Explain the observed reaction rates

TABLE 5.1

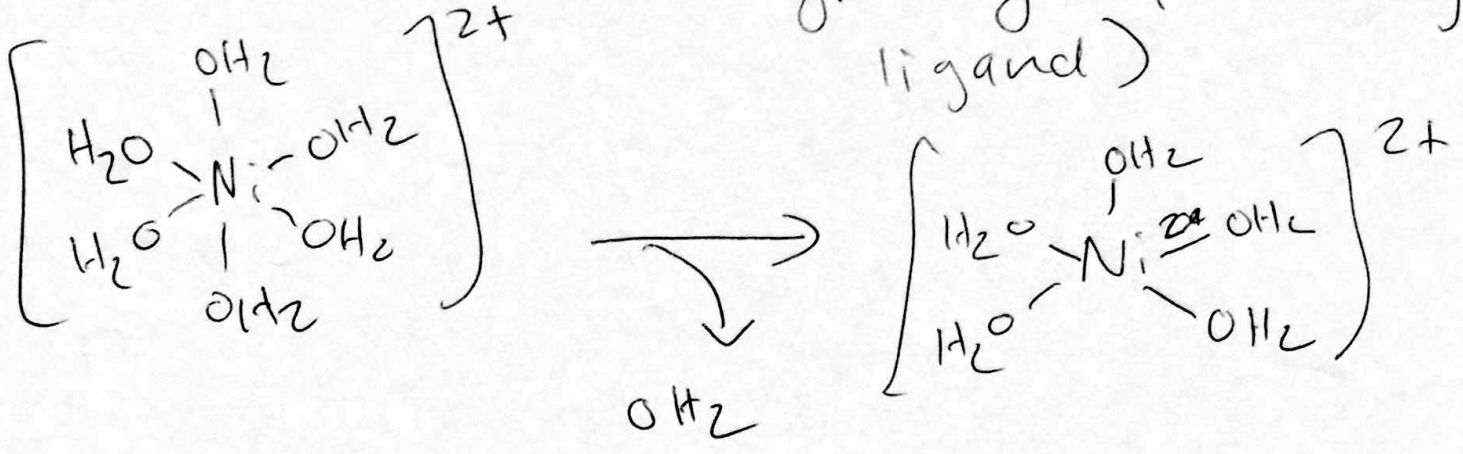
Rate Constants for Substitution Reactions of $[Ni(H_2O)_6]^{2+}$

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

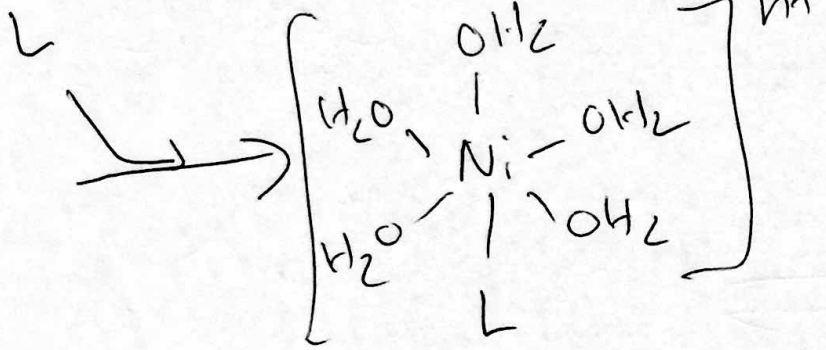
L	k, s^{-1}	log k
F^-	8×10^3	3.9
SCN^-	6×10^3	3.8
CH_3COO^-	30×10^3	4.3
NH_3	3×10^3	3.5
H_2O	25×10^3	4.4

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

— Dissociative (rates don't fluctuate greatly w/ incoming ligand)



✱ rate determining step



Ni^{2+} Oh d^8

eg^*: ↑ ↑

t_{2g}: ↑↓ ↑↓ ↑

- metal charge is not high (3+ or greater)
  → exchange tends to be faster
- d^8 Oh, not inert to substitution (because there are electrons in eg^* orbitals)

Explain the observed reaction rates

TABLE 5.2

Rate Constants for the Aquation of Pentaammine(ligand)cobalt(III) Complexes and Equilibrium Constants for the Anation of Pentaammineaquacobalt(III) with Various Anions

L	k, s^{-1}	K_a, M^{-1}
NCS^-	~~5.0×10^{-10}~~	470
F^-	8.6×10^{-8}	20
~~$H_2PO_4^-$~~	~~2.0×10^{-7}~~	7.4
Cl^-	1.7×10^{-6}	1.25
Br^-	6.3×10^{-6}	0.37
I^-	8.3×10^{-6}	0.16
~~NO_3^-~~	~~2.7×10^{-5}~~	0.077

Slowest rate of reaction

Fastest rate of reaction

Strongest M — L bonds

Weakest M — L bonds

The rate constants k refer to the following aquation reactions:

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

The equilibrium constants K_a refer to the following anation reactions:

$$[Co(NH_3)_5(H_2O)]^{3+} + L^- \overset{K_a}{\rightleftharpoons} [Co(NH_3)_5L]^{2+} + H_2O$$

The slowest rates of aquation correspond to the largest equilibrium constants for anation.

Source: Data from F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions, a Study of Metal Complexes in Solution*, 2d ed. (New York: Wiley, 1968), 164–166.

$[Co(NH_3)_5L]^{2+} + H_2O \rightleftharpoons [Co(NH_3)_5(H_2O)]^{3+} + L^{\ominus}$

$[Co(NH_3)_5L]^{2+} \longrightarrow [Co(NH_3)_5]^{3+} \xrightleftharpoons{H_2O}$

* rate determining step

L

$[Co(NH_3)_5(H_2O)]^{3+}$

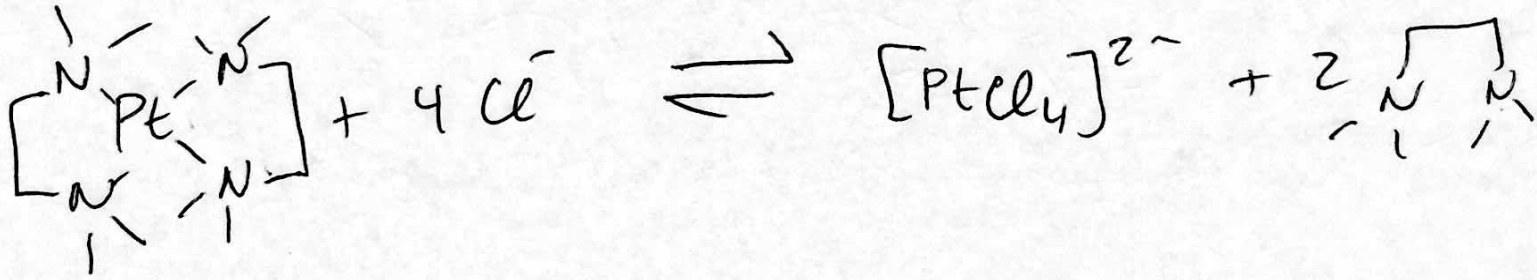
Co^{3+} → Hard acid

$I^{\ominus}$ soft ⟶ $F^{\ominus}$ hard

Hard-hard interactions stronger than hard-soft (generally)

Stronger M-L bond → slower exchange of L and H_2O in this reaction

Is ligand substitution at 4d ~~metal~~ metal centers faster or slower than 3d metal centers? How about 5d vs. 4d vs. 3d? WHY?



Which reaction is slower? WHY?

Ligand substitution rates

3d > 4d > 5d

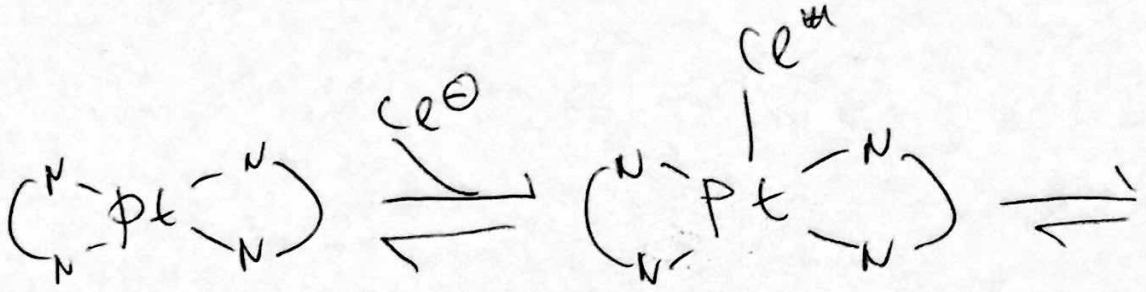
Δ_o 3d < Δ_o 4d < Δ_o 5d

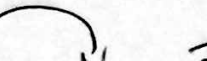
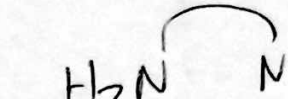
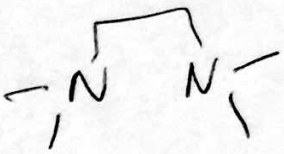
LFSE = (. – . –) Δ_o

for the same electron configuration

|LFSE 3d| < |LFSE 4d| < |LFSE 5d|

More LFSE (more negative) = slower ligand exchange rates



If  =  , reaction will be faster because this is less sterically bulky than 

Bulky ligands will prevent fast associated jun of incoming ligands

Trans effect

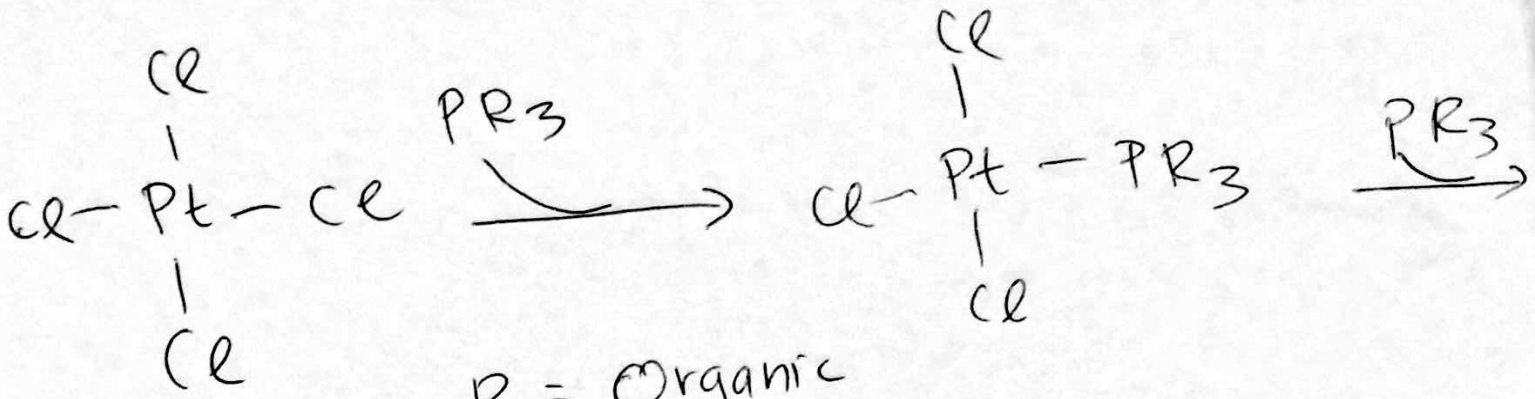
① Design two step syntheses to make cis and trans $[PtCl_2(NO_2)(NH_3)]^-$ starting from $[PtCl_4]^{2-}$

② Predict the products of the following:

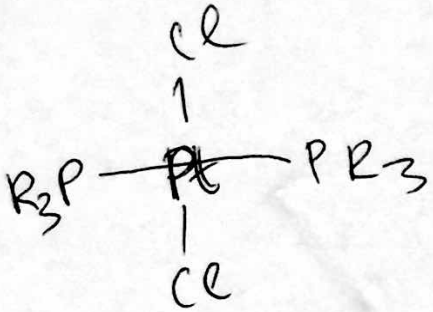
ⓐ $[Pt(PR_3)_4]^{2+} + 2Cl^- \longrightarrow$

ⓑ $[PtCl_4]^{2-} + 2PR_3 \longrightarrow$ ☆

ⓒ $cis\text{-}[Pt(NH_3)_2(py)_2]^{2+} + 2Cl^- \longrightarrow$



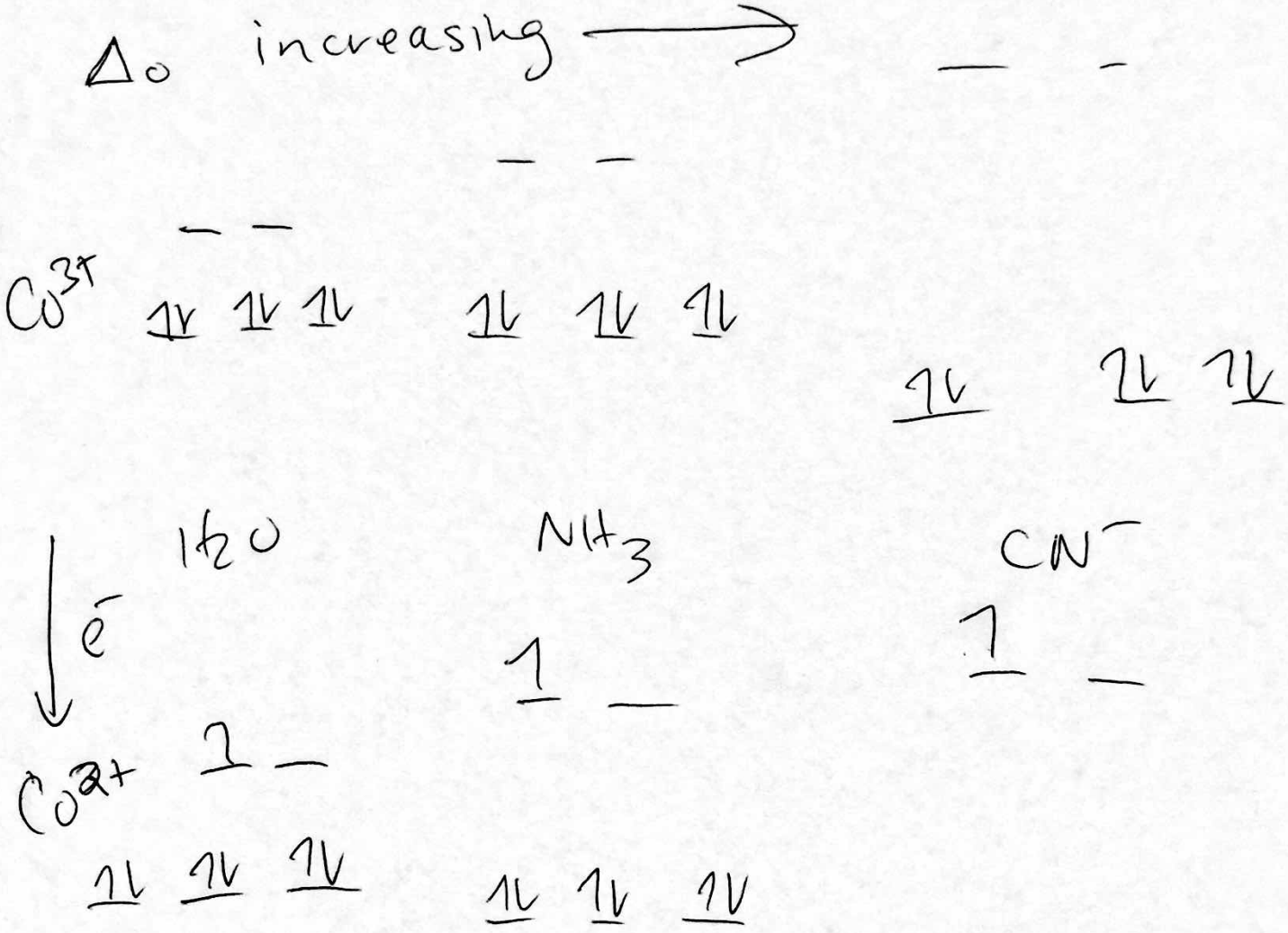
R = Organic group
(CH3, Ph etc)



CoL_6

H_2O, NH_3, CN^-

Δ_o increasing $\longrightarrow$



Hardest to reduce

$\rightarrow$ $\bar{e}$ add is going to the most destabilized e_g^* orbitals relative to t_{2g} (Δ_o is bigger)