Immobilisation of Ru-based metathesis catalysts and related aspects of olefin metathesis
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Citation for published version (APA):

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Chapte r 2

Preparation, Application
and EXAFS Structural Studies
of New Polystyrene-Supported
Ruthenium Carbene Catalysts
for Alkene Metathesis

**Keywords:** Ruthenium / Carbene complexes / Polystyrene-supported catalyst / Alkene metathesis / EXAFS

**Abstract:** Ruthenium carbene complexes 1 and 3 were immobilised via chlorine abstraction using polystyrene resins functionalised with silver carboxylate. The supported catalysts were applied in several types of metathesis reactions and could be also recycled. Their molecular structure was investigated by means of EXAFS spectroscopy.
2.1 Introduction

Since the discovery of the alkene metathesis reaction more than forty years ago, the bulk of the research carried out employed usually poorly defined transition metal species supported on various materials, silica and alumina being the most popular.\(^1\) During recent years impressive progress has been made in the development of well-defined homogeneous olefin metathesis catalysts\(^2\). This has mainly been due to the synthesis of new ruthenium carbene catalysts, such as the first-, Ru(=CHPh)Cl\(_2\)(PCy\(_3\))\(_2\) (1),\(^3\) and the second generation ruthenium metathesis catalysts, Ru(=CHPh)Cl\(_2\)(PCy\(_3\))L, where L is a N-heterocyclic carbene (NHC) ligand, e.g. 2 (L = IMes)\(^4\) and 3 (L = H\(_2\)IMes),\(^5\) as well as the Hoveyda modifications of the system – complexes 4\(^6\) and 5.\(^7\)

These catalysts have found wide application in organic synthesis because of their ease of preparation, resistance towards oxygen and moisture, compatibility with many functional groups and relatively high activity, especially of the complexes containing a NHC ligand.

2.1.1 Literature Survey of Supported Ru Carbenes

2.1.1.1 The First Supported Ru Carbene

In the industrial processes, the large majority of the catalysts used are heterogeneous systems and metathesis is not an exception in this respect, employing usually supported metal oxides or chlorides.\(^1,8\) Immobilisation of the homogeneous catalysts 1 - 5 on solid supports would facilitate the work-up and make the metathesis reaction an even more attractive tool for industry-oriented, practical applications. Nguyen and Grubbs presented the first example of immobilising a well-defined ruthenium carbene on a solid support.\(^9\) Complex Ru(=CH-CH=CPh\(_2\))Cl\(_2\)(PPh\(_3\))\(_2\) (1a) was tethered to a series of phosphine-functionalised polystyrene-divinylbenzene (PS-DVB) solid supports by phosphine exchange to form, e.g. 1. These supported catalysts bring about the ring opening metathesis polymerisation (ROMP) of norbornene and cyclooctene, as well as the self-metathesis of cis-2-pentene, although at a much slower rate than their homogeneous analogues. When later the metathesis mechanism for Grubbs-type catalysts was elucidated, the poor activity of this system became evident.

Because of these somewhat disappointing results, the supported catalyst 1 was the only example until recently, when several publications appeared describing new approaches to immobilise ruthenium carbene complexes, including the second generation catalyst 3 and its analogues. The immobilisation efforts can be categorised according to the point of attachment of the ruthenium complex to the solid phase.
2.1.1.2 Immobilisation via the Carbene Moiety

In the majority of the undertaken immobilisation efforts, the carbene unit itself functions as the connection of the homogeneous complex to the solid phase. The so called ‘boomerang’ polymer-supported catalyst IIa was first presented by Barrett and co-workers\(^\text{10}\) who anchored catalyst I to a vinyl analogue of Merrifield resin. During metathesis the catalyst is released to the reaction medium, acts as a homogeneous catalyst, and is then recaptured by the support once the substrate has been consumed. This approach solved the problem of the low activity of heterogenised catalyst I and lowered the contamination of the final product with Ru residues. Recycling attempts, however, were disappointing and the addition of stabilising agents only partially prolonged the catalyst lifetime. Kiddle and co-workers\(^\text{11}\) assessed the activity of the supported catalyst IIa and found that it performed less well than catalyst I in microwave promoted ring closing metathesis (RCM). Better results were obtained using resin IIb with the more robust and active catalyst 2. This system allowed the catalyst to be recycled for five consecutive RCM runs, or even longer when additives, like 1-octene or PPh\(_3\), were added to stabilise the metathesis active species.\(^\text{12}\)

Nolan and collaborators immobilised complexes 1 – 3 and some analogues on poly(di-vinylbenzene) (poly-DVB, a macroporous, non-swelling resin with a defined porous structure, also in its dry state in contrast to polystyrene resins) to produce resins IIIa-d.\(^\text{13}\) The supported catalysts showed similar activity to their homogeneous parent complexes. The loss in activity during recycling was quite modest, mainly due to effective recapture of the released catalyst species back to the surface of the polymeric matrix containing a large excess of free vinyl groups. The authors noticed\(^\text{13b}\) that oxygen-containing substrates greatly affected the recapture mechanism due to chelate formation (similar to that in complex 4) and recycling was not feasible in these cases.

A better recyclability is obtained using the Hoveyda-type catalysts 4 and 5 that are very robust organometallic entities and can be even recovered by silica gel chromatography.\(^\text{6,7}\) The group of Hoveyda prepared catalysts IVa and IVb - the carbosilane dendrimer supported analogues of 4 and 5, respectively.\(^\text{7a}\) The dendritic catalysts were recycled by column chromatography for multiple consecutive runs, and despite leaching levels of ~10% of Ru per cycle, still performed well in the sixth run of a model RCM reaction. Catalyst 5, when
immobilised by sol-gel procedure on glass pellets, produced supported catalyst IVc, which displayed even better catalytic properties.\textsuperscript{14} It could be recycled at least fifteen times bringing the test RCM, ROM/CM and CM reactions to completion, though the reaction time increased from 3 to 14 h because of minor catalyst leaching and slow deactivation. Nevertheless, the product contamination with Ru residue was below 1\% of the initial loading and the tablet-like shape of the support allowed easy combinatorial screening of libraries of twenty-five RCM and ROM/CM reactions.

Several other groups immobilised the Hoveyda-type catalysts 4 and 5 via the carbene moiety on various supports.\textsuperscript{15} Yao\textsuperscript{15a} used poly(ethylene glycol) (PEG) for preparing the soluble supported catalyst Va that carried out RCM for at least up to eight runs with only minor loss of activity. Catalyst Va was recycled by precipitation from the reaction mixture and filtration. Recently, in the same group, isopropoxystyrene derivatised PEG was used to immobilise catalyst 3.\textsuperscript{15b} The obtained catalyst Vb took advantage of the high activity and robustness of 3, improving the recyclability to at least seventeen cycles in RCM with only slight catalyst deactivation.

\begin{center}
\begin{tikzpicture}
\node (VA) at (0,0) {Va (L = PCy$\textsubscript{3}$)}
\node (Vb) at (3,0) {Vb (L = H$_2$IMes)}
\end{tikzpicture}
\end{center}

Dowden and Savovic\textsuperscript{15c} employed a modified polystyrene resin, obtaining catalyst VI that was effective for seven consecutive runs of RCM performed in air, although with a substantial decrease in conversions. Use of TentaGel\textsuperscript{TM} to give a supported catalyst of the sort VI gave rather poor results in RCM in non-degassed methanol.

In a simplified procedure, requiring only two steps, catalyst VIIa was prepared and successfully used for the ethenolysis of methyl oleate.\textsuperscript{15d} PEG modified with a styrene moiety at the end of the chain was employed for tethering 1 and 3 resulting in soluble polymeric catalysts VIIb-d.\textsuperscript{15e} Catalyst VIIb released the active species to the solution, but it was not effective in recapturing after metathesis completion precluding recycling of the catalyst.
Catalysts VIIc and VIIId could be recycled for up to five cycles, although the return of the active species to complete the 'boomerang' mechanism was not fully completed at the end of each cycle resulting in high catalyst leaching. The lower stability of the supported species VIIc-d, as compared to complexes 4, 5 or VIII, in which the isopropoxy group provides for a better chelation, is to blame.

Blecher and co-workers\textsuperscript{15f} employed Wang resin modified with 2-isopropoxy-5-hydroxystyrene to attach complex 3. The resin VIIIa was successfully applied in CM and could be recycled up to five times. They made also use of a commercial PEGA-NH$_2$ resin as a support for 3.\textsuperscript{15g} The catalyst VIIIb performed quite efficiently in aqueous and alcoholic solutions for metathesis of polar substrates. Alternatively, complex 3 was employed in ROMP copolymerisation of two oxanorbornene derivatives, one of which contained the isopropoxystyrene moiety. Addition of copper chloride induced catalyst immobilisation on the polymer, thus obtaining a self-generating supported catalyst VIIIc.\textsuperscript{15h} The soluble catalyst VIIIc showed very good activity, recyclability (up to eight runs with just 1 mol\% catalyst, recovered by precipitation) and a low bleeding profile. Weberskirch and co-workers\textsuperscript{15i} further improved the performance of catalyst VIII in aqueous solutions by using an amphiphilic, water soluble block copolymer based on poly(2-oxazoline)s. The highest metathesis activity in water presented so far was measured for a model RCM. Recycling was feasible for up to five cycles with low Ru leaching but major catalyst deactivation. Grela and collaborators used butyldiethylsilyl polystyrene (PD-DES) derivatised with isopropoxystyrene moiety as a long handle to tether complex 3.\textsuperscript{15j} Catalyst VIIId had a lower activity than catalysts supported on soluble supports, but comparable recyclability and low contamination of the products by Ru residues.
Yao and Zhang\textsuperscript{16} have to date presented the only example of successful recycling of a Ru carbene using perfluorinated solvents. They prepared a poly(fluoroalkyl acrylate) functionalised with isopropoxystyrene groups to which complex 3 was bound. The fluorinated supported catalyst \textit{VIIIe} was soluble in the reaction medium PhCF\textsubscript{3}/CH\textsubscript{2}Cl\textsubscript{2} (1:19 v/v) allowing fast and clean RCM. The catalyst was extracted with perfluorohexanes and recycled up to twenty times with only a slight (~10\%) decrease in activity, remarkably. A drawback of this procedure is the intrinsic requirement of the relatively expensive fluorous solvents, although this is at least partially compensated by the ease of automation of the extraction protocol.

\begin{center}
\begin{tikzpicture}
\node (img) {\includegraphics[width=0.8\textwidth]{figure.png}};
\end{tikzpicture}
\end{center}

\textit{VIIIe}

Ionic liquids are valuable ‘green’ alternatives to standard solvent systems. Several groups performed metathesis in ionic liquids with success.\textsuperscript{11,17} The homogeneous catalysts 1, 3 and the cationic precursor of \textit{XIII}, when solvated in ionic liquids, could be reused after extraction of the reaction products with an organic solvent. However, significant decreases in activity were observed, because of partial extraction of the Ru carbene to the organic layer, allowing in the most favourable cases for up to 5-6 cycles. To alleviate this problem, the modified catalysts \textit{VIIIf} and \textit{VIIIf} were prepared by the groups of Guillemin\textsuperscript{18a} and of Yao\textsuperscript{18b} by tagging complex 4 with 3-methylimidazolium hexafluorophosphate. The almost identical ionic catalysts outperformed the regular Ru carbenes in terms of recyclability allowing for ten cycles of practically complete conversion of a model substrate to RCM product (total TON of ~400). Studies regarding the utility of this approach to catalyst 5 are underway in both groups.

\begin{center}
\begin{tikzpicture}
\node (img) {\includegraphics[width=0.6\textwidth]{figure2.png}};
\end{tikzpicture}
\end{center}

Verdonck and collaborators prepared carbosilane dendrimers with the ruthenium carbene 1 and its PPh\textsubscript{3} analogue bound via the carbene unit.\textsuperscript{19} Using this dendritic initiator they prepared star-polymers with a carbosilane core by controlled ROMP of norbornene. However, no attempts of application towards RCM nor recycling data have been reported.
Despite some very fine results, the ‘boomerang’ system has a limited scope, since it is not suitable for continuous processes, nor for metathesis reactions with thermodynamical equilibria between substrate(s) and product(s) as, for example, for the self-metathesis of internal alkenes. For these reasons, considerable effort has been made to permanently immobilise the ruthenium-based catalysts 1 - 5 on supports.

2.1.1.3 Immobilisation via the NHC Carbene

In the ruthenium carbenes bearing a NHC ligand, e.g. 2, 3, 5, the ligand itself is a good candidate for an attachment point to a support. Since the NHC is strongly bound to the metal centre and does not dissociate during the catalytic cycle (in contrast to the carbene or phosphine moieties), a permanently immobilised complex can be made. A drawback is the usually multistep preparation of a NHC ligand suitable for tethering to a support. The first report using this strategy came from Blechert and co-workers that anchored complex 1 to a Merrifield resin functionalised with a NHC ligand, producing the immobilised second generation catalyst IXa.\textsuperscript{20} The catalyst was shown to be active for RCM and ene-yn metathesis, though long reaction times were usually required for reactions to reach completion. This period needed to be further extended in recycling experiments with only up to four runs being practical. Complex 3 was also supported on a similar PS resin giving catalyst IXb that, compared to its ‘boomerang’ analogue VIIIa,\textsuperscript{15f} performed somewhat less well. The presence of an additional isopropoxy group (IXc) did not improve the catalyst activity and stability in CM.

\begin{center}
\begin{tikzpicture}
\node (a) at (-2,0) {\includegraphics[width=0.4\textwidth]{IXa}};
\node (b) at (0,0) {\includegraphics[width=0.4\textwidth]{IXb}};
\end{tikzpicture}
\end{center}

In the group of Buchmeiser the second generation catalyst 3 was permanently anchored to monolithic and silicious materials for application in continuous processes.\textsuperscript{21} The immobilisation protocol employed derivation of the support surface by ROMP of norbornene-type monomers using 1. Since this is a living polymerisation, norbornene-derivatised NHC ligands are grafted to the support upon addition to the reaction mixture. Adjusting the ratio of the monomers allows to control the microstructure and loading of the support. Capping of the ruthenium termini with ethyl vinyl ether followed by base-promoted reaction with ruthenium carbene 1 yields immobilised complexes of type X. They proved to be efficient catalysts in RCM and ROMP using a continuous system, could be recycled in a batch system and the
metal leaching was low. Some doubts have arisen regarding validity of the proposed structure of the Ru carbene Xb that employs a diadamantyl NHC ligand (see Chapter 4 of this thesis and reference 22).

\[
\begin{align*}
\text{Xa (R = Mes) } & \\
\text{Xb (R = Ad)}
\end{align*}
\]

2.1.1.4 Alternative Immobilisation Procedures

In the Verpoort group several ruthenium complexes with bidentate Schiff-base ligands were developed and immobilised on mesoporous matrix MCM-41.\(^\text{23}\) The supported catalysts of type XI and its \(p\)-cymene precatalyst analogue\(^\text{23a}\) showed good activity in ROMP and RCM (also in Kharasch addition and enol ether synthesis) and they could be recycled four times with only a small decrease in activity. The same group used phosphinated MCM-41 to bind 1 and its PPh\(_3\) analogue via one of the phosphine moieties.\(^\text{24}\) The catalysts XIIa, b act partly in the already discussed ‘boomerang’ mode (in this case by phosphine dissociation) and then the active species is recaptured to the support quite efficiently, so the leaching is low (1-3%). However, recycling was not attempted and the activity was substantially lower than that of catalyst 1 for certain substrates.

\[
\begin{align*}
\text{XIa (R = Ph) } & \\
\text{XIIb (R = Cy)}
\end{align*}
\]

Similarly, a linkage of 1 to silica via phosphine moieties was realised by Mingotaud and collaborators.\(^\text{25}\) They made an analogue of 1 in which one of the cyclohexyl groups in both phosphine moieties was replaced by 10-decanol-1-y1 chain. The complex was then allowed to react with silica grafted with carboxyl group, leading to catalyst XIIc immobilised via a particularly long tether. The catalyst exhibited good activity in ROMP of norbornene, but more challenging substrates were not mentioned, and the direct measurement of catalyst leaching and recycling were not addressed. It is also possible, at least to some extent, that the dangling chain of the second phosphine is involved in bonding to the silica surface giving a chelated species.
The polystyrene-supported cationic ruthenium allenylidene complex XIII was prepared from a polymer-supported arene-ruthenium complex and appropriate reagents by Akiyama and Kobayashi. The tethering is realised via the arene unit in this case. The catalyst was used in a range of RCM reactions and could be reused in several cycles. When the activity decreased, the immobilised catalyst could be regenerated by reaction with a carbene source.

In the group of van Koten functionalised lithiated carbosilane dendrimers with a 2-hydroxyalkylpirydil ligand were used to support complex 1 and its analogue. The bidentate ligand exchanged a chloride atom and a phosphine moiety in 1. Catalysts XIVa, b were found to have similar catalytic performance as their homogeneous parent compounds. In spite of their good activity, a preliminary trial reaction in a flow reactor equipped with a nanofiltration membrane resulted in extensive catalyst deactivation.

Microincapsulation in polystyrene for the immobilisation of carbene 3, applicable also to other organometallic complexes, was presented by Gibson and Swamy. The RCM reaction was performed in water/methanol 4:1 mixture giving high conversions in this medium and permitting the recycling for at least four cycles, although with declining activity due to catalyst leaching from the polymer matrix. Ease of preparation makes this method quite interesting for practical purposes.

2.1.1.5 Immobilisation via the Anionic Ligand

In our group we devised a different approach for the immobilisation of ruthenium carbenes. We anticipated that the anionic ligands, which remain bonded to the ruthenium throughout the entire catalytic cycle, are the most suitable groups to form a covalent link between the Ru(II) centres and the support. Therefore, we have replaced the chlorides in 1 with carboxylate groups to produce six-coordinate dimeric complexes of the kind $\text{Ru}_2(=\text{CHR})_2(\text{R'}\text{CO}_2)_2(\mu-\text{R'}\text{CO}_2)_2(\text{PCy}_3)_2(\mu-\text{H}_2\text{O})$ (XV), where $\text{R'}$ is a strongly electron-withdrawing group (e.g. $\text{CF}_3$, $\text{C}_2\text{F}_5$, $\text{CCl}_3$). These ruthenium carbenes were found to be highly active metathesis catalysts.
Following our disclosure\(^\text{31}\) of the preliminary results discussed in this chapter, the collaborating groups of Nuyken and Buchmeiser\(^\text{32}\) reported several times on the application of this approach for catalyst immobilisation. Monolithic and silicious materials were grafted by ROMP with oxanorbornene (di)carboxylate or norborn-5-ene-2-ylmethyl hexafluoroglutarate, transformed into their silver salts, and subsequently reacted with 3 or 5 to replace one chlorine atom, furnishing permanently immobilised catalysts of type XVI\text{a} or XVI\text{b}, respectively.\(^\text{32a,b}\)

The catalysts were applied in a continuous process to give TON’s only somewhat lower than observed for 3 (batch process) in RCM and the metathesis products were found to be practically free of Ru contamination.

In the two other publications from these groups\(^\text{32c,d}\) the procedure described is (almost) identical to that presented in this chapter\(^\text{31}\) making use of perfluoroglutaric anhydride to immobilise complex 5 on amphiphilic poly(2-oxazoline)-derived block copolymer or just polystyrene. The heterogeneous catalysts showed high activity (TON of 200 for RCM) and very low ruthenium leaching (ppb levels), also in aqueous media.

### 2.2 Results and Discussion

#### 2.2.1 First Batch of Catalyst Supported According to a New Protocol

We chose a polystyrene resin as the support because of its chemical neutrality and presumed site isolation that would prevent deactivation of the catalyst by clustering.\(^\text{33}\)

Consequently, to obtain the desired polymer-supported ruthenium carbene we developed the straightforward procedure illustrated in Scheme 1.

A polystyrene resin (cross-linked with 1% DVB) functionalised with hydroxyethyl groups (batch capacity of ~1.48 mmol OH/g) was transformed into a carboxylic-acid-functionalised resin by reaction with hexafluoroglutaric anhydride. Upon treatment with sodium bis(trimethylsilyl)amide, followed by ion exchange with silver nitrate, a silver salt of
the immobilised carboxylic acid was obtained. Finally, the ruthenium complex 1 was reacted with the resin, producing the supported ruthenium carbene PS-Ru as dark brown beads. Based on our studies of the reaction with soluble silver carboxylates, we assumed that at least one chlorine atom in 1 was substituted with the carboxylic group.

![Scheme 1. Synthetic procedure to PS-Ru.](image)

The ruthenium loading on the resin, as determined by ICP-AAS analysis, was equal to 0.35 ± 0.05 wt% (~0.035 mmol/g). Thus, in the procedure employed, complex 1 substituted only circa 6% of the functional groups with respect to the starting hydroxyethyl resin (the maximal theoretical loading of the catalyst resin PS-Ru is approximately 0.60 mmol/g, provided all steps proceed with 100% efficiency). From elemental analyses of the resins obtained in each step of the procedure we concluded that the esterification was practically quantitative and the rather low ruthenium loading resulted mainly from considerable cleavage of the ester linkage upon treatment with sodium bis(trimethylsilyl)amide. In the MAS $^1$H NMR spectrum the carbene signal was observed at 19.86 ppm as a broad singlet, which is slightly upfield with respect to complex 1 (20.02 ppm). In the MAS $^{31}$P NMR spectrum two peaks were observed: a broad one at 52.6 ppm and a narrow one at 51.2 ppm in the ratio of circa 2:1. Although a definitive identification of these two peaks was not possible, we tentatively assigned the broad peak to a Ru carbene linked to the support by two carboxylic groups and the narrow one to a Ru carbene linked by one carboxylic group. Alternatively, it is possible that these peaks correspond to complexes with unideterminate and bidentate coordination modes of one carboxylic group to the ruthenium centre. Unfortunately, we could not confirm the coordination from the IR spectrum of the supported catalyst since all characteristic stretches were missing due to the low loading of the metal species.

Our polymer-supported catalyst PS-Ru was a highly active and versatile metathesis catalyst (Table 1, Scheme 2). It was applied in self-metathesis of internal alkenes, such as trans-4-decene (7) and methyl oleate (8, methyl cis-9-octadecenoate). Catalyst PS-Ru converted 39% and 45% of the respective alkenes in 4 h, which is possibly even slightly better than for the homogeneous catalyst 1 (36% and 40%, respectively) under similar reaction conditions. After an additional few hours, both reactions reached their
thermodynamic equilibria (~50% conversion), while the selectivity to the expected products was still ≥ 98%. Catalyst PS-Ru was much more productive in the metathesis of internal alkenes (turnover frequency, TOF 54 h\(^{-1}\) and 60 h\(^{-1}\) for 7 and 8, respectively) than catalyst I (TOF 2 h\(^{-1}\) for cis-2-pentene).

![Scheme 2](image)

Scheme 2. Model metathesis reactions.

Catalyst PS-Ru was also tested in RCM of diethyl diallylmalonate (6) and gave 94% conversion in 2 h, which is better than e.g. for a supported homogeneous catalyst reported by Dowden and Savović (43% in 1.5 h).\(^{10^g}\) It is noteworthy that 1 mol % of PS-Ru furnished nearly the same conversion as 5 mol % of PS-Ru (Table 1, entries 3 and 4).

**Table 1. Activity of PS-Ru for metathesis of selected substrates.**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Time [h]</th>
<th>Conversion [%]</th>
<th>Residual Ru content [μg/mg product]</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-4-decene (7)(^{b})</td>
<td>4</td>
<td>39</td>
<td>0.156 ± 0.008</td>
</tr>
<tr>
<td>methyl oleate (8)(^{b})</td>
<td>4</td>
<td>45</td>
<td>n.d.</td>
</tr>
<tr>
<td>diethyl diallylmalonate (6)(^{c})</td>
<td>2</td>
<td>94</td>
<td>3.76 ± 0.12</td>
</tr>
<tr>
<td>diethyl diallylmalonate (6)(^{d})</td>
<td>2</td>
<td>93</td>
<td>0.80 ± 0.04</td>
</tr>
</tbody>
</table>

\(^a\) in CH\(_2\)Cl\(_2\) at rt; \(^b\) ratio alkene: PS-Ru 550:1; \(^c\) 5 mol % of PS-Ru; \(^d\) 1 mol % of PS-Ru.

A major advantage of catalyst immobilisation is that, in the ideal case, the metathesis products are free from contamination of the often difficult to remove ruthenium residues. Using the immobilised catalyst PS-Ru for RCM of diene 6 (100 equiv.), we could reduce the ruthenium level in the product to 0.80 ± 0.04 μg per mg of product. In the case of trans-4-decene (550 equiv.) the product contamination with ruthenium was 0.156 ± 0.008 μg/mg of the product mixture after just a simple catalyst filtration. These values are comparable or lower than those reported in the purification procedures by Maynard and Grubbs\(^{35}\) using a water-soluble, coordinating phosphine and by Paquette and co-workers\(^{36}\) employing lead acetate to remove the ruthenium residues from metathesis products. Barrett and co-workers\(^{10^b}\)
also reported similar contamination levels with their ‘boomerang’ system (−0.50 μg/mg product before chromatographic purification).

We also assessed the recyclability of PS-Ru in RCM of diene 6. The diene was allowed to undergo metathesis for 2 h, then the solution was drained off, the resin washed, and a new batch of a dichloromethane solution of the substrate was added. Table 2 shows the activity of catalyst PS-Ru upon recycling.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion&lt;sup&gt;b&lt;/sup&gt;</td>
<td>94</td>
<td>64</td>
<td>41</td>
<td>37</td>
<td>30</td>
<td>23</td>
</tr>
<tr>
<td>Conversion&lt;sup&gt;c&lt;/sup&gt;</td>
<td>93</td>
<td>47</td>
<td>29</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup> All runs in CH<sub>2</sub>Cl<sub>2</sub> for 2 h at rt using <sup>b</sup> 5 mol % or <sup>c</sup> 1 mol % of PS-Ru.

We observed a substantial decrease in activity after the first cycle, which can be attributed to catalyst leaching (up to 19% ruthenium loss from the resin, as measured by ICP-AAS). Possibly, a part of immobilised catalyst resembled the dinuclear Ru carbene species<sup>30</sup> that upon metathesis were irreversibly liberated to the reaction medium. In the following cycles the catalyst activity declined more slowly and in the sixth cycle still 23% conversion was reached after 2 h. The leaching of ruthenium in these cycles was less than 3% of the initial Ru loading per cycle. Product contamination by ruthenium residues was very low in this instance - less than 0.58 ± 0.02 and 0.124 ± 0.006 μg/mg of product for 5 mol % and 1 mol % of catalyst PS-Ru used, respectively. Although the reuse of 1 mol % PS-Ru was feasible, the activity decreased rapidly upon recycling (29% in third cycle). Still, in this experiment the catalyst was employed more efficiently since the total turnover number of at least 169 in three cycles compares favourably with TON of 58 over six runs in the experiment with 5 mol % of PS-Ru. The recycled catalyst drove the reaction to completion after prolonged reaction time (24 h), demonstrating its long-term stability. The shelf life of catalyst PS-Ru was also good. It was stored for more than six months under a protective atmosphere of nitrogen and did not show any sign of diminished catalytic activity.

2.2.2 Further Development of the Procedure

The first immobilised catalyst PS-Ru, made according to the above-described protocol (Scheme 1), demonstrated several promising features, but also suffered from a few shortcomings. The latter are: a rather low catalyst loading resulting from incomplete conversions in the synthetic steps (overall yield of ~6% of the theoretical value), leaching of the catalyst, especially in the first run of a recycling process, and the rather quick degradation of the supported catalyst upon recycling.

It was also interesting to investigate if application of our immobilisation protocol to the second generation catalyst 3 would yield a supported catalyst of superior properties as compared to supported first generation Grubbs catalyst PS-Ru. We set off to modify the
parameters of the procedure presented in Scheme 1 to give answers to these points. The following major parameters of the protocol could be adjusted: the sort of support, solvent and salts used, use of larger excesses of sodium and silver salts as well as increased amounts of 1 or 3 in order to drive the reactions to a higher conversion. During the course of the protocol optimisation, other factors, previously considered as having only minor influence, were also taken into account. Since the first and second step of the procedure applied to form PS-Ru proceeded almost quantitatively, as judged by mass increase of the resin, we decided to introduce no major modifications in these steps and concentrate on the more troublesome subsequent steps. This notion was further supported by the metal content analysis of the intermediate resins obtained in the preparation of a second batch of immobilised catalyst following the same protocol (with minor modifications). Hence, the efficiency of each step of the procedure could also be assessed by an analytical method. The content of sodium, silver and ruthenium in the resins Na/PS, Ag/PS and Ru/PS prepared on the way to a new batch of supported catalyst (1.50% Ru1-PS) was measured by ICP-AES. The obtained values and theoretical maximum capacities are collected in Table 3.

We can see from Table 3 that the sodium salt and thus the immobilised acid are formed quantitatively and even exceed the calculated theoretical value. Possibly, a part of the excess of the sodium amide salt used in this step did not get washed away from the beads by the solvents employed for rinsing: dichloromethane and hexanes (alternatively, the actual capacity of the starting OH resin is higher or the Na measurement falls outside the confidence limits). These residues should not interfere with the preparation of the immobilised silver salt in the next step, though formation of certain amounts of amide argentate species cannot be excluded.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Theoretical Na/PS [mmol/g]</th>
<th>Theoretical Na [mmol/g]</th>
<th>Theoretical Ag [mmol/g]</th>
<th>Theoretical Ru [mmol/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na/PS</td>
<td>1.087</td>
<td>1.39 ± 0.04</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ag/PS</td>
<td>0.995</td>
<td>0.011 ± 0.004</td>
<td>0.155 ± 0.007</td>
<td>-</td>
</tr>
<tr>
<td>Ru/PS</td>
<td>0.594</td>
<td>-</td>
<td>0.074 ± 0.005</td>
<td>0.148 ± 0.006</td>
</tr>
</tbody>
</table>

Table 3. ICP-AES analysis of resin intermediates to 1.50% Ru1-PS. 

*maximal theoretical capacity calculated based on 1.48 mmol/g loading of the hydroxyethyl PS resin used and the assumption of 100% effectiveness of all the protocol steps; 95% confidence interval reported for analytical data reported.*

In the next step, only circa 10% of the sodium in the supported carboxylate was subsequently replaced by silver. The silver loading of Ag/PS decreased to only ~15% of the maximum theoretical loading highlighting this step as a critical one. The last step towards the immobilised catalyst proceeded in quantitative yield with respect to Ag/PS (within the confidence limit of the results). The stoichiometry of this reaction is close to one silver atom replaced by one ruthenium atom. A remainder of silver was detected in the Ru/PS, but it was only ~5% of the silver loading of the Ag/PS resin. The achieved loading of 1.50 wt%, which

28
is 0.148 mmol/g, constitutes almost 25% of the theoretically achievable loading and it is more than a three-fold increase with respect to the first catalyst resin PS-Ru.

In the course of our research we prepared several new batches of the immobilised catalyst that we screened for their activity for three model reactions: RCM of 6 and self-metathesis of 7 and 8 (Scheme 2). The obtained results are summarised in Table 4. The following naming system of prepared batches of immobilised catalysts is introduced: the numerical part of the tag of each batch relates to the measured ruthenium loading (expressed in wt%) while Ru1-PS and Ru2-PS refer to polymer-supported first (1) and second (3) generation of Grubbs catalyst, respectively. The original catalyst batch PS-Ru described previously is accordingly renamed to 0.35% Ru-PS.

Table 4. Catalytic activity of the various batches of resin-supported complexes 1 and 3 prepared by modification of the original procedure.¹

<table>
<thead>
<tr>
<th>Catalyst batch</th>
<th>Loading [mmol/g]</th>
<th>Catalytic activity⁶ [%]</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>[wt% Ru-PS]</td>
<td>Ru</td>
<td>P</td>
<td>6</td>
</tr>
<tr>
<td>----------------</td>
<td>-------</td>
<td>-----</td>
<td>---</td>
</tr>
<tr>
<td>0.35% Ru-PS</td>
<td>0.035</td>
<td>-</td>
<td>96</td>
</tr>
<tr>
<td>0.49% Ru2-PS</td>
<td>0.048</td>
<td>0.008</td>
<td>13</td>
</tr>
<tr>
<td>0.52% Ru1-PS</td>
<td>0.051</td>
<td>0.074</td>
<td>12</td>
</tr>
<tr>
<td>0.54% Ru1-PS</td>
<td>0.053</td>
<td>0.048</td>
<td>17</td>
</tr>
<tr>
<td>0.64% Ru1-PS</td>
<td>0.063</td>
<td>0.065</td>
<td>4 (12)</td>
</tr>
<tr>
<td>0.82% Ru1-PS</td>
<td>0.081</td>
<td>0.077</td>
<td>83</td>
</tr>
<tr>
<td>0.83% Ru2-PS</td>
<td>0.082</td>
<td>0.036</td>
<td>41</td>
</tr>
<tr>
<td>1.02% Ru1-PS</td>
<td>0.101</td>
<td>0.126</td>
<td>85</td>
</tr>
<tr>
<td>1.36% Ru1-PS</td>
<td>0.135</td>
<td>0.152</td>
<td>20</td>
</tr>
<tr>
<td>1.50% Ru1-PS</td>
<td>0.148</td>
<td>0.210</td>
<td>78</td>
</tr>
<tr>
<td>1.79% Ru1-PS</td>
<td>0.177</td>
<td>0.165</td>
<td>5 (8)</td>
</tr>
<tr>
<td>2.01% Ru1-PS</td>
<td>0.199</td>
<td>0.184</td>
<td>15</td>
</tr>
<tr>
<td>2.22% Ru1-PS</td>
<td>0.220</td>
<td>0.236</td>
<td>36</td>
</tr>
<tr>
<td>2.38% Ru1-PS</td>
<td>0.235</td>
<td>0.249</td>
<td>26</td>
</tr>
<tr>
<td>2.90% Ru1-PS</td>
<td>0.287</td>
<td>0.297</td>
<td>21</td>
</tr>
</tbody>
</table>

¹ a more detailed description of protocol modification can be found in the experimental section;
² 22°C, metathesis of diethyl diallylmalonate, ratio substrate:Ru 100:1, 2 h (24 h); for internal alkenes ratio 550:1, 4 h (24 h); conversion determined by GC; — = not measured.
CHAPTER 2

The ruthenium loading of the new batches of the polymer-supported catalysts 1 and 3 varied from 0.048 mmol/g up to 0.287 mmol/g, that is from 8.2 to 48.4% of the theoretical maximum capacity. The final ruthenium loading and the activity of the immobilised catalyst were strongly dependent on even small changes in the preparation procedure. We obtained the highest increase in ruthenium loading when no alcohol (MeOH or EtOH) was used for rinsing of the resins after each reaction step, especially in the step when the sodium salt of supported carboxylic acid was prepared. Although alcohols seemed to be the solvent of choice for washing away the excess sodium amide salt NaN(SiMe3)2 from the resin, it is possible that reaction of the residue of this salt may form sodium methoxide that could cause cleavage of the ester moiety. The linker was extensively cleaved from the PS beads since we detected the resonances coming from the linker in the 19F NMR spectrum of the alcoholic washings of the resin. We observed a similar problem when we, at an earlier time, attempted the use of alcoholic NaOH for the generation of the immobilised sodium salt. Remarkably, Buchmeiser et al., in a similar protocol, used aqueous NaOH for the silver salt generation and did not report on any detrimental hydrolysis of the ester linkage.32c,d

The cleavage of the linker was unintended, but in our case it played a key role in giving immobilised catalysts of higher activity, albeit at the cost of a lower loading. The supported catalyst 1.02% Ru1-PS and 0.35% Ru-PS prepared using methanol or ethanol as one of the solvents for resin rinsing after each protocol step, exhibited higher activity than all other catalyst batches for which no protic solvent was used. When tetrahydrofuran or dichloromethane was used in place of methanol, no ester bond cleavage was observed and higher Ru loadings were achieved. A similar effect was observed when we omitted the second step of the procedure and prepared the silver salt Ag/Ru directly from the carboxylic acid. Relatively 'highly-loaded' resins 2.22% Ru1-PS and 2.38% Ru1-PS were then obtained.

However, one can notice that the higher the Ru loading of the immobilised catalyst, the worse its catalytic performance was per equimolar amounts of ruthenium used in metathesis; this trend is observed in Table 4 for RCM activity of batches of Ru1-PS. Although the matrix of the support provides for the site isolation by imitating the infinite dilution conditions,33 the increasing density of ruthenium species on the surface and in pores of a PS bead made the contact between the supported Ru carbene species more probable. For example, in the hydroxyethyl resin used in most of the experiments, the density of functional groups on the surface is approximately 0.2-1 per nm² (15-80% functionalisation range, as calculated for following support parameters: 700 m²/g surface area, capacity of 1.5 mmol/g). Considering also the typical pore size for PS of 4-9 nm and a relatively extended linker chain of approximately 1-1.5 nm in length, these interactions are possible. The formation of Ru clusters is often held responsible for catalyst deactivation.37 It could occur during immobilisation procedure and also during catalysis due to recombination reactions of catalytically active, coordinatively unsaturated Ru species. Thus, a faster depletion of the Ru carbenes for the batches of supported catalyst with a relatively high Ru loading is
understandable. The issue of cluster formation on the support of the ruthenium catalysts is also discussed in the EXAFS investigation of the supported catalysts (vide infra).

Table 4 includes also entries that do not follow the above-mentioned 'rule of thumb' due to reasons other than possible cluster formation. When the procedure was performed with the use of non-dried and non-degassed solvents the quality of the prepared catalyst batch 0.64% Ru1-PS suffered significantly in terms of catalytic activity. In spite of a low ruthenium loading, the supported catalyst showed only residual activity in RCM and CM (Table 4). The obvious conclusion is that the immobilising procedure is sensitive towards moisture and oxygen. On the other hand, once prepared, the catalyst was active in metathesis of non-purified olefin in commercial solvent in air, although slightly less than when the reaction was performed under a protective atmosphere. For example, 0.82% Ru1-PS catalyst batch converted 76% and 83% of diethyl diallylmalonate (100 equiv., 2 h), respectively. However, we also observed that prolonged (weeks) exposure to aerobic conditions degraded the activity of the supported catalysts (samples of 1.79% Ru1-PS and 2.90% Ru1-PS used in the EXAFS investigations).

Surprisingly, the second generation Grubbs catalyst 3 immobilised following our protocol, Ru2-PS, performed poorly in RCM of diene 6 when compared to the first generation analogue Ru1-PS. The lower activity must be the effect of the structure of the immobilised Ru carbene species (see later in the text). Even more puzzling is the fact that Ru2-PS is as excellent catalyst in self-metathesis as its homogeneous analogue 3 and much better than Ru1-PS.

Table 4 reports, alongside the loading of ruthenium, also that of phosphorus for the most of supported catalyst batches. The ratio P/Ru for the batches of first generation supported catalyst Ru1-PS varies from 0.83 for 0.82% Ru1-PS to 1.44 for 0.52% Ru1-PS, but the majority of them falls in the range 1.0 ± 0.1 P atom per one Ru atom. This is in contrast with the tentatively proposed linkage mode for PS-Ru, meaning that in PS-Ru and all other Ru1-PS resins the silver carboxylate scavenged not only a chlorine atom, but also a phosphine ligand in the process of immobilisation. Most probably, both a phosphine and a chloride are replaced at once, forming as a by-product the silver chloride - phosphine complex (AgCl*PCy₃) that had also been observed in the synthesis of the dinuclear complexes XV. If so, a bidentate mode of coordination of the carboxylate would be preferred if the pentacoordinated structure of the complex is to be preserved. The monodentate linkage mode must be formed to a much lesser extent than we anticipated in order to account for the P:Ru ratio close to 1:1. In the two relatively highly active resins 1.02% Ru1-PS and 1.50% Ru1-PS this ratio was substantially above one (1.25 and 1.41, respectively), thus more monodentate linkages should be expected in these two catalysts. The formation of AgCl*PCy₃ was not confirmed by ³¹P NMR analysis of the liquor from the last step of the procedure. Instead of the characteristic doublets at ~43 ppm, peaks at 30.1 (not positively identified), 36.7 (excess Grubbs catalyst 1) and 51.4 (most probably phosphine oxide O=PCy₃) in a ~2:2:1 ratio were observed in the preparation of 1.36% Ru1-PS batch.
In the case of the immobilised second generation Grubbs catalyst Ru2-PS data from only two samples are at our disposal: 0.49% Ru2-PS and 0.83% Ru2-PS. The former contained very low amounts of phosphorus (ratio P/Ru of only 0.17), strongly pointing a phosphine-free Ru carbene as the major Ru species present on the resin and thus AgCl*PCy3 formation. The P/Ru ratio of 0.43 for the 0.83% Ru2-PS batch was also rather low, what suggests formation of both AgCl and AgCl*PCy3 in close to equimolar amounts. Hence, the formation of both mono- and bidentate linkage modes of ruthenium to the solid phase and the existence of both phosphine-free and phosphine-bearing Ru carbenes is likely. The latter catalyst batch was also more active since it contained more phosphine moieties that upon dissociation formed the catalytically active species. The other ligands, possibly including species such as a η2-chelating carboxylato ligand, do not dissociate very effectively causing slow initiation. This statement accounts for the poor activity in RCM of Ru2-PS relative to Ru1-PS, but does not explain the excellent CM activity.

To test which of the hypothetical structures is the closest to reality, we have also performed EXAFS measurements of several ruthenium complexes including the carbenes, immobilised catalysts, and samples of spent catalysts. The findings are discussed in the following section of this chapter.

We also measured the silver content of some batches of the supported catalyst Ru-PS and we noticed that the activity correlated to some extent with the amount of residual silver in the final resins. The Ag content in the measured samples was between 0.3% up to 240% (mmol Ag/mmol Ru) with respect to the determined Ru loading. The sample showing the maximum extreme of this range – 1.07% Ru1-PS (not included in Table 4) was completely inactive in RCM and CM with all tested substrates. This was somewhat surprising since this batch was prepared following a similar procedure as for 1.50% Ru1-PS, except that only 0.10 equiv. of catalyst 1 was used in the last step of the protocol and no methanol was used for washing of the resins throughout the procedure. Using only 0.10 equiv. of complex 1 was apparently not sufficient to replace all the silver immobilised on the resin and that completely shut down the metathetic activity of supported carbenes, if any were present on the support. The resins 0.64% Ru1-PS and 1.79% Ru1-PS contained 21 and 33% of Ag with respect to the Ru content and their catalytic activity was also greatly impaired. The best performing batches, such as 0.64% Ru1-PS, 0.83% Ru1-PS or 1.02% Ru1-PS, contained below 1% Ag with respect to Ru. Thus, the content of residual silver present on the beads is clearly an important factor, influencing the catalytic activity of immobilised catalysts Ru-PS.

2.2.2.1 Use of a Non-perfluoro Linker

We were often asked the question if we really have to use a perfluorinated linker for the catalyst immobilisation. Initially, we thought that the complexes would not be formed on such a linker, since attempts to make the homogeneous dinuclear complexes XV with silver salts of non-fluorinated carboxylic acids had failed. Without the experimental proof this statement was ungrounded, therefore we have repeated the procedure leading to the 0.35% Ru-PS catalyst using glutaric anhydride instead of its perfluorinated analogue. Dark-green to brown
resins 2.85% Ru1-PS and 2.15% Ru2-PS were obtained with high ruthenium loading. The two new supported catalysts showed activity in RCM of 100 equiv. of diene 6, giving respectively 9 and 4% conversion after 4 hours. This is very low when compared to the original resins 0.35% Ru-PS or 1.50% Ru1-PS that showed almost full conversion after 4 hours. The ruthenium species that were deposited on these polymers probably consist mainly of metal clusters (rather high loading) and non-carbene species (low activity). The conclusion can be drawn that the findings for the homogeneous complexes did translate to the results obtained for the heterogenised catalysts, at least in these two instances.

2.2.2 Recycling Experiments

We carried out recycling experiments with some of the batches of the immobilised catalysts. The results for better performing catalyst batches are presented in Table 5. Diethyl diallylmalonate (6) was allowed to undergo metathesis using the beads from a batch of catalyst for two hours in dichloromethane, then the reaction mixture was filtered off, washed twice with dichloromethane and hexanes and the liquor tested for RCM conversion by GC. The resin was then reused with a new batch of substrate and solvent added.

We conclude from the recycling experiments that the catalysts with the lower loadings (0.35% Ru-PS and 1.50% Ru1-PS) that had performed well in the previous experiments, also generated the best catalytic results upon recycling. The recycling of the catalyst was feasible in the case of metathesis of diene 6, but the catalyst activity decreased with time, especially after the first run owing to catalyst leaching. The liquor from the first run was usually slightly coloured and we measured a maximum ruthenium leaching of up to ~25% in the case of the resin with the highest Ru loading. We suppose that also certain amounts of dinuclear ruthenium species might have formed and these species would also be released to the solvent during the first metathesis cycle. In the following cycles the activity decrease was less pronounced and catalyst leaching in the second and following cycles was below 3% of the initial loading. Presumably, in these cases the drop-off in activity was primarily a consequence of catalyst decomposition.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>run 1 (%)</th>
<th>run 2 (%)</th>
<th>run 3 (%)</th>
<th>run 4 (%)</th>
<th>run 5 (%)</th>
<th>run 6 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35% Ru-PS</td>
<td>94</td>
<td>64</td>
<td>41</td>
<td>37</td>
<td>30</td>
<td>23</td>
</tr>
<tr>
<td>0.83% Ru2-PS</td>
<td>59</td>
<td>39</td>
<td>28</td>
<td>24</td>
<td>19</td>
<td>16</td>
</tr>
<tr>
<td>1.50% Ru1-PS</td>
<td>83</td>
<td>34</td>
<td>18</td>
<td>15</td>
<td>11</td>
<td>7</td>
</tr>
<tr>
<td>2.22% Ru1-PS</td>
<td>90</td>
<td>53</td>
<td>35</td>
<td>33</td>
<td>21</td>
<td>13</td>
</tr>
</tbody>
</table>

Conditions: 20°C. resin suspension in CH2Cl2 (2.0 ml); molar ratio alkene:[Ru] = 20:1, [Ru] catalyst concentration ~1.0 mM.

We performed the following experiment to assess the catalytic activity of the Ru (carbene) species leaching from 2.22% Ru1-PS resin. After 15 minutes of the RCM experiment with 6 (100 equiv., catalyst concentration ~3.0 mM) half of the solution was moved to a second vessel under nitrogen equipped with a stirring bar taking care that no beads
were transferred. At this point the conversion was 9% by GC. After 4 h the conversion measured for the two experiments was of 89% (mixture containing beads) and only 20% for the mixture with no beads. Thus, the ruthenium species that got detached from the polymer surface did show a residual activity, but they accounted for only circa 10% of the total conversion achieved in the first cycle. Since the leaching of Ru was much lower in the following reuse cycles, we assume that solely the supported catalyst is responsible for the metathesis activity. In line with previous experiments, the second generation catalyst 0.83% Ru2-PS was also found to be less efficient than Ru1-PS with respect to recycling.

2.2.2.3 Exploring the Scope of Supported Catalysts

The best two performing resins with supported first and second generation Grubbs catalysts 1 and 3, respectively 1.02% Ru1-PS and 0.83% Ru2-PS, were tested for their metathesis activity towards several dienes. The results are collected in Table 6.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Conversion [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.02% Ru1-PS</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>85 (2h)</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td>97 (4h)</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>89 (1h)</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>100 (4h)</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td>76 (1h)</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td>96 (24h)</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td>96 (1h)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100 (4h)</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td>99 (1h)</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
<td>76 (1h)</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td>99 (4h)</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td></td>
<td>64 (1h)</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td></td>
<td>99 (22h)</td>
</tr>
</tbody>
</table>

Table 6. Activity of supported catalysts in RCM of various dienes.

Reaction conditions: 22°C, 1.0 mM suspension of [Ru=] in CH2Cl2; molar ratio alkene : [Ru=] = 100:1.
Both generations of supported catalyst 1.02% Ru1-PS and 0.83% Ru2-PS performed well in RCM formation of five- to seven-member rings, bringing the reactions to completion usually within 4 hours. The seven-member ring and the formation of the spiro system (entries 3 and 7) required prolonged reaction times (22-24 hours) to reach the complete conversion. The first generation supported catalyst 1.02% Ru1-PS was more active than the second generation 0.83% Ru2-PS, as it was already observed in RCM of 6. An exception was the metathesis of linalool (entry 6) for which the latter catalyst showed substantially higher activity than the former. The presence of trisubstituted double bond and hydroxyl group evidenced the higher activity and functional group tolerance of the second generation catalyst with respect to the first generation one.

The capability of the supported catalyst to carry out metathesis in solvent-free, and thus more environmentally friendly conditions, was also investigated. Due to the larger amounts of olefin needed to carry out this experiment, readily available and inexpensive 1-octene was used as the test substrate. Before the reaction, the substrate was passed through a column of alumina to remove traces of peroxides that are very detrimental to (ruthenium) carbenes in the low concentration range of Ru species that will be present during the experiments. Catalysts 1.02% Ru1-PS and 0.83% Ru2-PS gave 29% and 6% of conversion to 7-tetradecene after 24 h of exposure to 10,000 equiv. of 1-octene. The obtained turn over numbers (TON) of 2,900 and 600, respectively, are rather low, especially when results obtained in our group for the homogeneous systems are considered (TON at rt of 21,000 for 1 and 95,000 for 3). 38

1-octene is nonetheless an apolar molecule and the beads of polystyrene hardly swell in this medium thereby limiting the accessibility of the supported catalyst to the substrate. Indeed, when a similar experiment was performed using 1:1 v/v 1-octene and dichloromethane mixture, which has a much better swelling potential, 69% and 19% conversion was reached after 24 h, respectively. A respectable TON of 6,900 was recorded for catalyst 1.02% Ru1-PS, but catalyst 0.83% Ru2-PS proved to be disappointing again in terms of its activity (TON 1,900). Possibly, a higher reaction temperature (above 60°C) 38 would improve the numbers for catalyst 0.83% Ru2-PS, but this experiment was not conducted.

2.2.2.4 Modified Silicas as Support

We attempted to use functionalised silica gels as support. Two modified silicas were used: one bearing a 1,2-diolpropoxypropyl function and another one with aminopropyl group, on which the slightly modified standard protocol using complex 1 was applied. We obtained brown, free flowing solids for which the ruthenium content was established at 1.43 and 0.98 wt%, respectively for (Ru1-OCO)2-Si and Ru1-CONH-Si. Unfortunately, their metathesis activity was very low and only 8 and 13% conversion of diethyl diallylmalonate (after 24 h at rt, 1 mol% catalyst) was measured, respectively. One of the reasons of the inactivity might be
incomplete capping of the silanol groups to which complex 1 is sensitive, but by IR the support is deprived of these groups, at least to a major extent. In view of these poor results we must conclude that the silica support used is incompatible with the first generation Grubbs catalyst 1. We did not try to use the much more robust Hoveyda modified metathesis catalysts 4 or 5 that are known for their remarkable stability on silica gel.

2.2.2.5 MAS NMR Studies of Supported Catalysts

As already mentioned, we could obtain the crucial information about the ruthenium loading of the supported catalyst by AES-ICP and AAS-ICP, but these methods do not provide any data on the chemical nature of the immobilised Ru species. The tools attainable for the fast and routine analysis of heterogeneous catalyst are limited and one must resort to special techniques (see the subchapter on EXAFS) not available for every day routine. IR did not provide any clues on catalyst structure since the spectra of ruthenium species failed to display any of the expected (although usually weak) bands attributable to the Ru carbene complex. Actually, we did not observe any relevant changes in the infrared spectrum of 1.50% Ru-PS with respect to Ag/PS resin; probably due to the low loading of Ru species the expected bands failed to emerge. Standard NMR techniques also failed (though for perfluoroglutarate derived PS, Na/PS, and Ag/PS some signals could be observed, especially in the $^{19}$F spectra). Fortunately, a special nanoprobe was at our disposal that allows the implementation of the Magic Angle Spinning (MAS) NMR technique. The mentioned technique provides spectra of reasonable signal-to-noise ratio from the solvent-swollen resins. In particular, the outer shell of the beads that is sufficiently in contact with the solvent gives rise to peaks with diminished line broadening (less restricted motion and thus smaller anisotropic interactions and faster relaxation) as compared to the matrix of the polystyrene bead. Both $^1$H and $^{31}$P MAS spectra were measured for several of the supported catalysts (unfortunately, the $^{19}$F resonance was problematic in the set-up used and could not be measured). In Table 7 the obtained results are summarised.

We could not observe any or only very weak resonances attributable to the carbene proton in the $^1$H NMR for resins performing poorly in metathesis, e. g. 1.79% Ru1-PS, 2.15% Ru1-PS, 2.22% Ru1-PS. In the $^{31}$P NMR several peaks were observed for these batches of supported catalyst highlighting their great inhomogeneity. Nevertheless, the relative highly loaded resin 2.22% Ru1-PS, which revealed many peaks in $^{31}$P spectrum and a weak carbene proton signal, showed a respectable activity in RCM. For the resins that showed a better catalytic activity, distinct though broad (due to the inherently poorer resolution of MAS NMR technique with respect to liquid phase NMR) peak(s) of the carbene proton could be observed and up to three peaks in phosphorus spectrum. The carbene hydrogen signals appeared in a range from 18.5 to 20 ppm and the signals in $^{31}$P NMR in two groups at circa 32 and 52 ppm, usually with one resonance of dominant intensity. The position of the carbene resonance is
quite variable in Ru carbenes depending on minor structural changes, and the values measured for the immobilised catalyst do fit well in the normal range. The assignment of the peaks in $^{31}$P NMR is somewhat more problematic. They are not situated in the range observed for dinuclear complexes XV (43.2-46.6 ppm). For the first made catalyst batch 0.35% Ru-PS, we speculated that the two peaks around 52 ppm come from the Ru carbene linked to the support by one or two carboxylic acid groups. On the other hand, these resonances could arise from species linked in $\eta^1$ or $\eta^2$ fashion by one carboxylic group to the support. With the data available at this point we can not make the hard conclusions on the catalyst structure (see the next section on EXAFS)

<table>
<thead>
<tr>
<th>Catalyst batch</th>
<th>$^1$H MAS NMR data [ppm]</th>
<th>$^{31}$P MAS NMR data [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35% Ru-PS</td>
<td>19.9</td>
<td>52.6 (br, ~70%), 51.2</td>
</tr>
<tr>
<td>0.49% Ru1-PS</td>
<td>19.3 (br, w);</td>
<td>32.7 (vw)</td>
</tr>
<tr>
<td>0.83% Ru2-PS</td>
<td>19.1 (br d)</td>
<td>30.3, 32.5 (~5%)</td>
</tr>
<tr>
<td>0.89% Ru1-PS</td>
<td>20.0 (w)</td>
<td>53.2, 50.8, 37.2 (~80%)</td>
</tr>
<tr>
<td>1.02% Ru1-PS</td>
<td>18.4 (~70%), 17.9</td>
<td>55.2 (~20%), 53.0, 39.0 (~65%),</td>
</tr>
<tr>
<td>1.79% Ru1-PS</td>
<td>No carbene peak detected</td>
<td>58.7 (br, w), 51.7 (w)</td>
</tr>
<tr>
<td>2.15% Ru1-PS</td>
<td>No carbene peak detected</td>
<td>53.4, 50.5, 48.4, 47.4, 45.9, 42.9,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>36.3 (main), 28.5</td>
</tr>
<tr>
<td>2.22% Ru1-PS</td>
<td>20.7 (vw)</td>
<td>63.6 (main), 62.5, 61.4, 60.5,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>57.1, 47.7, 30.1</td>
</tr>
</tbody>
</table>

$br$ = broad, $w$ = weak, $vw$ = very weak

### 2.3 Structure Determination of Immobilised Catalysts by EXAFS

In the heterogeneous catalysis the characterisation of the supported species is usually more complicated than it is for homogeneous catalysis. In order to get insights about the structure of the immobilised catalysts Ru1-PS and Ru2-PS we made use of Extended X-ray Absorption Fine Structure (EXAFS). This technique has proven itself in probing the type of atoms surrounding a metal centre and their distance from the metal, irrespective of the state of aggregation of the sample.\(^{39}\) Both the electronic and geometric local states are determined. An advantage of this X-ray technique with respect to X-ray diffraction (XRD) is that it does not require a long range ordering of atoms (a crystalline material). This is not present in the supported organometallic complexes dealt with in this chapter. To the best of our knowledge, this is the first application of EXAFS in a study of ruthenium carbenes species.

#### 2.3.1 Data Acquisition and Ru K-edges

For the purpose of our study we have measured the absorption spectra of homogeneous ruthenium carbene complexes 1, 3, 5, 9, 10, and the PS immobilised catalysts 0.83% Ru2-PS, 1.02% Ru1-PS, 1.79% Ru1-PS, 2.22% Ru1-PS, as well as 2.90% Ru1-PS.
Ruthenium powder and several simple compounds of ruthenium, that is RuO₂, RuCl₃, RuCl₂(PPh₃)₃, Ru(acac)₃ were measured as reference materials needed for the EXAFS calculations. All samples were measured in the solid state at liquid nitrogen temperature at the Hasylab Synchrotron Laboratory in Hamburg (Germany). Figure 1 shows the Ru K absorption edge of the Ru metal, RuO₂, RuCl₃ and RuCl₂(PPh₃)₃.

Figure 1. Ru K-edge of the reference materials.

The energy of the edge inflection point is mainly determined by the effective oxidation state of the metal – the higher the oxidation state is, the higher the energy required to expel an electron from the K shell into the continuum. The reference ruthenium compounds obeyed this rule. We have found the inflection point of the edge on the spectrum of ruthenium(IV) dioxide – a sample with the highest formal oxidation state of the metal, on the extreme right side at 22130 eV, then ruthenium(III) trichloride at 22128 eV and ruthenium(II) tris(triphenylphosphine) dichloride at 22123 eV. The values are given with respect to the edge position of ruthenium metal, which was set as the reference at 22117 eV, that is also the lowest energy value concurrent to the oxidation state of metal in these materials. The difference between the two latter samples in the edge position (Figure 1) seems to be less pronounced as it is between the two other pairs. However, the first inflection point of the edge of metallic ruthenium is
already positioned at the base of the edge and serves as the reference point. The difference between edge position and formal oxidation state is of circa 3 eV per one unit.

**Figure 2.** Near-edge of Ru K-edge of several ruthenium carbene compounds.

The edges of ruthenium carbenes are preceded by a pre-edge feature (*vide infra*). The energies of the edges are in a range from 22124.6 (for complex 1) to 22125.8 eV (for complex 5, Figure 2). The comparison of the edge positions with the reference compounds suggests that the effective charge of the ruthenium in the carbene complexes discussed in this paper (Grubbs-type and its analogues) is +2 or somewhat above this value. The benzylidene ligand ‘=CHPh’ is electronically neutral (or possibly slightly electron accepting) to the metal centre thus confirming the Fisher carbene (low oxidation state) behaviour of the ruthenium carbenes. In complex 5 the presence of the oxygen atom of the ether moiety coordinated to the Ru centre increases the effective positive charge of the metal to a value close to +3.

### 2.3.2 The Pre-edge Feature

On closer inspection, one can notice that all carbene (both =CHPh carbene and NHC carbene ligand) containing complexes possess a characteristic feature – a pre-edge shoulder positioned for all the carbene-containing materials at ~22114.7 eV. Its nature is not fully clear and a theoretical study of the interacting orbitals would be necessary to shed more light on this issue. We suggest that it originates from the symmetry of the complexes that causes rehybridization of p and d orbitals of the metal and mixing with those of the ligands, similarly to Pd bidentate diphosphine allyl complexes.

A pronounced pre-edge is visible for all complexes that contain the carbene bond. Therefore, the pre-edge can be considered a signature for the metal-carbon bond. We quantified the size of the pre-edge by subtracting the tailing part of the edge from the spectra (Table 8).
Table 8. The position (eV) of the inflexion point of the Ru K-edge and intensity of the pre-edge shoulder (arbitrary units).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Inflection point (eV)</th>
<th>Area [a. u.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>22124.6</td>
<td>0.301</td>
</tr>
<tr>
<td>3</td>
<td>22125.5</td>
<td>0.442</td>
</tr>
<tr>
<td>5</td>
<td>22125.8</td>
<td>0.685</td>
</tr>
<tr>
<td>9</td>
<td>22124.9</td>
<td>0.297</td>
</tr>
<tr>
<td>10</td>
<td>22125.5</td>
<td>0.092</td>
</tr>
<tr>
<td>0.83% Ru2-PS</td>
<td>22125.3</td>
<td>0.362</td>
</tr>
<tr>
<td>1.02% Ru1-PS</td>
<td>22125.0</td>
<td>0.217</td>
</tr>
<tr>
<td>1.79% Ru1-PS</td>
<td>22126.0</td>
<td>0.075</td>
</tr>
<tr>
<td>2.22% Ru1-PS</td>
<td>22125.8</td>
<td>0.143</td>
</tr>
<tr>
<td>2.90% Ru1-PS</td>
<td>22126.0</td>
<td>0.134</td>
</tr>
<tr>
<td>Spent 1</td>
<td>22123.9</td>
<td>0.013</td>
</tr>
<tr>
<td>Spent 3</td>
<td>22124.2</td>
<td>0.119</td>
</tr>
</tbody>
</table>

The pre-edge shoulder was clearly visible for all samples containing ruthenium-carbon bonds and its intensity was higher for complex 3 and 5 (two carbene moieties) than those of 1 and 9 (just benzylidene; Figure 2). Resins with immobilised complex 1 and 3 also followed this trend and the intensity of this absorbance with respect to homogeneous counterparts could be an approximate measure of their purity and catalyst activity. When oxygen is coordinated to the metal (as for 5), the intensity of the pre-edge was much higher than for 3, but for complex 10 it was much lower. Likely, the presence of a bidentate phosphine in 10 constrains the geometry around ruthenium so that its symmetry prevents p-d hybridisation and minimises the pre-edge intensity. The Ru-O bond in 10 is elongated thus the Ru-O interaction is weaker than it is in 5.\(^{43}\) In 5 the overlap of Ru and O orbitals is probably enhanced allowing better orbital mixing and an increase in the pre-edge intensity.

The shoulder was also visible for the immobilised catalysts and its size showed correlation with the activity of the catalyst. In the lower loading resins 1.02% Ru1-PS and 0.83% Ru2-PS spectra the shoulder was relatively large while for the higher loading batches 1.79% Ru1-PS, 2.22% Ru1-PS and 2.90% Ru1-PS the pre-edge feature was substantially lower. This is in line with their lower activity in metathesis with respect to the two former resins. The 1.79% Ru1-PS catalyst, which showed only residual activity, also displayed only a minuscule pre-edge peak (Table 8 and Figure 3). The edge position for resins 1.02% Ru1-PS and 0.83% Ru2-PS was similar to its homogeneous counterparts 1 and 3, but for the other three resins the edge position was shifted to circa 21226 eV, thus towards a higher oxidation state of metal (closer to +3). Since these batches of immobilised catalyst showed the presence of several species in \(^{31}\)P MAS NMR (at relatively higher ppm values) the observed oxidation state of the metal is an average of all the species present. Nevertheless, this fact points out the presence of a substantial amount of ruthenium species in higher oxidation...
states, for example Ru(IV), that are not recognised as metathesis active species. Interestingly, in the samples of spent catalyst 1 and 3 the position of the inflection point of the edge was at somewhat lower energy values (~21224 eV) suggesting a decrease in the average oxidation state (reduction) of the Ru present in the spent catalyst.

Figure 3. Near-edge of Ru K-edge of several batches of immobilised ruthenium carbene complexes.

2.3.3 Structural Parameters Extracted from EXAFS Spectra

Having the K-edge absorption data in hand, the EXAFS spectra were extracted using the XDAP data analysis code. After Fourier transformation of the EXAFS data, spectra were fitted in k⁰ or k¹ as well as in k³ space to the experimental spectrum. The plots below (Figure 4 and 5) exemplify the EXAFS data and Fourier transformed data for complexes 1 and 3.

Figure 4. Ru K-edge k³-weighted EXAFS and Fourier transform of complex 1.

The quality of the experimental data was excellent and we could obtain accurate values of interatomic distances that correlated well with the crystal structure of these complexes. The distances found by EXAFS spectroscopy between the metal centre and the two heavy scatterers – phosphorus and chlorine are close to bond lengths determined by crystallographic analysis. The discrepancy usually was not exceeding 0.05 Å as compared to the X-ray
structures of an analogue of complex 1$^{3a}$ and complex 3.$^{45}$ The distances between ruthenium and the carbene carbons, being a light scatterer, proved to be more problematic. The distances for benzyldiene carbene could not be fitted properly because of its small contribution to the absorption spectrum with respect to the heavier scatterers. We solved this problem by assigning the arbitrary value for Ru=C bond reported for the crystal structures of Ru carbenes. The contribution of the carbon atom of NHC carbene in 3 could then be extracted and calculated with an acceptable disorder parameter (Debye-Waller factor).

Figure 5. Ru K-edge $k^3$-weighted EXAFS and Fourier transform of complex 3.

In the same manner we obtained Fourier transformed data of immobilised complexes Ru1-PS and Ru2-PS (Figure 6) and, after optimisation, we obtained good matches of the fits with the experimental data. The results of the best fits are summarised in Table 9. Thus, according to the data provided by EXAFS, the coordination sphere around the ruthenium centre in the immobilised first generation catalyst batch 1.02% Ru1-PS consists, in addition to the presumed carbene carbon atom, of two heavy scatterers, a phosphorus and a chlorine, and of two oxygen atoms. The latter fact means that a phosphine and a chlorine atom are replaced by a chelating carboxylic group in this batch of immobilised catalyst. The calculated distance of 2.09 Å is somewhat shorter than the typical C-O distance for chelating COO groups (2.172 Å in complex XV), but still within the expected accuracy limits of the method. For the catalyst batch 0.83% Ru2-PS the calculation of the coordination sphere was somewhat more complicated since not integer coordination numbers were obtained in the best fit. Minor (up to 0.2 - 0.3) alteration of these numbers did not cause a dramatic deterioration of the fit goodness. This suggests that not a single Ru species was present on the support.

Figure 6. Ru K-edge $k^3$-weighted Fourier transforms of immobilised catalysts 1.02% Ru1-PS and 0.83% Ru2-PS.
As a result, the error margin of the values obtained for the dominant species increased somewhat and the separation of individual contribution for the light scatterers was not always possible, especially for the alkylidene carbon. The sample of 0.83% Ru2-PS contained at least two major Ru species that could account for the values found by EXAFS: one with 1 Cl, 1 P, 1 O and two C's of both carbenes around Ru centre and the other one in which the P atom is replaced by an additional O atom from the chelating carboxylate group. The calculated bond lengths deviated somewhat more from the crystallographic data for 1, 3 and XV, but were still chemically sound. The lower accuracy of the obtained data is not surprising when taking into account the presence of more than one peak in the phosphorus NMR spectra of both batches of the resins arising from several Ru species (sample inhomogeneity).

Table 9. The data of best fits obtained for a selection of homogeneous and supported complexes.

<table>
<thead>
<tr>
<th>Shell</th>
<th>Coordination number N</th>
<th>Interatomic distance R, [Å]</th>
<th>Debye-Waller factor Δσ², [Å²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>2.0</td>
<td>2.36</td>
<td>-0.002</td>
</tr>
<tr>
<td>P</td>
<td>2.0</td>
<td>2.43</td>
<td>0.002</td>
</tr>
<tr>
<td>C</td>
<td>0.9</td>
<td>1.85</td>
<td>0.010</td>
</tr>
<tr>
<td>Ru(=CHPh)Cl2(PCy3)2 (1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.9</td>
<td>1.85</td>
<td>0.011</td>
</tr>
<tr>
<td>C</td>
<td>1.0</td>
<td>2.07</td>
<td>0.002</td>
</tr>
<tr>
<td>Cl</td>
<td>2.0</td>
<td>2.35</td>
<td>-0.004</td>
</tr>
<tr>
<td>P</td>
<td>1.0</td>
<td>2.47</td>
<td>-0.001</td>
</tr>
<tr>
<td>Ru(=CHR)Cl2(PCy3)(H2IMes) (3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.02% Ru1-PS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.9</td>
<td>1.85</td>
<td>0.006</td>
</tr>
<tr>
<td>O</td>
<td>2.1</td>
<td>2.09</td>
<td>-0.005</td>
</tr>
<tr>
<td>Cl</td>
<td>1.0</td>
<td>2.33</td>
<td>-0.006</td>
</tr>
<tr>
<td>P</td>
<td>1.0</td>
<td>2.45</td>
<td>0.000</td>
</tr>
<tr>
<td>0.83% Ru2-PS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.6</td>
<td>1.85</td>
<td>0.005</td>
</tr>
<tr>
<td>C/O</td>
<td>2.5</td>
<td>2.05</td>
<td>0.008</td>
</tr>
<tr>
<td>Cl</td>
<td>1.2</td>
<td>2.34</td>
<td>-0.003</td>
</tr>
<tr>
<td>P</td>
<td>0.8</td>
<td>2.47</td>
<td>0.000</td>
</tr>
</tbody>
</table>

In the case of catalyst batches with a higher ruthenium loading, no reasonable fits could be obtained. The calculated coordination numbers for the ligands were often non-integer, the distances not reliable and the goodness of fit unsatisfactory. The presence of certain amounts of Ru-Ru clusters could be detected for the highest loading resin 2.90% Ru1-PS demonstrating the clustering of Ru carbenes by the high loading. Since EXAFS is a bulk technique, the average of all species is determined and problematic fitting of the experimental data is usually a sign of the inhomogeneity of the sample. This observation was also confirmed by MAS NMR of the swollen 2.22% Ru1-PS batch, especially in 31P NMR spectrum, where several resonances were detected between 47 and 64 ppm. For the resins with lower Ru loading usually one dominant resonance in phosphorus spectrum was evidenced and the fitting procedure of EXAFS experimental data provided acceptable results.
We also measured the EXAFS spectrum of the samples of decomposed catalysts 1 and 3 as well as a sample of the spent resin 1.02% Ru1-PS. Both homogeneous catalysts were subjected to a large excess of 1-octene until their catalytic activity ceased and the solid residue was recovered. The spent catalyst resin was obtained after reaction with 550 equivalents of trans-4-decene. In the spectrum of the decomposed complex 1 almost no carbene Ru=C bond was present as the pre-edge shoulder had disappeared almost completely. For the decomposed catalyst 3, the shoulder was still present, although much smaller than for 1 and 3. The residual shoulder presumably originates from the presence of Ru-C bond of imidazolium carbene that survives the metathesis reaction conditions. In the Fourier transformed data of the decomposed complex 1 we observed the presence of Ru-Ru bonds (coordination number $N = \sim 0.5$) evidencing a bimolecular pathway for its decomposition, at least for a part of the catalyst. In the decomposition products of the second generation Grubbs catalyst 3 no clearly visible Ru clusters were observed. Regretfully, in the case of spent immobilised catalyst it was impossible to draw hard conclusion based on the EXAFS measurements due to a very troublesome fitting of the data indicating a complex mixture of species.

2.3.4 Discussion of Possible Structures of Immobilised Catalysts

As the immobilisation procedure should give an analogous product as XV, we expected that ruthenium in the first generation Grubb's catalyst 1 will be attached to the resin in one of the following, hypothetical modes A-D (limited to interactions with one linker moiety). Possibly, more than one coordination mode can exist in a sample.

![Diagram of structures A-D](image)

Our anticipation was that the silver carboxylate would displace one of the chlorine atoms leading to immobilised species A and silver chloride. We had proposed this structure in the disclosure of preliminary results on the subject, in spite of limited structural experimental data for 0.35% Ru-PS to support this hypothesis. Since the P/Ru ratio measured for the later prepared batches of the immobilised catalysts Ru1-PS was close to one, we now must discount the structures A and C. The six-coordinate structure D is rejected based on EXAFS that accounts only for two heavy scatterer atoms - a chlorine and a phosphorus. The remaining structure B is well corroborated by EXAFS fitting results as a plausible structure. Therefore, we conclude that the first generation Grubbs catalyst reacts with supported silver carboxylate forming chiefly immobilised species B together with AgCl*PCy$_3$ complex formation as a by-product.
We can propose similar coordination modes also for the second generation Grubbs catalyst 3 with an additional, hypothetical structure H in which a phosphine instead of a chlorine is replaced.

The P/Ru ratio determined for the two Ru2-PS catalyst batches was well below one (0.17 and 0.43) and, consequently, formation of AgCl*PCy3 most probably occurs as a major immobilisation pathway. We failed to detect this species in the reaction liquor, instead, we observed phosphine oxide that might originate from this complex upon oxidation by air. Structure J would account for this observation. Structure E is the most likely to account for the residual amounts of phosphorus in the immobilised resins Ru2-PS. Six-coordinate structure G cannot be excluded, however the fate of the silver cation is unclear in this case. Structures F and H are rather improbable since, respectively, AgCl2 formation would require a redox process to occur and an AgPCy3 entity has not yet been reported.

In terms of an explanation for the lower RCM reactivity of Ru2-PS catalyst, the structure J does not possess sufficiently labile ligands thus impeding the formation of the active species needed for alkene metathesis. Possibly, the steric factors have also influence disfavouring the backbiting of the other double bond of the diene to form the ring closed product. The CM reaction would not suffer from this influence and thus proceed quickly, even with a limited number of active sites. The results of Buchmeiser and co-workers, obtained using the same procedure to immobilise the phosphate-free catalyst 5, showed that a well-behaved system is obtained in which only AgCl formation occurs. No problems with the scavenging of two ligands are found as we did for the immobilisation of complexes 1 and 3. The robustness of complex 5 is also an advantage. Regretfully, we did not employ our protocol to 5 to perceive how this supported catalyst would behave in our hands.

2.4 Conclusions

In conclusion, we have reported a new approach for permanent immobilisation of ruthenium carbene complexes on a polymeric support using carboxylate ligands as the linking groups. The supported catalyst performed well in the self-metathesis of internal alkenes and RCM. It was easily separated from the metathesis products and reused without the addition of any stabilising agents, although some leaching and deterioration of the catalyst was observed.
Resin-immobilised ruthenium carbenes 1 and 3 were prepared using the original or modified protocol with metal loading on the support varying from 0.35 to 2.90 wt% of ruthenium. The supported catalyst 3 showed unexpectedly diminished activity in RCM, but was still a superior catalyst in CM of internal alkenes. With increasing ruthenium loading of the supported catalyst inferior activity was observed due to formation of unidentified, metathesis-inactive Ru complexes and clusters. The supported catalyst can be recycled, although upon recycling the activity decreases. In the first cycle this was caused by catalyst leaching and in the following cycles mainly by catalyst decomposition. Product contamination with ruthenium residues was relatively low, facilitating the work-up and purification of the metathesis products. Ru K edge EXAFS measurements elucidated the binding mode of ruthenium to the support. In the batches of catalyst Ru1-PS with a low metal loading the binding occurred via a chelating carboxylic group of one linker unit, which replaced a chlorine and a phosphine atom. In the case of immobilised complex 3 both chelating and monodentate tethers are needed to account for the experimental results.

2.5 Experimental Section

2.5.1 Materials and Techniques

Solvents (hexanes, tetrahydrofuran, dichloromethane, methanol, ethanol) were dried according to standard procedures. The polymeric and siliceous supports were used as received and degassed prior to derivatisation. The list of resins and silicas employed in the procedures follows:

- hydroxyethyl PS resin (PS-(CH$_2$)$_2$OH, 1% cross-linked DVB, 75-150 μm (100-200 mesh), batch capacity 1.48 mmol/g, RAPP Polymere; kindly provided by Floris Rutjes and Wim Meester);
- hydroxymethyl PS (batch capacity 0.87 mmol/g, 75-150 μm, polymer matrix is copoly(styrene-1% DVB), NovaBioChem);
- $p$-benzyloxybenzyl alcohol resin (Wang resin, 100-200 mesh, copoly(styrene-1% DVB), batch capacity 1.1 mmol/g, NovaBioChem);
- ArgoPore™.OH (benzyl alcohol, macroporous polymer-bound, bead size 60-140 mesh, batch capacity 0.68 mmol/g, Argonaut/Aldrich);
- 3-aminopropyl-functionalised silica gel (batch capacity 0.95 mmol/g, particle size 40-63 μm, Aldrich);
- 2,3-diolpropoxypropyl-functionalised (diol-3) silica gel (batch capacity ~1.1 mmol/g, particle size 40-63 μm, Acros).

Hexafluoroglutaric anhydride (ABCR), sodium bis(trimethylsilyl)amide (Aldrich), silver nitrate and triflate (Acros) were used as received. Diethyl diallylmalonate (Aldrich), methyl oleate (Fluka) and trans-4-decene (Fluka) were passed through a column of activated alumina and degassed prior to use. Ru(=CHPh)Cl$_2$(PCy$_3$)$_2$ (1) was synthesised following the literature procedure or purchased from Strem or Fluka. All other ruthenium carbenes were synthesised according to literature procedures. Unless stated otherwise, all manipulations were performed under an atmosphere of purified nitrogen using standard Schlenk techniques. The following instruments were used: Inova 500 spectrometer equipped with a nanoprobe for MAS NMR, Mercury 300 spectrometer for standard NMR, Carlo Erba 8000$^{\text{Top}}$ (DB-5 column from J&W Scientific) for GC analyses. IR spectra of the resins ground with KBr were measured using a DRIFT module. The ruthenium and phosphorus content in batches of
immobilised catalysts Ru1-PS and Ru2-PS and in metathesis products were determined by ICP-AES or ICP-AAS measurements.

2.5.2 Synthetic Routes to Immobilised Catalysts

**Step (a):** Hydroxyethyl PS resin (1.59 g, 2.36 mmol) was swollen in dry tetrahydrofuran (15 mL) and gently stirred with hexafluoroglutaric anhydride (11, 0.35 mL, 2.60 mmol, 1.1 equiv.) for 1.5 hour under a nitrogen atmosphere. The liquor was drained, while the resin was alternately washed four times with dichloromethane and ethanol, then with ether, and dried under vacuum for 1 h. Bright yellow beads were obtained. Selected spectroscopic data: IR (KBr): 1780 cm⁻¹ (COOR and COOH). ¹⁹F NMR (CH₂Cl₂/MeOH): -119 ppm (br), -125 ppm (br).

**Step (b):** Next, to a suspension of the resin in dry tetrahydrofuran (10 mL) a solution of 1.1 equiv. of NaN(SiMe₃)₂ (12) in the same solvent (10 mL) was added. The reaction mixture was stirred at room temperature for 2 h and worked-up as described above. Yellow beads were obtained. Selected spectroscopic data: IR (KBr): 1777 cm⁻¹ (COOR), 1678 cm⁻¹ (COONa). ¹⁹F NMR (CH₂Cl₂/MeOH): -118 ppm (br), -119 ppm (br), -126 ppm (br).

**Step (c):** AgNO₃ (1.1 equiv.) was dissolved in ethanol (20 mL) and added to the resin suspended in tetrahydrofuran (10 mL). This mixture was stirred at room temperature for 12 h, while protected against direct exposure to light. Within this period of time the solid became light brown. It was worked-up in the usual manner. IR (KBr): 1665 cm⁻¹ (COOAg).

**Step (d):** Finally, the functionalised resin from step (c) and the ruthenium carbene 1 (0.5 equiv.) were mixed in a Schlenk tube. Dry hexanes (10 mL) and dry THF (10 mL) were added and the suspension was stirred overnight (15 h) at room temperature. The liquid phase was still purple the next day. The resin was filtered off and repeatedly washed with portions of dichloromethane and methanol, until the washings were colourless, and dried under vacuum, giving dark-brown beads of 0.35% Ru-PS. IR (KBr): no particular changes in the spectrum with respect to the previous resin.

List of modification to the original procedure:

- 0.49% Ru₂-PS: a) as for 2.38% Ru₁-PS; b) as for 0.35% Ru₁-PS; d) as for 0.35% Ru₁-PS, but with 0.13 equiv. of complex 3.
- 0.52% Ru₁-PS: a) as for 1.79% Ru₁-PS; b) as for 2.38% Ru₁-PS; c) as for 1.50% Ru₁-PS, but using silver triflate and no MeOH wash; d) as for 1.50% Ru₁-PS, but with 0.5 equiv. 1.
- 0.54% Ru₁-PS: a) procedure as for 0.35% Ru₁-PS, but applied to Wang resin; b) as for 1.50% Ru₁-PS; c)-d) as for 0.35% Ru₁-PS, but with 0.3 equiv. 1 in DCM.
- 0.64% Ru₁-PS: a) as for 2.01% Ru₁-PS; b)-d) as for 0.35% Ru₁-PS; in all steps commercial, non-dried solvents used.
- 0.82% Ru₁-PS: a) as for 2.38% Ru₁-PS; b) as for 0.35% Ru₁-PS, but wash with DCM/hexanes; c) as for 0.35% Ru₁-PS; d) as for 0.35% Ru₁-PS, but with 0.3 equiv. 1.
- 0.83% Ru₂-PS: a)-d) as for 1.02% Ru₁-PS, but with complex 3 used in the last step.
- 1.02% Ru₁-PS: a)-d) procedure as for 0.35% Ru₁-PS repeated with 0.25 equiv. 1 used in the last step.
- 1.36% Ru₁-PS: a)-b) as for 0.52% Ru₁-PS; c) as for 0.35% Ru₁-PS, but with 3 equiv. AgNO₃ in EtOH; d) as for 1.50% Ru₁-PS.
- 1.50% Ru₁-PS: a) 2.0 equiv. 11, resin wash DCM/hexanes; b) 2.0 equiv. 12, work-up DCM/hexanes; c) 3 equiv. AgNO₃, 2.5 h, work-up DCM/MeOH/hexanes; d) 1.1 equiv. 1 in THF/DCM, 8 h, resin wash with DCM/hexanes.
1.79% **Ru1-PS**: a) procedure as for 2.38% **Ru1-PS** applied to macroporous ArgoPore™-OH resin; b) as for 0.35% **Ru-PS** in THF/DCM; c) as for 0.35% **Ru-PS**, but in EtOH and with ~10 equiv. NH₄OH; d) as for 2.38% **Ru1-PS**.

2.01% **Ru1-PS**: a) procedure as for 2.38% **Ru1-PS** applied to hydroxymethyl PS resin; b) as for 0.35% **Ru-PS** in THF/DCM; c) as for 0.35% **Ru-PS**, but with ~10 equiv. NH₄OH; d) as for 0.35% **Ru-PS**, but reaction in THF/DCM.

2.22% **Ru1-PS**: a)-b) as for 2.38% **Ru1-PS**; c) 2.0 equiv. AgNO₃, 3 h, work-up DCM/hexanes; d) 0.4 equiv. 1 in THF, 2 h, resin wash THF/pentane/DCM/MeCN.

2.38% **Ru1-PS**: a) 1.5 equiv. 11, resin wash DCM/hexanes; b) 0 equiv. 12; c) 2.0 equiv. AgNO₃ in MeCN/THF, 2.5 h, work-up DCM/MeCN; d) 1.5 equiv. 1 in THF, 2.5 h, resin wash THF/pentane/DCM.

2.90% **Ru1-PS**: a)-b) as 0.35% **Ru-PS**, but with hexanes instead of EtOH used for rinsing; c) 1.2 equiv. AgNO₃ in THF/DCM, rinsed with THF/DCM/hexanes; d) 0.8 equiv. 1 in DCM/hexanes for 5 h, wash with THF/DCM/hexanes.

**Catalysts supported using a non-perfluorinated linker:**

2.85% **Ru1-PS**: a) resin as in 0.35% **Ru-PS** with glutaric anhydride (2 equiv.) and dimethylaminopyridine (1 equiv.) in DCM for 24 h, rinsed with DCM/MeOH; b) as for 1.50% **Ru1-PS**; c) as for 0.35% **Ru1-PS**; d) as for 0.35% **Ru-PS** with 0.75 equiv. 1 used.

2.15% **Ru2-PS**: a)-d) as for 2.85% **Ru1-PS**, but with 0.5 equiv. 3 used in the last step.

**Silica-supported catalyst:**

1.43% (Ru1-OCO)₂-Si: a) as for 1.50% **Ru1-PS** using diol-3 functionalised silica gel, wash with THF; b) 2.50 equiv. of 12, wash with THF; c) 2.2 equiv. AgNO₃ in MeOH, wash MeOH/THF; d) 0.5 equiv. 1 in DCM, wash with DCM.

0.98% **Ru1-CNH-Si**: a) as for 1.50% **Ru1-PS** using 3-aminopropyl functionalised silica gel, wash with THF; b) 1.25 equiv. of 12, wash with THF; c) 1.1 equiv. AgNO₃ in MeOH, wash MeOH/THF; d) 1 equiv. 1 in DCM, wash with DCM.

**2.5.3 Metathesis Experiments**

**RCM of diethyl diallylmalonate**: In a typical experiment the alkene (5 μL, 0.020 mmol) was added to 29.5 mg (1.02 μmol Ru, 5 mol%) of supported catalyst **Ru-PS** suspended in CH₂Cl₂ (1.0 mL). The reaction mixture was stirred at room temperature. The progress of the reaction was followed by GC. In the reaction with 1 mol% of **Ru-PS** the amount of the diene was increased fivefold.

Recycling experiments were conducted as follows: after 2 h reaction time, the solution was carefully drained off by cannula filtration, the resin was alternately washed twice with a good swelling solvent (dichloromethane) and a poor swelling solvent (ethanol). Then a new batch of a dichloromethane solution of the diene was added.

**Self-metathesis of internal alkenes**: In a typical experiment, trans-4-decene (0.135 mL, 0.715 mmol, 550 equiv.) was added to a suspension of **Ru-PS** (37.5 mg, 1.30 μmol Ru) in dichloromethane (1.0 mL). The reaction progress was monitored by GC sampling.

**2.5.4 EXAFS Experimental Procedures**

Ru K-edge absorption spectra were taken at the station X1.1 of the Hamburger Synchrotronstrahlungs labor (HASYLAB) at DESY (Hamburg, Germany), using a Si(311) double
crystal monochromator. The measurements were performed in transmission mode using ion chambers filled with argon to have a $\mu x$ of 20 and 80% in the first and second ionisation chamber, respectively. The monochromator was detuned to 50% of its maximum intensity at the Ru K-edge to minimise the presence of higher harmonics. In order to minimise high and low frequency noise the counting time per data point was 1000 ms and three or four scans were averaged. A ruthenium powder sample mounted between adhesive tape windows was used for calibration of the edge position. Absorption spectra were calibrated at the position of the main-edge jump of ruthenium at 22117 eV.\(^1\) The sample was pressed into a self-supporting wafer and mounted in an \textit{in situ} EXAFS cell equipped with beryllium windows.\(^2\) The thickness of the wafer was chosen to give an absorption ($\mu x$) of $\sim$2.5 at the absorption edge for optimal signal-to-noise ratio. To prevent thickness effects for the highly loaded samples $\mu x$ was set to yield a step of 1.0 in absorption in the edge region. All samples were measured in the solid state at liquid nitrogen temperature. Typically, about 20 mg of homogeneous complex was used, accompanied with 40 mg of boron nitride (BN) to have a manageable amount of material; in the case of heterogeneous catalysts 50-100 mg of resin was mounted with no BN used.

Data reduction and data analysis were performed with the XDAP code developed by Vaarkamp \textit{et al.}\(^3\) The standard procedures were used to extract the EXAFS data from the measured absorption spectra. The pre-edge was subtracted using a modified Victoreen\(^4\) and the background was subtracted using cubic spline routines.\(^5\) Normalisation was performed by dividing the data by the height of the absorption edge at 50 eV. Averaging 3 or 4 scans of the individual data after background subtraction and normalisation gave the final EXAFS function.

Phase shifts and backscattering amplitudes from reference compounds were used to calculate the EXAFS contributions: RuO$_2$ for the Ru–O and Ru–C contributions, RuCl$_3$ for Ru–Cl contribution and Ru powder for the Ru–Ru contribution. The Ru–P contribution was calculated using FEFF8 code program.\(^6\) The fit parameters were determined by multiple shell fitting in R-space usually in a range 1.00-3.00 Å.\(^7\) The backscatterers were identified by applying the difference file technique after phase-corrected Fourier transformations.\(^8\) The final fit parameters were obtained after a full optimisation of all parameters in $k^0$ or $k^1$ as well as $k^2$ weighting in the Fourier transformations, usually in a range of 4.00-14.00 Å$^{-1}$. The accuracy in the fit parameters were estimated to be 20% in co-ordination number (N), 5% in distance (r), 20% in Debye–Waller factor ($\Delta \sigma^2$), and 10% in inner potential correction ($\Delta E_0$).

2.6 Acknowledgements and References

We thank Ron Barendregt for technical support. The EXAFS part of this work was financially supported by the IHP-Contract HPRI-CT-1999-00040 of the European Commission and experimentally assisted by Moniek Tromp, Jeroen A. van Bokhoven and Maarten Dinger. J. A. v. B. is also thanked for help in EXAFS data analysis and discussion thereof. Jaap Elgersma and Leo Hoitinga are thanked for ICP-AES and ICP-AAS measurements of supported catalysts, Jan Meine Ernsting and Jan Geenevasen for help with the nanoprobe for MAS NMR.


PREPARATION, APPLICATION AND EXAFS STRUCTURAL STUDIES OF NEW POLYSTYRENE-SUPPORTED RUTHENIUM CARBENE CATALYSTS FOR ALKENE METATHESIS


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Chapter 2