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Recent advances in the synthesis of supported metathesis catalysts

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The state of the art and recent developments in the synthesis of supported, well-defined metathesis catalysts are reviewed. In this context, their synthesis, selected properties and application to both polymer and organic chemistry are summarised. Special consideration will be given to aspects of activity [discussed in terms of turnover numbers (TONs) and turn over frequencies (TOFs)], regioselectivity and enantioselectivity as well as stability. The general applicability of these supported catalysts to either high-throughput technology or to the manufacture of continuous flow systems is discussed.

Introduction

During the past ten years, olefin metathesis has experienced dramatic development and is nowadays considered to be one of the most important C–C bond forming reactions,[1–4] allowing the synthesis of both well-defined, functional polymers and complex architectures, including medium-sized[5] and large ring structures.[6,7] The findings that these reactions can be carried out in an enantioselective way[8,9] widened the range of applications from commodity chemicals to the synthesis of chiral 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.[10–12] The development of well-defined, single-component metathesis catalysts smoothed the way for metathesis-based reactions such as ring-opening metathesis polymerisation (ROMP), 1-alkyne polymerisation, acyclic diene metathesis (ADMET), cross-metathesis (CM), tandem metathesis, enyne metathesis, and ring-opening cross metathesis (Scheme 1), and made them attractive for the scientific community.[7,9,13–18]

For various reasons, there is an increasing demand for supported versions of modern, highly selective and active metathesis catalysts. First, contamination of products with metal ions and/or ligands needs to be low, particularly in cases relevant to pharmaceutical chemistry. While Mo-based initiators and their decomposition products, respectively, are easily removed from both monomeric and polymeric products by simply adding a base,[19,20] the removal of Ru-based initiators requires tedious manipulations, in particular with polymeric products.[21–23] Second, modern metathesis catalysts significantly add to the total cost of a product, therefore regeneration or reuse are highly desirable. And third, supported catalysts offer access to high-throughput techniques and continuous flow reactors. Key issues associated with supported metathesis catalysts are (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. This article is intended to provide a comprehensive summary of the most significant achievements in this venture.

Supported metathesis catalysts

While organic chemists have been used to polymer-immobilised reagents for quite a long time,[24–26] it soon became obvious that ring-closing metathesis (RCM) and related reactions were best carried out with systems in which the catalyst could either be easily separated[27–35] or was polymer bound. Some summaries on supported metathesis catalysts have been given recently,[36–38] nevertheless, in view of the rapid developments in this field, the present state of the art in supported, well-defined metathesis catalysts as well as recent contributions to this field shall be summarised here. Doing this, the following types of immobilised catalysts will be included: (i) soluble

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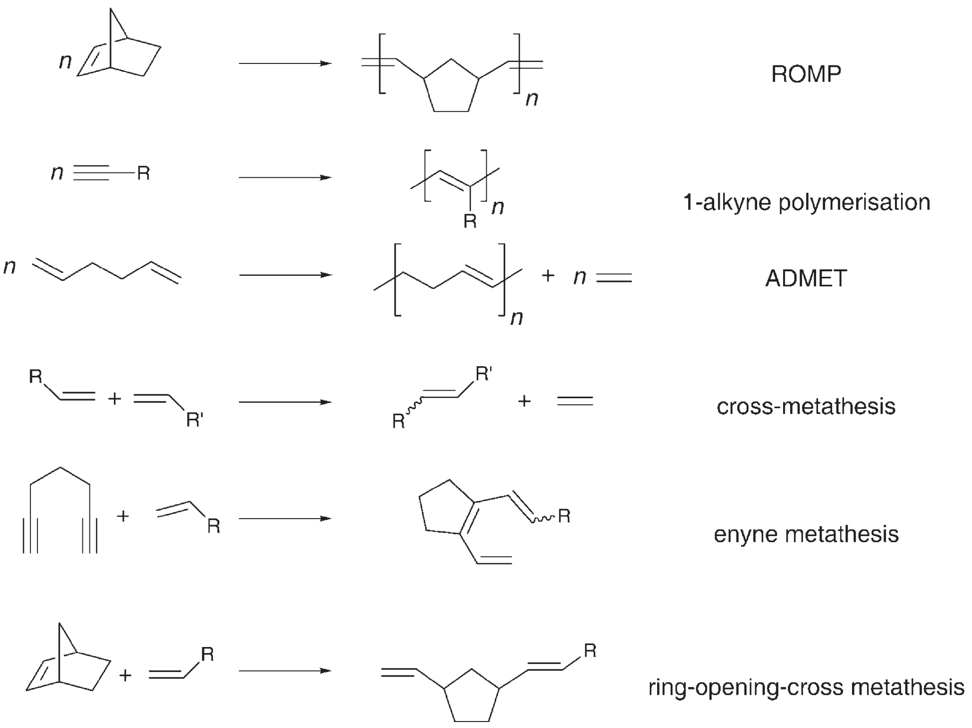


Scheme 1 Metathesis-based reactions.

polymer-bound catalysts [*e.g.*, poly(ethylene)glycol (PEG)-bound, poly(7-oxanorborn-2-ene)-bound] and (ii) supported catalysts [(polystyrene–divinylbenzene) PS–DVB-bound systems, monolith-immobilised systems, and silica-bound systems]. Nevertheless, in order to understand the developments in this area, they will be discussed in the context of their appearance and heterogenisation chemistry, respectively. In addition, Mo-, Ru- and Re-based catalysts shall be covered separately.

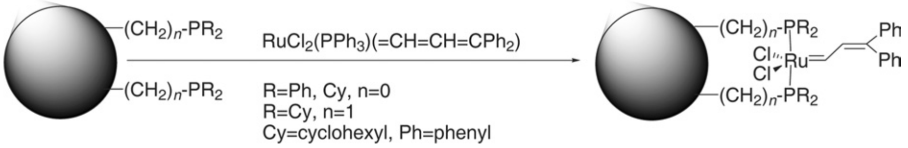
Ruthenium-based systems

Immobilisation *via* phosphine exchange. The first example of a supported Ru-based metathesis catalyst was reported by Grubbs *et al.*[39] They used various phosphine-derivatised, low-crosslinked (2%) PS–DVB resins for the immobilisation of $RuCl_2(PR_3)_2(=CH{-}CH{=}CPh_2)$ (Scheme 2). The supported catalyst showed significantly reduced activity both in the metathesis of *cis*-2-pentene and the polymerisation of norborn-2-ene for which mainly incomplete substitution of phosphine, respectively phosphine chelation effects, as well as limited diffusion were made responsible. Using the same approach, Verpoort *et al.* reported on the immobilisation of $RuCl_2(PCy_3)_2(=CHPh)$ on a phosphine-derivatised mesoporous silica support (P-MCM-41).[40] The phosphine groups were introduced by reaction of the support with $(EtO)_3SiCH_2CH_2PPh_2$. Not unexpectedly, poly(norborn-2-ene) prepared with this support showed 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, giving TONs up to 20.

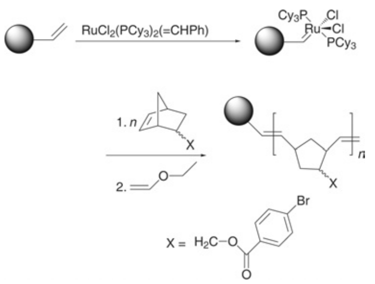
Immobilisation *via* alkylidene exchange. Barrett *et al.* described the use of vinyl-substituted supports [*i.e.*, poly(vinylstyrene-co-divinylbenzene)] in the exchange reaction with $RuCl_2(PCy_3)_2(=CHPh)$ (Scheme 3).[41] The resulting supported metathesis catalyst was used for the synthesis of poly(norborn-2-ene) loaded supports for use in combinatorial chemistry.

Through an identical approach, this type of supported catalyst was used as a "boomerang" catalyst in RCM.[42] Though the idea of a supported catalyst, acting in solution and returning to the support is certainly attractive, the inherent instability of intermediary formed ruthenium methylidenes is a severe impediment in the realisation of this concept (Scheme 4). Though the longevity of such systems can in fact be enhanced by the addition of "regenerating agents" such as styrene or bis(acetoxy)but-2-ene-1,4-diol,[43] their multiple use is hindered by continuous catalyst deterioration, thus preventing the back reaction with the vinyl-substituted support. In due consequence, ruthenium contamination of the products is high (up to 0.5 wt % without further purification). Similar results were found by Barrett *et al.* and Nolan *et al.* when using $RuCl_2(PCy_3)(SIMes)(=CHPh)$ and $RuCl_2(PCy_3)(IMes)(=CHPh)$, respectively (SIMes = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene, IMes = 1,3-dimesitylimidazol-2-ylidene), instead of $RuCl_2(PCy_3)_2(=CHPh)$. Nevertheless, with these new types of catalysts, Ru contamination levels were reported to be lowered by a factor of 10.[44–46]

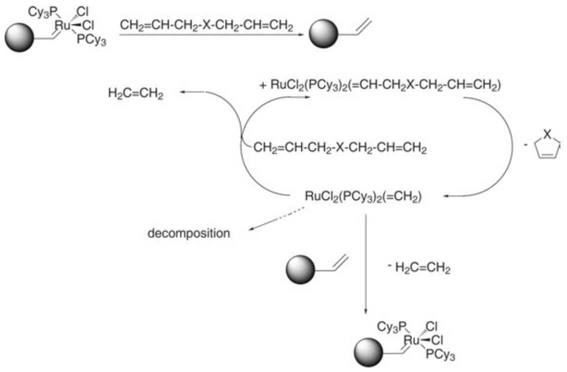
With the report of Hoveyda *et al.* on a recyclable, ruthenium-based metathesis catalyst[47] it became clear that the particular alkylidene used in this type of initiator, a 2-(2-PrO)-benzylidene, should also allow enhancement of the efficiency of supported, "boomerang"-type catalysts.



Scheme 2 Immobilisation of $RuCl_2(PPh_3)_2(=CH{-}CH{=}CPh_2)$ on phosphine-derivatised supports.



Scheme 3 Synthesis of a supported metathesis catalyst *via* alkylidene exchange.



Scheme 4 Mechanism and drawback of "boomerang" catalysts.

Yao, Hoveyda *et al.* and others were the first to report on such poly(ethylene glycol) (PEG) and dendrimer-bound systems, respectively (Figs. 1),[48–50] that showed significantly increased persistence in RCM. The same holds true for an aminomethyl-PS-DVB-supported Hoveyda-type catalyst (Fig. 2) reported by Dowden *et al.*[51] as well as for the Hoveyda system supported on 0.5 mm i.d. monolithic silica discs (Fig. 3).[52] Under argon, the latter could be used in 20 cycles.[53] The Ru content of the products was in the range of 40–60 ppm.

Quite recently, Blechert *et al.* reported on a "self-supporting" version of Hoveyda's catalyst.[54] The preparation entailed the reaction of 7-oxanorborn-2-ene-substituted 2-(2-PrO)styrene with $RuCl_2(PCy_3)(SIMes)(=CHPh)$, leading to the formation of a 7-oxanorborn-2-ene-substituted Hoveyda catalyst, which undergoes spontaneous polymerisation to from a (slightly crosslinked?) polar matrix of poly(7-oxanorbornene) with the catalyst bound to it (Scheme 5). 7-Oxanorborn-2-ene-5-ylmethyl benzoate was used as a co-monomer 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 Ru content in the polymer was 40 ppm.

Grela *et al.* reported on a butyldiethylsilyl polystyrene (PS–DES) supported Hoveyda-type catalyst (Fig. 4).[55] 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 non-terminal alkene groups.

Finally, Blechert *et al.* described the synthesis of a Hoveyda-type catalyst immobilised on a highly hydrophilic, commercially available ω-amino-poly(ethyleneglycol)amide (PEGA–NH_2) support (Scheme 6).[56] 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%.

Immobilisation *via* the *N*-heterocyclic carbene. The first Ru-based metathesis catalyst immobilised *via* the *N*-heterocyclic carbene was reported by Blechert *et al.*[57] 4-(PS–DVB–methyloxymethyl)-1,3-dimesityl-4,5-tetrahydrimidazolin-2-ylidene was used for the generation of the corresponding free carbene and reacted with $RuCl_2(PCy_3)_2(=CHPh)$ to form the supported catalyst (Fig. 5). This supported version of Grubbs' second-generation metathesis catalyst was successfully used in RCM and enyne metathesis reactions and was easy to handle. Reported TONs were in the range of 20. By switching to the Hoveyda version of this type of catalysts, an improved recyclability of the support was achieved.[58] Generally speaking, the Merrifield support that was chosen for the synthesis of these supported catalysts represents a swollen, low cross-linked network. Consequently, reactions are diffusion controlled and increased reaction times are required.

In order to overcome this problem, we aimed for the synthesis of non-porous supports suitable for continuous flow experiments, that is monolithic supports. Using a ROMP-based protocol, we were able to synthesise functionalised monoliths.[43,59,60] These were designed in such a way that only interparticle porosity was generated, whereas the structure-forming microglobules were virtually non-porous. Taking advantage of the "living" character of ruthenium-catalysed ROMP used for their synthesis and the high tolerance of the catalytic system towards different functional monomers, we were able to graft cationic *N*-heterocyclic carbene (NHC) precursors onto the surface. Tentacle-like polymer chains attached to the surface were formed. The free NHC necessary for catalyst formation was simply generated by passing a strong base such as 4-dimethylaminopyridine (DMAP) over the support. In a last step the catalyst was formed and simultaneously immobilised by passing a solution of $Cl_2Ru(CHPh)(PCy_3)_2$ over the rigid rod (Scheme 7). Loadings of up to 1.4% of Grubbs catalyst on NHC base were achieved.

Monolith-immobilised metathesis catalysts prepared by this approach showed high activity in various metathesis-based reactions such as ROMP and RCM. The use of chain-transfer agents (CTAs; *e.g.*, *cis*-1,4-diacetoxybut-2-ene, DEDAM, 2-hexene) allowed regulation of molecular mass, in particular in the case of cyclooctene. The presence of CTAs additionally enhanced the lifetime of the catalytic centres by reducing the average concentration of ruthenium methylidenes, thus allowing 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 high average TOFs of up to 0.5 s^{-1}.

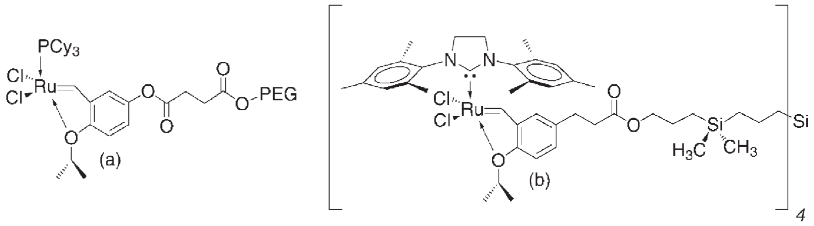


Fig. 1 (a) PEG- and (b) dendrimer-supported Hoveyda-type catalysts.

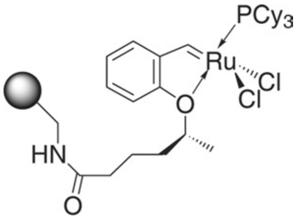


Fig. 2 Aminomethyl–PS–DVB-supported version of Hoveyda's catalyst.

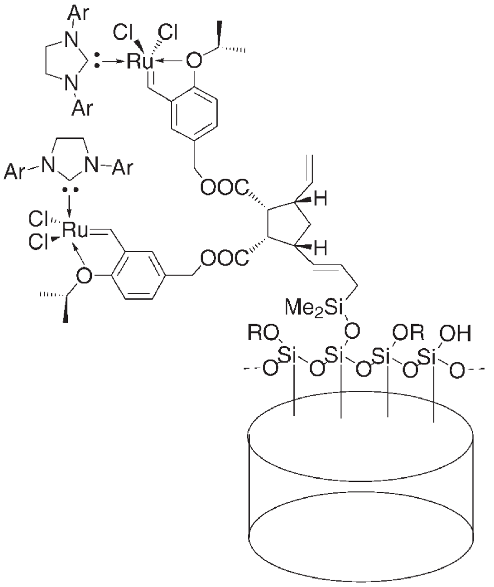
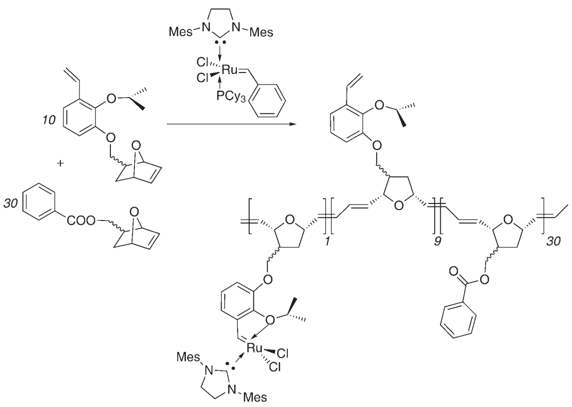


Fig. 3 Monolithic silica-supported Hoveyda catalyst.

In an effort to synthesise a silica-supported version of this catalyst, we polymerised 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. Reaction of this monomer with $\mathrm{Cl_2Ru(PCy_3)_2(CHPh)}$ in methylene chloride at 45 °C resulted in complete consumption of the initiator and formation of an oligomer with a DP of 7. Alternatively, polymerisations with the Schrock initiator $\mathrm{Mo(}N\text{-2,6-}i\text{-}\mathrm{Pr_2{-}C_6H_3)(CHCMe_2Ph)[OCMe(CF_3)_2]_2}$[61] were performed in methylene chloride at ambient temperature. The DP of 7 ± 1 found *via* end group analysis using ^{1}H-NMR was in excellent agreement with the theoretical DP of 7. 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 in THF at −30 °C yielded the free carbene, which was subsequently reacted with $\mathrm{Cl_2Ru(CHPh)(PCy_3)_2}$ to yield the immobilised second-generation Grubbs catalyst (Scheme 8).[62]



Scheme 5 "Self-supporting" catalyst formed *via* simultaneous alkylidene exchange-polymerisation reaction.

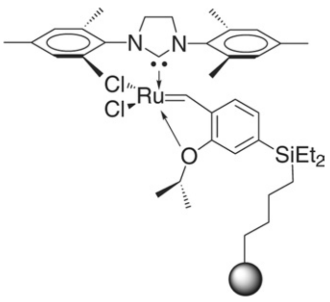
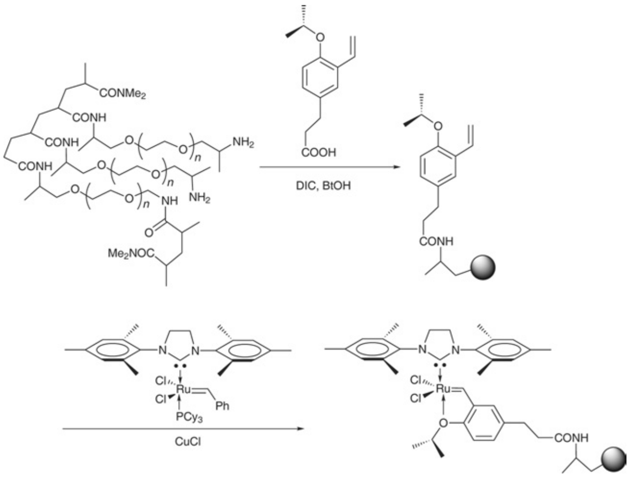


Fig. 4 PS–DES supported Hoveyda-type catalyst.



Scheme 6 Synthesis of a PEGA-supported Hoveyda-type catalyst.

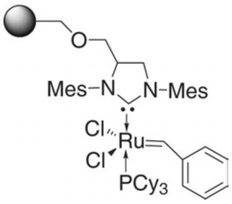
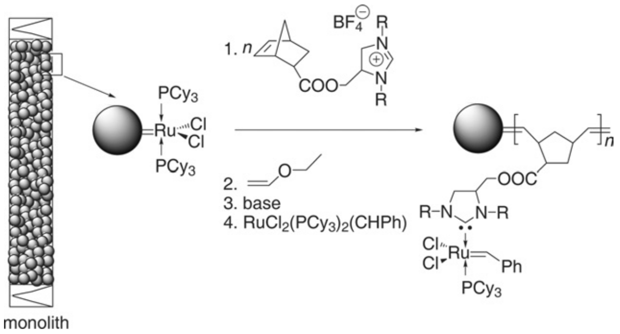
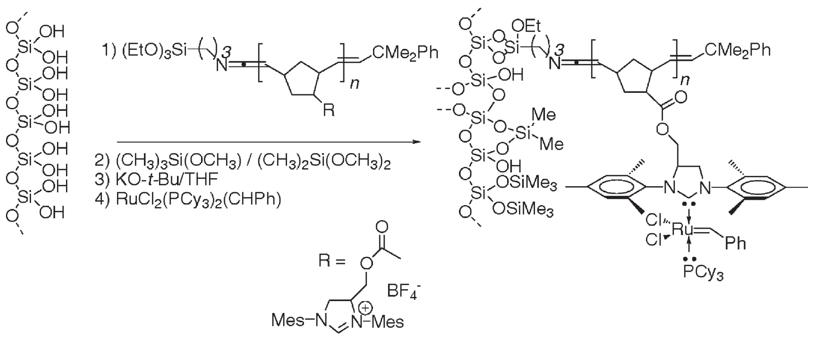


Fig. 5 PS–DVB-supported Grubbs' second-generation catalyst.



Scheme 7 Immobilisation of Grubbs' second-generation catalyst on a ROMP-derived monolith.



Scheme 8 Silica-supported version of Grubbs' second-generation catalyst.

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 $\leqslant$ 80 for a stirred batch, which is comparable to those in homogeneous systems.

Complementary to the above-mentioned grafting approach, coating techniques[63] 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-derivatised silica 60 containing 0.09 mmol of NHC precursor. Conversion into the initiator was carried out as described for the grafted analogue, resulting in a support containing 4.1 μmol ruthenium g^{-1}. Good results were obtained with these coated supports in the RCM of DEDAM and 1,7-octadiene with TONs of 210 and 55, respectively, 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 an attractive access to virtually metal-free products.[52]

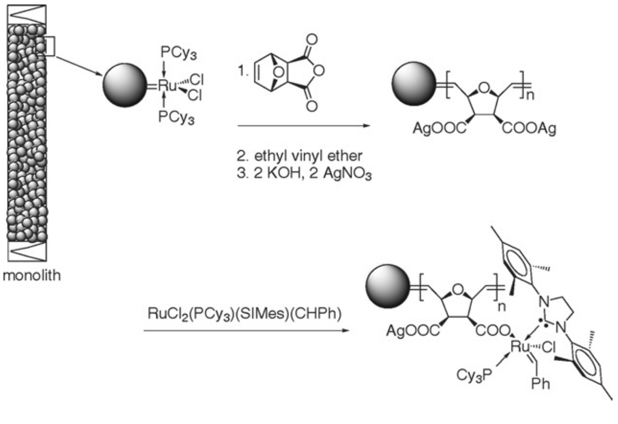
Immobilization through halogen exchange. In 2001, Mol *et al.* reported on the synthesis of a PS–DVB-supported version of $RuCl_2(PCy_3)_2(=CHPh)$.[64] It was obtained by reacting hydroxyethyl–PS–DVB (1% DVB) with hexafluoroglutaric anhydride. The intermediary formed polymer-bound carboxylic acid was converted into the silver salt and finally reacted with $RuCl_2(PCy_3)_2(=CHPh)$ to yield PS–DVB–$CH_2OCOCF_2CF_2CF_2COORuCl(PCy_3)_2(=CHPh)$. As for other ruthenium catalysts containing phosphine ligands, a rapid decrease in reactivity was observed during consecutive cycles in the RCM of DEDAM. A comparably low total TON of *ca.* 60 was reported for this reaction. In addition, the Ru content in the products was as high as 3800 ppm.

In an alternative approach, we prepared a monolith-supported second-generation Grubbs catalyst containing the saturated 1,3-dimesitylimidazolin-2-ylidene (SIMes) ligand by a synthetic protocol summarised in Scheme 9.[65,66] Surface derivatisation 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 the halogen exchange with the second-generation Grubbs catalyst $RuCl_2(PCy_3)(SIMes)(=CHPh)$. In the benchmark reaction with DEDAM, TONs close to 1000 were achieved.

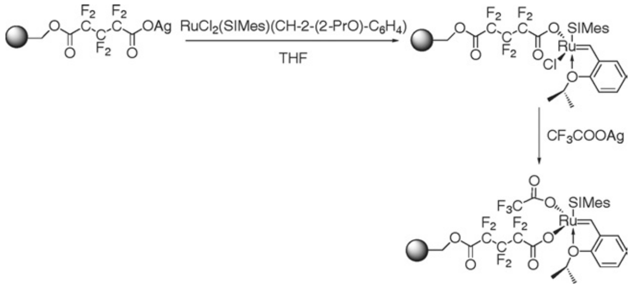
It is worth mentioning that these systems benefit from the presence of free silver carboxylate groups, which act as a reversible scavenger for phosphine. Thus, the use of monocarboxylic acids such as 7-oxanorborn-2-ene-5-carboxylic acid instead of the anhydride results in a supported catalyst that shows significantly reduced TONs in the RCM of DEDAM. Again, the use of silica as the support results in low TONs around 120. This comparably low activity of the silica-based systems is attributed to both the non-reversible scavenging of the phosphine by residual silanol groups and to diffusion-controlled reactions and can in fact be overcome by the use of the above-mentioned monolithic systems.

In view of these results we tried to further enhance the reactivity of Ru-based metathesis catalysts and to avoid the use of phosphine ligands. In due consequence, numerous variations in Hoveyda-type catalysts of the general formula $RuCl_2$(SIMes)[=CH–2-(2-PrO–C_6H_4)] were obtained. Among the most important findings was that the exchange of chlorine by a strongly electron-withdrawing group in fact enhanced the reactivity of these systems without sacrificing their high stability.[67] Thus, $Ru(CF_3CO_2)_2$(SIMes)[=CH–2-(2-PrO)–C_6H_4] was a highly active catalyst in RCM at both 45 and 20 °C, exceeding known ruthenium-based catalysts in catalytic activity. TONs of up to 1800 and 1400, respectively, were achieved in the RCM of DEDAM. High activity was also observed in enyne metathesis and ring-opening-cross metathesis using norborn-5-ene and 7-oxanorborn-5-ene derivatives. Supported versions were synthesised by immobilising $RuCl_2$(SIMes)[=CH-2-(2-PrO)-C_6H_4] on a perfluoroglutaric acid derivatised hydroxymethylated Merrifield resin (silver form).

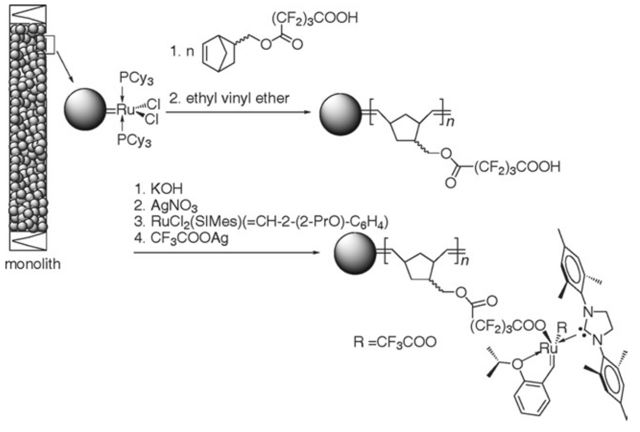
Ru(polymer–CH_2–O–CO–$CF_2CF_2CF_2$COO)(CF_3CO_2][=CH–2-(2-PrO)–C_6H_4](SIMes) was finally obtained by substitution of the remaining Cl ligand of the parent catalyst *via* addition of CF_3COOAg (Scheme 10). Excellent activity in RCM was observed; TONs up to 1100 were achieved in stirred batch RCM experiments. Leaching of ruthenium into the reaction mixture was low, resulting in a ruthenium content <70 ng g^{-1} in the final RCM-derived products. Finally, a monolith-supported version of this catalyst was prepared and used in continuous flow experiments (Scheme 11).[68] TOFs of 0.11 s^{-1} were observed and TONs were > 500. It is worth mentioning that the TONs obtained with these two supported versions so far exceed all published data on supported well-defined metathesis catalysts.



Scheme 9 Synthesis of a monolith-bound Hoveyda-type catalyst based on *vic*-dicarboxylates.

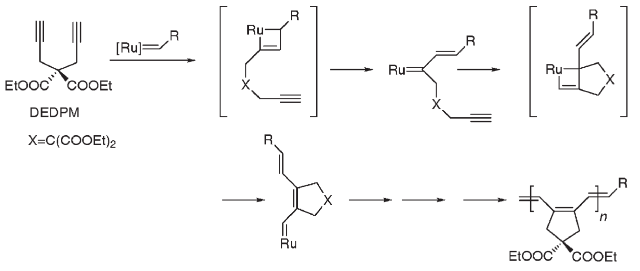


Scheme 10 Synthesis of a Hoveyda-type catalyst bound to a Merrifield support.



Scheme 11 Synthesis of a monolith-bound Hoveyda-type catalyst based on flourocarboxylates.

In view of the high reactivity of these systems and other ongoing projects in the stereo- and regioselective cyclopolymerisation of heptadiynes (Scheme 12),[69–71] we investigated whether these catalysts would be suitable for this purpose. Even to our surprise, Ru(CF$_3$COO)$_2$(SIMes) [=CH–(2,4,5-(MeO)$_3$-C$_6$H$_2$] turned out to be an excellent catalyst for the cyclopolymerisation of diethyl dipropargylmalonate (DEDPM), allowing class VI living polymerisations.[72]



Scheme 12 Cyclopolymerisation of DEDPM to yield poly(ene)s consisting solely of 5-membered rings.

A supported version of this catalyst was prepared by attaching it to a poly(2-oxazoline) derived block copolymer (Scheme 13). This supported catalyst allowed the cyclopolymerisation of DEDPM in water under micellar conditions. At this point it should be emphasised that these have been the first Ru-catalysed (cyclo-) polymerisations of alkynes ever reported.

Other immobilised Ru-based catalysts. Tremel *et al.* reported on a ruthenium catalyst precursor immobilised on gold colloids (Fig. 6) and its use in the polymerisation of norborn-2-ene.[73] Though TOFs of 75,000 h^{-1} were reported after initiation with ethyl diazoacetate, data on other substrates and PDIs of poly(norborn-2-ene) are lacking, impeding an evaluation of the value of this system.

Kobayashi *et al.* described a poly(styrene) supported version of [Ru-(η^6–C$_6$H$_5$COOEt)(PR$_3$)Cl$_2$] (R = Cy, Ph) (Scheme 14).[74] 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.

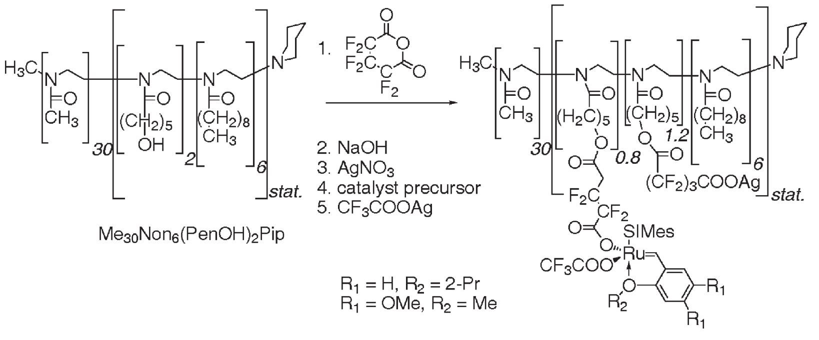
Recently, Fürstner *et al.* reported on a silica-immobilised NHC-based ruthenium catalyst (Fig. 7).[75] This system was reported to be reusable up to 3 times with TONs in the range of 15–20.

Finally, Verpoort *et al.* reported on a MCM-41 immobilised system shown in Fig. 8.[76] It was used in ROMP of norborn-2-ene and cyclooctene as well as in the RCM of various dienes. TONs in the range of 4–20 were reported.

Molybdenum-based systems

Due to the pronounced sensitivity of Mo-based systems towards oxygen and moisture, only a 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,[77,78] supported versions of well-defined catalysts, such as analogues of Schrock catalysts, are rare. Stelzer *et al.* reported on such a supported version prepared by the reaction of Mo[*N*-2,6-(*i*-Pr$_2$)–C$_6$H$_3$](CH–*t*-Bu)(OTf)$_2$·DME (DME = dimethoxyethane, OTf = CF$_3$SO$_3$) with methylalumoxane (MAO).[79] Significant ROMP activity was observed under continuous conditions,[80] nevertheless, the actual 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, Hoveyda and their coworkers[81] They used a polymerisable, that is *p*-styrylethyl substituted, enantiomerically pure biphenoxide. The bis-O-protected form of this ligand was subjected to radical copolymerisation with styrene. Subsequent deprotection, deprotonation and reaction with the



Scheme 13 Synthesis of a poly(2-oxazoline) bound Ru-based metathesis catalyst.

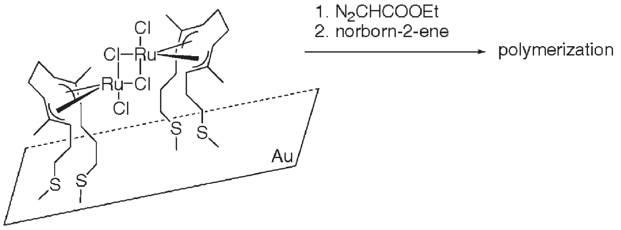
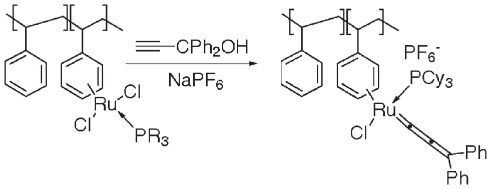


Fig. 6 Au colloid immobilised metathesis catalyst precursor.



Scheme 14 PS-supported Ru-allenylidene catalyst.

catalyst precursor Mo(N-2,6-i-Pr_2–C_6H_3)(=$CHCMe_2Ph$-)$(OTf)_2$·DME resulted in the desired supported catalyst (Scheme 15).[82]

A comparison of the results obtained in asymmetric RCM and selected desymmetrisation reactions, respectively, revealed no significant differences between the parent and the analogous supported systems 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 low leaching ($<5\%$), resulting in low contamination of the products with Mo. Unfortunately, the system showed reduced recyclability. Nevertheless, in view of the highly unstable Mo-methylidenes that are formed as intermediates 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 for a more straightforward synthesis, we recently reported on the synthesis of a supported version of a chiral Schrock catalyst prepared by ROMP.[83] For polymerisation, we prepared a bis(norborn-2-ene) substituted chiral phenoxide, which could be polymerised without any protection/deprotection steps using Ru$(CF_3COO)_2$[=CH-2-(2-PrO)–C_6H_4]-(SIMes).[67] Reaction of the polymeric support with KH followed by Mo(N-2,6-i-Pr_2–C_6H_3)(=$CHCMe_2$)Ph$(OTf)_2$·DME resulted in the desired supported catalyst (Scheme 16).

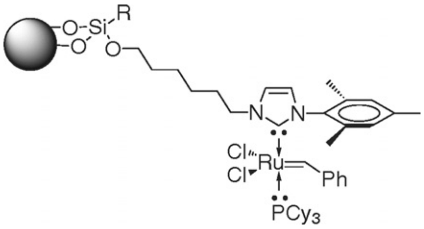


Fig. 7 Silica-supported catalyst described by Fürstner *et al.*

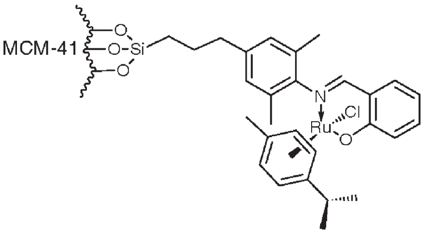
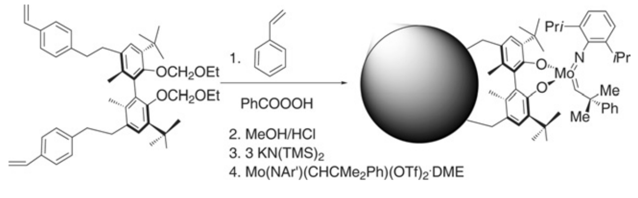


Fig. 8 MCM-41 supported catalyst.



Scheme 15 Synthesis of a supported enantioselective Schrock catalyst *via* radical polymerisation.

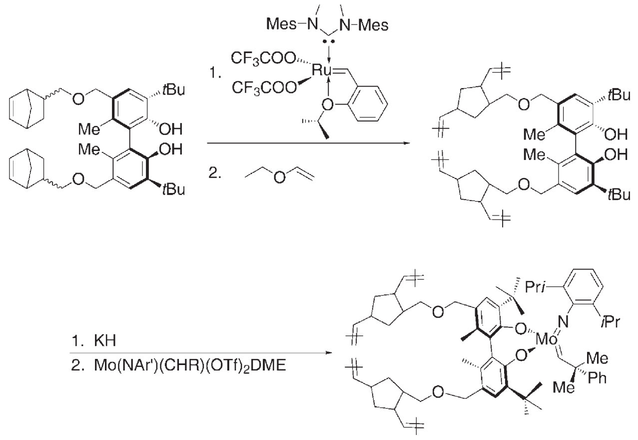
Due to the low crosslinked nature of the support, which showed a swelling of 700%, resulting in a solvent uptake of 2000%, the catalytic sites showed increased accessibility compared to the parent supported version. Consequently, lower amounts of catalyst were required, while yields and *ee*s were basically identical to those obtained with the supported system describe above. Again the Mo loss was $<5\%$.

Rhenium-based systems

While supported versions of Re_2O_7 (*e.g.*, Re_2O_7/Al_2O_3) are widely used in numerous industrial processes, reports on well-defined supported Re catalysts are very rare. Methyltrioxorhenium [$ReO_3(CH_3)$] was first reported to be active in olefin metathesis by Herrmann *et al.*,[84] and immobilised on Nb_2O_5. Though a surface-acidity-dependent metathesis activity for *cis*-2-pentene was found, the actual catalytic species remained unknown.[85,86] Bein *et al.* reported on the successful encapsulation of $ReO_3(CH_3)$ in zeolite-Y-type carriers.[87] With 1-hexene as substrate, metathesis activity was observed at low zeolite acidity, where $ReO_3(CH_3)$ was activated by the intrazeolite protons and simultaneously blocked their isomerisation activity.

Conclusion, summary and outlook

Supported catalysts for metathesis reactions will 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 to economical aspects, *i.e.* the price. Nevertheless, a steady and consequent development in homogeneous catalysis, that is the synthesis of highly active and stable



Scheme 16 Synthesis of a supported, enantioselective Schrock catalyst *via* ROMP.

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.

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References

1 R. H. Grubbs, S. J. Miller and G. C. Fu, *Acc. Chem. Res.*, 1995, **28**, 446.
2 M. Schuster and S. Blechert, *Angew. Chem.*, 1997, **109**, 2124; M. Schuster and S. Blechert, *Angew. Chem. Int. Ed.*, 1997, **36**, 2036.
3 R. H. Grubbs and S. Chang, *Tetrahedron*, 1998, **54**, 4413.
4 A. Fürstner, *Angew. Chem.*, 2000, **112**, 3140; A. Fürstner, *Angew. Chem. Int. Ed.*, 2000, **39**, 3012.
5 M. E. Maier, *Angew. Chem.*, 2000, **112**, 2153; M. E. Maier, *Angew. Chem. Int. Ed.*, 2000, **39**, 2073.
6 A. Fürstner and K. Langemann, *Synthesis*, 1997, 792.
7 R. H. Grubbs, Ed., *Handbook of Metathesis*, Wiley-VCH, Weinheim, 2003, vol.1–3.
8 T. J. Seiders, D. W. Ward and R. H. Grubbs, *Org. Lett.*, 2001, **3**, 3225.
9 A. H. Hoveyda and R. R. Schrock, *Chem.-Eur. J.*, 2001, **7**, 945.
10 M. R. Buchmeiser, *Chem. Rev.*, 2000, **100**, 1565.
11 R. R. Schrock, *J. Chem. Soc., Dalton Trans.*, 2001, 2541.
12 R. R. Schrock, *Chem. Rev.*, 2002, **102**, 14.
13 R. R. Schrock, *Acc. Chem. Res.*, 1990, **23**, 158.
14 R. H. Grubbs and S. H. Pine, in *Comprehensive Organic Synthesis*, eds. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, vol. 5, p. 1115.
15 R. R. Schrock, in *Ring-Opening Polymerization*, ed. D. J. Brunelle, Hanser, Munich, 1993, p. 129.
16 R. R. Schrock, *Pure Appl. Chem.*, 1994, **66**, 1447.
17 R. R. Schrock, *Polyhedron*, 1995, **14**, 3177.
18 T. M. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, 2001, **34**, 18.
19 M. R. Buchmeiser, N. Atzl and G. K. Bonn, *J. Am. Chem. Soc.*, 1997, **119**, 9166.
20 F. Sinner, M. R. Buchmeiser, R. Tessadri, M. Mupa, K. Wurst and G. K. Bonn, *J. Am. Chem. Soc.*, 1998, **120**, 2790.
21 H. D. Maynard and R. H. Grubbs, *Tetrahedron Lett.*, 1999, **40**, 4137.
22 Y. M. Ahn, K. Yang and G. I. Georg, *Org. Lett.*, 2001, **3**, 1411.
23 J.-Y. Cho and B. M. Kim, *Org. Lett.*, 2003, **5**, 531.
24 M. Schuster, J. Pernerstorfer and S. Blechert, *Angew. Chem.*, 1996, **108**, 2111; M. Schuster, J. Pernerstorfer and S. Blechert, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1979.
25 M. Schuster, N. Lucas and S. Blechert, *Chem. Commun.*, 1997, 823.
26 M. R. Buchmeiser, ed., *Polymeric Materials in Organic Synthesis and Catalysis*, Wiley-VCH, Weinheim, 2003.
27 D. Sémeril, H. Olivier-Bourbigou, C. Bruneau and P. H. Dixneuf, *Chem. Commun.*, 2002, 146.
28 D. F. Taber and K. J. Frankowski, *J. Org. Chem.*, 2003, **68**, 6047.
29 N. Audic, H. Clavier, M. Mauduit and J.-C. Guillemin, *J. Am. Chem. Soc.*, 2003, **125**, 9248.
30 M. Picquet, I. Tkatchenko, I. Tommasi, P. Wasserscheid and J. Zimmermann, *Adv. Synth. Catal.*, 2003, **345**, 959.
31 Q. Yao and Y. Zhang, *Angew. Chem.*, 2003, **115**, 3517; Q. Yao and Y. Zhang, *Angew. Chem. Int. Ed.*, 2003, **42**, 3395.
32 S. Csihony, C. Fischmeister, C. Bruneau, I. T. Horváth and P. H. Dixneuf, *New. J. Chem.*, 2002, **26**, 1667.
33 R. C. Buijsman, E. van Vuuren and J. G. Sterrenburg, *Org. Lett.*, 2001, **3**, 3785.
34 A. Fürstner, L. Ackermann, K. Beck, H. Hori, D. Koch, K. Langemann, M. Liebl, C. Six and W. Leitner, *J. Am. Chem. Soc.*, 2001, **123**, 9000.
35 S. E. Gibson and V. M. Swamy, *Adv. Synth. Catal.*, 2002, **344**, 619.
36 J. S. Kingsbury and A. H. Hoveyda, in *Polymeric Materials in Organic Synthesis and Catalysis*, ed. M. R. Buchmeiser, Wiley-VCH, Weinheim, 2003, pp. 467.
37 M. Mayr, B. Mayr and M. R. Buchmeiser, *Des. Monomers Polym.*, 2002, **5**, 325.
38 M. Mayr, B. Mayr and M. R. Buchmeiser, in *Studies in Surface Science and Catalysis: Scientific Bases for the Preparation of Heterogeneous Catalysts*, eds. E. Gaigneaux, D. E. DeVos, P. Grange, P. A. Jacobs, J. A. Martens, P. Ruiz and G. Poncelet, Elsvier, Amsterdam, 2002, vol. 143, pp. 305.
39 S. Nguyen and R. H. Grubbs, *J. Organomet. Chem.*, 1995, **497**, 195.
40 K. Melis, D. De Vos, P. Jacobs and F. Verpoort, *J. Mol. Catal. A: Chem.*, 2001, **169**, 47.
41 A. G. M. Barrett, S. M. Cramp and R. S. Roberts, *Org. Lett.*, 1999, **1**, 1083.
42 M. Ahmed, A. G. M. Barrett, D. C. Braddock, S. M. Cramp and P. A. Procopiu, *Tetrahedron Lett.*, 1999, **40**, 8657.
43 M. Mayr, B. Mayr and M. R. Buchmeiser, *Angew. Chem.*, 2001, **113**, 3957; M. Mayr, B. Mayr and M. R. Buchmeiser, *Angew. Chem. Int. Ed.*, 2001, **40**, 3839.
44 M. Ahmed, T. Arnauld, A. G. M. Barrett, D. C. Braddock and P. A. Procopiu, *Synlett*, 2000, 1007.
45 L. Jafarpour and S. P. Nolan, *Org. Lett.*, 2000, **2**, 4075.
46 L. Jafarpour, M.-P. Heck, C. Baylon, H.-M. Lee, C. Mioskowski and S. P. Nolan, *Organometallics*, 2002, **21**, 671.
47 J. S. Kingsbury, J. P. A. Harrity, P. J. Bonitatebus, Jr. and A. H. Hoveyda, *J. Am. Chem. Soc.*, 1999, **121**, 791.
48 Q. Yao, *Angew. Chem.*, 2000, **112**, 4060; Q. Yao, *Angew. Chem. Int. Ed.*, 2000, **39**, 3896.
49 S. B. Garber, J. S. Kingsbury, B. L. Gray and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2000, **122**, 8168.
50 S. Varray, R. Lazaro, J. Martinez and F. Lamaty, *Organometallics*, 2003, **22**, 2426.
51 J. Dowden and J. Savovic, *Chem. Commun.*, 2001, 37.
52 J. S. Kingsbury, S. B. Garber, J. M. Giftos, B. L. Gray, M. M. Okamoto, R. A. Farrer, J. T. Fourkas and A. H. Hoveyda, *Angew. Chem.*, 2001, **113**, 4381; J. S. Kingsbury, S. B. Garber, J. M. Giftos, B. L. Gray, M. M. Okamoto, R. A. Farrer, J. T. Fourkas and A. H. Hoveyda, *Angew. Chem. Int. Ed.*, 2001, **40**, 4251.
53 A. H. Hoveyda, D. G. Gillingham, J. J. Van Veldhuizen, O. Kataoka, S. B. Garber, J. S. Kingsbury and J. P. A. Harrity, *Org. Biomol. Chem.*, 2004, **2**, 8.
54 S. J. Connon, A. M. Dunne and S. Blechert, *Angew. Chem.*, 2002, **114**, 3989; S. J. Connon, A. M. Dunne and S. Blechert, *Angew. Chem. Int. Ed.*, 2002, **41**, 3835.
55 K. Grela, M. Tryznowski and M. Bienik, *Tetrahedron Lett.*, 2002, **43**, 9055.
56 S. J. Connon and S. Blechert, *Bioorg. Med. Chem. Lett.*, 2002, **12**, 1873.
57 S. C. Schürer, S. Gessler, N. Buschmann and S. Blechert, *Angew. Chem.*, 2000, **112**, 4062; S. C. Schürer, S. Gessler, N. Buschmann and S. Blechert, *Angew. Chem. Int. Ed.*, 2000, **39**, 3898.
58 S. Randl, N. Buschmann, S. J. Connon and S. Blechert, *Synlett*, 2001, 1547.
59 F. Sinner and M. R. Buchmeiser, *Angew. Chem.*, 2000, **112**, 1491; F. Sinner and M. R. Buchmeiser, *Angew. Chem. Int. Ed.*, 2000, **39**, 1433.
60 F. Sinner and M. R. Buchmeiser, *Macromolecules*, 2000, **33**, 5777.
61 J. H. Oskam, H. H. Fox, K. B. Yap, D. H. McConville, R. O'Dell, B. J. Lichtenstein and R. R. Schrock, *J. Organomet. Chem.*, 1993, **459**, 185.
62 M. Mayr, M. R. Buchmeiser and K. Wurst, *Adv. Synth. Catal.*, 2002, **344**, 712.
63 M. R. Buchmeiser, M. Mupa, G. Seeber and G. K. Bonn, *Chem. Mater.*, 1999, **11**, 1533.
64 P. Nieczypor, W. Buchowicz, W. J. N. Meester, F. P. J. T. Rutjes and J. C. Mol, *Tetrahedron Lett.*, 2001, **42**, 7103.
65 J. O. Krause, S. Lubbad, M. Mayr, O. Nuyken and M. R. Buchmeiser, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 2003, **44**, 790.
66 J. O. Krause, S. Lubbad, O. Nuyken and M. R. Buchmeiser, *Adv. Synth. Catal.*, 2003, **345**, 996.
67 J. O. Krause, K. Wurst, O. Nuyken and M. R. Buchmeiser, *Chem.-Eur. J.*, 2004, **10**, 778.
68 J. O. Krause, S. H. Lubbad, O. Nuyken and M. R. Buchmeiser, *Macromol. Rapid Commun.*, 2003, **24**, 875.
69 U. Anders, O. Nuyken, K. Wurst and M. R. Buchmeiser, *Angew. Chem.*, 2002, **114**, 4226; U. Anders, O. Nuyken, K. Wurst and M. R. Buchmeiser, *Angew. Chem. Int. Ed.*, 2002, **41**, 4044.

70 U. Anders, O. Nuyken, K. Wurst and M. R. Buchmeiser, *Macromolecules*, 2002, **35**, 9029.
71 U. Anders, M. Wagner, O. Nuyken and M. R. Buchmeiser, *Macromolecules*, 2003, **36**, 2668.
72 J. O. Krause, M. T. Zarka, U. Anders, R. Weberskirch, O. Nuyken and M. R. Buchmeiser, *Angew. Chem.*, 2003, **115**, 6147; J. O. Krause, M. T. Zarka, U. Anders, R. Weberskirch, O. Nuyken and M. R. Buchmeiser, *Angew. Chem. Int. Ed.*, 2003, **42**, 5965.
73 M. Bartz, J. Küther, R. Seshadri and W. Tremel, *Angew. Chem.*, 1998, **110**, 2646; M. Bartz, J. Küther, R. Seshadri and W. Tremel, *Angew. Chem. Int. Ed.*, 1998, **37**, 2466.
74 R. Akiyama and S. Kobayashi, *Angew. Chem.*, 2002, **114**, 2714; R. Akiyama and S. Kobayashi, *Angew. Chem. Int. Ed.*, 2002, **42**, 2602.
75 S. Prühs, C. W. Lehmann and A. Fürstner, *Organometallics*, 2004, **23**, 280.
76 B. De Clerq, F. Lefebvre and F. Verpoort, *New J. Chem.*, 2002, **26**, 1201.
77 K. J. Ivin and J. C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, San Diego, 1997.
78 E. M. Zahidi, H. Oudghiri-Hassani and P. H. McBreen, *Nature (London)*, 2001, **409**, 1023.
79 P. Preishuber-Pflügl, P. Buchacher, E. Eder, R. M. Schitter and F. Stelzer, *J. Mol. Catal.: A Chem.*, 1998, **133**, 151.
80 P. Preishuber-Pflügl, E. Eder and F. Stelzer, *e-Polymers*, 2002, 45.
81 K. C. Hultzsch, J. A. Jernelius, A. H. Hoveyda and R. R. Schrock, *Angew. Chem.*, 2002, **114**, 609; K. C. Hultzsch, J. A. Jernelius, A. H. Hoveyda and R. R. Schrock, *Angew. Chem. Int. Ed.*, 2002, **41**, 589.
82 R. R. Schrock and A. H. Hoveyda, *Angew. Chem.*, 2003, **115**, 4740; R. R. Schrock and A. H. Hoveyda, *Angew. Chem. Int. Ed.*, 2003, **42**, 4592.
83 R. M. Kröll, N. Schuler, S. Lubbad and M. R. Buchmeiser, *Chem. Commun.*, 2003, 2742.
84 W. A. Herrmann, W. Wagner, U. N. Flessner, U. Volkhardt and H. Komber, *Angew. Chem.*, 1991, **103**, 1704; W. A. Herrmann, W. Wagner, U. N. Flessner, U. Volkhardt and H. Komber, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1638.
85 R. Buffon, A. Choplin, M. Leconte, J.-M. Basset, R. Touroude and W. A. Herrmann, *J. Mol. Catal.*, 1992, **72**, L7.
86 R. Buffon, A. Auroux, F. Lefebvre, M. Leconte, A. Choplin, J. M. Basset and W. A. Herrmann, *J. Mol. Catal. A: Chem.*, 1992, **76**, 287.
87 T. Bein, C. Huber, K. Moller, C. G. Wu and L. Xu, *Chem. Mater.*, 1997, **9**, 2252.