

F Organometallic Reactions 2: Reactions at the Ligands

Again, there are three major classes of reactions:

1 Insertion / Deinsertion

- 1,1-insertion / deinsertion (eg. CO insertion)
- 1,2-insertion / deinsertion (eg. alkene insertion)

2 Attack by nucleophiles (Nu^-)

- addition (Nu^- adds to the complex)
- abstraction (Nu^- removes part of the ligand from the complex)

3 Attack by electrophiles (E^+)

- addition
- abstraction

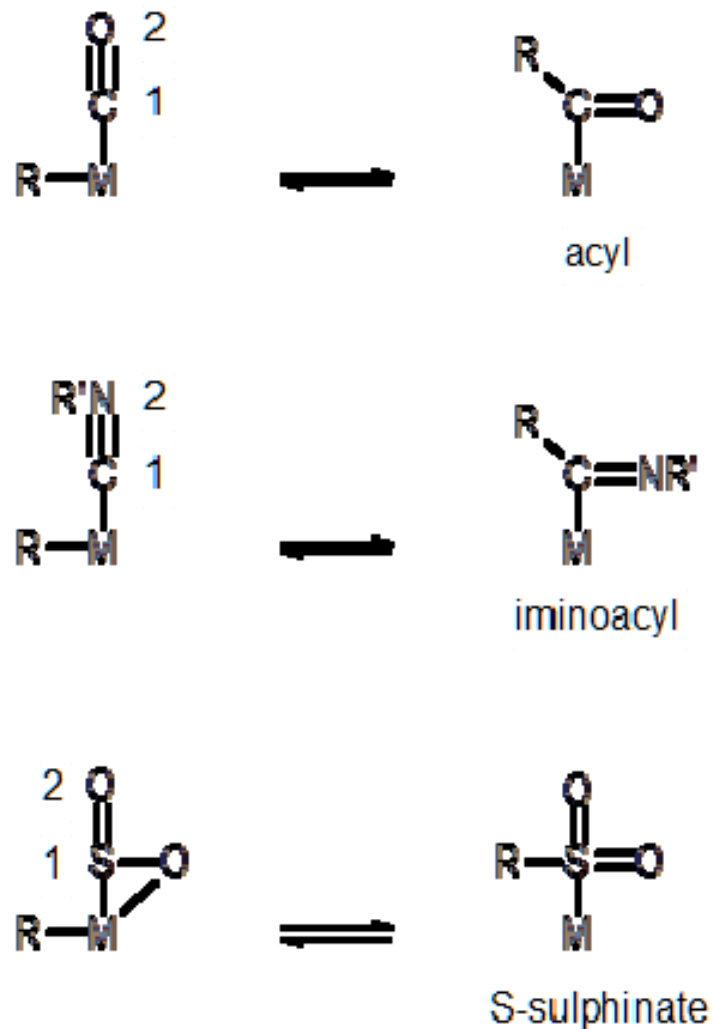
1. Insertion / Deinsertion

- 1,1-insertion / deinsertion



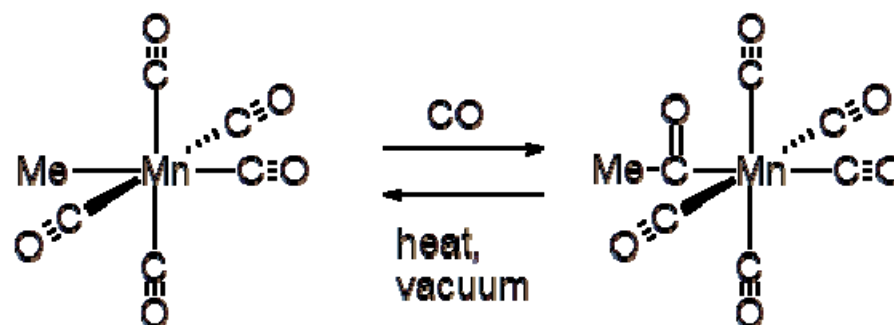
1,1-insertion because both **M** and **Y** end up bound to the atom in position 1 (**X**)

Specific examples:

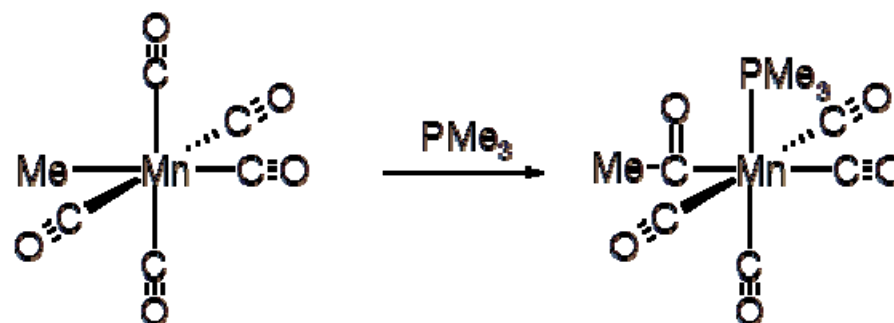


Migratory insertion of CO

- general reaction of M-C bonds
- important in the **'Oxo' hydroformylation** process and the **Monsanto acetic acid** process

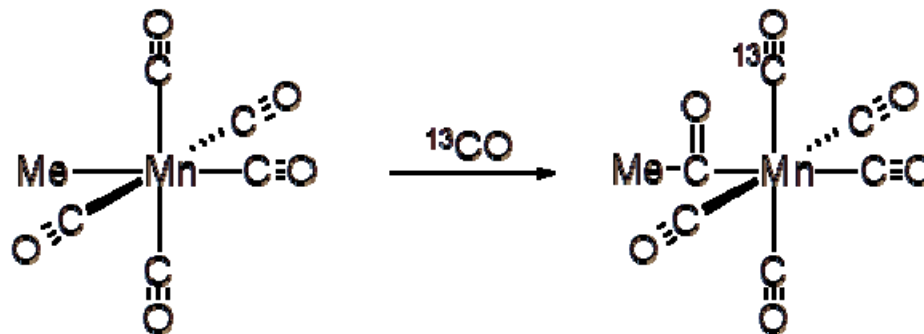


The classic example:



Suggests that direct CO insertion from the gas phase is NOT involved

Confirmed using ^{13}C labeled CO:



Mechanistic possibilities are:

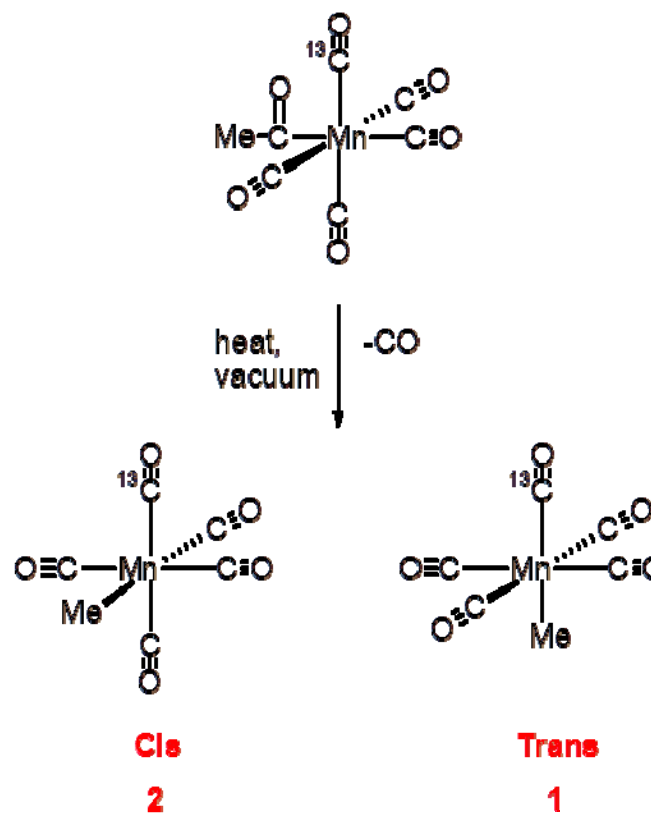
i) insertion of a cis CO into the metal-alkyl bond

OR

ii) migration of the methyl group onto a cis CO

These outcomes are *stereochemically* different.

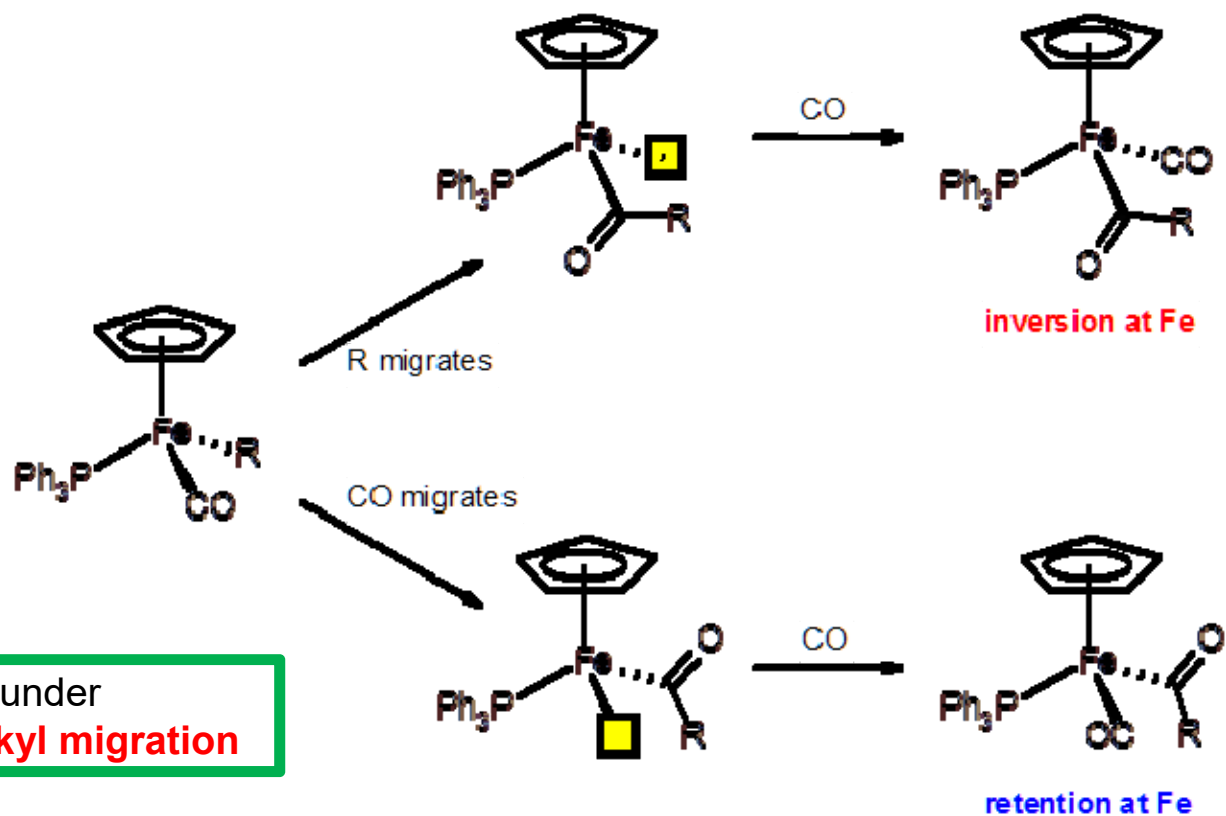
These two options can be distinguished by the **decarbonylation reaction** of the labeled compound:



For **i) expect only cis**

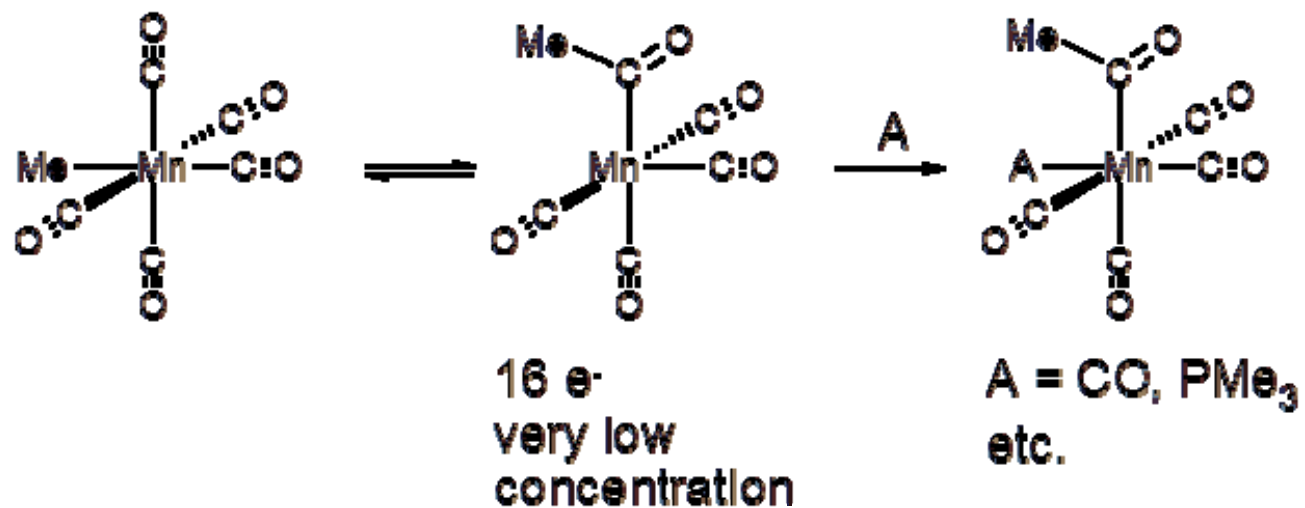
ii) expect 2:1 ratio of cis/trans (observed)

Chiral metal complexes can also be used to probe this reaction:

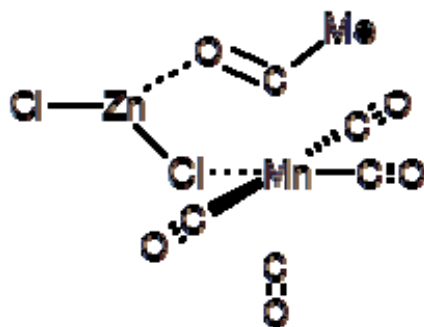


Inversion at Fe is observed under most conditions supporting **alkyl migration**

Accepted Mechanism:



Lewis acids catalyze methyl migration by stabilizing the 16 e⁻ intermediate:



- SO_2 insertion proceeds via an $\text{S}_{\text{E}2}$ -type mechanism:

