

Short communication

# Olefin metathesis transformations in thermomorphic multicomponent solvent systems



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## ABSTRACT

Homogeneous catalysis is a major actor of modern chemistry with a growing impact on clean and sustainable chemical processes. However, for many industrial applications of homogeneously catalyzed reactions, an easy separation and recovery of the catalyst should be guaranteed. Temperature-dependent multicomponent solvent (TMS) systems have been evaluated in ruthenium catalyzed olefin metathesis transformations. Propylene carbonate was found a suitable solvent for the ruthenium catalyzed ring-closing and cross-metathesis transformations of a variety of substrates including renewable fatty esters. The potential of a TMS system consisting of propylene carbonate/ethyl acetate/cyclohexane was then evaluated in the cross-metathesis of the renewable methyl 10-undecenoate with methyl acrylate and acrylonitrile.

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## 1. Introduction

Olefin metathesis is a powerful synthetic tool that has found a growing interest in the organic and polymer synthesis community [1–3]. As for many other catalytic transformations, post-treatment of the reaction media for catalyst/product separation is an important concern in particular when high catalyst loadings are required in the last or late stage of a synthetic sequence. Despite important progress in catalyst performances [4,5], the vast majority of ruthenium catalyzed transformations usually requires catalyst loadings of 1 mol% or higher as for the synthesis of macrocycles [6]. Consequently, several methods or processes have been designed for catalyst/product separation aimed at decreasing metal contamination of the final products [7] and in some cases for catalyst recycling [8] in particular using non-conventional solvents [9–13]. Over the last decade we have been investigating several processes for catalyst/product separation [9,10,14,15] and we have also searched for alternative greener solvents for olefin metathesis transformations. In particular, the findings that dimethyl carbonate was a suitable solvent for olefin metathesis transformations [16] prompted us to investigate the potential of temperature-dependent multicomponent solvent (TMS) systems using dialkyl carbonates as the polar phase. Since the first reports on thermomorphic catalysts by Bergbreiter in 1998 [17] and on temperature-dependent multicomponent solvent systems by Behr in 1999 [18], TMS systems have proven their interest and potential in a broad range of homogeneously catalyzed transformations [19–25].

To the best of our knowledge, only few studies on ruthenium-catalyzed olefin metathesis transformation in TMS system and thermomorphic polymer supported catalysts have been reported [26–28]. Herein, we present our results on olefin metathesis transformations in TMS system employing propylene carbonate as the polar phase.

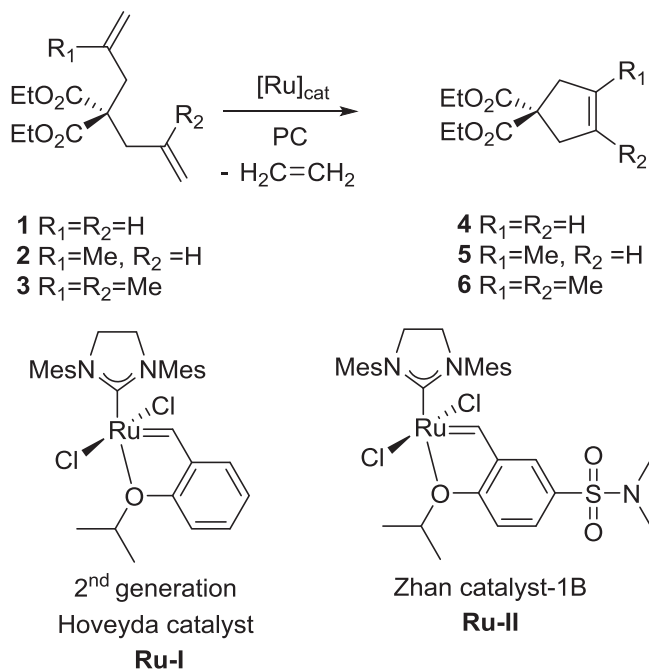
## 2. Results and discussion

Olefin metathesis transformations have been and are still essentially conducted in solvents with environmental and health issues, typically toluene or dichloromethane (DCM). Since 2008, we have shown that dimethyl carbonate (DMC) could be used as a greener and more environmentally acceptable solvent in metathesis transformations [16,29,30]. As opposed to DMC which is miscible with alkanes (C5, C6, C7) at room temperature, propylene carbonate (PC) is a solvent that can be used as the polar component of TMS systems. However, propylene carbonate displays very different physico-chemical properties from dimethyl carbonate (PC,  $\epsilon = 64.8$ ,  $\mu = 4.94$  D, DMC,  $\epsilon = 3.1$ ,  $\mu = 0.9$  D) [31], hence we first investigated the compatibility of propylene carbonate with a series a benchmark ring-closing and cross-metathesis reactions using two commercially available ruthenium catalysts (Scheme 1).

The RCM of **1** and **2** were conducted under experimental conditions established by Grubbs et al. for comparison of catalyst and process performances [32]. As depicted in Table 1, these transformations performed very well in propylene carbonate. If the efficiencies of catalyst **Ru-I** were slightly lower than those reported in dichloromethane (DCM), catalyst **Ru-II** was found more active in PC than in DCM (Table 1, entries 2, 3 and 5, 6). Without any catalyst solubility issue in PC and DCM, a

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Scheme 1. RCM in propylene carbonate (PC).

**Table 1**  
RCM reactions in propylene carbonate.

Entry	Substrate	Cat	t (min)	Solvent	Conv. (%) <sup>c</sup>
1 <sup>a</sup>	<b>1</b>	<b>Ru-I</b>	30	PC	84 (>95 in DCM) [32]
2 <sup>a</sup>	<b>1</b>	<b>Ru-II</b>	30	PC	99
3 <sup>a</sup>	<b>1</b>	<b>Ru-I</b>	30	DCM	86
4 <sup>a</sup>	<b>2</b>	<b>Ru-I</b>	60	PC	68 (>95 in DCM) [32]
5 <sup>a</sup>	<b>2</b>	<b>Ru-II</b>	60	PC	89
6 <sup>a</sup>	<b>2</b>	<b>Ru-II</b>	60	DCM	55
7 <sup>b</sup>	<b>3</b>	<b>Ru-I</b>	960 (16 h)	PC	22
8 <sup>b</sup>	<b>3</b>	<b>Ru-II</b>	960	PC	23
9 <sup>b</sup>	<b>3</b>	<b>Ru-II</b>	960	Toluene	36

<sup>a</sup> 0.2 mmol of substrate, 1 mol% of catalyst in 2 mL of solvent [substrate] = 0.1 M.

<sup>b</sup> 0.2 mmol of substrate, 2.5 mol% of catalyst in 2 mL of solvent [substrate] = 0.1 M.

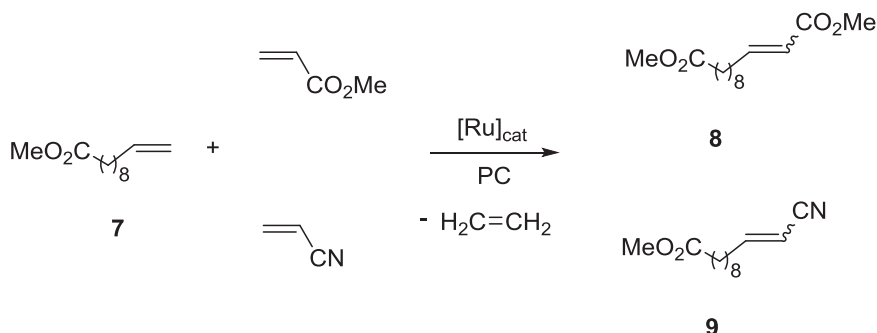
<sup>c</sup> Determined by gas chromatography using tetradecane as internal standard.

rationale for this observation may be found in the molecular structure of catalyst **Ru-II**. One peculiarity of catalyst **Ru-II** is the presence of a polar and electron withdrawing sulfonamide group at the *para*-position of the coordinating isopropoxy ether. This sulfonamide substituent is intended to boost the initiation of the catalyst upon weakening the Ru–O bond. Hence, one hypothesis to explain the observed results may be found in the exaltation of the activating properties of the polar sulfonamide group in a very polar solvent. The reluctant RCM of **3** was conducted with higher catalyst loading (2.5 mol%) at 80 °C for 16 h. Under these

conditions moderate conversions (22–23%) in agreement with modest results obtained with this type of catalysts were reached (Table 1, entries 7, 8). For comparison a slightly better conversion of 36% was obtained in toluene under identical conditions with **Ru-II** (Table 1, entry 9). Altogether these three examples clearly demonstrated the compatibility of propylene carbonate for ruthenium catalyzed metathesis transformations. Nevertheless, extraction of polar compounds such as **4–6** was not easy and required multiple extractions with cyclohexane.

The cross-metathesis of the renewable methyl undecenoate **7** [33] with functional olefin is an industrially relevant transformation since it provides an entry to bio-sourced polyester and polyamide monomers (Scheme 2) [34,35]. We anticipated that product extraction that was found tedious with small polar olefins **4–6** should be facilitated by the more lipophilic character of **7** and its cross-metathesis products **8** and **9**. If the cross-metathesis of **7** with acrylonitrile was not successful in PC, the cross-metathesis with methyl acrylate led to the expected diester **8**. Careful investigation and optimization of the experimental parameters demonstrated that both catalysts **Ru-I** and **Ru-II** enabled high conversions at high temperature with low catalyst loading (Table 2) (see Supplementary data). As observed in previous studies the reaction delivered the *E*-isomer as the major product [34,35].

Having demonstrated the compatibility of propylene carbonate with Ru-catalyzed metathesis transformations, we have then evaluated the potential of TMS for the industrially relevant transformations of fatty acid methyl ester derivatives employing propylene carbonate as the polar phase and cyclohexane (CH) as the non-polar component for the CM of **7**. Several semi-polar solvents were evaluated of which ethyl acetate (EA) enabled best phase separation when reaction mixtures were cooled to room temperature. Initial tests were conducted in a 1/1/1 mixture of PC/EA/CH at 80 °C with Zhan catalyst **Ru-II** (0.5 mol%). Interestingly, an improved conversion of 79% was obtained when compared to the same reaction conducted in pure propylene carbonate (conv. 46%, Table 2, entry 2). The performances of the reaction and phase separation were slightly improved by using a 1/1/2 mixture of PC/EA/CH. Under these conditions, a conversion of 88% was obtained. These results proved the suitability of a TMS system for olefin metathesis transformation. As anticipated, full recovery of the organic products was easier but still required 3 extractions with 5 mL of cyclohexane (ca. 95% weight of product recovered). After solvent removal, the product was analyzed by ICP to evaluate the metal leaching from the PC phase. As suggested by the colourless cyclohexane phase (see Supplementary data) suggested a very low metal leaching. Indeed, a 62 ppm ruthenium content was measured in the reaction product (theoretical ~ 2500 ppm). Further quick filtration on a short plug of silica (h × d = 2 cm × 1 cm) and elution with petroleum ether/ethyl acetate (1/1, v/v) was sufficient to lower the ruthenium content below 1 ppm. This flash filtration was also efficient in removing low amounts of propylene carbonate (ca. 5–10%) that was found in the cyclohexane extracts. Not only these encouraging results but also the drawbacks of this process related to product recovery prompted us to search for an alternative solvent composition. In particular, we foresaw that **7** featuring an aliphatic chain and a polar

Scheme 2. CM of methyl undecenoate **7** with functional olefins in PC.

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