

Olefin Metathesis: The Early Days (Nobel Lecture 2005)**

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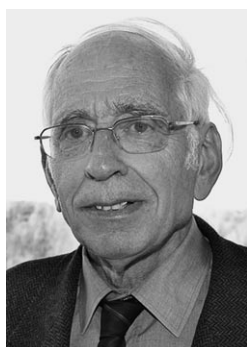
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Biographical Notes

I was born on October 10, 1930 in Menin (Menen in Flemish) in western Flanders, on the border between Belgium and France. My parents were French. To be more precise, they were not only both from the Tours region, but also descended from long-established families in the little village of Beaumont-la-Ronce. I used to spend my holidays there in my grandparents' large family house, with my numerous cousins. When I die, I am going to be buried in the village cemetery. My grandmother was fond of painting and playing the piano. She had been given lessons by Emmanuel Chabrier, who used to spend the summer months in nearby Membrolle. He said in his correspondence that he did not much care for his pupils on the whole and my grandmother found him very strict.



Most of my ancestors were small-scale farmers. My father was an electrical engineer. After three years of military service and quite a difficult time in the First World War, he was sent by the company that had taken him on after his demobilization to Ypres and then Menin, to work on rebuilding (building) the electricity network in this war-ravaged province. I remember him always being very motivated and working

very long hours. He was sent to war again in 1939 and taken prisoner. There were five brothers and sisters in the family and we had quite a strict upbringing.

From my bedroom, I looked out over our large garden (roses and vegetables) and the Lys river, which at that particular point separates France from Belgium and was where the flax was retted in tanks then dried in little bundles in a field (what a foul smell!). I watched the barges go past, towed by horses or even by men. It was a fascinating sight: the man pulling the rope remained bent over and unmoving for several minutes before the barge started to move. I also remember Vauban's fortifications in this land of invasions, and the smell of roasted chicory. I still have many paintings of Flanders that my father bought from contemporary painters—somewhat classical, but not devoid of charm.

I went to pre-school in Flanders and then the French primary school, which meant that I crossed the border every day. I then continued my secondary and higher education in various towns. During the war, I managed to come through the bombings unscathed, though sometimes only just. The war taught me to eat what there was; I am still not a fussy eater, although I do enjoy good food.

To be perfectly truthful, I was not a very brilliant student, even at chemistry school. I chose chemistry rather by chance, because I firmly believed (and still do) that you can become passionately involved in your work whatever it is. Various circumstances, mainly to do with my military service, prevented me from doing a PhD and I have often regretted it, though you do need to choose the "right" supervisor in the "right" discipline—no easy task when you are totally inexperienced.

So I took a job in industry, but the fact that process development consisted primarily of copying what already existed, with no possibility of exploring other fields, prompted me to resign. Furthermore, I discovered that this was a very common attitude among

managers. They are afraid of anything new: “Do what everyone else does and change as little as possible: at least we know it will work”. It is the opposite of my way of thinking, which, I must admit, is a bit of an obsession! I have often got into arguments about it. My motto is more, “If you want to find something new, look for something new!” There is a certain amount of risk in this attitude, as even the slightest failure tends to be resounding, but you are so happy when you succeed that it is worth taking the risk.

The whole contradiction of research (whether applied or fundamental) generally lies in the fact that we have to start out with the knowledge handed down by our predecessors, but be able to depart from it “at the right time”.

I joined Institut Français du Pétrole in 1960 and managed to focus my work on what I thought would be most interesting. I got married the same year and over the course of time we had two sons and five grandsons.

The oil industry essentially uses heterogeneous catalysis: cracking, reforming, hydrosulfurization, hydrogenation, etc., but that was not what interested me. I have always tried to avoid areas that have been perfected with time. At the time, nothing much was being done in France on coordination chemistry, organometallics, or homogeneous catalysis by transition metals and I was fascinated by the achievements in Italy (G. Natta), Great Britain (J. Chatt), Germany (at the Max Planck Institute in Mülheim), and the United States. As a result, I unwittingly became the French specialist in these disciplines, which brought me into contact with both the positive and the unwieldy aspects of the various commissions at the CNRS. I spent the best part of my time on applied chemistry, which was what I had been employed for and which I was quite happy about. This was how I came to develop two homogeneous catalysis processes. The first one, which uses a nickel-based catalyst, was called “Dimersol” and exists in two basic versions: The “gasoline” version (Figure 1) consists of dimerizing propene to high-octane isohexenes. There is, quite often, an excess of propene, especially in oil refineries that do not produce petrochemicals, as in the United States. There are currently 35 plants in operation (including 18 in the USA), with a combined annual output of 3.5 million tonnes. It was the first and only time that coordination catalysis had been used in refining.

The “chemical” version of the Dimersol process (Figure 2) consists of dimerizing *n*-butenes to isoocenes, basic inputs for plasticizers, using the “oxo” reaction. Current production levels stand at 400 000 tonnes a year.

The second process I developed, and which uses a titanium-based catalyst, was called “Alphabutol”. It consists of dimerizing ethylene to 1-butene (Figure 3),

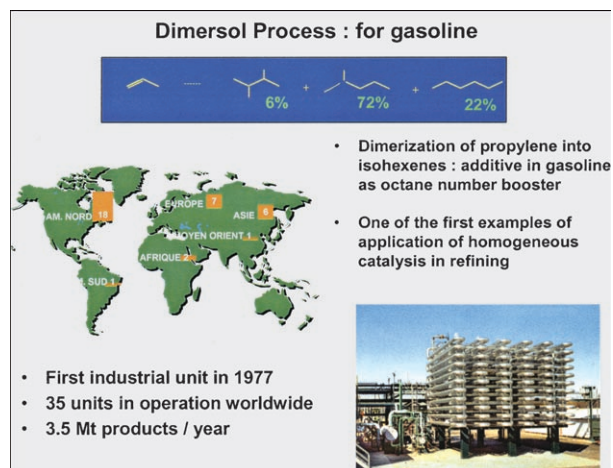


Figure 1.

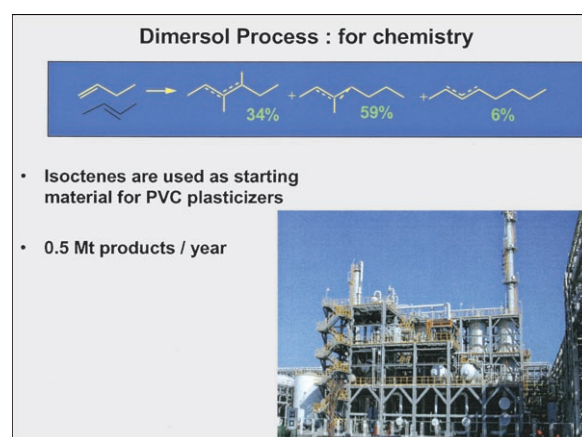


Figure 2.

the comonomer of low-density linear polyethylene. The benefits of such a process were not evident to begin with and stem from a number of causes. There are currently 20 plants operating worldwide, with a

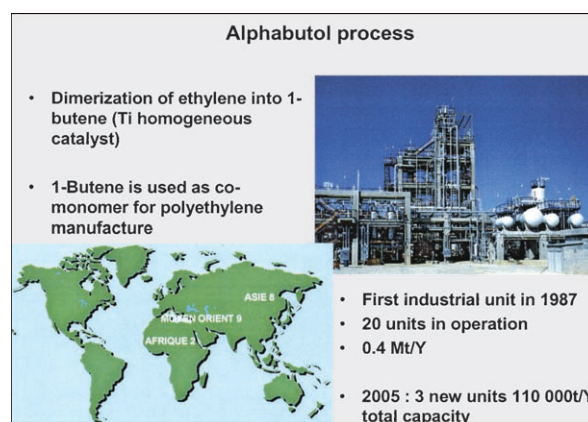


Figure 3.

combined output of 400 000 tonnes a year. However, others are under construction, which will take total output to over 0.5 million tonnes a year.

While there are obvious drawbacks to not having done a PhD (especially when you supervise those with them!), the advantage is that at least your mind is free to focus on whatever presents itself. At the time, I was working on batteries and, in particular, the non-aqueous electrolytes used to extend their electrochemical window. I thought it would be a good idea to try to use these electrolytes, which belong to the class of ionic liquids, as catalyst solvents. These liquids feature very low vapor pressure and virtual insolubility in hydrocarbons, paving the way for a biphasic catalysis. The mixture of alkylimidazolium chloride and aluminum chloride forms a liquid with a very low melting point (below ambient temperature; Figure 4). It proved to be a first-rate solvent for

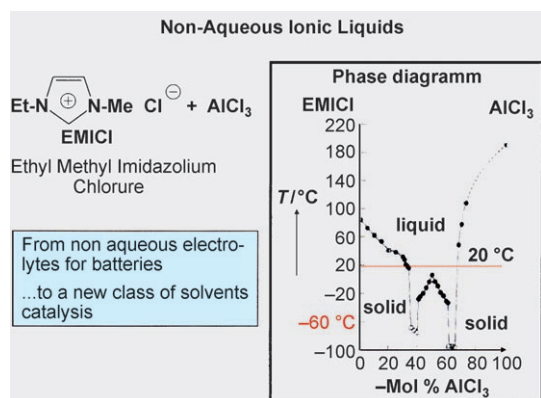


Figure 4.

nickel-based dimerization catalysts (Dimersol catalysts). The diagram for this process, called “Difasol”, is shown in Figure 5. The reaction volume required for a biphasic system is 10-times smaller than for a homogeneous system (important for safety: refineries do not like to have large volumes in reaction because they are potential “bombs”, especially at start-up); likewise for nickel consumption. This new process, dealt with in a PhD thesis in 1990, will see the light of day thanks to the inventiveness and determination of H  l  ne Olivier-Bourbigou, who took over from me in the laboratory.

What applied chemistry has taught me is the need for absolute solidarity between the research laboratory and the “downstream” side (pilot testing, marketing, setting up industrial plant): same enthusiasm, same determination, especially when everything goes wrong!

There is no difference between fundamental research and applied research. Although this is my

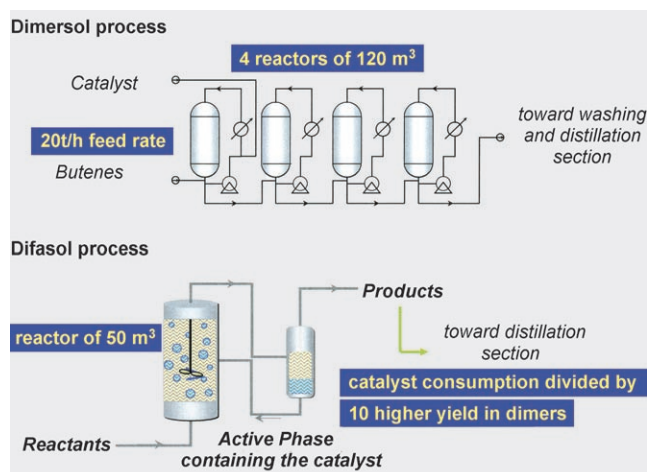


Figure 5.

view, based on personal taste and the areas I have worked in, it is not necessarily true for others. The PhD work either led to, or was derived from processes. I have spoken so much about “processes” because they took up about three-quarters of my working time.. However, I also took an interest in other aspects of coordination chemistry, such as palladium catalysis, rhodium catalysis, asymmetric amino acid synthesis, and so on. After retiring in 1995, I was invited to work in J.-M. Basset’s laboratory in Lyon, which allows me to pursue a reasonable level of activity.

Olefin Metathesis: Discovery and First Achievements

At no time in my life did I dream of such a prize. Indeed, as I explained in my biography, I had no training in research as such and as a consequence I am in a sense self-taught. What I owe to the Institut Français du Pétrole is some freedom to choose my research area. I have always been an avid reader of chemical literature, eager for what is new. Like all sciences, chemistry is marked by magic moments. For someone fortunate enough to live such a moment, it is an instant of intense emotion: an immense field of investigation suddenly opens up before you. There were very many of these moments in the course of my career. For example, the discovery of ferrocene, the stereospecific polymerization of olefins by G. Natta (I never failed to read any of his articles!), the homogeneous catalysis of hydrogenation by rhodium complexes (G. Wilkinson), the homogeneous catalysis of dimerization of olefins by nickel complexes (G. Wilke and B. Bogdanovic) and the catalysis of asymmetric hydrogenation. I experienced the latter with an especially keen intensity because we were in very

close touch with Henri Kagan, who came every month to tell us about his chemistry; it was outstanding! And 1964 was an especially magical year (Figure 6): a revelation for me, by R. L. Banks and G. C. Bailey of Phillips Petroleum, of the disproportionation of olefins catalyzed by a molybdenum- or tungsten-based heterogeneous catalyst deposited on

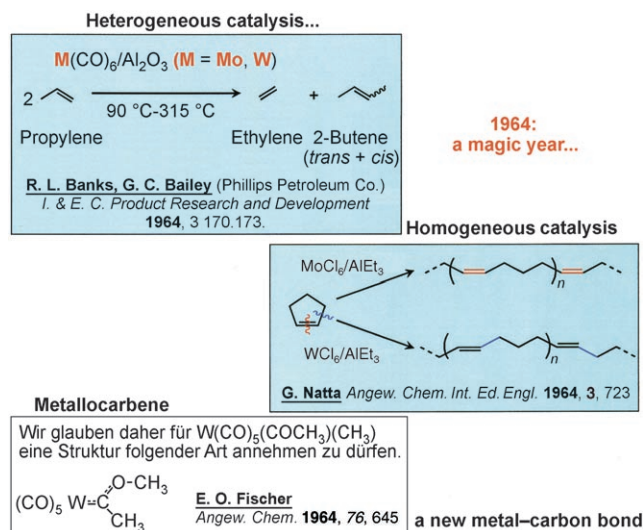


Figure 6.

alumina; the homogeneous catalysis of polymerization of cyclopentene by ring opening, published by G. Natta, and the existence of a new metal-carbon bond, the carbenes of E. O. Fischer. A priori these three had nothing in common.

The disproportionation of linear olefins (Banks and Bailey), since called metathesis, is an equilibrated reaction, governed basically by entropy. This is doubtless why, from the start, "pairwise mechanisms" were favored (Figure 7), which assume a perfect symmetry of the reaction intermediates. In addition, these intermediates are based on the only bonds known at the time: π bonds and σ bonds between hydrocarbons and transition metals. Other mechanisms were proposed (Figure 8).

The polymerization of cyclopentene into polypentenylene (Natta), for its part, is governed mainly by the enthalpy linked to the release of the ring strain when

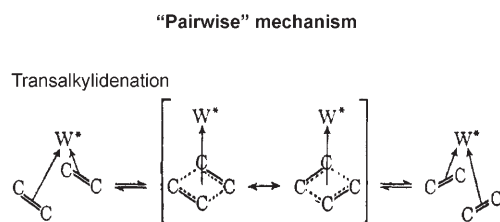


Figure 7.

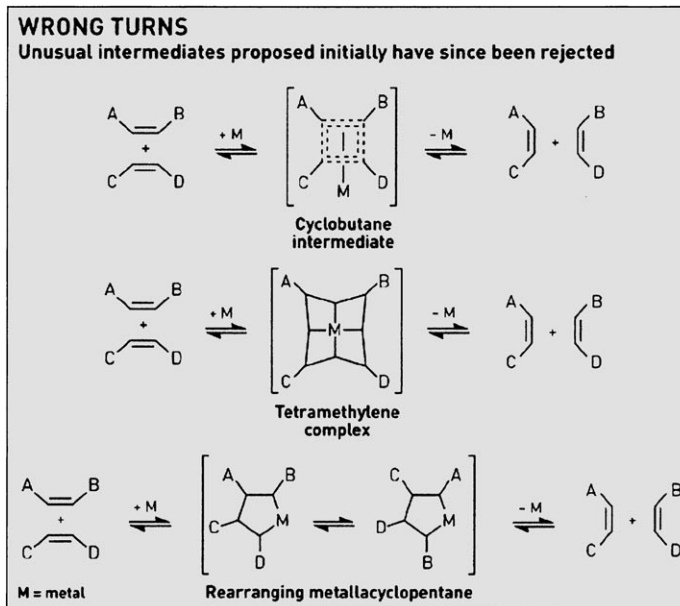


Figure 8.

the ring is cleaved; but entropy also plays a part there owing to the multiple conformations of the chain and, like the metathesis of acyclic olefins, the reaction is equilibrated. These factors are no longer the same in the case of the higher cycles, as we shall see later. To explain the high molecular weights observed from the start of the reaction, Natta assumed the existence of a σ bond between the transition metal and the growing chain, the proposed mechanism being an α -cleavage of the ring such as is often invoked in classic organic chemistry.

My immediate reaction back in 1964 was the thought that disproportionation and ring opening were part of the same reaction. In addition to the fact that both reactions preserved the number and type of double bonds (only the molecular weight of the products was changed), they used the same transition metals, molybdenum and tungsten. In fact, at the time, in a way that may be surprising today, there was a gap—a total lack of understanding—between homogeneous catalysis and heterogeneous catalysis (some people even attributed the fundamental role in the transformation to the catalyst support!). Since I was familiar with both types of catalysis in our Institute, that was not a real problem for me. But how could the statistical aspect of the one be reconciled with the chain growth of the other? Meanwhile, N. Calderon had also started building a bridge between homogeneous catalysis and heterogeneous catalysis.^[1] It then seemed obvious to associate the two reactions, where the enthalpy of ring opening would in a sense "freeze" the statistical reactivity of the acyclic olefin.^[2] Accordingly we treated cyclopentene with 2-pentene in the molar ratio 1:1 with the homogeneous

catalyst WOCl_4 and SnBu_4 or AlEt_2Cl . The result is shown in Figure 9 and Table 1: in addition to the C_{10} di-unsaturated product of the expected coupling of cyclopentene with 2-pentene (5+5 carbon atoms), there were other products, also di-unsaturated (5+4) and (5+6), the ratio was 1:2:1 for the $\text{C}_9/\text{C}_{10}/\text{C}_{11}$ species, then higher tri-unsaturated products containing (5+5+5), (5+5+4), and (5+5+6) carbon atoms; and

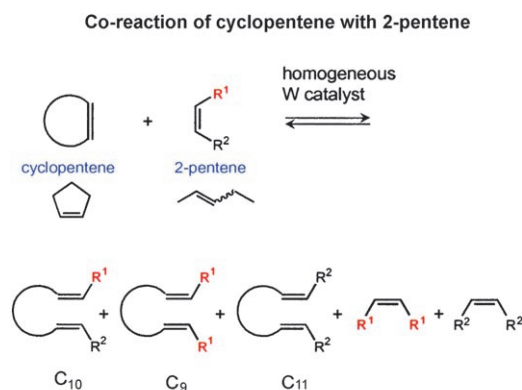


Figure 9.

Table 1. Telomerization of cyclopentene with 2-pentene.

Catalyst and reaction time	$\text{WOCl}_4/\text{Sn}(\text{C}_4\text{H}_9)_4$		$\text{WOCl}_4/\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	
	7 min	14 min	24 h	
<i>Relative molar quantity</i>				
cyclopentene	32	35	148	
butenes	9.3	18.7		
pentenes	58	31.3	159	
hexenes	8.8	17.7		
C_9H_{16}	4.5	8.1	16.8	
$\text{C}_{10}\text{H}_{18}$	9.5	18.3	18.1	34.4
$\text{C}_{11}\text{H}_{20}$	4.3	8.2	16.8	
$\text{C}_{14}\text{H}_{24}$	2.0	3.6	8.9	
$\text{C}_{15}\text{H}_{26}$	4.3	8.3	6.9	13.9
$\text{C}_{16}\text{H}_{28}$	2.0	3.4	8.6	
$\text{C}_{19}\text{H}_{32}$	1.0	1.5	5.0	
$\text{C}_{20}\text{H}_{34}$	2.8	4.8	3.0	6.0
$\text{C}_{21}\text{H}_{36}$	1	1.5	4.9	
$\text{C}_{24}\text{H}_{40}$		0.8	n.d.	
$\text{C}_{25}\text{H}_{42}$		1.6	3.1	n.d.
$\text{C}_{26}\text{H}_{44}$		0.7	n.d.	
chlorobenzene	30	90	–	
D %	24	54	–	
C %	29	46	44	

so on, in decreasing quantities, but in each case forming “triads”. This was, then, a “telomerization” reaction in which the telogene is *n*-pentene and the taxogene is cyclopentene. Since the participation of the 2-pentene in the telomerization reaction is at each instant equal to its participation in the metathesis reaction, the telomerization products are as a consequence not derived from the metathesis products. The reaction, like the metathesis and polymerization of cyclopentene, is equilibrated. The general characters of the telomerization reaction have been verified for many pairs of olefins, such as 2-pentene/cyclooctene, 2-hexene/cyclopentene, and 3-heptene/cyclopentene. α -Olefins, such as propene and 1-pentene are, as in the case of metathesis, less reactive, but the telomers form in ratios from 1:10:1 to 1:20:1.

1,5-cyclooctadiene (cod) and 1,5,9-cyclododecatriene (cdt) lead to telomers of the same type, but in this case the successive “triads” are separated by four atoms of carbon and not by an integral multiple of the number of carbon atoms forming the ring.

This situation therefore means that alkylidene “residues” are left on the transition metal. The most obvious hypothesis is the formation of a metallocarbene sequestering an olefin to form a metallacyclobutane intermediate (Figure 10).

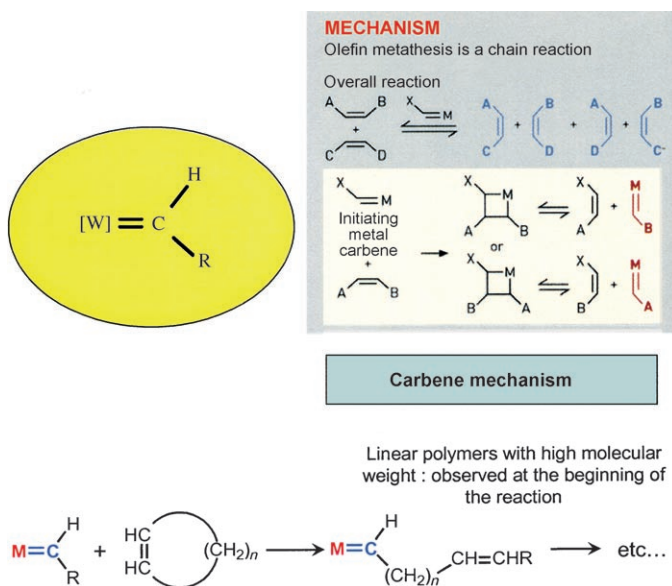


Figure 10.

The mechanism may be a little more complex in reality: the reactivity of cod and cdt as “butadienyldene” ($=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{}$) even at the very start of the reaction, so that it cannot be explained as a “back-biting” reaction (reaction of the metallocarbene with one of the double bonds of the growing chain), remains to be explained.

While the cyclopentene is in equilibrium with its polymer (polypentenylene), this is not true of the higher cycles, such as cyclooctene and cyclooctadiene: their polymers are in equilibrium with the cyclooligomers.^[3] This situation is due to the relative stability of the cycles, as P. J. Flory has shown in the case of the lactones (Figure 11).^[4] These macrocycles are formed by back-biting.

All three reactions (disproportionation, polymerization, telomerization) can be represented as shown in Figure 12. It remained to be shown how the initial

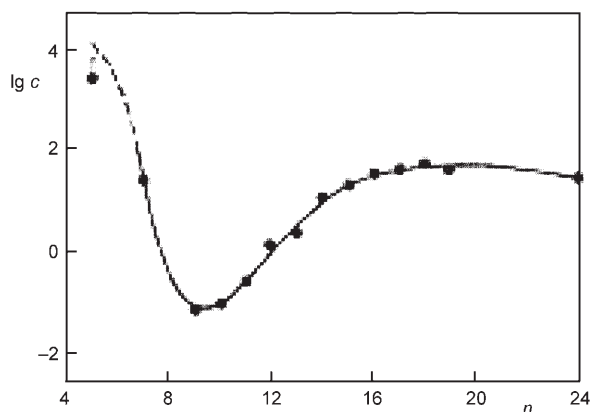


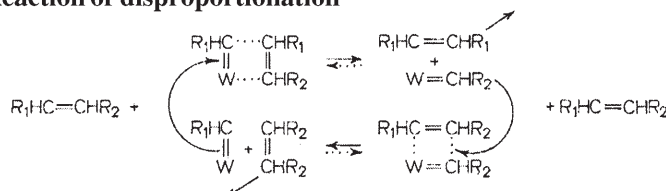
Figure 11. Logarithm of the cyclization constant C for the lactonization of ω -hydroxyacids versus ring size n .^[4]

metallocarbene forms when a tungsten halide and an organometallic species are mixed. For this investigation we chose methylated derivatives that cannot give rise to β -H elimination: methyl lithium and tetramethyltin. All that could be hoped for was to favor α -H elimination with the formation of a methyldene species that could simply be “trapped” by means of olefins with a di-substituted double bond: 2-butene, 2-pentene, 3-hexene. Figure 13 summarizes the results of these experiments.^[5] The formation of propene and of 1-butene clearly demonstrates the existence on the tungsten of a methyldene group. The formation of methane is explained by an α -H elimination, doubtless followed by a reducing elimination resulting from a double alkylation of the tungsten.

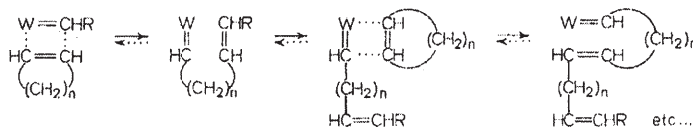
E. O. Fischer's carbene is itself a very active catalyst for the polymerization of cyclopentene in the presence of TiCl_4 when activated, probably photochemically, by chlorination of the tungsten (it is well known that TiCl_4 is photochemically reduced by alkanes).^[6]

It is also possible to characterize and count the metallocarbenes formed on rhenium peroxide impregnated on alumina, by means of reaction with a 1,2-disubstituted olefin. Subsequent reaction with ethylene leads to propene^[7] by a sequence of reactions that might be as given in Equations (1) and (2) (where r is a symbol formerly used by K. Ziegler).

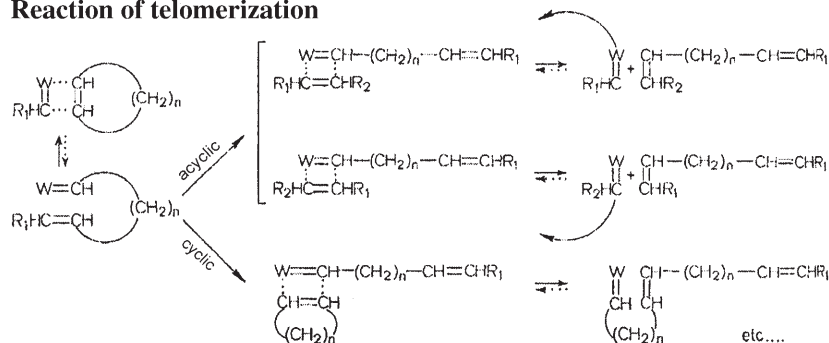
Reaction of disproportionation



Reaction of polymerization



Reaction of telomerization



J.-L. Hérisson, Y. Chauvin, *Makromolekulare Chemie* **1971**, 141, 161–176.

Figure 12.

Formation of the metallocarbene: $WCl_6 + Sn(CH_3)_n$

TABLEAU

Produits de réaction entre $W(Cl)_6$, $M(CH_3)_n$ et une oléfine

% molaires par rapport au tungstène mis en œuvre

Oléfine	W (Cl) ₆ (g)	Coréactif (**)	Solvant	T (°C)	Oléfine W (Cl) ₆	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.

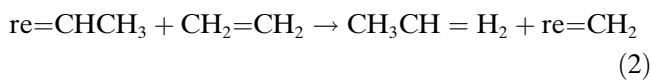
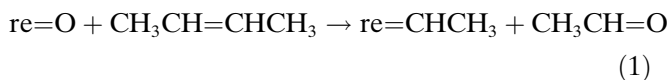
J.-P. Soufflet, D. Commereuc, Y. Chauvin, C. R. Acad. Sci. **1973**, 276, 169–171

[W]=CH₂

R¹CH=CHR²

formation of
α-olefins

Figure 13.



Concluding Remarks

Obviously, not everyone has the opportunity to witness the birth of a new bond like the one discovered by E. O. Fischer, and the event is likely to become increasingly rare! Nor are they likely to be present at the birth of a unified concept encompassing two types of catalysis that until then had not been on speaking terms. It was an opportunity that had to be seized!

I owe a great deal to everyone who took part in what I can rightly call an “adventure”, because at the start we could not be sure of reaching a significant result. And more particularly to the talented students directly involved—J.-L. Hérisson, J.-

P. Soufflet, and G. Zaborowski—without whom this work (and therefore the prize!) would not have existed.

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- [7] Y. Chauvin, D. Commereuc, *J. Chem. Soc. Chem. Commun.* **1992**, 462–464.
- [8] There have been many publications on metathesis; the last and without doubt the best documented of them is the *Handbook of Metathesis* by R. H. Grubbs (Wiley-VCH, Weinheim, **2003**).