imizing of $\Sigma w(F_o^2 - F_c^2)$ with $w = 1/[\sigma^2(F_o^2)+0.02P^2+1.1P]$ and $P = (F_o^2+2F_c^2)/3$, 483 refined parameter, $R_1 = 0.0442$, $wR_2 = 0.0953$, $\Delta\rho_{max}/\Delta\rho_{min}$: 0.405/−0.338 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-144043. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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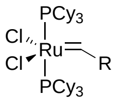
A Soluble Polymer-Bound Ruthenium Carbene Complex: A Robust and Reusable Catalyst for Ring-Closing Olefin Metathesis[**]

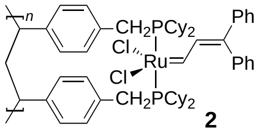
Qingwei Yao[*]

Facile catalyst separation and subsequent reuse are of prime importance in both industrial and academic settings. From the viewpoint of atom economy,[1] a catalyst should ideally be completely recoverable and reusable. In this respect, immobilized or heterogeneous catalysts offer inherent operational and economical advantages over their homogeneous counterparts. Herein we report the first soluble polymer-bound olefin-metathesis catalyst derived from Grubbs' ruthenium carbene complex and poly(ethylene glycol) (PEG). The new PEG-bound catalyst exhibits remarkable chemical stability and can be repeatedly used and recycled in the ring-closing metathesis (RCM) of a variety of α,φ-dienes.

The enormous recent success of olefin metathesis[2] catalyzed by metal carbene complexes stems from the availability of several well-defined catalysts,[2g] which include the Schrock molybdenum alkylidene[3] and the Grubbs-type ruthenium alkylidenes **1a**[4] and **1b**.[5, 6] Earlier attempts by Grubbs and Nguyen[7] to prepare polystyrene-supported catalysts based on **1a** met with only limited success and the resulting polymer-supported Ru carbene (for example, **2**) was found to be about two orders of magnitude less reactive than the homogeneous analogue **1a**. Moreover, recovery and reuse led to losses in activity (20% after each cycle). To the best of our knowledge, no further application of this catalyst has been reported in the literature. Very recently, Barrett and co-workers[8] have reported the immobilization of **1b** on vinyl polystyrene. Unfortunately, attempted recycling and reuse of the immobilized catalyst **3** led to a dramatic decrease in activity. The catalyst survives only a limited number of recyclings and completely loses its activity after the third cycle. Therefore, despite the obvious and much desired advantage, development of immobilized ruthenium carbene complexes as active, truly recyclable and reusable catalysts for olefin metathesis remains a challenging task.[9]



1a, R = CH=CPh₂
1b, R = Ph



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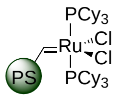

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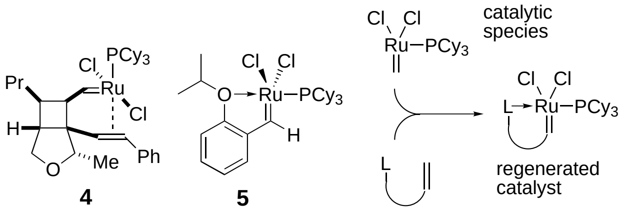
(Cy = Cyclohexyl)

In contemplating a novel approach to the immobilization of metathesis catalysts, we were attracted by two serendipitous findings from the groups of Snapper[10] and Hoveyda.[11] Thus, ruthenium carbenes **4**[10] and **5**[11] (Scheme 1), each bearing one phosphane ligand bound to the metal, were found to be remarkably stable and could be isolated and purified by silica-gel column chromatography. Hoveyda and co-workers also demonstrated[11] that **5** could be recycled by column chromatography and reused in olefin methathesis. Moreover, these complexes catalyze olefin metathesis with greater propagating rates than **1**. The bidentate nature of the non-phosphane ligands is particularly attractive in terms of catalyst regeneration since this should be entropically favored. We expected that attaching **5** to a polymeric support would give a recyclable and reusable olefin metathesis catalyst. We envisioned that it would be advantageous to use a soluble polymer[12] such as poly(ethylene glycol) as the support since this would allow the catalysis reaction to be carried out under standard homogeneous conditions and would enable the simple recovery of the catalyst by precipitation and filtration. However, it was not clear whether the backbone of the polymer would compete with substrate binding by chelating through its multiple ether functionalities.[13]



Scheme 1. Monophosphane-based metathesis catalysts[10, 11] and their regeneration at the end of the reaction.

Starting from the aldehyde **6**, the functionalized styrene **8** was prepared in a straightforward manner (Scheme 2). This material was then coupled to poly(ethylene glycol) monomethyl ether (MeO-PEG) derivatized with a succinate ester

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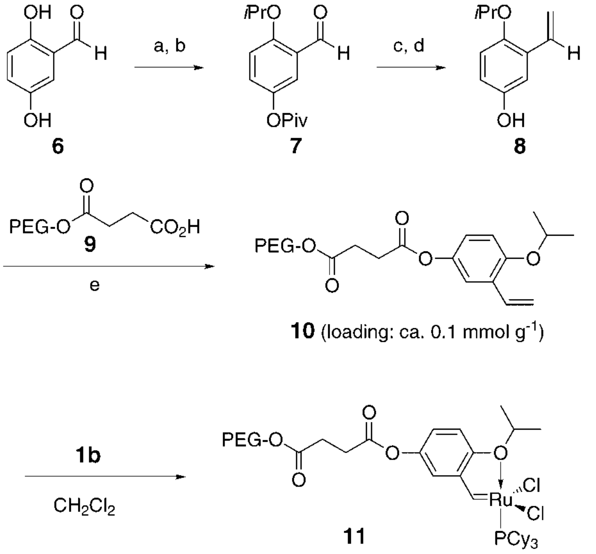
[**] Financial support by Northern Illinois University is acknowledged.

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

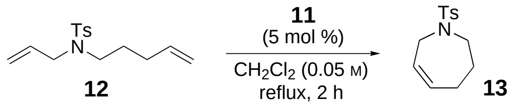


Scheme 2. Preparation of a soluble polymer PEG-bound ruthenium carbene complex: a) Et_3N, Piv-Cl, DMF, 0°C then RT, 6 h, H_2O, 65%; b) *i*PrI, Cs_2CO_3(cat.)/K_2CO_3, DMF, RT, 10 h, H_2O, 93%; c) $Ph_3(CH_3)P^+Br^-$, LHMDS, THF, 0°C then RT, 12 h, Et_2O, 75%; d) *t*BuO$^-$Na$^+$, MeOH, RT, 4 h, NH_4Cl, 99%; e) DCC, DMAP, CH_2Cl_2 reflux 12 h, 0°C Et_2O. Piv-Cl = trimethylacetyl chloride, LHMDS = lithium bis(trimethylsilyl)amide, DCC = 1,3-dicyclohexylcarbodiimide, DMAP = 4-dimethylaminopyridine, Cy = cyclohexyl. Full experimental details are available in the Supporting Information.

linker **9**[14] to give **10** (Scheme 2). The loading of the styrene moiety in **10** was estimated by 500 MHz ^{1}H NMR spectroscopy to be about 0.1 mmol g^{-1}.[15] Following Hoveyda's method[11] for the synthesis of **5** from **1b**, the polymer-bound catalyst **11** (Scheme 2) was prepared as a brownish powder by stirring an equimolar mixture of **10** and **1b** in refluxing CH_2Cl_2 followed by precipitation with dry diethyl ether.

When a solution of the diene **12** in CH_2Cl_2 was treated with 5 mol% of **11** for 2 h at reflux, **12** was converted cleanly to the cyclic olefin **13** in greater than 98% conversion, as determined by 500 MHz ^{1}H NMR spectroscopy (Table 1). Importantly, the catalyst is readily recovered[16] by precipitation with diethyl ether and, as shown in Table 1, the recycled material was used for the next cycle of metathesis, and gave a similarly high conversion. After up to eight runs of recycling and reuse, the catalyst remains active with only very slight loss of activity.

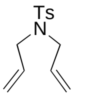
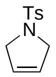
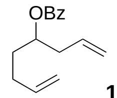
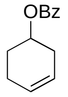
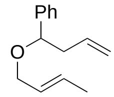
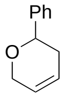
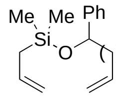
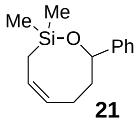
Table 1. Recycling and reuse of polymer-bound Ru complex **11** in the ring-closing metathesis of diene **12**.



cycle	1	2	3	4	5	6	7	8
conversion [%]	98	97.5	96.5	95	95	93	93	92

Table 2 lists the results of experiments with other substrates leading to the formation of different carbo- and heterocycles. Ring-closing metathesis of **14** goes cleanly, with high conversion, under conditions similar to those for the metathesis of **12** (cycles 1–3). Use of a reduced amount (2.5 mol%) of catalyst relative to the substrate in CH_2Cl_2 led to high conversion at elevated or room temperatures (cycles 4 and 5, respectively). The recycled catalyst from the reaction of **14** was subsequently used for the metathesis of a second substrate **16** (cycle 6). The crude product from **16** consists of only the cyclized product **17** and unreacted **16**, devoid of any contamination from the previous reaction. It should be noted that sequential use of the same batch of a catalyst in two different reactions is rarely possible, thus being able to do this represents a great practical advantage. The same strategy was applied to the metatheses of **18** and **20**. After the catalyst was used for the reaction of substrate **18**, the recycled catalyst was employed to catalyze the metathesis of the silicon-tethered[17] diene **20**. With 2.5 mol% of the recycled catalyst, **20** was converted to the cyclic silyl ether **21** in 98% conversion and 94% yield.

Table 2. Ring-closing metathesis catalyzed by polymer-bound Ru complex **11** in CH_2Cl_2.

Cycle	Substrate [conc]	Product	Catalyst [mol%]	Conditions	Conversion [%]
	 **14**	 **15**			
1	(0.05 M)		5	reflux, 2 h	96
2	(0.05 M)		5	reflux, 2 h	94
3	(0.05 M)		5	reflux, 2 h	92
4	(0.1 M)		2.5	reflux, 3.5 h	96.5
5	(0.1 M)		2.5	RT, 12 h	> 99
	 **16**	 **17**			
6	(0.1 M)		2.5	reflux, 2 h	90
	 **18**	 **19**			
1	(0.1 M)		2.5	reflux, 2 h	96
	 **20**	 **21**			
2	(0.1 M)		2.5	reflux, 3 h	> 98

While the data presented in Tables 1 and 2 show that the PEG-bound ruthenium carbene complex exhibits remarkable recyclability and can be repeatedly reused in the metathesis of various diene substrates, a slight decrease in catalytic activity is also evident. We attribute this to the slow but competing decomposition of the propagating species, presumably a monophosphane-based Ru carbene,[11] [$Cy_3PCl_2Ru{=}CHR$] (R = H or Me). A mechanistic study conducted by Grubbs and Ulman[18] has established that decomposition of ruthenium carbene based metathesis catalysts follows a bimolecular pathway involving a monophosphane ruthenium species, formed after the dissociation of one phosphane ligand.

In summary, we have developed a stable and readily recyclable, soluble, polymer-bound catalyst for olefin metathesis. 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.

Received: February 16, 2000
Revised: May 17, 2000 [Z14719]

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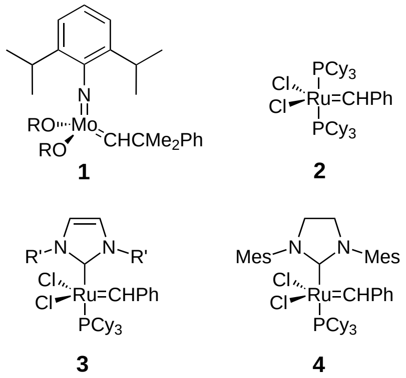
Synthesis and Application of a Permanently Immobilized Olefin-Metathesis Catalyst[**]

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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[**] This work was supported by the Fonds der Chemische Industrie. S.G. and N.B. would like to thank the Graduiertenkolleg "Synthetische, mechanistische und reaktionstechnische Aspekte von Metallkatalysatoren" for their Ph.D. grants.