Chem 241

Lecture 15

Homework

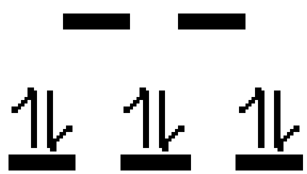
Start reading chapter 20

Recap

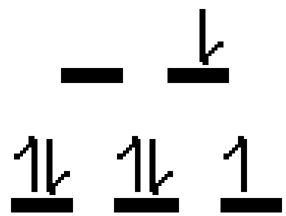
MOT with both σ and π orbitals
Absorption
LMCT/MLCT
Florescence and Phosphorescence

States

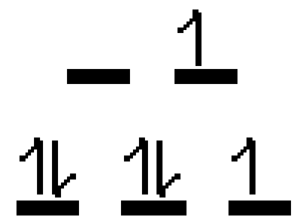
M_s = ½ for electron
S = add all the M_s
Multiplicity = 2S + 1



S= 0
Multiplicity = 1
Singlet



S= 0
Multiplicity = 1
Singlet



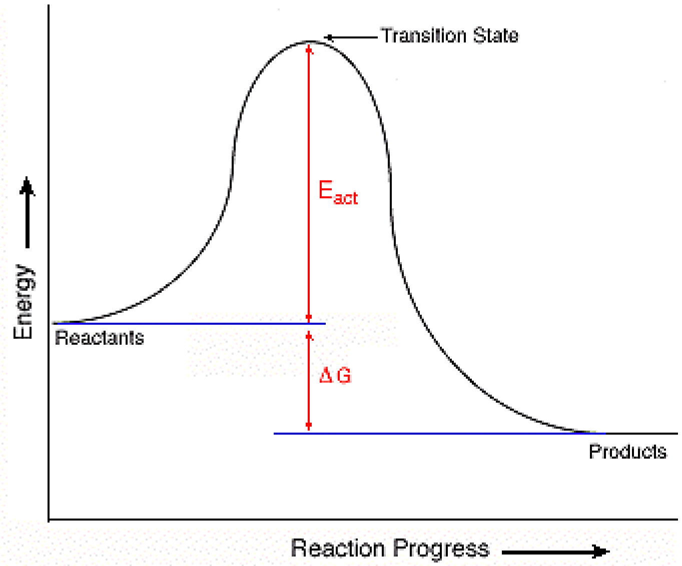
S= 1
Multiplicity = 3
Triplet

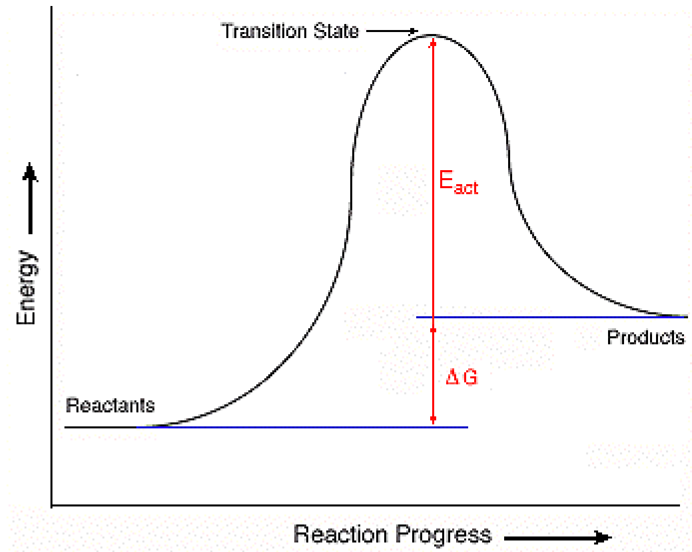
Reactions

Ligand substitution

Y + M-X → M-Y + X

Kinetics v Thermodynamic





Formation Constant

$$M + L \rightleftharpoons ML \qquad K_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \rightleftharpoons ML_2 \qquad K_2 = \frac{[ML_2]}{[ML][L]}$$

$$M + nL \rightleftharpoons ML_n \qquad B_n = \frac{[ML_n]}{[M][L]^n}$$

$$B_n = K_1K_2K_3 \ldots$$

Dissociation Constant

$$ML \leftrightharpoons M + L \qquad K_d = \frac{[M][L]}{[ML]}$$

Table 20.1 Formation constants for the reaction $[M(H_2O)_n]^{m+} + L \rightleftharpoons [M(L)(OH_2)_{n-1}]^{m+} H_2O$

Ion	Ligand	K_f	log K_f	Ion	Ligand	K_f	log K_f
Mg^{2+}	NH_3	1.7	0.23	Pd^{2+}	Cl^-	1.25×10^5	6.1
Ca^{2+}	NH_3	0.64	−0.2	Na^+	SCN^-	1.2×10^4	4.08
Ni^{2+}	NH_3	525	2.72	Cr^{3+}	SCN^-	1.2×10^3	3.08
Cu^+	NH_3	8.50×10^5	5.93	Fe^{3+}	SCN^-	234	2.37
Cu^{2+}	NH_3	2.0×10^4	4.31	Co^{2+}	SCN^-	11.5	1.06
Hg^{2+}	NH_3	6.3×10^8	8.8	Fe^{2+}	pyridine	5.13	0.71
Rb^+	Cl^-	0.17	−0.77	Zn^{2+}	pyridine	8.91	0.95
Mg^{2+}	Cl^-	4.17	0.62	Cu^{2+}	pyridine	331	2.52
Cr^{3+}	Cl^-	7.24	0.86	Ag^+	pyridine	93	1.97
Co^{2+}	Cl^-	4.90	0.69				

Trends in formation Constants

General Trends

$K_1 > K_2 > K_3$ ...

Chelating Effect – Greater stability once coordinated

Higher K formation because of entropy.

Rings

5 and 6 membered rings tend to be more stable

The Irving-William Series

Summarize stability of complexes based on electrostatic effects and LFSE

$Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Zn$

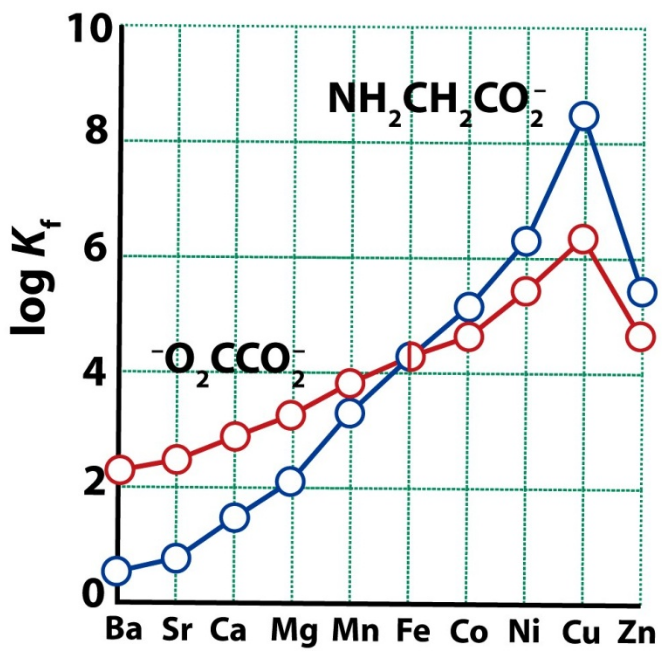
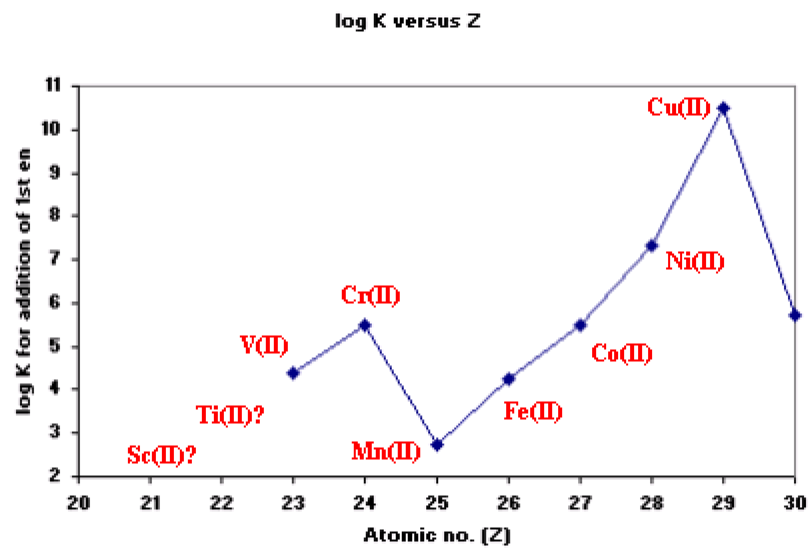


Figure 20-1
Shriver & Atkins Inorganic Chemistry, Fourth Edition



Ligand substitution

Complexes that lose their ligands easily = Labile
Complexes that keep their ligands = Nonlabile or Inert

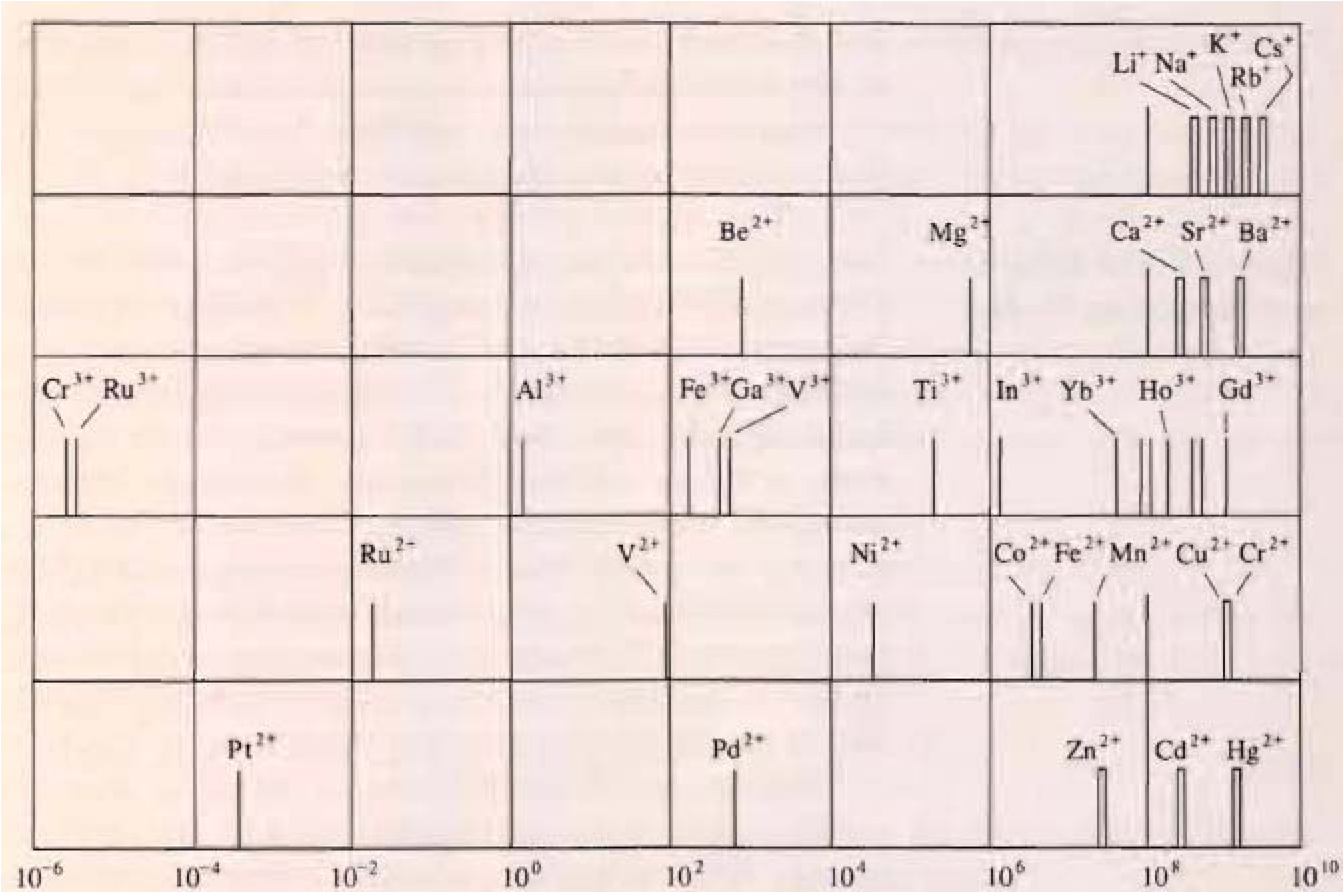


Fig. 13.5 Water excha... ...ured by NMR (solid bars) or derived from c... ...Docommun, Y.;

Mechanism

Rate Law links the rate of the reaction to the concentrations.

$xA + yB \rightarrow C \qquad r = k[A]^x [B]^y$

Elementary step represents the reaction at the molecular level not the overall reaction.

$2\,NO_2 + F_2 \rightarrow 2NO_2F$

$NO_2 + F_2 \rightarrow NO_2F + F$
$NO_2 + F \rightarrow NO_2F$

Rate-Determing Step slowest elementary step

Mechanism

Dissociative Mechanism is a reaction in which an intermediate of reduced coordination number is formed by the departure of the leaving group.

$ML_nX \rightarrow ML_n + X$

$ML_n + Y \rightarrow ML_nY$

Rate Determining Step:
Breaking the bond of the Leaving group

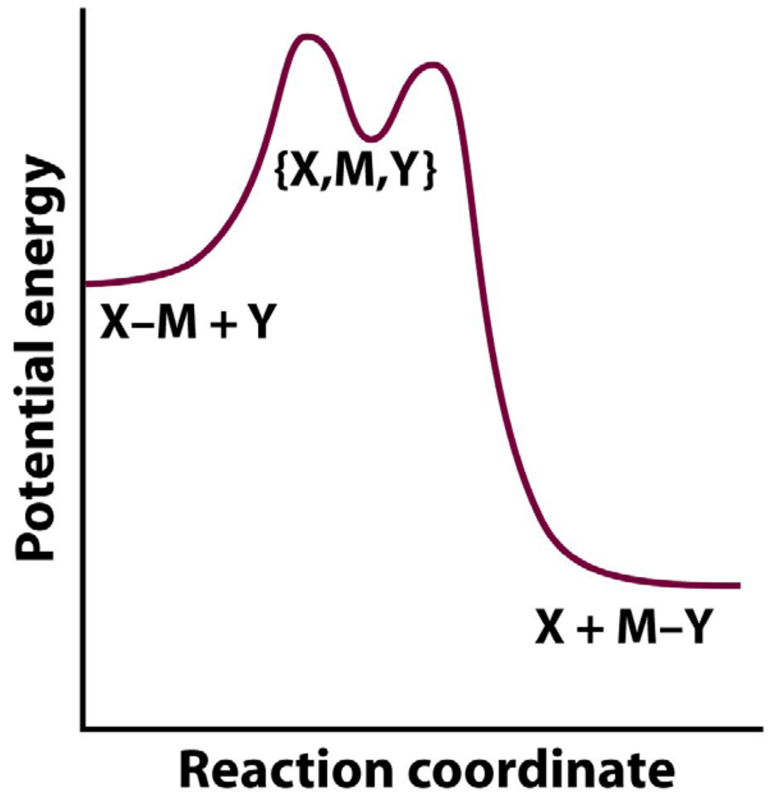
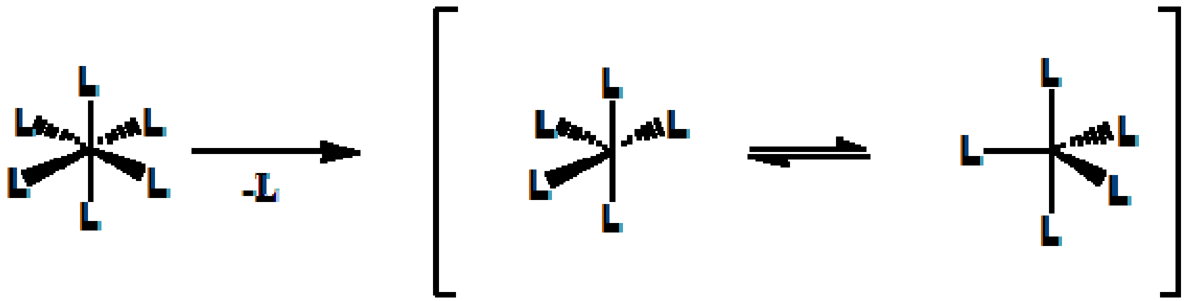
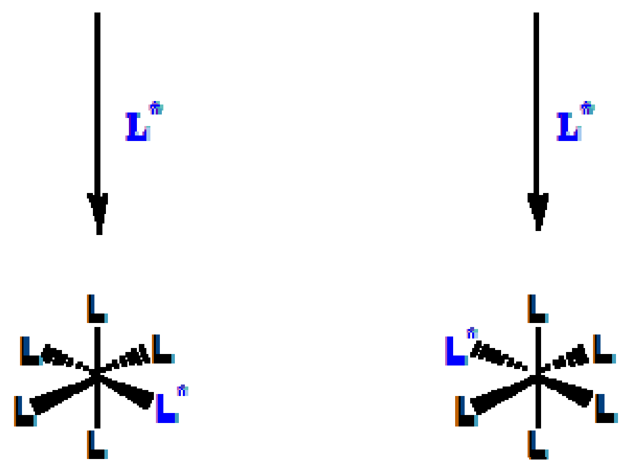


Figure 20-3
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Dissociative Mechanism



Happens if L can stabilize square planar, L is strong π-acceptor and/or strong σ-donor.



- The geometry of the end product can be different
- Reaction order is 1

Dissociative Mechanism

$$MX_n \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MX_{n-1} \xrightarrow{k_2[Y]} MX_{n-1}Y$$

$$rate = \frac{k_1\, k_2 [MX_n][Y]}{k_{-1}[X] + k_2[Y]}$$

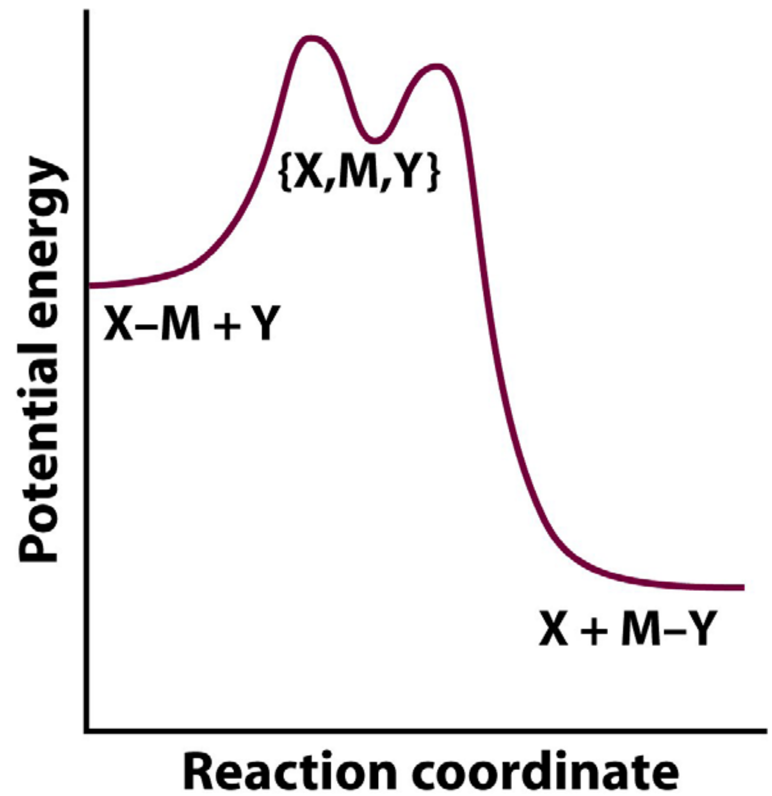


Figure 20-3
Shriver & Atkins Inorganic Chemistry, Fourth Edition

The first step is rate determining

$k_2 >> k_1$

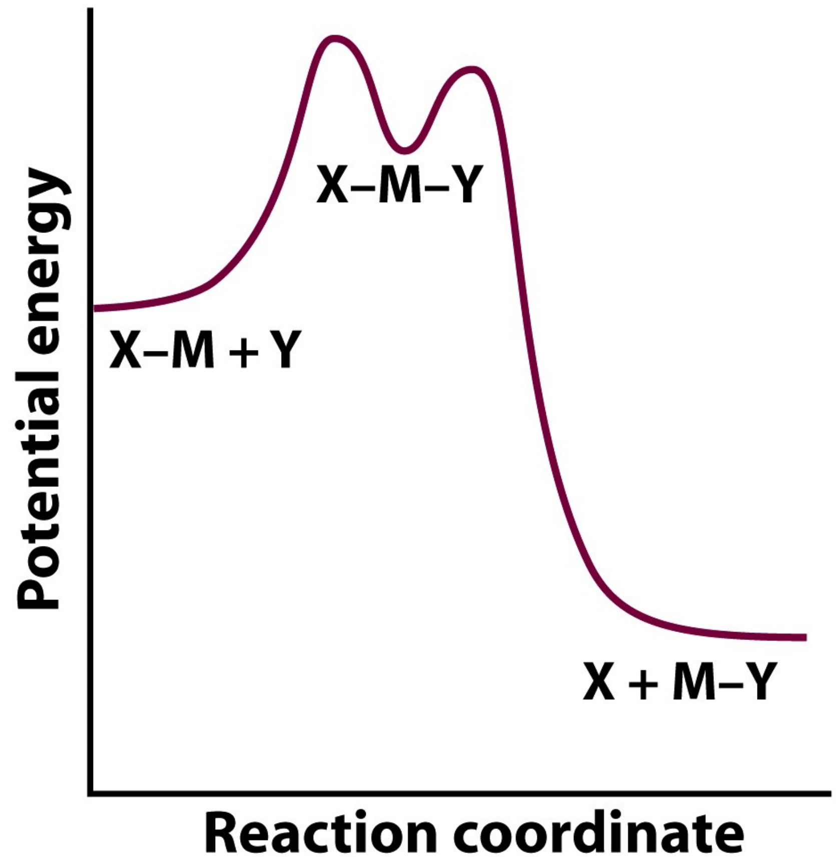
rate = k_1 [MX_n]

Mechanism

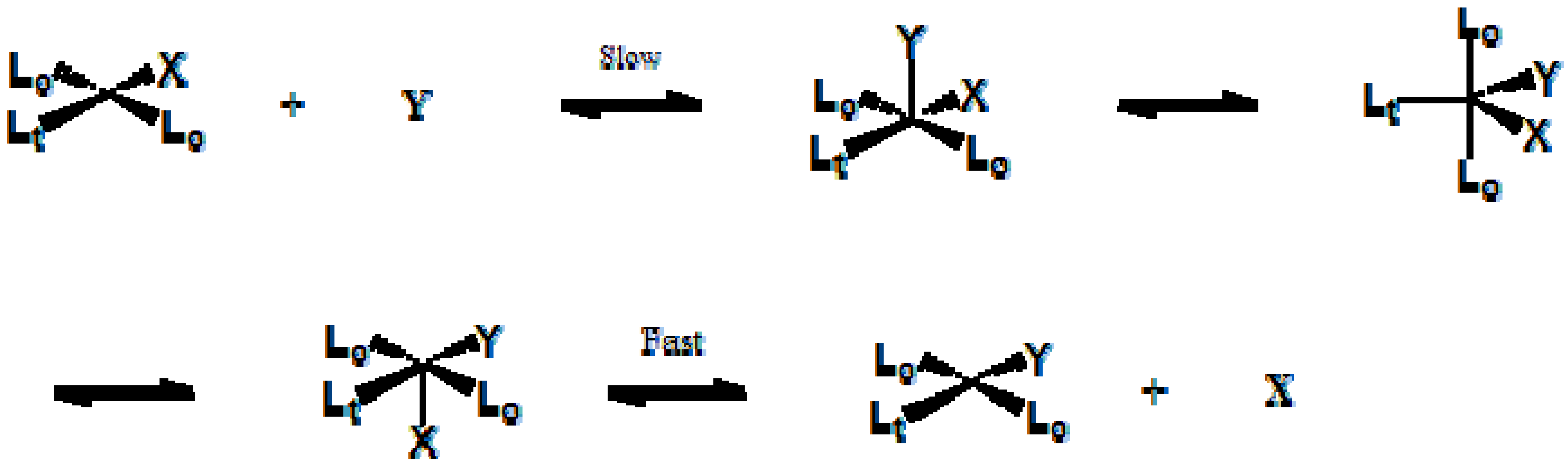
Associative Mechanism is a reaction in which an intermediate of higher coordination number is formed.

ML_nX + Y → ML_nXY
ML_nXY → ML_nY + X

Rate Determining Step:
Ligand attack



Associative Mechanism



- The geometry does not get scrambled
- Reaction order is 2

Dissociative Mechanism

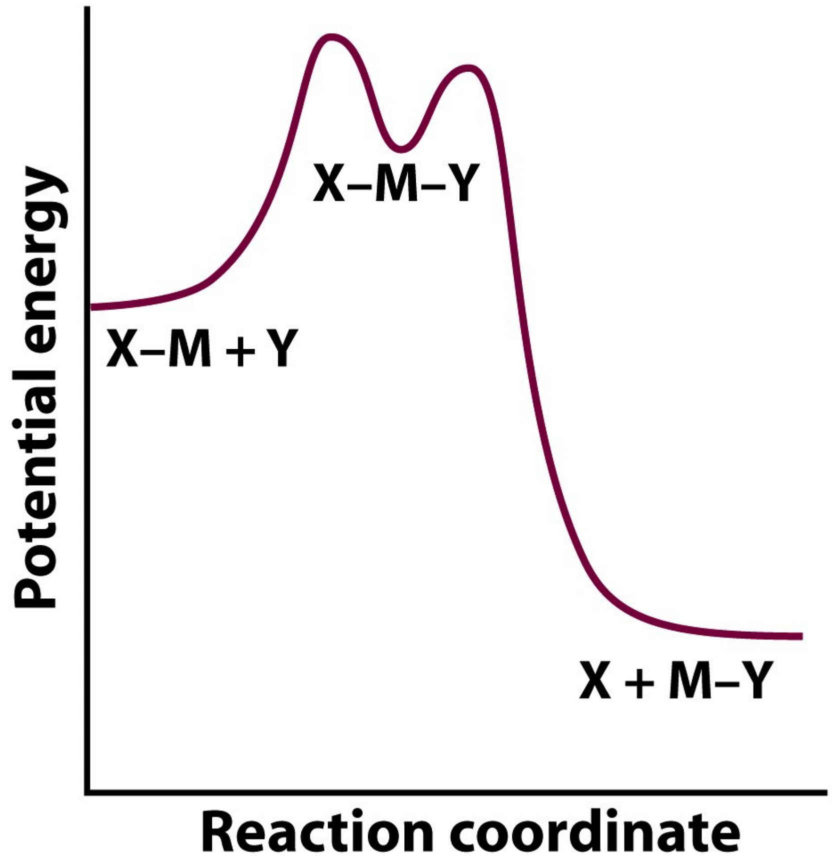
$$MX_n \underset{k_{-1}}{\overset{k_1[Y]}{\rightleftharpoons}} MX_nY \xrightarrow{k_2} MX_{n-1}Y$$

$$rate = \frac{k_1\, k_2 [MX_n][Y]}{k_{-1} + k_2}$$

The first step is rate determining

$k_2 >> k_1$

rate = k_1 $[MX_n][Y]$

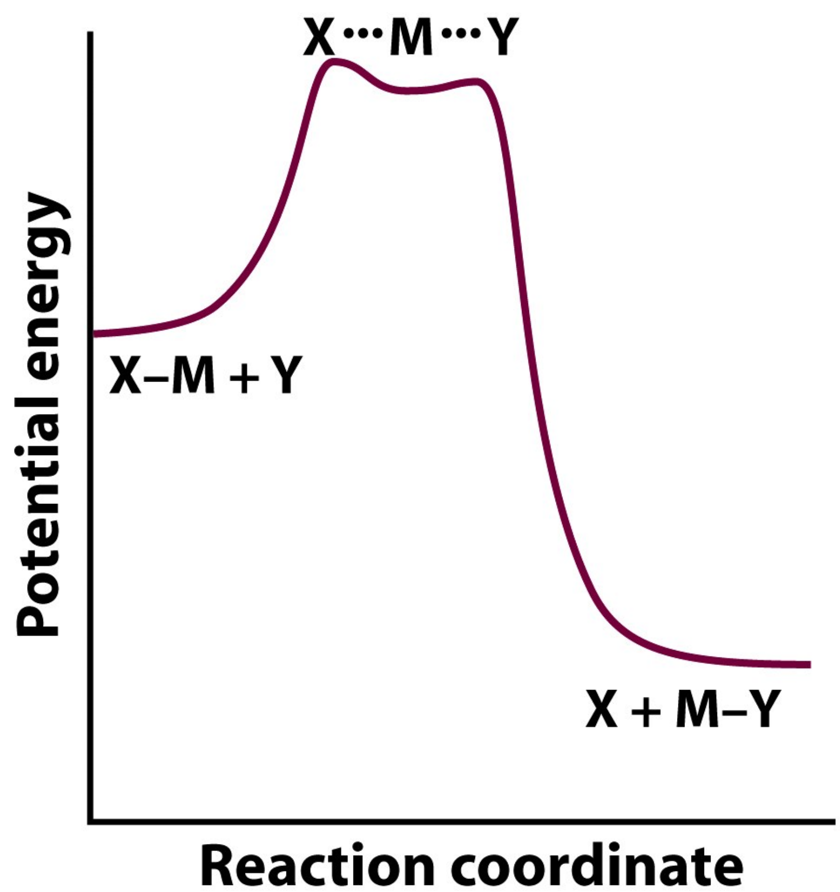


Mechanism

Interchange Mechanism takes place in one step.

$ML_nX + Y \rightarrow X\cdots ML_n\cdots Y$
$X\cdots ML_n\cdots Y \rightarrow ML_nY + X$

Often we don't have a pure associative or dissociative mechanism – instead the reaction involves concerted bond breaking and formation.



Square Planar

Platinum is an archetype

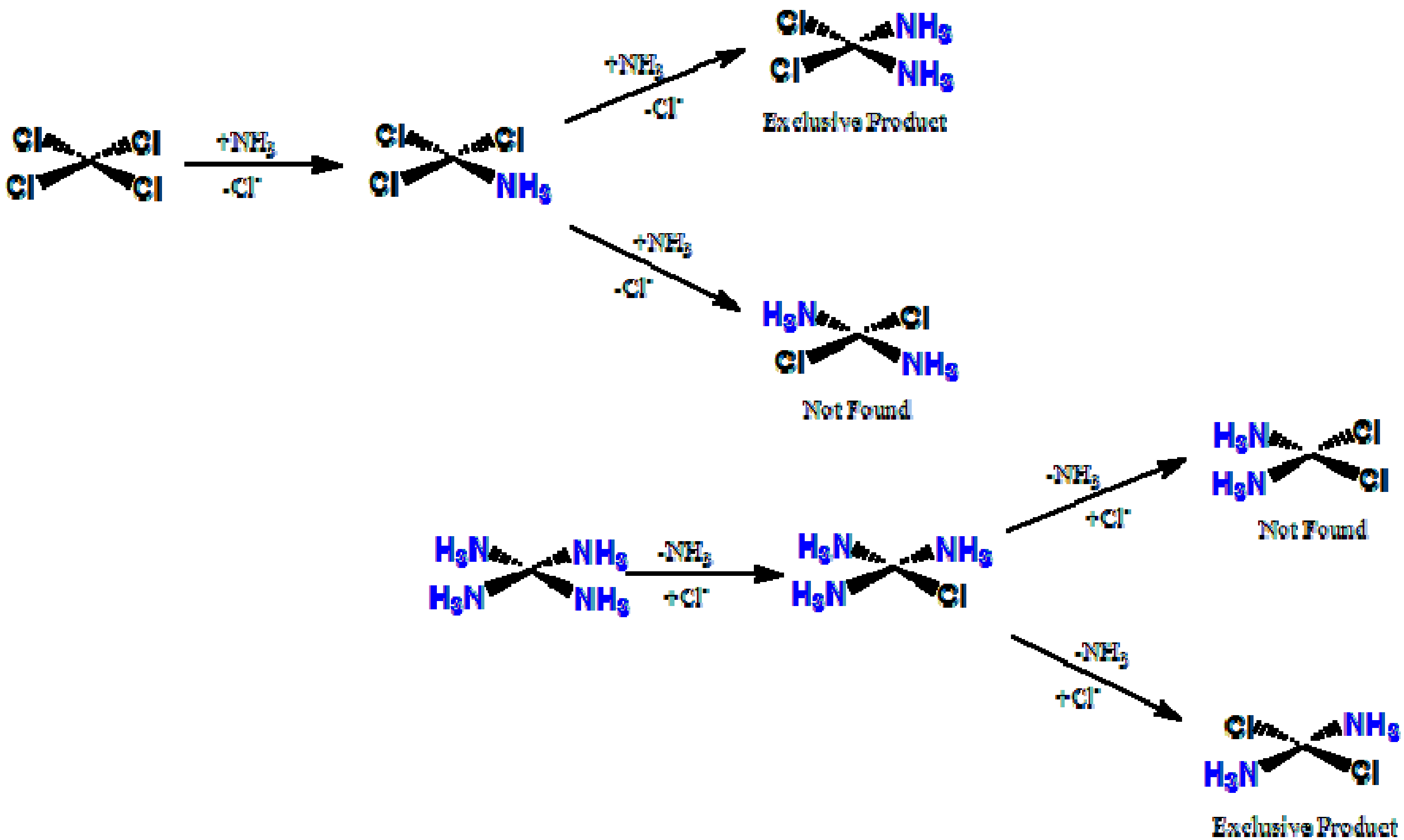
Nucleophilicity parameter

$$n_{Pt} = log \frac{k_2[Y]}{k_2^0}$$

Table 20.4 A selection of n_{Pt} values for a range of nucleophiles

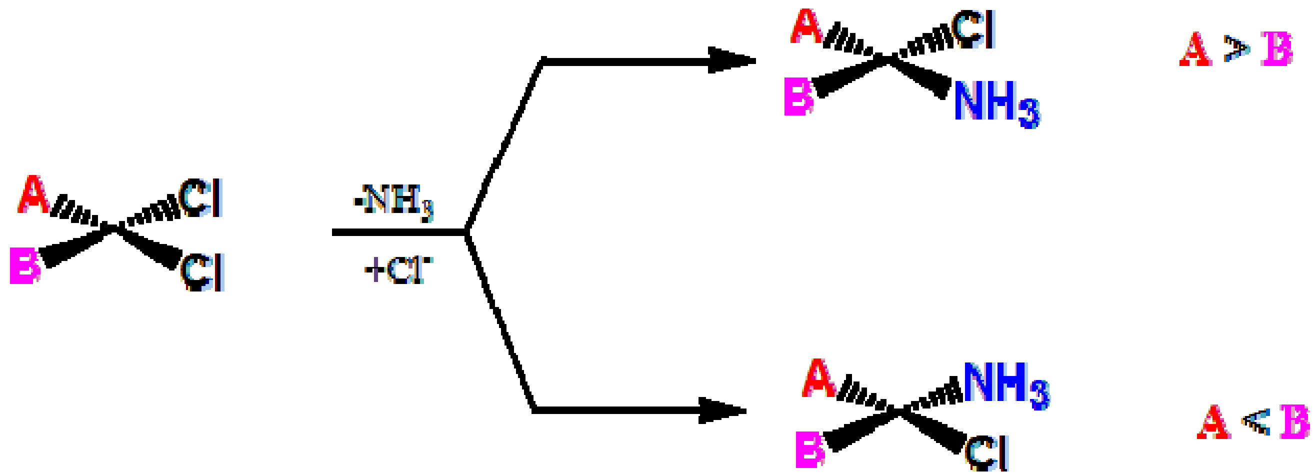
Nucleophile	Donor atom	n_{Pt}
Cl^-	Cl	3.04
I^-	I	5.42
CN^-	C	7.00
CH_3OH	O	0
C_6H_5SH	S	4.15
NH_3	N	3.06
$(C_6H_5)_3P$	P	8.79

Trans Effect



Trans Effect

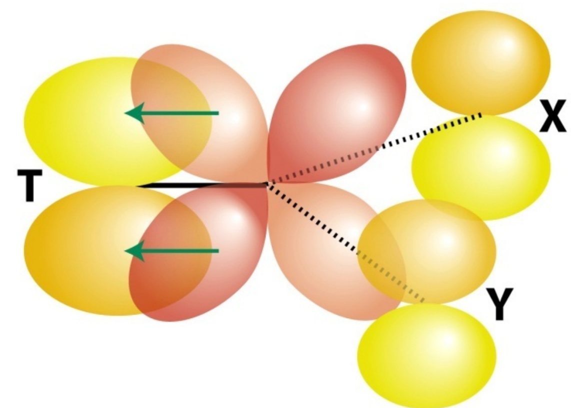
Is defined as the labilization of ligands trans to certain other ligands.



CN^-, CO, NO, C_2H_2 > 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

Trans Effect

Trans influence is the extent to which the ligand T weakens the bond *trans* to iteself in the ground state



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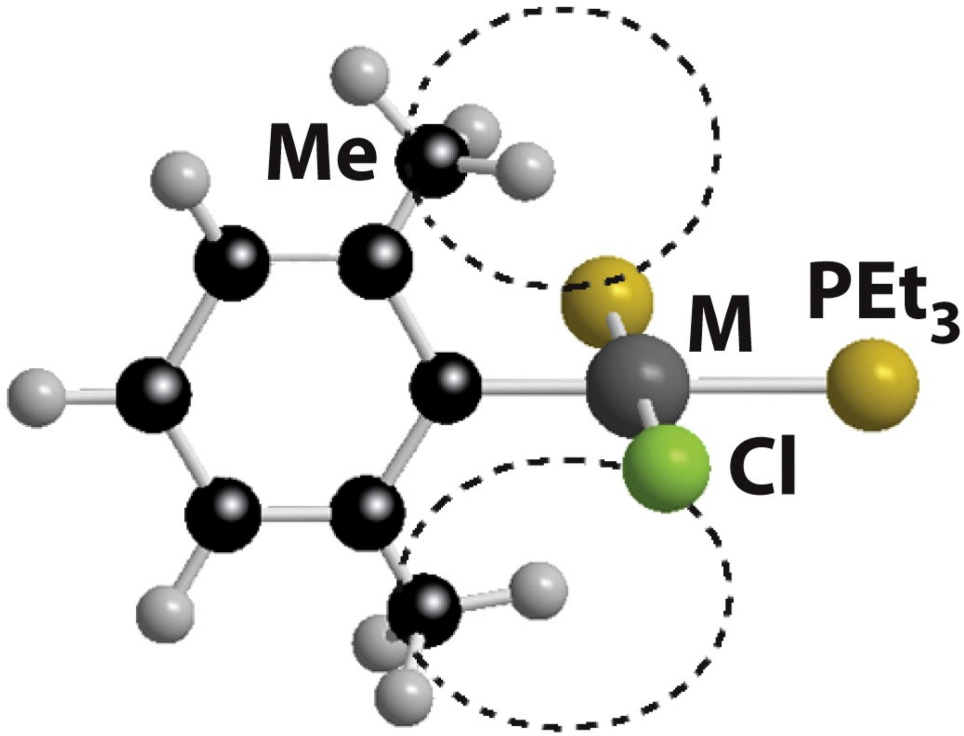
Structure 20-5

T σ-donor: $OH^- < NH_3 < Cl^- < Br^- < CN^-, CH_3^- < I^- <$ **S**$CN^- < PR_3$

T π-acceptor: $Br^- < I^- < NCS^- < NO_2^- < CN^- < CO, C_2H_2$

Steric Effects

Steric crowding usually hinders associative attacks.



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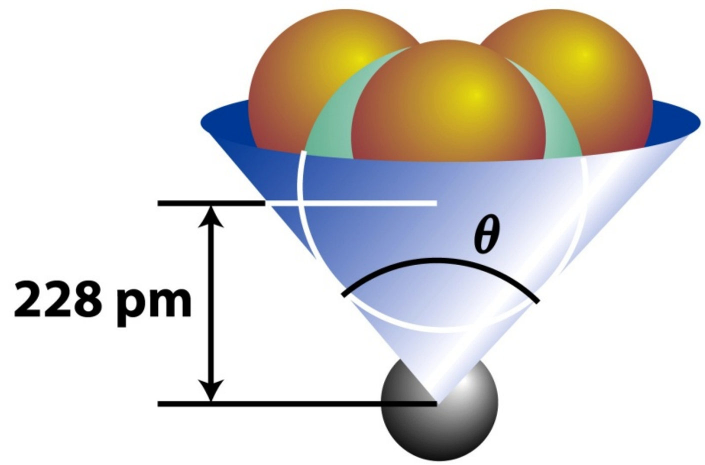
Structure 20-6

Tolman Cone Angle

Approximating the ligand as a cone.

Table 20.9 Tolman cone angles for various ligands

Ligand	$\theta/°$	Ligand	$\theta/°$
CH_3	90	$P(OC_6H_5)_3$	127
CO	95	PBu_3	130
Cl, Et	102	PEt_3	132
PF_3	104	η^5-C_5H_5(Cp)	136
Br, Ph	105	PPh_3	145
I, $P(OCH_3)_3$	107	η^5-C_5Me_5 (Cp*)	165
PMe_3	118	2,4-$Me_2C_5H_3$	180
t-Butyl	126	P(*t*-Bu)$_3$	182

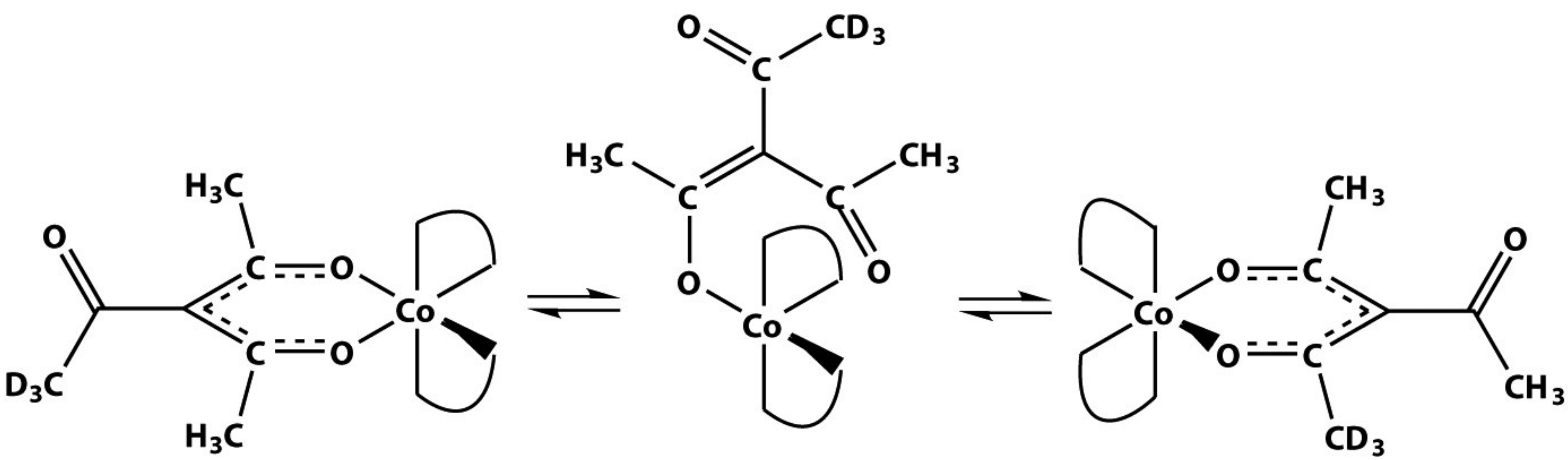


Isomerization

Go by a dissociative mechanism**:**

Bailer twist

Ray- Dust twist



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Redox Reactions

Reduction – Electron Gain
Oxidation – Electron Loss

Reducing Agent – Species that supplies electrons
Oxidizing Agent – Species that removed electrons

Groups 1 and 2 will do oxidation states of +1 and +2, respectively. While some d metals like Os can go from 0 to +8