Pergamon

Tetrahedron, Vol. 52, No. 7, pp. 2565-2572, 1996

0040-4020/96 $15.00 + 0.00

0040-4020(95)01082-3

The Formation of Catenanes.
The Möbius Strip Approach Revisited

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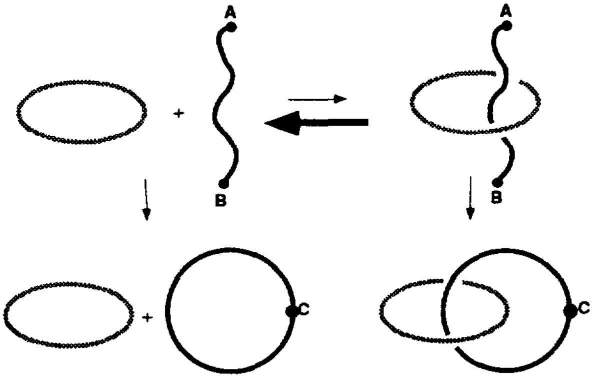
Abstract: The "Möbius strip approach" for the synthesis of catenanes requires that a ladder shaped molecule (doubly functionalized at both ends) twists twice prior to bimacrocyclization. A successful application of this strategy was claimed in the 1960's. However, the catenanes were *believed* to be formed via a *Möbius strip mechanism* since, at that time, a metal coordinated all carbon cyclobutane was assumed to be an intermediate in the olefin metathesis. Although the incompatibility of the Möbius strip mechanism and the (later proposed) actual metathesis mechanism has been pointed out, the original claim keeps being cited as a successful one even in the recent literature. In this paper, the background of this mechanistic misconception is discussed, and it is demonstrated that the formation of catenanes in olefin metathesis is resulting from a statistical threading process.

INTRODUCTION

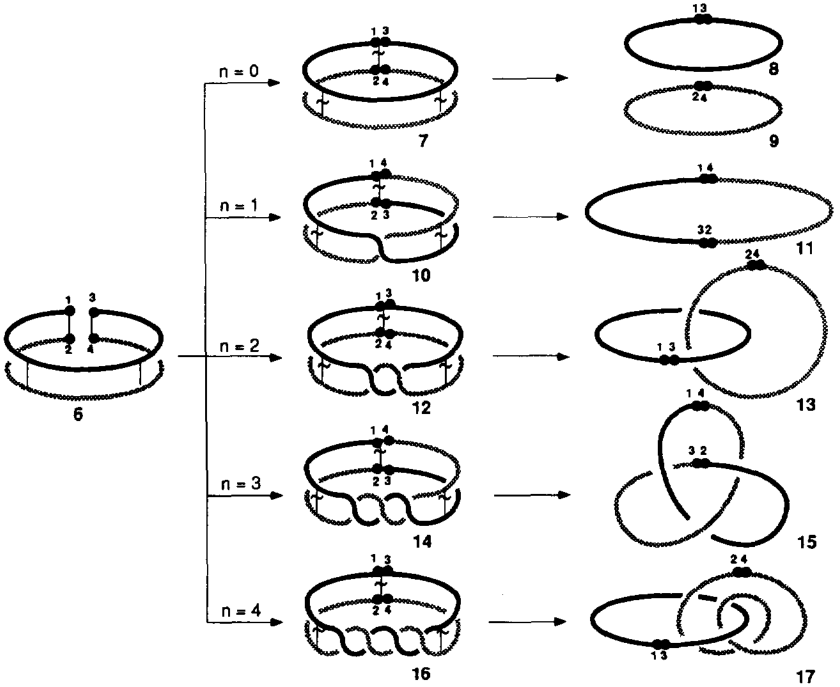
The literature concerning interlocking and knotted rings has been reviewed recently.[1-3] Today, several routes for the synthesis of catenanes are known. Four of these routes received considerable attention: statistical threading,[4-7] the Möbius strip approach,[8-12] multistep directed synthesis,[13-17] and template synthesis using either transition metals[18-25] or electron donor-acceptor interactions.[26-32] The first catenanes were synthesized by application of the very simple principle of statistical threading (Scheme 1). In this approach, a linear compound **1** is cyclized in the presence of a cyclic compound **2**. Compound **1** has two functionalities **A** and **B** that can react to give junction **C** resulting in the cyclic compound **3**. If **2** has a sufficiently large cavity, a certain, though very small amount of **1** will at any moment be threaded through **2** as shown in **4**. In this situation, cyclization of **1** interlocks the rings of **2** and **3** under formation of the catenane **5**. Note that to avoid oligomerization the cyclization of **1** requires the use of *high dilution* conditions, but that the threading process is favoured by *high concentrations*. It is therefore not surprising that yields of less than 1% were reported for synthesis using this methodology.

Almost simultaneously, a second route was claimed to be successful, namely the Möbius strip approach.[8] The principle of this method is based on the fact that a ladder shaped molecule **6** may twist n times prior to bimacrocyclization. Ring closure can occur according to 1-3/2-4 or 1-4/2-3, as shown in Scheme 2. If no twist occurs (n = 0), cyclization to **7** followed by cleavage of the rungs yields two unconnected rings **8** and **9**.

Scheme 1.



Scheme 2

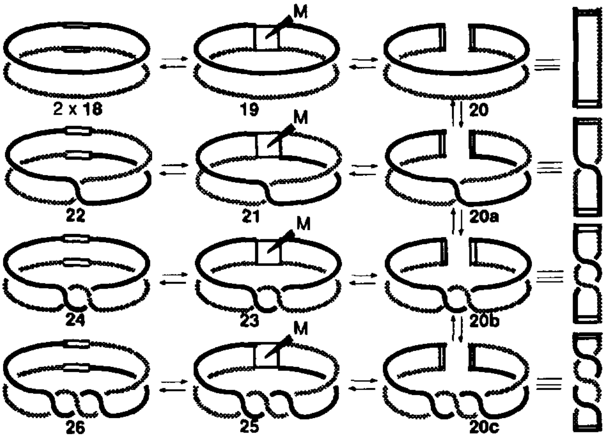


With a single twist (n = 1; 180°) as in **10**, a large cyclic molecule **11** is obtained after cleavage of the rungs. With a double twist (n = 2; 360°), a single fully twisted Möbius strip **12** is formed, which leads to catenane **13** after cleavage of the rungs. Note that a triple twist (n = 3; 540°) to **14** would yield the trefoil knot **15** and a quadruple twist (n = 4; 720°) to **16** would result in the doubly threaded catenane **17**. A singly twisted Möbius strip was synthesized by this method in 1982,[33] but the synthesis of a stable organic doubly twisted Möbius strip has to our knowledge not been reported.

DISCUSSION

A successful synthesis of catenanes was claimed to proceed via an olefin metathesis proces.[8-10] Wasserman *et al.* performed an olefin metathesis on cyclododecene using a tungsten catalyst. This process was reported to yield a mixture of large cyclic (poly)olefins $(C_{12}H_{22})_n$, the mass spectra of which provide convincing evidence that catenanes, e.g. a C_{72} + C_{72} catenane, are indeed formed in the metathesis of cyclic olefins. However, the *mechanism* presented by the authors for this catenane formation, which at that time was supposed to proceed via the intermediately double twisted Möbius strip **23** (Scheme 3), cannot be correct as will be elaborated below.

Scheme 3

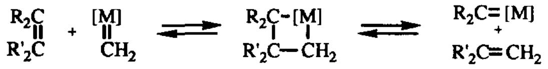


According to Scheme 3, which is based on the "old" olefin metathesis mechanism invoking a metal coordinated cyclobutane intermediate (such as **19**, **21**, **23**, or **25**), the dimer **20** plays a key role. It is formed from two n-membered olefins **18** in the first metathesis. The formation of n,n-catenanes **24** and 2n macrocylic diolefins **22** is attributed to twisting of the cyclic 2n-membered diolefin **20** prior to the second olefin metathesis. Note, however, that **22** is *in practice* indistinguishable from **20** (and **20a**) as they are conformational isomers and/or products of an identity reaction.

In order to form catenane **24** from two cyclic olefins **18**, the sequence **18** - **19** - **20** - **20a** - **20b** - **23** - **24** has to be completed. From **20** to **20a** the strip is twisted 180° and from **20a** to **20b** by another 180°. If the cyclobutane containing species like **19**, **21**, **23**, and **25** were indeed *intermediates* in the olefin metathesis process, this mechanism would be a feasible one. The yield of catenanes would depend on the statistical probability that **20** twists 360° prior to its intramolecular metathesis. The formation of the above mentioned C_{72} + C_{72} catenane would need 2 x 6 = 12 additive metathesis steps involving cyclododecene to obtain the C144 dodecaolefin (**20** in scheme 3); a 360° twist and a subsequent intramolecular metathesis would yield the catenane **24**.

However, after the development of the concept described in Scheme 3, it has become apparent that olefin metathesis *does not* proceed via the formation of a (metal-coordinated) cyclobutane ring, but via a transient metallacyclobutane species formed from a metal carbene complex and the C=C double bond of an olefin (Scheme 4).[34]

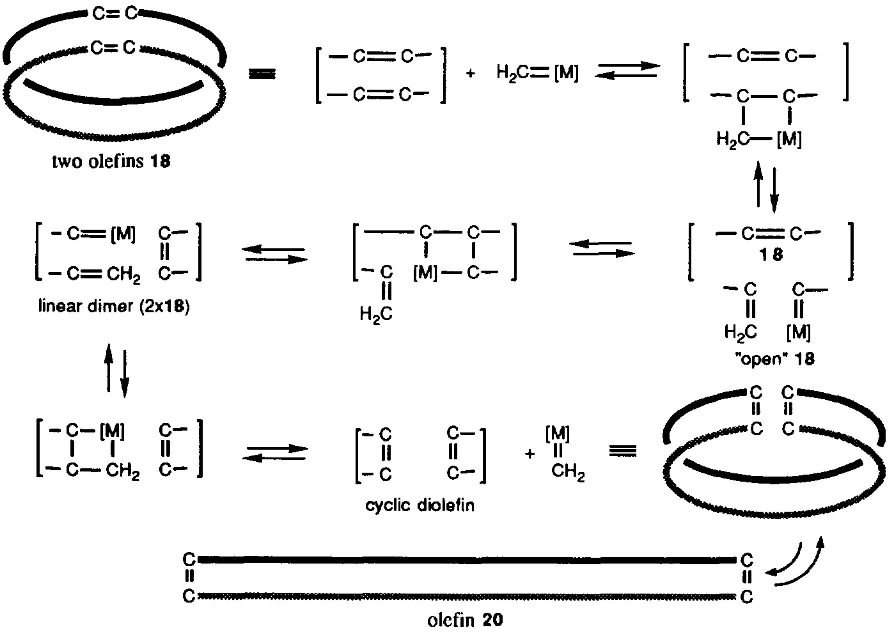
Scheme 4



The incompatibility of the Möbius strip mechanism and the actual metathesis mechanism has been noted incidentally. In 1975 Katz pointed out that "the formation of large rings and catenanes from smaller cyclic olefins can be interpreted as proceeding not through twisted intermediates" (like **23**, Scheme 3) "but by cyclization of the terminal carbene upon an internal double bond of a long chain."[35] In 1977 Katz published a similar statement in a review on olefin metathesis.[36] In 1985 Walba discussed an alternative mechanism in order to explain the formation of catenanes during a metathesis process. Walba considered a twisted acyclic alkylidene (like **27**, Scheme 6, *vide infra*) and he rejected a threading process as being too unfavourable.[37] Finally, in 1993 Breslow stated that a statistical threading process was responsible for the formation of catenanes: "By the carbene mechanism, formation of the catenane would result from a growing chain threading its way through an already formed oligomer and then backbiting".[38]

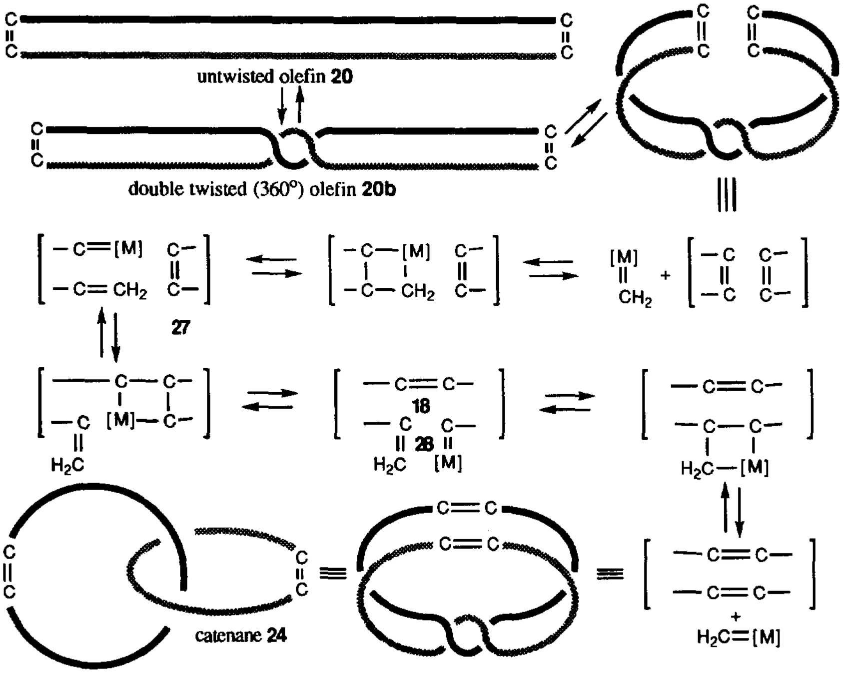
The considerable interest in this topic is apparent from the fact that Wasserman's paper has been cited 55 times (citations in books not included). Against this background, it is amazing that only the abovementioned 4 papers are based on the correct olefin metathesis mechanism and, moreover, that none of them refers to any of the others. The remaining 51 papers on this topic repeat the misconception that the (as such not challenged) formation of catenanes by olefin metathesis proceeds by the originally proposed Möbius strip mechanism. This is all the more remarkable because 45 of these, including recent state of the art reviews[1-3,39] and an editorial in Nature,[40] have appeared after Katz had in 1975 first pointed out the implications of the new, correct metathesis mechanism for this problem. It is for this reason that we believe that an explicit and comprehensive presentation of the chemistry actually involved is appropriate; it is outlined in Schemes 5 and 6.

Scheme 5



The formation of the cyclic diolefin **20** from two molecules of **18** involves three olefin metathesis steps: in the first step one of the olefins is opened, after which in the second step, a linear dimer is formed, and in the third metathesis, the linear dimer is cyclized to form the cyclic diolefin **20**. From **20** to **20b**, a double twist is involved. Next, from **20b** to catenane **24**, three olefin metathesis steps are required as outlined in Scheme 6. Even if the double twist is conserved *during all* of these steps, as suggested by Walba,[37] which is *extremely unlikely*, a Möbius strip is not involved *at any stage* because in the first metathesis of Scheme 6, the reaction of **20b** with a metal carbene gives an intermediate **27** in which *the ring has been opened*! After the second metathesis step in Scheme 6, a molecule of **18** is formed, threaded (or intertwined) by the α-ene-ω-carbene complex **28**. Ultimately, catenane **24** is produced after the third metathesis step.

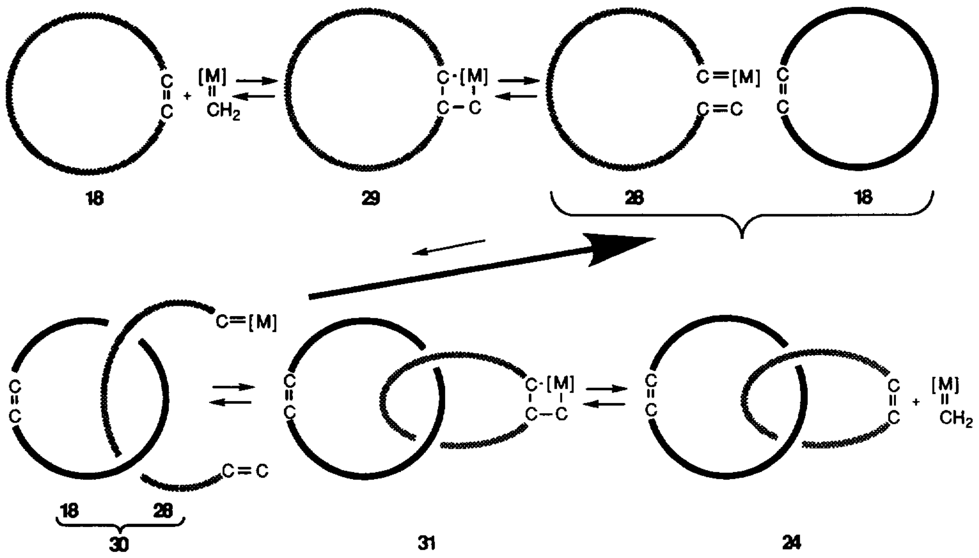
Scheme 6



Thus, the formation of **24** by twisting of **20** to **20b** followed by olefin metathesis, if applicable at all, would in the essential step come down to the ring closure of an acyclic entity through a ring, and it is therefore topologically equivalent to the original (statistical) threading mechanism. The only difference would be that in the process of Scheme 6, the threading - or intertwining - of the two non-bonded molecules has occurred by a twist in **20** followed by ring cleavage, which in turn would require the rather doubtful assumption that the double twist conformation survives during the last two metathesis steps.

Finally, the challenging question remains of how the catenane formation under olefin metathesis conditions actually does proceed. As outlined above, the pathway via **20b**, the doubly twisted conformer of **20** (Scheme 6), is highly unlikely for more than one reason. Based on the generally accepted mechanism of olefin metathesis,[34,41,42] the "old-fashioned", straightforward statistical threading mechanism (Scheme 1) appears to be the only reasonable alternative as elaborated in Scheme 7.

Scheme 7



In the first step of metathesis, addition of the metal-carbene carbene complex to **18** yields the metallacyclobutane **29** which cleaves to furnish the ring opened α-ene-ω-carbene complex **28** (cf. also Scheme 6). As indicated in the Introduction (cf. Scheme 1), a certain, low percentage of **28** will happen to be threaded through **18** as in **30**; presumably threading proceeds by piercing of the -CH=CH_2 unit of **28** through **18** because it is smaller than the -CH=[M] unit. Subsequent ring closure by a second metathesis via **31** then produces the catenane **24**. One would, incidentally, predict that catenanes smaller than those actually observed, e.g.(C_{72} + C_{12n}) with n = 1, 2, etc., are formed by analogous processes, but probably have escaped detection by the mass spectrometric analysis mentioned.[8]

CONCLUSION

It is obvious that the formation of catenanes in the olefin metathesis, claimed in the original papers[8-12] and cited in recent reviews,[2,3,39,41] cannot proceed by the original Möbius strip concept. Based on modern insight into the mechanism of olefin metathesis, it is argued that these reactions involve metallacyclobutanes and ring opened α-olefin-ω-carbene complexes such as **28** as the key intermediates. Catenanes are formed by the classical statistical threading process by which **28**, produced in a single olefin metathesis step from the cyclic olefin **18**, is piercing the cavity of another **18**, followed by metathetical ring closure.

ACKNOWLEDGEMENTS

This work was supported in part (G.-J. M. G) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO) which is gratefully acknowledged.

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(*Received in UK* 19 *April* 1995; *accepted* 14 *December* 1995)