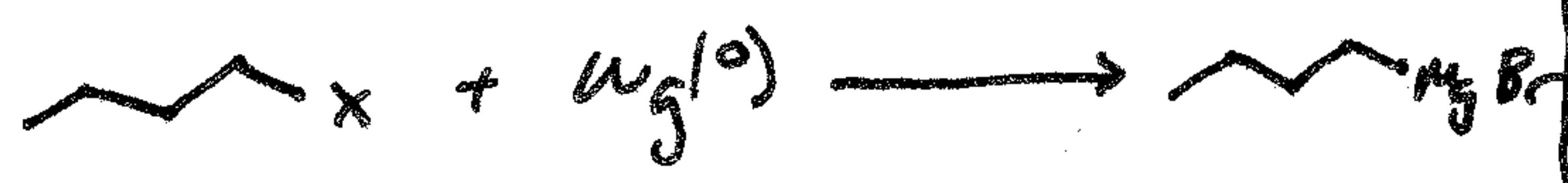
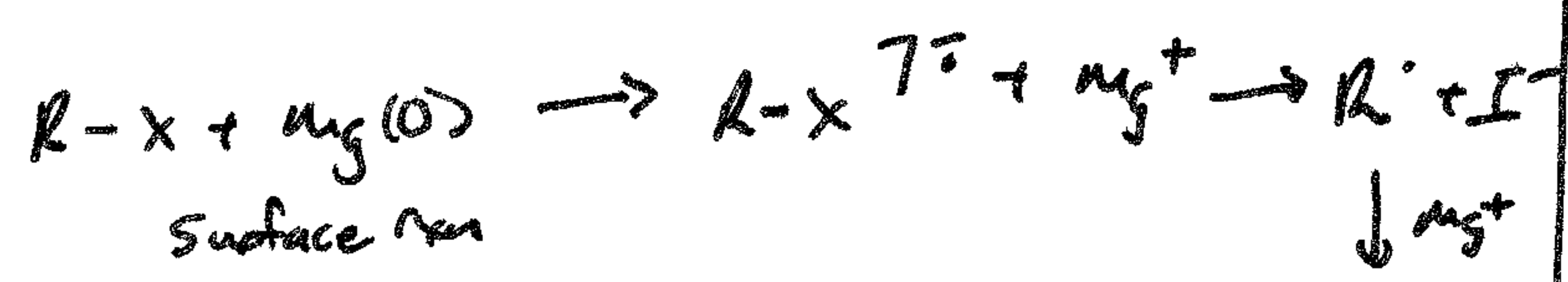


① Classical Organometallic Chem

Grignard rxn

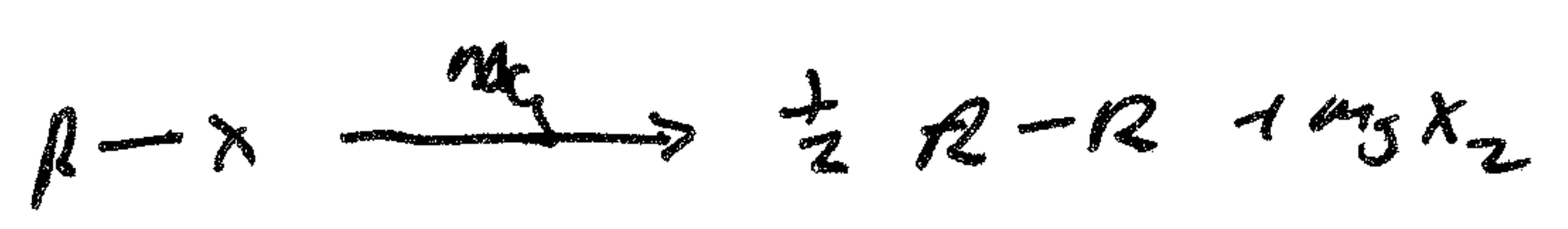


X: I > Br >> Cl >> F



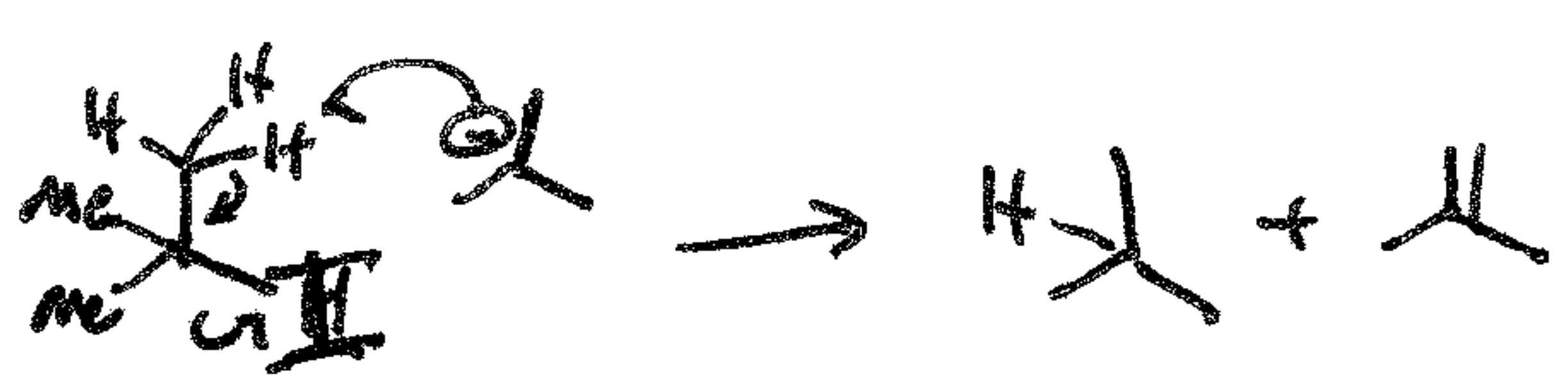
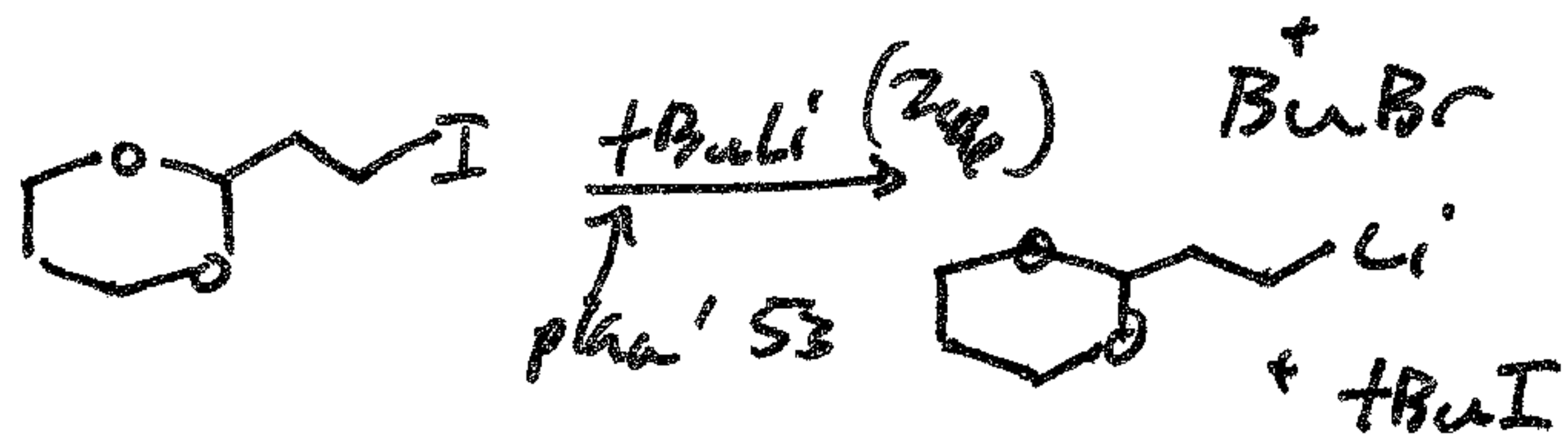
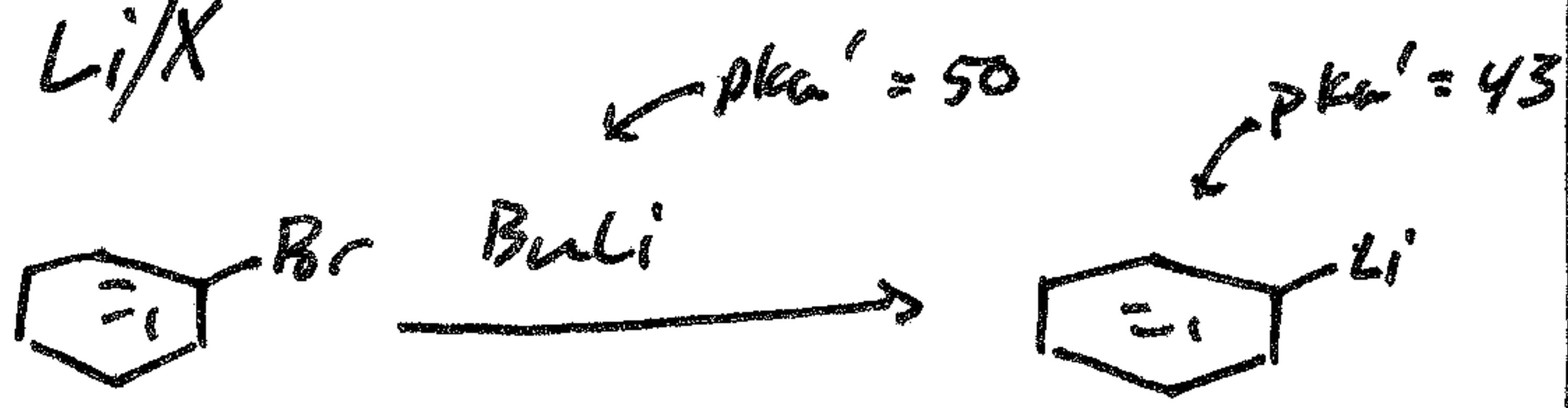
(also w/ C, Si, Zn)

② Wurtz coupling



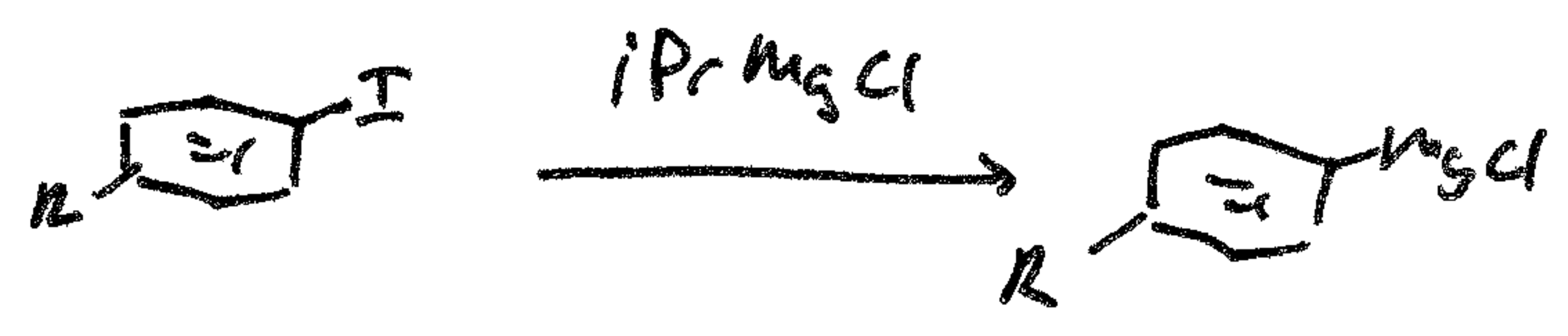
③ Metal-halide Exchange

Li/X



2nd eq of tBuLi prevents product from quenching on tBuI

④ Mg/X

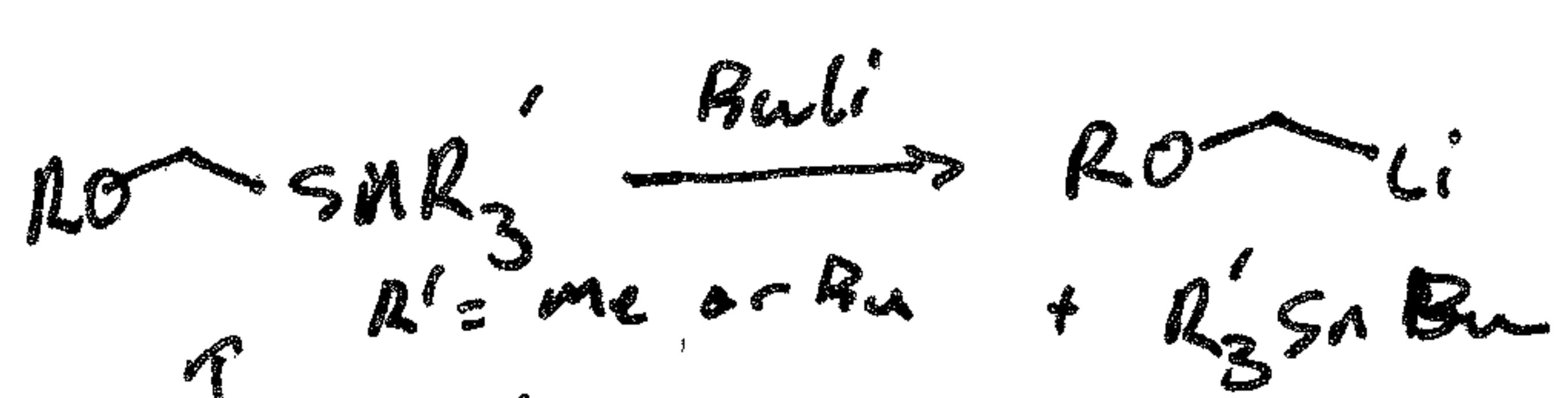


- typically low temp (R = EWG), ~-20°C

- low temp allows R = CO₂Me, NO₂, NO₂ etc

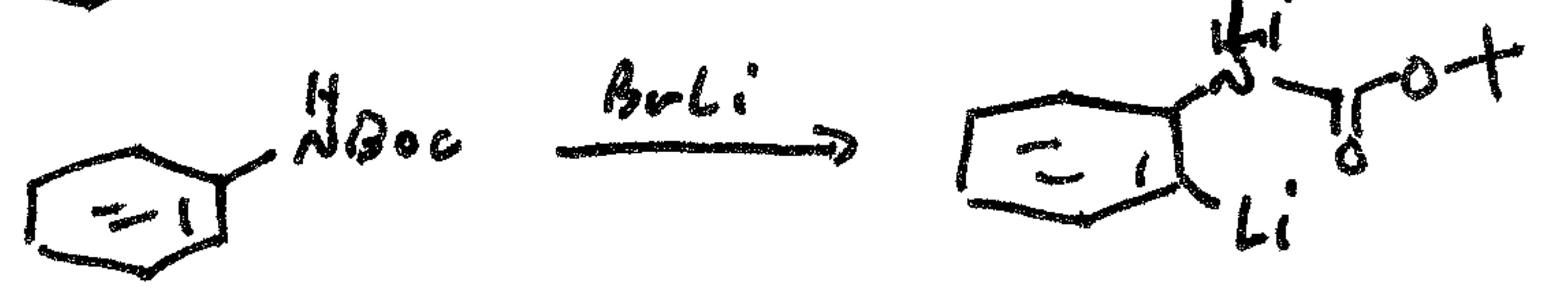
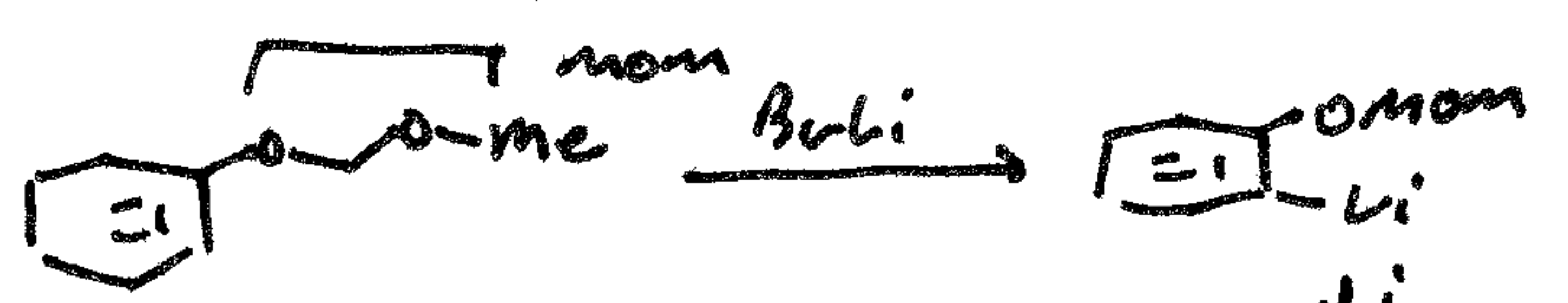
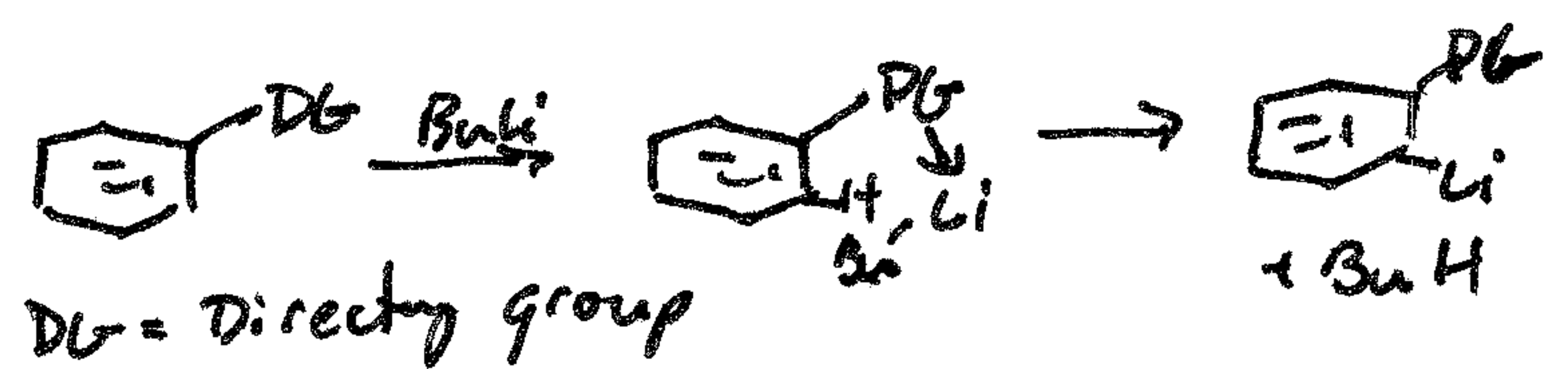
Knochel, ACIE, 2003, 42, 4302

⑤ Sn/Li



↑ or other stab. T. Fed allyl tin

⑥ Directed metalation



Snieckus, Chem Rev, 1990, 90, 979

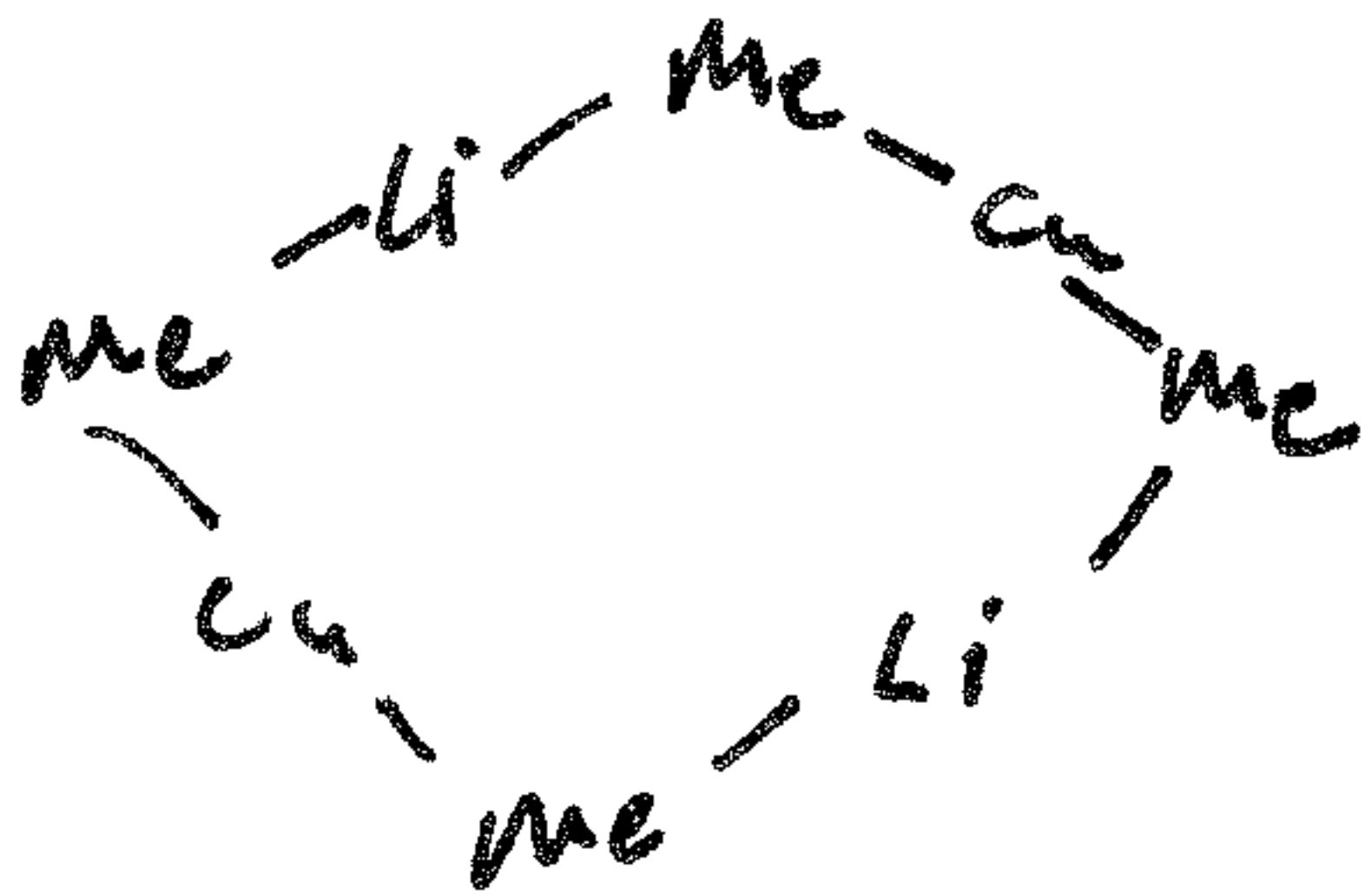
① Cuprates



X = I, Br, Cl, .

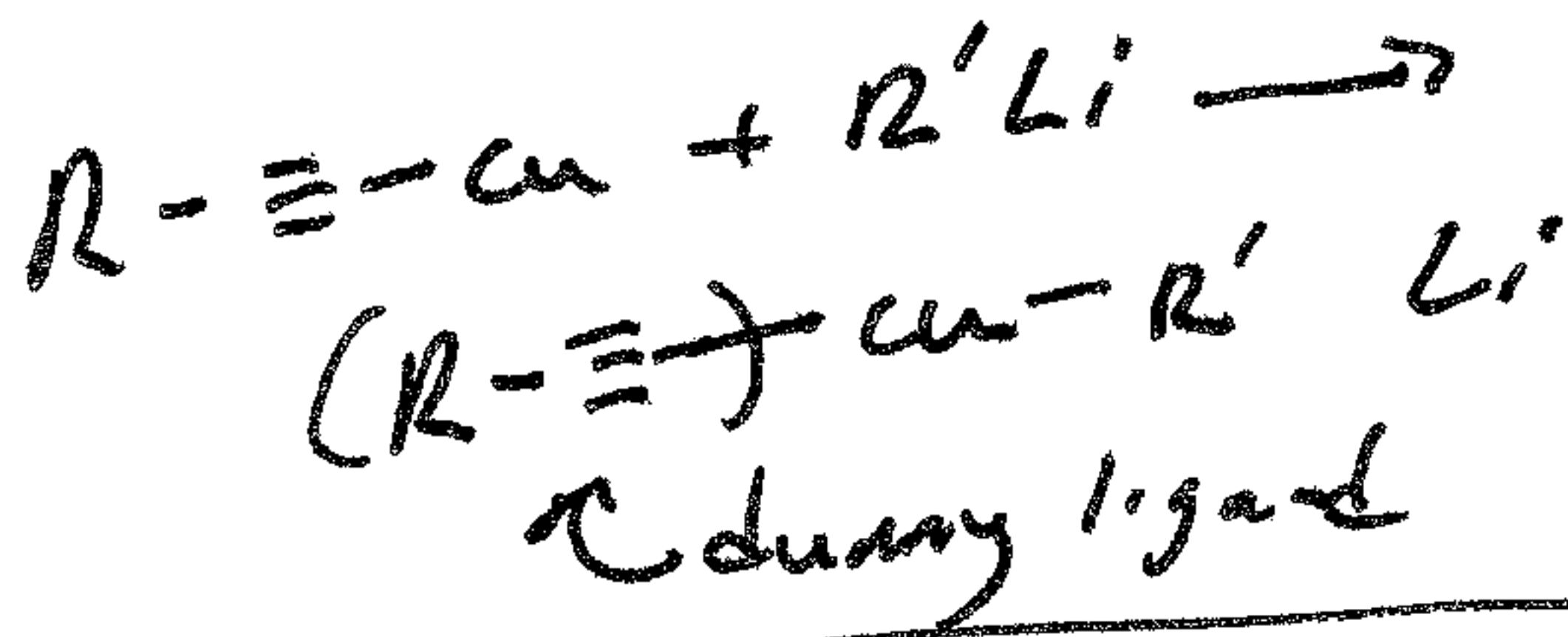
Gilman Cuprate

Soft, less basic



Modern Organocopper Chem, Ed Krause
Wiley, 2002

② other CuX



Cyano cuprates

"higher order"
Gilman cyanocuprate

③

④

⑤

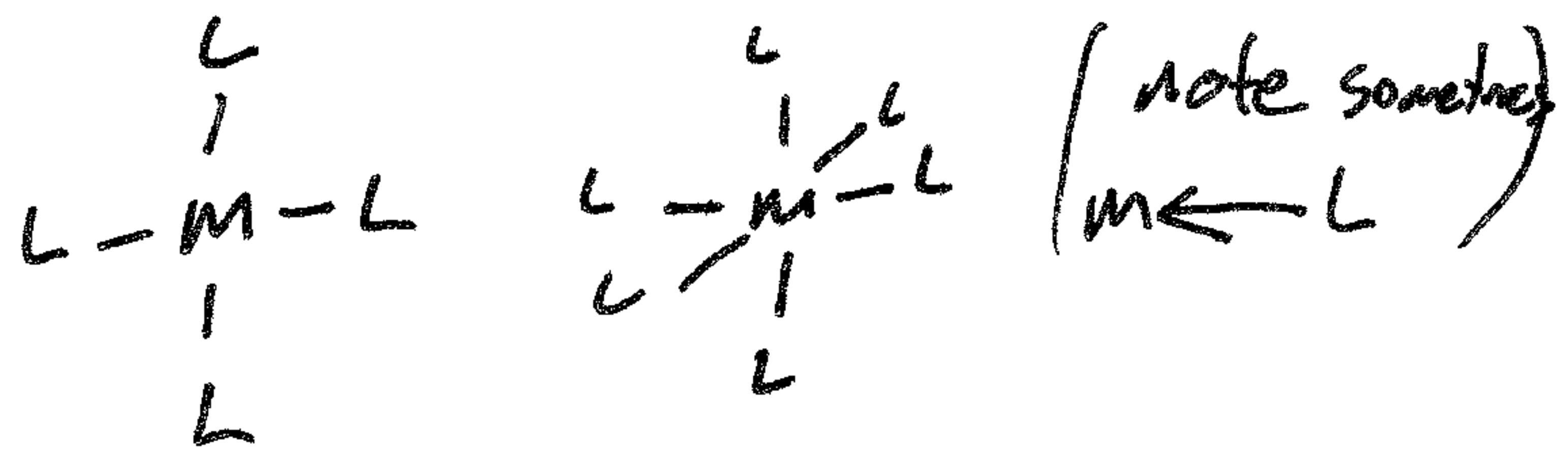
⑥

① Intro to organo-transition metal chemistry

1) Formal charge, d-electrons & ligand types

2) Basic mechanisms of organometallic rxns.

② Complexes of interest
mainly soluble molecules containing metal atoms



- Ligands support metal modulate reactivity

③ Assigning formal charge / d-electrons

1) ID metal center & Group to get d-electron count for $M(0)$

2) "Disconnected" ligands w/ electron. $M-L \rightarrow M :L$

3) Assign charges to ligands

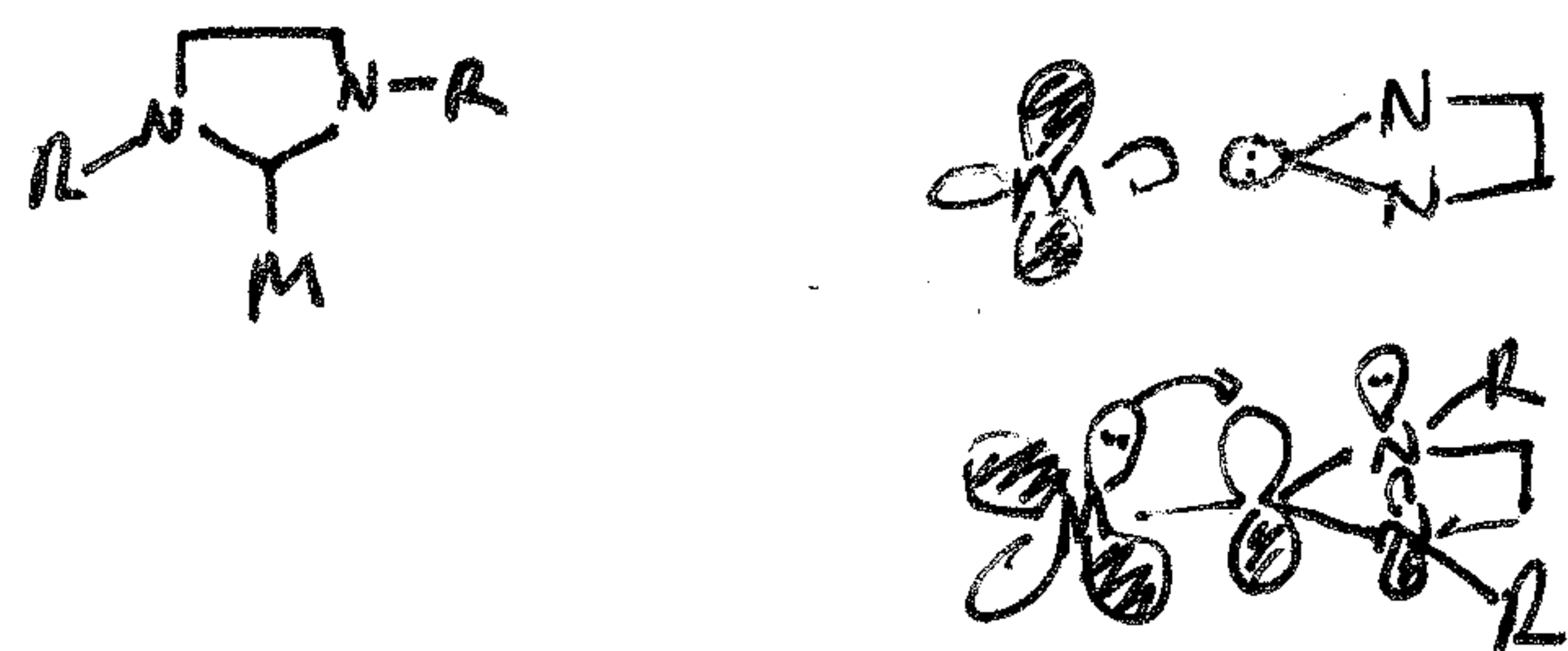
4) Balance charges on metal (don't forget overall charge)

5) Assign d-electrons to complex

④ Ligand Types

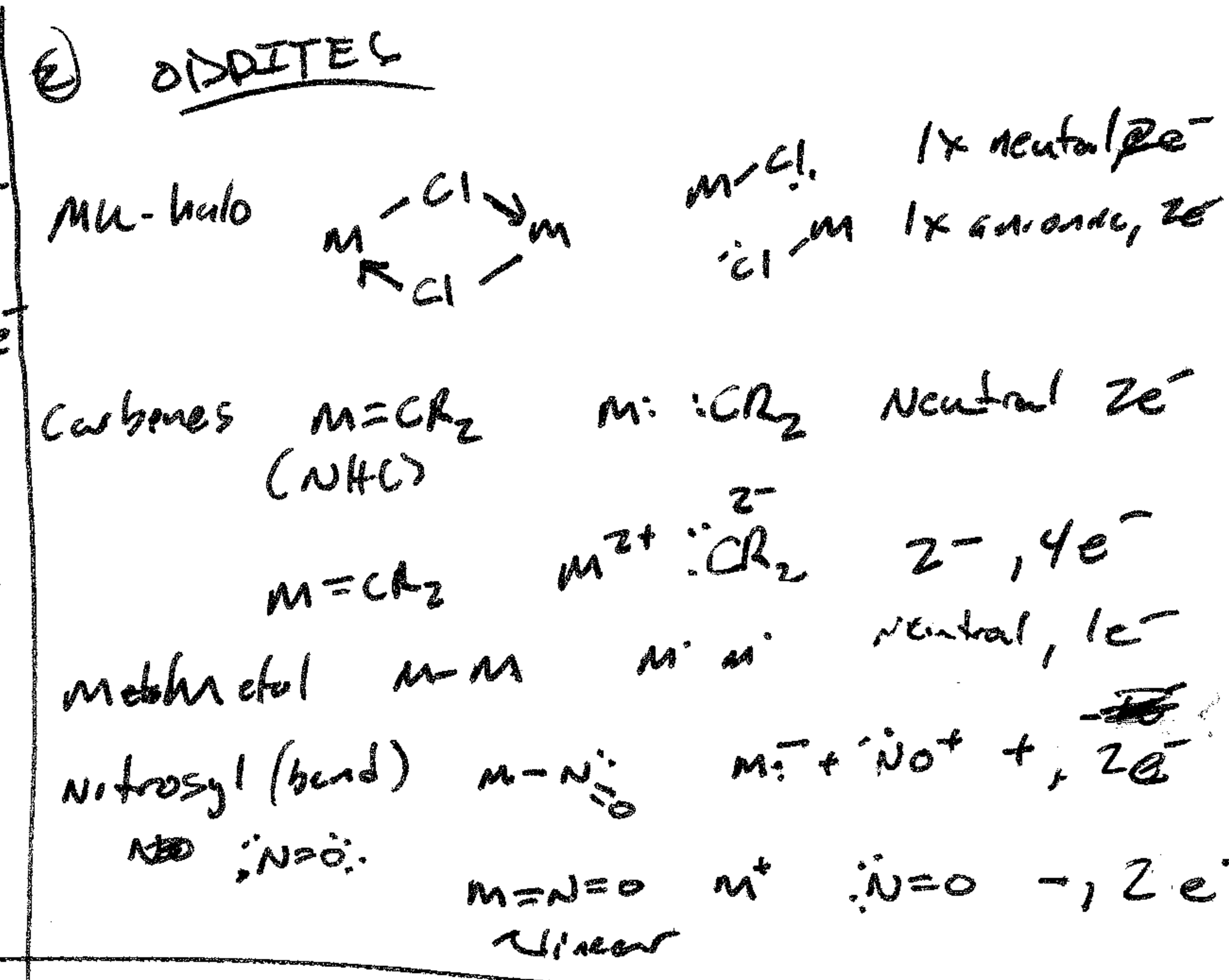
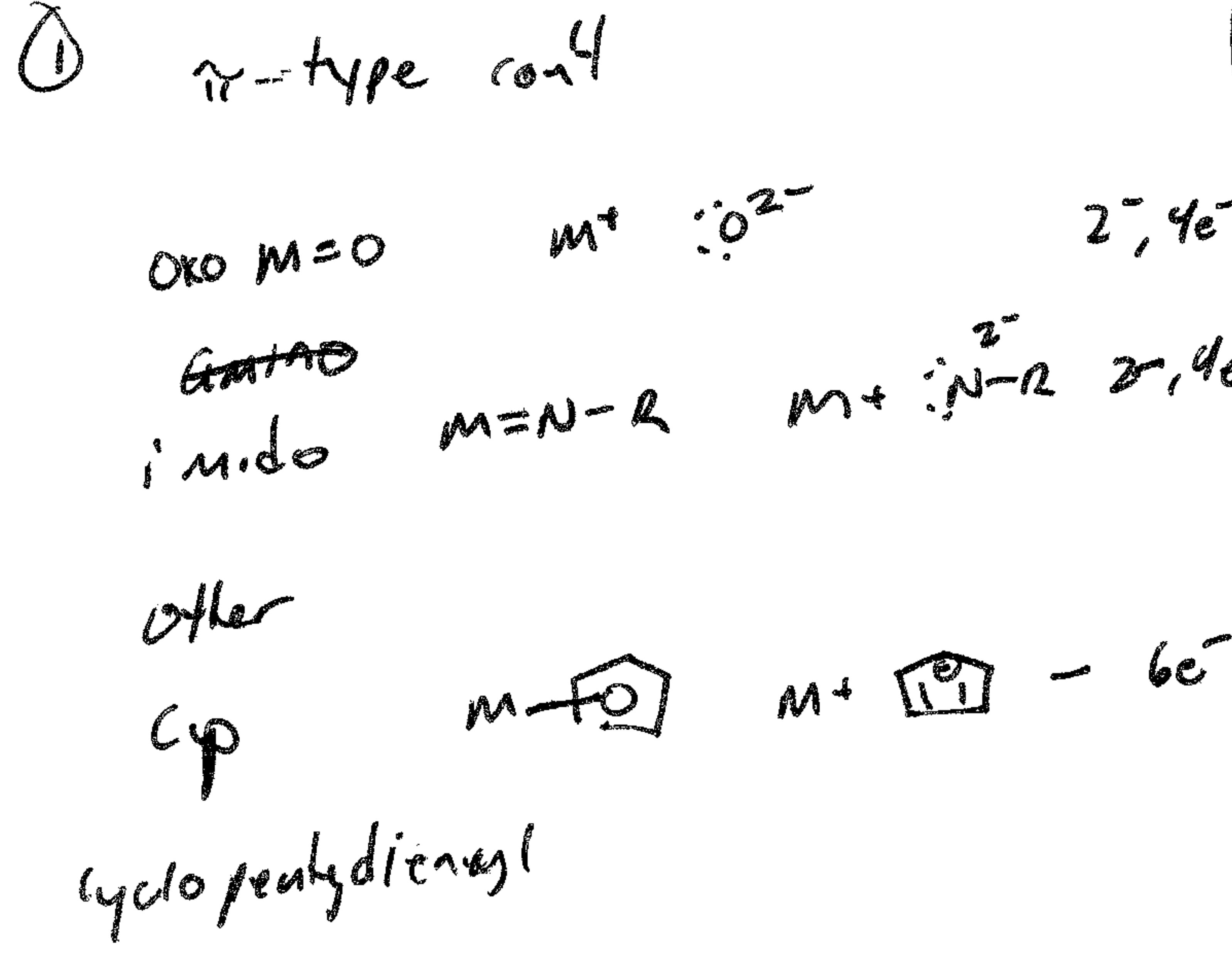
L-type (neutral)	disconnect charge	charge	d	e^-
Phosphine	$M-PPh_3$	$M+ :PPh_3$	0	$2e^-$
Amine	$M-NR_3$	$M+ :NR_3$	0	$2e^-$
Carbonyl	$M-C\equiv O$	$M+ :C\equiv O:$	0	$2e^-$
alkene	$M- $	$M+ \begin{array}{c} \text{C} \\ // \\ \text{C} \end{array}$	0	$2e^-$
C-H	$M-\begin{array}{c} H \\ \\ CR_3 \end{array}$	$M+ \begin{array}{c} H \\ \\ CR_3 \end{array}$	0	$2e^-$
Nitrile	$M-N\equiv C-R$	$M+ :N\equiv C-R$	0	$2e^-$
diene	$M \rightleftharpoons \text{C}=\text{C}$	$M+ \rightleftharpoons \text{C}=\text{C}$	0	$4e^-$
arene (η^6)	$M-\text{C}_6\text{H}_6$	$M+ \text{C}_6\text{H}_6$	0	$6e^-$
arene (η^2)	$M-\text{C}_2\text{H}_4$	$M+ \text{C}_2\text{H}_4$	0	$2e^-$

⑤ N-heterocyclic carbenes



X-type (anionic)

	charge	d	e^-
halide	$M-Cl^-$	$M+ :Cl^-$	$- 2e^-$
acetate (η^2)	$M-O-C(=O)Me$	$M+ :O-C(=O)Me$	$- 2e^-$
acetate (η^4)	$M-O-C(=O)Me$	$M+ O-C(=O)Me$	$- 4e^-$
allyl (η^2)	$M-CH_2-CH=CH_2$	$M+ \text{allyl}^-$	$- 2e^-$
allyl (η^4)	$M-CH_2-CH=CH_2$	$M+ \text{allyl}^-$	$- 4e^-$
amide	$M-NR_2^-$	$M+ :NR_2^-$	$- 2e^-$
alkoxide	$M-OR^-$	$M+ :OR^-$	$- 2e^-$



③ $18e^-$ rule

d-block - 5 d orbitals

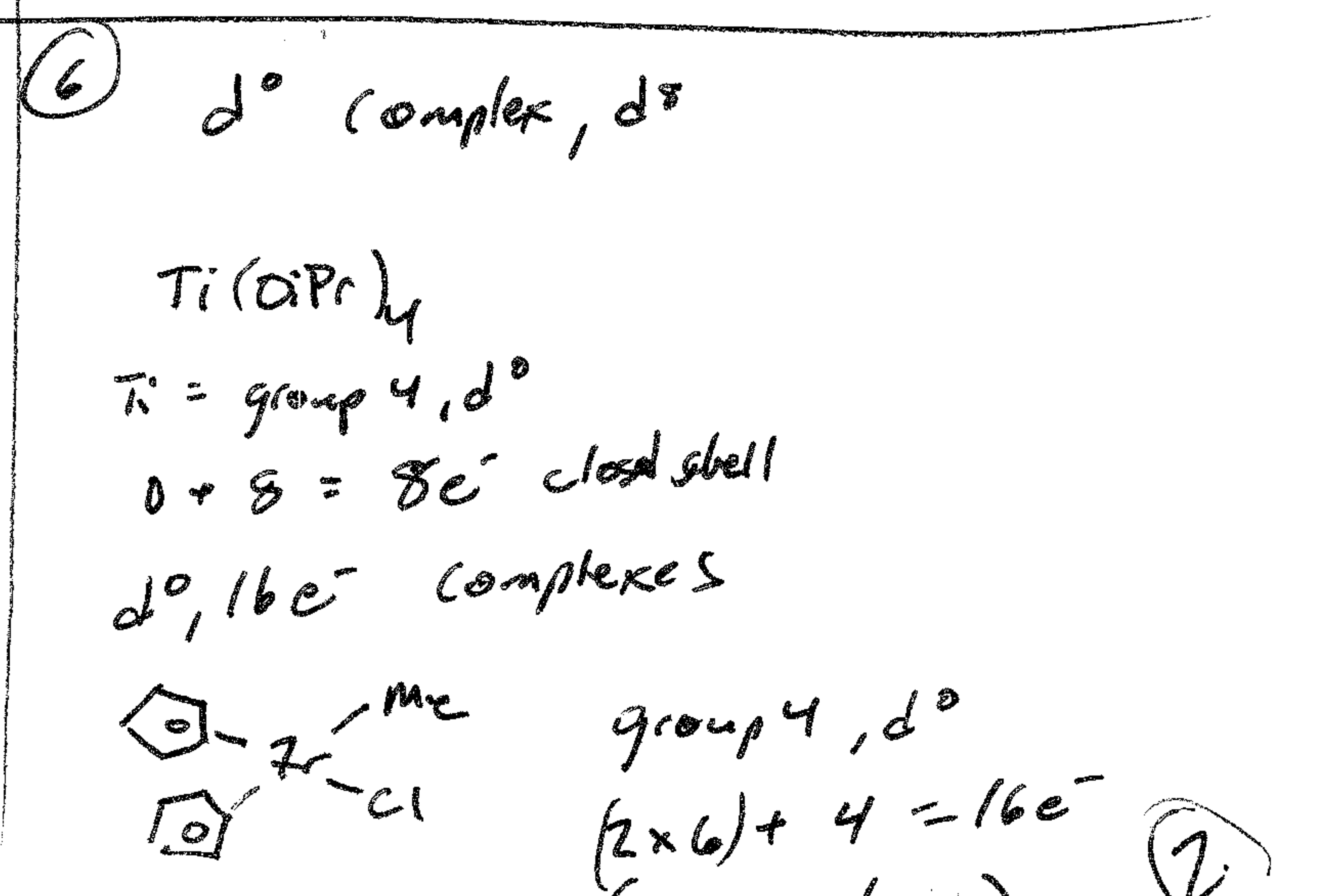
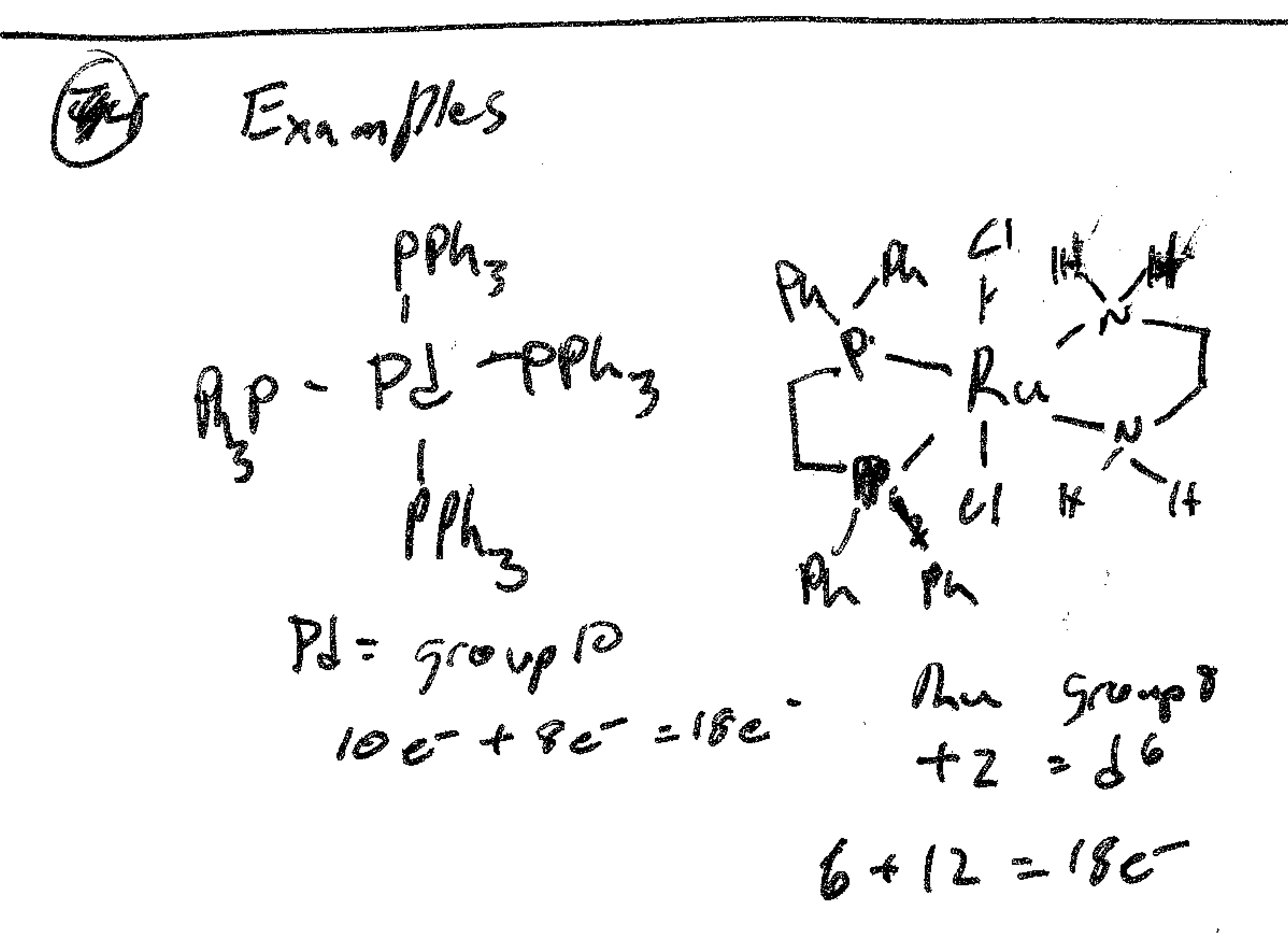
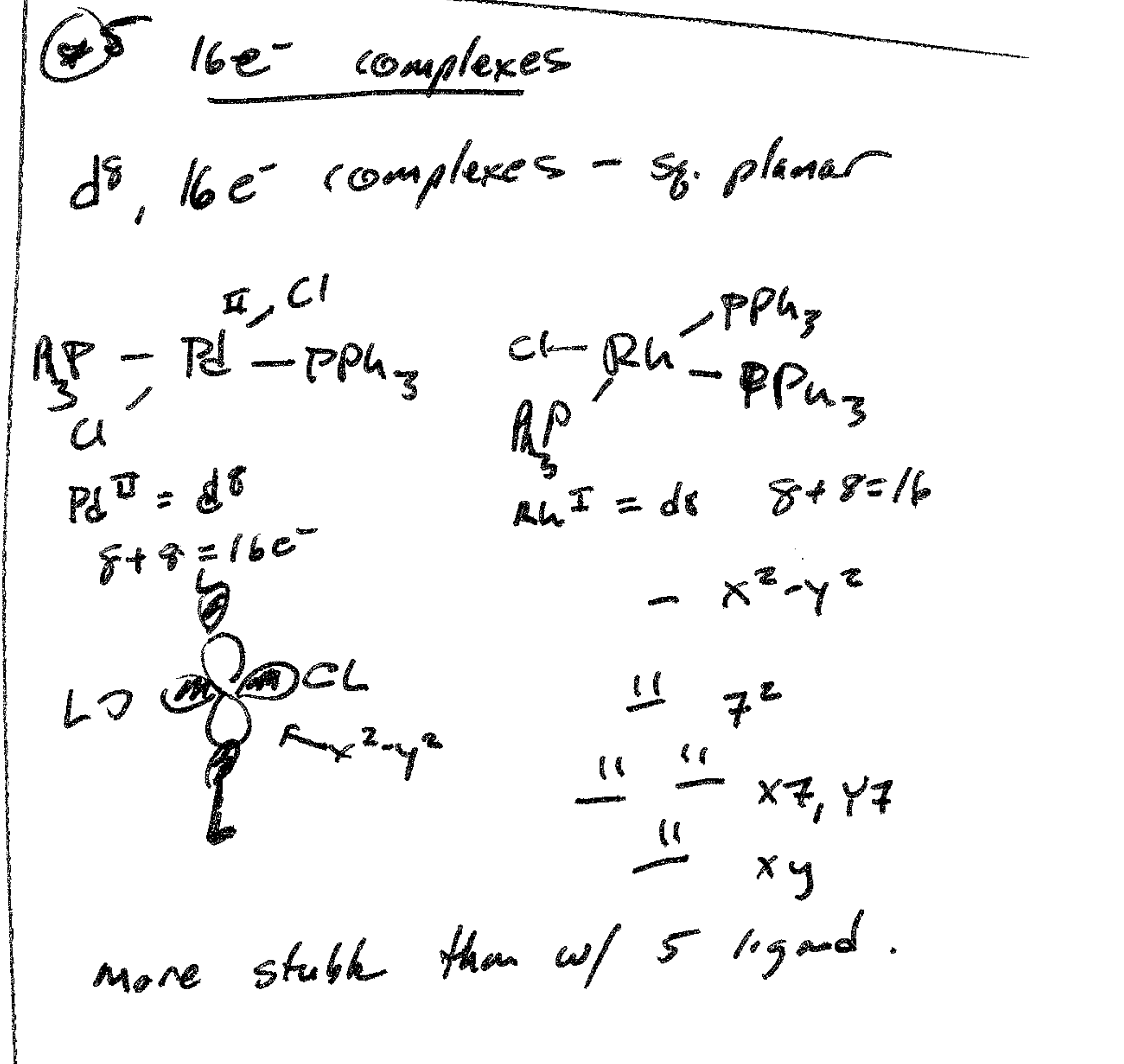
$S, 3P, 5D \equiv 2+6+10 = 18e^-$

Most transition metal complexes

Want $18e^-$.

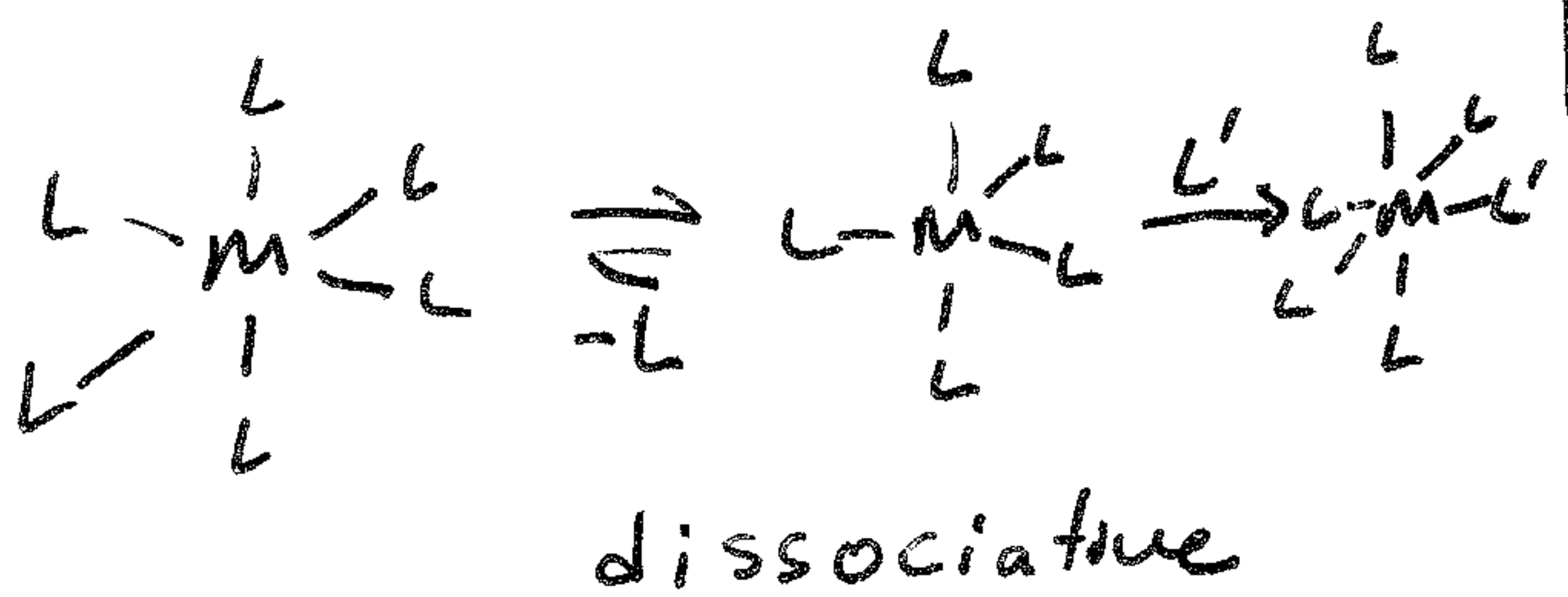
Note

Oxidation state is a formalism not rule



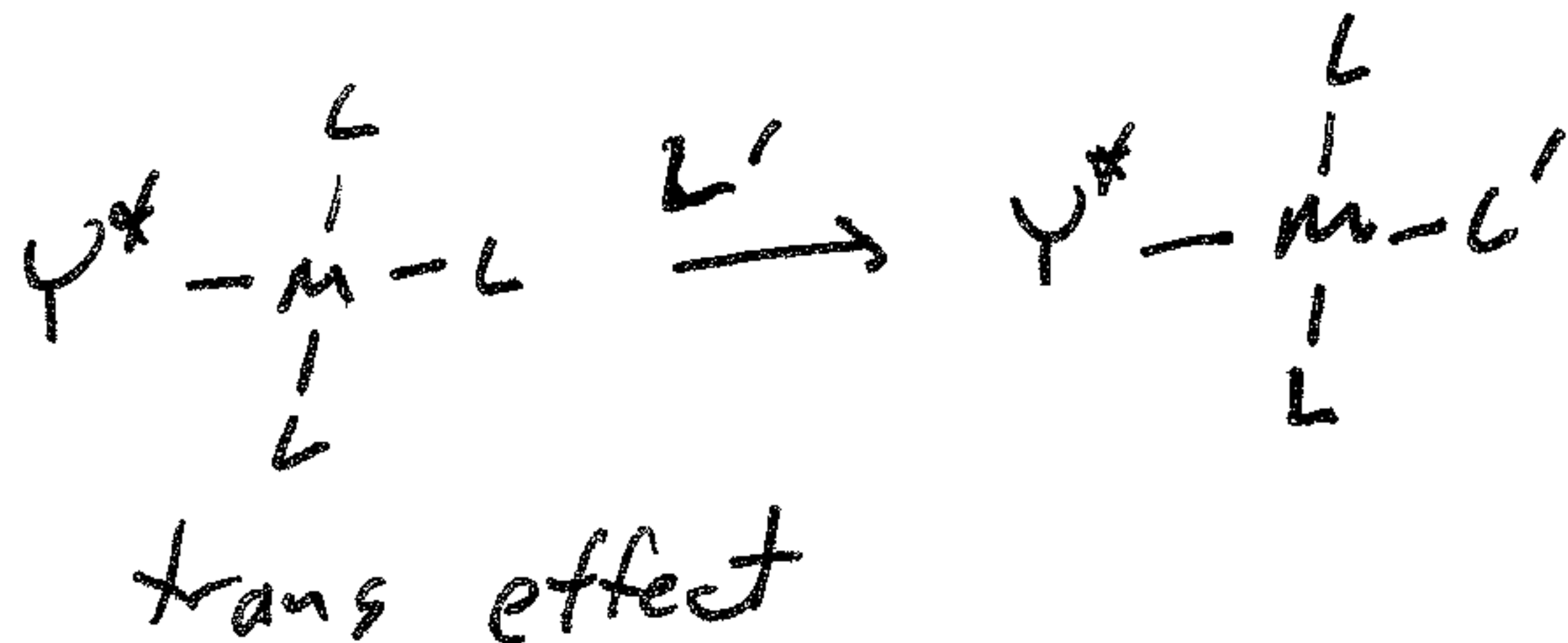
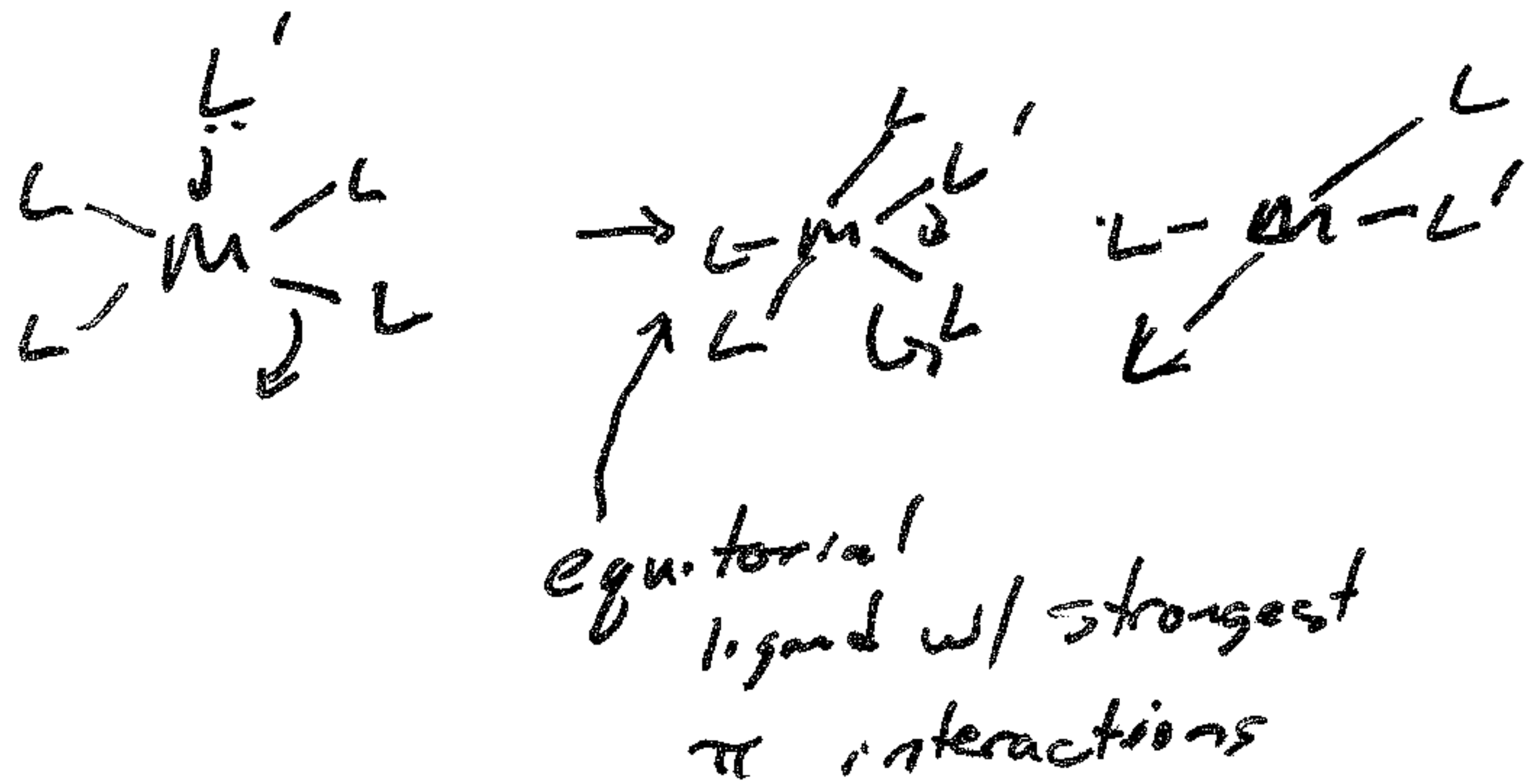
① Basic O.M mech's

Ligand substitution



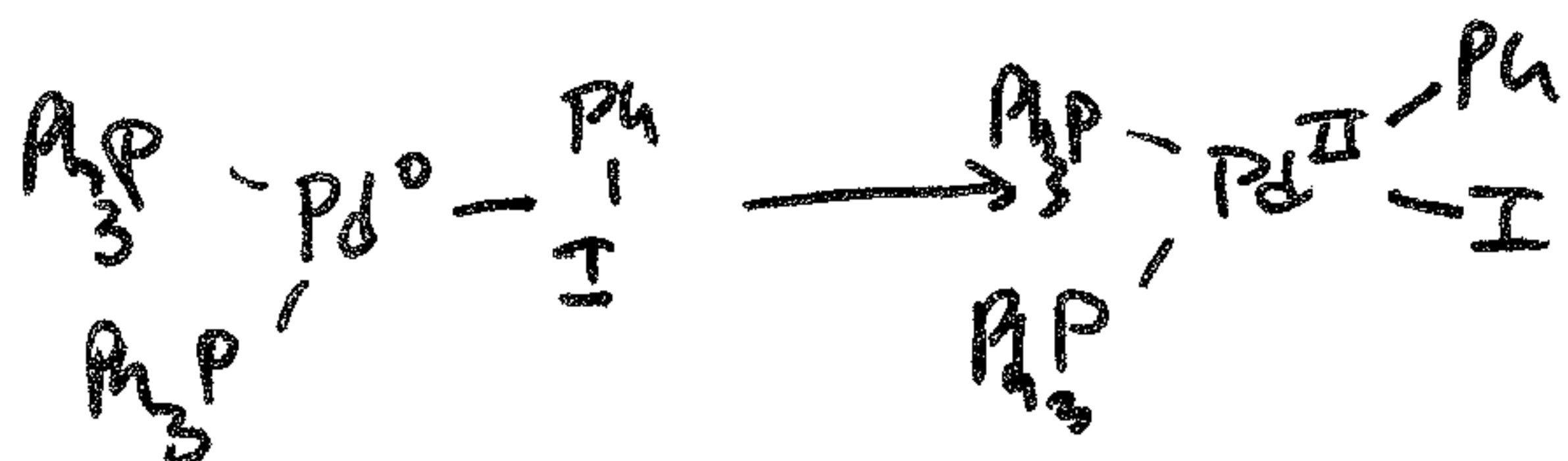
Common w/ coordinatively saturated
-oh
-18e- complexes

Associative



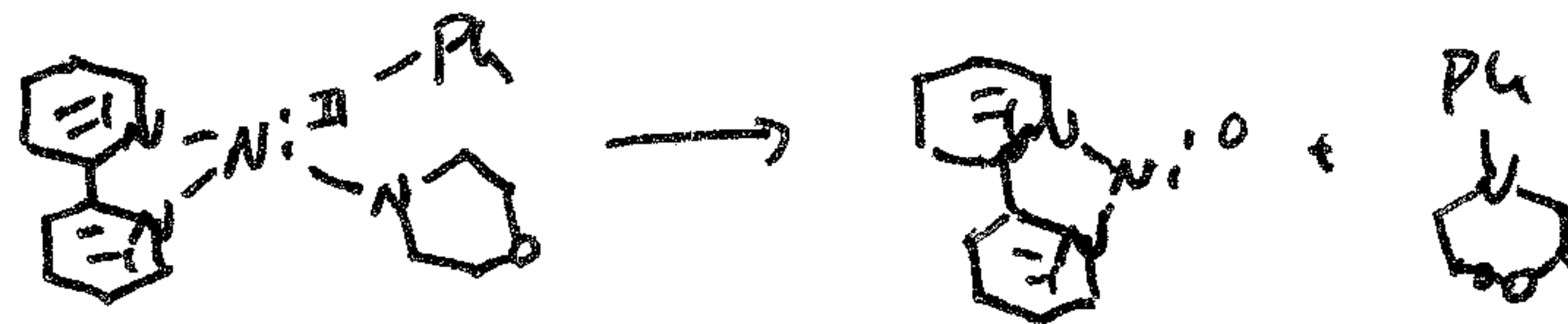
Oxidative addition

brackets mean details not specified



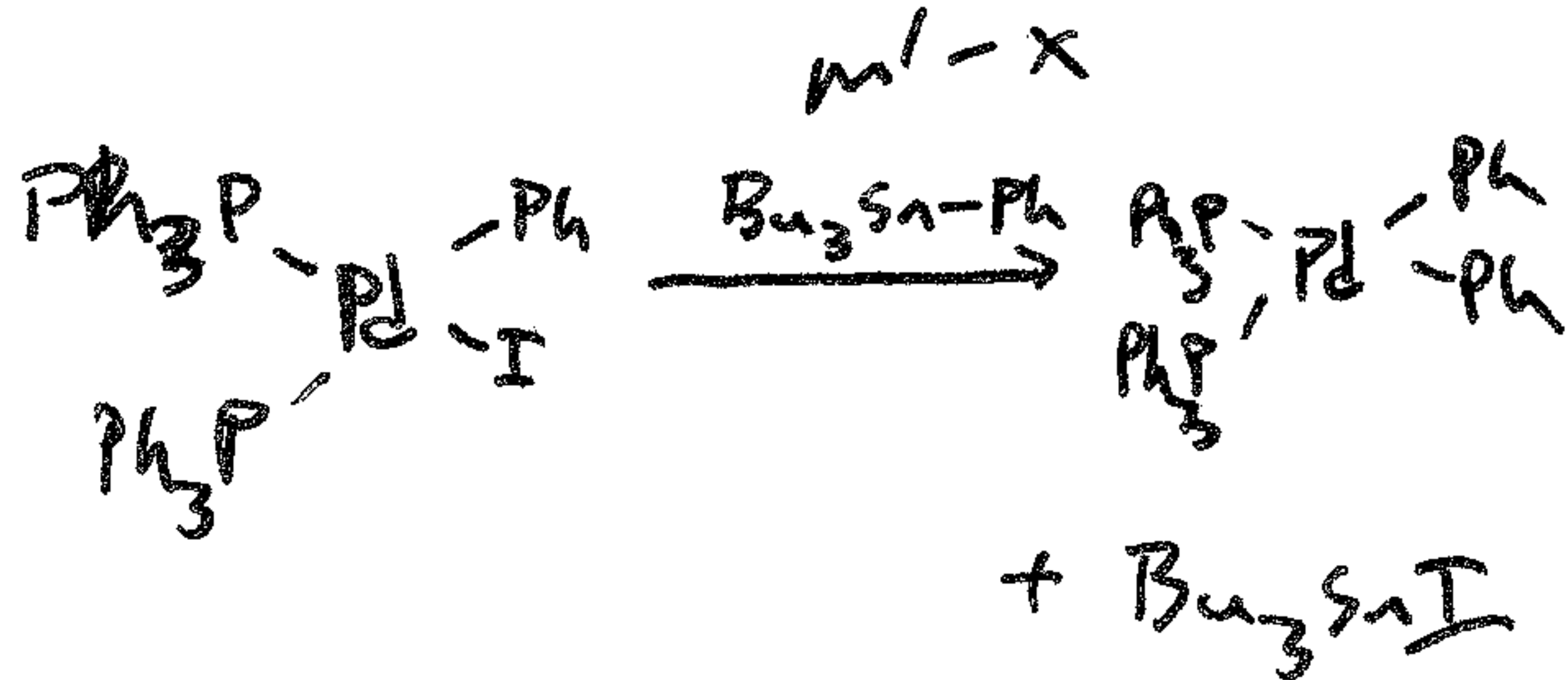
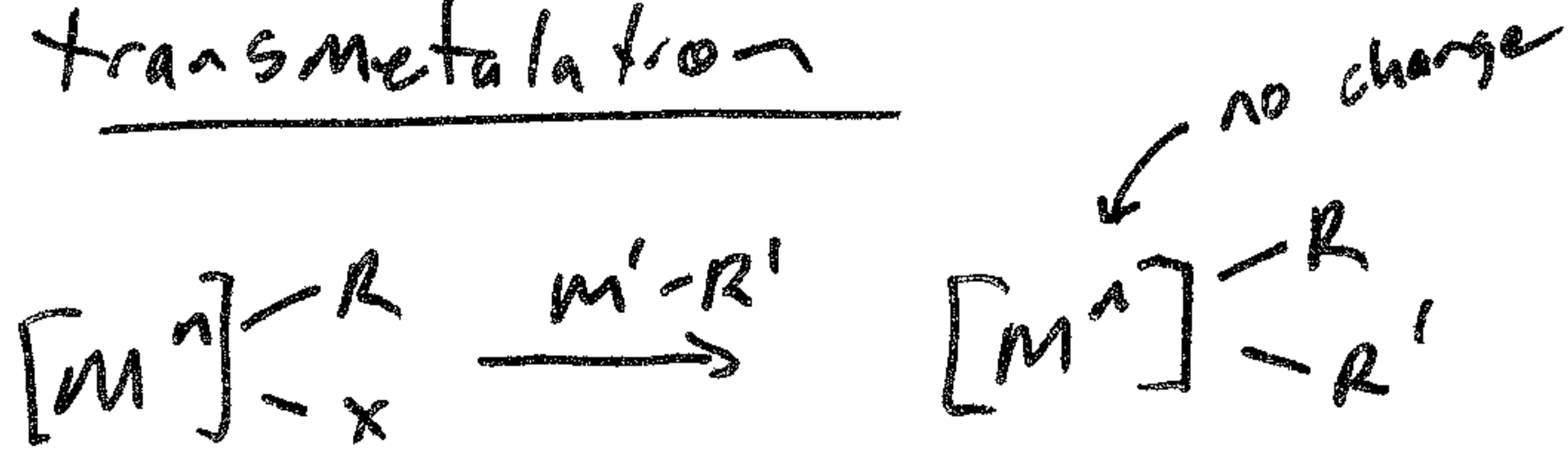
electron rich metal centers

Reductive Elimination

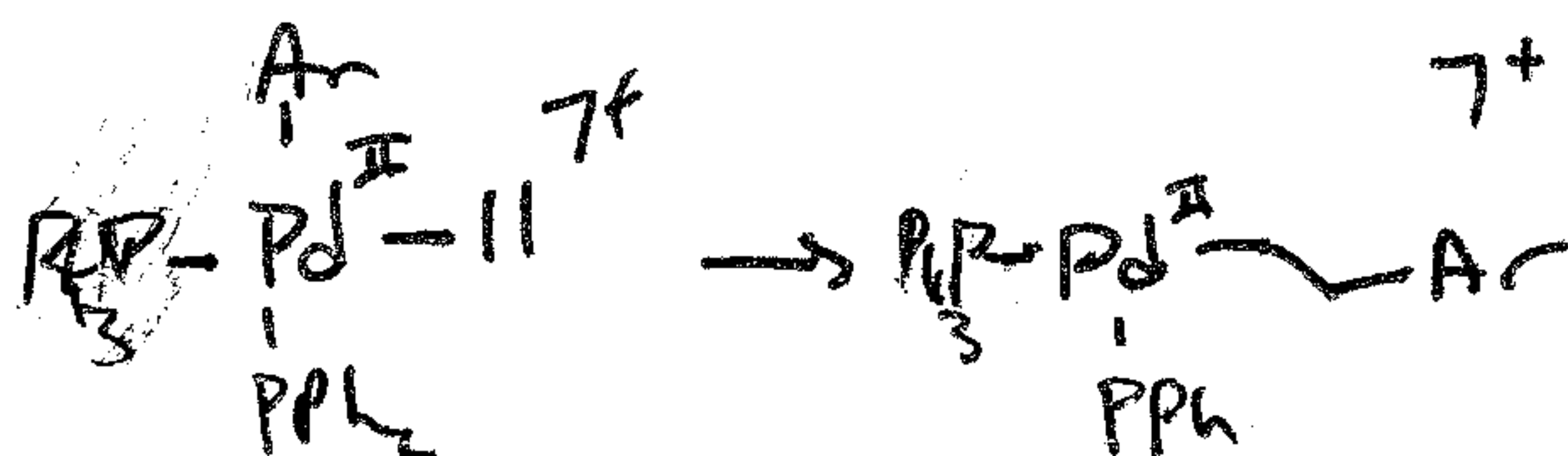
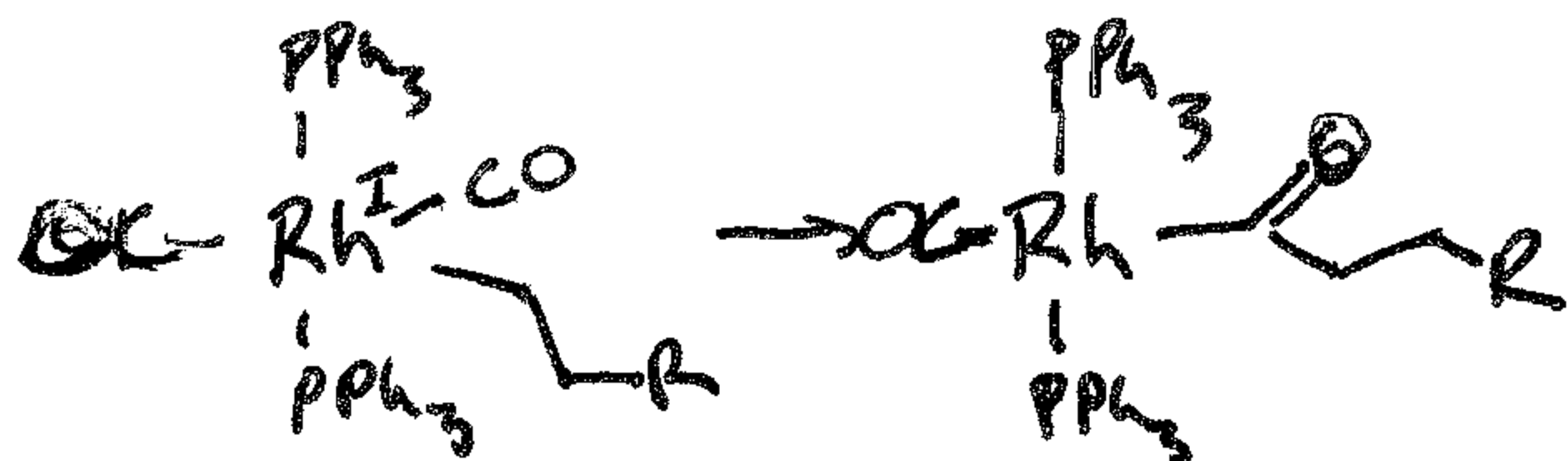


- Promoted by electron poor metal centers
- large ligands accelerate
- microscopic reverse of O.M.

transmetalation



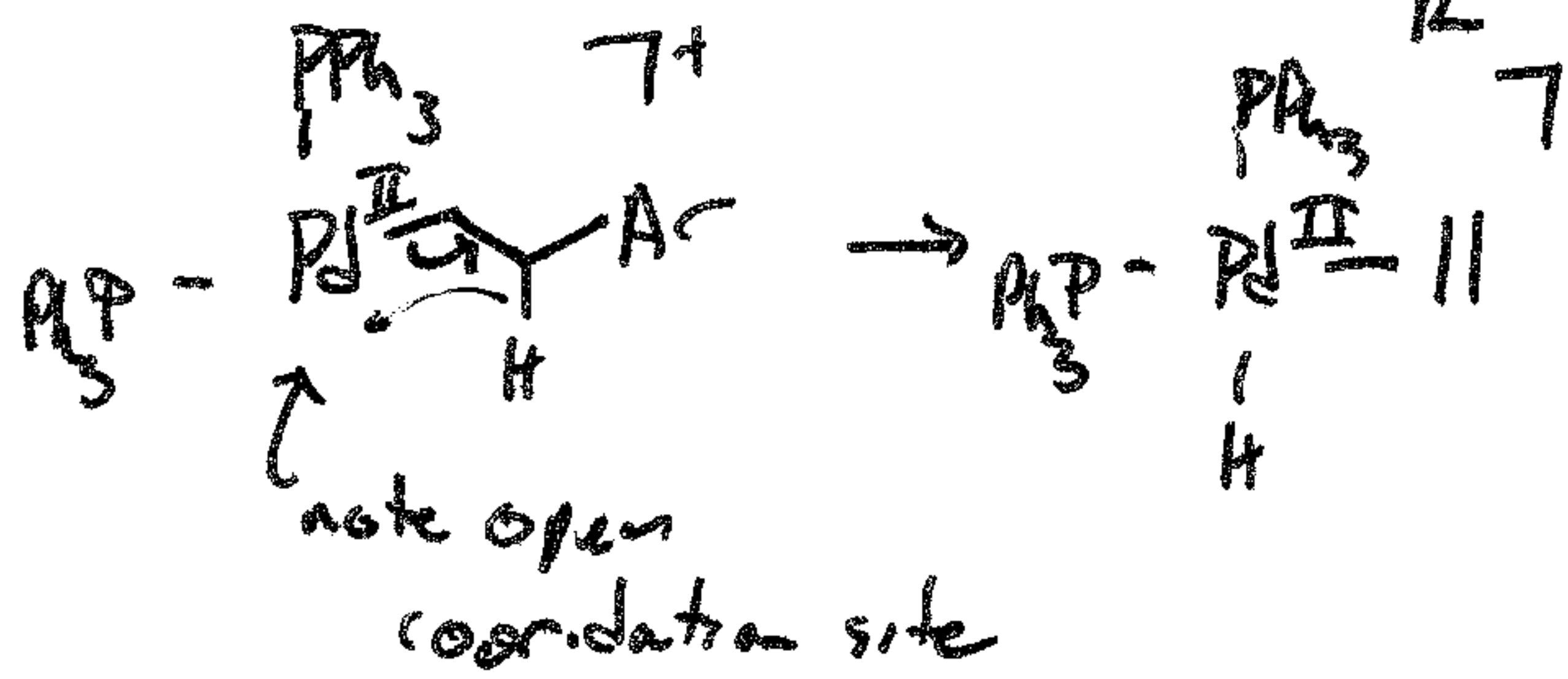
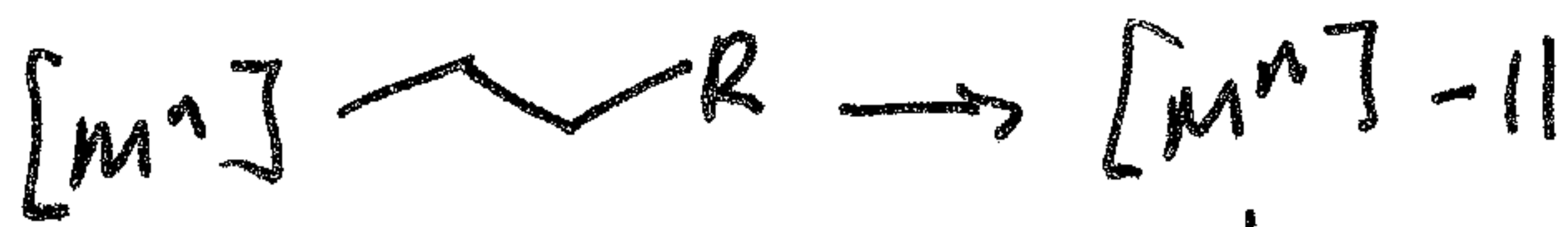
migratory insertion



(2)

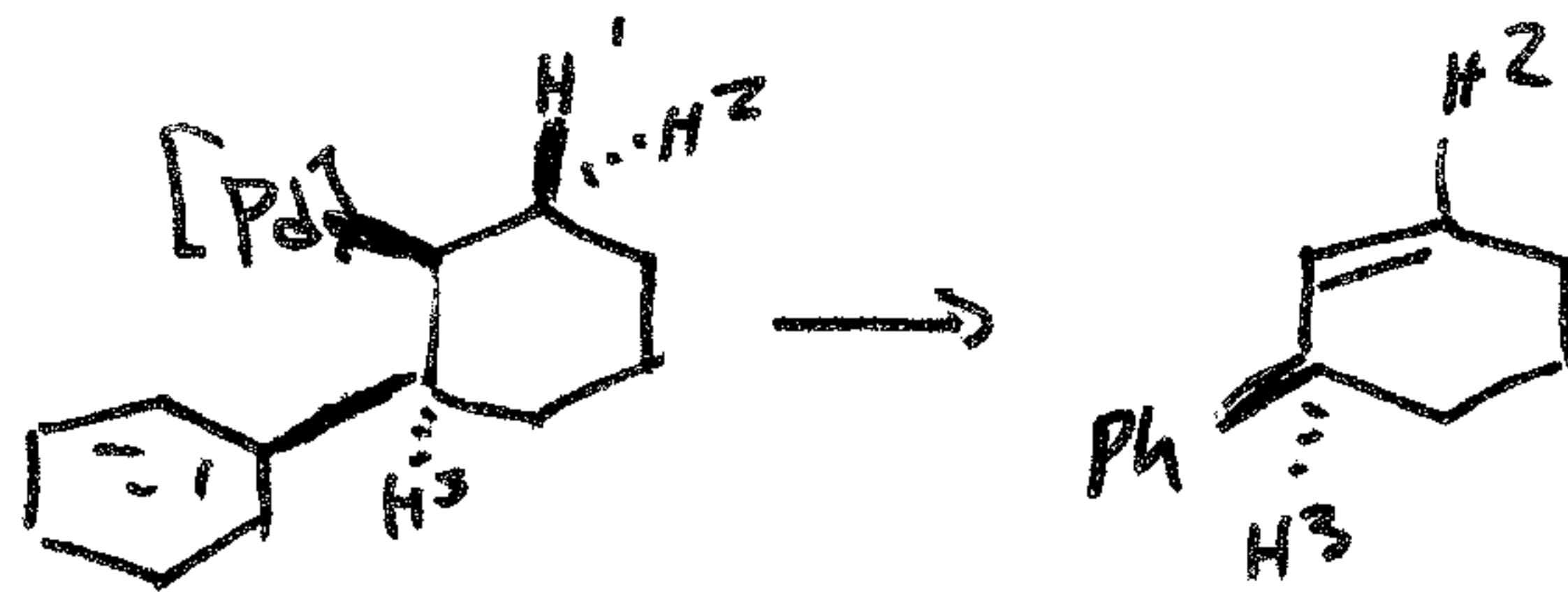
①

β -elimination (hydride)

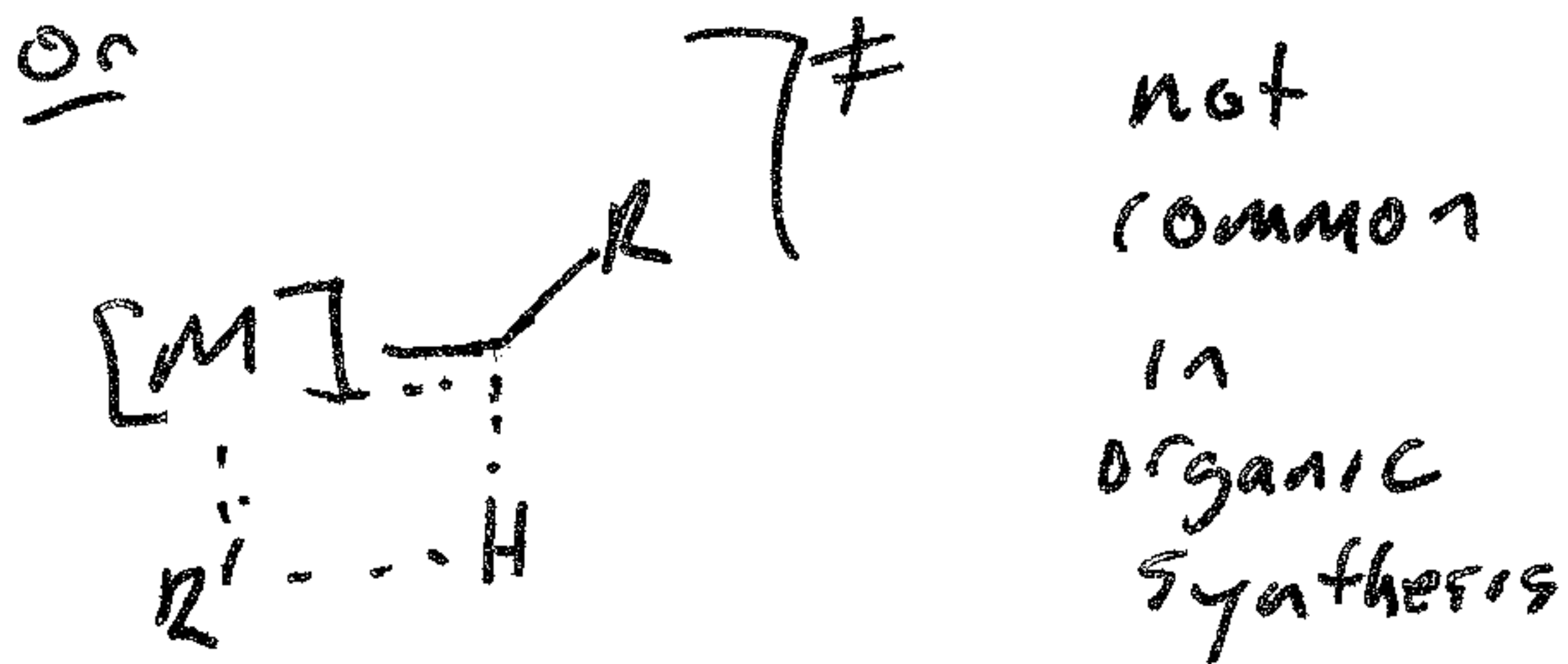
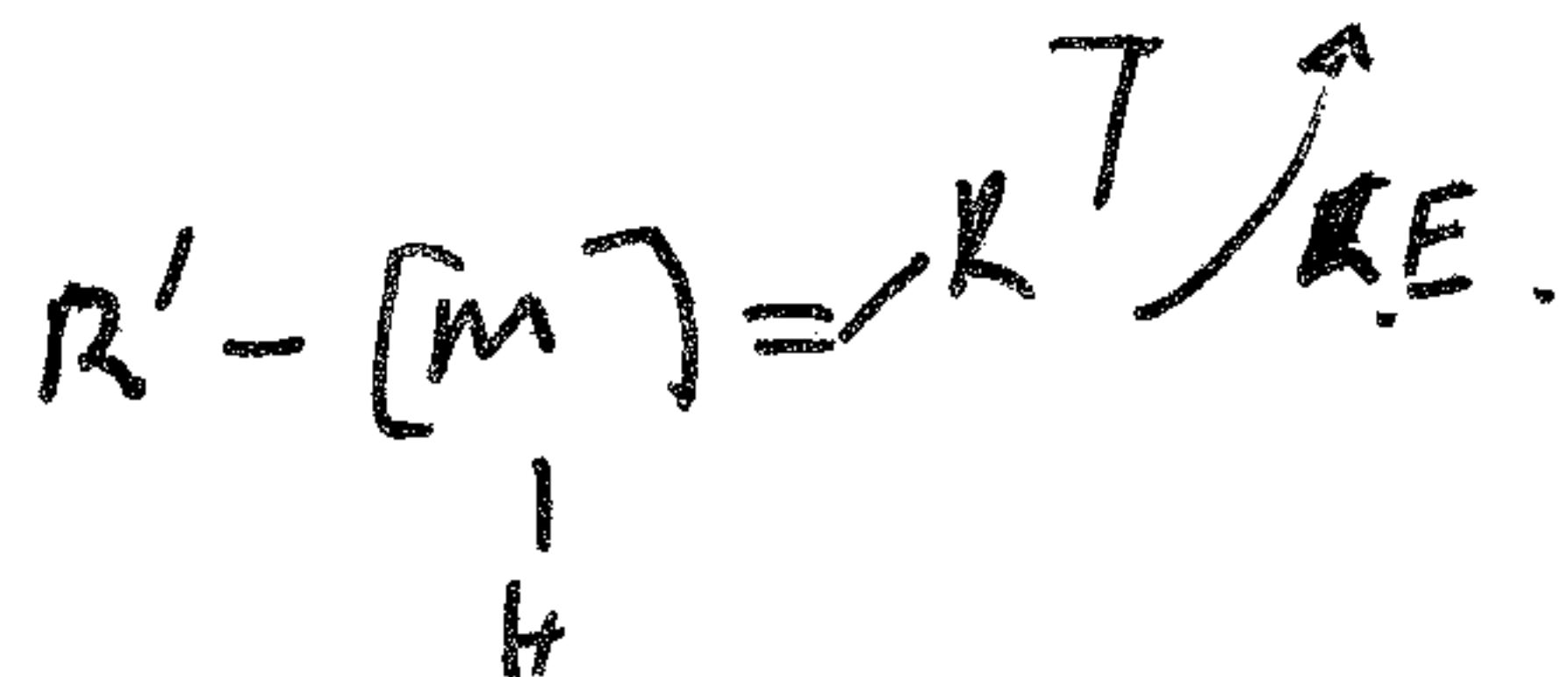
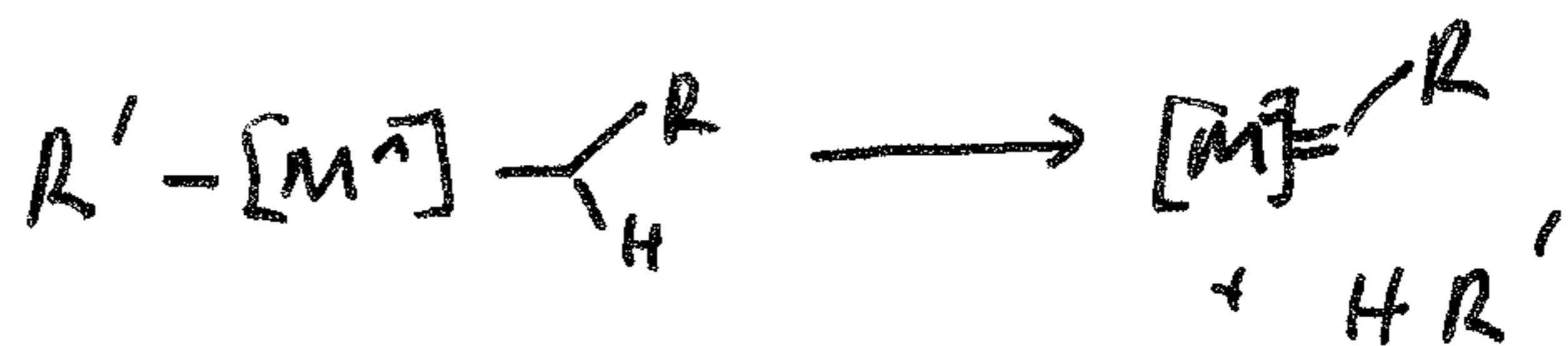


②

CIS-geometry required

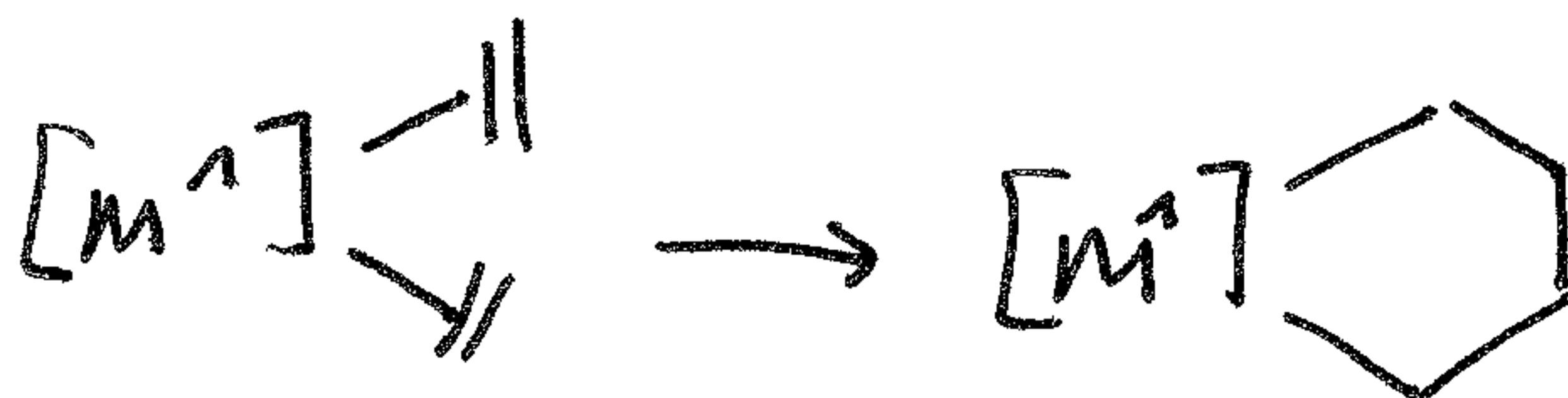


③ α -elimination

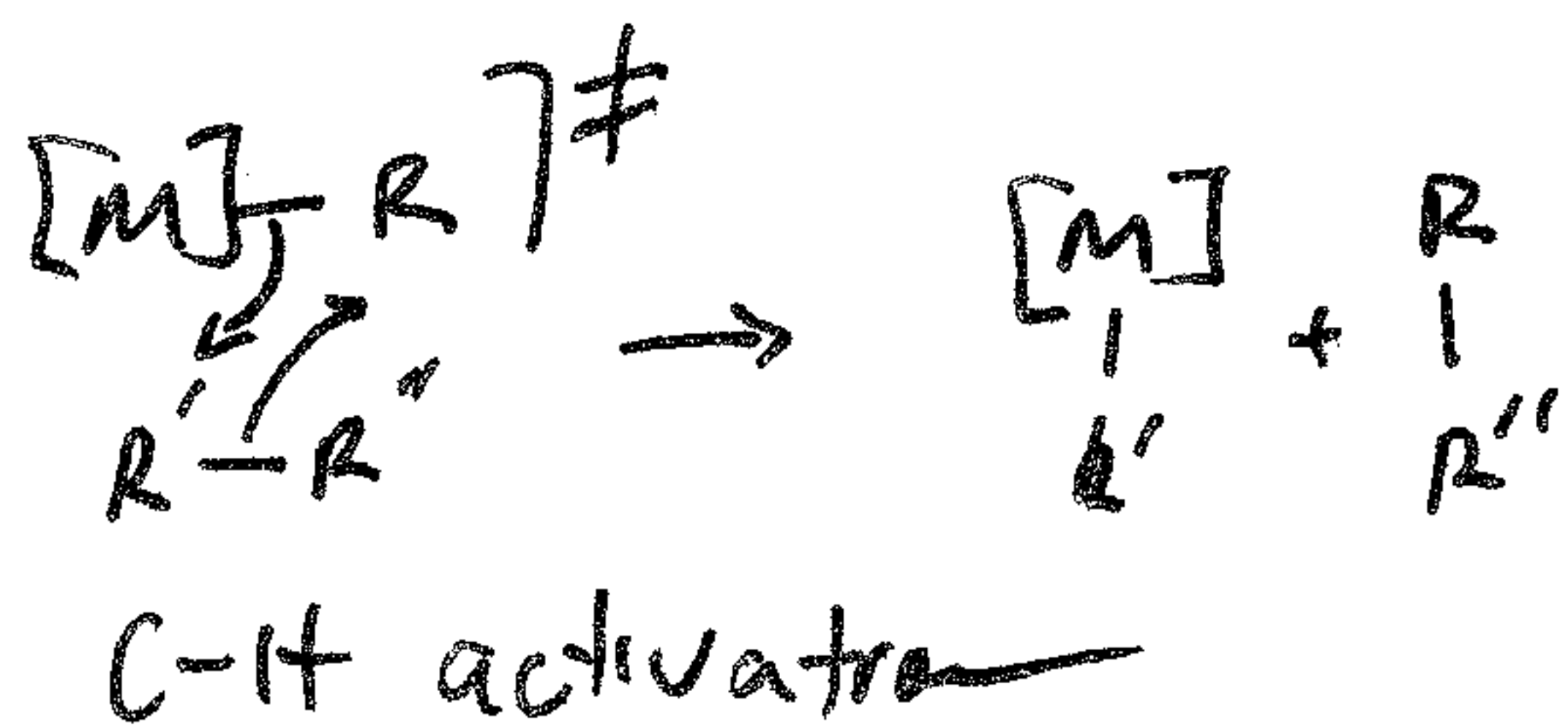
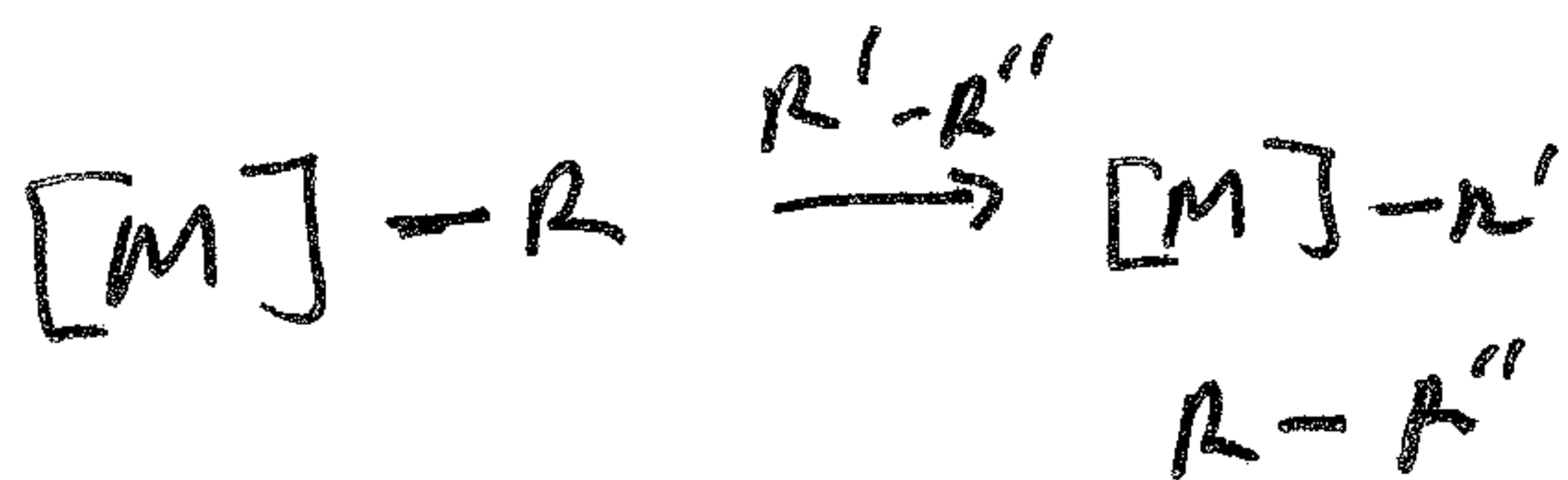


④

Oxidative coupling/cyclization



⑤ σ -bond metathesis



⑥

Reading

chs 7.1 & 7.3.1

3.5

~~12.1, 12.5, 12.7~~

12.1, 12.5, 12.7

④