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A recyclable 'boomerang' polymer-supported ruthenium catalyst for olefin metathesis

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Abstract

Polymer supported ruthenium catalyst **8** was found to be an effective catalyst for ring closing metathesis. The rate of reaction and activity was found to be comparable to that of homogeneous catalyst **1**. In addition, the catalyst could be recycled and re-used up to three times by simple filtration. The residual ruthenium/catalyst content in the product mixtures using catalyst **8** were found to be much reduced compared with the homogeneous catalyst **1**.

Keywords: polymer-supported; catalyst; ring-closing; olefin metathesis; recyclable.

The recent development of well-defined transition metal catalysts **1**[1] and **2**[2] for olefin metathesis has had a tremendous impact on synthetic organic chemistry.[3] The somewhat less active Grubbs catalyst **1** enjoys high popularity because of its ability to tolerate many functional groups, commercial availability, and due to its ease of handling. However, some acknowledged drawbacks still remain associated with catalyst **1**, especially from an industrial viewpoint.[4] Catalyst **1** is non-recyclable, is destroyed on reaction work-up, and frequently leads to highly coloured ruthenium residues in the product mixture which must be removed by chromatography. Similar constraints apply to the highly air and water sensitive Schrock carbene **2**.

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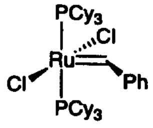

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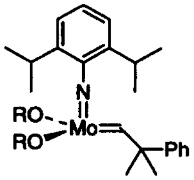
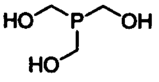


2 R = $C(CH_3)(CF_3)_2$



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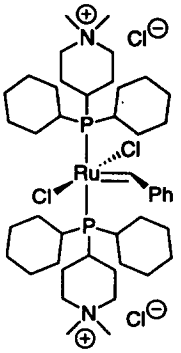

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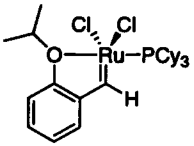

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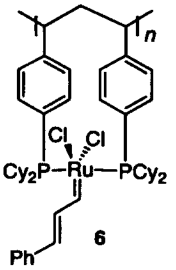

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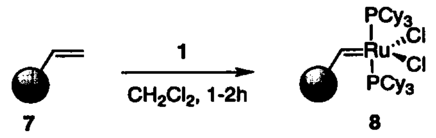
Some of these problems have been addressed by Grubbs[4,5] and separately by Hoveyda.[6] Grubbs has shown that the ruthenium residues can be sequestered by the addition of the very hydrophilic phosphine ligand **3** in the work-up procedure, thus allowing the metal residues to be extracted into aqueous media.[4] In an earlier paper Grubbs also describes the use of water soluble catalysts of the type **4**, with clear advantages.[5] Following his studies on chromenes,[7] Hoveyda introduced catalyst **5** which was found to be remarkably robust and could be recovered and purified by simple silica gel chromatography.[6]

We envisaged that immobilization of a metathesis catalyst onto a polymer support should in theory allow for complete abstraction of the catalyst from the product of olefin metathesis reactions by simple filtration. Furthermore, such polymer-supported catalysts seem ideally suited for recycling purposes without the need for chromatography or an aqueous work-up regime, thereby avoiding the need for removal of heavy metals from aqueous waste. In this context Grubbs has reported well-defined polymer supported catalyst **6**,[8] but was found to be at least two orders of magnitude less active than its homogeneous counterpart **1**. This has been attributed to a detrimental phosphine chelating effect, and by the need for the substrate to diffuse into the polymer cavities.

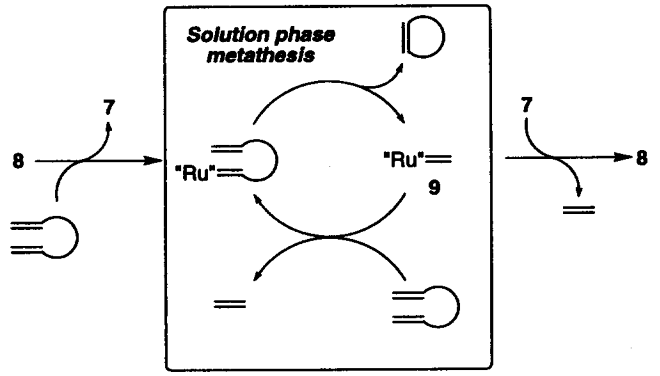
We now report a new polymer supported catalyst system that circumvents these rate limitations, allows for catalyst residue elimination, and is recyclable. Herein we describe a polymer-bound pro-catalyst that becomes homogeneous for the course of a ring closing metathesis (RCM) reaction, with concomitant reaction rate advantages, and is then recaptured by the resin after completion of the solution reaction: a 'boomerang' supported catalyst.

Polymer-supported ruthenium catalyst **8** was isolated as orange-brown beads by simply shaking a mixture of the Grubbs carbene **1** (approx. 10 mol% based on calculated vinyl resin sites) and vinyl polystyrene **7**,[9] for 1–2 h in CH_2Cl_2 followed by filtration (Scheme 1). The washings from the filtration were essentially colourless indicating complete incorporation of the Grubbs catalyst onto the support. Microanalysis of the beads gave a %P figure in accord with this observation. The catalyst-resin preparation time was found to be critical: longer catalyst-resin preparation times (>2 h) tended to lead to dark solutions with highly coloured washings, and the resin, once isolated was only poorly active for RCM. Once dried, the resin was found to be indefinitely stable under normal atmospheric conditions with no loss of activity.



Scheme 1.

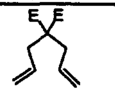
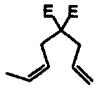
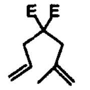
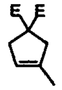
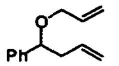
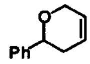
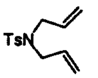
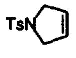
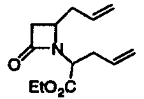
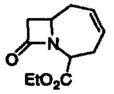
Polymer-supported catalyst **8** was employed for RCM of a set of representative diene substrates (Scheme 2 and Table 1). As can be seen from the results, the yields obtained with the 'boomerang' catalyst resin **8** were directly comparable to those achieved with the homogeneous catalyst **1**. For instance, both **1** and **8** quantitatively converted diethyl diallylmalonate to the ring closed product (Table 1, entry 1) in 40 min. Emphasis must be drawn to the practical simplicity with which the polymer-supported catalyst reactions were carried out: polymer-supported catalyst **8** was suspended in dichloromethane, the diene added and the mixture shaken for 40 min followed by filtration.[10] The washings were concentrated to provide the desired RCM product directly. Visual comparison of the products derived from polymer supported catalyst **8** versus those derived from homogeneous catalyst **1** was revealing. While the products produced using catalyst **1** were highly coloured the products produced using catalyst **8** were essentially colourless. Quantitative ruthenium residue analysis was obtained by ICP-MS analysis (Table 2). Employing homogeneous catalyst **1** (3 mol%) for the ring closing metathesis of diethyl diallylmalonate (40 min run) followed by simple evaporation gave the product contaminated with Ru at a level of 5100 ppm (Entry 1) which could be reduced to 330 ppm after chromatography (Entry 2). To our delight, the use of comparable quantities of polymer supported catalyst **8** followed simply by filtration and then evaporation gave a product where the Ru contaminant level was just 500 ppm (Entry 3), which could be further improved to 55 ppm after chromatography (Entry 4). This compares favourably to the procedure reported by Grubbs using phosphine **3** where the best case gave a Ru contaminant level of 200 ppm.[4]



Scheme 2.

An assessment of the recycling potential of catalyst **8** was also made, using diethyl diallylmalonate as the test substrate (Table 3). Quantitative ring closure was obtained (as expected) for the first run and the polymer was recovered by simple filtration (Table 3, entry 1). In the second run, over the same time period, the resin **8** was markedly less active and the solution containing the product was dark in colour. Inspection of our proposed mechanism (Scheme 2) reveals that the de facto catalytic carbene in solution is $Cl_2(PCy_3)_2Ru{=}CH_2$ **9**.[11] This is known to be relatively unstable with respect to unimolecular decomposition.[12] It is apparent that at the completion of any metathesis run, in the absence of any available terminal alkene *in the solution phase*, unimolecular decomposition of **9** can dominate

Table 1
RCM using polymer supported catalyst **8**[a]

Entry	Substrate[b]	Product	%Conversion[c]	Ref.[d]
1			100 (100)	4
2			95 (100)	4
3			60 (>90)[e]	5
4			85 (90)	-
5			100 (100)	14
6			100 (100)	15
7			40 (45)	-

[a] All runs performed with 50 mg substrate and 25 mg/0.1mmol substrate of polymer supported catalyst in CH_2Cl_2 for 40 minutes; [b] E = CO_2Et; [c] ^1H NMR analysis of crude reaction mixture after filtration and evaporation. The figure in parentheses represents the %conversion using homogeneous catalyst **1**; [d] All new compounds satisfactorily characterised; [e] Reactions performed for 22 h.

Table 2
Ru contaminant level for the RCM of diethyl diallylmalonate using catalysts **1** and **8**[a]

Entry	Catalyst (quantity)	Operation	Ru residue/ppm[b]
1	**1** (3 mol%)	evaporation	5100
2	**1** (3 mol%)	evaporation & chromatography	330
3	**8** (50 mg)	filtration & evaporation	500
4	**8** (50 mg)	filtration, evaporation & chromatography	55

a All runs performed in CH_2Cl_2 for 40 minutes; b Determined by ICP-MS.

prior to recapture by the resin. It should be noted that this is not a problem with the preparation of polymer-supported catalyst **8** since the precursor catalyst **1** is benzylidene-bound. With this in mind we reasoned that addition of styrene to the reaction mixture should retard catalyst decomposition by virtue of formation of the benzylidene catalyst which could then be recaptured by the resin before the onset of decomposition.

Table 3
Recycling of **8** for the RCM of diethyl diallylmalonate[a]

Entry	Additive (mol%)	Conversion[b]			
		Run 1	Run 2	Run 3	Run 4
1	none	100	40	0	0
2	styrene (3)	100	70	20	0
3	1-hexene (3)	100	100	40	0
4	1-hexene (9)	100	100	50	10
5	3,3-dimethyl-1-butene (3)	100	95	50	0
6	3,3-dimethyl-1-butene (9)	100	100	50	0

[a] All runs performed with 50 mg substrate and 50 mg of polymer supported catalyst in CH_2Cl_2 for 40 minutes; [b] ^1H NMR analysis of crude reaction mixture after filtration and evaporation.

To our pleasure, the addition of styrene (3 mol% based on diethyl diallylmalonate) led to an increased conversion for the second run and also allowed for slight activity in the third cycle (Table 3, entry 2). However, this excess styrene (bp 146°C) still remains in the crude product mixture after filtration, and is prone to polymerisation. The more volatile 1-hexene (bp 64°C) was explored as an alternative additive and proved to be superior (entries 3 and 4). Indeed, quantitative conversion for the second run could be obtained using this additive, and the resin was still active in the third run. 3,3-Dimethyl-1-butene, with a boiling point (41°C) very close to that of CH_2Cl_2 also proved effective (entries 5 and 6) and could be readily removed by evaporation.

In conclusion, we have reported a new 'boomerang' polymer supported catalyst which combines the advantages of solution phase chemistry with the ease of purification associated with solid phase chemistry. It compares favourably with other reported methods for catalyst recycling and ruthenium residue elimination. Further applications of the ruthenium catalyst **8** will be reported in due course.[13]

Acknowledgements

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