A simple approach to reduce the environmental impact of olefin metathesis reactions: a green and renewable solvent compared to solvent-free reactions

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Two widely-studied olefin metathesis reactions, the cross-metathesis of allyl benzene with *cis*-1,4-diacetoxy-2-butene and the ring closing metathesis of diethyl diallylmalonate, were studied under environmentally more benign reaction conditions. All studied catalysts allowed these reactions to be performed under bulk conditions, thus avoiding large amounts of solvent waste. Moreover, methyl decanoate, a fatty acid-derived, and thus renewable and non-toxic, solvent, was shown to be an environmentally friendly alternative solvent to the usually applied dichloromethane. Most interestingly, only the reactions performed under bulk conditions allowed a 25-fold catalyst loading reduction, thus offering the "greenest" alternative of the investigated reaction conditions.

Introduction

Since the development and continuous improvement of well defined, highly active and functional group-tolerant ruthenium based catalysts,[1–11] olefin metathesis has found manifold possible applications in organic and polymer synthesis.[12–16]

More recently, many methods for the reduction of the environmental impact of olefin metathesis reactions were reported in the literature. For instance, supported catalysts that facilitate catalyst removal and recycling were often reported.[17] Similarly, procedures for the removal of homogenous catalysts from the reaction mixture are being developed.[17] However, since the catalyst is not the only parameter that can influence the environmental impact of a reaction, many reports are available that describe olefin metathesis in alternative solvents. Most often, homogeneously-catalyzed metathesis reactions are carried out in dichloromethane (and, less frequently, in aromatic solvents) at high dilutions. Current investigations focus on the use of ionic liquids,[18,19] water,[20] other environmentally friendly solvents,[21] and supercritical fluids[22,23] for olefin metathesis reactions. All of these investigations claim the use of less toxic solvents and/or an easier recycling of the catalyst as environmental advantages. However, it should be mentioned here that a certain solvent should not generally be considered as "green", since all process parameters have to be carefully evaluated and compared (*e.g.* by using environmental factors) to each other before such a statement can be made.

Although the use of ruthenium based metathesis initiators under bulk conditions is a standard procedure for acyclic diene metathesis (ADMET) polymerization and, in some cases, for ring-opening metathesis polymerization (ROMP), very little has been reported on olefin metathesis reactions to yield defined low molecular weight organic compounds under solvent-free conditions. In 2002, Grubbs *et al*. reported a solvent free cross-metathesis procedure for the synthesis of trisubstituted olefins.[24] Practically, a non-dimerizing cross-metathesis reaction partner, isobutylene or 2-methyl-2-butene in this case, was used in excess and acted as solvent for these reactions, allowing a 5-fold catalyst loading reduction (from 5 to 1%). Along the same lines, we observed that low catalyst loadings of 0.1–1% were sufficient for the quite challenging cross-metathesis reactions of allyl chloride[25] and methyl acrylate[26] with fatty acid derivatives under bulk conditions to yield renewable monomers for step-growth polymerizations. Here, an excess of allyl chloride or methyl acrylate also acted practically as the solvent, but it is important to note that these reactions did not proceed well when performed in dichloromethane or other organic solvents. Moreover, a solvent-free ring-closing metathesis procedure under microwave conditions with 1% of catalyst that provided quantitative conversions in many cases was recently reported.[27] Despite these promising observations, no detailed studies on the performance of ruthenium-based metathesis initiators under bulk conditions is available.

With the aim of reducing the environmental impact of the reaction conditions commonly applied in olefin metathesis reactions, we investigated the use of a fatty acid-derived (and thus renewable) solvent, as well as solvent-free conditions, in detail for two commonly-studied metathesis reactions with three frequently-studied highly active second generation catalysts (see Fig. 1). The studied reactions were the cross-metathesis (CM) of allyl benzene with *cis*-1,4-diacetoxy-2-butene and the ring closing metathesis (RCM) of diethyl diallylmalonate (see Fig. 2), since both reactions were suggested by Grubbs *et al*. as standard reactions for the evaluation of a new catalyst.[28] However, here we used these widely-studied reactions to evaluate and compare more environmentally friendly reaction conditions.

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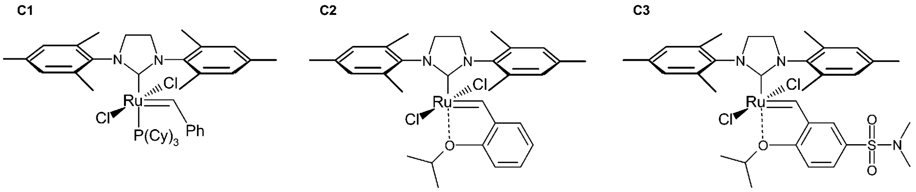

Fig. 1 Investigated second generation catalysts.

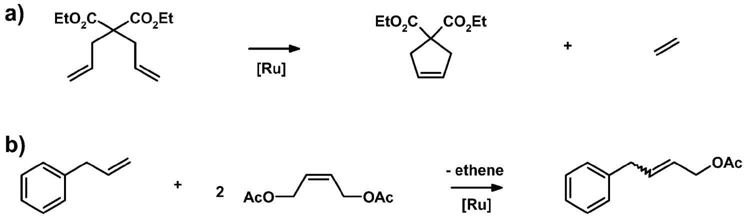

Fig. 2 Investigated metathesis reactions: (a) ring-closing metathesis of diethyl diallylmalonate; (b) cross-metathesis of allyl benzene with *cis*-1,4-diacetoxy-2-butene.

Results and discussion

We studied the CM of allyl benzene with *cis*-1,4-diacetoxy-2-butene and the RCM of diethyl diallylmalonate under bulk conditions and in a renewable and non-toxic solvent with the aim of reducing the environmental impact of metathesis reactions. Our findings were then compared to the conventionally-applied reaction conditions, *e.g.* reaction in the toxic solvent dichloromethane at high dilution.

In the case of the ring closing metathesis of diethyl diallylmalonate, Grubbs *et al.* suggested performing the reaction at a concentration of 0.1 mol L^{-1} in dichloromethane (DCM) with a catalyst loading of 1% at 30 °C.[28] These conditions were suggested to test and evaluate new catalysts. We used these conditions as a starting point and as a reference for our target to minimize the environmental impact of olefin metathesis reactions. Thus, we performed this reaction in methyl decanoate (MD) and in bulk under otherwise unchanged conditions with catalysts **C1**–**C3**.

All reactions were performed in triplicate and the averaged results of these investigations are provided in Table 1. The reproducibility of these reactions was good (<3% standard deviation). Only the reactions performed in MD showed somewhat larger deviations (up to 5%). It is obvious that all investigated catalysts were able to catalyze the reaction, as expected and reported many times in the literature. The standard conditions at high dilution in DCM with 1% catalyst loading resulted in almost full conversion for all catalysts. MD gives somewhat poorer results for all catalysts and at all catalyst loadings, if compared to the reactions in DCM. Therefore, MD is generally suitable as a solvent for this RCM reaction, but somewhat less than DCM, if high conversions are desired. Nevertheless, the choice of MD can offer significant environmental benefits. More interestingly, with the exception of **C1**, the solvent-free conditions also show full conversions and thus offer an environmentally friendly alternative to the reactions performed in solvent.

Table 1 Results of the RCM of diethyldiallyl malonate (T = 30 °C, t = 60 min, reactions performed in triplicate; averaged results are given) using standard conditions with different solvents

Catalyst	Catalyst loading/mol%[a]	Solvent[b]	C/%[c]
C1	1.0	DCM	97.8
C1	1.0	MD	79.3
C1	1.0	none	88.1
C2	1.0	DCM	95.9
C2	1.0	MD	66.4
C2	1.0	none	99.5
C3	1.0	DCM	99.6
C3	1.0	MD	71.5
C3	1.0	none	99.4

[a] Amount of catalyst in mol% relative to diethyldiallyl malonate. [b] DCM: dichloromethane ([diethyldiallyl malonate] = 0.1 mol L^{-1}); MD: methyl decanoate ([diethyldiallyl malonate] = 0.1 mol L^{-1}); none: reaction performed in bulk ([diethyldiallyl malonate] = 4.136 mol L^{-1}). [c] Conversion of diethyldiallyl malonate (by GC-MS).

In order to further reduce the environmental impact of these reactions, we investigated a 5-fold reduction in catalyst loading to 0.2 mol% (Table 2). We were pleased to still observe good to excellent results under these conditions in all solvent systems. Once more, the reactions performed in MD showed somewhat poorer results for all catalysts. However, the solvent-free reactions provided an advantage here, since the observed conversions remained high and were higher than in DCM in all cases.

Since diethyl diallylmalonate is an α,ω-diene one might expect ADMET as a side reaction, especially under these highly concentrated conditions. However, we did not observe the formation of oligomers or even polymers by GPC, ruling out this side reaction. Therefore, the RCM reactions with 0.2% of **C2** and **C3** avoid 46 L of toxic DCM per kg of obtained product without loss of catalyst activity. Inspired by these findings, we tried to reduce the loading of **C2** and **C3** even further to 0.04 mol%. **C2** was somewhat less active under these conditions than **C3**. Generally, this catalyst loading reduction resulted in decreased conversions, but **C3** remained highly active under bulk conditions. This is a very interesting and promising result, since not only does it save 46 L of DCM per kg of product, but also the amount of potentially toxic and expensive

Table 2 Results of the RCM of diethyldiallyl malonate ($T = 30$ °C, $t = 60$ min, reactions performed in triplicate; averaged results are given) at reduced catalyst loadings

Catalyst	Catalyst loading/mol%[a]	Solvent[b]	C/%[c]
C1	0.2	DCM	76.4
C1	0.2	MD	60.8
C1	0.2	none	81.5
C2	0.2	DCM	86.5
C2	0.04	DCM	62.4
C2	0.2	MD	49.9
C2	0.2	none	99.4
C2	0.04	none	15.9
C3	0.2	DCM	94.9
C3	0.04	DCM	76.5
C3	0.2	MD	66.0
C3	0.2	none	99.6
C3	0.04	none	97.0

[a] Amount of catalyst in mol% relative to diethyldiallyl malonate. [b] DCM: dichloromethane ([diethyldiallyl malonate] = 0.1 mol L^{-1}); MD: methyl decanoate ([diethyldiallyl malonate] = 0.1 mol L^{-1}); none: reaction performed in bulk ([diethyldiallyl malonate] = 4.136 mol L^{-1}). [c] Conversion of diethyldiallyl malonate (by GC-MS).

catalyst can be reduced at least 25-fold, compared to the classic literature conditions. Quite interestingly, the bulk reactions with low catalyst loadings showed a better reproducibility than the corresponding reactions in solvent, which is an additional advantage.

In order to evaluate if the above findings are only applicable to the investigated RCM reaction, or if they can be transferred to other metathesis reactions, we investigated the cross-metathesis of allyl benzene with *cis*-1,4-diacetoxy-2-butene in a similar set of experiments (see Table 3). Again, for these reactions, we used the reaction conditions suggested by Grubbs *et al.* as the starting point for our investigations: catalyst concentration of 2.5 mol%, 0.2 M allyl benzene in dichloromethane, 2 equivalents of *cis*-1,4-diacetoxy-2-butene, 25 °C.[28] In order to be able to compare the obtained results to the RCM reaction described above, we changed the concentration of allyl benzene to 0.1 M and left all other parameters unchanged. Starting from these conditions, we tested methyl decanoate and solventless reactions in a similar way as described above (Table 3). Under all reaction conditions, the observed formation of the allyl benzene self-metathesis product was below 1% and thus we will neglect this side-reaction in further discussions. The reproducibility was also good for these reactions (< 3% standard deviation). In contrast to the RCM reaction described above, MD is a very suitable solvent for this CM reaction for all catalysts and provides nearly full conversions of ally benzene, similar to the reactions performed in DCM and in bulk. Thus, either an environmentally friendly and renewable solvent can be used for this reaction, or solvent-free conditions that avoid solvent waste completely may be chosen without losing catalyst activity.

Table 3 Results of the CM of allyl benzene with *cis*-1,4-diacetoxy-2-butene ($T = 25$ °C, $t = 180$ min, reactions performed in triplicate; averaged results are given) using standard conditions with different solvents

Catalyst	Catalyst loading/mol%[a]	Solvent[b]	C/%[c]
C1	2.5	DCM	86.6
C1	2.5	MD	94.8
C1	2.5	none	85.8
C2	2.5	DCM	90.6
C2	2.5	MD	91.2
C2	2.5	none	90.6
C3	2.5	DCM	91.7
C3	2.5	MD	89.7
C3	2.5	none	90.2

[a] Amount of catalyst in mol% relative to allyl benzene. [b] DCM: dichloromethane ([allyl benzene] = 0.1 mol L^{-1}); MD: methyl decanoate ([allyl benzene] = 0.1 mol L^{-1}); none: reaction performed in bulk ([allyl benzene] = 2.216 mol L^{-1}). [c] Conversion of allyl benzene (by GC)

Table 4 Results of the CM of allyl benzene with *cis*-1,4-diacetoxy-2-butene ($T = 25$ °C, $t = 180$ min, reactions performed in triplicate; averaged results are given) at reduced catalyst loadings

Catalyst	Catalyst loading/mol%[a]	Solvent[b]	C/%[c]
C1	0.5	DCM	63.6
C1	0.5	MD	78.6
C1	0.5	none	81.9
C1	0.1	none	54.8
C2	0.5	DCM	87.7
C2	0.1	DCM	14.9
C2	0.5	MD	72.2
C2	0.5	none	88.4
C2	0.1	none	84.7
C3	0.5	DCM	71.7
C3	0.5	MD	79.7
C3	0.1	MD	35.9
C3	0.5	none	89.4
C3	0.1	none	81.8

[a] amount of catalyst in mol% relative to allyl benzene; [b] DCM: dichloromethane (c[allyl benzene] = 0.1 mol L^{-1}); MD: methyl decanoate (c[allyl benzene] = 0.1 mol L^{-1}); none: reaction performed in bulk (c[allyl benzene] = 2.216 mol L^{-1}); [c] Conversion of allyl benzene in % (by GC)

Similar to the RCM reaction described above, a reduction in catalyst loadings led to decreased conversions (Table 4). This effect was more pronounced for solvent reactions than for the bulk reactions. Moreover, MD gives good results for all catalysts and all catalyst loadings, comparable to, and sometimes better than, the corresponding reactions in DCM. However, the solvent-free reaction conditions show the highest conversions for all catalysts and at all catalyst loadings. A further 5-fold reduction in catalyst loading was then attempted with all systems that provided conversions higher than 80% with a catalyst loading of 0.5%. These results are also presented in Table 4. A 25-fold reduction in catalyst loading while still maintaining high conversions was only possible under bulk conditions. These results clearly show that the most environmentally benign reaction conditions are once more the solvent-free conditions.

The E : Z ratio of the formed product was ~9 : 1, quite independent of the reaction conditions. The only exceptions were the reactions at high dilution and low catalyst loading in solvent, where the E : Z ratio was ~4 : 1. These observations are probably due to a deactivation of the catalyst, which is also in accordance with the low observed conversions under these reaction conditions (data not presented in Table 4). If the catalyst is deactivated, it cannot perform secondary metathesis reactions, which would equilibrate the product to the more stable E isomer.[28] Moreover, the E : Z ratio of the bulk reactions with **C2** and **C3** was again ~9 : 1, which is in agreement with the high observed conversions for these reactions and, thus, the remaining high catalyst activity.

In summary, solvent-free conditions for this metathesis reaction also allowed for a straightforward 25-fold reduction of the amount of catalysts **C2** and **C3**. Moreover, MD was even better suited for this reaction than DCM and can provide a green alternative reaction medium, in case a solvent is required for the reaction. Furthermore, the solvent-free reactions showed significantly higher reproducibility, even at very low catalyst loadings.

Conclusions

The conclusions of these investigations are manifold. Most importantly, metathesis reactions in methyl decanoate and solvent-free metathesis reactions offer environmentally friendly alternatives to the commonly applied solvent dichloromethane. This finding seems to be of a general nature, but this has to be confirmed with different metathesis reactions in the future. In particular, the solvent free reaction conditions offer the most sustainable alternative by avoiding large amounts of solvent waste without losing catalyst activity. Along the same lines, only the bulk conditions allowed a straighforward 25-fold reduction of the amount of metathesis catalyst for both investigated metathesis reactions. This is not only interesting in terms of green chemistry, because large amounts of potentially toxic transition metal can be avoided, but also in terms of process economics, because the catalyst is by far the most expensive component of these reactions.

Experimental

Materials

Decanoic acid (Cognis, Edenor C10, 98%), methanol (VWR, 99%), sulfuric acid (Fluka, 95-97%), allylbenzene (Aldrich, 98%), *cis*-1,4-diacetoxy-2-butene (Aldrich, 95%), diethyl diallylmalonate (Aldrich, 98%), dichloromethane (Riedel-de Häen, 99.8%), tetradecane (Fluka, ≥99%), decane (Fluka, ≥99.8%), ethyl vinyl ether (Aldrich, 99%), tetrahydrofuran (Sigma, ≥99%), (1,3-*bis*-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)-dichloro(*o*-isopropoxyphenyl-methylene)ruthenium (**C2**, Aldrich), benzylidene[1,3-*bis*-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(tricyclohexylphosphine)ruthenium (**C1**, Aldrich), and 1,3-*bis*-(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene[2-(*i*-propoxy)-5-(*N*,*N*-dimethylaminosulfonyl)phenyl]methyleneruthenium(II)dichloride (**C3**, ABCR, 96%) were used as received. Methyl decanoate was prepared by esterification with methanol from the corresponding decanoic acid according to standard laboratory procedures.

Analytical equipment and methods. Thin layer chromatography (TLC) was performed on silica gel TLC-cards (layer thickness 0.20 mm, Fluka). Compounds were visualized by permanganate reagent. For column chromatography, silica gel 60 (0.035–0.070 mm, Fluka) was used.

^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AVANCE DPX spectrometer operating at 300 (75.5) MHz. Chemical shifts (δ) are reported in parts per million relative to the internal standard tetramethylsilane (TMS, $\delta = 0.00$ ppm).

Analytical GC characterization of reaction mixtures was carried out with a Shimadzu GC-2010 equipped with a fused silica capillary column (Stabilwax®, 30 m × 0.25 mm × 0.25 μm, Restek), using flame ionization detection. The oven temperature program was: initial temperature 50 °C, hold for 5 min, ramp at 10 °C min^{-1} to 250 °C, hold for 5 min (total analysis time: 30 min, cross-metathesis of allylbenzene with *cis*-1,4-diacetoxy-2-butene). Measurements were performed in the split–split mode (split ratio 45 : 1) using hydrogen as the carrier gas (linear velocity of 31.4 cm s^{-1} at 220 °C).

GC-MS (EI) chromatograms were recorded using a VARIAN 3900 GC instrument with a capillary column FactorFour™ VF-5ms (30 m × 0.25 mm × 0.25 μm, Varian) and a Saturn 2100T ion trap mass detector. Scans were performed from 40 to 650 m/z at rate of 1.0 scan s^{-1}. The oven temperature program was: initial temperature 95 °C, hold for 1 min, ramp at 10 °C min^{-1} to 200 °C, hold for 3 min (total analysis time: 14.5 min, ring-closing metathesis of diethyl diallylmalonate). The injector transfer line temperature was set to 250 °C. Measurements were performed in the splitless and split–split modes (split ratio 50 : 1) using helium as the carrier gas (flow rate 1.0 ml min^{-1}).

Mass spectra (ESI) were recorded on a VARIAN 500-MS ion trap mass spectrometer with the TurboDDS™ option installed. Samples were introduced by direct infusion with a syringe pump. Nitrogen served both as the nebulizer gas and the drying gas. Helium served as the cooling gas for the ion trap and collision gas for MS^n. Nitrogen was generated by a nitrogen generator Nitrox from Domnick Hunter.

Gel permeation chromatograms were measured on a SEC system LC-20A from Shimadzu equipped with a SIL-20A autosampler, PLgel 5 μm MIXED-D column (Polymer Laboratories, 300 mm × 7.5 mm), and a RID-10A refractive index detector in THF (flow rate 1 ml min^{-1}) at 50 °C. All determinations of molar mass were performed relative to poly(methylmethacrylate) standards (Polymer Standards Service, M_p 102–981.000 Da).

Cross-metathesis reaction (general procedure). In a typical experiment, allylbenzene and *cis*-1,4-diacetoxy-2-butene were mixed at a molar ratio of 1 : 2 and dichloromethane or methyl decanoate was added in different amounts. Some experiments were also performed in bulk, without the addition of solvent. Reactions were carried out in parallel using a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK) under stirring at 25 °C. The solid catalyst (**C1–C3**) was then added to the solution, in the quantities of 0.1, 0.5 and 2.5 mol% of the educt allylbenzene. All reactions were carried out without a nitrogen atmosphere. Samples were taken periodically and quenched with an excess of ethyl vinyl ether in order to stop the metathesis reaction. Tetradecane was used as an internal standard in the samples with solvent and decane as external standards in the solvent-free samples for GC analysis. After this procedure, a conversion and composition analysis was performed by GC. For isolation of the cross-metathesis product, this procedure was performed with 1.175 ml (1.05 g, 0.0089 mol) allylbenzene, 2.828 ml (3.05 g, 0.018 mol) *cis*-1,4-diacetoxy-2-butene and 0.1627 g (2.5 mol%) of **C3**. The reaction mixture was stirred magnetically at 25 °C. After 25 h reaction time the compound was purified by column chromatography on silica with a mixture of hexane and diethyl ether (1 : 10) as eluent.

4-Phenylbut-2-enyl acetate. MS (ESI-positive, CH_3OH, *m*/*z*): 213.1 (MNa^+, calc. 213.1). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.29–7.17$ (m, 5H, C_6H_5), 5.91 (m, 1H, $–CH{=}CH–$), 5.62 (m, 1H, $–CH{=}CH–$), 4.54 (d, 2H, $–CH_2–O–CO–$), 3.39 (d, 2H, $C_6H_5–CH_2–$), 2.05 (s, 3H, $–O–CO–CH_3$).

Ring-closing metathesis reaction (general procedure). In a typical experiment, diethyl diallylmalonate and dichloromethane or methyl decanoate as solvent were mixed in different concentrations. Some experiments were also performed in bulk, without the addition of solvent. Reactions were carried out in parallel using a carousel reaction station™ RR98072 (Radleys Discovery Technologies, UK) under stirring at 30 °C. The solid catalyst (**C1–C3**) was then added to the solution in the quantities of 0.04, 0.2 and 1.0 mol%. All reactions were carried out without a nitrogen atmosphere. Tetradecane was used as external standard for GC-MS analysis. Samples were taken periodically and quenched with an excess of ethyl vinyl ether in order to stop the ring-closing metathesis reaction. After this procedure, a conversion and composition analysis was performed by GC-MS. For isolation of the ring-closing metathesis product, this procedure was performed with 4 ml (3.98 g, 0.017 mol) diethyl diallylmalonate and 0.1037 g (1 mol %) of **C2**. The reaction mixture was stirred magnetically at 30 °C. After 25 h reaction time the compound was purified by column chromatography on silica with a mixture of hexane and diethyl ether (1 : 1) as eluate.

Diethyl cyclopent-3-ene-1,1-dicarboxylate. GC-MS (EI, *m*/*z*): 212.8 ($M^{+\bullet}$, calc. 212.2). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 5.60$ (m, 2H, $–CH_2–CH{=}CH–CH_2–$), 4.20 (q, 4H, 2× $–CO–O–CH_2–CH_3$), 3.01 (d, 4H, $–CH_2–CH{=}CH–CH_2–$), 1.26 (t, 6H, 2× $–CO–O–CH_2–CH_3$).

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