

# CH304 Industrial Chemistry 2008 -2009 P.McArdle

The following topics will be covered

Structure of the Chemical Industry

Economic Factors

Differences between lab. & industry

Conversion & selectivity v.s yield

Reactor Types

Catalyst Use and Material Balance

The Chlor-alkali Industry

Raw material sources and SynGas.  
T-metal Catalysed Processes

Getting O into organics  
Addition Polymers  
Chiral catalysis

## Sources:

Principles of Industrial Chemistry, C.A. Clausen & G. Mattson, Wiley 1978

Industrial Chemistry, C.A. Heaton, Blackie 1992.

C & E News, (Weekly) American Chemical Society.

# Raw Material Sources for the Chemical Industry

## Inorganics

Sulfur about  $70 \times 10^6$  tons p.a.

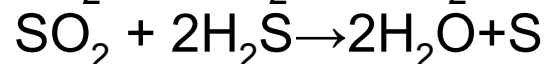
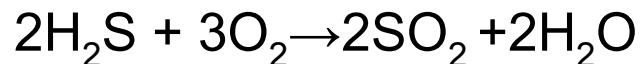
About 50% extracted from Nat. Gas & Oil

About 20% mined by Frasch process.

About 20% from pyrites  $\text{FeS}_2$  (Fool's gold)

About 10% from smelter gases.

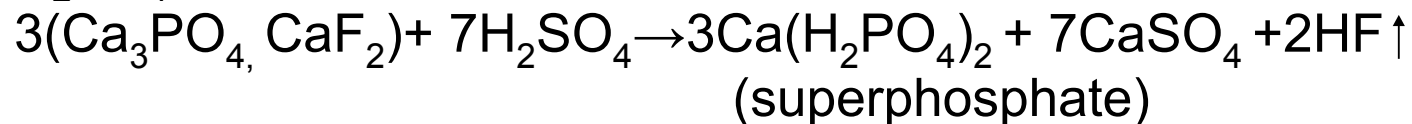
Nat. gas may be up to 20%  $\text{H}_2\text{S}$  (Canada)



90% of S is used to make  $\text{H}_2\text{SO}_4$ .

About 50% of  $\text{H}_2\text{SO}_4$  is used to make fertilizers

$\text{H}_2\text{SO}_4$  + Phosphate Rock



## Air Separation into N<sub>2</sub> & O<sub>2</sub>

The process has used liquefaction-fractional distillation and storage of N<sub>2</sub> & O<sub>2</sub> as cryogenic liquids or compressed gases for many years. Membrane separation of O<sub>2</sub>/N<sub>2</sub> has recently been developed.

Liquid air → N<sub>2</sub> (l) → steel, food, fertilizers (N<sub>2</sub> + 3H<sub>2</sub> = 2NH<sub>3</sub>)  
→ O<sub>2</sub> (l) → steel, medicine, etc.

100\*10<sup>6</sup> tons of liq N<sub>2</sub> & O<sub>2</sub> p.a.

Ammonia from N<sub>2</sub>

Haber (1918)-Bosch (1931) process

N<sub>2</sub>+3H<sub>2</sub> = 2NH<sub>3</sub> ΔH -ve but rate slow

World production was 1\*10<sup>6</sup> tons p.a. in 1950

It is now over 100 \*10<sup>6</sup> tons p.a.

The H<sub>2</sub> comes from steam reforming of natural gas.

Uses NH<sub>3</sub> O<sub>2</sub>/cat = HNO<sub>3</sub> converted to NH<sub>4</sub>NO<sub>3</sub> (fertilizer)

or NH<sub>3</sub> + CO<sub>2</sub> = Urea (fertilizer), nylon etc.

## Raw Material Sources for Carbon Based Compounds

There has been a trend towards Petroleum as a raw material source for the last 50-60 years, because oil was so cheap and pure. There are signs that this may change but the overall picture is

1. Oil Refineries still provide most chemical feedstock..
2. There has been a change to natural gas in some areas.  
Steam Reforming of Natural Gas is now an important raw material source.
3. Coal is used to a small extent but it is more expensive to use than oil.

**Synthesis Gas** or **Syngas** is any mixture of CO and H<sub>2</sub>

Some sources are:

- $C_nH_{2n+2} + \frac{1}{2}nO_2 \rightarrow (n+1)H_2 + nCO$
- Steam Reforming of nat. gas is  $CH_4 + H_2O = CO + 3H_2$
- Coal using WaterGas reaction  $C + H_2O = CO + H_2$

**Syngas** can be used to synthesise Methanol, and Ammonia

ICI low temperature Methanol Process

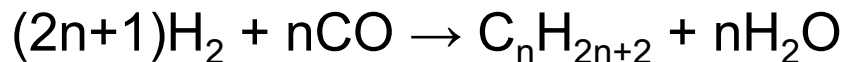


Coal can also be used as a raw material but it is still expensive relative to oil. The following was operated in Germany (1939-1945) and is current in South-Africa (Sasol1 and Sasol2).

$\text{C (coal)} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$  is the water gas reaction, gasification of coal. This can also be converted to **oil** by the Fischer Tropsch Process

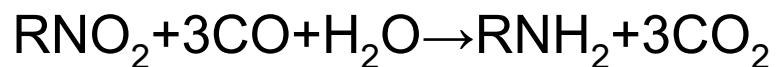
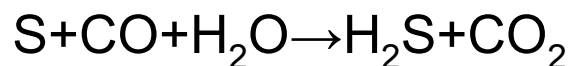
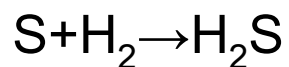


The Fischer-Tropsch process is described by the following equation



	Only CH <sub>4</sub> has -ΔG	ΔG kJ/mol
CO + 3H <sub>2</sub> = CH <sub>4</sub> + H <sub>2</sub> O		-96.22
CO + H <sub>2</sub> = HCHO		50.62
CO + 2H <sub>2</sub> = MeOH		21.23
2CO + 3H <sub>2</sub> = (CH <sub>2</sub> OH) <sub>2</sub>		65.92

Hydrogen  $H_2$  is required for many reactions, it is expensive  
 $CO + H_2O = H_2 + CO_2$  can sometimes be used in place of  $H_2$ .



Pure  $H_2$  is very expensive and hard to store. For this reason  
 $H_2$  fuelled cars are not easy to make. Steam reforming of  
natural gas or naphtha is the main source of  $H_2$

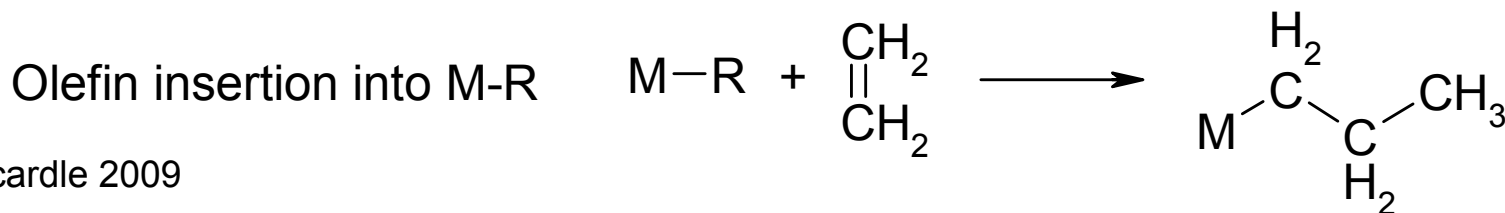
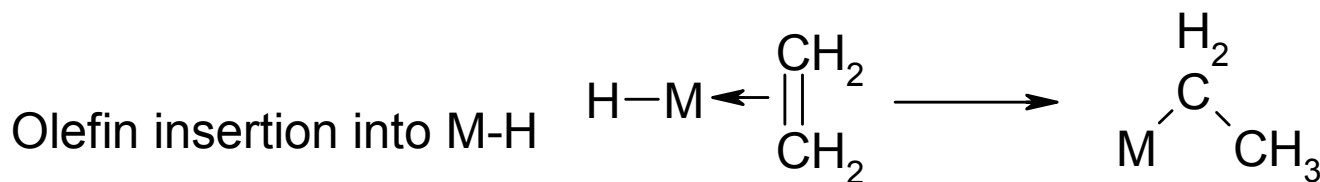
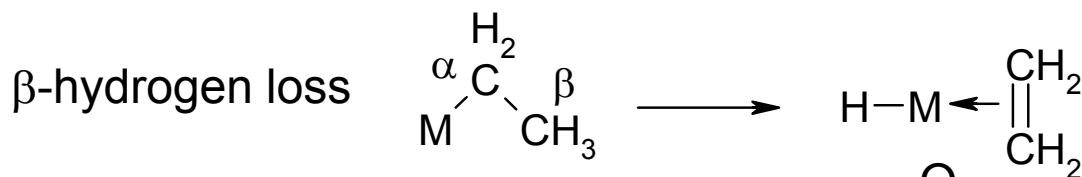
## Using transition metal catalysts

During 20<sup>th</sup> Century the price of commodities decreased by 0.6% per year every year.

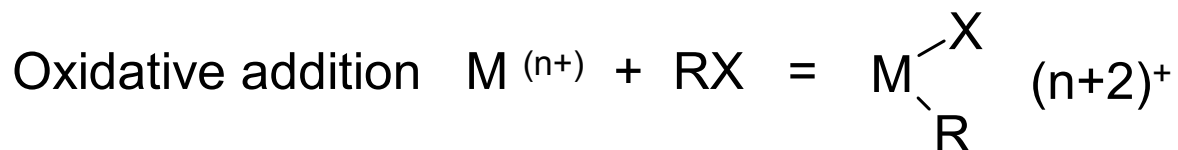
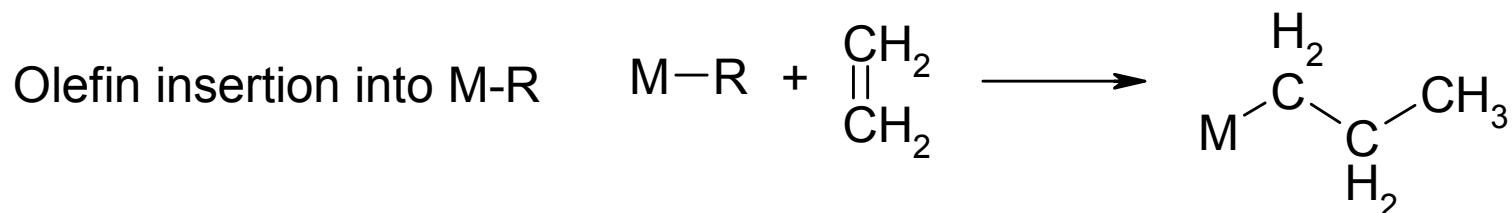
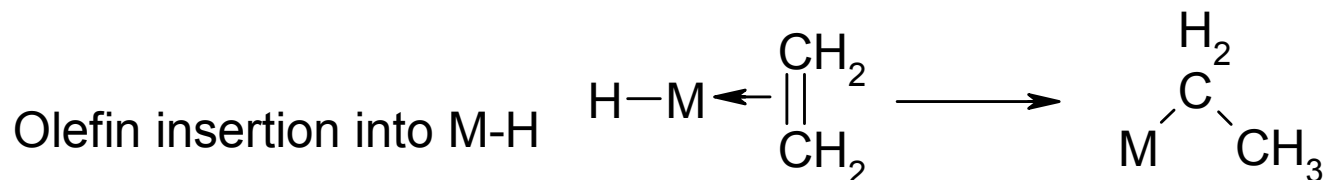
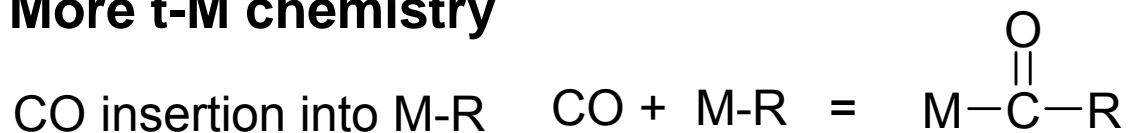
This trend puts a stress on the importance of constant improvements in efficiency. New and better catalysts is one way to remain competitive.

### Some t-metal chemistry

Simple M-R (e.g. M-CH<sub>3</sub>) were with a few exceptions unknown. In 1968 Wilkinson suggested that if complexes had no βH they would be stable



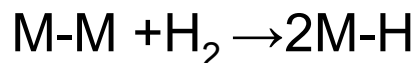
## More t-M chemistry



Coordinated olefins are susceptible to nucleophilic attack

Free olefins are not

M-M bonds can be reductively cleaved by  $\text{H}_2$



**Most t-M catalysed reactions involved a cycle of reactions in which the catalyst takes part and is regenerated.**

## Getting oxygen into organics

Without a catalyst this is not easy.

In the past butane was oxidized by partial combustion

Butane + O<sub>2</sub> → aldehydes + acids

### Reaction 1

The Oxo-process was developed since World War 2  
it converts olefins into aldehydes (hydroformylation).

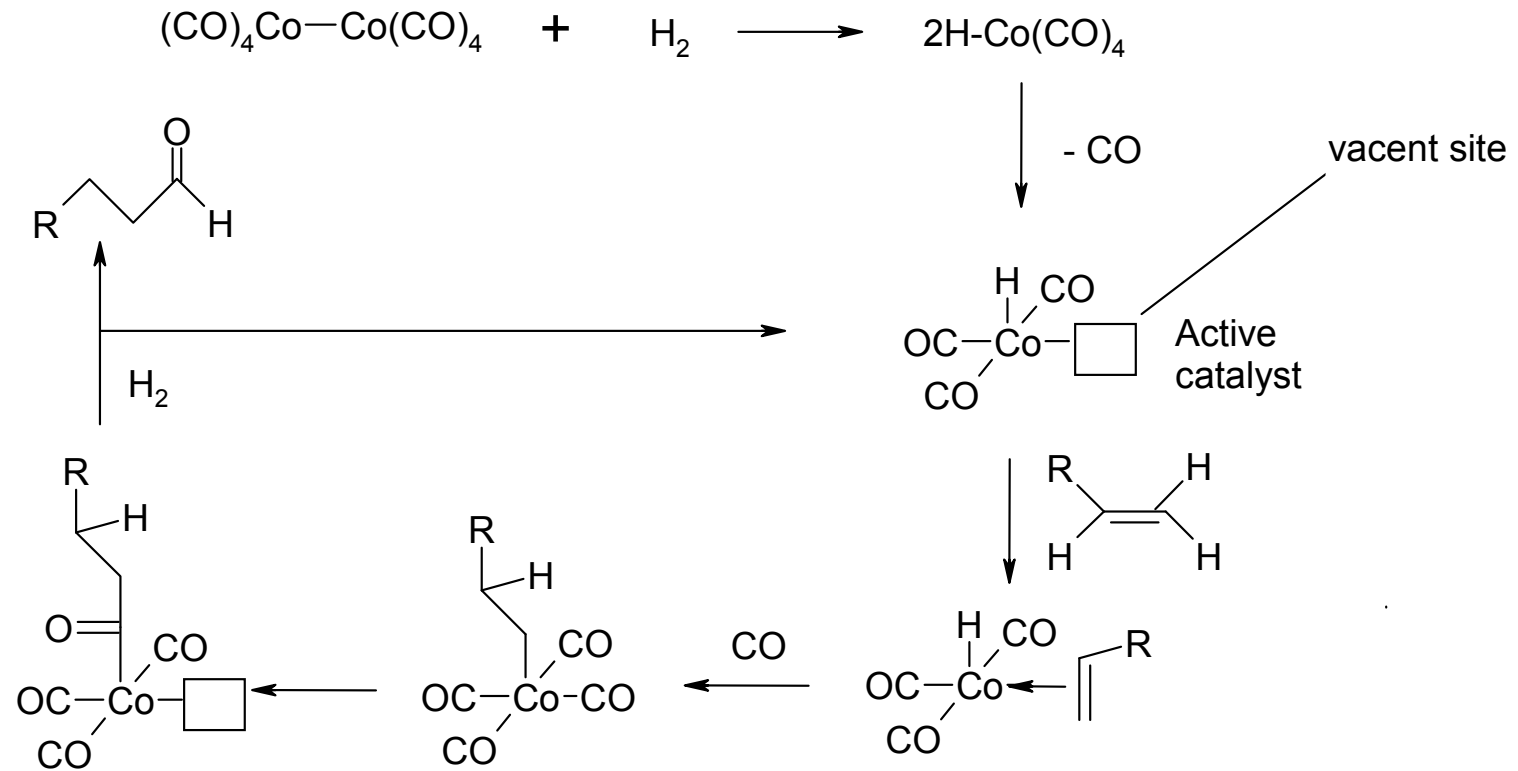


The catalyst was originally a Co<sup>II</sup> salt. and excess H<sub>2</sub> gives an alcohol.  
Under the reaction conditions Co<sup>II</sup> is reduced and Co<sub>2</sub>(CO)<sub>8</sub> is produced  
which is cleaved by H<sub>2</sub> to 2HCo(CO)<sub>4</sub>

### The oxo-process can be improved

1. by addition of PBu<sup>n</sup><sub>3</sub> to the cobalt catalyst (BP).
2. by a change to Rh based catalysts [Rh(PPh<sub>3</sub>)(CO)(H)]<sub>3</sub>.  
this gives more straight chain aldehyde than Co catalysts.
3. Rhone-Poulenc Two Phase process using water soluble  
(tri-m-sulphonato-phenyl)phosphine with rhodium cat.

# OXO-Process mechanism



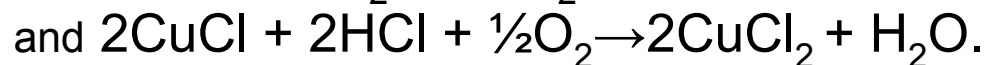
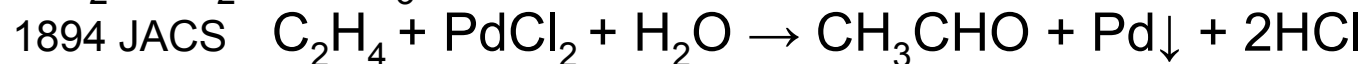
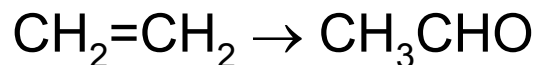
The Rhone-Poulenc catalyst is soluble in H<sub>2</sub>O (Na Salt)  
Using a phase transfer catalyst (long chain detergent)  
the reactants and products are in the organic phase and the catalyst  
is in the H<sub>2</sub>O phase (no sep. problem).

>95% selectivity and unlike classic OXO olefins >C<sub>3</sub> can be used.  
>99.9% recovery of precious metal.

## Reaction 2

Wacker process

J.D. Smidt at Wacker Chemie in 1960s



On summing these reactions the Pd, Cu, HCl and H<sub>2</sub>O cancel giving



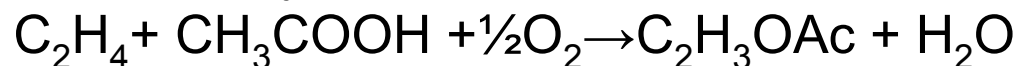
## Method - In a Batch Reactor

1. Mix  $C_2H_4$ ,  $PdCl_2$ ,  $H_2O$ ,  $CuCl_2$
2. Flush out  $CH_3CHO$  with air
3. Pass in Ethene, back to 1.

Mechanism involves nucleophilic attack on coordinated ethene by  $OH^-$ . This would not happen for free olefin.

The vinyl acetate process is a simple modification of this procedure with the solvent changed from  $H_2O$  to acetic acid.

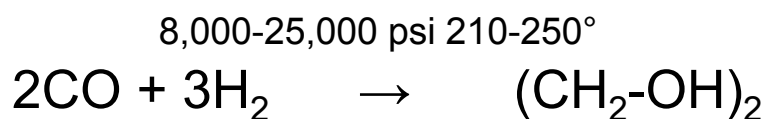
Same catalyst.



Here there is nucleophilic attack by  $OAc^-$  on coordinated ethene.

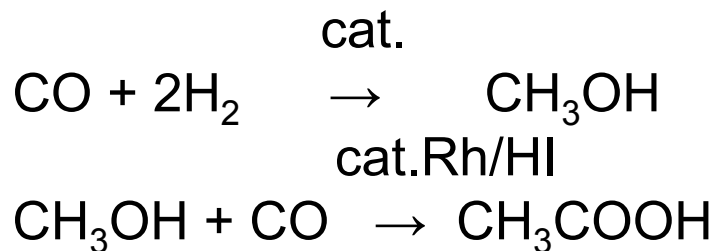
Processes which use Syn-Gas. CO/H<sub>2</sub>

Union Carbide Ethylene glycol HO-CH<sub>2</sub>-CH<sub>2</sub>-OH Process



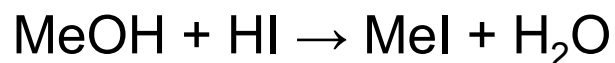
Catalyst Rh/C direct C-C bond formation is v. difficult hence the high pressure used.

MONSANTO acetic acid process – converts methanol to acetic acid. The methanol is available from syn-gas by the ICI low temperature methanol process

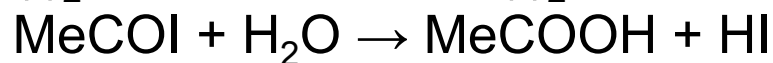
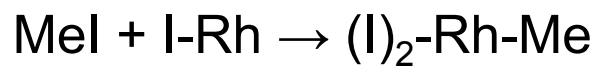
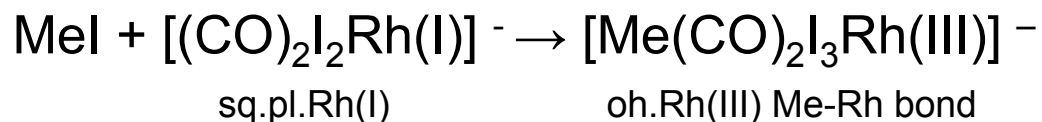


# Monsanto Acetic Acid Process

This reaction involves a very simple way to activate the MeOH  
MeOH does not react with Rh compounds.



MeI reacts with Rh(I)

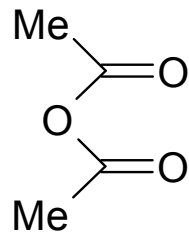


# Tennessee-Eastman Acetic Anhydride Process

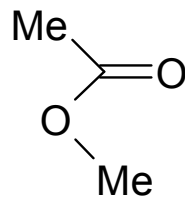
Change the solvent in the Monsanto acetic acid process from methanol to methyl acetate *i.e.* MeOH to MeCO<sub>2</sub>Me.



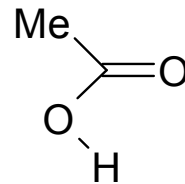
This is very similar to the switch from H<sub>2</sub>O, HOH, as solvent in the Wacker process to MeCO<sub>2</sub>H, AcOH, which changed the product from vinyl alcohol to vinyl acetate,



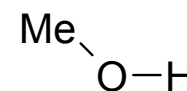
acetic anhydride



methyl acetate



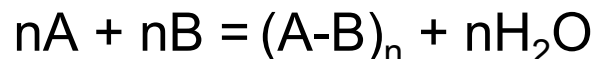
acetic acid



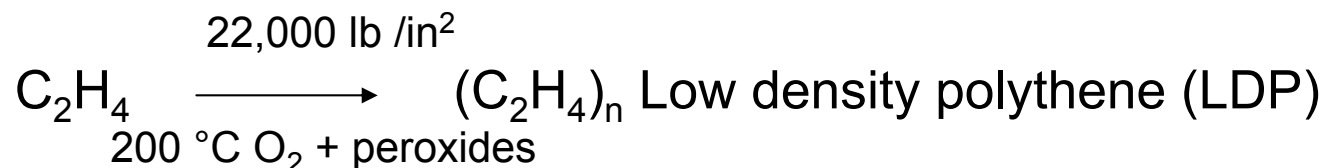
methanol

## Addition polymers $nA = A_n$

We will not discuss Condensation polymers of the type

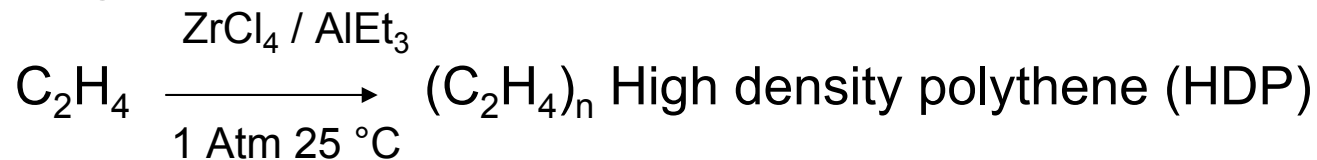


Ethene polymerisation (accidental discovery at ICI in the UK)



LDP has some cross-linking giving it flex and stretch properties

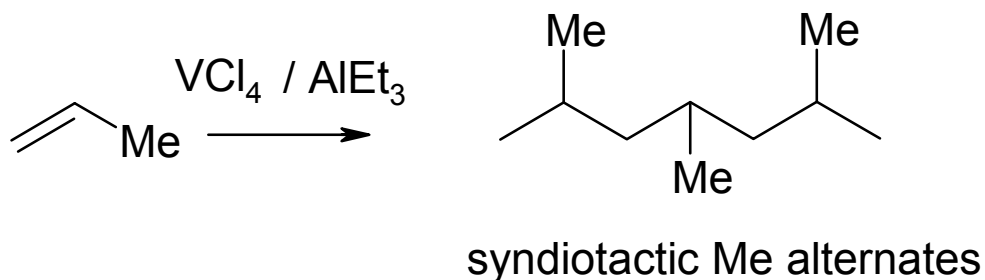
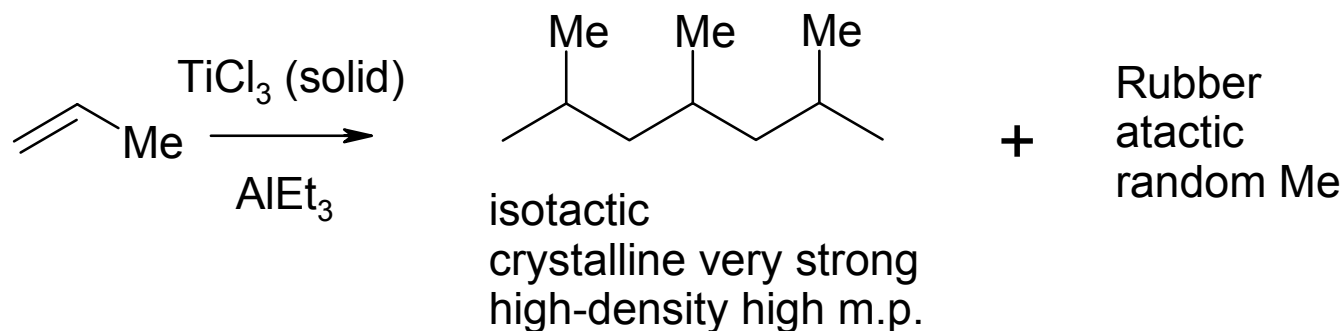
Ziegler Process (Karl Ziegler Max Planck-Institut für Kohlenforschung, Mülheim/Ruhr)



HDP has few cross-links, rattles when you shake it and is very strong.

# Ziegler-Natta Process

Use propene and change the catalyst to  $\text{TiCl}_3$  (solid) /  $\text{AlEt}_3$   
The product may be stereo regular high-density or rubber.



## Addition Polymers

Monomer	Method	Properties
Ethene	Free Rad. Ziegler	Low density polyethene, Stretches, tear resistant High density polymer Very Strong.
Propene	Ziegler	Very strong and high resistance to chemicals.
Isobutylene	$\text{AlCl}_3/\text{CH}_3\text{Cl}$	Butyl Rubber, crosslinking sites if isoprene Added.
Styrene	Free Rad. Ziegler	Atactic Polystyrene, wide uses. Divinyl benzene will crosslink Sulphonate $\rightarrow$ ion-exch.resins crystalline polymer m.p. 230 °C
$\text{CH}_2=\text{CH}-\text{Cl}$	Free Rad.	PVC usually plastized Upvc is unplastized very inert.
$\text{C}_2\text{F}_4$	Free Rad.	Teflon, Very very inert. m.p. 327 °C
$\text{CH}_2=\text{CMe}-\text{CO}_2\text{Me}$	Free Rad.	Perspex, good optical properties
$\text{CH}_2=\text{CH}-\text{OAc}$	Free Rad.	Chewing Gum, water soluble paint, adhesives.
Butadiene	Free Rad. Ziegler	Complex rubber Car tyres
Chloroprene	Free Rad.	Neoprene, hoses, gaskets. good oil

## Advantages / Disadvantages of Ziegler / Free Radical

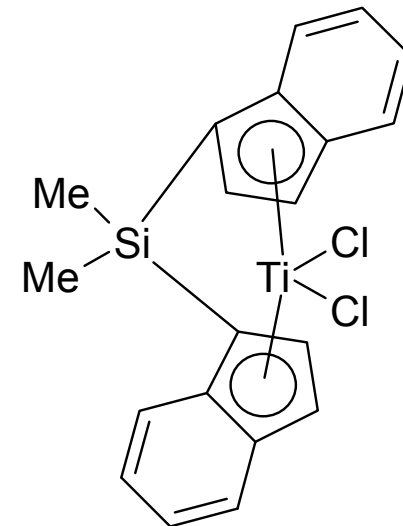
### Free Radical

1. Can be run in H<sub>2</sub>O. Emulsions are often used.
2. Produces cross-linked flexible film.
3. Processing energy 10 – 12 GJ/tonne
4. No tacticity control.

### Ziegler

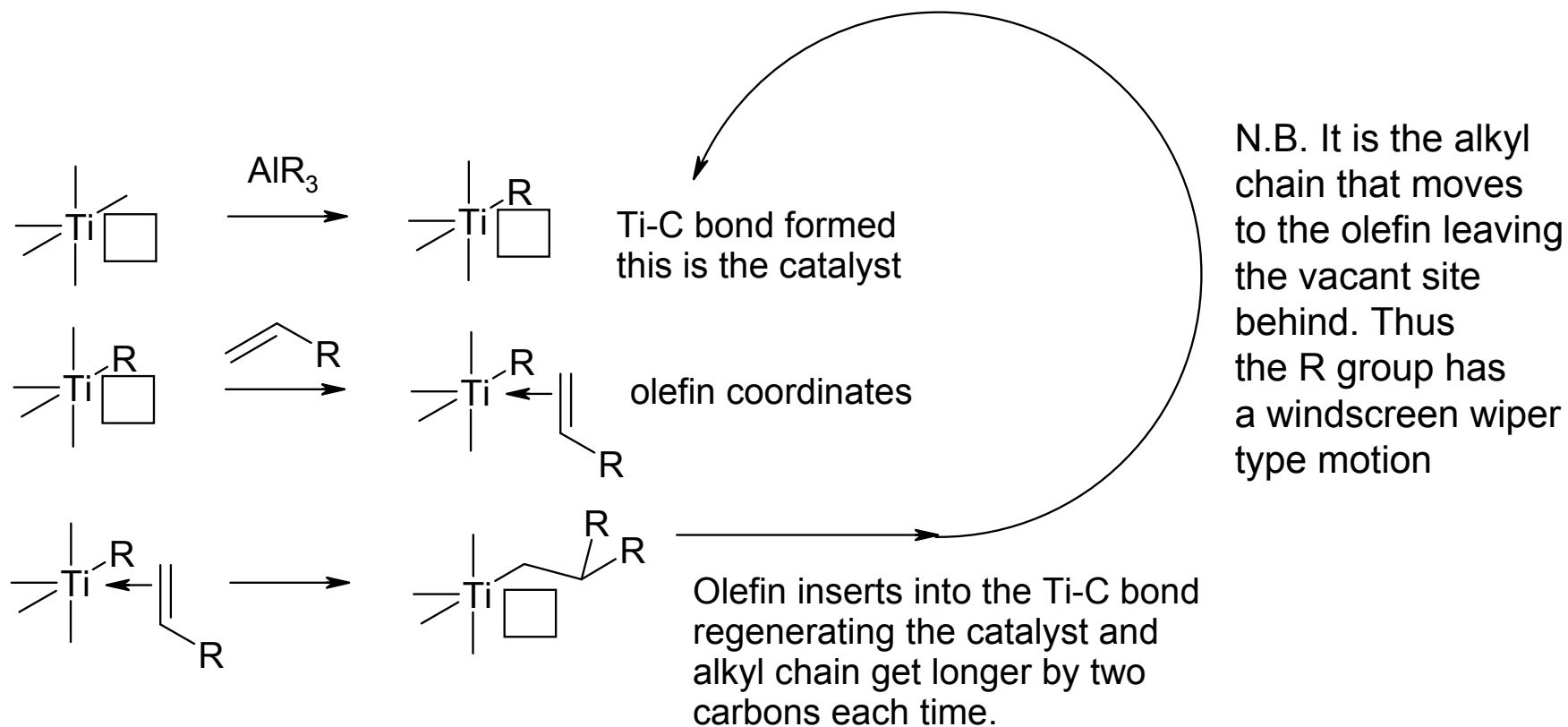
1. Linear high-density and low-density polymer.
2. Tacticity control possible.
3. Processing energy 6 – 7 GJ/tonne
4. Cannot be run in H<sub>2</sub>O.

The latest catalysts  
are metallocenes



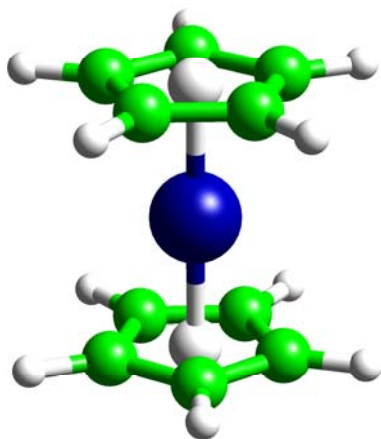
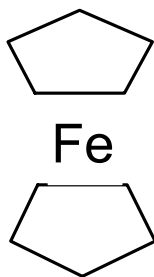
## Reaction Mechanism proposed by Cossee

TiCl<sub>3</sub> - octahedral geometry about a Ti on the surface with a vacant coordination site.

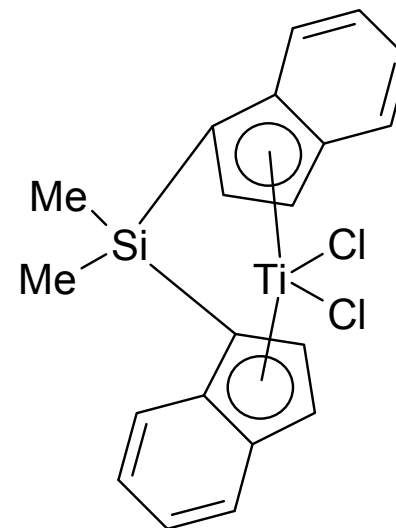


The origin of the stereo-regularity is much discussed - often in terms of the environment of the incoming olefin.

## Metallocene catalysts

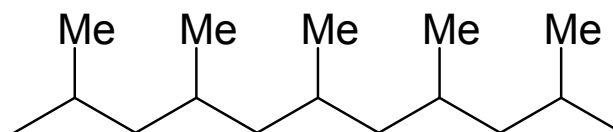
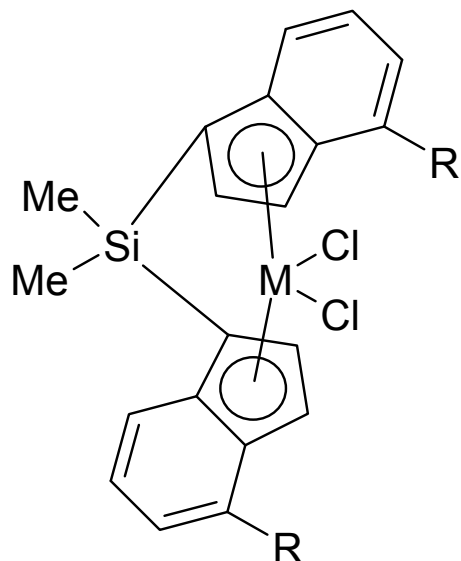


Ferrocene is the best known metallocene

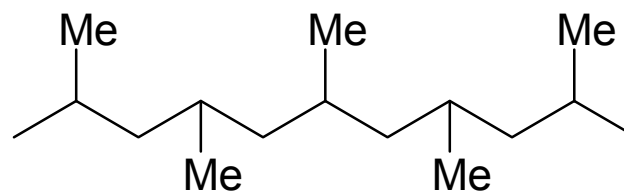


Metallocene Ziegler catalyst

[Kaminsky catalyst](#)



iso-tactic polypropylene

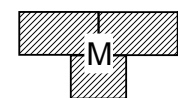
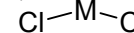
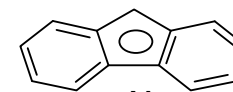
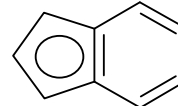
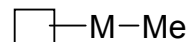
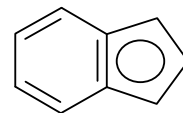
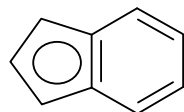
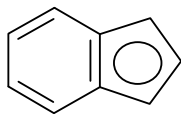
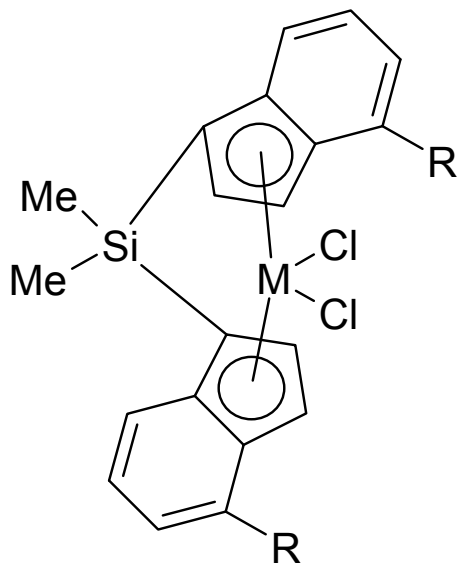


syndiotactic polypropylene

If  $M = \text{Ti}$  and  $R = \text{H}$  propene gives isotactic polypropylene

If  $M = \text{Zr}$  and  $R = \text{H}$  propene gives syndiotactic polypropylene

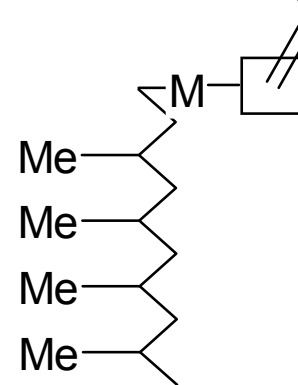
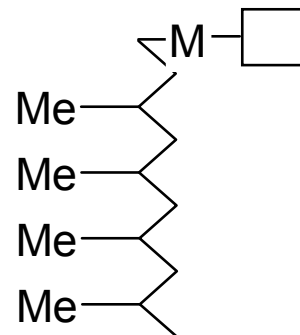
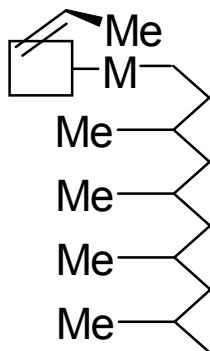
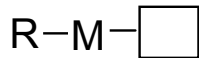
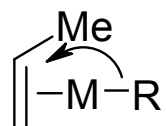
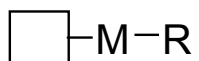
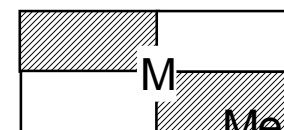
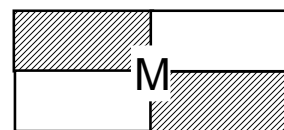
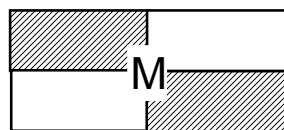
If  $M = \text{Zr}$  and  $R = \text{Bu}^t$  propene gives isotactic polypropylene



Catalyst precursor

actual catalyst is cationic

Product always syndiotactic



Windscreen wiper motion of alkylchain

No large steric interactions  
olefin coordinates

Alkyl migration to olefin  
vacant site restored

olefin coordinates other way up

# Co-polymers

If two or more monomers are used at the same time there are  
Many possibilities some of the more important types are:

Random copolymer: -A-A-B-B-A-A-A-B-A-A-B-B-A-B-A-A-A-B-A-A-A

Alternating copolymer: -A-B-A-B-A-B-A-B-A-B-, or  $-(-A-B-)_n-$

Block copolymer: -A-A-A-A-A-A-A-B-B-B-B-B-B-B-A-A-A-A-A-A-A-B-B-

Graft copolymer: -A-

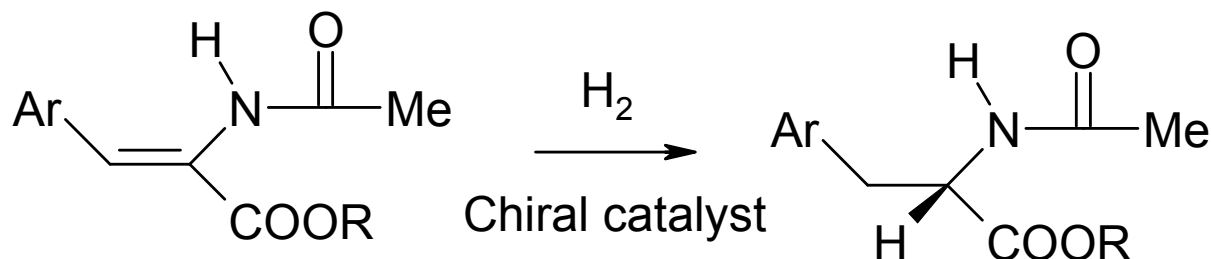


ABS - Poly(Acrylonitrile, Butadiene, Styrene) is a good example this is an attempt to do three things at the same time poly-acrylonitrile gives strong fibres, poly-butadiene is a rubber and poly-styrene is hard. If you hit ABS with a hammer it will not break (the rubber absorbs the shock).

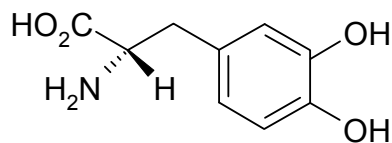
# Chiral Catalysis

Non-chiral starter + Chiral catalyst = Chiral product

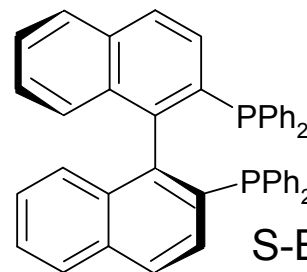
Nature does this very well – enzyme catalysts often produce chiral products. Two examples Hydrogenation and Epoxidation



Catalytic hydrogenation of olefins. The most effective heterogeneous catalyst is  $\text{PtO}_2$  (Adam's catalyst) and the best (and equally effective per mole of Pt) homogeneous catalyst is  $(\text{PPh}_3)_3\text{RhCl}$  (Wilkinson's catalyst). Putting chiral ligands on Wilkinson's catalyst makes the catalyst chiral.



L-DOPA



100mg €55  
Rh cpx 10mg €26

S-BINAP

C & E News September 5<sup>th</sup> 2005 Cover Story

Chiral catalysis.

Some extracts

"From a process development viewpoint, catalysis in the production of chiral compounds is essential, because we are always looking for cost-effective and environmentally friendly solutions," Trevor Laird, editor of *Organic Process Research & Development*, told C&EN.

"Catalysis offers the possibility of both."

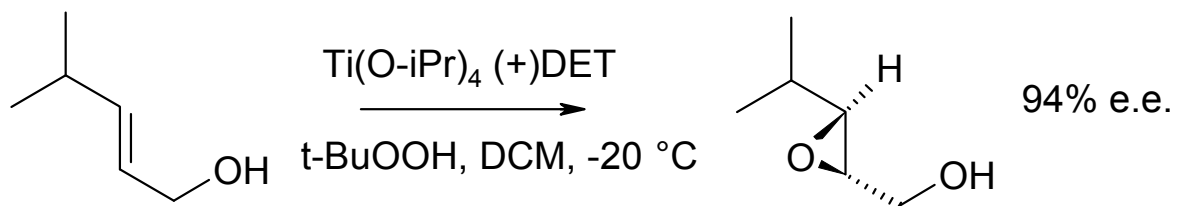
Yongkui Sun, director of [Merck's](#)

Catalysis & Reaction Discovery & Development Laboratory, presented his case for catalysis in the pharmaceutical industry.

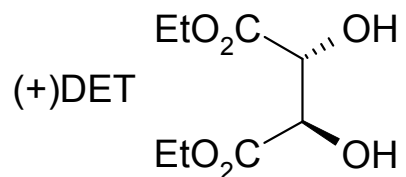
The Pfizer group has designed the C1-symmetrical bisphosphine ligand trichickenfootphos (TCFP), which is used in synthesizing Pfizer's new -amino acid-based drug, pregabalin.

"Then we added TCFP and continued the hydrogenation, and in about eight hours we had greater than 99% conversion and 96% ee,"

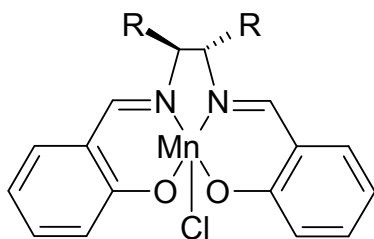
## Sharpless asymmetric epoxidation of allylic alcohols



allylic alcohol

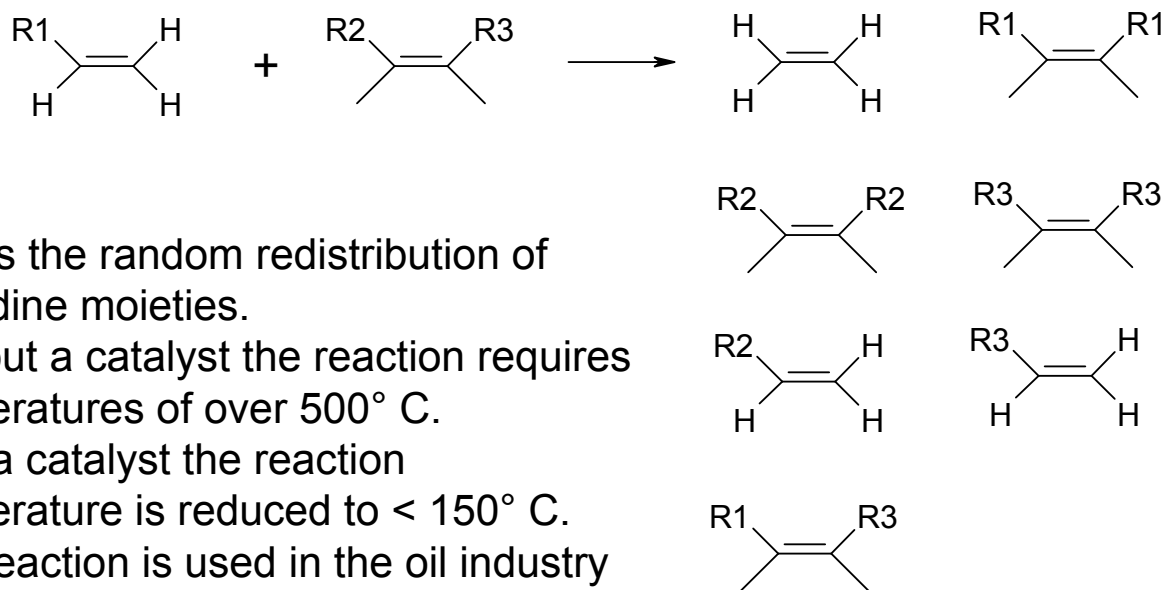


## Jacobsen asymmetric epoxidation of olefins



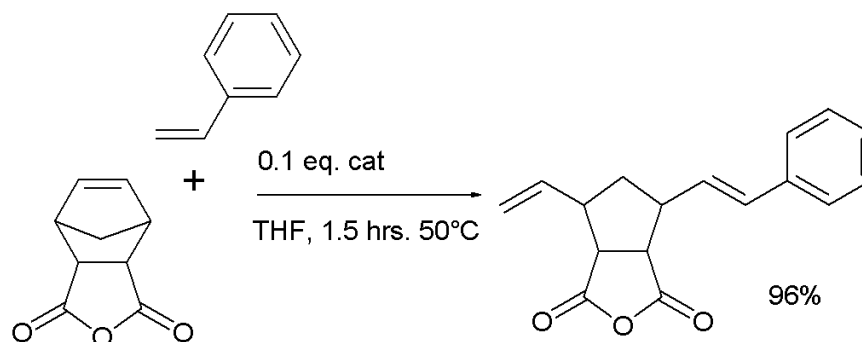
Household bleach is the oxidant

## Olefin or Alkene Metathesis



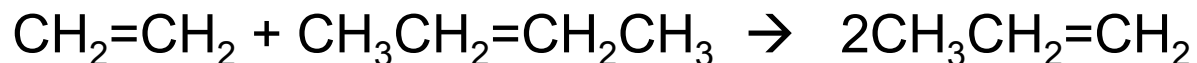
- This is the random redistribution of alkylidene moieties.
- Without a catalyst the reaction requires temperatures of over 500° C.
- With a catalyst the reaction temperature is reduced to < 150° C.
- The reaction is used in the oil industry and for synthesis.
- Catalysts for Industry use Mo halide + Lewis acid and for synthesis Grubbs and Schrock catalysts are used.
- Chauvin, Grubbs and Schrock got the Nobel prize for this in 2005.

### Synthetic example



## Some industrial applications of Olefin Metathesis

### 1. Propene production



### 2. In the polymer field ring-opening metathesis polymerization

(ROMP) of cycloalkenes. Dicyclopentadiene ROMP is an attractive process for making the polymer for golf carts, snow mobile hoods etc.

[Ref](#)