(35) **Today**

Chap 12.4.5
Chap 12.5

Next Class (36)

Chap 12.5, 12.7

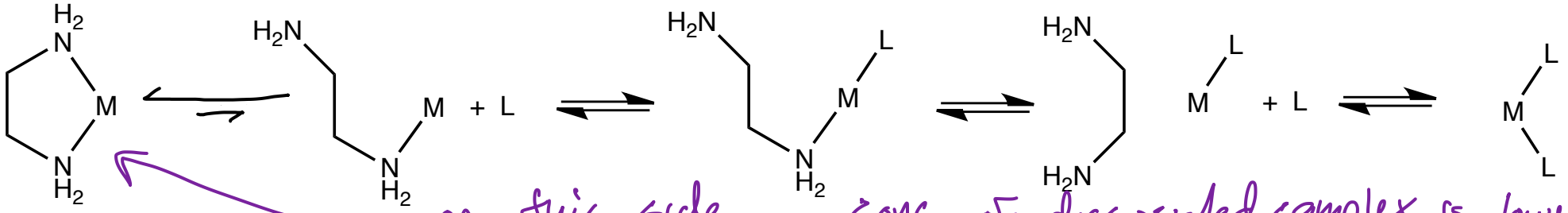
(37) **Second Class from Today**

Test 3

Third Class from Today (38)

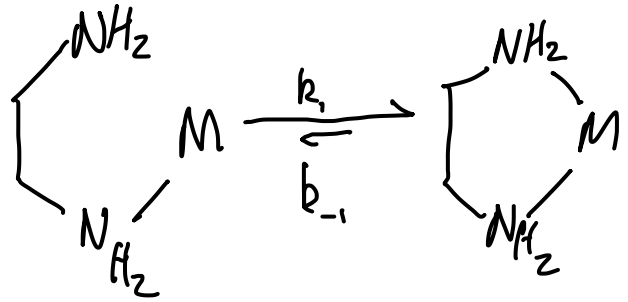
Chap 12.8

this rxn slows down because the equilib lies

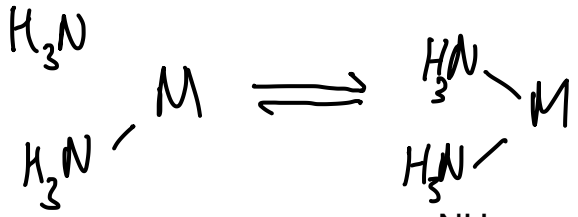


on this side ... conc of dissociated complex is lower

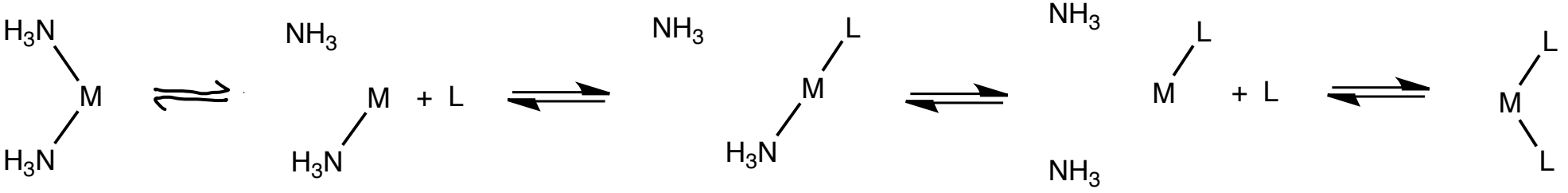
$K_{chelate} > K_{non\text{-}chelate}$

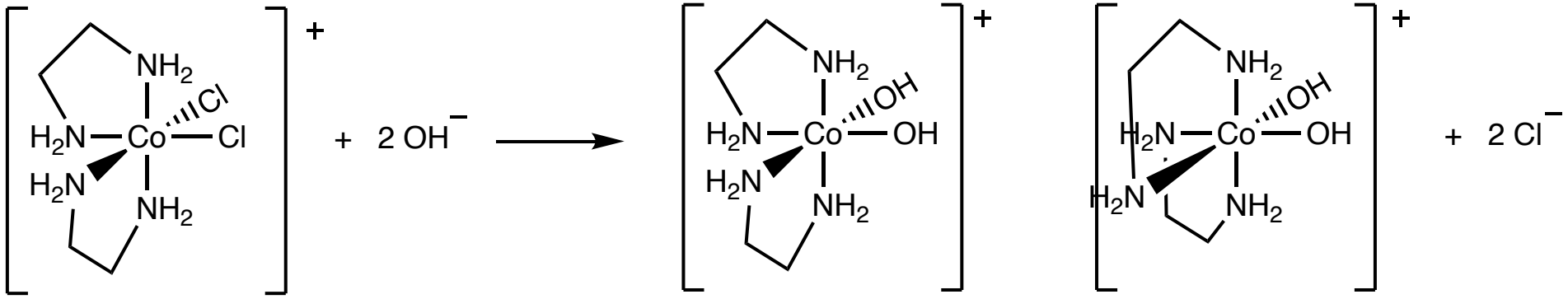


$K_{chelate}$



$K_{non\text{-}chelate}$





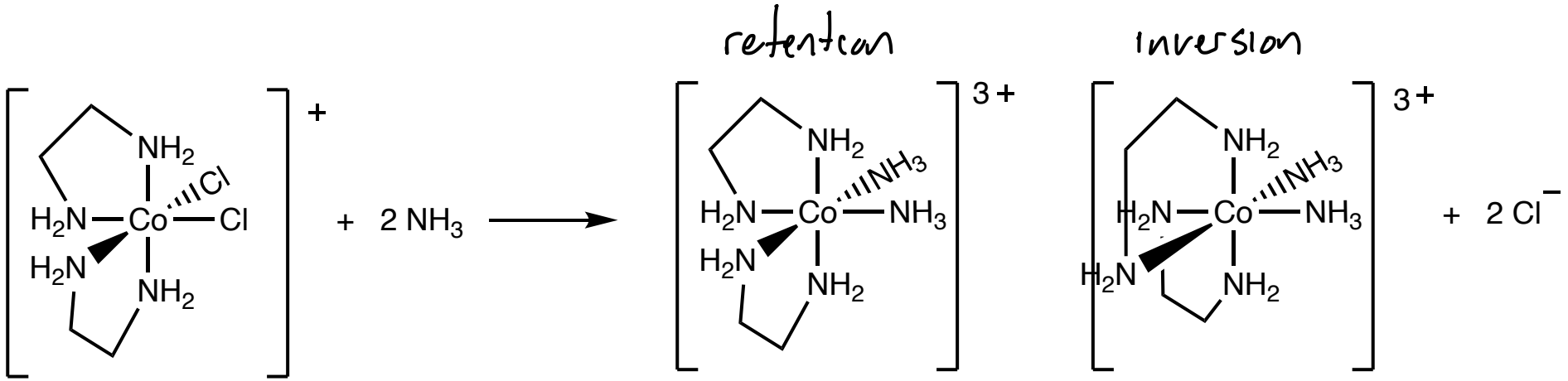
Λ-*cis*-$[Co(en)_2Cl_2]^+$

Λ-*cis*-$[Co(en)_2(OH)_2]^+$

$[OH^-] < 0.01$ M

Δ-*cis*-$[Co(en)_2(OH)_2]^+$

$[OH^-] > 0.25$ M



Λ-*cis*-$[Co(en)_2Cl_2]^+$

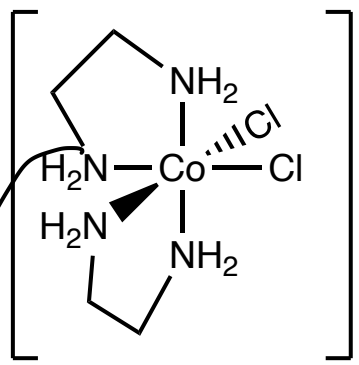
Λ-*cis*-$[Co(en)_2(NH_3)_2]^+$

> 25 °C in $NH_3(l)$

solid reacting with

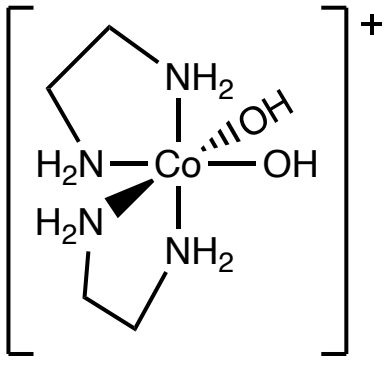
Δ-*cis*-$[Co(en)_2(NH_3)_2]^+$

< –33 °C in $NH_3(l)$

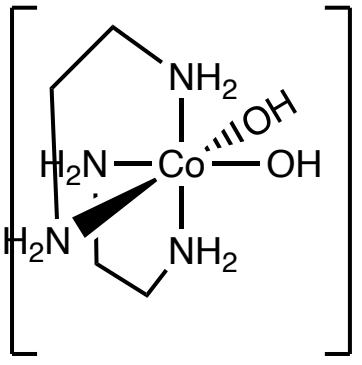


+ 2 OH^- →

retention



+



+ 2 Cl^-

Λ-*cis*-$[Co(en)_2Cl_2]^+$

Λ-*cis*-$[Co(en)_2(OH)_2]^+$

$[OH^-] < 0.01$ M

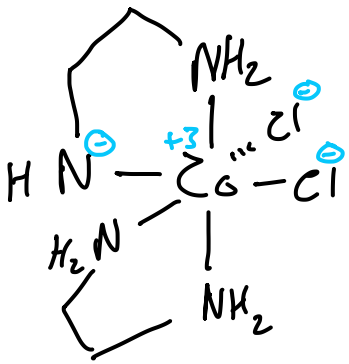
Δ-*cis*-$[Co(en)_2(OH)_2]^+$

$[OH^-] > 0.25$ M

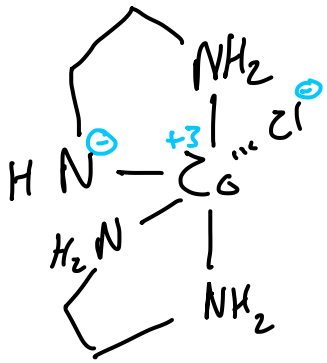
since N's lp e⁻ are being donated to the M the NH's are more acidic

dissociative mechanism?

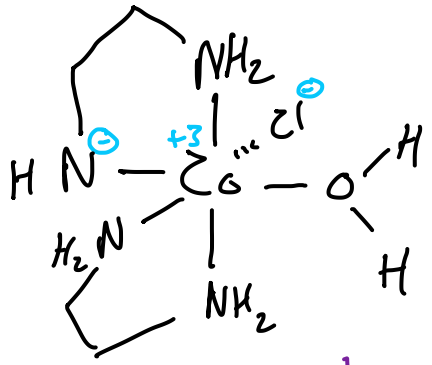
S_N1CB



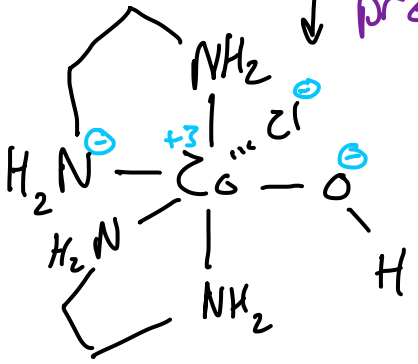
HOH



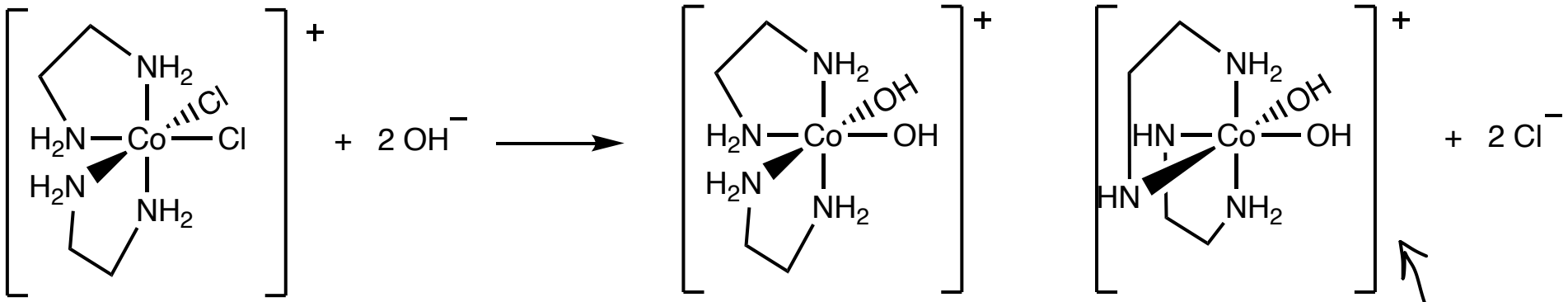
Cl^-



proton transfer



more common with molecules that can do S_N1CB



Λ-*cis*-$[Co(en)_2Cl_2]^+$

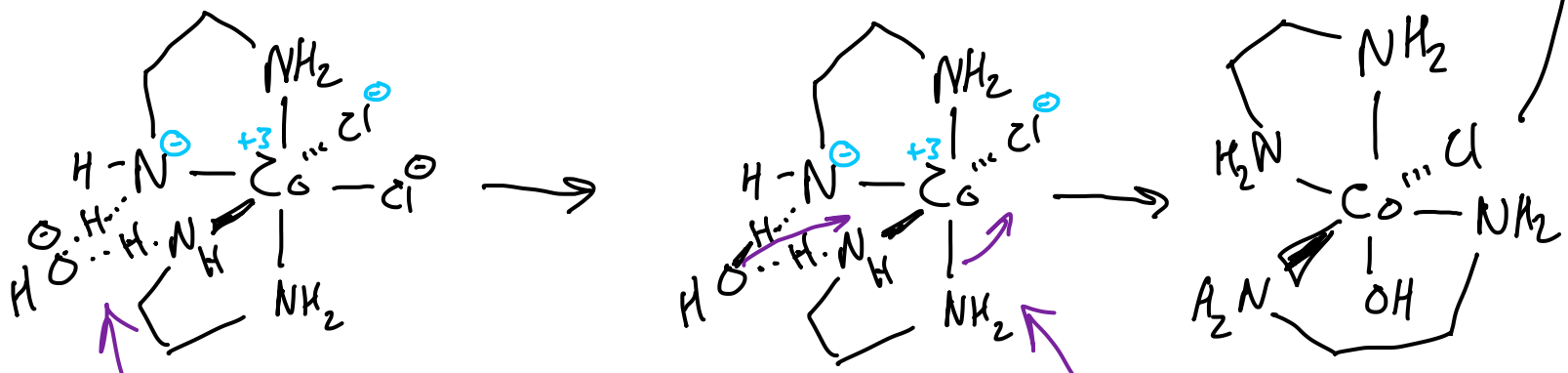
Λ-*cis*-$[Co(en)_2(OH)_2]^+$

$[OH^-] < 0.01$ M

Δ-*cis*-$[Co(en)_2(OH)_2]^+$

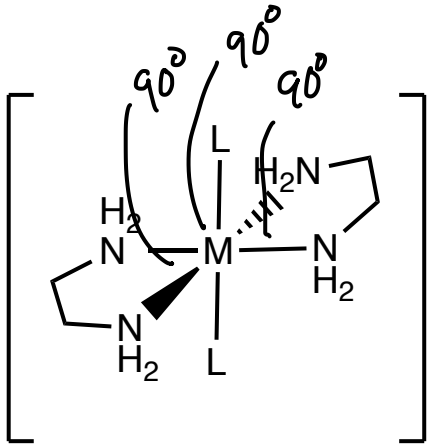
$[OH^-] > 0.25$ M

repeat



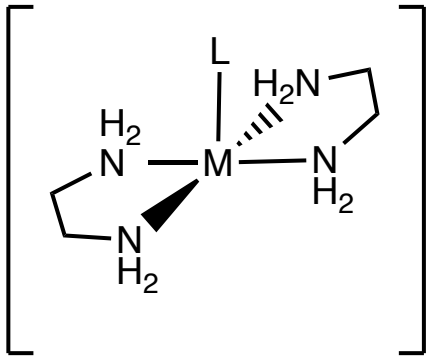
hydroxide grabs at H but because of high OH^- conc an ion pair forms $[OH^-][M^+]$

because OH is in the ion pair it pushes in after Cl^- leaves and inverts config



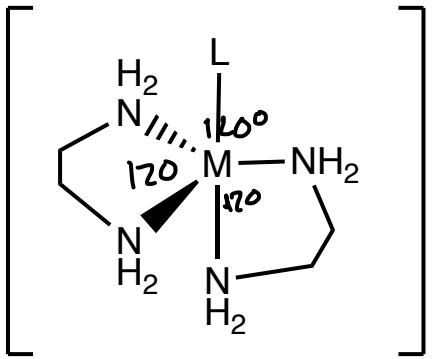
trans-$[Co(en)_2L_2]^+$

– L



square pyramidal

→ trans likely to form

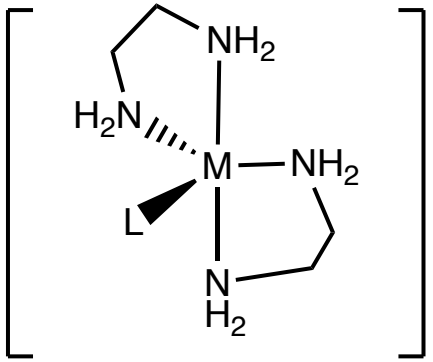


trigonal bipyramidal

least likely to form

→ creates 2 diff products

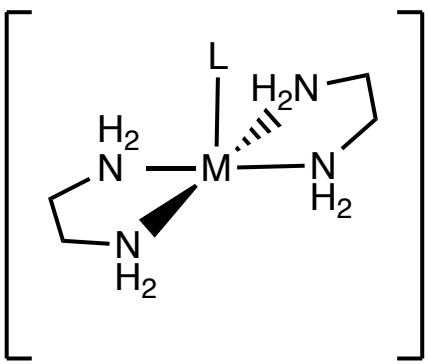
more bond angles must change to make this one



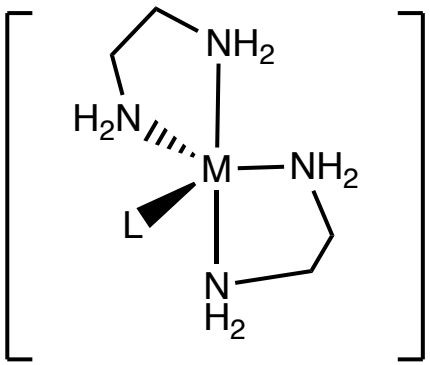
trigonal bipyramidal

– creats 3 diff products

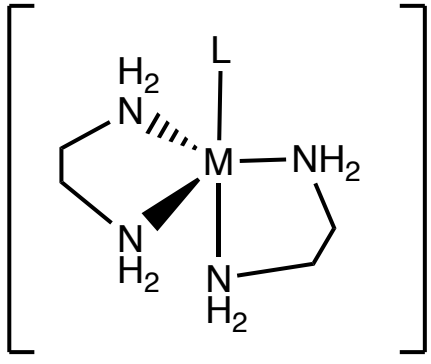
fewer bond angles change to make this one



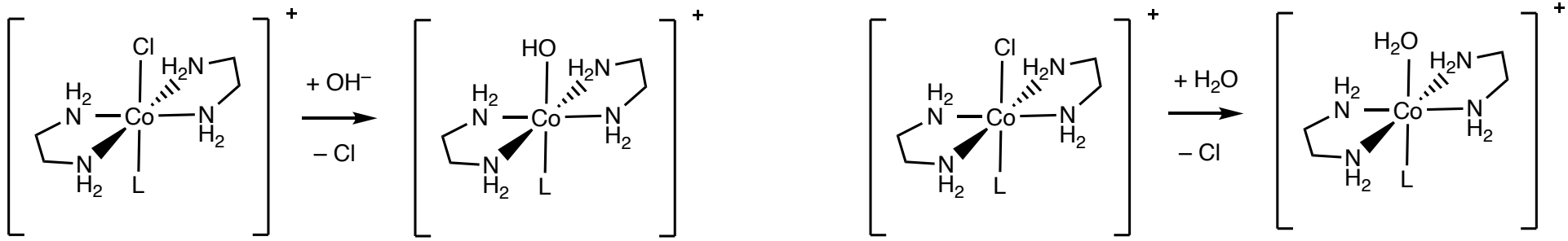
square pyramidal



trigonal bipyramidal



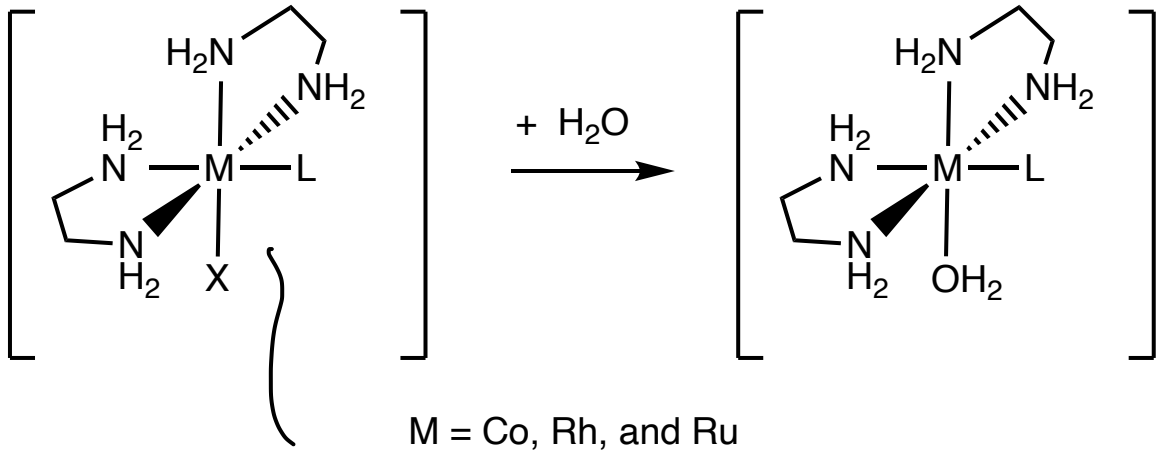
trigonal bipyramidal



trans are less likely to predictably retain their geometries

L^-	% trans product under acidic conditions (stereochemistry of reactant is retained)	% trans product under basic conditions (stereochemistry of reactant is retained)
OH^-	25	6
NCS^-	30-50	24
Br^-	50	100
Cl^-	65	95
NH_3^-	100	24
NO_2^-	100	94

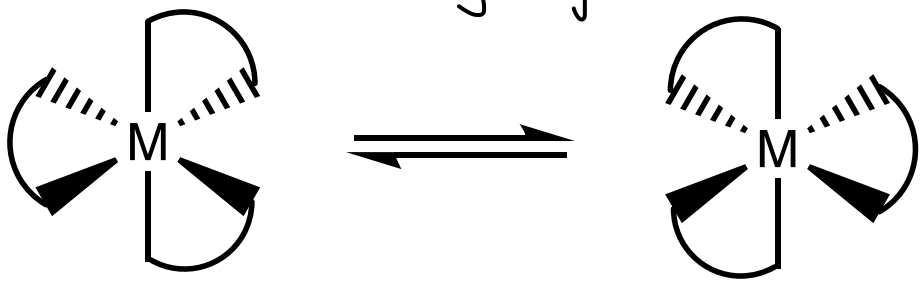
Data from Miessler, Fischer , and Tarr *Inorganic Chemistry, 5th ed.* Pearson, Boston, 2014, p.159. Table from Hass https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Inorganic_Chemistry_(LibreTexts)/12:_Coordination_Chemistry_IV_-_Reactions_and_Mechanisms/12.05:_Stereochemistry_of_Octahedral_Reactions/12.5.01:_Substitution_in_trans-en_octahedral_complexes



cis compounds are more likely to maintain cis geometry and

For Cobalt, Rhodium, Ruthenium they also retain their stereochemistry

labile metal complexes with chelating ligands can invert there stereochem

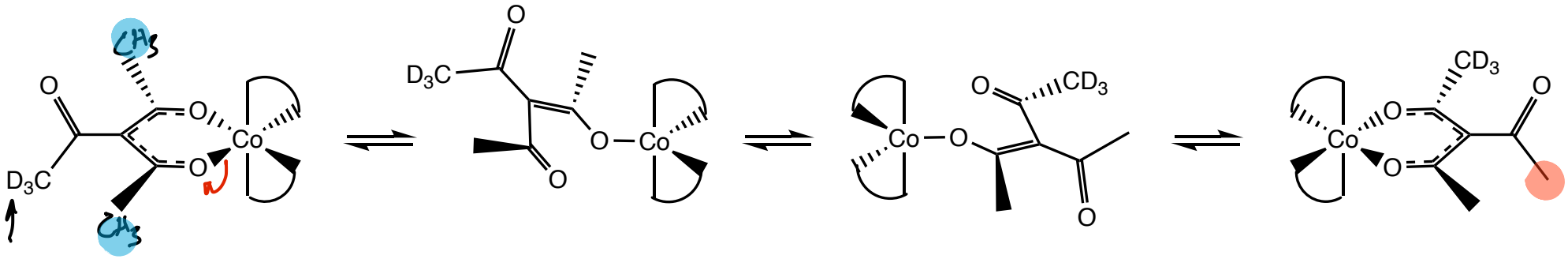


Dissociative Mechanisms

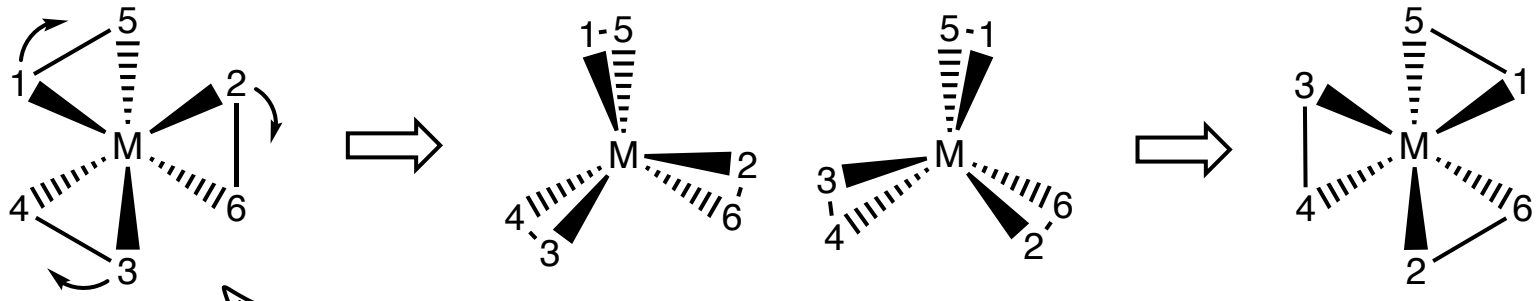
one part of the ligand dissociates, the ligands perform a pseudo rotation and reattach

Twisting Mechanism

the groups can just move



CH_3 and CH_3 are in different chemical environments and can be observed via spectroscopic technique



Front triangular face rotates past back triangular face ...