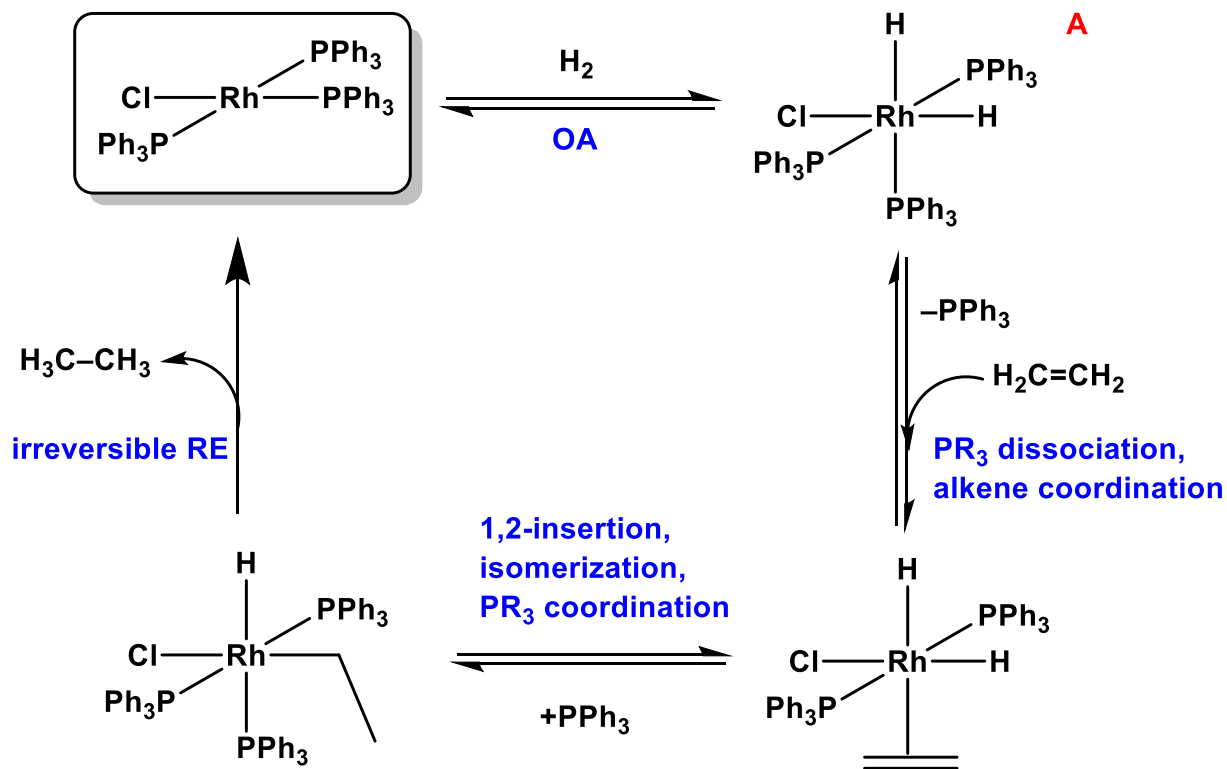


Alkene Hydrogenation (Dihydride Intermediate)

Rh or Ir

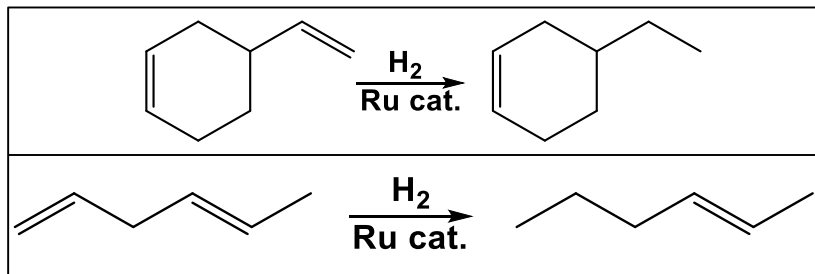
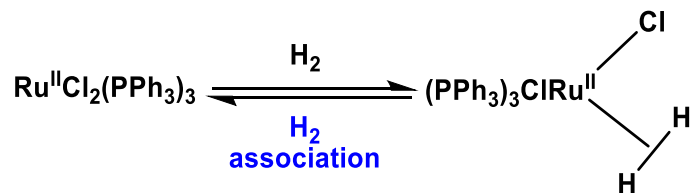
- $[\text{RhCl}(\text{PPh}_3)_3]$ (Wilkinson's Catalyst)
- $\{[\text{Rh}(\text{NBD})(\text{m-Cl})_2]\} + 4 \text{PR}_3$ or $\{[\text{Ir}(\text{COD})(\text{m-Cl})_2]\} + 4 \text{PR}_3$
- $[\text{Ir}(\text{COD})(\text{PMePh}_2)_2][\text{PF}_6]$ or $[\text{Ir}(\text{COD})(\text{PCy}_3)(\text{Py})][\text{PF}_6]$
- $[\text{Rh}(\text{NBD})(\text{bidentate phosphine})][\text{PF}_6]$
- (NBD = norbornadiene)
- (COD = 1,5-cyclooctadiene)



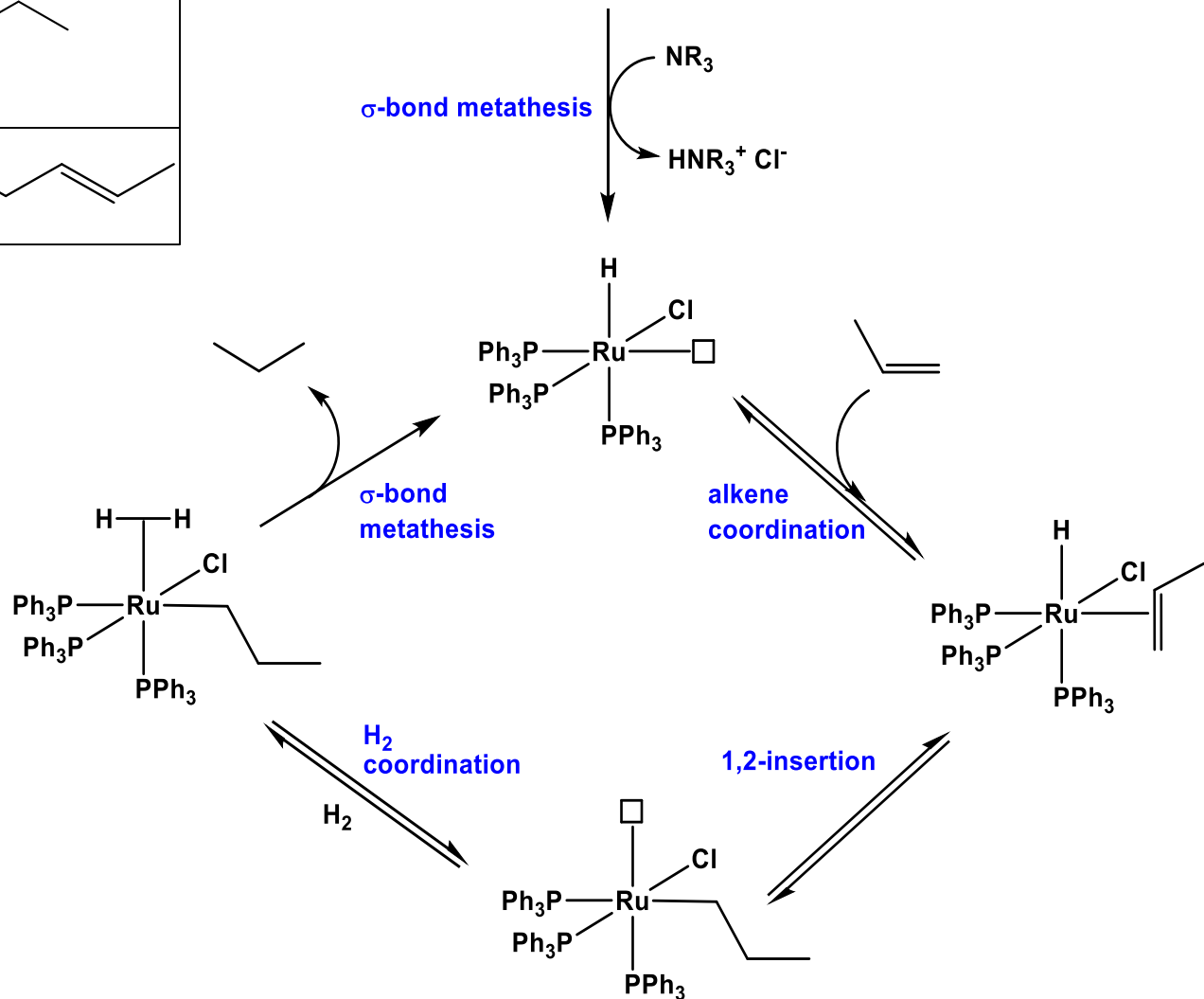
- Note: Hydrogenation involves 1,2-insertion, so *syn*-addition to the alkene is observed.
- Note: Less substituted alkenes are hydrogenated faster.

Alkene Hydrogenation (Monohydride)

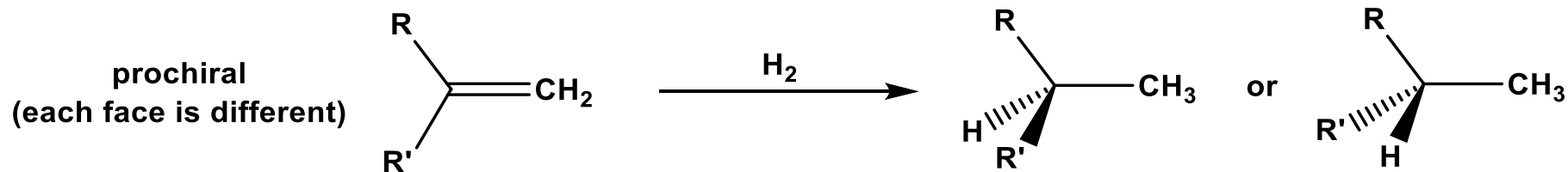
Ru



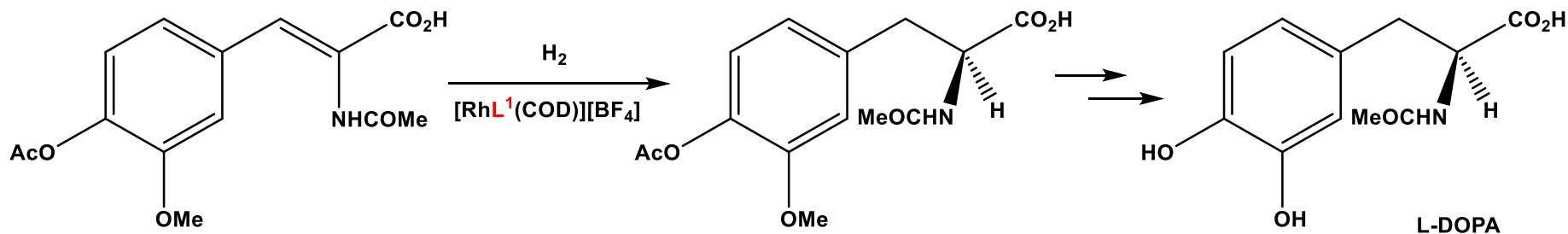
- Certain ruthenium(II) complexes, such as $[\text{RuCl}_2(\text{PPh}_3)_3]$ are active hydrogenation catalysts
- Operate by a different mechanism than Wilkinson's catalyst.
- They also show very high selectivity for terminal double bonds:



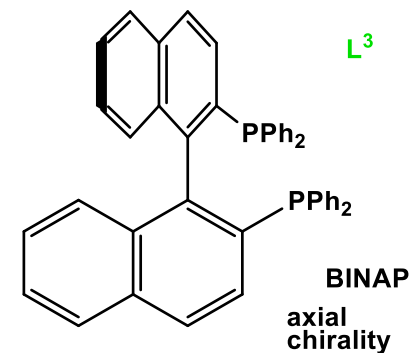
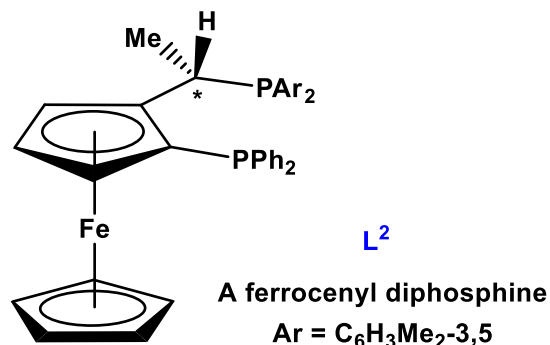
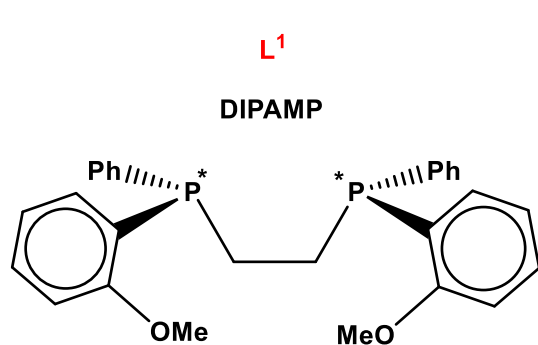
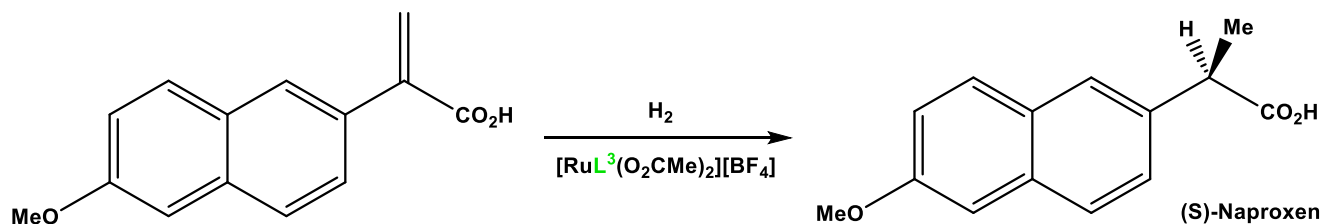
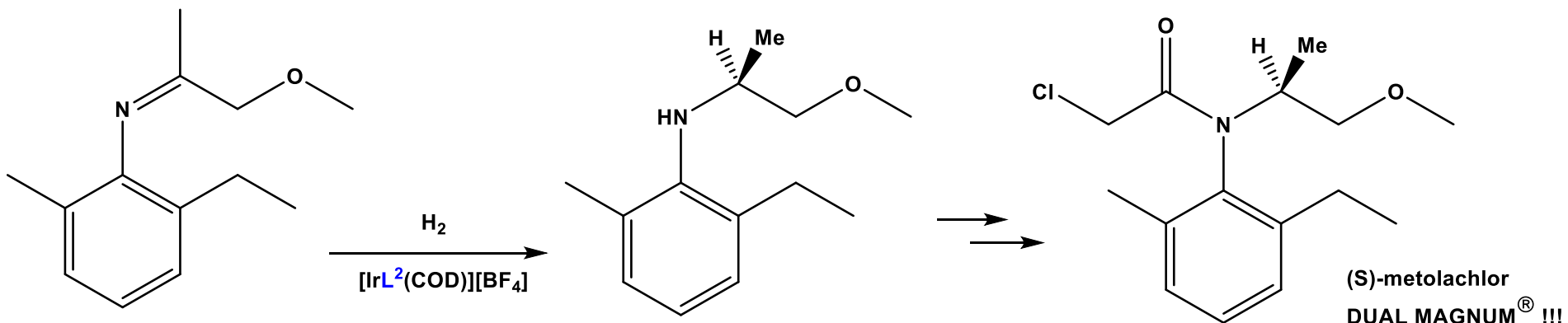
Asymmetric Hydrogenation



- Two enantiomers may be formed from a prochiral alkene (or ketone or imine)
- With a suitable chiral metal complex, the alkene will bind predominantly through one face. This is the face that is hydrogenated, giving predominantly a single enantiomer.
- Asymmetric hydrogenation is possible because the last step of the catalytic cycle is irreversible \rightarrow kinetic products.
- 2001 Nobel Prize for William Knowles and Ryoji Noyori.



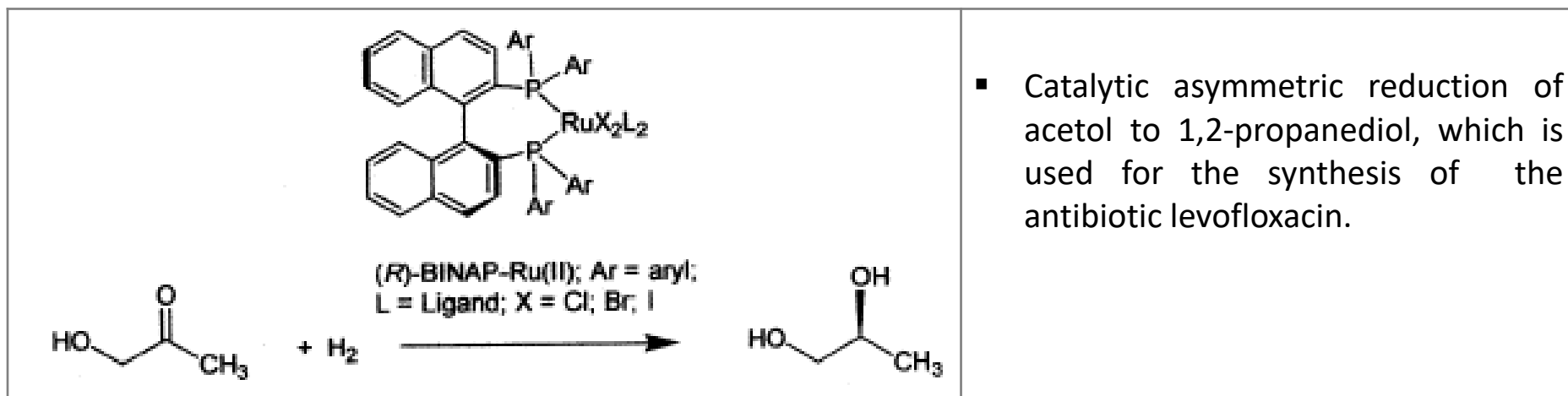
Asymmetric Hydrogenation



Hydrogenation

What about other substrates?

- The C=O and C=N bonds of ketones and imines are only reduced by certain catalysts {e.g. [M(diphosphine)]⁺ (M = Rh or Ir), [RuCl₂(diphosphine)] or [CpRe(CO)(PPh₃)⁺}

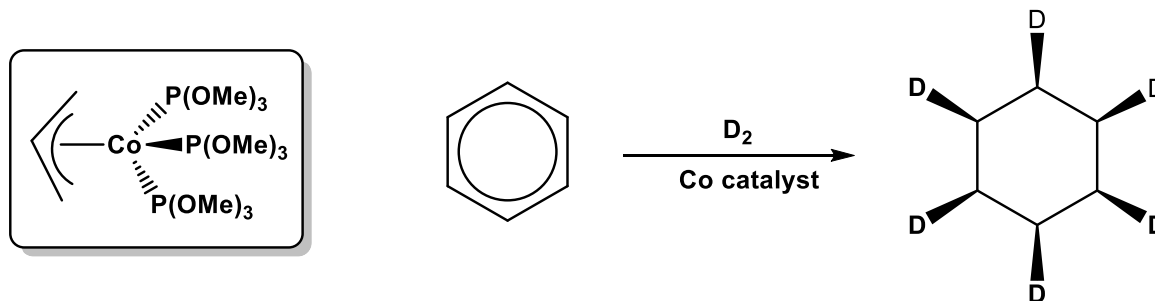


- Catalytic asymmetric reduction of acetone to 1,2-propanediol, which is used for the synthesis of the antibiotic levofloxacin.

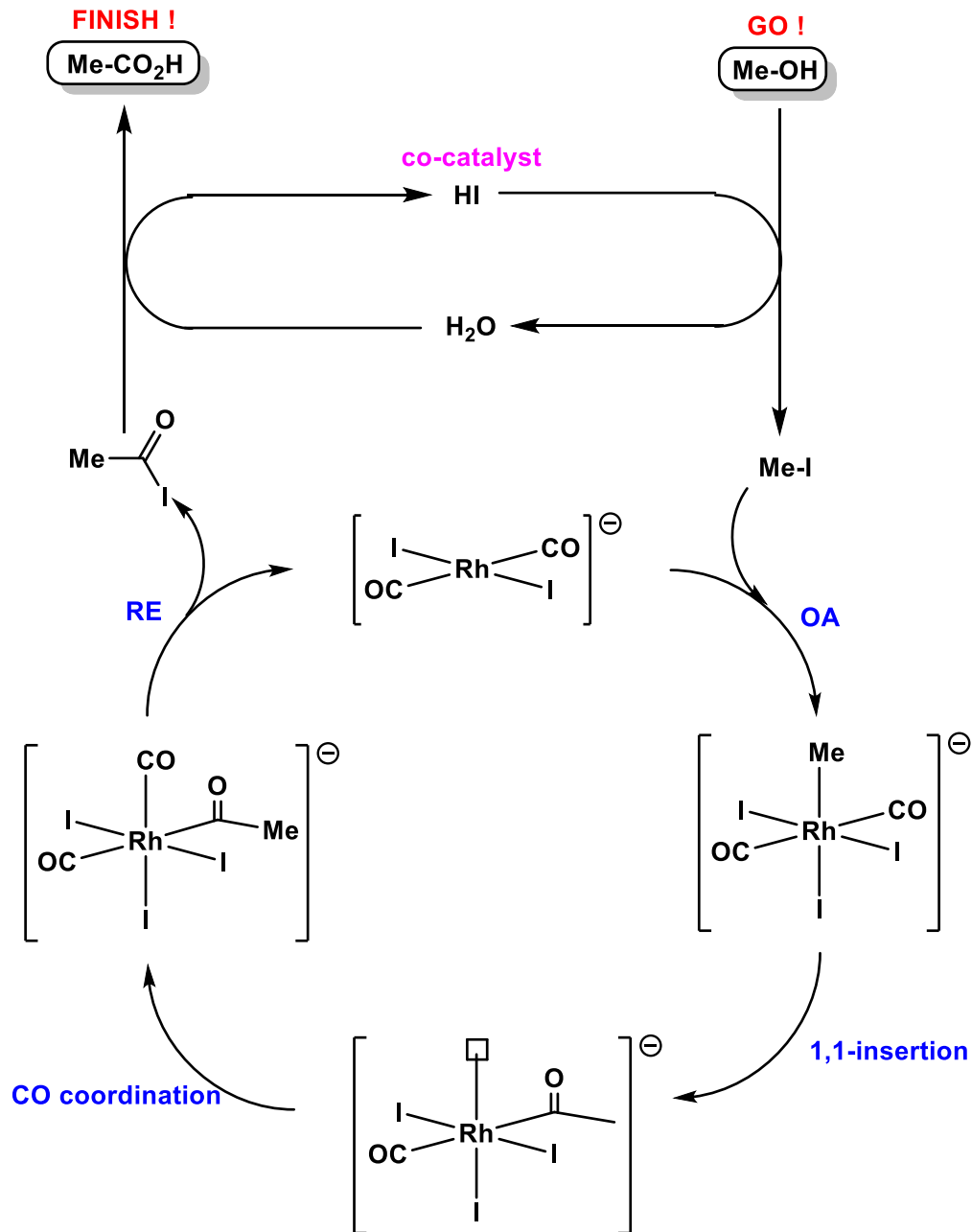
- Aryl rings are NOT reduced by the usual catalysts (see below).
- CN, NO₂, ester or amide groups are NOT reduced by the usual catalysts.

Arene Hydrogenation

- Several heterogeneous catalysts can do this (e.g. Rh/C)
- None of the catalysts discussed so far will hydrogenate arenes

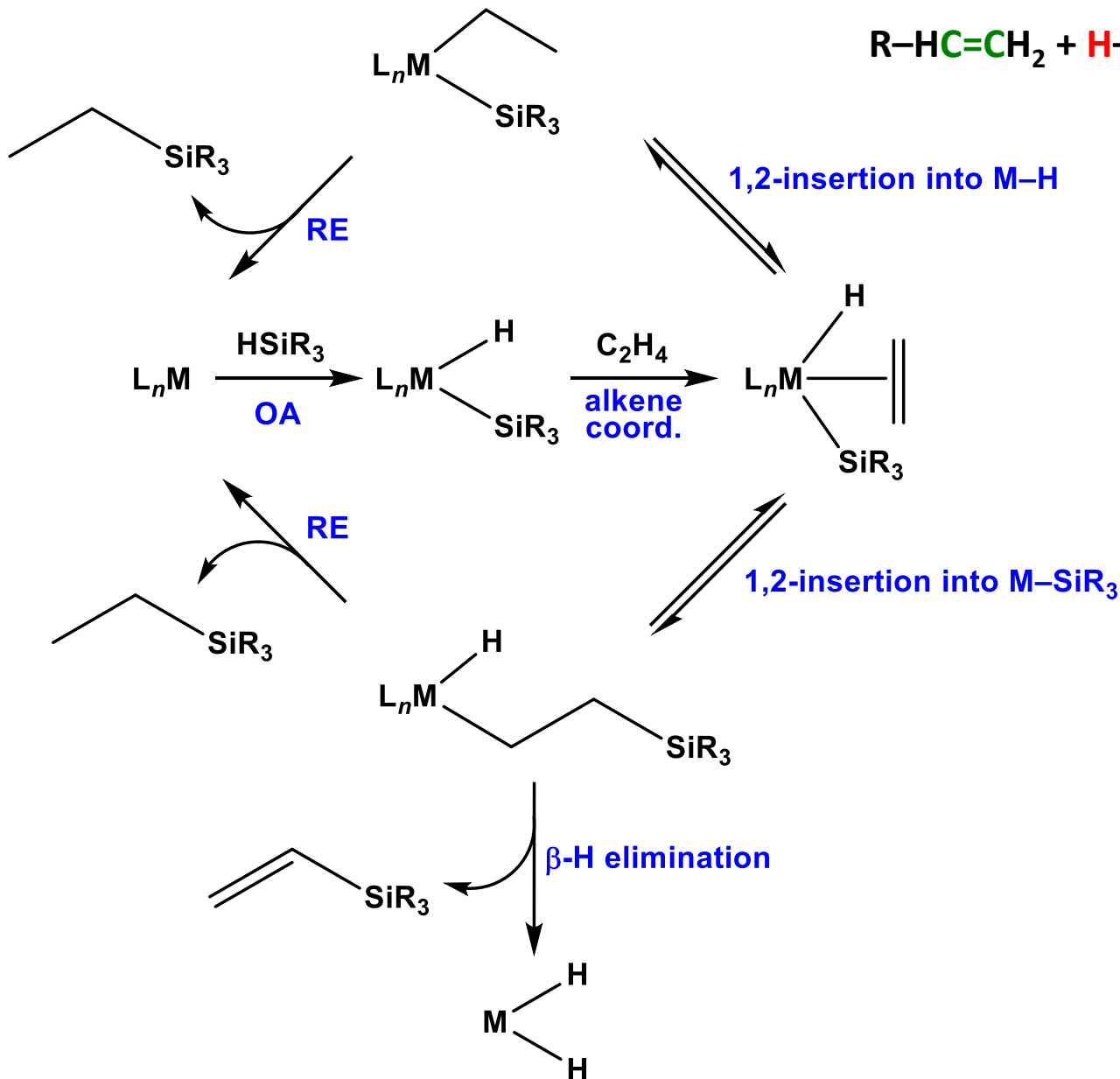
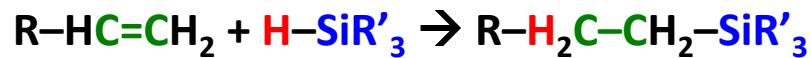


Monsanto Acetic Acid Process



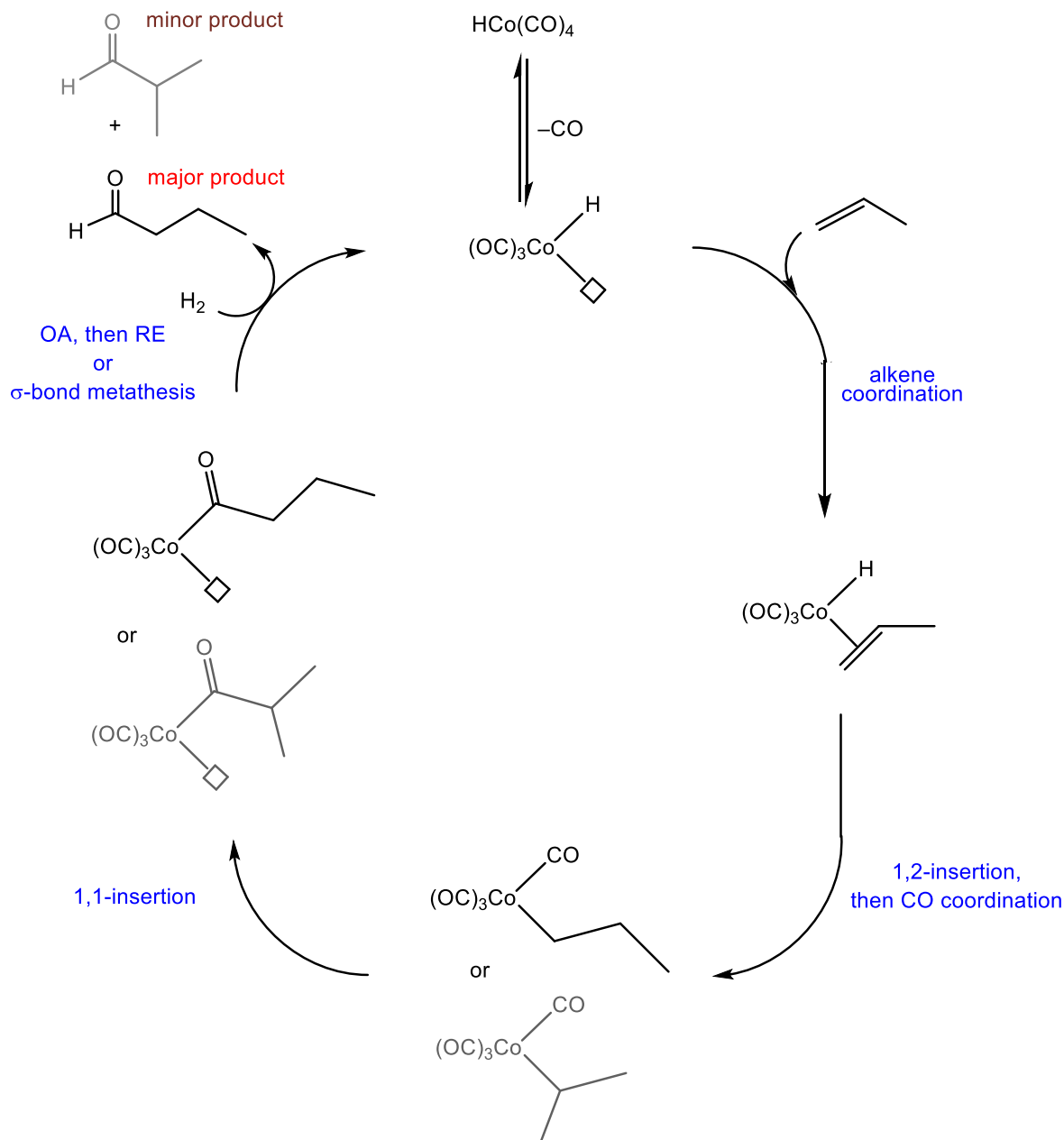
- Used to produce 3.8 million tonnes of MeCO_2H p.a. Most of this acetic acid is converted to acetic anhydride (used in the synthesis of cellulose acetate and asparin, *etc.*). Eastman has a similar process to the Monsanto process which produces acetic anhydride directly.
- Monsanto acetic acid process runs at 180 °C and 30-40 atm of CO .
- Rate determining step is oxidative addition of MeI .

Olefin Hydrosilylation



- One of the earliest catalysts was H_2PtCl_6 (Speier's Catalyst) – originally thought to be homogeneous but more likely that catalysis is due to colloidal platinum metal.
- Homogeneous catalysts include $Co_2(CO)_8$, $Ni(COD)_2$, $NiCl_2(PPh_3)_2$ and $RhCl(PPh_3)_3$

Co-Catalyzed Alkene Hydroformylation



- Discovered in 1938 by Otto Roelen at Ruhrchemie.
- Sometimes called the *oxo* process.
- 6.6 million tons p.a. (1998)
- Rhodium and cobalt catalysts used industrially.

Alkene Hydroformylation

Problems with the cobalt catalyzed hydroformylation reaction:

- Ratio of linear to branched aldehydes is 4:1 at best.
- Catalyst is unstable, so its separation and recovery are difficult
- High temperature (140-180 °C) and pressure (200-300 atm) of CO required → plants are expensive to build and operate

HRh(CO)(PPh₃)₃ has many advantages over cobalt catalysts:

- 100 to 1000 times more active
- Pressure (15 to 25 atm) and temperature (80 to 120 °C) are much lower than needed for cobalt catalysts (200-300 atm and 140-180 °C).
- Linear to branched ratios as high as 14:1 are obtained. Only the linear product is commercially valuable.
- HRh(CO)(PPh₃)₃ is also an excellent isomerization catalyst. Therefore, in the hydroformylation of H₂C=CH-CH₂-Me or Me-CH=CH-Me, the major product is Me-CH₂-CH₂-CH₂-CHO.
- Advantages far outweigh the drawback of having to recover the expensive Rh catalyst {rhodium is 500 to 5000 times more expensive than cobalt (depends on the year)}.

Rh-Catalyzed Alkene Hydroformylation

