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Metathesis

Cyclooctane Metathesis Catalyzed by Silica-Supported Tungsten Pentamethyl [(≡SiO)W(Me)$_5$]: Distribution of Macrocyclic Alkanes

Nassima Riache,[a] Emmanuel Callens,*[a] Manoja K. Samantaray,[a] Najeh M. Kharbatia,[b] Muhammad Atiqullah,[c] and Jean-Marie Basset*[a]

Abstract: Metathesis of cyclic alkanes catalyzed by the new surface complex [(≡SiO)W(Me)$_5$] affords a wide distribution of cyclic and macrocyclic alkanes. The major products with the formula C_nH_{2n} are the result of either a ring contraction or ring expansion of cyclooctane leading to lower unsubstituted cyclic alkanes ($5 \leq n \leq 7$) and to an unprecedented distribution of unsubstituted macrocyclic alkanes ($12 \leq n \leq 40$), respectively, identified by GC/MS and by NMR spectroscopies.

Introduction

Macrocyclic alkanes are a class of molecules with high value interest in industry. For instance, macrocyclic alkanes and their methylated analogues are biomarkers isolated from torbanite of *Botryococcus braunii* used in studies of environmental change.[1] Macrocyclic alkanes could also serve as building blocks in the synthesis of macrolides. In fact, the carbon skeleton is found in several macrocyclic musk (muscone, civetone, exaltolide, etc.) used as olfactory molecules.[2] Today, a facile access to various macrocyclic alkanes size remains a synthetic challenge. The late valuable transformation, which converts given linear alkanes to higher linear alkanes, namely alkane metathesis is an interesting strategic tool.[3] To date, two alkane metathesis catalytic systems have been reported.[4] The alkane metathesis through a single catalytic system was discovered in the 90s with silica-supported tantalum hydride[5] and extended to oxides supported group VI hydrides later on. These systems act as multifunctional supported catalysts, which transform acyclic light alkanes into a mixture of their lower and higher homologues.[6] Another catalytic system employs a tandem strategy with two different metals, one metal for alkane (de)hydrogenation step and another one for olefin metathesis transformation. This tandem catalytic system generally operates at high temperature[7] until the recent development of an homogeneous iridium-based pincer complex with an olefin metathesis catalyst.[8]

Thus, it was envisaged that cyclooctane metathesis would offer a rapid and facile access to these cyclic structures. In 2008, cyclooctane metathesis in a tandem system employing the pincer-ligated iridium complexes acting as hydrogenation/dehydrogenation catalysts combined with Schrock-type Mo-alkylidene complexes as olefin metathesis catalyst has been reported.[9] Although the cyclooctane conversion was 27–80%, this tandem catalytic system suffers from the formation of polymeric products (>80%), which renders the isolation of macrocyclic compounds difficult. Besides, these alkanes correspond essentially to cyclooctane oligomers (cC_{16}, cC_{24}, cC_{32}, and cC_{40}).[9] In the following work, we envisage that employing a single multifunctional silica-supported catalyst **1** would be an alternative catalytic system for the synthesis of a wider distribution of macrocyclic alkanes (Figure 1).[10] We report here our findings showing remarkable results on cycloalkane metathesis with this W catalyst.

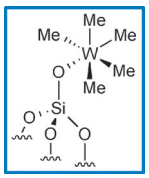

Figure 1. Silica-supported W catalyst precursor **1**.

Results and Discussion

In a typical experiment, cyclic alkane (3.7 mmol) and the catalyst precursor **1** (6.5 μmol) were added using a glovebox into an ampoule. Each ampoule was then sealed under vacuum and heated at 150 °C. At the end of the catalytic run, the reaction was allowed to cool to −78 °C. After filtration, an aliquot was analyzed by GC and GC-MS techniques (for a calibration Table see Figures S1 and S2 in the Supporting Information). To

[a] *N. Riache, E. Callens, M. K. Samantaray, J.-M. Basset*
KAUST Catalysis Center, King Abdullah University of Science and Technology, Thuwal 23955-6900 (Kingdom of Saudi Arabia)
E-mail: emmanuel.callens@kaust.edu.sa
jeanmarie.basset@kaust.edu.sa

[b] *N. M. Kharbatia*
Analytical Core Laboratory, King Abdullah University of Science and Technology, Thuwal 23955-6900 (Kingdom of Saudi Arabia)

[c] *M. Atiqullah*
Center for Refining & Petrochemicals
Center of Research Excellence in Petroleum Refining & Petrochemicals
King Fahd University of Petroleum & Minerals
Dhahran 31261 (Saudi Arabia)

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ensure that the nature of the catalytic site is heterogeneous, we analyzed the filtrate at the end of the reaction and found that the concentration of W was less than 0.1 ppm.[11] Besides, no reaction could be observed when adding cyclooctane to this filtrate. To analyze the higher oligomers, a suitable GC methodology was developed allowing the detection up to pentamers of cyclooctane.[12]

The typical GC chromatogram of cyclooctane metathesis displays a distribution of peaks. The most intense ones have molecular formula C_nH_{2n}: 1) Three peaks with lower retention time than cyclooctane (on GC) correlate with the peaks with lower molecular weight ($< C_8$) (on GC-MS) and 2) other peaks with longer retention time and higher molecular weight (Figure 2).

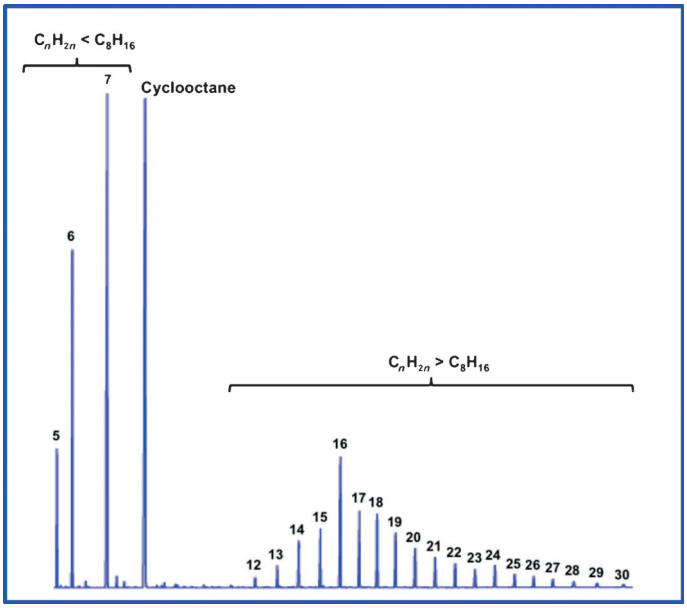


Figure 2. GC chromatogram of cyclooctane metathesis products catalyzed by **1**. Reaction conditions: Batch reactor, compound **1** (300 mg, 23 μmol, W loading: 1.4 wt%), cyclooctane (2 mL, 14.88 mmol), 190 h, 150 °C. Conversion = 70%, TON = 450. The turnover number (TON) is the number of mol of cyclooctane transformed per mole of W.

Lower cycloalkanes with a molecular weight ranging from C_5 to C_7 are attributed to cyclopentane, cyclohexane, and cycloheptane. They result from the ring contraction of cyclooctane (see below for the mechanism). With very few literature data available, the compounds with chemical formula of C_nH_{2n} ranging from C_{12} to C_{40} required more thought concerning their characterizations. From the molecular formula, they could be either macrocyclic alkanes or linear olefins as well as branched cyclic alkanes. Firstly, proton and carbon NMR spectra of the resulting solution at the end of the catalytic run shows the absence of olefinic protons and sp^2 carbons that would correspond to a double bond (see Figures S3 and S4, the Supporting Information). Macrocyclic alkanes from C_{12}–C_{15}, C_{24}, C_{28}, and C_{30} were identified by comparison with the mass spectra of the corresponding library references.[13] They exhibit similar fragmentation pattern and ion ratio. However, EI spectral libraries were not found for most of the other alkanes requiring ion fragmentation interpretation. We noticed a similar ion fragmentation pattern for most of alkane products in the range of C_{12} to C_{40}. The comparison between their ion fragmentation pattern with the only cycloeicosane (cC_{20}) and cycloheneicosane (cC_{21}) patterns disclosed in literature[1b,14] supports that C_{20} and C_{21} from the mixture are macrocyclic alkanes, and therefore strongly support that the other alkanes from C_{12} to C_{40} belong to this same family. Secondly, we examine the correlation of the logarithm of the relative retention time versus the carbon atom numbers, known as Kovats retention index.[15] The experimental linear correlation found (0.996) corroborates with the assignment for macrocyclic alkanes series as major products (see the Supporting Information, Figure S6).

In addition with ^1H and ^{13}C NMR spectroscopies, the distortionless enhancement by polarization transfer (DEPT-135) NMR spectroscopy of the reaction mixture displays weak signals corresponding to CH and CH_3 groups suggesting also the presence of substituted cyclic alkanes or linear alkanes (see Figure S5, the Supporting Information). To unambiguously distinguish between the pure macrocyclic alkanes and the branched ones, we compared the ion fragmentation of octylcyclooctane and cyclohexadecane. For this purpose, octylcyclooctane was synthetized starting from cyclooctanone (see the Supporting Information).[16] As expected, octylcyclooctane and cyclohexadecane exhibit different retention times (t_R: 13.35 and 13.56 min, respectively). More importantly, their ion fragmentation pattern differs significantly (Figure S7, the Supporting Information). In fact, the mass spectrum of octylcyclooctane shows a low intense molecular ion at *m/z* 224 and higher intensity of a characteristic ion fragment corresponding to cyclooctane carbocation secondary fragmentation peak at *m/z* 111, which represents the loss of alkyl chain (see Figures S8 and S9, the Supporting Information, for EI spectra of cyclic and branched cyclic alkanes). Lately, we employed a GC preparative fraction collector to isolate two macrocyclic alkanes from our reaction mixture, cycloheptadecane (cC_{17}) and cycloheneicosane (cC_{21}) (Figure 3). ^1H and ^{13}C NMR spectroscopies of these two samples gave single resonance signals, respectively (see Figures S10 and S11, the Supporting Information). These experiments confirm unambiguously the structure of cyclooctane metathesis products as purely cyclic compounds.

Thus, overall, these results demonstrate that the major products of cyclooctane metathesis in the range of C_{12} to C_{40} are pure macrocyclic alkanes. We observe a different distribution compared with the tandem catalytic system with a wider distribution of macrocyclic alkanes. Finally, traces of linear alkanes and *n*-alkyl cyclohexanes compounds were also observed (GC/GC-MS, molar fraction: less than 1% for each family; see Figure S12, the Supporting Information). Further analysis by gel-permeation chromatography (GPC) of the crude reaction mixture shows the absence of polymeric products (see Figure S13, the Supporting Information).

A kinetic study of the cyclooctane metathesis catalyzed by **1** was carried out at 150 °C. The plots of turnover numbers (TONs) and conversion versus time are given in Figure 4. A final conversion of 60% is reached with 340 TONs. The catalyst

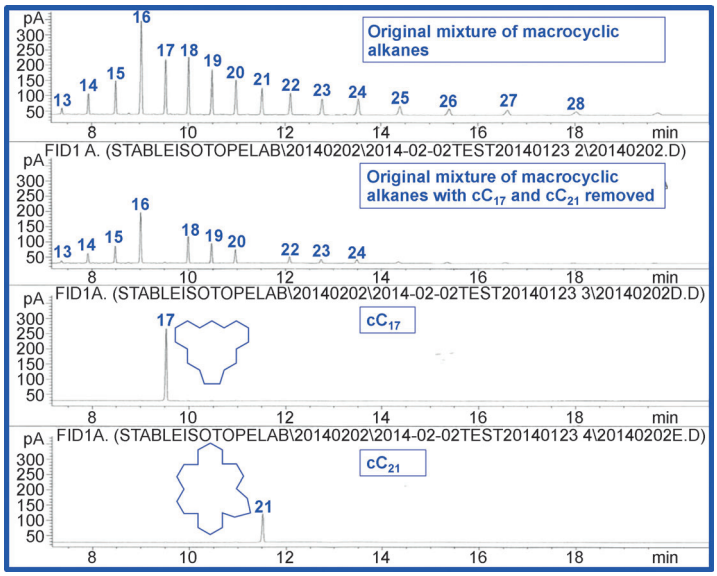


Figure 3. GC chromatogram of the original mixture; of the mixture after isolation of cC_{17} and cC_{21} and their corresponding chromatograms.

In addition, the first hours of this cyclooctane metathesis were also examined (Figure 6 and see the Supporting Information, Figure S14). Interestingly, we found that our W catalytic-supported system is selective for the formation for cC_{16} (cyclic dimer) (molar fraction: 30% for the dimer and up to 60% for all the macrocyclic alkanes). The selectivity toward macrocyclic oligomers decreases with time, which is illustrated by ring contraction at the expense of ring expansion (see Figure S15, the Supporting Information).

Metathesis of cyclodecane gave also similar distribution of lower and higher cyclic alkanes (see Figures S16 and 17, the Supporting Information). In this case, the ring-contraction products are cyclooctane, cycloheptane, cyclohexane, and cyclopentane. A distribution of macrocyclic alkanes is also observed from cyclododecane (cC_{12}) to cyclotetracontane (cC_{40}). It should be noted that formation of cyclononane from contraction of cyclodecane was not observed. Under the same reaction conditions, no metathesis products were observed when cyclopentane, cyclohexane, and cycloheptane were used as substrate.

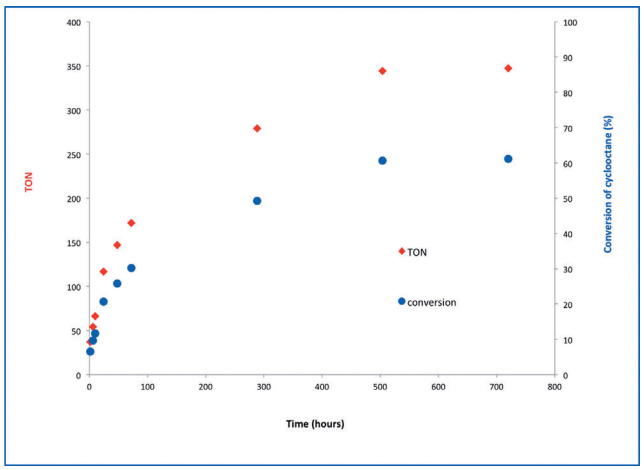


Figure 4. Cyclooctane metathesis catalytic performance catalyzed by **1**: TON (◆) and conversion (●) of cyclooctane versus time. Reaction conditions: Batch reactor, compound **1** (50 mg, 6.5 μmol, W loading: 2.4 wt%), cyclooctane (0.5 mL, 3.7 mmol), 150 °C.

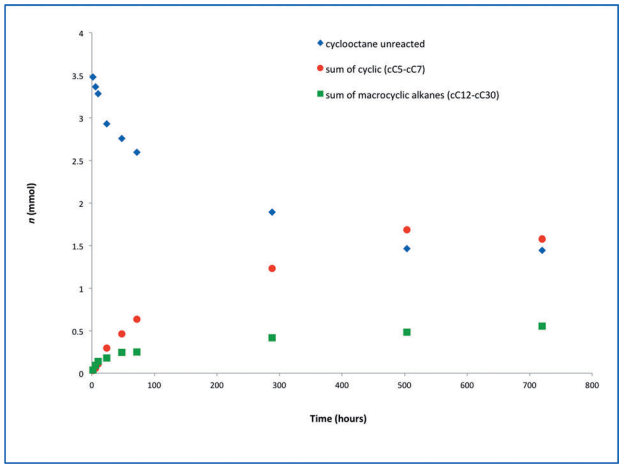


Figure 5. Cyclooctane metathesis products selectivity catalyzed by **1**: Sum of cyclic alkanes (cC_5–cC_7) (●), sum of macrocyclic alkanes (cC_{12}–cC_{30}) (■), and the conversion of cyclooctane (◆). Reaction conditions: Batch reactor, compound **1** (50 mg, 6.5 μmol, W loading: 2.4 wt%), cyclooctane (0.5 mL, 3.7 mmol), 150 °C.

remains active over a long period of time (up to minimum 500 h), which could correspond to a thermodynamic equilibrium or the deactivation of the catalysts. An initial turnover frequency of 40 mol of cyclooctane $(mol_W)^{-1}\ h^{-1}$ is obtained. Two independent runs confirmed the reproducibility of this catalytic reaction.

Cyclooctane conversion and cyclooctane metathesis product selectivity (cyclic and macrocyclic alkanes) versus time are shown in Figure 5. The cyclic/macrocyclic alkane ratio is not constant with time. After 24 h, the plateau corresponding to macrocyclic alkanes is attained. At this time, cyclooctane is likely to be transformed mainly into cyclic alkanes. Above 500 h, 24% of the total number of mol produced corresponds to higher macrocyclic alkanes.

Metathesis reaction of cyclooctane or cyclodecane catalyzed by **1** produces a distribution of higher and lower cyclic alkanes. On the basis of the seminal work on light alkane metathesis, our multifunctional precursor catalyst for this transformation operates as follows: 1) C–H Bond activation;[2,21–22] 2) α or β-H elimination to give W-carbene hydride and an olefin; 3) Intermolecular reaction of this in situ formed olefin with the carbene, which after cycloreversion [2+2] of the metallacycle gives a new carbene and a new olefin and finally two different hydrocarbons[17] through 4) stepwise hydrogenation of double bond.[4a,6a] Thus, for cyclooctane metathesis, a C–H activation followed by β-H elimination should lead to the dehydrogena-

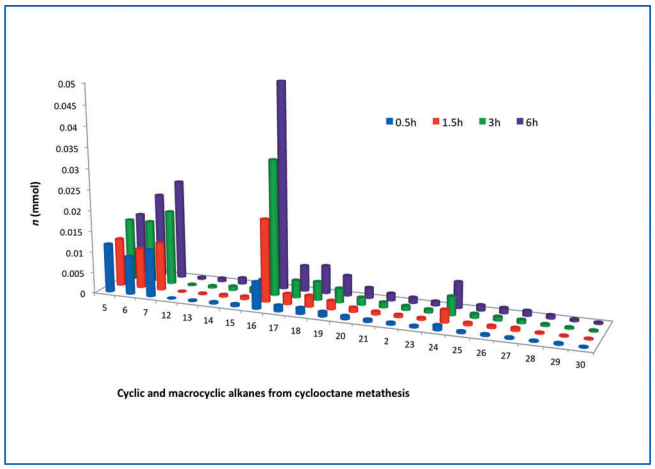
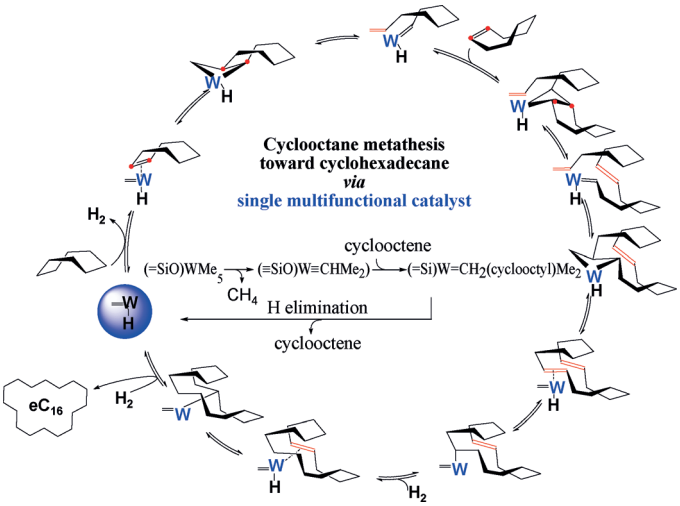


Figure 6. Products distribution of cyclooctane metathesis from 0.5 to 6 h catalyzed by **1**. Reaction conditions: Batch reactor, compound **1** (50 mg, 6.5 μmol, W loading: 2.4 wt%), cyclooctane (0.5 mL, 3.7 mmol), 150 °C.



Scheme 1. Postulated mechanism for cyclohexadecane formation from cyclooctane metathesis.

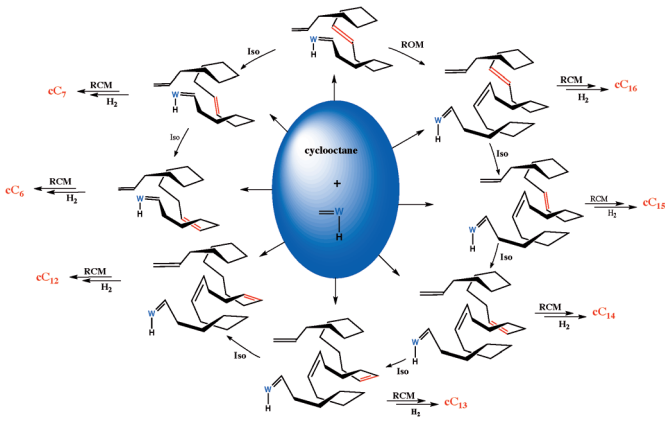
tion of cyclooctane to cyclooctene.[18] This olefin would undergo successive ring-opening–ring-closing metathesis reactions (ROM–RCM). Finally, a hydrogenation step of these double bonds gives the corresponding macrocyclic alkanes. Since the mechanism postulated involves the formation of cyclooctene, which is not detected at the end of a typical catalytic run, we performed this metathesis in a NMR Young tube in which the hydrogen formed was released continuously over a long period of time. Indeed, after 10 days, ^{13}C NMR spectroscopy displays a very weak signal at $\delta = 130$ ppm assigned to cyclooctene (GC and GC-MS) (see Figure S18, the Supporting Information). These results point out that the cyclooctene is effectively formed in situ as an intermediate, which supports our initially proposed mechanism.[19]

Additionally, a catalytic run with cyclooctene lead only to a ring-opening metathesis polymerization (ROMP) with a polymer of M_n 23107 g mol^{-1} (based on polystyrene standard calibration; see Figure S19, the Supporting Information). The ROMP of cyclooctene is well-known and could afford either cyclic[20] or linear polyoctenamers.[21] The high polydispersity index (PDI) of 5.05 obtained allows us to suggest that in our catalytic system, secondary alkene metathesis reaction occurs in the polymer chains, as already reported.[22] Moreover, the thermal properties of this polymer were determined by using differential scanning calorimeter (DSC) (see Figure S20, the Supporting Information). The peak melting temperature, the peak crystallization temperature, and the crystallization fraction were 37.20, 18.91, and 9.83%, respectively. These values are much lower than what has been reported in the literature.[20,23] ^{13}C NMR spectroscopic experiments supported by DSC show a *trans*/*cis* composition of 55:45 (see Figure S21, the Supporting Information). Therefore, no polymeric product is observed in our catalytic system because of the steady state formation of cyclooctene.

In the cyclooctane metathesis, this cyclooctene intermediate would coordinate to W-methylidene, which is generated from pre-catalyst **1** as reported earlier (Scheme 1). The next step would follow a classical ROM–RCM of cyclooctene by backbiting of terminal double bond to produce 1,9-cyclohexadecadiene. Finally, hydrogenation of this macrocyclic diene intermediate would lead to the observed cyclohexadecane. Successive insertions of cyclooctene by ROM and RCM would generate other macrocyclic alkanes with multiple carbon numbers of 8. In this catalytic system, a steady state concentration of minute amounts of coordinated cyclooctene prevents the formation of polymeric products.

The formation of cyclic alkanes and the other macrocyclic alkanes is resulting from double bond isomerization process prior to RCM. W-hydride is likely responsible for this isomerization step. For instance, starting from C_8 W-alkylidene, an isomerization of the terminal olefin followed by RCM and hydrogenation steps would provide cycloheptane (Scheme 2).

We should point out that high selectivity of cyclohexadecadiene (dimer) is obtained in the earlier hours of this reaction. It has been observed with both supported and unsupported Ru catalysts that selective formation of cyclic dimer requires a ki-



Scheme 2. Proposed mechanism for selected cyclic and macrocyclic alkanes formation from cyclooctane metathesis. (ROM: Ring-opening metathesis; RCM: Ring-closing metathesis; Iso: double bond isomerization).[24]

netic-reaction regime, low temperature, and high dilution of cyclooctene to avoid the undesirable polymerization reaction.[25] This multifunctional alkane metathesis allows the use of directly neat cyclooctane without dilution. Moreover, if the reaction is carried out without stirring, the conversion is decreased and one needs 24 h to reach the conversion obtained within 6 h (under stirring conditions) with dimer selectivity up to 41%. This result highlights the important effect of stirring and the mean residence time.[26] We are currently investigating these effects in the view of better selectivity on macrocyclic versus cyclic alkanes.

To see whether the formation of observed ring contraction cyclic alkanes could also arise from secondary metathesis of macrocyclic alkanes, we examined the reactivity of a fraction of cC_{12}–cC_{40}. This colorless oil was easily isolated by removal of cyclic alkanes under reduced pressure (see Figure S22, the Supporting Information). No ring contraction of cyclic products was observed with **1** after 48 h at 150 °C. Thus, this would suggest that the formation of cC_5, cC_6, and cC_7 results directly from the isomerization of a C_8 W-alkylidene intermediate (see Scheme 2) and they accumulate over a long period of time. It is known that ROMP of cyclic olefins depends on the ring strain of the monomer as well as the reaction conditions (temperature, concentration of monomer, pressure, etc.).[27] In our case, there is a competition between ROM/double bond isomerization/RCM leading to cyclic alkanes and ROM/backbiting affording the macrocyclic alkanes.

Conclusion

We have demonstrated that the cyclic alkane metathesis catalyzed by a multifunctional supported W single catalytic system leads to an unprecedented distribution of macrocyclic alkanes in the range of C_{12} to C_{40}. The main advantage of our catalyst system is the fact that we used a W single catalyst able to promote different elementary steps. Furthermore, no polymeric products were detected. Future studies will be aimed at post functionalization of these macrocyclic alkanes.

Experimental Section

General considerations

All experiments were conducted under argon atmosphere using glovebox techniques. The syntheses and the treatments of the surface species were carried out using high vacuum lines ($< 10^{-5}$ mbar) and glovebox techniques. Pentane and dichloromethane were distilled from Na and CaH_2, respectively. Elemental analyses were performed at the London Metropolitan University in London and Mikroanalytisches Labor Pascher in Remagen. Cyclic alkanes were purchased from Aldrich, distilled from sodium/potassium alloy under nitrogen, degassed by several freeze–pump–thaw cycles, filtered over activated alumina, and stored under nitrogen. Octylidenecyclooctane was synthesized in two steps from cyclooctanone according to a literature report.[16] The supported pre-catalyst [(≡SiO)W(Me)$_5$] **1** was prepared according a literature report.[10] NMR spectra were recorded on Bruker 500 and 600 MHz instruments. ^{1}H and ^{13}C were reported in ppm downfield from tetramethylsilane and were referenced to deuterated solvent. GC measurements were performed with an Agilent 7890 A Series (FID detection). Method for GC analyses: Column HP-5; 30 m length × 0.32 mm ID x 0.25 μm film thickness; Flow rate: 1 mL min^{-1} (N_2); split ratio: 50:1; Inlet temperature: 250 °C, Detector temperature: 250 °C; Temperature program: 40 (1 min), 40–250 (15 °C min^{-1}), 250 (1 min), 250–300 (10 °C min^{-1}), 300 °C (30 min); Cyclic alkanes retention time: t_R (cyclooctane): 6.51 min, t_R (cyclohexadecane, dimer): 13.56 min, t_R (cyclotetraeicosane, trimer): 19.30 min.

GC-MS measurements were performed with an Agilent 7890A Series coupled with Agilent 5975C Series. GC/MS equipped with capillary column coated with none polar stationary phase HP-5 MS was used for molecular weight determination and identification that allowed the separation of hydrocarbons according to their boiling points differences. GC response factors of available cC_5–cC_{12} standards were calculated as an average of three independent runs. The plots of response factor versus cyclic alkanes carbon number were determined and a linear correlation was found. Then, we extrapolated the response factors of this plot for the other cyclic alkanes (Figures S1 and S2, the Supporting Information).

General procedure for cyclic alkane metathesis catalytic runs

All the reactions were carried out following the same way: An ampoule was filled with the catalyst (50 mg, 6.5 μmol, W loading: 2.4 wt%, 0.2% equiv) in a glovebox and the cyclic alkane (0.5 mL, 3.7 mmol) was then added. The ampoule was sealed under vacuum, immersed in an oil bath, and heated at 150 °C. At the end of the reaction, the ampoule was allowed to cool to −78 °C. Then, the mixture was diluted by addition of external standard *n*-pentane, and, after filtration, the resulting solution was analyzed by using GC and GC-MS. For kinetic studies, each analysis represents an average of two independent runs.

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Keywords: alkanes · NMR spectroscopy · macrocycles · metathesis · tungsten

[1] a) M. Audino, K. Grice, R. Alexander, C. J. Boreham, R. I. Kagi, *Geochim. Cosmochim. Acta* **2001**, *65*, 1995; b) M. Audino, K. Grice, R. Alexander, R. I. Kagi, *Org. Geochem.* **2001**, *32*, 759; c) M. Audino, K. Grice, R. Alexander, R. Kagi, *Org. Geochem.* **2004**, *35*, 661.

[2] A. Gradillas, J. Perez-Castells, *Angew. Chem.* **2006**, *118*, 8264; *Angew. Chem. Int. Ed.* **2006**, *45*, 8086.

[3] J. M. Basset, C. Coperet, D. Soulivong, M. Taoufik, J. Thivolle-Cazat, *Angew. Chem.* **2006**, *118*, 6228; *Angew. Chem. Int. Ed.* **2006**, *45*, 6082.

[4] a) J. M. Basset, C. Copéret, D. Soulivong, M. Taoufik, J. T. Cazat, *Acc. Chem. Res.* **2010**, *43*, 323; b) M. C. Haibach, S. Kundu, M. Brookhart, A. S. Goldman, *Acc. Chem. Res.* **2012**, *45*, 947.

[5] V. Vidal, A. Theolier, J. Thivolle-Cazat, J. M. Basset, *Science* **1997**, *276*, 99.

[6] a) C. Copéret, *Chem. Rev.* **2010**, *110*, 656; b) C. Copéret, M. Chabanas, R. P. Saint-Arroman, J. M. Basset, *Angew. Chem.* **2003**, *115*, 164; *Angew. Chem. Int. Ed.* **2003**, *42*, 156.

[7] R. L. Burnett, T. R. Hughes, *J. Catal.* **1973**, *31*, 55.

[8] a) A. S. Goldman, A. H. Roy, Z. Huang, R. Ahuja, W. Schinski, M. Brookhart, *Science* **2006**, *312*, 257; b) J. Choi, A. H. R. MacArthur, M. Brookhart, A. S. Goldman, *Chem. Rev.* **2011**, *111*, 1761.
[9] R. Ahuja, S. Kundu, A. S. Goldman, M. Brookhart, B. C. Vicente, S. L. Scott, *Chem. Commun.* **2008**, 253.
[10] M. K. Samantaray, E. Callens, E. Abou-Hamad, A. J. Rossini, C. M. Widdifield, R. Dey, L. Emsley, J. M. Basset, *J. Am. Chem. Soc.* **2014**, *136*, 1054.
[11] R. H. Crabtree, *Chem. Rev.* **2012**, *112*, 1536.
[12] Column HP-5; 30 m length × 0.32 mm ID × 0.25 μm film thickness; temperature program: 40 (1 min), 40–250 (15 °C min^{-1}), 250 (1 min), 250–300 (10 °C min^{-1}), and 300 °C (15 min), t_R (cyclooctane): 6.5 min, t_R (cyclohexadecane, dimer): 6.5 min (13.6), t_R (cyclotetradecane, trimer): 19.3 min.
[13] NIST standard reference database: http://webbook.nist.gov/chemistry/.
[14] Y. L. Wang, X. M. Fang, Y. Bai, X. X. Xi, S. L. Yang, Y. X. Wang, *Org. Geochem.* **2006**, *37*, 146.
[15] N. H. Ray, *J Appl Chem.* **1954**, *4*, 21.
[16] W. Giencke, O. Ort, H. Stark, *Liebigs Ann. Chem.* **1989**, 671.
[17] Y. Chauvin, J. L. Herisson, *Bull. Soc. Chim. Fr.* **1970**, 34.
[18] D. Michos, X. L. Luo, J. W. Faller, R. H. Crabtree, *Inorg. Chem.* **1993**, *32*, 1370.
[19] J. M. Basset, C. Coperet, L. Lefort, B. M. Maunders, O. Maury, E. Le Roux, G. Saggio, S. Soignier, D. Soulivong, G. J. Sunley, M. Taoufik, J. Thivolle-Cazat, *J. Am. Chem. Soc.* **2005**, *127*, 8604.
[20] C. W. Bielawski, D. Benitez, R. H. Grubbs, *Science* **2002**, *297*, 2041.
[21] N. Calderon, *Acc. Chem. Res.* **1972**, *5*, 127.
[22] J. Kress, *J. Mol. Catal. A* **1995**, *102*, 7.
[23] C. D. Liu, S. B. Chun, P. T. Mather, L. Zheng, E. H. Haley, E. B. Coughlin, *Macromolecules* **2002**, *35*, 9868.
[24] Only the formation of some products is depicted. It is an example of how ROM, RCM, and the isomerisation process could evolve during the reaction, indeed, each internal olefin could be isomerized and successive ROM/RCM could occur at any time providing miscellaneous cyclic and macrocyclic alkanes. For example, isomerization of the terminal olefin before RCM (backbiting) could also explain the distribution of cyclooctane metathesis reaction products. However, the same process could explain all macrocyclic alkanes resulting from the cyclooctane metathesis reaction: Successive ROM and RCM reactions in competition of internal olefins isomerization involving either the carbene or the hydride functions of the propagative species.
[25] a) S. Kavitake, M. K. Samantaray, R. Dehn, S. Deuerlein, M. Limbach, J. A. Schachner, E. Jeanneau, C. Coperet, C. Thieuleux, *Dalton Trans.* **2011**, *40*, 12443; b) M. K. Samantaray, J. Alauzun, D. Gajan, S. Kavitake, A. Mehdi, L. Veyre, M. Lelli, A. Lesage, L. Emsley, C. Coperet, C. Thieuleux, *J. Am. Chem. Soc.* **2013**, *135*, 3193.
[26] a) M. Bru, R. Dehn, J. H. Teles, S. Deuerlein, M. Danz, I. B. Muller, M. Limbach, *Chem. Eur. J.* **2013**, *19*, 11661; b) J. Cabrera, R. Padilla, M. Bru, R. Lindner, T. Kageyama, K. Wilckens, S. L. Balof, H. J. Schanz, R. Dehn, J. H. Teles, S. Deuerlein, K. Muller, F. Rominger, M. Limbach, *Chem. Eur. J.* **2012**, *18*, 14717; c) S. Warwel, H. Katker, C. Rauenbusch, *Angew. Chem.* **1987**, *99*, 714; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 702.
[27] P. V. Schleyer, J. E. Williams, K. R. Blanchard, *J. Am. Chem. Soc.* **1970**, *92*, 2377.

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