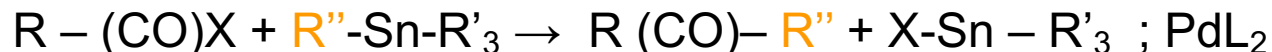
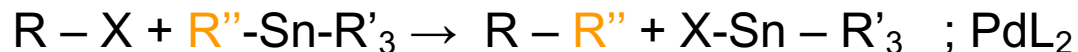


REACTIONS INVOLVING CO

Transmetallation with palladium

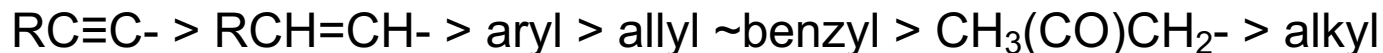
Three general coupling reactions are possible using organotin and palladium.



These coupling reactions are called generally **Stille-coupling**.

Almost any organic iodide and bromide will serve as electrophile and undergo coupling with the organotin reagent (no hydrogen in sp^3 β -carbon).

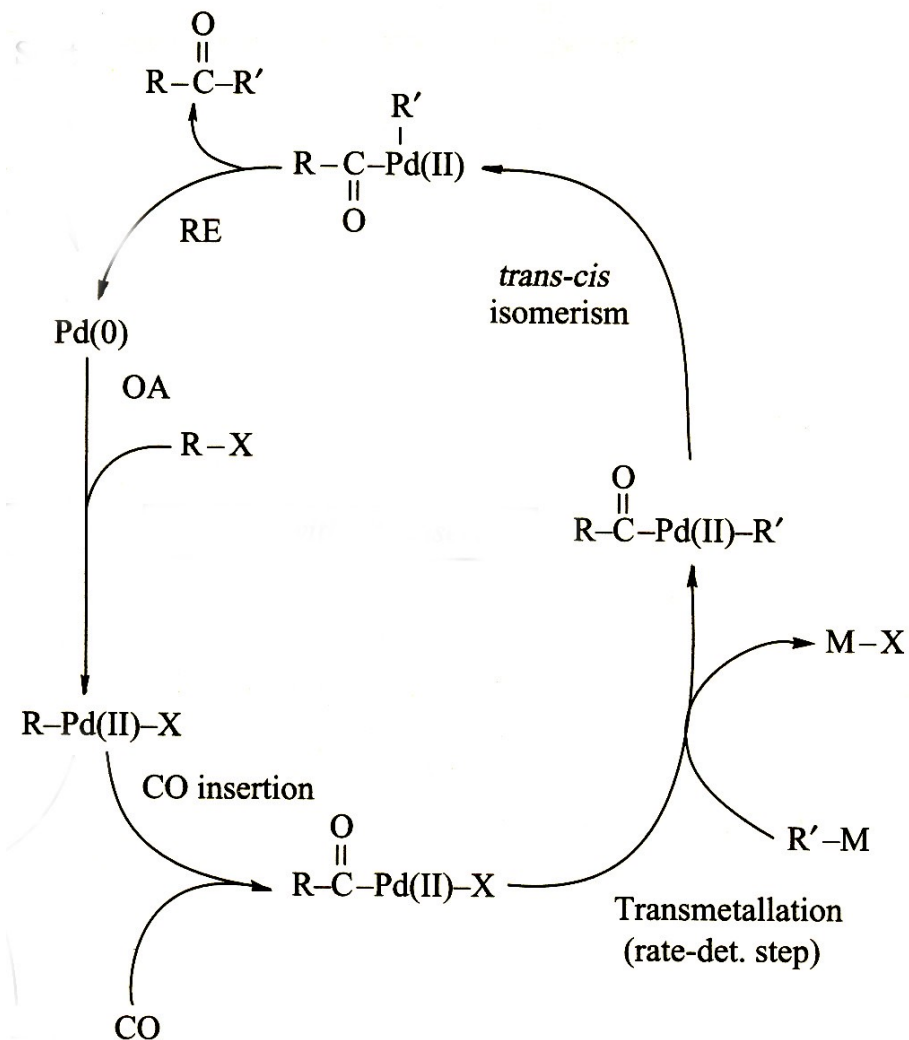
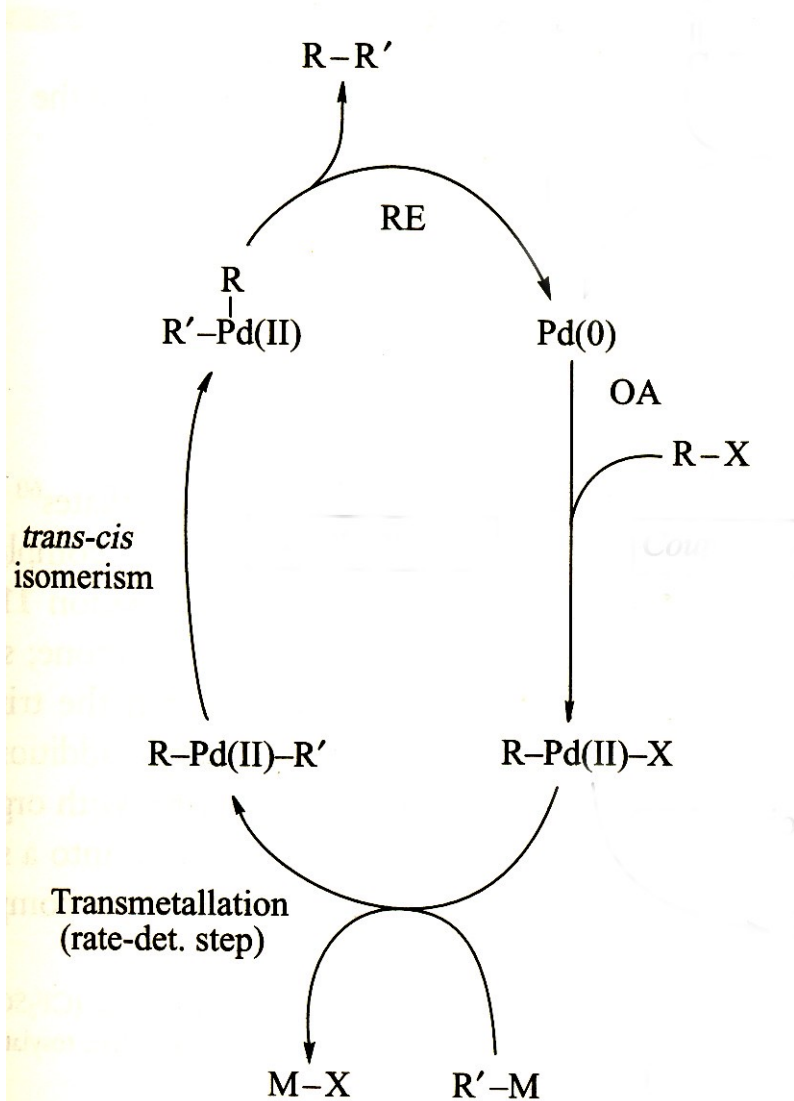
Usually organotin complexes are designed so that one of the ligands is reactive.



Methyl or n-butyl groups on Sn are typically the nontransferable groups.

REACTIONS INVOLVING CO

Transmetallation with palladium



REACTIONS INVOLVING CO

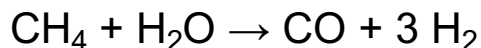
Acetic acid

For many years, the major production method of acetic acid was based on Wacker Chemie process. The ready availability of CH_3OH from syngas using heterogeneous processes sparked interest in to develop **acetic acid directly from methanol by inserting CO into C-O bond**.

Methanol

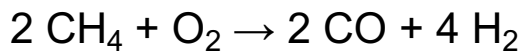
Today synthesis gas is most commonly produced from the methane (natural gas) rather than from coal. **Three processes are commercially practiced.**

(I) At moderate pressures of 40 atm and high temperatures (around 850 °C), methane reacts with steam on a nickel catalyst to produce syngas :



Steam-methane reforming (SMR), is endothermic and the heat transfer limitations place limits on the size of and pressure in the catalytic reactors used.

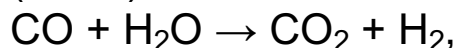
(II) Methane can also undergo partial oxidation with molecular oxygen to produce syngas:



This reaction is exothermic and the heat given off can be used *in-situ* to drive the steam-methane reforming reaction.

(III) When the two processes are combined, it is referred to as *autothermal reforming*.

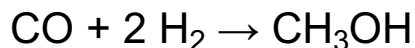
The ratio of CO and H₂ can be adjusted to some extent by the water-gas shift reaction (WGS),



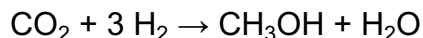
to provide the appropriate stoichiometry of H₂ and CO for methanol synthesis.

Methanol

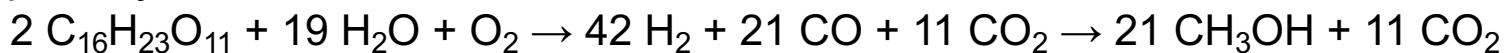
CO and H₂ then react on a second catalyst to produce methanol. Today, the most widely used catalyst is a mixture of copper, zinc oxide, and alumina first used by ICI in 1966. At 50–100 atm and 250 °C, it can catalyze the production of methanol from carbon monoxide and hydrogen with high selectivity:



It is worth noting that the production of syngas from methane produces 3 moles of hydrogen for every mole of carbon monoxide, while the methanol synthesis consumes only 2 moles of H₂ for every mole of carbon monoxide. One way of dealing with the excess hydrogen is to inject carbon dioxide into the methanol synthesis reactor, where it, too, reacts to form methanol :



Although natural gas is the most economical and widely used feedstock for methanol production, many other feedstocks can be used to produce syngas via steam reforming. Coal is increasingly being used as a feedstock for methanol production, particularly in China. In addition, mature technologies available for biomass gasification are being utilized for methanol production. For instance, woody biomass can be gasified to water gas (a hydrogen-rich syngas), by introducing a blast of steam in a blast furnace. The water-gas / syngas can then be synthesized to methanol using standard methods. *“The net process is carbon neutral since the CO₂ byproduct is required to produce biomass via photosynthesis”.*

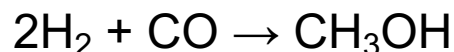


REACTIONS INVOLVING CO

Acetic acid

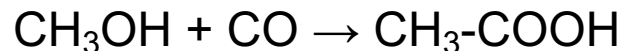
For many years, the major production method of acetic acid was based on Wacker Chemie process. The ready availability of CH_3OH from syngas using heterogeneous processes sparked interest in to develop acetic acid directly from methanol by inserting CO into C-O bond.

After all, such process would be based entirely on syngas:



$$\text{RhCl}_3 = 248 \text{ € /g}$$

$$\text{CoCl}_2 = 6 \text{ € /g}$$

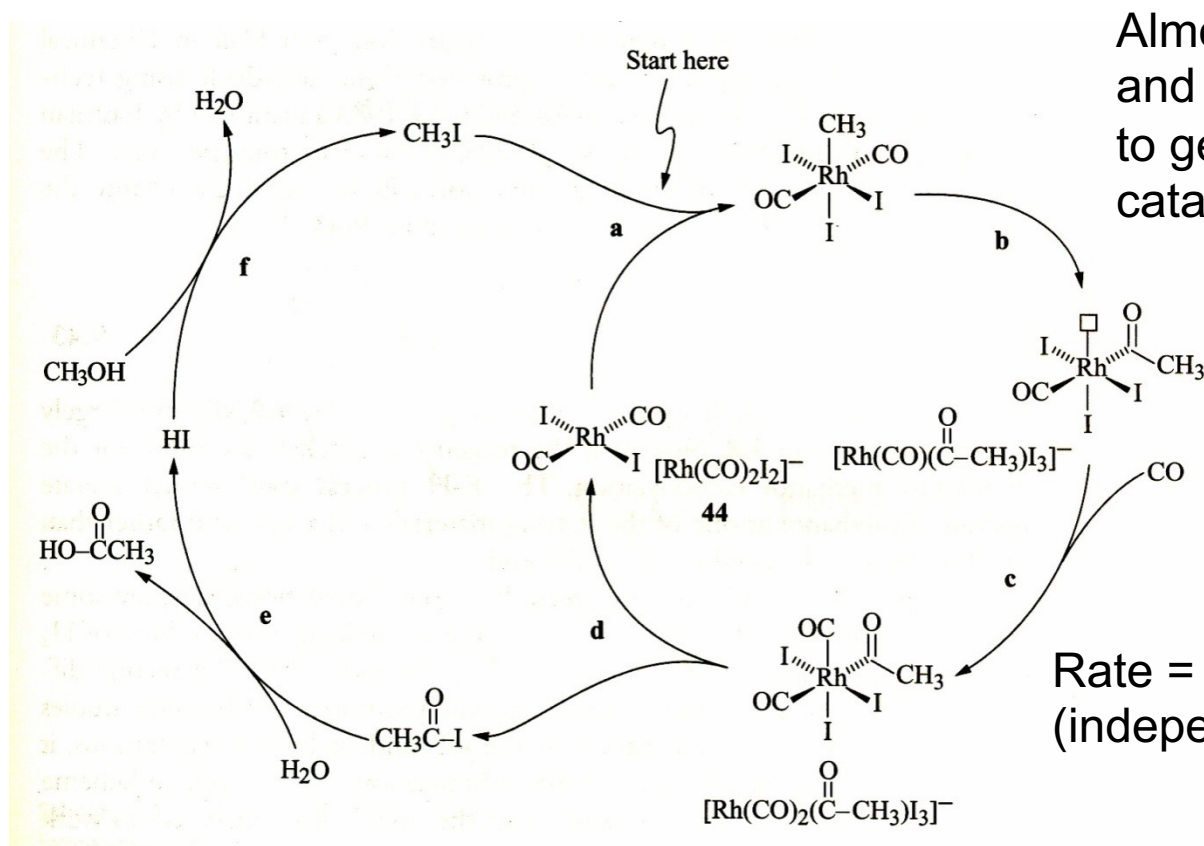


In mid 1960s BASF developed a methanol carbonylation process using a mixture of $\text{Co}_2(\text{CO})_8$ and HI as catalyst. 210 °C and 700 atm were required to produce CH_3OH rapidly enough.

Few years later Monsanto developed a process based on Rh and HI and methanol, having needed catalytic activity at 180 °C and 30-40 atm. The molar concentration of the catalyst was 100 times less than in BASF process.

REACTIONS INVOLVING CO

Monsanto Acetic acid process



Oxidative addition of CH₃I on Rh(I) is the rate limiting step.
(S_N2 displacement of I⁻ on CH₃I by negatively charged and highly nucleophilic **44**).

REACTIONS INVOLVING CO

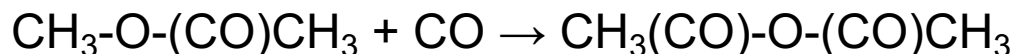
Acetic acid is produced industrially on a large scale. Although useful in some commercial processes as it is, most of the acetic acid is converted to **acetic anhydride**.

As indicated by its organic chemistry, Ac_2O is mainly used for acetylations leading to commercially significant materials. Its largest application is for the conversion of cellulose to cellulose acetate, which is a component of photographic film and other coated materials. Similarly it is used in the production of aspirin, acetylsalicylic acid, which is prepared by the acetylation of salicylic acid. It is also used as a wood preservative via autoclave impregnation to make a longer lasting timber.

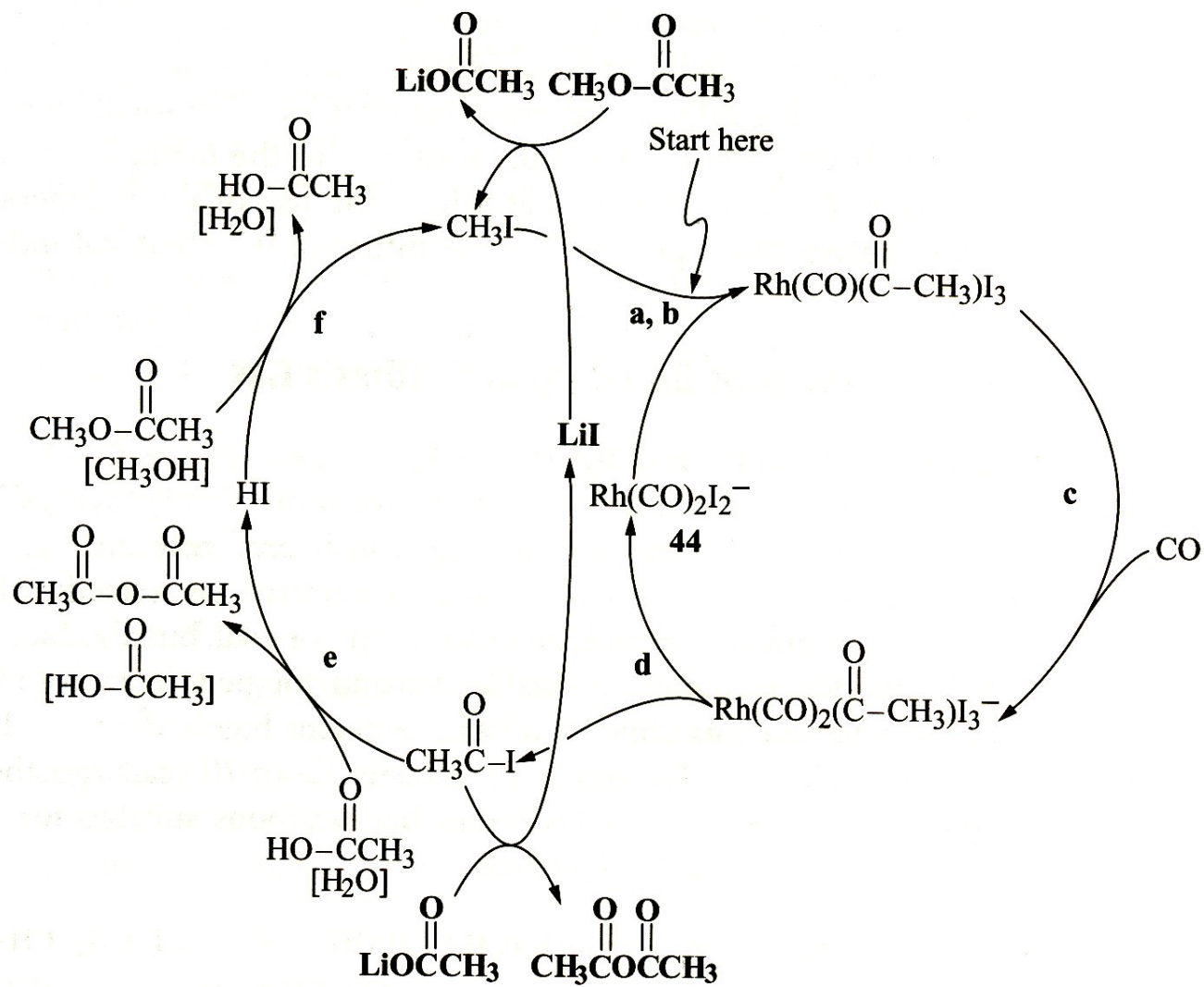
In starch industry, acetic anhydride is a common acetylation compound, used for the production of modified starches (E1414, E1420, E1422).

Therefore, a process giving directly acetic anhydride would be desirable.

Halcon Chemical company together with Eastman Chemicals designed a process similar to Monsanto process, where formally CO is inserted C-O bond of methyl acetate:



REACTIONS INVOLVING CO

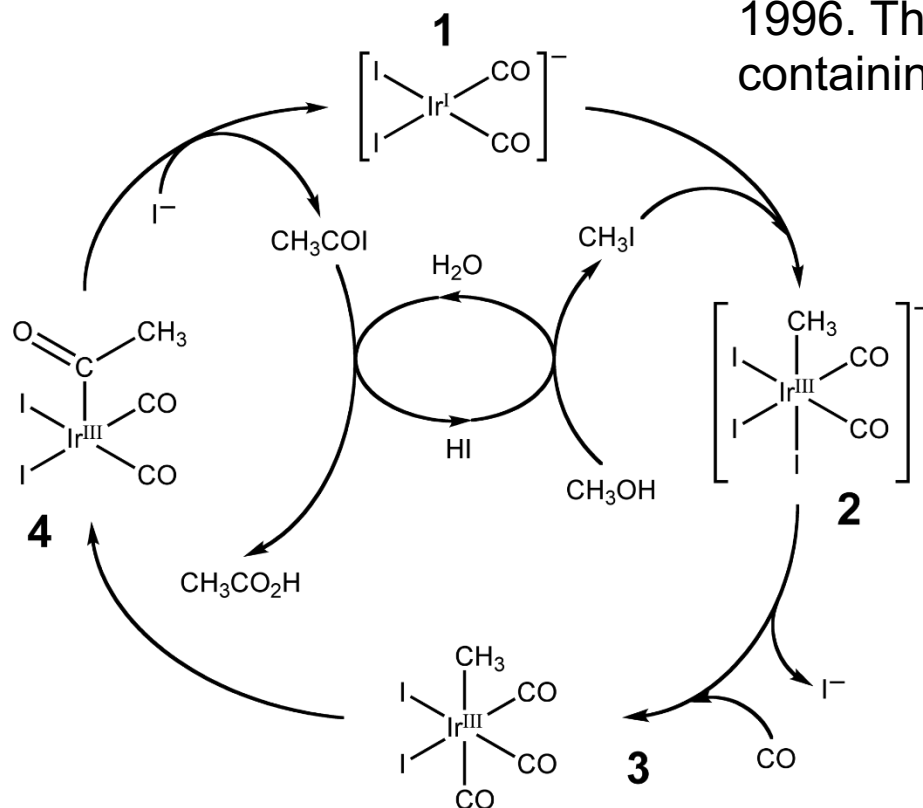


The products in brackets belongs to Monsanto cycle.

REACTIONS INVOLVING CO

Cativa process

The process is similar to the Monsanto acetic acid process and was developed by BP Chemicals in 1996. The process is based on an iridium-containing catalyst, such as the $[\text{Ir}(\text{CO})_2\text{I}_2]^-$ (**1**).



$\text{IrCl}_3 = 56 \text{ € /g}$
 $\text{RhCl}_3 = 215 \text{ € /g}$
 $\text{CoCl}_2 = 6 \text{ € /g}$

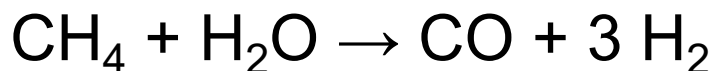
Initial studies by Monsanto shown that iridium to be less active than rhodium. Subsequent research, however, showed that the iridium catalyst could be promoted by ruthenium, and this combination leads to a catalyst that is superior to the rhodium-based systems.

The switch from rhodium to iridium also allows the use of less water in the reaction mixture. This change reduces the number of drying columns necessary, decreases formation of by-products, such as propionic acid, and suppresses the water gas shift reaction.

Methanol

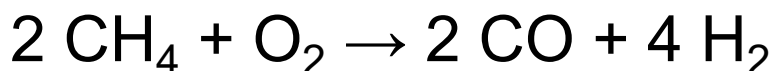
Today synthesis gas is most commonly produced from the methane (natural gas) rather than from coal. **Three processes are commercially practiced.**

(I) At moderate pressures of 40 atm and high temperatures (around 850 °C), methane reacts with steam on a nickel catalyst to produce syngas :



Steam-methane reforming (SMR), is endothermic and the heat transfer limitations place limits on the size of and pressure in the catalytic reactors used.

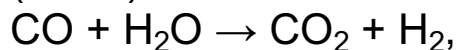
(II) Methane can also undergo partial oxidation with molecular oxygen to produce syngas:



This reaction is exothermic and the heat given off can be used *in-situ* to drive the steam-methane reforming reaction.

(III) When the two processes are combined, it is referred to as *autothermal reforming*.

The ratio of CO and H₂ can be adjusted to some extent by the water-gas shift reaction (WGS),



to provide the appropriate stoichiometry of H₂ and CO for methanol synthesis

REACTIONS INVOLVING CO

Water gas shift reaction



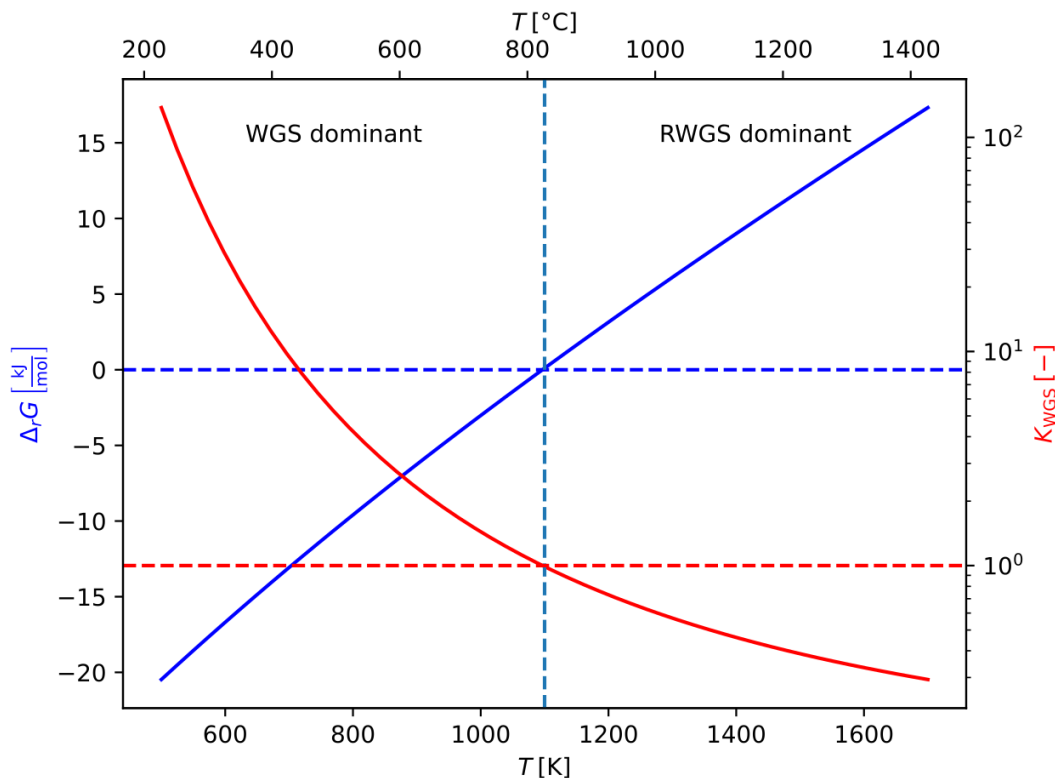
For some processes H_2 is the more valuable of the two components of syngas, e.g. in methanol production and in Haber Bosch process for production of NH_3 from N_2 and H_2 .

Thus chemistry for production of H_2 over CO has great economic value.

WGSR is rather slow in RT, but favors products. Industrially reaction is run using heterogeneous catalysts (chromium activated iron oxide or Co-Mo oxides) and requires severe conditions ($>400^\circ\text{C}$ and $>200 \text{ atm}$). High temperature required is bonded to negative entropy change ($\Delta S_{298} = -10 \text{ eu}$), making $T\Delta S$ term large and positive (position of equilibrium becomes less favorable toward products).

REACTIONS INVOLVING CO

Water gas shift reaction



Free energy	$\Delta G^\ominus = -6.82 \text{ kcal}$
Enthalpy	$\Delta H^\ominus = -9.84 \text{ kcal}$
Entropy	$\Delta S^\ominus = -10.1 \text{ cal/deg}$

The water gas shift reaction is a moderately exothermic reversible reaction. Therefore, with increasing temperature the reaction rate increases but the CO_2 production becomes less favorable. The water-gas shift reaction is sensitive to temperature, with a tendency to shift towards CO as temperature increases due to Le Chatelier's principle. Over the temperature range 600–2000 K, the equilibrium constant for the WGSR has the following relationship:

$$K_{\text{eq}} = e^{-2.4198 + 0.0003855T + \frac{2180.6}{T}}$$

REACTIONS INVOLVING CO

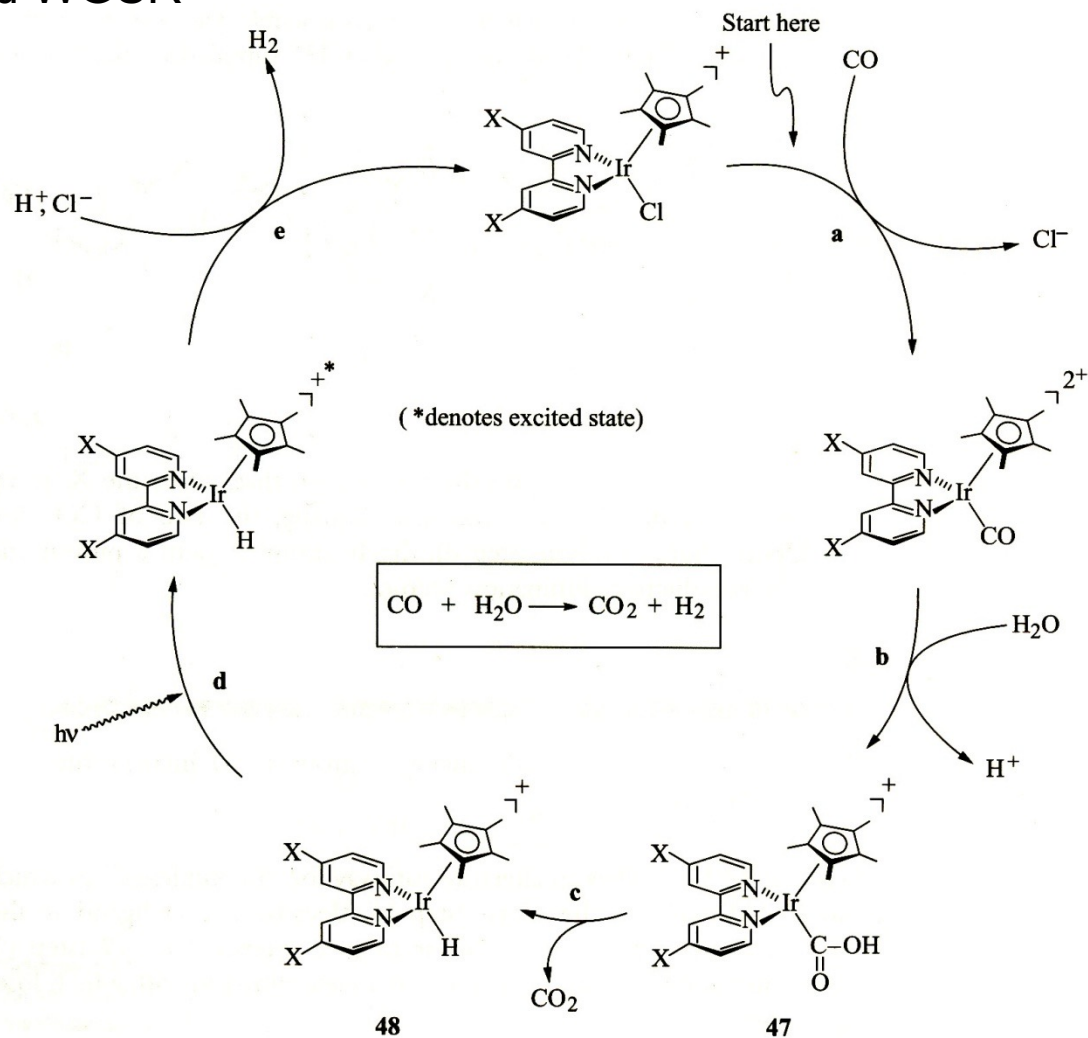
Water gas shift reaction

Several homogeneous catalysts exist (e.g. Ru(II)-carbonyl and $\text{Pt}(\text{i-Pr}_3\text{P})_3$) and they work under milder reaction conditions than heterogeneous catalysts.

None of the homogeneous catalysts is used commercially, but mechanistic studies are worth.

REACTIONS INVOLVING CO

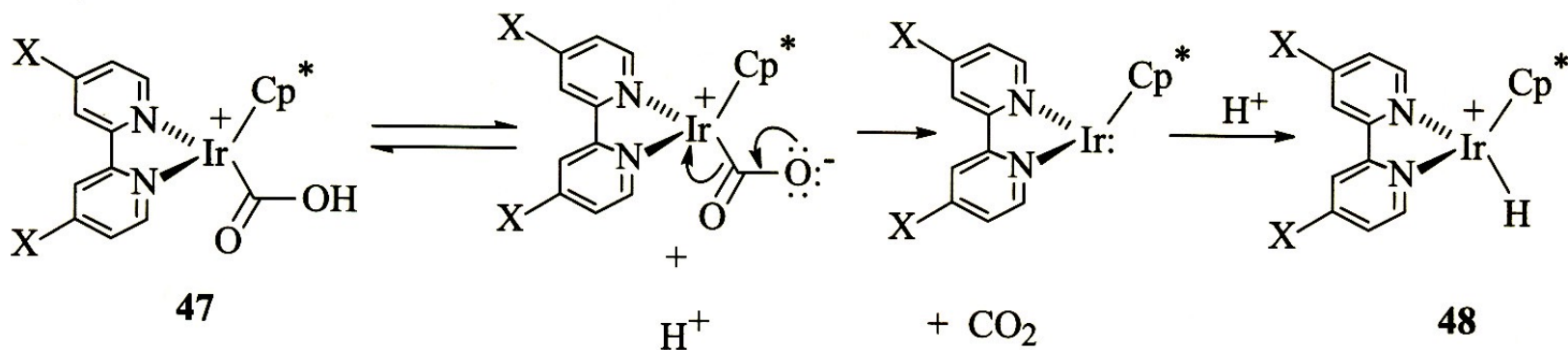
Ir-catalyzed WGSR



REACTIONS INVOLVING CO

Ir-catalyzed WGS

“It is tempting to ascribe the loss of CO₂ to a β-hydrogen elimination, but this would require a ligand dissociation in order to create an active site. This is not likely since the ligands already present are Cp* and bipyridyl (bipy).”



“It is considered that a more reasonable pathway for loss of CO₂ goes through η¹-CO₂ ligand that is replaced by H⁺ supplied by the reaction medium”.

Photocatalysis

The photocatalysis is the acceleration of a photoreaction in the presence of a photocatalyst, the excited state of which "repeatedly interacts with the reaction partners forming reaction intermediates and regenerates itself after each cycle of such interactions."

In many cases, the catalyst is a solid that upon irradiation with UV- or visible light generates electron–hole pairs that generate free radicals.

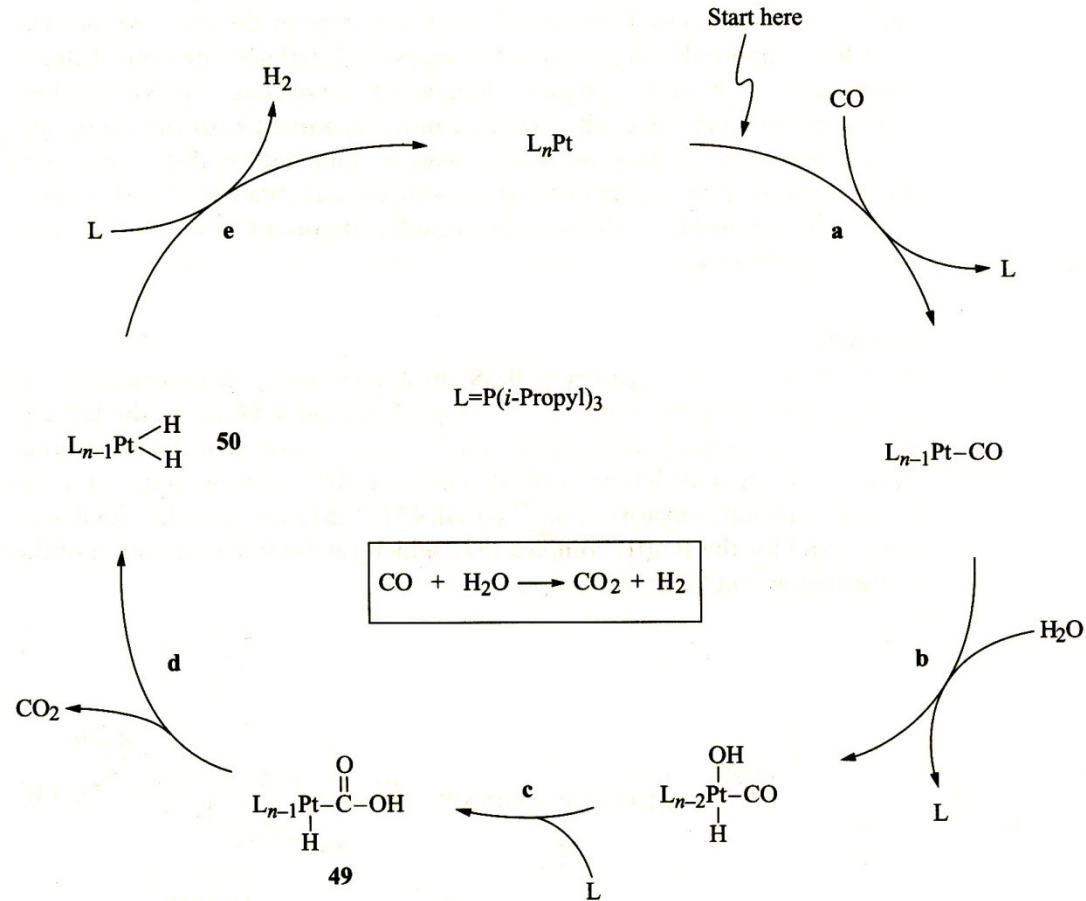
Photocatalysts belong to three main groups; heterogeneous, homogeneous, and plasmonic antenna-reactor catalysts.

REACTIONS INVOLVING CO

Pt-catalyzed WGSR,

An alternative mechanism

RE



OA

REACTIONS INVOLVING CO Hydroformylation

Among all of the homogeneous processes catalyzed by transition metals, hydroformylation stands out in two respects:

It is the oldest process still in use today and it is responsible for producing the largest amount of material resulting from a homogeneous transition metal-catalyzed reaction.

Discovered in 1938 by Otto Roelen (Ruhrchemie, Germany)

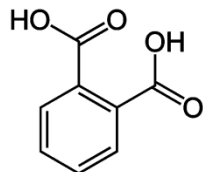
Co-catalyzed hydroformylation, was used in WW II to produce aldehydes from alkenes, H_2 and CO.

In 1945 US and British obtained details of the process and since then hydroformylation plants have been built worldwide to produce millions of tons of alcohols .

REACTIONS INVOLVING CO Hydroformylation

Propene is most common feedstock for hydroformylation and is transformed into butanal and 2-methylpropanal (the former is much more valuable product).

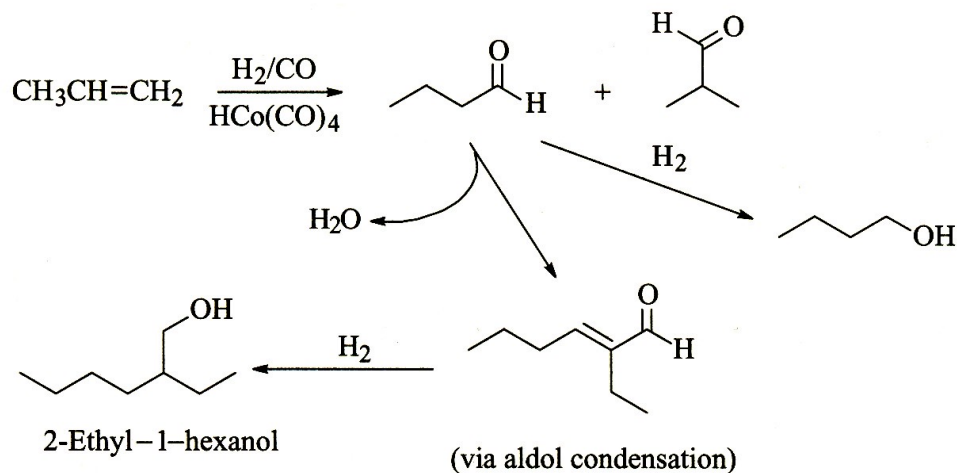
Aldol condensation followed by hydrogenation gives 2-ethyl-1-hexanol, needed for synthesis of a diester of phthalic acid, a plasticizer for PVC.



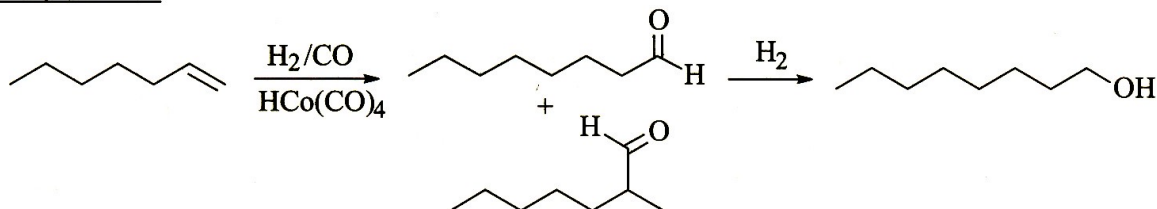
Useful plasticizers.

These alcohols serve as a basis for surfactant compounds with domestic and industrial uses.

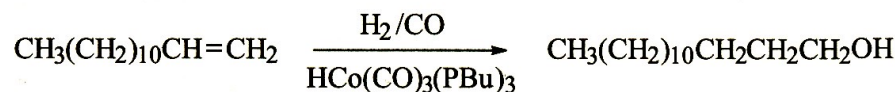
Propene:



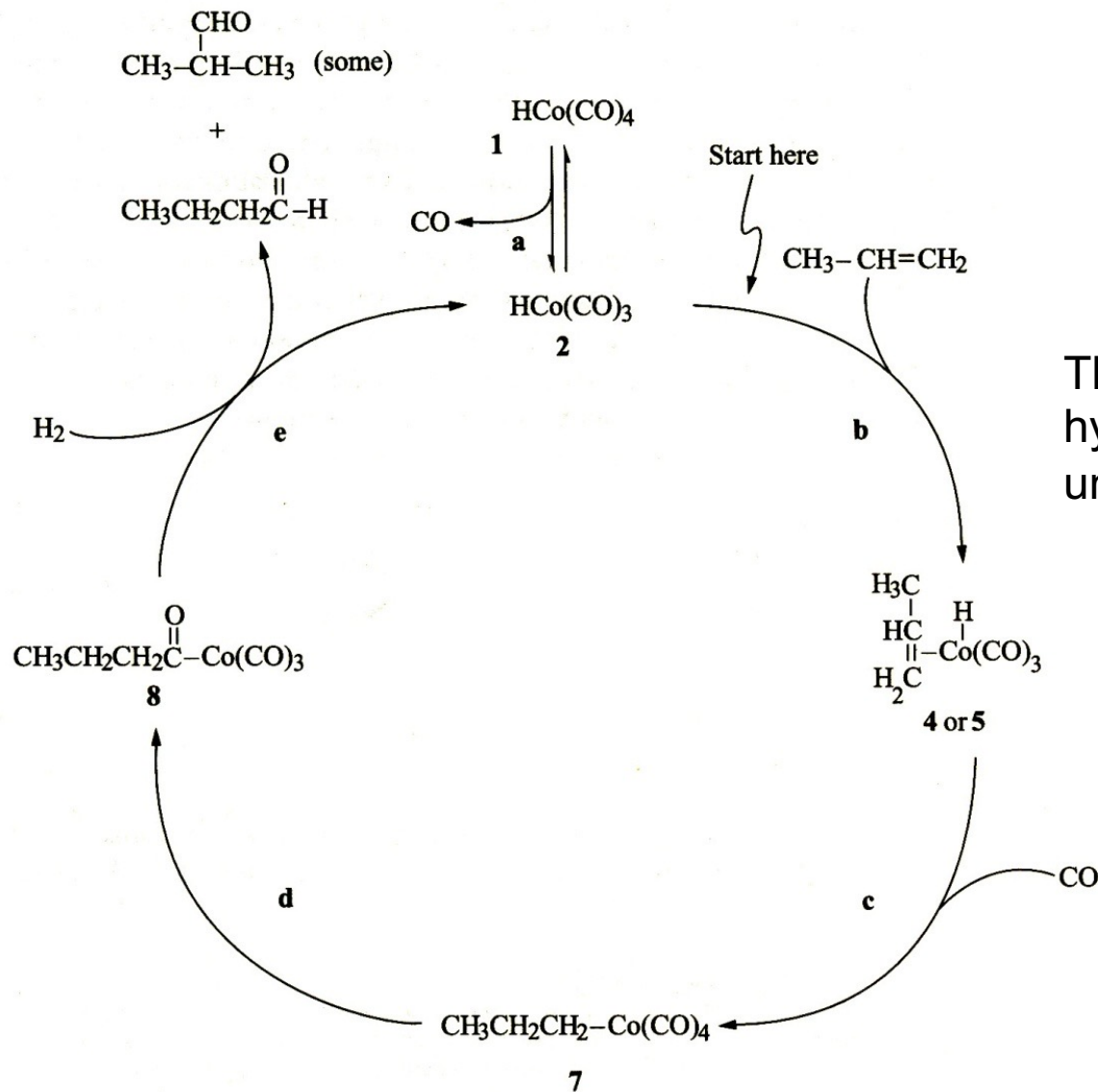
C₇–C₉ Alkenes:



C₁₁–C₁₅ Alkenes:



REACTIONS INVOLVING CO Hydroformylation

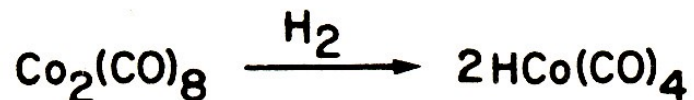


The mechanism for hydroformylation is rather well understood.

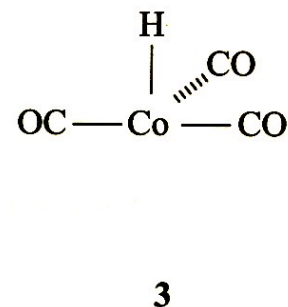
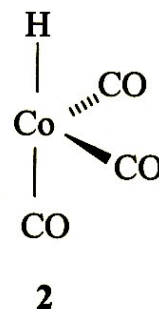
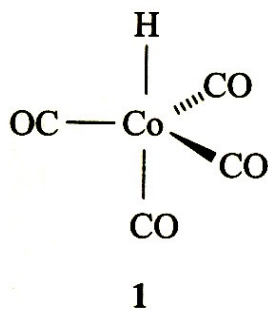
Process conditions:
120-170 °C
200-300 bars

REACTIONS INVOLVING CO Hydroformylation

Adding H_2 on $\text{Co}_2(\text{CO})_8$ generates *in situ* exceptional acidic metal hydride:



By losing one of the CO ligands the catalytic active species, 16 electron complex is formed



Step b

Sometimes **1** is prepared in a separated step and introduced to the alkene in the presence of syngas. This allows hydroformylation to be run at a lower temp. (90-120 °C instead of 120-170 °C).

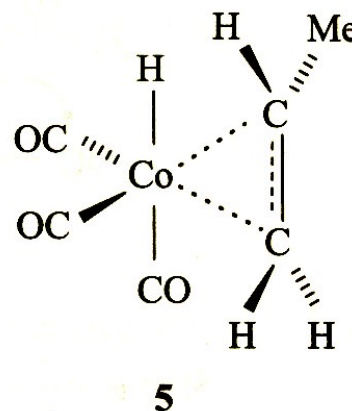
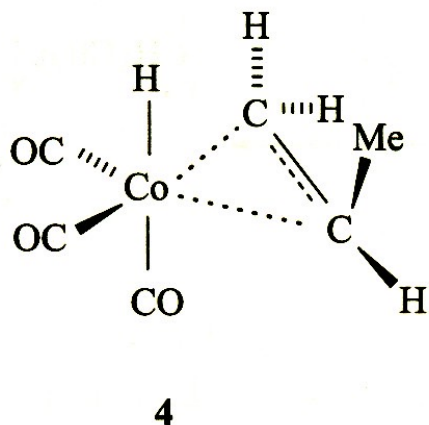
According to calculations, geometry **2** is more preferred than **3**.

Dissociation of CO occurs with relatively high energy and is inhibited by high CO concentrations. The reaction is run, anyhow under 200-300 atm. to stabilize later intermediates in the catalytic cycle. (Balance between activation and reaction rate).

REACTIONS INVOLVING CO

Hydroformylation

Binding of alkene (propene) form 18 electrons hydride-alkene complexes, that can have two structures **4** and **5**.

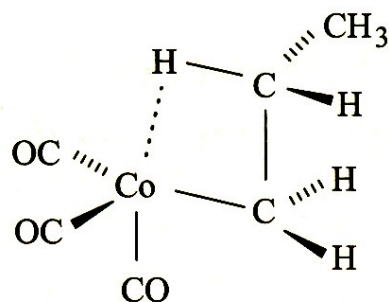


Step c

Although **4** is a little more stable than **5**, only **5** has the requisite geometry (Co, H and C=C in the same plane for further insertion). Overall, the change from **1** to **5** is ligand exchange reaction via dissociation of CO.

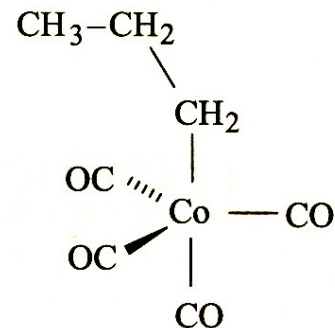
REACTIONS INVOLVING CO Hydroformylation

Insertion gives a 16 electron complex **6**. High concentration of CO gives **7** and possibility to reverse β -elimination is reduced.



6

Step d

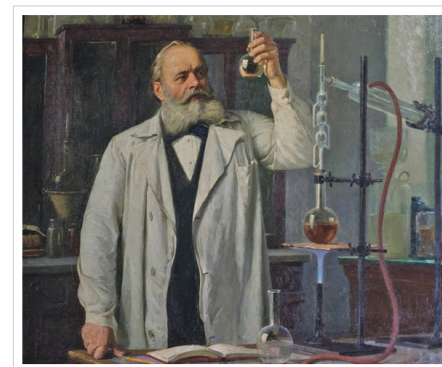


7

Structures **6** and **7** show the result of “anti-Markovnikov” insertion from which linear aldehyde will result.

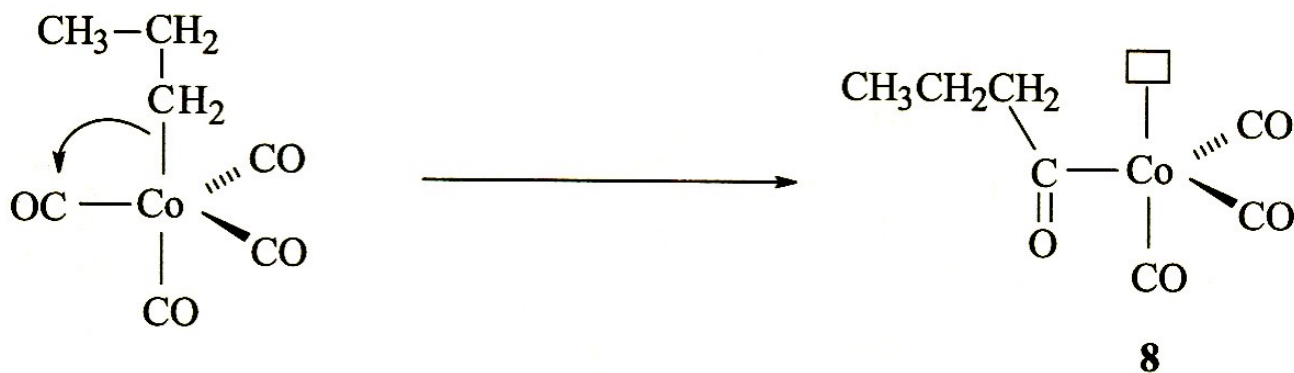
Markovnikov “Experience shows that the haloid adds to the least hydrogenated carbon, that is, to the one most susceptible to the influence of other carbon units”

Angew chem Int. Ed., **2019**, 4778-4789



REACTIONS INVOLVING CO Hydroformylation

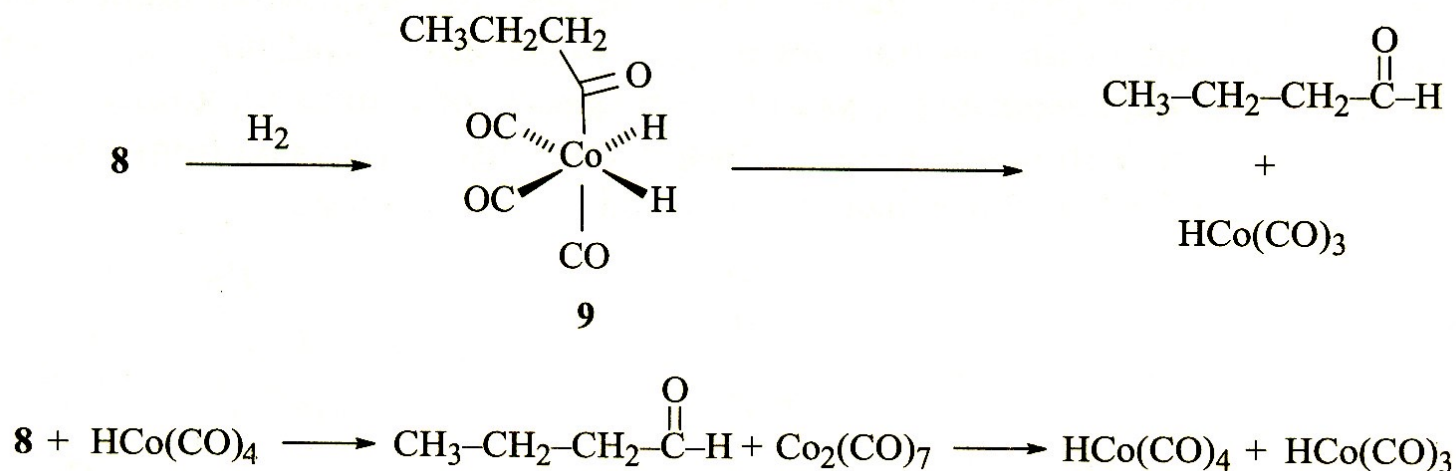
1,2 migratory insertion of the alkyl group to CO in a *cis*-position give the metal acyl. The reaction has low activation energy and is endothermic. Under high CO pressure **8** reversibly add CO to form $(\text{RCO})\text{Co}(\text{CO})_4$, which is the only detectable intermediate (by IR).



Step e

REACTIONS INVOLVING CO Hydroformylation

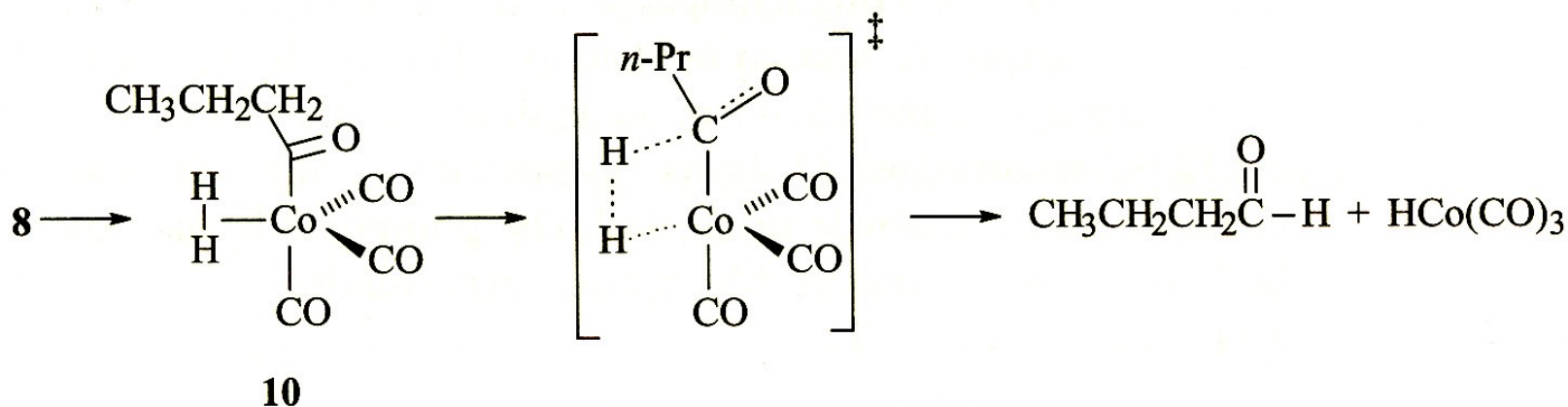
8 with vacant coordination site and 16 electrons can activate hydrogen through oxidative addition. The aldehyde is released via reductive elimination. One of them seems to be the rate limiting step in the cycle. Also a bimolecular process between **8** and **1** has been suggested.



Low concentration of catalytic species under catalytic reaction conditions argues against the bimolecular model (but it works under stoichiometric conditions). On the other hand hydrogen activation occurs with a rather high activation energy.

REACTIONS INVOLVING CO Hydroformylation

Low energy process seems to go via η^2 dihydrogen complex **10** followed by a four-center rearrangement to HCo(CO)_3 and aldehyde.



This original process is still in use, although there are following problems:

The ratio between linear and branched aldehydes is 4:1.

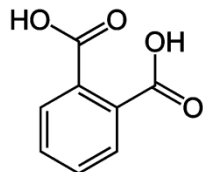
Active catalyst is unstable and its separation and recovery are difficult.

High CO pressure requirement means that plants are expensive to build and operate.

REACTIONS INVOLVING CO Hydroformylation

Propene is most common feedstock for hydroformylation and is transformed into butanal and 2-methylpropanal (the former is much more valuable product).

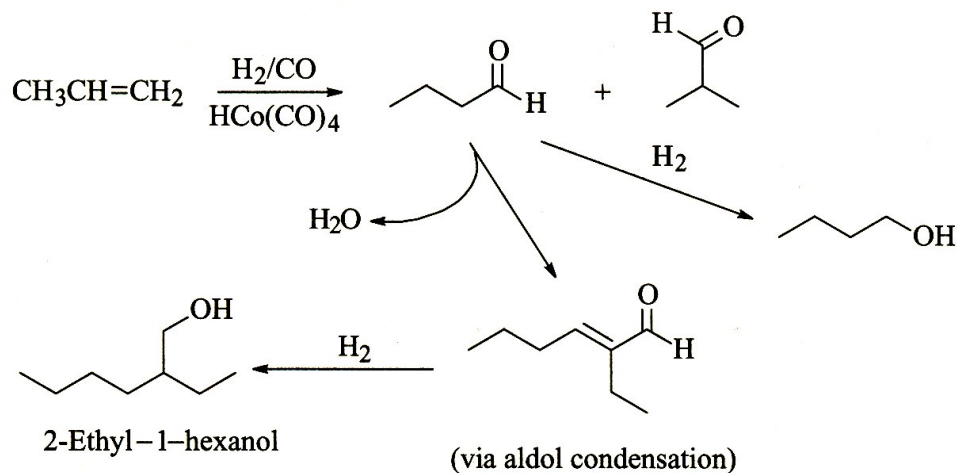
Aldol condensation followed by hydrogenation gives 2-ethyl-1-hexanol, needed for synthesis of a diester of phthalic acid, a plasticizer for PVC.



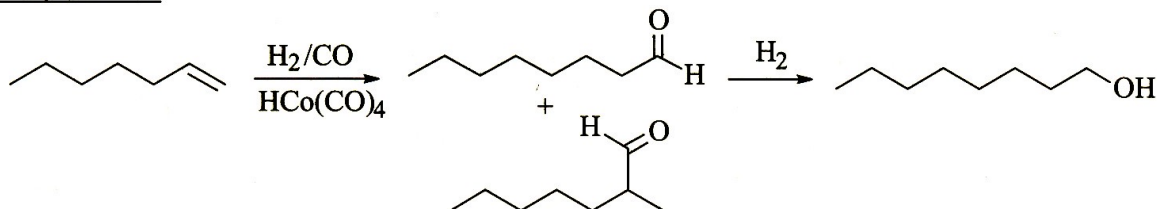
Useful plasticizers.

These alcohols serve as a basis for surfactant compounds with domestic and industrial uses.

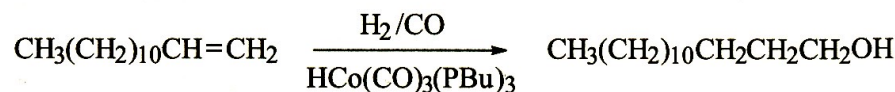
Propene:



C₇-C₉ Alkenes:



C₁₁-C₁₅ Alkenes:



REACTIONS INVOLVING CO Hydroformylation

Phosphine modified catalyst

In 1968 Shell Oil Company reported that adding phosphine ligands, such as PBU_3 , resulted benefits for hydroformylation reactions compared to the original process.

- * The reaction takes place now in 100 bars (vs. the 200-300 bars)
- * Although the phosphine modified catalyst is not so active as $\text{HCo}(\text{CO})_3$, it is more active towards hydrogenation and no separate catalysts are needed.
- * The ratio between linear and branched aldehydes is 9:1 (vs. 4:1)
- * The modified catalyst $\text{HCo}(\text{CO})_3\text{PBU}_3$ turned out to be more stable

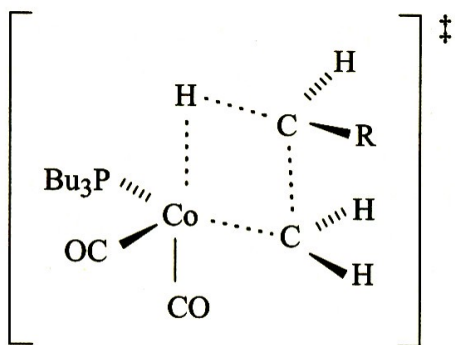
Drawbacks:

- * Process needs higher temperature (160 – 200 °C)
- * Because facile hydrogenation, around 15 % of olefins are converted to alkanes.

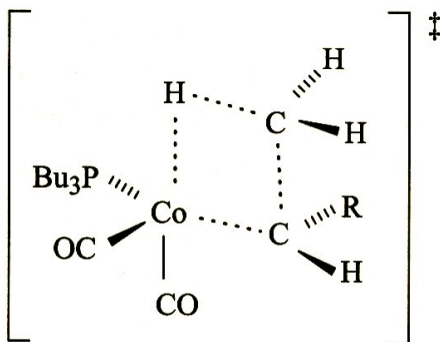
REACTIONS INVOLVING CO Hydroformylation

Phosphine modified catalyst

Selectivity of phosphine modified catalysts towards **anti-Markovnikov** products is due mainly to steric factors. The large steric bulk of the $\text{P}(\text{Bu})_3$ (compared to CO) must influence the course of the insertion of alkene to Co-H bond.



11



12

Insertion via **11** would lead to linear product. The phosphine points away from the R group on the alkene.

12 gives sterically more hindrance intermediate

REACTIONS INVOLVING CO Hydroformylation

Phosphine modified catalyst

Also electronic factors may play a role in the rate and orientation of phosphine modified hydroformylation.

As σ donors, phosphines undoubtedly donate more electron density to the Co-center. This is taken up by other CO ligands, thus making the Co-CO interaction stronger and improving the stability of the catalyst.

The key intermediates in phosphine modified hydroformylation, instead of acyl- and alkyl-cobalt complexes typical in the unmodified process, are phosphine substituted carbonyl species. Presumably the rate determining step is then alkene insertion.

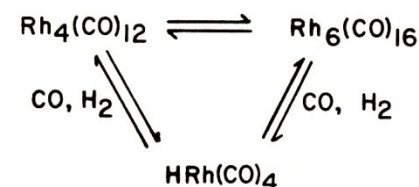
REACTIONS INVOLVING CO Hydroformylation

Phosphine modified Rh catalyst

As development of suitable Co catalyst occurred, work was also carried out to create corresponding Rh complexes that could serve as suitable catalysis.
(Compare the idea with acetic acid synthesis)

Under appropriate reaction conditions (in the presence of H_2 , CO) $\text{HRh}(\text{CO})_4$ forms from Rh-carbonyl cluster compounds. The ratio between linear and branched products tend to be low.

The $\text{HRh}(\text{CO})_4$ has also hydrogenation activity (see below).



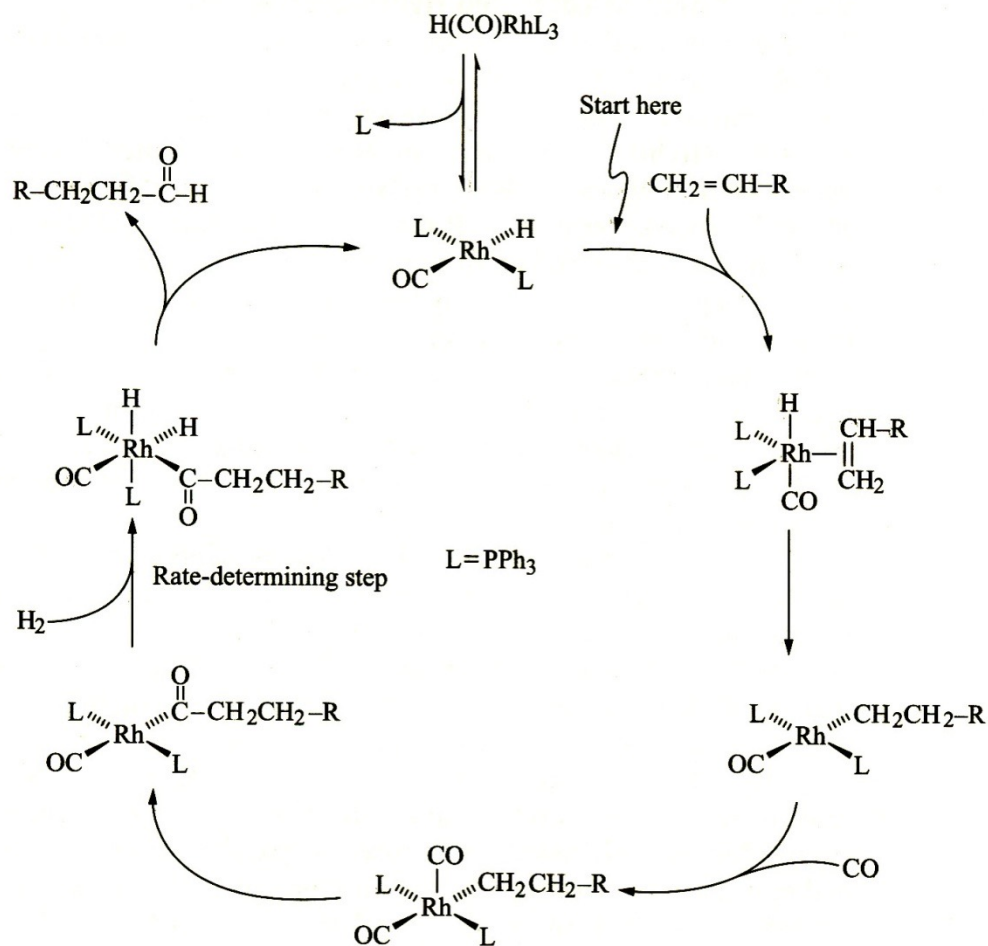
Adding of phosphine, as with Co, significantly improved the catalyst's properties.

- The reaction occurs even at atmospheric pressure and at relatively low temperatures (in process 15 to 25 bars and 80 - 120°C).
- With appropriate phosphines high linear : branched ratios (14:1 for 1-olefin)
- No significant hydrogenation of starting material (and neither aldehydes)
- 100-1000 times more active than Co-based catalyst

REACTIONS INVOLVING CO

Hydroformylation

Phosphine modified *Rh* catalyst



Active species is H(CO)RhL_3 or $\text{H(CO)}_2\text{RhL}_2$ depending on CO/PR_3 concentrations.

The rate limiting step is likely hydrogen activation in the acylmetal intermediate (as in Co, too). The mechanism for the OA/Re step is not completely understood.

It is important to note that this catalyst is good hydrogenation catalyst (see also Wilkinson's catalyst). When CO pressure exceeds 10 bars, capability of the complex to hydrogenate alkenes is suppressed.

REACTIONS INVOLVING CO Hydroformylation

Phosphine modified Rh catalyst

If linear aldehydes are the desired products, the Rh catalyst is optimal choice

If alcohols are the goal, then Co catalyst is preferred, because hydroformylation and hydrogenation can be done in the same reaction vessel.

In contrast to Co catalyst, optimal phosphine for Rh is PPh_3 .

PBu_3 is **too good** at donating electron density to the Rh catalyst and intermediate catalyst species are too stable for efficient catalysis.

PPh_3 seems to have the right combination of steric (during the insertion step) and electronic properties (right order to stabilize coordination of CO ligands)

Effectiveness of other metals in hydroformylation reaction:

Rh > Co > Ru > Mn > Fe > Cr, Mo, W, Ni						
Rel. Reactivity:	10^2 - 10^3	1	10^{-2}	10^{-4}	10^{-6}	0

PHOSPHINES

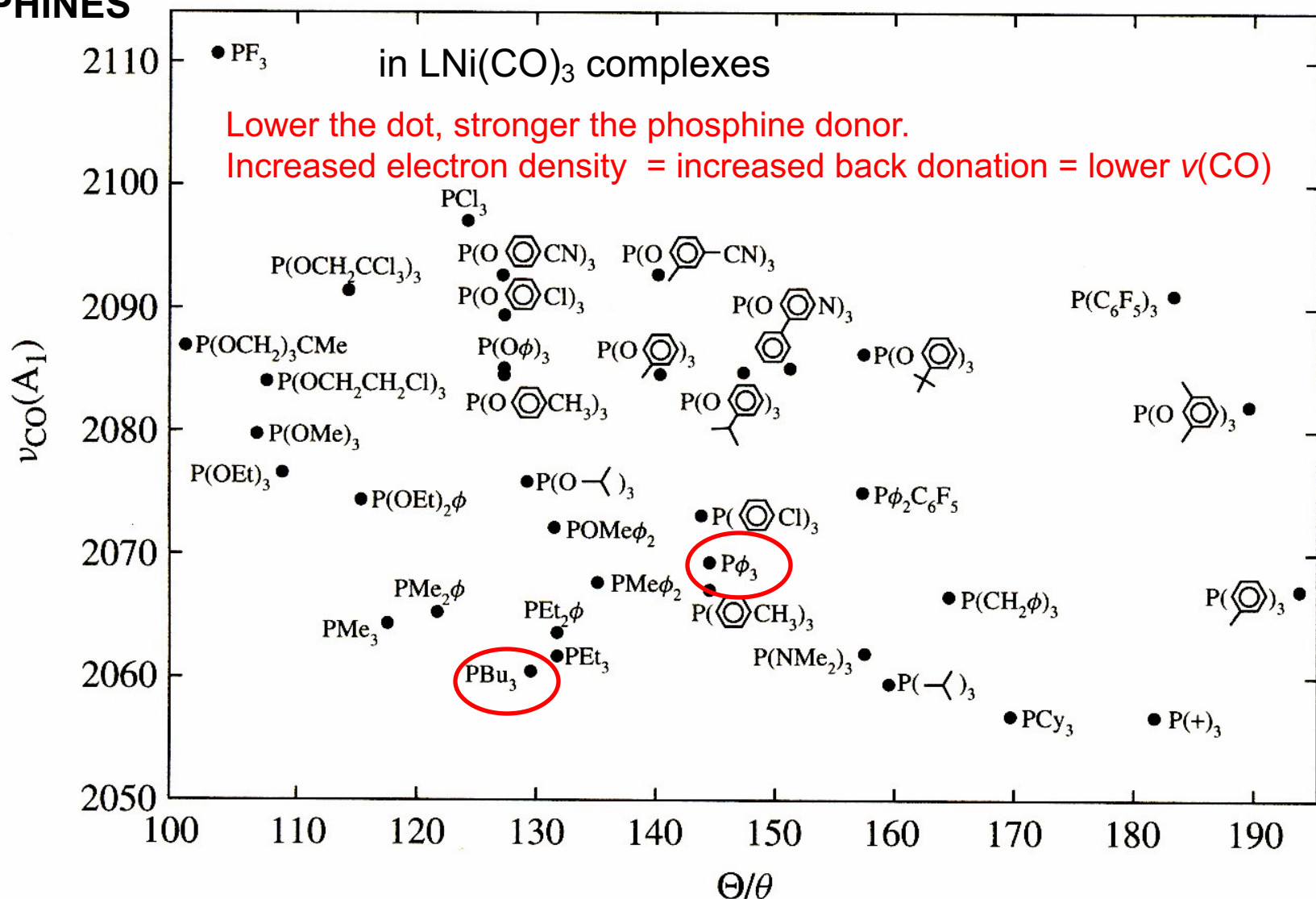


FIGURE 4.4 Electronic and steric effects of common P-donor ligands plotted on a map according to Tolman (ν in cm^{-1} , θ in degrees). Reproduced from Ref. 26 with permission of the American Chemical Society.)

Hydroformylation of cyclopentenenes, novel strategy for total synthesis of carba-D-fructofuranose

Mohindra Seepersaud,^a Mika Kettunen,^b Adnan S. Abu-Surrah,^c Timo Repo,^b Wolfgang Voelter^d and Yousef Al-Abed^a *

^aLaboratory of Medicinal Chemistry, The Picower Institute for Medical Research, 350 Community Drive, Manhasset, NY 11030, USA

^bDepartment of Chemistry, University of Helsinki, FIN-0014 Helsinki, Finland

^cDepartment of Chemistry, Hashemite University, PO Box 150459, Zarqa 13115, Jordan

^dPhysiologisch-chemisches Institut der Universitat, Hoppe-Seyler-Strasse 4, D-72076 Tübingen, Germany

Received 10 December 2001; revised 17 January 2002; accepted 18 January 2002

Carba-D-fructofuranose (**2a**) is a carbasugar that, if phosphorylated (**2b**), mimics fructose 2,6-bisphosphate in polarity and shape, and thus may act as a stable modulator of iPFK-2 activity with potentially useful therapeutic effects on cancer cell metabolism.

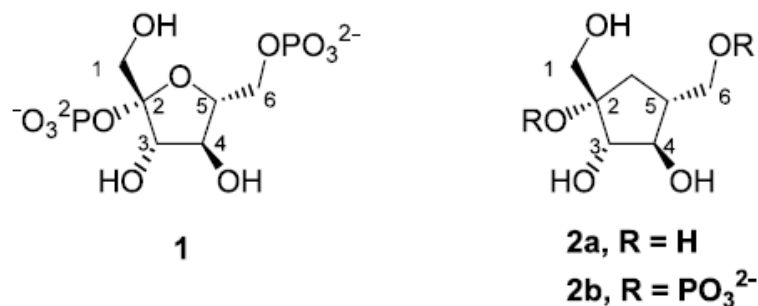
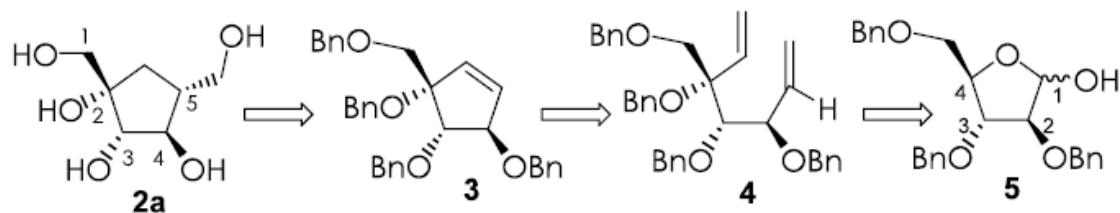


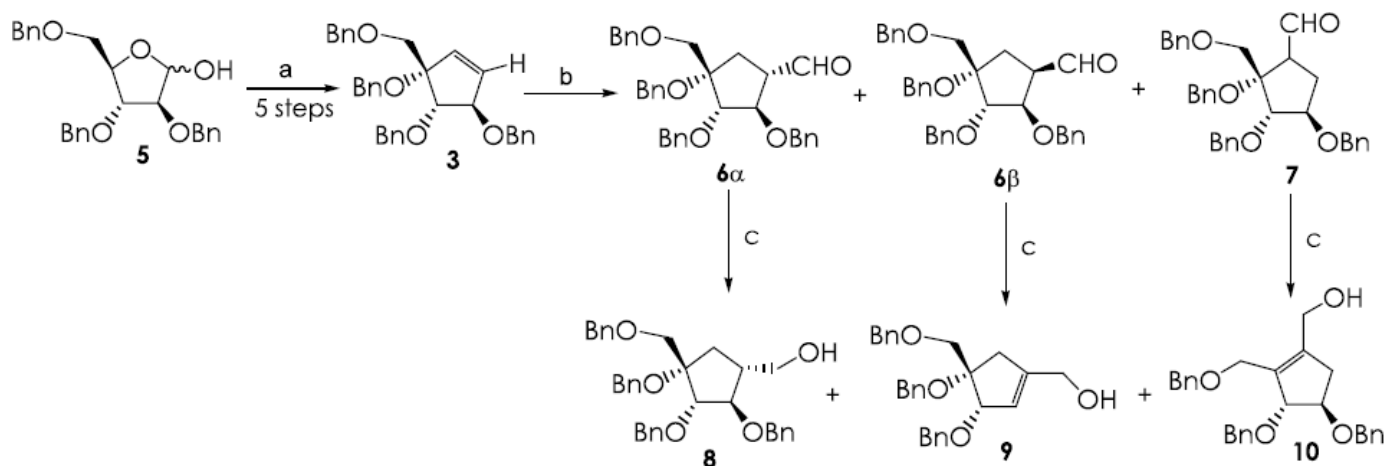
Figure 1. Structures of fructose 2,6-bisphosphate and carbafructofuranose.

These pseudo-sugars have been shown to enhance metabolic stability and potential clinical utility.

A 12-step total synthesis of carba-D-fructofuranose (**2a**) in **16%** yield employing a free radical cyclization was initially demonstrated.



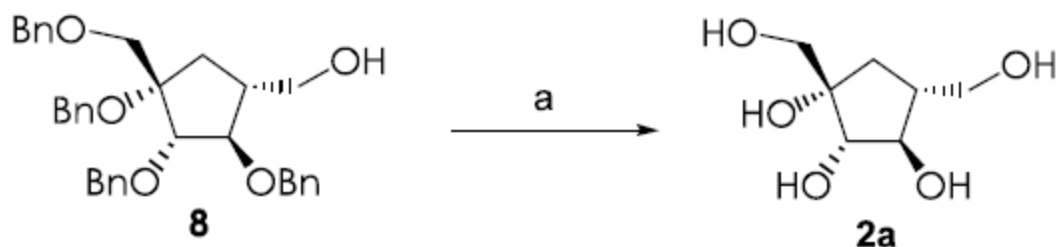
Scheme 1. Retrosynthetic route to carba-D-fructofuranose.



Scheme 2. Synthesis of substrates **6**, **7**. (a) Five steps, 90%; (b) Wilkinson's catalyst, CO, H₂, 80°C, 24 h, quant.; (c) NaBH₄, MeOH, 100%.

The hydroformylation reaction employed Wilkinson's catalyst $[(\text{Ph}_3\text{P})_3\text{RhCl}]$, a mixture of carbon monoxide (40 bar) and hydrogen (40 bar) at 80°C for 24 h. Under these reaction conditions the functionalized cyclopentene **3** was converted quantitatively to the corresponding aldehyde (Scheme 2).

The catalytically active species for the carbonylation reaction, $[(\text{Ph}_3\text{P})_3\text{Rh}(\text{CO})\text{H}]$, is postulated to be formed as an intermediate complex in situ. Attempts to carry out the reaction using $\text{Co}_2(\text{CO})_8$ as catalyst were unsuccessful.

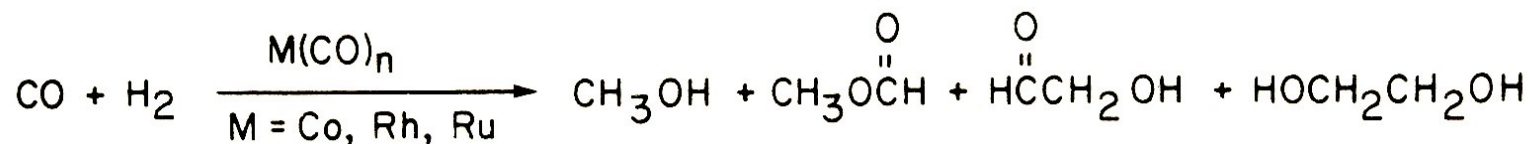


Scheme 3. Hydrogenation of compound **8**. (a) Pd/H_2 , EtOH, 98%.

“This is the first demonstration of the hydroformylation of a highly oxygenated cyclopentene. With this strategy **2a** was synthesized in eight steps with a yield of 32%” (vs. 12 steps and 16% yield).

HYDROGENATION OF CO

Soluble **metal carbonyl compounds**, especially those of Rh, Ru and Co can catalyze the transformation of syngas into wide variety of oxygenated products. High pressures and temperatures are needed.



The primary products, methanol, methyl formate, glycoaldehyde and glycol are thought to form via parallel pathways. Glycol aldehyde is precursor for glycol which is the most attractive commercial target.

Selectivity depends on the nature of the metal, additives and the reaction conditions.

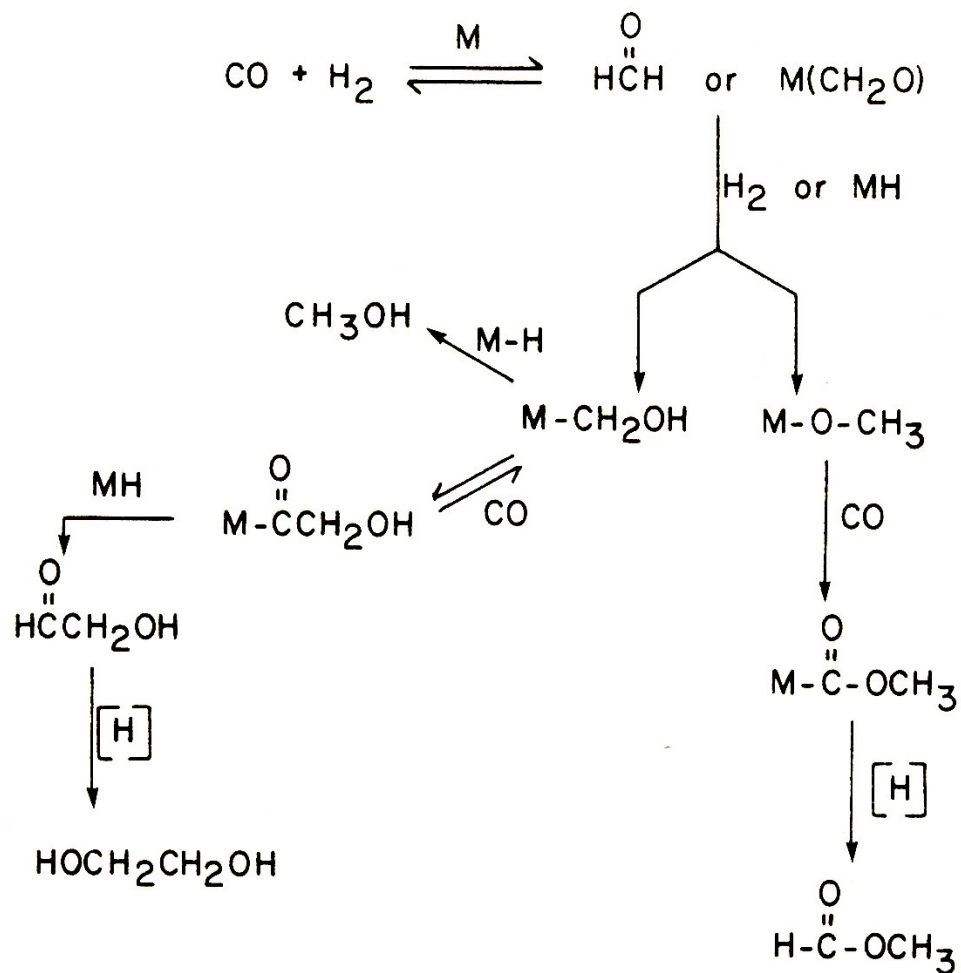
Ru and Rh catalysts give much higher rates than Co, but even the fastest systems are slow, unselective and need so drastic reaction conditions that they are unattractive for commercial scale (220-280 °C and 550-1000 bars).

HYDROGENATION OF CO

Formation of formaldehyde is considered as a rate limiting step. In fact, formation free formaldehyde from CO and H₂ is thermodynamically uphill ($\Delta G^\circ = 6.5 \text{ kcal/mol}$ at 25 °C = 12.1 kcal/mol at 227 °C).

Even the fastest catalysts can give only very small equilibrium conc.

Either of two tautomeric complexes M-CH₂OH and MOCH₃ is formed. As shown, hydroxymethyl intermediate can form either methanol or glycolaldehyde. Other route leads to methyl formate.

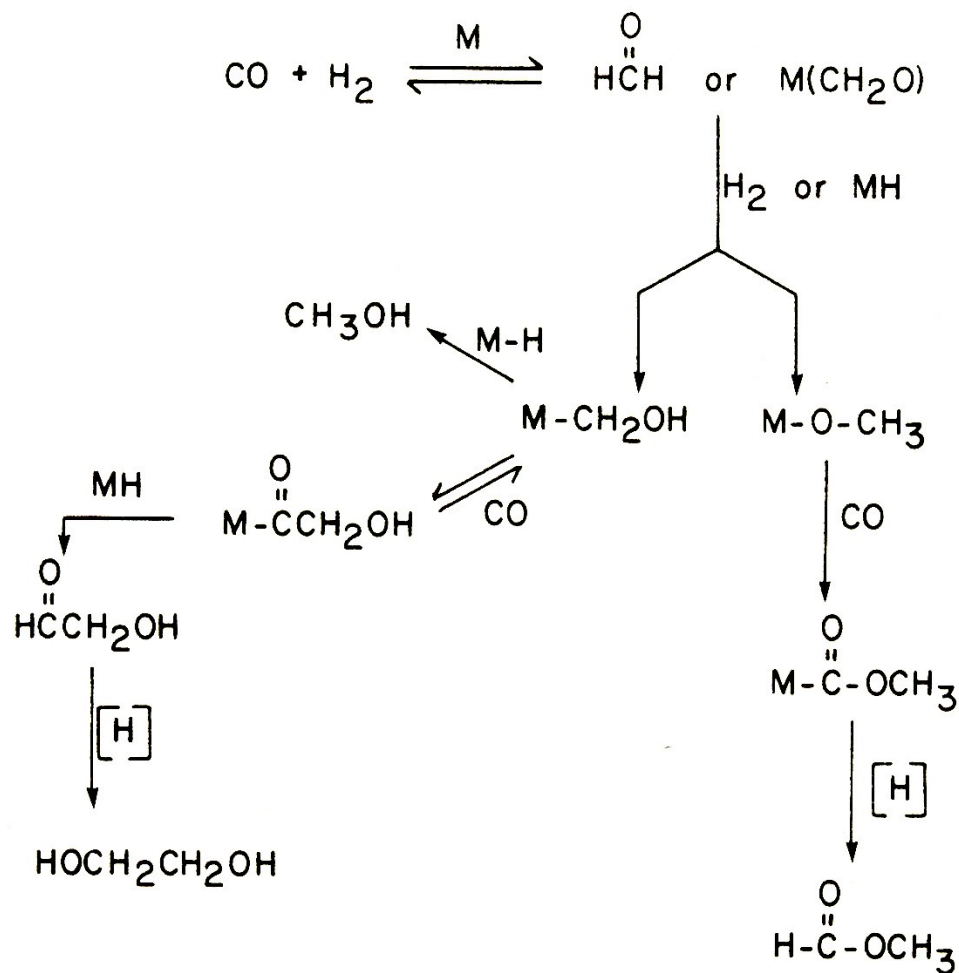
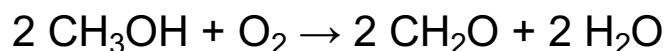


M = a soluble carbonyl complex of Co, Rh or Ru

HYDROGENATION OF CO

Formaldehyde is produced industrially by the catalytic oxidation of methanol. The most common catalysts are silver metal or a mixture of an iron and molybdenum or vanadium oxides.

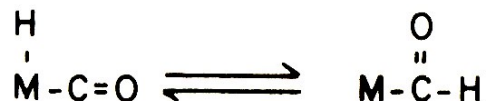
In the commonly used *Formox process*, methanol and oxygen react at ca. 250–400 °C in presence of iron oxide in combination with molybdenum and/or vanadium to produce formaldehyde according to the chemical equation:



M = a soluble carbonyl complex of
Co, Rh or Ru

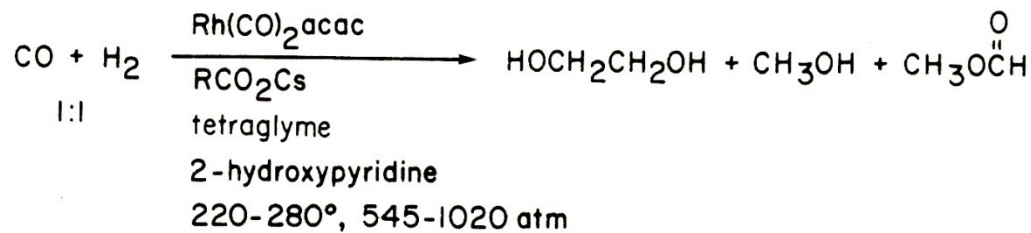
HYDROGENATION OF CO

Formation of formaldehyde involves the prior formation of a formyl complex. Insertion of CO to M-H bond is usually thermodynamically uphill (formyl complexes can be prepared from strongly reducing hydrides (Ti, Al, Zr) + electrophilic carbonyl ligands (intermolecular reactions)) is considered as a **rate limiting step**.



In the course of catalytic reaction a very small (undetectable) quantities of formyl complex is thought to form. On the other hand, formaldehyde reacts very fast and generates a formyl complex. The catalytic reaction therefore squeezed to this very narrow thermodynamic and kinetic window. conc.

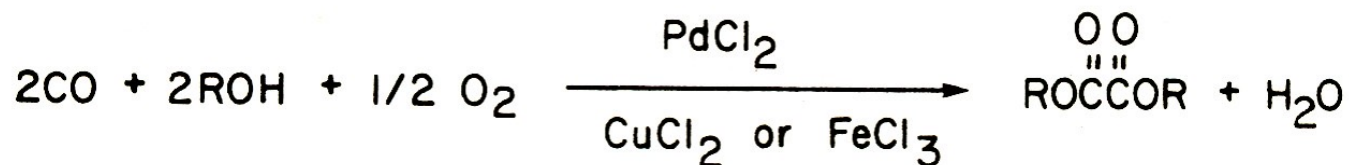
Typical reaction conditions for Rh catalyst are below:



Role of Cs carboxylates may relate to formation of Rh cluster. This is rare example where TM clusters could work as a homogeneous catalyst.

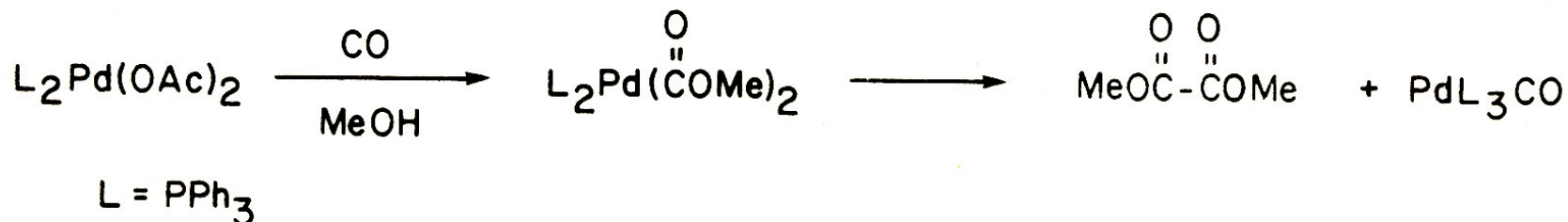
OXIDATIVE COUPLING OF CO

An alternative direct synthesis of glycol from CO and H₂ is an oxidative coupling of CO. This complicate, multistep process affords oxalate esters along with dialkylcarbonate byproducts. The oxalates are subsequently hydrogenated to ethylene glycol using heterogeneous catalysts.



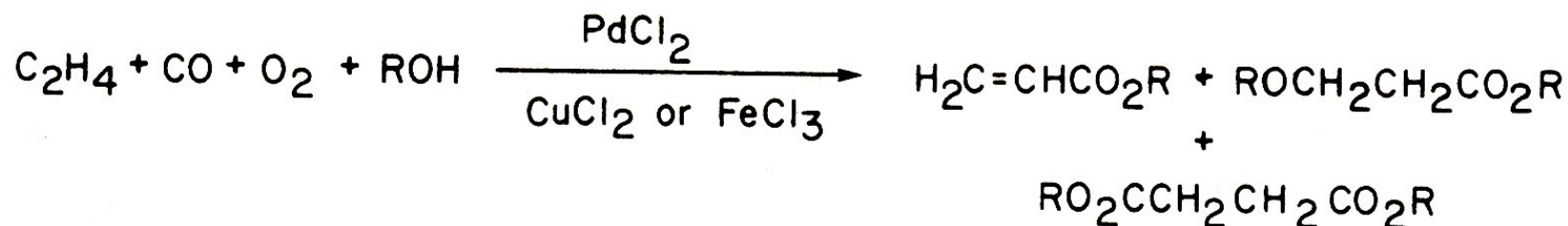
The first step is catalyzed by mixture of Pd complex with CuCl₂ or FeCl₃. The role of Cu or Fe salt is to reoxidize Pd(0) back to Pd(II), using dioxygen as the oxidant. This is reminiscent for Wacker-Smid process (see below).

The key step is oxidative dimerization is reductive elimination of a bis(carbomethoxy)Pd(II) complex.



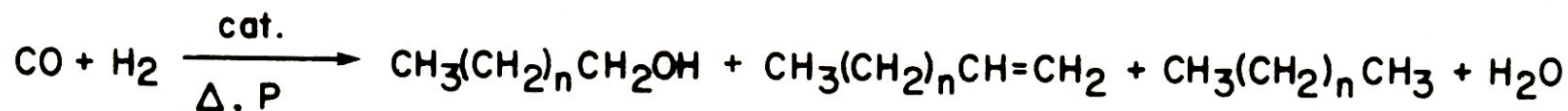
OXIDATIVE COUPLING OF CO

Similar oxidative coupling between alcohols and ethene provides a potential route for acrylate and succinate esters. The latter can be obtained with 90% selectivity.



THE FISCHER-TROPSCH REACTION

Reductive polymerization of CO in the presence of H₂ to form linear hydrocarbons, olefins, alcohols is an old process which has recently attracted great interest because of the possibility that biomass (and coal) could be used as a source of fuel or liquid chemical feedstock. The reaction is exothermic.

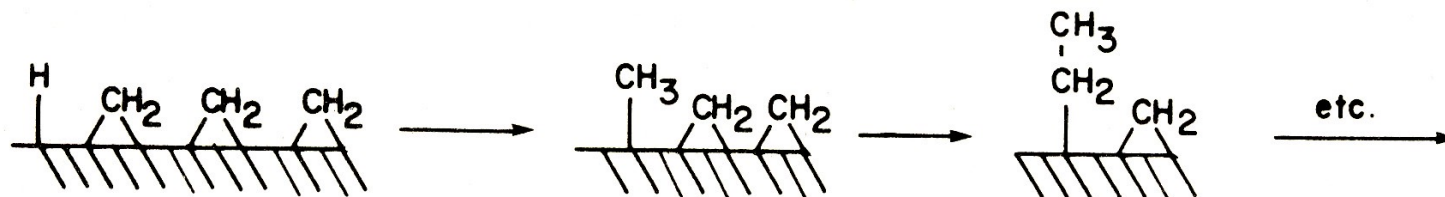


Franz Fischer and Hans Tropsch discovered alkali-iron catalyzed reaction in 1923 and from 1936 the first commercial plant was operated in Germany. During WW II substantial portion of liquid fuels was produced with this technology in Germany.

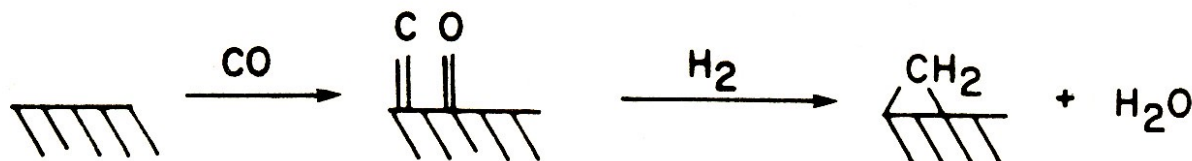
Product selectivity depends on many factors, such as CO/H₂ ratios, pressure, temperature, the catalyst (heterogeneous) and method of preparation and the presence of promoters such as alkali metals. *The lack of product selectivity and statistical molecular weight range are major drawbacks of the FT reaction.* Additionally a large quantity of the carbon content of coal must be discarded as CO₂ to form H₂ necessary for the FT (water-gas shift reaction).

THE FISCHER-TROPSCH REACTION

Extensive efforts have been focused on the mechanism. There are three mechanistic contenders. The first one (by Fischer and Tropsch) suggest that CH_2 (carbene) fragments form and polymerize on the catalyst surface: hydride first inserts CH_2 to form a methyl group, which then inserts CH_2 again in the chain propagation step.



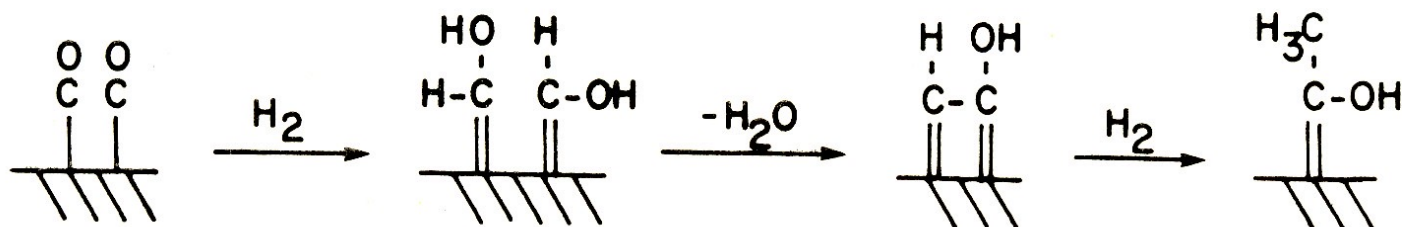
The carbene fragments are proposed to originate from surface carbides, which in turn derive from dissociative chemisorption of CO as outlined below.



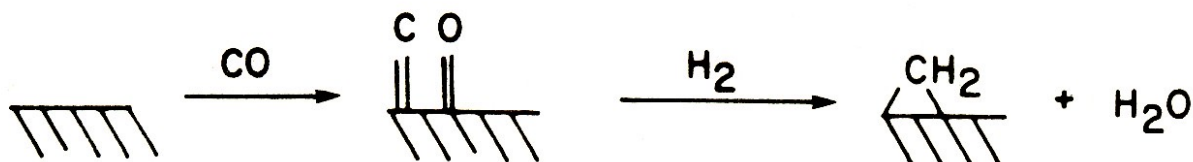
This mechanism is supported by several observations: using ^{13}CO , and CH_2N_2 . Most of the products contain labeled C and in the absence of hydrogen, ethene is formed from diazomethane (with hydrogen typical products with right distribution).

THE FISCHER-TROPSCH REACTION

Another mechanism includes hydroxymethylene groups on the surface. The C-C bonds are constructed by condensation reaction between the hydroxymethylene groups. Although some hydroxy carbene complexes are known, the condensation reaction is not.

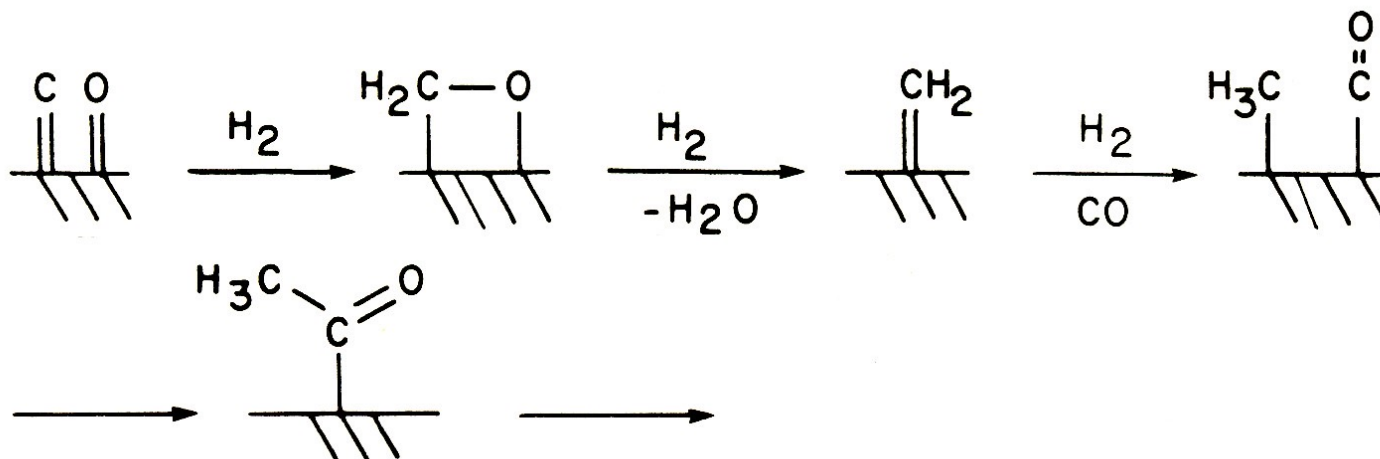


We might think, that these species are rather alternative intermediates related to parallel reaction pathway to dissociative chemisorption of CO.



THE FISCHER-TROPSCH REACTION

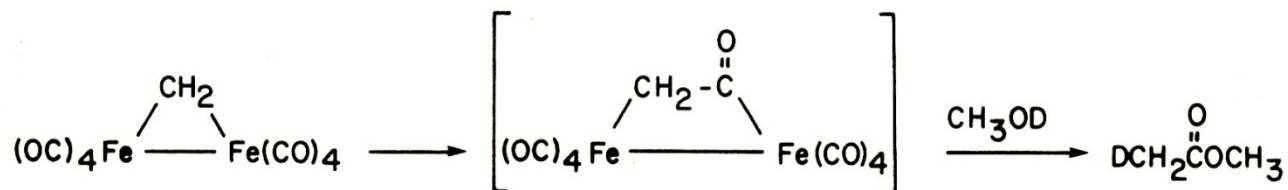
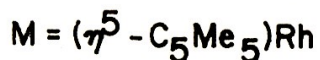
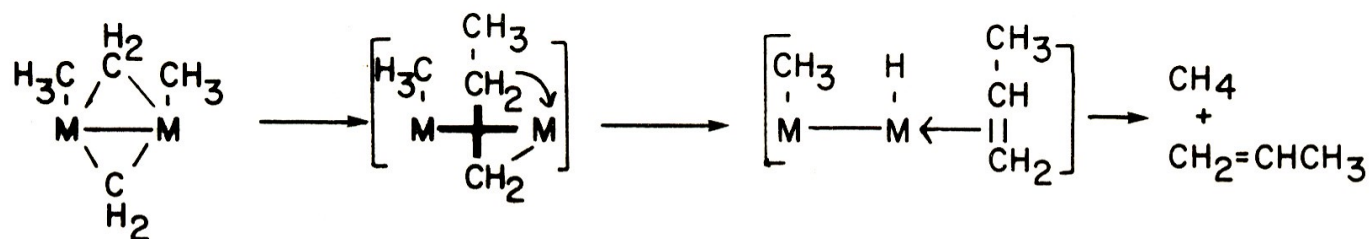
The third mechanism is via formaldehyde. In this reaction the C-C bond is formed via “classical” migration of the methyl group to CO.



At the present, there is no general agreement on the dominating pathway. A mass of evidence is accumulated to support the carbide/methylene mechanism.

THE FISCHER-TROPSCH REACTION

Some homogeneous models for FT



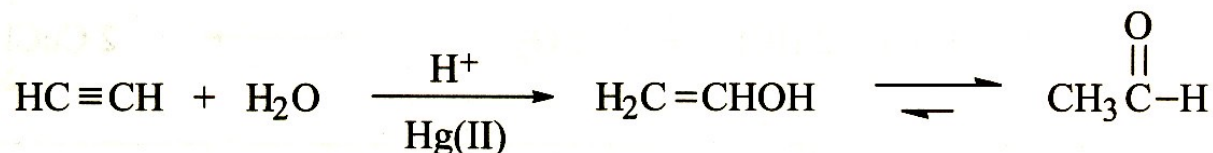
THE FISCHER-TROPSCH REACTION



SASOL 2008 in Qatar

WACKER SMIDT SYNTHESIS OF ACETALDEHYDE

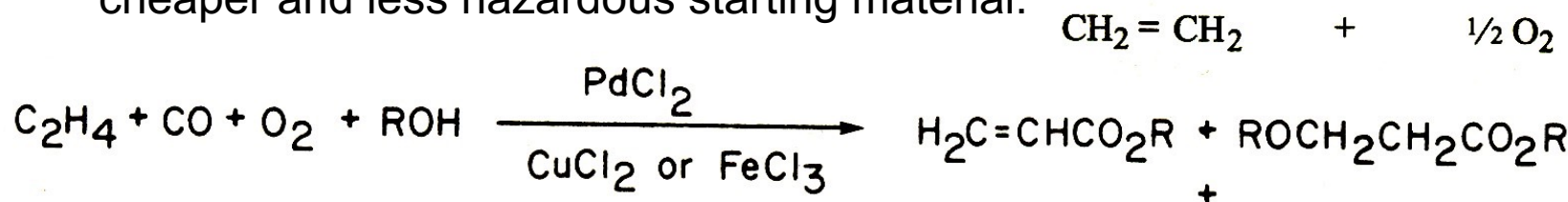
Acetaldehyde (ethanal) is commercially important aldehyde. It is originally produced by hydration of acetylene with a high yield.



Problems of process are related to acetylene. Acetylene is produced from hydrocarbons with high temperature, sometimes in the presence of electric arc (high amount of energy is needed).

Acetylene is also thermodynamically unstable, and must be handled with extra care to prevent explosion.

Therefore, there have been incentives to develop a process based on cheaper and less hazardous starting material.



WACKER SMIDT SYNTHESIS OF ACETALDEHYDE

It has been long known that acetaldehyde can be produced from ethene and water in the presence of stoichiometric amount of PdCl_2 .



In 1950s Smidt in Wacker Chemie resolved the problem.

By adding CuCl_2 and HCl and O_2 the reaction turns to catalytic.

WACKER SMIDT SYNTHESIS OF ACETALDEHYDE

The overall reaction is oxidation of ethylene by oxygen.



The process is run in one or two stages depending whether the catalyst is regenerated in situ or separately.

WACKER SMIDT SYNTHESIS OF ACETALDEHYDE

The Wacker-Smidt process, leading ultimately to acetic acid and acetic anhydride has enjoyed considerable success, but nowadays its importance is declining

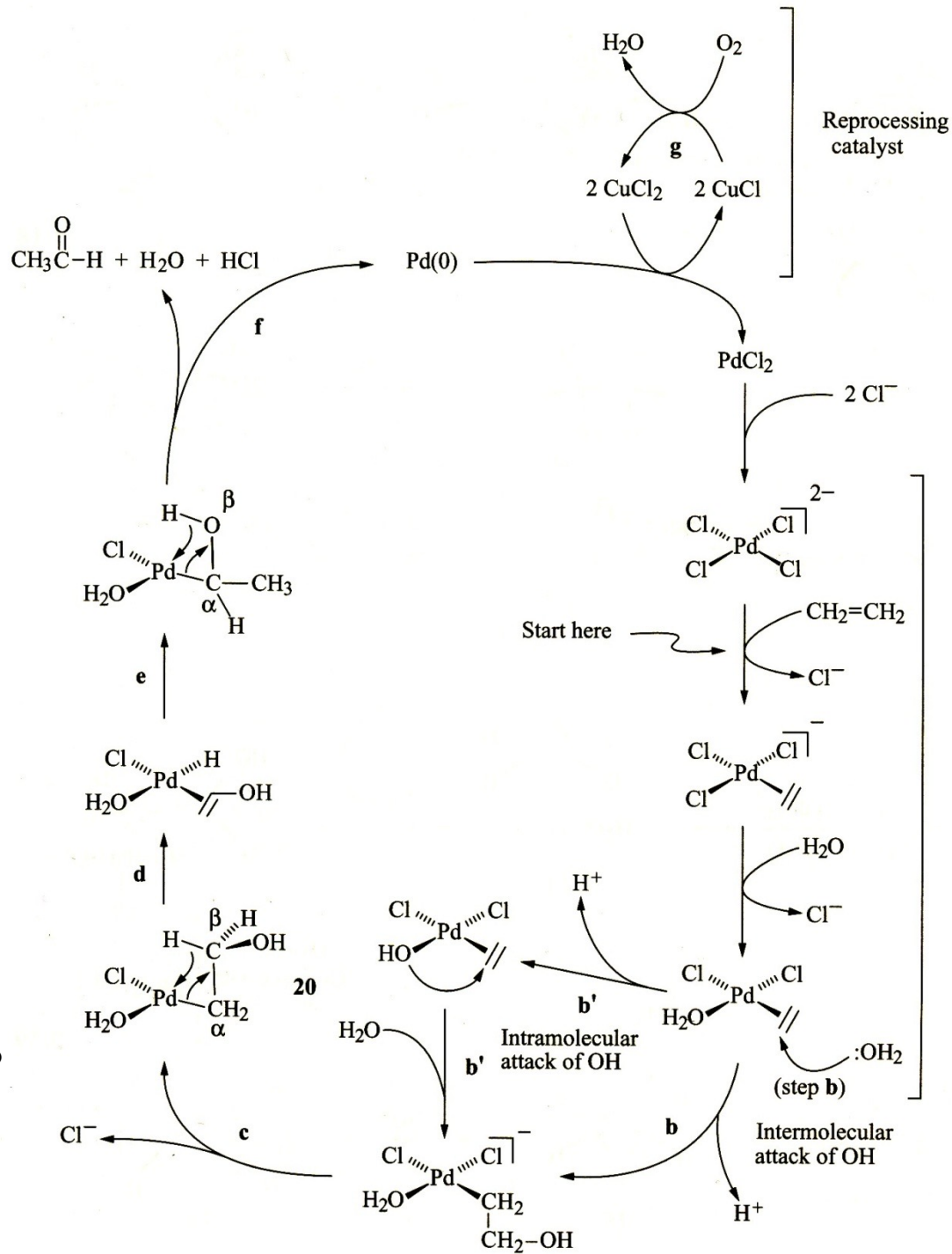
- Because of the corrosive conditions (HCl) the operational costs are high.
- Monsanto acetic acid process + Halcon-Eastman

WACKER SMIDT SYNT ACETALDEHYDE

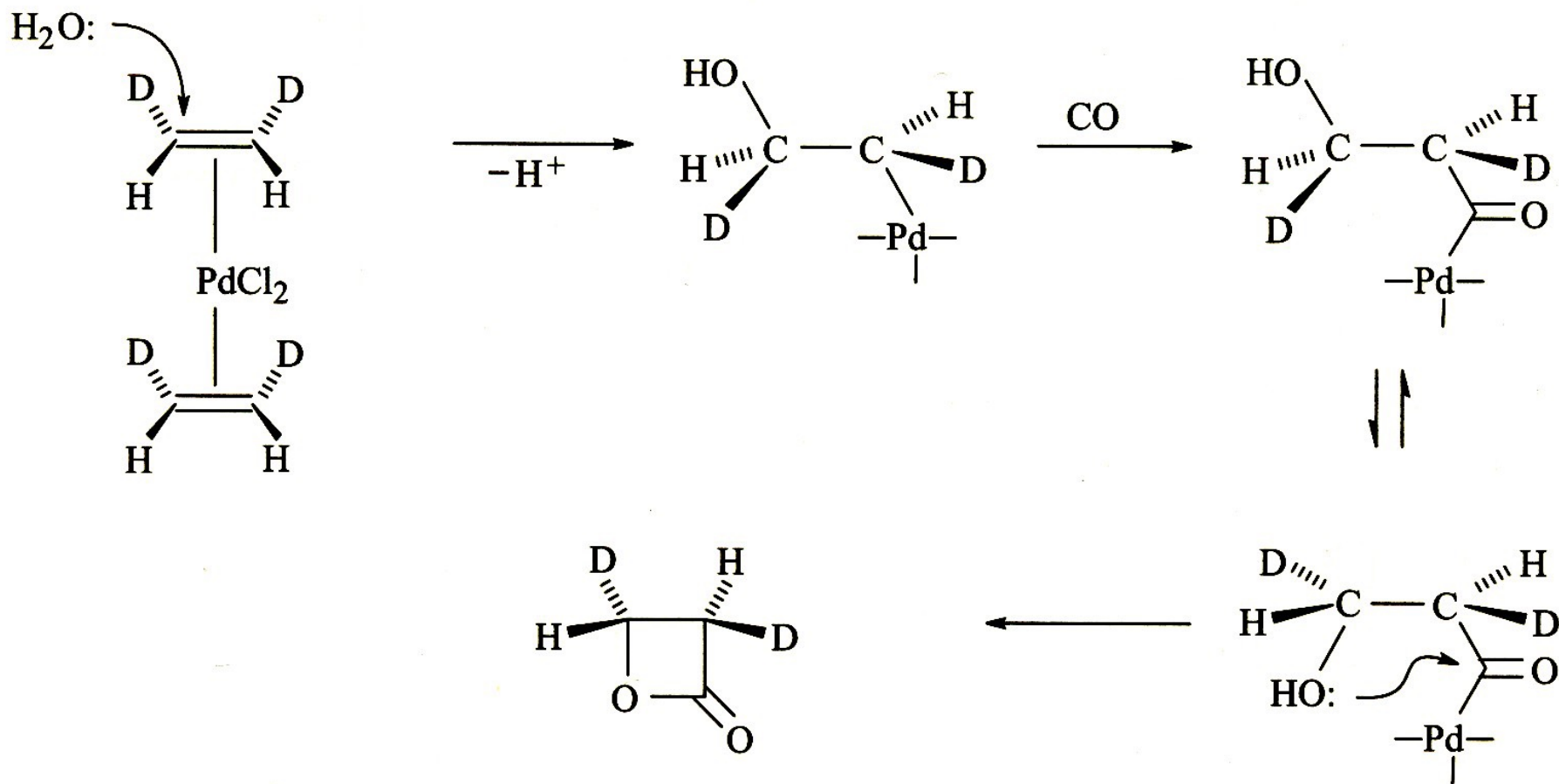
Exact mechanism for acetaldehyde formation is not completely clear.

$$\text{Rate} = \frac{k[\text{CH}_2=\text{CH}_2][\text{PdCl}_4^{2-}]}{[\text{H}^+][\text{Cl}^-]^2}$$

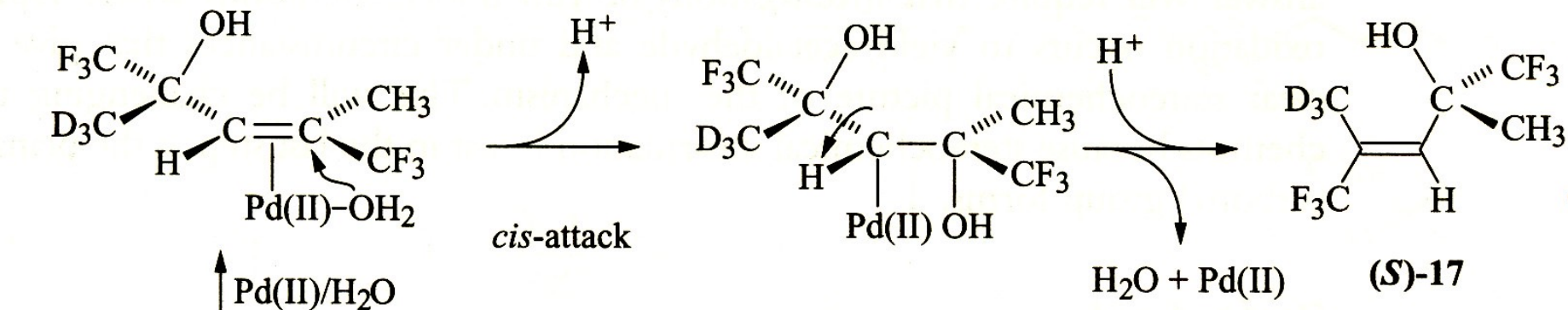
Step c is the rate limiting. Why?



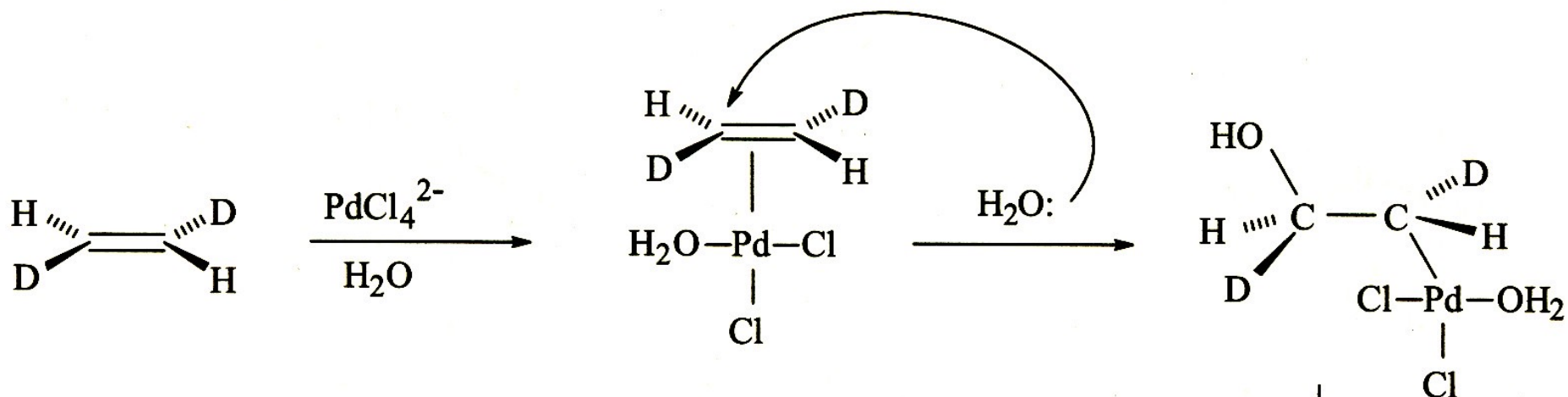
WACKER SMIDT SYNTHESIS OF ACETAL DEHYDE



WACKER SMITZ SYNTHESIS OF



Bond rotation and *cis*-elimination



Oxidative
Cleavage with
Inversion

$\text{CuCl}_2 / \text{LiCl}$

WACKER SMIDT SYNTHESIS OF ACETALDEHYDE

