

Lecture 10

Inorganic chemistry

β -hydrogen elimination

σ -bond metathesis

Homogeneous versus Heterogeneous Catalysis

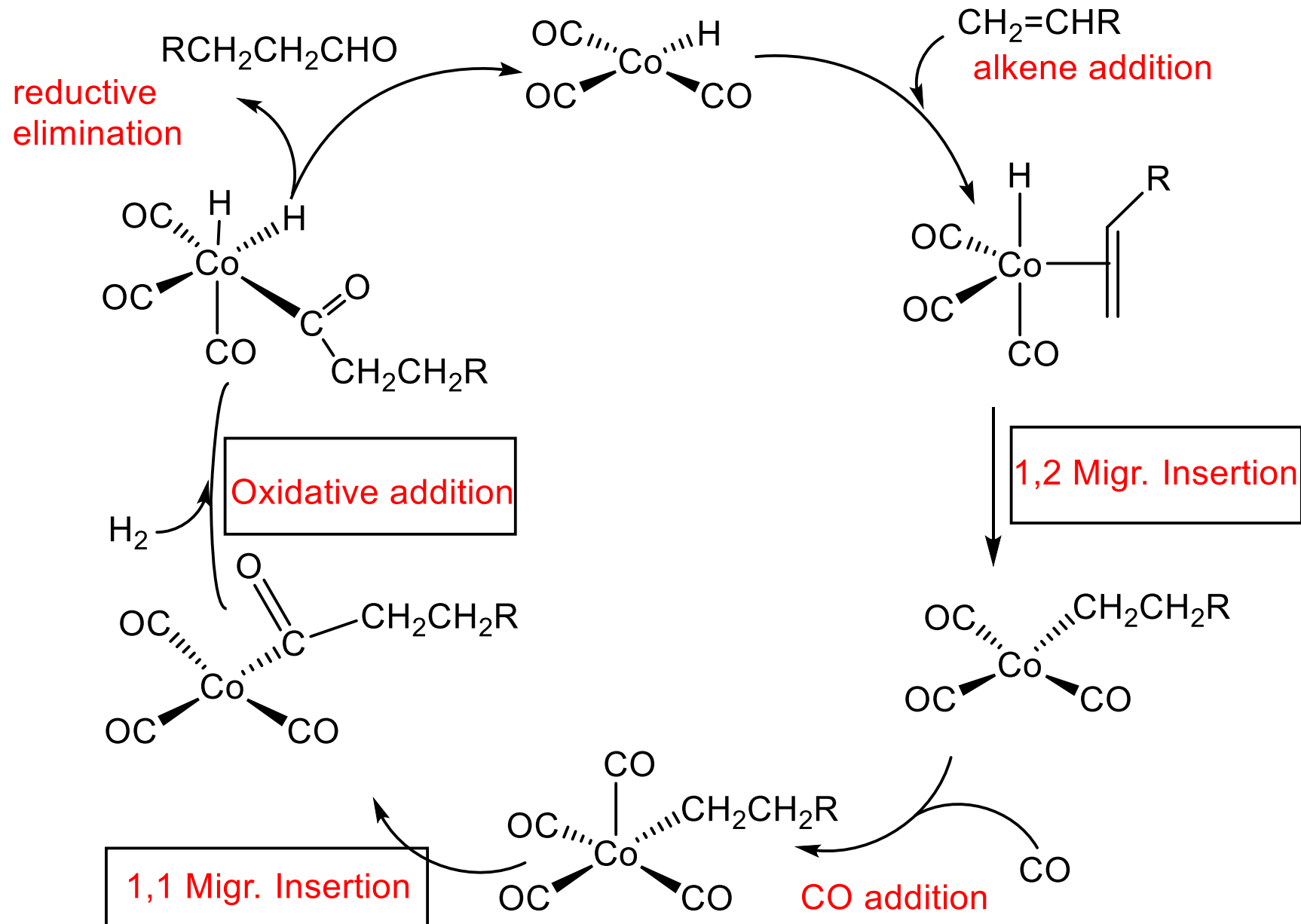
Wilkinson's Catalyst

Hydroformylation (Oxo-process)

Carbonylation of methanol: Monsanto Process

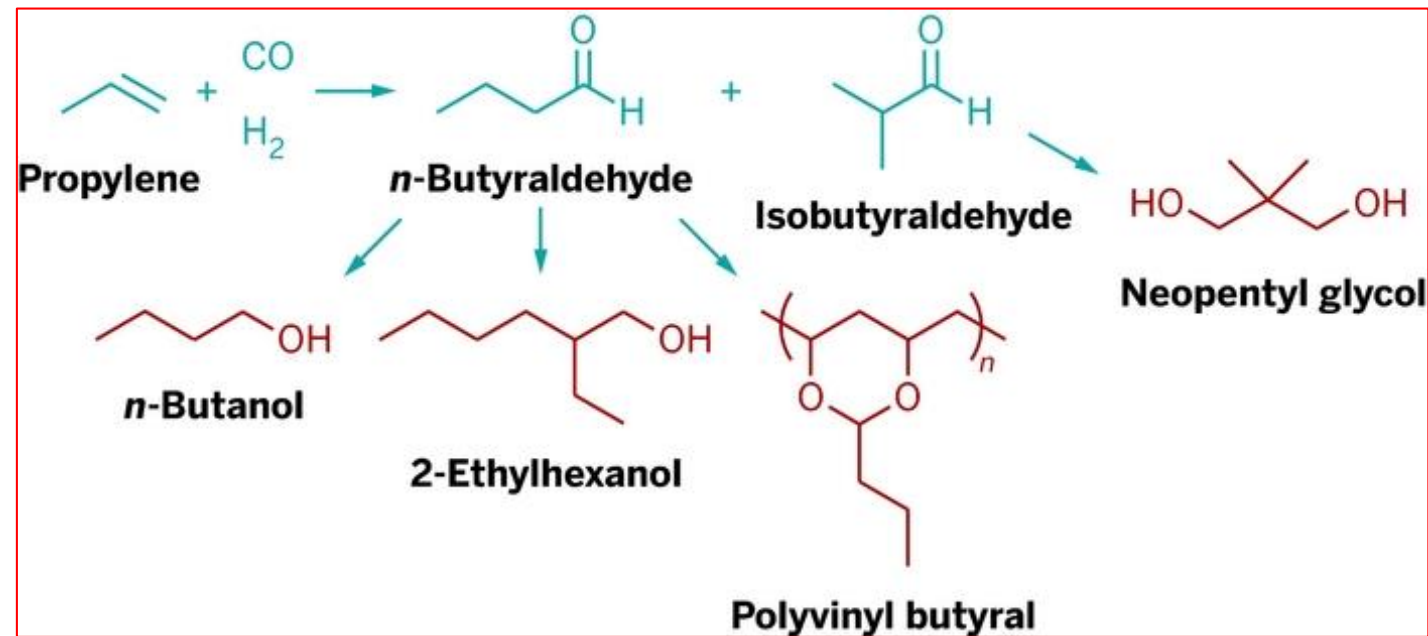
Cativa Process

Problem solving- fill in the blanks



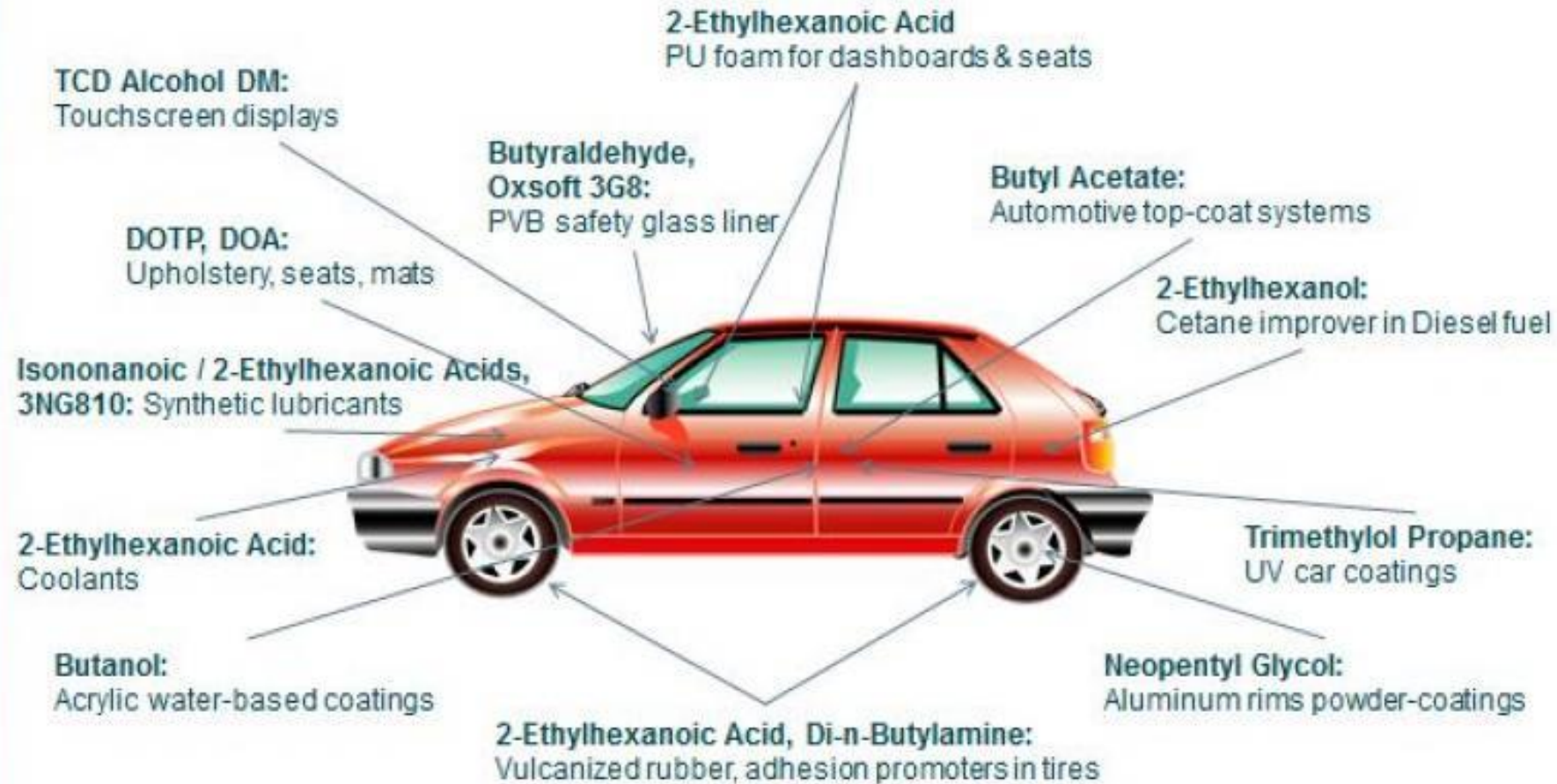
Hydroformylation (Oxo-process)

Hydroformylation - often called the oxo process- is used to describe the addition of H_2 and CO to an olefinic double bond resulting in the formation of an aldehyde which has one carbon atom more than the olefin.



Actually aldehydes are not the end products they get further reduced to alcohol and other value added products

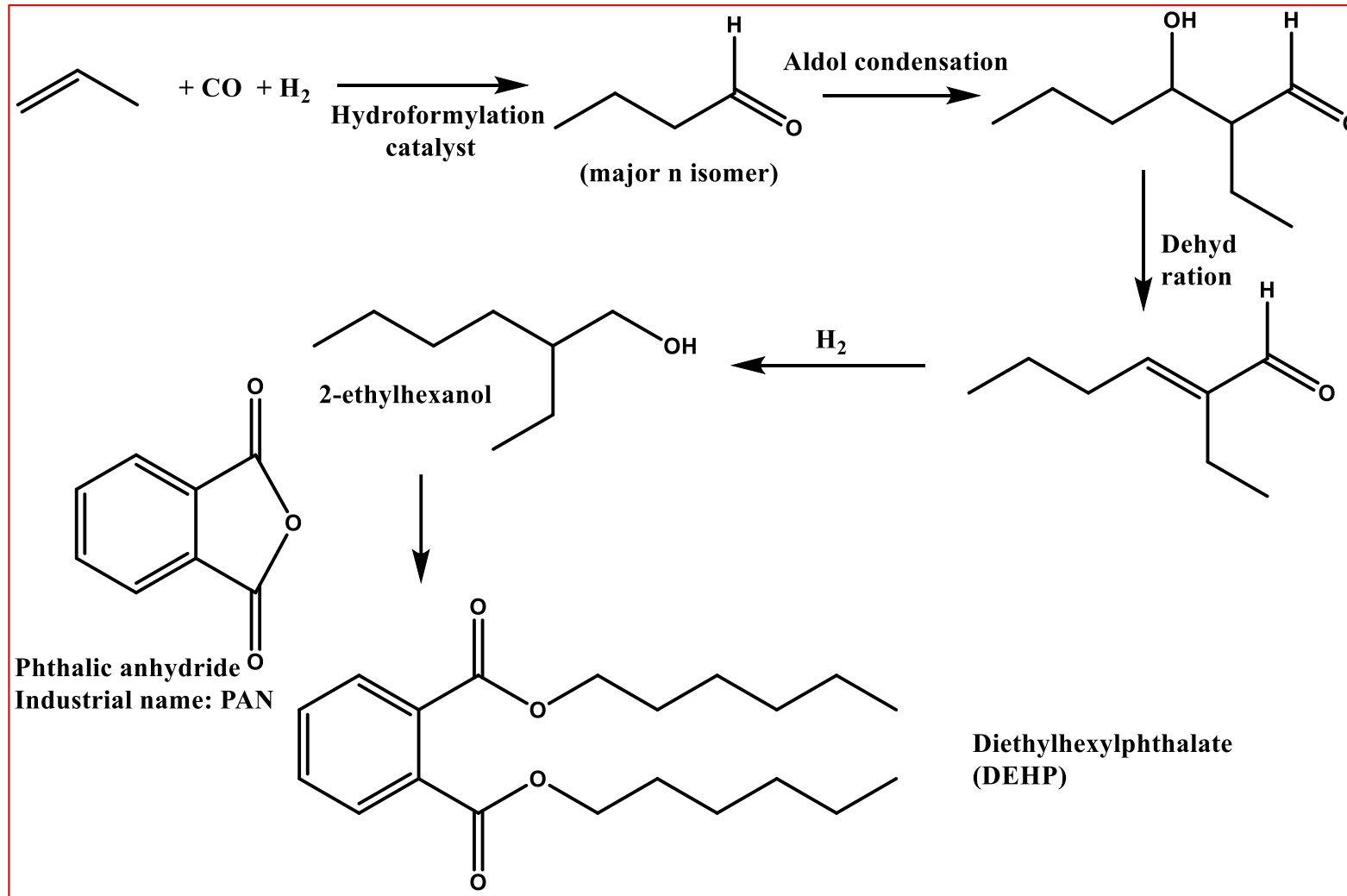
OXEA in our daily lives: example automotive vehicles



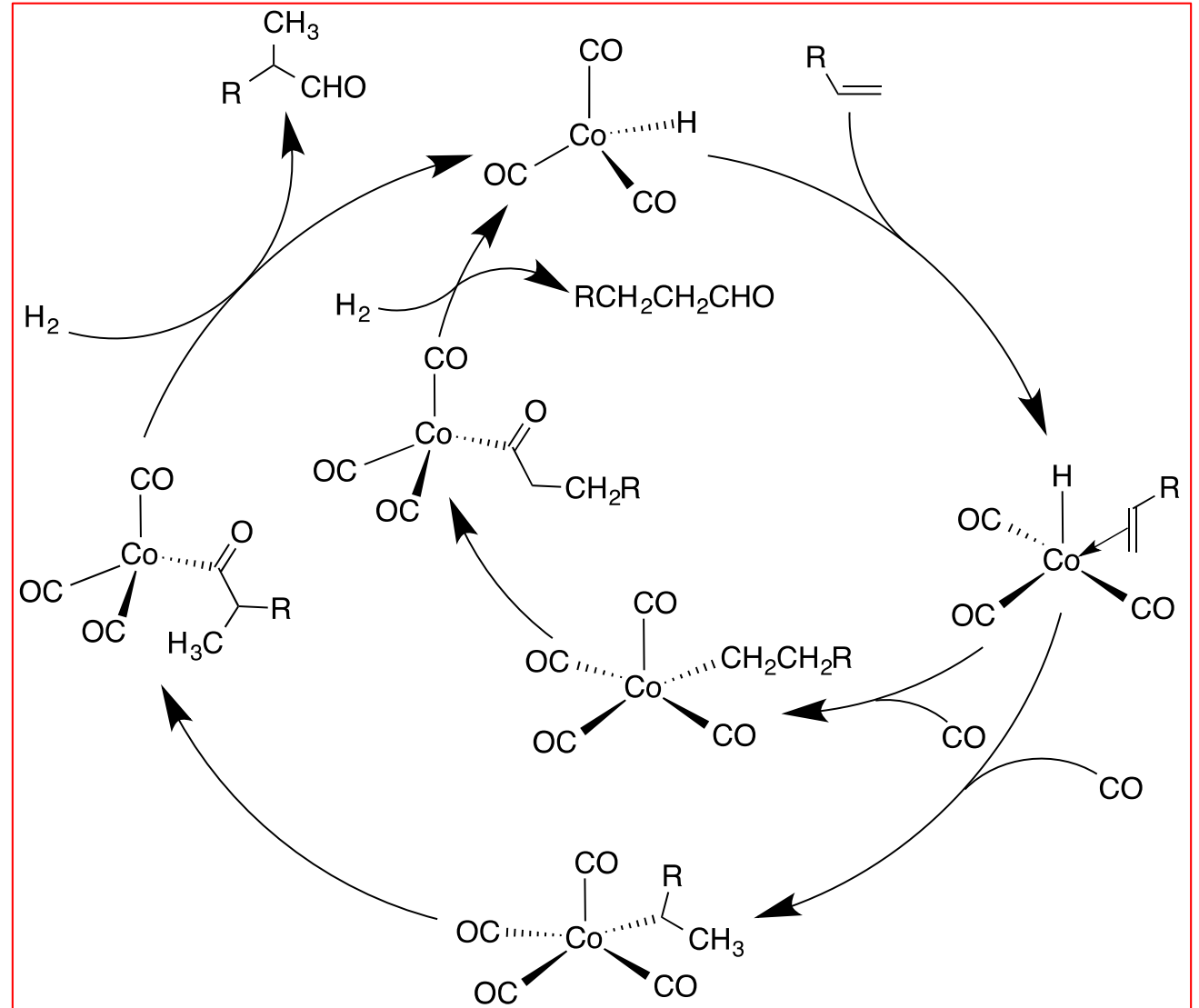
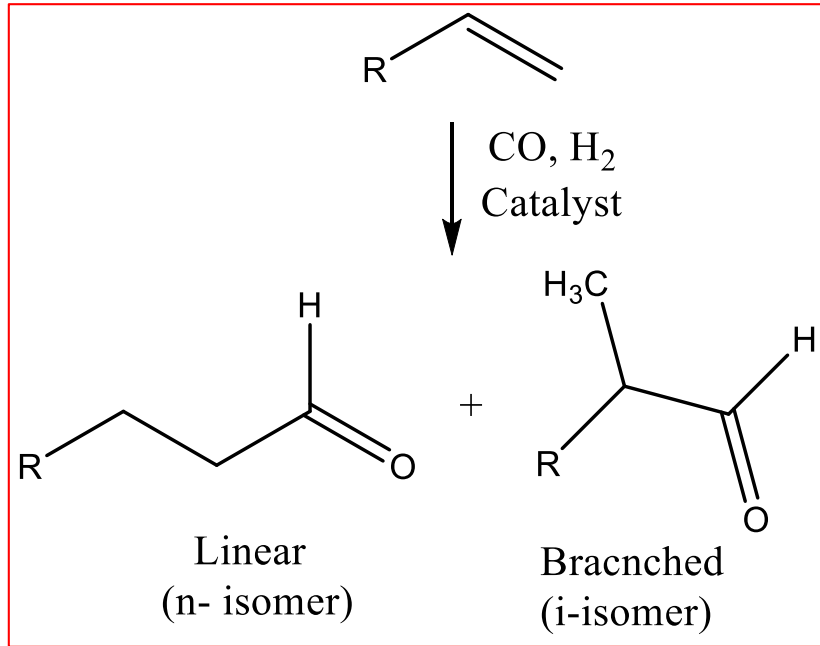
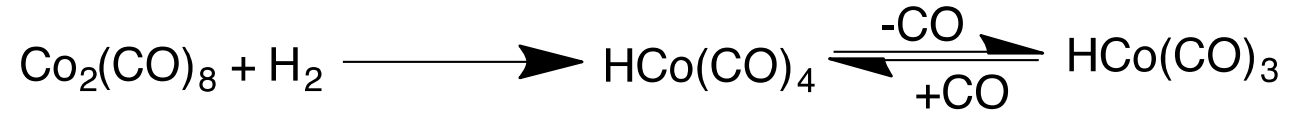
There are ~7,5 kg of Oxea chemicals on average in a car

Plasticisers and industry

A plasticiser is a substance which when added to a material – usually a hard plastic such as PVC – makes it flexible, elastic and easier to handle. Early examples of plasticisers include water to soften clay and oils to plasticise pitch used for waterproofing ancient boats. Modern plasticisers are manmade organic chemicals, the majority of which are esters such as adipates and phthalates.



Hydroformylation (Oxo-process): Mechanism



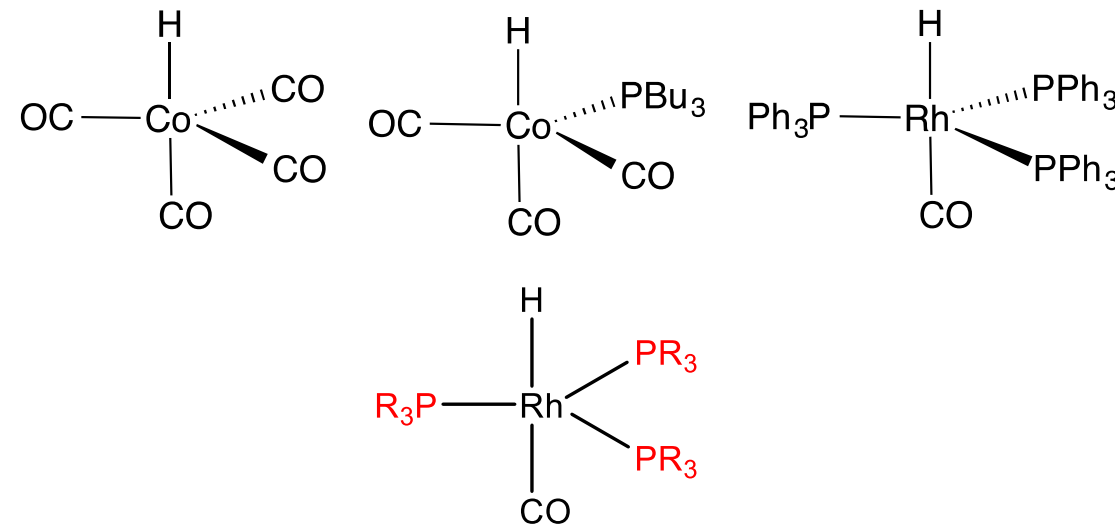
Catalyst design

Over the years, four catalytic processes have come into prominence for hydroformylation reactions

Catalysts:

Comparison of hydroformylation catalysts

Conditions	HCo(CO)_4	$\text{HCo(CO)}_3(\text{PBu}_3)$	$\text{HRh(CO)(PPh}_3)_3$
Temp/K	410–450	450	360–390
Pressure/bar	250–300	50–100	30
Regioselectivity $n : i$	$\approx 3 : 1$	$\approx 9 : 1$	$> 10 : 1$



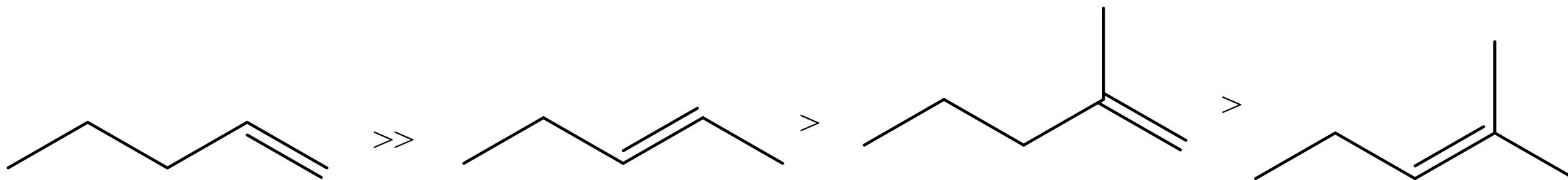
The major differences between these processes are (i) The operating temperature and pressure (ii) The ratio of the products formed (n-aldehyde vs iso-aldehyde) (iii) The rate of the reaction and the control of side reactions such as hydrogenation (III) ease of catalyst recovery

If the partial pressure is not kept high enough, metallic cobalt gets deposited due to the thermal instability of HCo(CO)_4

Unlike the $\text{HCo}(\text{CO})_4$ based hydroformylation (n:iso 3:1), the PBu_3 added catalyst $\text{HCo}(\text{CO})_3\text{PBu}_3$, provides a better n:iso ratio of products (7:1). Explain this observation on the basis steric on the catalyst.

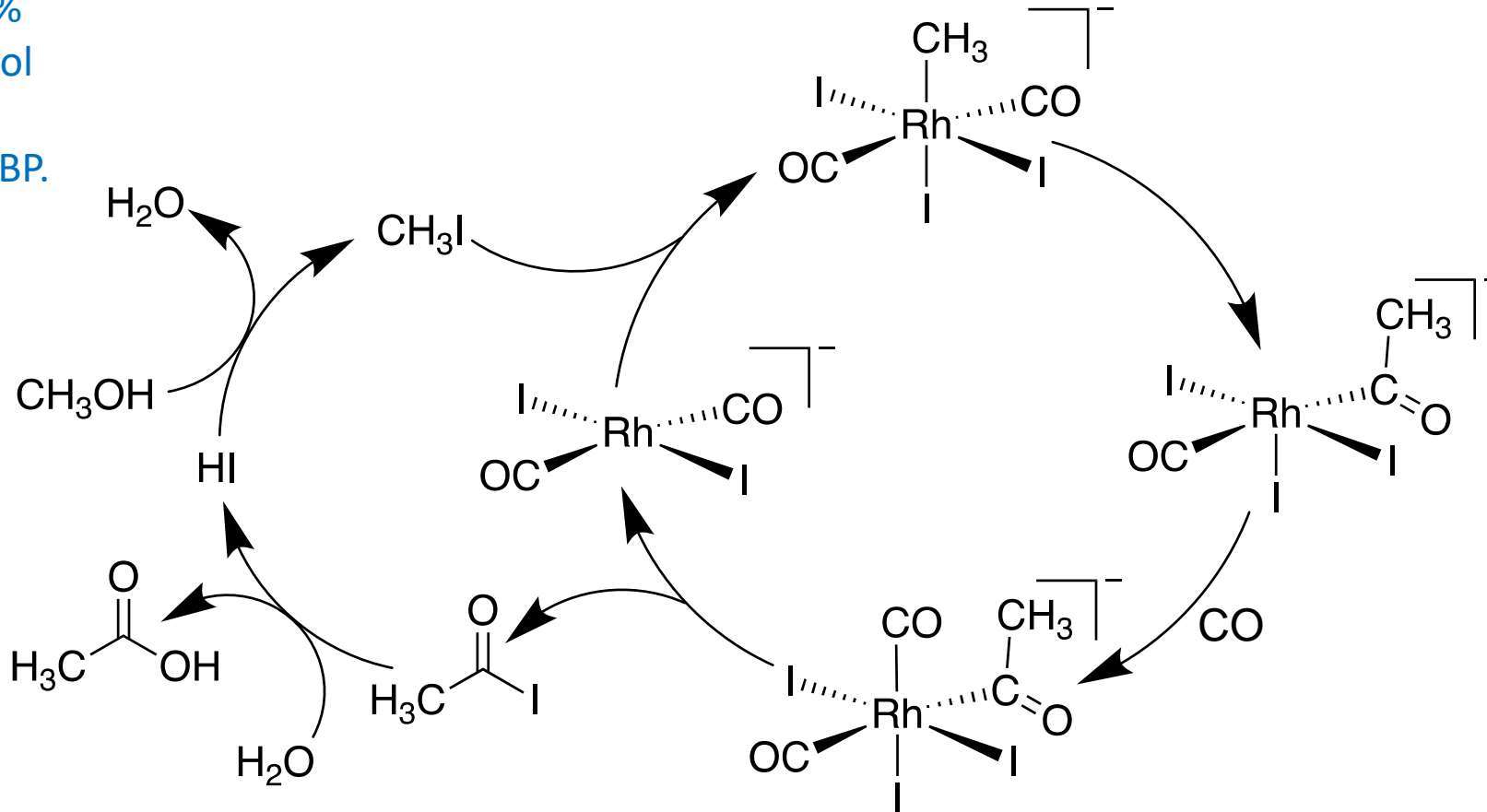
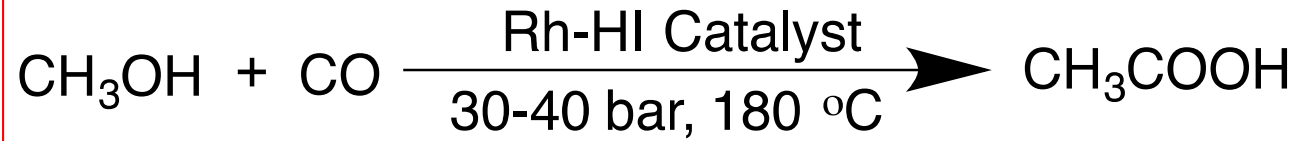
Since PBu_3 is sterically bulkier than CO , the linear alkyl complex is preferentially formed. The secondary Co-Alkyl intermediate if formed is not stable.

The general reactivity of alkenes for hydroformylation is as follows



Carbonylation of methanol: Monsanto Process

In 1966, Monsanto established that a rhodium based catalyst with iodide as a co-catalyst could give 99% conversion of methanol to acetic acid. This process was taken by BP.

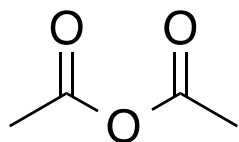


Most of Rh(III) salt and source of I^- , are suitable for the generation of active catalyst, $[\text{Rh}(\text{CO})_2\text{I}_2]^-$. OA of CH_3I to the later complex, is rate determining step in the reaction.

Importance of Acetic Acid

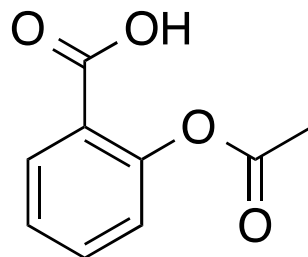
cellulose acetate films

Material for photographic emulsion.

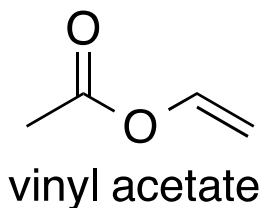


Acetic anhydride

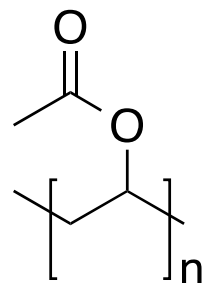
Acetylating agent
in synthetic chemistry



Aspirin



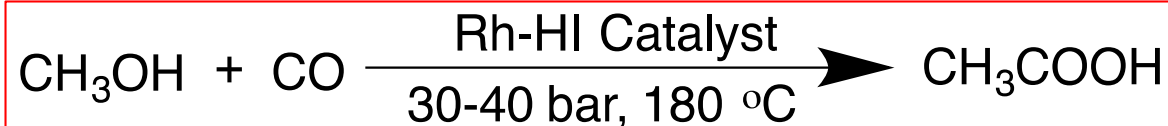
vinyl acetate



Polyvinyl acetate

Currently, 7 Mt per year of acetic acid are consumed worldwide, with the formation of vinyl acetate, is the precursor to polyvinylacetate.

Advantages



This process was first commercialized in 1970 and was a great advance on the previous processes in several respects:

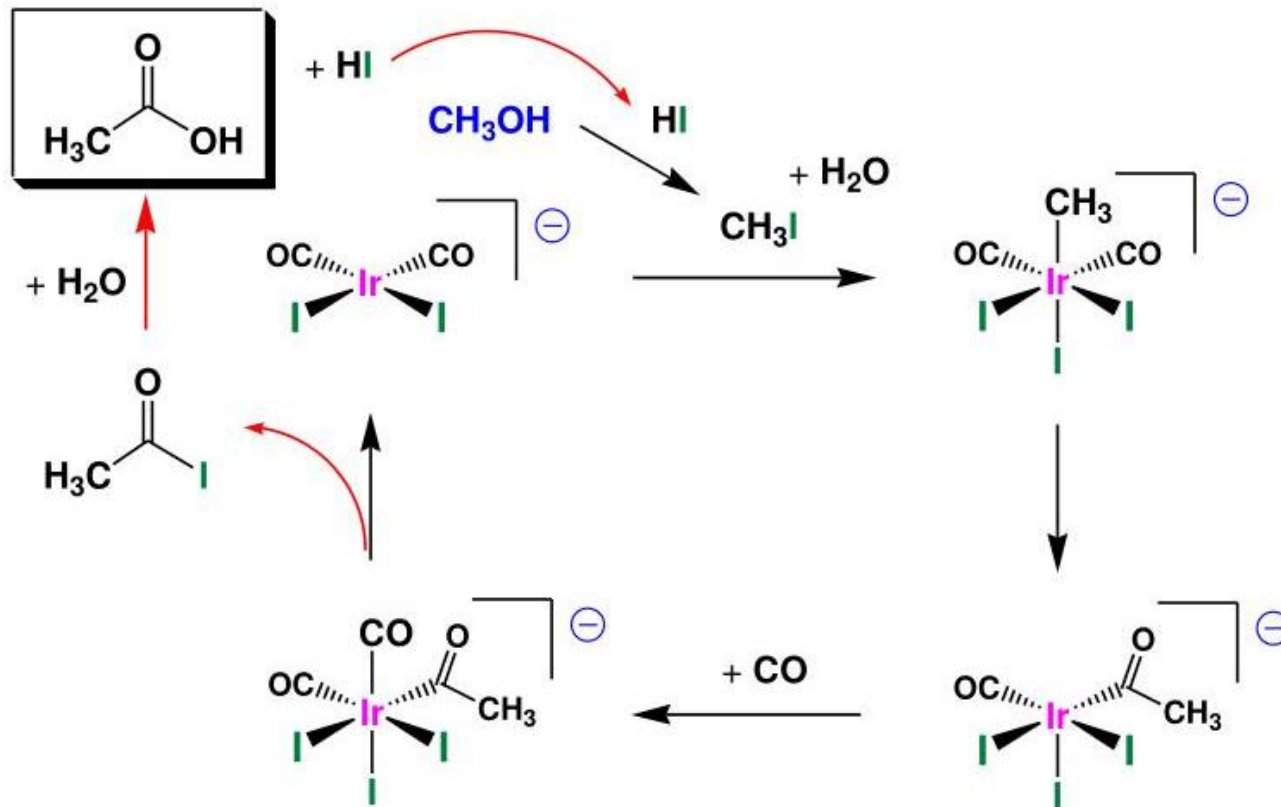
- It has an atom economy of 100%, with all atoms in the reactants going into the product (see equation above). In contrast, the older direct oxidation of butane and naphtha had a very poor atom economy with respect to ethanoic acid (about 35%). Consequently, there is a huge reduction in waste, and purification of the product is much easier
- The whole process uses less energy
- Has a high yield, approximately 98% based on methanol (90% based on carbon monoxide).
- Uses methanol, a cheaper feedstock than the previous naphtha/ butane.
- Although methanol is usually manufactured from synthesis gas, produced from oil, it can also be produced from biomass (wood), municipal wastes and sewage. This may eventually lead to the process being no longer dependent on oil.
- The reaction is extremely fast, and the catalyst has a long life

The Monsanto process has been the dominant process used in the production of ethanoic acid from 1970 to the late 1990s.

BP Ir-based Cativa Process

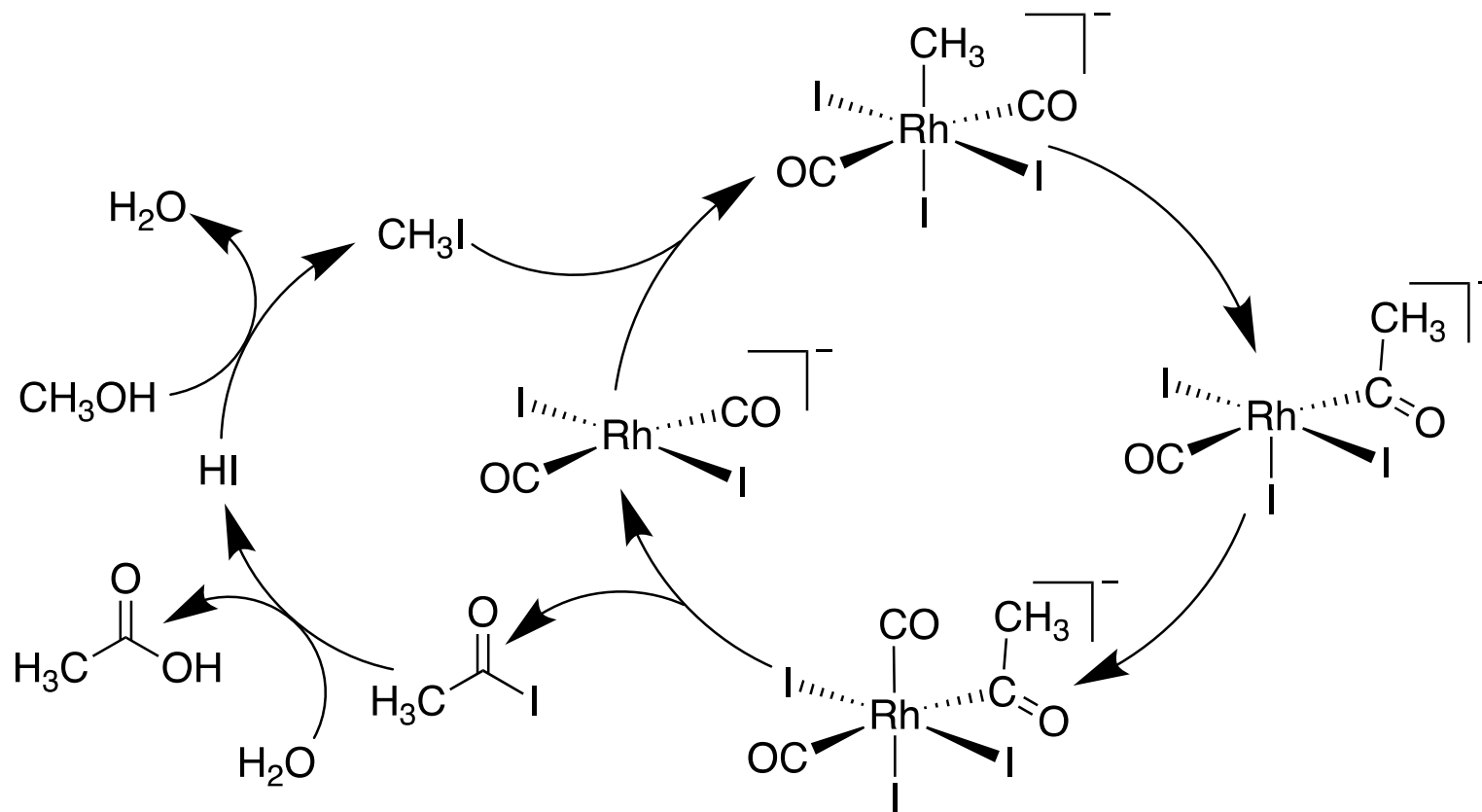
Advantage:

The Cativa Ir-based acetic acid catalyst system was announced with much fanfare in 1999. However, much of this catalytic chemistry was part of the original Monsanto Acetic Acid patent. The Ir cycle was originally studied in considerable detail by Forster (along with the Rh system) in 1979 (*JCS Dalton*, 1979, 1639). The fundamental mechanism is essentially the same as the Rh cycle:



- (1) Retrofitting of the plant
- (2) Ir (Rs 10000/g) is much cheaper compared to Rh (Rs 60,000/g)
- (3) Purification of acetic acid from water
- (4) The process is much faster and effective and require less amount of catalyst

$[\text{Rh}(\text{CO})_2\text{I}_2]^-$ and $\text{Rh}(\text{CO})_3\text{I}$ are both square planar complexes with rhodium in the +1 oxidation state. Both can act as active catalysts in the conversion of methanol to acetic acid. However, the reaction rate is much lower when $\text{Rh}(\text{CO})_3\text{I}$ is used in the Monsanto process. Give reasons for the same.



For the rhodium catalyst, oxidative addition of MeI is slow and is the rate determining step. Oxidative addition is much more facile in electron rich anionic complexes. Hence the rate of the reaction is higher when the anionic complex is used.