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Grafted metallo-carbynes as bifunctional pre-catalysts for ROMP of *cyclo*-octene and cyclic alkane metathesisWiebke Wackerow^[a], Manoj K. Samantaray^[a], Jean-Marie Basset^{[a]*}

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Abstract: Metallo-carbynes grafted on mesoporous fibrous silica are active towards alkane metathesis. We are comparing the activity of well-defined grafted pre-catalysts ($\equiv\text{Si-O-}W(\equiv\text{CCMe}_3)(-\text{CH}_2\text{CMe}_3)_2$, ($\equiv\text{Si-O-}W(\equiv\text{CH})(-\text{CH}_3)_2$ and ($\equiv\text{Si-O-}Mo(\equiv\text{CCMe}_3)(-\text{CH}_2\text{CMe}_3)_2$ 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*-octane 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.¹⁻⁶ 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 °C (KCC-1₍₇₀₀₎) (**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-carbyne 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.

Catalyst	Time [min]	Conv [%]	M _w [g/mol]	PDI	Trans/Cis
1	30	100	9510	1.14	0.97
2	30	95	11680	1.19	0.87
3	30	92	8850	1.15	0.82

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 σ -donors like PMe_3 promote the α -H transfer between alkyl ligand and metallo-carbyne triple bond of alkyl-alkylidyne complexes.¹⁸ In addition, due to the coordination of the stronger σ -donor PMe_3 to the $d^{(0)}$

Figure 1. Grafted metallocarbyne complexes **1** - **3**.

Scheme 1. Activation of C-H bonds by metallo-carbenes formed as intermediates of the catalyst precursor

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Scheme 2. Coordination of the internal cis double bond with respect to the propagating metallocarbene. 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.

metal center, the metallo-biscarbene isomer is stabilized and can be spectroscopically observed.^{18, 19} It is well known that olefins act as σ -donor ligand, albeit weaker than PMe_3 , and promote the α -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*-configured 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).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 metallocarbene have almost equal probability. This is generally the case for highly active catalysts.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.²¹ (Scheme 2) But in the case of ROMP it is possible that a secondary metathesis occurs between the acyclic

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

double bond in the polymer chain and the metallocarbene (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 carbyne triple bond into a bis-carbene via α -H transfer and C-H addition of the cyclic substrate to the metallo-biscarbene are energetically unfavored compared to the C-H addition of the substrate to the metallo-carbyne triple bond.^{22, 23} The C-H addition to the metallo-carbyne is followed by a β -H-elimination and the coordinated *cyclo*-olefin is released. In Scheme 4 the remaining metallo-carbene-hydride undergoes

Figure 2. Product distribution of cyclooctene metathesis with grafted carbyne complexes **1-3**

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Scheme 4. Metallacycles for ROM-RCM alkane metathesis of complexes **1**, **2** and **3**

the classical reaction cycle ROM-RCM of cyclic alkane metathesis as depicted *Cyclo*-octene can be formed by either reaction of *cyclo*-octane (cC_8) with the metallo-carbyne triple bond or by reaction of cC_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 be observed in **Figure 2**. The metallo-carbyne 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 C₈ to C₇, C₆, C₅, 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

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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.²⁵ Regarding cyclic olefin metathesis, six-membered rings do not undergo ROMP due to their low strain energy.²⁶⁻³¹

Table 2. Conversion of reactions with cyclic alkanes and cyclic alkenes.

Cat	Conversion of cyclic alkanes ^[a] [TON]					Conversion [mol %] cyclic alkenes	
	C ₅	C ₆	C ₇	C ₈ ^[a]	C ₈ ^[b]	<i>cis</i> -C ₈ ^[c]	C ₆ ^[d,e]
1	---	---	---	369	103	100	---
2	---	---	---	224	82	95	---
3	---	---	---	109	63	92	---

Catalysis conditions: a) cyclic alkanes: 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 β -H elimination step, too high to allow β -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 polyoctenamers 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 polyoctenamers. Obviously, the concentration of *cyclo*-octene is too low in *cyclo*-octane metathesis.

We have shown here that grafted d⁽⁰⁾ metallo-carbyne complexes are highly reactive precursors towards ROMP of *cyclo*-octene, 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 metallocarbyne triple-bond, leading to a carbene-hydride and cyclic alkane metathesis. In the case of an olefinic double bond (*cyclo*-octene), 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.

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There is no conflict of interest.

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

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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.