

OLEFIN METHATHESIS

An alkene dance

Catherine S. J. Cazin 

The seminal paper by Yves Chauvin and Jean-Louis Hérisson on the mechanism of alkene metathesis is elegant, simple and insightful. Published more than 50 years ago, it deserves appreciation and admiration even today.

Refers to Hérisson, J.-L. & Chauvin, Y. Catalyse de transformation des oléfines par les complexes du tungstène. II. Télomérisation des oléfines cycliques en présence d'oléfinés acycliques [French]. *Makromol. Chem.* **141**, 161–176 (1971).

In 2005, the Nobel Committee awarded the Prize in Chemistry to Yves Chauvin, Robert Grubbs and Richard Schrock for their seminal work on olefin metathesis, a reaction that has greatly helped synthetic chemists assemble complex molecules in very few steps. It is not the two latter awardees, whose key discoveries were made in the late 1980s and early 1990s and whose contributions have been reported in a large number of prominent journal articles, who we focus on, but on the former chemist whose work precedes that of our more contemporary colleagues. A 1971 paper by Chauvin paved the way to the later discoveries and still guides and inspires research efforts today¹. On the manuscript, the year is instead indicated as 1970, which explains why this paper in *Die Makromolekulare Chemie* has been largely wrongly cited. Here, I took the liberty to spell out the journal name. Yes, you read it correctly: the journal name is in German and is about macromolecular chemistry, a subject that is relevant to the article, whose underlying chemistry concerns polymer formation through what is now known as ring-opening metathesis polymerization (ROMP) of cyclic alkenes. What is also fascinating is that this article was written in French, with the abstract provided in German and French. The journal then published papers in French, German and English. That it was not written in English or entirely in German surely hindered the dissemination of its discovery and mechanistic proposal. This is also an example of many gems in the open literature that should be found, read and appreciated wherever they are published.

In an age of hyped-up science and banal ‘unprecedented’ and ‘first’ examples, Chauvin’s contribution was not to be found in *Science*, *Nature*, *Proceedings of the National Academy*

of Sciences of the USA, *Angewandte Chemie International Edition* or the *Journal of the American Chemical Society* but in a more specialized journal. It was written in a sober, humble and matter-of-fact manner — clearly reflecting the character of the lead author. This was a collaboration between Mr Hérisson, a thesis student, and Mr Chauvin, an employee of the Institut Français du Pétrole (IFP), which was then located near Paris². The work is a classic example of meticulously performed physical organic chemistry to elucidate a reaction mechanism by quantifying, using gas chromatography and mass spectrometry (rudimentary analytical tools for us nowadays), the product distribution of a reaction between cyclic and acyclic alkenes catalysed by a metal catalyst. The observation of mixed alkenes produced through cross-metathesis using a tungsten catalyst is what led to the mechanistic proposal now known as the Chauvin mechanism, which helps us rationalize oligomerization, polymerization and ring-opening and ring-closing events. In fact, it explains all alkene metathesis reactions in their numerous incarnations. Chauvin’s name is associated with this paper and the mechanism of olefin metathesis derived from these simple and elegant experiments. Hérisson and Chauvin’s ‘olefin dance’ is an exchange of partners between cyclic and acyclic alkenes and the resulting exchange of alkene termini (FIG. 1a).

Prior to publication of their paper, olefin metathesis was incorrectly thought to occur through a [2+2]-type cycloaddition in which the metal just sat at the centre of this all-carbon cyclic intermediate. Since the first observation of this reaction in 1960 (REF.³), the reaction had been thought of as a curiosity, especially in view of the multicomponent catalyst mixture required⁴. The discovery

“it explains all alkene metathesis reactions in their numerous incarnations”

of this unusual reaction in an industrial setting surely led IFP management to question whether this could lead to a viable process. But it was simply too early for the reaction to develop into something financially rewarding because the lack of control, selectivity and productivity remained serious issues. For these reasons (and surely many others), such projects became more interesting to researchers in academia. In this regard, Chauvin’s approach, curiosity and desire to find out how things worked were traits that are nowadays common among academics. The early days of olefin metathesis — with its ill-formulated catalyst compositions (or need for catalyst and activator) — with hindsight, were very much influenced by advances in Ziegler–Natta chemistry. Ever the humble man, Chauvin acknowledged this very fact in his Nobel address.

In the Chauvin paper, a tungsten alkylidene forms *in situ* and affords a putative metallacyclobutane intermediate (which would later be explored by Grubbs in 2006)⁵, leading to a novel metal alkylidene and a new alkene with a new substitution pattern. The involvement of a metal–alkylidene as an initiator or catalyst for this reaction was a crucial lesson — if Chauvin were correct, then such well-defined species could be the key to overcoming numerous obstacles (including those mentioned above) that hindered the evolution of olefin metathesis from a mere curiosity into a practical organic transformation.

The next big developments in olefin metathesis came with the preparation of well-defined catalysts. Schrock first reported robust molybdenum alkylidene complexes⁶ in 1990, with Grubbs describing more air- and water-stable ruthenium catalysts⁷ in 1992 (FIG. 1b). The teachings of Chauvin, not least in terms of how the nature of the catalyst affects activity, were exemplified in the work of Nolan, who in 1999 used a *N*-heterocyclic carbene (NHC) supporting ligand to stabilize the Ru–alkylidene and broaden its scope in olefin metathesis⁸. Nolan, at the time a physical inorganic chemist, conducted solution calorimetry studies on a model

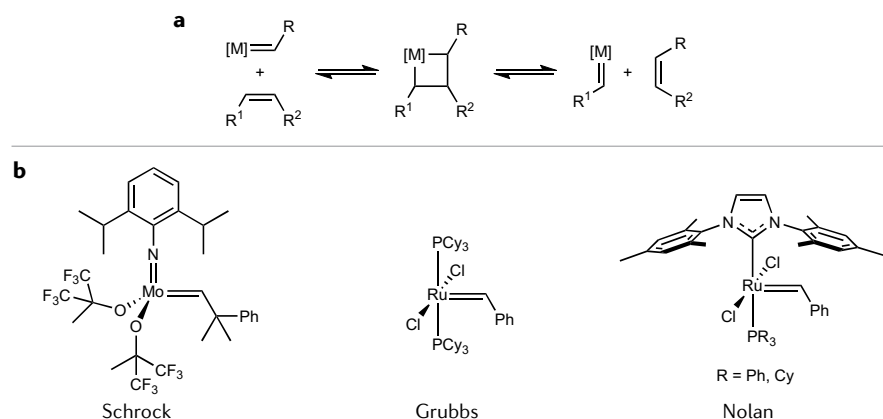


Fig. 1 | The Chauvin mechanism and molecular catalysts that operate through this ‘olefin dance’. **a** | The exchange of olefin partners, despite being linked by strong double bonds, readily occurs in the presence of a metal alkylidene. **b** | Prominent transition metal (pre)catalysts include Mo complexes developed by Schrock and Ru complexes pioneered by Grubbs and tuned by Nolan.

ruthenium system and found that replacing a PCy_3 with a more basic NHC ligand was exothermic by $\sim 5 \text{ kcal mol}^{-1}$. In turn, the Grubbs catalyst bore a PCy_3 ligand and was obtained by ligand substitution of a precursor complex featuring PPh_3 , an even weaker base. Examining the thermodynamic data, Nolan reasoned that it would be enthalpically possible to obtain a Ru-NHC system by ligand substitution of either Ru-PPh_3 or Ru-PCy_3 precursors. Steric arguments and other thermochemical data, namely the M-L bond dissociation enthalpies of NHCs being substantially higher than those of tertiary phosphines, led Nolan to suspect that NHCs would increase catalyst stability and longevity. Both lines of reasoning proved to be correct — second-generation Ru benzylidenes bearing a NHC can be obtained from the Ru-PR_3

benzylidenes and they do indeed exhibit higher stability. Nolan was first to report such a second-generation catalyst, followed very shortly by reports of the same architectures by Grubbs⁹ and Herrmann¹⁰. Great minds apparently do think alike!

The Chauvin paper concludes by stating that their observations do not fit well with polymerization results known at the time, giving an insightful and premonitory analysis that the degree of control in product distribution depends strongly on the nature of the catalyst. Such catalyst design efforts ensued and took nearly 20 years to come to fruition. The teachings centred on understanding the reaction mechanism and how catalyst composition can affect stability, reactivity and selectivity. This seminal paper influences our thinking even nowadays in olefin metathesis

but also in several transition-metal-catalysed reactions. The approach of understanding how things work allows catalyst design and redesign and is a lesson that still resonates with us today.

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Competing interests

The author declares no competing interests.