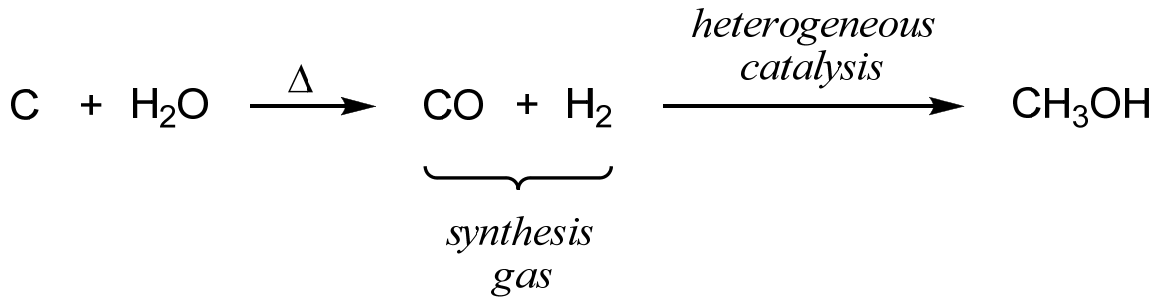
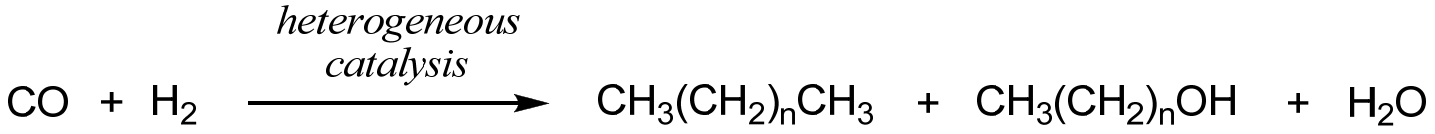
CO_2 and CO activation

- Most organic chemicals are currently made commercially from ethylene, a product of oil refining.
- It is possible that in the next several decades we may have to shift toward other carbon sources for these chemicals as depletion of our oil reserves continues.
- Either coal or natural gas (methane) can be converted into CO/H_2 mixtures with air and steam, and it is possible to convert such mixtures, variously called "***water–gas***" or "***synthesis gas***" to methanol and to alkane fuels with various heterogeneous catalysts.

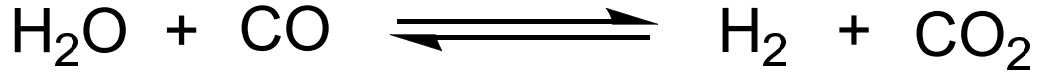


- In particular, the Fischer–Tropsch reaction converts synthesis gas to a mixture of long-chain alkanes and alcohols using heterogeneous catalysts *(typically Co, Fe or Ru)*.



Water-gas shift reaction

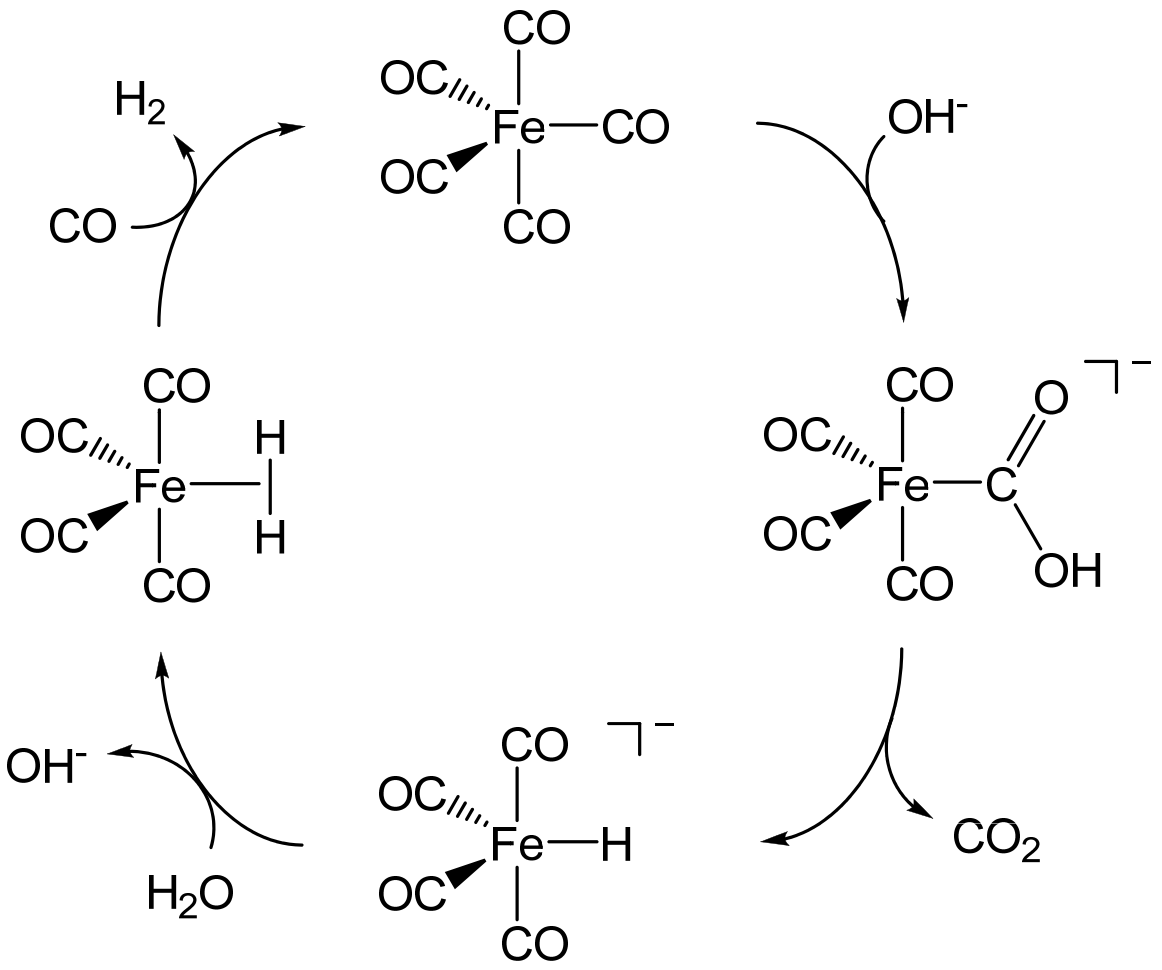
- It is often useful to change the CO:H_2 ratio in synthesis gas, and this can be accomplished by the ***water–gas shift reaction***, which can be catalyzed heterogeneously (Fe_3O_4 or Cu/ZnO) or by a variety of ***homogeneous catalysts, such as $Fe(CO)_5$ or $Pt(i\text{-}Pr_3P)_3$.***

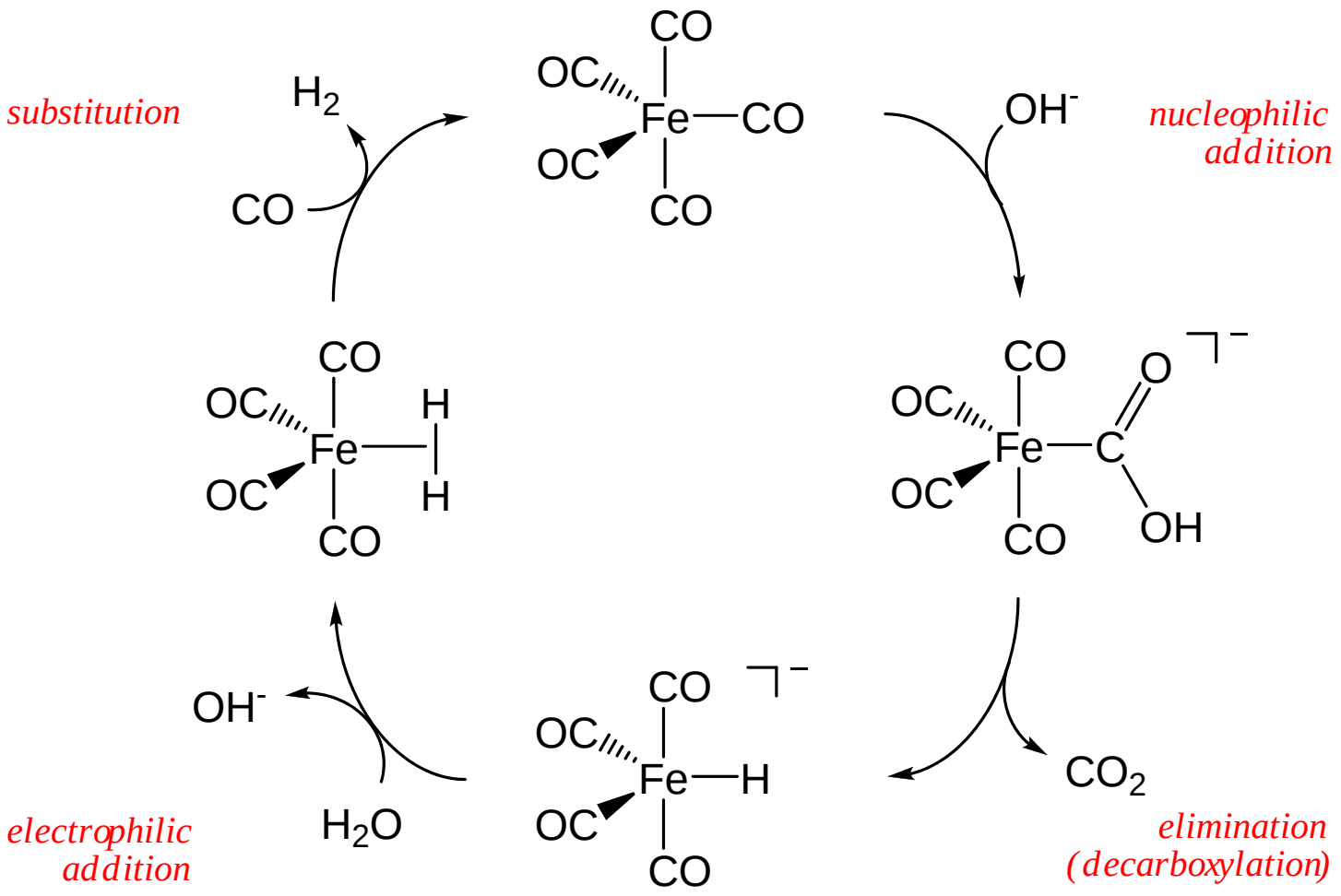


- The ***reagents and products have comparable free energies***; the reaction can therefore be run in either direction and this can be regarded as both CO and CO_2 activation.

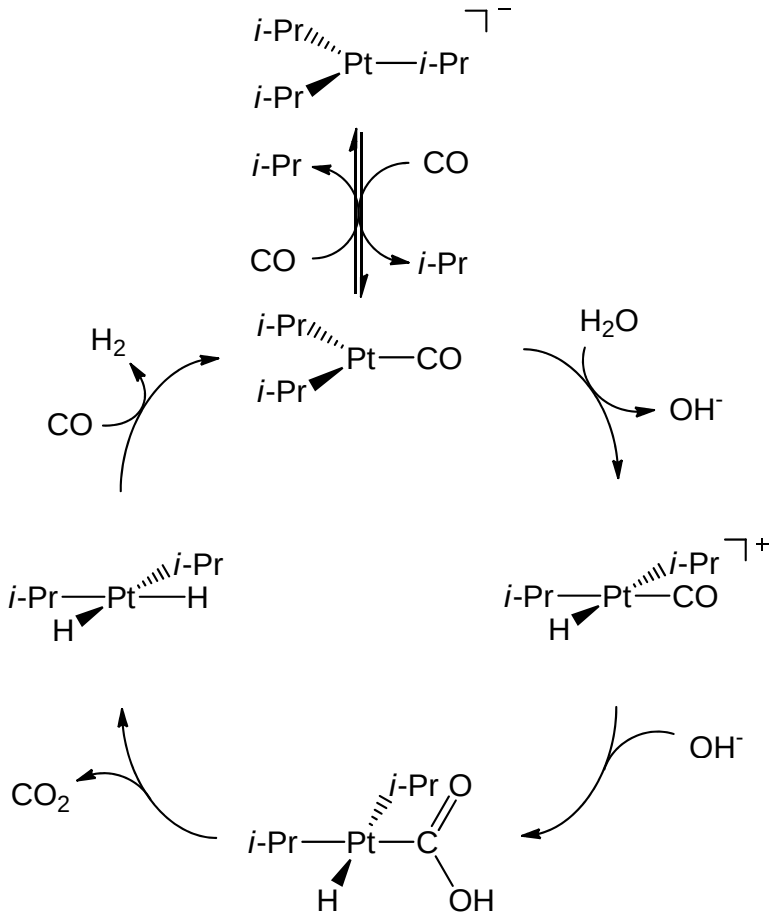
- In the mechanism proposed for the homogeneous iron catalyst, CO binds to the metal and so becomes ***activated for nucleophilic attack*** by OH^- ion at the CO carbon.

- ***Decarboxylation*** of the resulting metalacarboxylic acid probably does not take place by β *elimination* because this would require prior loss of CO to generate a vacant site; instead, deprotonation may precede loss of CO_2, followed by reprotonation at the metal to give $HFe(CO)4^-$.


CO
OC
Fe
CO
OC
CO
OH-
CO
O
OC
Fe
C
OC
CO
OH
CO2
CO
OC
Fe
H
OC
CO
OH-
H2O
H2
CO


substitution
H2
CO
CO
OC
Fe
CO
OC
CO
OH-
nucleophilic addition
CO
OC
H
Fe
OC
H
CO
CO
OC
O
Fe
C
OC
CO
OH
electrophilic addition
OH-
H2O
CO
OC
Fe
H
OC
CO
CO2
elimination (decarboxylation)

- Using a platinum catalyst for the same ***water-gas shift*** reaction is perhaps more interesting in that it ***activates both the water and the CO***, so no added base is needed.
- This happens because the platinum complex is sufficiently basic to deprotonate the water, leading to a cationic hydride complex.
- The ***cationic charge activates the CO for nucleophilic attack*** by hydroxide ion to give the metalacarboxylic acid (M−COOH).



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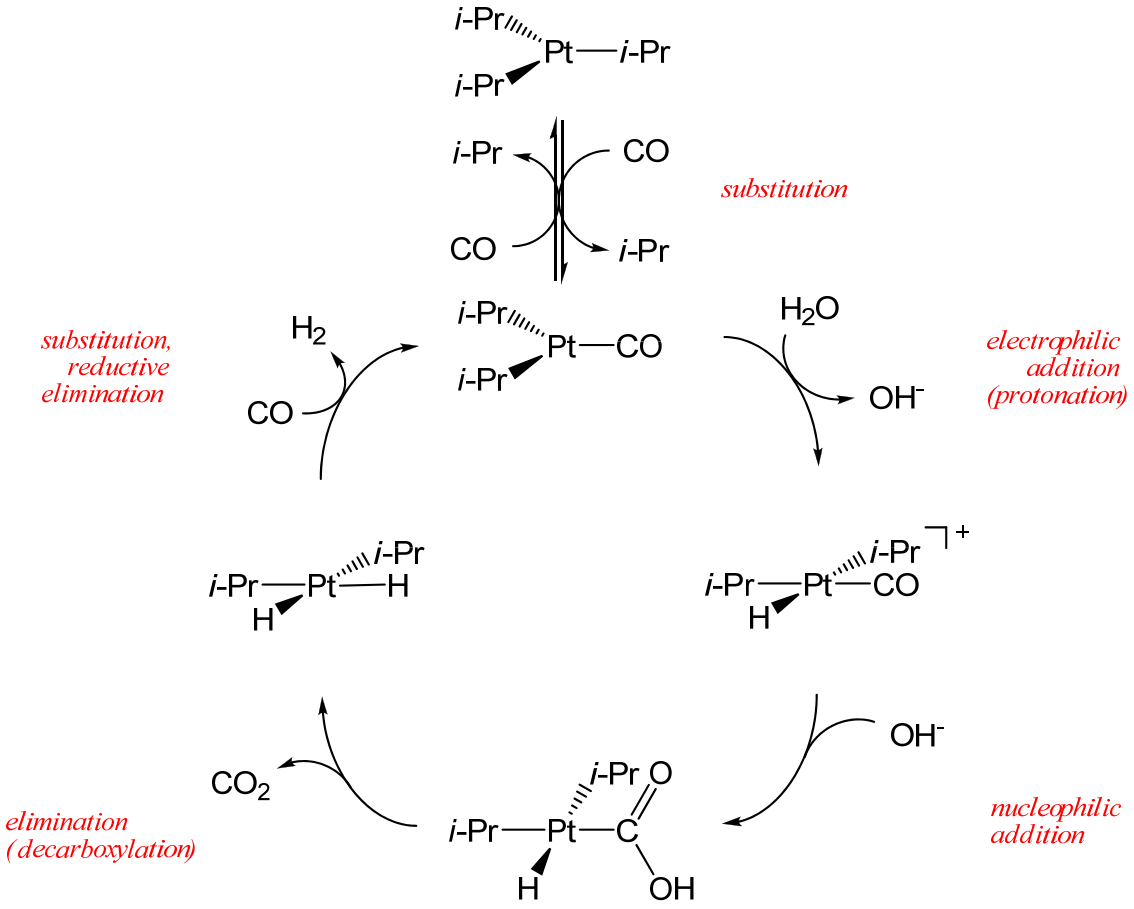
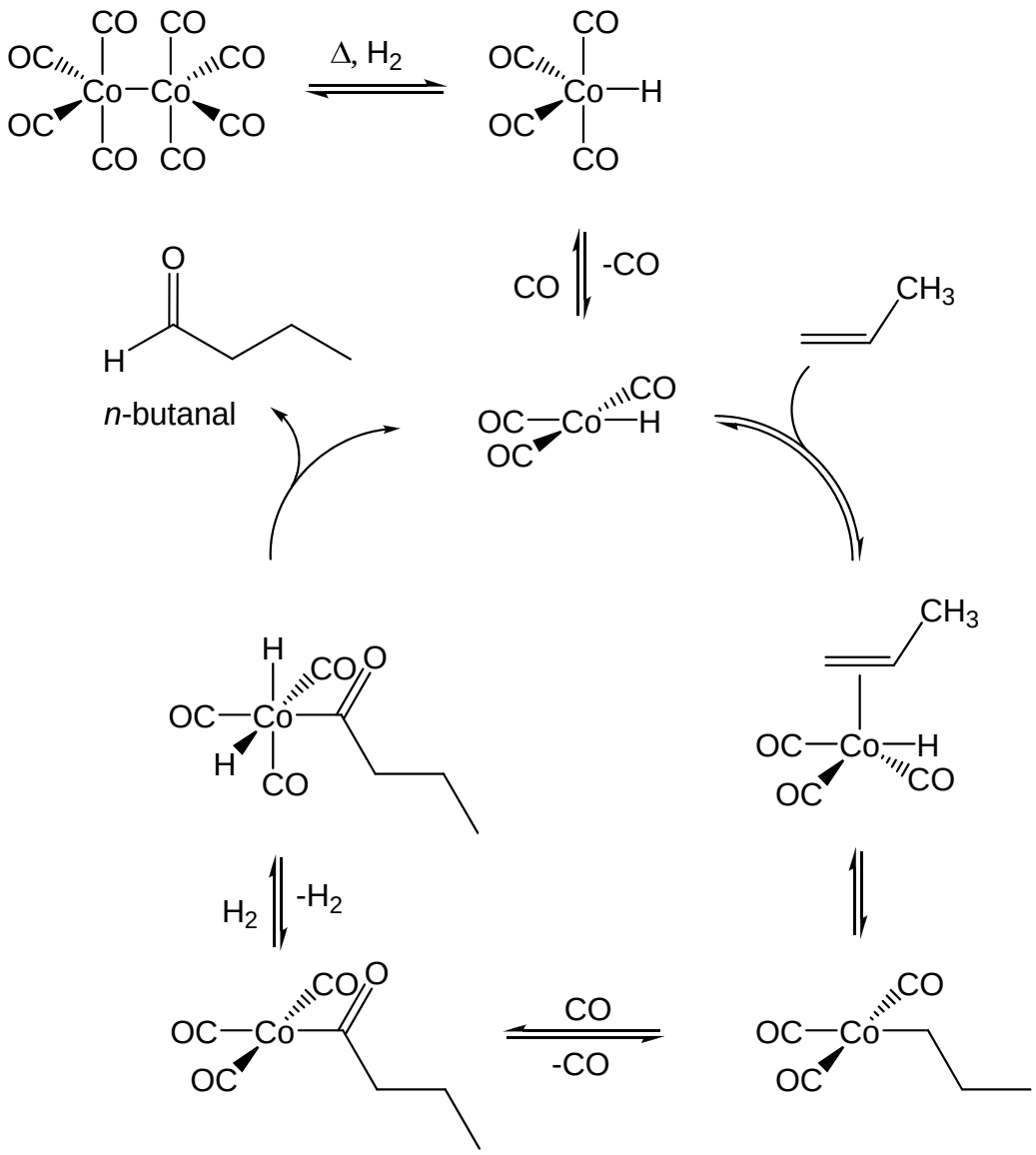


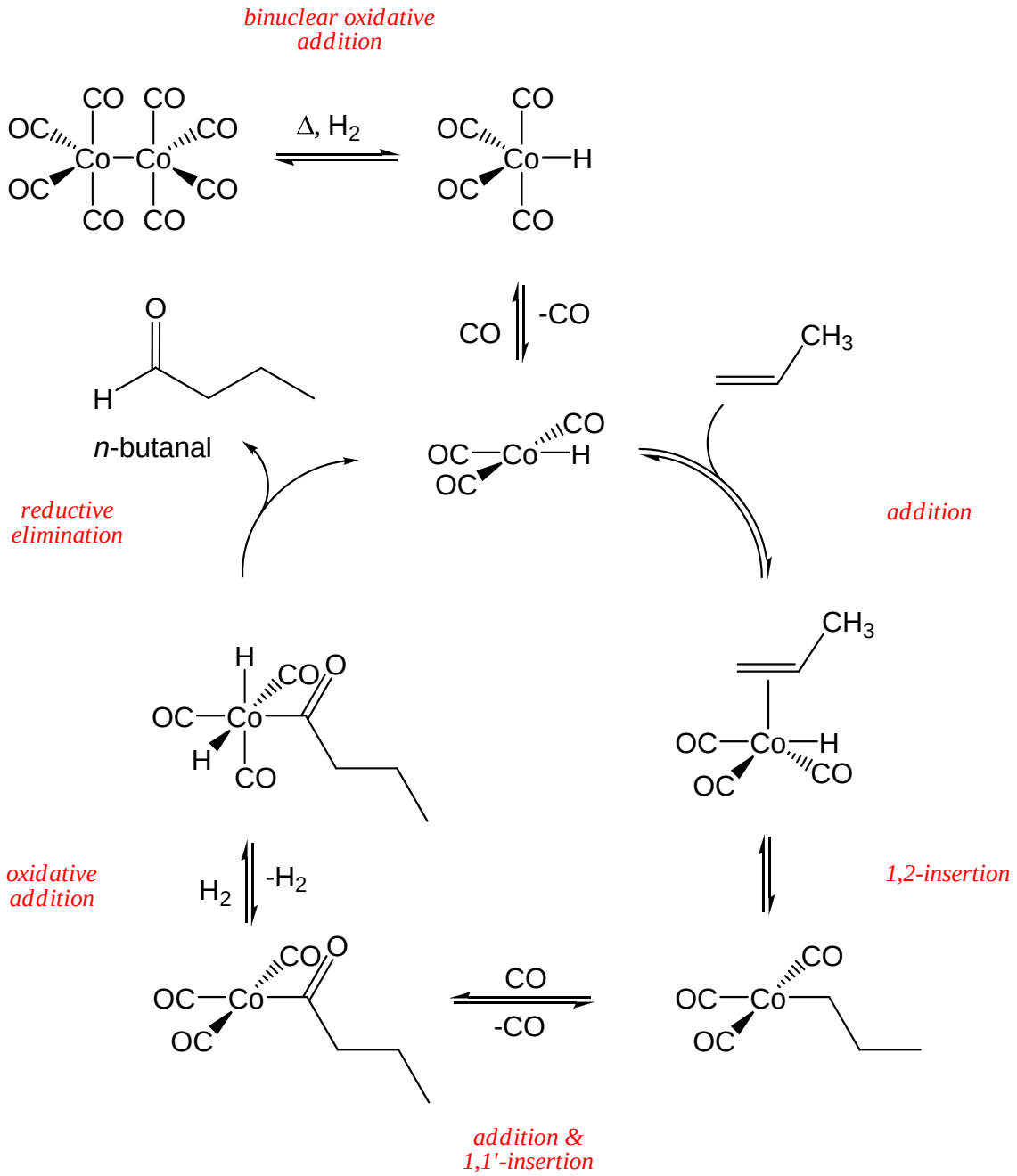
Alkene hydroformylation *(oxo process)*

- The catalysis of alkene hydroformylation (Roelen 1938), with 4 million tonnes per year, is one of the most industrially relevant applications of organometallic chemistry.

- The aldehyde products are further reacted via hydrogenation for alcohol synthesis, which are used for detergent, plastics and carboxylic acids (via further oxidation) production.

- The irreversibility of the overall hydroformylation cycle is due to the irreversibility of the final reductive elimination step, releasing an aldehyde from the intermediate metal-hydride-formyl species. The latter being generated by oxidative addition of H_2.


CO
OC
Co
Co
Δ, H2
H
n-butanal
-CO
CH3
H2
-H2

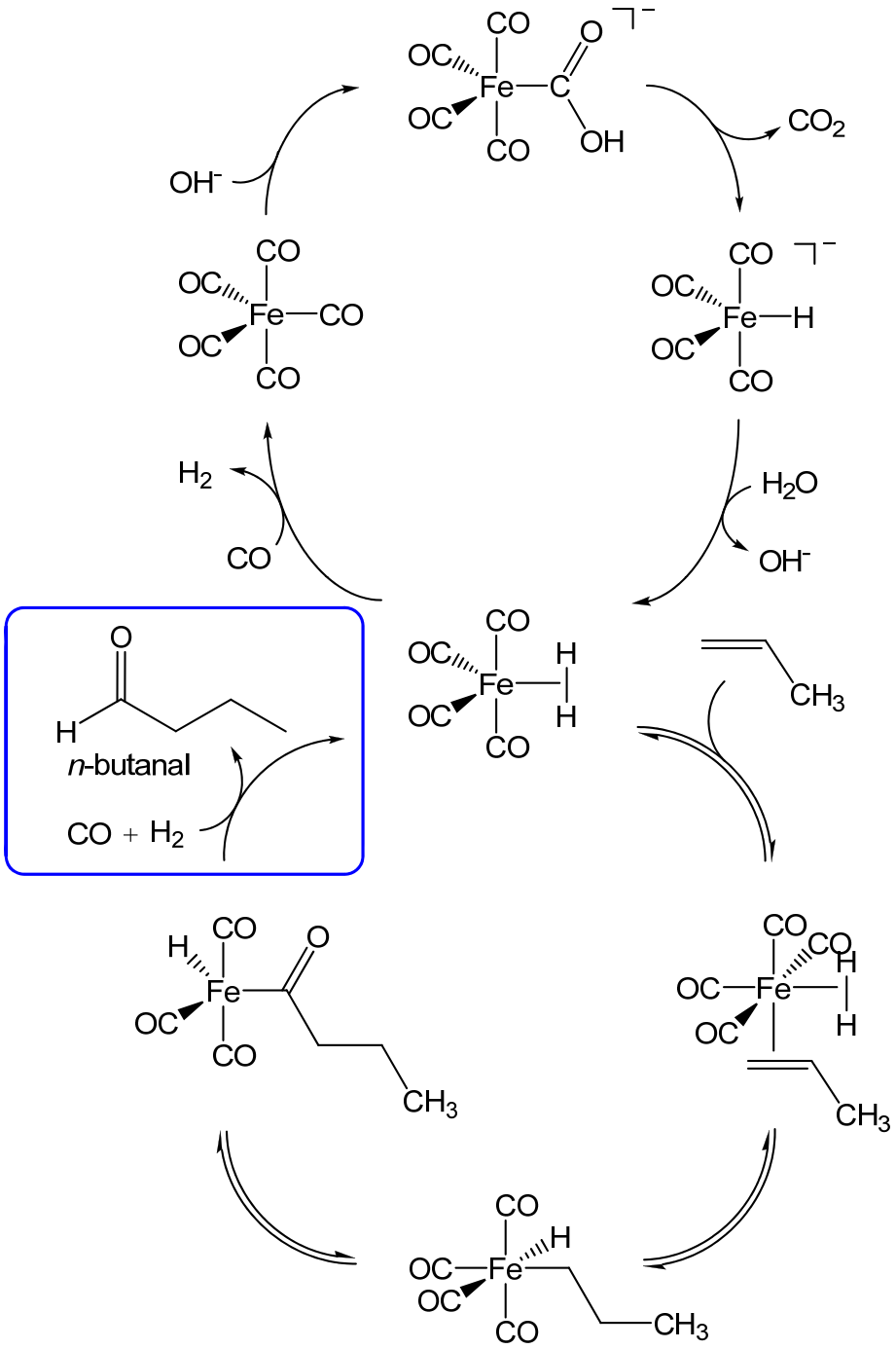

binuclear oxidative addition
Δ, H2
CO
-CO
n-butanal
reductive elimination
addition
oxidative addition
H2
-H2
1,2-insertion
addition & 1,1'-insertion

Alkene hydroformylation *(Reppe reaction)*

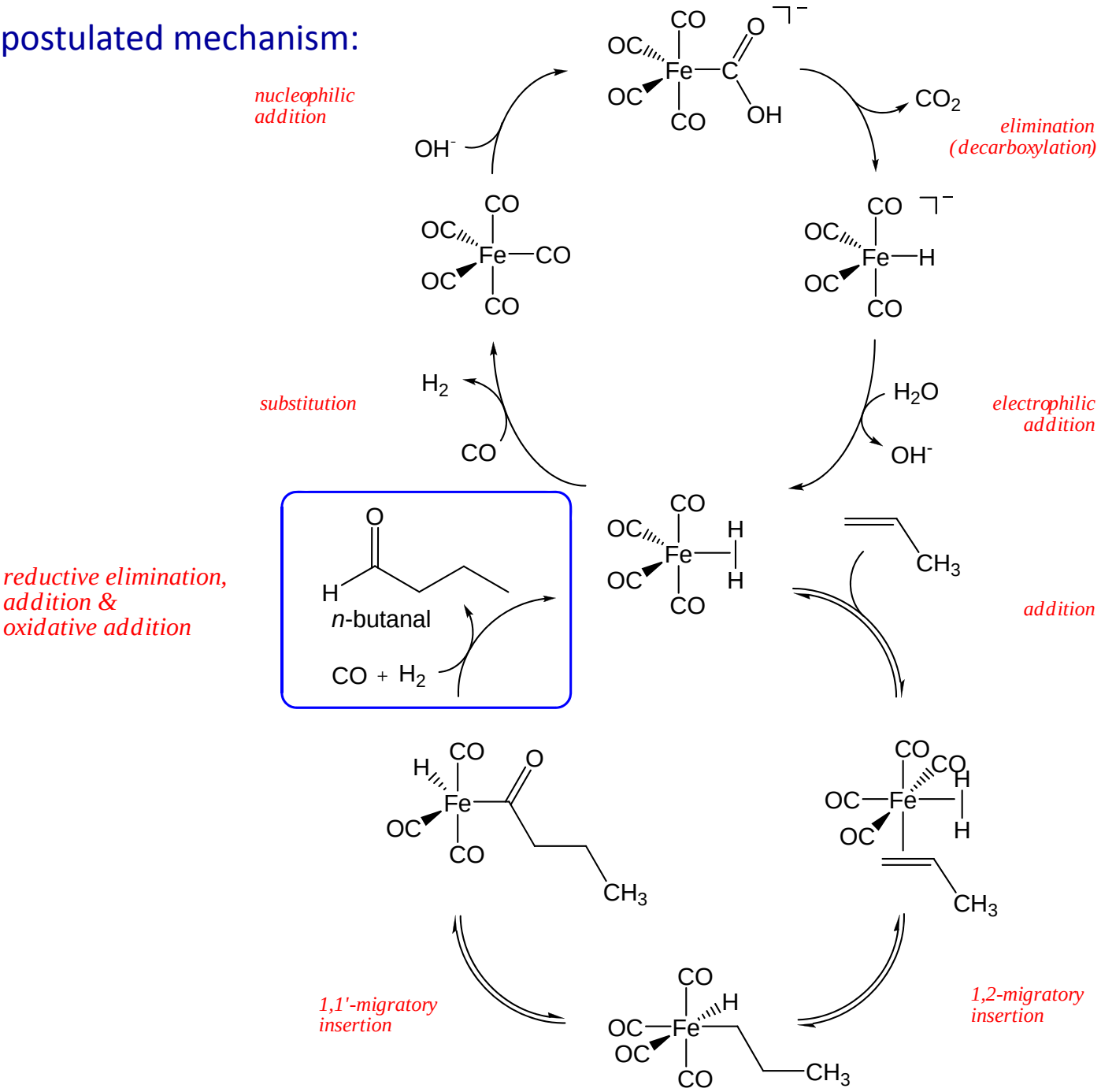
- The Reppe reaction ***uses the water–gas shift reaction to generate*** **H_2/CO** for subsequent hydroformylation of the substrate alkene to give an aldehyde, followed by hydrogenation to give an alcohol.
- With the $Fe(CO)_5$/base catalyst mentioned above, the product is the linear alcohol.

$$RCH{=}CH_2 + 3CO + 2H_2O \xrightarrow{KOH,\ Fe(CO)_5,\ 15\ atm,\ 100^\circ C} RCH_2CH_2CH_2OH + 2CO_2$$

- The alkene is believed to insert into an Fe−H bond of the active catalyst, $H_2Fe(CO)_4$, followed by migratory insertion to give $(RCH_2CH_2CO)FeH(CO)_3$, which in turn reductively eliminates the aldehyde RCH_2CH_2CHO.
- This aldehyde is then hydrogenated to the alcohol with $HFe(CO)_4^-$ as catalyst.
- By itself, $Fe(CO)_5$ is not a hydroformylation catalyst because H_2 cannot displace CO to form $H_2Fe(CO)4$, hence the need for the base to remove the CO.

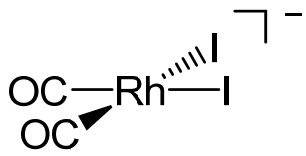

CO
OC
Fe
C
O
OH
CO
OC
CO
CO2
OH-
H2O
OH-
H2
CO
H
n-butanal
CO + H2
CH3

….postulated mechanism:

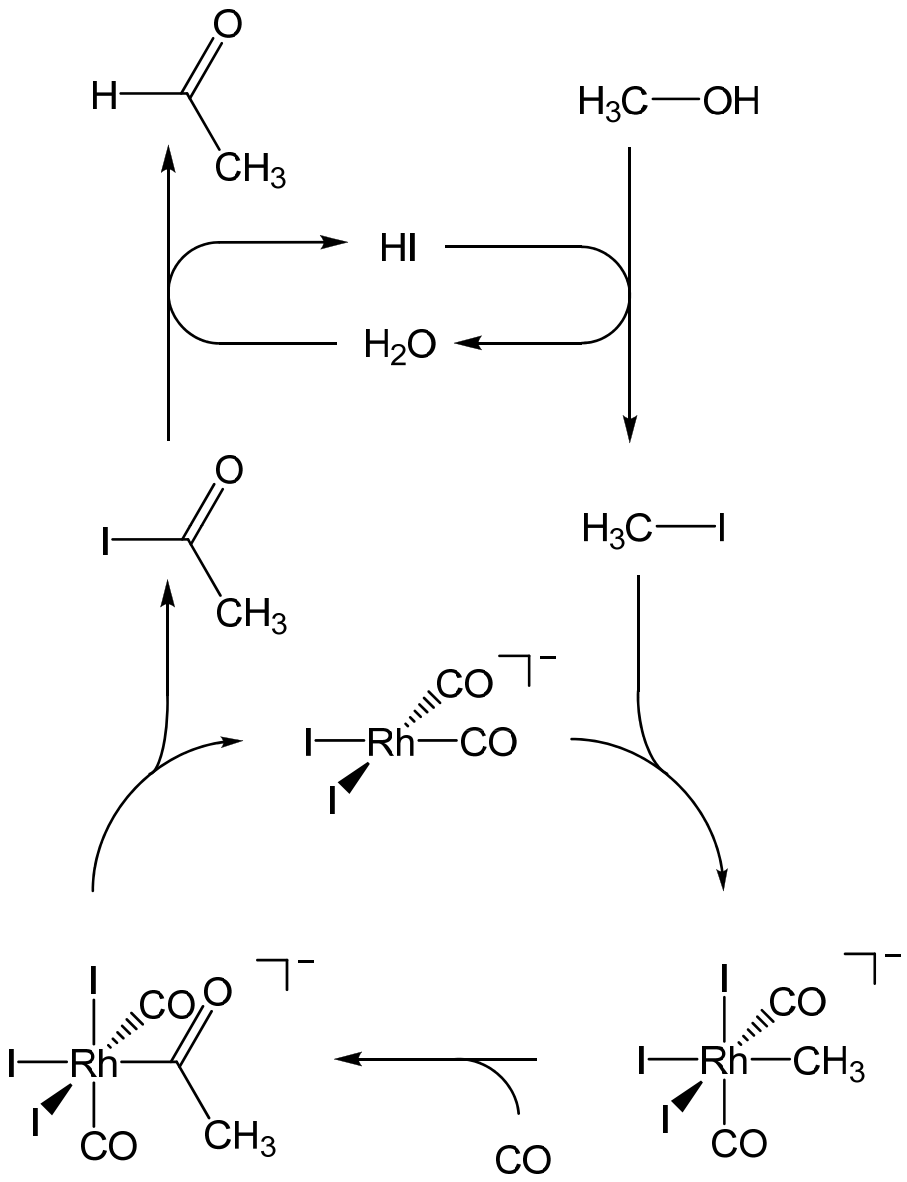


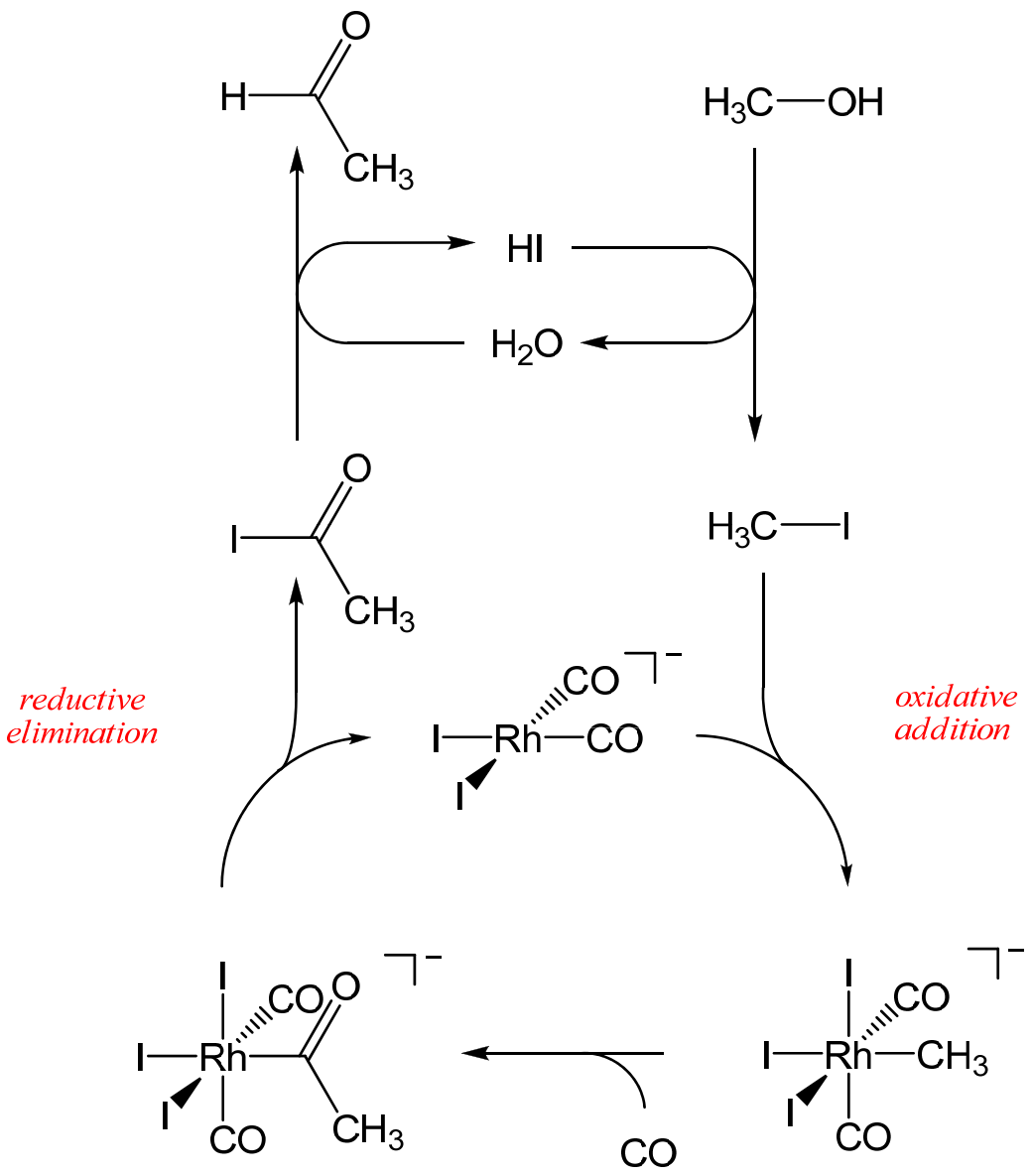
Monsanto acetic acid process

- Over two million tons of acetic acid a year are produced by carbonylation of methanol, which happens in *>99% selectivity with a rhodium catalyst. The active* catalyst is



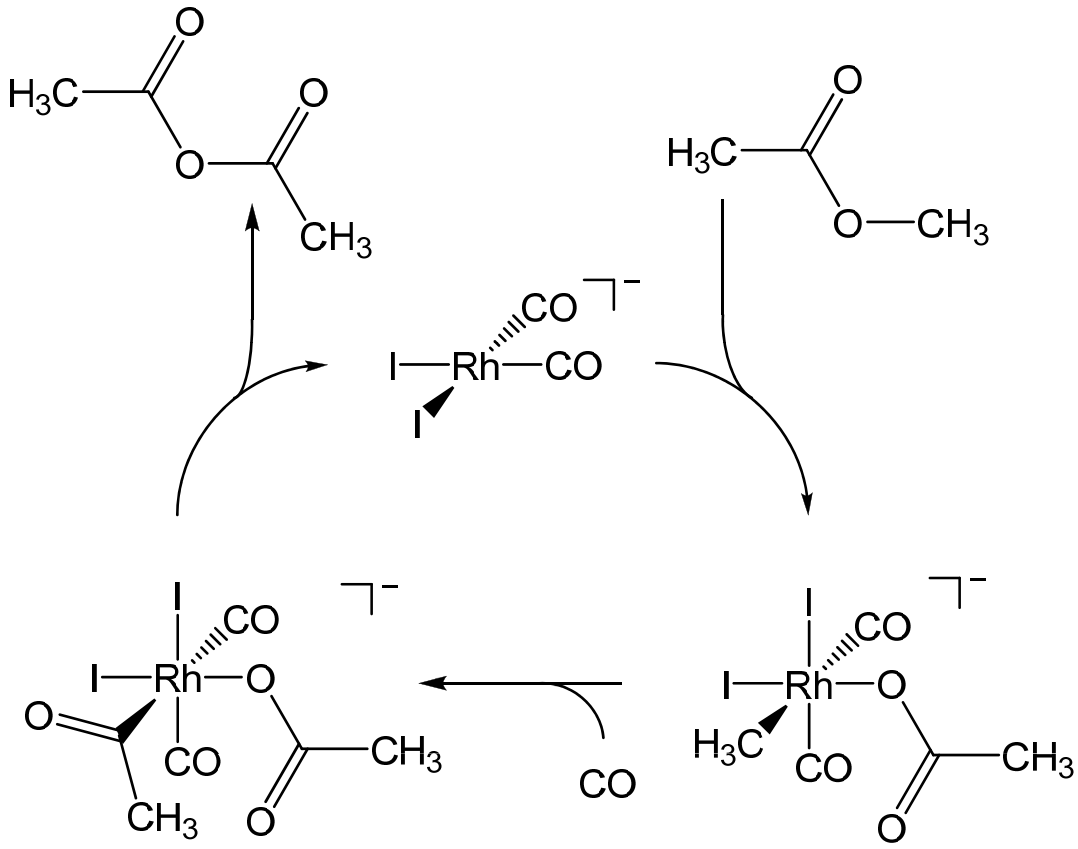
- The net effect is the ***cleavage of the methanol C–O bond and insertion of a CO***.
- To be carbonylated, the methanol has to bind to the catalyst and this requires adding a certain amount of HI to the system, which produces an equilibrium concentration of MeI, which can in turn oxidatively add to the metal in the turnover limiting step.
- Once we have the rhodium methyl, migratory insertion can take place with CO to give an acetylrhodium iodide. Reductive elimination of the acyl iodide completes the cycle.
- The free acyl iodide is hydrolyzed by the methanol to give methyl acetate and can be ultimately converted to acetic acid with water.
- The resulting acetic acid can be entirely derived from synthesis gas.


O
H
CH3
H3C—OH
HI
H2O
O
I
CH3
H3C—I
CO
I—Rh—CO
I
I
CO
O
I—Rh
I
CO
CH3
CO
I
CO
I—Rh—CH3
I
CO


H3C—OH
HI
H2O
reductive elimination
oxidative addition
1,1′-insertion & addition
CO

- In a very closely related reaction, CH_3COOMe can be carbonylated to acetic anhydride $(CH_3CO)_2O$…

...postulated mechanism:



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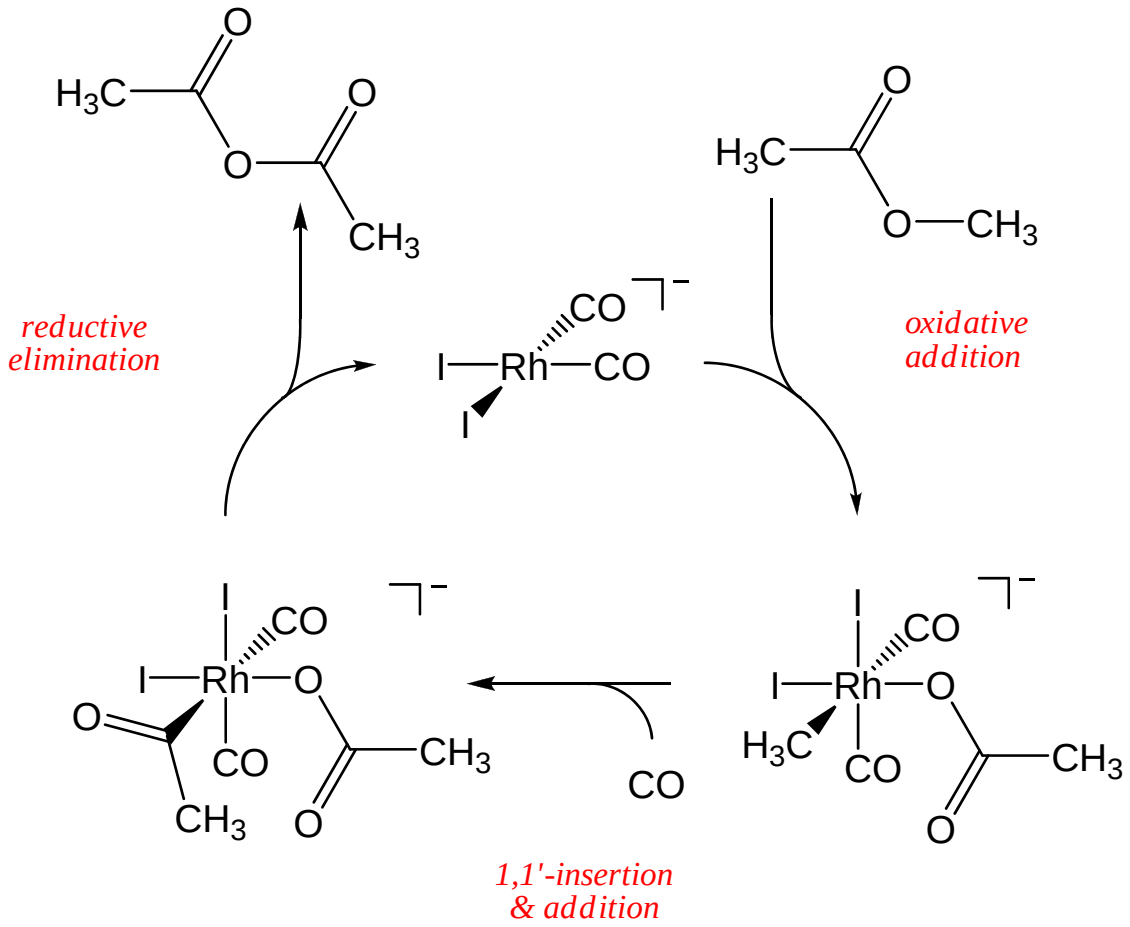
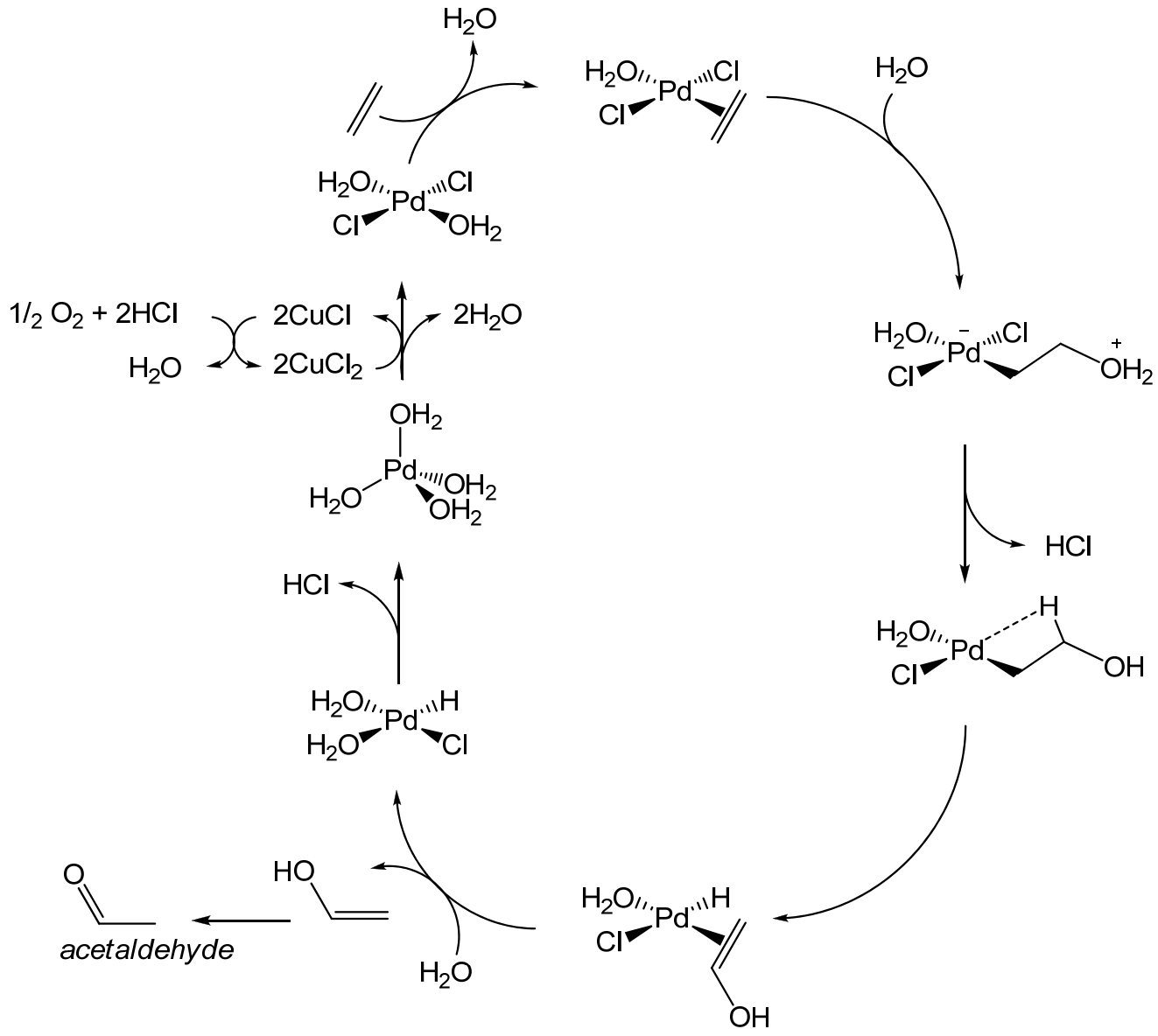
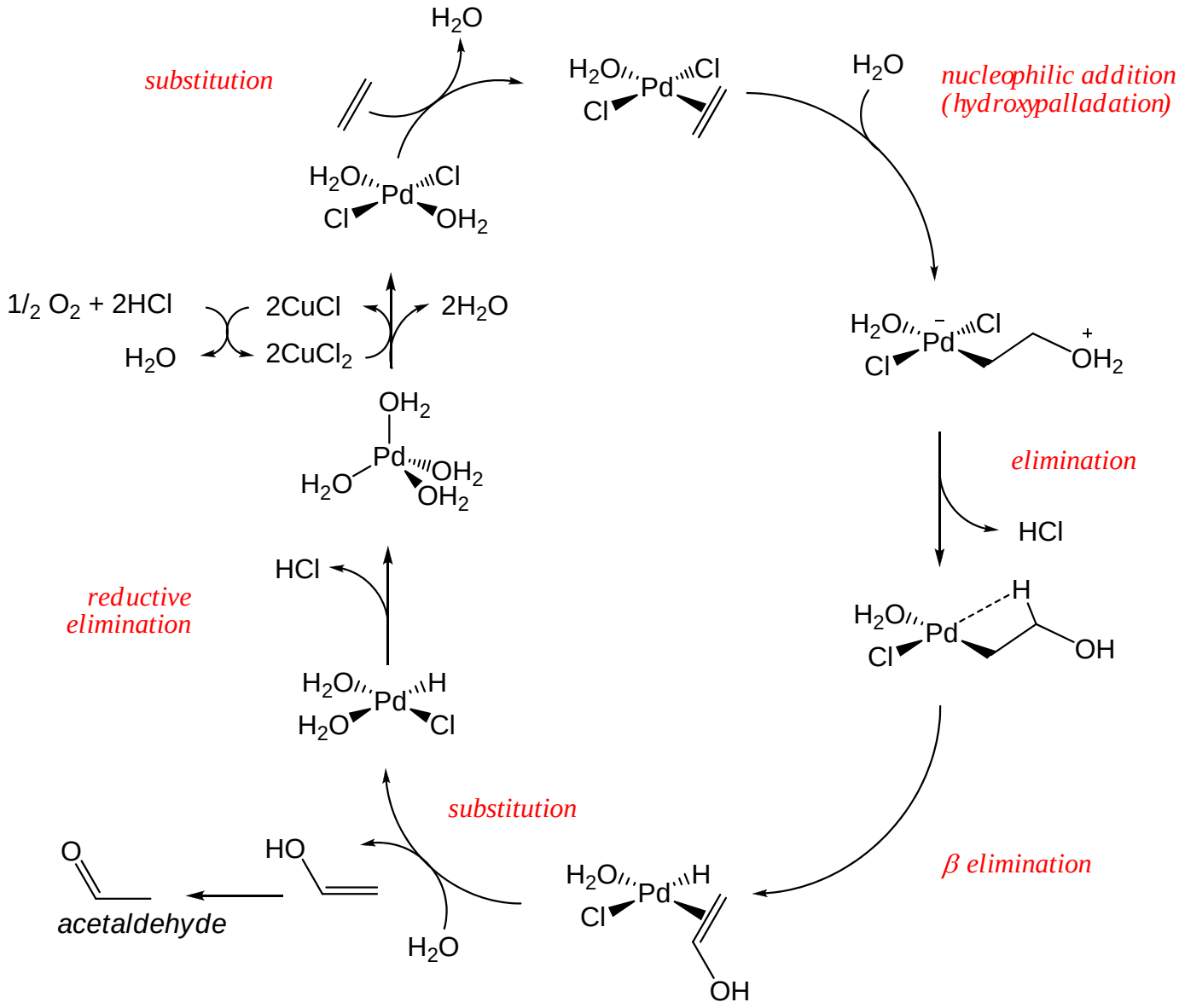


- The Monsanto process for making acetic acid is replacing the older route that goes from ethylene by ***the Wacker process*** to acetaldehyde, which is then oxidized to acetic acid in a second step.
- This example shows how important it is that chemical companies carry out research into possible alternative ways to make a compound, even though the current route is working well; otherwise their competitors may discover a better one.
- An improved process based on iridium has been developed by BP-Amoco.

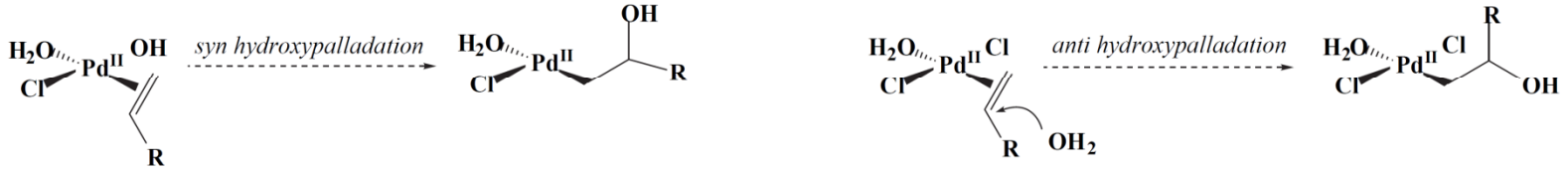
Wacker oxidation
(*Nucleophilic addition of H_2O at ethylene*)

- Alkene complexes undergo ***nucleophilic attack to give metal alkyls***, which can often rearrange to give other products. This is the basis of an important industrial process, the Wacker process, now used to make about 4 million tons of aldehydes from alkenes annually.
- The fact that aqueous $PdCl_2$ oxidizes ethylene to acetaldehyde had been known (although not understood) since the nineteenth century.
- The reaction consumes the $PdCl_2$ and deposits metallic Pd(0). It took considerable imagination to see that such a reaction might be useful on an industrial scale because $PdCl_2$ is far too expensive to use as a stoichiometric reagent in the synthesis.
- The key is catalysis, which allows the Pd to be recycled almost indefinitely.
- J. Smidt of Wacker Chemie realized in the late 1950's that it is possible to intercept the Pd(0) before it has a chance to precipitate by using $CuCl_2$, which reoxidizes the palladium and is itself reduced to cuprous chloride.
- This is air sensitive and is reoxidized back to Cu(II). The resulting set of reactions are an elegantly simple solution to the problem and resemble the coupled reactions of biochemical catalysis.


H2O
H2O
Pd
Cl
Cl
OH2
H2O
H2O
Pd
Cl
Cl
1/2 O2 + 2HCl
H2O
2CuCl
2CuCl2
2H2O
H2O
Pd
Cl
Cl
OH2
OH2
H2O
Pd
OH2
OH2
HCl
H2O
Pd
Cl
H
OH
HCl
H2O
Pd
H2O
H
Cl
H2O
Pd
Cl
H
OH
O
HO
acetaldehyde
H2O


substitution
nucleophilic addition
(hydroxypalladation)
elimination
HCl
β elimination
substitution
reductive
elimination
HCl
1/2 O2 + 2HCl
H2O
2CuCl
2CuCl2
2H2O
acetaldehyde
H2O
Pd
Cl
OH2
OH
H

- The currently accepted mechanism involves attack of a free water molecule from the solvent on the coordinated ethylene, which, in the process, inverts the stereochemistry at one of the carbons.
- 2 mechanistic possibilities for hydroxypalladation:



- Deuterium labeling study indicates that hydroxypalladation proceeds *via palladium-nucleophile anti-addition.* No deuterium is incorporated into the acetaldehyde when the reaction is carried out in D_2O, which would happen if vinyl alcohol were released.