Enhancement of ruthenium-catalyzed olefin metathesis reactions: Searching for new catalyst or new reaction conditions?*

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Abstract: Olefin metathesis as a catalytic process constantly gains interest among organic chemists. Over the last decade, it became an efficient tool to accomplish the synthesis of many complex molecules. The development of new well-defined catalysts and continuous examination of novel ligands led to the establishment of metathesis methodology in a group of widespread chemical transformations. Not only does the selection of the catalyst seem to be of crucial importance, but modifying the reaction conditions, such as choice of the solvent and temperature, also allows one to make olefin metathesis a practical industrial process. This contribution, based on examples from our research, is devoted to answering the question "What may have a greater impact on the performance of metathesis reaction: a sophisticated catalyst design or unique reaction conditions?" Based on the data reported in the paper, we discuss two complementary strategies concerning the tuning of the olefin metathesis process.

Keywords: catalysis; fluorinated aromatic hydrocarbons; Lewis acids; ligands; microwave irradiation; *N*-heterocyclic carbenes; olefin metathesis; reaction conditions; ruthenium.

INTRODUCTION

The appearance of well-defined ruthenium-based complexes for olefin metathesis prompted an extraordinary scientific knockout, which revolutionized the area of both fine chemicals and polymer industry [1,2]. Synthetic chemists were provided with ruthenium complexes that present enhanced functional group tolerance, activity, and stability combined with fast initiation rate in a range of metathesis reactions (Fig. 1). Unfortunately, in some applications relatively high loadings of the ruthenium pre-catalysts, which are often required, lead sometimes to suboptimal use of this powerful methodology. In the respect of greener chemistry, it is desirable to use these costly and potentially toxic complexes more efficiently in order to protect the environment and to reduce costs of industrial processes.

Most ruthenium initiators can be handled in air and are compatible with various functionalized substrates, such as esters, amides, ketones, aldehydes, and even alkenes bearing protic functionalities like hydroxy or carboxylic groups [3]. Besides evolutionary improvement of the catalyst structure, the research aiming at finding some new reaction conditions that allow more optimal use of known catalysts can be considered as a complementary approach. Contemporary ruthenium complexes promote metathesis not only in neutral organic solvents traditionally used for metathesis (dichloromethane and
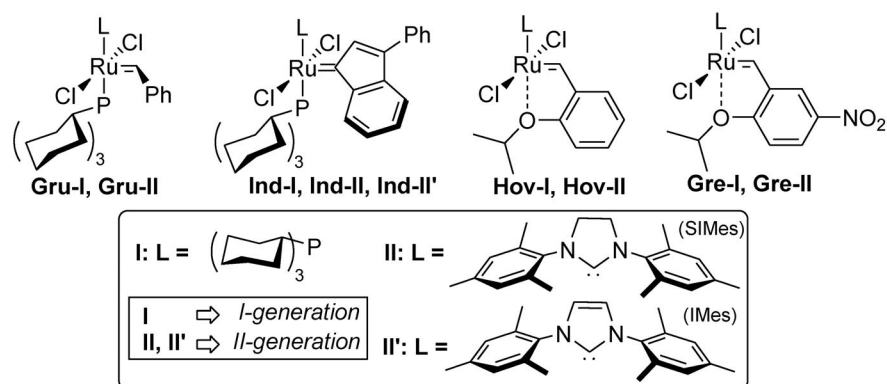
Fig. 1 Several commercially available ruthenium pre-catalysts.

toluene), but also in protic organic solvents, water [4], and fluorinated solvents [5]. Testing various catalysts in a specific reaction is time-consuming, but there are other ways of reaching high yields. Careful optimization of reaction conditions can also be very helpful in promoting olefin metathesis reactions on demanding substrates, and examples are presented in this article.

CATALYST DESIGN

The design of novel ligands for catalysts is directed to create perfect initiators tailored to specific applications. Changes in steric strain, chelating ring size, chelating heteroatom, and electron density on the aromatic ring of the chelating benzylidenes allow one to obtain catalysts with various reactivity ranges [6–9]. The great impact of a N → Ru or O → Ru chelation in metathesis initiators **1–5**, and their influence on catalytic activity was examined widely in detail (Fig. 2) [10–12].
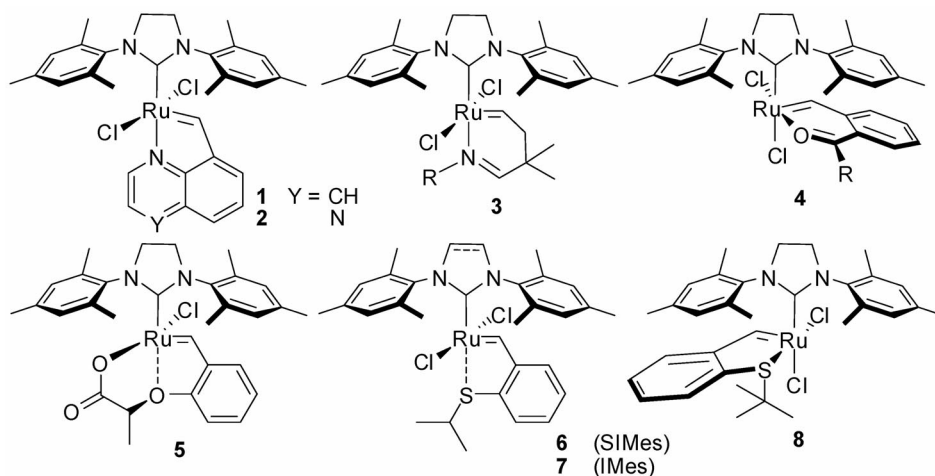

Fig. 2 Examples of ruthenium catalysts bearing chelating alkylidene ligands.

Recently, a new class of sulfur-containing Ru catalysts **6–8** was disclosed independently by Lemcoff and our group [13–15]. Initiators **6–8** prove to be extremely stable and can be useful in high-temperature applications, although they do not show activity at room temperature.

Continuing our research, we decided to formally oxidize the sulfur-chelating atom so that sulfoxide and sulfone complexes could be obtained. Based on previous results, the best stabilizing effect was observed in the presence of *tert*-butyl group. We decided that due to mentioned steric factors this bulky group will be the best choice for further investigation, so a series of initiators was synthesized.

Routes to ligands and catalysts containing -S(O) or -S(O)$_2$ moieties

For the synthesis of ligands for new ruthenium initiators (illustrated in Fig. 3), we used the commercially available 2-bromothiophenol **9** as a starting material for preparation of the corresponding sulfoxide **11a** and sulfone **11b** via a straightforward process of alkylation-oxidation [16,17]. In the next step, compounds **11a** and **11b** were transformed into styrenes **12a** and **12b** using Suzuki–Miayura cross-coupling as an olefination method [18].
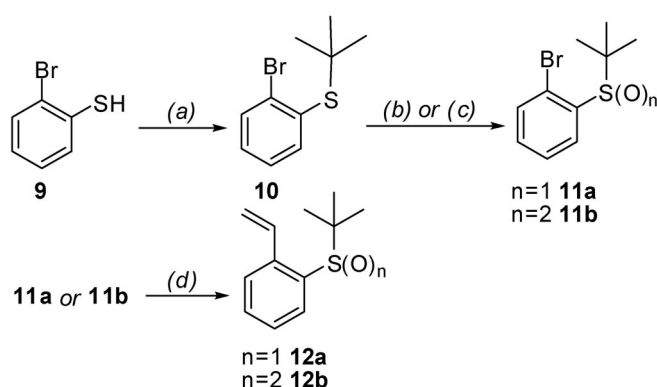
Fig. 3 Synthetic routes of ligands **12a** and **12b**. Reagents and isolated yields: (a) *t*-BuOH, H$_2$SO$_4$/H$_2$O, –10 °C to RT, 24 h (58 %); (b) 1 equiv Oxone^{TM}, MeOH/ H$_2$O, 5 °C to RT, 4 h (70 %); (c) 2 equiv Oxone^{TM}, MeOH/H$_2$O, 5 °C to RT, 6 h (80 %); (d) Pd(PPh$_3$)$_2$Cl$_2$, C$_2$H$_3$BF$_3$K, Cs$_2$CO$_3$, THF/H$_2$O, 85 °C, 22 h (**4a** 70 %), (**4b** 82 %).

Having prepared the styrene derivatives, we attempted to synthesize catalysts **13–16**. A simple ligand-exchange reaction, performed with the ligand **12a** stirred with **Ind-II** or **Ind-II'** in toluene at 85 °C in the presence of a phosphine scavenger CuCl, resulted in formation of initiators **13** and **14** (Fig. 4).
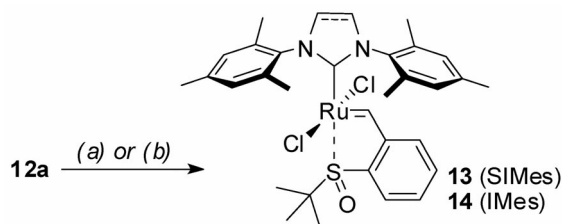
Fig. 4 Synthesis of catalysts **13** and **14**. Reagents and isolated yields: (a) **Ind-II**, CuCl, 85 °C toluene, 0.5 h, (62 %); (b) **Ind-II'**, CuCl, 85 °C toluene, 0.5 h (57 %).

Both pre-catalysts (**13** and **14**) were obtained with good yields (62 and 57 %, respectively) and found to be perfectly stable in air and during storage. Full characterization of the new complexes was performed by spectral techniques and elemental analysis followed by X-ray determination of their solid-state structures (Fig. 5).
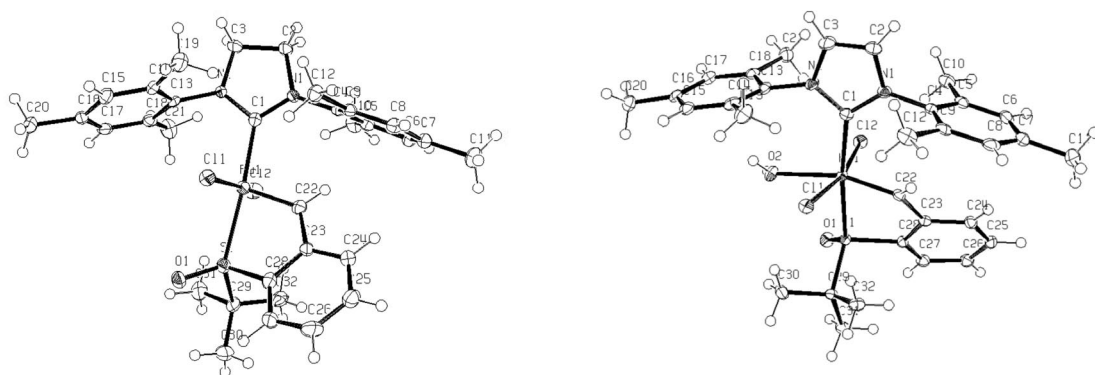

Fig. 5 ORTEP presentations of initiators **13** (left) and **14** (right). Thermal ellipsoids were drawn with 50 % probability.

The sulfoxide initiators **13** and **14** have *trans*-chloro geometry and do not show a tendency for *trans* → *cis* isomerization [19]. Solid-state structures show that the chelating ligand is coordinated to the ruthenium center through the sulfur atom, not through the sulfoxide's oxygen atom, which corresponds to a geometry reminiscent of that of the parent Hoveyda complex (**Hov-II**). In case of the **14** structure, there is another ligand coordinating to the ruthenium center—a water molecule. To our best knowledge, such structures of a Hoveyda-type pre-catalyst are very rare in the literature [20]. The introduction of the water molecule probably occurred during crystallization from high-performance liquid chromatography (HPLC) solvents, which were not dried beforehand. The appearance of the next ligand changed considerably the geometry of the metal surroundings. A separate work on this subject will appear soon in the specialist literature [21].

Our initial studies focused on sulfoxide derivatives, but then based on the obtained results we decided to synthesize the sulfone analogues. We presumed that the greater lability of the ligand would increase significantly the reactivity of the initiator. Using catalysts **Ind-II** and **Ind-II'** (Fig. 6) and the sulfone ligand **12b** (Fig. 3) we performed a ligand-exchange reaction. Complexes **15** and **16** were obtained but the yield was rather unsatisfactory (30 %), and what is more, their stability can be described as moderate compared to that of sulfoxide derivatives.
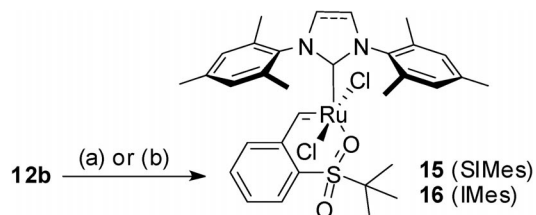

Fig. 6 Synthesis of catalysts **15** and **16**. Reagents and isolated yields: (a) **Ind-II**, CuCl, 85 °C toluene, 0.5 h (30 %); (b) **Ind-II'**, CuCl, 85 °C toluene, 0.5 h (30 %).

It seems obvious that the ruthenium atom is chelated by an oxygen atom. However, solid structures of complexes **15** and **16** were not confirmed by X-ray measurements. Efforts to crystallize the sulfone derivatives are still made due to the required conclusion of the whole issue [22].

Catalyst performance

Diethyl diallylmalonate (DEDAM) **17** has been widely used as a benchmark ring-closing metathesis (RCM) substrate for assessment of the relative activity of a metathesis-initiating complex. While its utility declines as metathesis activity increases, it provides a basis for comparison of factors such as solvent, concentration, catalyst's loading and screening of temperatures. All of the initiators previously described in the paper were tested in RCM of **17** at a catalyst's loading of 1 mol % within 15 min in CD_2Cl_2 at 22 °C, monitored by ^1H NMR spectroscopy. Results shown in Fig. 7 demonstrate that **15** gave a maximum yield of 94 % and **16** only 71 %. In case of sulfoxide ligands, complex **13** presented just 20 % of conversion after 15 min. However, after 1 h of metathesis performance, the activity of this analogue increased to 99 %. In contrast to former outcomes, the congener **14** turned out to be inactive under these conditions, even if the reaction was prolonged to 24 h.
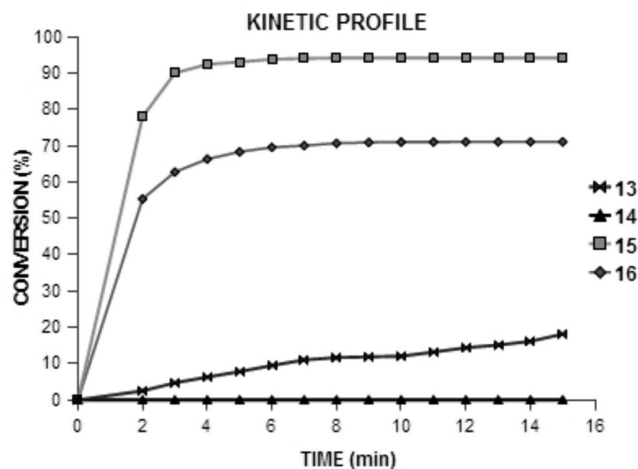

Fig. 7 Kinetic profile of catalysts **13–16** in RCM of DEDAM. Conditions: $c[17] = 0.1$ M, 1 mol % of catalyst, CD_2Cl_2, 22 °C, 15 min.

The data in Fig. 7 illustrate the sensitivity of the catalyst's performance to the nature of the *N*-heterocyclic carbene (NHC) ligand and the obvious influence of the alkylidene moiety. This phenomenon is explored in more detail in Fig. 8, which shows that, as expected, complexes bearing saturated NHC were found to be more active than the derivatives containing unsaturated NHC. Sulfone analogues were characterized by faster initiation rates, which were associated with lower stability, especially in solution and at higher temperatures. For the same reasons, complexes **15** and **16** operated successfully at lower temperatures (from 0 to 22 °C). On the contrary, sulfoxide congeners possess very good thermal stability in different solvents, which makes them useful in higher-temperature applications (from 80 to 110 °C). Entry **III** in Fig. 8, which presents a cyclization of a very demanding substrate **21** can serve as a good example of these theses. Catalyst **14** provided metathesis transformation of **21** at 110 °C in toluene with 40 % of conversion, while use of the commercially available **Gru-II** resulted in total yield of 32 %. Such features of **14** can be beneficial if the catalyst's initiation step is required to be controllable in reasonable manner. For example, during some industrial set-ups of the
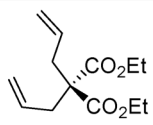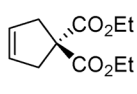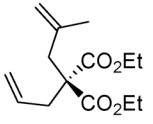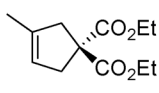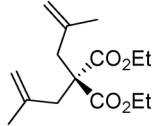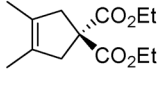
Entry	Substrate	Product	Catalyst/Loading (mol %)		Time	Temperature (°C)	Conversion (%)
I	**17**	**18**	**13**	(1)	15 min	0	0
			14	(1)	15 min	0	0
			15	(1)	15 min	0	70
			16	(1)	15 min	0	26
II	**19**	**20**	**13**	(1)	15 min	0	0
			13	(1)	1 h	80	99
			14	(1)	15 min	0	0
			14	(5)	6 h	80	92
			15	(1)	15 min	0	51
			16	(1)	15 min	0	27
III	**21**	**22**	**14**	(1)	24 h	110	40

Fig. 8 RCM of DEDAM (**17**) and its derivatives using complexes **13–16**. Conditions: $c = 0.1$ M, CH_2Cl_2 (0 °C), toluene (80 and 110 °C). For entries **I–III**, conversion was determined by GC using internal standard.

ring-opening metathesis polymerization (ROMP) reaction it is required that a mixture of a monomer and an initiator can be processed, or stored, before the metathesis process occurs [23–25].

NEW REACTION CONDITIONS

As focusing only on the synthesis of new catalysts would be a mistake, we searched for other ways of improving the reaction results. Many researchers consider optimization of reaction conditions as obvious values that already fixed and underestimate this "tedious" app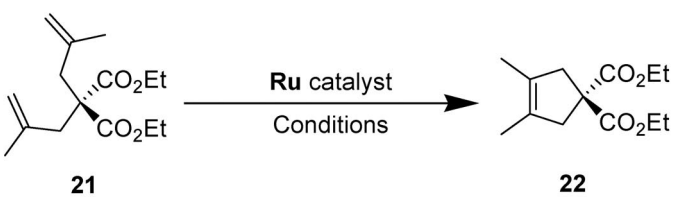roach. Having considered all the factors that usually determine a positive reaction outcome (such as concentration, temperature, and catalyst loading, to list only a few), we decided to devote a part of our research to explore some solvent effects and other nonclassical reaction conditions.

Fluorinated aromatic hydrocarbon (FAH) activation effect

In 2007 we observed a remarkable enhancement of activity in catalytic olefin metathesis when second-generation ruthenium pre-catalysts were applied in FAHs as solvents (e.g., hexafluorobenzene, octafluorotoluene) [26]. Challenging metathesis transformations such as formation of tetrasubstituted C–C double bonds (Fig. 9) were made possible in these media using standard commercially available ruthenium pre-catalysts.

The data presented in Fig. 9 clearly show that the reaction outcome is related to the number of the fluorine atoms in the aromatic solvent molecule. It was previously published that olefin metathesis reactions work better in aromatic solvents comparing to aliphatic chlorinated solvents [27]. We reported recently that the best results can be obtained in octafluorotoluene as a solvent when using phosphine-containing ruthenium complexes, especially **Ind-II** [5]. The search for full explanation of the FAH activation effect is ongoing in our laboratory and will be published in due course. Our research efforts in this area are focused on X-ray structure analysis, computational studies, and probing the initiation step of phosphine-containing pre-catalyst using ^{31}P NMR [28].

Fig. 9 RCM of demanding substrate **21** using commercially available complexes. Conditions: $c = 0.02$ M, 2 mol % catalyst, 70 °C, 3 h. Yield was determined by GC using internal standard.

	solvent	Gru-II	Gru-II'	Ind-II	Ind-II'	Hov-II	Gre-II
'classical' solvents	$C_2H_4Cl_2$	21	nd	28	38	4	19
	$C_6H_5CH_3$	20	nd	27	56	33	29
	$C_6H_5CF_3$	36	nd	48	61	13	nd
FAH	C_6F_6	61	77	91	74	58	nd
	$C_6F_5CF_3$	72	nd	94	85	72	49

Lewis acid additive

Encouraged by positive outcomes of the FAH project, we decided to undertake a greater challenge. We selected a class of compounds that are difficult to prepare via conventional synthetic methods—substituted β,γ-nitroolefins, which are useful and versatile building blocks in organic synthesis [29]. We decided to use CM of 3-nitropropene (**23**) to obtain new allylic nitro compounds. In order to do so, we studied the CM reaction of **23** with **24**, leading to a β,γ-nitroolefin **25**, under various reaction conditions (Fig. 10). First, we looked into the activity of the commercial catalysts to find the most promising one in the desired transformation. Interestingly, catalyst **Gru-II** failed in studied CM (entry **I**), while its phosphine free analogue **Hov-II** (entry **II**) in refluxing CH_2Cl_2 worked reasonably. However, the best results were achieved by using **Gre-II**. In this case, we tried to modify the conditions in order to get a higher conversion. Entries **IV** and **V** show that using a higher loading of ruthenium pre-catalyst as well as applying higher temperature in toluene did not improve the yield as expected [27]. Another hope of optimizing the reaction conditions lay in using octafluorotoluene as a solvent (entry **VI**) [5,26]. This caused the CM reaction to work better, but still not as well as we expected.

Finally, we decided to use a Lewis acid additive (entry **VII**) [30]. This is a known approach toward the metathesis reaction of molecules containing a substituent which behaves as a Lewis base [30]. When such a group is situated close to the double bond, it may "arrest" the active catalytic species acting in the reaction as a Lewis acid. This kind of interaction inactivates the catalyst and makes further reaction impossible. To prevent this, we decided to introduce an external Lewis acid into the reaction. Based on our research, we concluded that boron-containing Lewis acids are the most capable ones [29]. Triphenyl borate (25 mol %) was the most promising acid we tested, combined with 5 mol % of **Gre-II** created optimal conditions for promoting the CM reaction of 3-nitropropene leading to a broad variety of β,γ-nitroolefins with very good isolated yields [29].
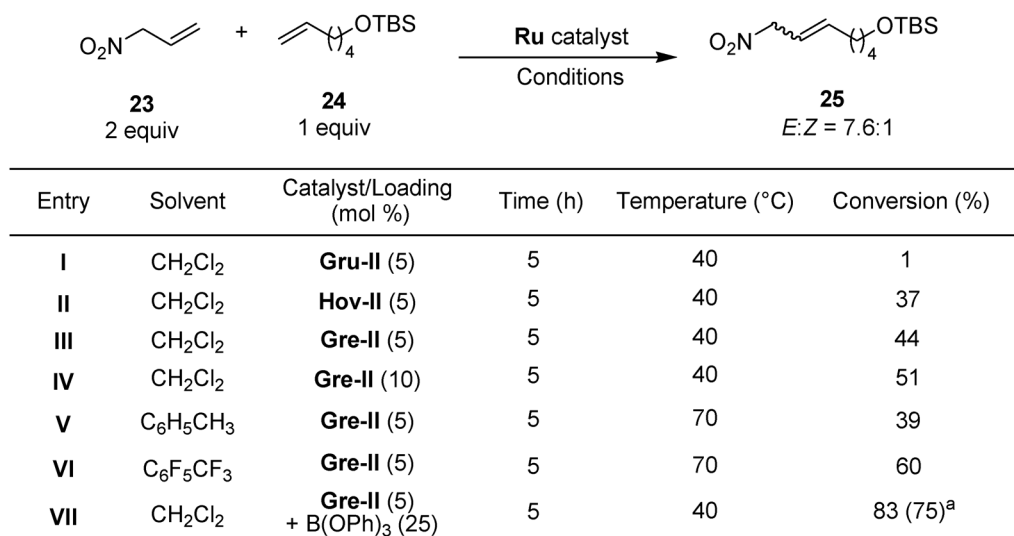
Fig. 10 Optimization of CM reaction of 3-nitropropene using commercially available ruthenium complexes. Conversion of **24** was determined by GC using internal standard. [a]Isolated yield.

Entry	Solvent	Catalyst/Loading (mol %)	Time (h)	Temperature (°C)	Conversion (%)
I	CH_2Cl_2	**Gru-II** (5)	5	40	1
II	CH_2Cl_2	**Hov-II** (5)	5	40	37
III	CH_2Cl_2	**Gre-II** (5)	5	40	44
IV	CH_2Cl_2	**Gre-II** (10)	5	40	51
V	$C_6H_5CH_3$	**Gre-II** (5)	5	70	39
VI	$C_6F_5CF_3$	**Gre-II** (5)	5	70	60
VII	CH_2Cl_2	**Gre-II** (5) + $B(OPh)_3$ (25)	5	40	83 (75)[a]

Microwave-assisted reactions

Microwave-assisted reactions are another method of optimizing the reaction conditions used in laboratory practice [31]. This approach toward olefin metathesis resulted in shortening the reaction time and improved yield. There is also some evidence that it may affect the selectivity of the reaction [32]. However, it should be noted that the beneficial effect of microwave irradiation in general, and particularly on olefin metathesis reactions, is poorly understood. We decided to use the combination of the FAH activation effect with microwave irradiation in RCM of one of the most demanding RCM substrates (Fig. 11) [33]. Ester **26** was reported as a reluctant molecule for very active ruthenium complexes, however, when the reaction was performed in hexafluorobenzene, it led to a satisfactory conversion [33]. We decided to apply **26** in RCM using fluorinated aromatic solvents in a microwave-assisted environment [34]. This part of the work (microwave-irradiated olefin metathesis reactions) has been made in the collaboration with Dr. Marc Mauduit in his laboratories (CNRS Rennes, France).

Entry **I** shows that RCM of molecule **26** performed in benzene-d_6 with 2 mol % of ruthenium complex **Ind-II** is indeed ineffective. However, simple switching of the reaction medium from a "classical" solvent to hexafluorobenzene and octafluorotoluene using an oil bath as heating source led to low conversion, 15 and 33 %, respectively (entries **II** and **III**). When a reaction performed in FAH was heated using microwave irradiation, with the same catalyst **Ind-II** loading, it resulted in improved conversion of 31 and 57 %, respectively (entries **IV** and **V**). In the end, we decided to supply the reaction with a fresh portion of **Ind-II**. Entry **VI** shows that after the mixture was heated again in the microwave reactor the expected product **27** was formed after 30 min with 81 % of conversion and 80 % of isolated yield.
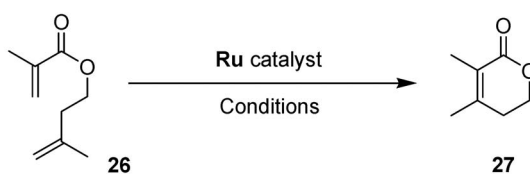
Entry	Solvent	Catalyst/Loading (mol %)	Time	Temperature (°C)	Conversion (%)
I	C_6D_6	**Ind-II** (2)	24 h	80	0
II	C_6F_6	**Ind-II** (2)	15 min	100	15
III	$C_6F_5CF_3$	**Ind-II** (2)	15 min	120	33
IV	C_6F_6	**Ind-II** (2)	15 min	100 μW (200 W)	31
V	$C_6F_5CF_3$	**Ind-II** (2)	15 min	120 μW (200 W)	57
VI	$C_6F_5CF_3$	**Ind-II** (2 × 2)	2 × 15 min	120 μW (200 W)	81 (80)[a]

Fig. 11 Optimization of RCM reaction leading to lactone **27** using commercially available ruthenium complexes. Conversion of **26** was determined by ^1H NMR using internal standard. [a]Isolated yield.

CONCLUSIONS

The problem of finding the clear answer to the question "What are the future topics in olefin metathesis?" is not yet fully addressed. Considering the presented research, the answer can be based on one's idea of tuning metathesis. One can either try to change the catalyst's structure parameters or the conditions of the reaction. The paper presents a new series of ruthenium catalysts containing variously oxidized sulfur atoms. The described synthetic pathways allowed us to modify the size of the chelating ring and the chelating heteroatom, resulting in a high degree of tunability of the catalyst's initiation step. Current synthetic work aims at modifying the substituents of the chelating ring of sulfone analogues from steric to electronic factors as well as changing the nature of NHC ligand once again. Further studies of initiation efficiency and catalytic activity of sulfur-based complexes are expected to shed light on optimum electronic and steric properties of alkylidene ligands in ruthenium metathesis catalysts.

On the other hand, searching for new reaction conditions is a valuable alternative for catalyst design in difficult olefin metathesis reactions. Solvent, temperature, and concentration are almost obvious factors that affect the reaction results. We showed that less popular solvents such as FAHs can enhance reactions significantly. An addition of Lewis acid is a next alternative in enhancing the reaction results, especially useful when the reagents are specific molecules bearing substituents that could "arrest" catalyst active species. However, taking all methods into consideration, the microwave-assistance seems to be the most universal one for olefin metathesis as it simultaneously allows one to reduce the time of the reaction, improve yield, and sometimes change its selectivity. The search for new catalysts is crucial, when olefin metathesis reaction performance can be enhanced by an appropriate selection of solvents (FAH), additives (co-catalyst) or utilization of microwave irradiation. For some demanding molecules, the combination of these techniques (designing new catalysts and improving reaction conditions) can be important for the performance of reactions and both approaches could be

considered not as "alternative" solutions but as "cumulative" methods. Further research devoted to finding even more optimal reaction conditions for olefin metathesis is ongoing in our laboratory.

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REFERENCES

1. (a) R. H. Grubbs. *Handbook of Metathesis*, Wiley-VCH, Weinheim (2003); (b) C. Samojłowicz, M. Bieniek, K. Grela. *Chem. Rev.* **109**, 3708 (2009); (c) C. E. Diesendruck, E. Tzur, G. Lemcoff. *Eur. J. Inorg. Chem.* 4185 (2009); (d) H. Clavier, K. Grela, A. Kirschning, M. Mauduit, S. P. Nolan. *Angew. Chem., Int. Ed.* **46**, 6786 (2007); (e) P. H. Deshmukh, S. Blechert. *Dalton Trans.* 2479 (2007).
2. (a) T. M. Trnka, R. H. Grubbs. *Acc. Chem. Res.* **34**, 18 (2001); (b) A. Leitgeb, J. Wappel, C. Slugovc. *Polymer* **51**, 2927 (2010).
3. P. Śledź, M. Mauduit, K. Grela. *Chem. Soc. Rev.* **37**, 2433 (2008).
4. D. Burtscher, K. Grela. *Angew. Chem., Int. Ed.* **121**, 2433 (2008).
5. C. Samojłowicz, M. Bieniek, A. Zarecki, R. Kadyrov, K. Grela. *Chem. Commun.* 6282 (2008).
6. (a) K. Grela, S. Harutyunyan, A. Michrowska. *Angew. Chem., Int. Ed.* **41**, 4038 (2002); (b) A. Michrowska, R. Bujok, S. Harutyunyan, V. Sashuk, G. Dolgonos, K. Grela. *J. Am. Chem. Soc.* **126**, 9318 (2004); (c) H. Clavier, F. Caijo, E. Borré, D. Rix, F. Boeda, S. P. Nolan, M. Mauduit. *Eur. J. Org. Chem.* 4254 (2009).
7. (a) H. Wakamatsu, S. Blechert. *Angew. Chem., Int. Ed.* **41**, 2403 (2002); (b) H. Wakamatsu, S. Blechert. *Angew. Chem., Int. Ed.* **41**, 794 (2002).
8. M. Bieniek, R. Bujok, M. Cabaj, N. Lugan, G. Lavigne, D. Artl, K. Grela. *J. Am. Chem. Soc.* **128**, 13652 (2006).
9. X. Gstrein, D. Burtscher, A. Szadkowska, M. Barbasiewicz, F. Stelzer, K. Grela, C. Slugovc. *J. Polym. Sci., Part A: Polym. Chem.* **45**, 3494 (2007).
10. M. Barbasiewicz, A. Szadkowska, R. Bujok, K. Grela. *Organometallics* **25**, 3599 (2006).
11. C. Slugovc, B. Perner, F. Stelzer, K. Mereiter. *Organometallics* **23**, 3622 (2004).
12. R. Gawin, A. Makal, K. Woźniak, M. Mauduit, K. Grela. *Angew. Chem., Int. Ed.* **46**, 7206 (2007).
13. A. Ben-Asuly, E. Tzur, C. E. Diesendruck, M. Sigalov, I. Goldberg, N. G. Lemcoff. *Organometallics* **27**, 811 (2008).
14. R. Kadyrov, A. Rosiak, J. Tarabocchia, A. Szadkowska, M. Bieniek, K. Grela. In *Catalysis of Organic Reactions: Twenty-second Conference*, M. L. Prunier (Ed.), p. 568, CRC Press, Boca Raton (2008).
15. R. Kadyrov, A. Szadkowska, K. Grela, M. Barbasiewicz. DE Patent 102007020694.3, filed 3 May 2007, issued 6 Nov. 2008.
16. S. B. Harkins, J. C. Peters. *J. Am. Chem. Soc.* **126**, 2885 (2004).
17. J. R. McCarthy, D. P. Matthews, J. P. Paolini. *Org. Synth.* Coll. Vol. **9**, 446 (1998).
18. G. A. Molander, A. R. Brown. *J. Org. Chem.* **71**, 9681 (2006).
19. A. Poater, F. Ragone, A. Correa, A. Szadkowska, M. Barbasiewicz, K. Grela, L. Cavallo. *Chem.—Eur. J.* **16**, 14354 (2010).
20. A. Szadkowska, A. Makal, K. Woźniak, R. Kadyrov, K. Grela. *Organometallics* **28**, 2693 (2009).
21. A. E. Pazio, A. Makal, A. Szadkowska, K. Grela, K. Woźniak. Manuscript in preparation.

22. A. Szadkowska, K. Żukowska, A. E. Pazio, K. Woźniak, R. Kadyrov, K. Grela. Manuscript in preparation.
23. A. Hejl, M. W. Day, R. H. Grubbs. *Organometallics* **25**, 6149 (2006).
24. A. Szadkowska, K. Grela. *Curr. Org. Chem.* **12**, 1631 (2008).
25. A. Szadkowska, X. Gstrein, D. Burtscher, K. Jarzembska, K. Woźniak, C. Slugovc, K. Grela. *Organometallics* **29**, 117 (2010).
26. (a) R. Kadyrov, M. Bieniek, K. Grela. Verfahren zur Metathese in electroarmen aromatischen Lösungsmitteln, Pat. Appl., DE 102007018148.7, 11 April 2007; (b) M. Jacoby. *Chem. Eng. News* **86**, 36 (2008); (c) D. Parker. *Chem. Sci.* **6**, C4 (2009).
27. M. Bieniek, A. Michrowska, D. L. Usanov, K. Grela. *Chem.—Eur. J.* **14**, 806 (2008).
28. C. Samojłowicz, M. Bieniek, A. Pazio, A. Makal, K. Woźniak, A. Poater, L. Cavallo, J. Wójcik, K. Zdanowski, K. Grela. Manuscript in preparation.
29. T. Wdowik, C. Samojłowicz, M. Jawiczuk, A. Zarecki, K. Grela. *Synlett* 2931 (2010).
30. For a chelation of ruthenium active species in olefin metathesis reactions, see: (a) A. Fürstner, K. Langemann. *J. Am. Chem. Soc.* **119**, 9130 (1997); (b) A. K. Ghosh, J. Cappiello, D. Shin. *Tetrahedron Lett.* **39**, 4651 (1998); (c) E. Vedrenne, H. Dupont, S. Oualef, L. Elkaim, L. Grimaud. *Synlett* 670 (2005).
31. General reviews on microwave-assisted reactions: (a) C. O. Kappe. *Chem. Soc. Rev.* **37**, 1127 (2008); (b) T. Razzaq, C. O. Kappe. *ChemSusChem* 123 (2008); (c) Microwave irradiation used in olefin metathesis: Y. Coquerel, J. Rodriguez. *Eur. J. Org. Chem.* 1125 (2008).
32. (a) O. Debleds, J.-M. Campagne. *J. Am. Chem. Soc.* **130**, 1562 (2008); (b) K. Grela. *Angew. Chem., Int. Ed.* **47**, 5504 (2008); (c) S. Fustero, D. Jiménez, M. Sánchez-Roselló, C. del Pozo. *J. Am. Chem. Soc.* **129**, 6700 (2007).
33. (a) J. M. Berlin, K. Campbell, T. Ritter, T. W. Funk, A. Chlenov, R. H. Grubbs. *Org. Lett.* **9**, 1339 (2007); (b) I. C. Stewart, T. Ung, A. A. Pletnev, J. M. Berlin, R. H. Grubbs, Y. Schrodi. *Org. Lett.* **9**, 1589 (2007); (c) D. Rost, M. Porta, S. Gessler, S. Blechert. *Tetrahedron Lett.* **49**, 5968 (2008).
34. C. Samojłowicz, E. Borré, M. Mauduit, K. Grela. Manuscript in preparation.