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## ARTICLE

# Striking difference between alkane and olefin metathesis by the well-defined precursor [ $\equiv\text{Si-O-WMe}_5$ ]: indirect evidence in favour of a bifunctional catalyst W alkylidene-hydride

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Metathesis of linear alkanes catalyzed by the well-defined precursor ( $\equiv\text{Si-O-WMe}_5$ ) affords a wide distribution of linear alkanes from methane up to triacontane. Olefin metathesis with the same catalyst and under the same reaction conditions gives a very striking different distribution of linear  $\alpha$ -olefins and internal olefins. This shows that olefin and alkane metathesis occur by very different pathways.

## Introduction

Alkane metathesis, a promising reaction to convert light alkanes into more valuable higher molecular weight hydrocarbons, has aroused strong interest during the last decade.<sup>1,2</sup> Two catalytic systems were developed, one employing a single site multifunctional catalyst<sup>3</sup> and the other one using a tandem catalytic approach.<sup>4,5</sup> The first catalytic system used notably group V and VI transition metals supported on various metal oxides synthesized by Surface Organometallic Chemistry. It was found to be an efficient precatalyst for the metathesis of light alkanes ( $\text{C}_2\text{-C}_4$ ).<sup>1,6,7</sup> For instance, supported Ta mono or polyhydrides catalyze *n*-butane metathesis into  $\text{C}_1\text{-C}_3$  light hydrocarbons as well as liquid hydrocarbon fuels ( $\text{C}_5\text{-C}_{10}$ ) in a pressurized fixed bed reactor.<sup>8</sup> In such supported system it has been observed that an initial C-H bond activation occurs on the metal hydride with hydrogen evolution.<sup>9</sup> Next,  $\alpha$ - or  $\beta$ -H elimination from the resulting alkyl species would give the corresponding carbene or olefin. To account for the overall features of the reaction, a propagative bi-functional alkylidene/hydride species was proposed.<sup>10</sup> The metal alkylidene converts alkene intermediates *via* a metallacyclobutane while the W-hydride is needed to release  $\text{H}_2$ , for the hydrogenation of newly formed olefins to new alkanes.<sup>10</sup> Recently, we disclosed the synthesis of a well-defined silica supported catalyst [ $\equiv\text{Si-O-WMe}_5$ ] **1** (Fig. 1).<sup>11</sup> We have shown that **1** is thermally transformed into a W-methyl carbyne species [ $\equiv\text{Si-O-W}(\equiv\text{CH})(\text{CH}_3)_2$ ] **2** at 150 °C (Fig. 1). Moreover, in the presence of an olefin, an equilibrium with this W-carbyne and the corresponding bis-carbene [ $\equiv\text{Si-O-W}(\equiv\text{CH})_2(\text{CH}_3)$ ] **3**, (needed for olefin metathesis) is also observed (Fig. 1).<sup>12</sup> Complex **1** was found to be an efficient pre-catalyst for propane<sup>11</sup> and cycloalkane metathesis.<sup>13</sup> As mentioned for W-polyhydrides species, **1** is able to promote several elementary steps:  $\sigma$ -bond metathesis on the W-methyl,  $\alpha$ - and  $\beta$ -H elimination from the resulting W-alkyl group, olefin metathesis *via* the carbene functionality and double bond

hydrogenation *via* a classical 1,2 insertion mechanism. Thus, we envisaged employing this multifunctional system for higher alkane metathesis and comparing its behaviour with the corresponding pure  $\alpha$ -olefins metathesis.

Herein we wish to report the metathesis of different linear alkanes and their corresponding  $\alpha$ -olefins catalyzed by **1**. Our results support the multifunctional character of this supported catalyst with a W carbene hydride playing a crucial role in this transformation.

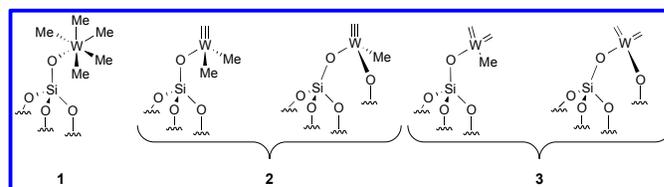
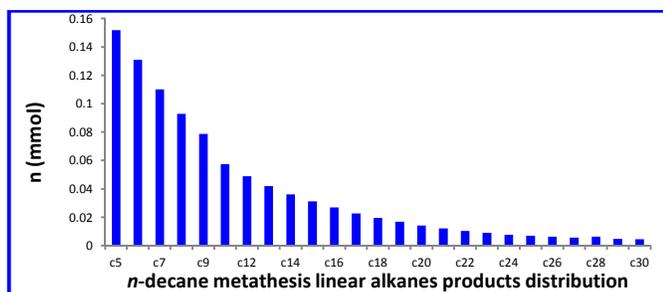


Fig. 1 Well-defined supported W methyl **1**,<sup>11</sup> W methyl-carbyne **2** and bis-carbene species **3**.<sup>12</sup>

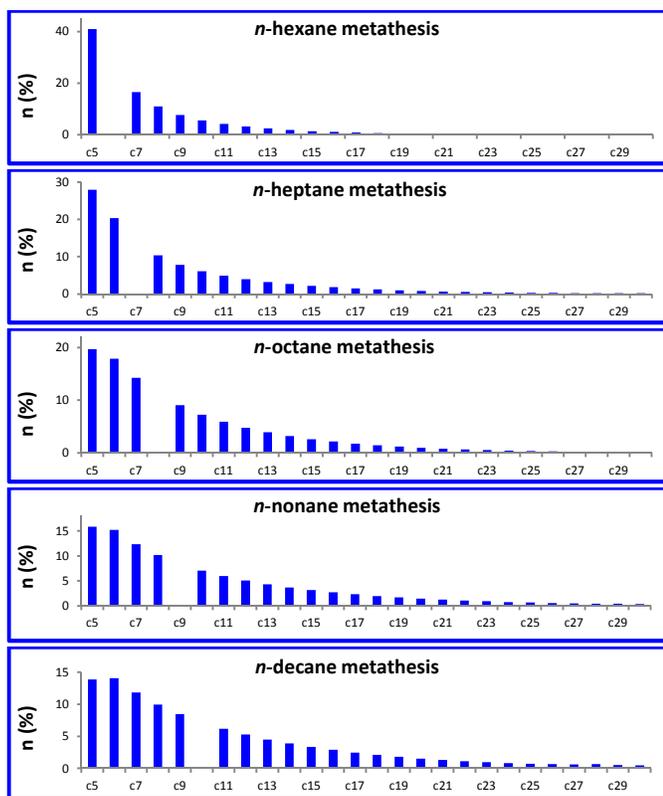
## Results and discussion

In a batch reactor at 150 °C, metathesis of *n*-decane produces a broad distribution of linear alkanes ranging from methane to triacontane ( $\text{C}_{30}$ ). These linear alkanes were assigned (by GC and GC-MS) according to their retention time and fragmentation pattern by comparison with available references.<sup>14</sup> Traces of branched alkanes (molar fractions <1%) were also observed, while no cyclic or olefinic products were detected by GC-MS and NMR spectroscopy. In a typical catalytic run, a conversion of 38% is reached with 142 TONs after 5 days period. Product distribution curve of molar quantity of *n*-decane metathesis products *versus* carbon number (from  $\text{C}_5$ ) is shown in Fig. 2.



**Fig. 2** Distribution of *n*-decane metathesis products from C<sub>5</sub> to C<sub>30</sub> catalyzed by **1**. Reaction conditions: batch reactor, **1** (50 mg, 6.7 μmol, W loading: 2.48 wt%), *n*-decane (0.5 mL, 2.57 mmol), 120 h, 150°C. Conversion= 38%, TON=142. The turnover number (TON) is the number of mol of *n*-decane transformed per mol of W.

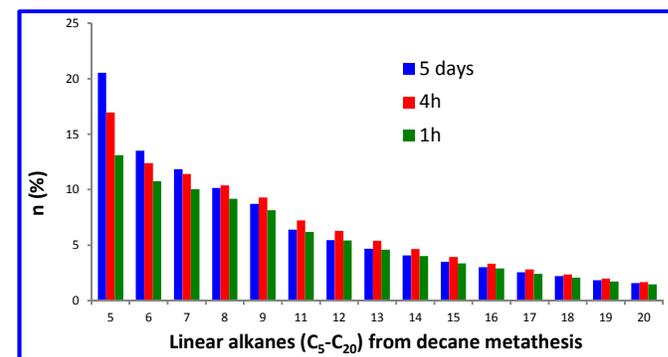
A narrow distribution centred on *n*-decane is not observed in this liquid/solid interface catalytic system in sharp contrast with propane metathesis.<sup>1</sup> Actually, this observed selectivity is closer to the one reported with fully heterogeneous tandem system.<sup>15, 16</sup> Noteworthy, our catalytic system is also active for the transformation of other linear alkanes, from hexane to nonane. Metathesis of each C<sub>n</sub> alkane afforded a similar distribution of higher and lower linear hydrocarbons (**Fig. 3**, for corresponding chromatograms, see **Fig. S1**). The molar ratio of  $\Sigma(C_{n+1}, C_{n+5})/C_n$  is 0.29 for octane and 0.30 for decane metathesis at similar conversions. At lower conversions, molar ratios of 0.74 for hexane and 0.8 for nonane were obtained. These results indicate that the distribution is independent from the alkane carbon number.



**Fig. 3** Alkane metathesis products distribution from C<sub>5</sub> to C<sub>30</sub> catalyzed by **1**. Conversion= 30-45%; TON=150-300. Reaction conditions: batch reactor, **1** (50 mg, 6.7 μmol, W loading: 2.48 wt%), *n*-alkane (0.5 mL, 3.83-2.57 mmol), 120 h, 150°C. The

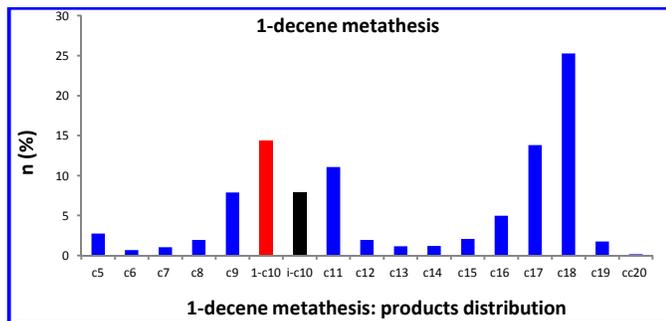
turnover number (TON) is the number of mol of a given alkane transformed per mol of W.

In addition, *n*-decane metathesis products were examined in function of time of reaction. The plot of molar fraction of linear alkane products at 1h, 4h and 5 days is shown in **Fig. 4**. The initial distribution of alkanes remains similar with time, suggesting no distinction between kinetic and thermodynamic products for these reaction times. Furthermore, the metathesis of a mixture of octane and decane did not follow the alkane selectivity distribution (C<sub>n-1</sub>/C<sub>n+1</sub> as major products) observed for gas phase reaction (see **Fig. S2**)



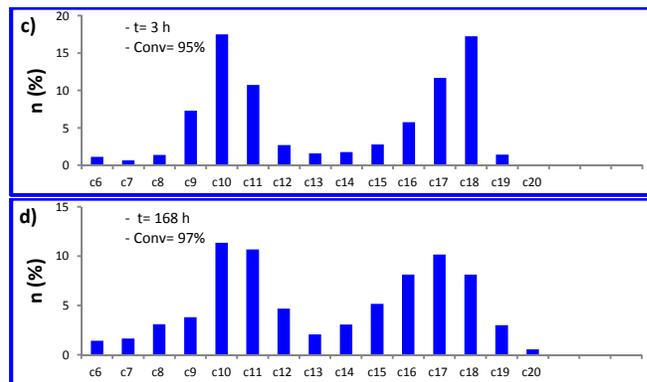
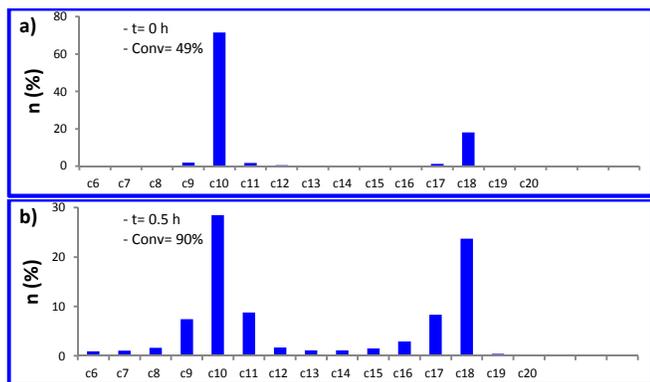
**Fig. 4** Molar fraction of decane metathesis products in function of time catalyzed by **1**. Reaction conditions: batch reactor, **1** (50 mg, 5.73 μmol, W loading: 2.11 wt%), decane (0.5 mL), ■ 5 days; ■ 4h and ■ 1h, 150°C.

Since it has been demonstrated that olefins are key intermediates in alkane metathesis transformation, we also studied the direct metathesis of solely  $\alpha$ -olefins catalyzed by **1** to compare their reactivity with their homologous alkanes. Although 1-decene is the thermodynamically less favoured olefin, we have chosen 1-decene as a comparison for the following reason: we have shown that in alkane metathesis linear paraffin are the only products, which means that *n*-alkyl are preferred over secondary alkyls. This is a well-known fact since the Wilkinson catalyst due to steric crowding of secondary alkyls. Therefore, the simplest olefin to be considered is the one resulting from a beta-H elimination of linear alkyl chains. The olefin metathesis having a low activation barrier, **1** catalyzed the self-metathesis of 1-decene at room temperature (76% conversion) (See **Fig. S3** and **S4**). Under the alkane metathesis reaction conditions, 1-decene is transformed into olefins of shorter (C<sub>2</sub>-C<sub>9</sub>) and longer carbons (C<sub>11</sub>-C<sub>20</sub>) (**Fig. 5**). A higher conversion of 1-decene (90%) is obtained after only 0.5 h with 1650 TONs. An initial turnover frequency of 150 min<sup>-1</sup> is obtained. These TONs could reach 5500 by increasing the alkene/**1** ratio. With time, GC chromatograms exhibit two clearly distinguishable regions: one comprising olefins from C<sub>7</sub> to C<sub>12</sub> and another from C<sub>13</sub> to C<sub>20</sub> as major products (**Fig. 5**). We identified that these two regions should correspond to regioisomers of given alkenes (C<sub>7</sub> to C<sub>11</sub>) and to higher internal olefins (C<sub>15</sub> to C<sub>18</sub>). The self-metathesis of 1-decene is followed by secondary cross metathesis of newly formed olefin from isomerization of the 1-decene to internal isomers of decene. With such olefin distribution from 1-decene, we examined other  $\alpha$ -olefins from 1-hexene to 1-nonene. Olefin metathesis chromatograms indicate similar distribution curve as shown in **Fig. S5** and **S6**. Olefin metathesis chromatograms indicate similar distribution curve with a limitation in the olefin carbon number (C<sub>2n+2</sub>) as shown in **Fig. S4** and **S5**.

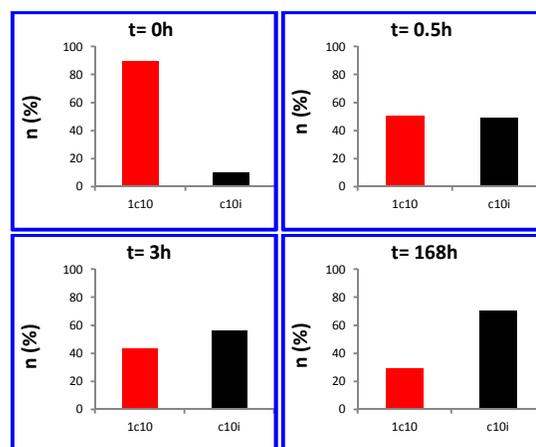


**Fig. 5** Molar fraction of  $\alpha$ -decene metathesis products catalyzed by **1**. Conversion= 90%; TON= 1650. Reaction conditions: batch reactor, **1** (25 mg, 1.44  $\mu$ mol, W loading: 1.06 wt%), 1-decene (0.5 mL, 2.64 mmol), 0.5 h, 150 °C. The turnover number (TON) is the number of mol of 1-decene transformed per mol of W.

Next, we monitored the reaction of 1-decene metathesis *versus* time. A plot of molar fraction of the medium at different periods of time is shown in **Fig. 6** (For products distribution *versus* time, see **Fig. S7**). At  $t=0$  h (defined by the time where the reactor temperature reaches 150 °C) the predominant reaction is the self-metathesis of 1-decene leading to 9-octadecene and ethylene (**Fig. 6** and **S7**). 51 % of reacted 1-decene is transformed into 9-octadecene as primary product. After 15 min, the peaks of  $C_9$  and  $C_{11}$  olefins become apparent due to a competitive isomerization/metathesis process. Those olefins (secondary metathesis products) should result from the cross-metathesis of 1-decene.  $C_{17}$  olefin peak formed from secondary metathesis of 1-decene with 1-nonene is also observed. After 3 h, the conversion reaches an apparent plateau but the reaction has not reached thermodynamic equilibrium. At this point, the self-metathesis of 1-decene is overcome by secondary reactions. In the early stage 1-decene accounts for 90 % of total fraction of  $C_{10}$  while it decreases to 30 % after 3 h (**Fig. 7**). These substituted  $C_{10}$  isomers would react consecutively to form secondary olefin metathesis products as depicted in **Fig. S10**. The plots of TONs and conversion *versus* time are given in **Fig. 8**. A final conversion of 97 % is reached after several days whereas after only 3h, 95% of the substrate is converted. Final TONs of 1790 are obtained (several days period reaction). In addition, 5-decene metathesis was examined under the same reaction conditions. This experiment led to a Gaussian distribution of olefins with only  $C_{20}$  as the higher alkene in contrast to  $> C_{30}$  for decane (**Fig. S8**). And, a cross-metathesis of 1-decene and 5-decene (v/v, ratio of 1:1) catalytic run was conducted (**Fig. S9**). We found that in the early stage no significant amount of  $C_{18}$  (homo coupling of 1-decene product) was observed supporting a preferential olefin metathesis between 1-decene and 5-decene (see additional supporting information).

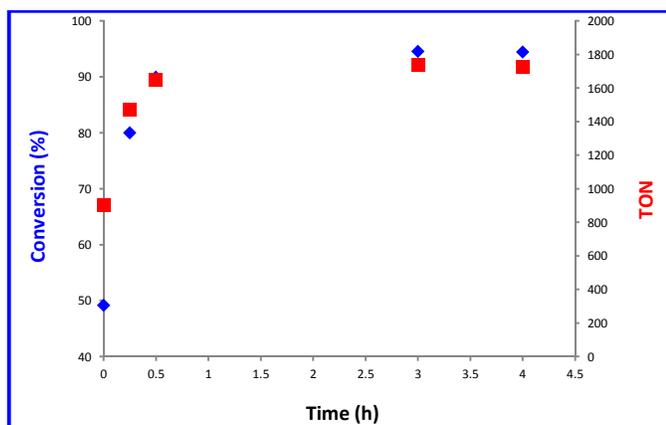


**Fig. 6** Molar fraction of 1-decene metathesis products in function of time catalysed by **1**, 0 h, 0.5 h, 3 h and 163 h. Reaction conditions: batch reactor, **1** (25 mg, 1.44  $\mu$ mol, W loading: 1.06 wt%), 1-decene (0.5 mL, 2.64 mmol), 150 °C. For clarity,  $C_{10}$  represents all decene regioisomers.



**Fig. 7** Molar fraction of 1-decene (red) and isomers of 1-decene (black) at different time: 0 h, 0.5 h, 3 h and 163 h. Reaction conditions: batch reactor, **1** (25 mg, 1.44  $\mu$ mol, W loading: 1.06 wt%), 1-decene (0.5 mL, 2.64 mmol), 150 °C.

Additionally, the terminal  $sp^3$  C-H bond of 1-decene could theoretically be active for CH activation *via* sigma-bond elementary step, as observed for *n*-decane, to generate either a diene or a W-alkylidene with a terminal olefin. Thus, we examined the direct reaction of 1,9-decadiene catalyzed by **1**. In this case, we observed cyclic olefins (cyclohexene and cycloheptene) resulting from intramolecular ring-closing metathesis of dienes. The formation of such 6 and 7 membered carbocycles have been reported for cyclooctane metathesis in which lower cyclic alkanes (from cyclopentane to cycloheptane) were observed. Since with 1-decene no cyclic products were detected, the *in situ* formation of a diene seems unlikely under these reaction conditions. Olefin metathesis/isomerization must be the predominant elementary steps at the expense of  $sp^3$  carbon activation, when using a terminal olefin as a substrate.

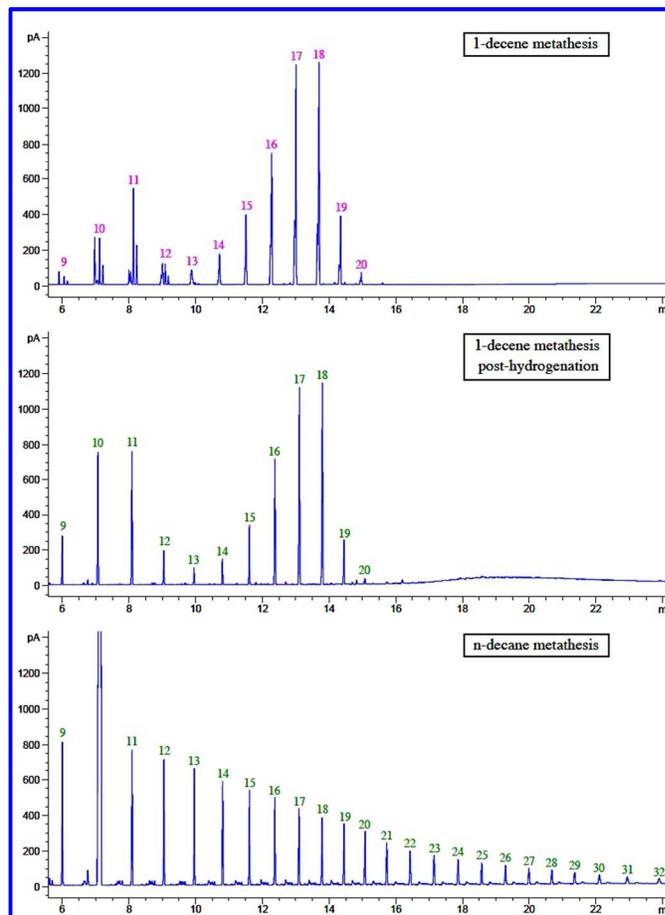


**Fig. 8.** Plot of conversion (◆) and TON (■) versus time of 1-decene metathesis catalyzed by **1**. Reaction conditions: batch reactor, **1** (25 mg, 1.44  $\mu$ mol, W loading: 1.06 wt%), 1-decene (0.5 mL, 2.64 mmol), 150 °C.

We also compared the 1-decene metathesis of a multifunctional catalyst composed of a typical Grubbs first generation Ru-based catalyst impregnated on alumina under our reaction conditions.<sup>17, 18</sup> This catalyst possesses the alkylidene function without coordinated alkyl groups. After 24 h, the GC chromatogram indicates mainly the self-metathesis of 1-decene with only traces of isomers (see **Fig. S11**).

In order to compare the product distribution of metathesis of *n*-decane and 1-decene, hydrogenation of an olefin mixture resulting from 1-decene metathesis with catalyst **1** was also carried out in methanol in the presence of Pd/C under atmospheric pressure of hydrogen. The hydrogenated products are linear alkanes (**Fig. 9**). It is noteworthy that this alkane distribution resulting from olefin metathesis differs totally from the decane metathesis with the same catalyst. In the latter, we observe products up to C<sub>30</sub> (**Fig. 8**). This could be attributed to the different amount of hydrogen released in a catalytic cycle in these two systems. Interestingly, addition of a hydrogen acceptor tertbutylethylene (tbe) with pre-catalyst **1** (W/tbe molar ratio: 1/13) led to no activity in *n*-decane metathesis over a 3 days period, while with the same ratio of W/tbe, metathesis of 1-decene is occurring.

This result is the proof of a strong mechanistic difference between alkane and olefin metathesis. For the alkane metathesis, the olefin formed by a succession of  $\sigma$ -bond metathesis and  $\beta$ -H elimination steps does not decoordinate rapidly from the W catalyst as would be expected on a d<sup>0</sup> system. To the contrary, it would immediately undergo a [2+2] cycloaddition on the coordinated carbene. After cycloreversion of the metallacycle, there is a fast reaction of the resulting olefin with the coordinated hydride to form an alkyl group. This implies the importance of the low steady state olefin concentration in alkane metathesis.



**Fig. 9.** GC chromatogram of 1-decene metathesis, hydrogenation of 1-decene metathesis mixture and *n*-decane metathesis.

We propose the following mechanism pathway to account for the formation of heptacosane (C<sub>27</sub>) starting from *n*-decane (**Fig. 10**). An initial  $\sigma$ -bond metathesis generates methane and the W bis-decyl species.<sup>19-21</sup> A classical  $\beta$ -H elimination gives the W-H and the coordinated olefin. Next, the well-established  $\alpha$ -hydrogen transfer from the alkyl to alkylidene forms the W-carbene.<sup>22-24</sup> A [2+2] cycloaddition, followed by the cycloreversion leads to the internal alkene and the W-bis-carbene. Successive insertion/elimination steps (by chain walking) give the terminal alkene, which reacts to a new W-alkylidene.<sup>25, 26</sup> The CH activation of the pendant W-hydride with *n*-decane followed by  $\beta$ -H elimination provides 1-decene. A second 1-decene metathesis with newly formed W-alkylidene and hydrogenolysis affords heptacosane (C<sub>27</sub>). For the olefin metathesis, an H-transfer of the W methylidyne generates the corresponding W bis-carbene. Next, successive [2+2] cycloaddition of olefin and [2+2] cycloreversion steps lead to W-alkylidene. The latter reacts with an additional olefin to release the substituted olefin. The major difference between the olefin and the alkane mechanisms is the amount of hydrogen produced which is higher for alkanes.

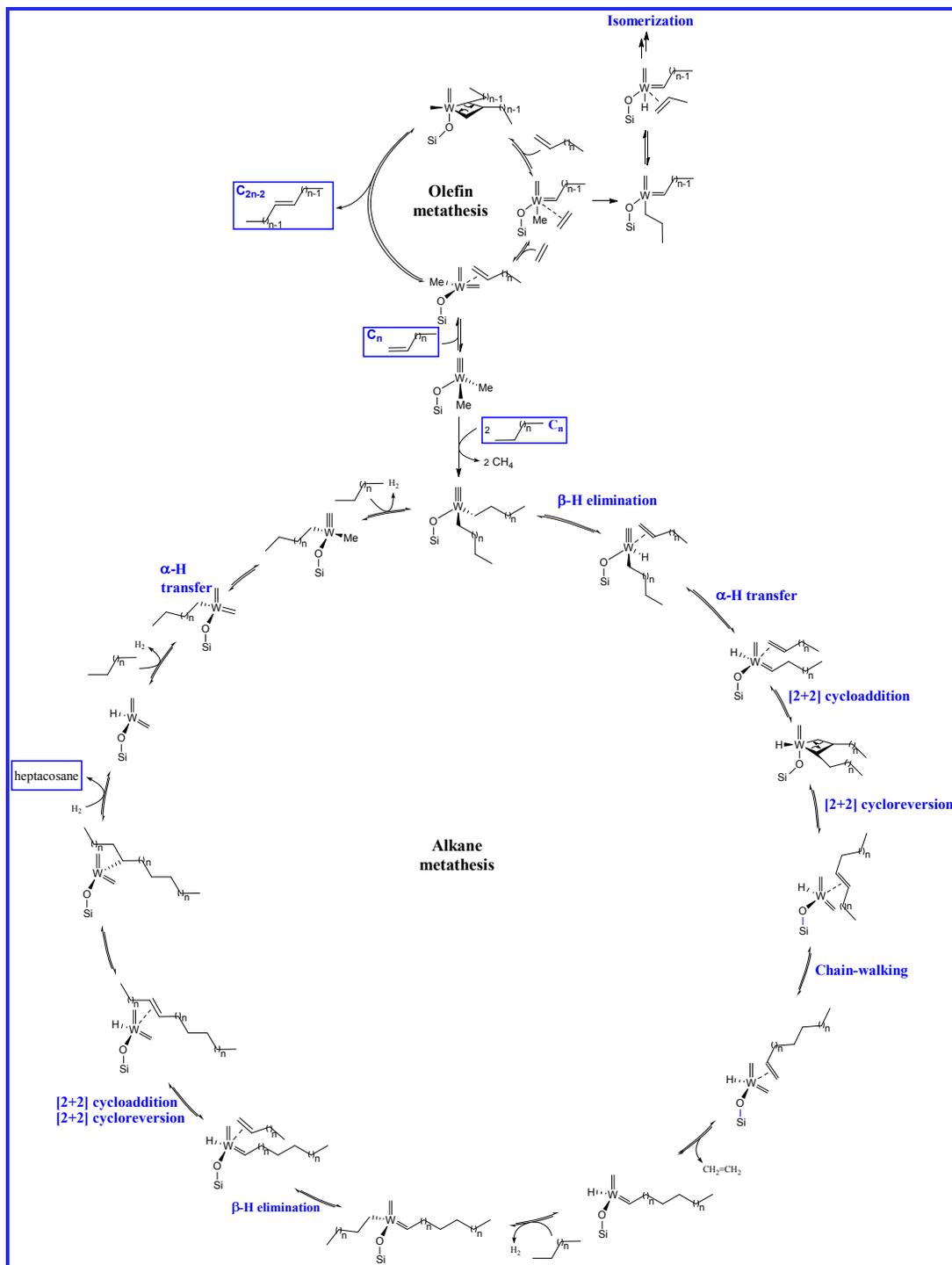


Fig. 10. Plausible mechanism for linear decane metathesis and  $\alpha$ -decene metathesis from common pre-catalyst **2**. ( $n=7$  for  $n$ -decane and 1-decene metathesis).

## Conclusion

We have demonstrated the efficiency of **1** and **2** in *n*-alkane metathesis leading to a distribution of linear alkanes in the range of C<sub>1</sub> to C<sub>30</sub>. By comparing the homologous terminal alkenes, we found a strong difference of product distribution between *n*-decane and 1-decene metathesis. This shows the striking difference between alkane metathesis and olefin metathesis. This difference is attributed to the very small amount of olefin produced freely on the single site catalyst due to the supposedly very fast 2+2 intramolecular cycloaddition of the formed olefin to the metallocarbene followed again by a fast reinsertion of the resulting olefin to the metal hydride. Considering the tandem catalytic system, our single-site system is certainly a convenient protocol to upgrade hydrocarbons.

## Acknowledgements

Research reported in this publication was supported by the King Abdullah University of Science and Technology.

## Notes and references

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

- J. M. Basset, C. Coperet, D. Soulivong, M. Taoufik and J. T. Cazat, *Accounts Chem Res*, 2010, **43**, 323-334.
- M. C. Haibach, S. Kundu, M. Brookhart and A. S. Goldman, *Accounts Chem Res*, 2012, **45**, 947-958.
- V. Vidal, A. Theolier, J. Thivolle-Cazat and J. M. Basset, *Science*, 1997, **276**, 99-102.
- A. S. Goldman, A. H. Roy, Z. Huang, R. Ahuja, W. Schinski and M. Brookhart, *Science*, 2006, **312**, 257-261.
- R. L. Burnett and T. R. Hughes, *J Catal*, 1973, **31**, 55-64.
- C. Coperet, *Chem Rev*, 2010, **110**, 656-680.
- E. Le Roux, M. Taoufik, C. Coperet, A. de Mallmann, J. Thivolle-Cazat, J. M. Basset, B. M. Maunders and G. J. Sunley, *Angew Chem Int Edit*, 2005, **44**, 6755-6758.
- K. C. Szeto, L. Hardou, N. Merle, J. M. Basset, J. Thivolle-Cazat, C. Papaioannou and M. Taoufik, *Catal Sci Technol*, 2012, **2**, 1336-1339.
- F. Quignard, A. Choplin and J. M. Basset, *J Chem Soc Chem Comm*, 1991, 1589-1590.
- 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 and J. Thivolle-Cazat, *J Am Chem Soc*, 2005, **127**, 8604-8605.
- M. K. Samantaray, E. Callens, E. Abou-Hamad, A. J. Rossini, C. M. Widdifield, R. Dey, L. Emsley and J. M. Basset, *J Am Chem Soc*, 2014, **136**, 1054-1061.
- E. Callens, E. Abou-Hamad, N. Riache and J. M. Basset, *Chem Commun*, 2014, **50**, 3982-3985.
- N. Riache *et al.* Cyclooctane metathesis catalyzed by silica supported tungsten pentamethyl ( $\equiv\text{SiO}(\text{Me})_5$ ): distribution of macrocyclic alkanes, *Chem. Eur. J.*, 2014, *in press*.
- NIST Standard Reference Database: <http://webbook.nist.gov/chemistry/>
- S. Kundu, Y. Choliy, G. Zhuo, R. Ahuja, T. J. Emge, R. Warmuth, M. Brookhart, K. Krogh-Jespersen and A. S. Goldman, *Organometallics*, 2009, **28**, 5432-5444.
- Z. Huang, E. Rolfé, E. C. Carson, M. Brookhart, A. S. Goldman, S. H. El-Khalafy and A. H. R. MacArthur, *Adv Synth Catal*, 2010, **352**, 125-135.
- M. Bru, R. Dehn, J. H. Teles, S. Deuerlein, M. Danz, I. B. Muller and M. Limbach, *Chem-Eur J*, 2013, **19**, 11661-11671.
- B. Van Berlo, K. Houthoofd, B. F. Sels and P. A. Jacobs, *Adv Synth Catal*, 2008, **350**, 1949-1953.
- P. L. Watson, *J Am Chem Soc*, 1983, **105**, 6491-6493.
- C. Coperet, O. Maury, J. Thivolle-Cazat and J. M. Basset, *Angew Chem Int Edit*, 2001, **40**, 2331-.
- F. Rascon and C. Coperet, *J Organomet Chem*, 2011, **696**, 4121-4131.
- K. G. Caulton, M. H. Chisholm, W. E. Streib and Z. L. Xue, *J Am Chem Soc*, 1991, **113**, 6082-6090.
- L. A. Morton, S. J. Chen, H. Qiu and Z. L. Xue, *J Am Chem Soc*, 2007, **129**, 7277-7283.
- Z. L. Xue and L. A. Morton, *J Organomet Chem*, 2011, **696**, 3924-3934.
- C. M. Killian, D. J. Tempel, L. K. Johnson and M. Brookhart, *J Am Chem Soc*, 1996, **118**, 11664-11665.
- L. K. Johnson, C. M. Killian and M. Brookhart, *J Am Chem Soc*, 1995, **117**, 6414-6415.

