

# New concepts for the non covalent immobilisation of Ru-based olefin metathesis catalysts

Anna Michrowska,<sup>a</sup> Karol Grela,<sup>\*a</sup> Andreas Kirschning,<sup>\*b</sup> Klaas Mennecke,<sup>b</sup>

[a] Institute of Organic Chemistry, Polish Academy of Science, Kasprzaka 44/52, 01-224, Warsaw, Poland.

Fax: +48-22-632-6681; E-mail: grela@icho.edu.pl

[b] Institut für Organische Chemie, Universität Hannover, Schneiderberg 1B, D-30167 Hannover, Germany

Telefax: int. (+)-(0)511-762 3011; E-mail: andreas.kirschning@oci.uni-hannover.de

## Introduction

During recent years, olefin metathesis has gained a position of increasing significance. The development of modern ruthenium metathesis catalysts, such as Grubbs (1-2) and Hoveyda-Grubbs carbenes (3-4, Figure 1) combining high activity with an excellent tolerance to a variety of functional groups has been the key to widespread applications of olefin metathesis in organic synthesis and polymer chemistry.<sup>[1]</sup>

**Figure 1.** Ruthenium-based catalysts 1-7 for olefin metathesis.



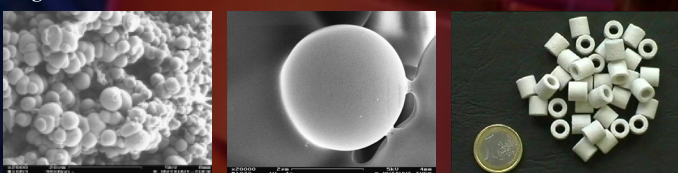
Cy = cyclohexyl, Mes = 2,4,5-trimethylphenyl.

Despite the major advantages offered by this family of catalysts, they share some disadvantages: during the reaction they form various ruthenium byproducts, which are difficult to remove from the reaction products<sup>[2]</sup> and the cost of such catalysts are very high. Immobilization of homogeneous catalysts offer inherent operational and economic advantages over the parent soluble catalysts.<sup>[3]</sup> For practicability reasons non-covalent attachment of catalysts to a solid phase is highly desirable. The possibility of reloading the solid phase opens the door for utilizing solid supports. It should be noted that this concept is of particular relevance in continuous flow processes<sup>[4]</sup> using reactors filled with heterogeneous or immobilized homogeneous catalysts.<sup>[5]</sup> The attachment ought to be strong enough in order to suppress leaching of the catalyst. However, after inactivation of the catalyst it is beneficial if it can be removed and the solid phase can be reactivated with fresh catalyst.

## Results and Discussion

Herein we report on a monolithic highly porous polymer/glass composite material, obtained by precipitation polymerization of sulfonated polystyrene, which should be suited for ion exchange based immobilization of catalysts.

**Figure 2.**

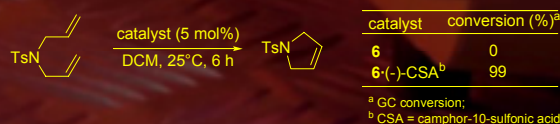


a) Sulfonated polymer particles (1–5 μm diameter) and b) bridging to neighbouring polymer particles (SEM) c) Megaporous glass Raschig rings.

The precipitation polymerisation was carried out in the presence of megaporous Raschig glass rings which are widely utilized in industrial applications (Figure 2).

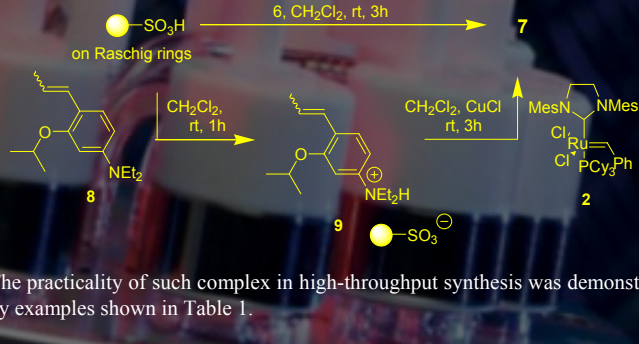
Recently, we demonstrated that the 5-nitro-substituted complex **5** initiates metathesis dramatically faster than the parent Hoveyda-Grubbs catalyst **4**.<sup>[6-7]</sup> We proposed that the electron-withdrawing nitro-group in the benzylidene fragment of **4** would weaken O→Ru chelation and facilitates faster initiation of the catalytic cycle.<sup>[6-7]</sup> In accordance with this assumption we observed that complex **6** (Figure 1), bearing the electron-donating diethylamino group shows no or very little activity in olefin metathesis with model substrates (Scheme 1). However it can be immobilized by ion exchange which results in the active catalyst **7**. In this novel strategy for ruthenium-based metathesis catalysts immobilisation the amino group plays a twofold role, being first an active anchor for immobilisation (vide supra) and secondly, after protonation, activating the catalysts (*electron donating* to *electron withdrawing activity switch*).

**Scheme 1.**



As shown on Scheme 2, Raschig rings-bound Ru complex **7** can be obtained by direct immobilisation of diethyl amine containing Hoveyda-type complex **6** in the presence of polymeric sulfonic acid or by ion exchange of easily accessible styrene derivative **8** to yield functionalized polymer **9** which then was subjected to cross olefin metathesis conditions in the presence of Grubbs II catalyst **2**.

**Scheme 2.** Different approaches for the preparation of catalyst **7**.



The practicality of such complex in high-throughput synthesis was demonstrated by examples shown in Table 1.

**Table 1.** RCM and CM with Raschig rings bound catalyst **7**.

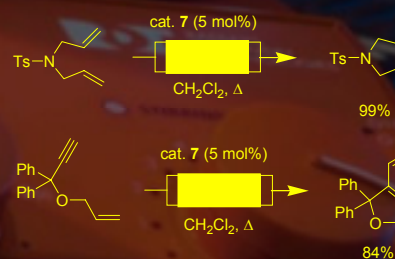
Entry <sup>[b]</sup>	Substrate	Product	Temp. [°C] (time [h])	Conversion (%) <sup>[a]</sup>
1			45 (18)	99
2			45 (18)	97
3			45 (2)	99
4			45 (4)	99
5			22 (18)	95 E:Z=1.2:1
6			45 (24)	68 <sup>[c]</sup> E:Z=11:1
7			45 (16)	99

Conditions: one Raschig rig with catalyst **7** (loading 3 μmol Ru/ring, 5 mol%) per tube was used. All the reactions were carried out in Radleys Carousel reactor (www.radleys.com). <sup>[b]</sup>crude products from entries 1 – 7 were obtained after removal of Raschig ring washing with dichloromethane and evaporation of solvent under reduced pressure. Conversions were calculated by <sup>1</sup>H NMR spectroscopy and/or GC-analysis. <sup>[c]</sup>one Raschig ring with catalyst **7** (loading 3 μmol Ru/ring, 10 mol%) was used

## PASSflow example

The concept of non-covalent attachment of catalysts to a solid phase is of particular relevance in continuous flow processes<sup>[4]</sup> using reactors filled with immobilized homogeneous catalysts (Scheme 3).<sup>[5]</sup>

**Scheme 3.** RCM under continuous flow conditions with solid phase bound catalyst **7**.



## Conclusions

We have described a new strategy for the non covalent immobilization of Ru-based olefin metathesis catalyst which rely on electrostatic binding. The solid-phase bound catalyst shows very good chemical reactivity and good recyclability.

## Notes and references

- [1] General reviews: a) R. R. Schrock, A. H. Hoveyda, *Angew. Chem., Int. Ed.* **2003**, *42*, 4592-4633. b) T. M. Trnka, R. H. Grubbs *Acc. Chem. Res.* **2001**, *34*, 18-29
- [2] H. D. Maynard, R. H. Grubbs, *Tetrahedron Lett.* **2000**, *40*, 4137-4140.
- [3] W. Solodenko, T. Frenzel, A. Kirschning, in *Polymeric Materials in Organic Synthesis and Catalysis*, (Ed.: M. R. Buchmeiser), Wiley-VCH **2003** pp 201-240.
- [4] A. Kirschning, G. Jes, in *Immobilized Catalysts* (Ed.: A. Kirschning), *Top. Curr. Chem.* **2004**, *242*, 209.
- [5] U. Kunz, S. Leue, F. Stuhlmann, G. Soukouni-Argirasi, H. Wen, G. Jas, A. Kirschning, *Eur. J. Org. Chem.* **2004**, 3601-3610.
- [6] K. Grela, S. Harutyunyan, A. Michrowska *Angew. Chem., Int. Ed.* **2002**, *41*, 4038-4040 (*Angew. Chem.* **2002**, *114*, 4210-4212).
- [7] A. Michrowska, R. Bajok, S. Harutyunyan, V. Sashuk, G. Dolgonos, K. Grela, *J. Am. Chem. Soc.* **2004**, *126*, 9318-9325.

## Acknowledgement

The work was funded by the Deutsche Forschungsgemeinschaft-Polish Academy of Sciences joint project "Synthetische Nutzung von immobilisierten Ruthenium-Carben-Katalysatoren in Durchflussmikroreaktoren" (436 POL/113/109/0-1) and the Fonds der Chemischen Industrie. We thank Prof. J. Wicha and Mr. M. Michalak for providing the sample of diene **22** and Prof. U. Kunz for preparation of the polymeric phases. I would like to thank Sanofi Aventis for [f]lab initiative-Grants for greater mobility.