



**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 CO₂

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

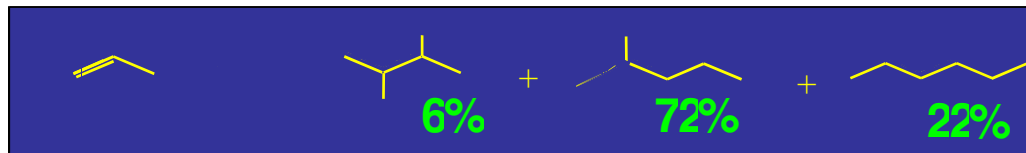
Recent achievements :

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

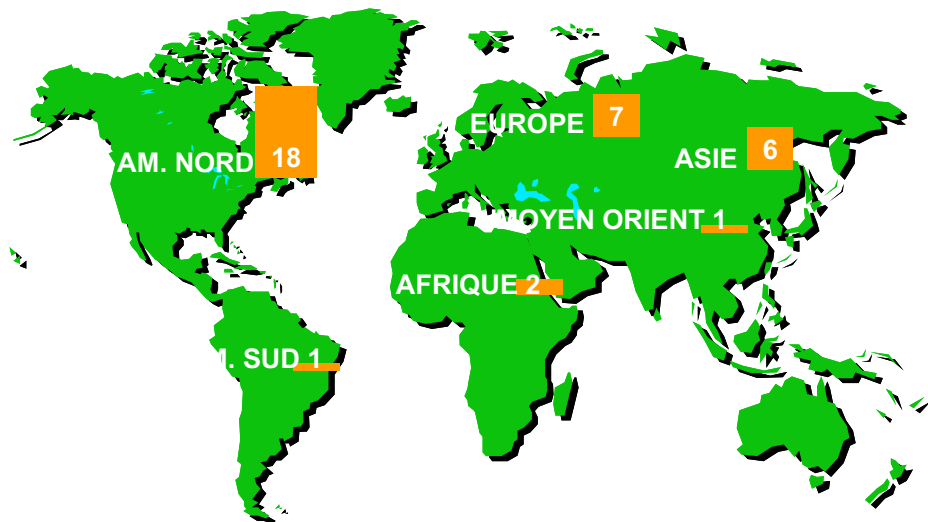


Esterfip-H unit under construction in Sète, France.

Dimersol Process : for gasoline



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

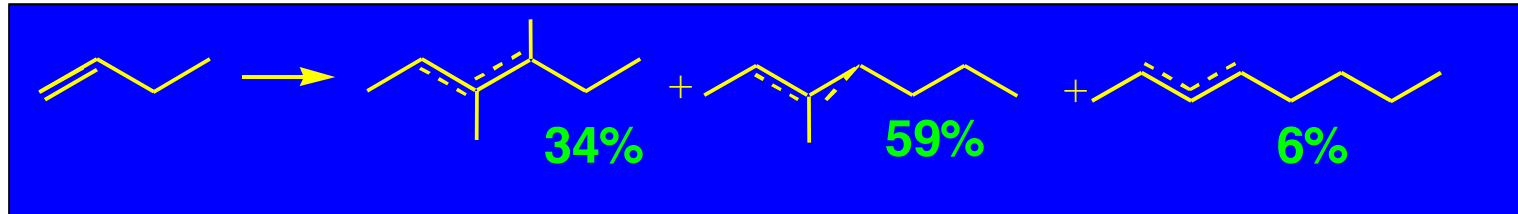


- One of the first examples of application of homogeneous catalysis in refining industry

- 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

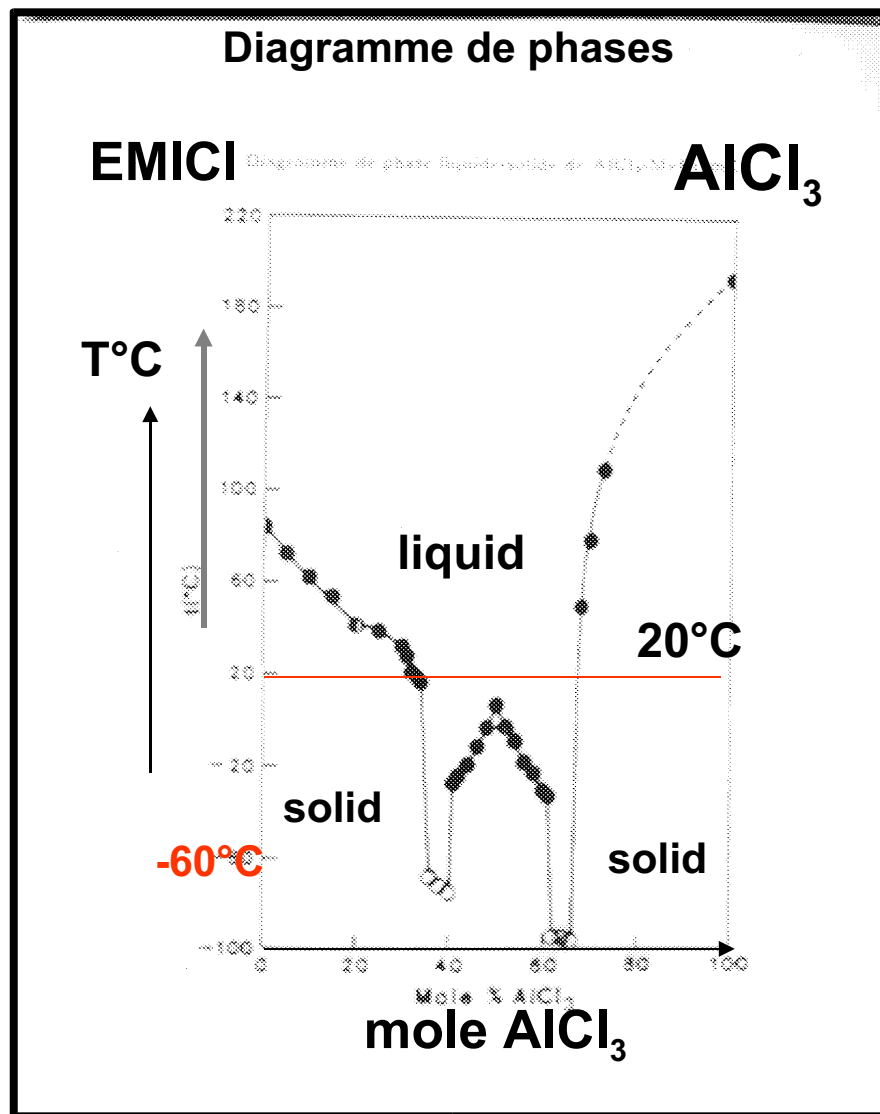


EMIC

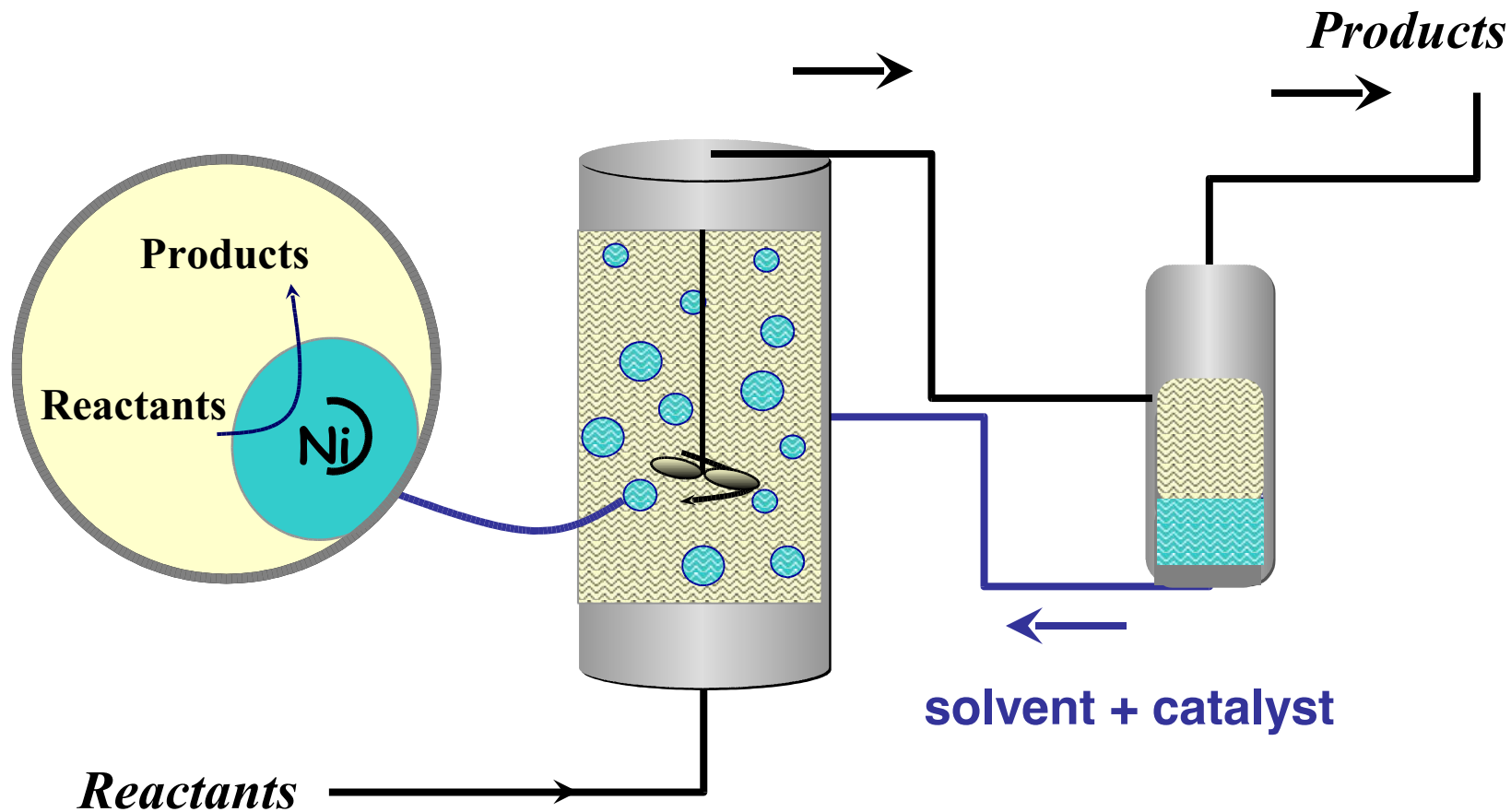
Ethyl Methyl Imidazolium
Chlorure

From non aqueous electrolytes
for batteries

...to a new class of solvents for
catalysis



Liquid-Liquid Biphasic Catalysis



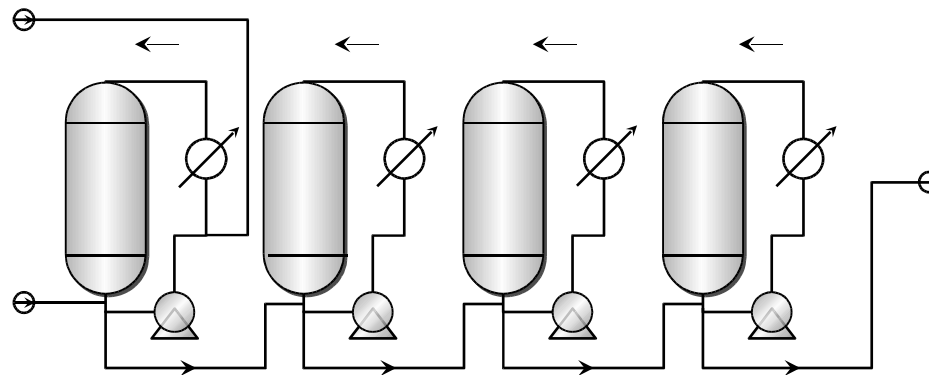
Dimersol process

20t/h feed rate

4 reactors of 120 m³

Catalyst

Butenes



toward washing
and distillation
section

Difasol process

reactor of 50 m³

Products

toward distillation
section

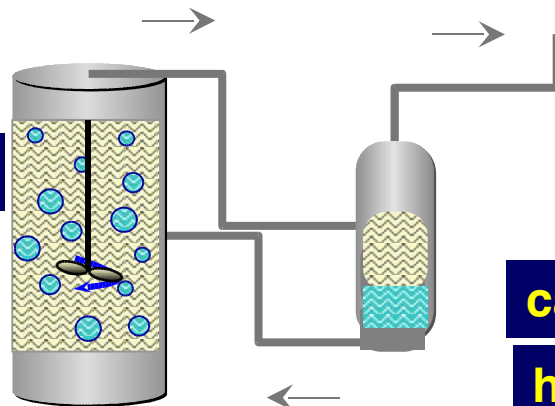
catalyst consumption divided by 10

higher yield in dimers

Reactants

Active Phase

containing the catalyst



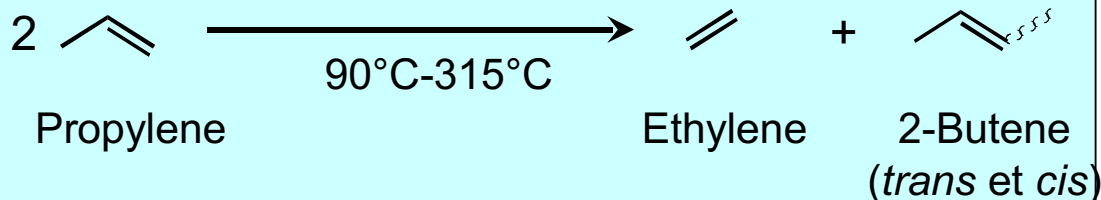
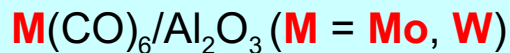
Alphabutol process

- **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**

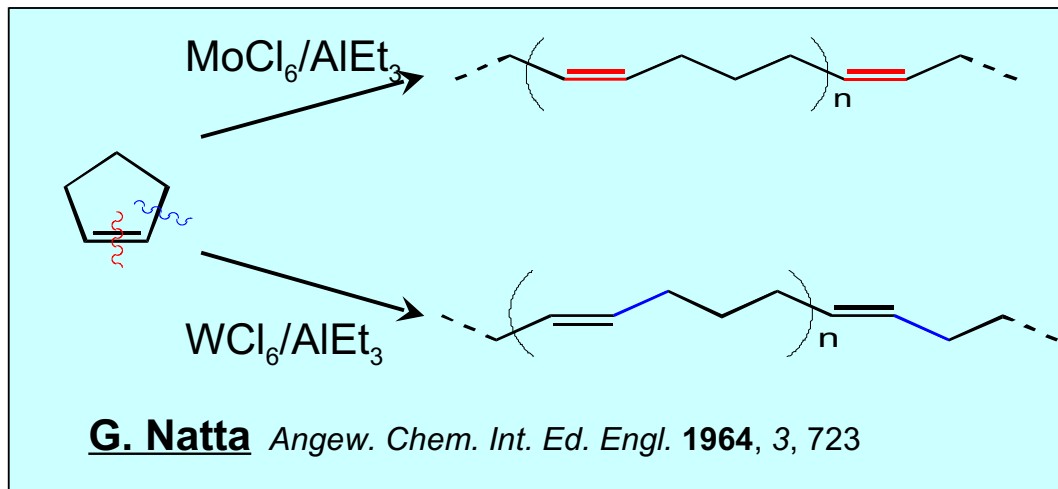
Heterogeneous catalysis...



1964 :
a magic year...

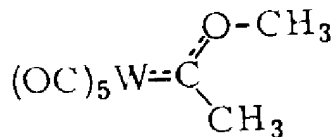
Homogeneous catalysis

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



Metallocarbene

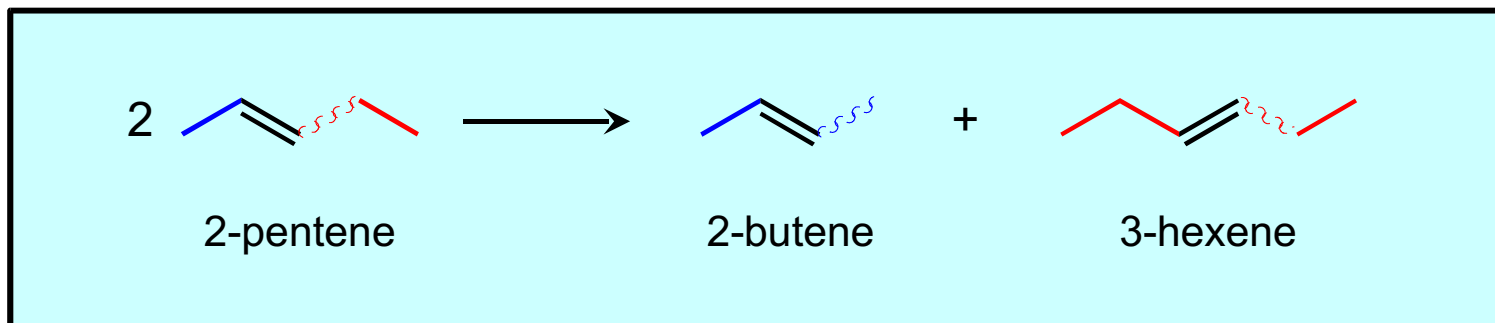
Wir glauben daher für $W(CO)_5(COCH_3)(CH_3)$ eine Struktur folgender Art annehmen zu dürfen.



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

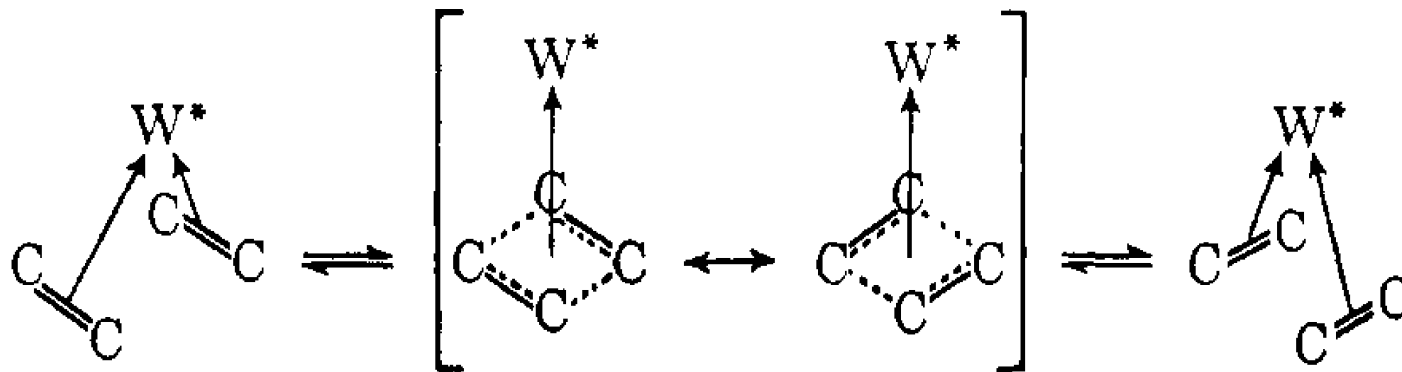
a new metal-carbon bond

Disproportionation of olefins



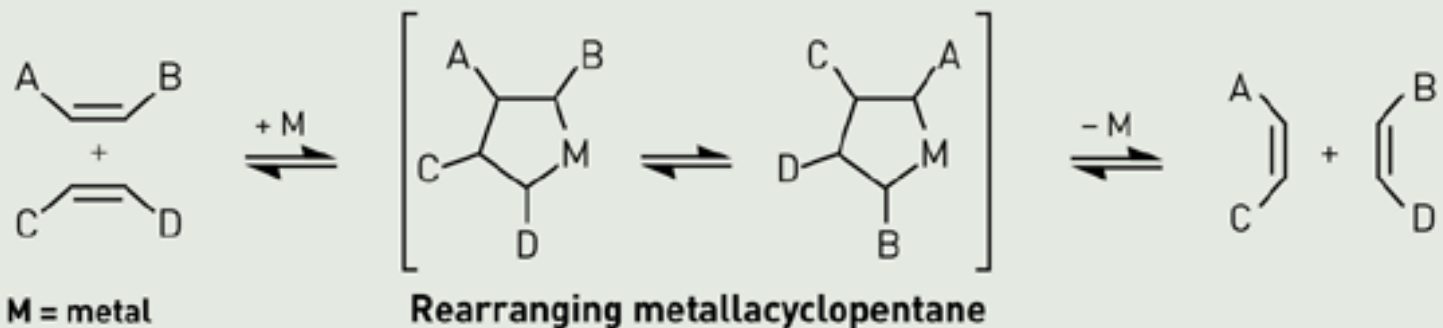
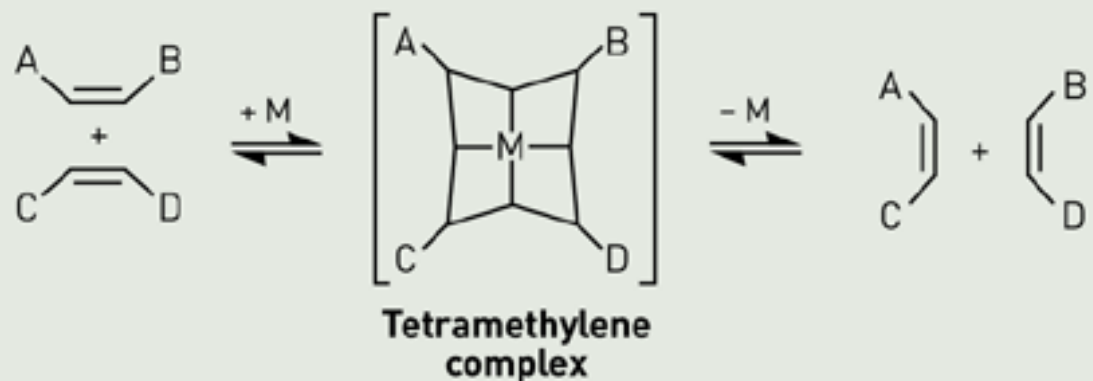
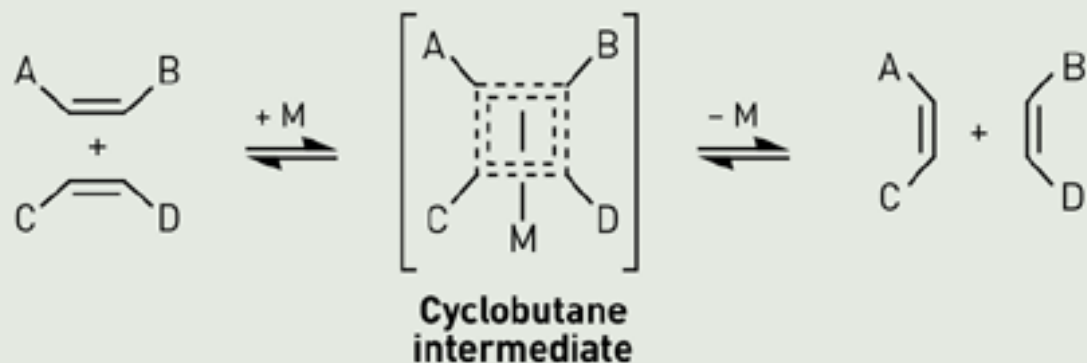
"Pairwise" mechanism

Transalkylidenation

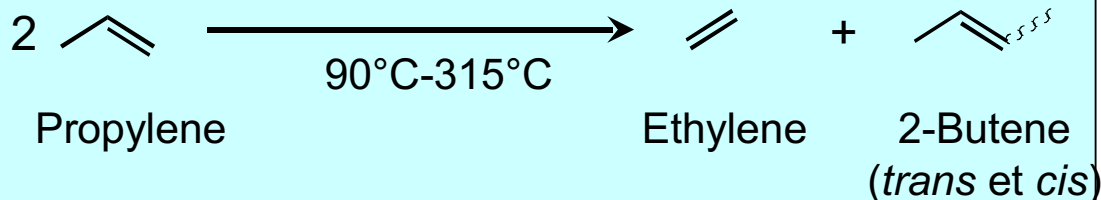
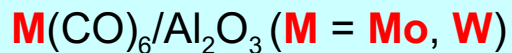


WRONG TURNS

Unusual intermediates proposed initially have since been rejected



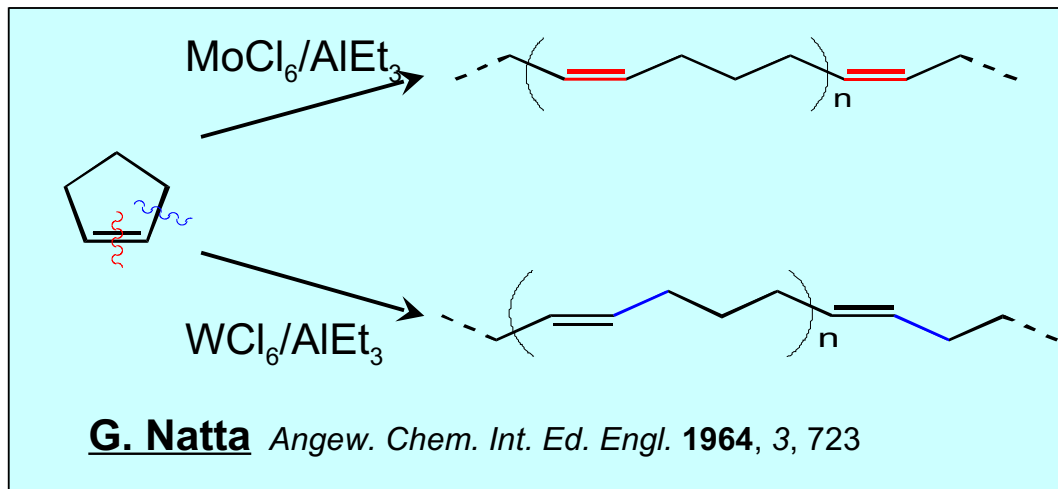
Heterogeneous catalysis...



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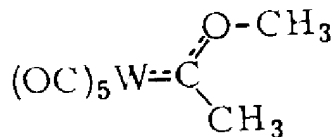
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Metallocarbene

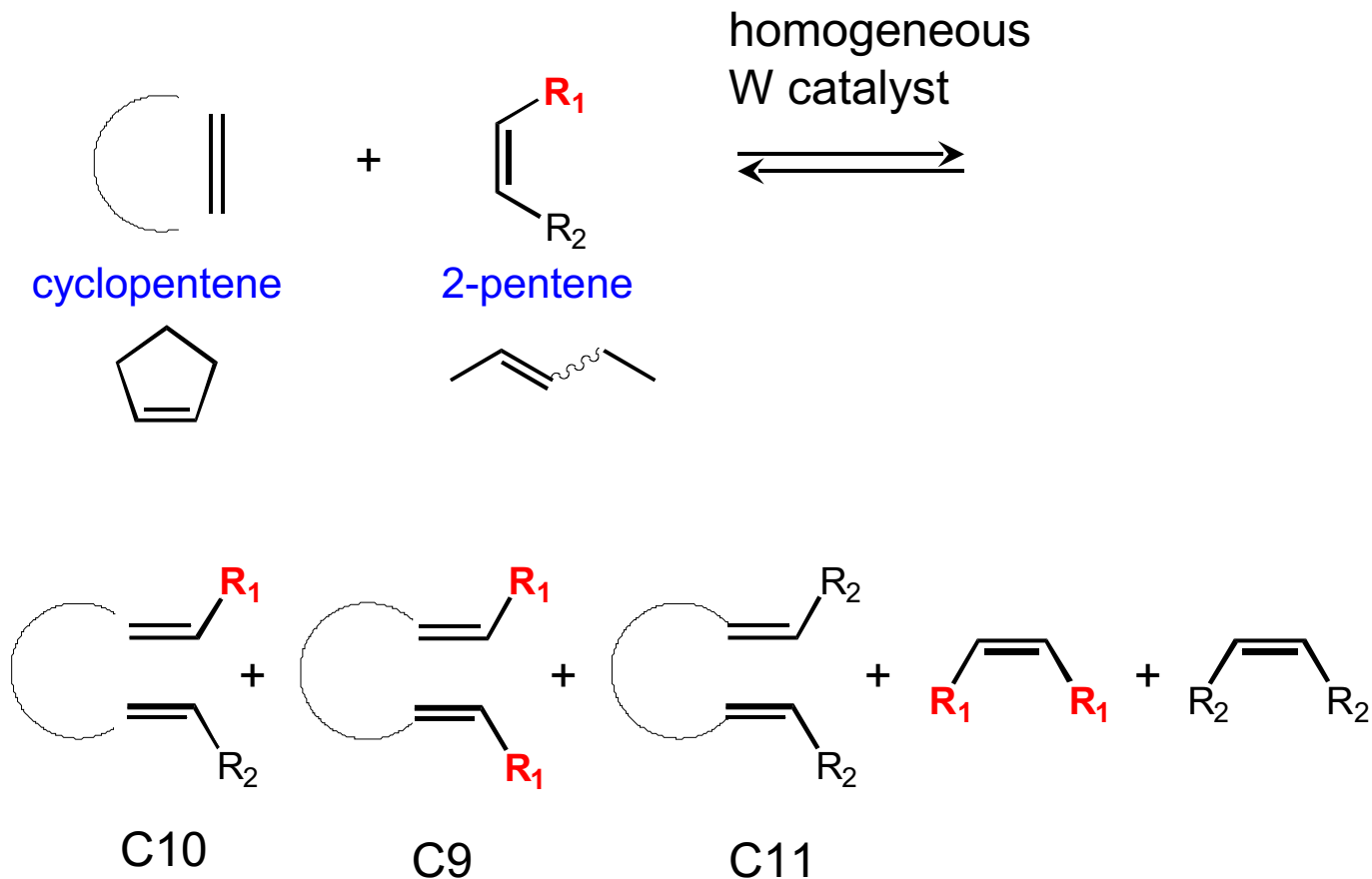
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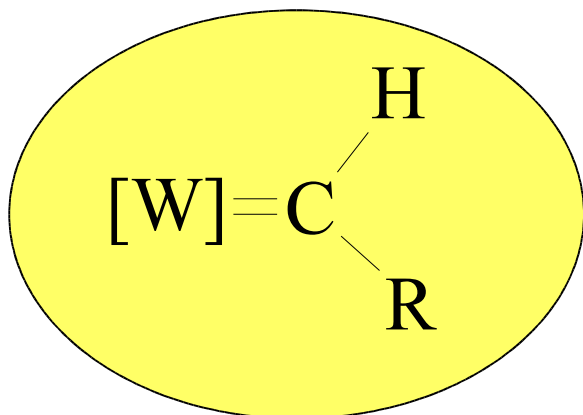
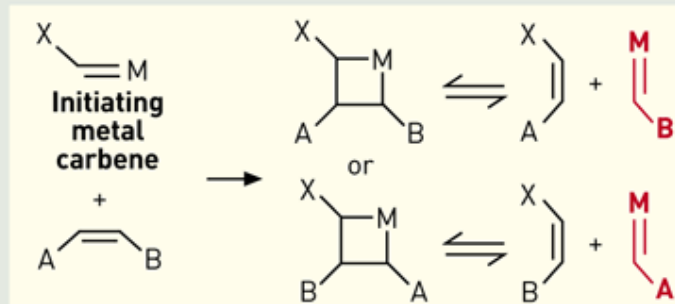
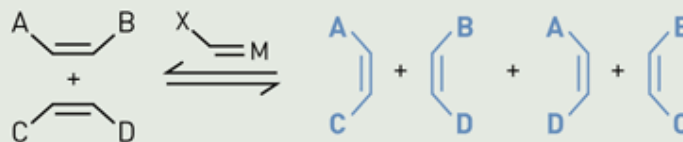
Co-reaction of cyclopentene with 2-pentene



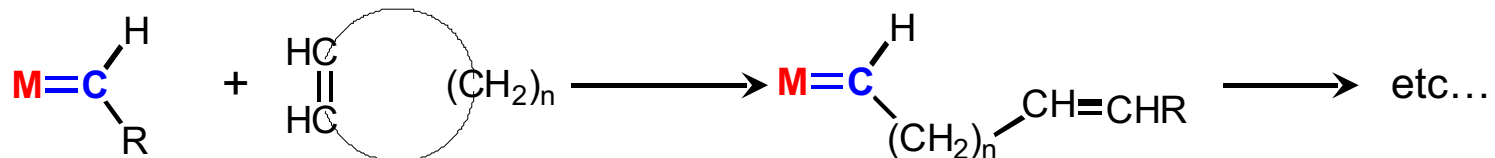
MECHANISM

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 :



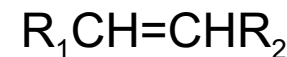
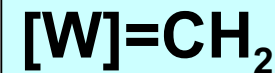
TABLEAU

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

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

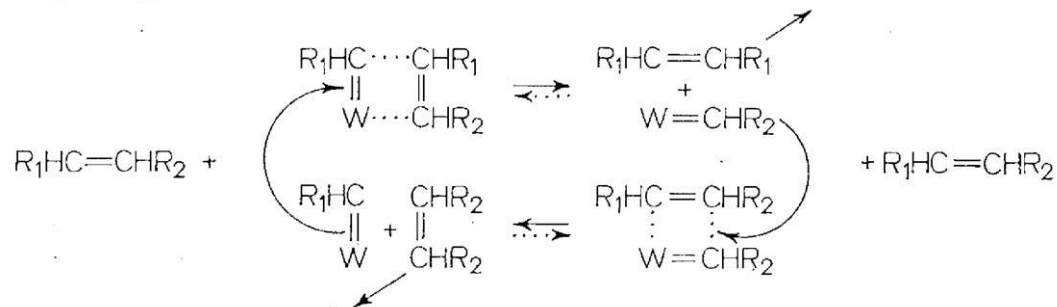
(*) On observe la formation de butène-2 et d'hexène-3 issus de la disproportion du pentène-2 en excès.

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

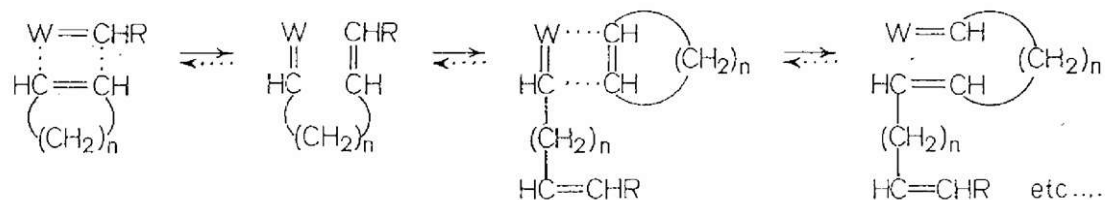


formation of
 α -olefins

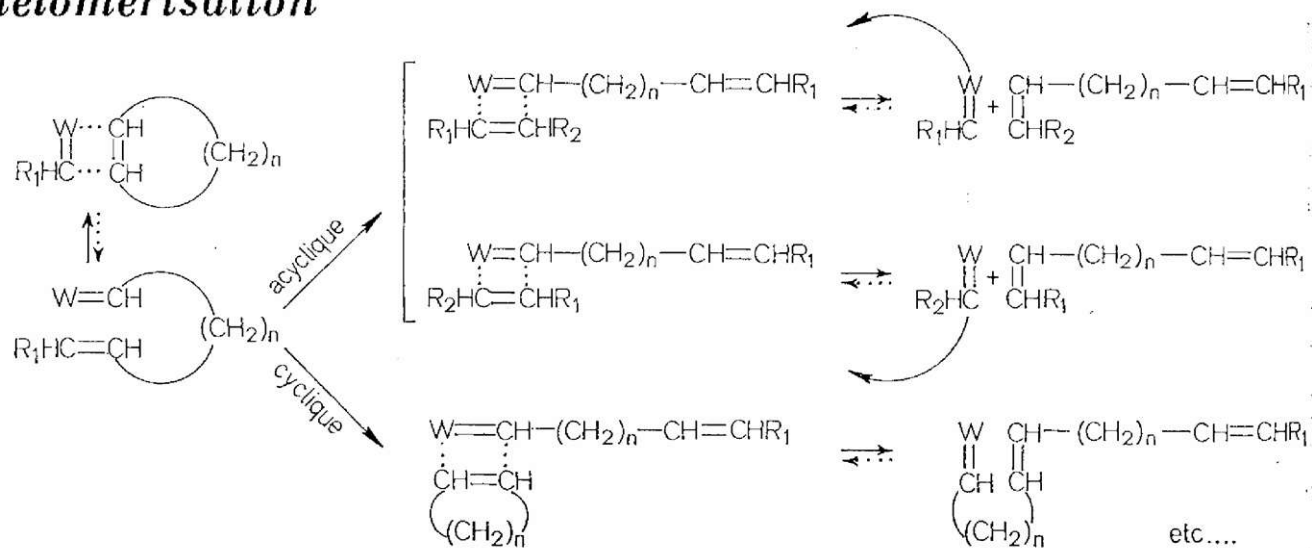
Réaction de disproportion



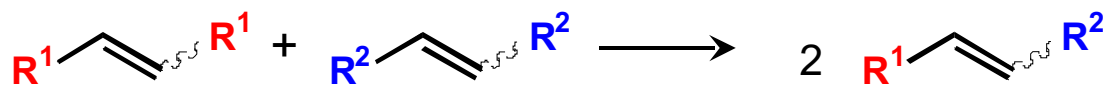
Réaction de polymérisation



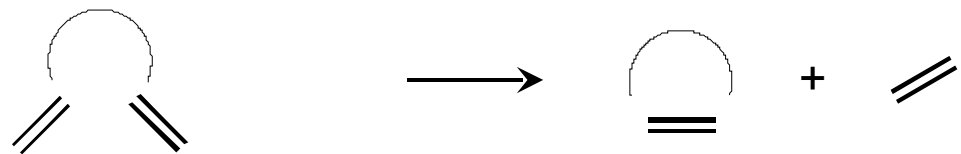
Réaction de télomérisation



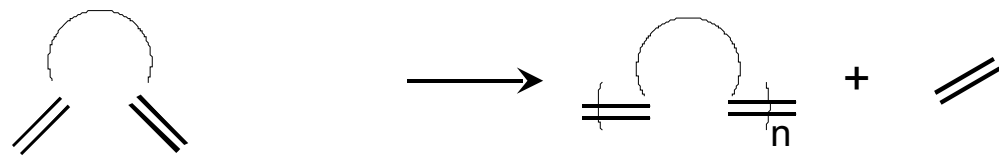
Cross Metathesis (CM)



Ring Closing Metathesis (RCM)



Acyclic Diene Polymerization (ADMET)



Ring Opening Metathesis (ROMP)

