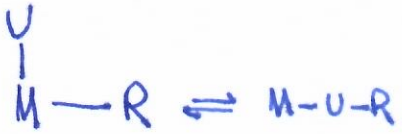
Insertion & Elimination Rxns lecture 14



U : unsaturated: CO, NO, CNR, NCR, =, ≡, O_2, CR_2, CR

R: H, alkyl, aryl, acyl, ...

no change in ox. state

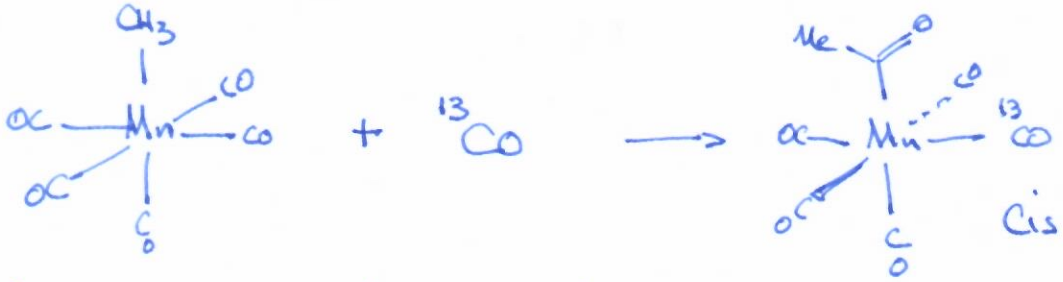
will change Coord #, but can be trapped by ligands

1,1 insertion 1,2 insertion

CO-insertions F. Calderazzo (IR) T. Flood (^{13}C)

experiments

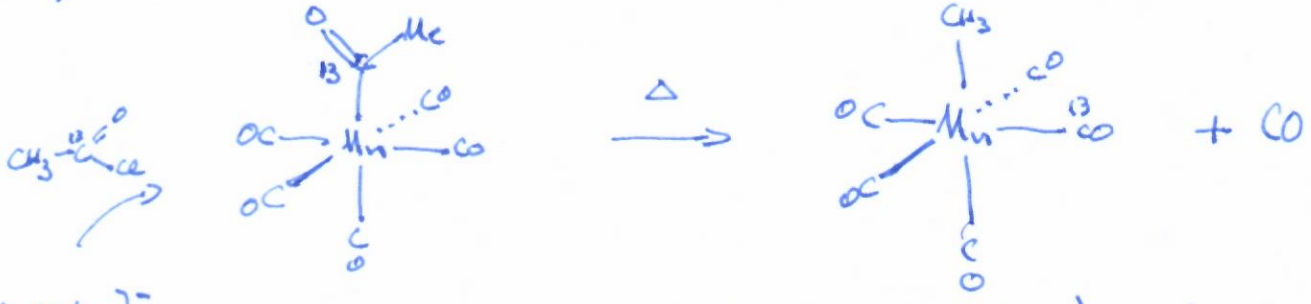
1)



intramolecular, formation of open coord site cis to acyl

⟹ cis Me & CO get together!?

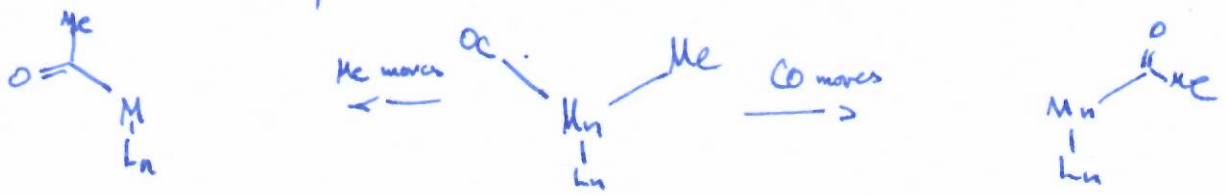
2)

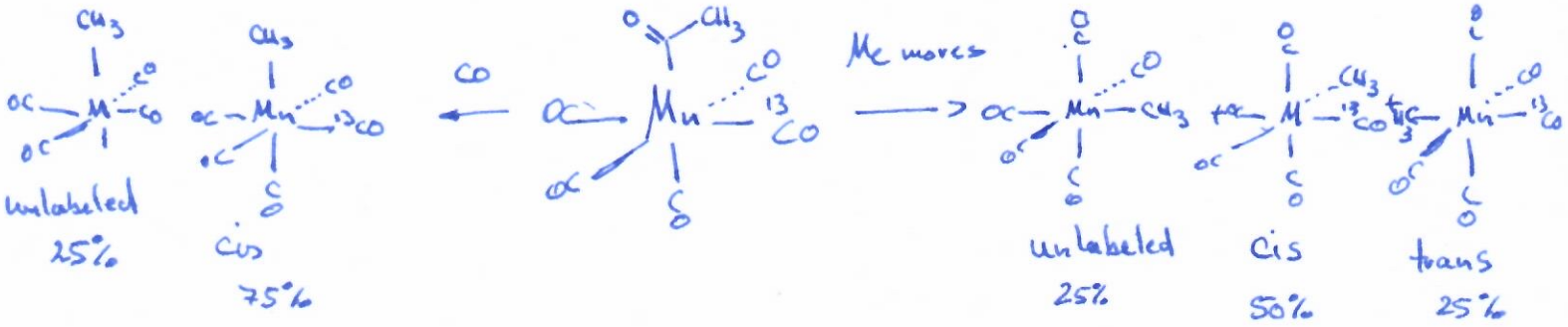


$[Mn(CO)_5]^-$

by PMR insertion (reverse of above) & involves cis Me & CO

3) Which moves, CO or Me





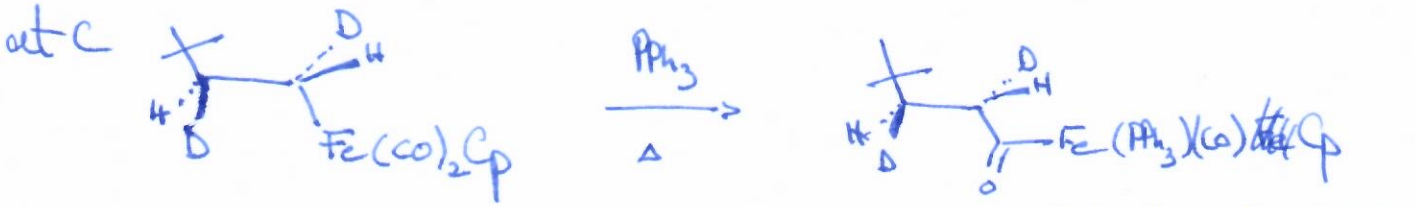
Experiment: 2 : 1 cis/trans Me moves !!!

→ migratory insertion

---

stereochemistry

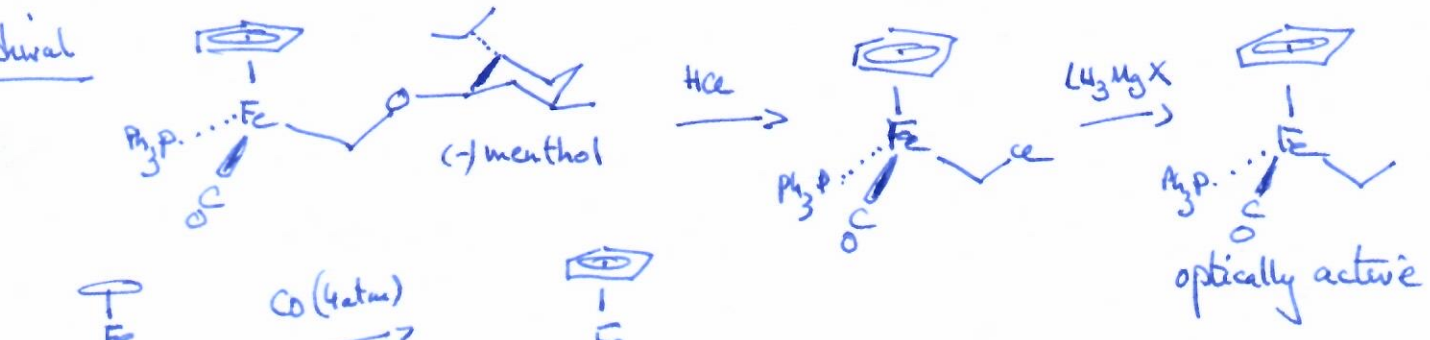
at C

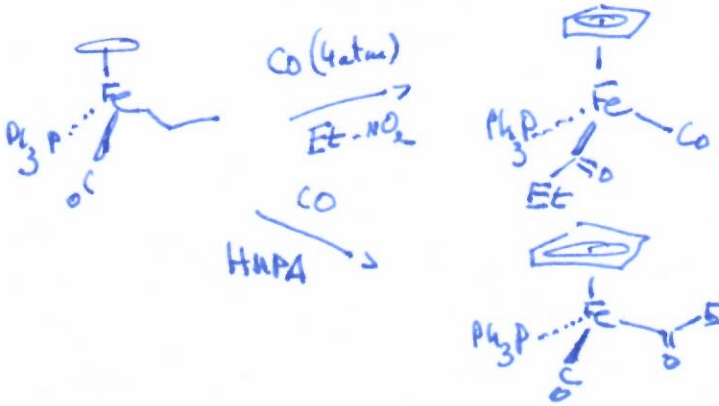


retention of configuration

at M used enantiopure metal complex

chiral





migratory aptitudes

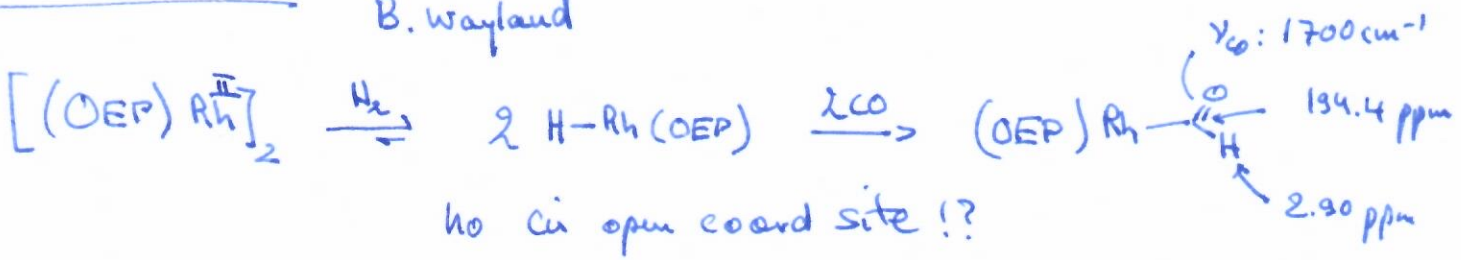
- sterically hindered R. groups are faster
- alkyl faster than aryls
- some groups don't! : $M-R_F$, $M-\overset{O}{\overset{\|}{C}}-R$, $M-H$ ←

thermodynamics: breaking strong bonds to replace w/ acyl is unfavorable

reverse?

M-H/CO insertions:

B. Wayland



no ci open coord site !?

Halpern JACS 1988, 107, 4333

↯ catalyzed by $[(OEP)Rh]_2$

radical chain mech.

initiation & termination $[(OEP)Rh]_2 \rightleftharpoons 2\,(OEP)Rh^{\cdot}$ / $H-Rh(OEP) + Q^{\cdot} \rightarrow Rh(OEP)^{\cdot} + QH$

propagation:

$(OEP)Rh^{\cdot} + CO \longrightarrow (OEP)Rh^{II}(CO)$

$(OEP)Rh(CO) + H-Rh(OEP) \longrightarrow (OEP)Rh-\overset{O}{\overset{\|}{C}}-H + Rh(OEP)^{\cdot}$