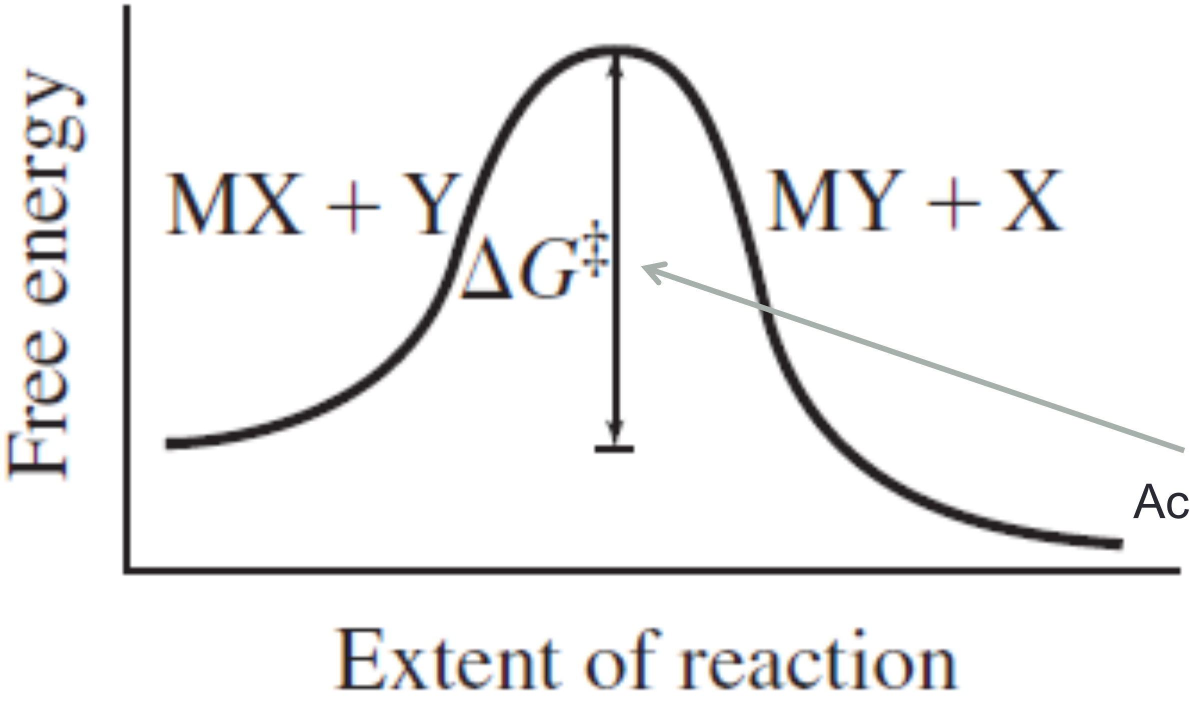
# LIGAND SUBSTITUTION REACTIONS IN COORDINATION COMPOUNDS

CH431

MFT Ch 12

# Reaction coordinate for ligand substitution



Activation energy

# Vocabulary for reaction kinetics

- **$\Delta G$**: overall free energy change of a reaction (difference in free energy of reactants and products)
  - Thermodynamically favorable reactions: **$\Delta G < 0$**
  - Thermodynamically unfavorable reactions: **$\Delta G > 0$**

- **Rate constant**: constant that describes how quickly a reaction proceeds
- **$\Delta G^{\ddagger}$** : free energy of activation, composed of the enthalpy (**$\Delta H^{\ddagger}$**) and entropy (**$\Delta S^{\ddagger}$**) of activation.

- Reaction rate (kinetics) depends on **$\Delta G^{\ddagger}$** and not **$\Delta G$**
- Equilibrium constant (thermodynamics) depends on **$\Delta G$**

$$[M(H_2O)_6]^{n+} + H_2O \rightleftharpoons [M(H_2O)_5(H_2O)]^{n+} + H_2O$$

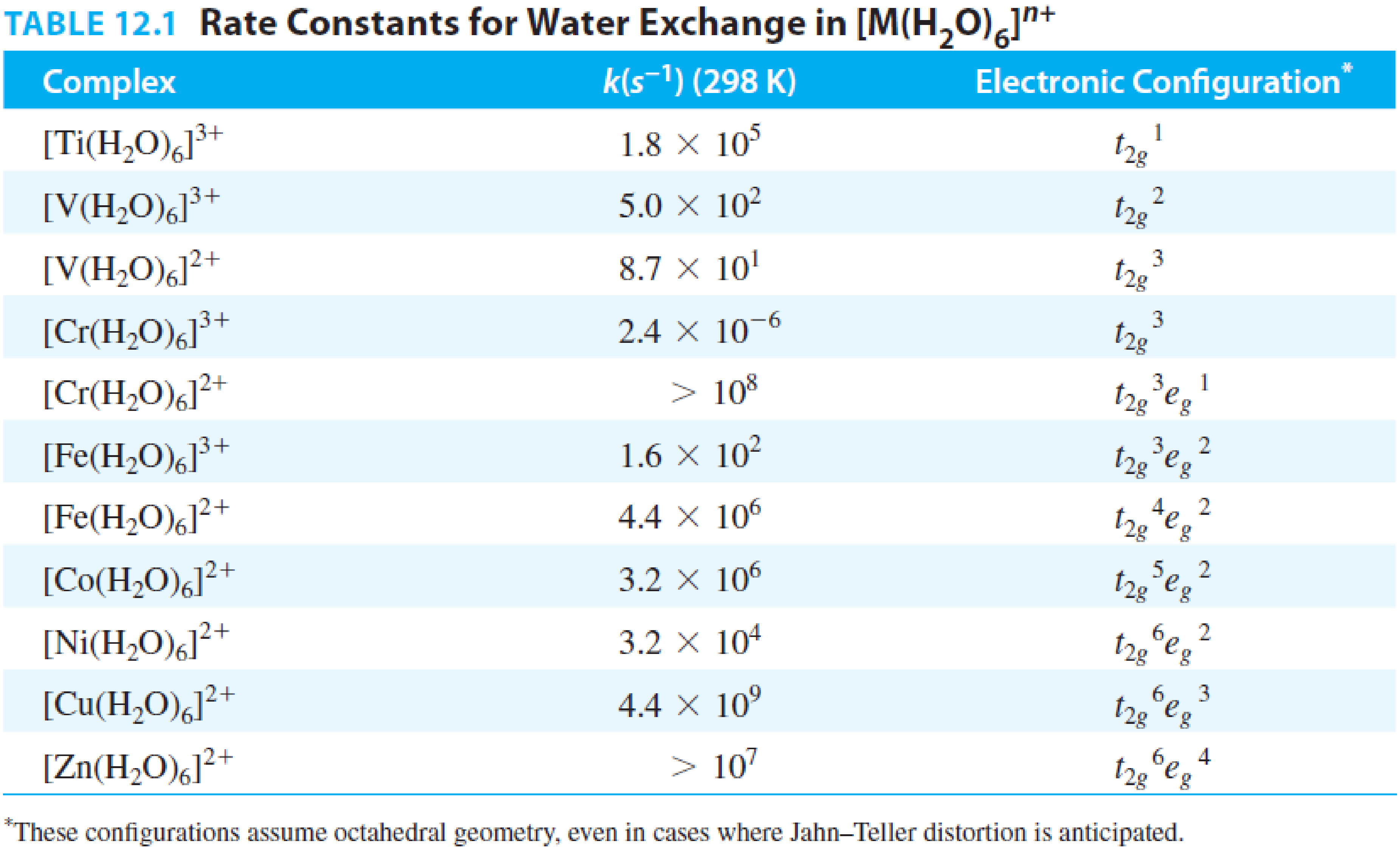


**TABLE 12.1** **Rate Constants for Water Exchange in $[M(H_2O)_6]^{n+}$**

| Complex | $k(s^{-1})$ (298 K) | Electronic Configuration* |
|---|---|---|
| $[Ti(H_2O)_6]^{3+}$ | $1.8 \times 10^5$ | $t_{2g}{}^1$ |
| $[V(H_2O)_6]^{3+}$ | $5.0 \times 10^2$ | $t_{2g}{}^2$ |
| $[V(H_2O)_6]^{2+}$ | $8.7 \times 10^1$ | $t_{2g}{}^3$ |
| $[Cr(H_2O)_6]^{3+}$ | $2.4 \times 10^{-6}$ | $t_{2g}{}^3$ |
| $[Cr(H_2O)_6]^{2+}$ | $> 10^8$ | $t_{2g}{}^3 e_g{}^1$ |
| $[Fe(H_2O)_6]^{3+}$ | $1.6 \times 10^2$ | $t_{2g}{}^3 e_g{}^2$ |
| $[Fe(H_2O)_6]^{2+}$ | $4.4 \times 10^6$ | $t_{2g}{}^4 e_g{}^2$ |
| $[Co(H_2O)_6]^{2+}$ | $3.2 \times 10^6$ | $t_{2g}{}^5 e_g{}^2$ |
| $[Ni(H_2O)_6]^{2+}$ | $3.2 \times 10^4$ | $t_{2g}{}^6 e_g{}^2$ |
| $[Cu(H_2O)_6]^{2+}$ | $4.4 \times 10^9$ | $t_{2g}{}^6 e_g{}^3$ |
| $[Zn(H_2O)_6]^{2+}$ | $> 10^7$ | $t_{2g}{}^6 e_g{}^4$ |

*These configurations assume octahedral geometry, even in cases where Jahn–Teller distortion is anticipated.

Data from R. B. Jordan, *Reaction Mechanisms of Inorganic and Organometallic Systems*, 3rd ed., Oxford (New York), 2007, p. 84

# Labile and inert electronic configurations

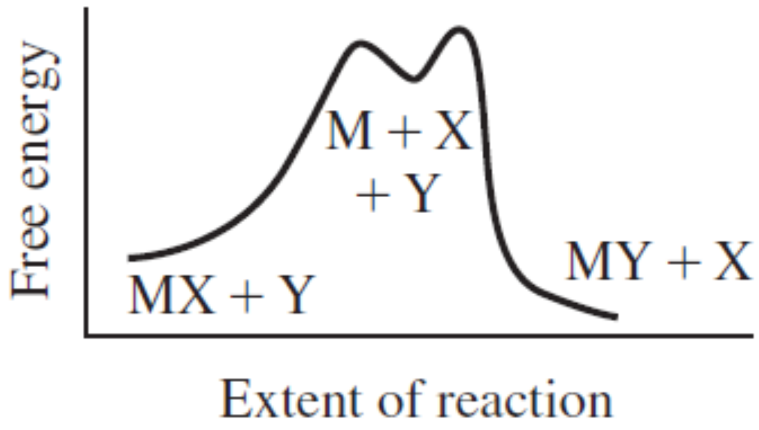
| Slow Reactions (Inert) |
|---|
| $d^3$, low-spin $d^4$, $d^5$, and $d^6$ |
| Strong-field $d^8$ (square planar) |

| Moderate Rate |
|---|
| |
| Weak-field $d^8$ |

| Fast Reactions (Labile) |
|---|
| $d^1$, $d^2$, high-spin $d^4$, $d^5$, and $d^6$ |
| $d^7$, $d^9$, $d^{10}$ |

# Mechanisms of ligand substitution

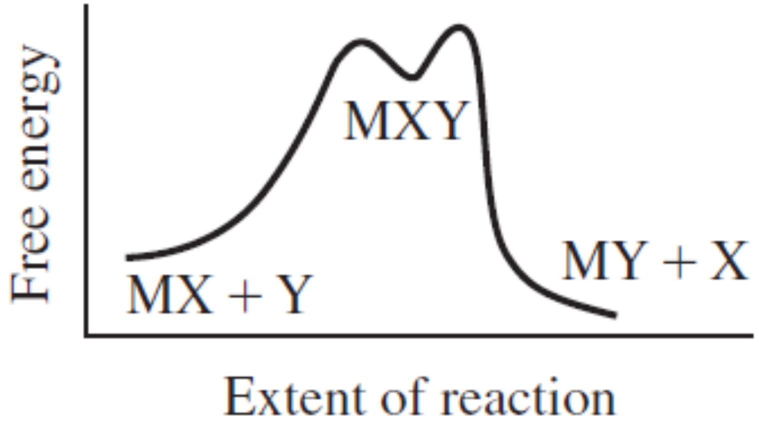
**Dissociative mechanism**



$MX_6 + Y \rightarrow MX_5 + X + Y \rightarrow MX_5Y + X$

Five coordinate intermediate

**Associative mechanism**



$MX_6 + Y \rightarrow MX_6Y \rightarrow MX_5Y + X$

Seven coordinate intermediate

# Other factors that influence octahedral dissociative substitution rates

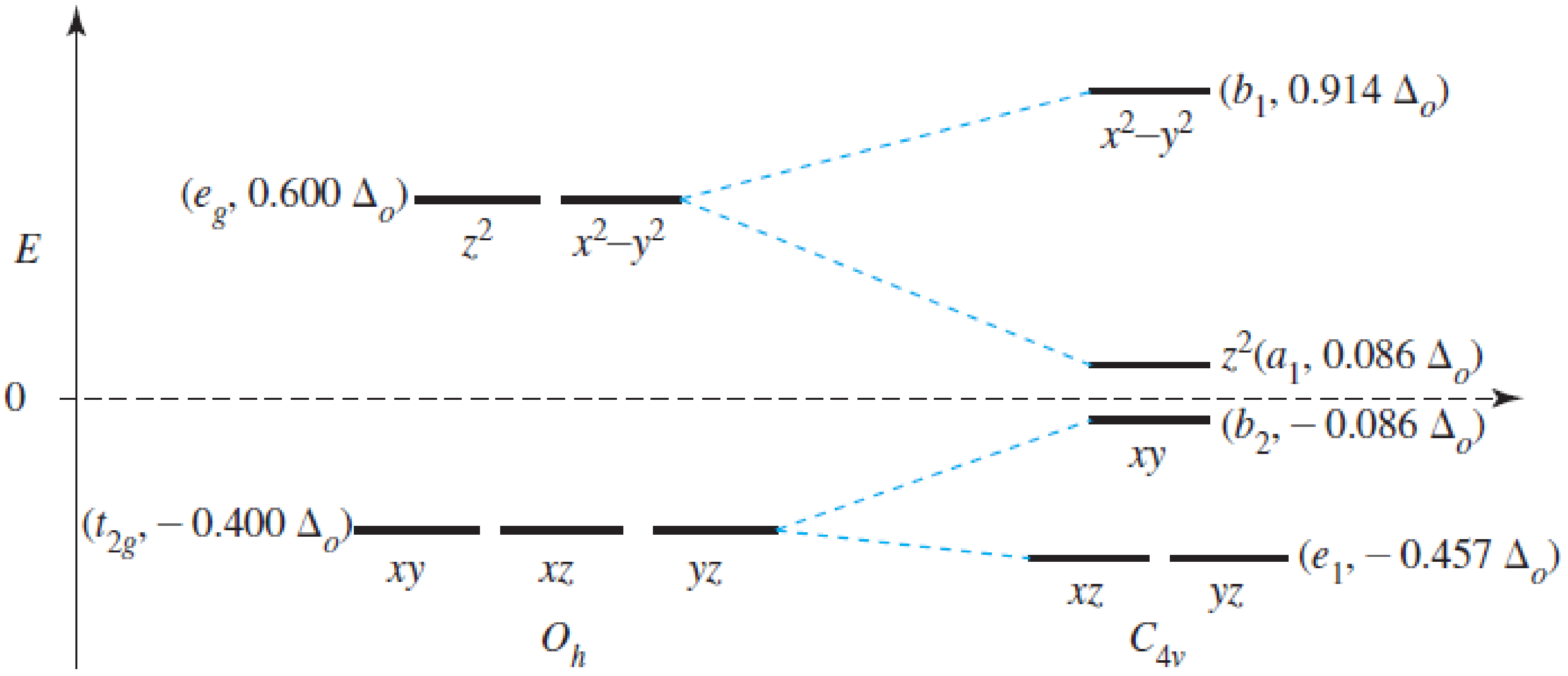
- **Oxidation state of the central ion**: central atoms with higher oxidation states have slower ligand exchange
  - Note: as we just discussed, must factor in d electron configuration when transition metals are the central atom
- **Ionic radius**: smaller ions have slower exchange rates

- Why?
  - Higher electrostatic attraction between central atom and ligands
  - This means stronger M-L bonds
  - Rate determining step in dissociative mechanism is initial breaking of M-L bond
  - The stronger the bond, the slower the rate

# Evidence that suggests a substitution reaction might be dissociative

- The rate of the reaction changes only slightly with changes in the incoming ligand (two rates differ by less than a factor of 10)
- Making the charge of the reactive complex more positive decreases the rate of substitution
- Steric crowding of the reactant complex increases the rate of reaction

# Ligand field activation energy in dissociative mechanism for octahedral complexes



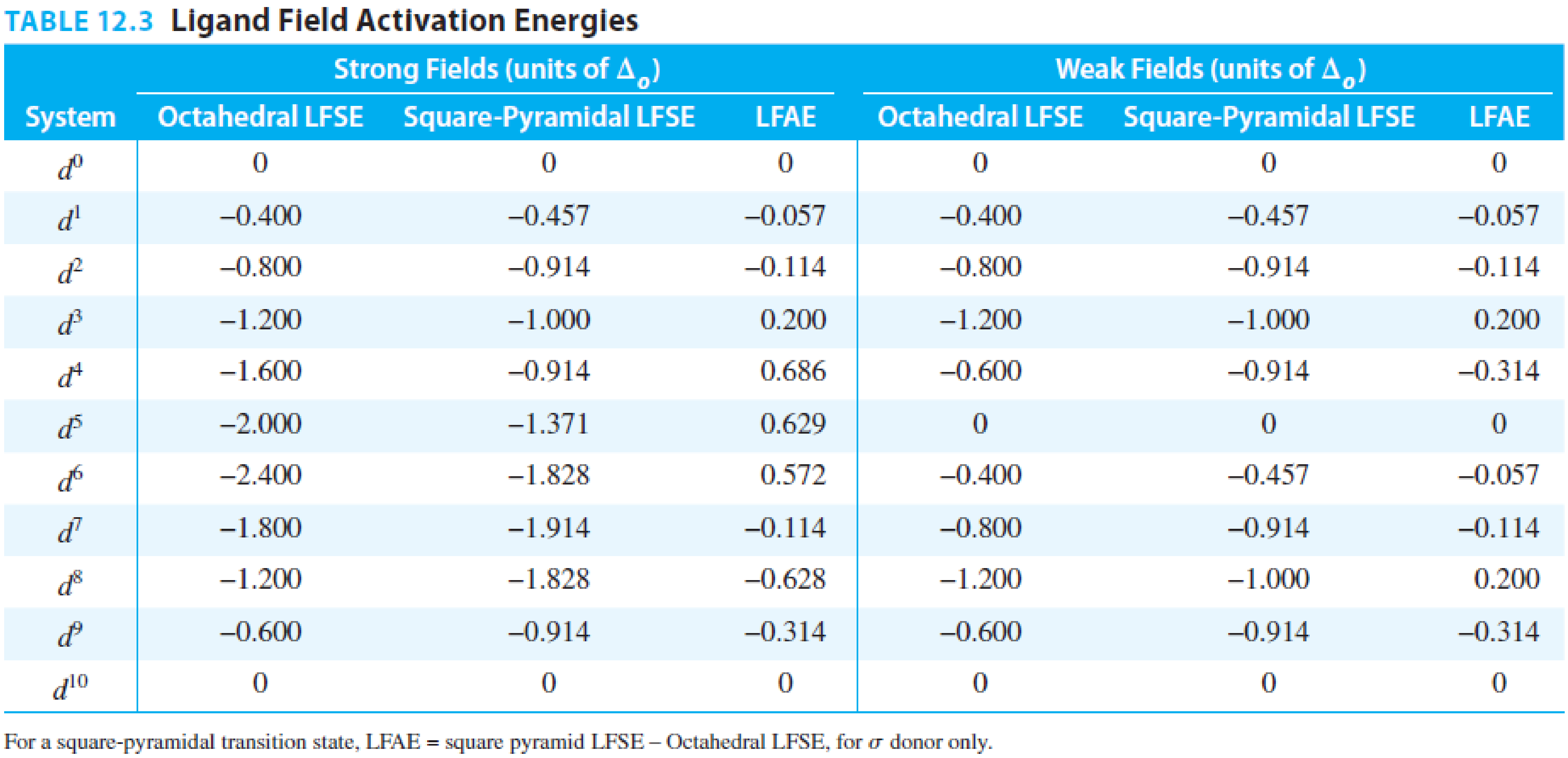


**TABLE 12.3 Ligand Field Activation Energies**

| | Strong Fields (units of $\Delta_o$) | | | Weak Fields (units of $\Delta_o$) | | |
|---|---|---|---|---|---|---|
| System | Octahedral LFSE | Square-Pyramidal LFSE | LFAE | Octahedral LFSE | Square-Pyramidal LFSE | LFAE |
| $d^0$ | 0 | 0 | 0 | 0 | 0 | 0 |
| $d^1$ | –0.400 | –0.457 | –0.057 | –0.400 | –0.457 | –0.057 |
| $d^2$ | –0.800 | –0.914 | –0.114 | –0.800 | –0.914 | –0.114 |
| $d^3$ | –1.200 | –1.000 | 0.200 | –1.200 | –1.000 | 0.200 |
| $d^4$ | –1.600 | –0.914 | 0.686 | –0.600 | –0.914 | –0.314 |
| $d^5$ | –2.000 | –1.371 | 0.629 | 0 | 0 | 0 |
| $d^6$ | –2.400 | –1.828 | 0.572 | –0.400 | –0.457 | –0.057 |
| $d^7$ | –1.800 | –1.914 | –0.114 | –0.800 | –0.914 | –0.114 |
| $d^8$ | –1.200 | –1.828 | –0.628 | –1.200 | –1.000 | 0.200 |
| $d^9$ | –0.600 | –0.914 | –0.314 | –0.600 | –0.914 | –0.314 |
| $d^{10}$ | 0 | 0 | 0 | 0 | 0 | 0 |

For a square-pyramidal transition state, LFAE = square pyramid LFSE – Octahedral LFSE, for $\sigma$ donor only.

# Associative mechanism for ligand substitution

- Less common than dissociative mechanism for octahedral complexes
- If rate depends on incoming ligand, likely associative

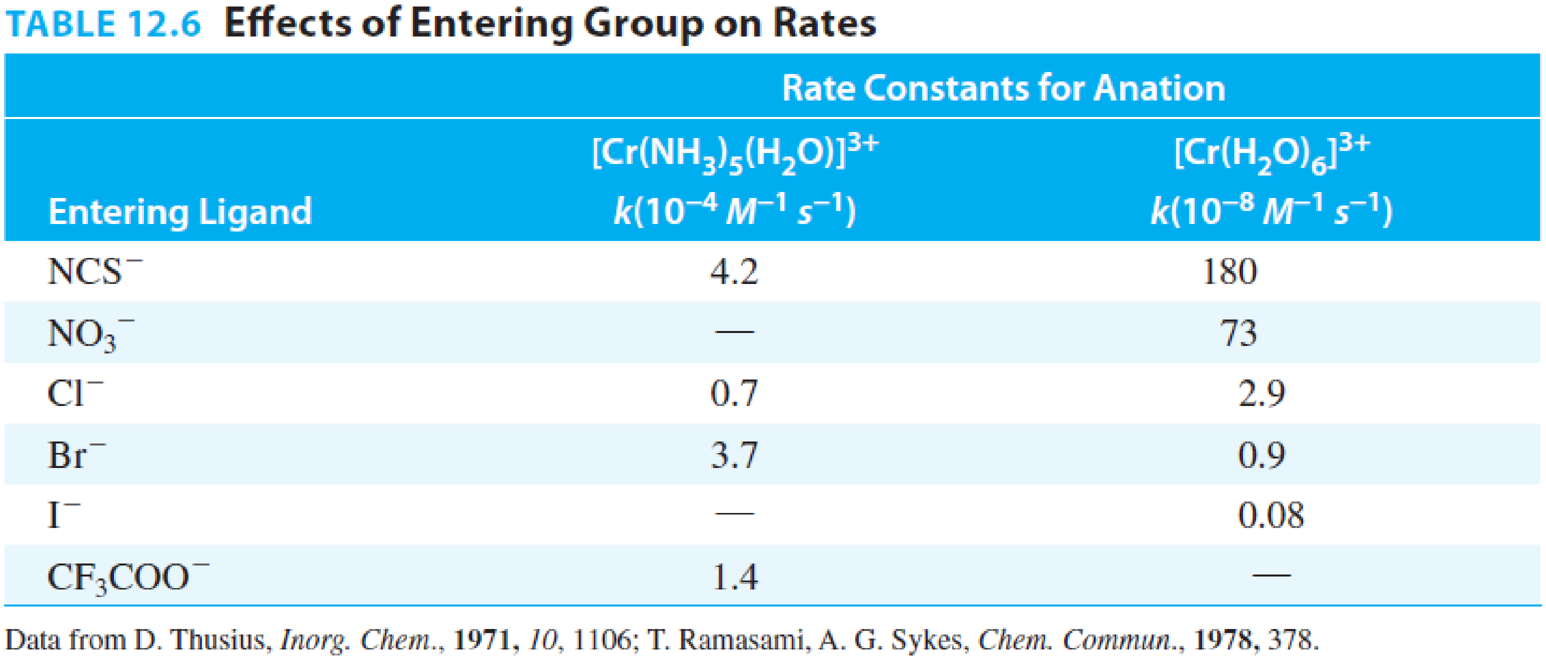


**TABLE 12.6 Effects of Entering Group on Rates**

| | Rate Constants for Anation | |
|---|---|---|
| Entering Ligand | $[Cr(NH_3)_5(H_2O)]^{3+}$ $k(10^{-4}\ M^{-1}\ s^{-1})$ | $[Cr(H_2O)_6]^{3+}$ $k(10^{-8}\ M^{-1}\ s^{-1})$ |
| $NCS^-$ | 4.2 | 180 |
| $NO_3^-$ | — | 73 |
| $Cl^-$ | 0.7 | 2.9 |
| $Br^-$ | 3.7 | 0.9 |
| $I^-$ | — | 0.08 |
| $CF_3COO^-$ | 1.4 | — |

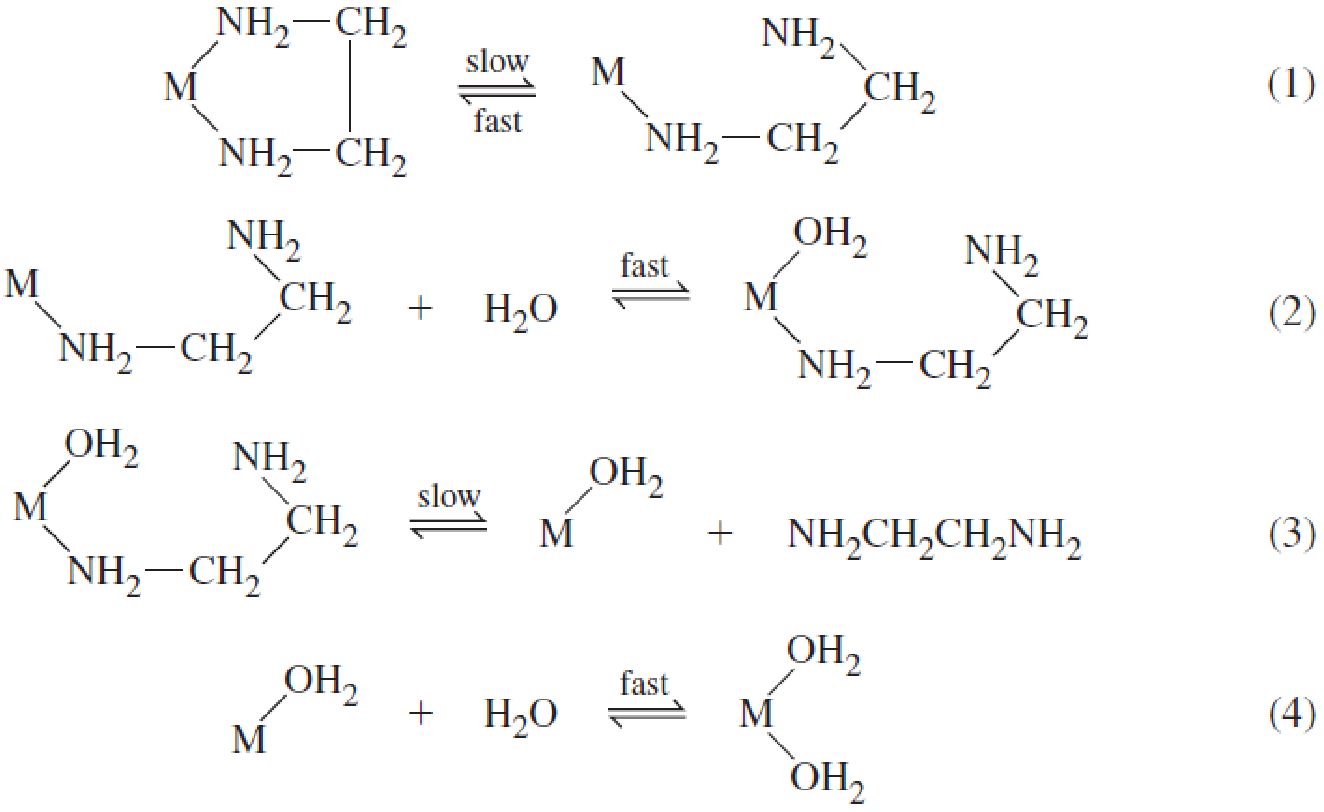
Data from D. Thusius, *Inorg. Chem.*, 1971, *10*, 1106; T. Ramasami, A. G. Sykes, *Chem. Commun.*, 1978, 378.

Dissociative

Associative

# The kinetic chelate effect

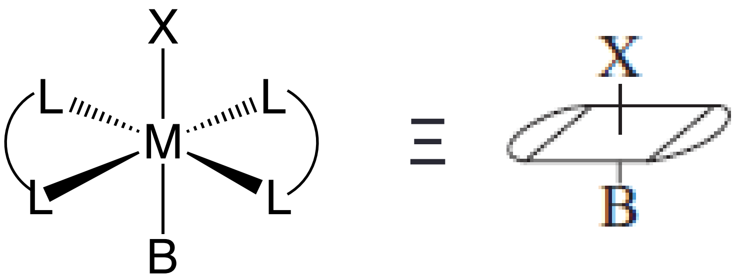
- In addition, once first atom detaches from metal center, kinetic barrier for reattachment is lower (rate faster) than for an additional atom to detach from the metal



# Stereochemistry of Reactions

# Dissociative substitution in *trans* octahedral metal complexes

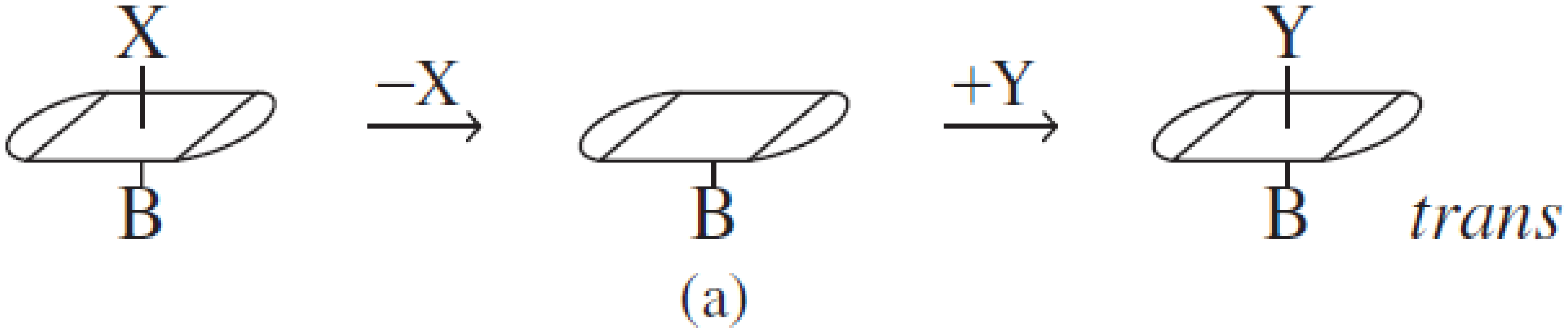
*trans* $M(LL)_2BX \;+\; Y \;\rightarrow$ ?? $M(LL)_2BY \;+\; X$



Three potential dissociative pathways

# Dissociative substitution in *trans* octahedral metal complexes

*trans* $M(LL)_2BX$ + Y → ?? $M(LL)_2BY$ + X

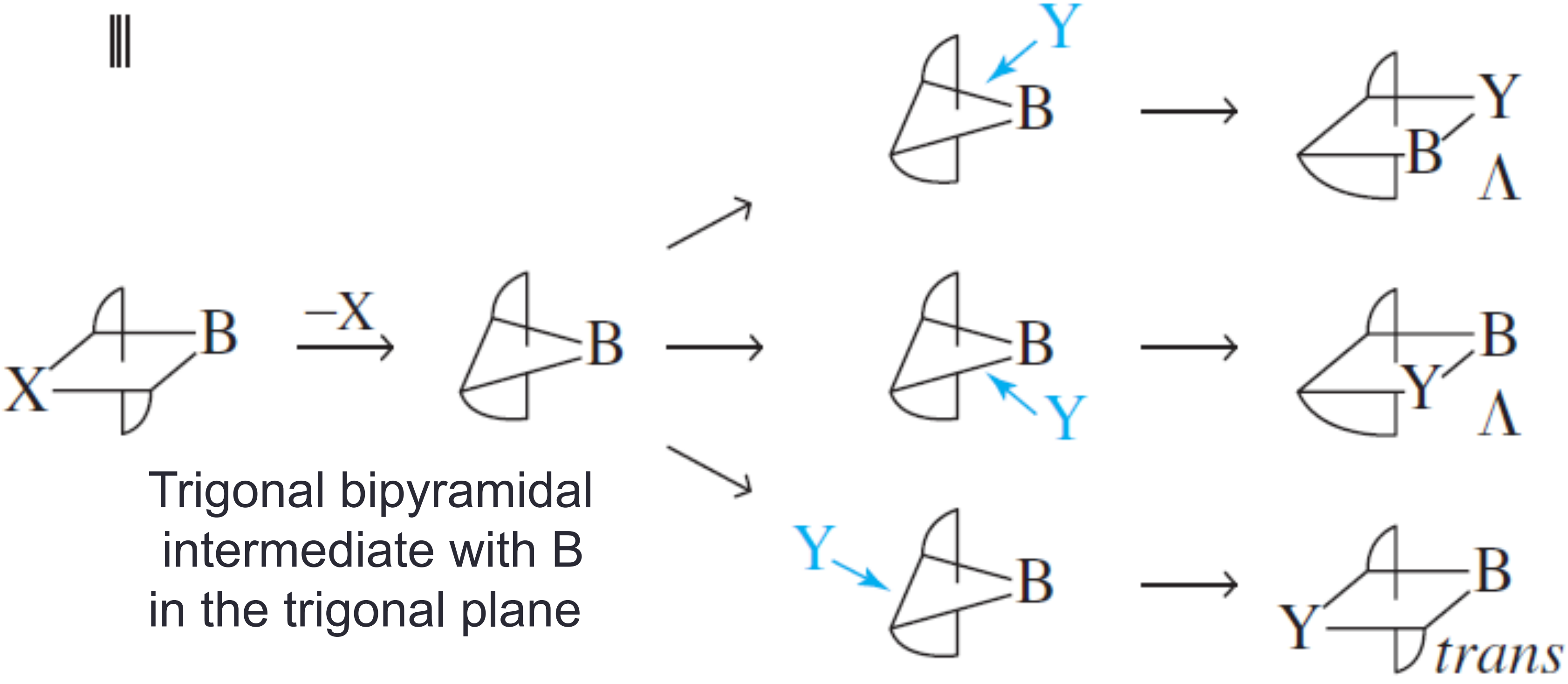


Square pyramidal intermediate

Incoming ligand binds to open site, *trans* configuration retained

# Dissociative substitution in *trans* octahedral metal complexes

*trans* $M(LL)_2BX$ + Y → ?? $M(LL)_2BY$ + X



Trigonal bipyramidal intermediate with B in the trigonal plane

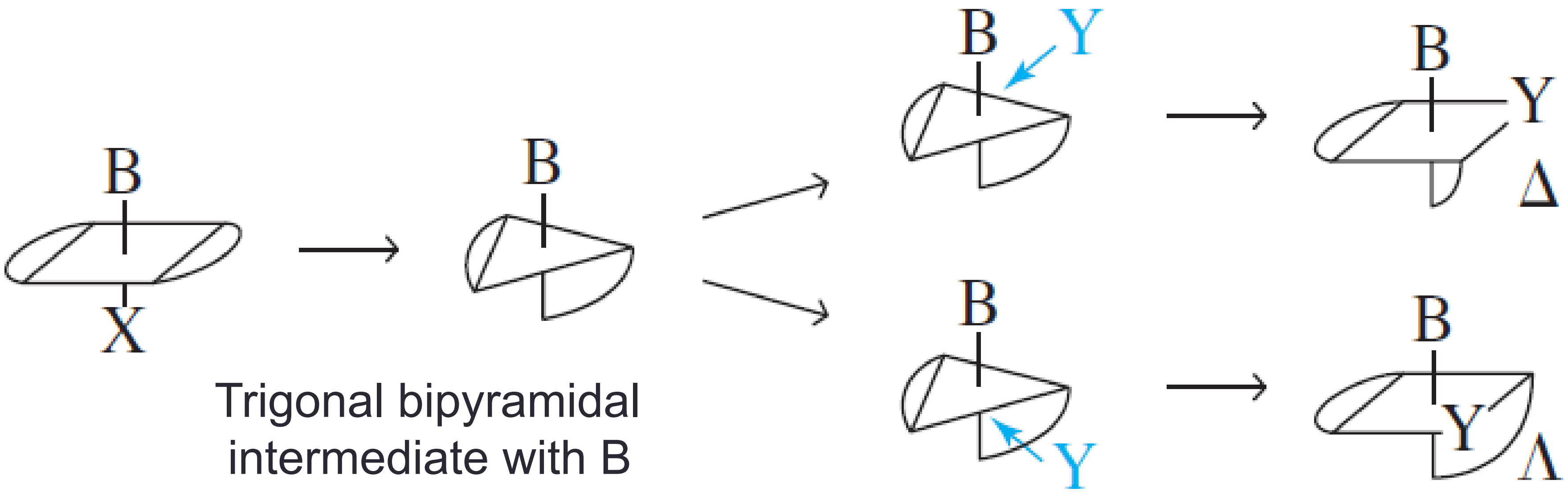
Y can attack from any side of the trigonal plane

Mixture of *cis* and *trans* products

# Dissociative substitution in *trans* octahedral metal complexes

*trans* M(LL)$_2$BX + Y → ?? M(LL)$_2$BY + X

⦀



Trigonal bipyramidal intermediate with B in axial position

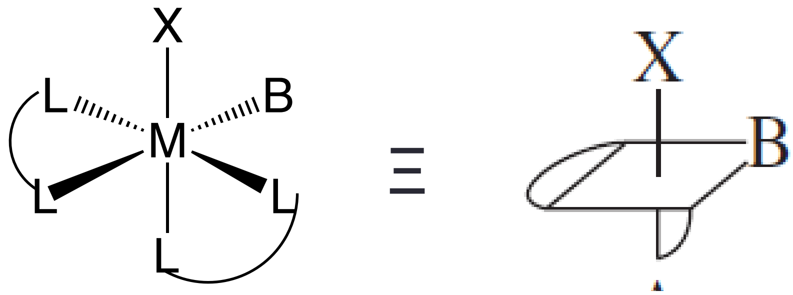
(c)

Y can attack at two positions

Only *cis* products

# Dissociative substitution in *cis* octahedral metal complexes

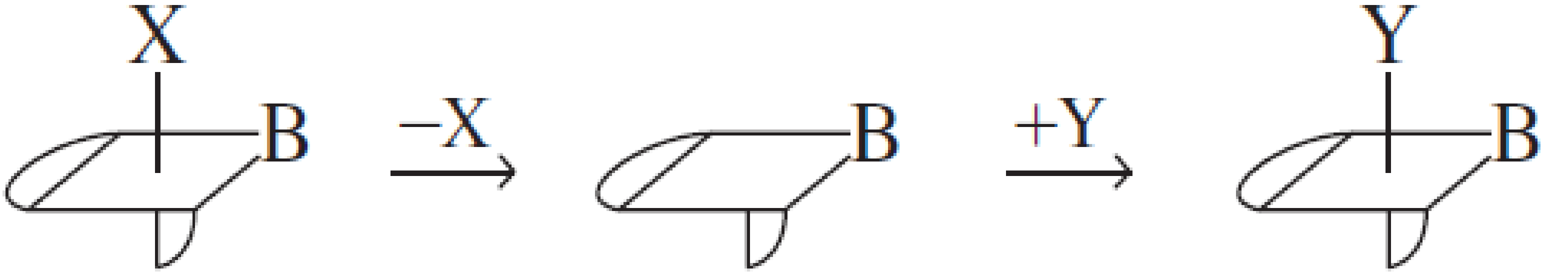
*cis* $M(LL)_2BX$ + Y → ?? $M(LL)_2BY$ + X



Three potential dissociative pathways

# Dissociative substitution in *cis* octahedral metal complexes

*cis* M(LL)$_2$BX + Y → ?? M(LL)$_2$BY + X

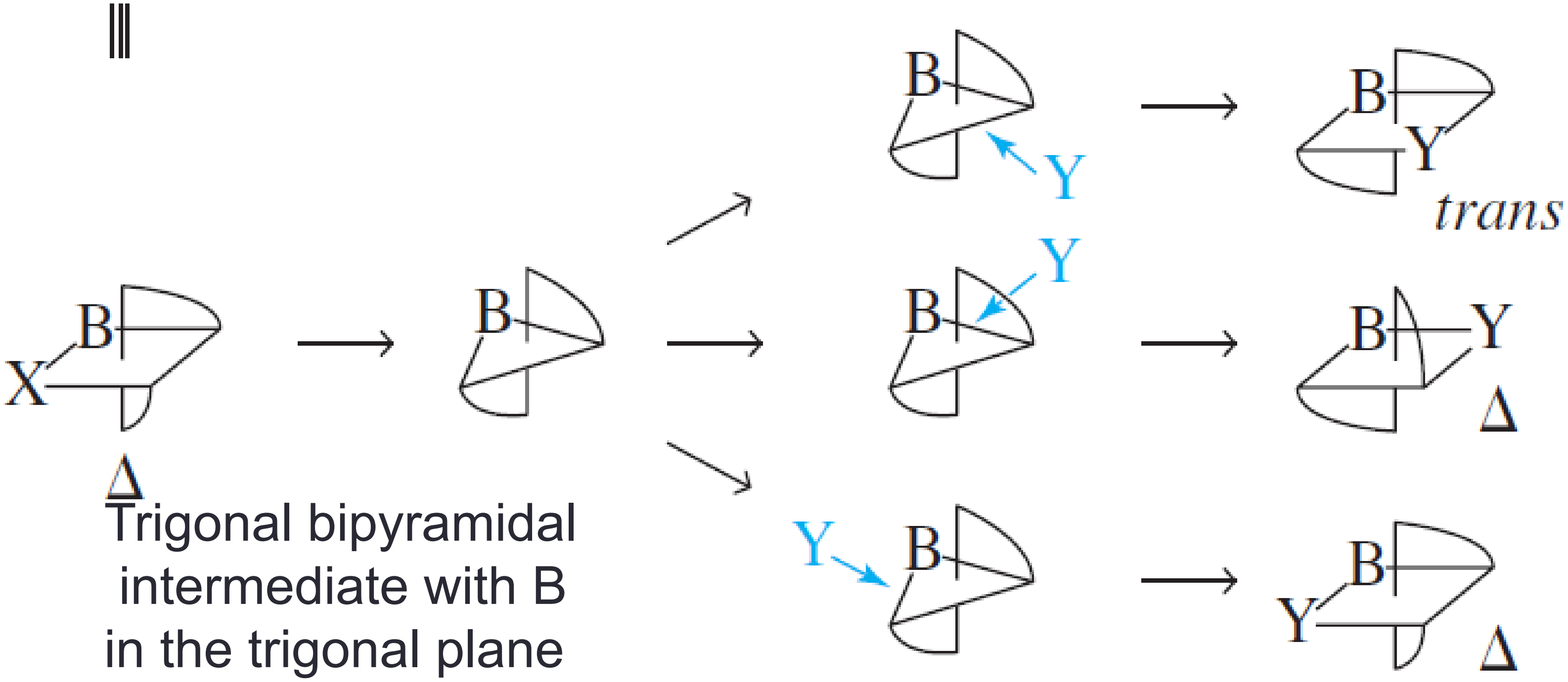


Square pyramidal intermediate

Incoming ligand binds to open site, *cis* configuration retained

# Dissociative substitution in *cis* octahedral metal complexes

*cis* $M(LL)_2BX + Y \rightarrow ?? M(LL)_2BY + X$



Trigonal bipyramidal intermediate with B in the trigonal plane

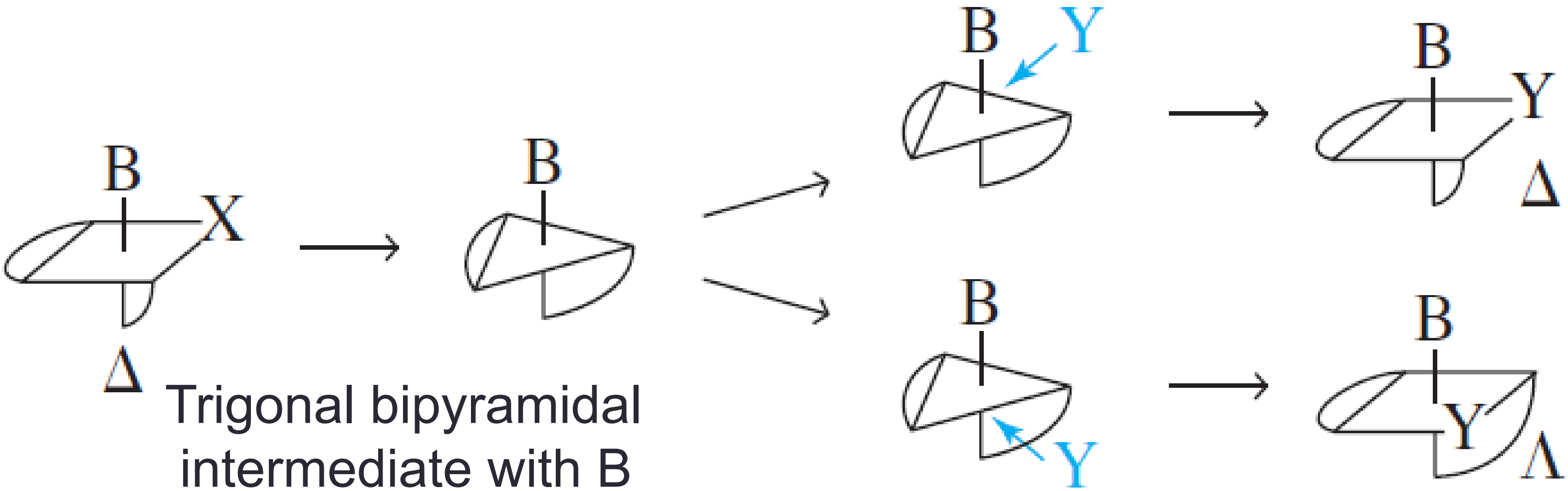
Y can attack from any side of the trigonal plane

Mixture of *cis* and *trans* products

# Dissociative substitution in *cis* octahedral metal complexes

*cis* $M(LL)_2BX$ + Y → ?? $M(LL)_2BY$ + X

⦀



Trigonal bipyramidal intermediate with B in axial position

(c)

Y can attack at two positions

Only *cis* products

# Substitution reactions in square-planar complexes

- In square planar complexes, substitution reactions tend to follow an associative-type mechanism
- Evidence for this comes from the large effect the incoming ligand has on reaction rates (Table 12.12)

$$ML_2TX + Y \rightarrow ML_2TXY \rightarrow ML_2TY$$

*Before going in to a specific example, we need to learn a little bit about hard soft acid base theory, which helps explain why certain M-L bonds are stronger than others*

Description of hard and soft acids and bases, section 6.6.1 MFT, Tables 6.14 and 6.15

# Hard Soft Acid Base Theory

- Metal-ligand bonds are a result of the interaction between a Lewis acid and a Lewis base
- These acids and bases can be described as either *hard* or *soft*
- Hard acid or base: small, compact, non-polarizable
  - Hard acids: typically cations with large postive charge (3+ or larger), cations whose d electrons aren't available for π bonding (e.g. alkali and alkaline earth cations)
  - Hard bases: smaller anions, like $F^-$
- Soft acid or base: larger, less compact, more polarizable
  - Soft acids: typically cations with d electrons are available for π bonding, neutral metals, 1+ cations, 2+ cations that are heavier
  - Soft bases: larger anions, like $I^-$

Description of hard and soft acids and bases, section 6.6.1 MFT, Tables 6.14 and 6.15

# Hard Soft Acid Base Theory

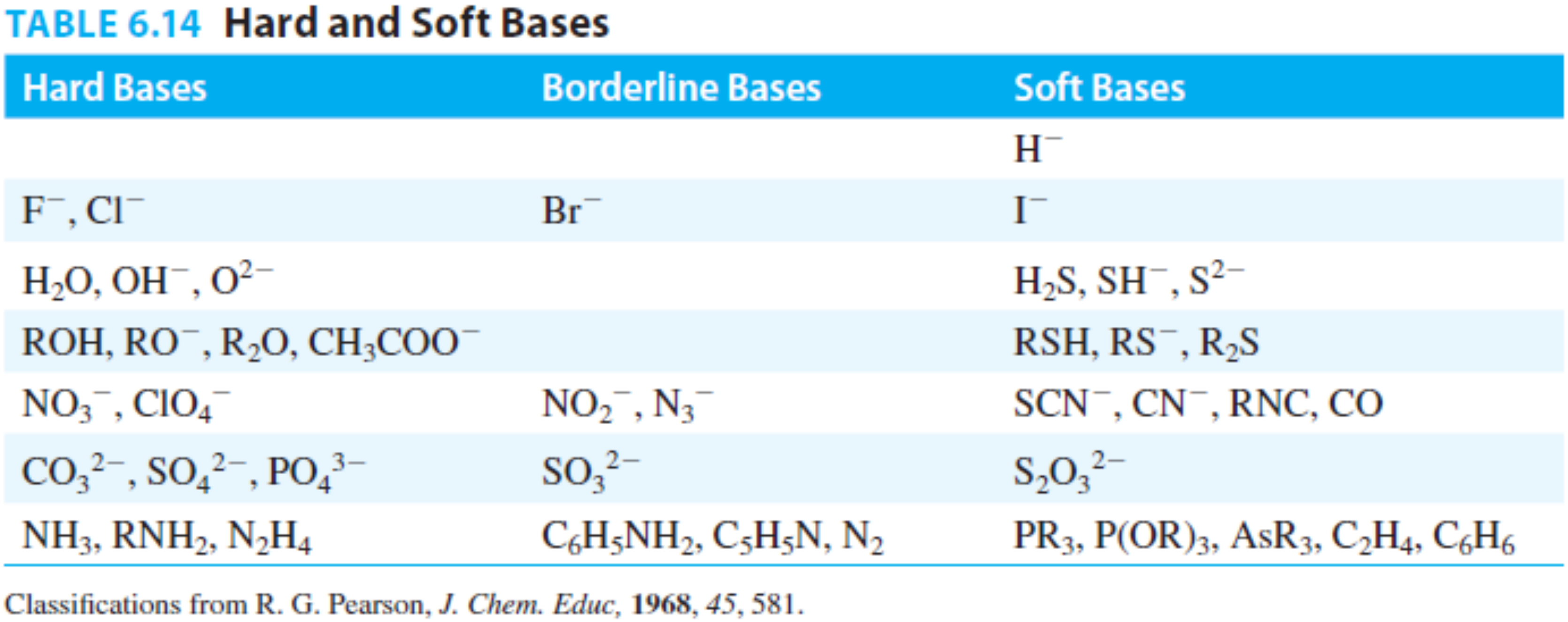


**TABLE 6.14 Hard and Soft Bases**

| Hard Bases | Borderline Bases | Soft Bases |
|---|---|---|
| | | $H^-$ |
| $F^-$, $Cl^-$ | $Br^-$ | $I^-$ |
| $H_2O$, $OH^-$, $O^{2-}$ | | $H_2S$, $SH^-$, $S^{2-}$ |
| $ROH$, $RO^-$, $R_2O$, $CH_3COO^-$ | | $RSH$, $RS^-$, $R_2S$ |
| $NO_3^-$, $ClO_4^-$ | $NO_2^-$, $N_3^-$ | $SCN^-$, $CN^-$, $RNC$, $CO$ |
| $CO_3^{2-}$, $SO_4^{2-}$, $PO_4^{3-}$ | $SO_3^{2-}$ | $S_2O_3^{2-}$ |
| $NH_3$, $RNH_2$, $N_2H_4$ | $C_6H_5NH_2$, $C_5H_5N$, $N_2$ | $PR_3$, $P(OR)_3$, $AsR_3$, $C_2H_4$, $C_6H_6$ |

Classifications from R. G. Pearson, *J. Chem. Educ*, **1968**, *45*, 581.

Hard bases: O donors, amines, F-, Cl-

Borderline bases: Br-, pyridine

Soft bases: S, P donors, pi acceptors, I-

Description of hard and soft acids and bases, section 6.6.1 MFT, Tables 6.14 and 6.15

# Hard Soft Acid Base Theory

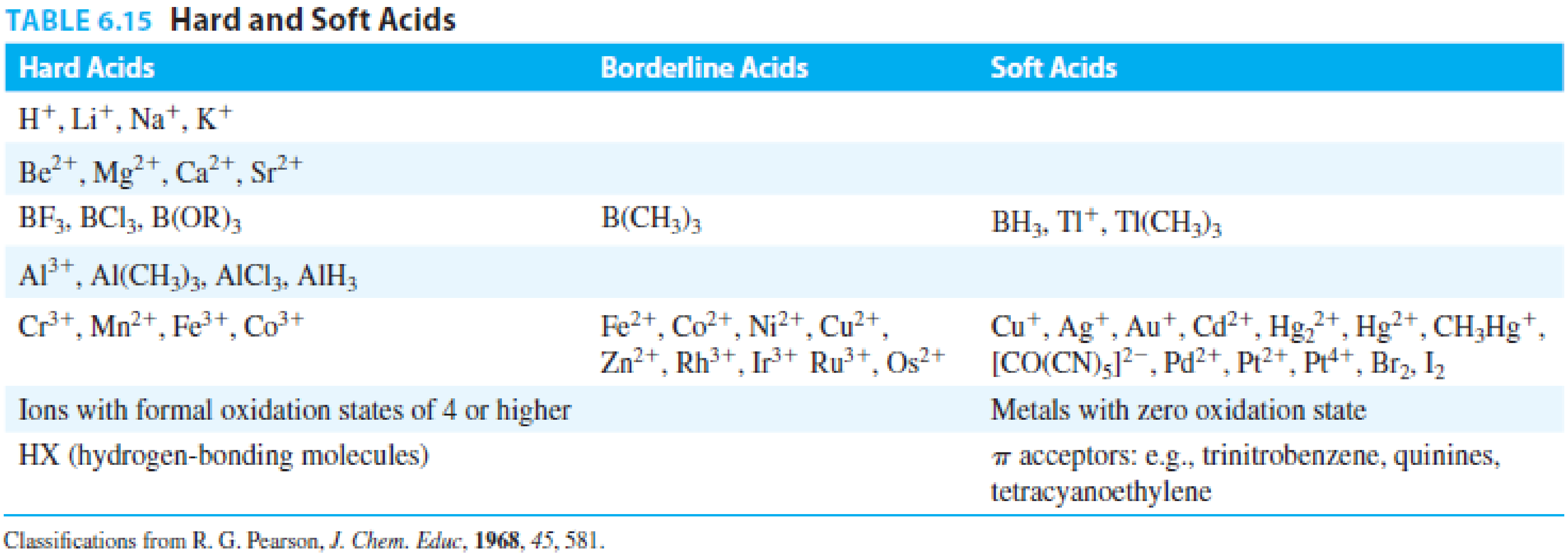


**TABLE 6.15 Hard and Soft Acids**

| Hard Acids | Borderline Acids | Soft Acids |
|---|---|---|
| $H^+$, $Li^+$, $Na^+$, $K^+$ | | |
| $Be^{2+}$, $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$ | | |
| $BF_3$, $BCl_3$, $B(OR)_3$ | $B(CH_3)_3$ | $BH_3$, $Tl^+$, $Tl(CH_3)_3$ |
| $Al^{3+}$, $Al(CH_3)_3$, $AlCl_3$, $AlH_3$ | | |
| $Cr^{3+}$, $Mn^{2+}$, $Fe^{3+}$, $Co^{3+}$ | $Fe^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Rh^{3+}$, $Ir^{3+}$ $Ru^{3+}$, $Os^{2+}$ | $Cu^+$, $Ag^+$, $Au^+$, $Cd^{2+}$, $Hg_2^{2+}$, $Hg^{2+}$, $CH_3Hg^+$, $[CO(CN)_5]^{2-}$, $Pd^{2+}$, $Pt^{2+}$, $Pt^{4+}$, $Br_2$, $I_2$ |
| Ions with formal oxidation states of 4 or higher | | Metals with zero oxidation state |
| HX (hydrogen-bonding molecules) | | $\pi$ acceptors: e.g., trinitrobenzene, quinines, tetracyanoethylene |

Classifications from R. G. Pearson, *J. Chem. Educ*, **1968**, *45*, 581.

Hard acids: $Fe^{3+}$, $Co^{3+}$, $Mn^{2+}$, $M^{4+}$

Borderline acids: $Fe^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$

Soft acids: $Cu^+$, $Ag^+$, $Au^+$, $Pd^{2+}$, $Pt^{2+}$

Description of hard and soft acids and bases, section 6.6.1 MFT, Tables 6.14 and 6.15

# Hard Soft Acid Base Theory

- In metal-ligand complexes, hard-hard and soft-soft interactions tend to be stronger (have higher thermodynamic stability) than hard-soft interactions

- Example: $Cu^+$ will form stronger interactions with $S^{2-}$ than with $F^-$

- This can affect the reactivity properties of your metal complexes

# Substitution reactions in square-planar complexes

- In square planar complexes, substitution reactions tend to follow an associative-type mechanism
- Evidence for this comes from the large effect the incoming ligand has on reaction rates (Table 12.12)

$$ML_2TX + Y \rightarrow ML_2TXY \rightarrow ML_2TY$$

For example, if M is Pt(II): the identity of Y affect rate of reaction:

$Cl^- < Br^- < I^- < SCN^- < PR_3$

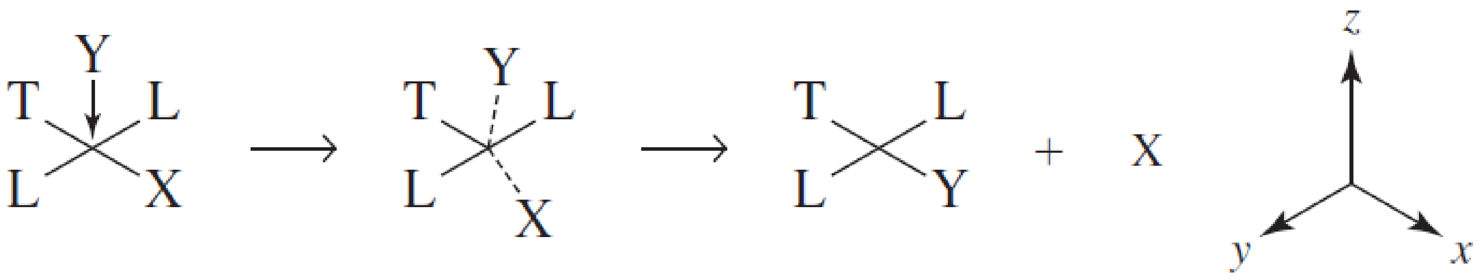
Trend follows HSAB (Pt(II) is soft)

# Substitution reactions in square-planar complexes

- Mechanism 1:

1) Formation of trigonal bipyramidal intermediate following association of Y
2) Dissociation of X to form square planar complex $ML_2TX$

$$ML_2TX + Y \rightarrow ML_2TXY \rightarrow ML_2TY$$



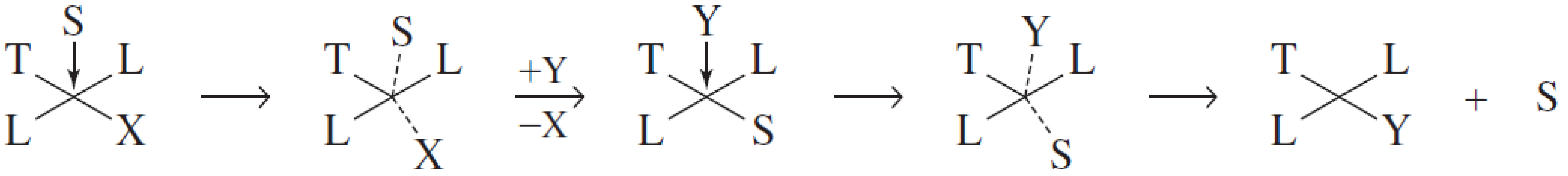
(a)

# Substitution reactions in square-planar complexes

- Mechanism 2:

1) Association of solvent (S),
2) Dissociation of ligand X
3) Association of ligand Y
4) Dissociation of solvent (S)

$$ML_2TX + S \rightarrow ML_2TXS \rightarrow ML_2TS + Y \rightarrow ML_2TSY \rightarrow ML_2TY$$

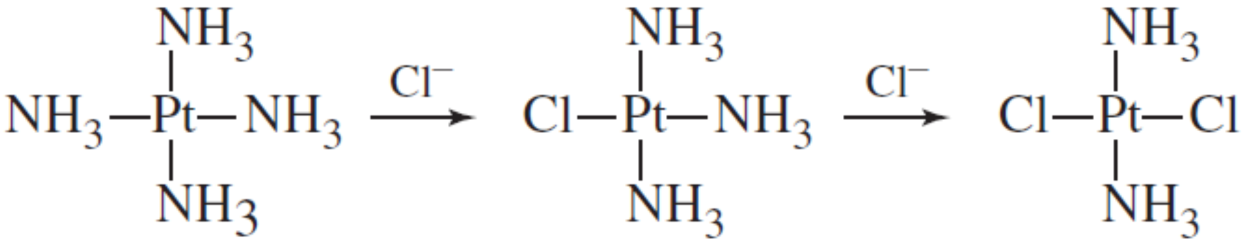


(b)

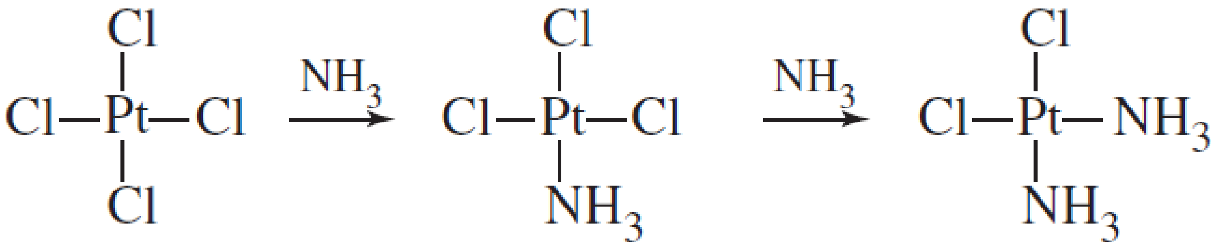
# The *trans* effect

- Observation by Chernyaev: in square planar Pt(II) compounds, certain ligands are more easily replaced than others (faster kinetics)

(a)



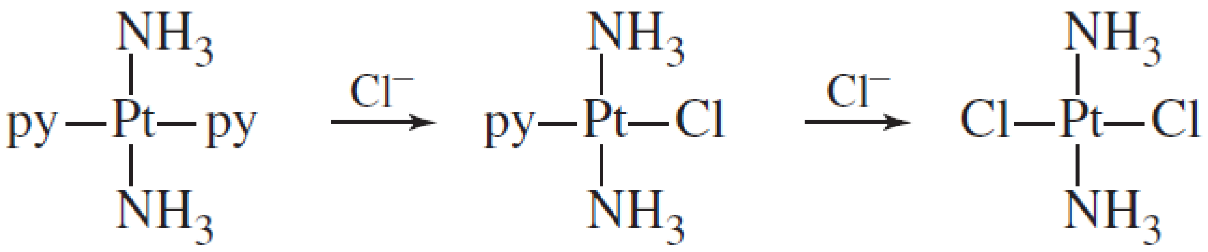
(b)



# The *trans* effect

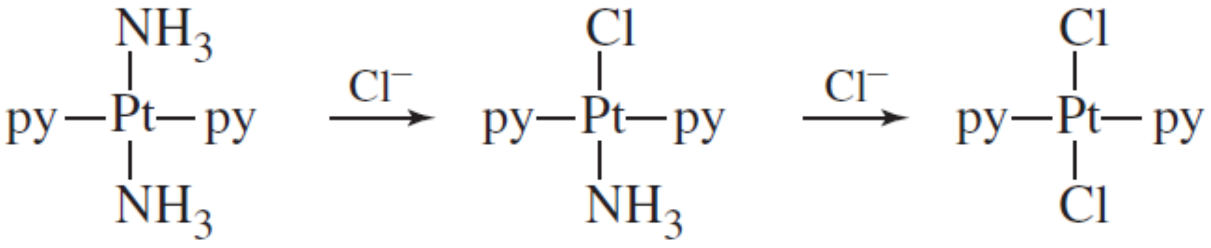
- Observation by Chernyaev: in square planar Pt(II) compounds, certain ligands are more easily replaced than others (faster kinetics)

(c)



$$\begin{array}{c}\mathrm{NH_3}\\ |\\ \mathrm{py{-}Pt{-}py}\\ |\\ \mathrm{NH_3}\end{array}\xrightarrow{\mathrm{Cl^-}}\begin{array}{c}\mathrm{NH_3}\\ |\\ \mathrm{py{-}Pt{-}Cl}\\ |\\ \mathrm{NH_3}\end{array}\xrightarrow{\mathrm{Cl^-}}\begin{array}{c}\mathrm{NH_3}\\ |\\ \mathrm{Cl{-}Pt{-}Cl}\\ |\\ \mathrm{NH_3}\end{array}$$

(d)



$$\begin{array}{c}\mathrm{NH_3}\\ |\\ \mathrm{py{-}Pt{-}py}\\ |\\ \mathrm{NH_3}\end{array}\xrightarrow{\mathrm{Cl^-}}\begin{array}{c}\mathrm{Cl}\\ |\\ \mathrm{py{-}Pt{-}py}\\ |\\ \mathrm{NH_3}\end{array}\xrightarrow{\mathrm{Cl^-}}\begin{array}{c}\mathrm{Cl}\\ |\\ \mathrm{py{-}Pt{-}py}\\ |\\ \mathrm{Cl}\end{array}$$

# The *trans* effect

- Observation by Chernyaev: in square planar Pt(II) compounds, certain ligands are more easily replaced than others (faster kinetics)

## Ligand ranking for trans effect

$$\mathrm{CN^- \sim CO \sim C_2H_4 > PH_3 \sim SH_2 > NO_2^- > I^- > Cl^- > NH_3 \sim py > OH^- > H_2O}$$

**Large trans effect**

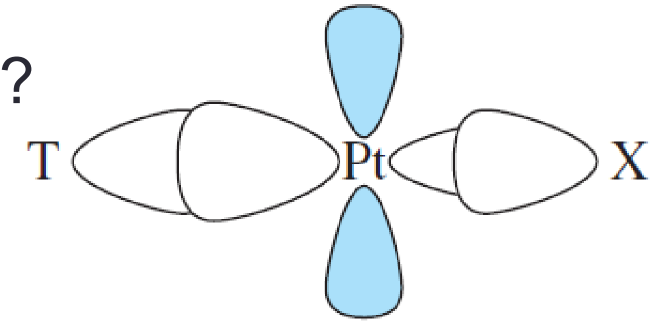
**Small trans effect**

# Explanations of *trans* effect: sigma bonding

- Sigma bonding effects:
  - the Pt-X bond will be influenced by the Pt-T bond (both X and T ligands sigma bond with the $d_{x^2-y^2}$ orbital)

  - When the Pt-T bond is stronger (if T is a better sigma donor), the P-X bond is weaker: this thermodynamic effect is called *trans* influence

  - What makes a good sigma donor?

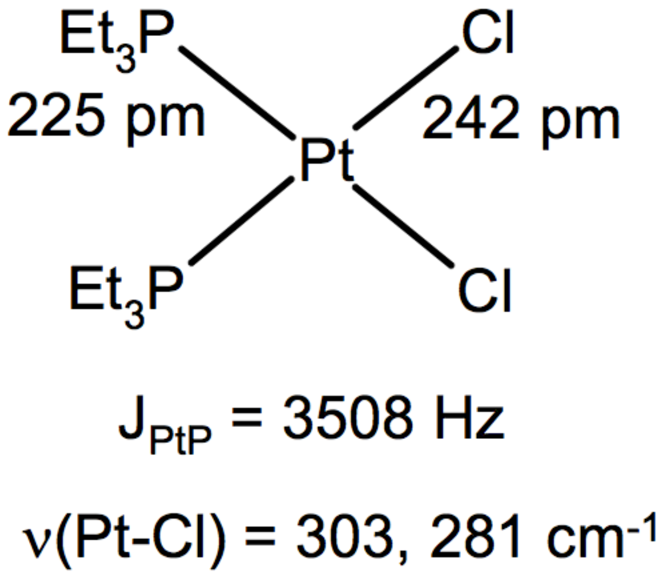


# Explanations of *trans* effect: sigma bonding

- Sigma bonding effects:
  - Strong sigma donors include $H^-$, $PR_3$, $I^-$, $CH_3^-$

$H^- > PR_3 > SCN^- > I^- \sim CH_3^- \sim CO \sim CN^- > Br^- > Cl^- > NH_3 > OH^-$

**Ranking of sigma donor strength**



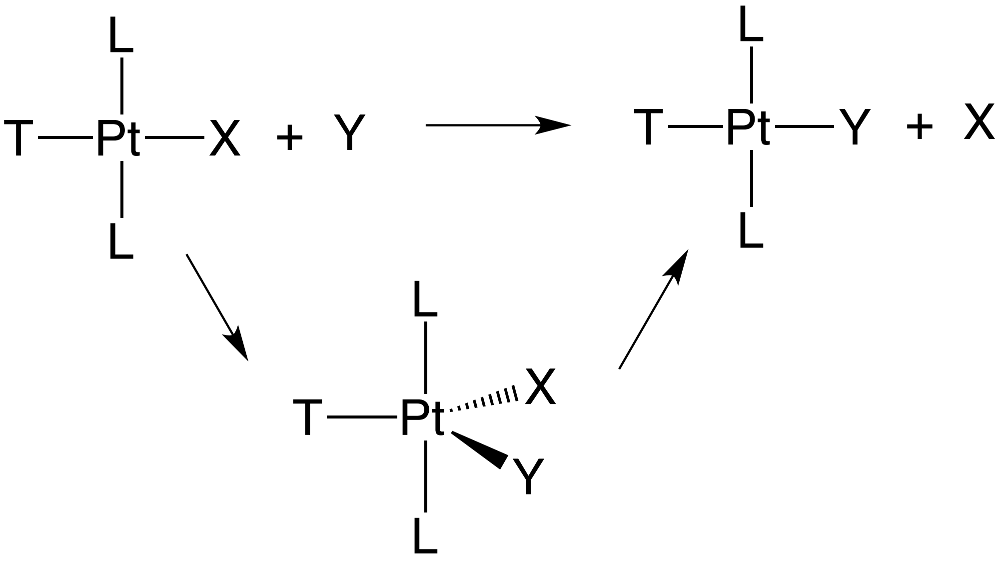
Bonds *trans* to a ligand are affected by that ligand. Strong sigma donor weakens the trans bond and thus lengthens it

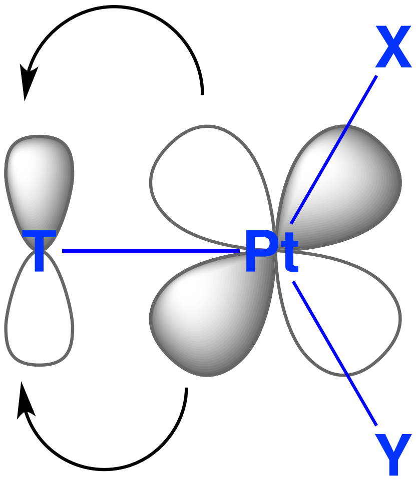
# Explanations of *trans* effect: pi bonding

- Pi bonding effects:
  - Pi acceptors pull electron density away from the metal center, stabilize 5-coordinate transition state during ligand substitution

$C_2H_4 \sim CO > CN^- > NO_2^- > SCN^- > I^- > Br^- > Cl^- > NH_3 > OH^-$

**Ranking of pi acceptor ability**





# The *trans* effect

- Final ligand ranking a result of both pi and sigma effects

## Ligand ranking for trans effect

$CN^- \sim CO \sim C_2H_4 > PH_3 \sim SH_2 > NO_2^- > I^- > Cl^- > NH_3 \sim py > OH^- > H_2O$

**Large trans effect** **Small trans effect**

Strong pi acceptor → strong sigma donor → neither strong sigma donor or pi acceptor

# Take home messages 2

- Reaction stereochemistry is influenced by geometry of transition state
  - In octahedral:square pyramidal vs. trigonal bipyramidal intermediate influences the product distribution

- In square planar complexes, the *trans* effect results in the preferential substitution of certain ligands over others
  - Result of sigma and pi interactions between the metal and ligands.

- You can use this information to predict what products will form in reactions