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Polymer-Supported Well-Defined Metathesis Catalysts

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1. Introduction

Since its discovery, olefin metathesis[1] has experienced dramatic developments and is nowadays considered to be one of the most important C−C bond-forming reactions,[2−5] allowing for the synthesis of both well-defined, functional (block co-) polymers and complex organic molecules including medium-sized[6] and large ring structures.[1,7] The fact that these reactions can be carried out in an enantioselective way[8−12] widened the range of applications from commodity chemicals to the synthesis of optically active compounds relevant to pharmaceutical chemistry.

From a synthetic chemist's point of view, the applicability of metathesis to both polymer and organic chemistry must be regarded as a direct consequence of the achievements in organometallic chemistry, i.e., of catalyst and initiator development.[13−15] The development of well-defined, single-component metathesis catalysts paved the way for all types of metathesis-based reactions such as ring-opening metathesis polymerization (ROMP), 1-alkyne polymerization, cyclopolymerization, acyclic diene metathesis (ADMET) polymerization, cross-metathesis (CM), tandem metathesis, enyne metathesis, and ring-opening cross metathesis (Scheme 1).[1,9,16−21] In 2005, the main of this protagonists chemistry were awarded the Nobel Price in Chemistry.[22−24]

Michael R. Buchmeiser was born in Linz, Austria. He received his Ph.D. degree in Inorganic Chemistry in 1993 from the University of Innsbruck, Austria, working on early and late transition metal metallocenes. He was awarded an “Erwin Schrödinger Fellowship” and spent 1 year at the Massachusetts Institute of Technology (MIT, Cambridge, MA) within the group of Professor Richard R. Schrock (Chemistry Nobel Prize 2005) working on poly(metallocenylacetylene)s and fluorinated organomolybdenum compounds. In 1995 he accepted a position as an Assistant Professor at the University of Innsbruck, where he finished his “Habilitation” in Macromolecular Chemistry in 1998. From 1998 to 2004 he held a Faculty Position as Associate Professor. He received the 1998 Professor Ernst Brandl Research Award, the START Award-2001, as well as the Novartis Award 2001. He was offered Faculty Positions (Full Professor of Polymer Chemistry, Chair of Polymer Chemistry) at the University of Halle (Germany) in 2004, the University of Leoben (Austria) in 2005, and the Dresden University of Technology (Germany) in 2007, which he all declined. Instead, since December 2004 he holds a Faculty Position (Full Professor) at the University of Leipzig, Germany. In addition, since February 2005 he has been Vice Director and Member of Board at the Leibniz Institute of Surface Modification (IOM), Leipzig, Germany. His research interests focus on transition-metal-catalyzed polymerizations, surface modifications in general, heterogeneous polymeric systems and their applications in the areas of heterogeneous catalysis, separation and life sciences, as well as diagnostics. Since 2002 he has been a Member of the International Advisory Board of *Macromolecular Rapid Communications* and *Macromolecular Chemical Physics*; since 2007 he has been a Member of the Editorial Board for *The Open Macromolecules Journal*. Thus far he has published some 200 research papers and filed 15 patents.

Synthetic organic chemists have used polymer-immobilized reagents for quite a long time;[25−27] it soon became obvious that those metathesis reactions relevant to synthetic organic chemistry were best carried out with systems where the catalyst either could easily be separated[28−36] or was polymer bound. The use of supported catalysts in general entails some potential advantages. Thus, in the case where catalyst immobilization is permanent, contamination of the products with metal ions and/or ligands is low, particularly in the case where the deactivated species remains polymer bound. This is of particular relevance in pharmaceutical chemistry. While molybdenum-based initiators and their

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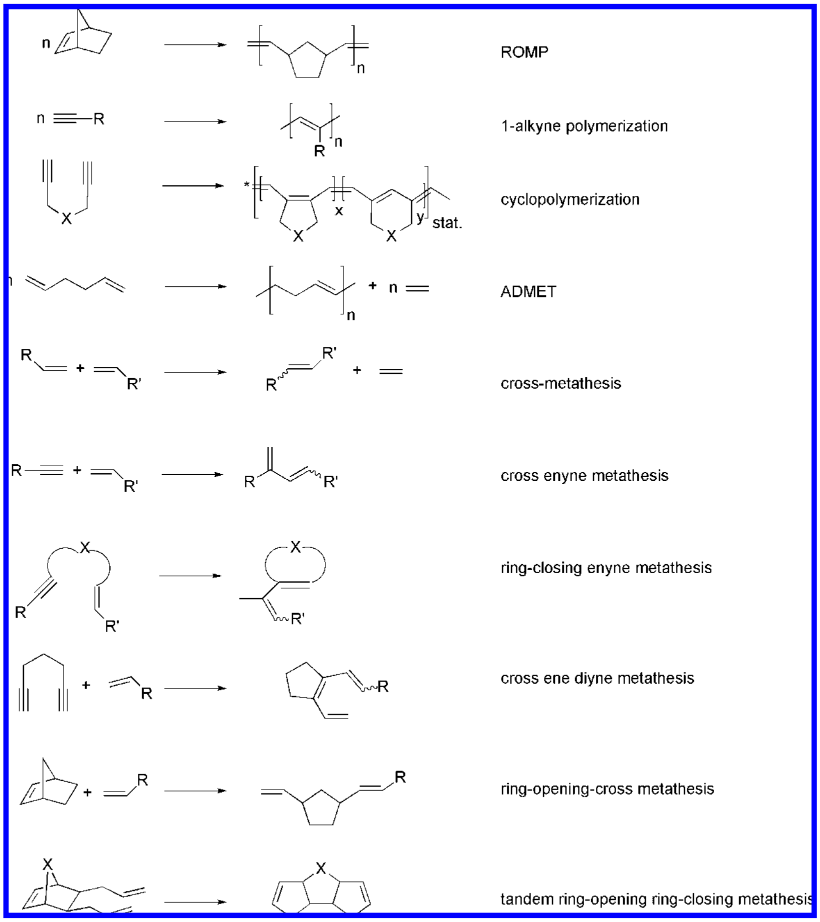
Scheme 1. Metathesis-Based Reactions



decomposition products, respectively, are easily removed from both monomeric and polymeric products by simply adding a base,[37,38] removal of ruthenium-based initiators requires tedious manipulations, in particular with polymeric products.[39−43] Apart from purity issues, modern metathesis catalysts significantly add to the total costs of a product; therefore, regeneration or reuse is highly desirable. Finally, supported catalysts in general offer access to high-throughput techniques and continuous flow reactors. Key issues associated with supported metathesis catalysts are the same as for other polymer-supported organometallics catalysts, i.e., (i) preservation of the high activities, (enantio-) selectivities, and reaction rates observed with homogeneous catalysts, (ii) ease of catalyst separation, (iii) (multiple) catalyst recycling, and (iv) metal- and contaminant-free products. In his introduction to a special issue in *Chemical Reviews*,[44] John A. Gladysz outlined the importance of distinguishing between a catalyst precursor and the active catalyst. As another critical point he identified the fact that the recycled species is (at least in most cases) the catalyst rest state which is seldom equivalent to the catalyst precursor. Additional critical issues summarized in his introduction were related to the quantitative evaluation of recycling efficiencies and reaction times. Within this context, he suggested rate measurements as a good criterion for recyclability and finally also addressed the importance of leaching measurements. Unfortunately, information on these points is only scarcely provided by most authors and can therefore not comprehensively be covered in this review, too.

However, this review intends to provide at least a comprehensive summary of the achievements made in the chemistry of polymer-supported, well-defined metathesis catalysts. It will *not* address any accomplishments made in the area of metathesis catalysts immobilized on metallic or inorganic supports such silica, alumina, or others. Similarly, immobilized binary or even ternary mixtures of precatalysts, auxiliaries, and activators on polymeric supports are not within the scope of the review and will, if at all, only be briefly mentioned.

Some excellent summaries on supported metathesis catalysts and related chemistry have been given recently;[45−54] nevertheless, in view of the rapid developments in this field, the present state of the art in supported, well-defined metathesis catalysts shall be summarized. The developments in this area will be discussed chronologically in terms of heterogenization methodology. Polymer-supported (immobilized) ruthenium-based Grubbs-type catalysts,[4,21,22,55] molybdenum-based Schrock-type catalysts,[11,14−16,18,19,23,56,57] as well as other catalytic systems shall be covered separately.

2. History of Polymer-Supported Metathesis Catalysts

The first reports on polymer-supported metathesis catalysts occurred in the early days of metathesis, i.e., in the 1970s, when metathesis catalysts still consisted of binary mixtures of a metal salt and an alkylating agent. Grubbs et al. described a poly(styrene)-supported molybdenum-based catalyst, which was obtained via treatment of polymer-bound diphenylphosphine with the progenitor $Mo(PPh_3)Cl_2(NO)_2$.[58] It was, after activation with $Me_3Al_2Cl_3$, active in the ring-closing metathesis (RCM) of 1,7-octadiene. Alternatively, a

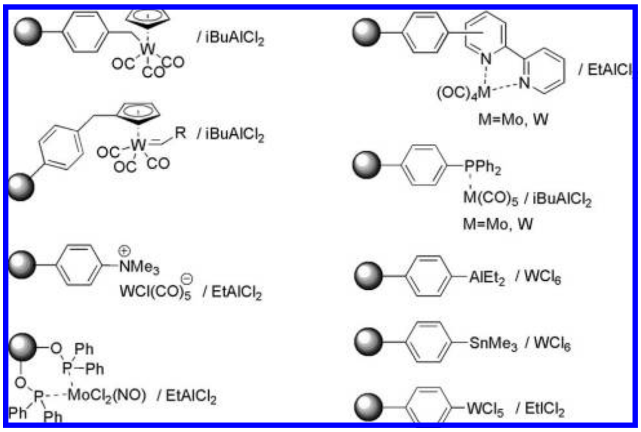


Figure 1. Representative selection of polymer-bound binary metathesis catalysts.

polymer-supported cocatalyst, i.e., polymer$-C_6H_4-SnMe_3$, was prepared, reacted with WCl_6, and used in the same reaction. Products were reported to be colorless after filtration. Neckers et al. also used polymer-bound biphenyl groups for immobilization of $Mo(CO)_6$ and $W(CO)_6$.[59] After activation with $EtAlCl_2$, the supported systems were used in the metathesis of 2-pentene in which the W-based system was the more active one. Repeated use of both systems was reported. Similarly, Buschmeyer et al. also described the immobilization of $W(CO)_6$ via polymer-bound diphenylphosphines. (Figure 1).

In an alternative route chloromethylated poly(styrene-*co*-divinylbenzene) (PS-DVB) was reacted with $Na[W(CO)_3(Cp)]$ (Cp = cyclopentadienyl).[60] Both supported catalysts were activated with *i*-$BuAlCl_2$ and used for the metathesis of *trans*-3-heptene. In these experiments the $[W(CO)_3(Cp)]$ fragment covalently bound to PS-DVB was found to be the only recyclable supported catalyst. In 1985 Uchida and Kori reported on the use of polymer-bound Et_2Al, Me_3Sn, and WCl_5 species.[61] The former two systems, however, did not show any metathesis activity in the presence of an olefin and WCl_6. The presence of additional free aluminum compounds was necessary to observe metathesis activity versus *cis*-2-octene. In contrast, polymer-bound $WCl_5EtAlCl_2$ showed some moderate metathesis activity. Berglund and Andersson used polymer-bound phosphanes to substitute a pyridine ligand in $Mo(NO)_2(pyridine)_2Cl_2$ and immobilize the catalyst. Addition of $EtAlCl_2$ gave the active species; however, large amounts of aluminum reagents were necessary to block the polar (hydroxyl) sites of the polar polymer.[62] Plessis et al. supported $W(CO)_6$ on a strong anion exchanger.[63] $EtAlCl_2$ was used as activator for the metathesis of 1-octene. Heveling reported on a poly(styrene)-supported $W(Cp)(CO)_3-$alkyidene, its activation with *i*-$BuAlCl_2$, and application of the thus formed metathesis catalyst in the metathesis of *trans*-3-heptene.[64] In general, activities and selectivities of these supported systems were comparably poor, which is in view of the properties of the parent binary catalytic systems not surprising. Basically no information on the metal content of the final products was provided; however, it may well be considered to be high. Finally, Li et al. reported on the ROMP of dicyclopentadiene (DCPD) on PS-supported WCl_6 and $(ArO)_3WCl_3$.[65,66] Activation was performed using Et_2AlCl. However, the nature of the supported catalyst remained unclear.

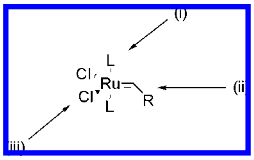
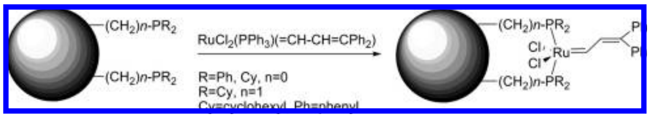


Figure 2. Possibilities of immobilizing Grubbs-type catalysts.

Scheme 2. Immobilization of $RuCl_2(PPh_3)_2(=CH-CH=CPh_2)$ on Phosphine-Derivatized Supports



Shortly after the appearance of well-defined, (mostly) high oxidation state metathesis catalysts,[13] their first supported versions appeared. Over a period of 10 years, the supports, catalysts, and immobilization techniques improved. The resulting supported metathesis catalysts are now finding their way into organic and pharmaceutical chemistry as well as chemical engineering.

3. Immobilized Grubbs-Type Catalysts

3.1. General Considerations

In principle, Grubbs-type catalysts can be immobilized via (i) one of the neutral, 2-electron donor ligands, i.e., the phosphine, the (substituted) pyridine, or the N-heterocyclic carbene (NHC), (ii) the alkylidene ligand, (iii) halogen exchange, and (iv) noncovalent interactions (Figure 2). In the following the different concepts are outlined in detail.

3.2. Immobilization via Phosphine Exchange

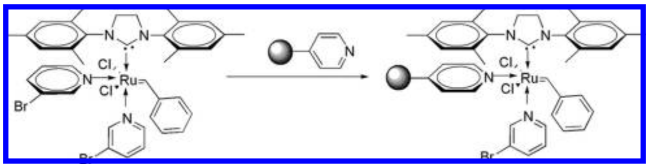
The first example of a supported Grubbs-type metathesis catalyst was reported by the group of Grubbs et al.[67] They used various phosphine-derivatized, low-cross-linked (2%) poly(styrene-*co*-divinylbenzene) (PS-DVB) resins for immobilization of $RuCl_2(PR_3)_2(=CH-CH=CPh_2)$ (Scheme 2).

The supported catalyst showed a significantly reduced activity in the metathesis of *cis*-2-pentene as well as in the ROMP of norborn-2-ene. Mainly the incomplete substitution of phosphine, phosphine chelation effects, and limited diffusion were made responsible for that. No information on the metal content of the products was provided. For purposes of comprehensiveness, it shall be stated that such a phosphine exchange was also found to be suitable for immobilizing the first-generation Grubbs catalyst on mesoporous silica (P-MCM.41) supports.[68] Not unexpectedly, poly(norborn-2-ene) prepared with this support shows broad polydispersities (PDIs) up to 7.2. In addition, the supported catalyst was reported to possess low RCM activity for diethyl diallylmalonate (DEDAM) and diallylamine, respectively, resulting in turnover numbers (TONs) ≤ 20.

3.3. Immobilization via Pyridine Exchange[69]

Kirschning et al. reported on the immobilization of both $RuCl_2(PCy_3)_2(=CHPh)$ and $RuCl_2(3\text{-}Br\text{-}py)_2(IMesH_2)(=CHPh)$ on a poly(vinylpyridine)-based resin (Scheme 3).[70] The latter was prepared via free-radical copolymerization of vinylpyridine with divinylbenzene aiming on a low degree of cross-linking. Turnover numbers were reported to be <20 in various RCM reactions. A reduction in activity to 10% after the fifth cycle was reported for the multiple reuse of

Scheme 3. Immobilization of a Grubbs-Type Catalyst via Pyridine Exchange



the thus supported system in the RCM of DEDAM. No information on the ruthenium content of the products was provided.

3.4. Immobilization via the N-Heterocyclic Carbene (NHC)[69]

The first ruthenium-based metathesis catalyst immobilized via the N-heterocyclic carbene was reported by Blechert et al.[71] 4-(Poly(styrene-*co*-divinylbenzene)methyloxymethyl)-1,3-dimesityl-4,5-tetrahydrimidazolin-2-ylidene was used for generation of the corresponding free carbene and reacted with $RuCl_2(PCy_3)_2({=}CHPh)$ to form the supported catalyst (Figure 3).

This supported version of Grubbs' second-generation metathesis catalyst was successfully used in RCM, ring-opening-cross and enyne metathesis reactions, and easy to handle. Reported TONs were in the range of 20. By switching to the Hoveyda version of this type of catalyst, an improved recyclability of the support was achieved.[72] Since the Merrifield support that was chosen for the synthesis of these supported catalysts represents a swollen, low-cross-linked network, reactions were diffusion controlled and increased reaction times were required.

In order to overcome this problem, both the groups of Buchmeiser et al. and Hoveyda et al. aimed at the synthesis of nonporous supports suitable for either high-throughput screening or continuous flow experiments, e.g., monolithic supports. Hoveyda et al. immobilized the Grubbs−Hoveyda catalyst on monolithic silica rods.[73] Using a ROMP-based protocol, Buchmeiser et al. were able to synthesize polymeric functionalized monoliths.[46,74−78] These were designed in a way that only interparticle porosity was generated, whereas the structure-forming microclobules were virtually nonporous. Taking advantage of the "living" character of ruthenium-catalyzed ROMP used for their synthesis and the high tolerance of the catalytic system toward different functional monomers, cationic N-heterocyclic carbene (NHC) precursors were grafted onto the surface. Tentacle-like polymer chains attached to the monolith's inner surface were formed. The free NHCs necessary for catalyst formation were generated by passing a strong base such as 4-dimethylaminopyridine (DMAP) over the support. In a last step, the catalyst was formed and simultaneously immobilized by passing a solution of $RuCl_2(PCy_3)_2({=}CHPh)$ over the rigid rod (Scheme 4).

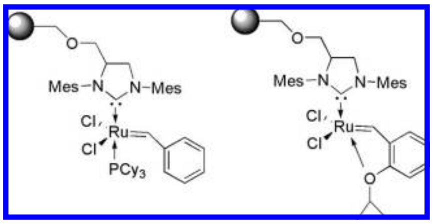
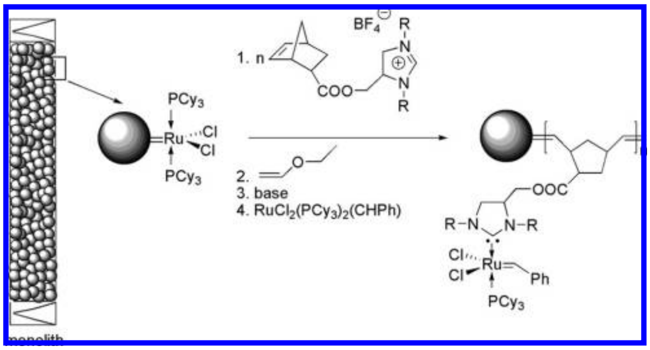


Figure 3. Grubbs- and Grubbs−Hoveyda-type catalyst immobilized via the NHC.

Scheme 4. Immobilization of Grubbs' Second-Generation Catalyst on a ROMP-Derived Monolith

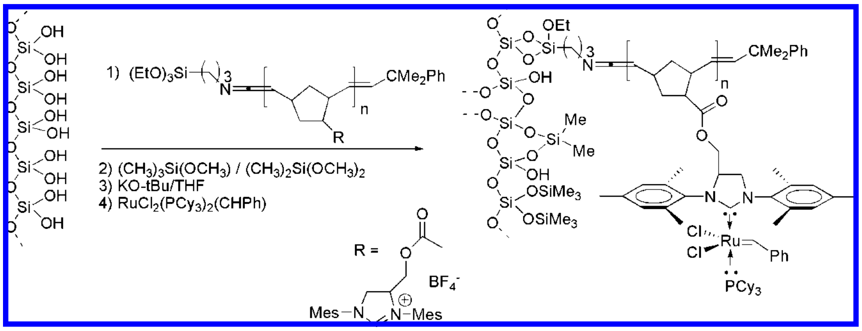


Loadings of up to 1.4 wt % of Grubbs catalysts were achieved. Monolith-immobilized metathesis catalysts prepared by this approach showed high activity in various metathesis-based reactions such as ROMP and RCM. Use of chain-transfer agents (CTAs, e.g., *cis*-1,4-diacetoxybut-2-ene, DEDAM, 2-hexene) allowed for regulation of the molecular weight of the polymers, in particular that of poly(cyclooctene). The presence of CTAs additionally enhanced the lifetime of the catalytic centers by reducing the average concentration of ruthenium methylidenes, thus allowing for prolonged use of these systems. Additionally, both the tentacle-type structure and the designed microstructure of the support reduced diffusion to a minimum. In a benchmark reaction with DEDAM, these properties directly translated into comparably high average turnover frequencies (TOFs) of up to 0.5 s^{-1}.

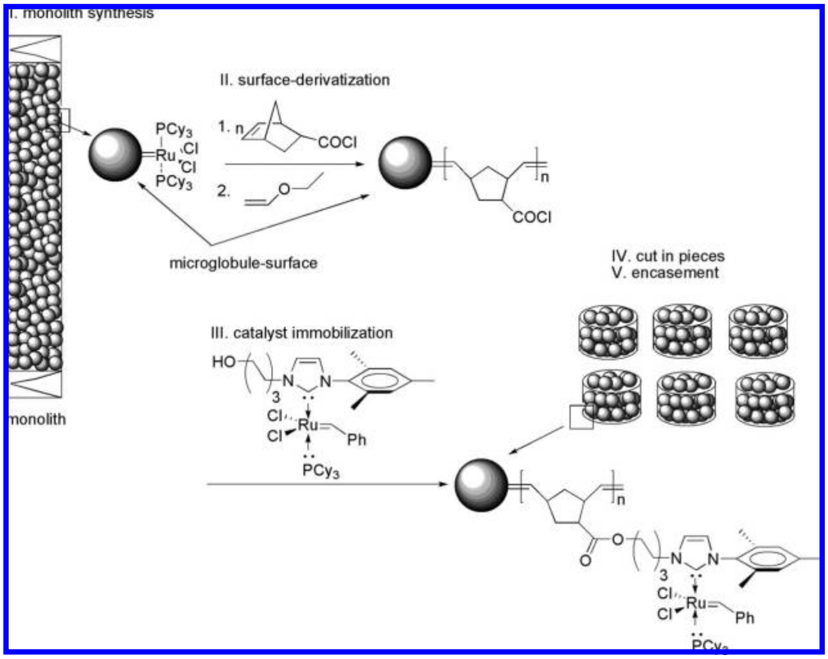
In an effort to synthesize a polymer/silica hybrid-supported version of this catalyst, Buchmeiser et al. polymerized the cationic NHC precursor 1,3-di(1-mesityl)-4-{[(bicyclo[2.2.1]hept-5-en-2-ylcarbonyl)oxy]methyl}-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate.[79] Reaction of this monomer with $RuCl_2(PCy_3)_2({=}CHPh)$ in methylene chloride at 45 °C resulted in complete consumption of the initiator and formation of an oligomer with a degree of polymerization (DP) of 7. Alternatively, polymerizations with the Schrock initiator $Mo(N\text{-}2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$[80] were performed in methylene chloride at ambient temperature. The theoretical DP of 7 was in excellent accordance with a DP of 7 ± 1 found via end-group analysis using ^1H NMR. An end group suitable for oligomer grafting on silica was introduced by reacting the living polymer with an excess of *ω*-(triethoxysilyl)propylisocyanate. Next, telechelic oligo-(1,3-di(1-mesityl)-4-{[(bicyclo[2.2.1]hept-5-en-2-ylcarbonyl)oxy]methyl}-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate) was reacted with silica. Reaction of the grafted supports with KO−*t*Bu yielded the free carbene which was subsequently reacted with $Cl_2Ru({=}CHPh)(PCy_3)_2$ to yield the immobilized second-generation Grubbs catalyst (Scheme 5).

The ruthenium content of the solution as measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) revealed catalyst loadings of 0.1−0.5 wt %. RCM carried out with DEDAM as a benchmark gave TONs ≤ 80 for a stirred batch. Complementary to the above-mentioned grafting approach, coating techniques[81] using oligo-(1,3-di(1-mesityl)-4-{[(bicyclo[2.2.1]hept-5-en-2-ylcarbonyl)oxy]methyl}-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate) were applied, leading to a surface-derivatized silica 60 containing 90 *μ*mol of NHC precursor. Conversion into the initiator was carried out as described for the grafted

Scheme 5. Polymer/Silica Hybrid-Supported Version of Grubbs' Second-Generation Catalyst



Scheme 6. Immobilization of a Second-Generation Grubbs-Type Catalyst via the NHC on a Monolithic Support



analogue, resulting in a support containing 4.1 μmol of catalyst/g. Good results were obtained with these coated supports in the RCM of DEDAM and 1,7-octadiene. Thus, TONs were 210 and 55, respectively, for these compounds under batch conditions. In all cases, ruthenium measurements by means of ICP-OES revealed quantitative retention of the original amount of ruthenium at the support within experimental error, thus offering attractive access to virtually metal-free products.[79] Finally, Buchmeiser and Fürstner et al. reported on the immobilization of a Grubbs-type catalyst on a ROMP-derived monolith.[82] The synthetic concept entailed the manufacture of the monolithic structure via ROMP, its in situ functionalization with norborn-2-ene carboxylic chloride, and reaction with $RuCl_2(PCy_3)(NHC)({=}CHPh)$ (NHC = 1-(2,4,5-trimethylphenyl)-3-(6-hydroxyhexyl)-imidazol-2-ylidene)[83] (Scheme 6).

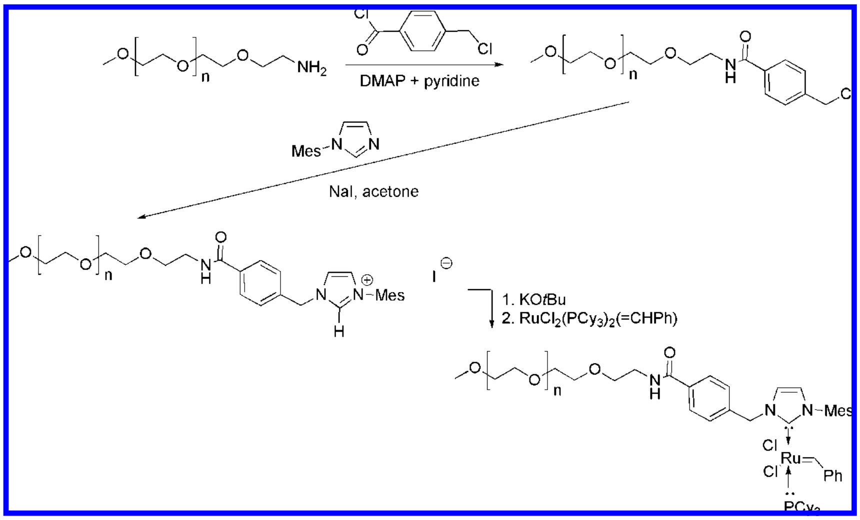
The monolithic disk-immobilized catalyst was used in various metathesis-based reactions including RCM, ring-opening cross metathesis, and enyne metathesis. Using 0.23−0.59 mol % of the supported catalyst, TONs up to 330 were achieved. Metal leaching was reported to be <3%.

In 2005 Grubbs et al. reported on the synthesis of a water-soluble Grubbs-type catalyst bound to poly(ethylene glycol) (PEG). Synthesis was accomplished by transforming the amino-telechelic PEG into an imidazolium-telechelic one. This precursor was transformed into the free NHC and subsequently reacted with $RuCl_2(PCy_3)_2({=}CHPh)$ to yield the desired PEG-supported catalyst (Scheme 7).[84]

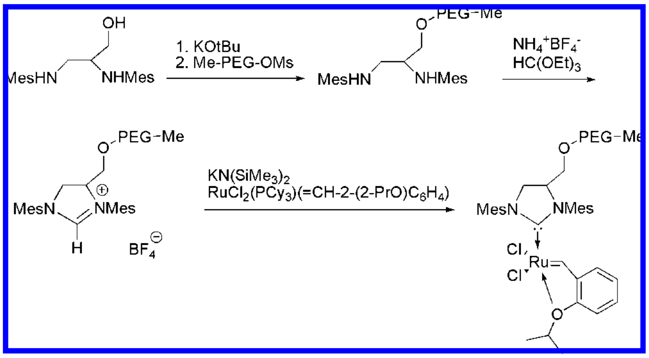
It was used for both the ROMP of water-soluble norborn-2-ene-based monomer as well as various RCM reactions. Using 5 mol % of the polymer-bound catalyst TONs in RCM, however, were comparably low (<17). An alternative approach to PEG-bound second-generation Grubbs catalyst was reported by the same group.[85] Here, instead of linking the catalyst via the N-substituent of the NHC to the PEG support, they chose an approach that entailed the use of 4-hydroxymethyl-1,3-dimesitylimidazolium tetrafluroborate[79] linked via an ether linkage to the PEG support (Scheme 8). Additionally, they employed the first-generation Grubbs−Hoveyda catalyst for immobilization, thus generating a PEG-supported version of the second-generation Grubbs−Hoveyda catalyst.

With this catalyst in hand, a series of RCM and cross-metathesis reactions was reported to proceed in high yields using 5 mol % of the supported catalyst. No information on the metal content of the products was provided. Finally, Weck et al. reported on the synthesis of a poly(norborn-2-ene)-supported version of a Grubbs-type catalyst (Figure 4) via copolymerization of *N*-mesityl-*N′*-(norborn-5-ene-2-ylcarbonyloxyundecyl) imidazolium bromide with octyl(norborn-5-ene-2-yl)carboxylate followed by deprotonation and reaction with $RuCl_2(PCy_3)_2({=}CHPh)$.[86] The final supported catalyst was reported to be active in the RCM

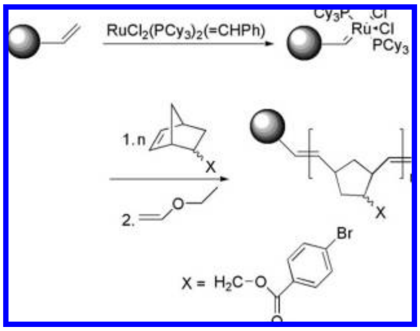
Scheme 7. PEG-Supported Unsymmetrical Second-Generation Grubbs-Type Catalyst



Scheme 8. PEG-Supported Symmetrical Second-Generation Grubbs−Hoveyda-Type Catalyst



Scheme 9. Synthesis of a Supported First-Generation Grubbs Catalyst via Alkylidene Exchange and Use for the Surface Grafting of Norborn-2-ene Derivatives



of DEDAM to yield ruthenium-free products. However, neither the ruthenium content of the products nor the limits of detection for ruthenium were provided.

3.5. Immobilization via Alkylidene Exchange[69]

In 1999 Barrett et al. reported on the reaction of vinyl-substituted supports (i.e., poly(vinylstyrene-*co*-divinylbenzene)) with $RuCl_2(PCy_3)_2({=}CHPh)$ (Scheme 9).[51,87]

The resulting supported metathesis catalyst was used for the synthesis of high-capacity, functional poly(norborn-2-ene)-loaded supports for use in combinatorial chemistry and resembled both the precipitation polymerization-derived systems and the ROMP-derived monolithic supports described by the group of Buchmeiser et al. in terms of capacity (expressed in mmol/g).[37,38,88−93]

Through an identical approach this type of supported catalyst was used as a boomerang catalyst in RCM.[94,95] Thus, the polymer-supported catalyst $[\text{polymer}-CH{=}RuCl_2(PCy_3)_2]$ was used in various RCM reactions. However, fast reduction in catalyst activity was observed, thus preventing effective recycling. Though the longevity of such systems can in fact be enhanced by adding “regenerating agents” such as styrene or bis(acetoxy)but-2-ene-1,4-diol,[76] their multiple use was still hindered by continuous catalyst deterioration, thus preventing the back reaction with the vinyl-substituted support. As a consequence, ruthenium contamination of the products was high (up to 0.51 wt % = 5100 ppm without further purification). In principle, the idea of such a supported catalyst acting in solution and returning to the support is in fact very attractive; however, the inherent instability of intermediate formed ruthenium methylidenes[96] is a severe impediment in the realization of this concept (Scheme 10). At this point it is worth mentioning that Hoveyda et al. provided full evidence for the general applicability of the boomerang concept.[97] In an appealing study, they silica-immobilized Grubbs−Hoveyda catalysts based on different (deuterated) NHCs. Cross-over was clearly observed by NMR spectroscopy, thus proving the boomerang mechanism.

These intrinsic properties were in fact confirmed by work of Barrett et al. and Nolan et al.[98−101] They extended this concept by the use of $RuCl_2(PCy_3)(IMesH_2)({=}CHPh)$, $RuCl_2(PCy_3)(IMes)({=}CHPh)$, $RuCl_2(PCyp_3)(IMes)({=}CHPh)$, and $RuCl_2(PCy_3)(P\textit{i}Pr_3)({=}CHPh)$ (where $IMesH_2$ = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene, IMes = 1,3-dimesitylimidazol-2-ylidene, Cyp = cyclopentyl) instead of $RuCl_2(PCy_3)_2({=}CHPh)$. Though ruthenium contaminations were reported to be lowered by a factor of 10 with these systems, no real breakthrough in terms of activity was achieved. With the report of Hoveyda et al. on a recyclable, ruthenium-based metathesis

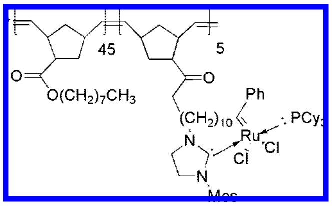
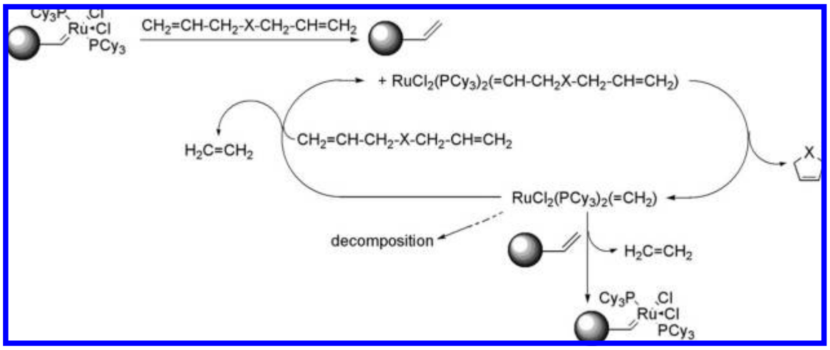


Figure 4. ROMP-derived supported unsymmetrical second-generation Grubbs-type catalyst.

Scheme 10. Concept and Drawbacks of Polymer-Supported Boomerang Catalysts

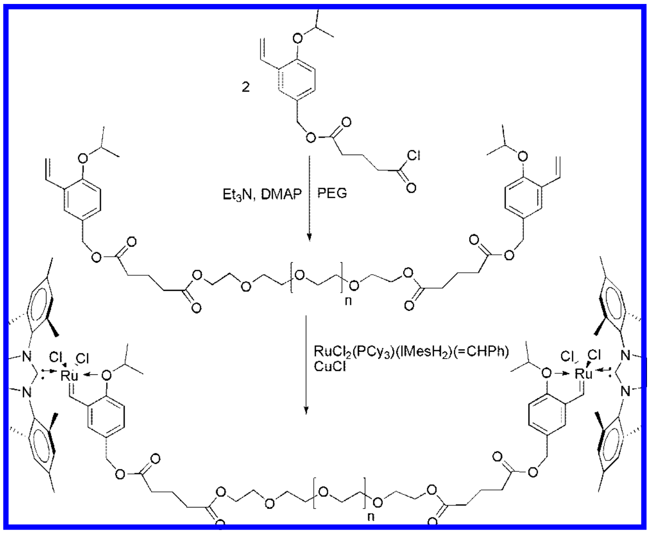


catalyst[102] it became clear that the particular alkylidene used in this type of initiator, i.e., a 2-(2-PrO)-benzylidene, should also allow for an enhanced efficiency of supported boomerang-type catalysts. Yao, Hoveyda et al., Blechert et al., Dowden et al., and Lamaty et al. investigated such systems.[54,103−105] Thus, Yao prepared a soluble poly(ethylene glycol) (PEG)-supported boomerang version of the Grubbs−Hoveyda catalyst (Figure 5).[103] It could be recycled up to 8 times without significant loss in activity. No information on the ruthenium content of the product was provided.

The same group also reported on α,ω-ditelechelic PEG with two Grubbs−Hoveyda moieties attached to both ends of the polymer.[106] The synthesis entailed reaction of PEG with glutaric acid chloride mono-3-vinyl-4-(2-PrO)-benzylester in the presence of triethylamine and 4-dimethylaminopyridine (Scheme 11). The thus obtained divinyl compound was then reacted with $RuCl_2(PCy_3)(IMesH_2)(=CHPh)$ to yield the supported system. It was used up to 10 times in RCM reactions (52 and 5 mol % catalyst) without significant reduction in educt conversion. They also pointed out the relevance of the structure of the alkyl group in the 2-alkoxybenzylidene ligand on the stability and thus recyclability of the catalyst by comparing their ligand to the one prepared by Lamaty et al. (vide infra).[105]

This very similar approach chosen by Lamaty et al.[105] entailed immobilization of both the first- and the second-generation Grubbs catalyst on poly(ethylene glycol). The resulting PEG-bound second-generation Grubbs−Hoveyda catalyst was reported to display superior recyclability in RCM compared to the corresponding PEG-bound first-generation Grubbs−Hoveyda system. However, no information on the ruthenium content of the products was provided. Hoveyda et al. described a dendrimer-bound system (Figure 5) that showed significantly increased persistence in RCM, ring-opening−ring closing, and ring-opening−cross (ROC) metathesis reactions. The ruthenium loss was comparably high (≤8%); however, the authors did not make clear whether this was a result of the inherent instability of the supported catalyst or of its comparably good solubility in organic solvents.

Scheme 11. Synthesis of a Ditelechelic PEG-Supported Grubbs−Hoveyda Catalyst



Dowden described a “self-supporting” version of the Grubbs−Hoveyda catalyst using amino-functionalized Tentagel as support.[107,108] The latter was used to synthesize a 2-alkyloxystyryl derivative which was then reacted with the first-generation Grubbs catalyst to form the supported Grubbs−Hoveyda-type catalyst (Figure 6).[109] The supported catalyst was applied to various RCM and cross-metathesis

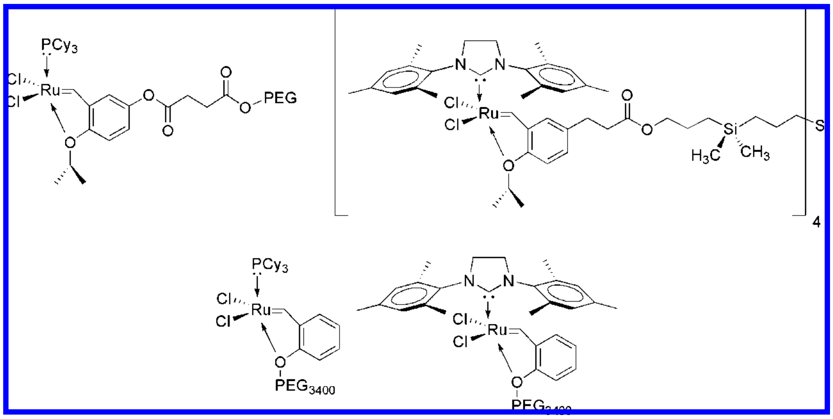


Figure 5. Synthesis of PEG- and dendrimer-supported Grubbs−Hoveyda-type catalysts.

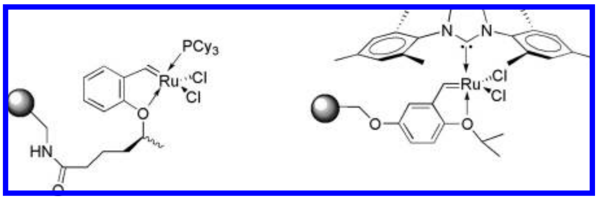
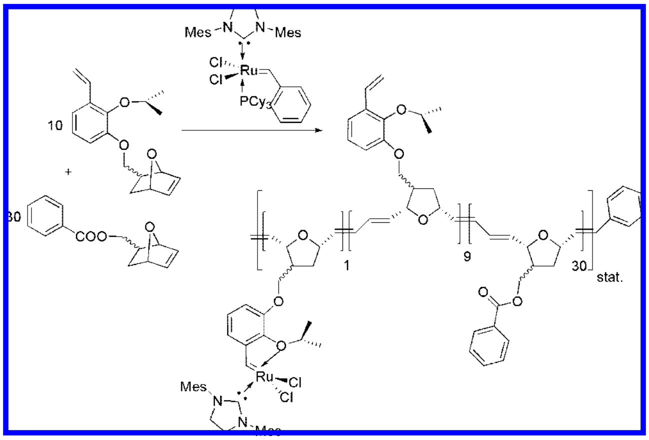


Figure 6. Tentagel- and PS-DVB-supported first-generation Grubbs and Grubbs−Hoveyda catalysts.

Scheme 12. "Self-Supporting" Catalyst Formed via Simultaneous Alkylidene Exchange−Polymerization Reaction



reactions. In contrast to other supported Grubbs−Hoveyda catalysts, yields were comparatively low. In addition, the supported catalyst displayed a quite limited recycling propensity. No information on the metal content of the products was provided.

Blechert et al. described a Merrifield resin-supported version of the Grubbs−Hoveyda catalyst (Figure 6).[72] It was used in various cross-metathesis reactions and could in fact be multiply reused. However, prolonged reaction times were necessary after the second run in order to obtain quantitative yields, suggesting catalyst deterioration. Blechert et al. also reported on a "self-supporting" version of Hoveyda's catalyst.[107,108] It entailed reaction of 7-oxanorborn-2-ene-substituted 2-(2-PrO)-styrene with $\mathrm{RuCl_2(PCy_3)(IMesH_2)}$ (═CHPh), leading to formation of a 7-oxanorborn-2-ene-substituted Grubbs−Hoveyda catalyst, which undergoes spontaneous polymerization to form a polar matrix of poly(7-oxanorborn-ene) with the catalyst bound to it (Scheme 12). The good solubility in organic solvents that was reported suggests a low degree of cross-linking (if any).

7-Oxanorborn-2-ene-5-ylmethyl benzoate was used as comonomer to avoid formation of vicinal catalytic sites that might undergo bimolecular decomposition. In the RCM of *N*-tosyl-*N*,*N*-diallylamine this system could be recycled 7 times with a total TON of 760. The ruthenium content in the polymer was <40 ppm as determined by total reflection X-ray fluorescence (TRXF) analysis. This example is another very nice, yet rare illustration on the importance of "vacant sites" that can be used for the rebinding of catalytic species.[88] Grela et al. reported on a butyldiethylsilyl polystyrene (PS-DES) supported Hoveyda-type catalyst (Figure 7).[110]

It could be recycled 5−6 times, resulting in TONs of up to 110 in the synthesis of cyclic structures based on trisubstituted double bonds. Disappointingly, no activity was observed in the RCM of dienes with two nonterminal alkene groups. The products were reported to contain up to 1000 ppm of ruthenium. Finally, Blechert et al. described the synthesis of a Grubbs−Hoveyda-type catalyst immobilized on a highly hydrophilic, commercially available PEGA-NH$_2$ support (Scheme 13).[111] Using 5 mol % of this supported catalyst various cross-metathesis and RCM reactions were successfully run in both methanol and water. Reported yields were in the range of 6−100%.

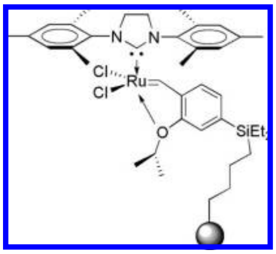
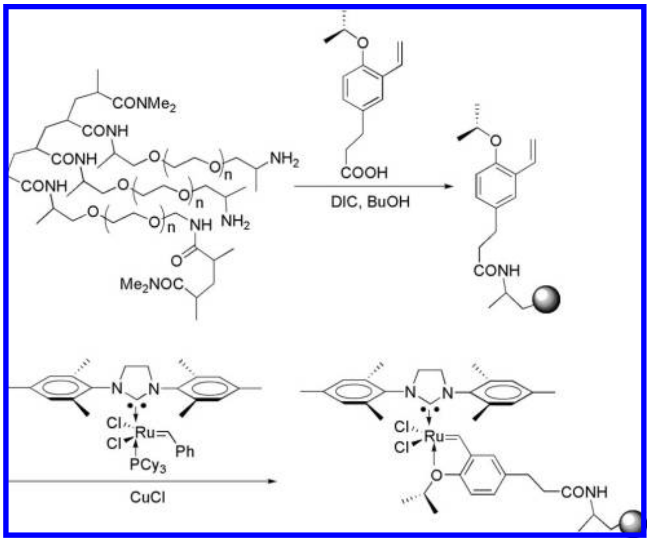


Figure 7. PS-DES-supported Grubbs−Hoveyda-type catalyst.

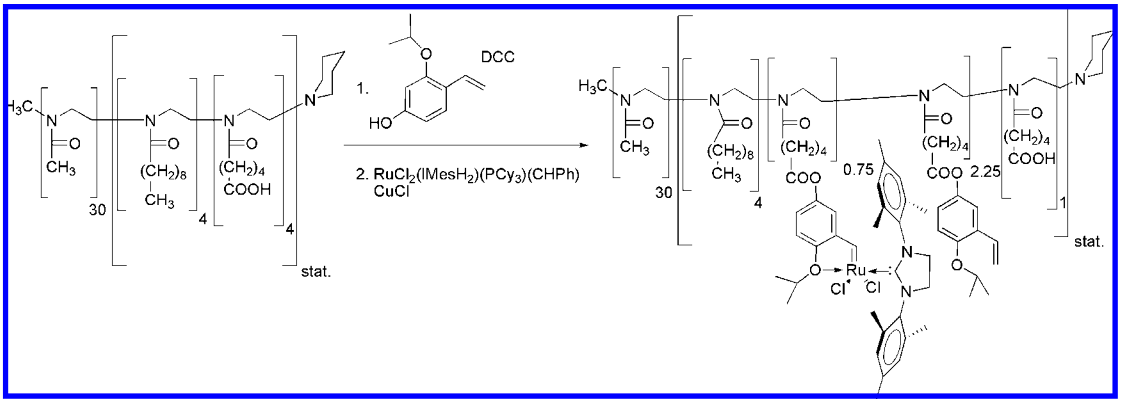
Scheme 13. Synthesis of a PEGA-Supported Hoveyda-Type Catalyst



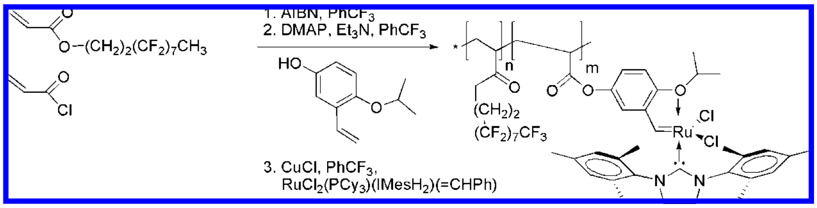
Weberskirch et al. reported on the synthesis of a poly(2-oxazoline)-derived block-copolymer-immobilized Grubbs−Hoveyda catalyst.[112] The block copolymer was designed in a similar way to the one reported by Buchmeiser et al. (vide infra)[113] and should probably allow for running RCM reactions under micellar conditions. However, only simple RCM reactions were reported. 2-(2-PrO)-4-hydroxystyrene was bound to the block copolymer via an ester linkage and used for catalyst immobilization (Scheme 14).

Unfortunately, no information on the critical micellar concentration was provided by the authors. Therefore, the reason for the rapid decrease in activity that was observed cannot be rationalized. Ruthenium concentrations in the product, however, were reported to be <1%, indicating a virtually quantitative retention of the metal inside the block copolymer in any form ever. The first polymer-supported system that could be used in a fluorous, biphasic system was elaborated by the group of Yao et al. They reported on the synthesis of poly(fluoroacrylate)-modified Grubbs−Hoveyda catalysts and their use in biphasic reactions.[114] The synthesis entailed copolymerization of a fluroacrylate with acrylic chloride followed by esterification with 2-(2-PrO)-5-hydroxystyrene. In a final step, the supported catalyst was prepared via reaction with $\mathrm{RuCl_2(PCy_3)(IMesH_2)}$(═CHPh) (Scheme 15). Excellent recyclability and yields were reported for a series of RCM, cross-, and enyne metathesis reactions.

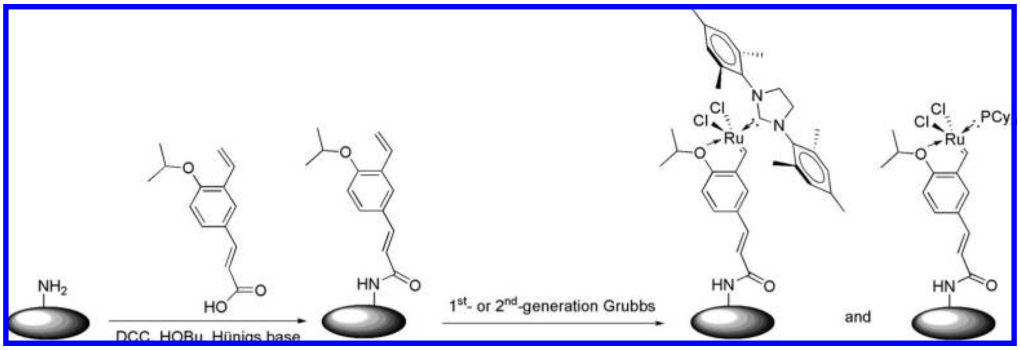
Scheme 14. Grubbs−Hoveyda Catalyst Supported on a Poly(2-oxazoline)-Derived Block Copolymer for Use in Micellar Catalysis



Scheme 15. Poly(fluoroacrylate)-Supported Grubbs−Hoveyda Catalyst for Use in Biphasic Catalysis



Scheme 16. First- and Second-Generation Grubbs−Hoveyda Catalysts Immobilized onto PE and PP Surfaces



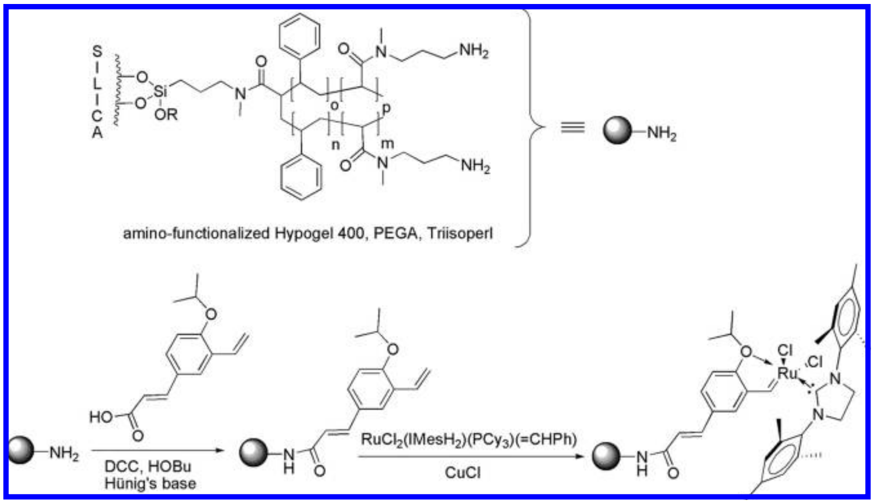
Haag et al. reported on a concept for the surface immobilization of both the first- and the second-generation Grubbs−Hoveyda catalyst onto various polymeric surfaces such as amino-functionalized poly(ethylene) (PE) and poly(propylene) (PP) membranes.[115] These were reacted with 3-vinyl-4-(2-PrO) cinnamic acid under standard peptide coupling conditions to yield the Hoveyda-ligand-functionalized polymer supports. These were then in a final step reacted with the first- or second-generation Grubbs catalyst to yield the corresponding polymer-supported first- and second-generation Grubbs−Hoveyda catalysts (Scheme 16). Recycling experiments carried out in form of selected RCM reactions, however, revealed a relatively poor recyclability. No information on the ruthenium content of the final product was provided.

More recently, Bannwart et al. called the critical role of the nature of a support for the performance of boomerang-type, supported first- and second-generation Grubbs−Hoveyda catalysts into mind.[116,117] For their investigations they used four different types of amino-functionalized supports, i.e., a Hypogel 400, poly(acrylamide-*co*-ethelene glycol) (PEGA), and Trisoperl as well as a hybrid polymer/silica support (Scheme 17).

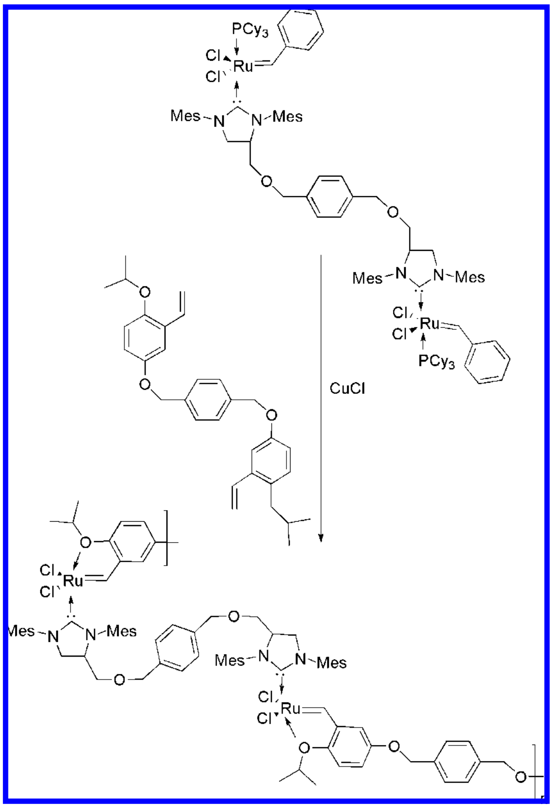
Several RCM, cross-metathesis, and ROC-metathesis reactions were carried out using 1 and 2.5 mol % of the supported catalysts, respectively. The ruthenium contamination of the products was reported to be within the range of 285−685 ppm. While the second-generation Grubbs−Hoveyda catalyst supported on the hybrid polymer−silica support was reported to perform best, no information on the porosity, pore size distribution, or any other physical data of the support was provided, thus making any correlations of catalyst structure and activity with the support hard to perform. Using the same supported systems, these authors performed various RCM reactions in CO_2 under supercritical conditions.[118] Aside from some positive yet not spectacular effects on recyclability, use of this medium allowed for reducing the ruthenium contaminations to 20 ppm. Lee et al. reported on the synthesis of a self-supported oligomeric Grubbs−Hoveyda catalyst using both dimeric NHC ligands and dimeric 2-(2-PrO-vinyl)styrenes (Scheme 18).[119] The resulting oligomeric, insoluble species consisted mainly of catalyst and was used in the RCM of *N*,*N*-diallyl-*N*-tosylamine. Multiple use, however, on a 5 mol % of catalyst base was reported. Product contamination with ruthenium as determined by ICP-OES was 16 ppm.

Bergbreiter et al. reported on the use of 2-(2-PrO)-styr-4-yl-terminated poly(isobutylene) and its use as a support for the second-generation Grubbs catalyst. The resulting poly(isobutylene)-supported second-generation Grubbs−

Scheme 17. Immobilization of a Second-Generation Grubbs−Hoveyda Catalyst on a Polymer−Silica Hybrid Support



Scheme 18. Self-Supported Grubbs−Hoveyda-Type Catalyst Based on Dimeric NHCs and Benzylidene Ligands



Hoveyda catalyst (Figure 8) was successfully used in various RCM reactions and in the ROMP of 7-oxanorborn-5-ene-2,3-dicarboxylic anhydride and 7-oxanorborn-5-ene-2,3-dicarbimide. The products obtained from RCM contained up to 1000 ppm ruthenium; nevertheless, a successful recycling was reported, however, again on a 5 mol % of catalyst base.

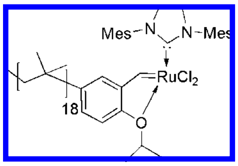
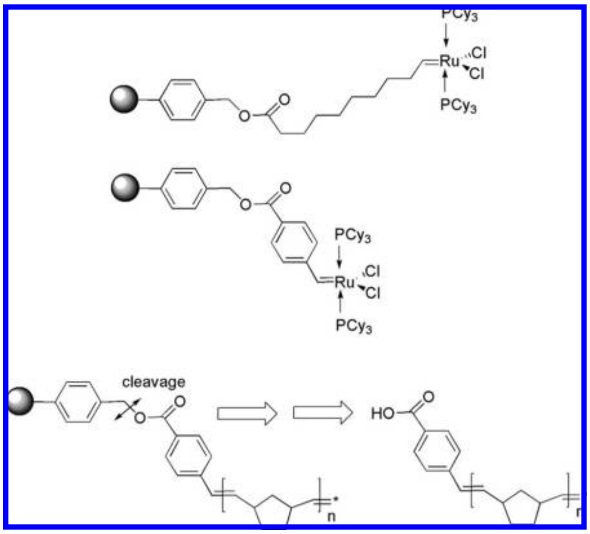


Figure 8. Poly(isobutylene)-supported Grubbs−Hoveyda catalyst.

Scheme 19. Surface ROMP/Cleavage Protocol Using Polymer-Supported Metathesis Catalysts

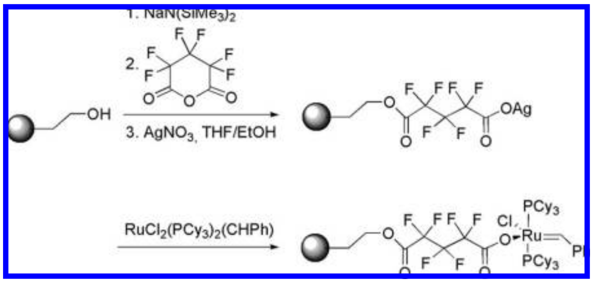


Finally, for purposes of completeness, it is worth mentioning that Fontaine et al. described undec-8-ene-1-oylated poly(styrene-*co*-divinylbenzene) and its use for immobilization of the first-generation Grubbs catalyst (Scheme 19).[120] The supported system that was very similar to the original one established by Barrett et al.[51,87] was used for the surface ROMP of norborn-2-ene. The poly(norborn-2-ene) that was formed could be cleaved from the support via hydrolysis of the ester moiety.

3.6. Immobilization Through Halogen Exchange[69]

On the basis of their work on carboxylic acid derivatives of the first-generation Grubbs catalyst,[121] the group of Mol et al. was the first to report on the synthesis of a poly(styrene-*co*-divinylbenzene)- (PS-DVB) supported version of $RuCl_2(PCy_3)_2({=}CHPh)$ using a perfluorated dicarboxylate.[122] Hydroxyethyl-PS-DVB (1 wt % DVB) was reacted with hexafluoroglutaric anhydride. The intermediate formed polymer-bound carboxylic acid was converted into the silver salt and finally reacted with $RuCl_2(PCy_3)_2({=}CHPh)$ to yield PS-DVB-$CH_2OCOCF_2CF_2CF_2COORuCl(PCy_3)_2({=}CHPh)$ (Scheme 20).

Scheme 20. Immobilization of the First-Generation Grubbs Catalyst on a Hydroxyl-Functionalized PS-DVB Support via Halogen Exchange



A rapid decrease in reactivity was observed during consecutive cycles in the RCM of DEDAM, and a comparably low total TON of ca. 60 was reported for this reaction. In addition, the ruthenium content of the products was as high as 3800 ppm. It is worth mentioning that the greatest loss in activity was observed after the first cycle. This in fact supports the structure of the catalyst proposed by the authors. Further information on that system was provided by Buchmeiser et al. They demonstrated that Grubbs-type catalysts containing the ruthenium monochloro-mono(trifluoroacetate) motif are in fact unstable in solution and rearrange into the corresponding ruthenium dichloro and ruthenium bis(trifluoroacetate) complexes (Scheme 21).[123]

A similar rearrangement of the supported catalyst would in fact account for the high ruthenium concentrations in the first batch since it would result in release of substantial amounts of the initially polymer-bound catalyst into solution. In an alternative approach, Buchmeiser et al. prepared a monolith-supported second-generation Grubbs catalysts containing the saturated IMesH$_2$ ligand by the synthetic protocol summarized in Scheme 22.[77,124−126]

Surface derivatization of the monolith was carried out with 7-oxanorborn-2-ene-5,6-dicarboxylic anhydride followed by conversion of the grafted poly(anhydride) into the corresponding poly silver salt. This poly silver salt was used for halogen exchange with the second-generation Grubbs catalyst RuCl$_2$(PCy$_3$)(IMesH$_2$)(=CHPh). In the benchmark reaction with DEDAM TONs close to 1000 were achieved. The ruthenium content in the final products was as low as 3.5 ppm, illustrating the high stability of this supported system.

Model reactions revealed that only one chloride is exchanged by the silver carboxylate, while the second chloride remains unaffected. However, it is worth mentioning that these systems benefit from the presence of free silver carboxylate groups, which actually acted as a reversible scavenger for phosphine. Thus, use of monocarboxylic acids such as 7-oxanorborn-2-ene-5-carboxylic acid instead of the 7-oxanorborn-5-ene-2,3-dicarboxylic anhydride resulted in a supported catalyst that showed significantly reduced TONs in the RCM of DEDAM. In addition and in contrast to supported systems based on pendant silver carboxylates, high concentrations of phosphine were monitored in the effluent applying a continuous flow setup. Again, use of silica as support results in low TONs around 120. This comparably low activity of silica-based systems was attributed to both the nonreversible scavenging of the phosphine by residual silanol groups and diffusion-controlled reactions and can in fact be overcome by use of the above-mentioned monolithic systems.

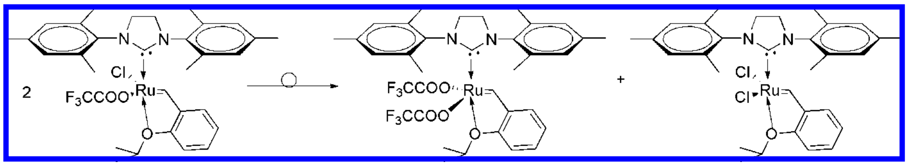
In an effort to further enhance the reactivity of ruthenium-based metathesis catalysts and avoid the use of phosphine ligands, Buchmeiser et al. reported on numerous variations in Grubbs−Hoveyda-type catalysts of the general formula RuCl$_2$(IMesH$_2$)(=CH-2-(2-PrO-C$_6$H$_4$)). Among the most important findings was that exchange of chlorine by a strongly electron-withdrawing group in fact enhanced the reactivity of these systems without sacrificing their high stability.[123] Thus, Ru(CF$_3$CO$_2$)$_2$(IMesH$_2$)(=CH-2-(2-PrO)-C$_6$H$_4$) was a highly active catalyst in RCM both at 45 and 20 °C, respectively, exceeding known ruthenium-based catalysts in catalytic activity. TONs up to 1800 and 1400, respectively, were achieved in the RCM of DEDAM. High activity was also observed in enyne metathesis and ROC metathesis using norborn-5-ene and 7-oxanorborn-5-ene derivatives. Supported versions were also synthesized by immobilizing RuCl$_2$(IMesH$_2$)(=CH-2-(2-PrO)-C$_6$H$_4$) on a perfluoroglutaric acid-derivatized hydroxymethylated Merrifield resin.[123] An immobilization protocol very similar to the one reported by Mol et al.[122] was chosen. The final supported catalyst, i.e., Ru(polymer−CH$_2$−O−CO−CF$_2$−CF$_2$−CF$_2$−COO)(CF$_3$CO$_2$)(=CH-2-(2-PrO)-C$_6$H$_4$)(IMesH$_2$), was finally obtained by substitution of the remaining Cl ligand of the parent catalyst via addition of CF$_3$COOAg (Scheme 23).

Excellent activity in RCM was observed; TONs up to 1100 were achieved in stirred batch RCM experiments with this supported catalyst. Leaching of ruthenium into the reaction mixture was low, resulting in a ruthenium content < 70 ng/g in the final RCM-derived products. The authors again underline the necessity of substitution of the second chlorine ligand by trifluoroacetate in order to obtain active supported catalysts. Finally, a monolith-supported version of this catalyst was prepared and used in a continuous flow setup,[127] which was considered to be of utmost significance for industrial applications[128,129] (Scheme 24).

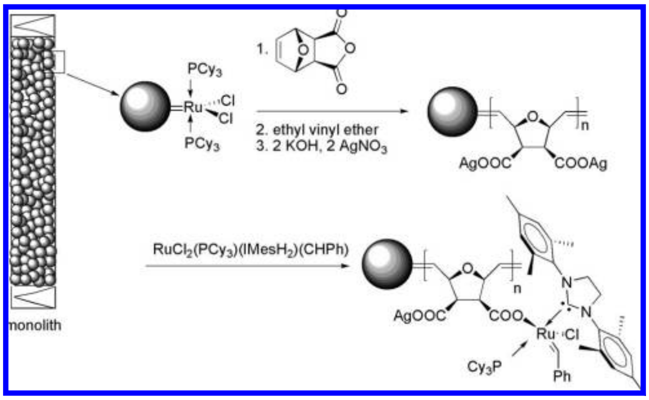
With this system, the initial TOF in the RCM of DEDAM was 0.11 s^{-1}, TONs were >500. It is worth mentioning that the TONs obtained with these two supported versions exceeded all published data on TONs of supported well-defined metathesis catalysts at that time. Equally important, contamination of the products with ruthenium was (at that time) unprecedentedly low, i.e., 1.8 ppm. The same group also reported on an extension of this work using 1,3-dimesityltetrahydropyrimidin-2-ylidenes instead if the IMes or IMesH$_2$ ligand. Immobilization of the corresponding catalysts was accomplished on both Merrifield- and ROMP-derived monolithic supports (Scheme 25).

The latter were used as disks (vide infra).[130] Metal leaching was reported to be low with both types of supports. Thus, the ruthenium content of the final products measured by ICP-OES was as low as 0.14 ppm. In view of the high reactivity

Scheme 21. Ligand Scrambling in Monotrifluoroacetato Derivatives of the Second-Generation Grubbs−Hoveyda Catalyst



Scheme 22. Synthesis of a Monolith-Bound Grubbs-Type Catalyst Based on *vic*-Dicarboxylates



of these systems, Buchmeiser et al. investigated whether these catalysts would be suitable for the stereo- and regioselective cyclopolymerization of heptadiynes (Scheme 26).[131−133]

In fact, $Ru(CF_3COO)_2(IMesH_2)({=}CH\text{-}(2,4,5\text{-}(MeO)_3\text{-}C_6H_4)$ and related systems turned out to be an excellent catalyst for cyclopolymerization of diethyl dipropargylmalonate (DEDPM), allowing for living polymerizations.[113,134−137] Supported versions of some of these catalysts (initiators) were prepared by attaching them to a poly(2-oxazoline)-derived block-copolymer (Scheme 27). Again, a protocol that entailed reaction of the polymer's hydroxyl group with hexafluoroglutaric anhydride followed by conversion of the monocarboxylate into the corresponding silver salt was chosen. The latter was then reacted with various Grubbs−Hoveyda-type initiators. An important step, however, was to react the remaining second chlorine moiety of the initiator with another equivalent of silver trifluoroacete in order to prevent initiator rearrangement (vide supra).

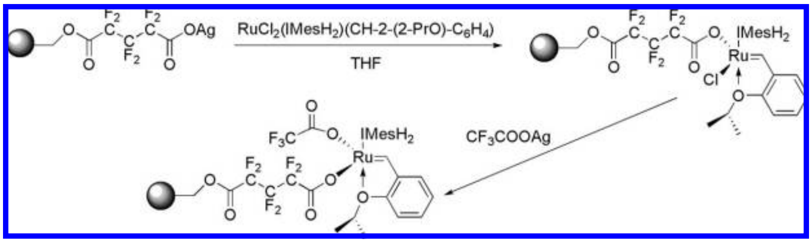
The supported initiator polymer−$Ru(CF_3COO)(IMesH_2)({=}CH\text{-}(2,4,5\text{-}(MeO)_3\text{-}C_6H_4)$ allowed for cyclopolymerization of DEDPM in water under micellar conditions.[138] A prerequisite, however, was the careful choice of the size of the corresponding polar and apolar poly(2-oxazoline) blocks. Reaction kinetics were enhanced by a factor of 4, and a significant reduction in the polydispersity of the polymers was concomitantly observed. These findings were attributed to the micellar polymerization setup leading to high monomer concentrations within the micelle. Immobilization of the initiator to the block copolymer in turn may be expected to result in a reduced number of bimolecular initiator decomposition reactions as well as chain-transfer reactions, which was in fact suggested by the lower PDI indices. At this point it should be emphasized that these have been the first ruthenium-catalyzed (cyclo-) polymerizations of 1,6-heptadiynes ever reported. TEM measurements further supported the micellar setup.

In an extension of their work Buchmeiser et al. reported on the synthesis and immobilization of a series of first- and second generation Grubbs and Grubbs−Hoveyda-type catalysts on Merrifield supports (Scheme 28).[139] In a series of RCM reactions the supported catalysts allowed for reaching TONs of 4200. Ruthenium contaminations of the final products were <85 ppb (sic!).

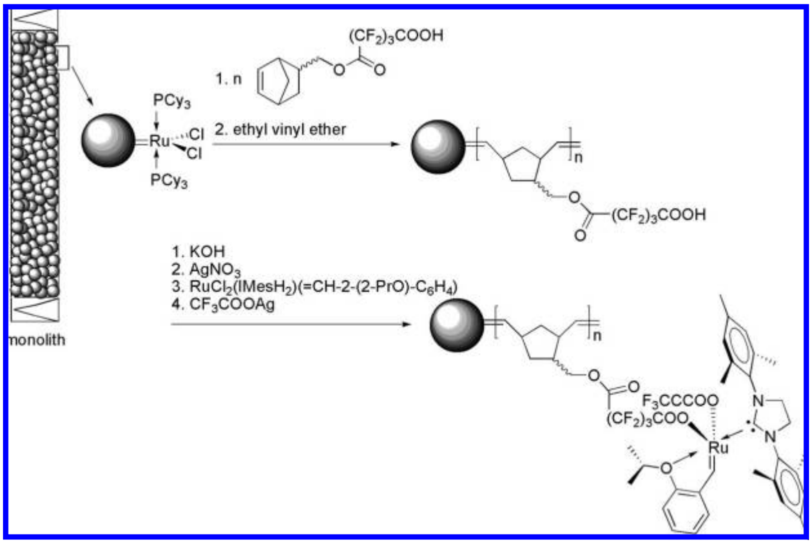
Braddock at al. reported on the synthesis of a polymer-supported perfluorocarboxylic acid via treatment of brominated PS-DVB resins (1 wt % cross-linking) according to a method published by Spring et al.,[140] and reaction of the intermediate formed aryl−magnesium species with hexafluoroglutaric anhydride followed by quenching with trifluoroacetic acid (Scheme 29).[141]

This support was then treated with $Ru(CF_3COO)_2(IMesH_2)$ $({=}CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)$[123] under vacuum. Due to the rapid

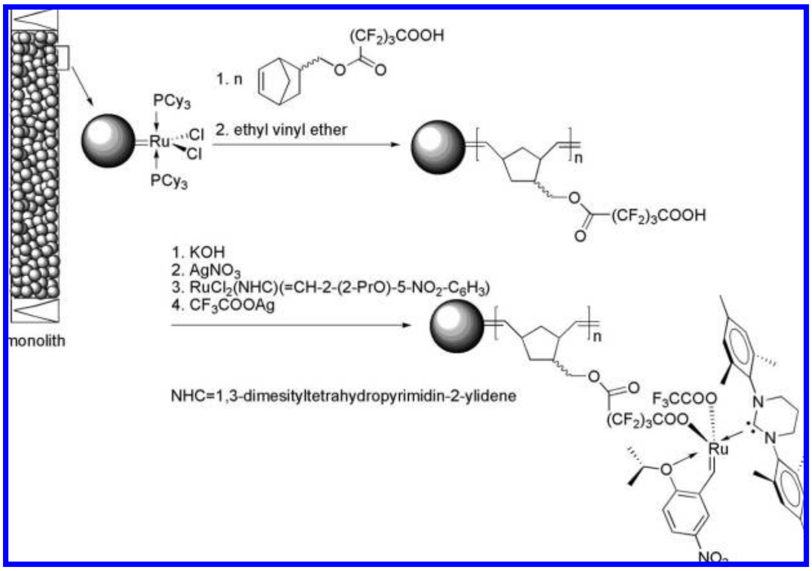
Scheme 23. Immobilization of a Second-Generation Grubbs−Hoveyda Catalyst on PS-DVB via Halogen Exchange



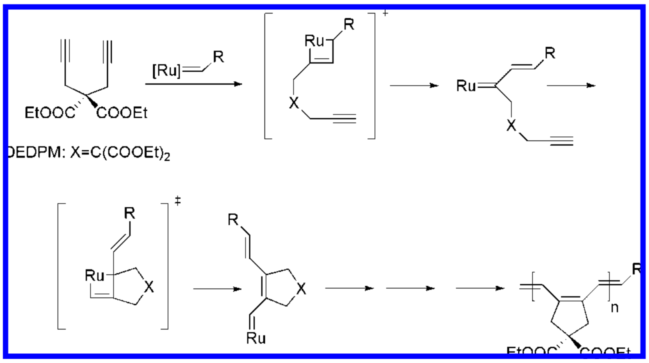
Scheme 24. Synthesis of a Monolith-Bound Second-Generation Grubbs−Hoveyda-Type Catalyst Based on Fluorocarboxylates



Scheme 25. Synthesis of Monolith-Bound Metathesis Catalysts Based on Ru−Tetrahydropyrimidin-2-ylidene Bis(trifluorocarboxylate)s



Scheme 26. Cyclopolymerization of DEDPM To Yield Poly(ene)s Consisting Solely of Five-Membered Repeat Units



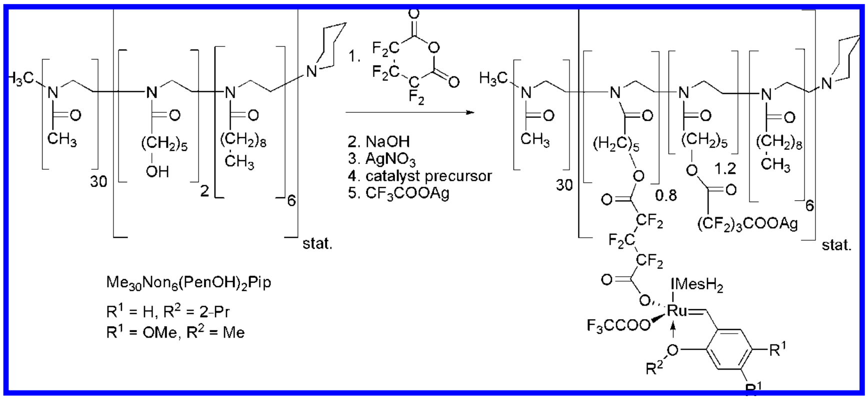
exchange of different anionic ligands that is also responsible for the instability of $RuCl(CF_3COO(IMesH_2)({=}CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)$ in solution,[123] at least one trifluoroacetate was replaced by the polymer-bound flurocarboxylic acid to yield another analogue of the above-mentioned supported systems. TONs in RCM with this supported catalyst were comparably low. In addition, no information on the ruthenium content of the products was provided. For purposes of completeness, it shall be mentioned that the Blechert group used trialkoxysilyl-substituted fluorinated carboxylates for immobilizing Grubbs catalysts on silica.[142]

3.7. Other Immobilized Ruthenium-Based Catalysts

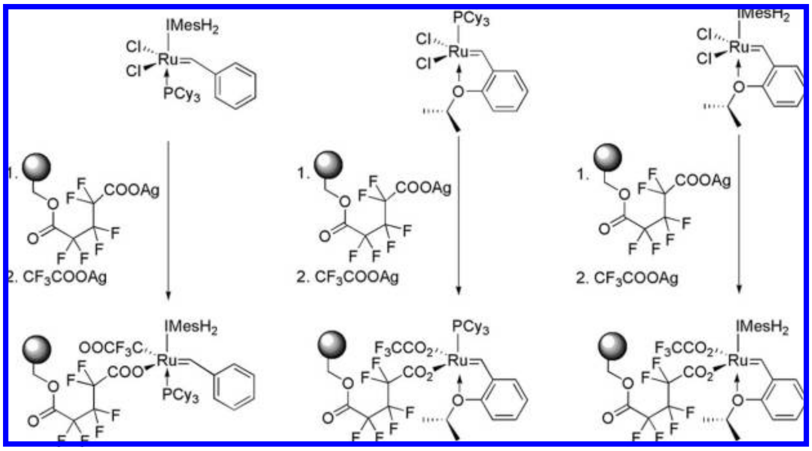
Kobayashi et al. described a poly(styrene)-supported version of [Ru-(η^6-C_6H_5COOEt)(PR_3)Cl_2] (R = Cy, Ph) (Scheme 30).[143] It was reported to be active in the RCM of various dienes and could be recycled without loss of activity for at least 3 cycles. However, significant amounts of precatalyst were used in the RCM reactions reported (20 mol %!), which translates into TONs < 5.

Kirschning and Grela et al. reported on an appealing alternative concept for immobilization of a Grubbs−Hoveyda catalyst. It was mainly based on the work performed by the groups of Grela et al.[144−150] and Blechert et al.[107,151−154] and entailed chemical modification of the benzylidene ligand. They designed a system based on noncovalent interactions[155] between the support and the catalyst.[156,157] For this purpose, a second-generation Grubbs−Hoveyda catalyst bearing an diethylamino group in the 4 position of the benzylidene ligand was reacted with both a commercial and a tailormade sulfonated poly(styrene-*co*-divinylbenzene)-based support to yield the corresponding supported catalyst (Figure 9). In addition, synthesis of a supported system based on a polymer−glass composite was reported. The supported catalyst was multiply used in the RCM of *N*,*N*-diallyl-*N*-tosylamide. A significant loss in activity was observed running the reactions at a 5 mol %

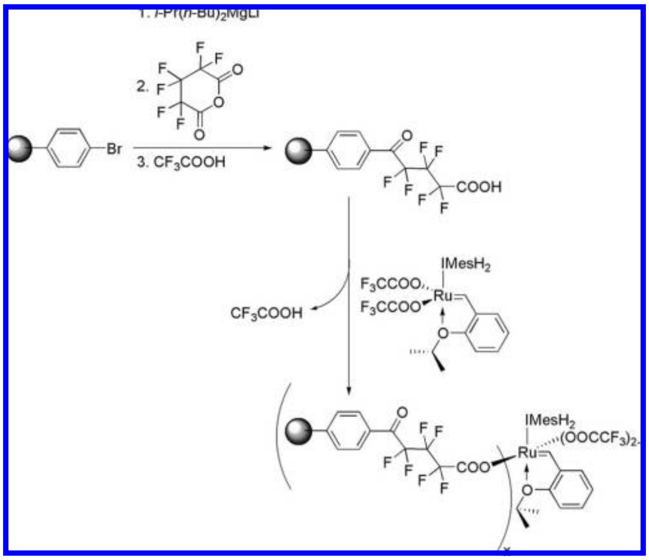
Scheme 27. Synthesis of a Poly(2-oxazoline)-Bound Second-Generation Grubbs−Hoveyda Catalyst for Use in Micellar Catalysis



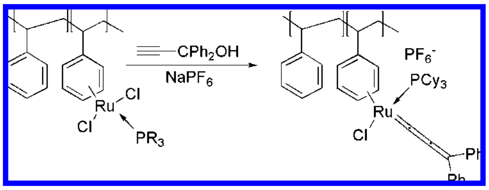
Scheme 28. Synthesis of Grubbs- and Grubbs−Hoveyda-Type Catalyst Bound to Fluorocarboxylate-Derivatized Merrifield Supports



Scheme 29. PS-Supported Grubbs−Hoveyda Catalysts Prepared from Ru(CF$_3$COO)$_2$(IMesH$_2$)(=CH-2-(2-PrO)-C$_6$H$_4$)



Scheme 30. PS-Supported Ru−Allenylidene Catalyst



catalyst base; product contamination with ruthenium was reported to be 100 ppm.

4. Immobilized Schrock-Type Catalysts

4.1. General Considerations

In principle, Schrock catalyst may be supported via three independent routes (Figure 10).

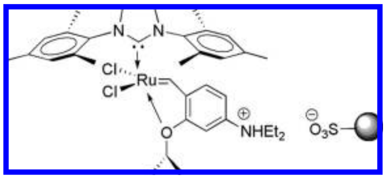


Figure 9. Second-generation Grubbs−Hoveyda catalyst immobilized via noncovalent interactions.

The first entails immobilization via the alkoxide or, in case of chiral catalysts, biphenyl or binaphthyl ligand. This route has extensively been used for immobilization of Schrock catalysts on inorganic supports.[158−160] Nevertheless, only recent approaches by the groups of Schrock, Basset, and Copéret allowed for realizing well-defined systems.[161−167] The silica-supported, Mo(*t*-BuArN)$_3$(CCEt)-derived alkyne metathesis catalyst described by Moore et al. also deserves to be mentioned here.[168] Alternatively, boomerang systems might be considered, i.e., immobilization is to be accomplished via alkylidene exchange with a suitable vinyl-derivatized support. However, no reports on this type of catalyst have appeared so far. Finally, immobilization via the arylimido ligand was demonstrated to be a viable alternative. In the following, the different concepts shall be outlined in more detail.

4.2. Immobilization through the Alkoxide Ligand

Due to the pronounced sensitivity of molybdenum-based systems versus oxygen and moisture, few examples of supported, metathesis active systems have been reported so far. While various supported versions of MoO$_3$-based catalysts are widely used in industrial petrochemical processes including the SHOP process,[169,170] supported versions of well-defined catalysts, i.e., analogues of Schrock catalysts, are rare. Significant ROMP activity was observed under continuous conditions;[158] nevertheless, the actually active species remained unknown, and cis/trans selectivities opposite to the ones found with similar complexes in solution were observed.

The first well-defined polymer-supported and recyclable catalyst for enantioselective olefin metathesis was reported by Schrock and Hoveyda et al.[171] They used a polymerizable, i.e., *p*-styrylethyl-substituted, enantiomerically pure biphenoxide. The bis-O-protected form of this ligand was

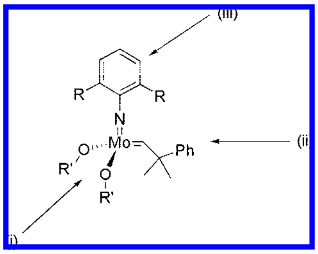
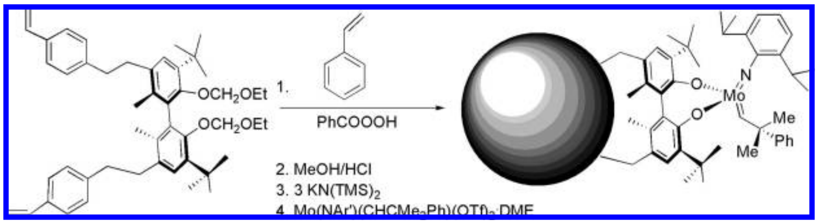


Figure 10. Possibilities of immobilizing Schrock-type catalysts.

Scheme 31. Synthesis of a Supported Enantioselective Schrock Catalyst via Free-Radical Polymerization

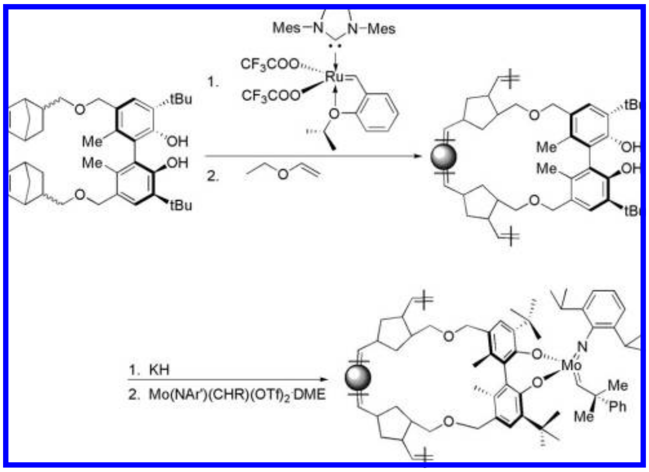


subject to a radical copolymerization with styrene. Subsequent deprotection, deprotonation, and reaction with the catalyst precursor Mo(N-2,6-*i*-Pr_2-C_6H_3)(═$CHCMe_2Ph$)-$(OTf)_2$·DME resulted in the desired supported catalyst (Scheme 31).[10]

A comparison of the results obtained in asymmetric RCM and selected desymmetrization reactions, respectively, revealed no significant differences between the parent and the analogous supported system in both yields and ee. These results indicated that (i) there was no change in the geometrical constraints relevant for catalysis and (ii) the catalytic sites were accessible to a reasonable extent. The supported system showed comparably low leaching (<5%), resulting in low contamination of the products with Mo. Unfortunately, the system showed a reduced recyclability. Nevertheless, in view of the highly unstable molybdenum methylidenes that are the intermediates formed in the course of every catalytic cycle and the supported nature of the system, where diffusion is a major issue, these findings are not surprising and must be regarded as an intrinsic property.

Aiming at a more straightforward synthesis, Buchmeiser et al. reported on the synthesis of a supported version of a chiral Schrock catalyst prepared by ROMP.[172] For polymerization they prepared a bis(norborn-2-ene)-substituted chiral phenoxide which could be polymerized without any protection/deprotection steps using $Ru(CF_3COO)_2$(═CH-2-(2-PrO)-C_6H_4)($IMesH_2$).[123,173] Reaction of the polymeric support with potassium hydride followed by addition of Mo(*N*-2,6-*i*-Pr_2-C_6H_3)(═$CHCMe_2Ph$)$(OTf)_2$·DME resulted in the desired supported catalyst (Scheme 32).

Scheme 32. Synthesis of a Poly(norbornene)-Supported, Enantioselective Schrock Catalyst via ROMP



Due to the low cross-linked nature of the support, which showed a swelling of 700%, resulting in a solvent uptake of 2000 wt-%, the catalytic sites showed excellent accessibility. Consequently, lower amounts of catalyst were required, while yields and ee's were basically identical to those obtained with the supported system described above. Again, the molybdenum loss was <5%.

Using the same bis(norborn-2-ene)-functionalized chiral biphenyl ligand, Buchmeiser et al. reported on its immobilization on monolithic supports. These were designed in a way that they could be cut into pieces and, after encasement, be used for high-throughput screening (Scheme 33).

The high porosity (ca. 60% pore volume) of the monolithic supports guaranteed for a sufficient void volume to take up solutions of the corresponding educt. The monolithic supports thus served simultaneously as catalyst supports, reactions vessels, and filtration units. A series of asymmetric RCM reactions and desymmetrization reactions was carried out. Using the supported chiral Schrock catalyst, very similar enantioselectivity was found as for the parent homogeneous system.[82] Metal leaching was reported to be <3%.

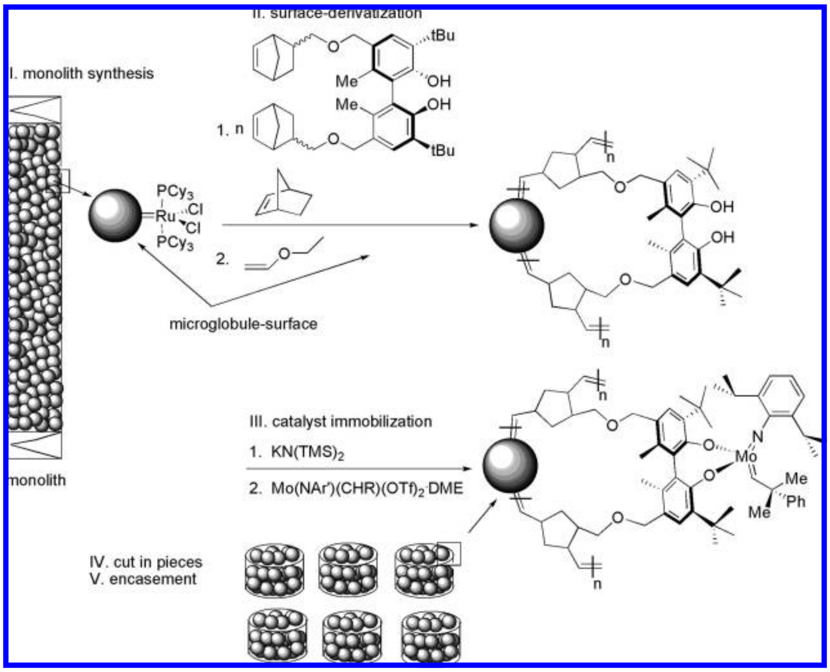
In an extension of their own work, the Schrock and Hoveyda group reported on the synthesis of a set of poly(styrene)- and poly(norborn-2-ene)-supported Schrock-type catalysts. Following the synthetic route described for synthesis of a polymer-supported chiral biphenyl-based Schrock catalyst, analogous systems based on the 2,6-dichlorophenylimido and adamantylimido ligand were prepared (Figure 11)

In addition, chiral binaphthyl-based Schrock catalysts containing the 2,6-dichlorophenylimido and adamantylimido ligand were synthesized (Scheme 34).[174]

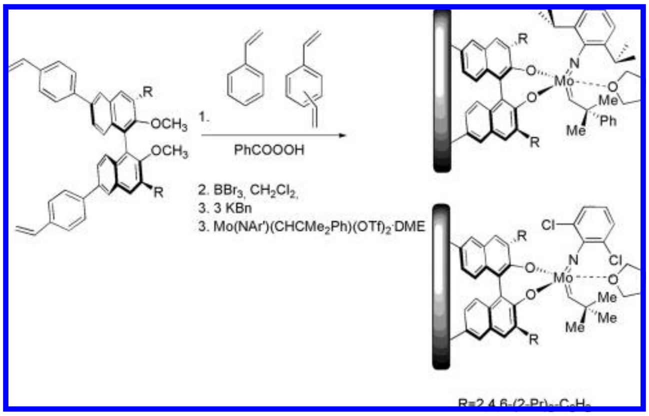
Finally, in a synthetic protocol very similar to the one reported by Buchmeiser et al., the Schrock and Hoveyda groups also reported on supported, chiral Schrock catalysts prepared via ROMP. Similar to the approach reported by Buchmeiser et al., they used a bis(norborn-2-ene)-substituted unprotected chiral biphenyl that they subjected to ROMP in the presence of a crosslinker, i.e., 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo*,*endo*-dimethanonaphthalene (DMN-H6)[175] and the catalyst precursor, i.e., Mo(NR′)($CHCMe_2Ph$)$(OTf)_2$·DME (R′ = 2,6-*i*Pr_2−C_6H_3, 2,6-Cl_2-C_6H_3, adamantyl; Scheme 35).[174]

The desired catalyst formed immediately and initiated ROMP, and thus, support formation occurred. With all the systems reported by these two groups the enantiomeric excess obtained in a series of asymmetric RCM, ROC, and desymmetrization reactions was in most cases very similar to the one obtained with the parent, unsupported ones, indicating that immobilization did not put any steric constraints onto

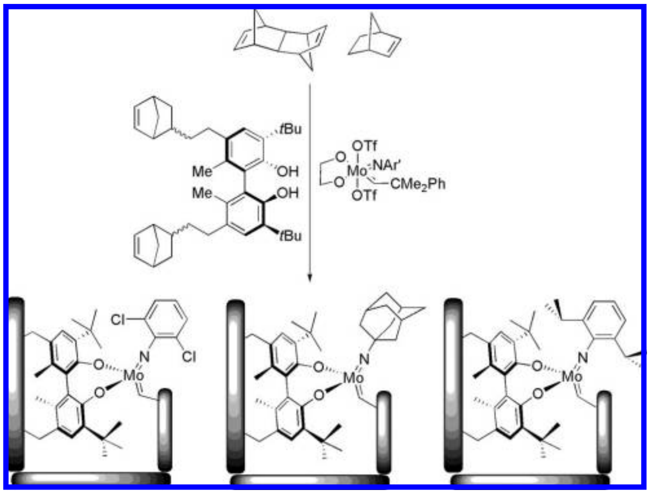
Scheme 33. Monolith-Supported Chiral Schrock Catalyst



Scheme 34. Polymer-Supported Chiral Binaphthyl-Based Schrock Catalysts



Scheme 35. Chiral Biphenyl-Based Schrock Catalysts Immobilized on ROMP-Derived Supports



the chiral center since this might certainly well be expected to lead to significant changes in stereoselectivity.

4.3. Immobilization Through the Arylimido Ligand

From a synthetic point of view, immobilization of a Schrock catalyst via the arylimido ligand is a challenging task. However, in case of realization of such an approach allows for a wider and in fact complementary variability in catalyst structure, since both reactivity and selectivity of chiral Schrock-type catalysts are mainly (but not exclusively)[9,176,177] governed by the nature of the alkoxides, (bi-) phenoxides, and binaphtholates. Thus, such a supported version of a Schrock catalyst, where heterogenization is realized via the arylimido ligand, allows for an ultimate variability in catalyst tuning. The only successful realization of that route so far has been reported by the Buchmeiser group.[178] A set of 2,6-disubstituted anilins containing an additional ω-halogenoalkyl group in the 4 position was designed. These anilins were subject to the standard synthesis for Schrock-type catalysts,[80] leading to the corresponding set of molybdenum triflates of general formula $Mo(NAr')(CHCMe_2Ph)(OTf)_2 \cdot DME$ ($Ar' = 2,5\text{-}Me_2\text{-}4\text{-}[(CH_2)_6\text{-}Br]\text{-}C_6H_3$; $2,5\text{-}i Pr_2\text{-}4\text{-}[(CH_2)_6\text{-}Br]\text{-}C_6H_3$; $2,5\text{-}i Pr_2\text{-}4\text{-}[(CH_2)_6\text{-}Cl]\text{-}C_6H_3$ (Scheme 36)).

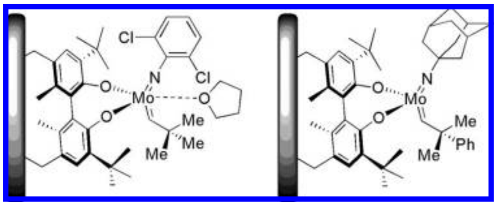
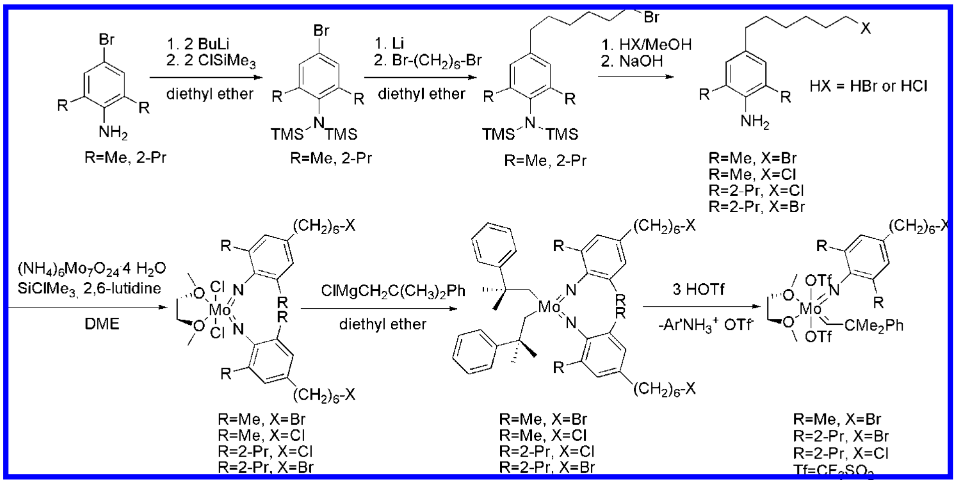


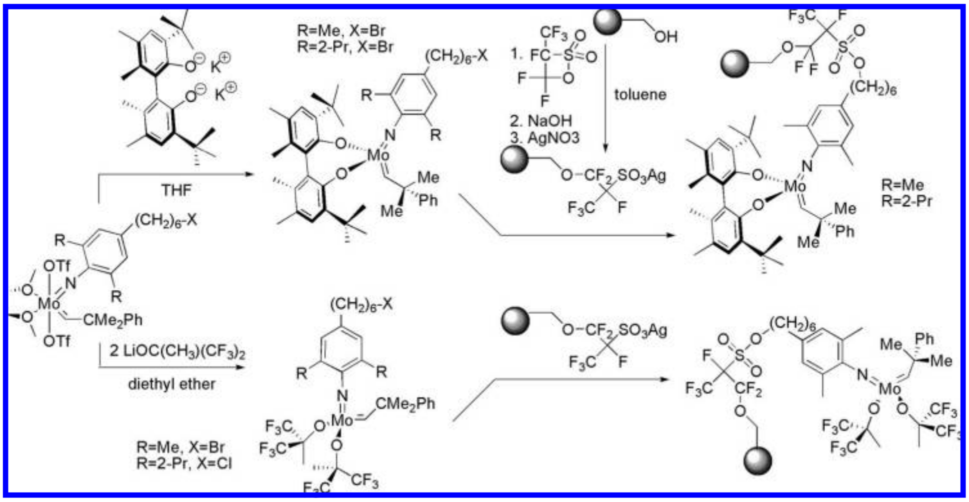
Figure 11. Polymer-supported chiral 2,6-dichlorphenylimido- and adamantylimido-based Schrock catalysts.

The molybdenum triflates were then converted into a set of four different chiral catalysts, i.e., $Mo(N\text{-}2,6\text{-}Me_2\text{-}4\text{-}(\omega\text{-}Br\text{-}C_6H_{12})\text{-}C_6H_2)(CHCMe_2Ph)(BIPHEN)$, $Mo(N\text{-}2,6\text{-}Me_2\text{-}4\text{-}(\omega\text{-}Br\text{-}C_6H_{12})\text{-}C_6H_2)(CHCMe_2Ph)(BIPHEN)$, $Mo(N\text{-}2,6\text{-}Me_2\text{-}4\text{-}(\omega\text{-}Br\text{-}C_6H_{12})\text{-}C_6H_2)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$, and $Mo(N\text{-}2,6\text{-}i Pr_2\text{-}4\text{-}(\omega\text{-}Br\text{-}C_6H_{12})\text{-}C_6H_2)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$ (BIPHEN = 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-2,2′-biphenolate), which were then, in a single step, subject to heterogenization. For these purposes, a

Scheme 36. Synthesis of Mo−Triflates Based on 4-(ω-Halogenoalkyl)phenylimido Complexes



Scheme 37. Synthesis of Chiral Schrock Catalysts and Immobilization via the Phenylimido Ligand via Ester Formation



fluorosulfonated poly(styrene-*co*-divinylbenzene) support was transformed into the corresponding poly(silver) salt and reacted with the progenitors (Scheme 37).

Halogen exchange yielded the corresponding perfluorosulfonesters and thus the supported catalysts which were characterized in a series of asymmetric RCM and desymmetrization reactions. The enantioselectivity observed was found to be very similar to the one of the corresponding parent, unsupported catalysts. Metal leaching was reported to be <6%.

5. Conclusions

Supported catalysts for metathesis reactions facilitate synthesis and will thus certainly be of further interest to both academia and industry. Since some highly active systems with good persistence and recyclability are already available, it is believed that the main future focus in this area of research will lie in the development of catalysts for asymmetric reactions as well as for large-scale metathesis reactions. Considerable attention will be given to low-bleeding systems as well as economical aspects, i.e., price. Nevertheless, a steady and consequent development in homogeneous catalysis, i.e., synthesis of new, highly active and stable organometallic compounds, will still be the prerequisite to any success in this area. If done properly, all this will certainly result in the permanent improvement of existing systems and techniques as well as in new applications in many areas of chemistry and materials science.

6. Acknowledgments

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