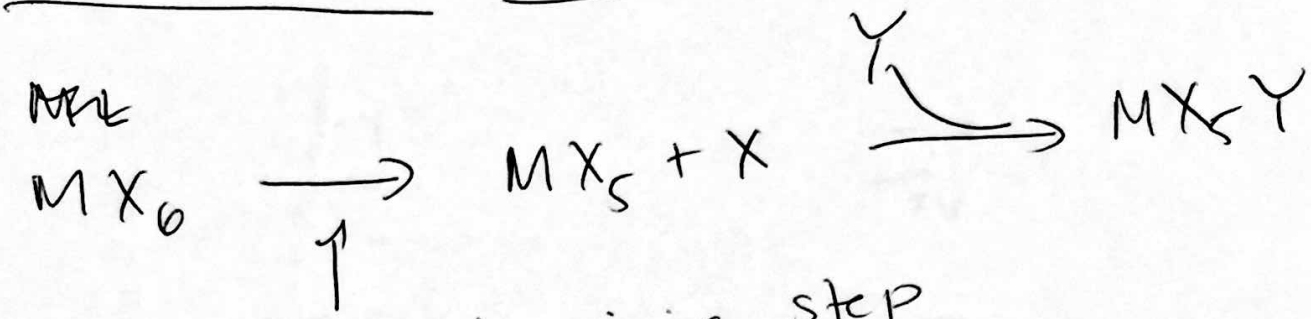
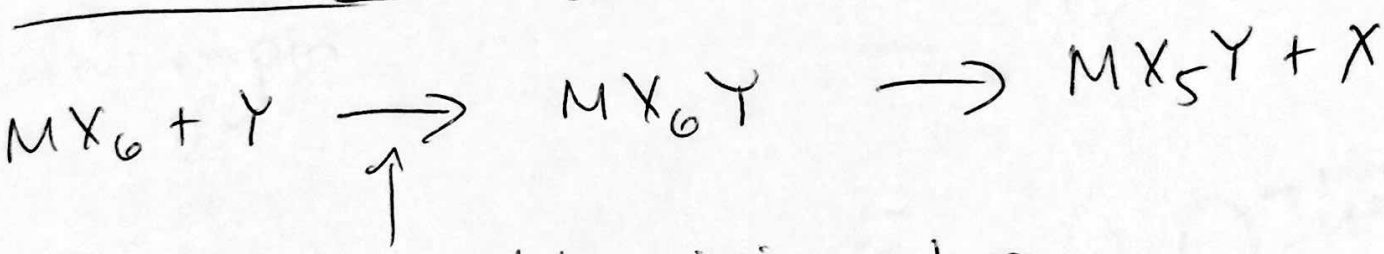
CH 431 Lecture 20 11/8/16

Dissociative mechanism

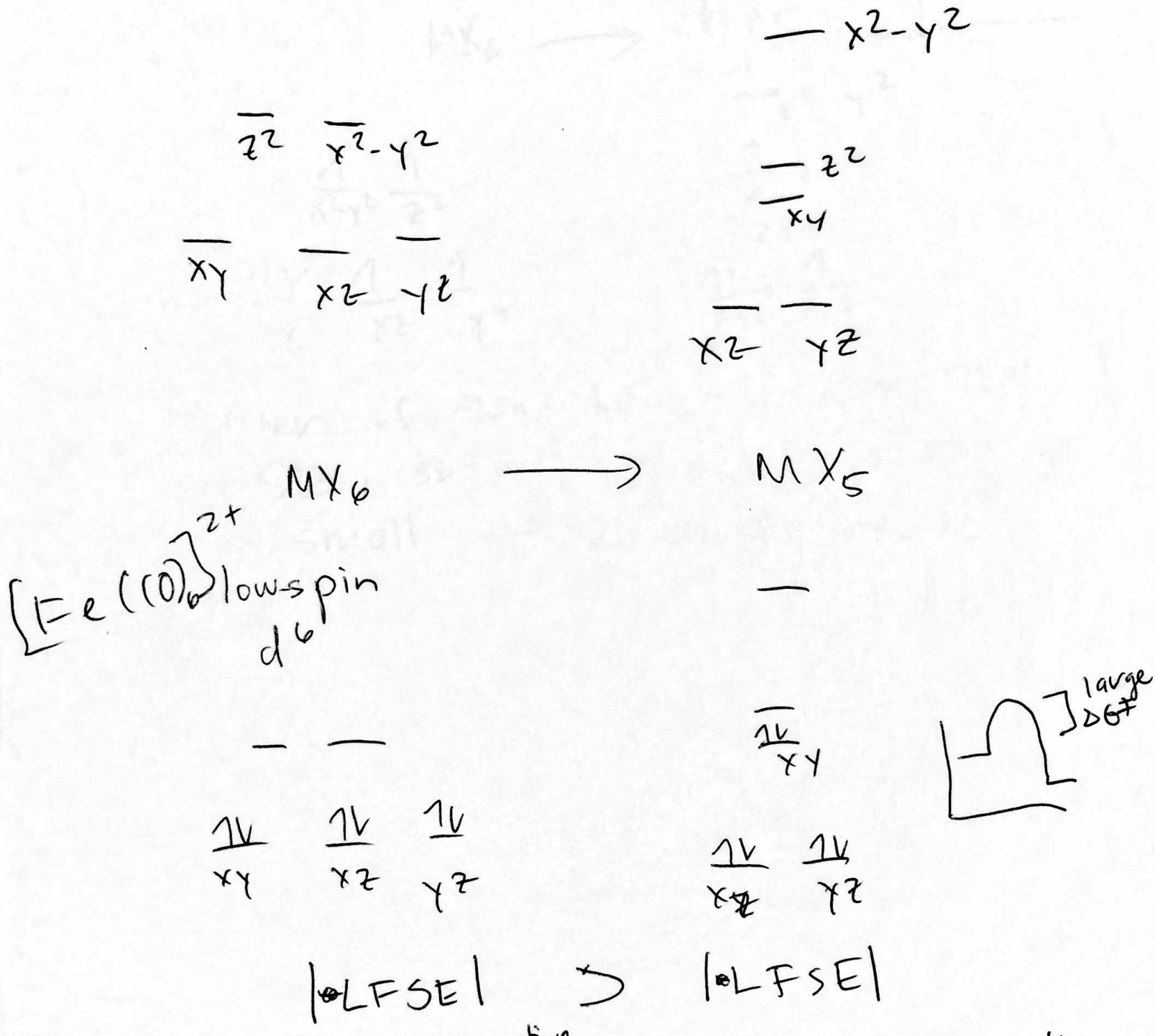


Rate determining step
(this is the step with largest activation energy)

Associative mechanism



Rate determining step



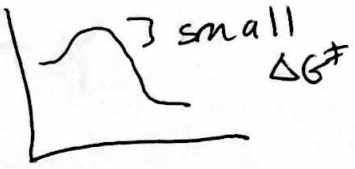
∴ more negative
LFSE ~~greater~~ in octahedral configuration, so activation energy to form 5-coordinate intermediate is large → kinetically inert

high spin d6

$[FeCl_6]^{4-}$

Fe^{2+}

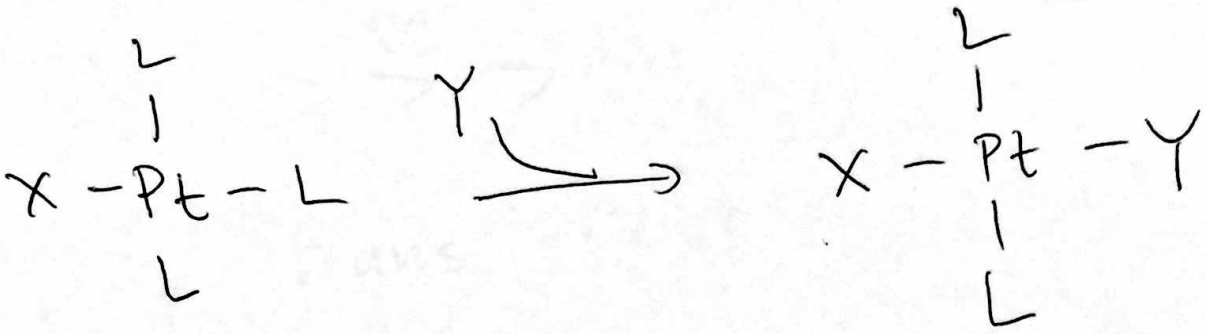
$MX_6 \longrightarrow MX_5$



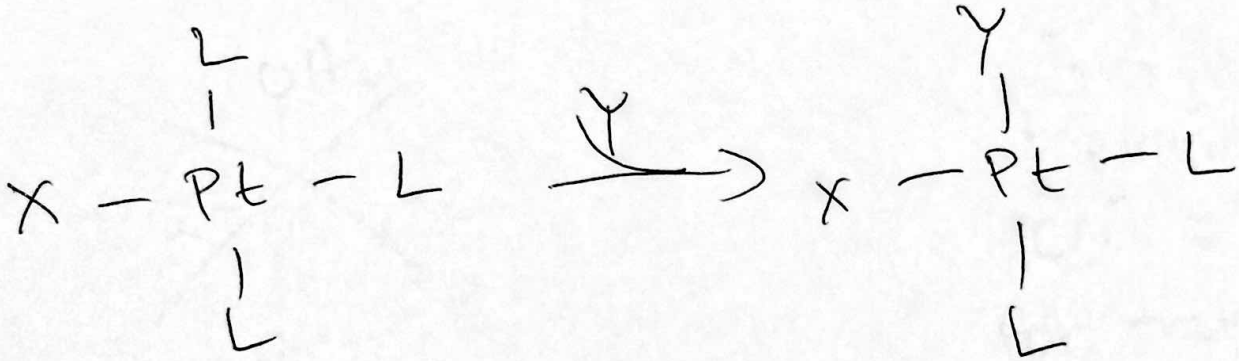
MX_6: $\uparrow$ x^2-y^2, $\uparrow$ z^2, $\uparrow\downarrow$ xy, $\uparrow$ xz, $\uparrow$ yz

MX_5: $\uparrow$ x^2-y^2, $\uparrow\downarrow$ z^2, $\uparrow\downarrow$ xy, $\uparrow\downarrow$ xz, $\uparrow$ yz

neither of these have very negative LFSE, so activation energy is small $\rightarrow$ kinetically labile



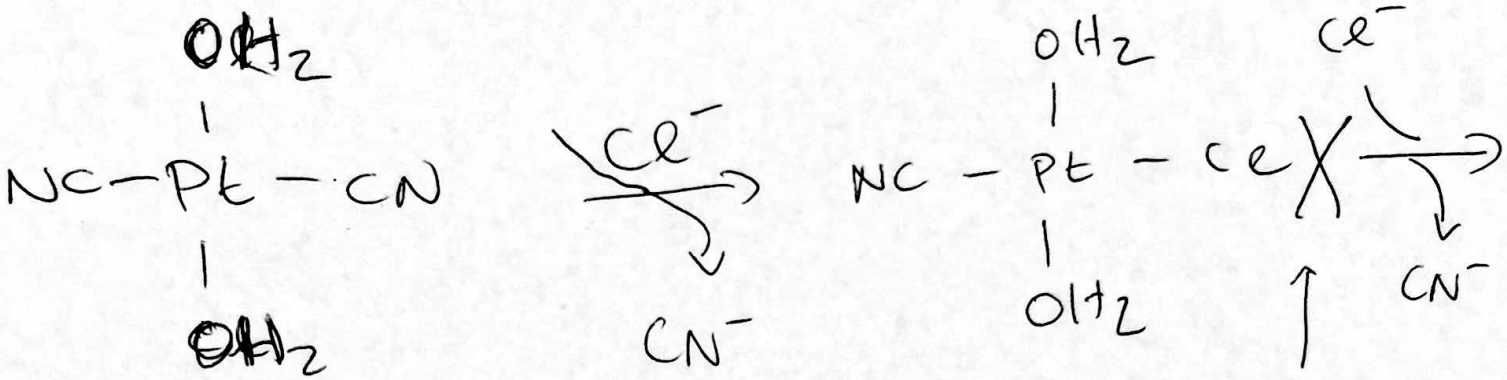
if X has strong trans effect (ligand trans to X will be substituted)



if X has a weak trans effect (ligand trans to X not as likely to be substituted → can form cis product instead)

$CN^- > Cl^- > H_2O$

trans effect



stop at this stage because CN^- > Cl^- for trans effect