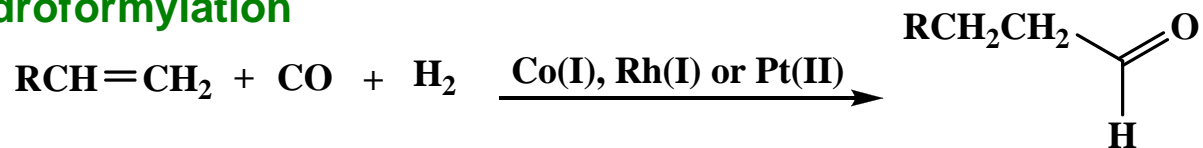
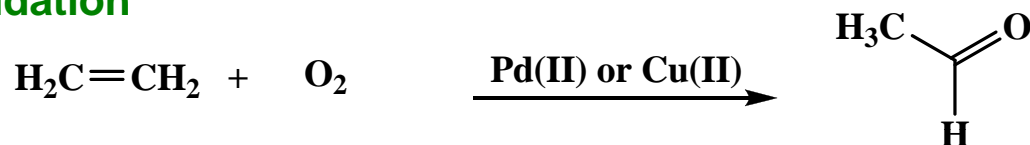


Homogeneous Catalytic Processes

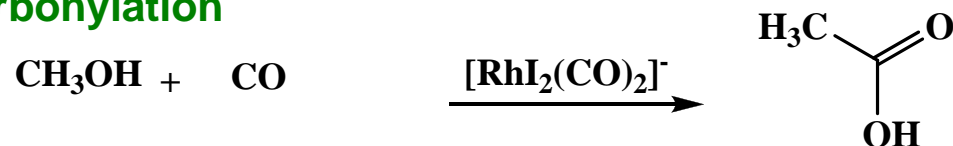
Hydroformylation



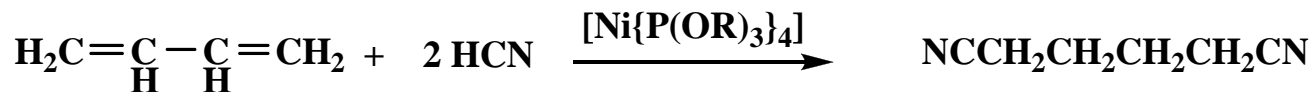
Oxidation



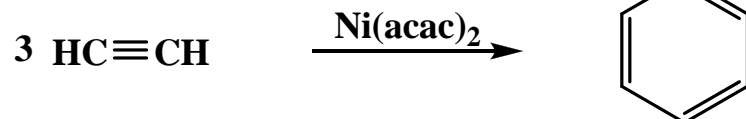
Carbonylation



Hydrocyanation



Cyclotrimerization



Hydrogenation of Alkenes



The most commonly used catalyst is the Wilkinson's Catalyst



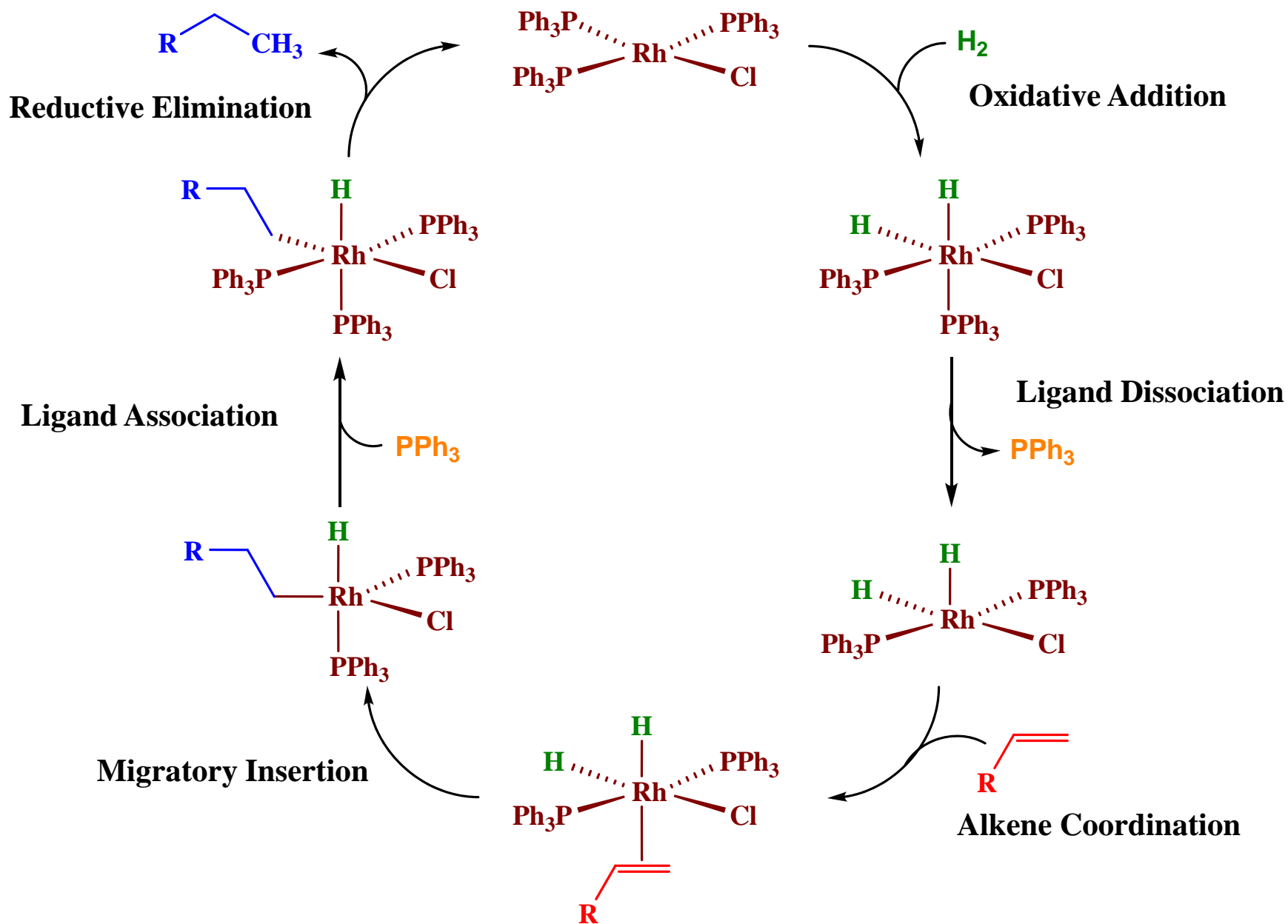
Many alkenes are hydrogenated with hydrogen at 1 atm pressure or less.

Wilkinson's catalyst is highly sensitive to the nature of the phosphine ligand and the alkene substrate.

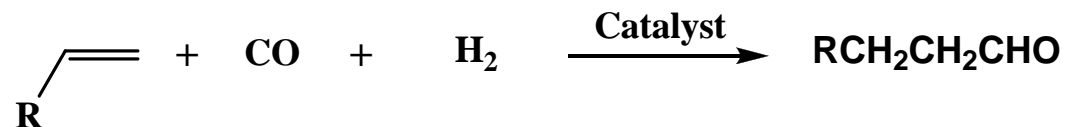
Analogous catalysts with alkyl phosphine ligands are inactive

Highly hindered alkenes and ethylene are not hydrogenated by the catalyst

Wilkinson's Catalyst



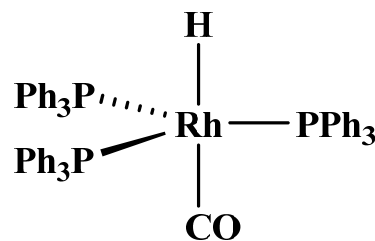
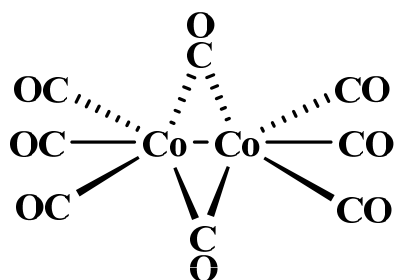
Hydroformylation



A less common, but more appropriate name is hydrocarbonylation

Both cobalt and rhodium complexes are used as catalysts.

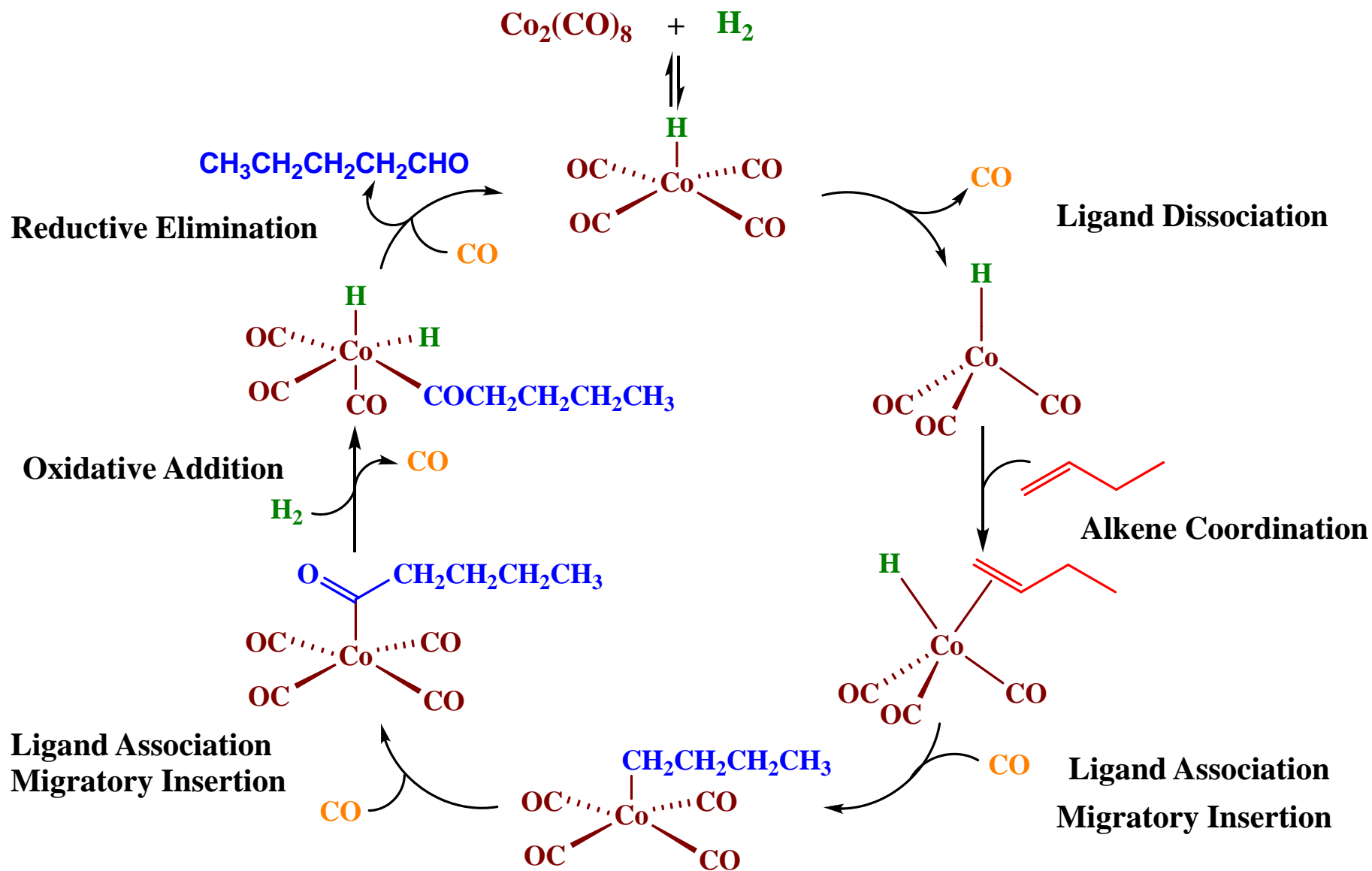
Alkene isomerization, alkene hydrogenation and formation of branched aldehydes are the possible side reactions.



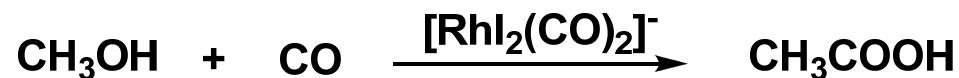
Cobalt catalysts operate at 150 °C and 250 atm, whereas Rhodium catalysts operate at moderate temperatures and 1 atm.

Rhodium catalysts promote the formation of linear aldehydes. Cobalt catalysts do so if modified with alkylphosphine ligands.

Hydroformylation



Monsanto Acetic Acid Synthesis



All three members of the group 9 (Co, Rh and Ir) can catalyze this reaction.

A cobalt complex was initially used, which was replaced with the rhodium complex later on.

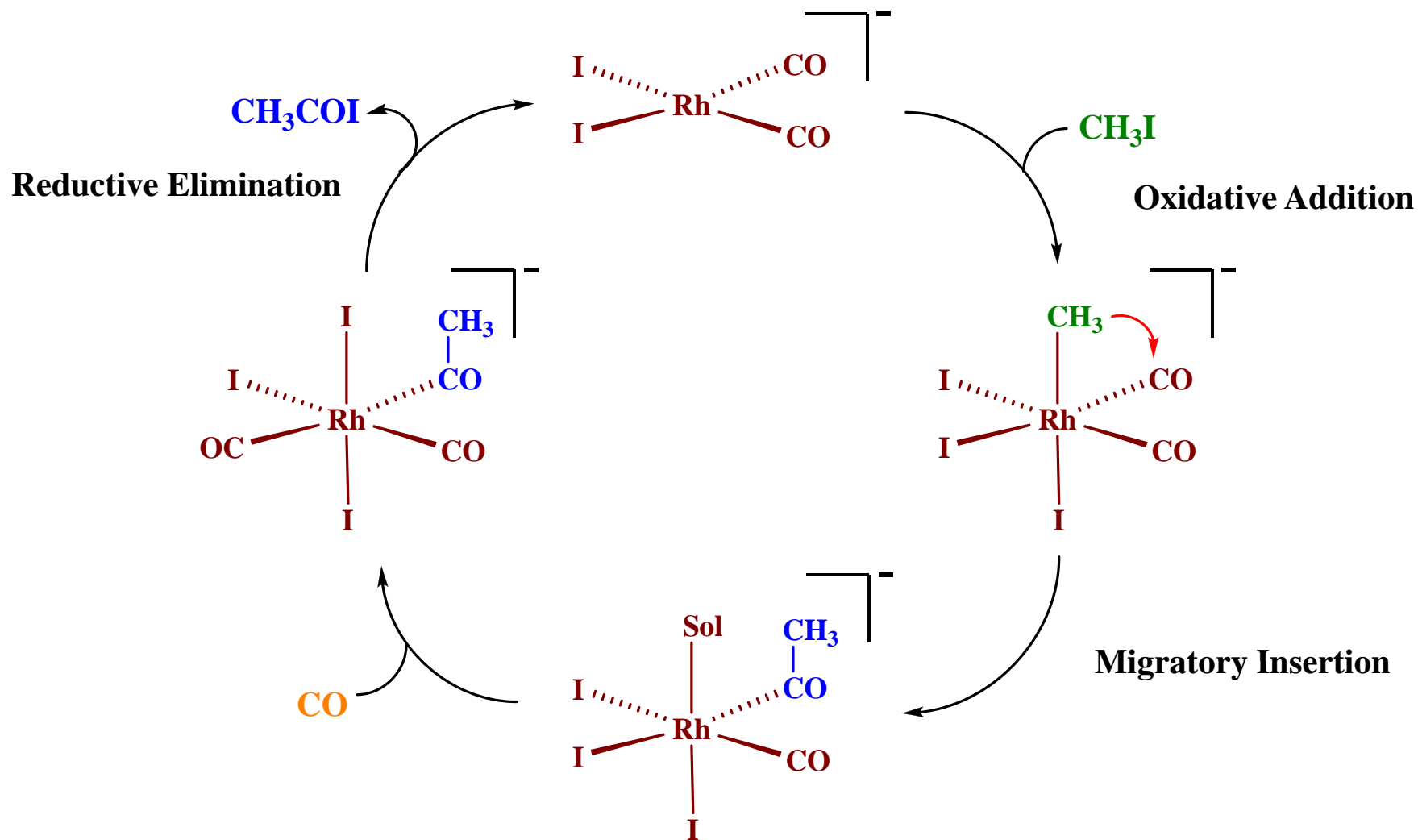
Methanol initially reacts with hydroiodic acid to give methyl iodide and H₂O. Methyl iodide reacts with the 16e⁻ catalyst, which forms the rate-determining step.



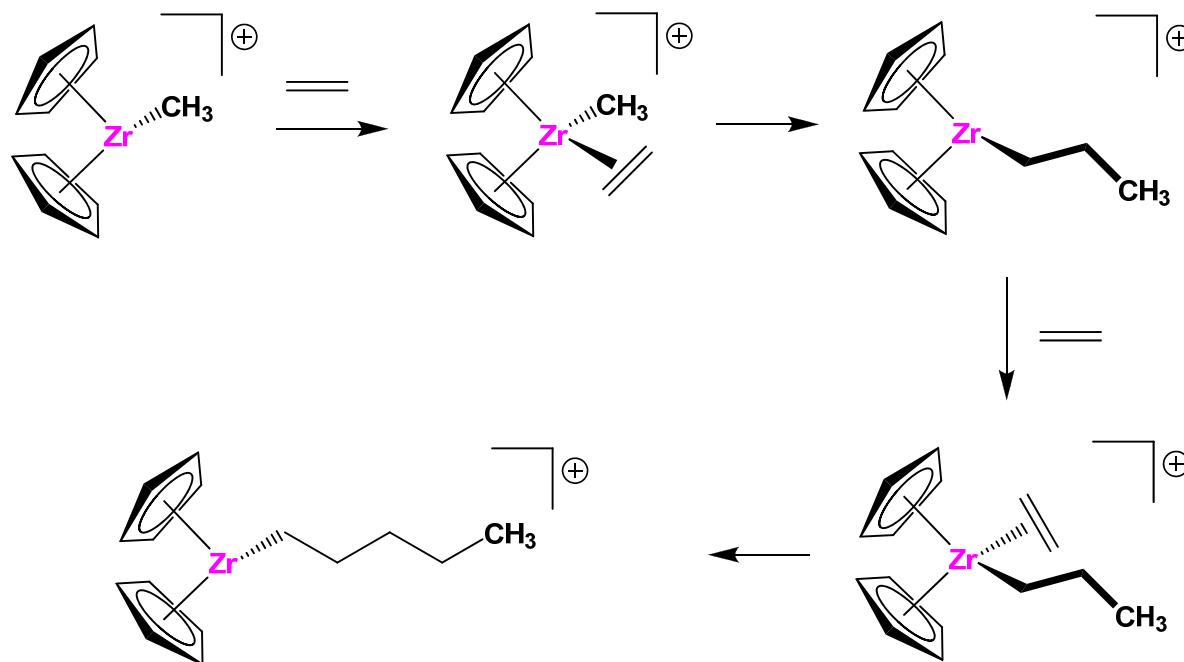
The final product formed after the catalytic cycle is acetyl iodide, which is hydrolyzed by water to acetic acid and HI.



Monsanto Acetic Acid Synthesis



Alkene Polymerization



The commonly used catalyst has a tetrahydrofuran molecule occupying the fourth coordination site of zirconium.

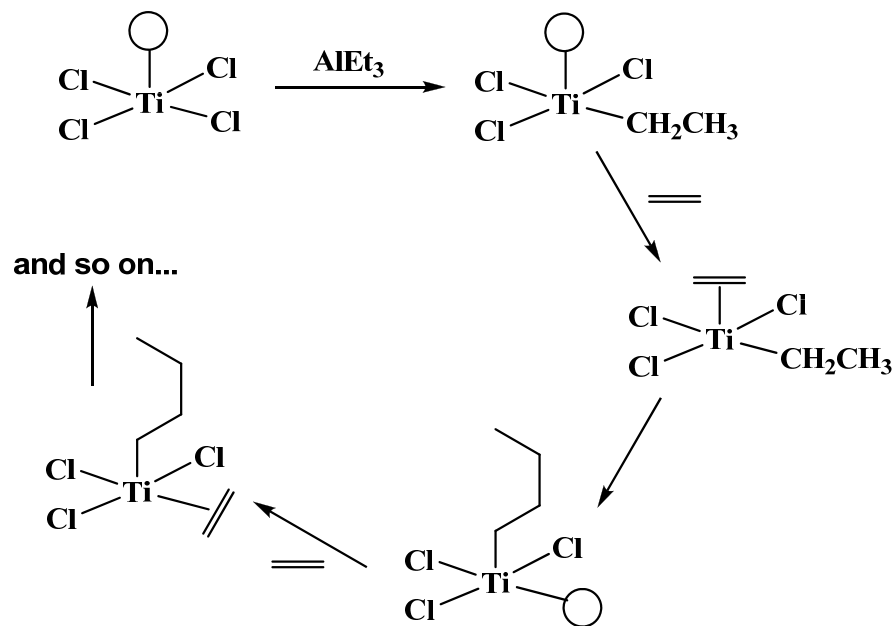
Ziegler-Natta Catalyst

Karl Ziegler in 1953, discovered a catalyst based on TiCl_3 and AlCl_3 for the polymerization of ethylene.

Giulio Natta extended the method for the polymerization of other olefins like propylene and made a number of different variations.

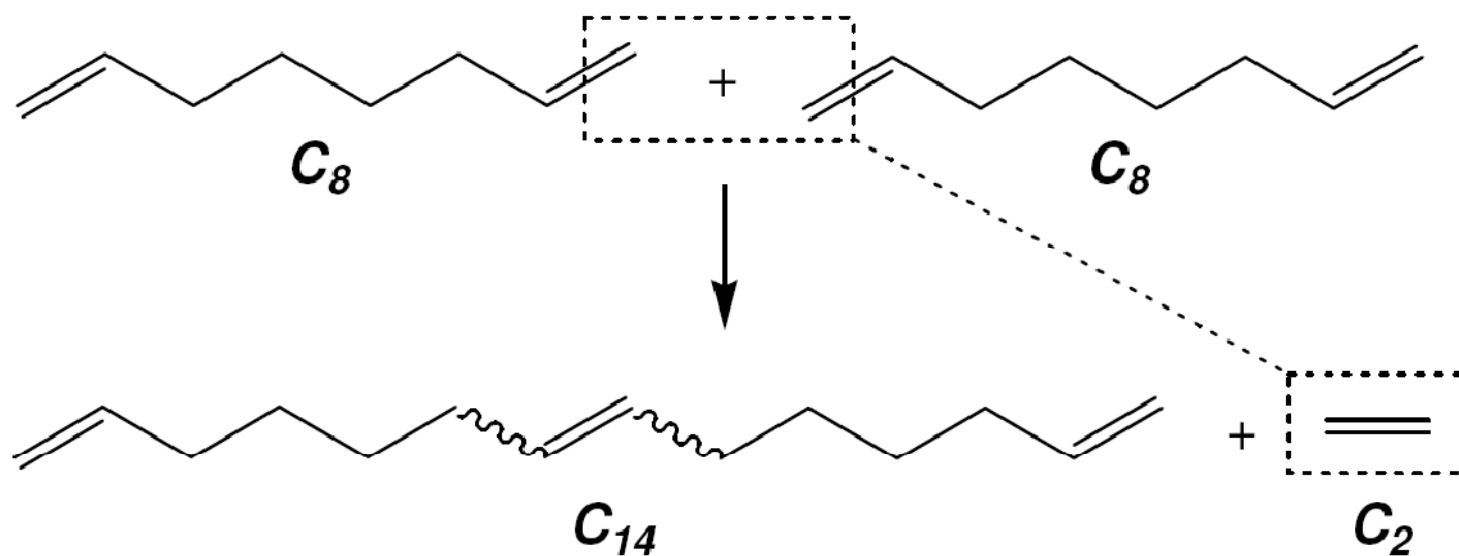
The Ziegler-Natta catalyst family includes halides of titanium, chromium, vanadium and zirconium, typically activated by aluminum halide compounds.

Ziegler and Natta received the Nobel Prize in Chemistry in the year 1963.

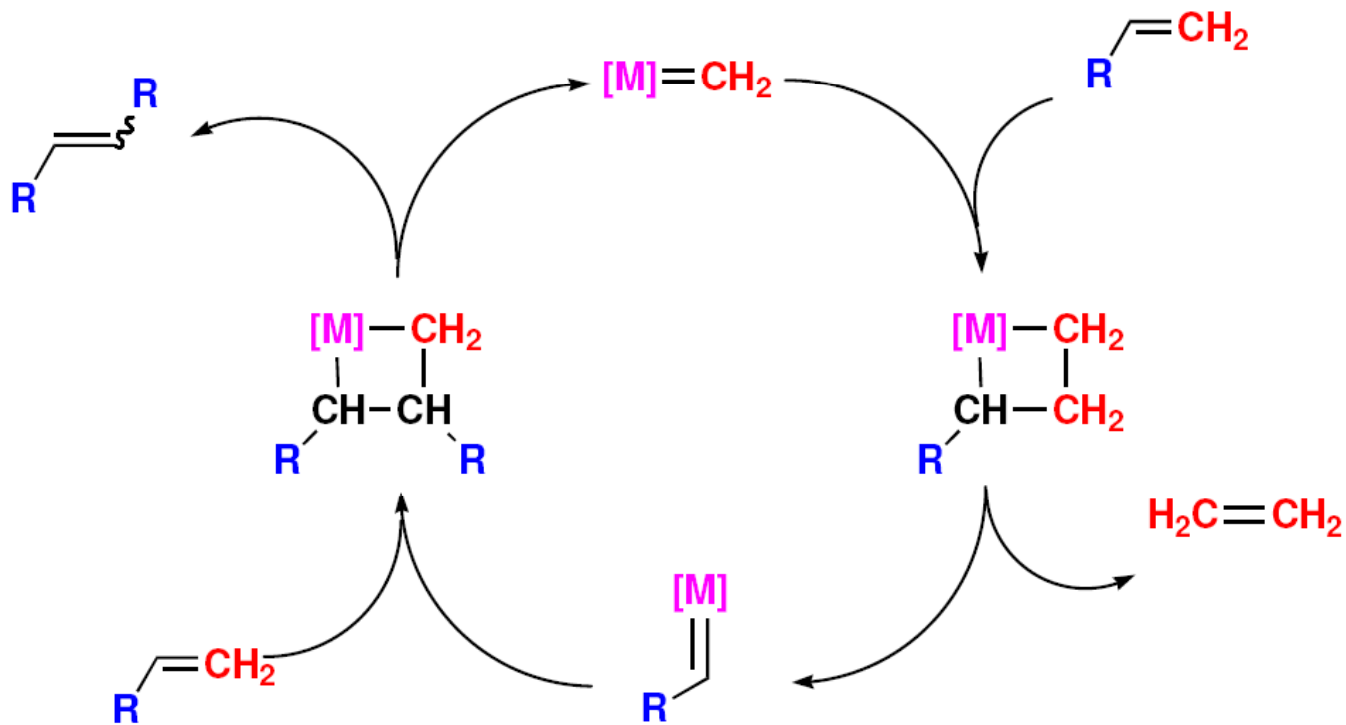
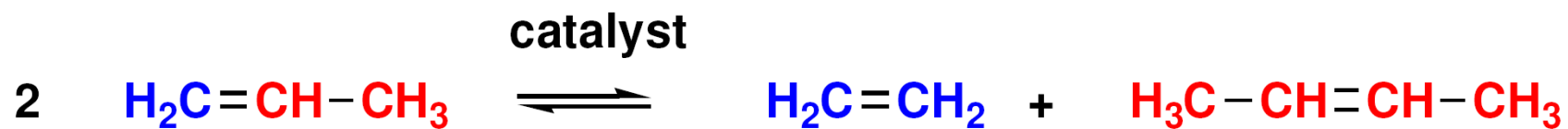


Alkene Metathesis

Metathesis catalysis refers to the reaction of two unsaturated substrates (typically alkenes or alkynes) that leads to a switching of the atom groups on each end of the bond with the unsaturation. This is shown below for the reaction of two C_8 dienes.



Alkene Metathesis



Alkene Metathesis

Nobel Prize in Chemistry 2005.



Yves Chauvin
Institut Français du
Pétrole,
Rueil-
Malmaison,
France

Photo: Patrick
Chevolat/
Photo France



Robert H.
Grubbs
California
Institute of
Technology
(Caltech),
Pasadena,
CA, USA

Photo: Robert
Paz/Caltech

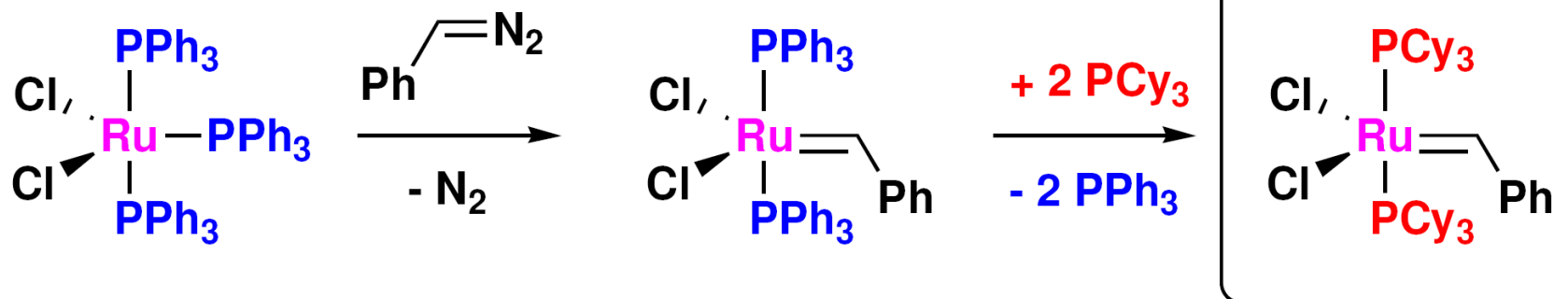


Richard R.
Schrock
Massachusetts
Institute of
Technology
(MIT), Cam-
bridge, MA,
USA

Photo: Donna
Coveney/MIT
News Office

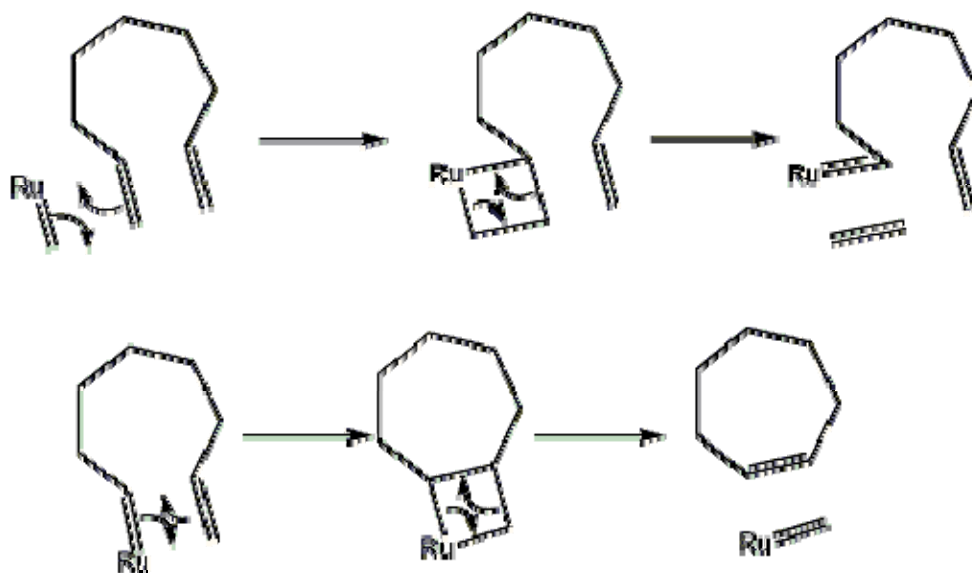
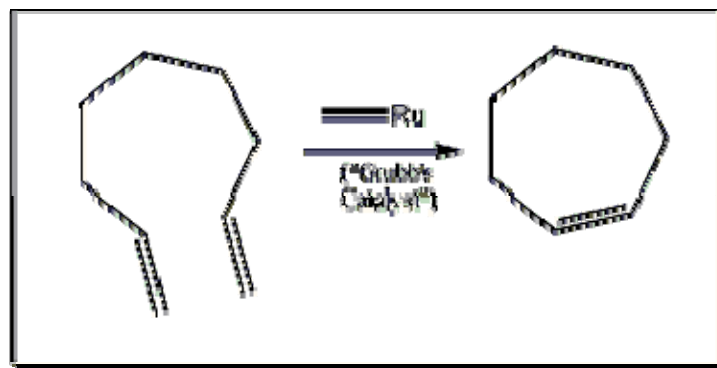
Metathesis – a molecular dance

The atoms let go of each other for a moment – the bonds are broken. All of a sudden a new molecule approaches. A new bond, or...? Everything happens at breakneck speed and the dancers are so exceedingly small... This makes the challenge of working out what really happens all the greater. That's what chemistry is all about – keeping up with the dancing molecules.

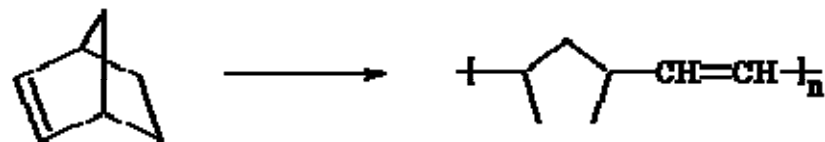
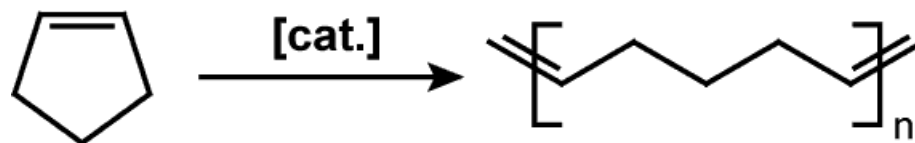


Grubbs Catalyst

Ring Closing Metathesis

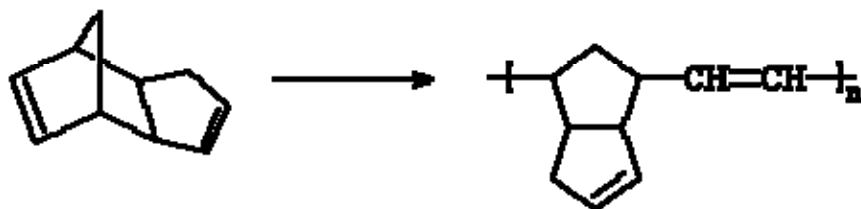


Ring Opening Metathesis Polymerization



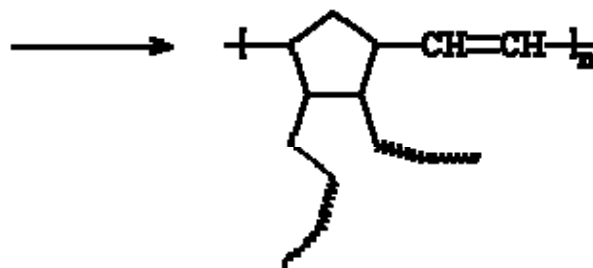
norbornene

polynorbornene



endo-dicyclopentadiene

poly(endo-dicyclopentadiene)



crosslinked polymer