View Article Online / Journal Homepage / Table of Contents for this issue

Corrections to a history of olefin metathesis

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Many assertions in an article titled "The metathesis reactions: from a historical perspective to recent developments" by Didier Astruc (*New J. Chem.*, 2005, 29, 42) are incorrect and misrepresent the history of the olefin metathesis reaction. Despite the availability of differing accounts, the errors in Astruc's article have not been recognized. I point to some of them here.

Introduction

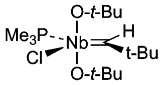
Many assertions in an article titled "The metathesis reactions: from a historical perspective to recent developments" by Didier Astruc[1] are incorrect and misrepresent the history of the olefin metathesis reaction. Despite the availability of differing accounts,[2,3] the errors in Astruc's article have not been recognized.[4] I point to some of them here.

Metal-carbene initiators of olefin metathesis

Tantalum and niobium initiators

With respect to initiations of olefin metathesis by tantalum-carbenes, Astruc states (on page 46) that "it was in 1980 that Dick Schrock's group at MIT reported a tantalum-alkylidene complex, $[Ta({=}CH{-}t\text{-}Bu)(Cl)(PMe_3)(O{-}t\text{-}Bu)_2]$, which catalyzed the metathesis of *cis*-2-pentene.... The reason that this complex catalyzes the metathesis reaction, whereas the other members of the family of niobium- and tantalum-alkylidene complexes failed to do so, was the presence of alkoxide ligands." However, the facts are that neither this tantalum-carbene nor any other tantalum-carbene, whether possessing alkoxide ligands or not, has ever been reported to initiate (or catalyze) the metathesis of *cis*-2-pentene or any other simple alkene. The experiments cannot be found in the literature Astruc cites, and they cannot be found anywhere else either.[3a] Because they are nonexistent, the experiments could not have involved "transition-metal-alkylidene complexes ... that [are] those really involved in metathesis catalysis" (page 44), could not "have provided the very first proof for Chauvin's mechanism of olefin metathesis" (page 46), and could not have "clearly established the validity of the Chauvin mechanism" (page 44).

Astruc claims two different metal-carbenes to have been the "1^{rst} [isolated] unimolecular metal-alkylidene metathesis catalyst." Neither of them was, even if "unimolecular" is taken to be a misnomer[5] for "single component." One of these metal-carbenes, in Astruc's Fig. 1, is the tantalum-derivative $[Ta({=}CH{-}t\text{-}Bu)(Cl)(PMe_3)(O{-}t\text{-}Bu)_2]$, whose claimed efficacy is nullified by the considerations in the paragraph above. The other, in Fig. 4, is a niobium-carbene (reproduced here as structure **1**) that is not a known substance.[6] The closest approach to published fact is that a material said to be an isomer of niobium-carbene **1** (there was no evidence for its purity), when mixed with unspecified amounts of trimethylphosphine, initiated metathesis of *cis*-2-pentene.[6] But the mixture cannot be said to be a single component, and the role of the trimethylphosphine has not been explained. (Is it a reducing agent?) The first single-component initiator of olefin metatheses, $[(C_6H_5)_2C{=}W(CO)_5]$, a metal-carbene that had been synthesized by Casey and Burkhardt,[7] was reported by Katz and his students in 1976.[8,9]



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Tungsten initiators

Although the experiments of Katz *et al.* demonstrated for the first time that olefin metatheses of a number of alkenes could be initiated by pure well-characterized tungsten-carbenes, Astruc alludes to them only vaguely and states (on page 46) that "these experiments cannot be considered as really significant" because "as we know ... almost any tungsten-containing molecular compound catalyzes alkene metathesis, eventually after decomposition of the precursor." Besides, "the complexes that were used by Katz [for which experiments is not said] contained particular carbenes that were different from alkylidenes" (page 44). No evidence is provided—nor is there any—to support the assertion that almost any decomposed tungsten-containing compound catalyzes olefin metathesis. Neither the inadequacy of "particular carbenes" nor the difference between the synonyms "carbenes" and "alkylidenes"[10] is explained.

Although Astruc's criticisms could have been applied to other experiments involving tungsten-carbenes, they were not. At the same time, deficiencies of these other experiments were overlooked. Thus, a "search for stable molecular alkylidene ... complexes ... that would catalyze the metathesis of unsaturated hydrocarbons," conducted long after the experiments above turned some up, is declared by Astruc to have been "successful" (page 46) when this search resulted in the publication of the statement that the tungsten-carbene $[W(CHt\text{Bu})(O)Cl_2(PEt_3)]$ in unspecified amounts initiated unspecified short-lived metatheses of unspecified terminal and internal olefins.[11] Similarly, "Chauvin himself," we are told (on page 44), "reported in 1976 that even some Fischer-type carbene could promote metathesis"—a misleading statement considering that what Chauvin

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showed was that tungsten-carbenes are effective only if they are first combined with 150 moles of titanium tetrachloride (!), then heated or photoirradiated, and that such recipes work even with tungsten compounds that do not have carbene ligands.[12,13]

The importance of metallacyclobutanes

Astruc repeatedly stresses Chauvin's recognition of the importance of metallacyclobutanes in organometallic reactions. His abstract points out how "the Chauvin metathesis mechanism, with formation of a metallacyclobutane, has been generalized to many organometallic reactions." Page 42 emphasizes "the little known implication of [Chauvin's] metallo-squares in most organometallic catalysis mechanisms." Page 53 asserts that "Chauvin['s] ... metallo-square mechanistic schemes are not only important in the olefin metathesis reaction, but for most organometallic reactions involved in catalysis." Page 44 states that "the intermediacy of the metallacyclobutane" is a "very important aspect of the Chauvin mechanism," and the legend to Scheme 1 says that the scheme shows "Chauvin's mechanism, proposed in 1971, for the catalyzed olefin metathesis involving metal alkylidene and metallacyclobutane intermediates."

However, the magnitude of these claims appears unjustified considering that in Chauvin's papers metallacyclobutanes were at best implied intermediates. None of his papers either shows or mentions them. None shows the mechanism displayed in Astruc's Scheme 1.

Early history of olefin metathesis

The early history of olefin metathesis is misrepresented. Pages 42–43 say that "the first polymerization of norbornene by the system $WCl_6/AlEt_2Cl$ was independently reported in 1960 by Eleuterio and by Truett *et al.*" However, neither Eleuterio nor Truett reported using $WCl_6/AlEt_2Cl$. Eleuterio used molybdenum oxide on alumina treated with hydrogen and lithium aluminium hydride.[14] Truett used $LiAl(heptyl)_4$ + $TiCl_4$,[15] a variant of a procedure (employing $LiAlBu_4$ + $TiCl_4$) that Anderson and Merckling had described in 1955 for the polymerization of norbornene.[16] The use of WCl_6 combined with $AlEt_2Cl$ as an initiator for cycloolefin polymerization was first reported by Natta *et al.* in 1966.[17]

Substrates for olefin metathesis

The kinds of molecules that undergo useful metatheses are misrepresented. Although page 43 states that "in fine chemical synthesis ... metathesis of a terminal ... alkyne ... displaces the reaction towards the product ... [so] terminal bis-alkynes ... selectively lead to cycloalkynes," the fact is that metathesis cannot be applied usefully to terminal alkynes.[18]

Stereoselectivity of olefin metathesis

The stereoselectivity achieved by metal-carbene initiators is misrepresented. Page 49 says that "one advantage of Schrock-type catalysts, also developed by Basset's group, ... is the extremely high stereoselectivity (up to 99%)." However, the stereoselectivities achieved with Schrock metal-carbenes have usually been poor.[19,20] A tungsten-carbene made by Basset induced high stereoselectivity in metatheses of *cis*-2-pentene and one (but not another) derivative of norbornene,[21] and a tungsten-carbene made by Schrock induced high stereoselectivity in the metathesis of 2,3-dicarbomethoxynorbornadiene.[22] But neither of these initiators is a derivative of the so-called "Schrock catalyst." By contrast, more than fifteen years before the earliest of these experiments, Katz *et al.* showed that high stereoselectivities are achieved in metatheses of many olefins when the metal-carbene initiator is pentacarbonyl(diphenylmethylene)tungsten.[3,8,9*a*]

Evidence for the mechanism of olefin metathesis

The evidence for the mechanism of olefin metathesis is misrepresented. According to Astruc, "Chauvin and Hérisson ... published several experiments to confirm it. For instance, the reaction of a mixture of cyclopentene and 2-pentene led to C-9, C-10 and C-11 dienes in the ratio 1 : 2 : 1" (page 44). Astruc is wrong to say that this experiment confirms the mechanism. It has been known for three decades that, contrary to Hérisson and Chauvin's assertions,[23] a 1 : 2 : 1 ratio should be obtained only at thermodynamic equilibrium and therefore has no mechanistic implication.[9,24]

Astruc adds that, unlike the reaction of cyclopentene with 2-pentene, "the reaction of a mixture of cyclooctene and 2-pentene led almost exclusively to the C-13 product." But it is not the substitution of cyclooctene for cyclopentene that leads to one product in place of three. It is the substitution of a terminal alkene for an internal alkene. Contrary to what Astruc says, 2-pentene does not give this result; 1-pentene does. And although Hérisson and Chauvin stated that the result was incompatible with the metal-carbene-propagated mechanism,[23] it is in fact compatible with this mechanism.[3*b*,24]

Astruc reports that another of Chauvin's experiments confirmed the mechanism: "In 1973, Chauvin [showed] that the WCl_6 + MeLi mixture catalyzes [*sic*[25]] the formation of propene by reaction of 2-butene, which was proposed to proceed [by forming] $W{=}CH_2(H)$." What he does not mention is that Chauvin also reported that the same experiments, while giving similar results when Me_4Sn was used in place of MeLi, failed when the organometallic compound was either Et_4Sn or Bu_4Sn.[26] All these tin compounds in combination with WCl_6 initiate olefin metatheses.[27] Astruc also fails to tell the reader about later studies that call into question the significance of these results: one shows that, in an experiment like Chauvin's, olefin metathesis starts only long after the propene forms;[28] another shows that in such experiments a $W{=}CH_2$ derivative forms only slowly and is not an efficient initiator of olefin metatheses.[29]

Scientific process

Astruc's history appears to be faulty. The following is from page 43. "In the process of thinking about the metathesis mechanism, Yves Chauvin from the Institut Français du Pétrole, had taken into account the report of E. O. Fischer on the synthesis of a tungsten-carbene complex, that of Natta on the polymerization of cyclopentene by ring opening catalyzed by a mixture of WCl_6 and $AlEt_3$ and that of R. L. Banks and G. C. Bailey on the formation of ethylene and 2-butene from propene catalyzed by $[W(CO)_6]$ on alumina. Consequently, Yves Chauvin and his student Jean-Louis Hérisson published their proposition of metathesis mechanism in 1971 (Scheme 1).'' No record of Chauvin's thinking is cited, but in his paper with Hérisson[23] he did not mention E. O. Fischer's tungsten-carbene complexes.

There are other historical inaccuracies. On page 47: "Grubbs … had noticed Natta's 1965 publication on the catalysis by $RuCl_3$" (the evidence is that he had not[30]); and further, "this process (in butanol) had been developed by Norsorex." (Norsorex is the brand name of a polynorbornenamer made by the procedure of Michelotti and Keaveney,[31,32] who were the first to polymerize norbornene with $RuCl_3$ in ethanol.) And on page 53: "Dick Schrock combined these two essential aspects of inorganic chemistry [Wilkinson's ideas about organometallic synthesis and Osborn's on homogeneous catalysis] to bring to the chemical community the first stable metal-methylene, -alkylidene and -alkylidene [*sic*; -alkylidyne ?] complexes." Schrock did indeed synthesize the first stable metal-methylene (the metal was tantalum and the year was 1975).[33] However, it was E. O. Fischer who synthesized the first stable metal-carbene (the metal was tungsten and the year was 1964)[34] and the first stable metal-carbynes (the metals were chromium, molybdenum, and tungsten and the year was 1973).[35]

References

1 D. Astruc, *New J. Chem.*, 2005, **29**, 42.

2 (*a*) K. J. Ivin and J. C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, San Diego, 1997, ch. 1; (*b*) R. H. Grubbs, *Tetrahedron*, 2004, **60**, 7117; (*c*) K. C. Nicolaou and S. A. Snyder, *Classics in Total Synthesis II*, Wiley-VCH, Weinheim, 2003, pp. 163–172; (*d*) *Handbook of Metathesis*, ed. R. H. Grubbs, Wiley-VCH, Weinheim, 2003, vols 1–3; (*e*) A. M. Rouhi, *Chem. Eng. News*, December 23, 2002, p. 34; (*f*) M. Schuster and S. Blechert, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2036 (*Angew. Chem.*, 1997, **109**, 2124).

3 (*a*) T. J. Katz, *Angew. Chem., Int. Ed.*, 2005, **44**, 3010 (*Angew. Chem.*, 2005, **117**, 3070); (*b*) T. J. Katz, *Adv. Organomet. Chem.*, 1977, **16**, 283.

4 For example, both the Royal Swedish Academy and C. P. Casey recommended the article for reading and incorporated portions of it in their writings. (*a*) http://nobelprize.org/chemistry/laureates/2005/chemreading.html; (*b*) http://nobelprize.org/chemistry/laureates/2005/adv.html; (*c*) C. P. Casey, *J. Chem. Educ.*, 2006, **83**, 192. Others claim the article supports the research in their publications.

5 A catalytic transformation cannot be unimolecular.

6 A material assigned the formula of **1** exhibits two ^1H NMR signals for the *tert*-butoxy groups, while structure **1** would exhibit only one. S. M. Rocklage, J. D. Fellmann, G. A. Rupprecht, L. W. Messerle and R. R. Schrock, *J. Am. Chem. Soc.*, 1981, **103**, 1440.

7 (*a*) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, 1973, **95**, 5833; (*b*) C. P. Casey, T. J. Burkhardt, C. A. Bunnell and J. C. Calabrese, *J. Am. Chem. Soc.*, 1977, **99**, 2127.

8 This and related tungsten-carbenes initiated metatheses of a variety of olefins. (*a*) J. McGinnis, T. J. Katz and S. Hurwitz, *J. Am. Chem. Soc.*, 1976, **98**, 605; (*b*) T. J. Katz, J. McGinnis and C. Altus, *J. Am. Chem. Soc.*, 1976, **98**, 606; (*c*) T. J. Katz, S. J. Lee and N. Acton, *Tetrahedron Lett.*, 1976, 4247; (*d*) T. J. Katz and N. Acton, *Tetrahedron Lett.*, 1976, 4251; (*e*) S. J. Lee, J. McGinnis and T. J. Katz, *J. Am. Chem. Soc.*, 1976, **98**, 7818; (*f*) T. J. Katz and W. H. Hersh, *Tetrahedron Lett.*, 1977, 585.

9 For reviews, see: (*a*) T. J. Katz, in *Handbook of Metathesis*, ed. R. H. Grubbs, Wiley-VCH, Weinheim, 2003, vol. 1, ch. 1.5; (*b*) ref. 3*b*.

10 Some have recognized that the synonyms cannot be distinguished: (*a*) K. H. Dötz, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 587 (*Angew. Chem.*, 1984, **96**, 573); (*b*) F. Zaragoza Dörwald, *Metal Carbenes in Organic Synthesis*, Wiley-VCH, New York, 1999, p. 1; (*c*) M. Brookhart and W. B. Studabaker, *Chem. Rev.*, 1987, **87**, 411; (*d*) S. T. Nguyen, L. K. Johnson, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1992, **114**, 3974.

11 J. H. Wengrovius, R. R. Schrock, M. R. Churchill, J. R. Missert and W. J. Youngs, *J. Am. Chem. Soc.*, 1980, **102**, 4515.

12 For example, $(C_2H_5NH_2)W(CO)_5$ combined with 150 moles of $TiCl_4$.

13 Y. Chauvin, D. Commereuc and D. Cruypelinck, *Makromol.Chem.*, 1976, **177**, 2637.

14 H. S. Eleuterio, *Ger. Pat.* 1,072,811, 1960.

15 W. L. Truett, D. R. Johnson, I. M. Robinson and B. A. Montague, *J. Am. Chem. Soc.*, 1960, **82**, 2337.

16 A. W. Anderson and N. G. Merckling, *US Pat.* 2,721,189, 1955.

17 G. Natta, G. Dall'Asta, I. W. Bassi and G. Carella, *Makromol. Chem.*, 1966, **91**, 87.

18 A. Mortreux, F. Petit, M. Petit and T. Szymanska-Buzar, *J. Mol. Catal. A: Chem.*, 1995, **96**, 95.

19 P. Dounis, W. J. Feast and A. M. Kenwright, *Polymer*, 1995, **36**, 2787, reported that a not fully specified Schrock tungsten-carbene converts cyclooctene in unspecified yield into 90%-*cis*-polyoctenamer and cyclopentene, cyclodecene, and cyclododecene into 55-, 20-, and 20%-*cis*-polyalkenamers. Cycloheptene gives no polymer. Schrock molybdenum-carbenes give polymers whose double bonds are mainly *trans*.

20 Norbornene derivatives have sometimes given high stereoselectivities. (*a*) R. R. Schrock, J. Feldman, L. F. Cannizzo and R. H. Grubbs, *Macromolecules*, 1987, **20**, 1169; (*b*) W. J. Feast, V. C. Gibson and E. L. Marshall, *J. Chem. Soc., Chem. Commun.*, 1992, 1157; (*c*) E. Khosravi and A. A. Al-Hajaji, *Polymer*, 1998, **39**, 5619; (*d*) R. R. Schrock, J.-K. Lee, R. O'Dell and J. H. Oskam, *Macromolecules*, 1995, **28**, 5933; (*e*) J. G. Hamilton, in *Handbook of Metathesis*, ed. R. H. Grubbs, Wiley-VCH, Weinheim, 2003, vol. 3, ch. 3.5, and references therein.

21 (*a*) J.-L. Couturier, C. Paillet, M. Leconte, J.-M. Basset and K. Weiss, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 628 (*Angew. Chem.*, 1992, **104**, 622); (*b*) two related initiators induce lesser stereoselectivity: F. Quignard, M. Leconte and J.-M. Basset, *J. Chem. Soc., Chem. Commun.*, 1985, 1816.

22 M. B. O'Donoghue, R. R. Schrock, A. M. LaPointe and W. M. Davis, *Organometallics*, 1996, **15**, 1334.

23 J. L. Hérisson and Y. Chauvin, *Makromol. Chem.*, 1971, **141**, 161.

24 (*a*) T. J. Katz and J. McGinnis, *J. Am. Chem. Soc.*, 1975, **97**, 1592; (*b*) T. J. Katz and J. McGinnis, *J. Am. Chem. Soc.*, 1977, **99**, 1903; (*c*) See also: http://www.columbia.edu/cu/chemistry/fac-bios/katz/group/pages/publications.html#N10478.

25 The word "catalyzes" is misused here. The yield of propene was 3% based on MeLi, 6% based on WCl_6, and 0.6% based on 2-butene.

26 J.-P. Soufflet, D. Commereuc and Y. Chauvin, *C. R. Seances Acad. Sci., Ser. C*, 1973, **276**, 169.

27 (*a*) For Bu_4Sn, see: C. P. C. Bradshaw, *Ger. Pat.* DE1909951, 1969; (*b*) for Et_4Sn, see: G. Pampus, G. Lehnert and D. Maertens, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 1972, **13**, 880; (*c*) tetraphenyltin, which cannot produce a tungsten-carbene by a mechanism analogous to the one postulated, is also effective. See: J. Sedláček, J. Vohlídal, J. Kares, M. Pacovská and B. Máca, *Collect. Czech. Chem. Commun.*, 1994, **59**, 2454, and references therein; (*d*) for some comparisons among these coinitiators, see: M. Dimonie, S. Coca and V. Drăguţan, *J. Mol. Catal.*, 1992, **76**, 79.

28 E. Thorn-Csányi, *Angew. Makromol. Chem.*, 1981, **94**, 181.

29 K. J. Ivin and B. D. Milligan, *Makromol. Chem., Rapid Commun.*, 1987, **8**, 269.

30 (*a*) B. M. Novak and R. H. Grubbs, *J. Am. Chem. Soc.*, 1988, **110**, 960, refer to ; (*b*) H. T. Ho, K. J. Ivin and J. J. Rooney, *J. Mol. Catal.*, 1982, **15**, 245.

31 F. W. Michelotti and W. P. Keaveney, *J. Polym. Sci., Part A: Gen. Pap.*, 1965, **3**, 895.

32 J. Vergne, L. Solaux, J.-C. Robinet and P. Lacroix, *US Pat.* 3,676,390, 1972.

33 R. R. Schrock, *J. Am. Chem. Soc.*, 1975, **97**, 6577.

34 E. O. Fischer and A. Maasböl, *Angew. Chem., Int. Ed. Engl.*, 1964, **3**, 580 (*Angew. Chem.*, 1964, **76**, 645).

35 E. O. Fischer, G. Kreis, C. G. Kreiter, J. Müller, G. Huttner and H. Lorenz, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 564 (*Angew. Chem.*, 1973, **85**, 618).