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Solid Supported Ruthenium Complexes for Olefin Metathesis

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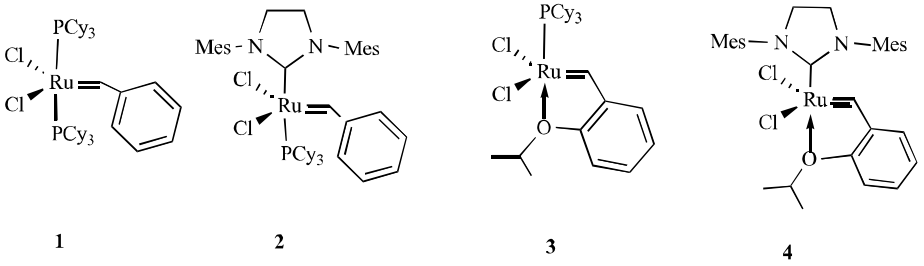
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Abstract: Immobilization of ruthenium metathesis catalysts on solid supports has attracted much attention in recent years since it opens up the possibility for easy catalyst–product separation and catalyst reuse as well as reduction of the residual ruthenium content in the organic product. The state of the art on immobilization of ruthenium based metathesis initiators on solid supports is surveyed in this review. In addition, a comparison of the performance of the heterogenized catalysts with homogeneous analogues is made.

Keywords: Alkylidene, Immobilization, Inorganic supports, Heterogeneous catalysis, Olefin Metathesis, polymeric supports, ruthenium carbenes, ruthenium.

1. INTRODUCTION

The development of easy to handle, well-defined ruthenium-based alkylidene complex **1** [1] which combine remarkable tolerance towards functional groups and moisture with high activity has tremendously broaden the scope of metathesis reactions as a powerful synthetic tool [2]. The optimization of the activity of the catalysts for various applications in metathesis reactions normally proceeds by tuning the ligand sphere around the corresponding metal center. Thus replacement of a phosphine by a highly electron donating N-Heterocyclic carbene (NHC) has afforded catalyst **2** with increased reactivity by many orders (Fig. **1**) [3].



1 **2** **3** **4**

Fig. (1). Ruthenium alkylidene metathesis initiators.

Similarly, the introduction of the bidentate alkylidene by Hoveyda resulted in metathesis catalysts **3** and **4** with increased stability and excellent recyclability (Fig. **1**) [4]. On the other hand, the advance of the 1st and 2nd generation ruthenium indenylidene **5** [5] and **6** [6] proved to have higher thermal stability than their benzylidene counter parts. Additionally, Verpoort *et al.* reported ruthenium indenylidene Schiff base complexes **7** and **8** as stable and effective metathesis initiators (Fig. **2**) [7].

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However, in spite of the highly favorable properties of the homogeneous well-defined ruthenium metathesis initiators, they are difficult to separate from the reaction mixture and often impose significant challenges. Very recently, different strategies for the sequestration of ruthenium impurities from olefin metathesis post-reaction mixtures have been reviewed by G. C. Vougioukalakis [8]. Nonetheless, the residual ruthenium complex may cause problems such as olefin isomerization, decomposition of the product, and increased toxicity of the final materials. Therefore, immobilization on various supporting materials combines the advantages of conventional heterogeneous catalysts with the versatility of homogeneous ones as heterogeneous catalysts not only allow for easiness of separation and recovery from the reaction medium but also show repeated recycling potential, good stability and ease of handling.

Up to now, different soluble polymers and solid supports are used as carriers to recover catalysts. Furthermore, various solvent systems such as perfluorinated solvents, ionic liquids, and supercritical CO_2 are also employed for this purpose. The present review describes the current state of the art on immobilization of ruthenium based metathesis initiators on solid supports. The immobilisation of the catalysts on polymeric beads, monolithic materials and siliceous supports both mesoporous as well as nonporous will be discussed. In addition, the performance of the supported catalysts will be compared with the homogeneous analogues.

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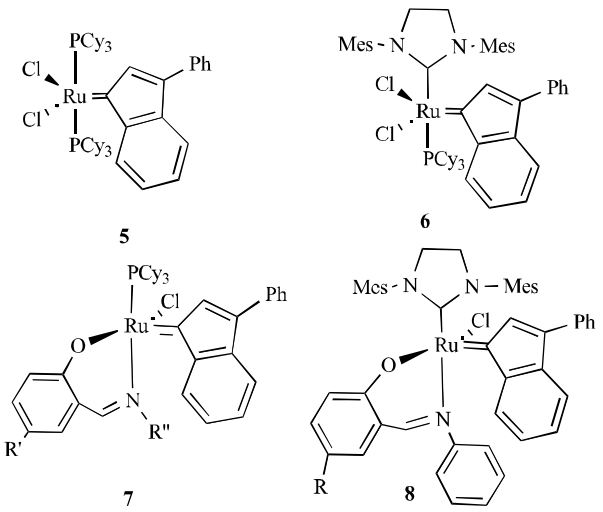


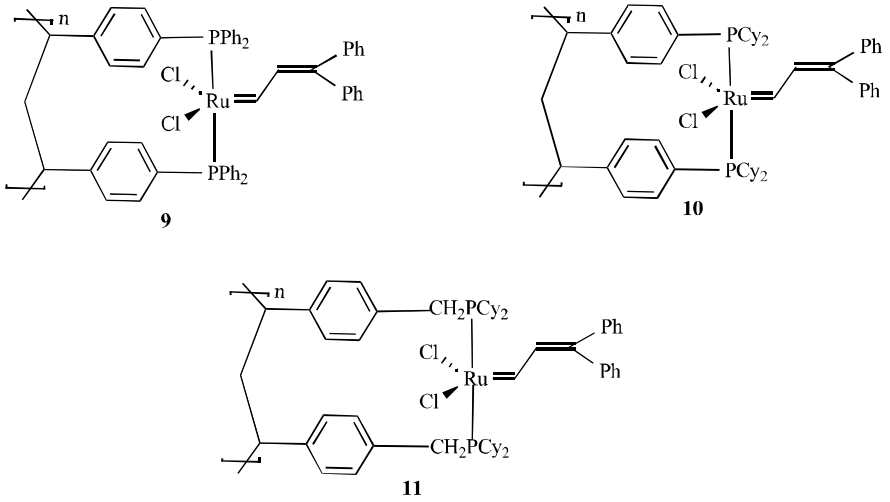
Fig. (2). Ruthenium indenylidene metathesis initiators.

2. POLYMER BEADS SUPPORTED RUTHENIUM METATHESIS CATALYSTS

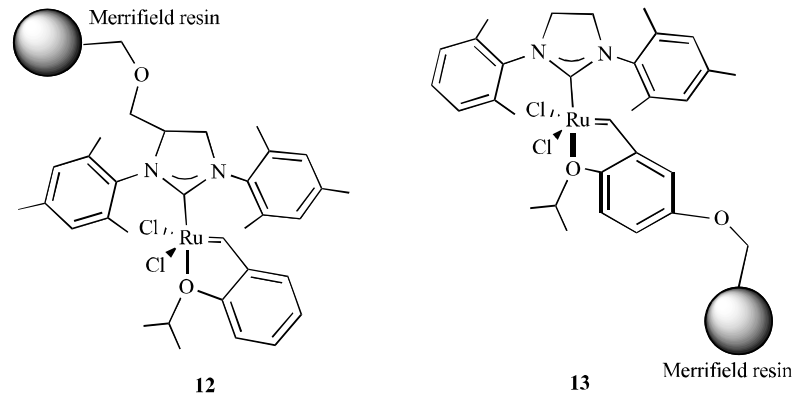
Functionalised polystyrenes present as linear or cross-linked polymers are very often used as catalyst support [9]. They are available in different bead sizes (50-500 mm) and degrees of functionalisation and cross-linking [10].

Grubbs and coworkers described the first example of a polymer supported well-defined olefin metathesis catalysts [11]. They reported a series of olefin metathesis catalysts based on a ruthenium vinyl carbene complex attached on a 2 % cross linked polystyrene divinyl benzene solid support (DVB-PS) (Scheme **1**). The ability of vinyl carbene complexes to exchange its phosphine ligands with a variety of phosphines allowed the convenient synthesis of PS-DVB supported ruthenium bis-phosphine vinyl carbene catalysts **9-11**. However, the supported catalysts turned out to be less appropriate for polymerization relative to their homogeneous counter parts, which was attributed to phosphine chelation effects, diffusion limitations and incomplete substitution of phosphine. The general decrease in metathesis activity of these PS-DVB-supported catalysts is offset by the extended lifetime of the supported catalysts. The PS-DVB-supported ruthenium catalysts are long-lived and can be re-used in practical circumstance.

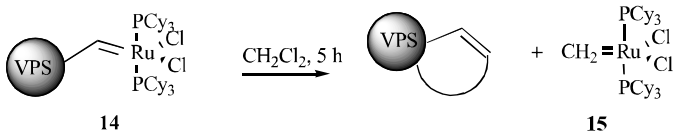
Blechert *et al.* [12] reported for the first time Merrifield polystyrene (1% divinyl benzene) (DVB) bound catalyst **12** anchored by a NHC ligand. They anticipated that anchorage of the catalyst through the NHC ligand could result into permanently immobilized and highly active metathesis initiator since NHC ligands remain bounded to the ruthenium center during metathesis reactions. The supported catalyst **12** was synthesized with a loading level between 0.14 and 0.4 mmol.g^{-1} of Grubbs' catalyst **2** by ligand exchange with the polymer supported 3,4-dimesityl-4-dihydroimidazoline chloride (Scheme **2**). The catalyst was tested on its ring-closing metathesis (RCM) activity towards various substrates and showed



Scheme 1. The PS-supported ruthenium vinylidene catalyst **9-11**.



Scheme 2. Merrifield resin immobilized Hoveyda type ruthenium catalysts **12** and **13**.



14 **15**

Scheme 3. Decomposition of vinyl polystyrene immobilized Grubbs' catalyst **14**.

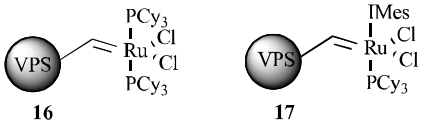
full cyclization. However, the rate of cyclization is lower relative compared to the homogeneous analogues. Highly pure products were obtained after filtration as the only purification step. The ease of isolation allows automation and makes catalyst **12** particularly suitable for combinatorial applications.

In addition, the same group also reported on the heterogeneous Hoveyda type ruthenium catalyst **13**, obtained by immobilization on a Merrifield resin via a styrene ligand [13]. The supported catalyst **13** is an excellent initiator in olefin metathesis reactions, re-usable and tolerates a wide variety of functional groups. Krischning and coworkers applied a similar approach however the linkage to the polymer is of ionic character [14].

A ruthenium alkylidene metathesis catalyst has been supported on a vinyl polystyrene polymer by means of metathesis between Grubbs' catalyst **1** and vinyl polystyrene to afford heterogeneous catalyst **14** [15]. Nevertheless, the immobilized catalyst was found to be unstable and degrades over a period of about 5 hours and if then isolated by filtration from the resin, found to be inactive. It has been suggested that the decomposition is due to the ring-closing metathesis between ruthenium alkylidene and free vinyl groups present in the resin releasing the unstable ruthenium methylidene **15** in solution (Scheme **3**). This immobilized catalyst has been used to initiate ring-opening metathesis polymerization (ROMP) of norbornene derivatives onto a polymer support to prepare novel high-loading resins for use in combinatorial chemistry.

Procopiou reported vinyl polystyrene polymer supported ruthenium pro-catalysts **16** and **17** that becomes homogeneous in the course of ring closing metathesis (RCM), with concomitant reaction rate advantages, and then recaptured by the resin after completion of the reaction in solution, a 'boomerang' catalysts (Scheme **4**). In the preparation of the 1st generation boomerang catalyst **16** preparation time was found to be critical, longer catalyst-resin preparation times (>2 h) tended to lead to poorly active catalyst for RCM [16].

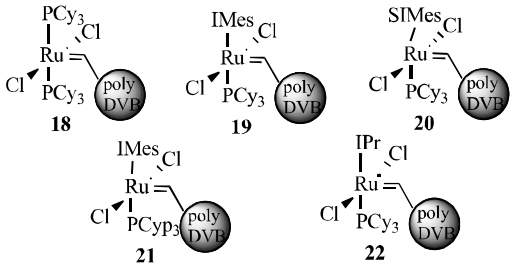
Compound **16** was found to be an effective catalyst for ring closing metathesis. The reaction rate and activity was found to be comparable to the homogeneous Grubbs' catalyst **1**. In addition, the catalyst could be recycled and re-used up to three times by simple filtration. However, deterioration of the catalyst activity was noticed and could be reduced by addition of volatile hexane. The ruthenium residues in the product mixtures were much lower compared with the reported values using catalyst **1** and comparable to the procedure reported by Grubbs applying phosphine [17]. In contrast to **16**, the second-generation boomerang catalyst **17** still retained activity in RCM after three consecutive runs [18] (Scheme **4**).



16 **17**

Scheme 4. 1st and 2nd generation boomerang catalysts.

Nolan's group reported additional boomerang catalysts [19], they used macroporous poly-DVB to prepare heterogeneous ruthenium catalysts **18-22** (Scheme **5**). Macroporous poly-DVB has advantages over lightly cross-linked Merrifield resins in that the permanent well-developed porous structure in macroporous resins can be easily accessed by solvents and reactants without any need for swelling [20]. In ring-closing metathesis the immobilized catalysts show comparable or better reactivities than their homogeneous counterparts, they perform very well with dienes and moderately well with highly hindered substrates. The macroporous poly-DVB supported catalysts tolerate functional groups very well and in some cases they are recyclable.



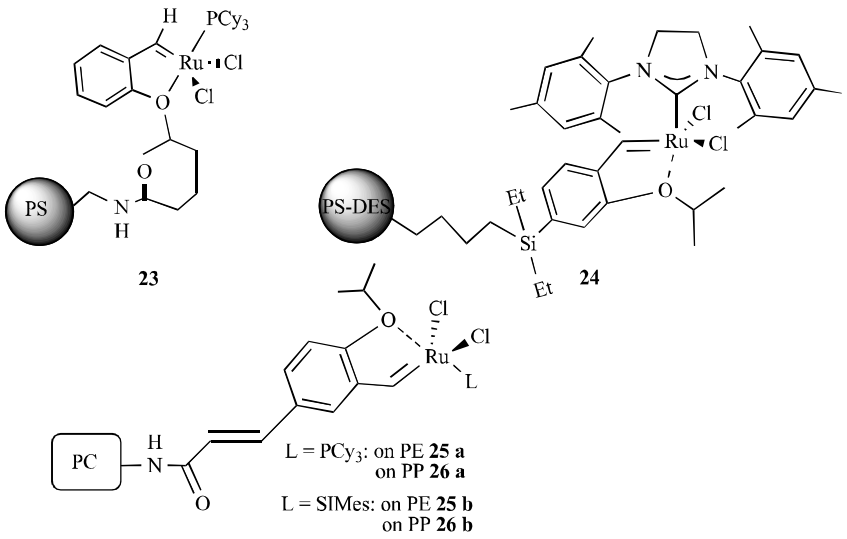
Scheme 5. Macroporous poly-DVB supported boomerang ruthenium catalysts **18-22**.

A number of polymer supported catalysts (**23-26**) that can operate in a range of reagent grade, non-degassed solvents and in an air atmosphere have been reported (Scheme **6**). The novel polystyrene supported catalyst **23** is a robust pro-catalyst in RCM of the representative dienes and easy to use [21]. However, the reaction rates were somewhat lower relative to Grubbs catalyst **1** nonetheless catalyst **23** could be recycled without the use of stabilizing additives.

Butyldiethylsilyl polystyrene (PS-BES) supported ruthenium carbene **24** has been prepared with ruthenium loadings between 0.22 - 0.33 mmol.g^{-1} [22] (Scheme **6**). The catalyst is robust in ring closing metathesis of representative substrates and easily recyclable. However, the reaction rate obtained from catalyst **24** is lower compared with the rate of the soluble analogue.

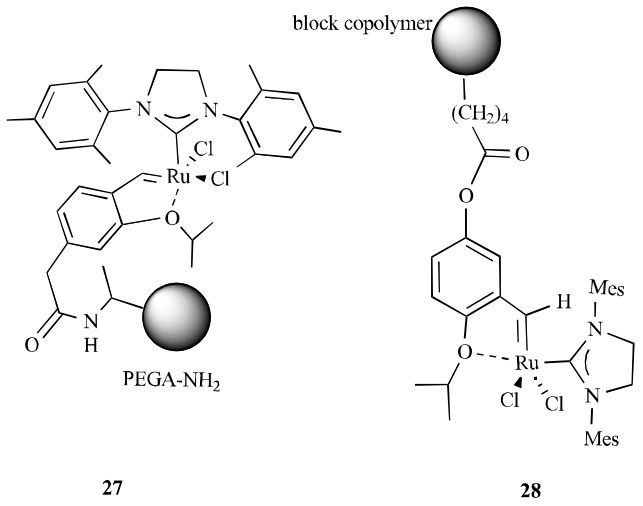
Furthermore, new heterogeneous Hoveyda type catalysts **25a-b and 26a-b** attached to the surface of amino-modified sintered polyethylene plates or polypropylene membranes via an amide bond have been reported (Scheme **6**). The polymeric chip is highly porous avoiding the swelling of the polymer resulting in the applicability of **25** and **26** in continuous flow-type processes. The catalysts were found to be very efficient for ring closing metathesis of various substrates in reagent grade solvent and without an inert atmosphere [23].

An innovation in the field of polymer supported metathesis initiators has led to the advent of water-soluble catalysts **27** and **28**. PEGA-NH_2 supported ruthenium alkylidene metathesis initiator **27** (Scheme **7**) has been reported which serves as an active catalyst for RCM and CM in methanol and even exhibits some activity in water under air atmosphere and in non-degassed solvents [24]. The hydrophilic, PEGA-NH_2 (Fig. **3**) support swells four times more per unit mass in water than the polystyrene/polyethylene glycol-based



23 24

Scheme 6. Moisture stable polymer supported ruthenium catalysts **23-26.**



27 28

Scheme 7. Hydrophilic polymer supported ruthenium alkylidene metathesis initiators.

TentaGel resin due the presence of amino functionalized dimethyl acrylamide and mono-2-acrylamidopropyl polyethyleneglycol, and proved to be perfectly stable under metathesis conditions.

A new amphiphilic, polymer-bound variant of the Hoveyda-Grubbs catalyst was synthesized **(28)** via the coupling reaction of a carboxylic acid-functionalized poly(2-oxazoline) block copolymer with 2-isopropoxy-5-hydroxystyrene and subsequent reaction of the resulting macroligand (Fig. **4**) with Grubbs' catalyst **2** [25]. A turnover number (TON) of up to 390 was achieved for the ring-closing metathesis of diethyl diallyl malonate in water resulting in the first high value for an aqueous RCM reaction. For the first time, recycling of a ruthenium initiator in an aqueous RCM reaction has been successful to some extent. In addition, the micellar conditions accelerate the conversion of the hydrophobic diene and at the same time stabilize the active alkylidene species, although competing decomposition of the catalyst in water still impairs the catalyst performance. The residual ruthenium content was determined to be below 1ppm in the product suggesting a very low leaching of the polymeric catalyst system.

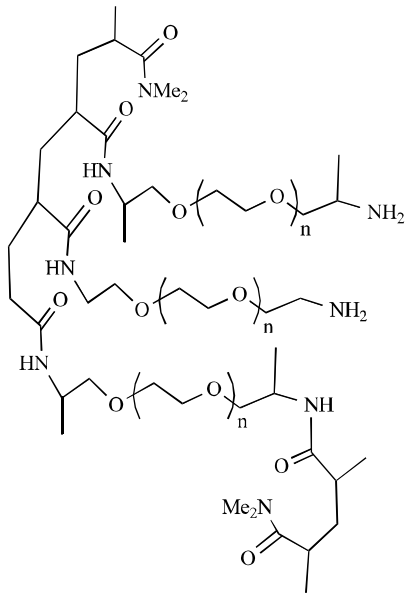


Fig. (3). PEGA-NH_2 resin.

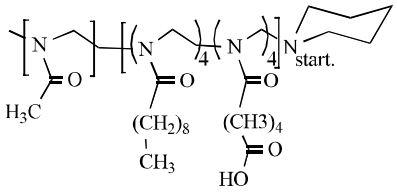
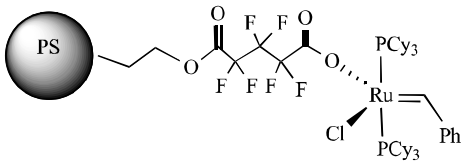
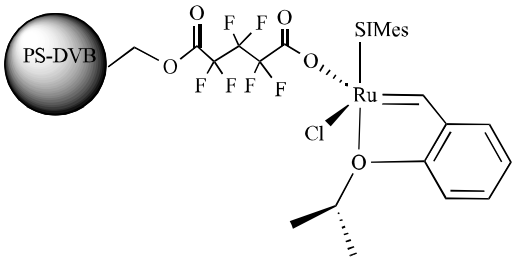


Fig. (4). Carboxylic acid-functionalized block copolymer.

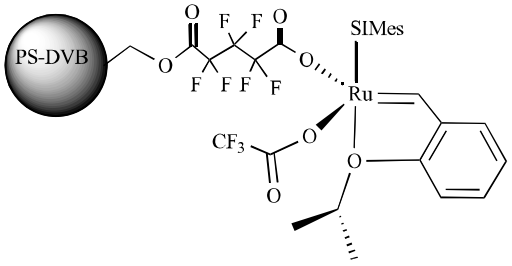
A series of ruthenium carbene complexes were permanently immobilized on polymer supports using carboxylate ligands as linking groups. For this objective one or both chloride ligands from parent ruthenium complexes were replaced with an immobilized carboxylic acid. For instance, polystyrene (PS) resin supported catalyst **29** was afforded as a new heterogeneous catalyst with a ruthenium loading of about 0.035 $mmol.g^{-1}$ by replacing one chloride ligand from complex **1** [26] (Scheme **8**). The supported catalyst is highly active in self-metathesis of internal alkenes and performed



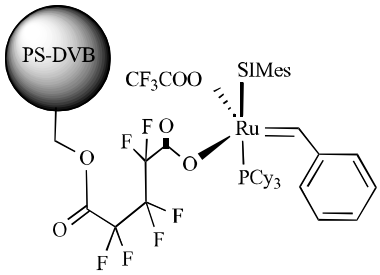
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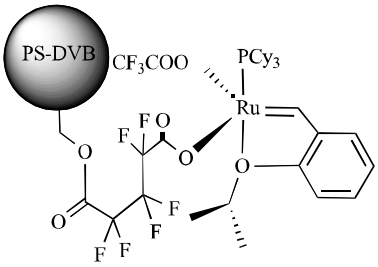
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32



33

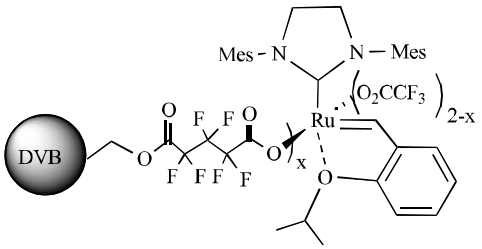
Scheme 8. Heterogeneous catalysts prepared by replacing 1 or 2 chloride ligands from the parent catalyst.

even better than Grubbs' catalyst **1**. In the RCM of diethyl diallylmalonate, applying catalyst **29**, better results were accomplished compared with for example catalyst **23** reported by Dowden and Savovic [21]. Catalyst **29** was easily separated from the metathesis products and reused without the addition of any stabilizing agents, although some leaching and deterioration of the catalyst was observed.

The Grubbs-Hoveyda type metathesis catalysts have also been immobilized on a perfluoroglutanic acid derivatized polystyrene-divinylbenzene (PS-DVD) by chlorine exchange [27]. While the substitution of one chloride ligand of the parent Grubbs-Hoveyda catalyst afforded catalyst **30** the substitution of both chloride ligands by addition of CF_3COOAg to **30** led to catalyst **31**. In RCM of representative substrates both catalysts possesses high activities, catalyst **31** being the superior system with TONs up to 1100 while with catalyst **30** TONs of 380 were achieved. For both systems, **30** and **31,** the leaching of ruthenium into the reaction mixture was unprecedentedly low, resulting in a ruthenium content < 70 ppb in the final RCM-derived products.

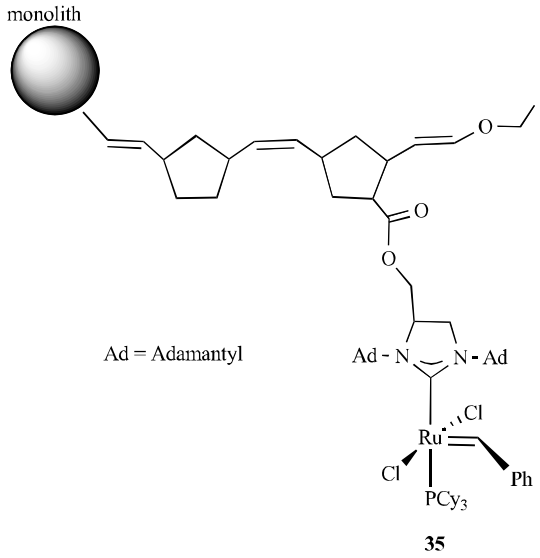
Furthermore catalysts **32, 33** were synthesized by reaction of Grubbs catalyst **2** and Grubbs-Hoveyda catalyst **3** respectively, with a perfluoroglutaric acid-derivatized poly(styrene-*co*-divinylbenzene) (PS-DVB) support [28]. Supported catalysts were prepared with high loadings (2.4 and 22.1 mg of catalyst.g^{-1} PS-DVB for **32** and **33** respectively). Catalysts **32** and **33** represent the first permanently bound versions of both Grubbs' catalyst **2** and the Grubbs-Hoveyda catalyst **3**. Catalyst **32** exhibited a higher activity while catalysts **31** and **33** displayed significantly reduced activities in RCM compared to their homogeneous analogues. Hence, with **32**, turnover numbers (TONs) up to 4200 were realized in stirred-batch (carousel) RCM experiments. Leaching of ruthenium into the reaction mixture was low, resulting in ruthenium contents of 70, 83 and 15 ppb, respectively for catalysts **31, 32** and **33**.

Polymer supported ruthenium catalyst **34** was prepared via vacuum-driven anionic ligand exchange of a polymer supported perfluorocarboxylic acid with ruthenium-bound perfluorocarboxylates in mesitylene [29] (Scheme **9**). The polymer-supported catalyst **34** is active for RCM of DEDAM and can be recycled. However, the activity is considerable reduced compared to its homogenous counterpart.



34

Scheme 9. Vacuum-driven immobilized catalysts **34**.



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Scheme 10. Monolithic supported metathesis catalyst **35**.

3. MONOLITH SUPPORTED RUTHENIUM METATHESIS INITIATORS

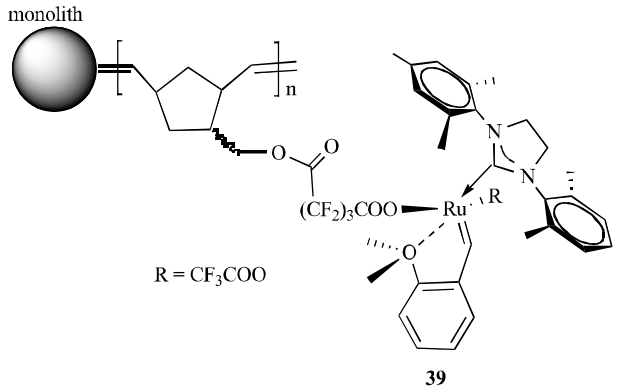
In order to overcome the problems commonly related to heterogeneous systems, such as diffusion controlled reactions and catalyst bleedings among others, Buchmeiser was able to immobilize Grubbs' type ruthenium initiators on non-porous, ring opening metathesis polymerization derived monolithic materials generated by well-defined transition metal alkylidenes. This polymerization method allows for the synthesis of monolithic materials with controlled and highly reproducible porosity characteristics. In addition, it allows for the development of monolithic supports with diversity of functional groups [30].

Using Grubbs' catalyst **1** ROMP initiator, they managed to synthesize a number of functionalized monolith supports suitable for catalysts immobilization. For instance, a N-heterocyclic carbene precursor was successfully grafted onto the surface of monolithic materials [31]. The immobilized catalyst **35** (Scheme **10**) with a loading of up to 1.4 $mg.g^{-1}$ was achieved from immobilized NHC following the standard procedure. The catalyst possesses a high activity towards RCM as well as towards ROMP. The cis/trans ratio of the polymers is exactly the same as the one obtained in homogeneous polymerizations (90 % *trans*).

The prepared monolithic systems may be used either as pressure-stable reactors or (in miniaturized form) as cartridges for applications in combinatorial chemistry. Additionally, the use of NHC ligands even in RCM successfully suppresses any bleeding of the column, consequently allowing the synthesis of virtually ruthenium-free cyclization products with a ruthenium content ≤ 70 ppm.

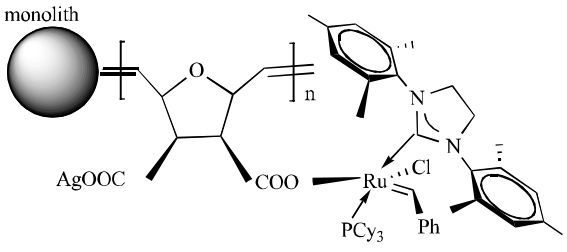
Different versions of monolith supported metathesis catalysts were obtained by chloride exchange between Grubbs' catalyst **2** and monolith supported silver carboxylates [32] (Scheme **11**). Heterogeneous catalysts **36**, **37** and **38** with loading of 10, 7 and 9 $mg.g^{-1}$ respectively were realized using this protocol. The catalysts were used in ring-closing metathesis of various substrates allowing turnover numbers (TON's) close to 1000. In a flow-through set-up, an auxiliary effect of pendant silver carboxylates was observed with catalyst **38**, where the silver moiety functions as a (reversible) phosphine scavenger that both accelerates initiation and stabilizes the catalyst by preventing phosphine elution. In all RCM experiments ruthenium leaching was low, resulting in a ruthenium content of the RCM products ≤ 3.5 $\mu g.g^{-1}$ (3.5 ppm).

The Grubbs-Hoveyda catalyst **4** has been immobilized on a monolithic support by exchanging chloride ligands between the ruthenium initiator and a monolith supported fluorinated carboxylate [33]. For this purpose norborn-2-ene-based perfluorinated acid was grafted onto the surface of the monolith before being deprotonated and converted into the corresponding silver salt. Reaction of the thus modified support with complex **4** resulted in the formation of a mono-carboxylate substituted complex. Finally, the remaining chloride ligands were reacted with CF_3COOAg to yield the corresponding bis-carboxylate substituted catalyst **39** (Scheme **12**). In this manner a ruthenium loading of the monolith-supported catalyst **39** of 0.41 $mg.g^{-1}$ was obtained.



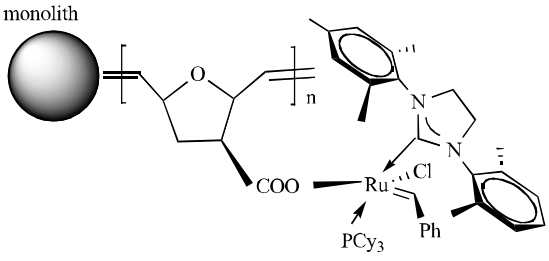
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Scheme 12. Monolith supported Grubbs-Hoveyda type catalyst.



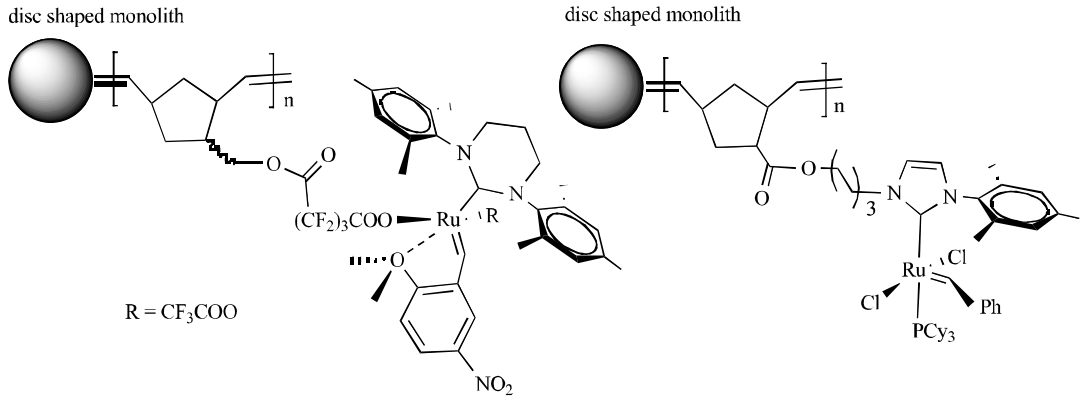
Cross-linker DMN-H_6: **36**

Cross-linker (NBE-CH_2-O)$_3$SiMe: **37**



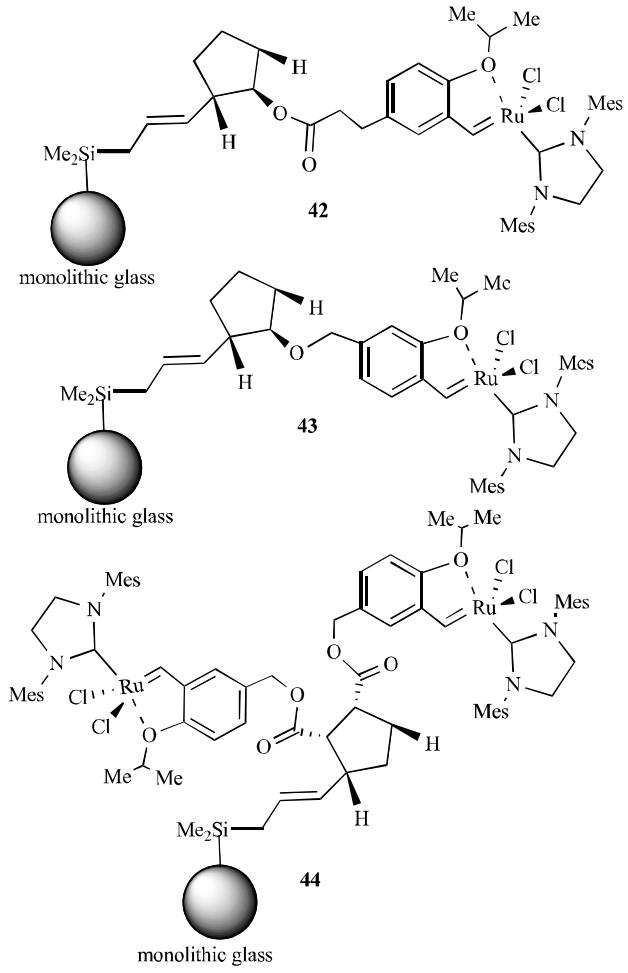
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Scheme 11. Monolith-supported catalysts obtained via chloride exchange.



40 **41**

Scheme 13. Disc-shaped monolith-supported catalysts **40** and **41**.



Scheme 14. Monolithic porous sol-gel glass supported ruthenium complexes **42-44**.

This monolith supported Grubbs-Hoveyda catalyst **39** was successfully used in continuous flow experiments. For instance, in the RCM of diethyl diallylmalonate, turnover numbers of up to 500 were achieved. It is worth mentioning that the turnover numbers obtained with this supported version are very similar to the ones obtained with the homogeneous analogues.

Most importantly, only pure product as well as unreacted adduct could be found in the eluent, which directly translates into an increased long-term stability of the catalysts. Extremely low leaching (<0.2%) was observed resulting in product contamination with ruthenium and silver of 1.8 and 0.01 ppm, respectively.

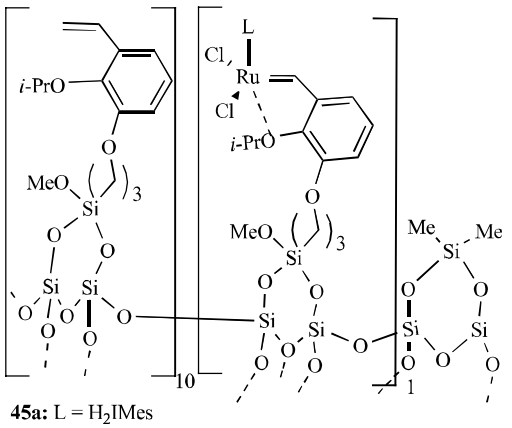
Buchmeiser and co-workers extended the study by focusing on disc-shaped monoliths to immobilize ruthenium initiators in contrast to previously reported one. The disc-shaped monoliths were developed by cutting the parent monolith into pieces of 1 cm in height and subsequently used in the preparation of catalysts **40** and **41** (Scheme **13**).

The supported catalyst **40** was prepared with loadings of about 2.5 wt% [34]. Excellent reactivities were observed in RCM and ROCM of various substrates. The monolithic disk immobilized catalyst **40** showed somewhat reduced activity, yet compared to the homogenous analogue, still can be regarded as good. In terms of product purity, it is noteworthy that ruthenium leaching from the supported systems **40** was very low, resulting in ruthenium contaminations of less than 0.14 ppm.

With the disc shaped monolith supported catalyst **41** [35] on the other hand, TONs in the range of 60-330 were obtained in the ring-closing metathesis of representative substrates which are comparable to those obtained with the homogeneous analogue.

These relatively low activities clearly stems from the fact that reactions within the disks were not stirred and, therefore, depended on diffusion of the substrates to the catalytic site. Nevertheless, the reactivity observed with these systems definitely justifies the use of such monolith-supported catalysts in high-throughput screening, where the disk serves simultaneously as support, reaction vessel, and filtration unit and can, in principle, be directly used in combination with commercially available machines.

Hoveyda and co-workers [36] disclosed the one-pot synthesis of ruthenium complexes **42-44** supported on commercially available monolithic samples of porous sol-gel glass (Scheme **14**). The supported catalysts can effectively promote various olefin metathesis reactions and can be easily employed in a library synthesis format without multiple weighing, in air and with undistilled commercial reagent-grade solvents. Catalyst recovery is simply carried out with a pair of tweezers; it does not require filtration and generates minimal solvent waste. The catalyst retains its activity after multiple



Scheme 15. Immobilized Hoveyda–Grubbs' type catalysts on silica gel.

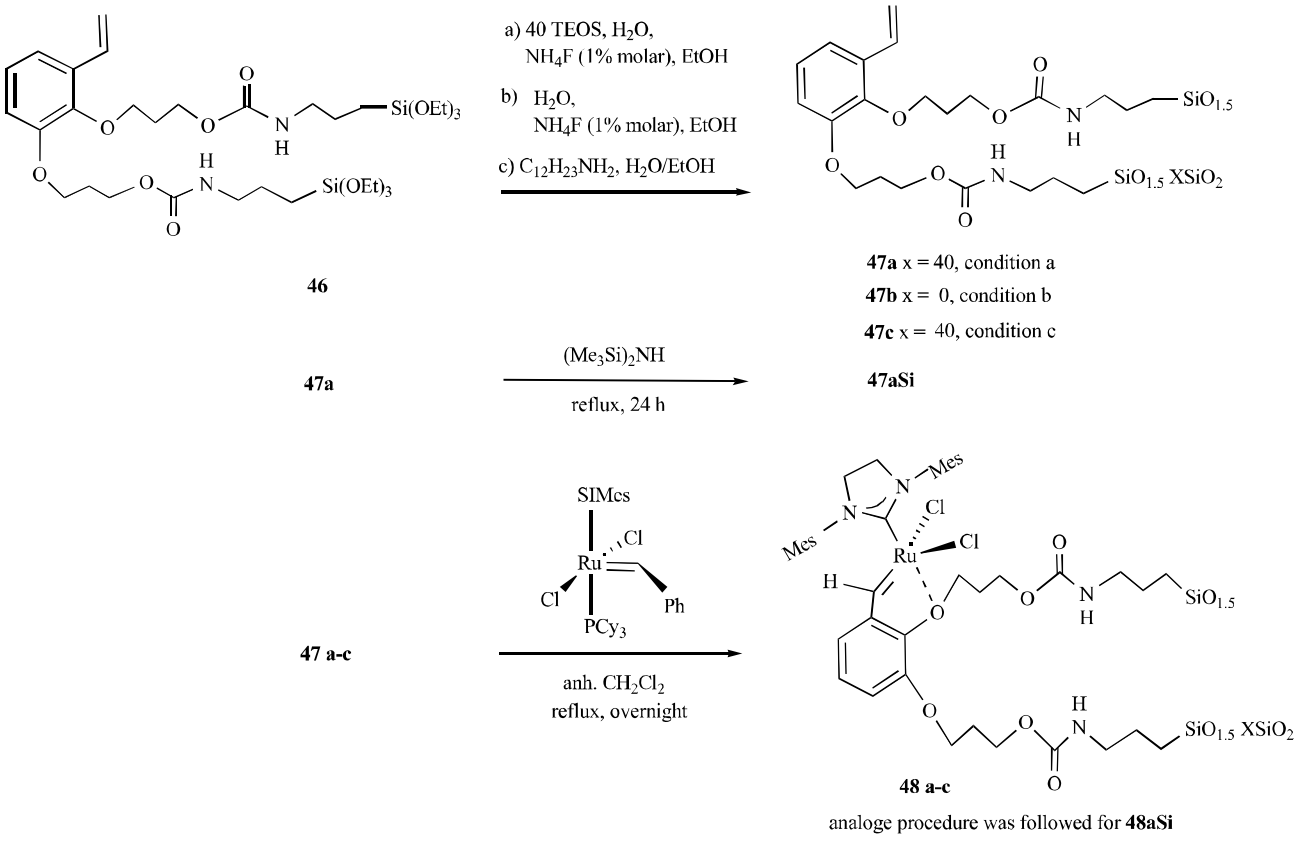
cycles (>15), affording products that are of high purity without recourse to any purification steps.

4. NON POROUS SILICA SUPPORTED RUTHENIUM METATHESIS INITIATORS

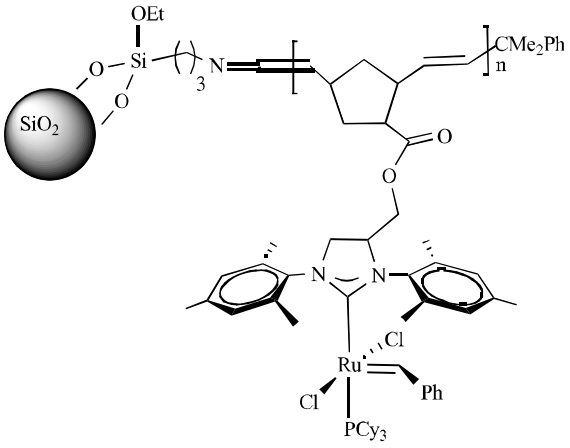
Inorganic silica material is a common support for the heterogenization of molecular catalysts. It offers a considerable advantage over other supporting materials due to its excellent thermal and chemical stability, low cost, and broad solvent compatibility. It has a rigid structure, does not swell in solvents, and can be used at both high and low temperatures and pressure.

Silica-gel immobilized Hoveyda–Grubbs type catalysts **45a** and **45b** synthesized by alkylidene exchange between commercially available Grubbs' catalysts **(1** and **2)** and silica gel immobilized isopropoxystyrene has been reported by Blechert *et al.* [37] (Scheme **15**). The supported catalysts showed good stability on storing at 4 °C under nitrogen over two weeks without any sign of decomposition. However, when quantitative loading of the styrene with ruthenium was achieved the catalysts decomposed within days at -20 °C. The catalysts demonstrate higher activity in a number of metathesis test reactions than the parent Grubbs' catalysts and they can be easily separated by simple filtration of the non-swelling material.

The hybrid organic-inorganic silicas obtained as bridged silsesquioxanes from a bis-silylated Hoveyda-type monomer via the sol-gel process have been prepared for the first time by Moreau [38]. Important to note is that the sol-gel process allows the control of not only the loading of organic groups but also their distribution in the matrix in contrast with grafting approach. Three different types of hybrid materials were prepared from bis-silylated compound **46** (Scheme **16**). Co-gelification with tetraethoxysilane (TEOS) afforded **47a**, whereas hydrolytic polycondensation of monomer **46** without TEOS in the same nucleophilic conditions gave **47b**. Another sol-gel condition was tested with neat monomer **46** in order to get an organized and porous material, using dodecylamine both as basic catalyst and surfactant, and gave rise to material **47c**. Capping of the residual silanol groups was performed before charging with the metal in order to test if improved materials could be obtained, as the silylated hybrid is less hygroscopic than its parent one and gave rise to **47aSi**. All materials (**47a-c** and **47aSi**) were charged with the metal by treating them with the Grubbs' catalyst **2**. The cata-



Scheme 16. Preparation of ruthenium heterogeneous catalysts **48a-c** and **48aSi**.



49 = on nonporous silica
50 = on porous silica

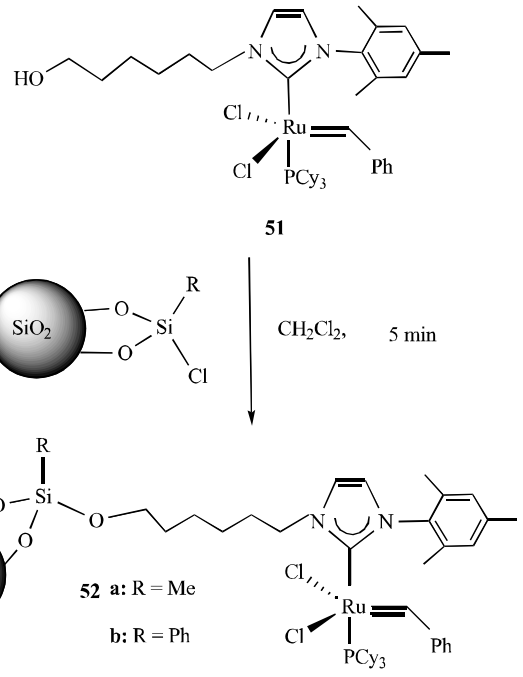
Scheme 17. Silica gel supported catalysts **49** and **50**.

lysts proved their efficiency as recyclable catalysts in the ring-closing metathesis of dienes and enynes. The materials prepared from the sol-gel are superior to the same catalysts deriving from anchorage to meso-structured silica. Furthermore, end capping of residual silanol groups before charging with the metal does not improve the materials.

The second-generation Grubbs catalyst type has been successful immobilized on both porous and non-porous silica via the NHC ligand [39]. For this purpose the porous and nonporous silica were functionalized with a NHC-precursor and subsequently converted to heterogeneous **49** and **50** applying the standard procedure (Scheme **17**). Ruthenium loadings of 5.3 and 1.3 mol.g^{-1} were realized. Additionally, coating techniques were applied, where C_{18}-derivatized silica-60 was used to attain a heterogeneous catalyst with a 4.1 mol.g^{-1} ruthenium loading.

In RCM of DEDAM, the catalysts immobilized onto non-porous silica reached the maximum turnover number (TON) of 75. Interestingly, basically identical results (TON = 80) were obtained with catalysts immobilized onto porous silica. Nevertheless, the low TON's (5!) obtained with other less reactive compounds such as 1,7-octadiene, N,N-diallyl trifluoroacetamide, diallyl ether, and diallyl diphenylsilane suggest that the stirred batch setup with this type of support is highly diffusion controlled, where reaction is too slow and decomposition of the intermediary ruthenium methylidene dominates.

Catalytic results obtained with coated supports exceed the data for TON of all other silica supports by far. This can be interpreted in a way that a support containing only macropores facilitates diffu-

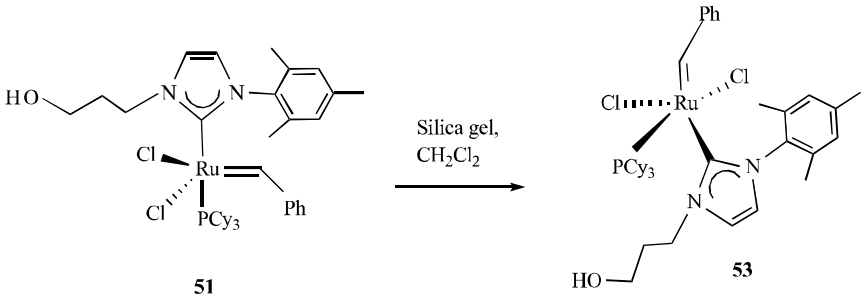


Scheme 18. Immobilization of complex **51** by chemisorption.

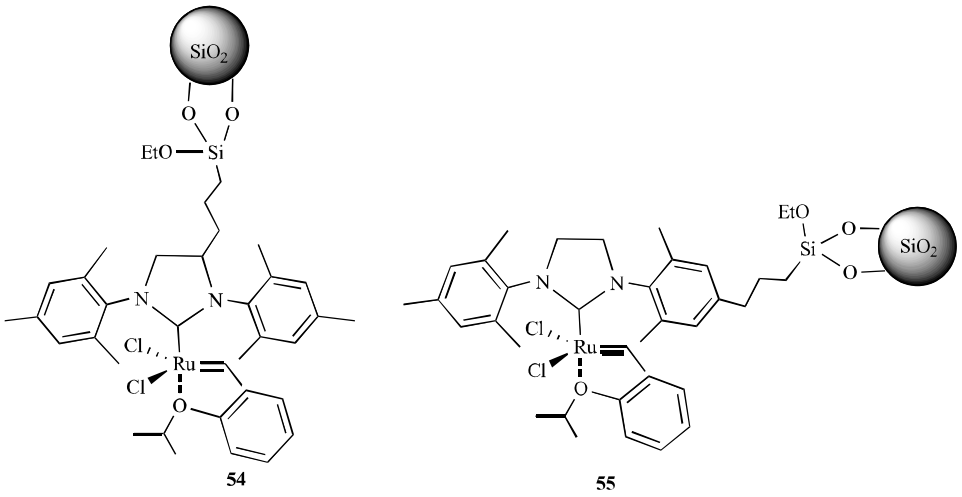
sion. It is worth mentioning that in all cases a quantitative retention of the original amount of ruthenium at the support was revealed thus offering access to metal-free products.

A ruthenium-carbene complex **51** bearing a hydroxyalkyl group on the N-substituent of its NHC ligand reported by the Fürstner group [39] has been covalently immobilized on chloro-functionalized silica (Scheme **18**). Although a longer reaction time is necessary to reach complete conversion, the immobilized catalysts **52a-b** possess a RCM performance comparable to its homogeneous analogues. These catalysts **52a-b** offer the advantage to be reusable up to three times. However, in case the immobilization of the hydroxyalkyl-functionalized ruthenium carbene complex is done by physisorption rather than chemisorption, rearrangement of **51** to isomer **53** was observed bearing the neutral ligands in a *cis* rather than the usual *trans* position (Scheme **19**), which is a characteristic of the highly conserved structural feature of the Grubbs type ruthenium carbene complexes.

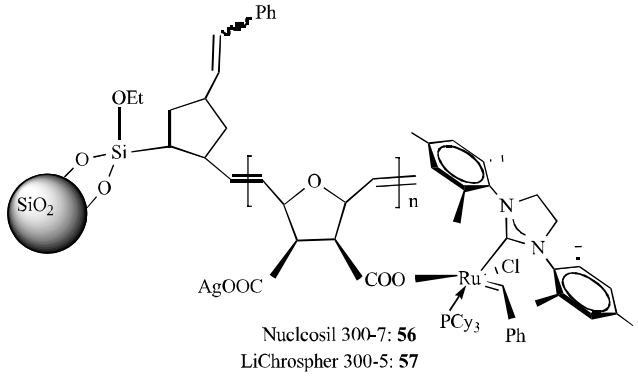
The silica-supported catalysts **54** and **55** have been successfully prepared via triethoxysilyl-functionalized NHC ligands [40] (Scheme **20**). These species were shown to be competent catalysts for a variety of olefin metathesis reactions, mimicking their homogeneous counterparts. Likewise, the activity of the supported cata-



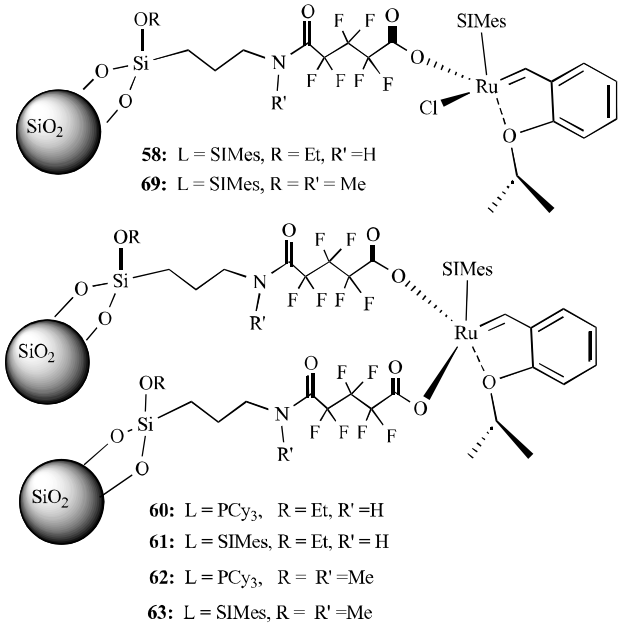
Scheme 19. Immobilization of complex **51** by physisorption.



Scheme 20. Silica-supported catalysts **54** and **55**.



Scheme 21. Preparation of heterogeneous catalyst **56** and **57**.



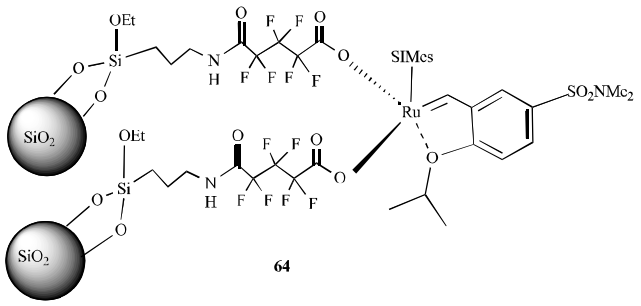
Scheme 22. Mixed anionic ligands catalysts **58**, **59** and disubstituted catalysts **60-63**.

lysts is truly heterogeneous in nature as revealed by split tests, moreover, they can be recycled multiple times. More significant is that the catalysts do not leach ruthenium under the standard reaction conditions as ruthenium concentration of the filtrate of less then 5 ppb in all cases are obtained.

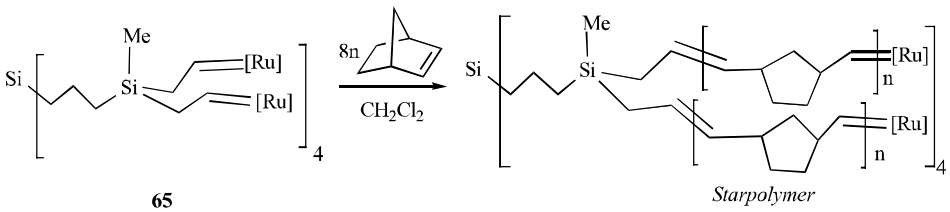
Buchmeiser *et al.* [41] reported catalysts **56** and **57** developed by exchange of chloride from Grubbs' catalyst **2** with immobilized silver carboxylates (Scheme **21**). Interesting to mention is that only one chloride ligand was exchanged. Catalyst loadings of 42 and 63 $mg.g^{-1}$ respectively were achieved. These heterogeneous catalysts are competent catalysts in ring-closing metathesis of various substrates allowing turnover numbers (TONs) close to 1000. In all RCM experiments ruthenium leaching was low, resulting in a ruthenium content in the RCM products $\leq 3.5\ g.g^{-1}$ (3.5 ppm).

One or both chlorides in the Hoveyda-Grubbs type catalysts have also been selectively substituted in the preparation of heterogeneous catalysts containing mixed anionic ligands as well as disubstituted catalysts. After heterogenization of the catalysts, the remaining free SiOH groups on the silica surface were subsequently capped with dimethoxydimethylsilane.

Loadings between 31 and 65 $\mu mol\ g^{-1}$ were achieved for catalysts **58-63** [42] (Scheme **22**). These heterogeneous catalysts showed good stability when stored at +4 °C under argon for 4 weeks without any sign of decomposition. The silica gel bound catalysts containing mixed anionic ligands **58** and **59** were more active in RCM reaction with N,N-diallyl-4-methylbenzenesulfonamide than their disubstituted counterparts **60** and **61**, however, there was not such a marked difference. The supported catalysts **58-**



Scheme 23. Immobilized ruthenium complex **64**.



Scheme 24. G1-dendrimer ruthenium initiator **65** and its star polymer.

63 displayed considerable lower TONs than their homogeneous counterparts. Nonetheless, compared to similar polymer-bound systems reported by Buchmeiser *et al.* the prepared silica bound catalysts performed better.

On the other hand, heterogeneous metathesis catalyst **64** was prepared with a ruthenium loading of about 0.78 wt % [43] (Scheme **23**). The catalyst demonstrated its activity and high selectivity in ring closing metathesis of 1,7-octadiene and diethyl diallylmalonate, as well as in the ring opening metathesis polymerization of norbornene and cyclo-octene, both carried out in a batch stirred reactor. Almost negligible leaching of ruthenium was observed and successful catalyst reusing was achieved. However, the reaction rate was lower in comparison with its SBA-15 supported analogue.

Synthesis of a new metathesis initiator **65** by coupling ruthenium-complexes to low generation carbosilane dendrimers, 0^{th} generation (G0–Ru) and first generation (G1–Ru) has been reported by Verpoort *et al.* [44] (Scheme **24**). The attachment of the ruthenium complexes to the boundary of the dendrimer is performed by olefin metathesis. With a dendrimeric support the regular occupation of the surface and the good accessibility of all the active catalytic sites for the reactants favors a high activity and selectivity. Besides, product separation is possible via ultra filtration. This dendrimer supported initiator shows a very high activity for the ROMP of norbornene. By using this dendrimeric initiator multi-arm star polymers can be developed in a controlled manner.

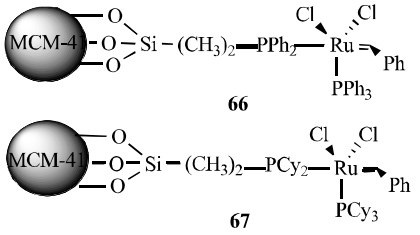
The Hoveyda-Grubbs catalyst **4** was successfully immobilized on commercial silica in pellet and powder form following a practical and fast synthesis procedure [45]. A solution of 2^{nd} generation Hoveyda-Grubbs catalyst was brought in contact with a suspension of silica and stirred at 293 K for two hours. A bright greenish powder was acquired with a ruthenium loading of about 0.1 wt %.

The activity of the solid system is truly efficient in various metathesis reactions and stable for at least 4000 TONs. Ruthenium contamination of the products was very low (ppb level). The catalyst can be recycled up to four cycles with full conversion in each cycle. The successful use of the robust system has even been demonstrated in a continuous reactor set-up.

5. MESOPOROUS MOLECULAR SIEVES SUPPORTED RUTHENIUM METATHESIS INITIATORS

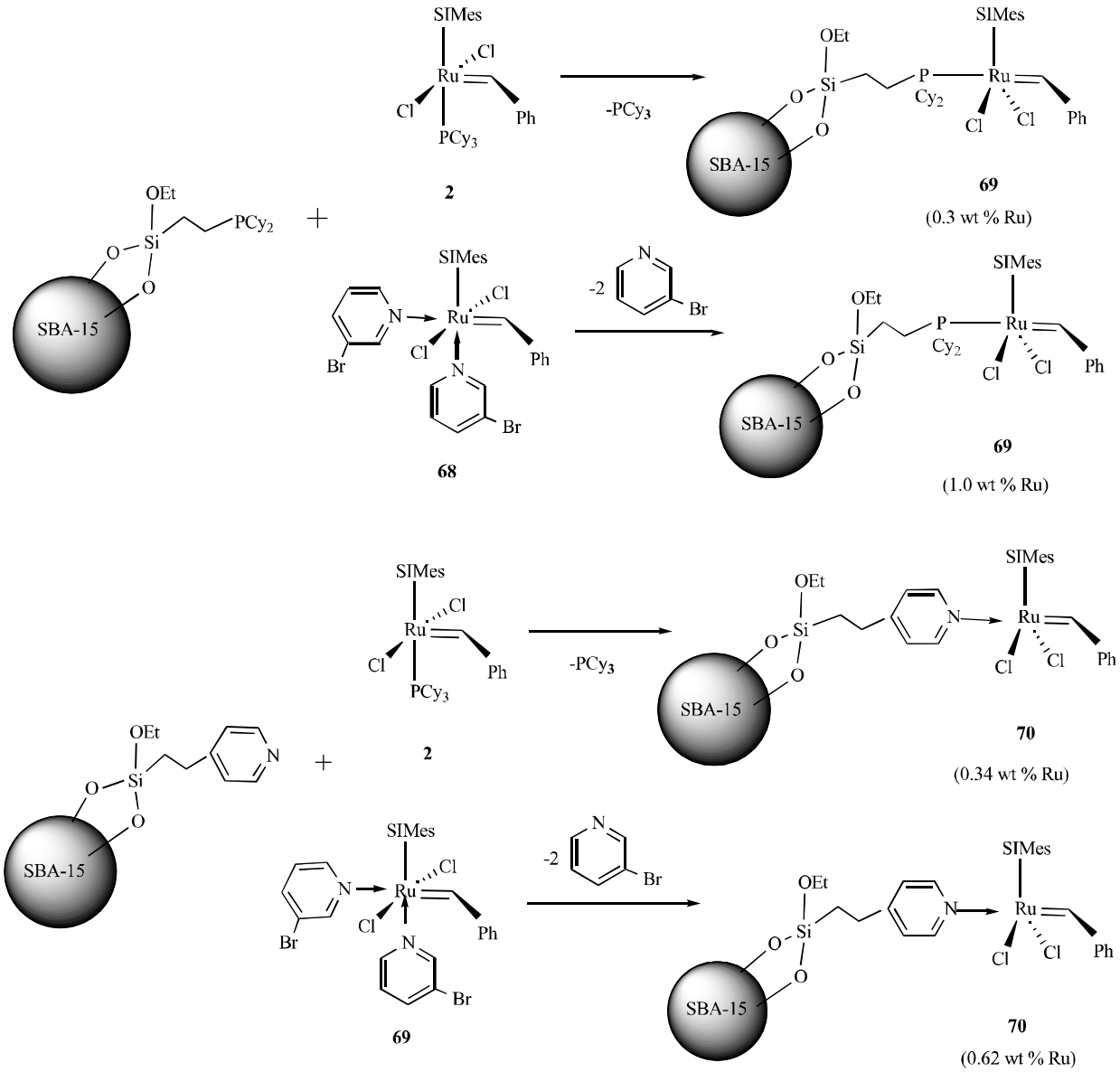
In 1992, the preparation of MCM-41 denotes a groundbreaking development in hybrid catalysis [46]. The creation of a uniform mesoporous skeleton delivers a new mean of immobilization. The large pore size allows large organic and organometallic molecules to pass through the channels and provides optimal contact with the surface. In addition, the regular pore size of MCM-41 can provide shape selectivity not provided by classical inorganic supports. This feature has led to a continuous increase in a number of reports about immobilization of ruthenium metathesis initiators on mesoporous materials.

For instance, heterogeneous catalysts **66** and **67** have been prepared by phosphine exchange between Grubbs' type ruthenium-alkylidene complexes and a phosphinated mesoporous matrix (P-MCM-41) [47] (Scheme **25**). The exchange of a phosphine ligand of the homogeneous complex by a P-functionalized spacer molecule was favored due to the increased pKa or donor capacity of the immobilized phosphine ligand. Both catalysts **66** and **67** reveal activity in ROMP of norbornene, however, due to diffusion limitations an enhancement in polydispersity was exhibited for the ROMP of norbornene catalyzed by **66**. Noteworthy is that catalyst **67** even exposes metathesis activity in aquatic environment. The RCM activity of catalysts **66** and **67** is in agreement with that of their homogeneous analogues.



Scheme 25. MCM-41 supported Grubbs' type metathesis catalysts.

Ligand exchange between phosphinated mesoporous silica (SBA-15) and either complex **2** or complex **68** has resulted into catalysts **69** with ruthenium attached to the surface via a PCy_2-



Scheme 26. Synthesis of SBA-15 supported catalysts **69** and **70**.

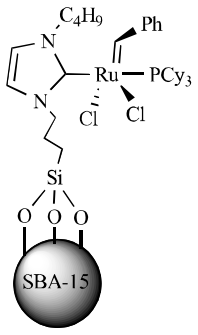
linker. On the other hand, catalyst **70** with ruthenium attached via a pyridine ligand has been prepared by ligand exchange between pyridinated mesoporous silica and either complex **2** or complex **68** [48]. Both complexes **2** and **68** generated catalysts with the same structure, however, the usage of complex **68** is preferable since catalysts with high loadings are more easily achieved (Scheme **26**).

Hybrid catalysts with ruthenium attached to the surface via PCy_2-linkers exhibited a higher activity and stability in metathesis than those having ruthenium attached via pyridine linkers. The former catalysts displayed a high activity in a series of metathesis reactions (RCM, ROMP and CM), reaching turnover numbers from 200 to 2000 at nearly 100 % selectivity and being reusable for several times. Catalysts with pyridine linkers tended to decompose rapidly at incomplete conversions. The filtration tests for all catalysts suggested that the immobilized catalysts were responsible for the catalytic activity during the reactions. Ruthenium leaching in the final reaction mixture was very low for catalysts coordinated to PCy_2-linkers and even negligible for catalyst with pyridine-linkers.

Shi and coworkers reported catalyst **71,** where the ruthenium catalyst is covalently anchored inside the pore channels of SBA-15 via an NHC-ligand [49] (Scheme **27**). The outer surface of SBA-15 was masked with Si-CH_3 groups before being functionalized with the ruthenium complex guaranteeing that the immobilization took place inside the pore and not outside. This approach was made in order to avoid the decomposition of the catalyst.

The heterogeneous catalyst **71** displays activities in RCM of DEDAM comparable with its homogeneous analogue proving that the reaction, most probably, is not diffusion-controlled due to the three-dimensional channels and high porosity of SBA-15. The immobilized catalyst can be repeatedly used without any apparent decrease in catalytic activity along with the cycle times.

MCM-41 supported Grubbs-Hoveyda type ruthenium complexes **72** and **73** have been reported by Moreau. These heterogeneous catalysts were realized by anchoring a *bis*-silylated monomer on meso-structured silica MCM-41 followed by the metalation

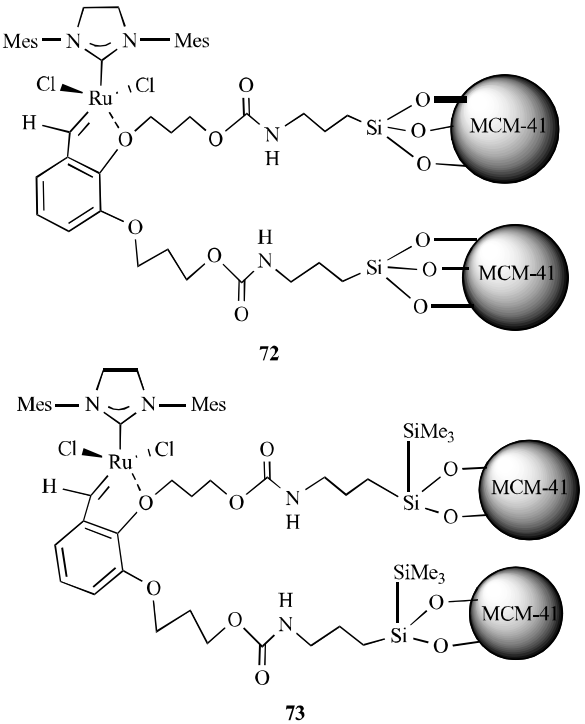


71

Scheme 27. SBA-15 immobilized ruthenium complex **71**.

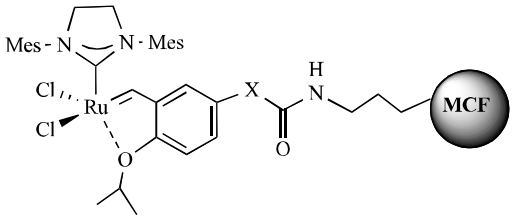
applying standard procedures [50] (Scheme **28**). End capping of the residual silanol groups was performed before charging with the metal in order to test if improved materials could be obtained. A ruthenium content of 0.113 mmol Ru/g for catalyst **72** and 0.0494 mmol Ru/g for catalyst **73** was achieved.

These catalysts were evaluated as recyclable catalysts in the RCM reactions of dienes and enynes. For the RCM of N,N-diallyl-4-methylbenzenesulfonamide complex **72** offers milder conditions and better results than previous works based on catalysts anchored to insoluble solid supports. RCM of a more challenging substrate, N,N-bis(2-methylallyl)-4-methylbenzene-sulfonamide, gave rise to the tetrasubstituted alkene. Moreover, the catalytic material is easy recyclable for the ring-closing enyne metathesis performed on 1-allyloxy-1,1-diphenyl-2-propyne. This is for the first time in the literature that a catalyst is described, which can be recycled in the ring-closing enyne metathesis reaction. However, silylation of residual silanol groups before charging with the metal does not improve the materials. Although the reaction time in the first cycle is lowered, the efficiency upon recycling decreases very rapidly.



Scheme 28. MCM-41 supported catalysts **72** and **73**.

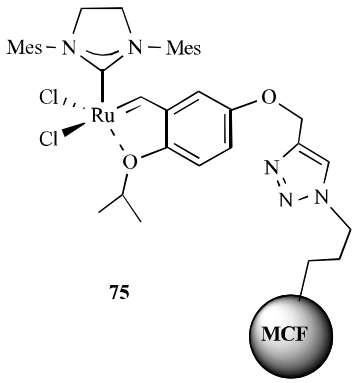
Mesocellular foam (MCF) supported Hoveyda-Grubbs catalysts have been successfully developed by Yinga *et al.* [51]. The ultra large pores and high surface area of MCF allowed the ligands and catalytic complexes to be immobilized without steric hindrance, and facilitated the diffusion of bulky substrates during reaction. The resulting novel heterogeneous catalysts **74a** and **74b** demonstrated excellent activity and reusability for the RCM of various types of substrates (Scheme **29**). Although the gradual loss of activity was unavoidable in multiple recycling runs, introducing additional MCF-supported free ligand significantly enhanced the reusability of the heterogeneous catalyst.



74a X = CH_2O
74b X = O

Scheme 29. MCF immobilized catalyst **74**.

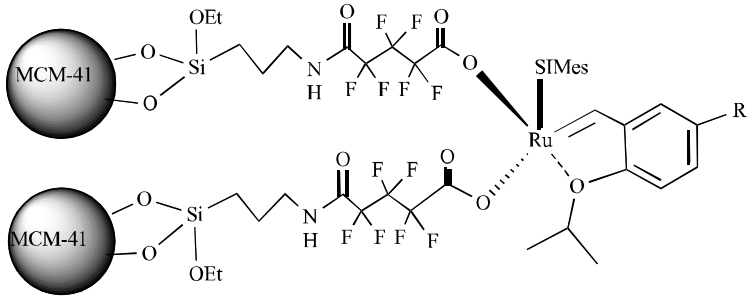
A siliceous mesocellular foam (MCF) immobilized ruthenium metathesis catalyst **75** was efficiently achieved by using click chemistry for linkage with the support [52] (Scheme **30**). A ruthenium loading of 0.16 $mmol.g^{-1}$ was obtained for catalyst **75**, while the ligand density of immobilized ligand was 0.19 $mmol.g^{-1}$ implying that more than 80% of the immobilized ligand was loaded with ruthenium. The supported catalyst **75** is applicable to a designed reactor system that made use of immobilized catalysts in a continuous process by just circulating the reaction mixture to facilitate the removal of in situ generated by-products [53]. The catalyst exhibited good activity and recyclability in RCM of various substrates. In most cases, good catalytic activities were maintained for 5 to 10 runs at 50 °C in DCM.



75

Scheme 30. MCF immobilized catalyst **75**.

Heterogeneous metathesis catalysts **76a** and **76b** were prepared by immobilization of commercially available Hoveyda-Grubbs type catalyst on siliceous mesoporous molecular sieves SBA-15 via exchange of chloro-ligands by silver(I) carboxylate [43] (Scheme **31**). The catalysts proved their activity and high selectivity in ring closing metathesis of 1,7-octadiene and DEDAM, as well as in the ring opening metathesis polymerization of norbornene and cylcooctene, both carried out in batch stirred reactor. Almost negligible

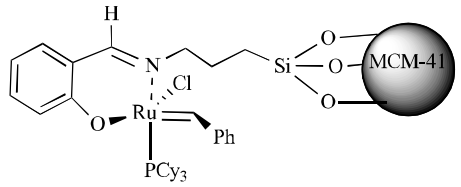


76a: R = H

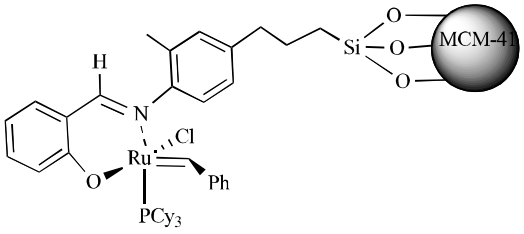
76b: R = SO_2NMe_2

Scheme 31. SBA-15 immobilized catalyst **76**.

leaching of ruthenium was observed and successful catalyst reusing was achieved. However, the reaction rate was slower in comparison with the parent Hoveyda-Grubbs alkylidenes under the same reaction conditions. In ROMP, high molecular weight poly(NBE) and poly(COE) were prepared in good or moderate yields.



77



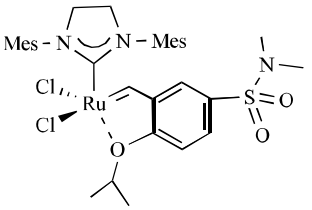
78

Scheme 32. MCM-41 supported N,O-bidentate Schiff base complexes **77** and **78**.

Verpoort reported the immobilization of homogeneous N,O-bidentate ruthenium complexes bearing a Schiff base as ancillary ligand onto MCM-41 by treatment of the inorganic support with a tris(alkoxy)silyl functionalized ruthenium complex [54]. They envisaged that the chemical tethering of organometallic compounds to a solid support to be one of the best strategies with respect to catalyst leaching. Applying this approach two multifunctional Schiff base-containing ruthenium carbene complexes, catalysts **77** and **78** supported on MCM-41 were generated from their homogeneous precursors (Scheme **32**).

RCM of various dienes substrates induced by catalysts **77** and **78** allowed cyclization to five-, six- and larger rings, in moderate to high yields, mainly depending on the dienic substrate, catalyst and reaction temperature. Catalyst **78** proved to be more active, however, both catalysts led easily to quantitative conversions of 1,7-octadiene, DEDAM and diallyl ether to give the corresponding cyclic products, when working at 85°C.

Importantly, work-up of the RCM reaction simply consisted of the removal of the catalyst through filtration and evaporation of the solvent under vacuum. It is noteworthy that both strained and low strained cyclo-olefins (e.g. norbornene or norbornene derivatives and cyclo-octene) displayed a high reactivity in ROMP by using both catalytic systems **77** and **78**, under normal reaction conditions. Interestingly, in ROMP, catalyst **77** proved to be more active than catalyst **78**. This result is in sharp contrast to the results obtained from RCM reactions using the same catalytic systems.



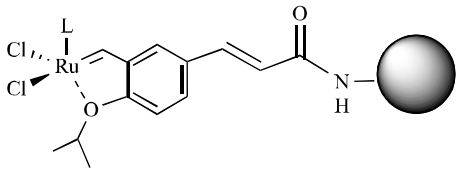
79

Fig. (5). Hoveyda-Grubbs type catalyst **79**.

Zhan catalyst **79** developed by Zannan (Fig. **5**) was immobilized on mesoporous molecular sieves MCM-41 and SBA-15 by mixing a suspension of **79** and mesoporous sieves in toluene at room temperature [55]. The immobilization proceeded quickly in a nearly quantitative way. Heterogeneous catalysts prepared in this way exhibited a high activity and 100% selectivity in the RCM of various substrates, and in the ROMP of cyclo-octene. Ruthenium leaching was found to depend on the polarity of the used substrates and solvents. For instance, the lowest leaching (0.04% of the catalyst ruthenium content) was found for the RCM of 1,7-octadiene in cyclohexane. On the other hand, for the RCM of DEDAM in dichloromethane, leaching reached up to 14 % of the initial ruthenium content. Results from UV-Vis and XPS studies suggested that catalyst **79** was attached to the mesoporous sieve surface by non-covalent interactions. Approximately 76% of the ruthenium content could be recovered from the sieve as **79** by washing heterogeneous **79** with THF at room temperature.

6. SUPPORTED RUTHENIUM METATHESIS INITIATORS ON OTHER SOLID SUPPORTS

Bannwarth presented for the first time, RCM reactions employing covalently immobilized Hoveyda-type catalysts in $scCO_2$ as the sole reaction medium [56]. He designed a new hybrid support material with a rigid core structure covered by an ultra-thin layer (~10 nm) of an acrylamide-styrene copolymer (Fig. **6**). The new support



80

Scheme 33. Heterogeneous ruthenium catalyst **80**.

was evaluated in comparison with commercially available amino-modified HypoGel 400, PEGA and Trisoperl. The new hybrid supported catalyst **80** (Scheme **33**) was superior to amino-modified silica gel (Trisoperl) and PEGA catalytic materials. This might be explained by swelling properties and polarity effects influencing the accessibility of catalytic sites on the support. None of the solid bound catalyst reached the excellent performance of Grubbs catalysts **1** and **2**. In addition, the catalysts allowed for repetitive cycles with remarkably low level of ruthenium leaching into the crude product (20 ppm).

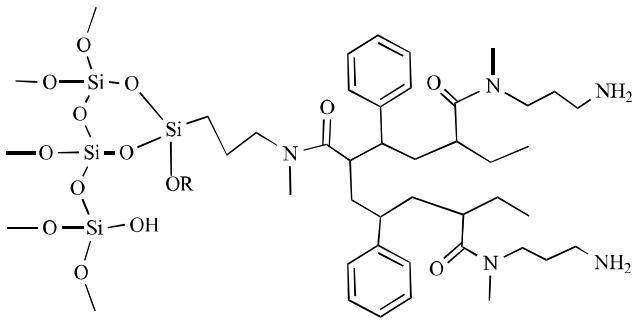
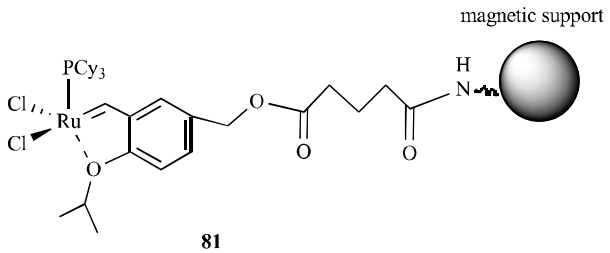


Fig. (6). Novel hybrid support.

Assembling magnetic nanoparticles with Grubbs catalyst **1** resulted in a novel type of Hoveyda–Grubbs catalyst (Scheme **34**) [57]. The ruthenium loading level of the obtained magnetic catalyst amounts to 0.025 mmol g/L. The heterogeneous catalyst **81** was found to be effective in the synthesis of a series of cyclic olefins, and found to be active without any loss of catalyst efficiency after repeated use.



81

Scheme 34. Magnetic ruthenium catalyst **81**.

CONCLUSION AND OUTLOOK

Different strategies on immobilization of well-defined ruthenium carbenes on different solid supports have been designed and resulted in active and recyclable heterogeneous olefin metathesis initiators. These catalysts can provide products that are of high purity, and some of them can be employed even in air and with reagent-grade commercial solvents. Nevertheless, the performance of the supported catalysts found to be dependent on parent homogeneous catalysts, the nature of the support materials as well as immobilization techniques employed. The obtained information concerning the different supported catalysts might be helpful in the design of further immobilized catalysts.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

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