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Development of new ruthenium catalysts for homogeneous and heterogeneous olefin-metathesis

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„Nur wer erwachsen wird und ein Kind bleibt, ist ein Mensch.“

Erich Kästner (1899-1974)

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Abbreviations

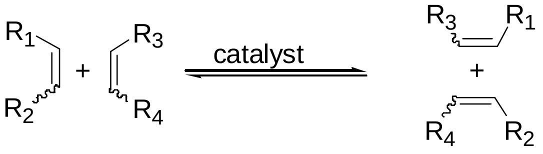
?̃	wave number in cm^{-1}
Ad	adamantyl
ADMET	acyclic diene metathesis
Ar	aryl
b	broad
Bu	butyl
Cat	catalyst
CM	cross-metathesis
Cp	cyclopentadienyl
CTA	chain transfer agent
Cy	cyclohexyl
d	doublet
dd	doublet of doublets
DEDAM	diethyl diallylmalonate
DEDPM	diethyl dipropargylmalonate
DMF	*N,N*-dimethylformamide
DMN-H6	1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo-endo*-dimethanonaphthalene
DMSO	dimethylsulfoxide
dt	doublet of triplets
DVB	divinylbenzene
E	energy gap between the valence and conduction band
ECMCH	4-(ethoxycarbonyl)-4-(1*S*, 2*R*, 5*S*)-(+)-menthoxycarbonyl-1,6-heptadiyne, dimethyldipropargylmalonate
EI	electron impact
FT-IR	Fourier-transform infrared
fw	formula weight
GC-MS	gas-chromatography-mass spectrometer
h	hour
Hz	Hertz
ICP	inductively coupled plasma
IMes	1,3-bis-2,4,6-trimethylphenyl-imidazol-2-ylidene

SIMes	1,3-bis-2,4,6-trimethylphenyl-4,5-dihydroimidazol-2-ylidene
LS	light scattering
m	multiplet
MALDI-TOF	matrix assisted laser desorption-ionization/time of flight
Mes	2,4,6-trimethylphenyl
MHz	mega Hertz
M_n	molecular weight in g/mol (number average)
n	degree of polymerization
NBE	norbornene
NHC	N-heterocyclic carbene
NMR	nuclear magnetic resonance spectroscopy
OCT	olefins conversion technology
OLED	organic light emitting device
PEEK	poly-ether-ether-ketone
PEG	polyethyleneglycol
Ph	phenyl
ppm	parts per million
PS	polystyrene
q	quartet
RCM	ring-closing metathesis
RI	refraction index
ROM	ring-opening metathesis
ROMP	ring-opening metathesis polymerization
RT	room temperature
s	strong in IR or singulet in NMR
SHOP	Shell-higher-olefins process
SIMes	1,3-bis-Mes-4,5-dihydroimidazol-2-ylidene
TEM	transmission electron microscopy
THF	tetrahydrofuran
TMS	tetramethylsilane
TMSCl	trimethylchlorosilane
TOF	turnover frequency

TON	turnover number
vs	very strong
vw	very weak
w	weak
d	shift in NMR

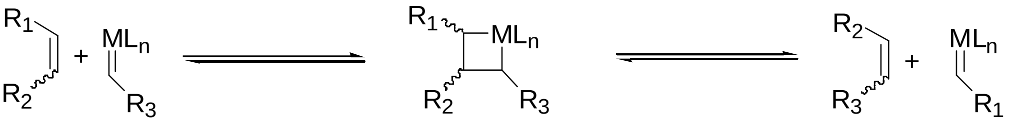
1 Introduction

In 1950 chemists at DuPont's petrochemicals department obtained a mixture of propylene, ethylene and 1-butene by passing remaining propylene from radical polymerization over a molybdenum catalyst immobilized on alumina. In 1955 the first patent on olefin-metathesis was granted.[1] In 1960, the disproportionation of propylene to ethylene and butenes led to a patent by the Standard Oil Co.[2,3] This process is generally referred to as the Phillips triolefin process. Today the SHOP (Shell-higher-olefins process) with 1.2 million tons of linear olefins per year is the most important industrial process for olefin-metathesis. Today, there is great interest in propylene, so that propylene is produced from ethylene and 2-butene in a process known as olefins conversion technology (OCT), which will be operated soon at BASF Fina Petrochemicals. In 1967, Calderon presented the mechanism of olefin metathesis and introduced it as a new reaction (scheme 1-1).[4,5]



Scheme 1-1. General reaction of olefin-metathesis.

In 1971, Chauvin postulated that during metathesis a metal carbene is formed and that it acts through formation of a metallacyclobutane as intermediate of the reaction (scheme 1-2)[6]. The final proof was given by Katz and Dall'Asta.[7-9]

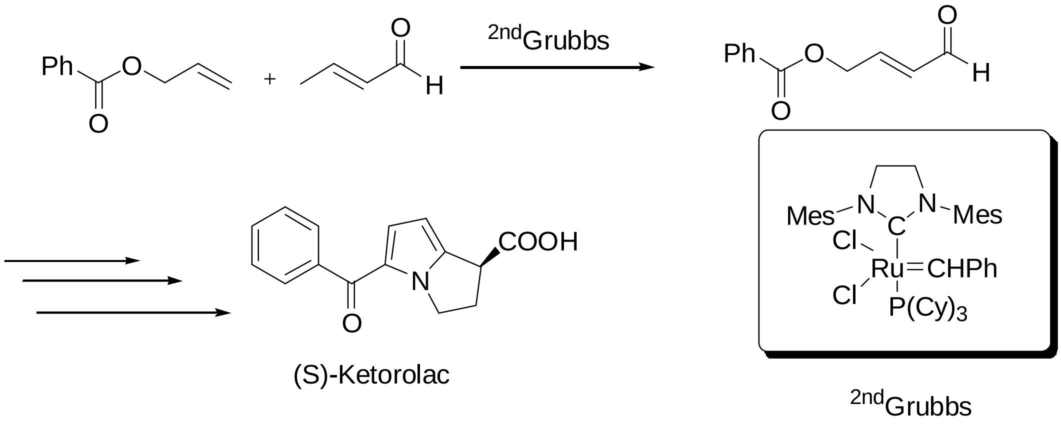


Scheme 1-2. Mechanism according to Chauvin.

Of course, the synthesis of $(CO)_5W{=}C(CH_3)(OCH_3)$ by Fischer was an important detail for Chauvin that led him to his hypothesis.[10-14]

With the development of well-defined catalysts by Grubbs and Schrock, olefin-metathesis could be introduced into organic chemistry.[15-21] The ruthenium based Grubbs catalysts have high preference for carbon-carbon double bonds and are indifferent to alcohols, amides, aldehydes and carboxylic acids in contrast to the Schrock catalysts that must be handled in a dry box.

Today, there are even highly active catalysts for asymmetric reactions reported by Hoveyda, Schrock and Grubbs.[22-29] To catalyze specific organic reactions, the Grubbs catalyst becomes of increasing interest for industrial application, as is here demonstrated in the synthesis of a,ß-unsaturated aldehydes (scheme 1-3).[30,31]



Scheme 1-3. Example of an industrial application of the well defined Grubbs catalyst.

As these highly active and well-defined catalysts are used in industrial synthesis of fine chemicals, permanently bound mimics of these catalysts are of great interest to prevent contamination of products with catalyst waste.

2 Background

2.1 Types of olefin metathesis

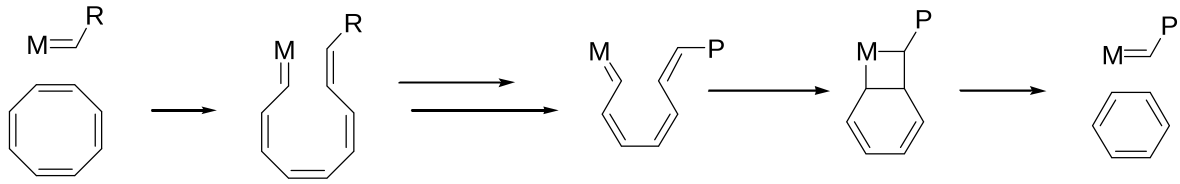
2.1.1 Ring closing metathesis (RCM)

In recent years, the RCM reaction became an important synthetic tool for organic chemists, who built up their molecules with double bounds, which could be introduced at an early stage of the synthetic protocol into their molecules.[21,32-41] In the key step rings are formed. As the RCM process involves equilibria, the RCM reaction requires running the experiment at high dilution so that most of the reactions are intra- rather than intermolecular (ADMET). In most cases the release of a gas such as ethene is the driving force of this reaction.

2.1.2 Ring-opening metathesis polymerization (ROMP)

As the name implies, this is the opposite of the RCM reaction. This type of reaction involves a cyclic olefin (norbornene or similar). In contrast to RCM, the relief of ring strain is here the main driving force.[42-56] Consequently, olefins such as cyclohexene with little ring strain can not be polymerized. Most prominent monomers are Diels-Alder adducts such as norbornenes.[57-61] The polymers produced by ROMP typically show a very narrow molecular weight distribution, something that is very difficult to achieve by standard polymerization methods such as free radical polymerization. Thus, the polydispersities are typically in the range of 1.03 to 1.10. An important feature of this mechanism is that ROMP systems are typically living polymerization catalysts.[62,63] Therefore, even the synthesis of block-copolymers is possible.[64]

However, one has to be a little more careful when selecting a ROMP catalyst. If the catalyst is too active, it can metathesize the unstrained olefinic bonds in the growing polymer chain (a process called "back-biting"), thereby reducing the molecular weight and increasing the molecular weight distribution (polydispersity). During the synthesis of polyacetylene by ROMP of cyclooctatetraene, backbiting occurs if the growing polymer chain can orient itself to undergo an intramolecular metathesis and generate benzene (scheme 2-1).[65-71] With a catalyst that can not react with internal olefins this reaction can not occur.

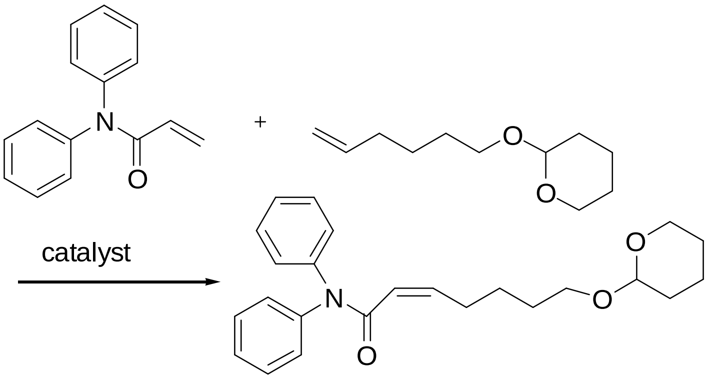


Scheme 2-1. Side reaction in the ROMP of cyclooctatetraene.

Technical applications of ROMP are the Norsorex-process[72] (ROMP of norbornene) and Vestenamer polymerization (ROMP of cyclooctene) using ill-defined tungsten catalysts. The polymers are used as elastomers.

2.1.3 Cross-metathesis (CM)

As described in the introduction, CM (cross-metathesis) is of great interest for building up organic molecules for industrial applications.[73-77] With the development of the Grubbs-Herrmann catalyst, trisubstituted and more importantly, functionalized olefins could be reacted. A good example is the cross-metathesis of a-ß-unsaturated amides with terminal olefins such as styrene. It is an important fact that the catalyst tolerates the coordination of the amides (scheme 2-2). As the Grubbs-Herrmann catalyst is highly stable, this reaction can be performed at elevated temperatures (40 °C).[78-81]

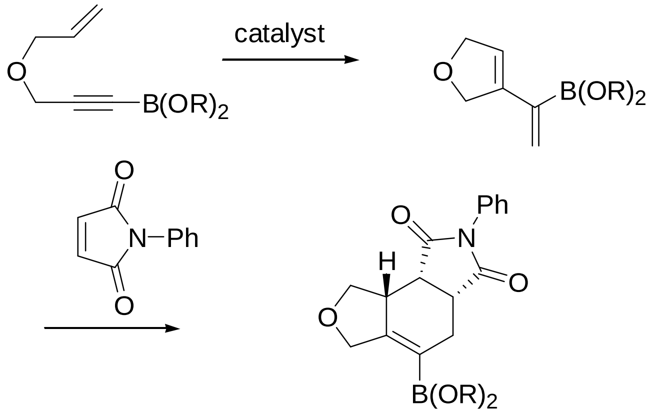


Scheme 2-2. CM of electron poor amides.

Examples of large industrial applications of CM such as the SHOP[82], FEAST (further exploitation of advanced Shell technology)[83] or the Phillips triolefins process and the OCT are mentionend in the introduction.

2.1.4 Enyne metathesis

Enyne metathesis is a variant of RCM, with the advantage of building a ring with an exocyclic olefin bound.[84-88] The obtained structures can be used as educts for Diels-Alder reactions as is shown in scheme 2-3.[89]

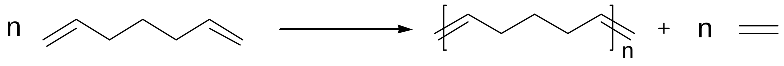


Scheme 2-3. Example of enyne metathesis followed by Diels-Alder reaction.

The boronic ester can be further used as an educt for Suzuki reactions,[90-94] so that large molecules can be built up in three steps using metal catalyzed reactions.

2.1.5 Acyclic diene metathesis (ADMET)

In the ADMET (acyclic diene metathesis) a,? -dienes are used to produce polymers. Driving force of this reaction is the release of ethene as in the RCM, normally accelerated by introducing nitrogen into the system. In contrast to RCM, one has to use high concentrations to run this intermolecular reaction instead of the intramolecular ones (scheme 2-4).

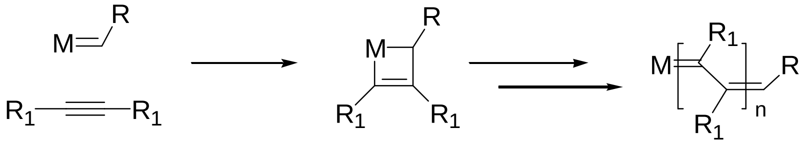


Scheme 2-4. ADMET of 1,6-heptadiene.

The reverse of this reaction (reacting an unsaturated polymer with excess ethylene in the presence of a metathesis catalyst), is of great interest for recycling automobile tires.[95] The Grubbs-Herrmann catalyst would tolerate the functional groups in tires and is able to react with internal olefins, but is too expensive. It remains to be seen if this method will become commercially viable.

2.1.6 Acetylene Polymerization

During acetylene polymerization a metallacyclobutene - instead of a metallacyclobutane as in ROMP - is formed via a [2+2] addition. If this metallacycle opens in a productive fashion, the result is a growing polymer chain (scheme 2-5).[96-109]

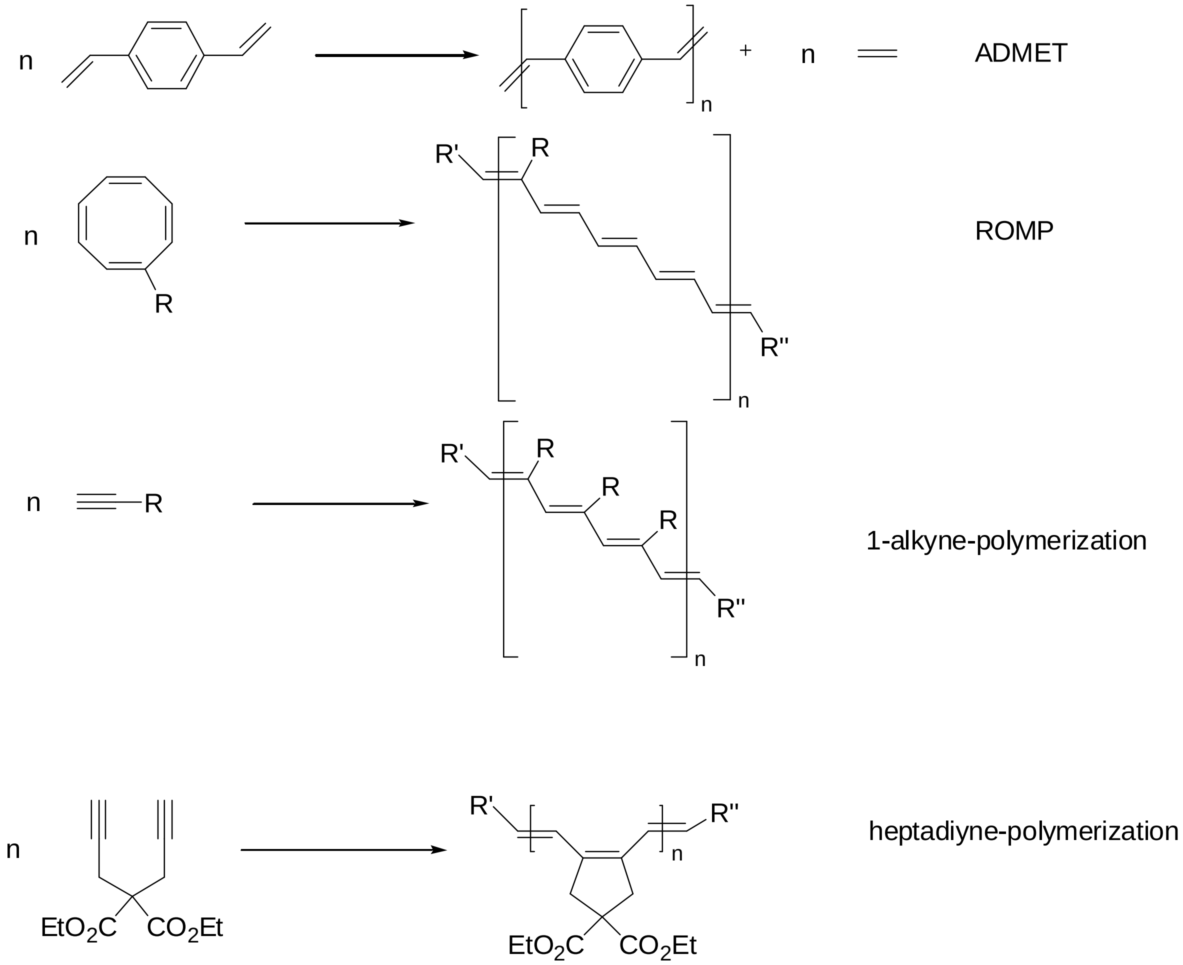


Scheme 2-5. Polymerization of acetylenes.

This reaction typically only works well with 2-butyne or terminal acetylenes and was totally unknown for ruthenium catalysts so far. Polymerization of terminal acetylenes is complicated by the potential for the R group to insert a or ß with respect to the metal. It is always extremely challenging to get one type of insertion and generate a polymer with reproducible properties.

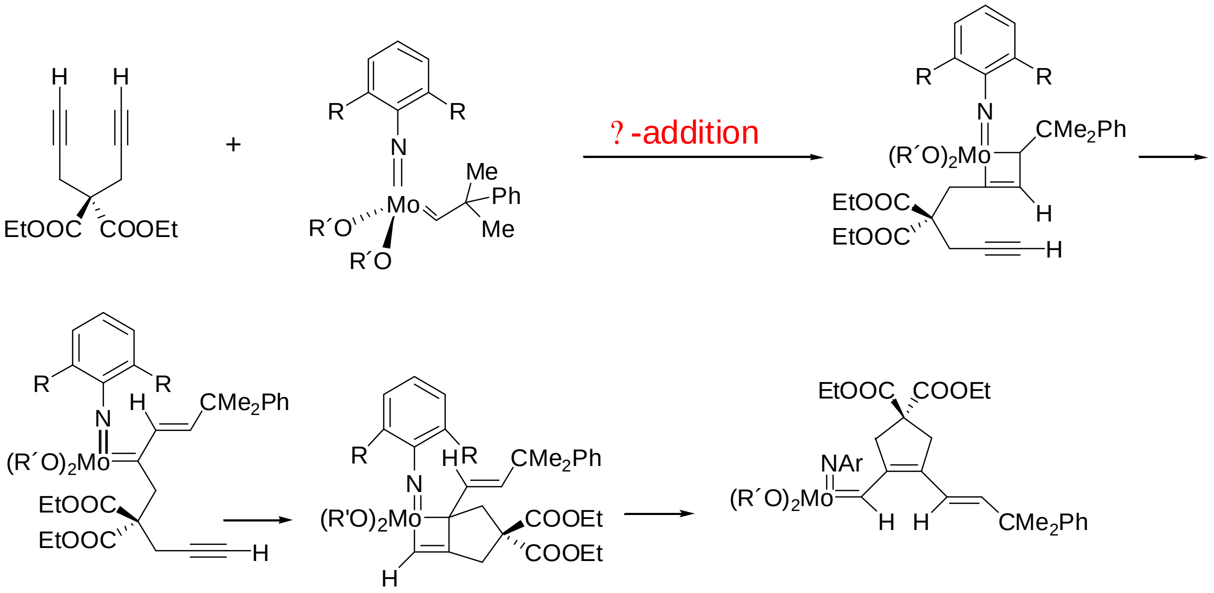
2.1.7 Polymerization of heptadiynes

Initiated by the discovery of the conductive properties of doped polyacteylene,[107-109] conjugated polymers are widely used in organic light-emitting diodes (OLEDS), solar cells, photovoltaic devices, field effect transistors and lasers.[107-112] Despite significant improvements, polyacteylene-derived materials still suffer from one or more drawbacks from a technological point of view such as insufficient stability and processability, random composition in terms of connectivity, end groups, molecular weight or reduced synthetic accessibility. On the one hand, any successful utilisation of these systems strongly depends on a high degree of definition and variability in monomer structure as well as stability and processability of the final polymeric material. On the other hand, these tasks must be accomplished via straightforward synthetic routes in order to allow commercialization. In contrast to 1-alkyne polymerization, the cyclopolymerization of 1,6-heptadiynes offers an attractive access to polyacetylenes with cyclic recurring units along the backbone where 1,3-interactions of the substituents, responsible for low effective conjugation lengths in poly(1-alkyne)s, are absent.[113,114] Examples of conjugated polymers obtained via ADMET, ROMP, 1-alkyne-polymerization and cyclopolymerization are shown in scheme 2-6.

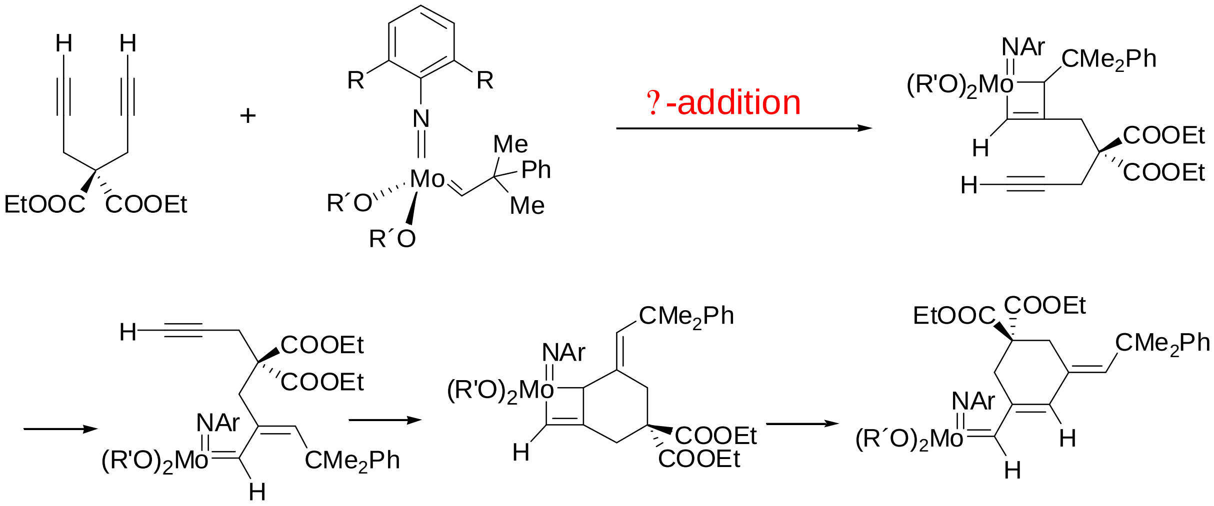


Scheme 2-6. Synthesis of conjugated polymers.

Cyclopolymerization-derived polyacetylenes display good solubility in common organic solvents (e.g. C_6H_6, toluene, CH_2Cl_2, $CHCl_3$), good long-term stability towards oxidation and low energy transitions between the valence and conductivity band.[101,113-115] They can be synthesised using Ziegler-type catalysts,[116,117] Pd-catalysts,[118] anionic polymerization[119] and binary/ternary Mo- or W-based catalysts.[120] Well-defined high oxidation-state molybdenum carbenes ("Schrock catalysts") must be regarded as superior since they cyclopolymerize 1,6-heptadiynes in a living manner[46,120] and can be tuned in a way that only one single repetitive unit, i.e. 1,3-(cyclopent-1-enylene)vinylens (5-membered rings, scheme 2-7))[121,122] or 1,3-(cyclohexen-1-enylene)methylidenes (6-membered rings, scheme 2-8),[101,115] respectively, are obtained .



Scheme 2-7. Polymerization of DEDPM (diethyldipropargylmalonate) to yield 5-membered rings.



Scheme 2-8. Polymerization of DEDPM to yield 6-membered rings.

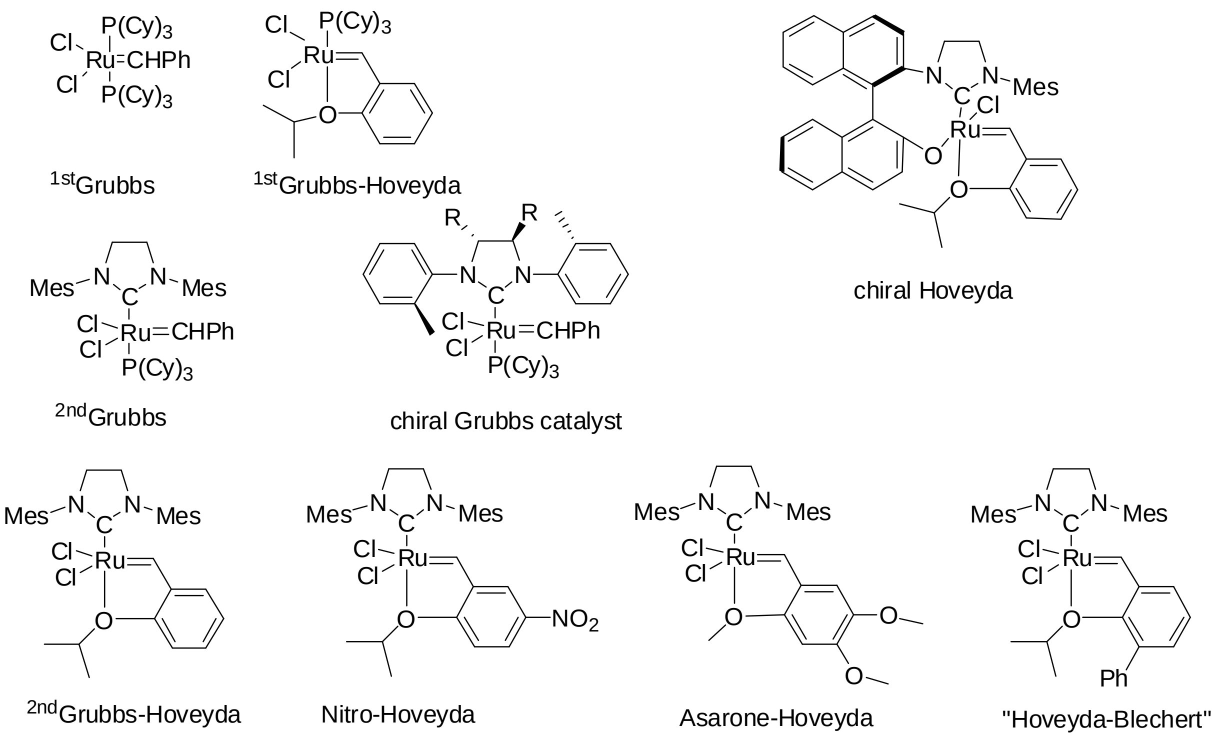
Despite their unique catalytic properties, the strictly air- and moisture-free conditions that are required in the use of Schrock catalysts are certainly a major limitation for technically relevant applications. Therefore, keeping any potential technological use in mind, such syntheses have to be accomplished by more straightforward routes. Grubbs-Herrmann (e.g. $RuCl_2$(1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolin-2-ylidene)(CHPh)(PCy_3)) respectively Grubbs-Hoveyda catalysts (e.g. $RuCl_2$(=CH(2-(2-PrO-C_6H_4)(1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolin-2-ylidene))[123] in fact represent air and moisture-stable metathesis catalysts with remarkable activity, sometimes rivalling that of highly active Schrock catalysts.[43] Nonetheless, despite their activity in ROMP, ring-closing, enyne and ring-opening cross metathesis reactions, none of the existing systems was capable of polymerizing alkynes or cyclopolymerizing 1,6-heptadiynes so far. Though polyacetylenes may in principle be prepared with these catalysts, their synthesis can still only be accomplished by ROMP-based routes.[66] The synthesis of a modified Grubbs-Hoveyda catalyst that can accomplish the cyclopolymerization of 1,6-heptadiynes in both a living and stereoregular way would close the last gap between molybdenum- and ruthenium-based metathesis catalysts.

2.2 Catalysts

Today there are still numerous heterogeneous catalysts in use, usally consisting of a high valent transition metal halide, oxide or oxo-halide with an alkylating co-catalyst such as alkyl zinc, alkyl tin or alkyl aluminum.[124] Some of these catalyst systems are immobilized on an alumina or silica support. Classic examples include $WCl_6/SnMe_4$ and Re_2O_7/Al_2O_3 ("green catalyst")[125].

More important are the well-defined molybdenum based Schrock catalysts and the ruthenium based Grubbs catalysts. Today, there is a broad spectrum of catalysts available. Ruthenium based catalysts consists of first and second generation Grubbs catalysts, with the second generation catalyst bearing an electron rich N-heterocyclic carbene (NHC) instead of a phosphine. Sometimes, the Grubbs second generation catalyst is named Grubbs-Herrmann catalyst, because Herrmann first introduced the NHC ligand into the first generation Grubbs catalyst.[53,62,126-130] Unfortunately, naming is arbitrarily.

Molybdenum based Schrock catalysts are highly active but intolerant towards many functional groups. In any case, glove-box conditions or at least Schlenk conditions are required. Nevertheless, there are two advantages of Schrock catalysts. First, one can easily obtain chiral catalysts and secondly they can polymerize 1-alkynes and this even in a living manner. In the following figure some Grubbs catalysts are given, such as the ^{1st}Grubbs[131-133], ^{1st}Grubbs-Hoveyda[134], a chiral Hoveyda[23,24] as well as a chiral Grubbs catalyst[25], ^{2nd}Grubbs[53,135,136], ^{2nd}Grubbs-Hoveyda[123], Nitro-[137], Asarone-[138] and Blechert-Hoveyda[139,140] (figure 2-1).



1stGrubbs

1stGrubbs-Hoveyda

chiral Hoveyda

2ndGrubbs

chiral Grubbs catalyst

2ndGrubbs-Hoveyda

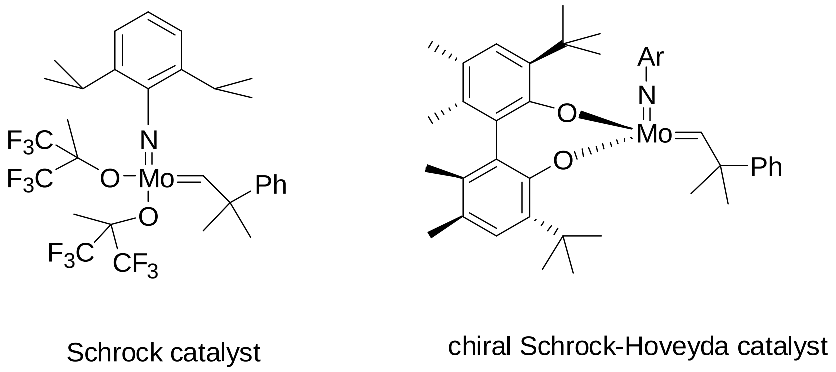
Nitro-Hoveyda

Asarone-Hoveyda

"Hoveyda-Blechert"

Figure 2-1. List of some Grubbs catalysts.

In the next figure the standard Schrock catalyst and the chiral Schrock-Hoveyda catalyst are shown.



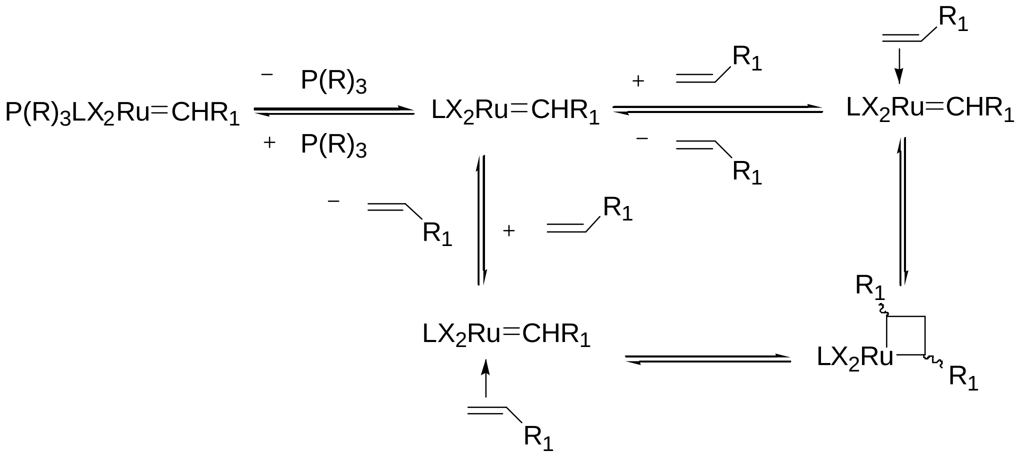
Schrock catalyst

chiral Schrock-Hoveyda catalyst

Figure 2-2. List of Schrock catalysts[27,141,142].

2.3 Mechanism

Based on the results by Chauvin[6], Katz[8,9], Dall'Asta[7], Sanford et al.[143,144] could present a mechanism for olefin metathesis with the Grubbs catalyst. Initiation proceeds by dissociative substitution of a phosphine ligand with an olefinic substrate (scheme 2-9).



Scheme 2-9. Mechanism of olefin metathesis with Ru-based catalysts according to Sanford and Grubbs.[143,144]

In the first step, the instable 14 electron ruthenium species is formed by phosphine dissociation. In the second step, the olefin coordinates to the ruthenium core and subsequently forms the metallacyclobutane. The metallacyclobutane can be isolated using a sterically demanding olefin. Crystals from this structure were grown for X-Ray measurements.[145] The reaction rate is decreased by the addition of phosphine and increased by the addition of CuCl (a phosphine scavenger).[146,147] All steps in this mechanism are reversible, which is an important and general detail of olefin metathesis.

2.4 Fixation to supports

Fixation of well-defined homogeneous catalysts combines the advantages of homogeneous catalysis such as high activity and selectivity with the simple removal of catalysts (in order to avoid metal contamination) in the case of heterogeneous catalysis.

Insoluble, two-phasic or amphiphilic supports such as PEG (polyethylene glycol)[148], monoliths[149-152], crosslinked polystyrene[153] and supports prepared by ring-opening metathesis precipitation polymerization[154] can be used. Some are used for catalysis in water[155-158] or in ionic liquids[159].

For the Grubbs catalyst, in principle all ligands could be used for fixation, but a difference had to be made between permanent and “boomerang” fixation[160-162]. Boomerang fixation can be achieved via the iso-propoxy group[160-162], a styrenyl (or vinyl) functionality[163] or the phosphine[162] ligand. The fixation possibilities are presented in the following scheme for the

^2nd^Grubbs-Hoveyda and Grubbs-Herrmann catalyst; for the Grubbs-Herrmann catalyst a reversible fixation using the phosphine is possible.[162]

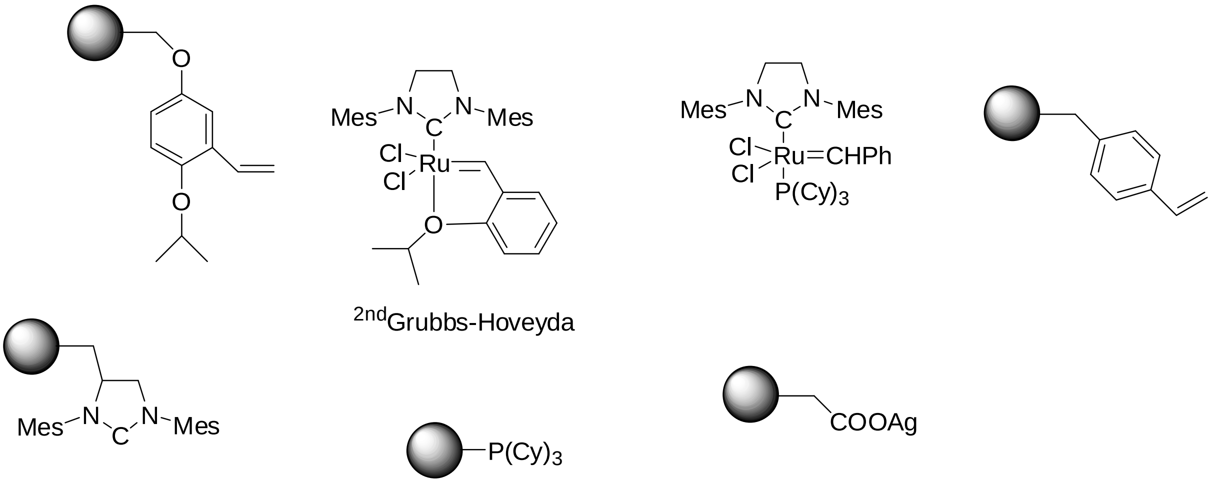


Figure 2-3. Possible fixations of ruthenium catalysts.

The first permanently bound Grubbs-Herrmann catalyst was realized by Blechert using a functionalized NHC, which was bound to a crosslinked polystyrene (figure 2-4).[164]

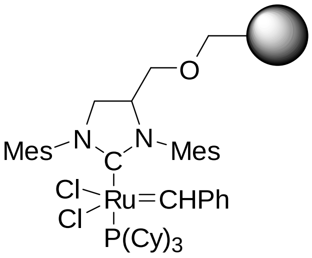


Figure 2-4. Fixation of the Grubbs-Herrmann catalyst via the NHC.

A major disadvantage of this system, was the low catalyst loading and the pressure instability. The fixation to a monolithic support via a polymerizable NHC resulted in high TONs (turn-over numbers) and TOFs in flow-through catalysis (figure 2-5).[151]

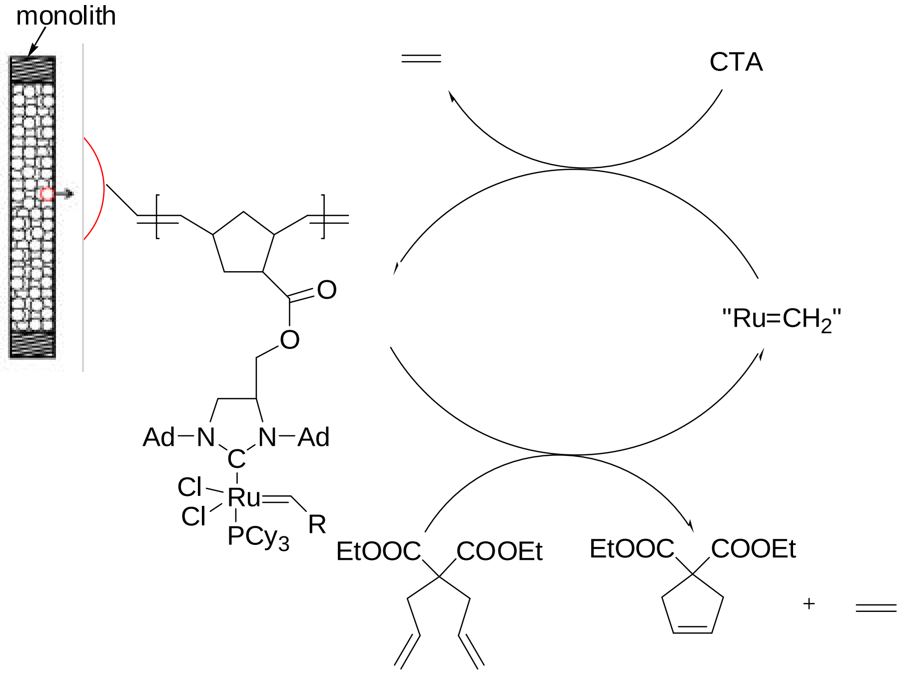


Figure 2-5. Flow-through catalysis using a monolithic support developed in the Buchmeiser group.[151]

The monoliths developed in the Buchmeiser group were prepared via *in situ* polymerization of NBE (norbornene) and 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo*,*endo*-dimethanonaphthalene (DMNH-6) as crosslinker using $RuCl_2(CHPh)(PCy_3)_2$ as catalyst in a solvent mixture of dichloromethane (polymer soluble) and 2-propanol (polymer insoluble) (figure 2-6).[165]

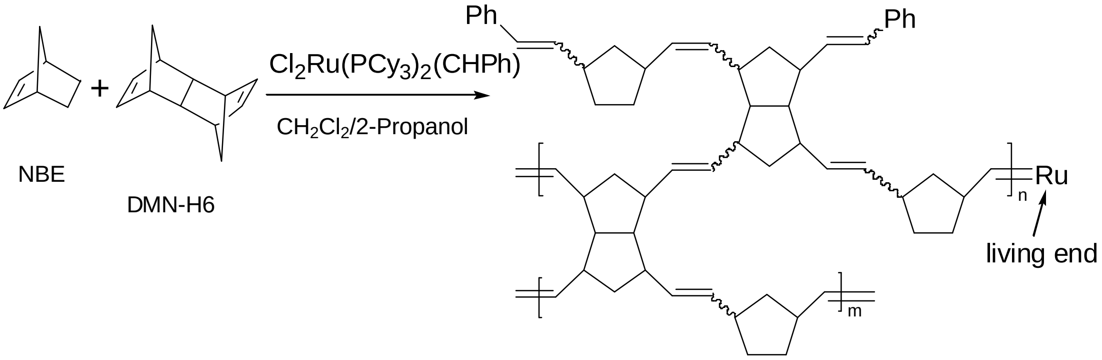


Figure 2-6. Structure of the monolithic support developed in the Buchmeiser group.[165]

All ruthenium-alkylidenes were on the surface of the monolith so that further grafting of a monomer was possible.

The chlorine exchange offers a relatively new and elegant approach to permanently bound ruthenium catalysts. In contrast to heterogenization via the NHC, side reactions connected to the generation of a free carbene could be avoided.

Buchowicz could show, that the chlorine ligands in the ^{1st}Grubbs catalyst can be exchanged with strong electron withdrawing silver salts.[166] Unfortunately, only dimeric, bridged catalysts could be isolated (figure 2-7).

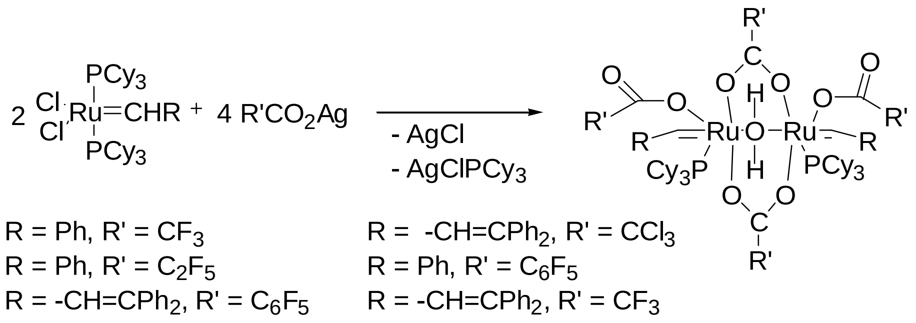


Figure 2-7. Chlorine exchange in the ^{1st}Grubbs catalyst.

Nevertheless, the main advantage of this modification is the simple access of a heterogeneous analogue which can be prepared in the following manner (figure 2-8).[167]

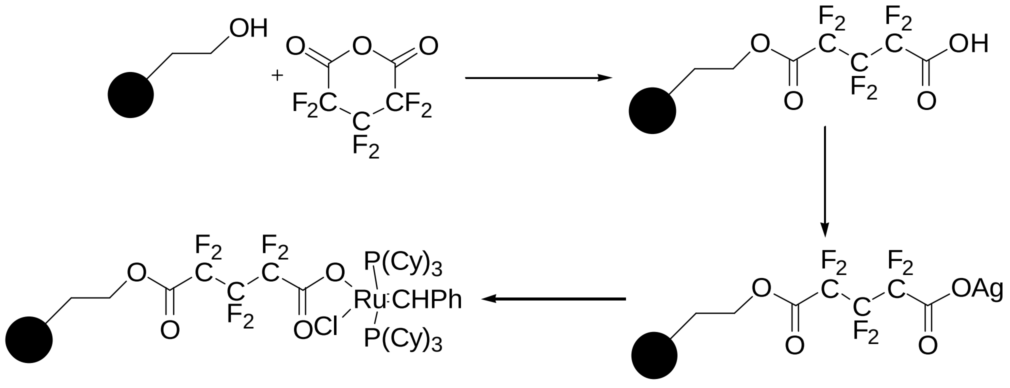


Figure 2-8. Fixation of ^{1st}Grubbs via chlorine exchange.[167]

Since RuCl$_2$(=CHPh)(PCy$_3$)$_2$ is less active and for some substrates even inactive compared to RuCl$_2$(=CH-2-(2-PrO)-C$_6$H$_4$)(SIMes), a fixation as shown in figure 2-9 is of general desire.[149]

We were able to use this support for the fixation of the Grubbs-Herrmann catalyst via chlorine exchange.[149] In flow-through catalysis the highest TONs of the ring closing reaction ever for DEDAM (diethyldiallylmalonate) of a heterogeneous catalyst have been reported that nearly reached the homogeneous ones (figure 2-9).

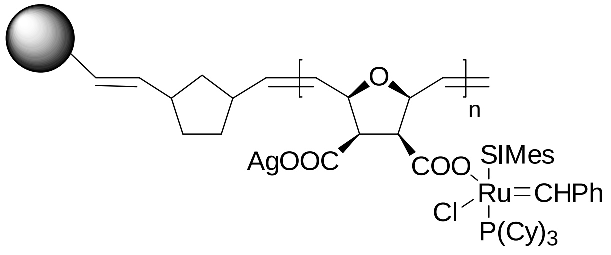


Figure 2-9. Fixation via chlorine exchange by us.[149]

The chlorine exchange has also been a key step in the synthesis of a chiral Grubbs-Hoveyda catalyst.[23,24] The chlorine exchange stops the rotation of the NHC and chirality can be used in synthesis (figure 2-10). Unfortunately, this alkoxide causes an extreme loss of activity.

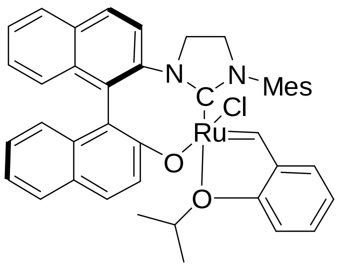


Figure 2-10. Chiral Grubbs-Hoveyda catalyst.

An exchange of the second chlorine in this catalyst could be used as possible fixation to any support, but as the synthesis of this catalyst requires more than 20 steps, it seems to be quite daunting. Consequently, it has to be mentioned that the fixation of chiral catalysts is still the area of Schrock catalysts. Again, Schrock was the first to present a supported, chiral catalyst for olefin metathesis (figure 2-11).[26]

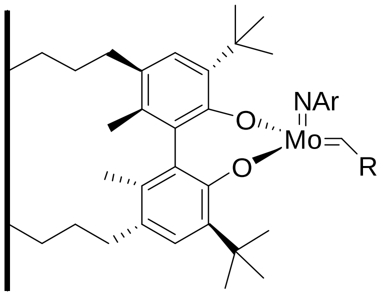


Figure 2-11. Permanently bound chiral Schrock catalyst.

A similar approach was used by Kröll et al. using a polymerizable chiral ligand via ring-opening metathesis precipitation polymerization.[168]

3 Motivation

The aim of this work was the design of new homogeneous ruthenium-alkylidene catalysts, that can be permanently bound to supports such as crosslinked polystyrene, monoliths, silica or poly(2-oxazoline)s. As precursor catalysts highly active and commercially available second generation, ruthenium catalysts such as the Grubbs-Herrmann catalyst were to be used.

The chlorine exchange of these catalysts with electron-withdrawing silver-carboxylates was to be used as the key-step for two reasons. First, the activity should be increased with stronger electron-withdrawing ligands. Second, fixation to any support is to be simplified and perfect mimics of the homogeneous compounds to be obtained.

In the chlorine exchange in second-generation systems the influence and kind of ligand variation on the activity is not predictable, new reactions were to be searched.

For flow-through catalysis, monolithic supports were to be used and their long-term stability to be investigated. Since water is an environmentally benign solvent, catalysis in water is of general interest. Amphiphilic poly(2-oxazoline) block copolymers are well-defined compounds, that are well soluble in water, and can furthermore solubilize hydrophobic compounds through micellation.[169-171] Nanoreactors obtained therefrom should increase reactivity. As a permanently bound amphiphilic ruthenium-alkylidene catalyst was unknown, a fixation via chlorine exchange was to be established.

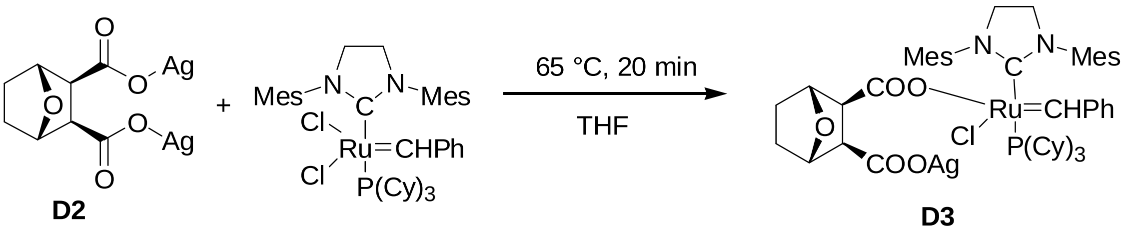
As supports for slurry reactions that can be used in organic solvents and easily be filtered off, silica as well as crosslinked polystyrene were to be used.

4 Results

4.1 Synthesis of homogeneous catalysts

4.1.1 Modification of the Grubbs-Herrmann-catalyst

Halogen exchange of the starting compound **D2** with the 2nd-generation Grubbs-Herrmann catalyst proceeded smoothly at elevated temperature (65 °C) to form the new catalyst **D3**. Interestingly, only one chlorine ligand was exchanged (scheme 4-1).[149,172-175]



Scheme 4-1. Synthesis of **D3**.

All efforts to substitute both chlorines, e. g. by using the bis-Tl or bis-Cs salts, by adding excess of PCy_3 or by using a phosphine scavenger failed, only decomposition of the catalyst was observed. One can attribute this to the phosphine-scavenging property of the second Ag-carboxylate group (*vide infra*), which results in the formation of $AgCl{\cdot}PCy_3$ in course of the (slow) reaction with the second chlorine ligand. Synthesis and derivatization of **D3** are already described in the diploma thesis[175], but more substrates were subject to catalysis as shown in table 4-1. Catalyst **D3** was used in RCM of diethyl diallylmalonate (DEDAM), 1,7-octadiene, diallyldiphenylsilane, *trans*-3-methylpentenoate, *N*,*N*-diallyltrifluoroacetamide and *N*,*N*-diallyl-*t*butylcarbamide allowing turn over numbers (TONs) close to 1000. The turn-over numbers (TONs) that were achieved (= 520, table 4-1, entries 7-13) were found to be reduced by a factor of 2 compared to the ones obtained with the Grubbs-Herrmann catalyst (table 4-1, entries 1-6) indicating that substitution of one chlorine ligand does in fact change the catalytic activity of the system. The importance of appropriate reaction conditions was illustrated by the low values for TON accomplished in complementary experiments carried out in a different (coordinating) solvent such as THF and different conditions such as higher monomer concentrations (table 4-1, entries 14-20).

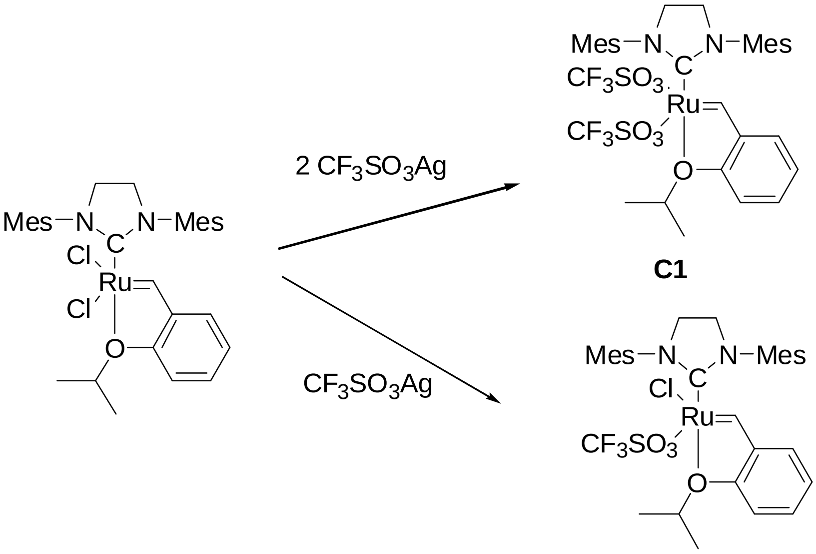
Table 4-1. Summary of catalytic activity of homogeneous systems.

#	**Compound**	Catalyst	Solvent (mol-% compound)	TON (45 °C)
1	**DEDAM**	2nd-Grubbs	CH_2Cl_2 (0.05)	1300
2	**1,7-octadiene**	2nd-Grubbs	CH_2Cl_2 (0.1)	1000
3	**diallyldiphenylsilane**	2nd-Grubbs	CH_2Cl_2 (0.1)	400
4	***trans*-3-methylpentenoate**	2nd-Grubbs	CH_2Cl_2 (0.01)	600
5	***N,N*-diallyl-*t*butylcarbamide**	2nd-Grubbs	CH_2Cl_2 (0.1)	770
6	***N,N*-diallyltrifluoroacetamide**	2nd-Grubbs	CH_2Cl_2 (0.1)	150
7	**DEDAM**	**D3**	CH_2Cl_2 (0.05)	520
8	**1,7-octadiene**	**D3**	CH_2Cl_2 (0.1)	520
9	**diallyldiphenylsilane**	**D3**	CH_2Cl_2 (0.1)	140
10	**diallylethanol**	**D3**	CH_2Cl_2 (0.1)	25
11	***trans*-3-methylpentenoate**	**D3**	CH_2Cl_2 (0.01)	280
12	**diallylether**	**D3**	CH_2Cl_2 (0.1)	50
13	***N,N*-diallyltrifluoroacetamide**	**D3**	CH_2Cl_2 (0.1)	190
14	**DEDAM**	**D3**	THF (9.3)	40
15	**1,7-octadiene**	**D3**	THF (3.8)	20
16	**diallyldiphenylsilane**	**D3**	THF (9.1)	30
17	**diallylethanol**	**D3**	THF (4.3)	10
18	***trans*-3-methylpentenoate**	**D3**	THF (5.6)	10
19	**diallylether**	**D3**	THF (3.4)	90
20	***N,N*-diallyltrifluoroacetamide**	**D3**	THF (6.0)	2

Due to the fact that catalyst **D3** was unstable due to $AgCl\cdot PCy_3$ precipitation, the next modification aimed on a chlorine exchange with more electron withdrawing ligands. When adding CF_3COOAg or CH_3COOAg to the Grubbs-Herrmann catalyst only precipitation of $AgCl\cdot PCy_3$ and decomposition was observed. The addition of one equivalent of PCy_3 could stabilize the catalyst, but only an unstable product could be isolated. To prevent $AgCl\cdot PCy_3$ precipitation and allow a “clean” reaction, the phosphine-free Hoveyda-Grubbs catalyst was used, as is shown in the next chapter.

4.1.2 Modification of the Grubbs-Hoveyda-catalyst

Though accessible and highly active, any phosphine-containing catalyst suffers from lack of stability due to formation of AgCl and AgCl(PCy$_3$), respectively, during reaction with silver salts. The aim was to apply the concept of chlorine replacement by ligands containing electron-withdrawing groups (e. g. fluorinated carboxylates and sulfonates) to a phosphine-free catalyst. The synthesis of a new generation of metathesis catalysts accessible *via* replacement of one or both chlorines in the phosphine-free Grubbs-Hoveyda catalyst by trifluoroacetate and trifluoromethanesulfonate groups was easily achieved. Thus, catalysts **C1** and **C2** were obtained by adding two respectively only one equivalent of CF_3SO_3Ag to $RuCl_2$(=CH-(2-(2-PrO)-C_6H_4)(SIMes) (scheme 4-2).



C1

C2

Scheme 4-2. Synthesis of catalysts **C1** and **C2**.

While the substitution of the first ligand proceeds smoothly, replacement of the second requires prolonged reaction times. Both compounds are obtained in virtually quantitative yields as demonstrated by in situ ^{1}H-NMR experiments and can be used *without any purification*. In case AgCl needs to be removed, the protocol described in the Experimental Section offers access to a silver-free catalyst, nevertheless, reduced yields (52-56 %) have to be accepted. In order to retrieve structural information, **C2** was subjected to x-ray crystallographic analysis (figure 4-1).

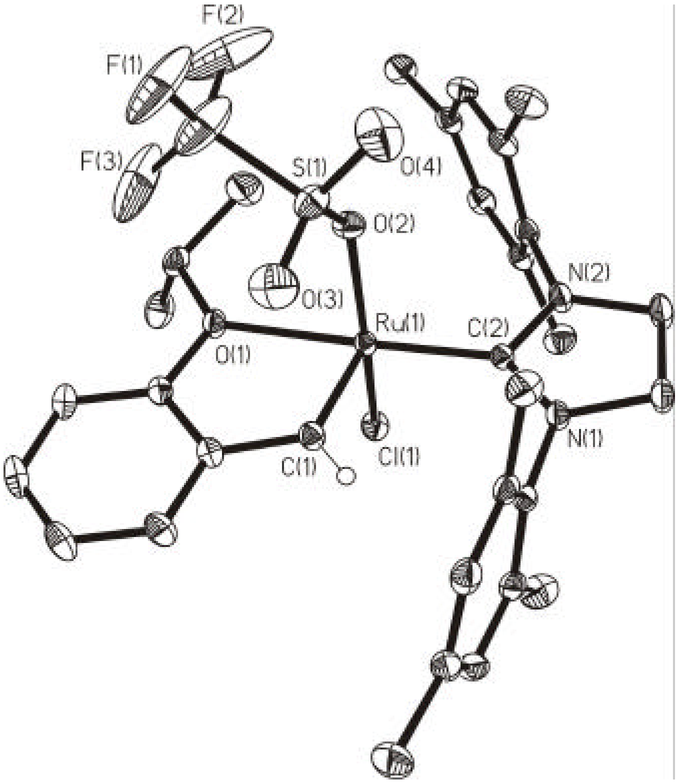


Figure 4-1. X-Ray structure of **C2**.

C2 crystallizes in the monoclinic space group $P2_1/c$, *a* = 1234.41(3) pm, *b* = 1604.50(3) pm, *c* = 1704.55(3) pm, ? = 91.077(2)°, Z = 4. Selected x-ray data are summarized in table 4-3, selected bond lengths and angles are given in table 4-2.

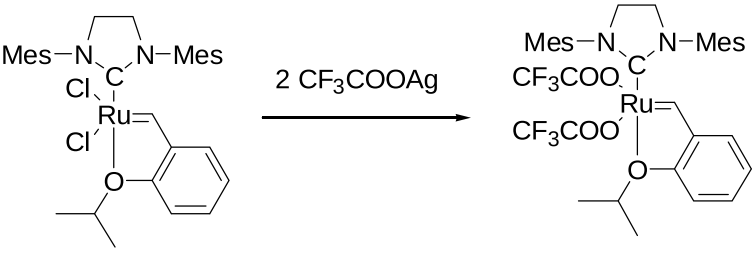
Table 4-2. Selected bond lengths [pm] and angles [°] for **C2**.

Bond lengths [pm]	
Ru(1)-C(2)	198.4(2)
Ru(1)-O(2)	209.86(19)
Ru(1)-O(1)	224.99(17)
Ru(1)-Cl(1)	231.82(7)

Angles [°]	
C(1)-Ru(1)-C(2)	102.34(11)
C(1)-Ru(1)-O(2)	98.87(10)
C(2)-Ru(1)-O(2)	93.50(9)

C(1)-Ru(1)-O(1)	79.31(10)
C(2)-Ru(1)-O(1)	178.17(8)
O(2)-Ru(1)-O(1)	85.43(7)
C(1)-Ru(1)-Cl(1)	97.21(9)
C(2)-Ru(1)-Cl(1)	93.12(7)
O(2)-Ru(1)-Cl(1)	160.87(6)
O(1)-Ru(1)-Cl(1)	87.44(5)

The Ru-Cl distances of 232.79(12) and 233.93(12) pm, respectively,[123] in the parent complex $RuCl_2(=CH-(2-(2-PrO)-C_6H_4)(SIMes)$ are reduced to 231.82(7) pm for Ru(1)-Cl(1) in **C2**. As a consequence of this stronger binding, substitution of the second chlorine is less favored. In addition, replacement of the second Cl-ligand is hampered due to the lower pK_a of the conjugated acid (CF_3SO_3H) of the ligand to be introduced, which in summary results in longer reaction times. Similar to **C3** (*vide infra*), the angle O(1)-Ru(1)-C(2) is close to 180° (178.17(8)°). Compared to the parent complex $RuCl_2(=CH-(2-(2-PrO)-C_6H_4)(SIMes)$[123] and **C3**, the angle between the chlorine ligand and the trifluoromethanesulfonate group is widened to 160.87(6)°. For the synthesis of catalyst **C3**, a similar procedure was used. Presumably, because of the softer character of the CF_3COO-ligand according to the HSAB-principle and the higher pK_a of the corresponding conjugated acid (CF_3COOH), both chlorines can be substituted in a clean reaction (scheme 4-3).



C3

Scheme 4-3. Synthesis of catalyst **C3**.

All attempts to isolate the mono-trifluoroacetate substituted catalyst failed, under all chosen conditions between –196 °C and room temperature and with varying stoichiometry only a 1:1:8 mixture of educt, bis-, and monoadduct (identified by means of ^1H-NMR) could be isolated. Only the bis(trifluoroacetate)-substituted catalyst **C3** could be isolated in a pure form (figure 4-2). The reaction of CH_3COOAg with the Grubbs-Hoveyda catalyst resulted in no reaction. As for **C1** and **C2**, **C3** is obtained in virtually quantitative yield as again demonstrated by *in situ* ^{1}H-NMR experiments and can be used *without any purification*. In case AgCl needs to be removed to obtain analytically pure catalyst, reduced yields (71%) have to be accepted.

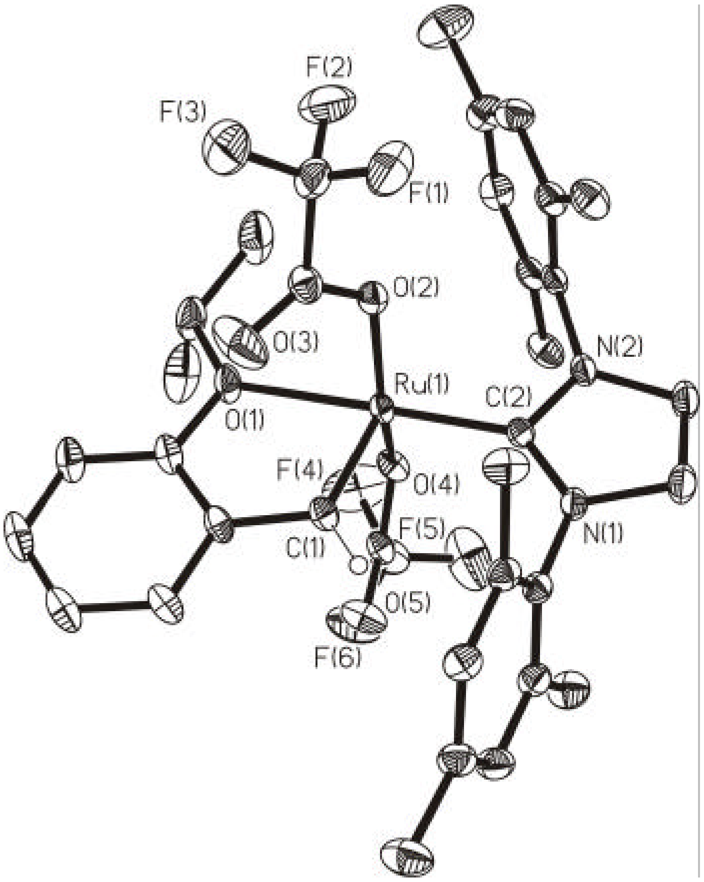


Figure 4-2. X-ray structure of **C3**.

Compound **C3** (figure 4-2) crystallizes in the space group $P2_1/n$, a = 1189.39(3) pm, b = 1664.62(3) pm, c = 1862.86(3) pm, ? = 90.086(2)°, Z = 4. Selected x-ray data are summarized in table 4-3, important bond lengths and angles are given in table 4-4.

Table 4-3. Selected x-ray data for compounds **C2** and **C3**.

	C2	**C3**
mol formula	$C_{32}H_{38}ClF_3N_2O_4RuS$	$C_{35}H_{38}F_6N_2O_5Ru$
fw	740.22	781.74
cryst syst	monoclinic	monoclinic

space group	P2$_1$/c (No. 14)	P2$_1$/n (No. 14)
a (pm)	1234.41(3)	1189.39(3)
b (pm)	1604.50(3)	1664.62(3)
c (pm)	1704.55(3)	1862.86(3)
? (deg)	90	90
? (deg)	91.077(2)	90.086(2)
? (deg)	90	90
vol (nm^3)	3.37545(12)	3.68824(13)
Z	4	4
temp (K)	233(2)	233(2)
density (calcd) (Mg/m^3)	1.457	1.408
abs coeff (mm^{-1})	0.660	0.496
color, habit	yellow plate	reddish prism
no. of rflns with $I > 2?(I)$	5211	6169
goodness-of-fit on F^2	1.052	1.054
R indices $I > 2?(I)$	R$_1$ = 0.0315	R$_1$ = 0.0300
	? R^2 =0.0789	? R^2 =0.0749

Table 4-4. Selected bond lengths [pm] and angles [°] for **C3**.

Bond lengths [pm]	
Ru(1)-C(1)	182.6(2)
Ru(1)-C(2)	197.9(2)
Ru(1)-O(4)	202.58(15)
Ru(1)-O(2)	203.65(16)
Ru(1)-O(1)	224.58(15)

Angles [°]

C(1)-Ru(1)-C(2)	100.83(9)
C(1)-Ru(1)-O(4)	97.91(8)
C(2)-Ru(1)-O(4)	92.26(7)
C(1)-Ru(1)-O(2)	103.11(8)
C(2)-Ru(1)-O(2)	92.31(7)
O(4)-Ru(1)-O(2)	157.23(6)
C(1)-Ru(1)-O(1)	79.20(8)
C(2)-Ru(1)-O(1)	178.93(8)
O(4)-Ru(1)-O(1)	86.67(7)
O(2)-Ru(1)-O(1)	88.73(7)

The angle formed by O(2)-Ru(1)-O(4) is 157.23(6)°, which is similar to the angle of 156.47(5)° found for Cl(1)-Ru-Cl(2) in the parent complex of $RuCl_2$(=CH-2-(2-PrO)-C_6H_4)(SIMes).[123] The Ru(1)-O(1) distance is basically not changed (2.261(3) Å in the parent complex *vs* 2.2458(15) Å in **C3**), which is in accordance with the high stability of **C3**. As for the parent complex, both the high reactivity and stability of **C3** can be explained by the *trans*-effect of the NHC-ligand on the 2-PrO-group (O(1)-Ru(1)-C(2) = 178.93(8)°, parent complex 176.22(14)°).

The fact that only monomeric compounds are obtained is in strong contrast to the findings of Buchowitz et al. for the $RuCl_2(=CHPh)(PCy_3)_2$-derived catalysts.[166] The clear advantage of such monomeric catalysts is that no dissociation of any dimeric catalyst precursor is necessary, thus enhancing both reaction rates and stability of the entire catalytic setup. In contrast to the work of Hoveyda[123], where a weaker electron donating character of the oxygen in the 2-PrO-group should result in an upfield shift of the benzylidene proton, no correlation could be observed in catalysts **C1**, **C2** or **C3**. Though **C2** and **C3** could be characterized by X-ray analysis, none of the complexes gave satisfactory elemental analyses. This is a result of the non-quantitative removal of AgCl, leading to low values for C and N (see Experimental).

In order to benchmark the new systems, their catalytic activity in RCM using a set of 6 different compounds was tested. Diethyl diallylmalonate (DEDAM), 1,7-octadiene, diallyldiphenylsilane, *trans*-3-methylpentenoate, *N*,*N*-diallyltrifluoroacetamide, and *N*,*N*-diallyl-*t*-butylcarbamide were used. Catalysts **C1** and **C2** displayed lower activities compared to the parent catalyst (table 4-5, entries 21-32). Nevertheless, using **C3**, RCM experiments could be carried out with high turn-over numbers (TONs) even at room temperature. As can be deduced from table 4-5, TONs obtained with **C3** at 45°C (table 4-5, entries 11-18) exceed in most cases those obtained with the Grubbs-Herrmann catalyst or the parent Grubbs-Hoveyda catalyst (table 4-5, entries 6 – 10). Even more interesting, high TONs (600 for DEDAM and 1380 for 1,7-octadiene, see table 4-5, entries 17-18) were obtained at 20°C, underlining the high activity of this catalytic system. Since the activity of a new metathesis catalyst is best demonstrated by the RCM of tri- and tetra-substituted dienes, RCM of diethyl allylmethallyl malonate and diethyl dimethallylmalonate (table 4-5, entries 19-20) were conducted. TONs of 80 and 70 respectively, were achieved. Though slightly higher numbers (TON = 99) were obtained by other groups using $RuCl_2(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}5\text{-}NO_2\text{-}C_6H_3)(SIMes)$,[137] these data still exceed or at least rival the activity of $RuCl_2(=CHPh)(SIMes)(PCy_3)$, $RuCl_2(=CH\text{-}(1\text{-}(2\text{-}(2\text{-}PrO)\text{-}naphth\text{-}1\text{-}yl)\text{-}2\text{-}(2\text{-}PrO)\text{-}naphth\text{-}3\text{-}yl)(SIMes)(PCy_3)$, and $Mo(N\text{-}2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$.[139-141]

Table 4-5. Summary of catalytic activities.

#	Compound	Catalyst	mol-% compound	TON
1	**DEDAM**	Grubbs-Herrmann[a]	0.05	1300
2	**1,7-octadiene**	Grubbs-Herrmann[a]	0.08	1000
3	**diallyldiphenylsilane**	Grubbs-Herrmann[a]	0.10	400
4	**methyl *trans*-3-pentenoate**	Grubbs-Herrmann[a]	0.01	600
5	***t*-butyl *N,N*-diallylcarbamide**	Grubbs-Herrmann[a]	0.10	770
6	**DEDAM**	Grubbs-Hoveyda[a]	0.05	1500
7	**1,7-octadiene**	Grubbs-Hoveyda[a]	0.05	1700
8	**diallyldiphenylsilane**	Grubbs-Hoveyda[a]	0.10	180
9	**methyl *trans*-3-pentenoate**	Grubbs-Hoveyda[a]	0.10	60
10	***t*-butyl *N,N*-diallylcarbamide**	Grubbs-Hoveyda[a]	0.10	100

11	**DEDAM**	**C3**[a]	0.05	1400
12	**1,7-octadiene**	**C3**[a]	0.05	1800
13	**diallyldiphenylsilane**	**C3**[a]	0.10	750
14	**methyl *trans*-3-pentenoate**	**C3**[a]	0.01	300
15	***t*-butyl *N,N*-diallylcarbamide**	**C3**[a]	0.10	780
16	***N,N*-diallyltrifluoroacetamide**	**C3**[a]	0.10	1000
17	**DEDAM**	**C3**[b]	0.10	590
18	**1,7-octadiene**	**C3**[b]	0.05	1400
19	**diethyl allylmethallylmalonate**	**C3**[c]	0.10	80
20	**diethyl dimethallylmalonate**	**C3**[c]	0.10	70
21	**DEDAM**	**C2**[a]	0.05	600
22	**1,7-octadiene**	**C2**[a]	0.05	300
23	**diallyldiphenylsilane**	**C2**[a]	0.10	10
24	**methyl *trans*-3-pentenoate**	**C2**[a]	0.01	300
25	***t*-butyl *N,N*-diallylcarbamide**	**C2**[a]	0.10	710
26	***N,N*-diallyltrifluoroacetamide**	**C2**[a]	0.10	630
27	**DEDAM**	**C1**[a]	0.05	500
28	**1,7-octadiene**	**C1**[a]	0.05	500
29	**diallyldiphenylsilane**	**C1**[a]	0.10	20
30	**methyl *trans*-3-pentenoate**	**C1**[a]	0.01	500
31	***t*-butyl *N,N*-diallylcarbamide**	**C1**[a]	0.10	110
32	***N,N*-diallyltrifluoroacetamide**	**C1**[a]	0.10	190

[a] 2 h, 2 mL CH_2Cl_2, 45°C; [b] 2 h, 2 mL CH_2Cl_2, 20°C.

A comparison between catalysts **M1a** (Hoveyda-Grubbs) and **C1-3** is presented in diagram 4-1. DEDAM (A), 1,7-octadiene (B), diallyldiphenylsilane (C), methyl trans-3-pentenoate (D), t-butyl N,N-diallylcarbamide (E).

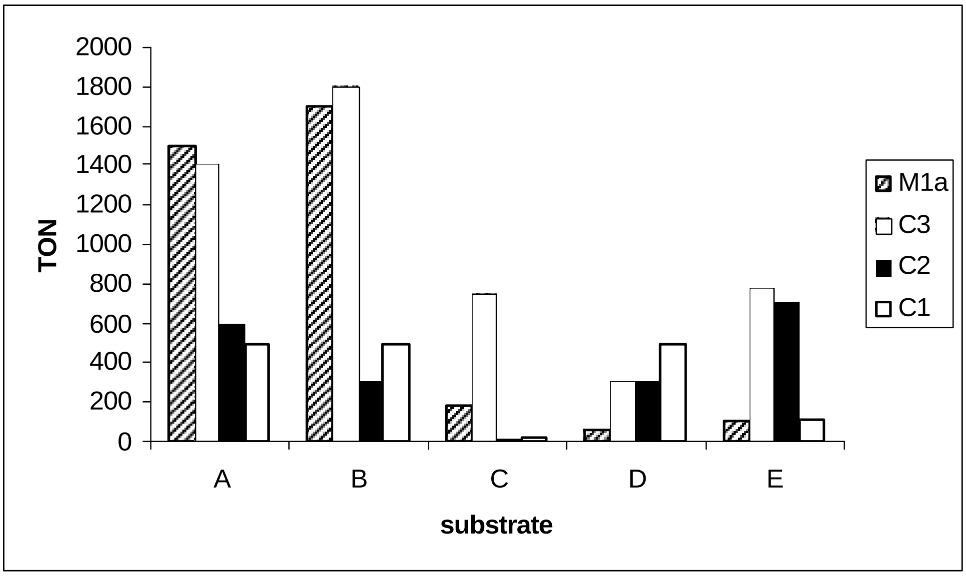


Diagram 4-1. Comparison of catalyst **M1a** and **C1-3**.

The comparison between **C1-3** and **D3** shows the high activity of **C3** in RCM of DEDAM (diagram 4-2).

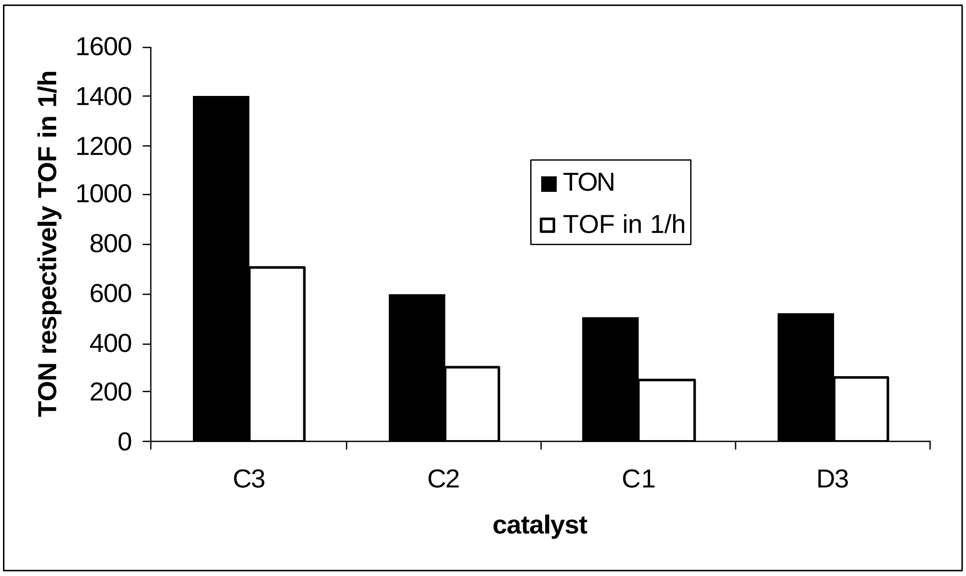
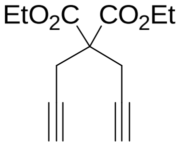
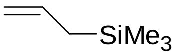
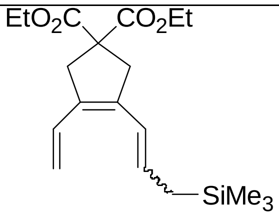
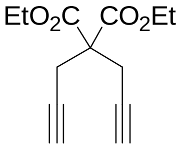
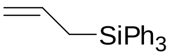
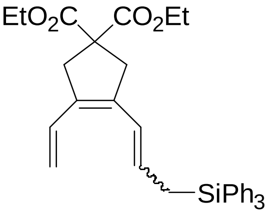
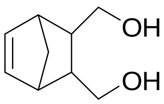
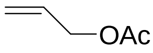
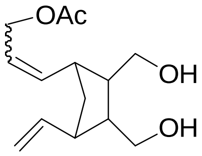
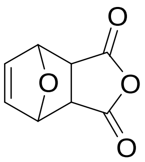
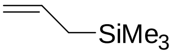
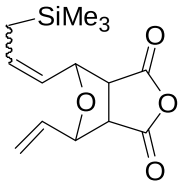


Diagram 4-2. TON and TOF for DEDAM using catalysts **C1-3** and **D3**.

In addition to RCM experiments, enyne metathesis reactions were carried out. Diethyl dipropargylmalonate (DEDPM) was reacted with trimethylallylsilane and triphenylallylsilane, respectively. The corresponding products were obtained in high yields (95 %). Conditions identical to those reported in the literature[176,177] were chosen in order to allow the comparison with reported yields. As can be deduced from table 4-6 (entries 43 and 44), **C3** again exhibited enhanced activity. Finally, ring-opening-cross metathesis reactions carried out with both norborn-5-ene and 7-oxanorborn-5-ene derivatives were investigated (table 4-6, entries 45-45). Again excellent yields (95 %) were obtained.

Table 4-6. Enyne and ring-opening-cross-metathesis reactions using **C3**.

#	reactants			product	conditions	E/Z	yield1)
43		+			[a]	1:3.5	95 % (65 %)
44		+			[a]	1:6	95 %
45		+			[b]	1:2	95 % (58 %)
46		+			[b]	1.1	95 %

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1) Yields in parenthesis are those reported by other groups using standard Ru-based metathesis catalysts. [a] CH_2Cl_2, 12 hours, room temperature, 10 mol-% catalyst; [b] 2 mol-%, 2 hours, $CDCl_3$, room temperature.

In order to investigate the influence of the catalyst structure, and to apply the concept of chlorine exchange, fourteen metathesis initiators, the Hoveyda catalyst $RuCl_2(SIMes)(=CH\text{-}2\text{-}(2\text{-}PrO\text{-}C_6H_4))$ (**M1a**), as well as $Ru(CF_3COO)_2(=CH\text{-}2\text{-}(2\text{-}PrO\text{-}C_6H_4))(SIMes)$ (**M1b**), $Ru(CF_3CF_2COO)_2(=CH\text{-}2\text{-}(2\text{-}PrO\text{-}C_6H_4))(SIMes)$ (**M1c**), $Ru(CF_3CF_2CF_2COO)_2(=CH\text{-}2\text{-}(2\text{-}PrO\text{-}C_6H_4))(SIMes)$ (**M1d**), $RuCl_2(=CH\text{-}2,4,5\text{-}(MeO)_3\text{-}C_6H_2)(SIMes)$ (**M2a**), $Ru(CF_3COO)_2(=CH\text{-}2,4,5\text{-}(MeO)_3\text{-}C_6H_2))(SIMes)$ (**M2b**), $Ru(CF_3CF_2COO)_2(=CH\text{-}2,4,5\text{-}(MeO)_3\text{-}C_6H_2)(SIMes)$ (**M2c**), $Ru(CF_3CF_2CF_2COO)_2(=CH\text{-}2,4,5\text{-}(MeO)_3\text{-}C_6H_2)(SIMes)$ (**M2d**), $RuCl_2(=CH\text{-}2\text{-}(2\text{-}PrO\text{-}C_6H_4))(IMes)$ (**M3a**), $Ru(CF_3COO)_2(=CH\text{-}2\text{-}(2\text{-}PrO\text{-}C_6H_4))(IMes)$ (**M3b**), $RuCl_2(=CH\text{-}2\text{-}(2\text{-}PrO\text{-}5\text{-}NO_2\text{-}C_6H_3))(SIMes)$ (**M4a**), $Ru(CF_3COO)_2(=CH\text{-}2\text{-}(2\text{-}PrO\text{-}5\text{-}NO_2\text{-}C_6H_3))(SIMes)$ (**M4b**), $Ru(CF_3CF_2COO)_2(=CH\text{-}2\text{-}(2\text{-}$

PrO-5-NO_2-C_6H_3))(SIMes) (**M4c**), and Ru($CF_3CF_2CF_2COO$)$_2$(=CH-2-(2-PrO-5-NO_2-C_6H_3))(SIMes) (**M4d**), designed for the living polymerization of diethyldipropargylmalonate (DEDPM), were prepared (figure 4-3).

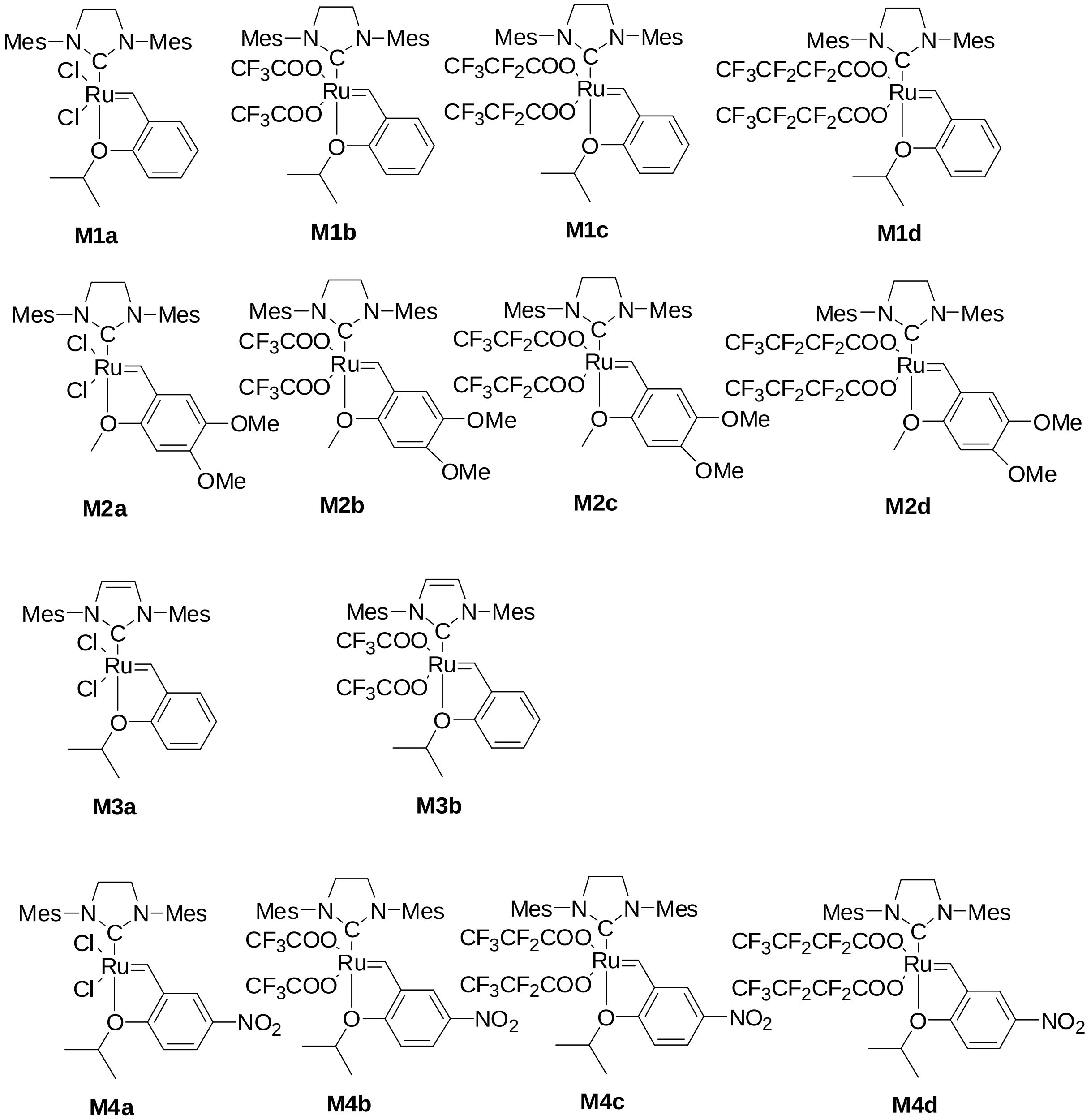


Figure 4-3. Structures of initiators **M1a-d**, **M2a-d**, **M3a-b**, **M4a-d**.

As shown above, a phosphine-free initiator turned out to be a prerequisite, because substitution of the chlorines e.g. in $RuCl_2$(CHPh)(PCy)$_3$(SIMes) by CF_3COOAg resulted in the precipitation of AgCl·PCy_3, and formation of the unstable 14-electron species Ru(CF_3COO)$_2$(CHPh)(SIMes). Thus, starting from $RuCl_2$(=CH-2-(2-PrO-C_6H_4))(SIMes), initiators **M1b-d** (figure 4-3) were prepared *via* reaction of **M1a** with CF_3COOAg,

CF_3CF_2COOAg and $CF_3CF_2CF_2COOAg$, respectively. It is worth mentioning that all initiators **M1b-d**, **M2b-d**, **M3a-b** and **M4b-d**, were obtained in quantitative yield as determined by means of ^{1}H-NMR and can be used without further purification. If desired or necessary, column chromatography can be applied to remove any impurities of remaining AgCl (e.g. for elemental analysis). In this case isolated yields are reduced to ca. 65 %. The chemical shifts of the alkylidene protons of initiators **M2a-d**, **M3a-b**, **M4a-d** were in the range of 17.14-17.59. Contradictory to previous reports,[134] no correlation between pK_a of the carboxylic acid and/or the chemical shift of the alkylidene protons could be found. More details are given in the polymerization part of diethyl dipropargylmalonate.

4.2 Supported catalysts

4.2.1 Grubbs-Herrmann-catalyst

Many concepts of monolithic supports are published by Buchmeiser and can be found in the literature.[151,165,178-188] The synthesis of the heterogeneous supports **D4-9** is described in the diploma thesis.[175] More catalytic details will be given below. Two polymerizable, carboxylate-containing ligands, *exo, exo*-7-oxanorborn-2-ene-5,6-dicarboxylic anhydride and 7-oxanorborn-2-ene-5-carboxylic acid were surface-immobilized onto silica- and ROMP-derived monolithic supports using "grafting-from" techniques. The "1st-generation Grubbs catalyst", $RuCl_2(=CHPh)(PCy_3)_2$, was used for these purposes. In addition, a poly(norborn-2-ene-*b*-*exo, exo*-norborn-2-ene-5,6-dicarboxylic anhydride)-coated silica 60 was prepared. The polymer-supported carboxylate anhydride groups were converted into the corresponding mono- and disilver salts respectively and reacted with the "2nd-generation Grubbs catalyst" $RuCl_2(=CHPh)(SIMes)(PCy_3)$. Heterogenization was accomplished by exchange of one chlorine ligand with the polymeric, immobilized silver carboxylates to yield the monolith-supported catalysts **D4**, **D5**, and **D6** as well as the silica-supported systems **D7**, **D8** and **D9**.

The next figures show the structure of the systems **D4-D8** (figure 4-4, 4-5, 4-6) synthesized according to the procedures published by Buchmeiser, who developed the ROMP-based monoliths.[151,165,178-188] **D9** is a coated silica of a structure similar to **D7-8**.

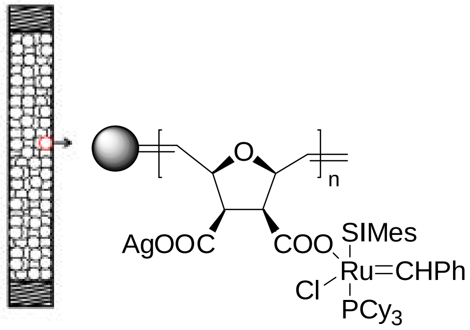


Figure 4-4. Structures of monoliths **D4** and **D5**.

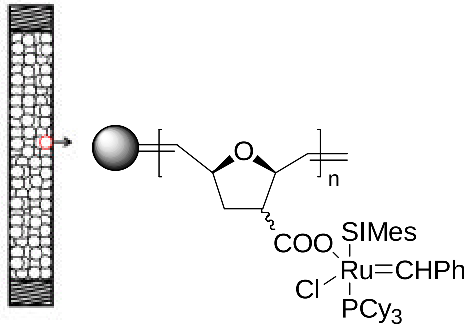


Figure 4-5. Structures of monolith **D6**.

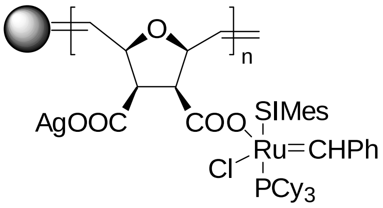


Figure 4-6. Structures of monolith **D7-8**.

All heterogeneous catalysts were used in RCM of DEDAM, 1,7-octadiene, diallyldiphenylsilane, *trans*-3-methylpentenoate, *N*,*N*-diallyltrifluoroacetamide and *N*,*N*-diallyl-*t*butylcarbamide allowing TONs close to 1000. In a flow-through setup, an auxiliary effect of pendant silver carboxylates was observed with catalyst **D5**, were the silver moiety functions as a (reversible) phosphine scavenger that both accelerates initiation and stabilizes the catalyst by preventing phosphine elution. Detailed catalytic studies were carried out with the monolith-supported systems **D4** and **D6** in order to investigate the effects of temperature and chain-transfer agents (CTAs) such as *cis*-1,4-diacetoxy-but-2-ene. In all RCM experiments Ru-leaching was low, resulting in a Ru-content of the RCM products = 3.5 ? g/g (3.5 ppm). Monoliths **D4** and **D5** were prepared according to literature given by Buchmeiser[151,165,178-188] and special details of **D4** and **D5** are given in the diploma thesis.[175]

A catalyst loading of 10 mg/g was achieved for **D5**. In order to investigate whether the second ("free") silver carboxylate had any influence on either the stability or catalytic activity of this system, the same synthetic protocol was applied for the synthesis of a poly(7-oxanorborn-2-ene-5-carboxylic acid) grafted monolith, which was in due consequence used for catalyst immobilization to give **D6**. As expected, a similar ruthenium loading of 0.8 mg Ru/g support, corresponding to 9 mg catalyst/g were obtained, nevertheless, a significant difference was observed in catalytic reactivity (*vide infra*).

Silica-derived supports were fabricated according to a synthetic procedure elaborated in the Buchmeiser group[47] and details of the synthesis are given in the diploma thesis.[175] Briefly, the corresponding support was surface-derivatized with norborn-2-ene-5-yl-trichlorosilane (*exo/endo*-mixture) or norborn-2-ene-5-yl-triethoxysilane (*exo/endo*-mixture) to obtain surface-immobilized silyl-norborn-2-ene groups.[189] These were consecutively reacted with $RuCl_2(=CHPh)(PCy_3)_2$ and *exo, exo7*-oxanorborn-2-ene-5,6-dicarboxylic anhydride respectively 7-oxanorborn-2-ene-5-carboxylic acid. By this grafting-from approach, satisfactory amounts of both monomers were grafted onto the support. Thus, an anhydride loading of 0.22 mmol/g (LiChrospher 300-5) and 1.2 mmol/g (Nucleosil 300-7) were achieved. Conversion into the corresponding di- and mono-silver salts and reaction with $RuCl_2(=CHPh)(PCy_3)(SIMes)$ gave the desired supported catalysts **D7** and **D8**. The catalyst-loading was in the range 42 mg (Nucleosil 300-7) to 63 mg catalyst/g (Lichrospher). Complementary, a poly(norborn-2-ene-*b*-7-oxanorborn-2-ene-5,6-anhydride)-coated silica was prepared from silica-60 and poly(norbornene-*b*-7-oxanorborn-2-ene-5,6-dicarboxylate) and used for catalyst immobilization. The corresponding supported catalyst **D9**, containing 7.0 mg Ru/g silica, corresponding to 77 mg catalyst/g, was used as an additional benchmark in the ranking of the catalytic activity.

The catalytic activity of the carboxylate-based systems was first studied with a DMN-H_6-derived monolith-supported system **D4**. The TON found for DEDAM was 180 (table 4-7, entry 21). From previous investigations concerning the microstructure of DMN-H_6-derived monoliths it is known, that a significant percentage of this rigid crosslinker did not take part in the cross linking reaction, resulting in the presence of a substantial number of norborn-2-ene-subunits.[185] Since these are highly reactive, an interference with the RCM reactions of interest can not be ruled out. Therefore the polymeric matrix was changed by using the more flexible $(NBE-CH_2O)_3$-SiMe as a crosslinker instead of DMN-H_6. Due to a reduced mesoporosity,[185] smaller amounts of the anhydride respectively the catalyst (i.e. 7 mg/g) could be immobilized. Nevertheless, with the corresponding monolith-supported catalyst **D5** *the highest TONs ever reported for a supported system* could be achieved, partially reaching the TONs that were observed with the 2nd-generation Grubbs catalyst in solution (e.g. for 1,7-octadiene, table 5-7, entries 22-28). The finding that TONs were even higher than those obtained with **D3** is attributed to the immobilization itself, which eliminates bimolecular reactions between two catalyst moieties.[147] In depth investigations carried out with DEDAM revealed that neither higher or lower temperatures (table 4-7, entries 30-31) nor the use of a CTA (table 4-7, entry 29) had a positive influence on the persistence (reflected by the TON value) of this system.

In order to shed some light on the (potentially synergistic) role of the second silver-carboxylate ligand present in the system, a monolith-supported catalyst starting with a mono-silver carboxylate (**D6**) was prepared. As can be seen (table 4-7, entry 32), the TON for DEDAM (110) was comparably low under conditions identical to the ones previously used. In addition, increased amounts of free PCy_3 were observed in the eluent. This is in strong contrast to catalyst **D5**, were no PCy_3 was found. In view of this and the differences in catalytic activity of **D5** and **D6** one can conclude, that the second, pendant silver carboxylate functions as an internal reversible phosphine scavenger during the RCM process, which reduces the loss of phosphine and thus stabilizes the ruthenium core in the absence of a diene.

Synthetic routes based on combinatorial chemistry usually entail the use of combi-chem machines. If used in catalytical processes, stirred reactions are usually the preferred setup. For this purpose, the silica-based systems **D7**, **D8** and **D9** were prepared as described by Buchmeiser[189] and special details are given in the diploma thesis. After verifying the optimum conditions (table 5-7, entries 33-35), a surface-grafted system based on Nucleosil 300-5 was used in stirred batch RCM reactions. TONs in the range of 40-90 were achieved (table 5-7, entries 36-40). This definitely allows its use in combinatorial chemistry. Furthermore, the surface-grafting of silica provided supports that were really comparable to their monolithic analogues because of the identical setup. In view of the quite different catalytic data that are achieved with these two supports, one obtains a nice illustration of the superiority of monolith-based systems used in a flow-through setup over classic supports.

A more straightforward synthetic route to silica-based supports is the synthesis of coated analogues. These are easy to prepare, yet suffer from a reduced accessibility of the catalytic sites, since these are located within the polymer film deposited on the silica surface. Not unexpected, if used in a flow-through or stirred batch setup (table 4-7, entries 41-43), comparably low TONs were achieved with the coated support **D9**, which justifies the synthesis of defined surfaces via grafting techniques in heterogeneous catalysis.

Table 4-7. Summary of catalytic activity of heterogeneous systems.

#	Compound	Catalyst	T [°C]	Solvent (Conc. [wt.-%])	TON
21	**DEDAM**	**D4**	45[a]	$ClCH_2CH_2Cl$ (10)	180
22	**DEDAM**	**D5**	45[a]	$ClCH_2CH_2Cl$ (10)	940
23	**1,7-octadiene**	**D5**	45[a]	CH_2Cl_2 (10)	900
24	**diallyldiphenylsilane**	**D5**	45[a]	CH_2Cl_2 (10)	90
25	***trans*-3-methylpentenoate**	**D5**	45[a]	$ClCH_2CH_2Cl$ (47.5)	340
26	***trans*-3-methylpentenoate**	**D5**	45[a]	$ClCH_2CH_2Cl$ (10)	30
27	***N,N*-diallyltrifluoroacetamide**	**D5**	45[a]	$ClCH_2CH_2Cl$ (10)	70
28	***N,N*-diallyl-*t*butylcarbamide**	**D5**	45[a]	$ClCH_2CH_2Cl$ (10)	140
29	**DEDAM**	**D5**	45[a, c]	$ClCH_2CH_2Cl$ (10)	280
30	**DEDAM**	**D5**	35[a]	$ClCH_2CH_2Cl$ (10)	442
31	**DEDAM**	**D5**	55[a]	$ClCH_2CH_2Cl$ (10)	220
32	**DEDAM**	**D6**	45[a]	$ClCH_2CH_2Cl$ (10)	110
33	**DEDAM**	**D7**	50[b]	$ClCH_2CH_2Cl$ (1.5)	10
34	**DEDAM**	**D7**	65[b]	$ClCH_2CH_2Cl$ (1.5)	10
35	**DEDAM**	**D7**	50[b, c]	$ClCH_2CH_2Cl$ (1.5)	1
36	**DEDAM**	**D8**	45[b]	CH_2Cl_2 (2)	90
37	**1,7-octadiene**	**D8**	45[b]	CH_2Cl_2 (2)	50
38	**diallyldiphenylsilane**	**D8**	45[b]	CH_2Cl_2 (2)	40
39	***N,N*-diallyltrifluoroacetamide**	**D8**	45[b]	CH_2Cl_2 (2)	70
40	***N,N*-diallyl-*t*butylcarbamide**	**D8**	45[b]	CH_2Cl_2 (2)	60
41	**DEDAM**	**D9**	45[a]	CH_2Cl_2 (10)	20
42	**DEDAM**	**D9**	50a, d]	CH_2Cl_2 (10)	3
43	**DEDAM**	**D9**	50[b, c]	CH_2Cl_2 (5)	0.1

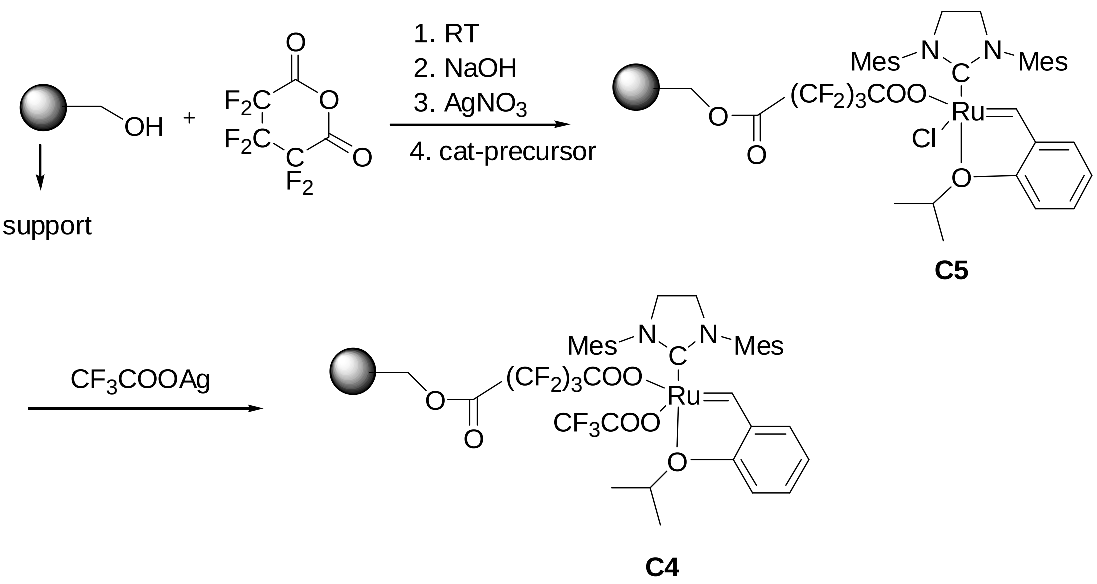
[a] flow-through; [b] stirred batch, [c] 1% *cis*-1,4-diacetoxy-2-butene, [d] 0.1 % *cis*-1,4-diacetoxy-2-butene.

Both the monolith- and silica-based catalytic systems turned out to be stable, allowing high TONs in RCM for a large number of compounds. Ruthenium leaching was low, resulting in virtually Ru-free products. The catalytic systems described here can be used as monolith-based flow-through reactors as well as surface-grafted silica-based supports in slurry type reactions. Together with their stability and high activity, this is believed to make them attractive for both combinatorial chemistry and large-scale industrial applications.

4.2.2 Grubbs-Hoveyda-catalyst

4.2.3 PS-DVB-based supports

Heterogeneous catalysts were synthesized by immobilizing $RuCl_2$(=CH-2-(2-PrO)-C_6H_4)(SIMes) on a perfluoroglutaric acid-derivatized polystyrene-divinylbenzene (PS-DVB) support (silver form) and details are given in the experimental part. The resulting supported catalyst RuCl(*polymer*-CH_2-O-CO-CF_2-CF_2-CF_2-COO)(=CH-2-(2-PrO)-C_6H_4)(SIMes) **C5** showed significantly reduced activities in RCM (TONs = 380) compared to the heterogeneous analogue of **C3**. The immobilized catalyst, Ru(CF_3CO_2)(*polymer*-CH_2-O-CO-CF_2-CF_2-CF_2-COO)(=CH-*o*-*i*Pr-O-C_6H_4)(SIMes) **C4** was obtained by substitution of both Cl-ligands of the parent Grubbs-Hoveyda catalyst via addition of CF_3COOAg to **C5**. **C4** can be prepared in high loadings (160 mg catalyst/g PS-DVB) and possesses excellent activity in RCM with TONs up to 1100 in stirred batch RCM experiments. Leaching of ruthenium into the reaction mixture was unprecedentedly low, resulting in a ruthenium content < 70 ppb (ng/g) in the final RCM-derived products. In detail: For purposes of heterogenization, hydroxymethyl-polystyrene (PS-DVB-CH_2-OH, 1.7 mmol CH_2-OH/g, crosslinked with 1% DVB) was reacted with perfluoroglutaric anhydride following a procedure published by Nieczypor et al.[167] Deprotonation and formation of the silver salt, was accomplished by reaction with aqueous sodium hydroxide followed by treatment with $AgNO_3$. $RuCl_2$(=CH-2-(2-PrO)-C_6H_4)(SIMes) was dissolved in THF and added to the silver salt. By this approach, RuCl(*polymer*-CH_2-O-CO-CF_2-CF_2-CF_2-COO)(=CH-2-(2-PrO)-C_6H_4)(SIMes) **C5** was obtained. In order to synthesize an almost identical analogue to **C3**, the second Cl-ligand was reacted with CF_3COOAg yielding Ru(*polymer*-CH_2-O-CO-CF_2-CF_2-CF_2-COO)(CF_3CO_2)(=CH-2-(2-PrO)-C_6H_4)(SIMes) **C4** as a lilac powder (scheme 4-4).



Scheme 4-4. Synthesis of heterogeneous catalysts C4 and C5.

A catalyst-loading of 160 mg/g (16 %) was determined for **C4**, indicating that more than 80 % of the polymer-bound silver perfluoroglutarate groups were accessible for reaction with $RuCl_2$(=CH-*o*-*i*-Pr-O-C_6H_4)(SIMes). This corresponds to a catalyst amount 5 times higher than reported for any other heterogeneous systems.[167] The fixation of $RuCl_2$(=CH-*o*-*i*-Pr-O-C_6H_4)(SIMes) to Nafion® was not successful.

Again, DEDAM, 1,7-octadiene, diallyldiphenylsilane, *trans*-3-methylpentenoate, and *N*,*N*-diallyl-*t*-butylcarbamide were used in heterogeneous RCM to benchmark the heterogeneous catalysts **C4** and **C5**. For most of these monomers, both catalyst **C5** and **C4** displayed high activities in RCM, the latter being the superior one reaching TON's close to 1100 (table 4-8, entries 31-35).

Table 4-8. Summary of catalytic activities.

#	**Compound**	Catalyst	mol-% compound	TON
33	**DEDAM**	**C4**[a]	0.05	200
34	**1,7-octadiene**	**C4**[a]	0.05	1100
35	**diallyldiphenylsilane**	**C4**[a]	0.10	100
36	***t*-butyl *N,N*-diallylcarbamide**	**C4**[a]	0.10	350
37	***N,N*-diallyltrifluoroacetamide**	**C4**[a]	0.10	70
38	**DEDAM**	**C5**[a]	0.05	200

39	**1,7-octadiene**	**C5**[a]	0.05	400
40	**diallyldiphenylsilane**	**C5**[a]	0.10	130
41	***t*-butyl *N,N*-diallylcarbamide**	**C5**[a]	0.10	190
42	***N,N*-diallyltrifluoroacetamide**	**C5**[a]	0.10	130

[a] 2 h, 2 mL CH_2Cl_2, 45°C; [b] 2 h, 2 mL CH_2Cl_2, 20°C. GH = Grubbs-Hoveyda catalyst $RuCl_2$(=CH-*o*-*i*-Pr-O-C_6H_4)(SIMes)

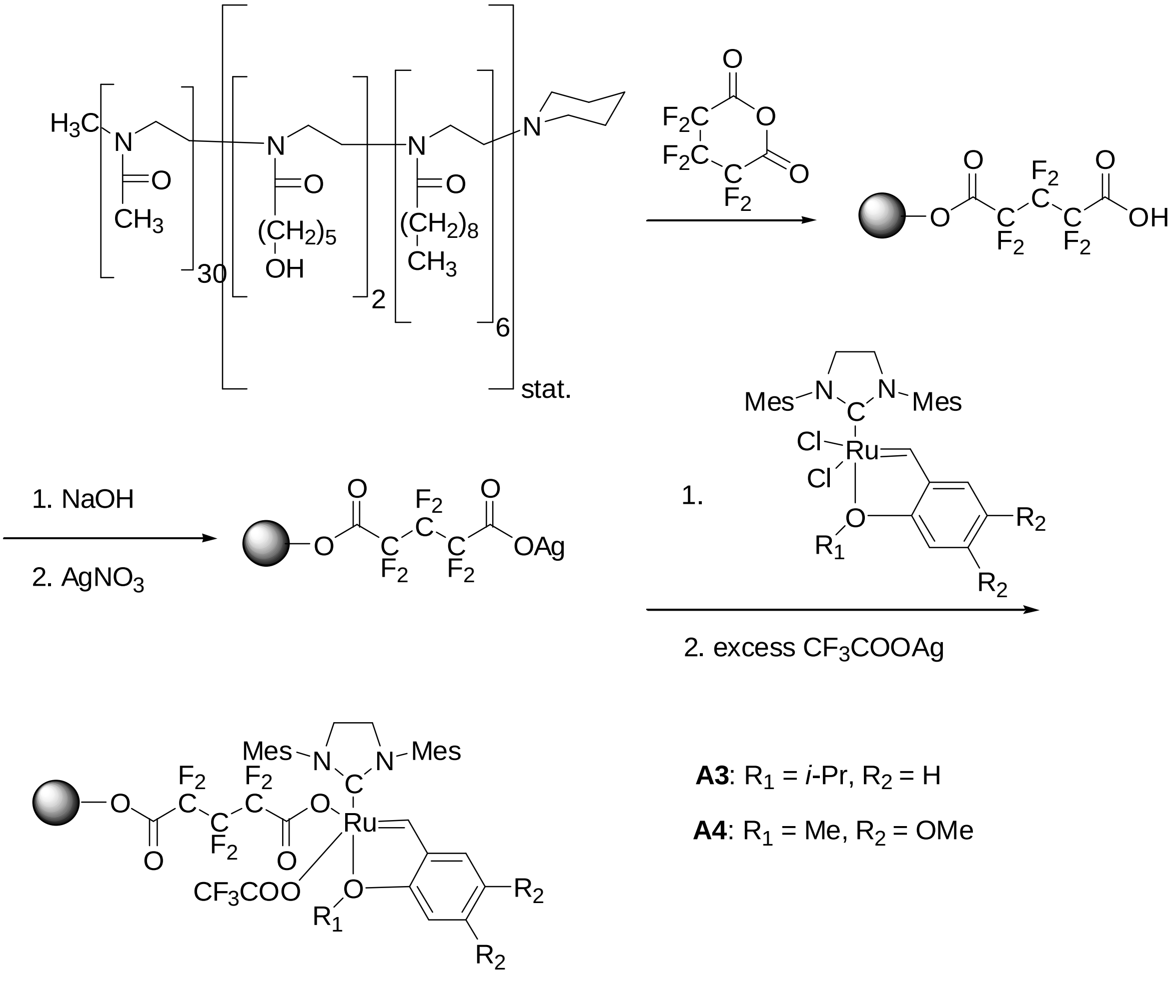
With **C5**, TONs = 380 were achieved (table 4-8, entries 36 – 40). With this catalytic activity, both heterogeneous systems exceeded by far any other existing one. The fact that **C4** exceeded **C5** in catalytic activity clearly documents the necessity of careful catalyst design, in our case the substitution of both chlorine ligands, which resulted in an almost perfect mimic of the homogeneous analogue **C3**. For both heterogeneous systems **C4** and **C5**, leaching of ruthenium into the various reaction mixtures was unprecedentedly low, resulting in a ruthenium content < 70 ppb (ng/g) in the final RCM-derived products.

Moreover, substitution of the chlorine ligands by trifluoroacetate groups respectively polymer-bound analogous ligands offered a simple access to heterogeneous catalysts as has been demonstrated with the synthesis of **C4** and **C5**. The high catalytic activity can be retained during the heterogenization process.

lock copolymer

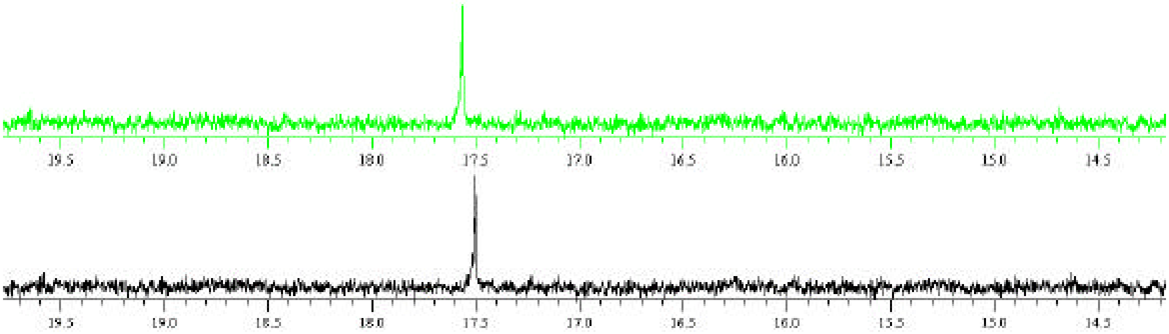
The synthesis of this part was done in a full cooperation with Tobias Zarka, TU München. The synthetic route necessary for the realization of a polymer-bound amphiphilic catalyst had to fulfill two requirements. On the one hand, perfect mimics of **C3** and **M2b** had to be generated in order to maintain their reactivity and stereoselectivity. On the other hand and in contrast to any suspension/emulsion polymerization, the catalyst had to be *permanently* linked to the block copolymer amphiphile.[169-171,190] Upon micelle formation of the functionalized block copolymer, the catalyst was located in the hydrophobic micellar core, where also the monomer was dissolved. Preparation of the functionalized block copolymers was accomplished by reacting first $Me_{30}Non_6(PenOH)_2Pip$,[191] bearing two randomly distributed hydroxyl groups in the side chain of the hydrophobic block with hexafluoroglutaric anhydride followed by deprotonation with aqueous NaOH and reaction with $AgNO_3$ to yield a polymer-bound silver carboxylate. The last steps entailed its reaction with the catalyst precursors

RuCl$_2$(=CH-2-(2-PrO)-C$_6$H$_4$)(SIMes) and RuCl$_2$(=CH-2,4,5-(OMe)$_3$-C$_6$H$_2$)(SIMes),[138] respectively, followed by reaction with silver trifluoroacetate to endcap the second, unreacted chloro group of the catalyst. In course of this two-step chlorine exchange, the corresponding ruthenium compounds were fixed to the support to yield the poly(2-oxazoline)-immobilized catalysts Me$_{30}$Non$_6$(PenOCO(CF$_2$)$_3$COO)(CF$_3$COO)Ru(=CH-2-(2-PrO)-C$_6$H$_4$)(SIMes))$_{0.8}$-(PenOCO(CF$_2$)$_3$COOAg)$_{1.2}$Pip **A3** and Me$_{30}$Non$_6$((PenOCO(CF$_2$)$_3$COO)-((CF$_3$COO)Ru(=CH-2,4,5-(OMe)$_3$C$_6$H$_2$(SIMES))))$_{0.8}$(PenOCO(CF$_2$)$_3$COOAg)$_{1.2}$Pip **A4**, respectively (scheme 4-5).



Scheme 4-5. Synthesis of **A3**.

Catalyst immobilization was followed by ^{1}H-NMR, which provided an exact measure for the quality and selectivity of this reaction. The alkylidene proton of the polymer bound catalyst **A3** gave a single signal at ?=17.51 ppm, which is in excellent agreement with the single signal at ?=17.58 ppm in the proton NMR spectrum of the free catalyst (scheme 4-6).

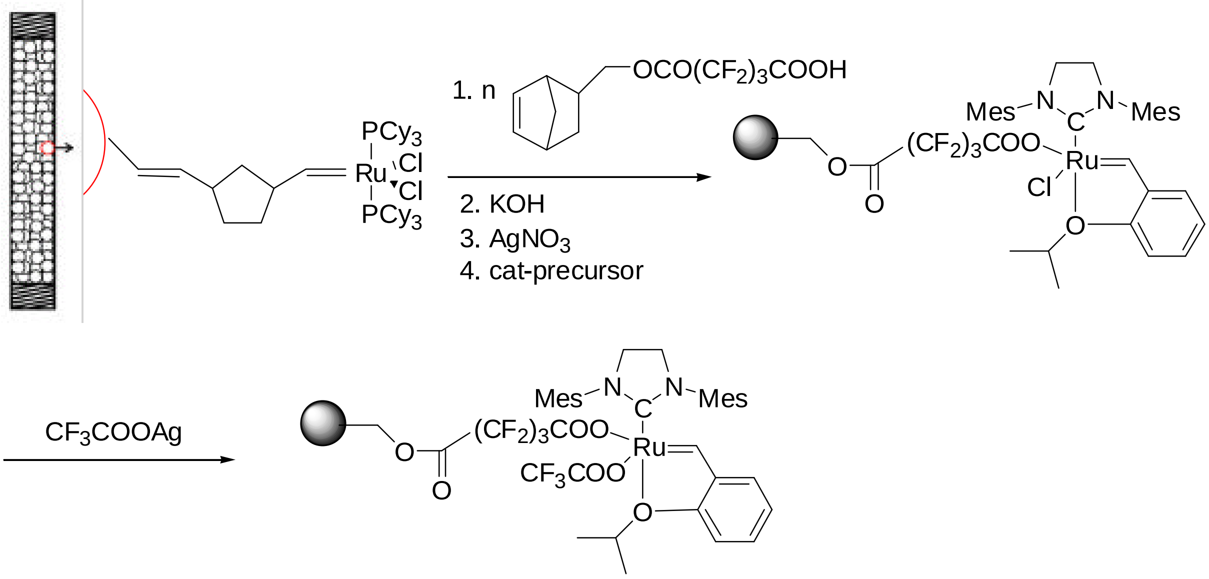


Scheme 4-6. ^{1}H-NMR (CD_3OD) of free catalyst **C3** (first), polymer-bound **A3** (last).

On the one hand, the similarity of these two chemical shifts was indicative of a selective immobilization, where neither any free catalyst nor any other catalytic species was observed. On the other hand, it underlined the degree of similarity between **C3** and its supported analogue **A3**, the more as the chemical shift for the alkylidene proton in this type of catalyst is very sensitive towards changes in the ligand sphere. It is worth mentioning that such a successful immobilization required both straightforward synthetic routes and the careful design of the block sizes in the amphiphilic copolymer. While $Me_{30}Non_4(PenOH)_4Pip$ already resulted in insoluble (in water), catalyst-loaded species, $Me_{30}Non_6(PenOH)_2Pip$ could be successfully used for these purposes. Quantification of ruthenium in **A3** and **A4** by means of ICP-OES (and NMR) measurements indicated that 40 % of the polymeric silver salt had reacted with the catalyst precursors **M1a** and **M2a**, leading to ruthenium loadings of the *block*-copolymer of 0.16 mmol/g.

A ROMP-based monolith was synthesized using Grubbs' first generation catalyst. The living termini were used for surface grafting of norborn-5-ene-2-ylmethyl hexafluoroglutarate. The free carboxylic acid groups of the graft polymer were converted into the corresponding silver salt and reacted with the Grubbs-Hoveyda catalyst $RuCl_2(=CH\text{-}(2\text{-}(2\text{-}PrO))C_6H_4)(SIMes)$ to yield a stable heterogeneous version of this catalyst for use in ring closing metathesis (RCM) under flow-through conditions.

The immobilization of metathesis catalysts on standard supports such as silica, monolithic or PS-DVB has already been addressed above, nevertheless, there are still few reports on the manufacture of supported systems suitable for *continuous* setups such as flow-through reactors. In flow-through reactors, "boomerang systems" derived via metathesis of various catalysts with surface vinyl groups are not suitable because they are released into the solvent during reaction and therefore prone to elution.[161,163,192] A similar fate had to be expected for the ligands responsible for catalyst stabilization, e.g. the phosphines. Above, a PS-DVB-supported metathesis catalyst system **C4** and **C5** that was fixed through substitution of two chlorine ligands in $RuCl_2(=CH\text{-}(2\text{-}(2\text{-}PrO)\text{-}C_6H_4)(SIMes)$ by fluorinated carboxylates was presented.[193] With this system, high turn-over numbers (TONs) around 250 in RCM of DEDAM in a stirred batch setup were achieved. In view of this high activity, generating a flow-through system with high long-term stability was interesting. For immobilization, a monolithic support was synthesized via ring-opening metathesis polymerization reaction (ROMP) of norborn-2-ene and tris(norborn-2-en-5-yl-methylenoxy)methylsilane in a suitable mixture of porogens applying Grubbs first generation catalyst ($RuCl_2(=CHPh)(PCy_3)_2$) according to published procedures.[149,151,172,194] Since the catalyst remained active on the inner surface of the monolithic matrix after rod formation is complete, it was used for grafting the perfluorinated ligand mono(norborn-5-ene-2-ylmethyl) hexafluoro-glutarate, which was prepared in situ. After deprotonation of the carboxylic acid groups of the graft polymer with KOH, the potassium salt was transformed into the corresponding Ag-salt using aqueous $AgNO_3$. After reaction with the Grubbs-Hoveyda catalyst $RuCl_2(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)(SIMes)$,[123] an excess of CF_3COOAg was added to substitute the second chlorine ligand (scheme 4-7).



R1

Scheme 4-7. Synthesis of **R1**.

The general applicability of such a consecutive chlorine substitution by two different carboxylates, one being polymer-bound, was demonstrated by NMR using low molecular weight polyoxazolines **A3** and **A4** with pendant carboxylic acid groups (M_n = 4000 g/mol) as shown above. In these experiments, the stepwise substitution of both chlorines was confirmed by monitoring the alkylidene proton of the corresponding species.[191] The formation of a single species with an alkylidene proton at ?=17.5 ppm (in CD_3OD) demonstrated that a perfect mimic of the homogeneous analogue ($Ru(CF_3COO)_2$(=CH-2-(2-PrO)-C_6H_4)(SIMes)) had been generated. The Ru-loading of the monolith-supported catalyst **R1** was 0.41 mg/g, corresponding to 2.54 mg catalyst/g support. This approach was much more straightforward and convenient than previous heterogenization methods, which entailed the heterogenization via the N-heterocyclic carbene (NHC). Since the critical step of NHC generation and reaction with suitable catalyst precursors was totally avoided, higher catalyst loadings were achieved. In addition, unreacted catalyst could be fully recovered.

For characterization of the support in flow-through catalysis and for purposes of comparison, again RCM of DEDAM was used for benchmarking. With the present system, TONs up to 500 and yields of 15 % even after 2 hours were achieved (figure 4-7).

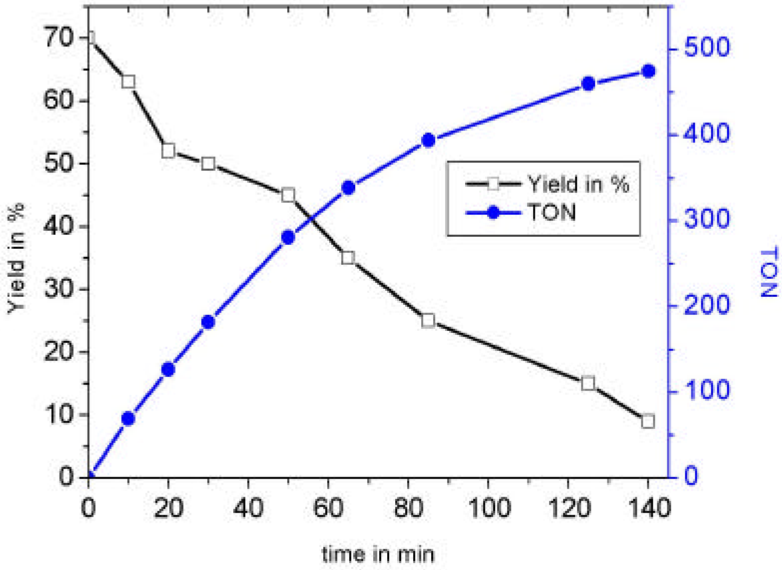


Figure 4-7. Flow-through catalysis using DEDAM.

Most important, only pure product as well as unreacted educt were found in the eluent, no metathesis derived ligand (i.e. 2-(2-PrO)-C_6H_4-CH=CH_2) or acyclic diene metathesis (ADMET) products were found. One can assume that back reaction of intermediaryly formed (2-(2-PrO)-C_6H_4-CH=CH_2) is fast, thus stabilizing the catalyst. This directly translates into an increased long-term stability. Thus, 15 % yield was observed even after 2 hours. Extremely low leaching (<0.2%) was found resulting in product contamination with Ru and Ag of 1.8 and 0.01 ppm, respectively.

A comparison with existing systems is given in table 4-9.

Table 4-9. Overview over catalytic activity in RCM of DEDAM of existing systems.

#	System	TON	Literature
1	$RuCl_2(=CHC_6H_5)(SIMes)(PCy_3)$/silica[a]	200	[150]
2	$RuCl_2(=CH\text{-}(2\text{-}R\text{-}O\text{-}C_6H_4)(PCy_3)$/PS-DVB	9	[195]
3	$RuCl_2(=CHC_6H_5)(SIMes)(PCy_3)$/PS-DVB[a]	= 20	[164]
4	$RuCl_2(=CHC_6H_5)(SIMes)(PCy_3)$/monolith[a]	250	[151]
5	$RuCl_2(=CHC_6H_5)(SIMes)(PCy_3)$/PS-DVB	= 100	[161,192,196]
6	$RuCl(RCOO)(=CHC_6H_5)(PCy_3)_2$/PS-DVB[a]	60	[167]
7	$RuCl_2(=CHC_6H_5)(PR_3)(PCy_3)$//MCM-41	= 20	[197]

[a] in principle suitable for flow-through catalysis

Diagram 4-3 gives a final comparison of supported catalysts.

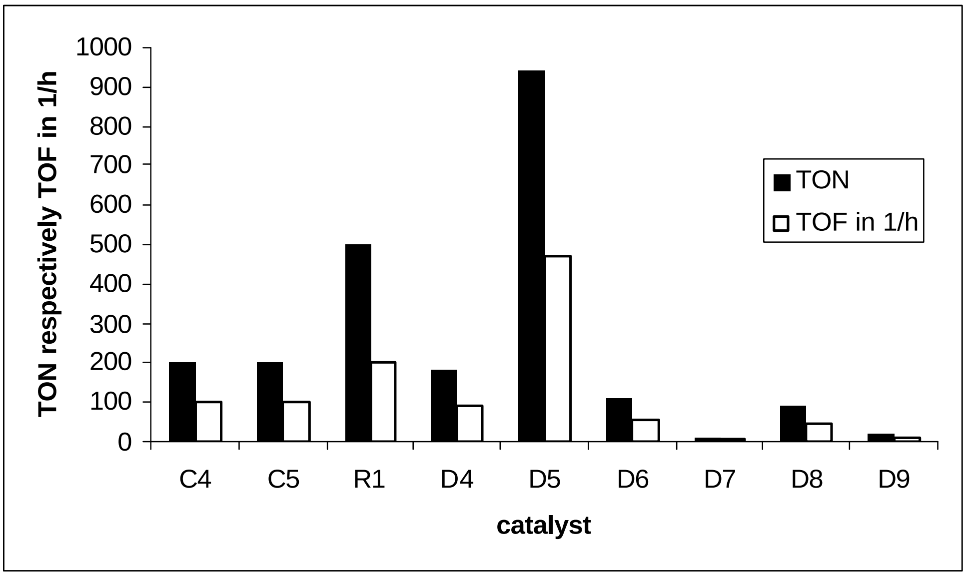


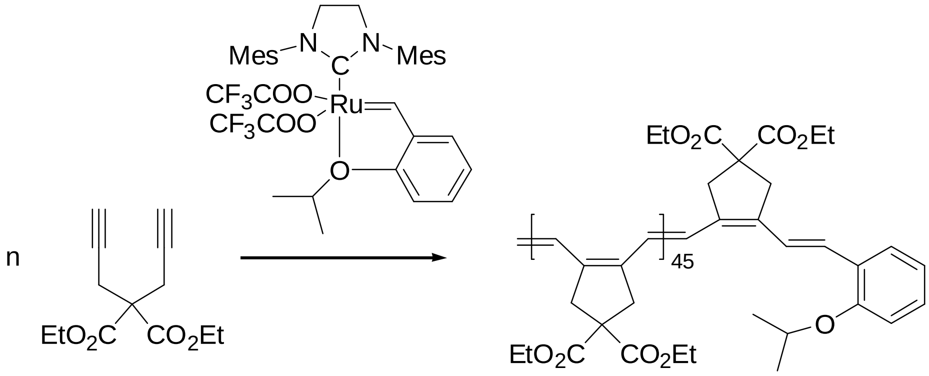
Diagram 4-3. Comparison of all supported catalysts.

The maximum TONs reported so far were in the range of 10 – 250, entry 4 in table 4-9 being the only system tested under flow-through conditions. With a TON of 500, the new supported modified Grubbs-Hoveyda catalyst exceeded existing heterogeneous catalysts by far, but in view of TON **D5** must be regarded as superior, in view of long-term stability and process ability system **R1**. First, it has a long-term stability giving even after 2 hours a conversion of DEDAM of 10 %. Second, during fixation of the catalyst no side-reactions occur and unreacted catalyst can be obtained in 100 % pure form. In conclusion, a long-term stable flow-through system for ring closing metathesis with a low leaching of ruthenium in the products was presented. This is the first example of a heterogenized Grubbs-Hoveyda catalyst in flow through catalysis.

4.3 Cylcopolymerization

4.3.1 Polymerization of diethyl dipropargylmalonate

The synthesis of a modified Grubbs-Hoveyda catalyst that can accomplish the cyclopolymerization of 1,6-heptadiynes in both a living and stereo regular way now closed the last gap between molybdenum- and ruthenium-based metathesis catalysts. $RuCl_2$(=CH-(2-(2-PrO)-C_6H_4)(SIMes) was converted into $Ru(CF_3COO)_2$(=CH-(2-(2-PrO)-C_6H_4)(SIMes) (**M1b**) by reaction of the parent complex with 2 equiv. of silver trifluoroacetate.[193] The enhanced polarization across the ruthenium-carbon double bond directly translated into an increased reactivity thus allowing the cyclopolymerization of DEDPM (scheme 4-8).



Scheme 4-8. Cyclopolymerization of DEDPM.

Interestingly, none of the existing ruthenium-metathesis catalysts such as $RuCl_2$(=CH-(2-(2-PrO)-C_6H_4)(NHC) and $RuCl_2$(=CH-C_6H_5)(PCy_3)(NHC) (PCy_3=tricyclohexylphosphine, NHC=1,3-dimesitylimidazolin-2-ylidene, 1,3-dimesityl-4,5-dihydroimidazlin-2-ylidene) nor $RuCl_2$(=CH-(2-(2-PrO)-C_6H_4)(1,3-dimesitylimidazolin-2-ylidene) or $RuCl_2$(=CH-(2,4,5-$(MeO)_3$-C_6H_4)(1,3-dimesityl-4,5-dihydroimidazolin-2-ylidene)] were reactive enough to accomplish this task. Though highly active, **M1b** did not allow a living polymerization setup in the polymerization of DEDPM. Irrespective of stoichiometry, molecular weights around 11000 g/mol were obtained (table 4-10, entries 1-2). A value for the ratio of the rate constant of propagation over the rate constant of initiation (k_p/k_i)[198] > 1000 was indicative of the negative role of the 2-(2-propoxy)benzylidene ligand. Its exchange by the 2,4,5-trimethoxybenzylidene ligand[138] lead to the formation of $Ru(CF_3COO)_2(=CH-(2,4,5-(MeO)_3-C_6H_4)(SIMes)$ **M2b**. This compound turned out to be an excellent catalyst for the cyclopolymerization of DEDPM, allowing full control over molecular weight. Thus, polymerizations of DEDPM initiated with **M2b** in methylene chloride proceeded in a class VI living manner.[199] An excellent agreement between the theoretical and experimentally determined molecular weights was observed. For all polymers the polydispersity index (PDI) was < 1.65. The value for k_p/k_i was 3, indicating a well-behaved system. In fact, the polymerization system **M2b**-DEDPM was living even after two days as shown by the stepwise addition of monomer (table 4-10 and digram 4-4, 4-5, 4-6). The unsaturated version of **M3b**, $Ru(CF_3COO)_2(=CH-(2-(2-PrO-C_6H_4))(IMes)$ **M3a** was totally inactive. Keeping all the (sometimes incremental) changes in the original Grubbs' 1st ($RuCl_2(=CH-C_6H_5)(PCy_3)_2$) respectively Herrmann catalyst ($RuCl_2(=CH-C_6H_5)(NHC)_2$, NHC=1,3-dimesitylimidazolin-2-ylidene) in mind, these results are illustrative for the drastic effects even small changes in a catalyst's environment can have.

Table 4-10. Summary of polymerization results.

polyacteylene	**cat**	**M_n(theor.)**	**M_n(LS)**	**PDI(LS)**	**$?_{max}$(nm)**	**E(eV)**
poly(DEDPM)$_{100}$	**C3**	11975	10400	1.62	584	2.123
poly(ECMCH)$_{50}$	**C3**	17485	11100	2.59	586	2.116
poly(DEDPM)$_5$	**M2b**	1389	5600	1.30	573	2.164
poly(DEDPM)$_{10}$	**M2b**	2571	7000	1.57	576	2.153
poly(DEDPM)$_{30}$	**M2b**	7296	13100	1.63	578	2.145
poly(DEDPM)$_{50}$	**M2b**	12021	16200	1.63	580	2.138
poly(DEDPM)$_{70}$	**M2b**	16747	20000	1.10	583	2.127
poly(DEDPM)$_{100}$	**M2b**	23835	27500	1.54	584	2.123
poly(ECMCH)$_{50}$	**M2b**	17517	13000	1.72	586	2.116

LS=light scattering. n=degree of polymerization. All molecular weights are in g/mol. All polymers were obtained in virtually quantitative (i.e.>95%) yield. $?_{max}$=UV-Vis absorption maximum. *E*= energy gap between the valence and conductivity band= E= 1.9368 + 8.4391/$_{\mathrm{Neff}}$ = E= hv.[198]

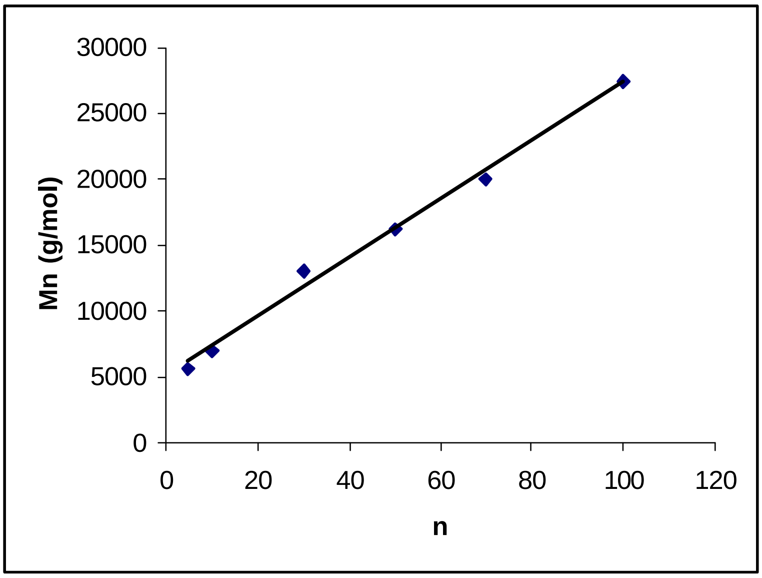


Diagram 4-4. Linear increase of molecular weight for poly(DEDPM)$_n$ prepared with **M2b**.

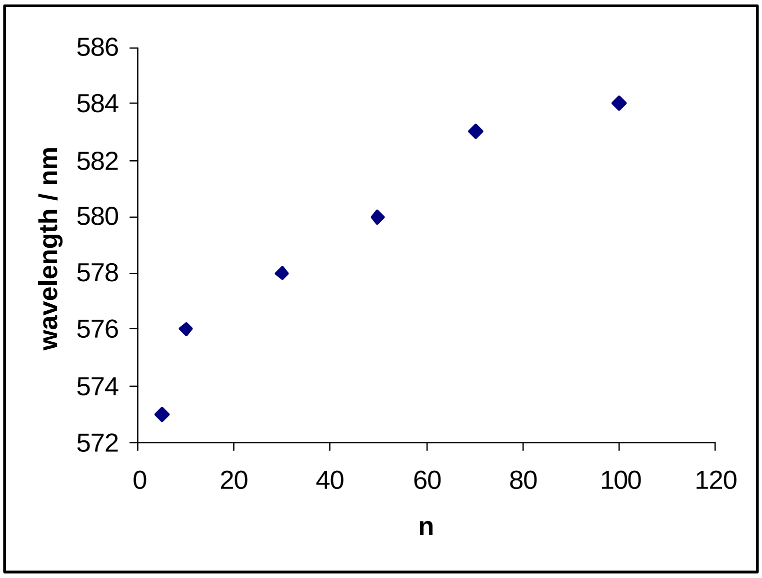


Diagram 4-5. Increase of wavelength (UV-vis) with n of poly(DEDPM)$_n$ prepared with **M2b**.

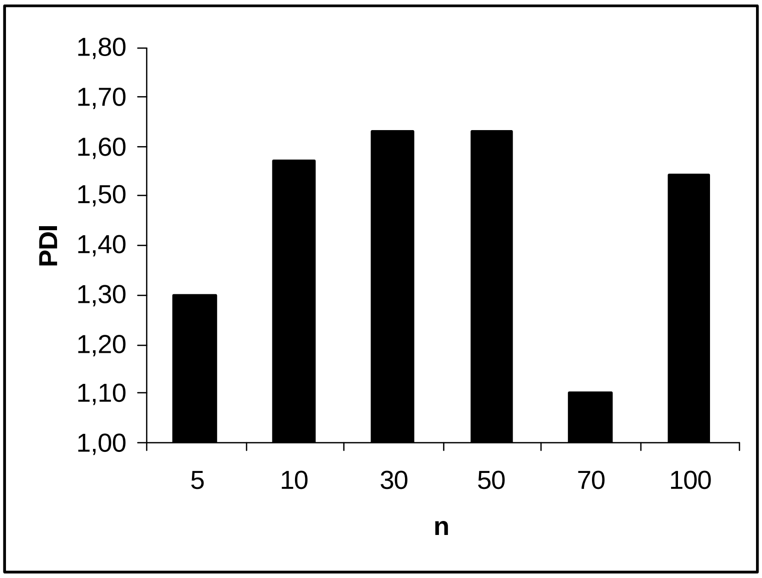


Diagram 4-6. PDI of poly(DEDPM)$_n$ prepared with **M2b**.

In terms of microstructure, poly(DEDPM) either prepared by **M1b** or **M2b** consisted virtually solely (>95%) of 1,3-cyclopent-1-enylenevinylene units as shown by $^{13}C\{^1H\}$-NMR measurements (figure 4-8).[121,122]

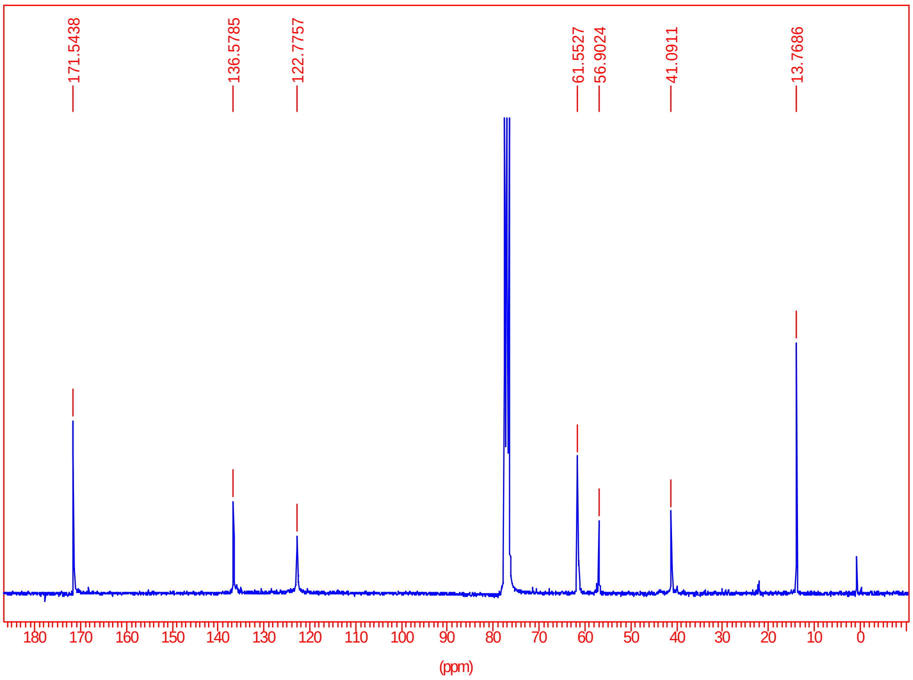
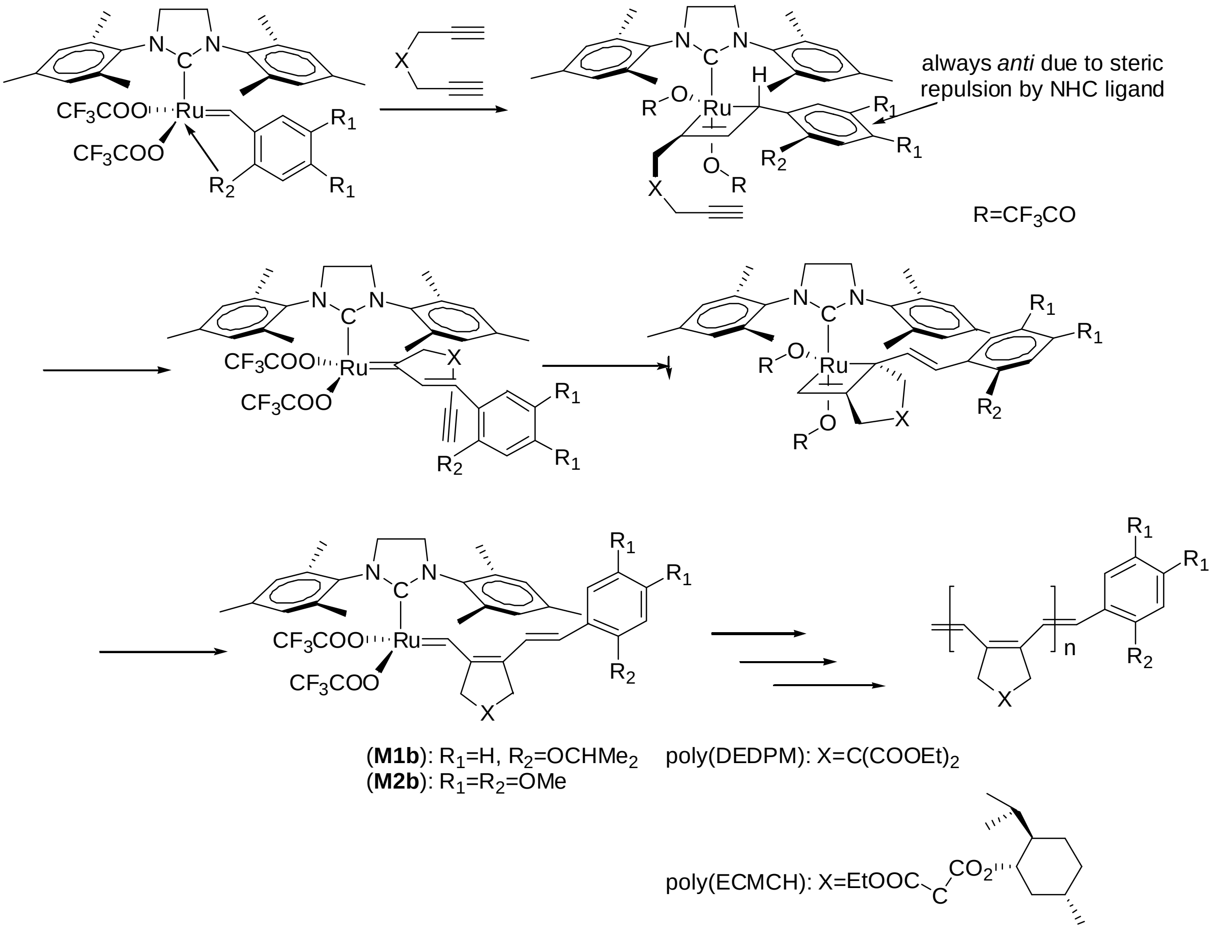


Figure 4-8. $^{13}C\{^1H\}$-NMR of poly(DEDPM) prepared with **M2b**.

A discussion of the NMR can be found in the literature.[121,122] Energy band gaps were calculated from the absorption maximum (?$_{max}$)[198] and are summarized in table 4-10. The polymerization mechanism certainly follows that of molybdenum-based cyclopolymerizations[113] and is shown in scheme 4-9.



Scheme 4-9. Mechanism of polymerization.

Upon addition of DEDPM to **M1b**, signals corresponding to the first insertion products at d=15.63, 18.67, 19.90, 20.84, 21.63 ppm, were observed by ^{1}H-NMR. The high *trans*-selectivity of the vinylene groups clearly originates from the steric repulsion of the 2-(2-PrO-C_6H_4)- and growing polyacetylene chain, respectively, by the NHC ligand, while the selective insertion mode is believed to be governed by the steric demands of the carboxylate groups. A conformation of the intermediary ruthenacyclobutene, with one carboxylate ligand in *trans*-position to the NHC ligand was assumed[25] and fits the stereochemical data.

Using MALDI-TOF spectroscopy, 2-propoxybenzylidene was found as endgroup in polymers prepared by the action of **M1b**, indicating the absence of any chain transfer reactions. In no case, any backbiting was observed. The polymerization of chiral 4-(ethoxycarbonyl)-4-(1*S*, 2*R*, 5*S*)-(+)-menthoxycarbonyl-1,6-heptadiyne (ECMCH) by this catalyst proceeded in a stereo- and regioselective way, resulting in tactic poly(*trans*-1,3-(cyclopent-1-

enylene)vinylene) with >95% stereoregularity as shown by ^{13}C-NMR spectroscopy (figure 4-9).[121,122]

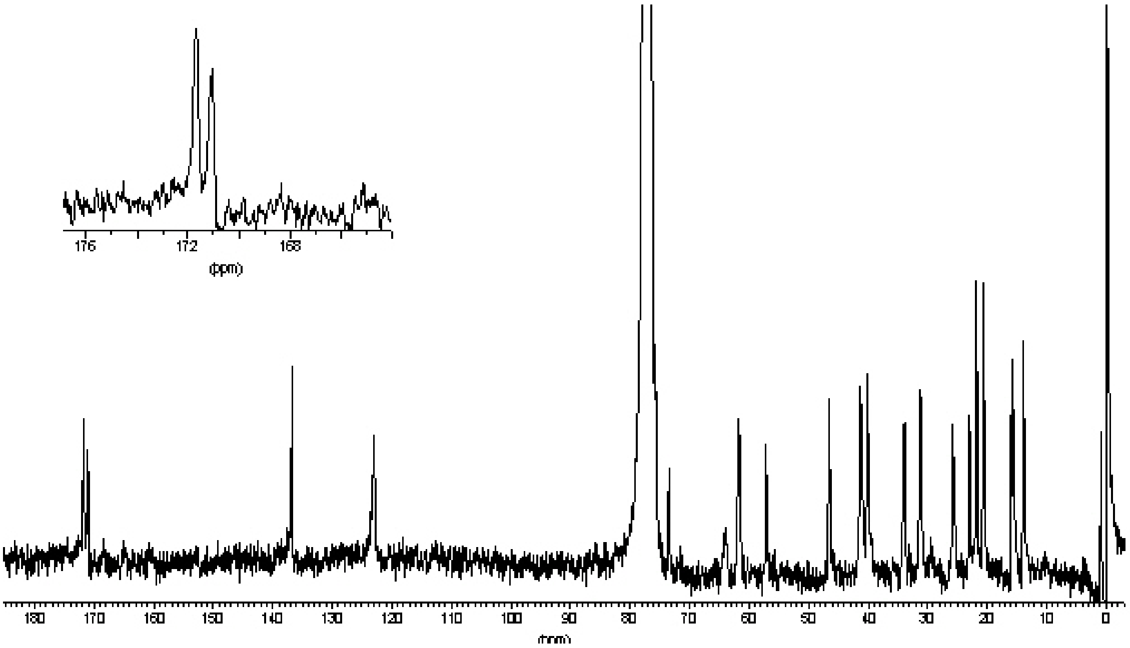


Figure 4-9. $^{13}C\{^{1}H\}$-NMR of Poly(ECMCH) prepared by **M2b**.

A discussion of the NMR can be found in the literature.[121,122] This finding was of particular interest, since polymers prepared via ring-opening metathesis polymerization (ROMP) using other Ru-based initiators revealed a *trans*-content = 90 % and low stereoregularity.[43,130]

Catalysts **M1-4** were designed by careful tuning of the electronic and steric situation of the ligands to investigate the character of the living polymerization of DEDPM in more detail. While **M1a**, **M2a**, **M3a, M3b**, and **M4a** were inactive in the cyclopolymerization of DEDPM and initiators **M1b-d** containing the (=CH-2-(2-PrO)-C_6H_4) group did not allow any control over molecular weight, initiators **M2b-d** containing the (=CH-2,4,5-$(OMe)_3$-C_6H_2) group and initiators **M4b-d** containing the (=CH-2-PrO-5-NO_2-C_6H_3) group offered access to class VI living polymerization systems, **M2b** and **M4d** being the preferred systems. The livingness of the systems was demonstrated by linear plots of M_n *vs* number of equivalents of monomer added (N), by ^{1}H-NMR as well as by addition of monomer to the living systems after 48 hours. For initiators **M2b-d** and **M4b-d**, values for k_p/k_i were in the range of 3-7, while **M1b**, **M1c** and **M1d** showed a k_p/k_i of >1000, 80 and 40, respectively. The use of non-degassed solvents showed no effect for these measurements and underlines the high stability of these initiators. The effective conjugation length (N_{eff}) was calculated from the UV-vis absorption maximum $(?_{max})$.[198] The final ruthenium content in the polymers was 3 ppm.

A typical UV-vis spectrum is given in figure 4-10.

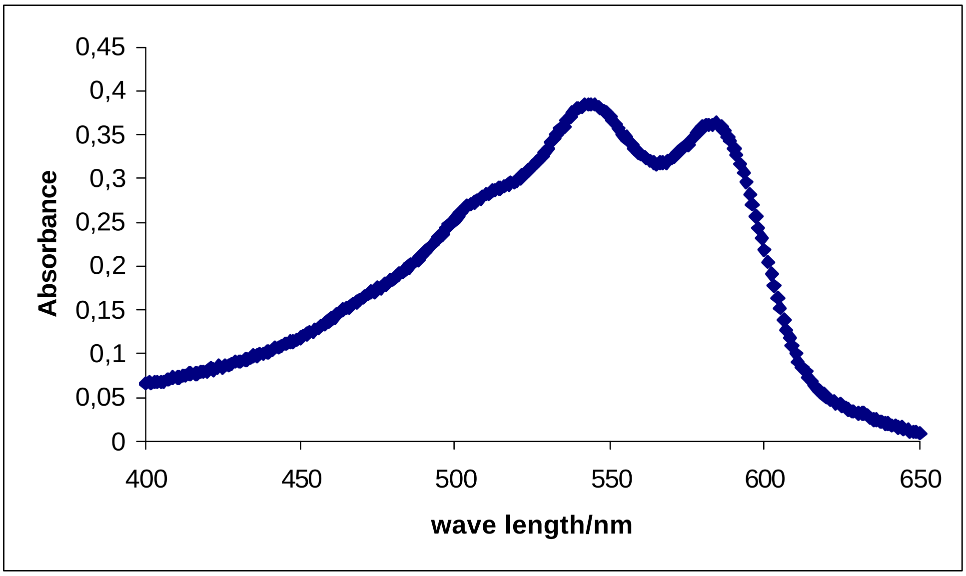


Figure 4-10. Typical UV-vis spectrum of poly(DEDPM)$_{50}$ prepared by **M2b**.

In detail the variations in the N-heterocyclic carbene (NHC) ligand (either electron rich or electron poor), the effect of substituting the chlorine ligands by electron withdrawing, fluorinated carboxylates was investigated and even more important, how the electronic and steric variations of the benzylidene moiety directly translated into a initiator's ability to form a class VI living system, allowing full control over molecular weight.

Similar to cyclopolymerizations catalyzed by a Schrock catalyst in the presence of a base such as quinuclidine, dissociation of the o-alkoxy group of the benzylidene ligand in Ru-based initiators had to be fast. Only in this case a well behaved system where the rate constant of initiation (k_i) was comparable to the rate constant of propagation (k_p), i.e. $k_p/k_i < 10$, could be established. In the following, the systematic variations that have been carried out in the ligand sphere of a ruthenium-based metathesis initiator were investigated.

While **M1a** did not polymerize DEDPM, initiators **M1b-d** were active in the cyclopolymerization of this monomer, indicating that electron withdrawing carboxylates were an important issue. Interestingly, values for k_p/k_i[198] were reduced from >1000 (**M1b**) to 80 (**M1c**), respectively 40 (**M1d**). Unfortunately, though polymerization active, none of these initiators allowed control over molecular weight. In all cases polymers with low PDIs (1.25-1.55) yet identical molecular weights around 11000 g/mol, irrespective of the stoichiometry of polymerization, were obtained. Nevertheless, in all cases polymers contained virtually solely 5-membered rings, indicating selective ?-addition for initiators **M1b-d**. This implied that irrespective of the size of the carboxylate groups used in this study, DEDPM can undergo selective ?-insertion.

Encouraged by the finding that it was possible to reduce the k_p/k_i in initiators **M1b-d** by simply changing the carboxylates the synthesis of an analogue to **M1b**, which beared the electron poorer unsaturated version IMes instead of the electron rich SIMes group was synthesized. This change was of particular interest since it is well-known from the literature that both ligands inherit a quite distinct reactivity in metathesis reactions, though it was in most cases not predictable for a particular substrate.[79] Interestingly, initiator **M3b** was found to be totally *inactive* in the cyclopolymerization of DEDPM, indicating that the NHC has to be electron rich in order to be suitable for cyclopolymerization of DEDPM.

With the finding that initiators of the general formula $Ru(CF_3(CF_2)_nCOO)_2$(=CH-2-RO-Ar)(SIMes) were in principle capable of cyclopolymerizing DEDPM, the design of these initiators in a way that would allow living polymerizations was challenging.[199] It was generally accepted that a *reduction* of the nucleophilic character of the oxygen atom in the 2-alkoxy fragment in RuX_2(=CH-2-RO-Ar)(SIMes) resulted in a dramatic increase in the catalytic activity in RCM and related reactions.[137,139,140] The reason was an adherent reduction of the chelating character of the oxygen group, thus facilitating the formation of the catalytically active 14-electron ruthenium species (figure 4-11).

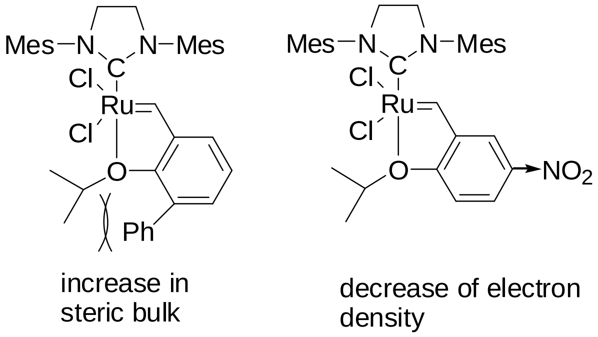


Figure 4-11. Reduction of chelating ability as postulated by Grela.[137]

On the one hand, quite impressive turn-over numbers (TONs) under mild conditions (0 °C to room temperature) in comparison to the parent Grubbs-Herrmann[43,53,62,126-128,130,200,201] catalyst or Grubbs-Hoveyda[123] catalyst could be achieved with such systems in RCM and related reactions. On the other hand, these systems decomposed more easily, particularly at higher temperatures, and must therefore be stored at 4 °C in a refrigerator. In view of this important background information, this concept should be transferred to initiators used for cyclopolymerizations and aimed on the synthesis of initiators that would show increased insertion rates, i.e. values of k_p/k_i < 10. One can easily imagine that the key reaction in reducing k_p/k_i is the insertion step, since the benzylidene would become the polymer end group and be transported away from the Ru-core once a monomer has undergone insertion. For this purpose, even any coordination of a 2-alkoxy group in the benzylidene has to be reduced to a minimum or even better suppressed in order to increase initiation rates while leaving propagation rates unaffected. Two pathways were independently pursued to improve the insertion efficiency. On the one hand, the nucleophilic character of the oxygen in the alkoxy group of the benzylidene moiety, on the other hand its steric hindrance was reduced. Such apparently incremental changes are not trivial at all. For example, changing from a (=CH-2-(2-PrO-C_6H_4) group in $RuCl_2$(=CH-2-(2-PrO-C_6H_4))(SIMes) to a (=CH-2-MeO-C_6H_4) group results in a totally unstable initiator, that was not suitable for any metathesis reaction.[123] It was shown by Grela et al. that introduction of additional two electron-donating methoxy groups could in fact stabilize this system,[138] yielding the stable Grubbs-Hoveyda-type catalyst **M2a**. Using the same ?-asarone-derived ligand, initiators **M2b-2d** were prepared. For DEDPM, values for k_p/k_i were in fact low, i.e. in the range of 2 to 6, which is lower than with Schrock catalysts.[121,122] As expected, these initiators cyclopolymerized DEDPM in a class VI[199] living manner. The fact that polymerizations proceeded in a living way was derived from the graphs that were obtained by plotting the number of equivalents of DEDPM (N) *vs* M_n.

The degree of livingness was determined by adding DEDPM to a living polymer after 48 hours. No bimodal GPC traces or any peak broadening was observed with respect to a reference sample. In an additional experiment, 2-3 molequiv. of DEDPM were added to initiators **M2b-2d** in $CDCl_3$. No change in NMR was observed after more than 48 hours. Interestingly, significant differences were found in the PDIs of the resulting polymers. Thus, poly(DEDPM) prepared by the action of **M2b-2d** showed PDIs < 1.8, while poly(DEDPM) prepared from **M2c** and **M2d** showed PDIs up to 2.1, indicating chain-transfer reactions, which in view of the stability of the living polymer must occur without initiator deterioration. The same high stability of living polymer chains was found for initiators **M1b-1d**.

In an extension to these investigations it was of interest whether the steric conditions provided by the methoxy group were the only factors responsible for insertion efficiency and the degree of livingness. And finally, it was of interest whether a reduction of the nucleophilic character of the 2-alkoxide could generate a truly living system. Grela et al. reported on the dramatic increase of reactivity in RCM reactions upon introduction of a nitro group in the 5-position of the (=CH-2-(2-PrO)-C_6H_4) moiety.[137] It was again to question whether this correlation was also true for cyclopolymerization. For this purpose, initiators **M4a-4d** were prepared. As all other chlorine bearing initiators, **M4a** was totally inactive, substitution of the chlorines by fluorinated carboxylates again increased the reactivity. As a matter of fact, initiators **M4b-4d** again cyclopolymerized DEDPM in a class VI living manner. Values for k_p/k_i of 4-7 were found. While the cyclopolymerization of DEDPM with **M4b** and **M4c**, respectively, gave rise to PDIs = 2.3 and 1.9, respectively, the action of **M4d** resulted in poly(DEDPM) with PDIs = 1.6. These results are interpreted in a way that large alkoxides apparently successfully suppress chain transfer reactions. Again, all polymers obtained with these initiators contained virtually solely (>96%) cyclopent-1-enylenevinylenes.

Since the synthesis of metal-free products is an important issue for any electronic and optical applications, all polymers were dissolved in aqua regia and subjected to ICP-OES measurements. A final ruthenium content of 3 ppm was found.

A final comparison of **M4b-d** with **M2b-d** goes in favor of **M2b** and **M4d** for two reasons. First, they show the best linear correlations between M_n and N, which is in fact a result of the low k_p/k_i values. Second, both initiators produce polymers with an excellent control over molecular weight and comparably low PDIs, **M4d** giving the lowest values. Nevertheless, from a synthetic point of view, it needs to be mentioned that initiator **M4d** was prepared *via* a two step synthesis, while **M2b** is conveniently accessible *via* commercially available ?-asarone. The properties of the polymers are summarized in table 4-11.

Table 4-11. Summary of polymerization results for initiators **M1-4**.

Initiator	**n**	**M_n(theor.)**	**M_n(RI)**	**PDI(RI)**	?$_{max}$	***E(eV)***	**N_{eff}**	**k_p/k_i**
M1a	10-100	no reaction	-	-	-	-	-	-
M1b	10-100	-	13200	1.51	584	2.123	45	> 1000
M1c	10-100	-	9900	1.25	584	2.123	45	80
M1d	10-100	-	10200	1.25	584	2.123	45	40
M2a	10-100	no reaction	-	-	-	-	-	-
M2b	10	2600	8400	1.79	576	2.153	39	3
M2b	30	7300	11500	1.26	578	2.145	41	-
M2b	70	16700	16100	1.46	583	2.127	44	-

M2b	100	23800	19700	1.48	584	2.123	45	-
M2c	10	2600	4700	1.70	577	2.149	40	6
M2c	30	7300	6700	1.84	583	2.127	44	-
M2c	70	16700	12200	1.65	584	2.123	45	-
M2c	100	23800	15100	1.94	584	2.123	45	-
M2d	10	2600	5400	1.61	576	2.153	39	2
M2d	30	7300	7900	1.65	581	2.134	43	-
M2d	70	16700	13000	1.99	585	2.119	46	-
M2d	100	23800	17500	2.11	585	2.119	46	-
M3a	10-100	no reaction	-	-	-	-	-	-
M3b	10-100	no reaction	-	-	-	-	-	-
M4a	10-100	no reaction	-	-	-	-	-	-
M4b	10	2600	1000	1.11	570	2.175	35	4
M4b	30	7300	5700	1.27	573	2.164	37	-
M4b	70	16700	9700	1.76	581	2.134	43	-
M4b	100	23800	12000	2.31	582	2.130	44	-
M4c	10	2600	4700	1.54	571	2.171	36	7.3
M4c	30	7300	6800	1.55	582	2.130	44	-
M4c	70	16700	11300	1.32	583	2.127	44	-
M4c	100	23800	12800	1.88	586	2.116	47	-
M4d	10	2600	4200	1.59	571	2.171	36	4.8
M4d	30	7300	7500	1.50	579	2.141	41	-
M4d	70	16700	14000	1.29	585	2.119	46	-
M4d	100	23800	17400	1.34	586	2.116	47	-

The following diagrams (4-7 - 4-12) give a final comparison of all data.

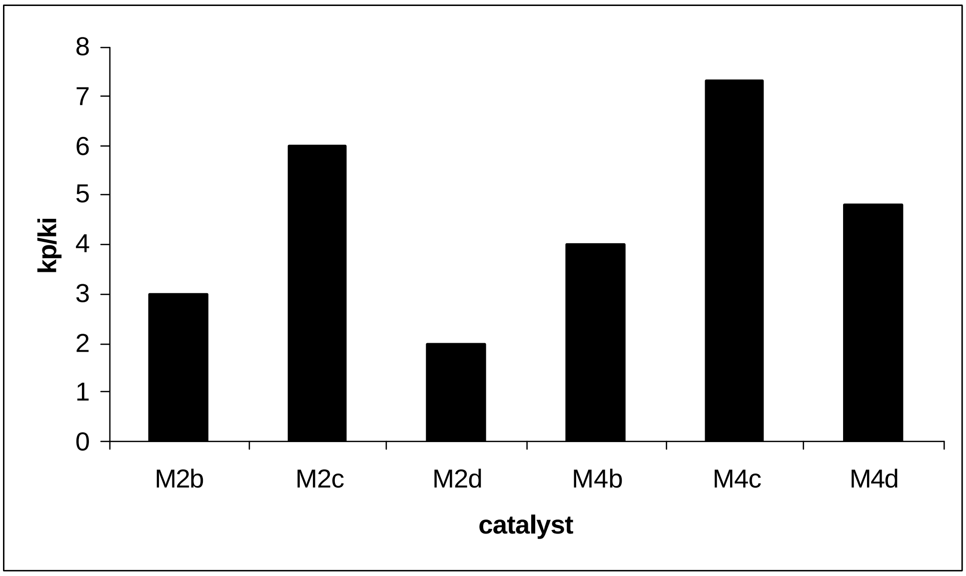


Diagram 4-7. Comparison of k_p/k_i for catalysts **M2-4**.

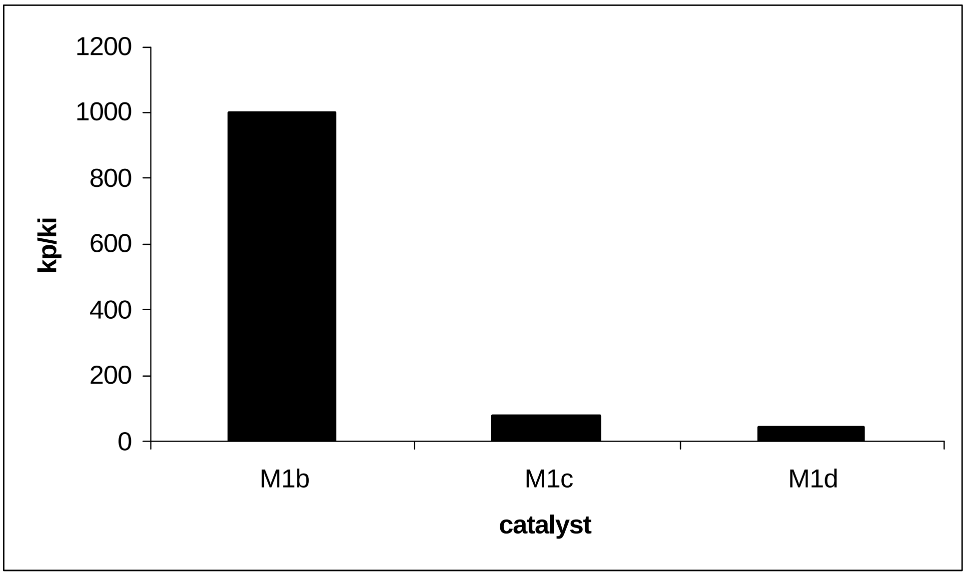


Diagram 4-8. Comparison of k_p/k_i for catalysts **M1b,c,d**.

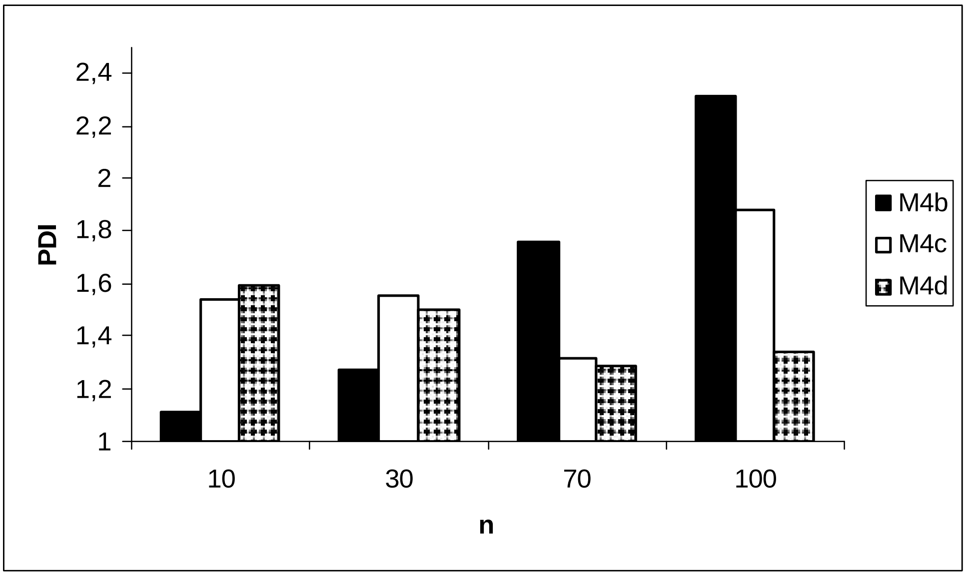


Diagram 4-9. Comparison of PDI of poly(DEDPM)$_n$ prepared with **M4**.

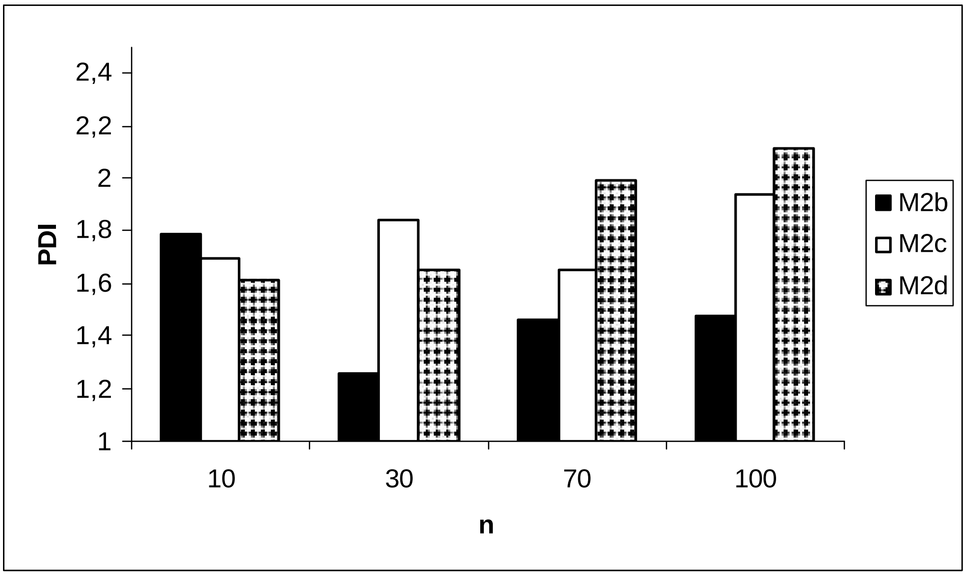


Diagram 4-10. Comparison of PDI of poly(DEDPM)$_n$ prepared with **M2**.

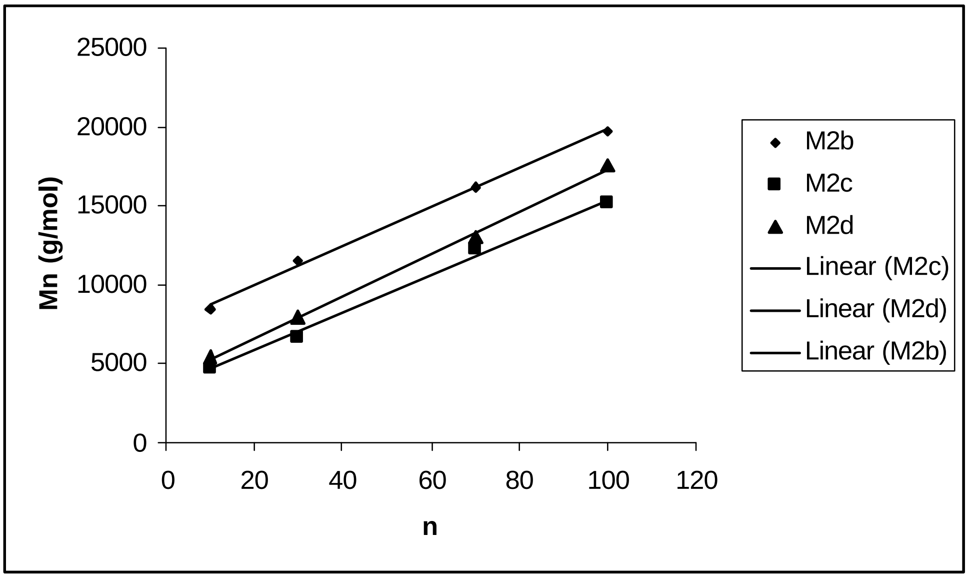


Diagram 4-11. Linear increase of molecular weigth of Poly(DEDPM)$_n$ prepared with **M2**.

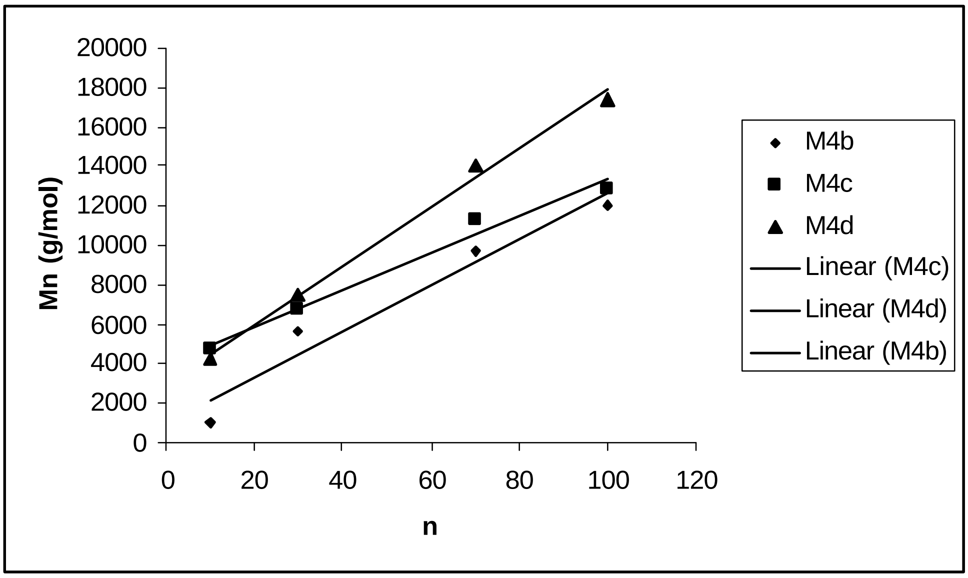


Diagram 4-12. Linear increase of molecular weigth of Poly(DEDPM)$_n$ with **M4**.

From the systematic variation of all ligands, the following requirements for cyclopolymerization-active systems were found: (i) the replacement of both chlorine ligands with strongly electron withdrawing carboxylic groups using salts such as $CF_3(CF_2)_{n=0-2}COOAg$ is required; (ii) the NHC has to be electron rich; (iii) the living character of the polymerization of DEDPM strongly correlates with the steric and electronic situation at the benzylidene ligand. Therefore, the weaker the coordination of the oxygen fragment to the Ru-core is, the lower the values for k_p/k_i are, resulting in increased insertion efficiencies. Two new types of initiators (**M2b-d** and **M4b-d**) that fulfill these criteria were prepared and found suitable for the class VI living polymerization of DEDPM. All initiators gave rise to 100 % of ?-insertion of the monomer, resulting in the formation of polyacetylenes containing virtually solely (>96%) 5-membered ring structures. The use of larger fluorinated carboxylates apparently further reduces chain-transfer reactions resulting in polyenes with low PDIs.

4.3.2 Polymerization of DEDPM using A3 and A4

One of the many advantages of ruthenium based catalysis is their tolerance to polar functional groups and water as a reaction medium. Poly(ene)s directly synthesized in form of stable aqueous dispersions are particularly attractive for many industrial applications, since they can be directly deposited on suitable supports such as clays. Therefore, establishing a system capable of polymerizing DEDPM under aqueous conditions, which provides stable latex in one single step is of great interest. The use of **C3** in combination with micelle forming compounds such as sodium dodecylsulfate (SDS) resulted only in the formation of oligomeric precipitates. As an alternative, an amphiphilic poly(2-oxazoline)-derived *block* copolymer, Me$_{30}$Non$_{6}$(PenOH)$_{2}$Pip, which is known to undergo micellisation in water,[202] was synthesized by living cationic polymerization.[170] Again, its use with **C3** only resulted in oligomeric precipitates. So, a fixation of the catalyst on these micelle-forming, amphiphilic *block* copolymers was attempted. Upon micelle formation of the functionalized block copolymer, the catalyst was to be located in the hydrophobic micellar core, where the monomer will be dissolved, too. While Me$_{30}$Non$_{4}$(PenOH)$_{4}$Pip resulted only in insoluble (in water), catalyst-loaded species, Me$_{30}$Non$_{6}$(PenOH)$_{2}$Pip could be successfully used for these purposes. For the polymerization of DEDPM, a value of 11 for k$_{p}$/k$_{i}$ was found for **A4**.

All experimental data can be found in table 4-12.

Table 4-12. Summary of polymerization results.

polyacteylene	**cat**	**solvent**	**M$_n$(theor.)**	**M$_n$(LS)**	**PDI(LS)**	**?$_{max}$(nm)**	***E*(eV)**
poly(DEDPM)$_{50}$	**A3**	water	11975	7700	2.08	584	2.123
poly(ECMCH)$_{50}$	**A3**	water	17485	8100	1.28	584	2.123
poly(DEDPM)$_{50}$	**A4**	water	12021	9500	1.38	580	2.138
poly(DEDPM)$_{100}$	**A4**	water	23835	12700	1.23	584	2.123

LS=light scattering. n=degree of polymerization. All molecular weights are in g/mol. All polymers were obtained in virtually quantitative (i.e.>95%) yield. $?_{max}$=UV-Vis absorption maximum. *E*=energy gap between the valence and conduction band.[198]

The next diagrams (4-13 - 4-14) give a final comparison of Poly(ECMCH)$_{50}$ obtained with catalyst **C3** and **A3** and show the decrease in PDI and increase of activity of the aqueous system.

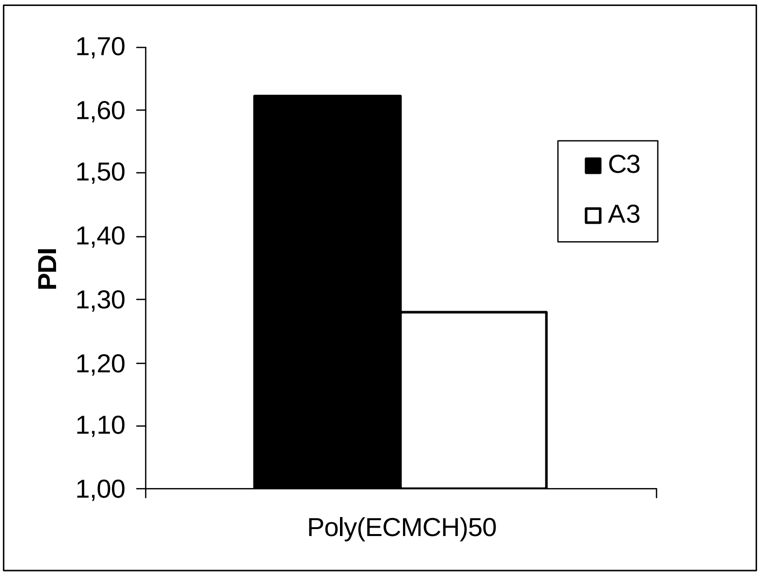


Diagram 4-13. PDI of Poly(ECMCH)$_{50}$ using **C3** and **A3**

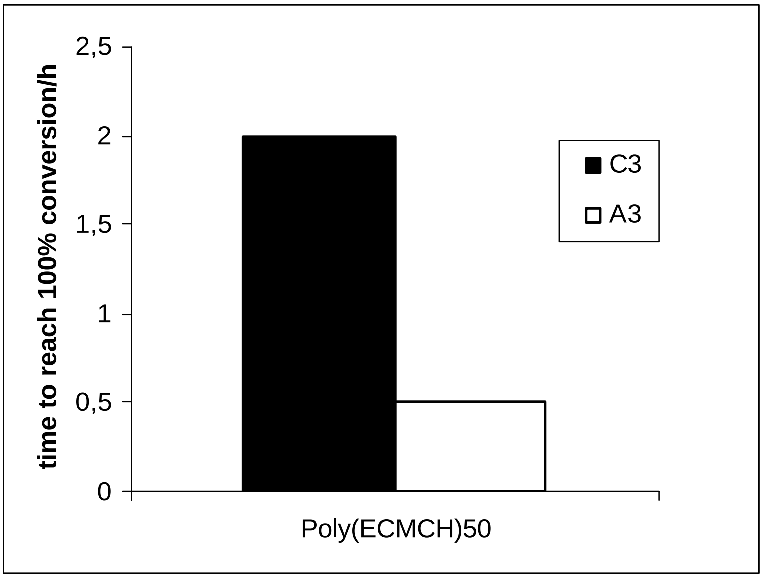


Diagram 4-14. Time to reach 100% conversion using **C3** and **A3** for Poly(ECMCH)$_{50}$.

Poly(DEDPM) prepared with **A4** in water was characterized by lower polydispersity indices (PDIs) < 1.40 compared to poly(DEDPM) prepared by **M2b** and due to the increased concentration of DEDPM within the micelles, reaction times required to reach complete conversion were reduced to 30 minutes using **A3** and **A4** compared to 2 hours with **M2b** illustrating the catalytic effect of the micellar nanoreactors formed in aqueous medium.

The polymerization can visually be followed through a color change to deep lilac as can be seen in figure 4-12.

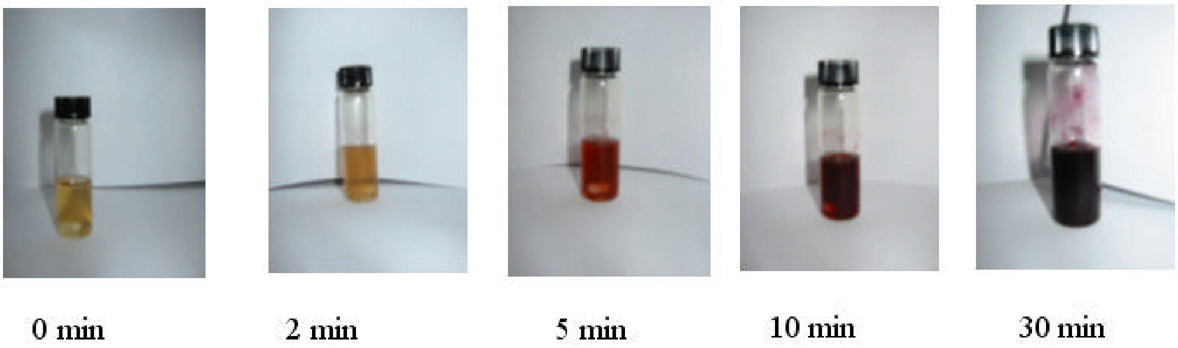

0 min 2 min 5 min 10 min 30 min

Figure 4-12. Color change during polymerization.

Nevertheless, the polymerization itself can not be regarded living. TEM analysis of the resulting polymer latex revealed particle sizes between 100 and 200 nm, which is typical for an emulsion based process (figure 4-13).

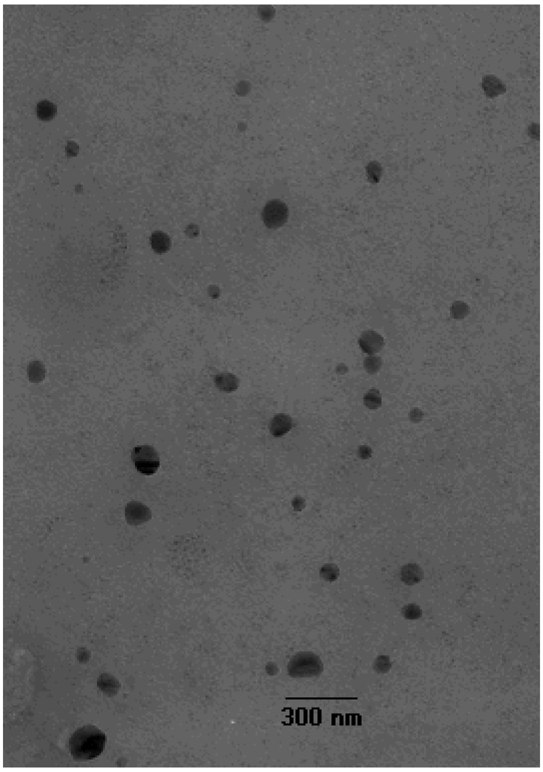


Figure 4-13. TEM-picture of stable latex.

Stabilized by the amphiphilic structure of the *block*-copolymer poly(DEDPM) could be stored over two weeks without any change in terms of latex particle size, molecular weight and UV-Vis absorption maximum. Complementary, the catalyst immobilization technique allowed also for catalyst/product separation to obtain virtually Ru-free polyacetylenes with a Ru-content = 0.35 ppm. Relevant for technical use, poly(DEDPM) prepared by any of the methods reported here was stable in the solid state under ambient conditions including air and moisture.

4.3.3 Other Heptadiynes

The following monomers were synthesized according to literature procedures to investigate the tolerance of the new catalysts towards functional groups and to get insight into the sterical demands of monomers (figure 4-14).

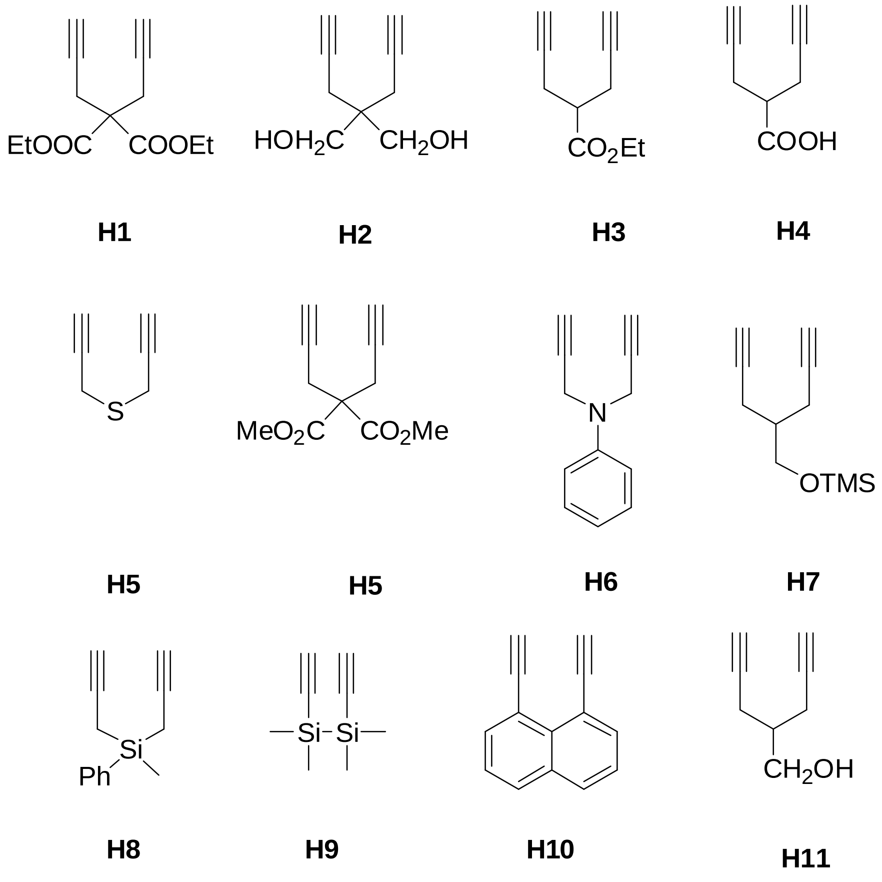


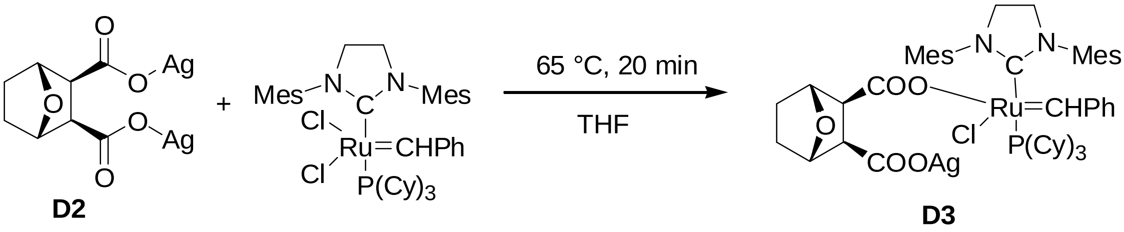
Figure 4-14. Heptadiynes used for polymerization.

For all reactions catalyst **M1b** was used. The use of **H1** is described above. With monomers **H3-H11** only insoluble polymers were isolated with **C3**. Only **H2** could be polymerized giving the following polymer (scheme 4-10).

6 Conclusion

The aim of this work was the synthesis of new homogeneous and heterogeneous second-generation Grubbs catalysts via chlorine exchange with electron-withdrawing groups using silver carboxylates.

The Grubbs-Herrmann catalyst can generally be employed in this transformation (scheme 6-1), precipitation of AgCl·PCy$_3$ during reaction was a major drawback.



Scheme 6-1. Synthesis of **D3**.

Whereas the homogeneous compound **D3** was not highly active, both the monolith- and silica-based (heterogeneous) catalytic systems turned out to be active and stable, allowing high TONs in RCM for a large number of compounds. Ruthenium leaching was low, resulting in virtually Ru-free products. The catalytic systems described here can be used as monolith-based flow-through reactors as well as surface-grafted silica-based supports in slurry type reactions (figure 6-1).

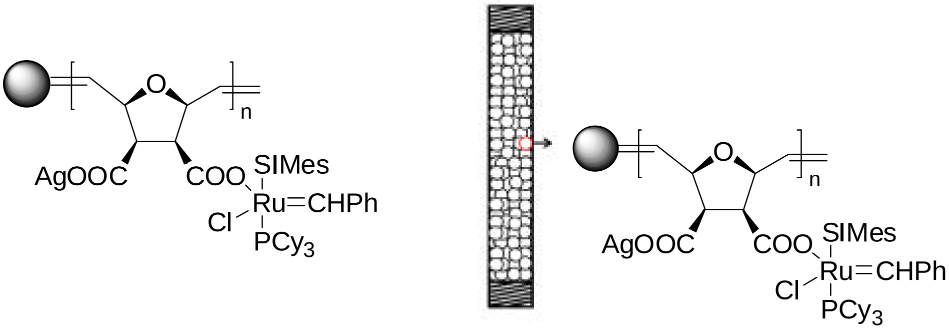
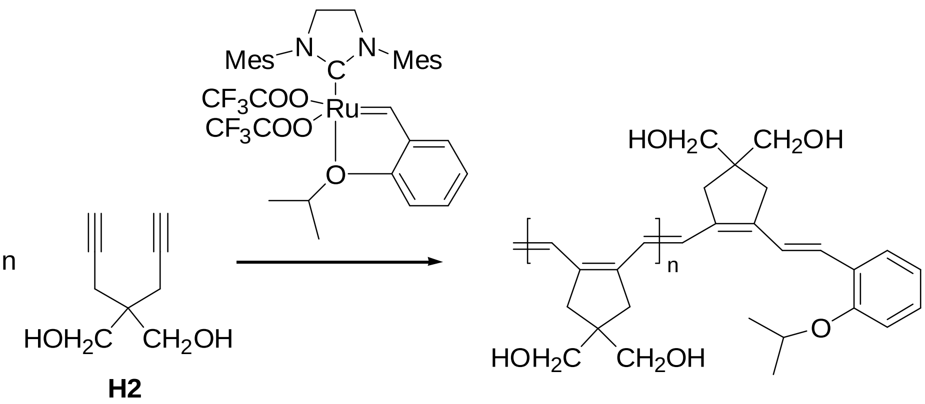


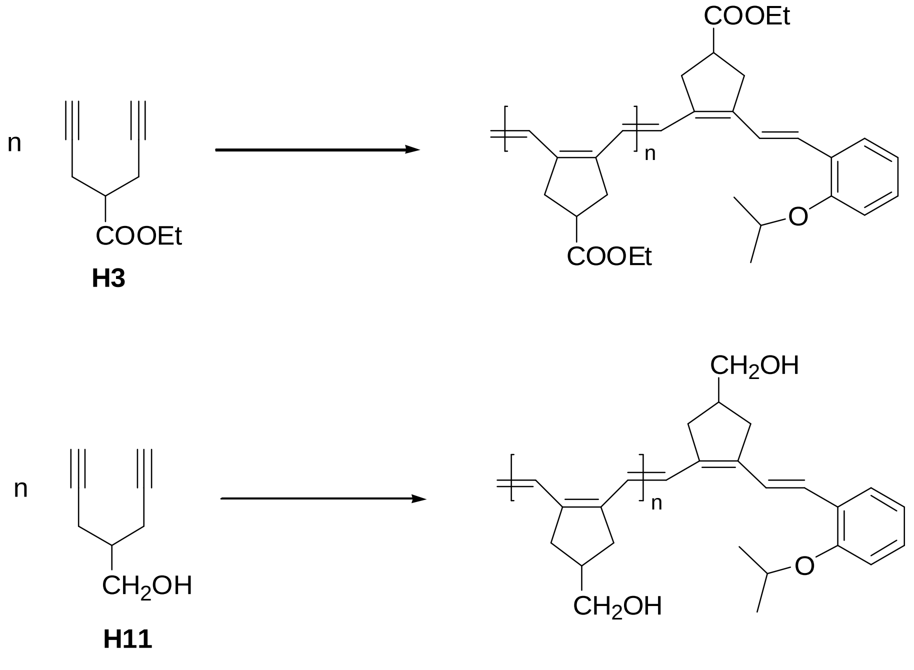
Figure 6-1. Heterogeneous systems: left silica based (**D7,8**) and right monolith based (**D4,5**).

Though accessible and highly active, any phosphine-containing catalyst suffers from lack of stability due to formation of AgCl(PCy$_3$) during synthesis. With the synthesis of catalysts **C1-3** and **M1-4(b-d)** the concept of the fixation via strongly electron withdrawing ligands that accelerate the catalytic activity of Grubbs-Hoveyda-type catalysts was shown. Thus, **C3** can be stored under ambient conditions (i.e. room temperature, air and moisture) without loss of activity. In various RCM, enyne metathesis and ring-opening cross metathesis experiments,



Scheme 4-10. Polymerization of **H2**.

As for the other monomers only highly conjugated, insoluble polymers could be isolated, the Grubbs-Herrmann as well as the Hoveyda-Grubbs catalyst, known to be inactive towards polymerization of **H1**, were used for the sterical less demanding monomers **H3** and **H11**. Interestingly, pure 5-membered soluble rings could be isolated. This is of major interest, because with highly active Schrock catalyst, only 77 % five-membered rings for **H3** can be isolated (scheme 4-11).



Scheme 4-11. Polymerization of sterical less demanding monomers **H3** and **H11**.

Until now, all polymerizations of 1-alkynes were unsuccessfully; monomers used are shown in the following figure.

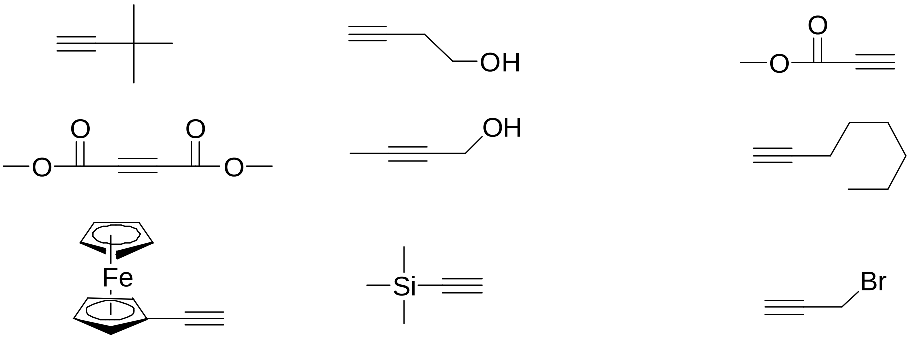


Figure 4-15. Monomers for 1-acetylene polymerization.

Only 1-octadiyne gave conversion of 5 % after 24 hours, yielding a soluble polymer of M_n=6000 g/mol.

5 Experimental section

5.1 General remarks

5.1.1 Analytics

NMR data were obtained at 300.13 MHz for proton and at 75.74 MHz for carbon in the indicated solvent at 25°C on a Bruker Spectrospin 300 and are listed in parts per million downfield from tetramethylsilane for proton and carbon. IR spectra were recorded on a Bruker Vector 22 using ATR technology. GC-MS investigations were carried out on a Shimadzu GCMS-QP5050, using a SPB-5 fused silica column (30 m x 0.25 mm x 25 ?m film thickness). Elemental analyses were carried out at the Institute of Physical Chemistry, University of Vienna and at the Mikroanalytical Laboratory, Anorganisch-Chemisches Institut, TU München, Germany. Mass spectra were recorded at the Anorganisch-Chemisches Institut, TU München, Germany. A Jobin Yvon JY 38 plus was used for ICP-OES (Universität Innsbruck) measurements, a MLS 1200 mega for microwave experiments. PEEK columns (100 x 4 mm i.d., 125 x 4 mm i.d., 100 x 7 mm i.d. and 150 x 4 mm i.d.) were purchased from Berger (Linz, Austria). MALDI-TOF experiments were carried out on a Bruker Biflex III using a N_2 laser (? = 337 nm). Dithranol was used as the matrix. Gel permeation chromatography (GPC) using UV/RI detection was carried out using PLgel 5 ?m MIXED-C columns (PLgel 5 ?m Guard, 50x7.5 mm, PLgel 5 ?m MIXED-C, 300x7.5mm, PLgel 5 ?m MIXED-C, 600x7.5 mm) using a Waters 410 differential refractometer detector and a Waters 484 UV-Detector for measurements in $CHCl_3$. The flow rate was 1.0 mL/min. Gel permeation chromatography (GPC) was carried out using PLgel 5µm MIXED-C and PLgel 5µm MIXED-E columns (PLgel 5µm MIXED-C, 300x7.5mm, PLgel 5µm MIXED-C, 300x7.5mm, PLgel 5µm MIXED-E, 300x7.5mm, PLgel 5µm MIXED-E, 300x7.5mm) using a 410 differential refractometer detector for measurements (from Waters) in DMAc (N,N-dimethylacetamide). The flow rate was 0.5 mL/min. GPC columns for DMAc were calibrated vs poly(methylmethacrylate) standards (Polymer Standards Service (PSS), molecular weights 960 to 1.64 x 10^6 g/mol). Samples were filtered through 0.2 ?m Teflon filters (Millipore) in order to remove particles. GPC columns for $CHCl_3$ were calibrated *vs* polystyrene standards

(Polymer Standards Service (PSS), molecular weights 580 to $1.57x10^6$ g/mol). Gel permeation chromatography (GPC) with light-scattering (Universität Innsbruck) detection was carried out in $CHCl_3$ using a Waters Styragel HR 4E column, a Waters 2414 differential refractometer, a Waters 484 UV-Detector and a Wyatt mini-dawn light scattering detector (? = 690 nm). The flow rate was 0.7 mL/min. Data were processed using a Millenium respectively ASTRA software. UV/vis spectra were recorded on a Varian Cary 3 spectrophotometer in the range 300-800 nm. TEM pictures were recorded on JEM 100 CX (Jeol) at 100 kV using copper gauze as carrier. The magnification was 66000 and 160000, respectively.

5.1.2 Chemicals

Synthesis of the ligands and polymerizations were performed under an argon atmosphere by standard Schlenk techniques or in an N_2- or Ar-mediated dry-box (MBraun, Germany) unless stated otherwise. Reagent grade diethyl ether, pentane, THF and toluene were distilled from sodium benzophenone ketyl under argon. Reagent grade triethylamine, dichloromethane, 1,2-dichloroethane, MeOH and chloroform were distilled from calcium hydride under argon. Other solvents and reagents were used as purchased. Deionized water was used throughout. Norborn-2-ene (NBE), ethynylferrocene, phenylacetylene, $RuCl_2(=CHPh)(PCy_3)_2$, CF_3SO_3Ag, CF_3COOAg, CF_3CF_2COOAg, $CF_3CF_2CF_2COOAg$, TlOEt, ?-asarone, PS-DVB-CH_2-OH (100 – 300 mesh, 1.7 mmol Ar-CH_2-OH/g, 1 % crosslinked), perfluoroglutaric anhydride, salicylaldehyde, 2-propyliodide, diethyldiallylmalonate (DEDAM), 1,7-octadiene, diallylether, *N*,*N*-diallyltrifluoroacetamide, diallyldiphenylsilane, *trans*-methyl-3-pentenoate, *t*butyl-*N*,*N*-diallylcarbamate, *cis*-1,4-diacetoxy-2-butene, ethylvinylether (EVE), 3,3-dimethyl-but-1-yne, but-3-yn-1-ol, propynoic acid methyl ester, but-2-ynedioic acid dimethyl ester, 1-octyne, 1,6-heptadiyne, ethynyl-trimethyl-silane, 1,2-diethynyl-1,1,2,2,-tetramethyl-disilane, propargylbromide, but-2-yn-1-ol were purchased from Fluka (Buchs, Switzerland). Norborn-2-ene-5-methanol was purchased form Greyhound Chromatography, UK. (R/S)-binaphthyl-2,2’-diol, 3,3’-di-tert-butyl-5,6,7,8-5’,6’,7’,8’-octahydro-[1,1’]binaphthalenyl-2,2’-diol, 3,3’-di-tert-butyl-5,6,5’,6’-tetramethyl-biphenyl-2,2’-diol, $IMesBF_4$ (IMes = 1,3-bis(2,4,6-trimethylphenyl)-imidazolin-2-ylidene) were purchased from Strem Chemicals. A ruthenium standard containing 1000 ppm of ruthenium was purchased from Alfa Aesar/Johnson Matthey (Karlsruhe, Germany). Bicyclo[2.2.1]hept-2-ene-5-yltrichlorosilane and bicyclo[2.2.1]hept-2-ene-5-yltriethoxysilane were purchased from ABCR (Darmstadt, Germany). Nucleosil 300-7 (300 Å, 7 ?m, pore volume 1.0 mL/g), LiChrospher wp300 (300 Å, 5 ?m, 80 m^2/g) and silica 60 (230-400 mesh, 40-63 ?m, 480-540 m^2/g, pore volume = 0.74 -0.84 mL/g) were purchased from Merck, Germany. 4-(Ethoxycarbonyl)-4-(1*S*, 2*R*, 5*S*)-(+)-menthoxycarbonyl-1,6-heptadiyne, dimethyldipropargylmalonate, trimethyl-(2-prop-2-ynyl-pent-4-ynyloxy)-silane were provided by Dr. Udo Anders (TU München). Methyl-phenyl-di-prop-2-ynyl-silane, 3-prop-2-ynylsulfanyl-propyne, 1,8-diethynyl-naphthalene, phenyl-di-prop-2-ynyl-amine were provided by Dr. Dongren Wang (Universität Innsbruck).

5.1.3 Synthesis according to literature

exo, exo-7-Oxanorborn-2-ene-5,6-dicarboxylic anhydride,[57] methyl-7-oxanorborn-2-ene-5-carboxylate,[203] 7-oxanorborn-2-ene-5-carboxylic acid,[204] tri(norborn-2-en-5-yl-methyloxy)methylsilane (NBE-CH$_2$O)$_3$-SiMe,[185] and 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo, endo*-dimethanonaphthalene (DMN-H$_6$)[205] were prepared according to literature procedures. RuCl$_2$(=CHPh)(SIMes)(PCy$_3$)[135,136] and RuCl$_2$(SIMes)(=CH-2-(2-PrO)-C$_6$H$_4$)[123] were purchased from Fluka (Buchs, Switzerland) or prepared according to literature. RuCl$_2$(SIMes)(=CH-2,4,5-(OMe)$_3$-C$_6$H$_2$),[138] RuCl$_2$(SIMes)(=CH-2-O*i*Pr-C$_6$H$_3$-5-NO$_2$),[137] isopropoxy-4-nitro-2-vinyl-benzene,[137] 2-ethoxy-biphenyl,[139] 2,3-difluoro-but-2-enedioic acid,[206] 3,4-difluoro-furan-2,5-dione,[206] 2-allyl-2-(2-methyl-allyl)-malonic acid diethyl ester,[207] 2,2-bis-(2-methyl-allyl)-malonic acid diethyl ester,[207] 2,4,6-trihydroxy-benzene-1,3,5-tricarbaldehyde,[208] 2-hydroxy-biphenyl-3-carbaldehyde,[139] 2-isopropoxy-biphenyl-3-carbaldehyde,[139] 2-isopropoxy-5-nitro-benzaldehyde,[137] 2-isopropoxy-3-vinyl-biphenyl,[139] 2-hydroxy-5-nitro-benzaldehyde,[137] RuCl$_2$(=CHPh)(SIMes)(Py),[209] RuI$_2$(=CHPh)(SIMes)(PCy$_3$)[144] were prepared according to literature. Compounds **A5-13** were synthesized by Tobias Zarka, experimental details are published and can be found in the supporting information there.[191] The synthesis of **D1-D6** and **D15** is described elsewhere.[149,172,174,175] The synthesis of heptadiyens: diethyldipropargylmalonate, 2,2-di-prop-2-ynyl-propane-1,3-diol, 2-prop-2-ynyl-pent-4-ynoic acid, 2-prop-2-ynyl-pent-4-yn-1-ol, 2-prop-2-ynyl-pent-4-ynoic acid ethyl ester is described in the literature.[210]

5.1.4 X-ray measurement and structure determination of C2 and C3

The data collection was performed on a Nonius Kappa CCD equipped with graphite-monochromatized Mo-K$_?$-radiation (? = 0.71073 Å) and a nominal crystal to area detector distance of 36 mm. Intensities were integrated using DENZO and scaled with SCALEPACK.[211] Several scans in ? and ? direction were made to increase the number of redundant reflections, which were averaged in the refinement cycles. This procedure replaces in a good approximation an empirical absorption correction. The structures were solved with direct methods (SHELXS86) and refined against F^2 (SHELX97).[212] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined at calculated positions with isotropic displacement parameters, except the hydrogen atoms at C(1), which were found and refined normally. For compound **C2** the fluorine atoms of the CF_3 groups and the methyl parts of the isopropyl group are 2:1 disordered. Relevant crystallographic data are summarized in part: results and discussion. Further crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication (CCDC-215 892 (**C2**) and -215 891 (**C3**)). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk)

5.1.5 ICP-OES measurements

Aqua regia (3.0 mL) was added to a sample of poly(DEDPM) (10.0 mg), the supported catalyst (10.0 mg) or to the combined effluents from which the solvent was removed. The mixture was placed inside high-pressure Teflon tubes and leaching was carried out under Microwave conditions (50, 600, and 450 *W* pulses, respectively, *t* = 32 minutes). After cooling to room temperature, the mixture was filtered and measured by ICP-OES for Ru (? = 240.272 nm, ion line). The background was measured at ? = 240.287 and 240.257 nm, respectively. Standardization was carried out with Ru standards containing 0, 5 and 10 ppm of Ru.

5.2 Catalysis

5.2.1 RCM-Experiments (Slurry Reactions, heterogeneous supports)

The following procedure is representative for all experiments. DEDAM (20 mg, 0.08 mmol) was dissolved in the corresponding solvent (e. g. 1,2-dichloroethane, 2 mL) and the supported catalyst (40 mg) was added. The reaction mixture was heated to 45°C for 2 hours. After removal of the catalyst by filtration, the yield was determined by GC-MS or ^{1}H-NMR in $CDCl_3$.

5.2.2 RCM-Experiments (Flow-Through Reactions, monoliths)

The following procedure is representative for all experiments. DEDAM (3.00 g, 12.48 mmol, 10 wt-%) was dissolved in the corresponding solvent (e. g. 1,2-dichloroethane) and this solution was pumped through a cartridge filled with the supported catalyst (either monolith- or silica-based) heated to 45°C at a flow rate of 0.1 mL/min unless stated otherwise. The effluent was collected in 0.5 mL portions and the yield was determined by GC-MS or ^{1}H-NMR in $CDCl_3$.

5.2.3 Polymerizations in solution

All polymer reactions were performed under Ar or N_2. A solution of $Ru(CF_3CO_2)_2$(=CH-(2-(2-PrO-C_6H_4))(SIMes) (**A1**, 1 equiv., 3.13 mg, 0.004 mmol) in 0.3 mL of CH_2Cl_2 was added to a solution of 3.0 mL of DEDPM (74 equiv., 70 mg, 0.30 mmol) or 4-(ethoxycarbonyl)-4-(1*S*, 2*R*, 5*S*)-(+)-menthoxycarbonyl-1,6-heptadiyne (70 mg, 0.202 mmol) in 5 mL of CH_2Cl_2. The mixture was stirred for 2 hours, then 0.5 mL of ethylvinyl ether was added and the mixture was stirred for another 30 minutes. The solvent was removed *in vacuo*, then 10 mL of MeOH were added. After sonification, stirring was continued for another 30 minutes. The product was centrifuged, dried *in vacuo* to give a lilac-gold powder (63.7 mg, 91 %).

5.2.4 Poly(2-oxazoline)-bound catalysts, organic solvent

Under Box conditions, the poly(2-oxazoline)-bound catalyst (**A3** and **A4**, respectively, 25 mg, 0.004 mmol ruthenium) was added to 3 mL of CH_2Cl_2 followed by DEDPM (74 equiv., 70 mg, 0.296 mmol) or 4-(ethoxycarbonyl)-4-(1*S*, 2*R*, 5*S*)-(+)-menthoxycarbonyl-1,6-heptadiyne (70 mg, 0.202 mmol) in 0.3 mL of CH_2Cl_2. The polymerization mixture was stirred for 2 hours, then 0.5 mL of ethylvinyl ether was added and the mixture was stirred for another 30 minutes. The solvent was removed *in vacuo*, then 10 mL MeOH was added to remove the poly(2-oxazoline)-bound catalyst as well as unreacted monomer, and after sonification the mixture was stirred for another 30 minutes. The product was centrifuged, dried *in vacuo* to give a lilac-gold powder (3.5 mg, 5 %).

5.2.5 Poly(2-oxazoline)-bound catalysts, micellar conditions

Under Schlenk conditions the poly(2-oxazoline)-bound catalyst (**A3** and **A4**, respectively, 25 mg, 0.004 mmol ruthenium) was added to 3 mL of degassed water followed by DEDPM (74 equiv., 70 mg, 0.296 mmol) or 4-(ethoxycarbonyl)-4-(1*S*, 2*R*, 5*S*)-(+)-menthoxycarbonyl-1,6-heptadiyne (70 mg, 0.202 mmol). One drop of toluene (0.01 wt %) was added. The mixture was stirred for 30 min, 0.5 mL of ethyl vinyl ether was added and the mixture was stirred for another 30 minutes. The latex was added to 10 mL of MeOH to remove the poly(2-oxazoline)-bound catalyst as well as unreacted monomer and stirring was continued for another 30 minutes. The product was centrifuged, dried *in vacuo* to give a lilac-gold powder (57.4 mg, 82 %).

5.2.6 Livingness

All manipulations were carried out under box conditions. **M2b** (48.2 mg for DP=5, 24.1 mg for DP=10, 8.0 mg for DP=30, 4.8 mg for DP=50, 3.4 mg for DP=70, 2.4 mg for DP=100) was dissolved in 3 mL of methylene chloride. A solution of DEDPM (70 mg, 0.296 mmol) in 0.5 mL of methylene chloride was added and the mixture was stirred for 4 h. EVE (0.5 mL) was added and stirring was continued for 30 minutes. Finally, the solvent was removed *in vacuo*, 10 mL of MeOH was added and stirring was continued for another 30 minutes. The product was centrifuged and dried *in vacuo*, yielding a lilac-gold powder (54.6-64.6 mg, 78-

92%). For the determination of the class of livingness, a sample with a *DP* of 50 was prepared as described above. A small aliquot was terminated with EVE and precipitated from methanol and subjected to GPC. The rest was stirred for 48 hours, and then DEDPM was added to give a theoretical degree of polymerization of 100. After termination with EVE and precipitation from methanol, the sample was subjected to GPC. No bimodal GPC traces or band broadening, indicative of termination reactions, were observed. $M_n(theor)$=23835. M_w=43700, M_n=25400, PDI=1.72.

5.2.7 RCM-, Ring-Opening-Cross Metathesis and Enyne-Metathesis Experiments (Slurry Reactions, homogeneous catalysts)

The following procedure is representative for all experiments. DEDAM (520 mg, 2.16 mmol) was dissolved in 2 mL CH_2Cl_2 and the homogeneous catalyst (0.01 – 0.10 mol-%) was added. The reaction mixture was heated to 45 °C for 2 hours. After removal of the catalyst by filtration, the yield was determined by GC-MS or ^{1}H-NMR in $CDCl_3$.

5.3 Synthesis and characterization

5.3.1 Synthesis and Derivatisation of $RuCl_2(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)(SIMes)$ (R1)

The monolith was made within the confines of a PEEK column using norborn-2-ene (20 wt-%) and methyl-tris(norborn-2-ene-5-yl-methoxy)silane ($(NBE\text{-}CH_2O)_3SiCH_3$) (20 wt-%) according to published procedures.[165] The monolith was kept in an ice-water bath for 30 minutes, then at room temperature for the same time before flushing it with freshly distilled toluene for 20 minutes at a flow rate of 0.2 mL/min. Argon was passed through the monolith for 20 minutes to elute the solvent. Hexafluoroglutaric anhydride (0.4 mL, 0.66 g, 2.98 mmol) was added dropwise to a solution of norborn-5-ene-2-yl-methanol (0.3 mL, 0.31 g, 2.48 mmol) in 6 mL of freshly distilled methylene chloride. The mixture was stirred for one hour in a Schlenk tube under argon at room temperature. 2 mL of this solution was introduced into the monolith, which was sealed and kept at 40 ^{o}C overnight. The following day, the monolith was flushed with ethyl vinylether (40 vol-% in THF), then with water, for 30 minutes. KOH

(25 mL, 4.6 mM) was passed through the monolith at a flow rate of 0.1 mL/min, followed by water until reaching neutral washings. Aqueous silver nitrate (3 mL, 21.7 mM) was introduced into the monolith using syringe technique, then the support was flushed until the effluent was free of silver as checked by aqueous sodium iodide solution. Then the monolith was flushed with dry THF. $RuCl_2(=CH-(2-2-Pr-O-)C_6H_4)(SIMes)$ (48 mg, 76.6 mmol) was dissolved in 1.5 mL of freshly distilled THF, the solution was introduced into the monolith, which was kept sealed at room temperature for 1 hour. Afterwards, silver trifluoroacetate (17.5 mg, 79.2 mmol) was dissolved in 1.5 mL of freshly distilled THF and the solution was introduced into the monolith, which was again kept sealed at room temperature for 1 hour. Finally, the monolith was flushed with freshly distilled THF until the effluent was colourless. Catalyst loading: 2.54 mg of $RuCl_2(=CH-(2-2-Pr-O-)C_6H_4)(SIMes)$/g.

5.3.2 $Ru(CF_3SO_3)_2(=CH-2-(2-PrO)-C_6H_4)SIMes)$ (C1)

Under Box conditions, $RuCl_2(=CH-2-(2-PrO)-C_6H_4)(SIMes)$ (200 mg, 0.32 mmol) was dissolved in 10 mL of THF and a solution of 2 equiv of CF_3SO_3Ag (164 mg, 0.64 mmol) in 2 mL of THF was slowly added to the stirred solution. Stirring was continued for 3 hours. A color change from green to red and the formation of a precipitate were observed. The precipitate was filtered off and the solution evaporated to dryness. The solid was re-dissolved in CH_2Cl_2 and flashed over a short pad of silica. Drying *in vacuo* provided a green powder (152 mg, 56 %, 0.18 mmol). FT-IR (ATR-mode): 2962 (br), 2910 (br), 1587 (s), 1481 (s), 1447 (s), 1331 (s), 1259 (vs), 1233 (w), 1190 (vs), 1088 (vs), 1015 (vs), 983 (s), 932 (w), 864 (w), 796 (vs), 754 (w) and 696 (w). ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C) ? 18.49 (s, 1H, Ru=CHAr), 7.51 (dd, 1H, aromatic CH), 7.10-7.19 (5H, aromatic CH), 6.97 (dd, 1H, aromatic CH), 6.78 (d, 1H, aromatic CH), 4.72 (septet, 1H, $(CH_3)_2C\mathit{H}OAr$), 4.16 (s, 4H, $N(CH_2)_2N$), 2.38 (m, 12H, mesityl o-CH_3), 2.17 (s, 6H, mesityl p-CH_3), 1.11 (d, 6H, $(C\mathit{H}_3)_2CHOAr$). ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C) ? 332.4, 203.9, 154.0, 145.5, 139.9, 138.6, 136.8, 135.1, 132.5, 130.8, 129.1, 122.1, 118.6, 114.4, 112.2, 52.1, 49.6, 24.8, 20.4, 19.4, 17.8, 17.1. Anal. Calcd for $C_{33}H_{38}F_6N_2O_7RuS_2$ (M_r = 853.85 g/mol): C; 46.42, H; 4.49, N; 3.28. Found: C; 40.07, H; 4.45, N; 2.64.

5.3.3 $RuCl(CF_3SO_3)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)(SIMes)$ (C2)

Under Box conditions $RuCl_2(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)(SIMes)$ (200 mg, 0.32 mmol) was dissolved in 10 mL of THF and a solution of 1 equiv of CF_3SO_3Ag (82 mg, 0.32 mmol) in 2 mL of THF was slowly added to the stirred solution. Stirring was continued for 90 minutes. A color change from green to green-yellow and the formation of a precipitate was observed. The precipitate was filtered off and the solution evaporated to dryness. The solid was re-dissolved in CH_2Cl_2 and flashed over a short pad of silica. Drying *in vacuo* provided a green powder (123 mg, 0.17 mmol, 52 %). Green crystals suitable for X-Ray analysis were obtained by layering pentane over a concentrated solution of CH_2Cl_2 at –36°C. FT-IR (ATR-mode): 2963 (br), 2915 (br), 1584 (s), 1479 (s), 1444 (s), 1389 (w), 1325 (w), 1261 (s), 1229 (w), 1190 (vs), 1100 (s), 1003 (vs), 934 (w), 848 (w), 801 (s), 749 (s) and 697 (w). ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C) ? 17.49 (s, 1H, Ru=CHAr), 7.46 (dd, 1H, aromatic CH), 7.18-6.95 (5H, aromatic CH), 6.86 (dd, 1H, aromatic CH), 6.73 (d, 1H, aromatic CH), 4.74 (septet, 1H, $(CH_3)_2C\mathit{H}OAr$), 4.12 (s, 4H, $N(CH_2)_2N$), 2.55-2.15 (m, 18H, mesityl CH_3), 1.25 (d, 3H, $(C\mathit{H}_3)_2CHOAr$), 1.04 (d, 3H, $(C\mathit{H}_3)_2CHOAr$). ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C) ? 313.8, 207.1, 152.1, 144.9, 139.4, 139.1, 138.8, 138.0, 136.8, 135.8, 131.6, 130.3, 128.8, 128.4, 121.7, 119.1, 114.9, 111.9, 74.7, 51.4, 49.4, 24.6, 20.2, 19.2, 19.0, 17.8, 17.2, 16.8. Anal. Calcd for $C_{32}H_{38}ClF_3N_2O_4RuS$ (M_r = 740.24 g/mol): C; 51.92, H; 5.17, N; 3.78. Found: C; 47.20, H; 5.83, N; 2.86.

5.3.4 $Ru(CF_3CO_2)_2(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)(SIMes)$ (C3)

Under dry box conditions, $RuCl_2(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)(SIMes)$ (200 mg, 0.319 mmol) was dissolved in 10 mL of THF and a solution of 2 equiv of CF_3CO_2Ag (141 mg, 0.64 mmol) in 2 mL of THF was slowly added to the stirred solution. Stirring was continued for 20 minutes. A color change from green to lilac and the formation of a precipitate were observed. The precipitate was filtered off and the solution evaporated to dryness. It was re-dissolved in 1 mL CH_2Cl_2, flashed over 5 cm silica and evaporated to dryness giving a lilac powder (177 mg, 0.23 mmol, 71 %). Lilac crystals suitable for X-Ray analysis were obtained by layering pentane over a diluted solution of Et_2O at –36 °C. FT-IR (ATR-mode): 2982 (br), 2925 (br), 1698 (s), 1609 (w), 1593 (w), 1577 (w), 1478 (w), 1451 (w), 1393 (s), 1260 (s), 1180 (vs), 1141 (vs), 1033 (w), 937 (w), 877 (s), 844 (s), 812 (w), 780 (w), 748 (s) and 722 (s). ^1H NMR

(300.13 MHz, CDCl$_3$, 25 °C) ? 17.38 (s, 1H, Ru=CHAr), 7.28 (dd, 1H, aromatic CH), 7.08 (s, 4H, mesityl aromatic CH), 7.00 (dd, 1H, aromatic CH), 6.86 (dd, 1H, aromatic CH), 6.56 (d, 1H, aromatic CH), 4.55 (septet, 1H, (CH$_3$)$_2$C*H*OAr), 4.05 (s, 4H, N(CH$_2$)$_2$N), 2.37 (s, 6H, mesityl p-CH$_3$), 2.20 (s, 12H, mesityl o-CH$_3$), 0.88 (d, 6H, (C*H*$_3$)$_2$CHOAr). ^{13}C NMR (75.47 MHz, CDCl$_3$, 25 °C) ?314.7, 209.1, 159.0, 152.1, 142.4, 138.4, 137.9, 133.4, 129.2, 128.7, 122.6, 121.8, 111.2, 109.9, 73.2, 50.3, 24.6, 19.1, 16.8. Anal. Calcd for $C_{35}H_{38}F_6N_2O_5Ru$ (M_r = 781.75 g/mol): C; 53.77, H; 4.90, N; 3.58. Found: C; 53.63, H; 4.90, N; 3.63.

5.3.5 Polymeric supports C4 und C5

Heterogenization on a PS-DVB support, generation of Ru(*polymer*-CH$_2$-O-CO-CF$_2$-CF$_2$-CF$_2$-COO)(CF$_3$CO$_2$)(=CH-*o*-*i*Pr-O-C$_6$H$_4$)(SIMes) (C4) and RuCl(*polymer*-CH$_2$-O-CO-CF$_2$-CF$_2$-CF$_2$-COO)(=CH-*o*-*i*Pr-O-C$_6$H$_4$)(SIMes) (C5): PS-DVB-CH$_2$-OH (1.00 g) was suspended in 20 mL of dry THF and 1 equiv of perfluoroglutaric anhydride (377 mg, 1.70 mmol) was added. Stirring was continued for 2 h, the product was filtered, and washed 3 times with THF. It was dried in high vacuum giving a white solid (1.33 g). FT-IR (ATR-mode): 3025 (br), 2920 (br), 2442 (br), 1772 (vs), 1600 (br), 1489 (w), 1448 (w), 1375 (w), 1312 (s), 1245 (s), 1175 (vs), 1145 (vs), 1044 (s), 915 (w), 867 (w), 823 (w), 755 (s) and 697 (vs). The solid was re-suspended in 10 mL of THF and excess NaOH (140 mg in 30 mL water) was added. The mixture was stirred for 2 h, the product was filtered and washed 3 times with water. The precipitate was suspended in 20 mL of water and 1.2 equiv of AgNO$_3$ (350 mg, 2.1 mmol) in 10 mL water was added. Stirring was continued for 2 h, the product filtered and washed 3 times with water, Et$_2$O and pentane. Drying *in vacuo* gave 0.85 g of a white solid. FT-IR (ATR-mode): 3056 (br), 3023 (br), 2918 (br), 2854 (br), 2336 (br), 1808 (w), 1596 (w), 1490 (w), 1446 (w), 1364 (w), 1285 (w), 1216 (s), 1067 (w), 1027 (w), 896 (w), 840 (w), 812 (w), 754 (s) and 694 (vs). The solid was re-suspended in 25 mL of THF and RuCl$_2$(=CH-2-(2-PrO)-C$_6$H$_4$)(SIMes) (99.8 mg, 0.159 mmol) was added. Stirring was continued for 90 min. RuCl(*polymer*-CH$_2$-O-CO-CF$_2$-CF$_2$-CF$_2$-COO)(=CH-*o*-*i*Pr-O-C$_6$H$_4$)(SIMes) (**C5**) was filtered off, washed with THF, dried *in vacuo* to yield an off-white powder. FT-IR (ATR-mode): 3057 (w), 3024 (w), 2917 (br), 2848 (w), 1600 (w), 1492 (w), 1451 (w), 1420 (w), 1180 (br), 1154 (w), 1027 (w), 1014 (w), 906 (w), 841 (w), 751 (s) and 697 (vs). 1 eq of CF$_3$COOAg (35.2 mg, 0.159 mmol) was dissolved in 2 mL of THF and the solution was added to **C5**, dissolved in 10 mL of THF, and the mixture was stirred for 90 min. Extensive washing with THF and drying *in vacuo* gave 0.7 g of Ru(*polymer*-CH_2-O-CO-CF_2-CF_2-CF_2-COO)(CF_3CO_2)(=CH-*o*-*i*Pr-O-C_6H_4)(SIMes) (**C4**) as a lilac powder. Ru-content 0.18 mmol/g, corresponding to 160 mg catalyst/g (16 % catalyst loading). FT-IR (ATR-mode): 3060 (w), 3023 (w), 2919 (br), 2852 (w), 2378 (w), 1942 (w), 1874 (w), 1805 (w), 1595 (w), 1488 (w), 1447 (w), 1365 (br), 1185 (br), 1019 (w), 817 (w), 754 (s) and 695 (vs).

5.3.6 2-(2-Propoxy)-styrene (C6)

Salicylaldehyde (10.3 g, 84 mmol), NBu_4Br (25.1 g, 78 mmol) and *i*-PrI (20 mL, 0.2 mol) were dissolved in 300 mL of CH_2Cl_2. NaOH (3.5 g, 88 mmol) dissolved in 150 mL of water were slowly added to the stirred solution. After stirring for 2 days, the organic phase was separated and the aqueous phase was washed 3 times with 50 mL of CH_2Cl_2. The combined organic phases were dried *in vacuo*, re-dissolved in ethyl acetate and filtered. The filtrate was dried over Na_2SO_4 and evaporated to dryness giving a yellow oil (5.7 g). $MePPh_3Br$ (13 g, 34.7 mmol) was dried in a Schlenk tube and put under argon. 50 mL of dry THF was added, followed by n-BuLi (2 n in pentane, 17.4 mL, 34.7 mmol) at 0 °C. It was stirred for 30 minutes at 0 °C and for another 30 minutes at room temperature. The aldehyde (5.7 g, 34.7 mmol) was slowly added at 0°C and stirring was continued for 12 h. Water (5 mL) was added to the yellow solution, which was then dried *in vacuo*. The product was extracted 3 times with 25 mL of Et_2O, dried over Na_2SO_4 and evaporated to dryness. Column chromatography over silica using ethyl acetate/pentane (2:98) as eluent provided the product in the first fraction (R_f = 0.5). It was dried over Na_2SO_4 and evaporated to dryness to give the product as a clear liquid in 23 % yield (3.2 g, 20 mmol). FT-IR (ATR-mode): 2978 (s), 2933 (br), 1625 (w), 1597 (w), 1484 (s), 1453 (s), 1383 (w), 1290 (w), 1240 (vs), 1118 (s), 997 (w), 955 (w), 906 (w), and 751 (w). ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C) ? 7.37 (d, 1H, Ar), 7.07 (m, 1H, Ar), 6.97 (dd, 1H, CH), 6.76 (m, 2H, Ar), 5.63 (dd, 1H, trans-CHC**H**$_2$), 5.12 (dd, 1H, cis-CHC**H**$_2$), 4.40 (sept, 1H, C**H**(CH_3)$_2$), 1.21 (d, 6H, C**H**(CH_3)$_2$). ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C) ? 155.0, 131.9, 128.6, 127.7, 126.4, 120.5, 114.0, 70.6, 22.1. GC-MS Calcd. for $C_{11}H_{14}O$: *m/z* = 162.1, found: 162.1.

5.3.7 Ru(CF$_3$CF$_2$CO$_2$)$_2$(=CH-2-(2-PrO)-C$_6$H$_4$)(SIMes) (M1c)

RuCl$_2$(=CH-2-(2-PrO)-C$_6$H$_4$)(SIMes) (300 mg, 0.479 mmol) was dissolved in 10 mL of THF and a solution of 2 equiv. of CF$_3$CF$_2$CO$_2$Ag (259.4 mg, 0.958 mmol) in 2 mL of THF was slowly added to the stirred solution. Stirring was continued for 30 minutes. The color changed from green to lilac and the formation of a precipitate was observed. The precipitate was centrifuged, the solution was filtered through a 0.2 ?m Teflon filter and evaporated to dryness. The following manipulations were done under air. The solid was re-dissolved in CH$_2$Cl$_2$ and flashed over a short pad of silica. Drying *in vacuo* provided a lilac powder (317.4 mg, 0.36 mmol, 75 %). FT-IR (ATR-mode): 2978 (br), 2922 (br), 2366 (w), 2108 (w), 1699 (s), 1586 (w), 1481 (m), 1433 (m), 1375 (m), 1311 (s), 1267 (s), 1210 (vs), 1154 (vs), 1021 (s), 938 (m), 847 (m), 809 (m) and 726 (m). ^{1}H NMR (CDCl$_3$) ? 17.59 (s, 1H, Ru=CHAr), 7.55 (dd, 1H, aromatic CH), 7.12-7.34 (5H, aromatic CH), 6.94 (dd, 1H, aromatic CH), 6.63 (d, 1H, aromatic CH), 4.57 (septet, 1H, (CH$_3$)$_2$C*H*OAr), 4.15 (s, 4H, N(CH$_2$)$_2$N), 2.47 (s, 12H, mesityl o-CH$_3$), 2.30 (s, 6H, mesityl p-CH$_3$), 1.10 (d, 6H, (C*H*$_3$)$_2$CHOAr). ^{13}C NMR (CDCl$_3$) ? 316.3, 209.2, 159.4, 152.2, 142.2, 138.4, 137.8, 133.4, 129.3, 128.7, 122.9, 121.8, 107.9, 73.4, 50.3, 20.1, 19.0, 16.8. Anal. calcd. for C$_{37}$H$_{38}$F$_{10}$N$_2$O$_5$Ru (M_r = 881.76 g/mol): C; 50.40, H; 4.34, N; 3.18. Found: C; 50.49, H; 4.28, N; 3.07. MS (CI) calcd. for C$_{37}$H$_{38}$F$_{10}$N$_2$O$_5$Ru: 882.2; found *m/z* = 883.2 (M+H)$^+$.

5.3.8 Ru(CF$_3$CF$_2$CF$_2$CO$_2$)$_2$(=CH-2-(2-PrO)-C$_6$H$_4$)(SIMes) (M1d)

RuCl$_2$(=CH-2-(2-PrO)-C$_6$H$_4$)(SIMes) (300 mg, 0.479 mmol) was dissolved in 10 mL of THF and a solution of 2 equiv. of CF$_3$CF$_2$CF$_2$CO$_2$Ag (307.4 mg, 0.958 mmol) in 2 mL of THF was slowly added to the stirred solution. Stirring was continued for 30 minutes. The color changed from green to lilac and the formation of a precipitate was observed. The precipitate was centrifuged, the solution was filtered through a 0.2 ?m Teflon filter and evaporated to dryness. The following manipulations were done under air. The solid was re-dissolved in CH$_2$Cl$_2$ and flashed over a short pad of silica. Drying *in vacuo* provided a lilac powder (343.3 mg, 0.35 mmol, 73 %). FT-IR (ATR-mode): 2978 (br), 2922 (br), 2366 (w), 2330 (w), 2114 (w), 1698 (s), 1589 (w), 1481 (m), 1446 (m), 1378 (m), 1320 (s), 1265 (s), 1208 (vs), 1153 (s), 1112 (s), 1084 (s), 1033 (m), 959 (m), 928 (s), 848 (m), 802 (m) and 719 (m). ^{1}H NMR (CDCl$_3$) ? 17.51 (s, 1H, Ru=CHAr), 7.44 (dd, 1H, aromatic CH), 7.03-7.26 (5H, aromatic

CH), 6.88 (dd, 1H, aromatic CH), 6.53 (d, 1H, aromatic CH), 4.46 (septet, 1H, $(CH_3)_2C\mathit{H}OAr$), 4.05 (s, 4H, $N(CH_2)_2N$), 2.37 (s, 12H, mesityl o-CH_3), 2.20 (s, 6H, mesityl p-CH_3), 0.91 (d, 6H, $(C\mathit{H}_3)_2CHOAr$). ^{13}C NMR ($CDCl_3$) ? 326.3, 219.0, 168.9, 162.0, 151.9, 148.2, 147.6, 139.0, 137.4, 132.7, 131.6, 119.7, 76.7, 60.1, 34.3, 29.9, 28.8, 26.5. Anal. calcd. for $C_{39}H_{38}F_{14}N_2O_5Ru$ (M_r = 981.78 g/mol): C; 47.71, H; 3.90, N; 2.85. Found: C; 47.51, H; 3.90, N; 2.71. MS (CI) calcd. for $C_{39}H_{38}F_{14}N_2O_5Ru$: 982.2; found *m/z* = 983.4 $(M+H)^+$.

5.3.9 $Ru(CF_3CO_2)_2(=CH\text{-}2,4,5\text{-}(OMe)_3\text{-}C_6H_2)(SIMes)$ (M2b)

$RuCl_2(=CH\text{-}2,4,5\text{-}(OMe)_3C_6H_2)(SIMes)$ (200 mg, 0.304 mmol) was dissolved in 10 mL of THF and a solution of CF_3CO_2Ag (2 equiv., 134 mg, 0.608 mmol) dissolved in 2 mL of THF was slowly added. Stirring was continued for 20 minutes. The color changed from green to yellow and the formation of a precipitate was observed. The precipitate was centrifuged and the solution evaporated to dryness. It was re-dissolved in 1 mL of CH_2Cl_2, flashed a short bed of silica and evaporated to dryness giving a yellow powder (150 mg, 0.184 mmol, 61 %). FT-IR (ATR-mode): 2961 (br), 2923 (br), 1679 (s), 1665 (w), 1502 (w), 1457 (w), 1354 (w), 1287 (w), 1260 (w), 1189 (vs), 1136 (vs), 1033 (w), 1007 (w), 885 (m), 840 (m) and 753 (s). ^{1}H-NMR ($CDCl_3$) ? 17.36 (s, 1H, Ru=CHAr), 7.72 (s, 1H), 7.07 (4H), 6.71 (s, 1H), 6.39 (s, 1H), 4.10 (s, 4H), 3.90 (s, 3H), 3.87 (s, 3H), 3.64 (s, 3H), 2.45 (s, 12H), 2.39 (s, 6H, mesityl o-CH_3). ^{13}C-NMR ($CDCl_3$) ? 303.0, 217.3, 177.7, 151.2, 144.6, 139.3, 138.8, 138.2, 130.0, 129.9, 107.2, 96.6, 57.1, 52.1, 34.5, 21.4, 18.2. MS (CI): *m/z* = calcd. 814.2, found 813.7 $[M]^+$.

5.3.10 $Ru(CF_3CF_2CO_2)_2(=CH\text{-}2,4,5\text{-}(OMe)_3\text{-}C_6H_2)(SIMes)$ (M2c)

$RuCl_2(=CH\text{-}2,4,5\text{-}(OMe)_3\text{-}C_6H_2)(SIMes)$ (140 mg, 0.213 mmol) was dissolved in 10 mL of THF and a solution of 2 equiv. of $CF_3CF_2CO_2Ag$ (115.1 mg, 0.425 mmol) in 2 mL of THF was slowly added to the stirred solution. Stirring was continued for 30 minutes. The color changed from green to yellow-green and the formation of a precipitate was observed. The precipitate was centrifuged, the solution was filtered through a 0.2 ?m Teflon filter and evaporated to dryness. The following manipulations were done under air. The solid was re-dissolved in ethyl acetate and flashed over a short pad of silica. Drying *in vacuo* provided a yellow-green powder (130.7 mg, 0.143 mmol, 67 %). FT-IR (ATR-mode): 2924 (br), 2856 (br), 2364 (w), 1955 (w), 1670 (m), 1599 (m), 1483 (m), 1458 (m), 1437 (m), 1409 (m), 1320 (m), 1255 (s), 1205 (vs), 1151 (s), 1024 (m), 915 (w), 852 (w), 813 (m) and 751 (m). ^{1}H NMR ($CDCl_3$) ? 17.19 (s, 1H, Ru=CHAr), 6.74-7.26 (4H), 6.42 (s, 1H), 6.26 (s, 1H), 4.02 (s, 4H), 3.90 (s, 3H), 3.75 (s, 3H), 3.49 (s, 3H), 2.32 (s, 6H), 2.22 (s, 12H, mesityl o-CH_3). ^{13}C NMR ($CDCl_3$) ? 311.1, 207.6, 187.1, 162.1, 150.1, 143.5, 137.9, 136.9, 135.9, 134.9, 128.7, 108.0, 104.6, 95.0, 58.2, 55.2, 50.7, 29.8, 20.1, 16.7. Anal. calcd. for $C_{37}H_{38}F_{10}N_2O_7Ru$ (M_r = 913.76 g/mol): C; 48.63, H; 4.19, N; 3.07. Found: C; 48.37, H; 4.42, N; 3.45.

5.3.11 $Ru(CF_3CF_2CF_2CO_2)_2$(=CH-2,4,5-$(OMe)_3$-C_6H_2)(SIMes) (M2d)

$RuCl_2$(=CH-2,4,5-$(OMe)_3$-C_6H_2)(SIMes) (140 mg, 0.213 mmol) was dissolved in 10 mL of THF and a solution of 2 equiv. of $CF_3CF_2CF_2CO_2Ag$ (136.4 mg, 0.425 mmol) in 2 mL of THF was slowly added to the stirred solution. Stirring was continued for 30 minutes. The color changed from green to yellow-green and the formation of a precipitate was observed. The precipitate was centrifuged, the solution was filtered through a 0.2 ?m Teflon filter and evaporated to dryness. The following manipulations were done under air. The solid was re-dissolved in ethyl acetate and flashed over a short pad of silica. Drying *in vacuo* provided a yellow-green powder (136.0 mg, 0.134 mmol, 63 %). FT-IR (ATR-mode): 2922 (br), 2361 (w), 1671 (m), 1599 (m), 1458 (m), 1407 (m), 1331 (m), 1266 (s), 1205 (vs), 1116 (s), 1079 (m), 1033 (m), 1014 (m), 964 (m), 928 (m), 852 (m) and 811 (w). ^{1}H NMR ($CDCl_3$,) ? 17.14 (s, 1H, Ru=CHAr), 6.78-7.26 (4H), 6.40 (s, 1H), 6.26 (s, 1H), 4.02 (s, 4H), 3.90 (s, 3H), 3.76 (s, 3H), 3.50 (s, 3H), 2.34 (s, 6H), 2.22 (s, 12H, mesityl o-CH_3). ^{13}C NMR ($CDCl_3$) ? 311.6, 208.0, 161.8, 143.4, 137.9, 137.0, 136.0, 135.0, 128.3, 108.0, 104.5, 95.0, 58.2, 55.2, 50.7, 28.2, 20.1, 16.7. Anal. calcd. for $C_{39}H_{38}F_{14}N_2O_7Ru$ (M_r = 1013.78 g/mol): C; 46.21, H; 3.78, N; 2.76. Found: C; 45.91, H; 4.12, N; 2.55.

5.3.12 $RuCl_2$(=CH-2-(2-PrO-C_6H_4)(IMes) (M3a)

Under Schlenk conditions, $RuCl_2$(=CHPh)(IMes)PCy_3 (1.03 equiv., 175 mg, 0.207 mmol) was dissolved in 10 mL of CH_2Cl_2 and CuCl (1 equiv., 19.9 mg, 0.201 mmol) as well as 2-(2-propoxy)styrene (0.97 equiv., 31.7 mg, 0.195 mmol) were added. The mixture was stirred for 1 hour at 45°C. The color changed from red to green. The solvent was removed *in vacuo* and the residue was purified under ambient conditions by column chromatography using

CH_2Cl_2:pentane =1:2 as eluent. After removal of the first fraction, the product was extracted with CH_2Cl_2. Drying over Na_2SO_4 and evaporation of the solvents *in vacuo* gave the product as a green powder (77 %, 100 mg, 0.16 mmol). FT-IR (ATR-mode): 2923 (br), 2862 (br), 1725 (m), 1584 (m), 1450 (s), 1383 (s), 1308 (vs), 1253 (s), 1224 (m), 1150 (m), 1103 (vs), 1031 (s), 971 (m), 930 (vs), 847 (s), 799 (m), 744 (m) and 696 (w). ^{1}H-NMR ($CDCl_3$) ? 16.71 (s, 1H, Ru=CHAr), 7.48 (dd, 1H, aromatic CH), 7.10-7.19 (5H, aromatic CH), 7.00 (d, 1H, aromatic CH), 6.85 (m, 1H, aromatic CH), 4.91 (septet, 1H, $(CH_3)_2C\mathit{H}OAr$), 4.23 (d, 2H, $N(CH_2)_2N$), 2.45 (s, 6H, mesityl p-CH_3), 2.27 (s, 12H, mesityl o-CH_3), 1.35 (d, 6H, $(C\mathit{H}_3)_2CHOAr$). ^{13}C-NMR ($CDCl_3$) ? 293.3, 175.8, 167.8, 152.4, 145.5, 139.5, 138.1, 135.9, 130.9, 129.0, 128.8, 124.7, 122.4, 112.9, 75.1, 68.1, 38.7, 30.3, 30.1, 28.9, 27.8, 23.7, 23.0, 21.1, 19.1, 14.0, 11.0. MS (FAB) calcd. for $C_{31}H_{36}Cl_2N_2ORu$: 624.12; found *m/z* = 623.3 ($M^{\cdot+}$-H).

5.3.13 $Ru(CF_3CO_2)_2(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)(IMes)$ (M3b)

Under Box conditions, $RuCl_2(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)(IMes)$ (58.8 mg, 0.094 mmol) was dissolved in 10 mL of THF and a solution of 2 equiv of CF_3CO_2Ag (41.6 mg, 0.19 mmol) in 2 mL of THF was slowly added to the stirred solution. Stirring was continued for 20 minutes. The color changed from green to lilac and the formation of a precipitate was observed. The precipitate was filtered off and the solution evaporated to dryness. The solid was re-dissolved in CH_2Cl_2 and flashed over a short pad of silica. Removal of the solvent *in vacuo* provided a lilac powder (55.4 mg, 75 %, 0.071 mmol). FT-IR (ATR-mode): 2925 (br), 2863 (br), 1702 (s), 1648 (s), 1589 (w), 1479 (w), 1390 (w), 1326 (w), 1295 (w), 1266 (w), 1183 (vs), 1137 (vs), 1021 (w), 940 (w), 841 (m), 807 (m), 786 (w), 749 (w) and 718 (s). ^{1}H-NMR ($CDCl_3$) ? 17.59 (s, 1H, Ru=CHAr), 7.31 (dd, 1H, aromatic CH), 7.05-7.19 (5H, aromatic CH), 6.94 (dd, 1H, aromatic CH), 6.60 (d, 1H, aromatic CH), 4.55 (septet, 1H, $(CH_3)_2C\mathit{H}OAr$), 3.70 (s, 2H, $N(CH_2)_2N$), 2.42 (s, 6H, mesityl p-CH_3), 2.00 (m, 12H, mesityl o-CH_3), 1.11 (d, 6H, $(C\mathit{H}_3)_2CHOAr$). ^{13}C-NMR ($CDCl_3$) ? 312.5, 174.3, 160.8, 153.6, 143.5, 140.3, 137.6, 134.6, 130.9, 129.9, 129.4, 128.8, 124.6, 122.7, 115.9, 112.0, 111.3, 74.6, 68.2, 68.0,. 38.7, 30.4, 28.9, 23.8, 23.0, 21.2, 20.1, 17.5, 14.0, 10.9. MS (FAB) calcd. for $C_{35}H_{36}F_6N_2O_5Ru$: 780.16, found *m/z* = 690.3 [$M^{+\cdot}$+Na-CF_3COO].

5.3.14 $Ru(CF_3CO_2)_2(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_3\text{-}5\text{-}NO_2)(SIMes)$ (M4b)

$RuCl_2(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_3\text{-}5\text{-}NO_2)(SIMes)$ (144 mg, 0.214 mmol) was dissolved in 10 mL of THF and a solution of 2 equiv. of CF_3CO_2Ag (94.8 mg, 0.429 mmol) in 2 mL of THF was slowly added to the stirred solution. Stirring was continued for 30 minutes. The color changed from green to brown and the formation of a precipitate was observed. The precipitate was centrifuged, the solution was filtered through a 0.2 ?m Teflon filter and evaporated to dryness. The following manipulations were done under air. The solid was re-dissolved in ethyl acetate and flashed over a short pad of silica. Drying *in vacuo* provided a brown powder (120 mg, 0.145 mmol, 68 %). FT-IR (ATR-mode): 2928 (br), 2855 (br), 2362 (w), 1959 (br), 1680 (m), 1482 (m), 1437 (m), 1336 (m), 1263 (s), 1189 (vs), 1138 (s), 1021 (m), 954 (m), 844 (m), 797 (m) and 723 (w). ^1H NMR ($CDCl_3$) ? 17.28 (s, 1H, Ru=CHAr), 8.42 (d, 1H), 8.03 (dd, 1H), 7.46 (d, 1H), 7.31 (t, 1H), 7.18 (t, 1H), 7.11 (s, 1H), 6.65 (d, 1H), 4.64 (septet, 1H), 4.09 (s, 4H), 2.40 (s, 6H), 2.20 (s, 12H), 0.90 (d, 6H). ^{13}C NMR ($CDCl_3$) ? 301.2, 206.2, 176.3, 156.2, 142.3, 137.9, 133.3, 132.3, 128.9, 127.7, 126.6, 124.2, 117.4, 109.8, 50.4, 31.0, 20.8, 19.1, 16.7. Anal. calcd. for $C_{35}H_{37}F_6N_3O_7Ru$ (M_r = 826.74 g/mol): C; 50.85, H; 4.51, N; 5.08. Found: C; 51.18, H; 4.31, N; 5.21. MS (CI) calcd. for $C_{35}H_{37}F_6N_3O_7Ru$: 827.2; found *m/z* = 826.3 $(M\text{-}H)^+$.

5.3.15 $Ru(CF_3CF_2CO_2)_2(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_3\text{-}5\text{-}NO_2)(SIMes)$ (M4c)

$RuCl_2(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_3\text{-}5\text{-}NO_2)(SIMes)$ (144 mg, 0.214 mmol) was dissolved in 10 mL of THF and a solution of 2 equiv of $CF_3CF_2CO_2Ag$ (115.9 mg, 0.428 mmol) in 2 mL of THF was slowly added to the stirred solution. Stirring was continued for 30 minutes. The color changed from green to brown and the formation of a precipitate was observed. The precipitate was centrifuged, the solution was filtered through a 0.2 ?m Teflon filter and evaporated to dryness. The following manipulations were done under air. The solid was re-dissolved in ethyl acetate and flashed over a short pad of silica. Drying *in vacuo* provided a brown powder (118.5 mg, 0.128 mmol, 60 %). FT-IR (ATR-mode): 2929 (br), 2856 (br), 2361 (w), 2124 (br), 1959 (br), 1690 (m), 1600 (w), 1484 (w), 1413 (m), 1328 (m), 1264 (s), 1213 (vs), 1162 (s), 1097 (m), 1025 (vs), 956 (m), 853 (w), 813 (m) and 730 (w). ^1H NMR ($CDCl_3$) ? 17.38 (s, 1H, Ru=CHAr), 8.42 (d, 1H), 7.88 (d, 1H), 7.44 (d, 1H), 7.30 (t, 1H), 7.19 (t, 1H), 7.11 (s, 1H), 6.64 (d, 1H), 4.56 (septet, 1H), 4.09 (s, 4H), 2.40 (s, 6H), 2.19 (s, 12H), 0.91 (d, 6H). ^{13}C

NMR (CDCl$_3$) ? 310.3, 214.8, 168.4, 164.7, 150.9, 150.6, 147.6, 146.4, 144.9, 140.9, 137.5, 136.3, 134.1, 132.9, 126.4, 118.4, 59.0, 46.4, 33.4, 28.7, 21.6, 18.5. Anal. calcd. for $C_{37}H_{37}F_{10}N_3O_7Ru$ (M_r = 926.76 g/mol): C; 47.95, H; 4.02, N; 4.53. Found: C; 48.23, H; 4.38, N; 4.74.

5.3.16 Ru(CF$_3$CF$_2$CF$_2$CO$_2$)$_2$(=CH-2-(2-PrO)-C$_6$H$_3$-5-NO$_2$)(SIMes) (M4d)

RuCl$_2$(=CH-2-(2-PrO)-C$_6$H$_3$-5-NO$_2$)(SIMes) (109.8 mg, 0.163 mmol) was dissolved in 10 mL of THF and a solution of 2 equiv. of CF$_3$CF$_2$CF$_2$CO$_2$Ag (104.9 mg, 0.327 mmol) in 2 mL of THF was slowly added to the stirred solution. Stirring was continued for 30 minutes. The color changed from green to brown and the formation of a precipitate was observed. The precipitate was centrifuged, the solution was filtered through a 0.2 ?m Teflon filter and evaporated to dryness. The following manipulations were done under air. The solid was re-dissolved in ethyl acetate and flashed over a short pad of silica. Drying *in vacuo* provided a brown powder (103.8 mg, 0.101 mmol, 62 %). FT-IR (ATR-mode): 2929 (br), 2857 (br), 2358 (w), 2121 (br), 1959 (br), 1681 (br), 1483 (w), 1404 (m), 1334 (m), 1262 (s), 1212 (vs), 1081 (m), 1023 (vs), 963 (m), 931 (m), 853 (w), 804 (m) and 752 (w). ^{1}H NMR (CDCl$_3$) ? 17.40 (s, 1H, Ru=CHAr), 8.42 (d, 1H), 7.88 (d, 1H), 7.44 (d, 1H), 7.29 (t, 1H), 7.19 (t, 1H), 7.12 (s, 1H), 6.64 (d, 1H), 4.55 (septet, 1H), 4.09 (s, 4H), 2.41 (s, 6H), 2.19 (s, 12H), 0.90 (d, 6H). ^{13}C NMR (CDCl$_3$) ? 301.7, 206.2, 156.2, 142.3, 142.0, 139.0, 137.9, 136.3, 134.5, 132.3, 128.9, 127.7, 127.1, 125.5, 124.2, 117.8, 109.8, 50.4, 31.0, 25.2, 24.8, 20.8, 19.0, 16.8. Anal. calcd. for $C_{39}H_{37}F_{14}N_3O_7Ru$ (M_r = 1026.77 g/mol): C; 45.62, H; 3.63, N; 4.09. Found: C; 45.99, H; 4.01, N; 4.39.

5.3.17 Me$_{30}$Non$_6$(PenOCO(CF$_2$)$_3$COOH)$_2$Pip (A14)

(**A11**) (1.5 g) was dissolved in 20 mL of dry CH$_2$Cl$_2$ and perfluoroglutaric acid anhydride (1 equiv., 158 mg, 0.71 mmol, 0.1 mL) was added at 0°C to the stirred solution under argon. Stirring was continued for 90 minutes. The solvent and unreacted anhydride were removed *in vacuo*. The yellow product was washed twice with 10 mL of dry diethyl ether, centrifuged and dried *in vacuo* to give a white powder (1.5 g). ^{1}H-NMR (MeOH-d$_4$) ? 4.28 (t, 4H, ^{3}J = 6.0), 3.43 (m, 152H), 3.01/2.96 (m, 3H), 2.01 (m, 98H), 1.67(m, 4H), 1.49 (m, 16H), 1.36 (m, 4H), 1.20 (m, 72H), 0.80 (t, 18H, ^{3}J = 6.87). FT-IR (ATR-mode): 2925 (br), 2854 (br), 1772 (m), 1633 (s), 1415 (s), 1359 (w), 1314 (br), 1235 (w), 1150 (br), 938 (br) and 729 (br). GPC (UV) M_n = 5974 g/mol, PDI 1.35. GPC (RI) M_n = 2025 g/mol, PDI 1.03.

5.3.18 $Me_{30}Non_6(PenOCO(CF_2)_3COOAg)_2Pip$ (A15)

(**A11**) (1.5 g) was dissolved in 20 mL of MeOH:H_2O (1:1) and 1 equiv of NaOH (0.2 N, 3.6 mL) was slowly added. Stirring was continued for 1 h and 1.1 equiv of $AgNO_3$ in 2 mL of water was added. It was stirred for another 2 h and dried at 60 °C *in vacuo* to give a reddish product, which was re-dissolved in 5 mL of MeOH, filtered 3 times over a Teflon filter (0.2 ?m) and evaporated to dryness to give a white powder (1.32 g). ^{1}H-NMR (MeOH-d_4) ? 4.27 (m, 4H), 3.43 (m, 152H), 3.02/2.95 (m, 3H), 2.06 (m, 98H), 1.67(m, 4H), 1.49 (m, 16H), 1.37 (m, 4H), 1.20 (m, 72H), 0.80 (t, 18H, ^{3}J = 6.87). FT-IR (ATR-mode): 2925 (br), 2855 (br), 1772 (m), 1624 (s), 1417 (s), 1364 (w), 1320 (br), 1253 (w), 1154 (br), 1029 (br), 938 (w) and 816 (w). GPC (UV) M_n = 3979 g/mol, PDI 1.14. GPC (RI) M_n = 1748 g/mol, PDI 1.03.

5.3.19 $Me_{30}Non_6((PenOCO(CF_2)_3COO)(CF_3COO)Ru(=CH\text{-}2\text{-}(2\text{-}PrO\text{-}C_6H_4))_{0.8}(SIMes)(PenOCO(CF_2)_3COOAg)_{1.2}Pip$ (A3)

$RuCl_2(=CH\text{-}2\text{-}(2\text{-}PrO\text{-}C_6H_4))(SIMes)$ (3 equiv., 80 mg, 0.128 mmol) was dissolved in 10 mL of dry THF. (A**11**) (1 equiv., 100 mg) dissolved in 10 mL of dry MeOH was added to the stirred solution. Stirring was continued for 15 minutes, then CF_3COOAg (6 equiv., 84 mg, 0.768 mmol) was added and the mixture was stirred for another 15 minutes. The solvent was removed *in vacuo*. The product was re-suspended in 10 mL of dry diethyl ether, centrifuged and dried *in vacuo*. The product was re-dissolved in 10 mL of dry MeOH, filtered 3 times through a Teflon filter (0.2 ?m) and evaporated to dryness to give a lilac powder (120 mg, 100 %). FT-IR (ATR-mode): 2926 (br), 2856 (br), 1884 (w), 1773 (w), 1625 (br), 1419 (s), 1367 (w), 1318 (w), 1254 (w), 1183 (s), 1134 (s), 1030 (w), 833 (w), 794 (w), 757 (w) and 721 (w). ^{1}H-NMR ? (CD_3OD) 17.51 (s, 0.8 H, Ru=CHAr), 6.6-7.1 (m, 4H), 4.27 (m, 4H), 3.43 (m, 152H), 3.02/2.95 (m, 3H), 2.06 (m, 98H), 1.67(m, 4H), 1.49 (m, 16H), 1.37 (m, 4H), 1.20 (m, 72H), 0.80 (m, 18H). GPC (UV) M_n = 11045 g/mol, PDI 1.20. GPC (RI) M_n = 1862 g/mol, PDI 1.03. ICP-OES: 40 % loading with ruthenium (0.16 mmol ruthenium/g). Leaching as determined by ICP-OES: 0.35 ppm Ru in poly(DEDPM)$_n$.

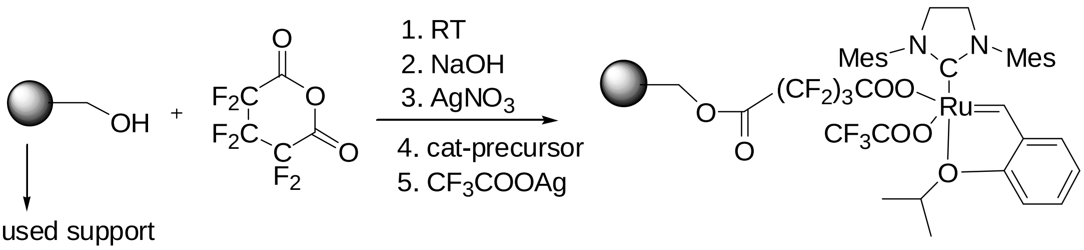
5.3.20 $Me_{30}Non_6(((PenOCO(CF_2)_3COO)(PenOCO(CF_2)_3COOAg)_{1.2}Pip))$-$(CF_3COO)Ru(=CH$-2,4,5-$(OMe)_3C_6H_2))_{0.8}$(SIMes) (A4)

This compound was prepared in analogy to **A3** using **A11** and $RuCl_2$(=CH-2,4,5$(OMe)_3$-C_6H_2)(SIMes). Yield (109 mg, 100 %). FT-IR (ATR-mode): 2967 (br), 2855 (br), 2060 (w), 2022 (w), 1670 (vs), 1594 (vs), 1487 (s), 1418 (s), 1272 (w), 1199 (s), 1130 (s), 1036 (w) and 837 (w). ^{1}H-NMR (CD_3OD) 18.03 (s, 0.5 H, Ru=CHAr), 6.4-7.2 (m, 6H), 4.27 (m, 4H), 3.43 (m, 152H), 3.02/2.95 (m, 3H), 2.06 (m, 98H), 1.67(m, 4H), 1.49 (m, 16H), 1.37 (m, 4H), 1.20 (m, 72H), 0.80 (t, 18H, ^{3}J = 6.87). ICP-OES: 40 % loading (0.16 mmol ruthenium/g). Leaching as determined by ICP-OES: 0.35 ppm Ru in poly$(DEDPM)_n$.

5.3.21 MALDI-TOF of poly$(DEDPM)_5$

Polymerization was terminated with excess ethylvinyl ether after 3 minutes. MALDI-TOF calcd. for $C_{63}H_{79}LiO_{17}$: *m/z* = 1114.55 (100 %), 1115.23 (70 %), found: 1115.96.

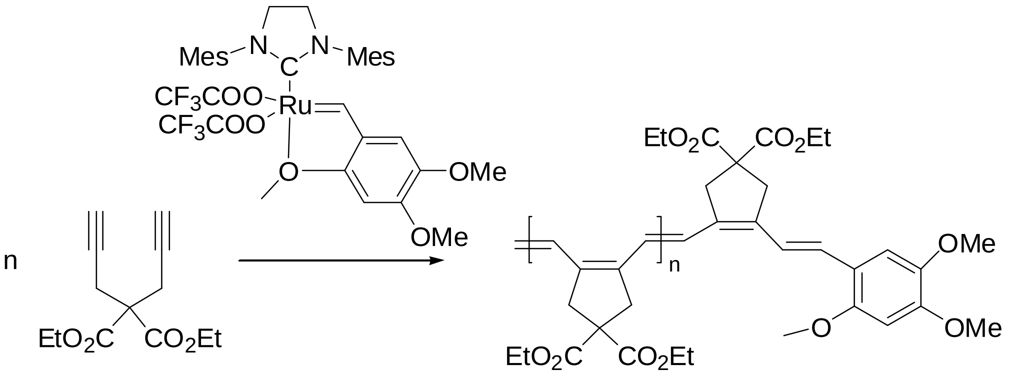
they revealed high activity both at elevated and room temperature. Moreover, substitution of the chlorine ligands by trifluoroacetate groups respectively polymer-bound analogous functions offer a simple access to heterogeneous analogues as has been demonstrated with the synthesis of **C4** and **C5**. The high catalytic activity is retained during the heterogenization process, and ruthenium leaching was unprecedentedly low, giving access to virtually Ru-free products. Apart from crosslinked polystyrene based catalysts **C4** and **C5**, with **R1**, **A3** and **A4** a monolithic (**R1**), as well as two amphiphilic based catalysts (**A3** and **A4**), could be generated using the same procedure (scheme 6-2).



Scheme 6-2. General procedure for immobilization of a Hoveyda-Grubbs catalyst.

For characterization of **R1** in flow-through catalysis and for purposes of comparison, RCM of DEDAM was used for benchmarking. With the present system, TONs up to 500 were achieved. This is the first example of a heterogenized Grubbs-Hoveyda catalyst in flow through catalysis. Regarding the fixation procedure, it has to mentioned, that no side reactions occur and unreacted catalyst can be obtained in 100 % pure yield for all supports. In view of this major advantage, **C4-5**, **R1**, **A3** and **A4** must be regarded superior in comparison to **D4-9** and literature systems.

Well-defined high oxidation-state molybdenum carbenes (Schrock catalysts) can be tuned in a way that only one single repetitive unit, i.e. 1,3-(cyclopent-1-enylene)vinylens[121,122] and 1,3-(cyclohexen-1-enylene)methylidenes,[101,115] respectively, is obtained in the polymerization of DEDPM. In contrast to other catalysts, they provide cyclopolymerization of 1,6-heptadiynes in a living manner. Despite their unique catalytic properties, the strictly air- and moisture-free conditions that are required in the use of Schrock catalysts are certainly a major limitation for technically relevant applications. In this work, the synthesis of the first ruthenium-based catalyst which can accomplish a cyclopolymerization is reported. Furthermore, the catalysts (**C3, M1-4 b-d**) can be tuned in a way that polymerization occurs in a living and stereoregular way. These catalysts now close one of the last gaps between molybdenum- and ruthenium-based metathesis catalysts (scheme 6-3).

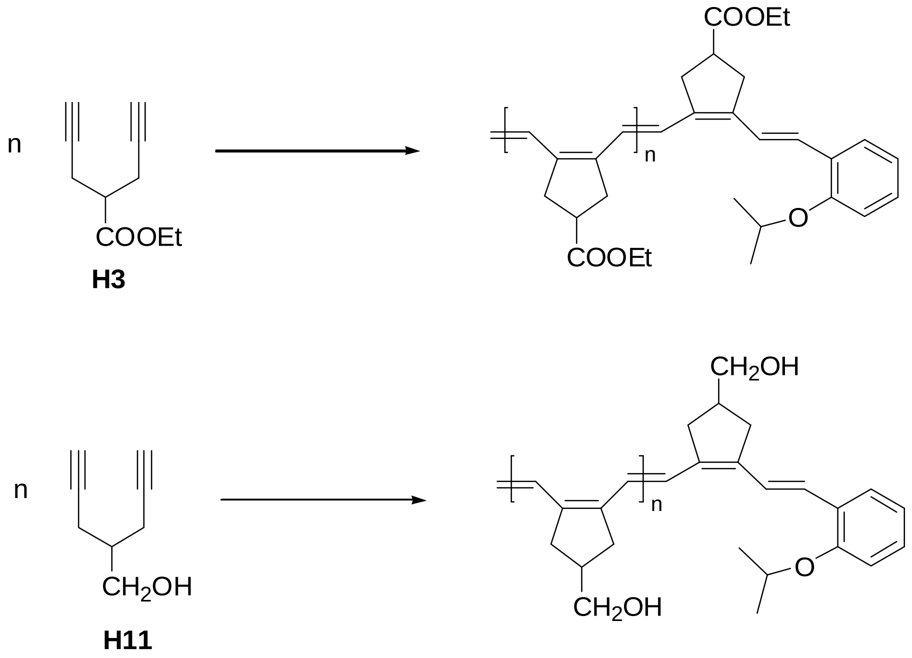


Scheme 6-3. Cyclopolymerization of DEDPM.

From the systematic variation of all ligands, the following requirements for cyclopolymerization-active systems were found: (i) the replacement of both chlorine ligands with strongly electron withdrawing carboxylate groups using salts such as $CF_3(CF_2)_{n=0-2}COOAg$ is required; (ii) the NHC has to be electron rich; (iii) the living character of the polymerization of DEDPM strongly correlates with the steric and electronic situation at the benzylidene ligand. Therefore, the weaker the coordination of the oxygen fragment to the Ru-core is, the lower the values for k_p/k_i are, resulting in increased insertion efficiencies. Two new types of initiators (**M2b-d** and **M4b-d**) that fulfill these criteria were prepared and found suitable for the class VI living polymerization of DEDPM. All initiators gave rise to 100 % of ?-insertion of the monomer, resulting in the formation of polyacetylenes containing virtually solely (>96%) 5-membered ring structures. With the synthesis of Poly(ECMCH) it could be shown, that the polymers consist of a cis-trans-structure. The use of larger fluorinated carboxylates apparently further reduces chain-transfer reactions resulting in polyenes with low PDIs.

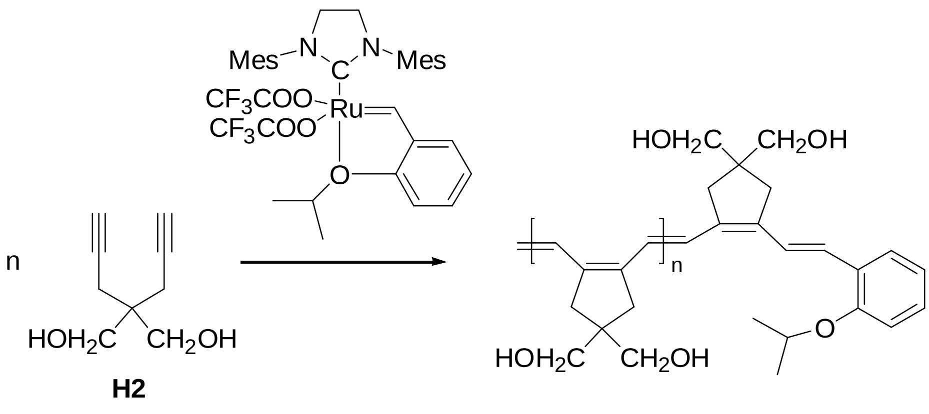
With the use of **A3** and **A4**, the polymerization could be transferred to aqueous media. On the one hand, perfect mimics of **C3** and **M2b** were generated so that the reactivity and stereoselectivity was maintained. On the other hand and in contrast to any suspension/emulsion polymerization, the catalyst was *permanently* linked to the amphiphilic block copolymer. This is the ***first*** ruthenium-alkylidene permanently bound to an amphiphilic support. Poly(DEDPM) prepared with **A4** in water was characterized by lower polydispersity indices (PDIs) < 1.40 compared to poly(DEDPM) prepared by **M2b**, and due to the increased concentration of DEDPM within the micelles reaction times required to reach complete conversion were reduced to 30 minutes using **A3** and **A4**, compared to 2 hours with **M2b**, illustrating the catalytic effect of the micellar nanoreactors formed in aqueous medium. Nevertheless, the polymerization itself can not be regarded living. TEM analysis of the resulting polymer latex revealed particle sizes between 100 and 200 nm, which is typical for an emulsion based process. Complementary, the catalyst immobilization technique allowed also for catalyst/product separation to obtain virtually Ru-free polyacetylenes with a Ru-content = 0.35 ppm.

Furthermore, it could be shown, that sterically less demanding polymers can be polymerized using directly the Hoveyda-Grubbs catalyst to give pure five-membered rings. This is in strong contrast to Schrock type catalyst for **H3**, where in the best cases only a 77 % yield of five-membered rings could be obtained (scheme 6-4).



Scheme 6-4. Polymerization of sterically less demanding monomers **H3** and **H11**.

As another interesting detail, polar/functional polymers can also be polymerized (scheme 6-5).



Scheme 6-5. Polymerization of functional monomer **H2**.

The ruthenium content in polymers obtained with homogeneous catalysts was around 3 ppm, with heterogeneous catalysts around 0.3 ppm.

In summary, a new class of reaction (polymerization of heptadiynes) has been introduced to ruthenium chemistry giving full control over molecular weight and microstructure. Furthermore, a simple access to heterogenization of these catalysts could be presented, giving not only perfect mimics and highly active catalysts but also access to virtually metal free products.[149,172-174,191,193,213-216]

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8 Publications from this work

1. J. O. Krause, O. Nuyken, K. Wurst, M. R. Buchmeiser, *Chemistry-A European Journal* **2004**, *10*, 777.
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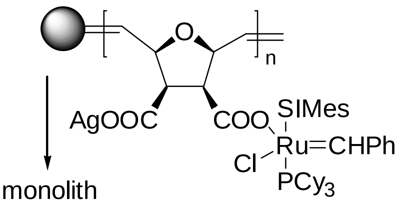

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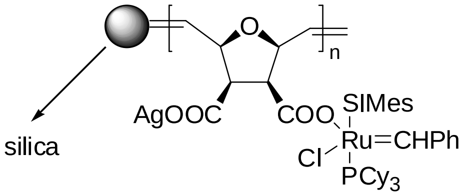

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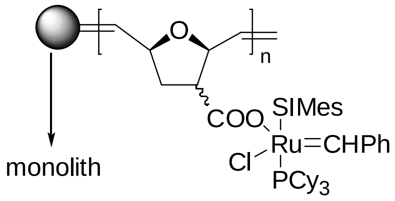

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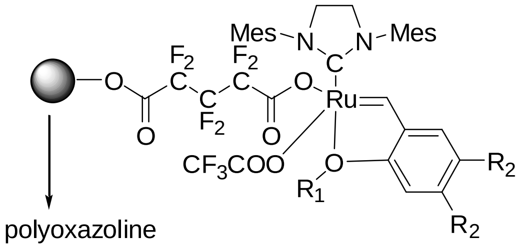

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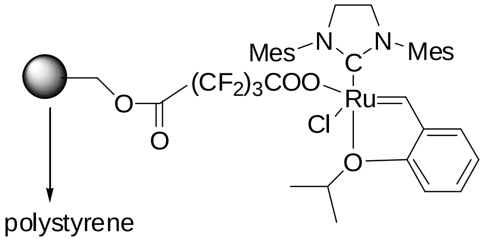

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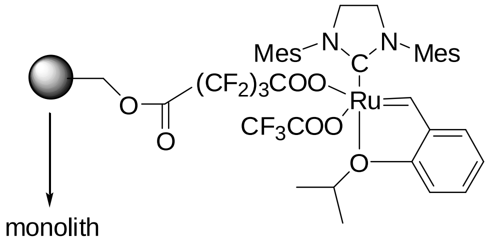

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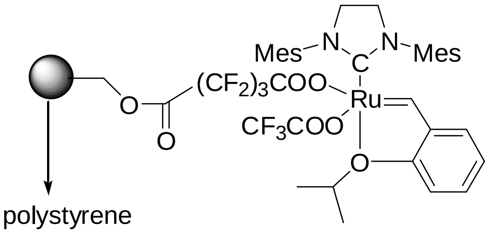

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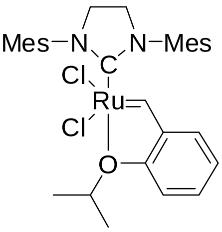

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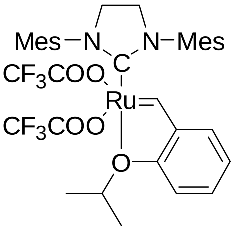

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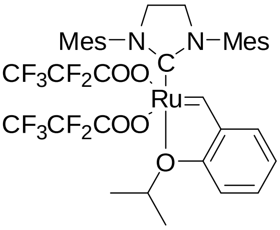

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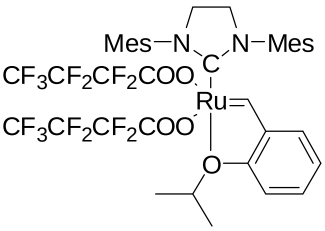

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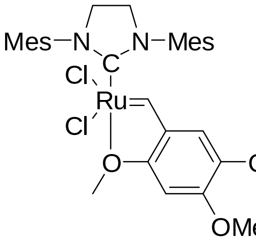

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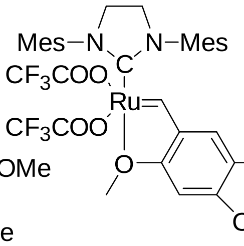

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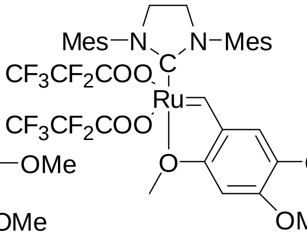

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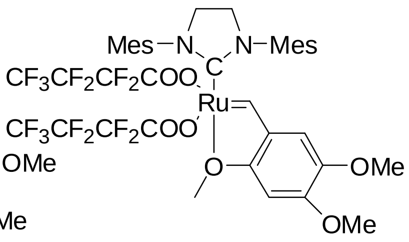

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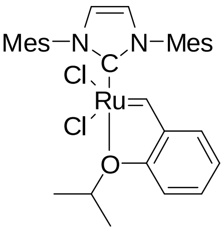

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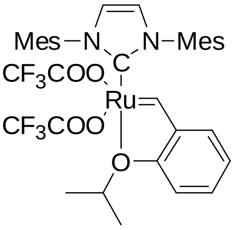

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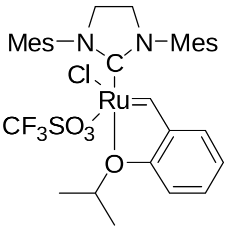

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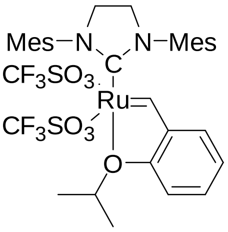

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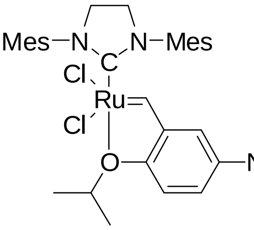

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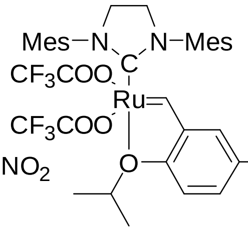

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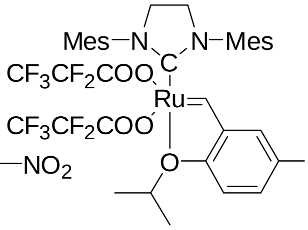

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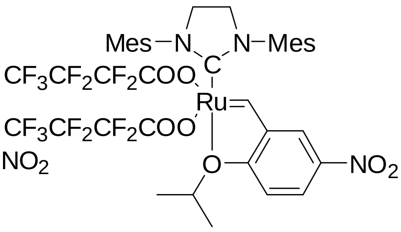

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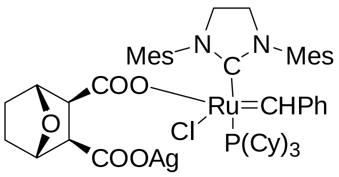

D3