Catalysis Communications 44 (2014) 80–84

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

2-Methyltetrahydrofuran: Sustainable solvent for ruthenium-catalyzed olefin metathesis

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ARTICLE INFO

Article history:
Received 9 April 2013
Received in revised form 1 June 2013
Accepted 18 June 2013
Available online 29 June 2013

Keywords:
Olefin metathesis
Ruthenium complexes
Hoveyda type catalysts
2-Methyltetrahydrofuran

ABSTRACT

Applicability of 2-methyltetrahydrofuran for olefin metathesis was examined with a set of ruthenium Hoveyda-type second generation catalysts. Influence of temperature was studied and the results were compared with those obtained in classical solvents for metathesis: dichloromethane and toluene.

1. Introduction

Catalytic olefin metathesis is an efficient synthetic method for the creation of new carbon–carbon double bond [1,2]. Main by-product of the whole catalytic cycle is typically ethylene, thus this process in comparison with other relevant synthetic approaches like Wittig reaction is much more economical and waste reducing. As the catalyst loading in preparative procedures usually does not exceed 1–5 mol% (loadings as low as 50 ppm are also possible [3]) the reaction mixture basically contains relatively pure product dissolved in a solvent. Typically this reaction is carried out in highly environmentally unfriendly solvents like dichloromethane or toluene (other halogenated solvents like 1,2-dichloroethane and fluorinated solvents are also used [4]). On the other hand there are several reports presenting the use of water as a reaction medium [5], but problems associated with solubility of typical olefins and catalysts pose a significant encumbrance. Alternative ionic liquids are considered [6], but their recycling is still a challenge [7]. It is also possible to conduct olefin metathesis in supercritical carbon dioxide ($scCO_2$) [8–10], however this requires pressurized reactors, not always available in research laboratories. The use of other renewable solvents like glycerol [11], polyethylene glycol [12] and methyl decanoate [13] has been also studied. However, the most interesting results concern dimethyl carbonate [14,15].

As olefin metathesis become an important part of industrial processes [16] there is a growing need for the search of eco-friendly solvents applicable in large scale synthesis. We turned our attention to 2-methyltetrahydrofuran (2-MeTHF), derived from renewable resources like oat hulls and corn cobs containing pentoses which after dehydrations give furfural catalytically reduced to 2-MeTHF. This solvent has already a broad application in organic chemistry including pharmaceutical industry [17]. In comparison with tetrahydrofuran, 2-MeTHF have several advantages like lower volatility, relatively high stability towards acids [18], and bases [19], low solubility in water (interestingly, decreasing with increasing temperature) making them easier to recycle than THF. Taking into account the low toxicity [20] and high biodegradability 2-MeTHF is considered as an environmentally friendly compound and their use is advocated by the ACS Green Chemistry Pharmaceutical Roundtable.

To the best of our knowledge, there are no reports on the use of 2-MeTHF as a medium for olefin metathesis reactions. In this study we present performance of selected newly synthesized second generation Hoveyda-type catalysts **5a**–**c** in comparison with commercially available second generation Hoveyda catalyst **6** in 2-MeTHF (Scheme 1). To extensively examine the performance of the catalysts we applied them in a set of model reactions. For comparison the same catalysts were also tested in common solvents used in olefin metathesis: dichloromethane and toluene.

2. Experimental

2.1. Materials

Solvents were dried by conventional methods. Substrates were used as obtained. For details see Appendix A.

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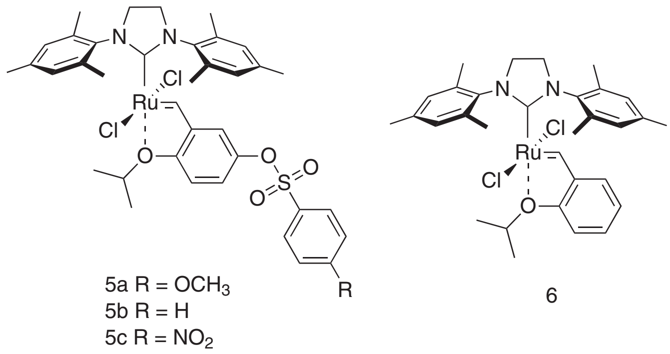
http://dx.doi.org/10.1016/j.catcom.2013.06.027



5a R = OCH_3
5b R = H
5c R = NO_2

6

Scheme 1. Newly synthesized second generation Hoveyda-type catalysts **5a**–**c** and second generation Hoveyda catalyst **6**.

2.2. Techniques

All experiments were carried out under argon atmosphere using standard Schlenk technique. NMR spectra were recorded on Agilent 400-MR DD2 400 MHz spectrometer. NMR experiments (reaction profiles for RCM of diethyl diallylmalonate **7**) were carried out using nondeuterated solvents [21] in typical NMR tubes closed with rubber septum and filled under argon with solution of substrate in dry solvent. Solution of catalyst (prepared in dry solvent under atmosphere of argon) was added through rubber septum just prior ^1H NMR measurement. The progress of the metathesis reactions was monitored by ^1H NMR spectroscopy on Agilent 400-MR DD2 400 MHz spectrometer. Conversions determined by gas chromatography were measured by PE Clarus 580 with InterCap 5MS-Sil column.

2.3. Catalyst preparation and reactivity studies

The styrene **1** was prepared according to the Yao procedure [22]. The reactions of **1** with appropriate arenesulphonyl chloride **2a**–**c** gave styrenes **3a**–**c** (Scheme 2).

The new Hoveyda-type second generation catalysts **5a**–**c** were obtained in the reaction of the appropriate styrenes **3a**–**c** with indenylidene ruthenium complex **4** in the presence of CuCl (Scheme 3).

2.3.1. Synthesis of **5a**

To a mixture of **3a** (80.9 mg, 0.232 mmol) and CuCl (25.3 mg, 0.253 mmol) dry toluene (5 mL) was added under atmosphere of Ar. Then reaction mixture was warmed up to 70 °C and **4** (200 mg, 0.211 mmol) was added. After 20 min the mixture was cooled down to room temperature and toluene was evaporated. The residue was purified by column chromatography (10% EtOAc/*c*-hexane and then 20% EtOAc/*c*-hexane). Then solvents were evaporated and product was crystallized two times from CH_2Cl_2/CH_3OH mixture, and once from CH_2Cl_2/*n*-hexane mixture, to afford **5a** (152 mg, 89%) as green crystals.

^1H NMR (400 MHz, CD_2Cl_2): $\delta = 16.21$ (s, 1H), 7.79–7.64 (m, 2H), 7.18 (dd, $J = 8.9, 2.8$ Hz, 1H), 7.06–6.93 (m, 6H), 6.72 (d, $J = 8.9$ Hz, 1H), 6.50 (d, $J = 2.8$ Hz, 1H), 4.81 (sept, $J = 6.1$ Hz, 1H), 4.15 (s, 4H), 3.90 (s, 3H), 2.41 (s, 12H), 2.38 (s, 6H), 1.20 (d, $J = 6.1$ Hz, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 291.5$, 209.1, 164.3, 150.2, 145.3, 144.8, 139.0 (ovl.), 130.8, 129.2, 126.2, 126.1, 122.2, 115.1, 114.4, 113.2, 76.1, 55.9, 51.6, 20.9, 20.9, 19.2. IR (KBr): $\nu = 3055$, 3042, 3002, 2979, 2957, 2917, 2845, 2735, 1594, 1577, 1495 cm^{-1}. Anal. Calcd. for $C_{38}H_{44}Cl_2N_2O_5RuS\cdot 2/5CH_2Cl_2$: C 54.47, H 5.33, N 3.31, S 3.79, Cl 11.72; Found: C 54.52, H 5.56, N 3.19, S 3.75, Cl 11.87.

2.3.2. Synthesis of **5b**

To a mixture of **3b** (70.0 mg, 0.220 mmol) and CuCl (24.0 mg, 0.240 mmol) dry toluene (5 mL) was added under atmosphere of Ar. Then mixture was warmed up to 70 °C and **4** (190 mg, 0.200 mmol) was added. After 15 min the mixture was cooled down to room temperature and toluene was evaporated. The residue was purified by column chromatography (10% EtOAc/*c*-hexane and then 20% EtOAc/*c*-hexane). After evaporation of solvents product was crystallized two times from CH_2Cl_2/CH_3OH, and once from CH_2Cl_2/*n*-hexane, to afford **5b** (138 mg, 88%) as green crystals.

^1H NMR (400 MHz, CD_2Cl_2): $\delta = 16.23$ (s, 1H), 7.87–7.78 (m, 2H), 7.78–7.70 (m, 1H), 7.64–7.51 (m, 2H), 7.17 (dd, $J = 8.9, 2.8$ Hz, 1H), 7.04 (s, 4H), 6.72 (d, $J = 8.8$ Hz, 1H), 6.53 (d, $J = 2.8$ Hz, 1H), 4.81 (sept, $J = 6.1$ Hz, 1H), 4.15 (s, 4H), 2.42 (s, 12H), 2.38 (s, 6H), 1.20 (d, $J = 6.1$ Hz, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 291.2$, 209.1, 150.3, 145.3, 144.8, 139.0 (ovl.), 135.1, 134.4, 129.3, 129.3, 128.5, 122.1, 114.9, 113.3, 76.2, 51.6, 20.9, 20.9, 19.1. IR (KBr): $\nu = 2980$, 2961, 2917, 2736, 1606, 1586 cm^{-1}. Anal. Calcd. for $C_{37}H_{42}Cl_2N_2O_4RuS\cdot 3/5CH_2Cl_2$: C 54.17; H 5.22; N 3.36; S 3.85; Cl 13.61; Found: C 54.24, H 5.52, N 3.32, S 3.99, Cl 13.36.

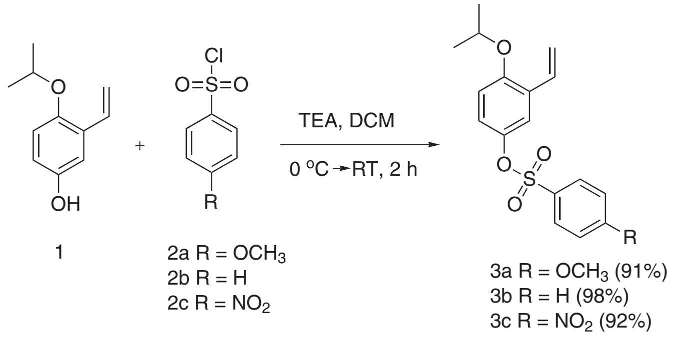
2.3.3. Synthesis of **5c**

To a mixture of **3c** (79.9 mg, 0.220 mmol) and CuCl (24.0 mg, 0.240 mmol), dry toluene (5 mL) was added under atmosphere of Ar. Then reaction mixture was warmed up to 70 °C and **4** (190 mg, 0.200 mmol) was added. After 25 min the mixture was cooled down to room temperature and toluene was evaporated. The residue was purified by column chromatography (10% EtOAc/*c*-hexane and then 20% EtOAc/*c*-hexane). Then solvents were evaporated and product was crystallized two times from CH_2Cl_2/CH_3OH, and once from CH_2Cl_2/*n*-hexane to afford **5c** (107 mg, 65%) as dark-green crystals.

^1H NMR (400 MHz, CD_2Cl_2): $\delta = 16.27$ (s, 1H), 8.49–8.28 (m, 2H), 8.12–7.90 (m, 2H), 7.16 (dd, $J = 9.0, 2.9$ Hz, 1H), 7.04 (s, 4H), 6.75 (d, $J = 8.9$, 1H), 6.63 (d, $J = 2.8$, 1H), 4.83 (sept, $J = 6.1$ Hz, 1H), 4.17 (s, 4H), 2.42 (s, 12H), 2.39 (s, 6H), 1.21 (d, $J = 6.1$ Hz, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 290.4$, 208.7, 151.1, 150.5, 145.4, 144.4, 140.7, 139.0 (ovl.), 130.1, 129.3, 124.5, 121.5 (ovl.), 114.7, 113.5, 76.4, 51.6, 20.9, 20.9, 19.1. IR (KBr): $\nu = 3108$, 3098, 3073, 3021, 2978, 2918, 2739, 1690, 1607, 1533 cm^{-1}. Anal. Calcd. for $C_{37}H_{41}Cl_2N_3O_6RuS\cdot 3/5CH_2Cl_2$: C 51.39, H 4.84, N 4.78, S 3.65, Cl 12.91; Found: C 51.23, H 5.01, N 4.74, S 3.69, Cl 12.96.

The second generation Hoveyda catalyst **6** was prepared according to our procedure [23].

Catalysts **5a**–**c** and **6** (1 mol% loading) were tested in standard RCM reaction performed in DCM, toluene and 2-MeTHF with initial concentration of diethyl diallylmalonate **7** equal to 0.1 M (Scheme 4). The formation of only one product was observed.



1

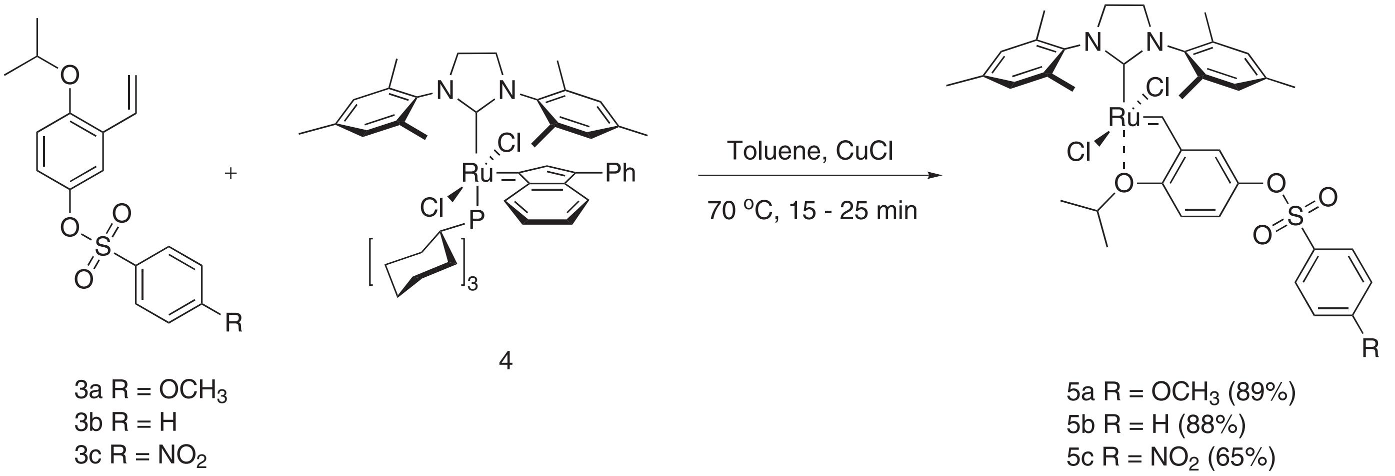
2a R = OCH_3
2b R = H
2c R = NO_2

3a R = OCH_3 (91%)
3b R = H (98%)
3c R = NO_2 (92%)

Scheme 2. Synthesis of styrenes **3a**–**c**.

2.3.4. General procedure for RCM and Ene–Yne reactions (Table 1, entries 1–4)

The comparative experiments with model substrates (Table 1, entries 1–4) were performed in 2-MeTHF at 70 °C with initial concentration of substrates c = 0.1 M and catalyst loadings 1 mol% (entries 2 and 3) or 2 mol% (entries 1 and 4). To a stirred solution of substrate (1 eq) and durene (1 eq, used as internal standard) in dry 2-MeTHF



Scheme 3. Preparation of second generation Hoveyda-type catalysts **5a**–**c**.

placed under atmosphere of Ar, solution of catalyst (**5a**, **5b**, **5c** or **6**) in dry 2-MeTHF was added in a single portion at 70 °C. The reaction mixture was left at 70 °C. After 5, 10, 30, 60 and 120 min aliquots (50 μL) were taken and quenched immediately with ethyl vinyl ether (100 μL). Then CH_2Cl_2 (500 μL) was added, and solution was analyzed by GC, using EP Clarus 580 chromatograph with InterCap MS5/Sil column.

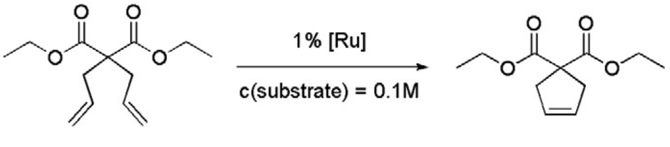
2.3.5. General procedure for CM (Table 1, entry 5)

The comparative experiment with model substrate (Table 1, entry 5) was performed in 2-MeTHF at 70 °C with initial concentration of substrate $c = 0.1$ M and catalysts loadings 2 mol%. To a stirred solution of allylbenzene (1 eq) and (*Z*)-1,4-diacetoxy-2-butene (2 eq) in dry 2-MeTHF placed under atmosphere of Ar, solution of catalyst (**5a**, **5b**, **5c** or **6**) in dry 2-MeTHF was added in a single portion at 70 °C. The reaction mixture was left at 70 °C for 30 min. After this time the mixture was immediately cooled down to room temperature. Then solvent was evaporated, and the residue was immediately purified by column chromatography (elution with 10% EtOAc/*c*-hexane). After evaporation of the solvents the residue was dried under vacuum. *E*/*Z* ratio was determined by ^{1}H NMR spectroscopy.

3. Results and discussions

Figs. 1 and 2 show the conversion profiles for RCM reaction of diethyl diallylmalonate **7** (Scheme 4) performed at 30 °C in DCM and toluene. All studied catalysts give high conversions in reasonable time and new catalysts **5a**–**c** outperform commercial second generation Hoveyda catalyst **6**. It is clearly seen that under the same conditions reactions in toluene are faster than in DCM, as 70% conversion was reached 1.5–2 times faster.

The effect of substituents in benzylidene part of Hoveyda-type catalysts was extensively studied and it was shown that strong electron withdrawing nitro group (Hammett σ_p value 0.78 [24]) in *para* position has the most beneficial effect on catalyst activity [25,26]. Phenylsulphonyloxy group exhibits also electron withdrawing properties (Hammett σ_p value 0.33 [24]). Unfortunately, to the best of our knowledge, constants for *para* substituted metoxy- and nitrophenylsulphonyloxy groups are not available in the literature.

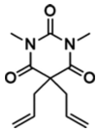
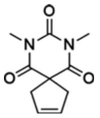
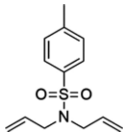
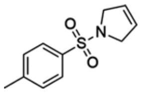
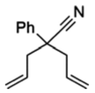
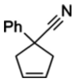
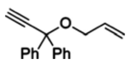
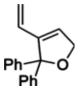
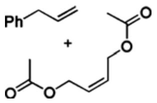
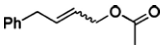


Scheme 4. RCM of diethyl diallylmalonate **7**.

Reaction profiles obtained in 2-MeTHF at 30 °C (Fig. 3) disclose significant differences in activities of studied catalysts. Catalyst **5a** is the most active one in this series whereas **6** is slightly less active. Reactivities of catalysts **5b** and **5c** are significantly suppressed under these conditions — conversions even after extended time were below 50%. As in DCM and toluene there are no such significant differences (Figs. 1 and 2) it seems that solvation by 2-MeTHF plays a crucial role in catalyst activity. However, it should be pointed out that activities of catalysts **6** and **5a** in 2-MeTHF at 30 °C (Fig. 3) are comparable with those in DCM at 30 °C (Fig. 1).

Next we examined the influence of temperature on the reactivity of catalysts in 2-MeTHF (Fig. 4). Surprisingly, catalysts **5b** and **5c** became very active at 50 °C. Catalyst **5b** reached full conversion after 6 min (the same as catalysts **5a**), and catalyst **5c** gives nearly 80% of conversion after 10 min. Complexes **5a** and **5b** definitely outperform commercial catalyst **6** in RCM reaction carried out in 2-MeTHF at 50 °C.

Table 1
Application of catalysts **5a**–**c** and **6** in RCM, CM and Ene–Yne reactions.[a]

Entry	Substrate	Product	Catalyst (mol%)	Time [min]	Conversion [%][b]
1			**5a** (2)	5 (10)	99 (>99)
			5b (2)	5 (10)	99 (>99)
			5c (2)	5	>99
			6 (2)	10 (30)	99 (>99)
2			**5a** (1)	5	85
			5b (1)	10	90
			5c (1)	10 (120)	86 (88)
			6 (1)	5 (30)	94 (97)
3			**5a** (1)	10	99
			5b (1)	5 (60)	95 (97)
			5c (1)	10 (60)	92 (94)
			6 (1)	10 (30)	99 (>99)
4			**5a** (2)	10 (120)	90 (93)
			5b (2)	5 (120)	90 (95)
			5c (2)	5 (120)	94 (96)
			6 (2)	10 (120)	94 (98)
5			**5a** (2)	30	70[c] 5.8:1[d]
			5b (2)	30	72[c] 6.1:1[d]
			5c (2)	30	70[c] 7.6:1[d]
			6 (2)	30	73[c] 6.6:1[d]

[a] All reactions were performed in 2-MeTHF at 70 °C.
[b] Conversion was determined by GC using durene as internal standard.
[c] Isolated yield.
[d] *E*/*Z* ratio was determined by ^{1}H NMR spectroscopy.

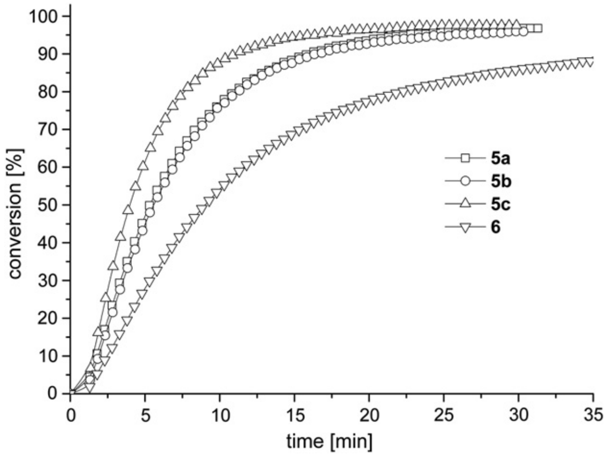


Fig. 1. Time-conversion profiles for RCM of **7** with **5a**–**c** and **6** catalysts (1 mol%) in DCM at 30 °C; initial concentration of substrate **7** equal to 0.1 mol/L.

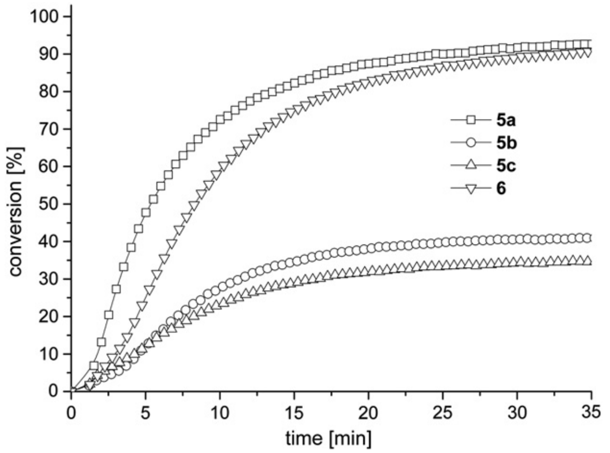


Fig. 3. Time-conversion profiles for RCM of **7** with **5a**–**c** and **6** catalysts (1 mol%) in 2-MeTHF at 30 °C; initial concentration of substrate **7** equal to 0.1 mol/L.

For comparison we also measured the reaction profiles for RCM with complexes **5a**–**c** and **6** in toluene at 50 °C (Fig. 5). All reactions were faster than in 2-MeTHF under the same conditions (for **5a** and **5b** observed differences are small). Much more surprising is that all catalysts show practically the same reactivity. Thus 2-MeTHF has significant influence on activity of catalysts, whereas toluene is much more innocent. This can be a consequence of coordinating ability of oxygen atom in 2-MeTHF, which structure mimics the coordinating part of 2-isopropoxybenzylidenes in Hoveyda type catalysts.

Results obtained with **5a**–**c** and **6** catalysts in model RCM reaction (Scheme 4) performed in 2-MeTHF at elevated temperature (Fig. 4) encouraged us to test these catalysts with broader spectrum of substrates and also in another types of metathesis reactions like cross metathesis (CM) and Ene–Yne reaction (Table 1). These reactions were performed at 70 °C to fully take advantage of the observed thermal switchability of our new catalysts in 2-MeTHF. In general, the reactions were monitored by GC with durene as internal standard. In RCM and Ene–Yne metathesis (Table 1, entries 1–4) formation of only one product was observed. In all RCM reactions (Table 1, entries 1–3) conversions are very high (from 85% up to full conversion) and are reached in very short time (up to 10 min). Conversions are not improved significantly by prolongation of reaction time. In Ene–Yne metathesis (Table 1, entry 4) conversions after 5 to 10 min are also very high and after 2 h there is only negligible increase. In CM reactions (Table 1, entry 5) conversions are high and there is strong preference for formation of isomer *E*.

4. Conclusions

Our investigations clearly demonstrate that typically used in metathesis solvents like DCM and toluene can be replaced by 2-MeTHF. For good performance of catalysts in this solvent it is recommended to carry out reactions at elevated temperature (50–70 °C). Among studied catalysts, for model reaction carried out in 2-MeTHF at 50 °C the best activity show new synthesized catalysts **5a** and **5b**, while for reaction carried out in DCM and toluene at 30 °C the most active is catalyst **5c**.

Reactions performed with a wider range of substrates (Table 1) clearly indicated, that the use of 2-MeTHF as a solvent for ruthenium catalyzed metathesis reactions is possible especially at elevated temperature. These results show that 2-MeTHF is an environmentally friendly solvent applicable for green olefin metathesis transformations.

Acknowledgments

M.K. and K.G. wish to acknowledge the TEAM project operated within the Foundation for Polish Science Team Program co-financed by the EU European Regional Development Fund, Operational Program Innovative Economy 2007-2013, while M.S. wish to thank The University of Warsaw (Grant No. 501/86-DSM-100100) for the financial support.

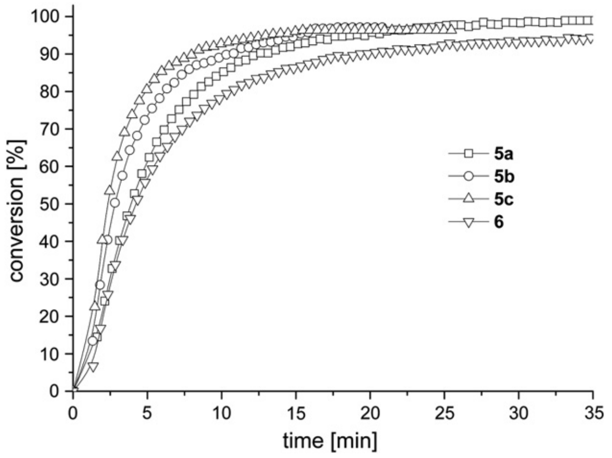


Fig. 2. Time-conversion profiles for RCM of **7** with **5a**–**c** and **6** catalysts (1 mol%) in toluene at 30 °C; initial concentration of substrate **7** equal to 0.1 mol/L.

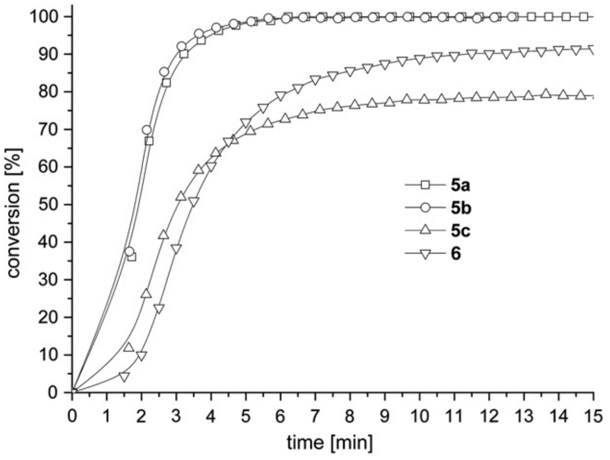


Fig. 4. Time-conversion profiles for RCM of **7** with **5a**–**c** and **6** catalysts (1 mol%) in 2-MeTHF at 50 °C; initial concentration of substrate **7** equal to 0.1 mol/L.

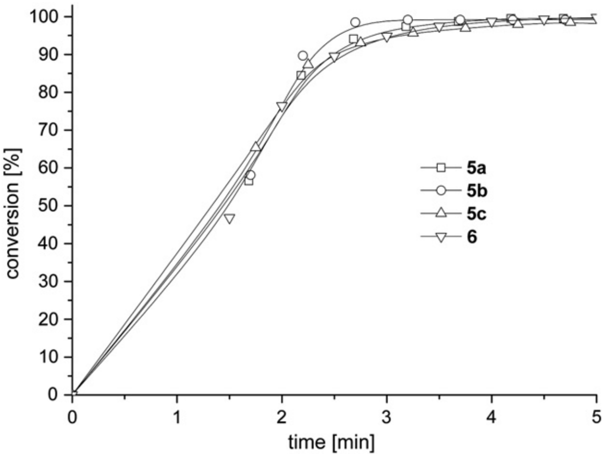


Fig. 5. Time-conversion profiles for RCM of **7** with **5a**–**c** and **6** catalysts (1 mol%) in toluene at 50 °C; initial concentration of substrate **7** equal to 0.1 mol/L.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2013.06.027.

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