

OLEFIN METATHESIS: THE EARLY DAYS*

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by

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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 1): a revelation for me, by R.L. Banks of Phillips Petroleum, of the disproportionation of olefins catalyzed by a molybdenum- or tungsten-based heterogeneous catalyst deposited on alumina, the homogeneous catalysis of polymerization of cyclopentene by ring opening, published by G. Natta, 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, since called *metathesis*, is an equilibrated reaction, governed basically by entropy. This is doubtless why, from the start, “*pairwise mechanisms*” was favored (Figure 2), 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 3).

The polymerization of cyclopentene into poly(pentenylenes), for its part, is

* The title is taken from the excellent article by A. Maureen Rouhi, a very competent scientific journalist, published in *Chemical & Engineering News* of 23 December 2002, a special issue on metathesis.

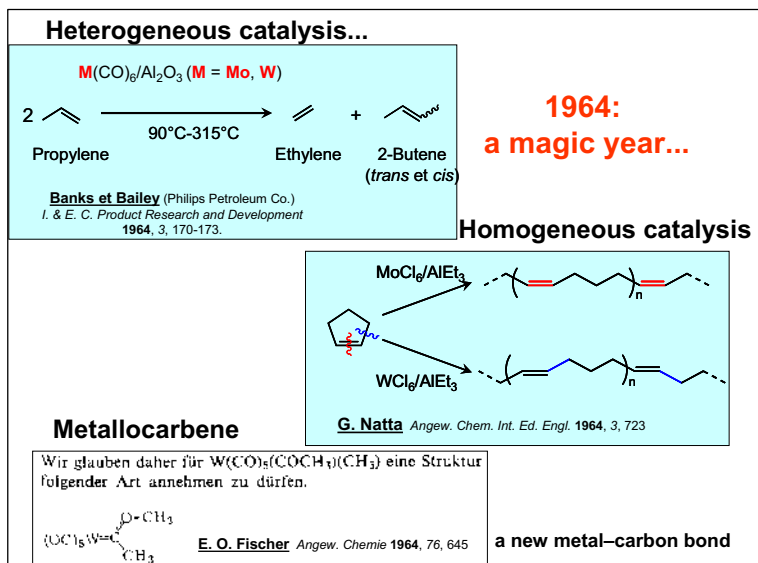


Figure 1.

governed mainly by the enthalpy linked to the release of the ring strain when the ring is cleaved, but entropy also plays a part there due to the multiple conformation of the chain and, like the metathesis of acyclic olefins, it 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, G. 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.

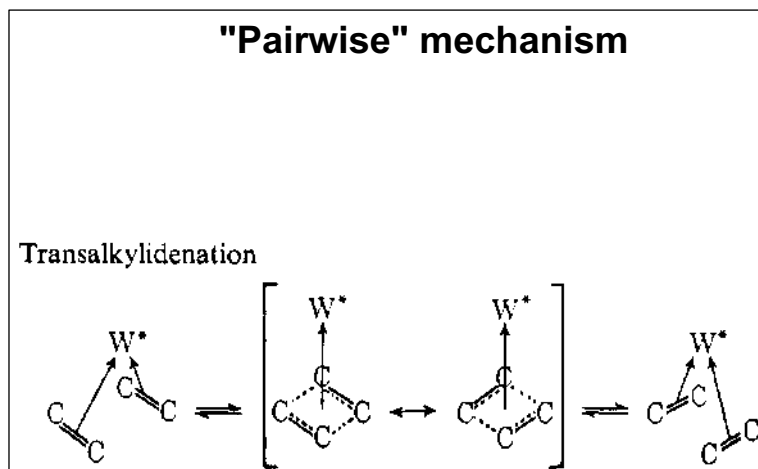


Figure 2.

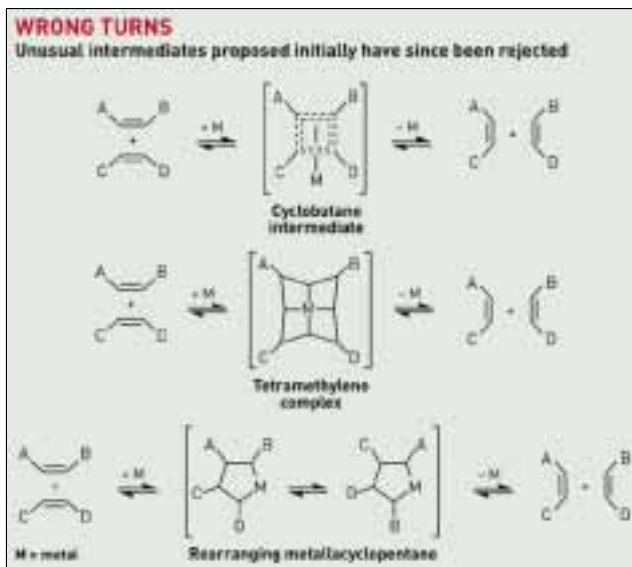
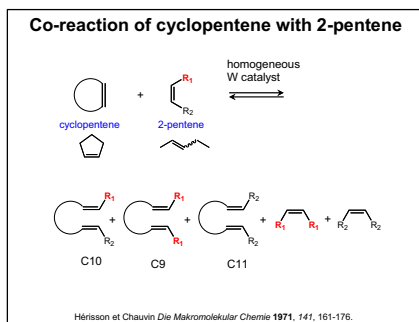


Figure 3.

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 Institut, 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 cyclopentene was associated with 2-pentene in the molar ratio 1:1 with the homogeneous catalyst WOCl_4 and SnBu_4 or AlEt_2Cl . The result was as follows (Figure 4): in addition to the di-unsaturated product of the expected coupling of cyclopentene with 2-pentene (5+5), there were other products, also di-unsaturated (5+4) and (5+6), in the ratio 1:2:1 for the condensations in carbon 9/10/11; then higher tri-unsaturated products containing (5+5+5), (5+5+4), and (5+5+6) carbon atoms; and so on, in decreasing quantities, thereby 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

Telomerization of cyclopentene with 2-pentene

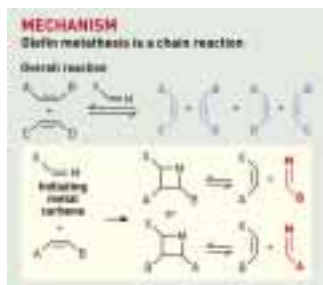
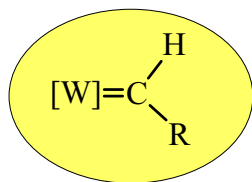


Catalyst Reaction time	WOCl ₄ /Sn(C ₄ H ₉) ₄		WOCl ₄ /Al(C ₂ H ₅) ₂ Cl
	7 min.	14 min.	24 h.
Relative Molar quantity			
Cyclopentene	32	35	108
Butenes	9,3	18,7	} 159
Pentenes	58	31,3	
Hexenes	8,8	17,7	} 70,4
CoH ₁₆	4,5	8,1	
C ₁₀ H ₁₈	9,5	18,1	} 34,4
C ₁₁ H ₂₀	4,3	8,2	
C ₁₄ H ₂₄	2,0	3,6	} 13,9
C ₁₅ H ₂₆	4,3	6,9	
C ₁₆ H ₂₈	2,0	3,4	} 8,6
C ₁₉ H ₃₂	1,0	1,5	
C ₂₀ H ₃₄	2,8	3,0	} 5,0
C ₂₁ H ₃₆	1	1,5	
C ₂₄ H ₄₀		0,8	} 4,9
C ₂₅ H ₄₂		1,6	
C ₂₆ H ₄₄		0,7	n.d.
Chlorobenzene	80	90	n.d.
D %			n.d.
(conversion of disproportionation reaction)	24	54	-
C %			
(conversion of cross-reaction)	29	46	

Figure 4.
Telomerization of cyclopentene with 2-pentene.

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 4 atoms of carbon and not by an integral multiple of the number of carbon atoms forming the ring.

This therefore means that alcoylidene "residues" are left on the transition metal. The most obvious hypothesis is the formation of a **metallo-carbene** sequestering an olefin to form a metallocyclobutane intermediate (Figure 5).



Carbene mechanism

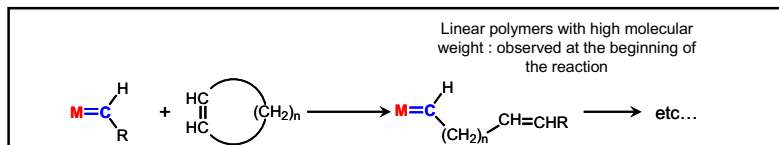


Figure 5.

The mechanism may be a little more complex in reality: the reactivity of cod and cdt as “butadienyldiene”



even at the very start of the reaction, so that it cannot be explained as a *back-biting* reaction (reaction of the metalcarbene with one of the double bonds of the growing chain), remains to be explained.

While the cyclopentene is in equilibrium with its polymer (polypentenyene), this is not true of the higher cycles such as cyclooctene and cyclooctadiene: their polymers are in equilibrium with the cyclooligomers [3]. This is due to the relative stability of the cycles, as P. J. Flory has shown in the case of the lactones (Figure 6) [4]. These macrocycles are formed by *back-biting*.

All three reactions can be represented as shown in Figure 7.

It remains to be shown how the initial metalcarbene forms when a tung-

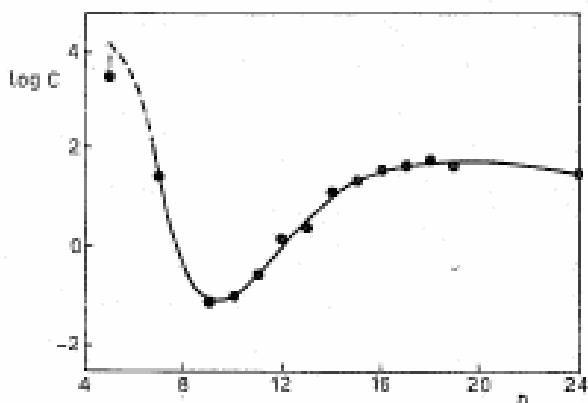
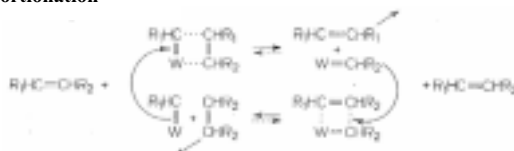


Figure 6. Log of the cyclization constant for the lactonization of ω -hydroxyacids vs. ring size (P. J. Flory).

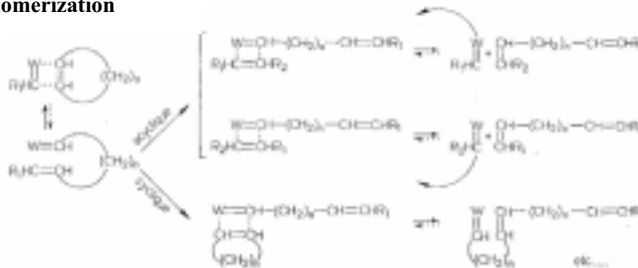
Reaction of disproportionation



Reaction of polymerization



Reaction of telomerization



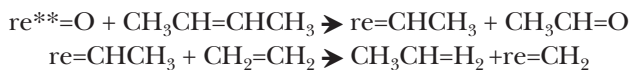
Hérisson et Chauvin *Die Makromolekular Chemie* **1971**, *141*, 161-176.

Figure 7.

sten halide and an organometallic of the principal series are mixed. For this 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 **methylidene** species that could simply be “trapped” by means of olefins with a di-substituted double bond: 2-butene, 2-pentene, 3-hexene. Here is what can be observed (Figure 8) [5]. The formation of propene and of 1-butene clearly demonstrates the existence on the tungsten of a **methylidene** 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.

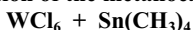
E.O. Fischer's carbene is itself a very active catalyst for the polymerization of cyclopentene in the presence of TiCl_4 activated, probably photochemically, by chlorination of the tungsten (it is well known that TiCl_4 is photochemically reduced by alkanes) [6].

It is also possible to characterize and count the metallocarbenes formed on rhenium peroxide impregnated on alumina, by means of a 1,2-disubstituted olefin, then a reaction with ethylene to lead to propene [7] by a sequence of reactions that might be:



** re: symbolic writing formerly used by K. Ziegler.

Formation of the metallocarbene :



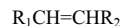
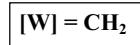
Products of reaction of WCl_6 , $\text{M}(\text{CH}_3)_n$ and an olefin
molar % relative to W

Olefin	WCl ₆ (g)	Co-reactants (***)	Solvent	T (°C)	Olefin WCl ₆	Methane + éthane	Propy- -lene	Butene-1
Butene-2	0,5	LiCH ₃	Benzene (15 ml)	4	10	22	6,3	-
Butene-2	0,5	Sn(CH ₃) ₄	Benzene (15 ml)	4	10	3,5	3,6	-
Hexene-3	0,2	Sn(CH ₃) ₄	Benzene (30 ml)	4	10	n.d.	-	2,6
Pentene-2 (*)	0,5	LiCH ₃	Benzene (15 ml)	4	10	22	4,4	4,7
	0,2	Sn(CH ₃) ₄	Benzene (30 ml)	4	10	10	9,6	10,4
	0,2	Sn(CH ₃) ₄	Chloro- benzene (30 ml)	-20	10	n.d.	8,5	6,4
	0,4	Sn(CH ₃) ₄	Chloro- benzene (30 ml)	-20	2,5	n.d.	6,8	6,9

(*) we observe the formation of butene-2et hexene-3 from the disproportion of pentene-2 in excess.

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

Soufflet, Commereuc et Chauvin C. R. Acad. Sc. 1973, 276, 169-171.



formation of
 α -olefins

Figure 8.

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 that 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!

ACKNOWLEDGEMENT

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 – Jean-Louis Hérisson, J.-P. Soufflet, and G. Zaborowski – without whom this work (and therefore the Prize!) would not have existed.

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There have been many works on metathesis; the last and without doubt the best documented of them is the book by R.H. Grubbs, “Handbook of Metathesis”, 2003, Wiley-VCH.

Portrait photo of Yves Chauvin by photographer U. Montan.