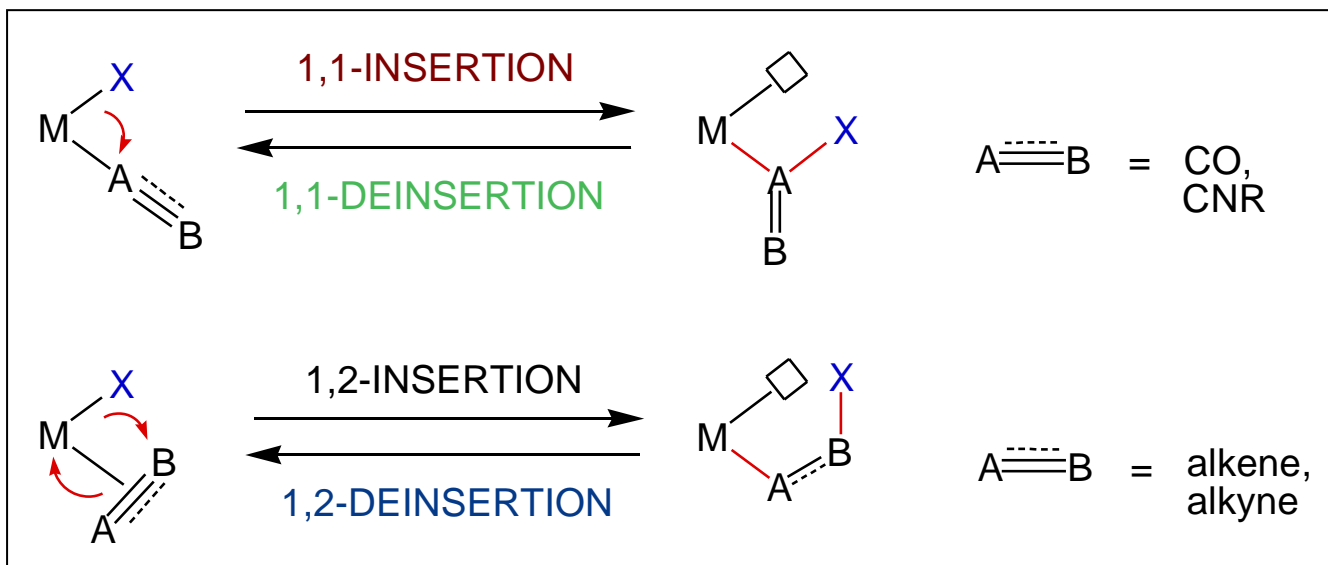


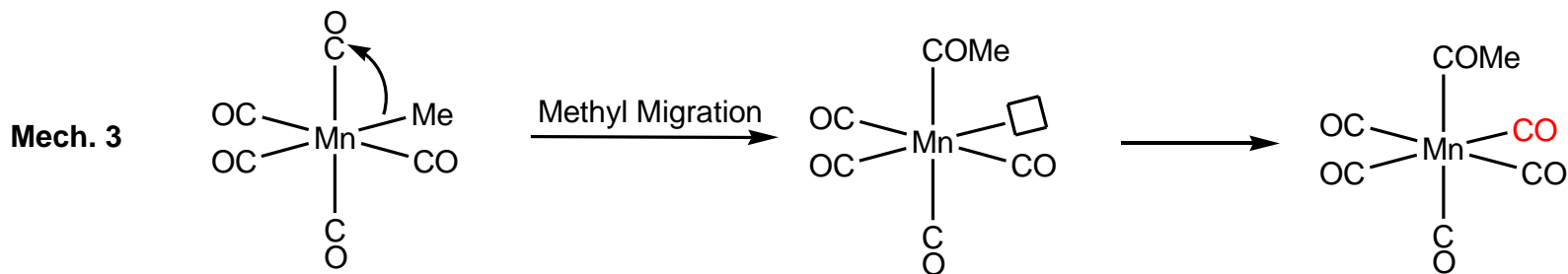
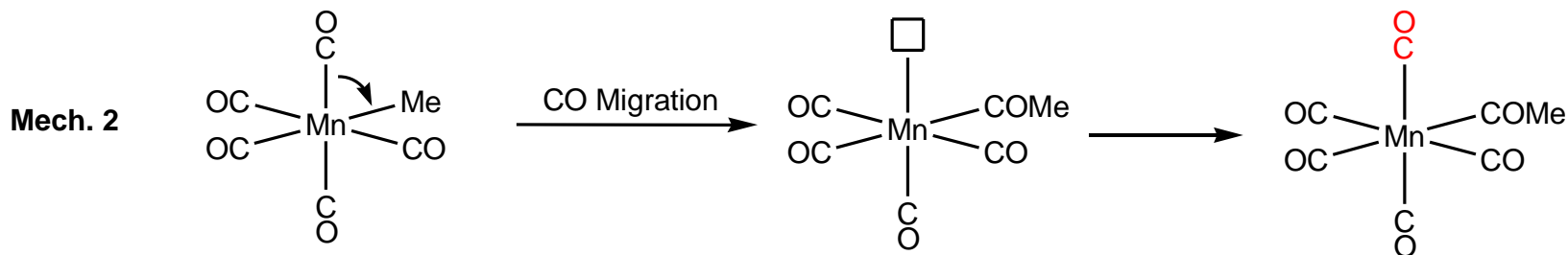
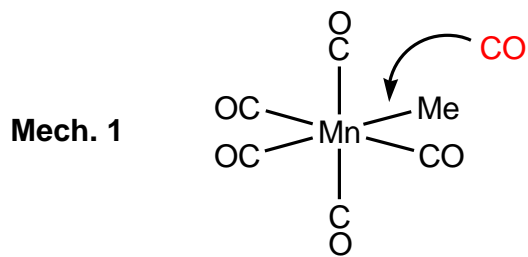
INSERTION AND DE-INSERTION REACTIONS



- **2 TYPES OF MIGRATORY INSERTION: 1,1- and 1,2-**

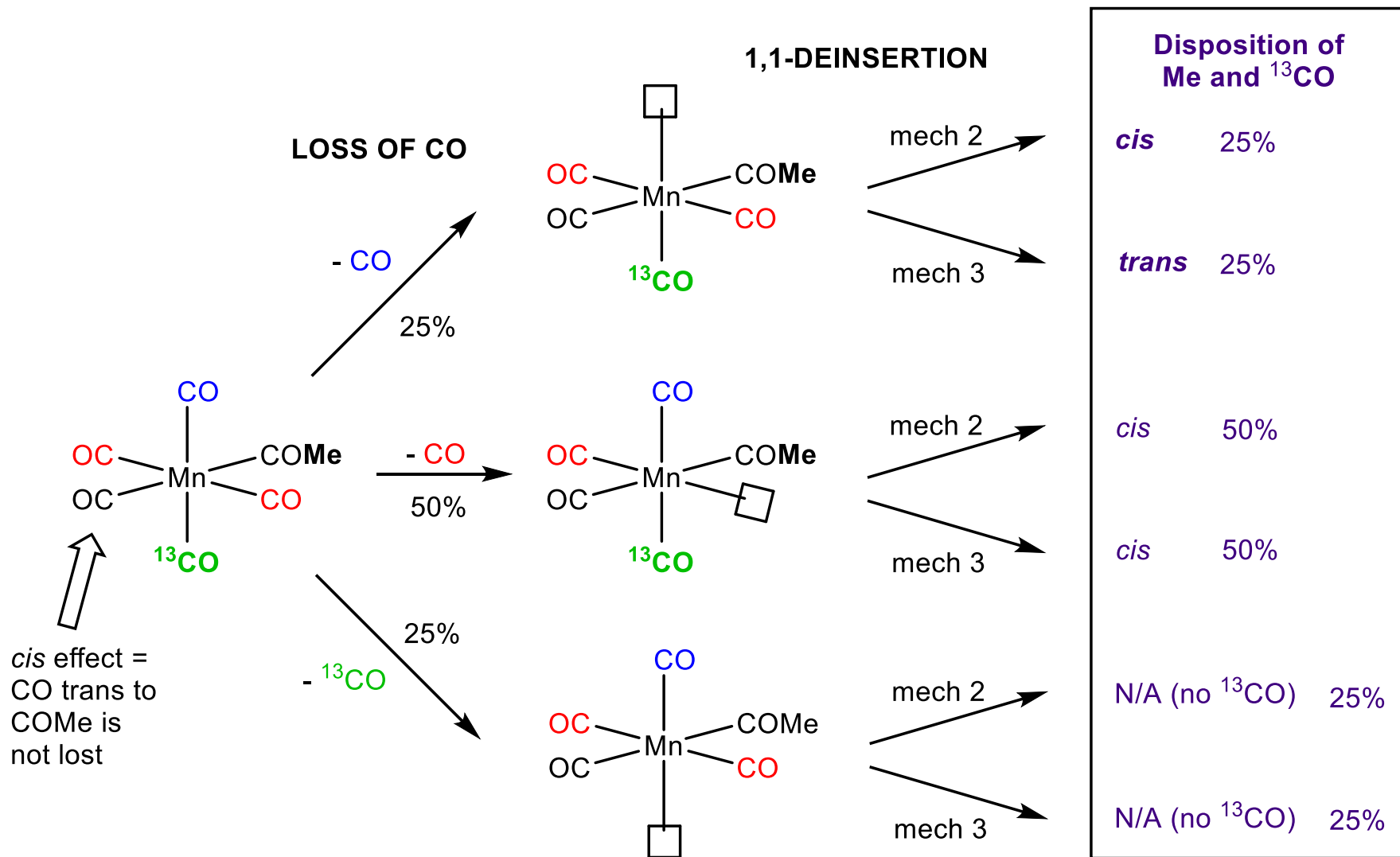
- Metal oxidation state is unchanged.
- Ligands must be cis for insertion to occur.
- Vacant site generated by insertion / required for de-insertion.
- 1,2-Insertion occurs via a 4-centered transition state, M-X addition across an alkene or alkyne occurs in a *syn*-fashion, and 1,2-insertion occurs with retention of configuration at X (e.g. for CHDPh)
- β -Hydride elimination is the most common type of 1,2-deinsertion.

1,1-INSERTION – Possible Mechanisms



- Under at atmosphere of ^{13}CO \rightarrow only one ^{13}CO in the product, which is *cis* to the COMe group \rightarrow rules out Mechanism 1.

1,1-INSERTION – Mechanism 2 or 3 ?



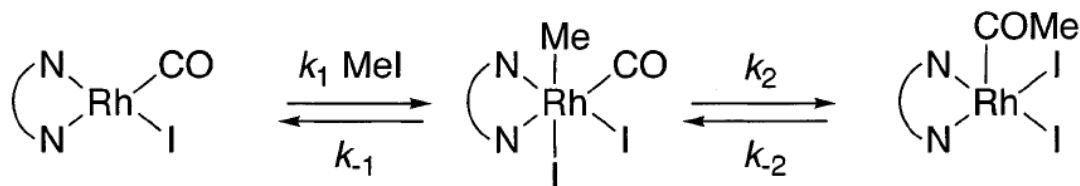
Mechanism 2 (CO migration) = 75% cis + 25% no ^{13}CO

Mechanism 3 (Me migration) = 50% cis + 25% trans + 25% no ^{13}CO = observed

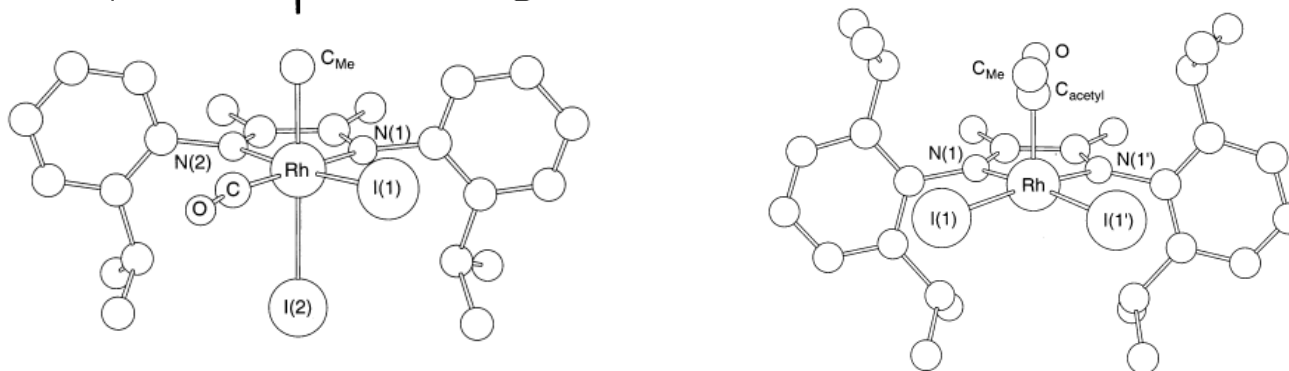
Enhancing 1,1-INSERTION

1,1-insertion is accelerated by:

- Steric bulk at the metal centre
- Less electron rich metals (less π -backdonation to CO or CNR)

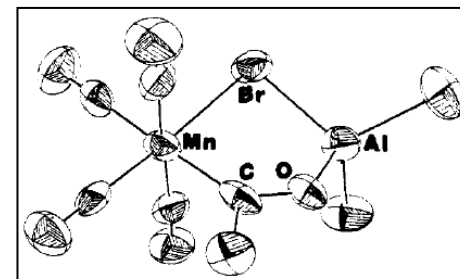
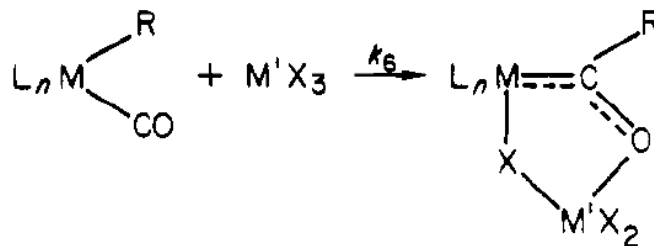


Haynes, *Organometallics*,
2003, 104.



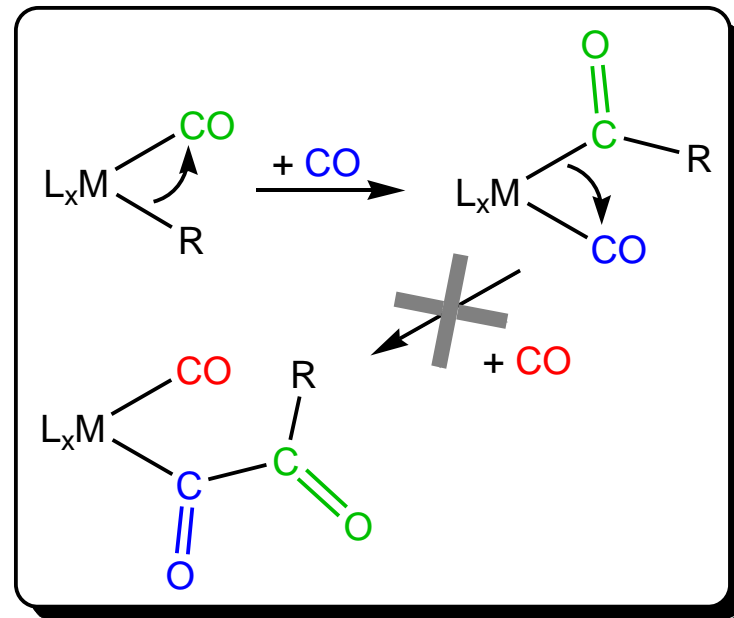
- Lewis acids can increase the rate of 1,1-insertion by up to 10^8

Shriver, *JACS*,
1980, 5093.

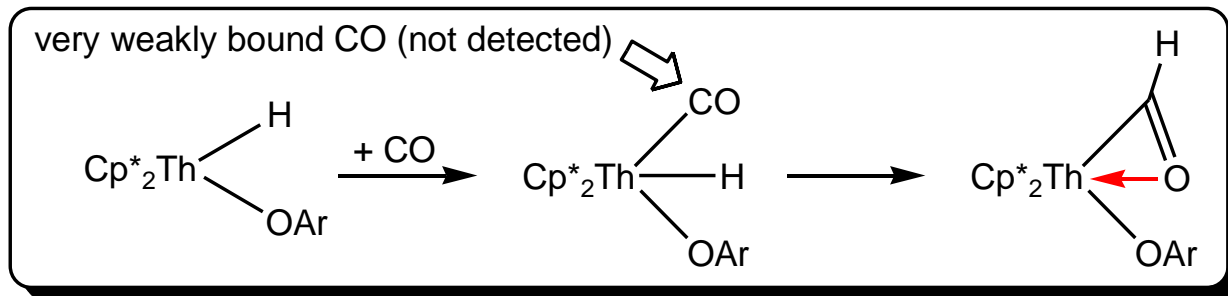


1,1-INSERTIONS WITH CO: Multiple Ins. or 1,1-Ins. with M-H or M-CF₃

- Reason for insertion: M-COME bonds are considerably stronger than M-Me
- For CO, only one insertion occurs.
- (CO)₅Mn(COCOMe) made by a diff. route readily eliminates CO.
- Polymeric L_xM(CO)_nR is believed to be unstable w.r.t. itself.
- The same situation applies to M-CF₃ bonds and M-H bonds →



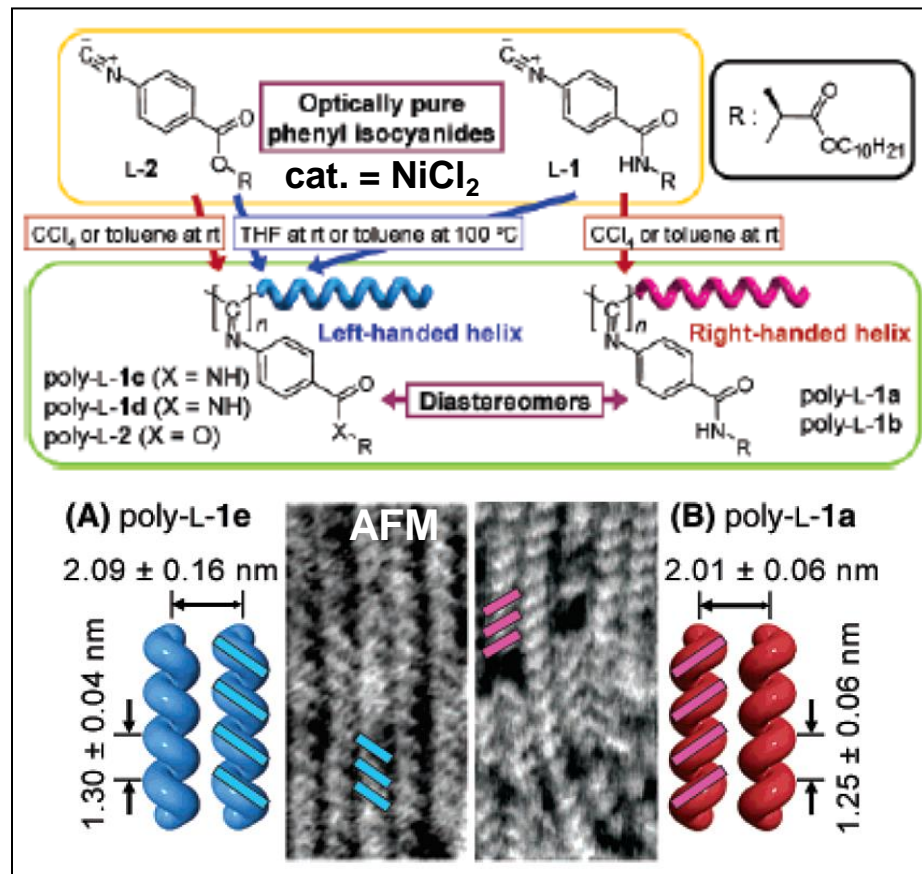
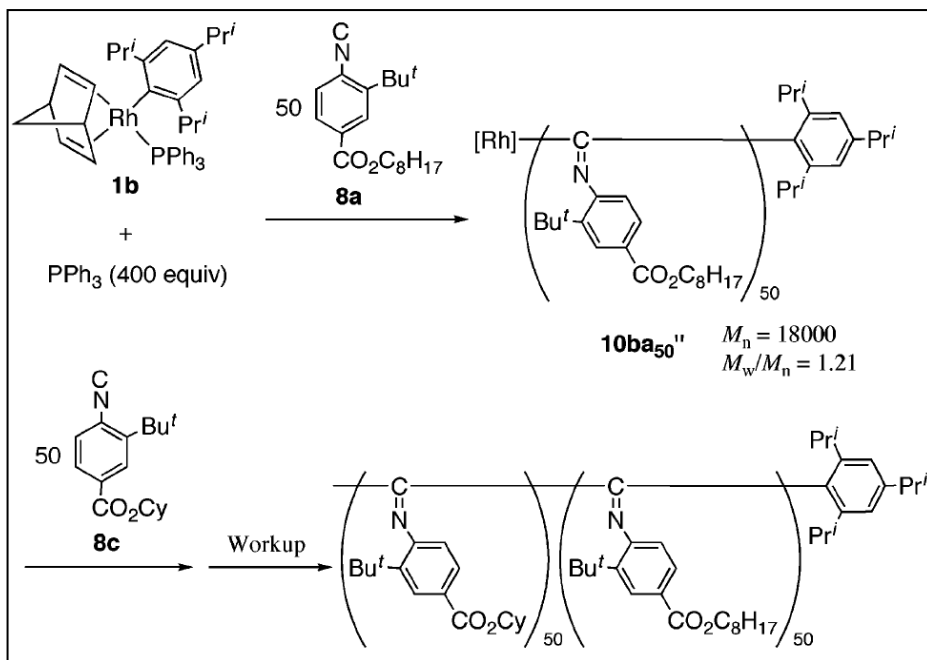
- For R = H or CF₃, even one insertion does not occur with CO unless M is an extremely Lewis acidic d⁰ metal (Sc^{III}, Y^{III}, Ln^{III}, Th^{IV}).



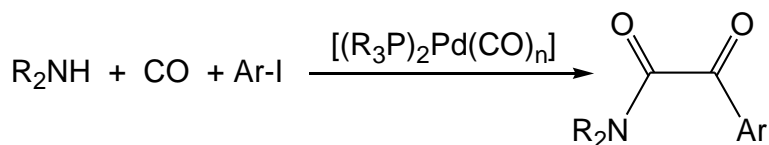
MULTIPLE 1,1-INSERTIONS WITH CNR – both early and late TMs

Okoshi, *JACS*, 2006, 708

Onitsuka, *Organometallics*, 2006, 1270



- Apparent double 1,1-insertions with CO go by a different mechanism:



Final Step Involves RE from:

