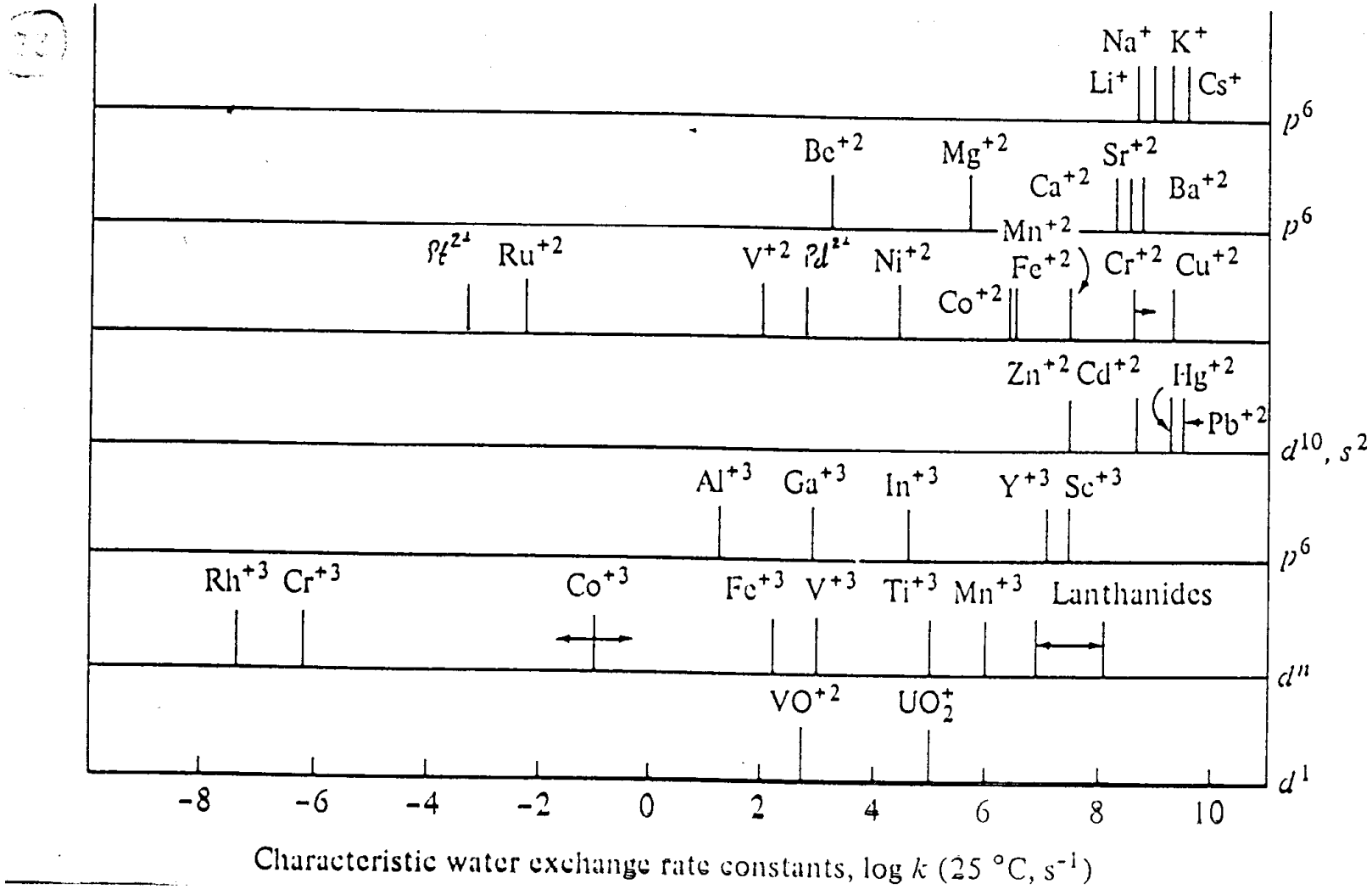
"Complexes that undergo complete ligand exchange within 1 minute at 25 ˚C are labile."

Henry Taube (1915-2005),
Nobel laureate of 1983



Which d^n configuration should provide inert octahedral complexes ?

Table 11.1 Change in LFSE (units *Dq*)[a] upon changing a 6-coordinate complex to a 5-coordinate (square pyramidal) or a 7-coordinate (pentagonal bipyramidal) species

	High spin		Low spin	
System	C.N. = 5	C.N. = 7	C.N. = 5	C.N. = 7
d^0	0	0	0	0
d^1	+0.57	+1.28	+0.57	+1.28
d^2	+1.14	+2.56	+1.14	+2.56
d^3	−2.00	−4.26	−2.00	−4.26
d^4	+3.14	−1.07	−1.43	−2.98
d^5	0	0	−0.86	−1.70
d^6	+0.57	+1.28	−4.00	−8.52
d^7	+1.14	+2.56	+1.14	−5.34
d^8	−2.00	−4.26	−2.00	−4.26
d^9	+3.14	−1.07	+3.14	−1.07
d^{10}	0	0	0	0

[a] The common convention is used: Negative quantities refer to *loss* of LFSE and destabilization of the complex.

SOURCE: Modified from F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed., Wiley, New York, 1967. Used with permission.

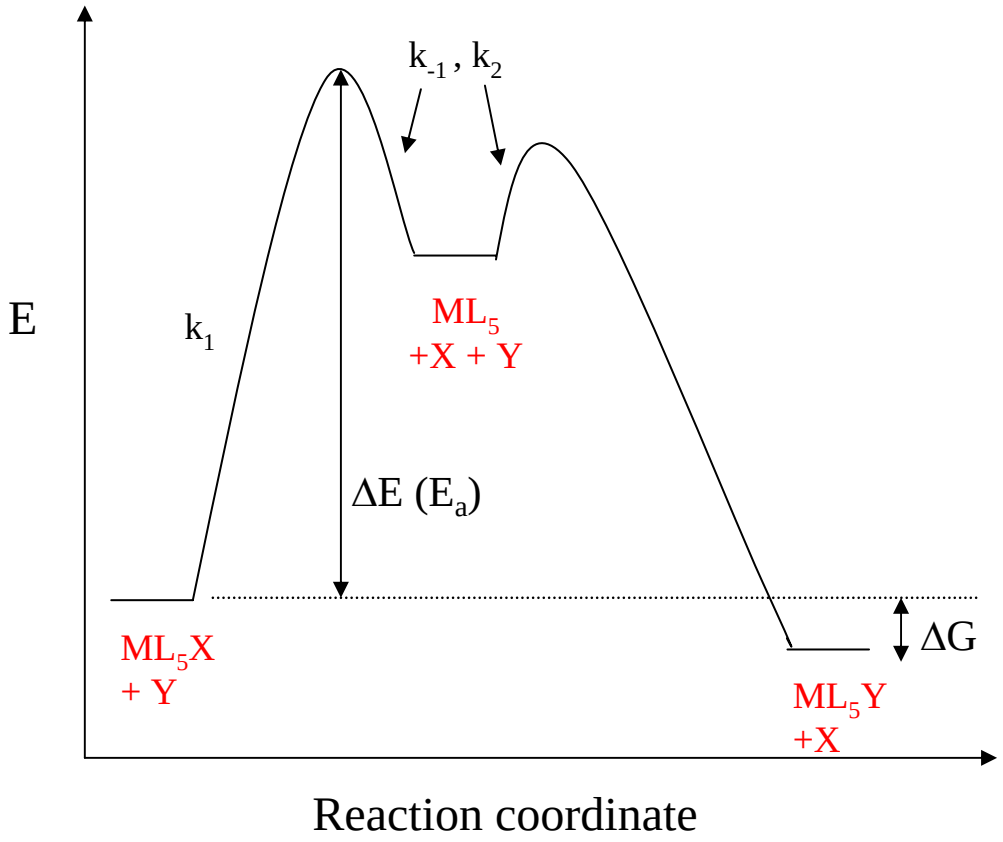
Inert Complexes
d^3 & d^8,
low spin d^4-d^6

Limiting Reaction Mechanisms for Ligand Substitution Reactions

D = Dissociative ~ S_N1

From C.N. = 6 to C.N. =5

Reaction Profile



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

$$ML_5 + Y \xrightarrow{k_2} ML_5Y$$

$k_1 << k_{-1} < k_2$

What are the kinetics of reactions proceeding via the **D** mechanism ?

Kinetics of reactions proceeding via the **D** mechanism

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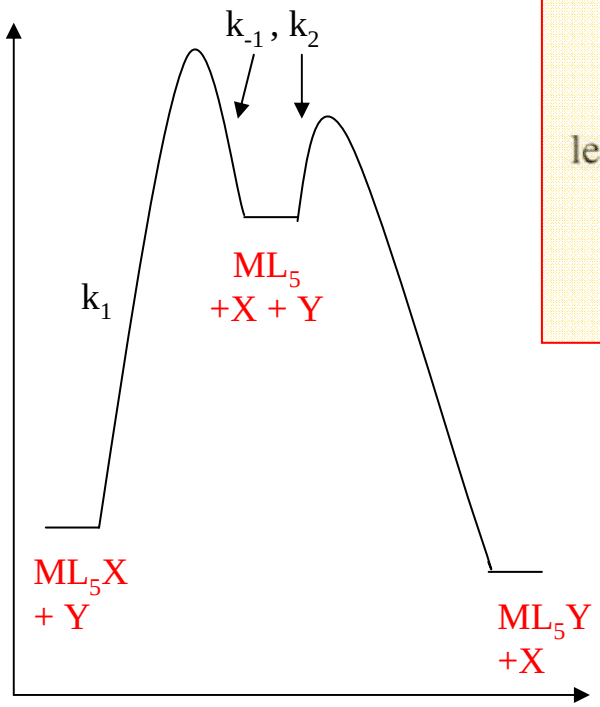
Reaction Profile



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

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:

$$\frac{d[ML_5Y]}{dt} = \frac{k_2k_1[ML_5X][Y]}{k_{-1}[X] + k_2[Y]}$$

But: $k_{-1}[X] << k_2[Y]$, because $k_{-1} < k_2$ and (usually) $[X] << [Y]$.

This leads to: **$d[ML_5Y]/dt = k_1[ML_5X]$**

The reaction is 1st order in substrate and hence, the rate of substitution should be independent of Y.

A simple case of a reaction proceeding via the **D** mechanism

Rate Constants for Substitution Reactions of $[Ni(H_2O)_6]^{2+}$

$$[Ni(H_2O)_6]^{2+} + L \xrightarrow{k} [Ni(H_2O)_5L]^{n+} + H_2O$$

L	k, s^{-1}	log k
F^-	8×10^3	3.9
SCN^-	6×10^3	3.8
CH_3COO^-	30×10^3	4.3
NH_3	3×10^3	3.5
H_2O	25×10^3	4.4

Source: Data from R. G. Wilkins, *Acc. Chem. Res.* 3 (1970): 408.

The rate is **independent** on the identity of L, the **entering ligand**

Another case of a reaction proceeding via the **D** mechanism

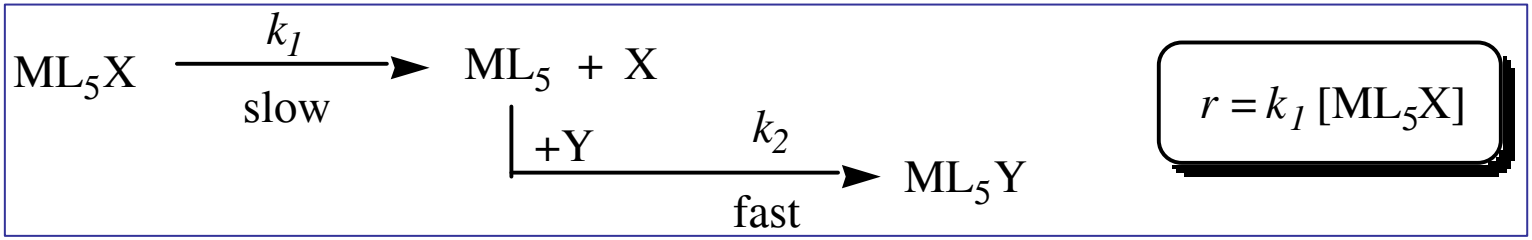
$$[Co(NH_3)_5L]^{2+} + H_2O \xrightarrow{k} [Co(NH_3)_5(H_2O)]^{3+} + L^-$$

	L	k, s^{-1}	K_a, M^{-1}	
Slowest rate of reaction				Strongest M — L bonds
↑	NCS^-	5.0×10^{-10}	470	↑
	F^-	8.6×10^{-8}	20	
	$H_2PO_4^-$	2.6×10^{-7}	7.4	
	Cl^-	1.7×10^{-6}	1.25	
	Br^-	6.3×10^{-6}	0.37	
	I^-	8.3×10^{-6}	0.16	
Fastest rate of reaction	NO_3^-	2.7×10^{-5}	0.077	Weakest M — L bonds

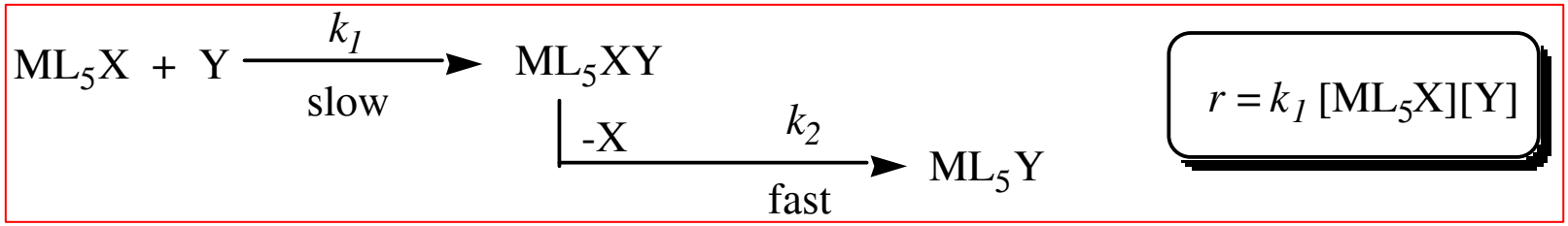
The rate is **dependent** on the identity of L, the **leaving ligand**

Kinetics of the two limiting reaction mechanisms for Ligand Substitution Reactions in octahedral complexes (r = dP/dt)

Dissociative (D)



Associative (A)



A reaction proceeding via the **A** mechanism

a. Rate constants for $[Ru(III)(EDTA)(H_2O)]^-$ substitution

Ligand	$k_1(M^{-1}\,s^{-1})$	$\Delta H^{\ddagger}(kJ\,mol^{-1})$	$\Delta S^{\ddagger}(J\,mol^{-1}\,K^{-1})$
Pyrazine	20,000 ± 1,000	5.7 ± 0.5	−20 ± 3
Isonicotinamide	8,300 ± 600	6.6 ± 0.5	−19 ± 3
Pyridine	6,300 ± 500		
Imidazole	1,860 ± 100		
SCN^-	270 ± 20	8.9 ± 0.5	−18 ± 3
CH_3CN	30 ± 7	8.3 ± 0.5	−24 ± 4

b. Rate constants for $[Ru(II)(EDTA)(H_2O)]^{2-}$ substitution

Ligand	$k_1(M^{-1}\,s^{-1})$
Isonicotinamide	30 ± 15
CH_3CN	13 ± 1
SCN^-	2.7 ± 0.2

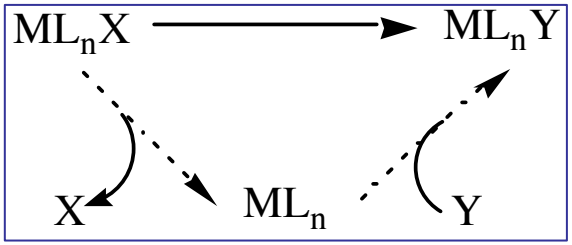
The identity of **entering ligand** influences the **rate** very much

$\Delta S^{\#}$ is negative, consistent with expectation for 2 molecules forming 1 new complex

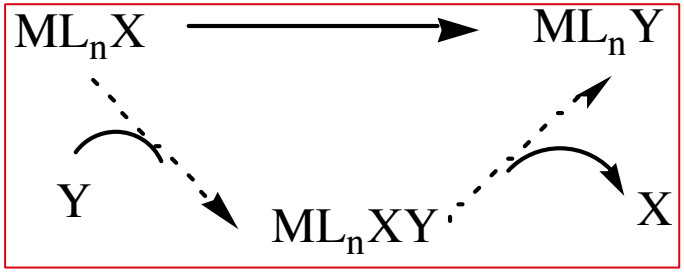
Summary of of ligand substitution (exchange) reaction mechanisms in octahedral complexes

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

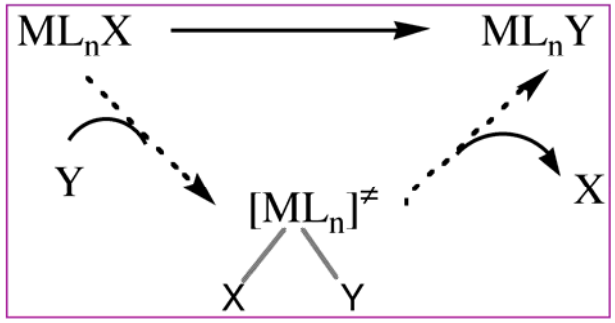
Dissociative (D)



Associative (A)



Interchange (I)



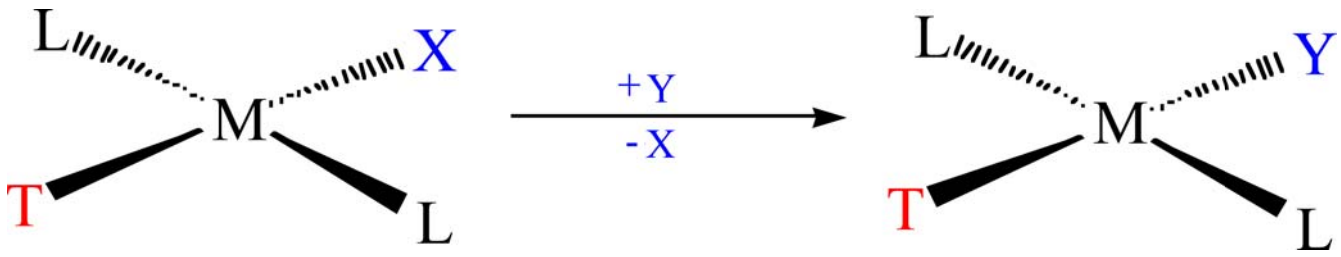
I_d if dissociation is more important

I_a if association is more important

Y assists the leaving ligand (X)
Dissociative Interchange (I_D)

Y strongly begins bond formation before X leaves
Associative Interchange (I_A)

Substitution reactions in square-planar complexes and the trans effect



Trans effect: The ability of a ligand (T) to labilize a ligand trans to it (X)

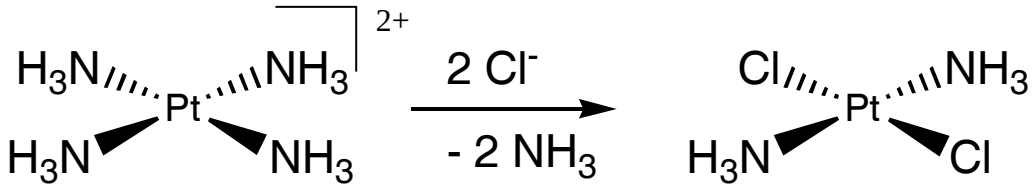
T = a trans-directing ligand

The trans effect series

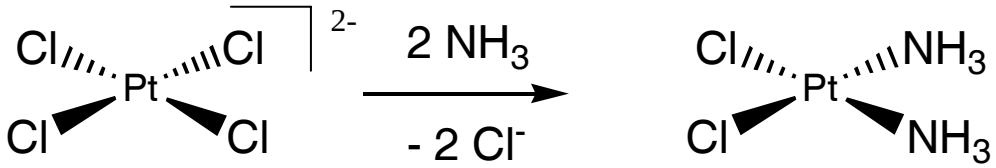
$$CO \sim CN^- \sim C_2H_4 > PR_3 \sim H^- > CH_3^- \sim SC(NH_2)_2 > C_6H_5^- >$$

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

Synthetically useful consequences of the trans effect

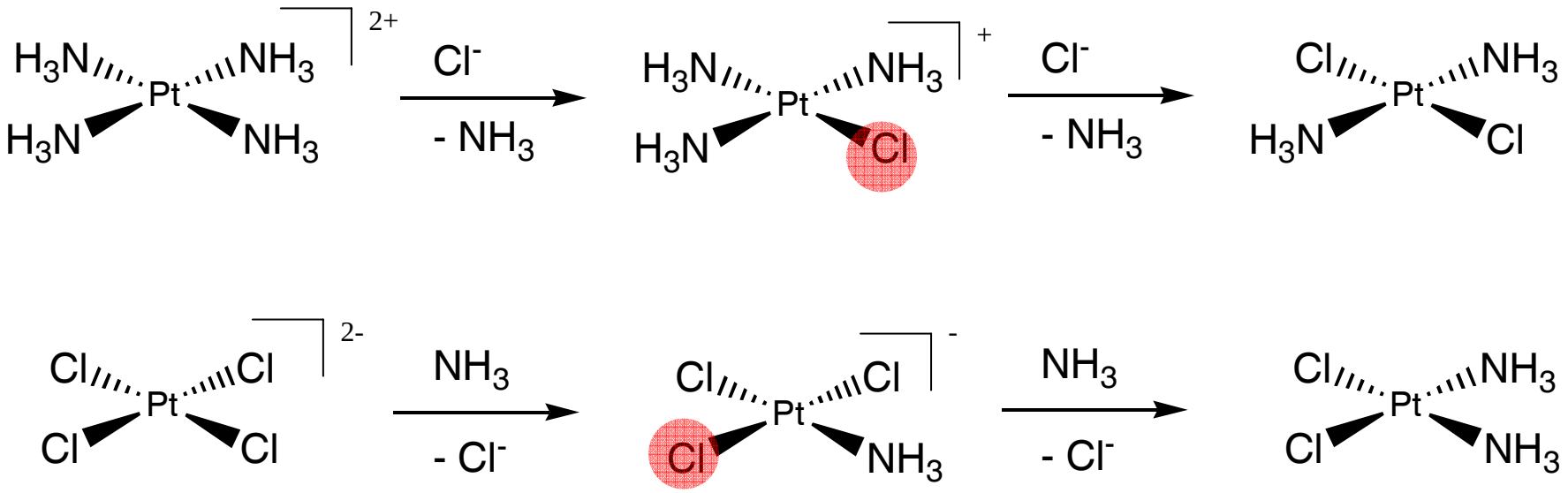


Trans only !!



Cis only !!

Synthetically useful consequences of the trans effect



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The trans effect series

CN^-, CO, NO, C_2H_4 > PR_3, H^- > CH_3^-, $C_6H_5^-$, $SC(NH_2)_2$, SR_2 > SO_3H^- > NO_2^-, I^-, SCN^- > Br^- > Cl^- > py > RNH_2, NH_3 > OH^- > H_2O

and the spectrochemical series

$I^- < Br^- < S^{-2} < SCN^- < Cl^- < NO_3^- < F^- < OH^- < ox^{-2} < H_2O < NCS^-$
$< CH_3CN < NH_3 < en < bipy < phen < NO_2^- < phosph < CN^- < CO$

Task 1

Note **similarities** and **differences** between the two series

Task 2

Let’s try understanding the trans effect by taking a closer look at a conceivable reaction mechanism

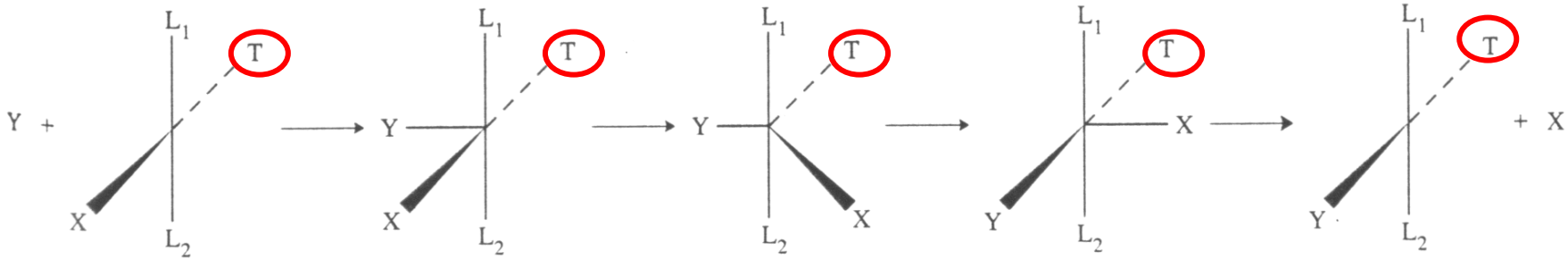

Fig. 13.2 Mechanism for nucleophilic substitution in square planar ML_1L_2XT complexes.

Note 1: the energies of square pyramidal and trigonal bipyramidal complexes are very similar and they interconvert very fast.

Note 2: π - accepting ligands prefer equatorial positions in trigonal bipyramidal complexes

Task 2

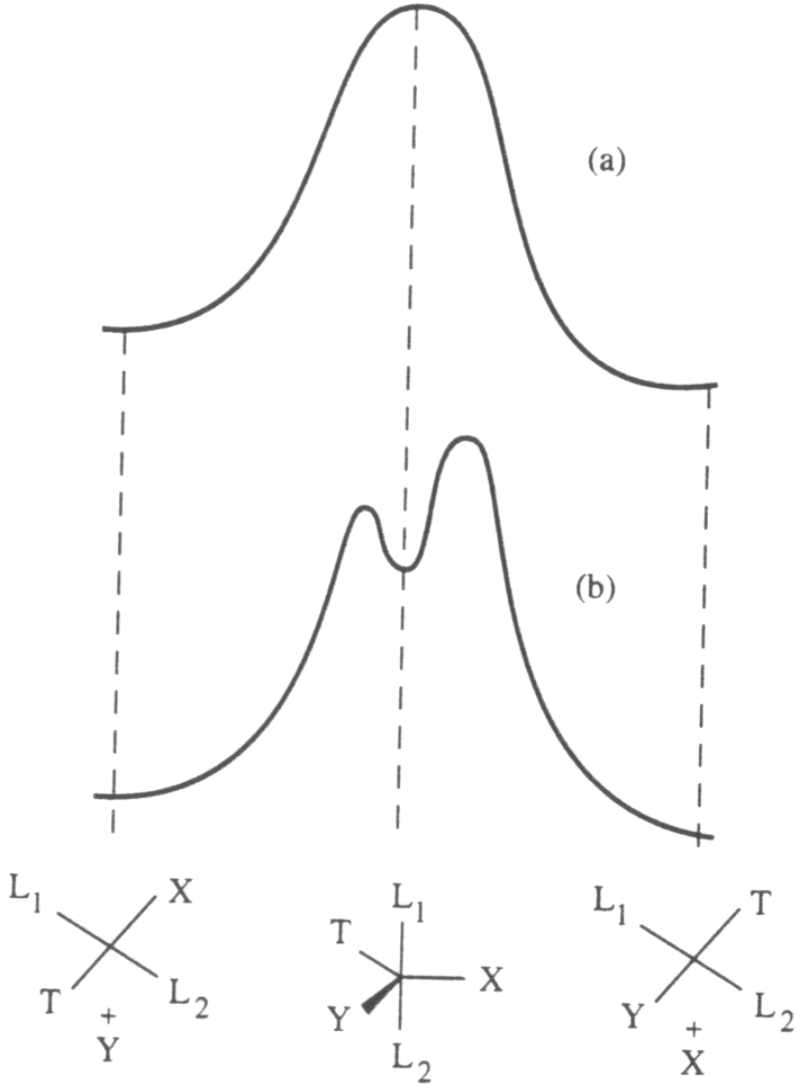

Fig. 13.3 Reaction coordinate/energy profile for a square planar substitution reaction having (a) a trigonal bipyramidal activated complex and (b) a trigonal bipyramidal intermediate. [From Burdett, J. K. *Inorg. Chem.* **1977**, *16*, 3013–3025. Used with permission.]

Note:
The barrier for tbp to spy is very small

Task 1 + Task 2

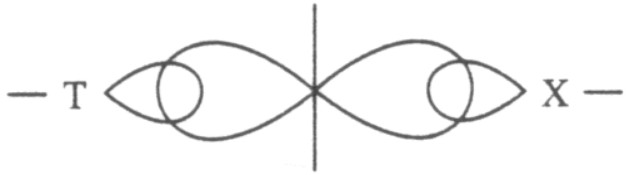

Fig. 13.4 Competition of trans ligand (T) and leaving group (X) for a metal p_x orbital in a square planar complex.

σ- donation by T weakens the M-X bond, hence
σ - donor strength:

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

π - acceptors prefer equatorial positions in bpy complexes, hence
π - acceptor series:

$$C_2H_2, CO > CN^- > NO_2^- > SCN^- > I^- > Br^- > Cl^- > NH_3 > OH^-$$

Conclusion

Both σ- donors and π-acceptors are expected to be strong *trans*-directing ligands

CN^-, CO, NO, C_2H_4 > PR_3, H^- > CH_3^-, $C_6H_5^-$, $SC(NH_2)_2$, SR_2 > SO_3H^- > NO_2^-, I^-, SCN^- > Br^- > Cl^- > py > RNH_2, NH_3 > OH^- > H_2O

Both σ- donors and π-acceptors are expected to be strong *trans*-directing ligands

Important notes:

a) Information about σ-donation is obtained from isolated complexes.

b) Information about π-acceptance is obtained from isolated complexes.

c) Information about preferred occupation in tbp complexes is obtained from isolated complexes.

d) Conclusion: Information for a-c is acquired from thermodynamic data.

But, information regarding *trans*-directing ligands is obtained from kinetic data. Remember that the trans-effect is defined as "The ability of a ligand (T) to labilize a ligand trans to it (X)"

Conclusion:

a) All information acquired about the effect of ligands on thermodynamic properties of other ligands trans to them is called the *trans*-influence.

b) Information acquired about the effect of ligands on kinetic properties of ligands trans to them is called the *trans*-effect.