thesis. In addition to the advantages discussed above, it is envisaged that this catalyst will find application in cases where the limited solubility of a substrate in organic solvents necessitates that the metathesis be carried out in aqueous media, a topic of current interest.[19] Full experimental details can be found in the Supporting Information.

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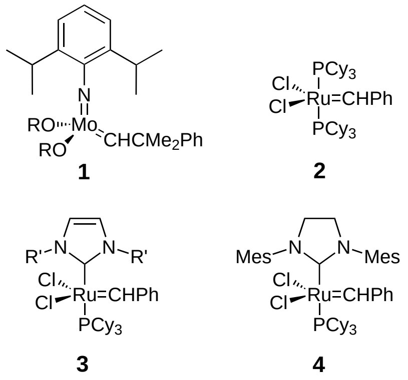
Synthesis and Application of a Permanently Immobilized Olefin-Metathesis Catalyst[**]

Stephan C. Schürer, Simon Gessler, Nicole Buschmann, and Siegfried Blechert[*]

Olefin metathesis has made a tremendous impact in synthetic organic chemistry[1] as a result of the availability of well-defined catalysts like **1**[2] and **2**[3](Scheme 1). The potential of ring-closing metathesis (RCM) for the construction of small, medium, and large rings has fully been recognized[1] and



Scheme 1. Metathesis catalysts. R = $CMe(CF_3)_2$; R' = *i*Pr, Cy, Mes; Cy = cyclohexyl; Mes = 2,4,6-$Me_3C_6H_2$.

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several applications of catalysts **1** and **2** to cross metathesis,[4] ring-opening metathesis,[5] and rearrangement reactions[6] have been published.

Catalyst **2** in particular enjoys high popularity because of its stability and tolerance towards functional groups. Nevertheless disadvantages remain associated with the use of homogeneous catalysts. After completion of a metathesis reaction the removal of the colored ruthenium complexes from the reaction products is often problematic and residual ruthenium may cause problems such as olefin isomerization, decomposition of the products over time, and increased toxicity of the final material. In addition to the separation of products and catalyst,[7] the recovery of the ruthenium catalyst has become a subject of interest.[8] Immobilization of a metathesis catalyst on a solid support would allow the catalyst to be separated from the reaction products simply and efficiently by filtration. Grubbs and Nguyen introduced phosphane ligands to attach ruthenium catalysts onto a polystryrene matrix, these systems have been used in living polymerization.[9] Barrett and coworkers have reported a "boomerang" catalyst, which was obtained by the reaction of **2** with vinyl polystyrene.[10] This precatalyst becomes soluble during the course of the reaction and can be recaptured by the polymer.

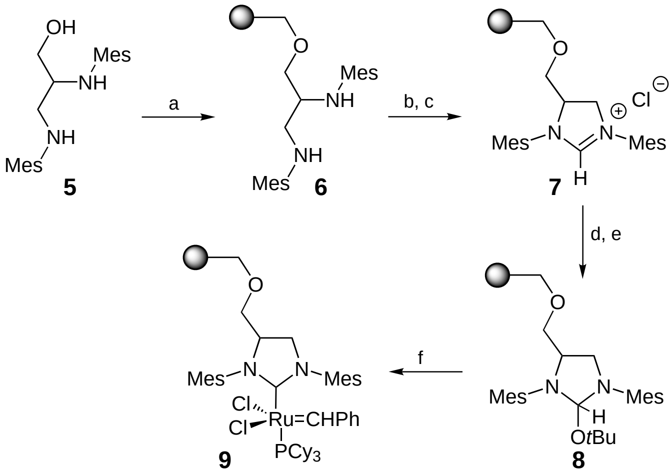
The need for further developments in this area led us to try an alternative approach to efficiently immobilize a metathesis catalyst, which is described herein. The potential of this catalyst is demonstrated by its application to different types of metathesis reactions.

Recently, new ruthenium-based alkylidene catalysts **3**[11] and **4**[12] bearing N-heterocyclic carbene (NHC) ligands have been reported (Scheme 1). These catalysts show an increased metathesis activity similar to that of **1** but have also retained the remarkable air and water stability of **2**.[12, 13]

The N-heterocyclic carbene ligands are stronger Lewis bases than the phosphane ligands, thus, the dissociation of a phosphane ligand in **3** or **4** has been proposed as initial step in the mechanism of olefin metathesis, which leaves the NHC ligand bound to the ruthenium center.[11a] The saturated 4,5-dihydroimidazole carbene (in complex **4**) shows even higher Lewis basicity than the imidazole carbene (in complex **3**). Therefore a permanently immobilized and highly active metathesis catalyst should result if **4** was attached to a polymeric support by its N-heterocyclic carbene ligand.

Such a support-bound ruthenium complex should be accessible from **2** by ligand exchange, similar to the synthesis of the soluble catalyst **4**.[12a] This approach requires the synthesis of a suitably immobilized ligand precursor, which could be obtained from the diamine **5** (see Scheme 2). Compound **5** can be prepared from 2,3-dibromo-1-propanol and 2,4,6-trimethylaniline.[14] After deprotonation of the hydroxy group compound **5** was attached to Merrifield polystyrene (1 % divinyl benzene (DVB)) by an ether linkage to quantitatively yield **6** (Scheme 2) as confirmed by elemental analysis. Compound **6** was then cyclized under acidic conditions, and anion exchange yielded the support-bound 3,4-dimesityl-4,5-dihydroimidazolium chloride **7**.

After treatment with TMSOTf/lutidine (TMSOTf = $Me_3SiOSO_2CF_3$) **7** was converted into the corresponding 2-*tert*-butoxy-4,5-dihydroimidazoline **8** (Scheme 2), obtained as an orange resin. 2-Alkoxy-imidazolidines undergo α-elimination at elevated temperatures and can thus be regarded as protected carbenes.[15] Therefore, in analogy to the synthesis of the soluble complex **4**,[12a] **8** was deprotected in situ in the presence of **2**, yielding the desired support-bound 1,3-dimesityl-4,5-dihydroimidazoline-2-ylide ruthenium complex **9** as a pinkish brown material. This four-step synthesis from **5** is particularly simple, because all the steps are performed on the solid support. Polymer-bound catalyst **9** is obtained with a loading level between 0.14 and 0.40 $mmol\,g^{-1}$ (determined by elemental analysis and mass increase) depending on the initial loading level of the Merrifield resin employed (0.50 to 0.90 $mmol\,g^{-1}$).

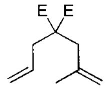
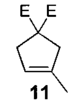
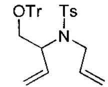
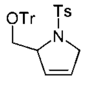
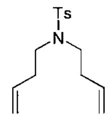
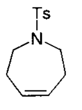
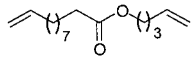
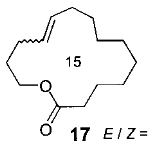
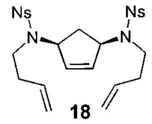
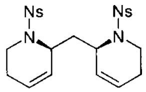
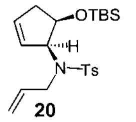
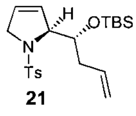
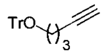
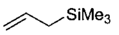
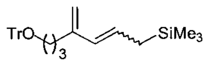
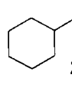
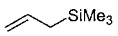
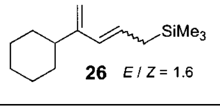


Scheme 2. Synthesis of support-bound catalyst **9**. a) 1.0 equiv KO*t*Bu, DMF, RT, 20 min, then 0.5 equiv Merrifield-polystyrene (1 % DVB), TBAI, DMF, 60 °C, 12 h; b) $HC(OMe)_3$, HCO_2H, toluene, 100 °C, 100 mbar, 15 h; c) 0.1 M HCl in THF, RT, 5 min; d) TMSOTf, 2,6-lutidine, CH_2Cl_2, RT, 30 min; e) KO*t*Bu, THF, RT, 60 min; f) 1.5 equiv **2**, toluene, 70–80 °C, 1 h. TBAI = tetrabutylammonium iodide.

As a first test diallyl malonic acid diethyl ester was cyclized using 5 mol % of catalyst **9**. At 45 °C in CD_2Cl_2 the RCM product was quantitatively formed after 40 min and could be isolated as a colorless oil after filtration and concentration. With the soluble catalyst **4** this reaction is complete in less than 5 min, which clearly suggests that fast metathesis reactions are diffusion controlled when the immobilized catalyst **9** is employed.

Various metathesis reactions have then been performed by using 5 mol % of support-bound catalyst **9** (Table 1). Substrate **10** was cleanly cyclized to give **11** as a colorless oil and accordingly the pyrroline derivative **13** was obtained from **12**. The RCM of **14** yielded the seven-membered heterocycle **15** as colorless crystals without need for further purification and the macrolactone **17** was obtained in 80 % yield from acyclic ester **16**. Apart from RCM we tested the capability of **9** to catalyze other types of metathesis. For example, triolefin **18** could be converted cleanly into **19** by double ring-closure using 5 mol % of catalyst **9** (entry 5). The enantiomerically pure diene **20** rearranged quantitatively in the presence of **9** and ethylene into **21**; upon concentration of the crude filtrate **21** crystallized immediately as a colorless solid.

Table 1. Results of metathesis reactions utilizing the immobilized catalyst **9**[a].

Entry	Substrate	Product	Yield [%]
1	 **10**	 **11**	100
2	 **12**	 **13**	90
3	 **14**	 **15**	100
4	 **16**	 **17** $E/Z = 1.4$	80
5	 **18**	 **19**	100
6[b]	 **20**	 **21**	100
7	 **22** +  **23** (3 Äquiv.)	 **24** $E/Z = 1.2$	100
8	 **25** +  **23** (3 Äquiv.)	 **26** $E/Z = 1.6$	80

[a] All reactions have been performed under standard conditions employing 5 mol% of **9** at 45°C in CH_2Cl_2 for 12– 18 h. [b] Reaction has been performed in the presence of ethylene. E = ester group, Tr = triphenylmethyl, Ts = *p*-toluenesulfonyl, Ns = *p*-nitrobenzylsulfonyl, TBS = *tert*-butyldimethylsilyl.

The catalyst **9** also catalyzes cross-metathesis reactions as demonstrated by the atom economical yne–ene metathesis[16] of the acetylene **22** with the allyl trimethylsilane (**23**) to yield the 1,3-disubstituted butadiene **24** (entry 7). After complete consumption of **22** compound **24** was isolated as a mixture of isomers (^{1}H NMR spectroscopy) by filtration and removal of the excess volatile allyl silane **23** under vacuum. The increased activity of catalyst **9** compared to **2** is demonstrated by the yne–ene cross metathesis of the sterically hindered cyclohexyl acetylene **25** and the allyl silane **23** (entry 8). In this reaction no products are obtained with **2**, whereas using **9**, the diene **26** was obtained in high yield as a colorless oil after removal of the excess starting material under vacuum.

The practical simplicity of product isolation when the polymer-supported catalyst **9** is used is clearly evident. Products of high purity (as determined by NMR spectroscopy) were obtained after filtration as the only purification step. This ease of isolation should allow automatization and makes catalyst **9** particularly suited to combinatorial applications.

As well as studying different types of metathesis reactions we were also interested in the potential recycling of catalyst **9**. For this purpose we varied the reaction conditions (reaction time, concentration, temperature) and the loading level. As a first substrate we chose **14** and obtained varying results. In the best case catalyst **9**, with a loading level of 0.14 mmol g^{-1}, gave the complete cyclization of **14** in four runs. The substrate (**14**; 0.025 M, CH_2Cl_2 solution) was refluxed together with 5 mol% of **9**, which was recovered by filtration under inert conditions. The reaction times for complete cyclization increased from 1.5 h in the first run, to 4 h in the second, 12 h in the third and two days in the fourth run. Investigations of the structure of the catalyst **9** (benzylidene or methylidene complex) are in progress. Detailed studies regarding further optimization of the recycling potential and stability of **9** and similar catalysts are also in progress.

Experimental Section

9: Polymer **6** (2.0 g; loading level 0.50–0.70 mmol g^{-1}) in a mixture of toluene (40 mL), trimethylorthoformate (10 mL, 91 mmol), and formic acid (0.5 mL, 13 mmol) was heated to 100°C under vacuum (100 mbar) for 15 h and shaken. The polymer was isolated by filtration, washed (2 × CH_2Cl_2, MeOH, THF, 3 × 0.1 M HCl in THF, 3 × THF, 3 × MeOH, 3 × CH_2Cl_2, 2 × MeOH, 2 × CH_2Cl_2, 2 × pentane), and dried. The IR spectrum indicated complete cyclization. The resulting polymer **7** was then shaken for 30 min in a solution containing TMSOTf (0.2 M) and 2,6-lutidine (0.3 M) in CH_2Cl_2 (30 mL) followed by filtration and washing (3 × CH_2Cl_2, 2 × pentane, 3 × CH_2Cl_2, 2 × pentane). The above capping step was repeated. The polymer was then suspended in THF (1 mL for 150 mg of support) and KO*t*Bu (3 mL; 1 M in THF (for 150 mg of support)) was added and the mixture slowly shaken for 1 h under exclusion of moisture and air. After filtration and washing (3 × THF) toluene (1 mL) and **2** (1.5 equivalents with respect to polymer **7**) were added and the suspension was then heated to 70–80°C for 1 h. The polymer was then collected by filtration, washed (5 × toluene, 3 × CH_2Cl_2, 2 × MeOH, 2 × CH_2Cl_2, 2 × MeOH, 2 × CH_2Cl_2, 3 × pentane), and dried to yield **9** as a pinkish brown resin.

^{31}P NMR (202.5 MHz, CH_2Cl_2/C_6D_6): $\delta = 28.4$ (br); IR (KBr pellet): $\tilde{\nu} = 1264$ (br, m) cm^{-1}.

Metathesis reactions utilizing **9**: The substrate was dissolved in CH_2Cl_2 and 5 mol% of catalyst **9** was added. The suspension was heated to 45°C for 12–18 h. The product was obtained as a colorless oil or solid after filtration and concentration. New compounds have been fully characterized (^{1}H and ^{13}C NMR, IR spectroscopy and high-resolution MS).

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Speciation in Solution: Silicate Oligomers in Aqueous Solutions Detected by Mass Spectrometry[**]

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Nucleation of solids from solution is one of the most challenging problems in solid-state chemistry. For a better understanding of processes taking place during crystallization, detailed knowledge about the species present in solution, such as particle size distribution and morphology, is mandatory to control the final properties of the solid.[1] However, only very few techniques are suited for such analyses, such as NMR spectroscopy for selected nuclei. Mass spectrometry could be a very versatile technique, since there are in principle no limitations with respect to the elements which can be analyzed. However, surprisingly only a few publications are available, in which mass spectrometry has been used for the analysis of speciation of crystallite precursors in solution. Most of the work reported to date has been limited to the investigation of partially hydrolyzed alkoxide solutions with predominantly alcohol as the solvent.[2] Herein we present for the first time data which show that oligomeric species in aqueous solutions can be reliably analyzed by using mass spectrometry. Electrospray ionization mass spectrometry (ESI-MS) has been used to study oligomer distribution in silicate solutions, since in this system the species can be independently analyzed with ^{29}Si NMR spectroscopy. However, in addition ESI-MS allows one to obtain information on oligomers and to address questions such as charge and degrees of hydrolysis of the species present in solution. Besides the availability of ^{29}Si NMR spectroscopy as an independent technique for analysis, the silicate system was chosen because of the importance of oligomeric species in zeolite synthesis,[3] sol–gel chemistry,[4] and silsesquioxane chemistry.[2c, 5]

Earlier studies showed the distribution of silicate oligomers depends on the alkyl chain length of the added tetraalkylammonium counterion.[3] Silicate solutions containing tetramethylammonium hydroxide (TMAOH) stabilize the cubooctameric double-four-membered ring (D4R), whereas in the presence of tetraethylammonium hydroxide (TEAOH) the formation of the double–three-membered ring (D3R) is preferred. Figure 1 depicts a typical ^{29}Si NMR spectrum and the corresponding negative-ion ESI mass spectrum for an aqueous/methanolic TMAOH solution containing dissolved silica. The ^{29}Si NMR spectrum indicates the high amount of D4R species (88.3 %), but there are also D3R (3.8 %), monomeric (3.0 %), dimeric (1.2 %), linear and cyclic trimeric (1.6 %), and different tetrameric (1.5 %) species present. The species detected in the ^{29}Si NMR are found in the ESI mass spectrum as well. The relative intensities of the peaks attributable to these species are in qualitative agreement for the two techniques. However, the intensity distribution in ESI-MS is somewhat dependent on the cone voltage and type of mass spectrometer used (see below), thus, full quantification is difficult. From the simple singly charged D4R oligomer at m/z 551 a series of peaks with a spacing of $\Delta(m/z)$ 73 to higher masses is observed. These can be assigned to species of higher charged cubic octamers that are clustered to TMA$^+$ ions. The series of peaks extends up to m/z 770, corresponding to a fourfold negatively charged D4R silicate clustered with three TMA$^+$ ions, while the doubly charged species clustered with one TMA$^+$ ion and the triply charged species clustered with two tetramethylammonium cations can be seen at m/z 624 and 697, respectively.

A second series of peaks starts at m/z 551. The following peaks at m/z 565, 579, and 593 shows a mass spacing of $\Delta(m/z)$ 14, which indicates a substitution of up to three hydroxyl groups at the silicon atoms by methoxy groups, which would be expected for highly alkaline solutions containing relatively large amounts of methanol. However, it can not be excluded

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