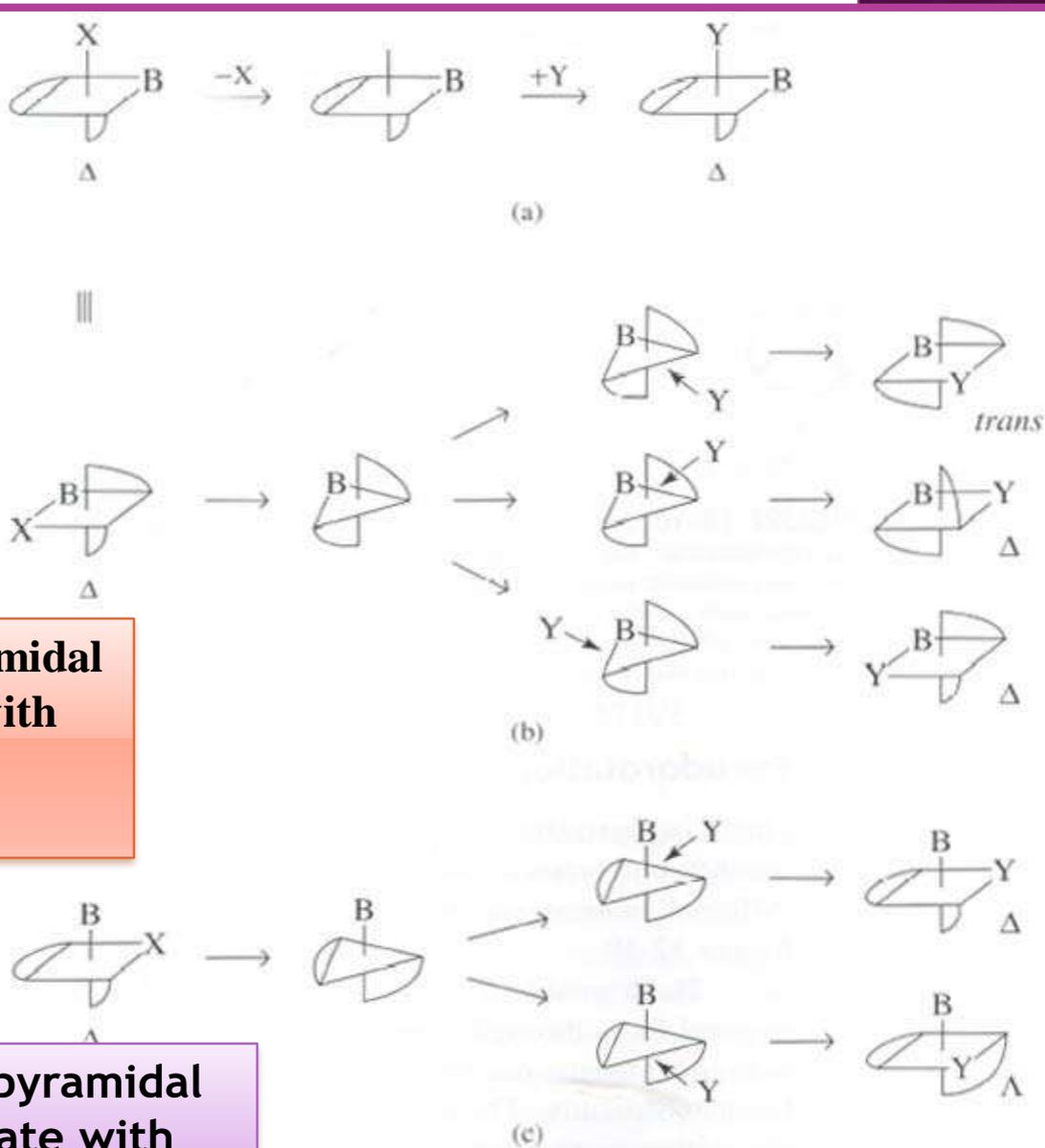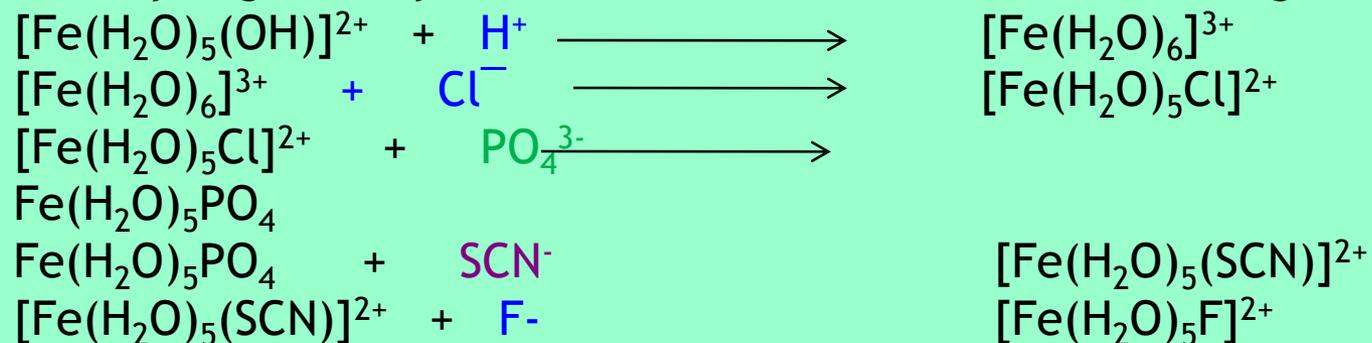
II. Substitution Reactions

Inert and Labile Complexes

Labile Complexes = those undergoing substitution with $t_{1/2}$ < 1 minute

Many analytically useful reactions are labile substitutions

$$[Cu(H_2O)_6]^{2+} + NH_3 \rightleftarrows [Cu(NH_3)_4(H_2O)_2]^{2+} + H_2O$$

$$[Fe(H_2O)_6]^{3+} + SCN^- \rightleftarrows [Fe(H_2O)_5(SCN)]^{2+} + H_2O$$

b) Lability is generally a function of the metal ion, not the ligands

$$[Fe(H_2O)_5(OH)]^{2+} + H^+ \longrightarrow [Fe(H_2O)_6]^{3+}$$

$$[Fe(H_2O)_6]^{3+} + Cl^- \longrightarrow [Fe(H_2O)_5Cl]^{2+}$$

$$[Fe(H_2O)_5Cl]^{2+} + PO_4^{3-} \longrightarrow Fe(H_2O)_5PO_4$$

$$Fe(H_2O)_5PO_4 + SCN^- \qquad [Fe(H_2O)_5(SCN)]^{2+}$$

$$[Fe(H_2O)_5(SCN)]^{2+} + F^- \qquad [Fe(H_2O)_5F]^{2+}$$

c) Often, the reaction happens at the diffusion limit = as soon as the reactants are mixed, they are done reacting. Diffusion = 10^{11} s^{-1}

d) Labile Metal ions = those with small or zero LFSE

a) d^1, d^2, d^7, d^9, d^{10}

b) High spin d^4-d^6

2)Inert Complexes = those undergoing substitution with $t_{1/2} > 1$ minute
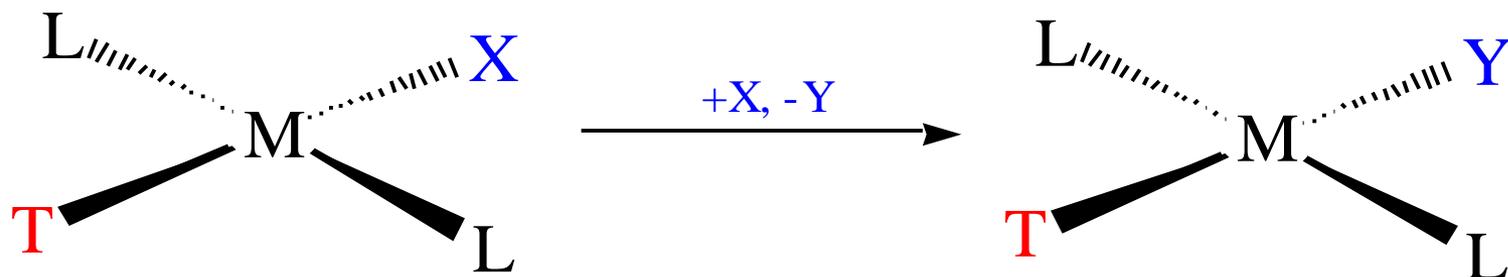
a) Inert doesn't mean unreactive; Inert doesn't mean thermodynamically stable

b) Inert does mean slow to react (also known as Robust)

$[Fe(H_2O)_5F]^{2+}$ = labile, but it is very thermodynamically stable

$[Co(NH_3)_6]^{3+}$ = inert, but thermodynamically unstable

c)Inert complexes react slowly, so their products can be isolated and studied

d)Inert metal ions = those with large LFSE

d^3, low spin d^4-d^6

"Low spin" (square planar, strong field) d^8

e)"High spin" (octahedral, weak field) d^8 metals are intermediate in lability
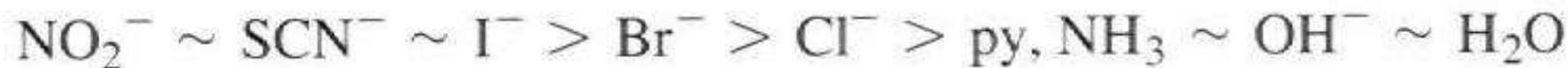
Labile or inert?

$$E_a$$

$$\Delta G$$
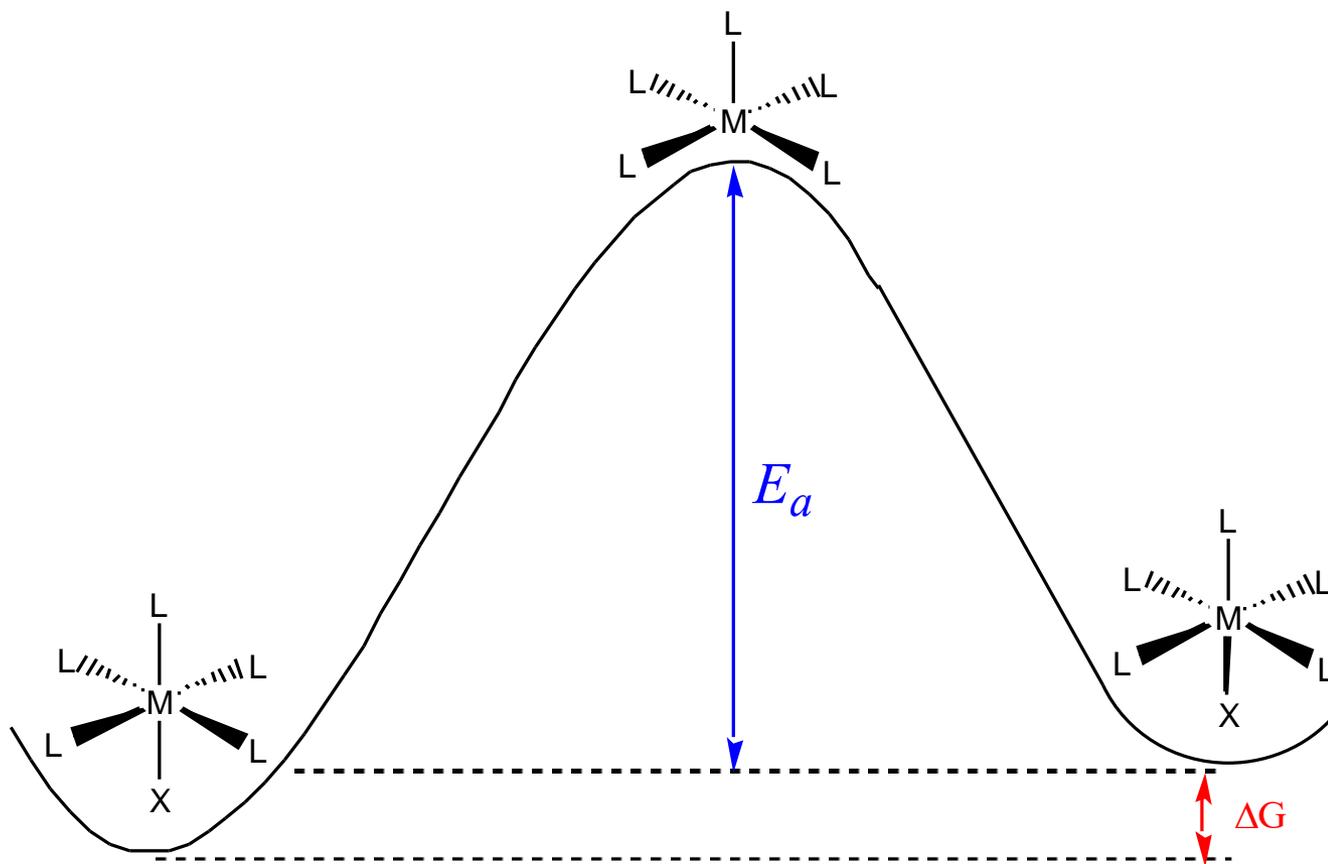
LFAE = LFSE(sq pyr) - LFSE(oct)

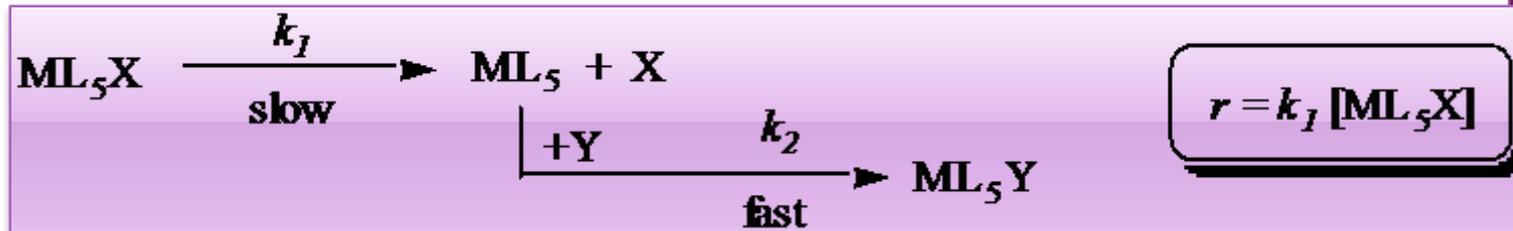# Substitution reactions in square-planar complexes
the trans effect

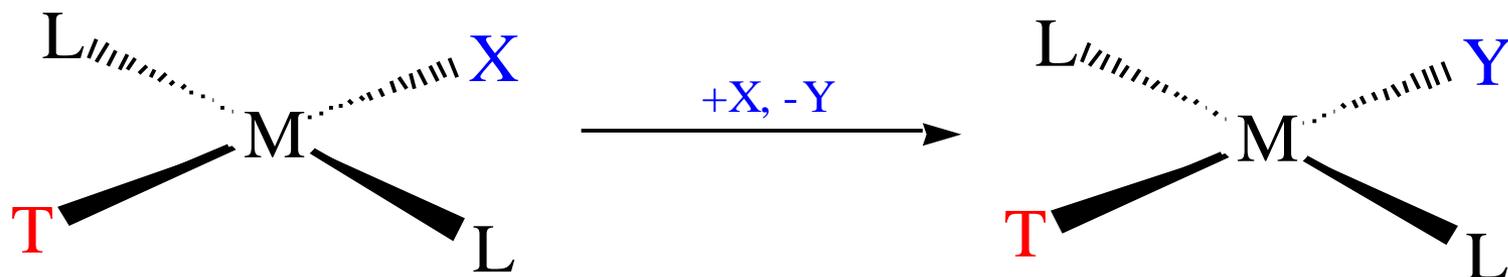*(the ability of T to labilize X)*

$$CO \sim CN^- \sim C_2H_4 > PR_3 \sim H^- > CH_3^- \sim SC(NH_2)_2 > C_6H_5^- >$$

$$NO_2^- \sim SCN^- \sim I^- > Br^- > Cl^- > py, NH_3 \sim OH^- \sim H_2O$$

Dissociative

$ML_5X \xrightarrow[\text{slow}]{k_1} ML_5 + X$

$\quad\quad\;\; \lfloor +Y \xrightarrow[\text{fast}]{k_2} ML_5Y$

$r = k_1\,[ML_5X]$

Associative

$ML_5X + Y \xrightarrow[\text{slow}]{k_1} ML_5XY$

$\quad\;\; \lfloor -X \xrightarrow[\text{fast}]{k_2} ML_5Y$

$r = k_1\,[ML_5X][Y]$

Substitution reactions in square-planar complexes the trans effect

(the ability of T to labilize X)

$$CO \sim CN^- \sim C_2H_4 > PR_3 \sim H^- > CH_3^- \sim SC(NH_2)_2 > C_6H_5^- >$$

$$NO_2^- \sim SCN^- \sim I^- > Br^- > Cl^- > py, NH_3 \sim OH^- \sim H_2O$$
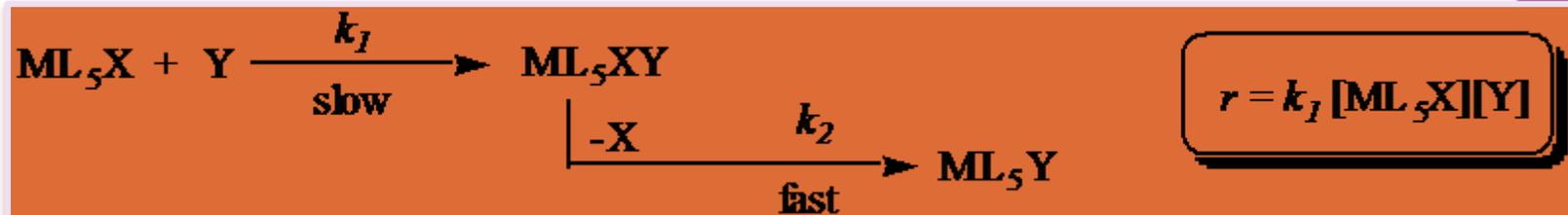
Synthetic applications of the trans effect

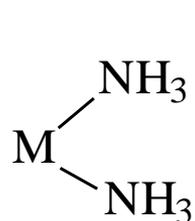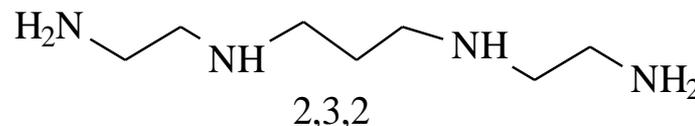$$-d[ML_3X]/dt = (k_s + k_y [Y]) [ML_3X]$$
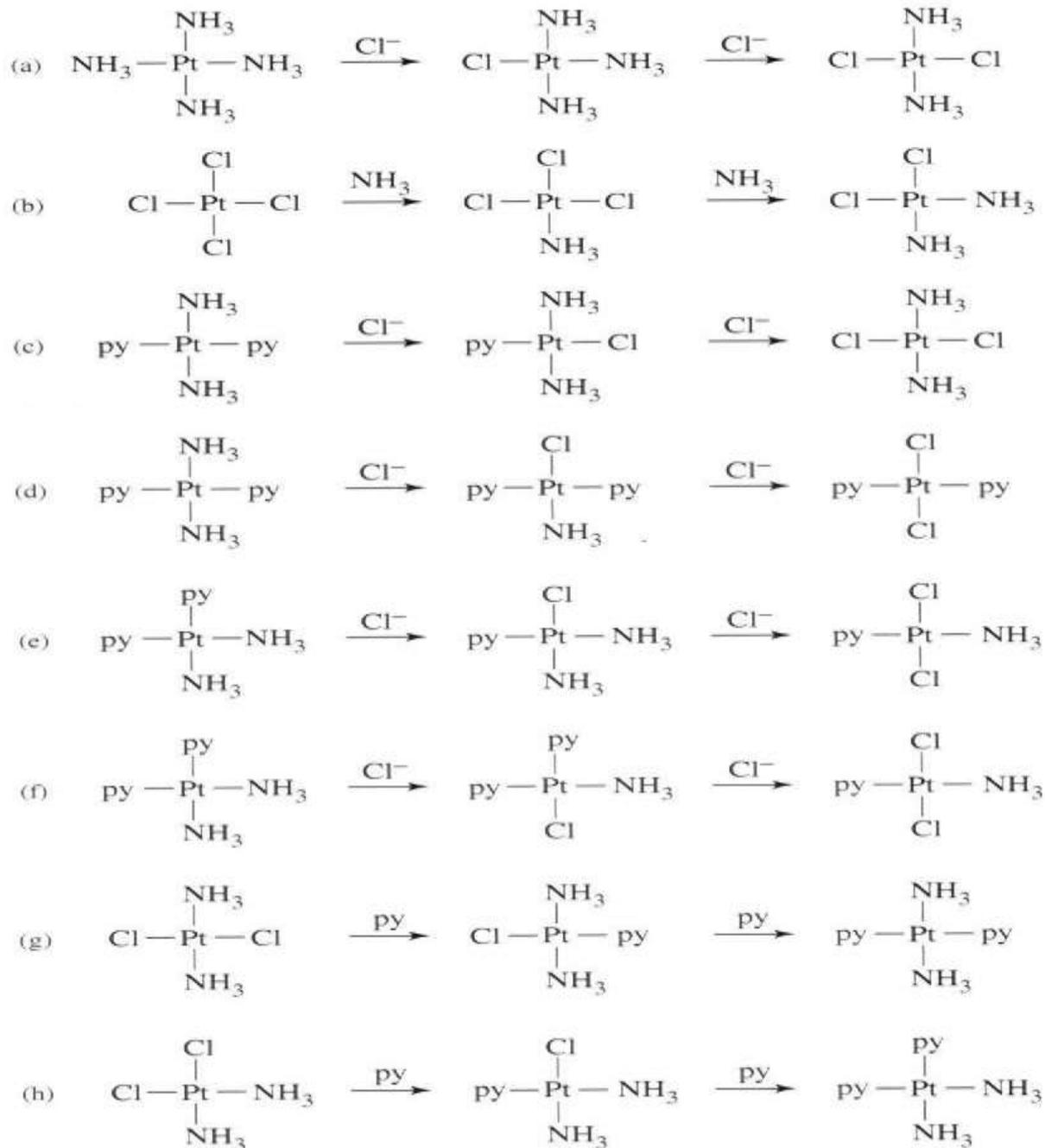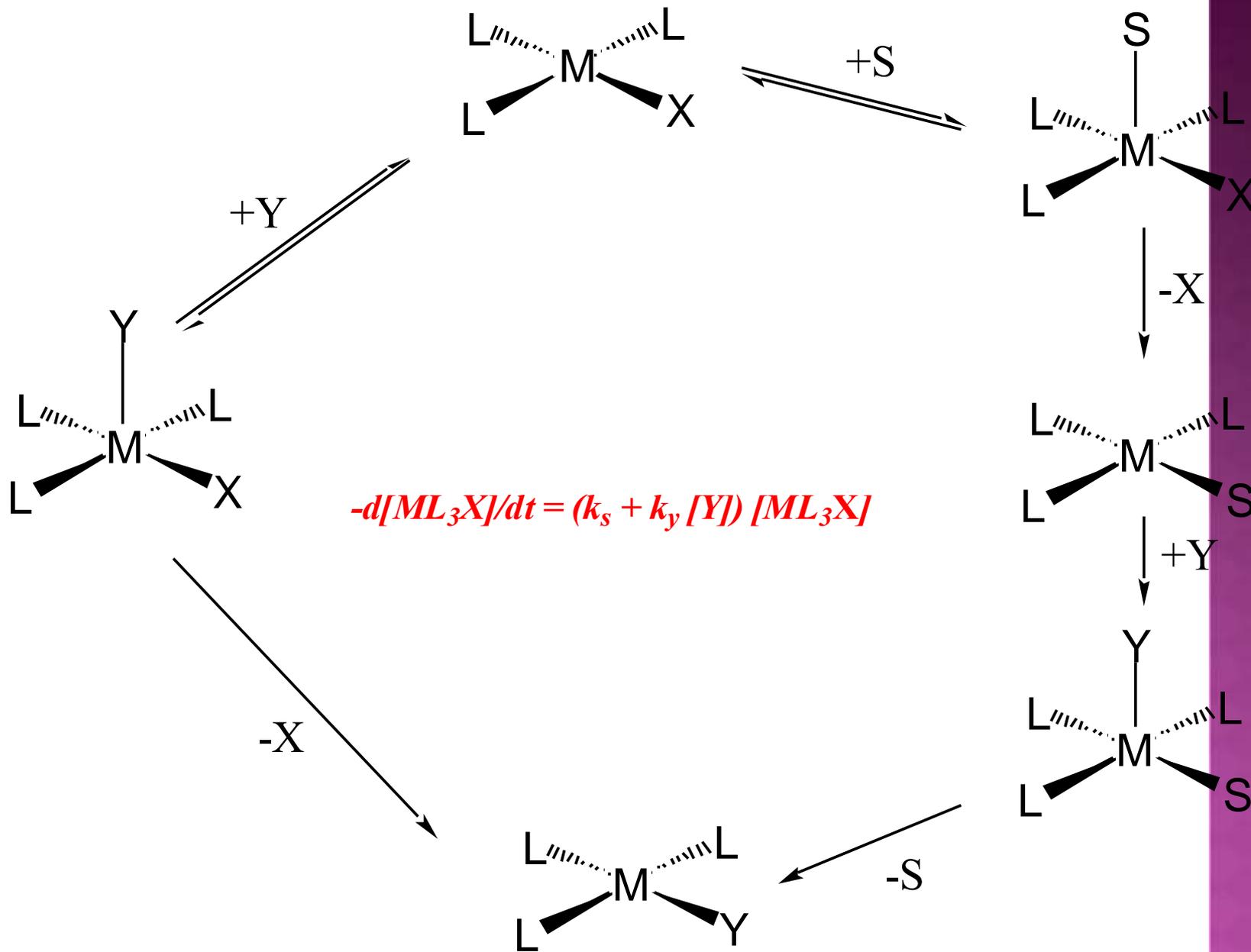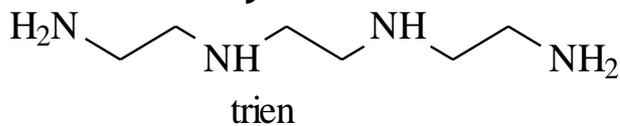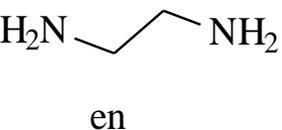
B. Topological Effects
- The Chelate Effect
  - Two donor atoms linked together = a chelate (claw)
  - Chelate ligands form much more stable metal complexes than monodentate related ligands (up to 10^5 times as stable)
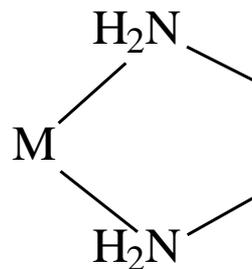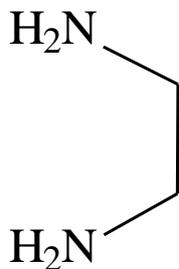
    Ni^{2+} + L Formation Constants:

L =	NH_3	en	trien	2,3,2
$\log \beta$	8.12	13.54	13.8	16.4

    Thermodynamic Reasons for the Chelate Effect = Entropy

H_2N⌒NH_2

en

H_2N⌒NH⌒NH⌒NH_2

trien

H_2N⌒NH⌒⌒NH⌒NH_2

2,3,2

$M\begin{smallmatrix}NH_3\\NH_3\end{smallmatrix}$ + $\begin{smallmatrix}H_2N\\H_2N\end{smallmatrix}$ ⟶ $M\begin{smallmatrix}H_2N\\H_2N\end{smallmatrix}$ + 2 NH_3

2 particles   3 particles

Rigidity Effects

- More rigid ligands(assuming complementarity) make more stable complexes
- Data

M	L	$t_{1/2}$	difference
Cu^{2+}	en	0.006 s	
Cu^{2+}	bipy	0.025 s	x 3
Cu^{2+}	spartiene	295 min	x 10^6
Ni^{2+}	dien	0.07 s	
Ni^{2+}	tach	7 min	x (6 x 10^3)
Ni^{2+}	TRI	90 days	x 10^8