Grafted metallo-carbynes as bifunctional pre-catalysts for ROMP of cyclo-octene and cyclic alkane metathesis

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Supporting information for this article is is available

Abstract: Metallo-carbynes grafted on mesoporous fibrous silica are active towards alkane metathesis. We are comparing the activity of well-defined grafted pre-catalysts (≡Si-O-W≡(CH₂)₂≡CMe₃)₂, (≡Si-O-W≡(CH₃)₂≡CMe₃)₂, and (≡Si-O-W≡(CH₃)₂≡CMe₃)₂ for Ring Opening Metathesis Polymerization of cyclo-octene and metathesis of cyclo-octane. This comparison is because olefins are assumed to be intermediate products in alkane metathesis. The three pre-catalysts are active in cyclo-octene metathesis, and give the higher, and lower cyclic homologues. However, with cyclo-octene the three catalysts give polyoctenamer by classical ROMP. It is assumed that the metallo-carbynes react differently towards cyclo-alkanes and cyclo-olefins. In one case, with cyclo-alkanes they give a metallo-carbene alkyl and in the other case with cyclo-olefins they give a bis-carbene.

Alkane and olefin metathesis have always been considered to be similar in terms of reaction mechanism.˜ The only difference being that alkane metathesis is multi-functional: one function (usually assumed to be a metallo-carbene-hydride) for C-H bond activation leads to olefin formation, the other function (a metallo-carbene) leads to olefin metathesis and olefin hydrogenation yielding new alkanes.3 7-10 The similarity between these two metathetical reactions is the olefin metathesis step,11, 12

Herein we report cyclo-octane metathesis and cyclo-octene ring opening metathesis polymerization using pre-catalysts 1, 2 and 3, supported on mesoporous silica, dehydroxylated at 700 ºC (KCC-1,1000) (Figure 1).13 We observed that with these well-defined silica supported precursors, cyclo-octane gives higher and lower cyclic alkanes, whereas cyclo-octene gives classical ring opening metathesis polymerization (ROMP). Metallo-carbony complexes 1, 2 and 3 (Figure 1) were synthesized according to the literature procedures and were fully characterized by advanced solid-state NMR, ICP, and CHNS analysis.14-16 To our knowledge, these pre-catalysts are the first time reported as cyclo-octene polymerization catalysts, even though metallo-carbynes were first discovered by E. O. Fischer.17 Catalytic experiments for ROMP experiments were set up in a 5 mL glass reactor at room temperature. Introduction of 0.5 mL cyclooctene to 15 mg of pre-catalyst 1, 2, 3 (metal loading 5 to 9 wt %) yielded a low-density molecular weight polymer within 30 minutes of reaction, with a molecular weight of approximately 10000 g/mol and a narrow PDI (1.14 to 1.19) (Table 1).

Table 1. Polyoctenamer characterisation.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time [min]</th>
<th>Conv [%]</th>
<th>Mₙ [g/mol]</th>
<th>PDI</th>
<th>Trans/ Cis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>100</td>
<td>9510</td>
<td>1.14</td>
<td>0.97</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>95</td>
<td>11680</td>
<td>1.19</td>
<td>0.87</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>92</td>
<td>8850</td>
<td>1.15</td>
<td>0.82</td>
</tr>
</tbody>
</table>

Catalysis conditions: 0.5 mL substrate, 15 mg catalyst, stirred at 400rpm at RT in glass reactor

The mechanism is assumed to proceed via the catalytically active metallo-biscarbene species (Scheme 1). This metallo-biscarbene is formed due to coordination of the cyclooctene to the metallo-carbene followed by α-H transfer from the alkyl fragment to the carbyne fragment.18 Indeed, it is known that α-donors like PME₃ promote the α-H transfer between alkyl ligand and metallo-carbene triple bond of alkyl-alkylidyne complexes.18 In addition, due to the coordination of the stronger α-donor PME₃ to the d₁⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻なのに

Figure 1. Grafted metallo-carbene complexes 1 - 3.
metal center, the metallo-biscarbene isomer is stabilized and can be spectroscopically observed.\textsuperscript{18,19} It is well known that olefins act as $\sigma$-donor ligand, albeit weaker than PMe$_3$, and promote the $\alpha$-H transfer between the alkyl ligand and the metal-carbyne, leading to a bis-carbene. The resulting metallo-biscarbene isomer then initiates the ROMP with the cyclic alkene. The reaction at room temperature proceeds so fast that cyclo-octene is polymerized to polyoctenamer in just 30 minutes. The resulting polyoctenamer is soluble in CDCl$_3$, this allowed us to analyse it by liquid state NMR. Cis- and trans-configurated double bonds in the polymer can be distinguished with the cis-isomer peak at 5.34 ppm and the trans-isomer peak at 5.38 ppm (Figure S1, SI).\textsuperscript{20} The cis/trans ratio of the resulting polymer is almost 1, meaning that cis or trans coordination and/or reaction of the double bond to the metalloalkene have almost equal probability. This is generally the case for highly active catalysts.\textsuperscript{21} However, slight changes in the cis/trans ratio were observed when comparing the bulky complexes 2 and 3 to the less bulky complex 1. It has been shown that the stereochemistry of acyclic olefin metathesis is governed at the metallacycle intermediate, or at the coordination step.\textsuperscript{21} (Scheme 2) But in the case of ROMP it is possible that a secondary metathesis occurs between the acyclic double bond in the polymer chain and the metalloalkene (backbiting). This can lead to cyclic polymer or double bond isomerization by a "degenerate metathesis". Due to a nonstereoselective repulsive interaction between the olefin and the ligands around the metal center, it can be observed that with bulky ligands the trans/cis ratio is different than with smaller ligands. For smaller ligands, the cis-trans isomerization of internal polymeric double bonds is more likely to occur. In conclusion, complex 1 with small methyl ligands has less repulsive interaction and the isomerization rate is higher, therefore the trans/cis ratio is closer to 1 (0.97). For complexes 2 and 3 with bulky neopentyl ligands, the repulsive interaction is higher, and the cis conformation of the substrate is retained, making the trans/cis ratio smaller (0.87 for complex 2 and 0.82 for complex 3).

In the case of cyclic alkane metathesis, the alkane substrate reacts with the metallo-carbyne via C-H addition on the metal-carbyne triple bond (Scheme 3). It is understood that for cyclic alkane metathesis, splitting of the carbene triple bond into a bis-carbene via $\alpha$-H transfer and C-H addition of the cyclic substrate to the metallo-carbene are energetically unfavored compared to the C-H addition of the substrate to the metallo-carbene triple bond.\textsuperscript{22,23} The C-H addition to the metallo-carbene is followed by a $\beta$-H elimination and the coordinated cyclo-olefin is released. In Scheme 4 the remaining metallo-carbene-hydride undergoes

![Scheme 2](image1.png)

**Scheme 2.** Coordination of the internal cis double bond with respect to the propagating metallo-carbene. This leads to degenerate cis trans isomerization for complexes 1 (left), and 2 and 3 (right) of the acyclic double bonds in the polymer chain. Molybdenum has been removed for clarity.

![Scheme 3](image2.png)

**Scheme 3.** C-H addition on metallo-carbene bond leading to the metallo-carbene-hydride.

![Figure 2](image3.png)

**Figure 2.** Product distribution of cyclooctane metathesis with grafted carbyne complexes 1 - 3.
the classical reaction cycle ROM-RCM of cyclic alkane metathesis as depicted. Cyclo-octene can be formed by either reaction of cyclo-octane (C_{8}) with the metallo-carbene triple bond or by reaction of C_{8} with the generated metallocarbene-hydride 4 (Scheme 4) and hydrogen release. The ring-opening of the cyclo-octene is depicted in the “Degenerate” reaction cycle, where 4 is forming a metallacycle with cyclo-octene and the cyclic double bond unit is opened to give 8 (Scheme 4). The step from 8 to 9 involves another ring opening metathesis. Here the cycle splits up in two pathways, “Ring expansion” (10a to 13a) and “Ring contraction” (10b to 14b). The difference between ring expansion and ring contraction is the terminal double bond coordination in 10a versus the internal double bond coordination to the metallo-carbene in 11b. In other words, DBM (10b to 11b) is competing with RCM, which influences the ring size of the product.22 24 This is the reason for the broad product distribution that can observed in Figure 2. The metallo-carbene complexes 1, 2 and 3 give a broader product distribution if the reaction proceeds for longer time. Conversion for cyclo-octane reaches up to 47 % with a TON of 350 and the product distribution shown in Figure 2 shows a tendency towards ring expansion. In case of cyclo-octane, no polymeric product was observed. This is in sharp contrast to tandem catalytic systems, where polymeric products were observed along with metathesis products.10 Additionally, it has been found that isomerization of the substrate cyclo-octane towards cyclo-hexane-ethyl takes place. This isomerization is again a consequence of double bond migration during the olefin metathesis step. Further experiments prove that the ring size of the substrate is critical for the metathesis reaction to proceed. Experiments depicted in Table 2 show that when the ring size is reduced from C_{8} to C_{7}, C_{6}, C_{5}, no alkane metathesis takes place. The right ring size of the substrate is critical for the metathesis reactions to proceed, because the β-H elimination leading to olefin formation is only possible if the M-C-C-H angle is small enough to...
enable the β-H elimination. For cyclic alkanes like cyclo-heptane, cyclo-hexane and cyclo-pentane this angle is not small enough due to the cyclic conformation of the alkane.\textsuperscript{25} Regarding cyclic olefin metathesis, six-membered rings do not undergo ROMP due to their low strain energy.\textsuperscript{26-31}

<table>
<thead>
<tr>
<th>Cat</th>
<th>Conversion of cyclic alkanes [TON]</th>
<th>Conversion [mol %] cyclic alkenes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C5</td>
<td>C7</td>
</tr>
<tr>
<td>1</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>2</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>3</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

Catalysis conditions: a) cyclic alkenes: 15 mg catalyst, 0.5 mL substrate, sealed glass ampoule, 3 days stirred at 150 °C, b) 1 day stirred at 150 °C, c) cyclic alkenes: 15 mg catalyst, 0.5 mL substrate, microwave vial, 30 min stirred at RT, d) 3 days stirred at RT, e) 3 days stirred at 100 °C.

Both reactions cyclo-octane metathesis and cyclo-octene metathesis have in common that reducing the ring size of the substrate is affecting the reaction rate. For cyclic alkane metathesis it is due to the large M-C-C-H angle of the beta-H elimination step, too high to allow beta-H elimination. For cyclic alkene metathesis it is due to the more stable ring conformation which hinders ring opening polymerization. This is a major difference here between cyclo-octane metathesis and cyclo-octene metathesis. It should be pointed out that cyclo-octane metathesis does not lead to polycarbene as occurs in cyclo-octene metathesis. Intramolecular coordination of the last double bond in the chain is favored versus the possible competitive step of cyclo-octene coordination which would lead to polycarbene. Obviously, the concentration of cyclo-octene is too low in cyclo-octane metathesis.

We have shown here that grafted d\(^{9}\) metallo-carbyne complexes are highly reactive precursors towards ROMP of cyclo-olefin, but in contrast they transform cyclo-octane to higher and lower homologs of cyclic paraffin. This behavior is related to the slight difference of mechanism of the two reactions; if there is no double bond present in the substrate (cyclo-octane), the C-H activation proceeds via C-H addition to the metallo-carbyne triple bond, leading to a carbene-hydrid and cyclic alkane metathesis. In the case of an olefinic double bond (cyclo-ocetene), the reactivity of the metallo-carbynes shifts towards formation of a metallo-biscarbene and ROMP. In addition, it could be shown that ring size reduction of the substrates hinders reactivity for cyclic alkane metathesis. The metallo-carbynes 1, 2 and 3 are inactive for cyclohexene metathesis.

**Acknowledgement**

We would like to acknowledge King Abdullah University of Science and Technology for funding. We also acknowledge the NMR core lab for their continuous help.

There is no conflict of interest.

**Keywords:** Carbonyl ligands • Heterogeneous catalysis • Ring-opening metathesis polymerization • Surface organometallic chemistry


\[24\] F. A. Pasha, A. Bendjerrou-Sedjerari, K.-W. Huang, J.-M. Basset Organometallics 2014, 33, 3320-3327.


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With this study of grafted metallo-carbyne complexes, light is shed on the activation mechanism of the carbyne functionality towards C-C bonds of cyclic olefins achieving ROMP versus activation of C-H bonds in cyclic alkanes yielding cyclic oligomers. Different isomers of the metallocarbynes define their reactivity.