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Answer to Katz's criticisms on the history of metathesis

Didier Astruc

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Answers are provided to all the points raised by T. J. Katz in his Opinion "Corrections to a history of olefin metathesis".

In October 2005 the Chemistry Nobel Prize was awarded to Yves Chauvin, Robert H. Grubbs and Richard R. Schrock "for development of the metathesis method in organic synthesis".[1] The catalysis of olefin metathesis by transition-metal compounds [$Mo(CO)_6$ on Al_2O_3] was first reported for propene in the 1950s by American industrial chemists (H. S. Eleuterio, E. F. Peters, B. L. Evering, R. L. Banks, and G. C. Bailey) working at DuPont, Standard Oil, and Philips Petroleum. The polymerization of cyclic olefins was found for norbornene in the 1960s to be catalyzed by WCl_6 + $AlEt_2Cl$. N. Calderon at Goodyear recognized that both reactions are of the same type and coined the expression "olefin metathesis".[2] Several mechanisms were suggested by organometallic chemists, but they turned out to be incorrect. It was Yves Chauvin and Jean-Louis Hérisson, in 1971, who proposed the now illustrious, simple and beautiful mechanism involving a metal-carbene that reversibly reacts with an olefin to form a metallacyclobutane.[3] This metallocycle can open in different ways to either regenerate the starting materials or form another metal-carbene complex and another olefin.[4] In 1974–1975, R. R. Schrock reported the first isolation of methylene and alkylidene complexes of transition metals[5a] and, in 1980, he showed that an alkylidene complex, now containing the key alkoxy ligands, catalyzed the metathesis of *cis*-2-pentene.[5b] In the 1980s, Schrock reported a family of very efficient Mo-alkylidene metathesis catalysts[5c] and, in the 1990s, Grubbs reported very efficient ruthenium benzylidene metathesis catalysts.[5d] Both families are complementary in terms of compatibility with functional groups and asymmetric versions have been reported by Schrock and Grubbs. Consequently, the Schrock and Grubbs catalysts have been shown to be invaluable for many applications in organic synthesis and polymer science.[2,4]

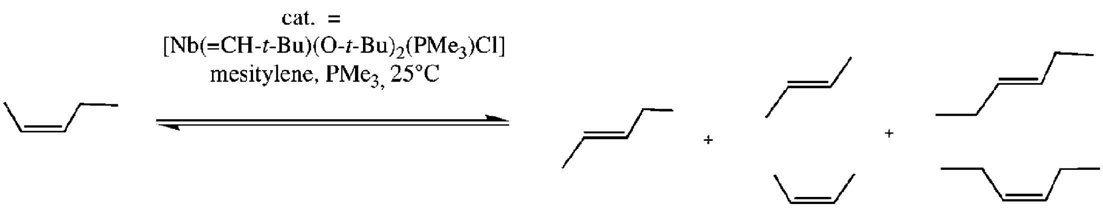
In January 2005, I published a short review article in *New J. Chem.* entitled "The metathesis reactions: from a historical perspective to recent developments" in which the first part was dedicated to historical aspects and the second part concentrated on the multiple applications.[4] This article has already been cited by many authors and was highlighted on the Nobel committee website.[1] In particular, it has been cited by Charles P. Casey, a well-known and distinguished organometallic chemist, former President of the American Chemical Society, among the six references of his four-page report on the Nobel Prize award to metathesis in the February issue of *Chem. Educ.*[6] It is precisely C. P. Casey and his student T. Burkhardt who reported in 1974 the first metathesis experiment between an isolated metal-carbene complex, [$W(CO)_5({=}CPh_2)$], and an alkene, in accord with the Chauvin mechanism.[7a] Other support for the Chauvin mechanism came from the groups of R. Grubbs, T. Katz and, as indicated above, R. R. Schrock. In my article, I recognized the contribution by Katz as follows (p. 44): "Katz also performed a number of experiments going in the direction of the Chauvin mechanism.[8] He was among the first chemists whose work led to the recognition of the Chauvin mechanism, but the complexes used by Katz contained particular carbenes that were different from alkylidenes." and p. 46, concerning Schrock's catalysis of *cis*-2-pentene in 1980: "Earlier, other catalysis experiments had been carried out with [$W(CO)_5({=}CPh_2)$], but as we know that almost any tungsten-containing molecular compound catalyzes metathesis, eventually after decomposition of the precursor, these experiments cannot be considered as really significant." In the following, I will address in detail each point raised by Katz in his Opinion,[9] in which he proposes "corrections" to my history of olefin metathesis.

Metal-carbene initiators of olefin metathesis

Tantalum and niobium initiators

Katz's denying that Schrock reported metathesis of *cis*-2-pentene or any other simple olefin with the tantalum and niobium complexes [$M(PMe_3)(O\text{-}t\text{-}Bu)_2Cl({=}CHt\text{-}Bu)$], M=Nb or Ta, in 1980 simply has no basis.[5b] Indeed, this work represents the first time that productive catalytic metathesis of a simple olefin starting with a well-characterized metal-alkylidene complex has been observed. Schrock's 1980 article is entitled: "Preparation and characterization of active niobium, tantalum and tungsten metathesis catalysts". It shows, on page 75, that [$Ta(PMe_3)(O\text{-}t\text{-}Bu)_2Cl({=}CHt\text{-}Bu)$] reacts with either ethylene or styrene to give olefin metathesis products only. Then, a test reaction with 1-butene is carefully developed with these Nb and Ta metathesis catalysts, leading to several conclusions on the understanding of how and why these catalysts are working in the absence of co-catalyst. Then, Fig. 1 on page 79 of that paper nicely shows the kinetics of the catalysis of metathesis of *cis*-2-pentene by [$Nb(PMe_3)(O\text{-}t\text{-}Bu)_2Cl({=}CH\text{-}t\text{-}Bu)$] in mesitylene in the presence of PMe_3 at 25 °C. For instance, after 24 h at 25 °C, 3400 mL of hexenes and 2560 mL of butenes are formed, and the *cis*/*trans* ratio of 2-pentenes (below) resulting from the isomerization of *cis*-2-pentene is 0.33 (eqn (1)):

Laboratoire de Chimie Organique et Organométallique (CNRS UMR 5802), Université Bordeaux I, 351 Cours de la Libération, 33405 Talence Cedex, France. E-mail: d.astruc@lcoo.u-bordeaux1.fr



(1)

Finally, Schrock also reports that terminal olefins (propene and styrene) are slowly metathesized at 25–50 °C by the tungsten complex $[W(O)(O\text{-}t\text{-}Bu)(PEt_3)_2Cl_2]$ in the absence of co-catalyst, and that these metathesis reactions are accelerated by the presence of a trace of $AlCl_3$; *cis*-2-pentene is also metathesized by this catalyst, but more slowly.

In his Opinion, Katz also states that "The first single-component initiator of olefin metathesis, a metal-carbene that had been synthesized by Casey and Burkhardt, was reported by Katz and his students in 1976." This is not correct because the first olefin-metathesis reaction using this complex $[(C_6H_5)_2C{=}W(CO)_5]$ was reported by C. P. Casey and T. J. Burkhardt in 1974[7a] with the olefin $CH_2{=}C(Ph)(OMe)$ (eqn (2)), two years after the report by the same authors of the synthesis of this carbene complex.[7b]2

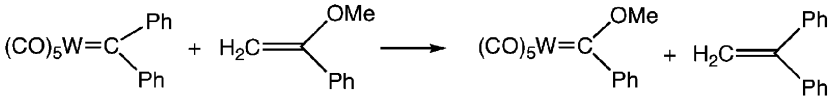
This report on a metathesis reaction by Casey and Burkhardt was the first one showing metathesis using a single-component metal-carbene complex, in agreement with the Chauvin mechanism, and it can be considered as the first American publication citing Chauvin's mechanism.[3] The above reaction of eqn (2), however, also gives other products, in particular decomposition products of the tungsten-carbene complex, which limit the yield of this stoichiometric reaction (*vide infra*).

Tungsten initiators

Concerning Katz's tungsten catalysts, my statement that "almost any tungsten-containing molecular compound catalyzes alkene metathesis, eventually after decomposition of the precursor", is contested by Katz in his Opinion. Katz used Casey's tungsten complex of eqn (1), $[(C_6H_5)_2C{=}W(CO)_5]$, as a metathesis catalyst. This work, despite its quality, did not prove the nature of the catalytically active species, which remained elusive, especially considering the decomposition of this complex during the stoichiometric reaction of eqn (2). In fact, such a statement has been formulated earlier in the *C&E News* article as follows:[2b] "...the metal in that carbene is not in a high oxidation state. Katz's work proved only what we knew already, that tungsten is an active metal for metathesis. It did not prove that the metal carbene is responsible for the reaction. It is possible that a very small amount of high-oxidation-state tungsten carbene species is formed under the reaction conditions described by Katz....If you put a metal complex in, you heat it up, and a reaction happens, you have no idea what's going on. It's not what you put in. What's important is showing that what you put in actually did the chemistry." Indeed, it could well be that an uncharacterized transient 16-electron species, $[W(CO)_4(C{=}CPh_2)]$, formed upon heating the precursor complex, was responsible for olefin binding and metathesis in Katz's reaction. It could as well be that another tungsten species, eventually produced by decomposition and/or oxidation of the latter in very small amounts, was responsible for initiating the reaction (tungsten-oxo complexes produced by reaction of air with tungsten compounds are excellent olefin metathesis catalysts[5b]). Along this line it should be noted, concerning the above metathesis reaction (eqn (2)), that the work by Casey and Burkhardt also showed a 45% yield of the decomposition product $[W(CO)_6]$ was obtained, in addition to the metathesis products, even when the metathesis reaction using $[(C_6H_5)_2C{=}W(CO)_5]$ was conducted for 3 h at a temperature as low as 31 °C. Thus, the stoichiometric Casey reaction of eqn (2) in no way indicates what the catalytically active tungsten species in the Katz system might be, even if the starting complex in Katz's system is the same as in Casey's reaction.

Katz uses the term "synonyms" to compare alkylidenes and carbenes and cites several references (see ref. 10 in Katz's Opinion[9]) to support this idea. I disagree with this usage, which is especially perturbing in the context of metathesis. Chemists know that alkylidenes (CHR, R = alkyl), a class of carbenes, are derived from alkanes and alkyls. All carbenes, however, are not alkylidenes. Carbenes that are not called alkylidenes are those bearing at least one atom different from carbon on the carbenic carbon, such as Fischer carbenes. The distinction between carbenes and alkylidenes is especially clear for the free ligand, which is not bonded to a transition metal. The difference between alkylidenes and heteroatom-stabilized carbenes is very important in terms of electronic structures: free alkylidenes, like free methylene CH_2, have a triplet ground state, and their complexes are best formulated as $M{=}CHR$.[10] On the other hand, free carbenes bearing a heteroatom on the carbenic carbon, such as Fischer carbenes, are singlets with large singlet–triplet energy gaps. As ligands, they are excellent σ-donors and weak π-acceptors and thus their transition-metal complexes should be formulated as $M \leftarrow CR(OR')$ although back donation should not be total. This difference in electronic structure has an influence on the reactivities of these complexes in catalysis.

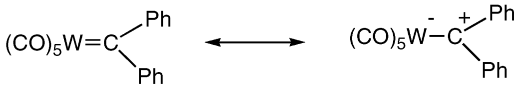
In terms of olefin metathesis activity, there is indeed a large body of data in the literature showing that, whereas many



(2)

alkylidene complexes are excellent metathesis catalysts, Fischer-type carbene complexes are at best very poor olefin metathesis catalysts.

The two phenyl substituents in Casey's carbene complex, $[(C_6H_5)_2C{=}W(CO)_5]$, are electron-withdrawing, contrary to the alkyl substituent in alkylidenes, which is electron-releasing. Thus, the diphenyl carbene complex bears a substantial amount of positive charge on the carbenic carbon, as shown by Casey,[11] although diphenylcarbene itself is a triplet.



The consequence for the reactivity with olefins is significant, because metal-carbenes bearing a substantial amount of positive charge on the carbenic carbon react with olefins in a specific way to form cyclopropanes.[12] In the case of $[(C_6H_5)_2C{=}W(CO)_5]$, its thermal instability at 31 °C has already been mentioned[10] and the metathesis experiments by Casey and Burkhardt (eqn (1)) also showed the concomitant temperature-dependent formation of some substituted cyclopropane derivatives.[7a] This is why it was justified to indicate, in the *NJC* review article, that the diphenylcarbene is somewhat different from an ordinary alkylidene ligand.[10]

The terms unimolecular and single-components (and possibly others) have been used to designate catalysts containing a single molecular compound as opposed to catalysts containing a mixture of two precursors such as WCl_6 + $AlEtCl_2$ or a tungsten complex + a Lewis acid. These terms do not refer to the kinetics and mechanism of the reaction, as Katz seems to indicate in ref. 5 of his Opinion.

Finally, the fact that Chauvin used excess $TiCl_4$ as a co-initiator does not contradict my statement that Chauvin promoted metathesis with Fischer carbene complexes, as opposed to what Katz states in his Opinion. Moreover, it is well-known by experts that Fischer-type carbene complexes are rather poor metathesis initiators (*vide supra*) and Katz himself published work confirming this point.[13]

The importance of metallacyclobutanes

According to Katz, stressing the importance of metallacyclobutanes in metathesis and other organometallic reactions is wrong, as in Chauvin's papers metallacyclobutanes were only implied intermediates. Indeed, while Chauvin drew a square scheme for his mechanism and metallacyclobutanes were sometimes isolated, most of the time they were transient intermediates that could not be isolated. Still, I do not see anything wrong with this. Moreover, the general importance of metallosquares in organometallic chemistry and catalysis is real. This is detailed in my book *Chimie Organométallique*[14a] (and its Spanish edition[14b]) and is further emphasized, together with some historical aspects, basic features and major applications of metathesis, in the forthcoming English version of this book.[14c]

Early history of metathesis

When discussing the early days of metathesis, Katz refers to Eleuterio's patent whereas I was referring to Eleuterio's historical review article[2a] in my *NJC* review paper, which is why some confusion may arise. The use of the WCl_6 + $AlEt_2Cl$ catalyst was first reported by Natta for the polymerization of cyclo-olefins, but at the time of Natta's publication, it was not recognized as being metathesis. According to Euleterio's historical review article, the fact that propylene was being selectively scrambled under remarkably mild conditions by promoted molybdena coordination-type catalysts was experimentally established for the first time by himself on November 21, 1956.[2a]

Substrates for alkyne metathesis

For applications to the synthesis of fine chemicals containing triple carbon–carbon bonds, the metathetic carbyne-exchange strategy using sacrificial terminal carbyne groups has indeed been relatively recently developed in a superb way, in particular by the groups of Fürstner in organic synthesis[15] and Bunz for molecular materials.[16] The terminal substituent usually is a methyl group and the alkyne formed is 2-butyne (eqn (3)):

$$2\,RC\equiv CMe \xrightleftharpoons{\text{cat.}} RC\equiv CR + MeC\equiv CMe \qquad (3)$$

Carbyne-exchange metathesis in which alkynes are terminated by a hydrogen atom has also been observed. For instance, in the article by Mortreux cited in Katz's Opinion, one can read, p. 99: "These results are consistent with the following metathesis reaction" {the catalyst was $[W(CCMe_3)(OCMe_3)]$ and the following equation was established after one minute at 21 °C (eqn (4))}:[18]

$$2\,C_5H_{11}C\equiv CH \xrightleftharpoons{\text{cat.}} C_5H_{11}C\equiv CC_5H_{11} + HC\equiv CH \quad (4)$$

Thus, this exchange metathesis is extremely efficient, contrary to what Katz says in his Opinion. Katz has nicely shown that polymerization of terminal alkynes occurs according to a metallosquare mechanism (the Katz mechanism, which is of the Chauvin type), which proceeds rapidly after carbyne-exchange metathesis. However, terminal alkynes also do undergo useful metathesis,[17] contrary to what is suggested by Katz in his Opinion. For instance, the first publication by Mortreux *et al.* in 1993,[18a] whose title is "Metathesis *vs.* polymerization of terminal acetylenes over $[W(CBu^t)(OBu^t)_3]$", showed how to favor catalytic carbyne-exchange metathesis of terminal alkynes using appropriate substituents and conditions (80 °C, ether). Since then, progress has been made in the specific field of efficient terminal alkyne-exchange metathesis to make it a useful organic reaction. Success has been obtained using quinuclidine together with the Schrock alkylidyne complex $[W(CCMe_3)(OCMe_3)]$: 80% of metathesis compounds were obtained at 80 °C within 1 min using 4 mol% of catalyst. Even phenylacetylene, which was earlier found to polymerize more easily than other terminal alkynes, gave several turnovers of carbyne-exchange metathesis. One can also find a literature report of a heterogeneous catalyst, $CoO\text{-}MoO_3\text{-}SiO_2$, for the carbyne-exchange metathesis of terminal alkynes such as 1-heptyne (eqn (5)):[19]

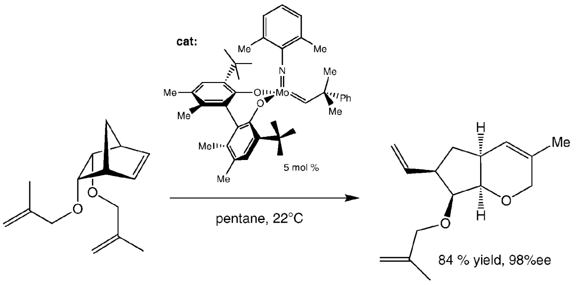
$$2\,RC\equiv CH \xrightleftharpoons{\substack{\text{cat.:}\\ CoO\text{-}MoO_3\text{-}SiO_2}} RC\equiv CR + HC\equiv CH \qquad (5)$$

$$R = \text{pentyl}$$

In all these catalyzed metathesis reactions of alkynes terminated by a hydrogen or even a methyl group, the formation of volatile acetylene or 2-butyne displaces the equilibrium towards the formation of the symmetrically disubstituted alkyne. This characteristic, together with the lack of stereoisomers (whereas stereoisomers are most often obtained in alkene metathesis), makes this alkyne metathesis reaction very useful.

Stereoselectivity of olefin metathesis

Katz denies that Schrock and Basset's catalysts are highly stereoselective, but they are. In his Opinion, Katz states that "the stereoselectivities achieved with Schrock metal-carbenes have usually been poor." In order to show that this statement is misleading, let me quote Schrock's chapter[20a] referring to his family of olefin metathesis catalysts [$Mo(NAr)(CHCMe_3)(OR)_2$] in Grubbs' handbook: "One of the more enlightening fundamental findings in this area was the elucidation of the origin of the *cis* or *trans* double bonds in the ROMP polymer prepared from norbornenes (or disubstituted norbornenes) and control of tacticity, *i.e.*, the stereochemical relationship between neighboring repeat units in the ROMP polymer. It was found that the *syn* isomer gave rise to the *cis* double bonds in the polymer, while the *anti* isomer gave rise to *trans* double bonds in the polymer.[20b] It was also found that the catalyst of the type [$Mo(NAr)(CHCMe_3)$(*rac*-diolate)] where *rac*-diolate is a racemic chiral diolate such as binaphtanoate, can control the tacticity of the polymer to a remarkable degree by enantiomorphic site control.[20c] In the process, it was also proven that an all *cis* polymer was isotactic, while an all *trans* polymer was syndiotactic.[20d] Perhaps most interesting from a fundamental point of view was the fact that the *anti* isomer in one example was estimated to be $\sim 10^5$ times more reactive than the *syn* isomer, even though the *anti* isomer could not be observed before or during the ROMP reaction[20a] ….Recent addition of molybdenum catalysts systems are those that contain a variety of enantiomerically pure biphenolate or binaphtanoate ligands and one or several imido ligands. Such species has been shown to catalyze a variety of ring-closing, ring-opening, and cross metathesis reactions efficiently.[20e] An example[20f] is shown…" (eqn (6)):



(6)

In the same handbook volume, one can find Basset's statement[21a] concerning his catalyst [$(ArO)_2W({=}CHt\text{-}Bu)(CH_2t\text{-}Bu)Cl(OR)_2$]: "In the case of the *o,o′*-diphenylphenoxy ligand, the product rearranges… to form another well-defined alkylidene… This complex displays good activity in olefin metathesis (500 equivalent of *cis* 2-pentene equilibrated in 1 min), but more importantly, the reaction is stereospecific (>99% stereoselectivity) *i.e.*, *cis* gives *cis* and *trans* gives *trans*… Conversely, the ROMP of 1-methylnorbornene provides a complete head-to-tail, predominantly syndiotactic polymer with 100% *cis* double bond.[21b] Moreover, this system is compatible with a wide range of functional groups, *i.e.* alkylsilanes, alkylstannanes, esters, ethers and, more surprisingly, phosphanes and thioethers in both RCM and self-metathesis or ROMP reactions.[21c]" This catalyst is a d^0 W^{VI} complex containing a neopentylidene and three aryloxy ligands, *i.e.*, it is also of the Schrock type.

Thus, comparison of Katz's work with Schrock and Basset's works is largely overestimated in favor of the author in Katz's Opinion.

Evidence for the mechanism of olefin metathesis

Chauvin has carefully detailed the experiments that led him to propose his mechanism and were consistent with it. The reader is invited to refer to Chauvin's papers[3] and for instance to the *C&E News* article that has already dealt with this issue.[2b] In addition, several authors have contributed to confirm the validity of Chauvin's mechanism. Among them, Casey's metathesis reaction was a key one in 1974.[7a] Stereochemical experiments that were independently reported by the groups of Grubbs[5d] and Katz[8] added confirmation. Finally, initiation of metathesis by Schrock's alkylidene complexes in 1980 completed the proof.[5b]

Scientific process

My mention of the fact that Chauvin had thought of Fischer's carbene complexes was not without precedent as this had already been stated in the *C&E News* article on the early days of metathesis.[2b] Concerning the question as to whether Grubbs has read Natta's article or not, the answer is that it is probable (but this is certainly not a matter much worth debating).

Katz's comments on this section end with the statement that if Schrock reported the first metal-methylene complex, it was E. O. Fischer who reported the first metal-carbene. Even if Fischer's discovery of Fischer carbene complexes was not emphasized in the *NJC* review, it was not hidden either. This is universally known and was cited in ref. 15 of my *NJC* review. But again, one must remember that Fischer carbene complexes are very poor metathesis initiators that are not used for such a purpose (*vide supra*),[10] whereas Schrock's families of tungsten-alkylidene complexes are excellent ones.

Conclusion

In my review, I have put the history of metathesis in perspective and no corrections are needed. When a research area is found to be sufficiently important to lead to a Nobel Prize, it is likely that several scientists have made key contributions to the field beside the actual Laureates. This is particularly true in the case of metathesis, for which American pioneers from industry contributed much, in particular Eleuterio who disclosed the first catalyzed metathesis reactions, N. Calderon who recognized and named metathesis, C. P. Casey who provided important confirmation of the fact that a metal-carbene complex could undergo the metathesis reaction, but also J.-M. Basset who remarkably linked the metal-alkylidene metathesis catalysts to surfaces and shown efficient catalysis herewith, A. Demonceau and A. F. Noels who generated and characterized the first arene-ruthenium-alkylidene metathesis catalyst in 1992–5, A. H. Hoveyda and K. Grela who have found extraordinarily efficient and easy-to-handle catalysts, W. A. Herrmann who has discovered that heterocyclic carbenes are formidable ligands for homogeneous catalysts, S. Nolan who has exploited Herrmann's idea and come up with a 2nd generation of Grubbs catalyst at about the same time as Grubbs, A. Fürstner who has brought a spectacular body of applications of alkene and alkyne metathesis in organic synthesis, A. Mortreux who first initiated alkyne metathesis, S. Blechert who disclosed stereoselectivity in cross-metathesis reactions, and the list goes on (see ref. 22). In addition, the memory of John Osborn and his seminal work on metathesis with tungsten-alkylidene complexes should be recalled. Of course, Thomas J. Katz clearly belongs to the detailed history of metathesis due to fine labeling and stereochemical experiments and his work on alkyne polymerization,[8,13,17a,23] but his attempts to overemphasize his own contribution by criticizing and denying others' are, in my opinion, counter productive.

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