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Simply Assembled and Recyclable Polymer-Supported Olefin Metathesis Catalysts

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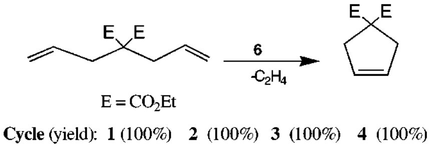
ABSTRACT



Polymer-supported ruthenium catalysts $(PCy_3)_2Ru(=C(H)Ph)Cl_2$, $(PCy_3)Ru(IMes)(=C(H)Ph)Cl_2$, and $(PCy_3)Ru(SIMes)(=C(H)Ph)Cl_2$, where IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene and SIMes = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene, have been prepared and found to be effective "boomerang" catalysts for ring-closing metathesis. They are recyclable, show comparable or better reactivity than their homogeneous counterparts, tolerate functional groups, and perform very well with dienes and moderately well with highly hindered substrates.

The formation of C−C bonds using olefin metathesis methodology (ring-closing metathesis, RCM; ring opening metathesis polymerization, ROMP; cross metathesis, CM; and combinations of these) is considered a powerful technique in organic synthesis and polymer chemistry.[1] Well-defined, single-component metal−carbene complexes of the Grubbs type $RuCl_2(=CHPh)(PCy_3)_2$ (**1**) are highly efficient catalyst precursors, moderately sensitive to air and moisture and very tolerant of many different organic functional groups.[2] However, they exhibit low thermal stability and decompose at high temperatures.[3] It has been shown that the replacement of one of the phosphine ligands in the Grubbs system with a sterically demanding nucleophilic carbene ligand (e.g. *N*,*N*′-bis(mesityl)imidazol-2-ylidene, IMes) to yield $RuCl_2(=CHPh)(IMes)(PCy_3)$ (**2**) leads to an increased thermal stability of the catalyst precursor and in an increased ring-closing activity toward tri- and tetrasubstituted substrates.[3,4] Grubbs et al. have recently prepared the saturated version of imidazol-2-ylidenes, the 4,5-dihydroimiazol-2-ylidene (SIMes). They propose that the higher basicity of the saturated imidazole ligand compared to that of its unsaturated analogue leads to an increased catalyst reactivity profile. The ruthenium complexes ($RuCl_2(=C(H)$-$Ph)(PCy_3)(1,3\text{-}R_2\text{-}4,5\text{-dihydroimidazol}-2\text{-ylidene})$, **3**) displayed increased ring-closing metathesis and cross metathesis activity compared to those of their phosphine analogues.[5]

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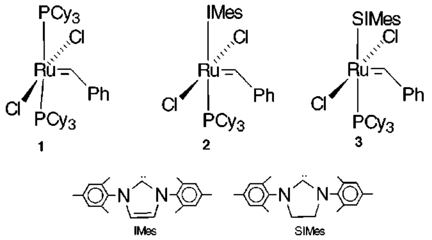
A common drawback of all above-mentioned catalyst precursors is the difficulty associated with their recovery from reaction mixtures. They usually decompose upon workup, giving rise to products that are highly colored by ruthenium residues. These issues have been addressed by sequestering the ruthenium residues via the addition of hydrophilic phosphine ligands[6] or lead compounds[7] in the workup procedure, by phosphine derivatization leading to water-soluble olefin metathesis catalyst use in biphasic systems,[8] and by development of recyclable monomeric[9] and dendritic[10] ruthenium-based catalysts. Grubbs reported a most promising approach to catalyst recyclability in 1995.[11] In this study a ruthenium complex was appended to a phosphine-modified polystyrene. Unfortunately, this polystyrene-supported olefin metathesis catalyst displayed activity 2 orders of magnitude lower than its homogeneous parent did. Most recently, Barrett and co-workers who have used vinyl-modified polystyrene beads as polymer support reported an exciting variation on this theme.[12] The catalysts are now bound to the polymer through the metathesis active carbene moiety. These researchers have recently demonstrated the use of the "Arduengo−Wanzlick" nucleophilic carbene[13] modified ruthenium catalyst in this polymer-supported approach with significant success.

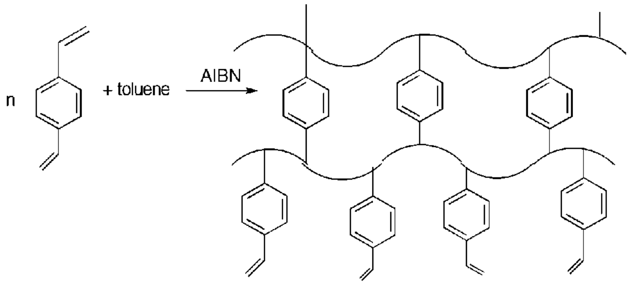
The use of macroporous polymers as support for transition metal catalysts has been explored.[14] Macroporous resins have a permanent well-developed porous structure even in a dry state.[15] Contrary to lightly cross-linked Merrifield resins[16] that need swelling solvents to access their interior volume, the pore structure in macroporous resins can be accessed by solvents and reactants without a need for swelling.[12] Herein, we report the immobilization of olefin metathesis catalysts precursors **1**, **2**, and **3** into macroporous polymers as well as their reactivity and recyclability in RCM reactions (Scheme 1).

Scheme 1. Homogeneous Catalysts



The macroporous resin employed in this study (poly-DVB) was synthesized from commercially available divinylbenzene with toluene as porogen (v:v = 1:1). The bulk polymer was ground into a fine powder and dried in vacuum. Poly-DVB has been characterized and found to possess a relatively large surface area (810 m^2/g polymer) and a high degree of cross-linking (55%), Scheme 2.[17]

Scheme 2. Poly-divinylbenzene (Poly-DVB)



Ring-closing metathesis catalyst precursors **1**, **2**, and **3** were immobilized onto this support using a simple impregnation protocol. A toluene solution of the catalyst precursor (ca. 100 mg) was added to a suspension of the polymer (ca. 1 g) and the mixture heated to 50 °C for 1 h. The slurry was then filtered and washed with toluene to yield light pink solids (**1** → **4**, **2** → **5**, and **3** → **6**). The catalyst loadings are determined by ruthenium elemental analysis of the polymers as 4 wt % for **4**, 3 wt % for **5**, and 10 wt % for **6**. The higher or more efficient catalyst loading for **6** is in line with the increased cross metathesis activity observed for the homogeneous catalyst bearing SIMes.[3] Polymer-supported catalyst precursors **4**, **5**, and **6** were used in RCM with a set of representative diene substrates.

With the diene substrate diethyl diallylmalonate (**7**), all three polymer-supported catalyst precursors **4**, **5**, and **6** exhibit RCM activity similar to that of their homogeneous parents (see Table 1). They can be recycled up to 4 times without significant loss of activity (Table 1 entries 2, 3, 5, 6, 9, and 10). This combined with the fact that the filtrates

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Table 1. RCM of Diethyl Diallylmalonate (**7**)[a]

entry	catalyst precursor	cycle	time (h)	yield[b] (%)
1	**1**		0.5	85[c]
2	**4**	1	0.5	97
3	**4**	4	0.5	81
4	**2**		0.5	92[c]
5	**5**	1	0.5	97
6	**5**	4	0.5	81
7	**5**[d]	1	20.0	65
8	**3**		0.5	100
9	**6**	1	0.5	100
10	**6**	4	0.5	100

[a] All reactions are performed in CH_2Cl_2 at room temperature. The catalyst loading is 5 mol %. [b] GC yield, average of two runs. [c] NMR yield, average of two runs. [d] Reaction was carried out in methanol.

and washes of four consecutive catalytic runs are ^{31}P and ^{1}H NMR silent indicate that there is little leaching of the ruthenium complex in the solution phase.[18]

The ruthenium content of the combined filtrates and washes (4) was determined by atomic absorption spectroscopy analysis. Results of these analyses show that 5% ruthenium (of the initial 4% loading) is lost after 4 cycles when **4** is used as the catalyst precursor. The loss in ruthenium content for **5** and **6** is 2% of the initial 3 and 10%, respectively. The nature of the polymer support allows RCM to be performed in methanol. RCM of substrate **7** performed with catalyst **5** also proceeds, albeit much slower than in CH_2Cl_2 (Table 1, entry 7).[19]

The RCM of diallytosylamine (**8**) is very slow when mediated by catalyst precursor **2**; however, the polymer-supported catalyst **5** ring closes **8** and can be recycled at least three times (Table 2, entries 4 and 5). Performing the reaction at elevated temperature (40 °C) increases the yield (Table 2, entry 6). Addition of CuCl as a phosphine sponge (catalyst: CuCl = 1:1) leads to an increase in catalytic activity,[20] but the resulting catalyst could not be successfully recycled (Table 2, entries 8 and 9). We believe CuCl irreversibly removes the coordinated phosphine from the ruthenium complex and hence gives rise to a very reactive 14-electron ruthenium complex that decomposes rapidly, leading to the marked decrease in the activity of the catalyst in subsequent cycles. The catalyst precursor **1** and its polymer-supported analogue, **4**, mediate this transformation very efficiently (Table 2, entries 1 and 2). The polymer-supported catalyst precursor **6** is also moderately active in this RCM reaction (Table 2, entry 6).

Table 2. RCM of Diallytosylamine (**8**)[a]

entry	catalyst precursor	cycle	temp (°C)	time (h)	yield[b] (%)
1	**1**		rt	0.5	100[c]
2	**4**	1	rt	0.5	88
3	**2**		rt	3.0	12[c]
4	**5**	1	rt	1.0	31
5	**5**	3	rt	1.0	30
6	**5**	1	40	3.0	71
7	**5**[d]	1	40	0.5	100
8	**5**[d]	2	40	0.5	0
9	**6**	1	rt	0.5	66

[a] All reactions were performed in CH_2Cl_2. [b] GC yield, average of two runs. [c] NMR yield, average of two runs. [d] One equivalent of CuCl was added to the reaction mixture

Highly substituted dienes have proven a challenge in RCM. To examine the performance of the supported catalysts, the tetrasubstituted substrate diethyl bis(2-methylallyl)malonate **9** was examined as an RCM substrate. The catalyst precursor **1** and the polymer-supported relative **4** show no reactivity in the RCM of **9** (Table 3, entries 1 and 2). However, **2** and the polymer-supported analogue **5** are active in this reaction (Table 3, entries 3 and 4). Moreover, **5** can be recycled up to four times without losing significant activity (Table 3, entries 4 and 5). Addition of CuCl to **5** does not increase the yield and results in the total loss of activity (Table 3, entries 5 and 6). The yield of the reaction using catalyst precursor **6** is low (Table 3, entry 7) and comparable to its nonsupported analogue, but it can be recycled.[8a] Although the activity of the supported catalysts is disappointing in general for this most hindered substrate, the lack of significant catalyst deactivation for **5** is noteworthy.

Table 3. RCM of Diethyl Bis(2-methylallyl)malonate (**9**)[a]

entry	catalyst precursor	cycle	time (h)	yield[b] (%)
1	**1**		3.0	0[c]
2	**4**	1	3.0	2
3	**2**		1.0	75
4	**5**	1	3.0	33
5	**5**	4	3.0	22
6	**5**[d]	1	3.0	2
7	**6**	1	3.0	17

[a] All reactions were carried out in toluene at 80 °C. [b] GC yield, average of two runs. [c] NMR yield, average of two runs. [d] One equivalent of CuCl was added to the reaction mixture.

The mechanism involved in the polymer-supported catalyst transformation is believed to occur as Barrett and co-workers have proposed for the modified polystyrene bead system.[12] The "boomerang" mechanism involving catalyst release into solution and RCM as in the homogeneous catalyst scenario followed by recapture of the ruthenium species by styrene vinyl groups appears consistent with the observed chemistry. The advantages of the poly-DVB system include the ease of polymer preparation and the larger number of sites

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(18) The amount of leaching was determined by AA and ICPMS.

(19) The effect of the polymer surface area on catalysis was examined by comparing the RCM results of the catalyst precursor **5** in fine powder and small segment (ca. 0.2(cm) × 0.2(cm) × 0.2(cm)) forms. When the fine powder form of **5** was used in the RCM of **7**, the reaction was complete in 30 min (Table 1, entry 5). The same reaction after 5 h yielded only 77% product when the small solid pieces of **5** were used.

(20) For references on use of CuCl as phosphine sponge, see ref 2c.

available for catalyst recapture (45% of vinyl group in the bulk polymer are available for recapture). Barrett and coworkers have used additives (1-alkenes and triphenylphosphine) to stabilize the ruthenium center in solution.[12b] It is believed that the ruthenium methylidene species, which decomposes through a unimolecular process,[21] is at the origin of catalyst death in these “boomerang” polymer-supported systems. A noted difference between the polystyrene and poly-DVB-supported systems is the high recovery rate of the poly-DVB system even in the absence of additives.

A comparison of the three supported catalysts indicates the relative activity to be substrate dependent, but for unhindered substrates, **6** appears to be most active. This is principally due to the increased basicity at the metal, which is responsible for improved cross metathesis activity. This improved activity in cross metathesis increases the likelihood of rebinding to the polymer surface. Probabilities of rebinding are also increased in view of the larger number of available vinyl sites on poly-DVB. It should be pointed out that in view of this increased activity, a lower polymer-supported catalyst loading could be used. Indeed, in standard experiments involving **4** and **5**, 100 mg of the supported catalyst was used. In the case of **6**, similar loadings are not necessary to obtain quantitative yield. In optimization experiments, loading as low as 12.5 mg of supported catalyst **6** were used and lead to quantitative yield in the RCM of **7**.

In summary, we have developed a simple heterogeneous catalytic system for RCM that is recoverable and recyclable. These polymer-supported catalysts display reactivity comparable to that of their homogeneous counterparts, tolerate functional groups, and perform very well with dienes and moderately well with highly hindered substrates. Studies aimed at exploring the extent of reactivity and mechanism of these and related supported catalysts are in progress.

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Supporting Information Available: Experimental procedures. This information is available free of charge via the Internet at http://pubs.acs.org.

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