



**IFP : a research and industrial development  
and training center**



**Active in the fields of :**

- oil, gas and coal, their uses, in particular in transport,
- the new energy and environmental technologies

**IFP's staff :**           1,125 researchers  
                                  239 doctoral and post doctoral researchers

**An applied research :** a portfolio of more than 12,000 living patents

**A policy of commercial development of the results** through the licensing of processes, software, equipment, etc.



# In refining-petrochemicals

## Objectives are :

- to design refining and petrochemical processes that are clean and efficient
- to diversify sources of energy for the production of fuels and hydrogen
- to control emissions of CO<sub>2</sub>

## Skill areas :

catalysis, separation technologies, analysis and physico-chemical characterization, thermodynamics, chemical engineering, modeling of processes, molecular modeling, high-flow tests and experiments

**1,800 industrial units worldwide**

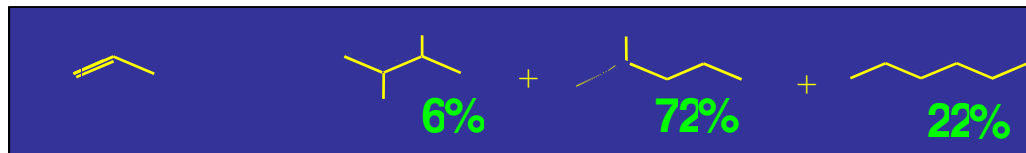
## Recent achievements :

**Esterfip-H:** biodiesel production process by transesterification of vegetable oils. Marketed by Axens.

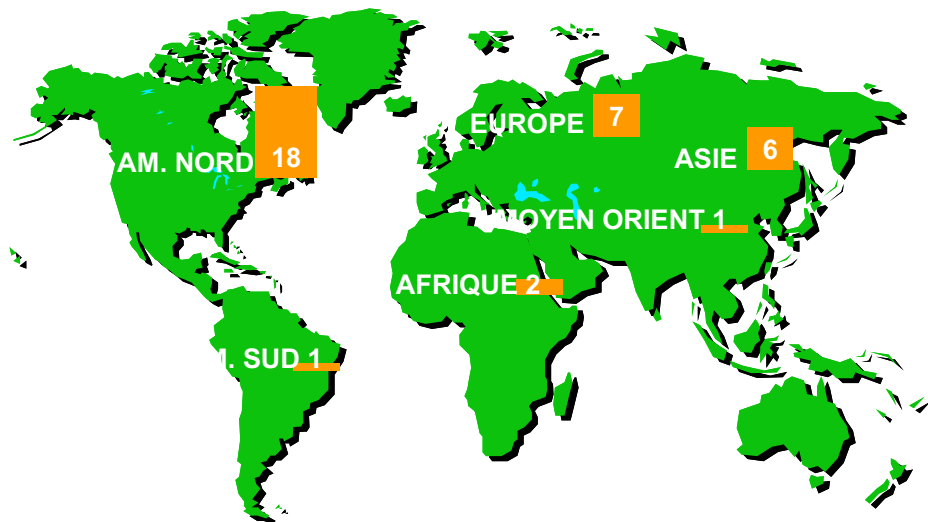


Esterfip-H unit under construction in Sète, France.

# Dimersol Process : for gasoline



Dimerization of propylene into iso-hexenes : octane booster for gasoline

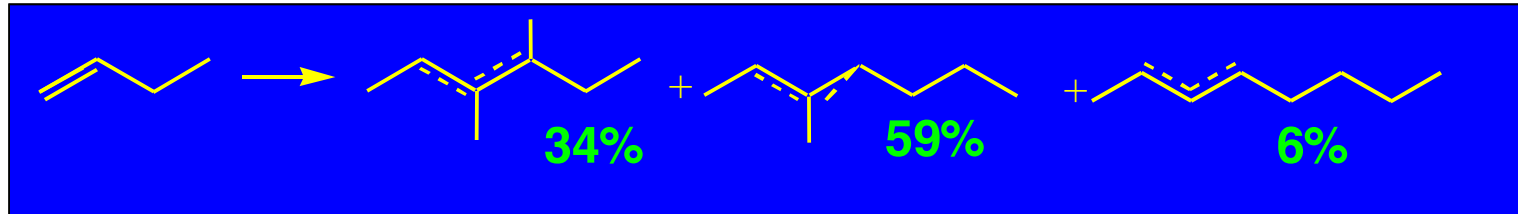


- One of the first examples of application of homogeneous catalysis in refining industry

- First industrial unit in 1977
- 35 units in operation worldwide
- 3.5 Mt products / year



# Dimersol Process : for chemistry



**Dimerization of butenes into octenes : raw materials for the production of PVC phthalate plasticizers**

- **First industrial unit in 1980**
- **0.4 Mt products / year**



# Non-Aqueous Ionic Liquids

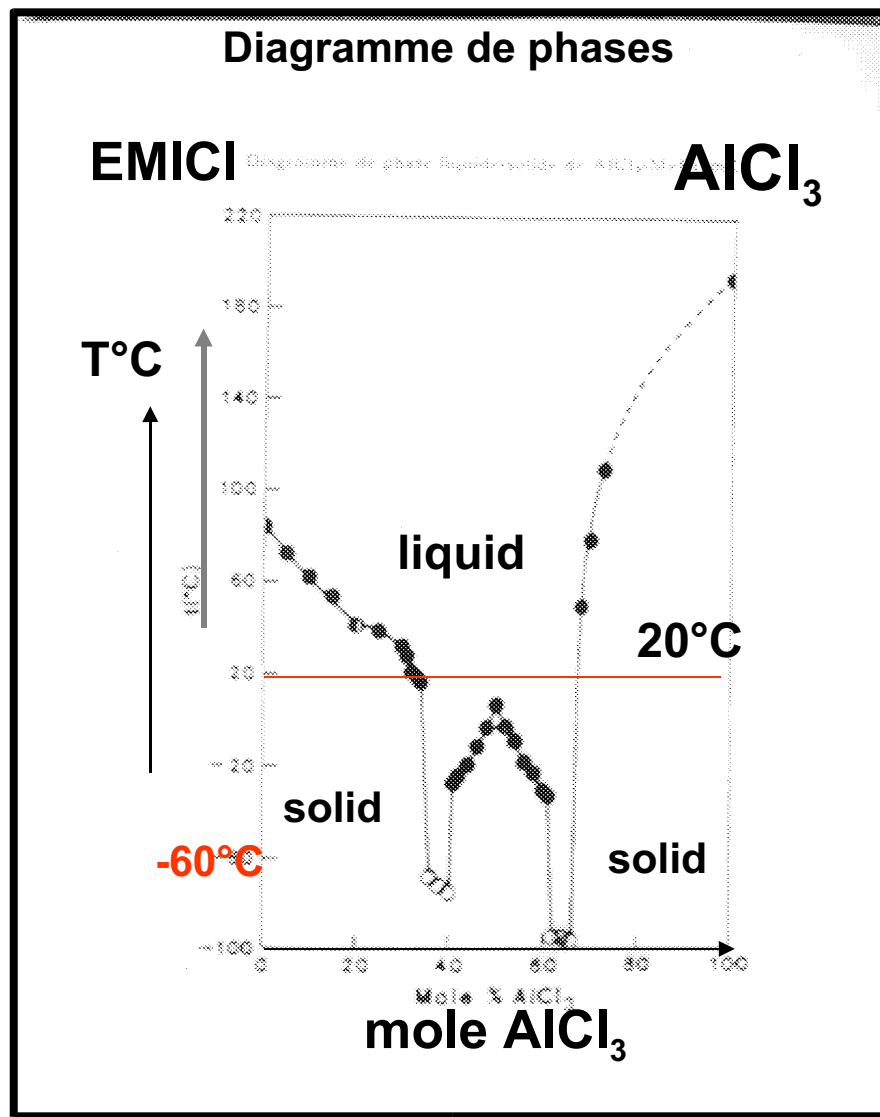


**EMIC**

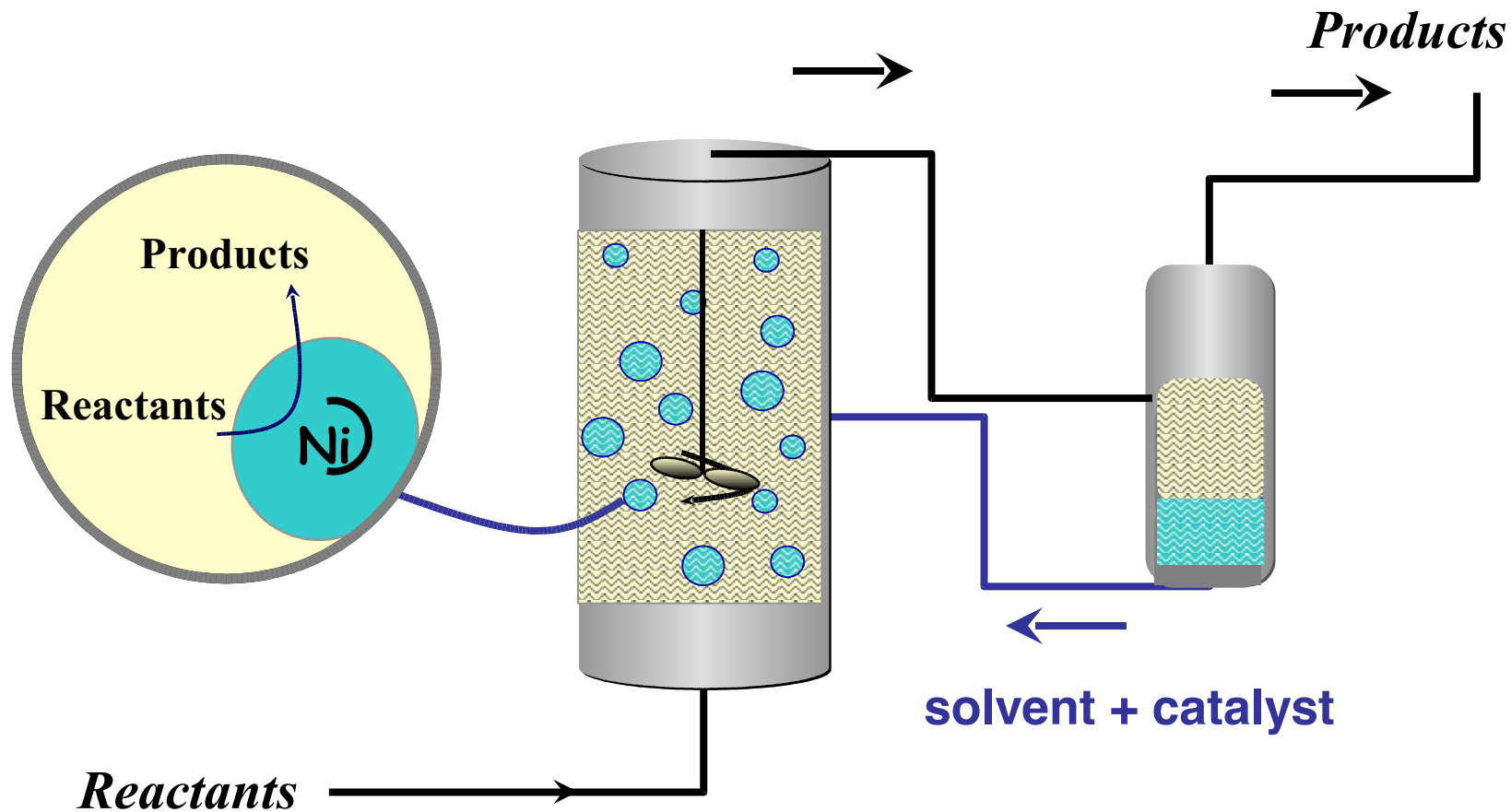
Ethyl Methyl Imidazolium  
Chlorure

From non aqueous electrolytes  
for batteries

...to a new class of solvents for  
catalysis



# Liquid-Liquid Biphasic Catalysis



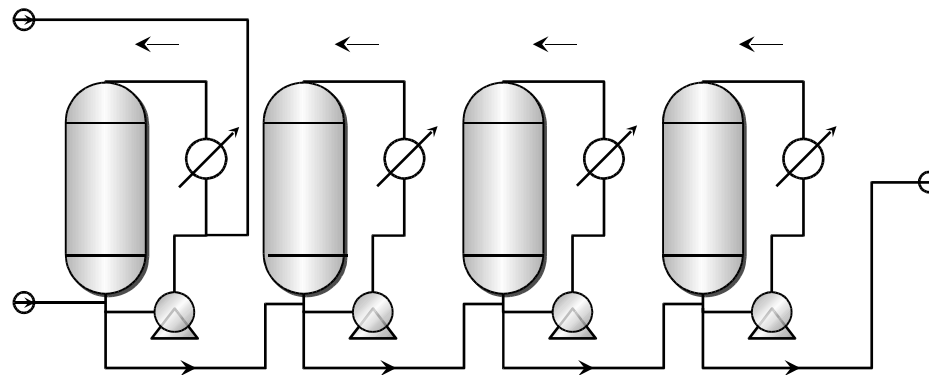
# Dimersol process

**20t/h feed rate**

**4 reactors of 120 m<sup>3</sup>**

*Catalyst*

*Butenes*



toward washing  
and distillation  
section

# Difasol process

**reactor of 50 m<sup>3</sup>**

*Products*

toward distillation  
section

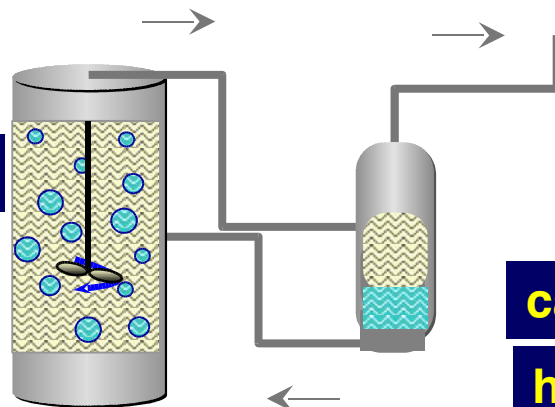
**catalyst consumption divided by 10**

**higher yield in dimers**

*Reactants*

*Active Phase*

*containing the catalyst*





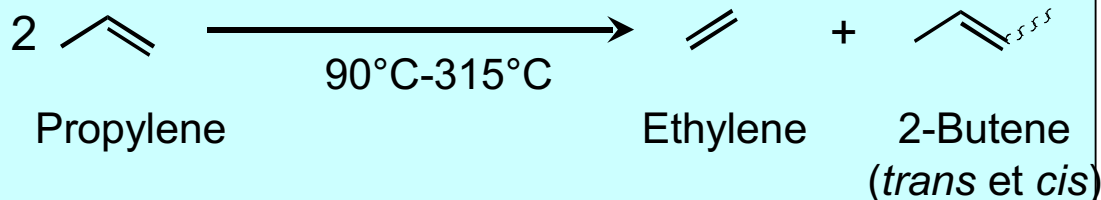
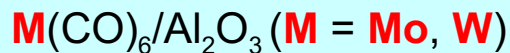
# Alphabutol process

- **Dimerization of ethylene into 1-butene (Ti homogeneous catalyst)**
- **1-Butene is used as co-monomer for polyethylene manufacture**



- **First industrial unit in 1987**
- **20 units in operation**
- **0.4 Mt/Y**
- **2005 : 3 new units 110 000t/Y total capacity**

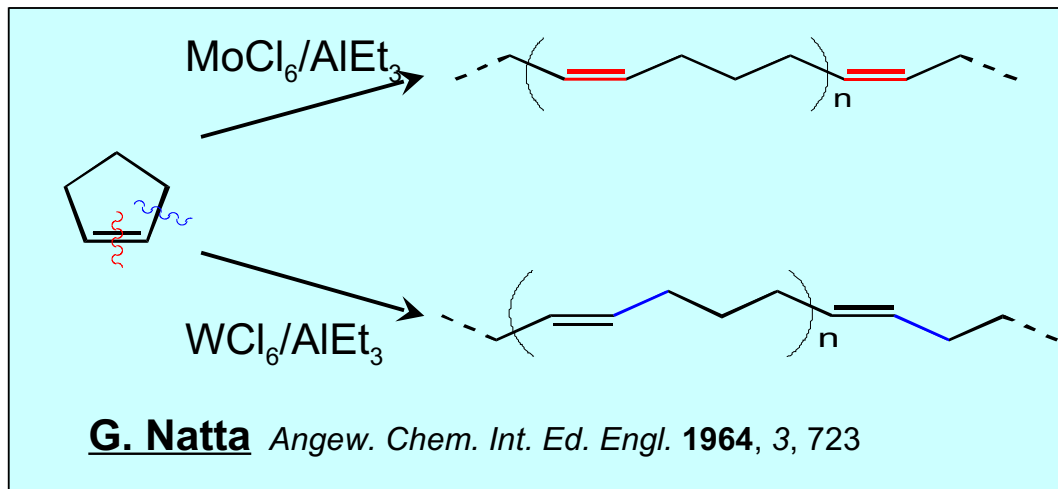
# Heterogeneous catalysis...



1964 :  
a magic year...

# Homogeneous catalysis

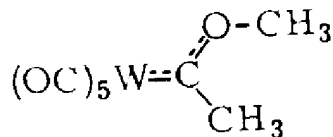
**Banks et Bailey** (Philips Petroleum Co.)  
*I. & E. C. Product Research and Development*  
1964, 3, 170-173.



**G. Natta** *Angew. Chem. Int. Ed. Engl.* 1964, 3, 723

# Metallocarbene

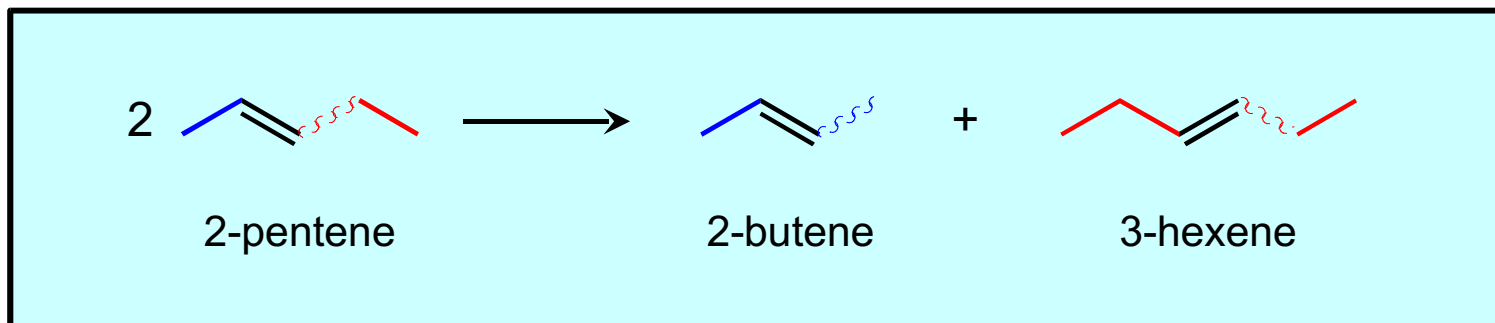
Wir glauben daher für  $W(CO)_5(COCH_3)(CH_3)$  eine Struktur folgender Art annehmen zu dürfen.



**E. O. Fischer** *Angew. Chemie* 1964, 76, 645

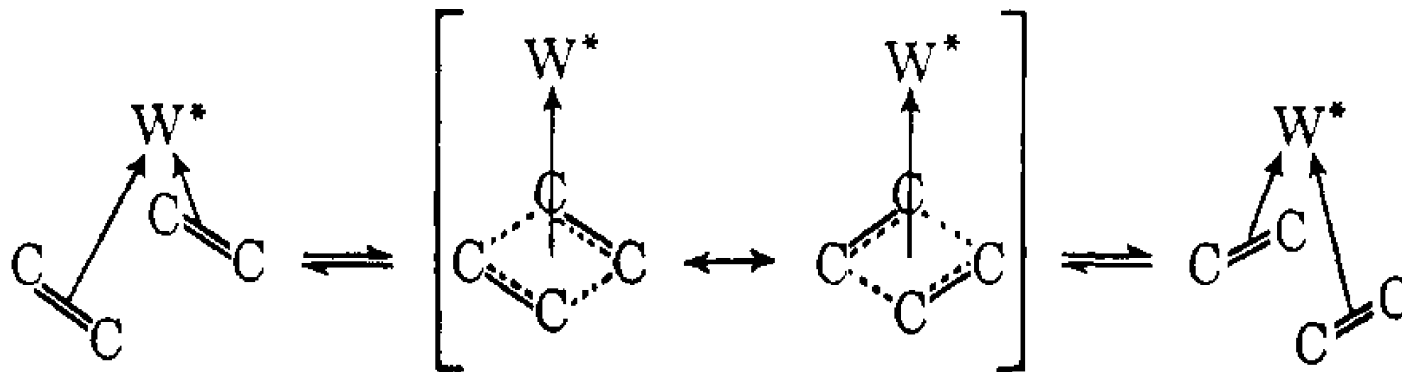
a new metal-carbon bond

# Disproportionation of olefins



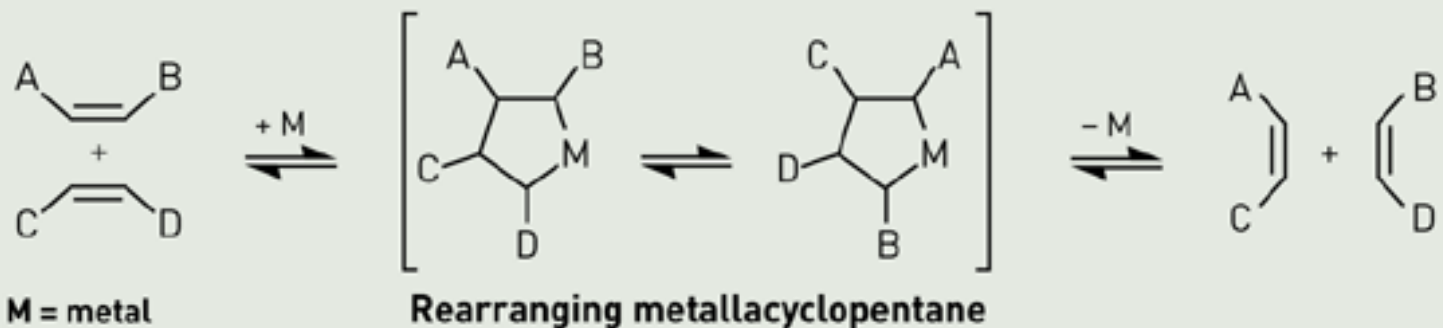
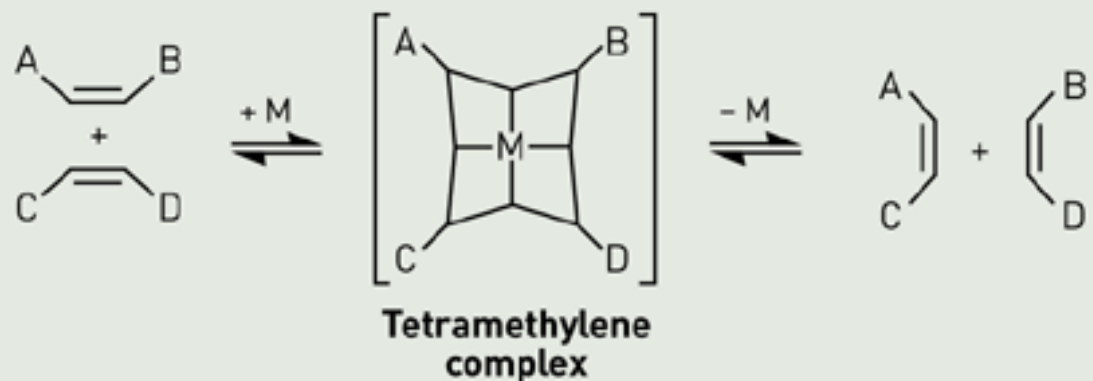
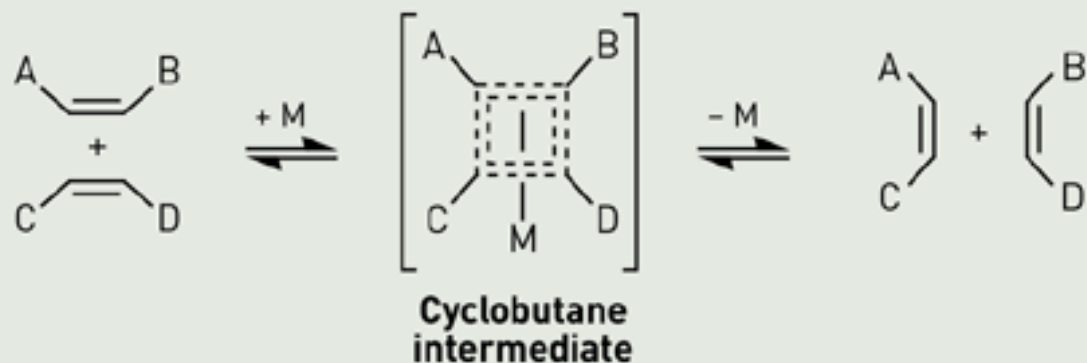
# "Pairwise" mechanism

Transalkylidenation

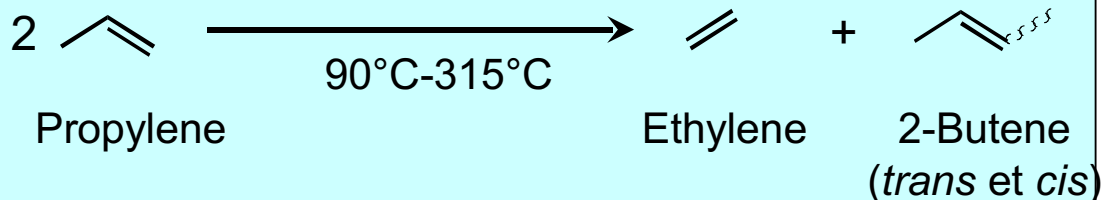
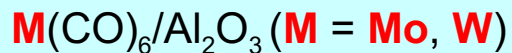


## WRONG TURNS

Unusual intermediates proposed initially have since been rejected



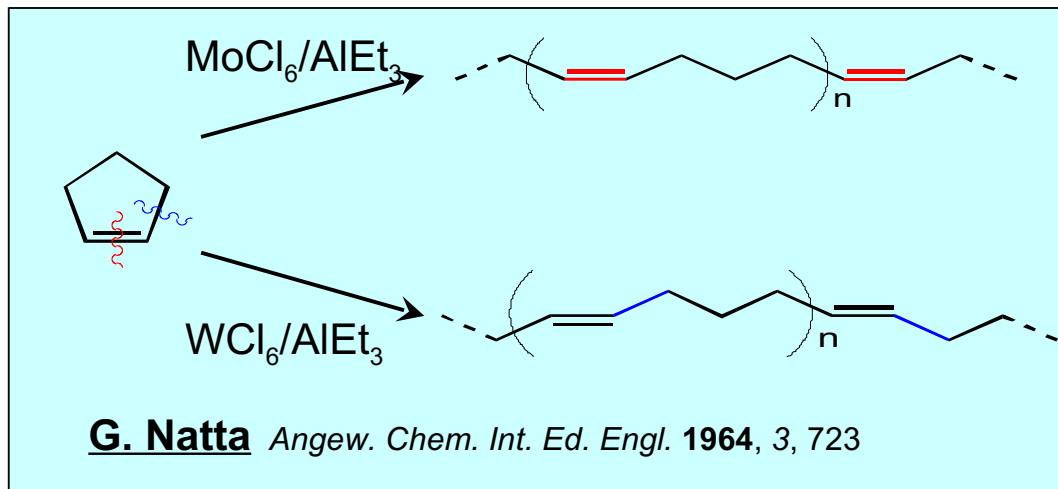
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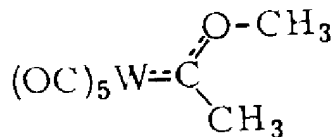
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**Banks et Bailey** (Philips Petroleum Co.)  
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# Metallocarbene

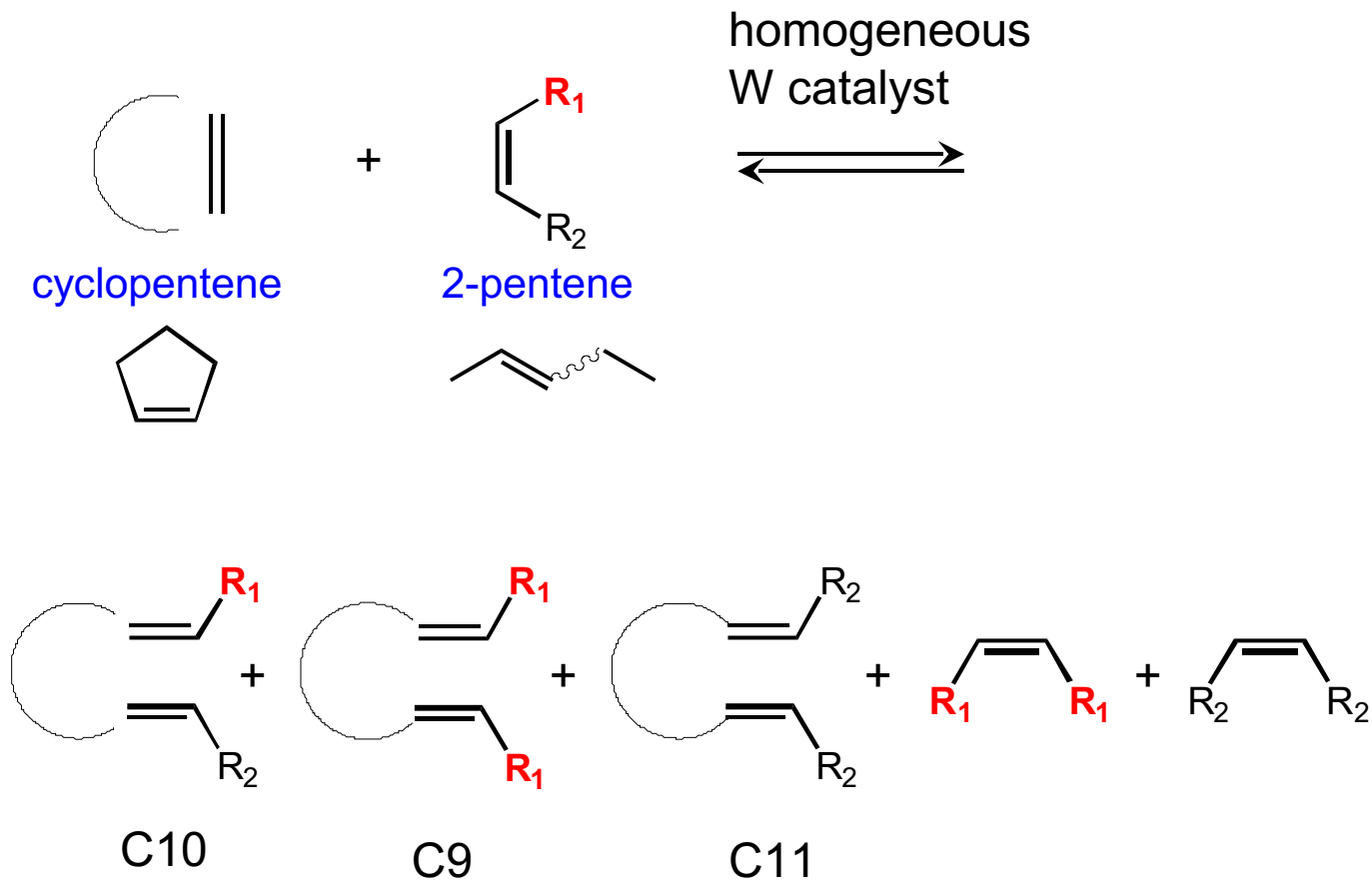
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a new metal-carbon bond

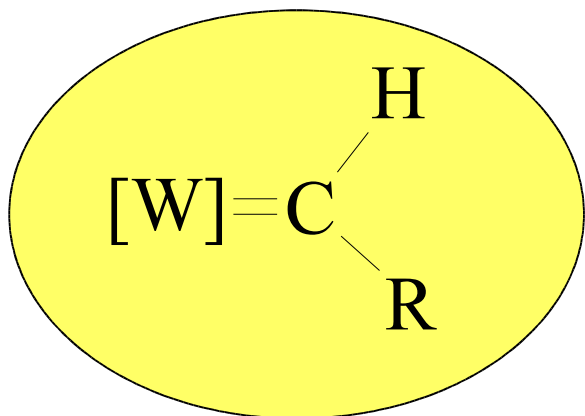
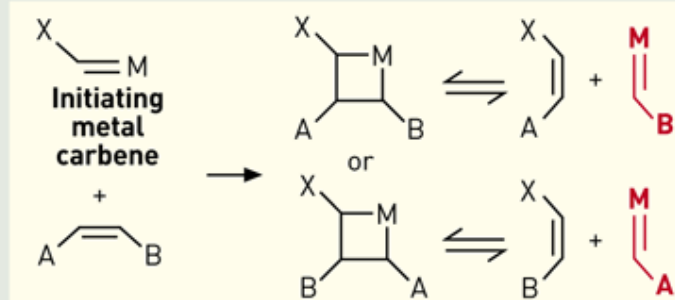
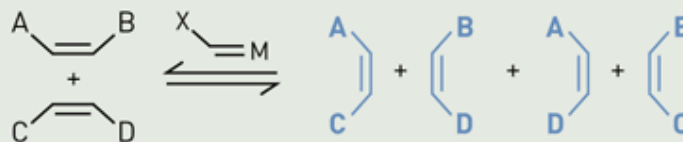
# Co-reaction of cyclopentene with 2-pentene



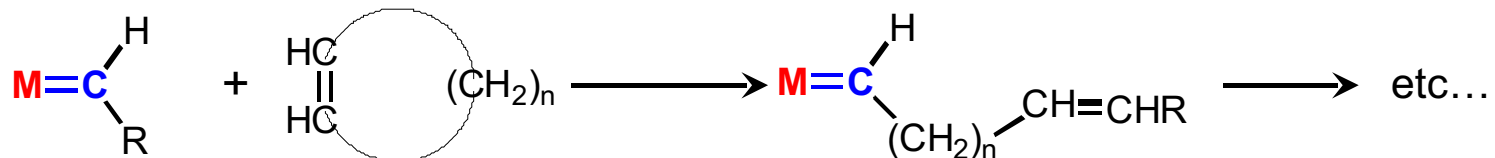
## MECHANISM

Olefin metathesis is a chain reaction

Overall reaction



## Carbene mechanism



Linear polymers with high molecular weight : observed at the beginning of the reaction



# Formation of the metallocarbene :



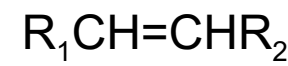
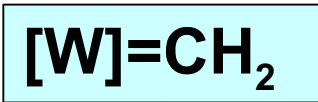
TABLEAU

*Produits de réaction entre  $\text{W}(\text{Cl})_6$ ,  $\text{M}(\text{CH}_3)_n$  et une oléfine*

Oléfine	W (Cl) <sub>6</sub> (g)	Coréactif (**)	Solvant	T (°C)	Oléfine W (Cl) <sub>6</sub>	% molaires par rapport au tungstène mis en œuvre		
						Méthane + éthane	Propy- lène	Butène-1
Butène-2 . . . . .	0,5	LiCH <sub>3</sub>	Benzène (15 ml)	4	10	22	6,3	-
Butène-2 . . . . .	0,5	Sn (CH <sub>3</sub> ) <sub>4</sub>	Benzène (15 ml)	4	10	3,5	3,6	-
Hexène-3 . . . . .	0,2	Sn (CH <sub>3</sub> ) <sub>4</sub>	Benzène (30 ml)	4	10	n. d.	-	2,6
Pentène-2 (*) . . .	0,5	LiCH <sub>3</sub>	Benzène (15 ml)	4	10	22	4,4	4,7
	0,2	Sn (CH <sub>3</sub> ) <sub>4</sub>	Benzène (30 ml)	4	10	10	9,6	10,4
	0,2	Sn (CH <sub>3</sub> ) <sub>4</sub>	Chloro- benzène (30 ml)	-20	10	n. d.	8,5	6,4
	0,4	Sn (CH <sub>3</sub> ) <sub>4</sub>	Chloro- benzène (30 ml)	-20	2,5	n. d.	6,8	6,9

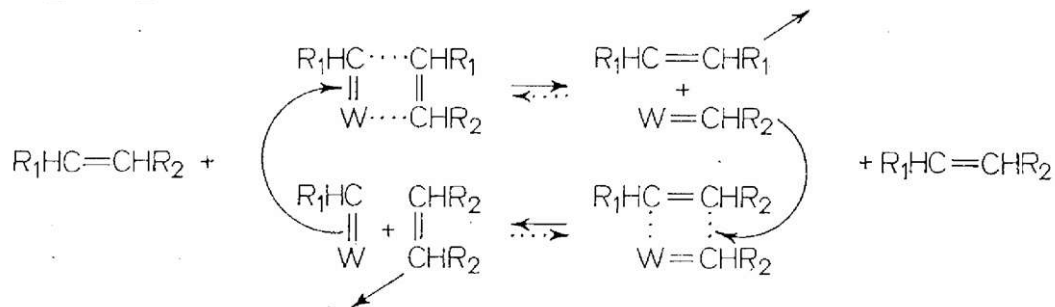
(\*) On observe la formation de butène-2 et d'hexène-3 issus de la disproportion du pentène-2 en excès.

(\*\*) Sn/W = 2; Li/W = 2.

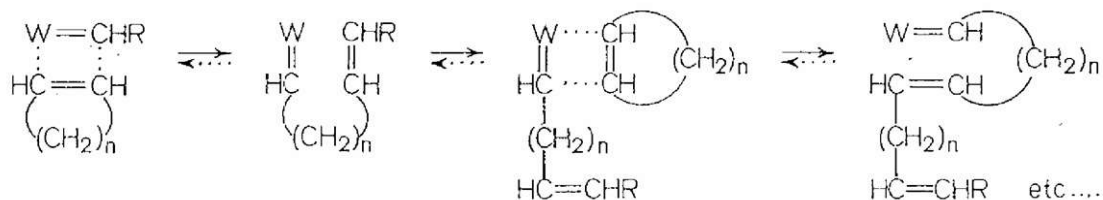


formation of  
α-olefins

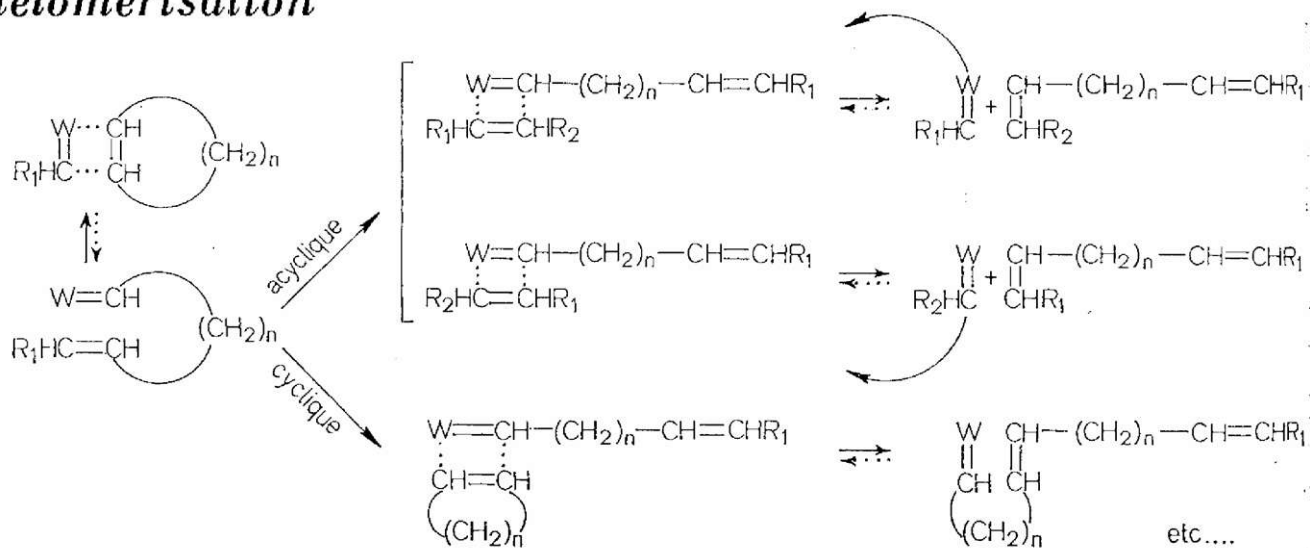
## Réaction de disproportion



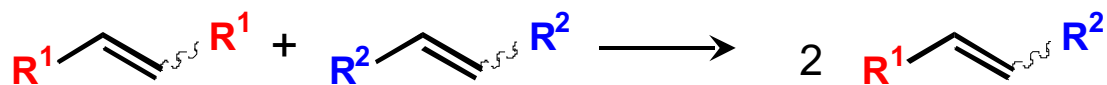
## Réaction de polymérisation



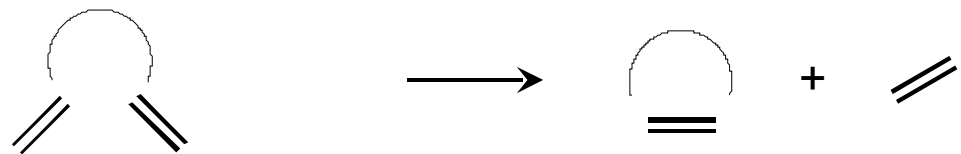
## Réaction de télomérisation



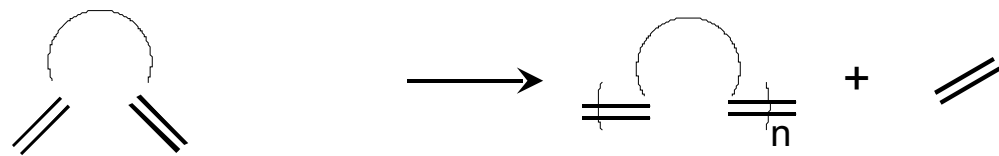
*Cross Metathesis (CM)*



*Ring Closing Metathesis (RCM)*



*Acyclic Diene Polymerization (ADMET)*



*Ring Opening Metathesis (ROMP)*

