Preparation and Activity of Recyclable Polymer-Supported Ruthenium Olefin Metathesis Catalysts

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The ruthenium catalysts $(PCy_3)_2Ru(=C(H)Ph)Cl_2$ (**1**), $(PCy_3)Ru(IMes)(=C(H)Ph)Cl_2$ (**2**), $(PCy_3)Ru(SIMes)(=C(H)Ph)Cl_2$ (**3**), $(PCyp_3)Ru(IMes)(=CHCH=C(CH_3)_2)Cl_2$ (**4**), and (PCy_3)-$Ru(IPr)(3$-phenylindenylid-1-ene$)Cl_2$ (**5**), where IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, SIMes = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, Cy = cyclohexyl, and Cpy = cyclopentyl, have been grafted to polymer supports and found to be effective heterogeneous catalysts for ring-closing metathesis. In some cases, they are recyclable, show comparable reactivity to their homogeneous counterparts, tolerate functional groups, and perform very well with unsubstituted dienes.

Introduction

The advent of well-defined, highly reactive catalysts for olefin metathesis (ring-closing metathesis, RCM; ring-opening metathesis polymerization, ROMP; cross metathesis, CM; and their combinations) has made this technique a powerful tool in organic synthesis and polymer chemistry.[1] Metal-carbene complexes of the Grubbs' type $(PCy_3)_2Ru(=C(H)Ph)Cl_2$ (**1**)[2] and its analogues modified with nucleophilic carbenes $(PCy_3)Ru$-$(IMes)(=C(H)Ph)Cl_2$[3] (**2**), $(PCy_3)Ru(SIMes)(=C(H)Ph)Cl_2$ (**3**),[4] and $(PCyp_3)Ru(IMes)(=CHCH=C(CH_3)_2)Cl_2$[3] (**4**), 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, are highly efficient cata-
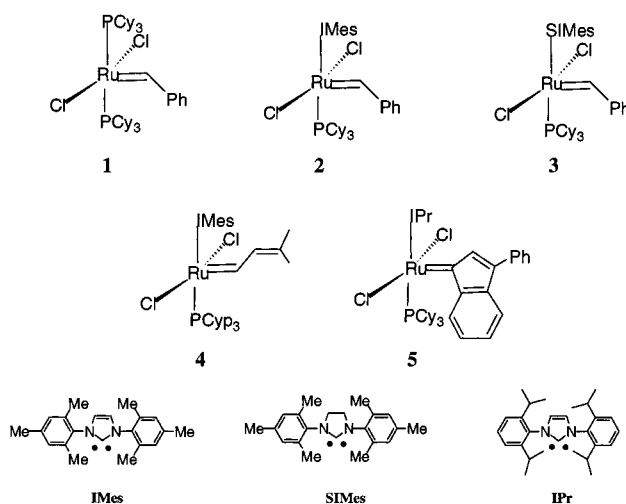

Figure 1. Homogeneous catalysts.

lyst precursors. We have shown that the complexes of unsaturated "C_α" ligands other than the alkylidenes such as $(PCy_3)Ru(IPr)(3$-phenylindenylid-1-ene$)Cl_2$ (**5**), where IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, are also active catalyst precursors in the ring-closing metathesis of dienes (Figure 1).[5]

However, the above-mentioned catalyst precursors are difficult to recover from reaction mixtures, usually

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decompose upon workup, and give rise to products that are highly colored by ruthenium residues. Considering the fact that these compounds are expensive to synthesize, devising methods to recover and recycle these catalysts could potentially lower the cost of olefin metathesis and facilitate the purification of the products. Several attempts have been made to immobilize these catalyst precursors on solid supports.[6] Anchoring a ruthenium complex to a moderately cross-linked, phosphine-modified polystyrene appeared promising, but this tethered catalyst was found to be at least 2 orders of magnitude less active than its homogeneous analogue.[7] Olefin metathesis catalysts can also be appended to a polymer support through their carbene rather than the phosphine moiety. Recently, a number of groups have made significant advances toward rendering ruthenium olefin metathesis catalyst recyclable. Most notable are the studies of Hoveyda and co-workers,[8] who have heterogenized ruthenium olefin metathesis catalysts through a pendant vinyl group on a dendritic scaffold, Yao,[9] who has used modified-PEG (poly(ethylene glycol)) resins as anchoring points, and Blechert,[10] who has used modified/tethered nucleophilic carbenes as a mode of "heterogenization". Barrett and co-workers have used vinyl-modified polystyrene beads as polymer supports. These approaches require a number of synthetic steps to produce the scaffold/anchoring portion of the catalyst. An intriguing system is the one reported by Barrett where olefin metathesis catalysts act as "boomerang" catalysts. These are thought to involve initial cleavage of the ruthenium center from the polymer support, with generation of the homogeneous catalytic species, and finally recapture by the support at the end of the catalytic reaction. To retain the recyclability of the catalyst precursor, it was determined that a terminal olefin additive should be added to the reaction mixture.[11] A more straightforward anchoring methodology could prove very useful. We thought a simple approach could be achieved using an appropriate polymer composition and morphology.

Macroporous polymers, polymers with a permanent pore structure, have been used as support for transition metal catalysts[12] where large surface areas that provide access to the catalytic sites are required. Contrary to lightly cross-linked Merrifield resins,[13] the pore structure can be accessed by essentially all solvents and reactants without a need for swelling.[14] Recently, we reported the use of macroporous resin, poly-DVB, as a support for olefin metathesis catalysts.[15] The polymeric support was synthesized from commercially available divinylbenzene (50%), using toluene as the porogen

Scheme 1. Poly-divinylbenzene (Poly-DVB)
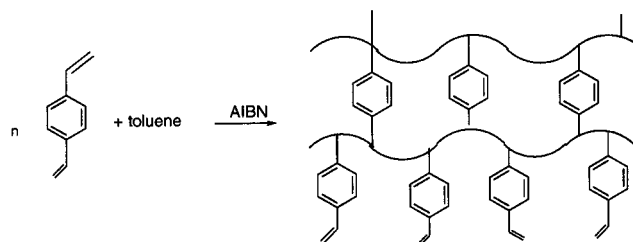
(v/v = 1:1) and AIBN as initiator (Scheme 1). This polymer has been characterized; it has a very large surface area (810 m^2/g),[16] a high degree of cross-linking (55%), and a large number of dangling vinyl groups (45% of initial vinyl groups),[10] which provide the cross metathesis sites for the ruthenium-carbene catalysts. It has been shown that the catalyst precursors **1**, **2**, and **3** could be immobilized on the above-mentioned polymer support and used in RCM reactions.[14] These show high catalytic activities and are recoverable and recyclable.

We now wish to expand on our initial studies and report results concerning the synthesis of polymer-bonded olefin metathesis catalyst precursors, **9** and **10**, and the reactivity and recyclability of polymer-supported catalyst precursors **6**−**10** in various RCM and self-metathesis reactions.

Results and Discussion

Synthesis of the Polymer-Supported Catalyst Precursors. The polymer is impregnated with the ruthenium complexes **4** and **5** by simply mixing a toluene solution of the catalyst precursors (100 mg) with a suspension of the polymer (1 g) and heating the mixture to 50 °C for 1 h. The slurry was filtered, washed with toluene, and dried in vacuum to yield light pink solids. Under these conditions, the ruthenium complexes undergo cross metathesis with poly-DVB and exchange their carbene moiety for the unbound vinyl groups of the supporting polymer, giving rise to polymeric compounds **9** and **10** (Scheme 2). The catalyst loadings were determined by ruthenium elemental analysis of the polymers and are shown in Table 1. The degree of loading for each catalyst precursor directly corresponds to the cross metathesis activity of its homogeneous congener. For example, the more efficient loading in **8** (12%) is in line with higher cross metathesis activity of **3**, and the low catalyst loading in **9** (1%) can be traced to the low cross metathesis activity of its homogeneous

(6) Another approach has recently been reported by Buijsman in performing RCM in ionic liquids followed by organic extraction which selectively removes the organic components from the reaction mixture: Buijsman, R. C.; van Vuuren, E.; Sterrenburg, J. G. *Org. Lett.* **2001**, *3*, 3785−3787.

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Table 1. Catalyst Loading onto Poly-DVB

polymer-supported complex	Ru (%)	loading (mmol g^{-1}($\times 10^2$))
6	0.60	5.0
7	0.38	3.5
8	1.20	12.0
9	0.12	1.2
10	0.32	4.6

Scheme 2.   Synthesis of the Polymer-Supported Catalyst Precursors

R = Cy, Cyp
R' = Ph, CHCH=C(Me)₂,

L = IMes, SIMes, IPr
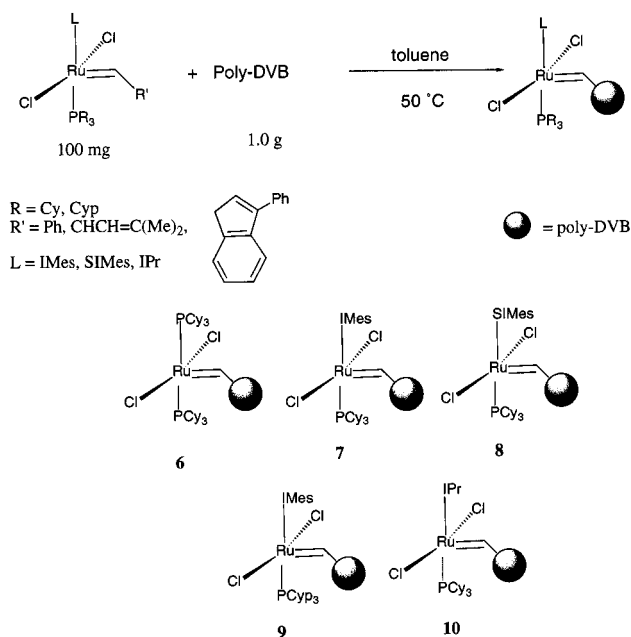
counterpart, **4**. The ruthenium content for the remaining entries lies intermediate to the two extremes and averages 5 wt %.

RCM Reactivity of the Polymer-Supported Catalyst Precursors. Polymer-supported catalyst precursors, **6**–**10**, were used in ring-closing metathesis with a set of representative diene substrates. Table 2 shows the RCM results of the polymer-supported catalyst precursors and their homogeneous analogues **1**–**5** with diethyldiallylmalonate **11** as substrate. RCM activity of **6**, **7**, and **8** is similar to that of their homogeneous parents (Table 2, entries 1, 2, 7, 8, 14, 15),[14] whereas **9** and **10** appear more reactive than their homogeneous analogues (Table 2, entries 19, 20, 24, 25). These results become more significant considering the fact that the catalyst loading of **9** is five times less than that of homogeneous parent, **4** (1 mol % vs 5 mol %). All heterogeneous catalysts can be recycled, some displaying effective recyclability and others displaying significant degradation after initial use (Table 2). Performing these reactions in air decreases the catalytic activity (Table 2, entries 6, 12, 29). The reaction can also be performed in methanol, albeit with lower yield and longer reaction time (Table 2, entry 13).

The filtrates and washes of four consecutive catalytic runs are ^{31}P NMR silent, indicating that there is little or no leaching of the ruthenium complex in the solution phase. The ruthenium content of the combined filtrates and washes (4 cycles) was determined by atomic absorption spectroscopy, and the results are shown in Table 3. Ruthenium leaching is highest for **6** and **9** and is 8

Table 2. RCM of Diethyldiallylmalonate (11)^a

E = CO₂Et

entry	catalyst precursor	cycle	yield^b (%)	entry	catalyst precursor	cycle	yield^b (%)
1	**1**		85^c	16	**8**	2	99
2	**6**	1	97	17	**8**	3	99
3	**6**	2	95	18	**8**	4	100
4	**6**	3	93	19	**4**		10
5	**6**	4	81	20	**9**^{f}	1	59
6	**6**^{d}	2	86	21	**9**^{f}	2	55
7	**2**		92^c	22	**9**^{f}	3	42
8	**7**	1	97	23	**9**^{f}	4	48
9	**7**	2	97	24	**5**		75
10	**7**	3	93	25	**10**	1	95
11	**7**	4	81	26	**10**	2	80
12	**7**^{d}	2	84	27	**10**	3	60
13	**7**^{e}	1	65	28	**10**	4	40
14	**3**		100	29	**10**^{d}	2	75
15	**8**	1	100				

^{a} All reactions are performed in CH₂Cl₂ at room temperature, the reaction time is 30 min, and the catalyst loading is 5 mol %. ^{b} GC yield, average of two runs. ^{c} NMR yeild, average of two runs. ^{d} The reaction is performed in air. ^{e} The reaction was carried out in methanol, and the reaction time was 20 h. ^{f} Catalyst loading is 1 mol %.

**Table 3. Catalyst Leaching Analysis by Atomic Absorption**

catalyst precursor	Ru in solution after 4 cycles (ppm)	(Ru in solution after 4 cycles)/ (initial Ru loading) (%)
6	330	8.0
7	90	3.0
8	200	2.0
9	65	6.0
10	70	2.0

and 6% of the initial ruthenium loading, respectively, and is only about 2% for the other catalyst precursors.

The polymer-supported catalyst precursors were tested for functional group tolerance when used in the RCM of diallytosylamine **12** and 4,5-bisacetoxyocta-1,7-diene **13**, and the results are displayed in Tables 4 and 5. Although the reaction is very slow when mediated by the homogeneous catalyst **2**, the polymer-supported analogue (**7**) is more reactive and can be recycled at least three times (Table 4, entries 3–6). Raising the reaction temperature to 40 °C increases the yield (Table 4, entry 7). Addition of CuCl, as a phosphine sponge, (catalyst:CuCl = 1:1) leads to an increase in catalytic activity,[17] but the resulting catalyst could not be successfully recycled (Table 4, entries 8, 9). We believe the coordinated phosphine is irreversibly removed from the ruthenium complex by CuCl, giving rise to a very reactive, coordinatively unsaturated compound that decomposes rapidly, leading to a marked decrease in the activity of the catalyst in subsequent cycles.[15] The polymer-supported catalysts **8**, **9**, and **10** mediate this transformation moderately (Table 4, entries 10, 11, 13), whereas **6** and its homogeneous analogue **1** are very efficient catalyst precursors (Table 4, entries 1, 2).

Homogeneous catalyst precursors **1**–**3** convert **13** into the ring-closed product very efficiently (Table 5, entries 1, 2, 9). The supported catalyst precursors **6**–**10** also

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

Table 4. RCM of Diallyltosylamine (12)[a]

12

TS = toluenesulfonyl
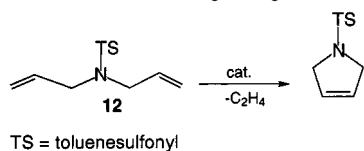
entry	catalyst precursor	cycle	temp (°C)	time (h)	yield[b] (%)
1	**1**		RT	0.5	100[c]
2	**6**	1	RT	0.5	88
3	**2**		RT	3.0	12[c]
4	**7**	1	RT	1.0	31
5	**7**	2	RT	1.0	38
6	**7**	3	RT	1.0	30
7	**7**	1	40	3.0	71
8	**7**[d]	1	40	0.5	100
9	**7**[d]	2	40	0.5	18
10	**8**	1	40	0.5	66
11	**9**[e]	1	40	3.0	58
12	**5**		RT	0.5	84[c]
13	**10**	1	RT	0.5	72

[a] All reactions are performed in CH_2Cl_2; the catalyst loading is 5 mol %. [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. [e] Catalyst loading is 1 mol %.

Table 5. RCM of 13[a]

13
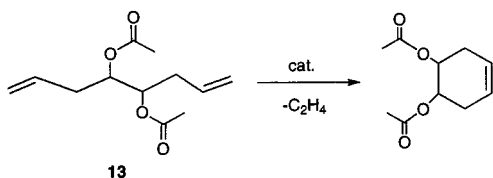
entry	catalyst precursor	cycle	time (h)	yield[b] (%)
1	**1**[c]		6.0	80[d]
2	**6**	1	1.25	90
3	**6**	2	12.0	10
4	**2**		1.25	92[d]
5	**2**		3.0	50[e]
6	**2**		12.0	88[e]
7	**7**	1	1.25	92
8	**7**	2	2.0	85
9	**3**		0.5	90
10	**8**	1	0.5	92
11	**8**	2	12.0	60
12	**9**	1	1.75	90
13	**9**	2	12.0	30
14	**10**	1	2.50	91
15	**10**	2	12.0	25

[a] All reactions are performed in toluene at 60 °C; the catalyst loading is 5 mol %. [b] GC yield, average of two runs. [c] Reaction was carried out in benzene, first at RT (3 h) and then at 60 °C (3 h). [d] NMR yield, average of two runs. [e] Reaction is carried out at room temperature.

exhibit high reactivity in this reaction (Table 5, entries 2, 7, 10, 12, 14). However, they show diminished activity in the second cycle (Table 5, entries 3, 11, 13, 15). Only catalyst precursor **7** performed well in the first and second cycles (Table 5, entries 7, 8).

Ring-closing metathesis of highly substituted diene substrates is most challenging. Performance of the supported catalysts was examined in the RCM of diethylbis(2-methylallyl)malonate **14**, and the results are shown in Table 6. Almost all catalyst precursors studied showed no or very poor reactivity in this transformation (Table 6, entries 1, 2, 8−12). The best result was obtained when the homogeneous catalyst precursor **2** was used (Table 6, entry 3); its polymer-

## Table 6. RCM of Diethylbis(2-methylallyl)malonate (14)[a]

14

E = CO_2Et
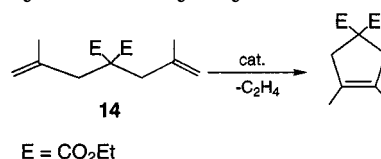
entry	catalyst precursor	cycle	time (h)	yield[b] (%)
1	**1**		3.0	0[c]
2	**6**	1	3.0	2
3	**2**		1.0	75[c]
4	**7**	1	3.0	33
5	**7**	2	3.0	36
6	**7**	3	3.0	28
7	**7**	4	3.0	22
8	**8**		3.0	17
9	**4**		3.0	7[c]
10	**9**[d]	1	3.0	9
11	**5**		3.0	19[c]
12	**10**	1	3.0	5

[a] All reactions are performed in toluene at 80 °C; the catalyst loading is 5 mol %. [b] GC yield, average of two runs. [c] NMR yield, average of two runs. [d] Catalyst loading is 1 mol %.

supported analogue **7** is less active but can be recycled up to four times without losing significant activity (Table 6, entries 4−7).[15]

While the use of ring-closing metathesis for the synthesis of unsaturated oxygen and nitrogen heterocycles is fully documented,[2a,b,18] these methods are generally limited to a single cyclization step leading to an unsaturated mono-heterocycle. Although there is literature precedent for the preparation of bicyclic compounds,[18a,19] these transformations involved either a two-step sequence[20] with introduction of the first ring followed by an intramolecular metathesis cyclization or a tandem ring-opening−ring-closing sequence[21] at slightly elevated temperature and in higher concentration conditions. Recently, the authors reported using **1** as double ring-closing metathesis precursor toward the synthesis of polycyclic unsaturated ethers.[22] In this process, two

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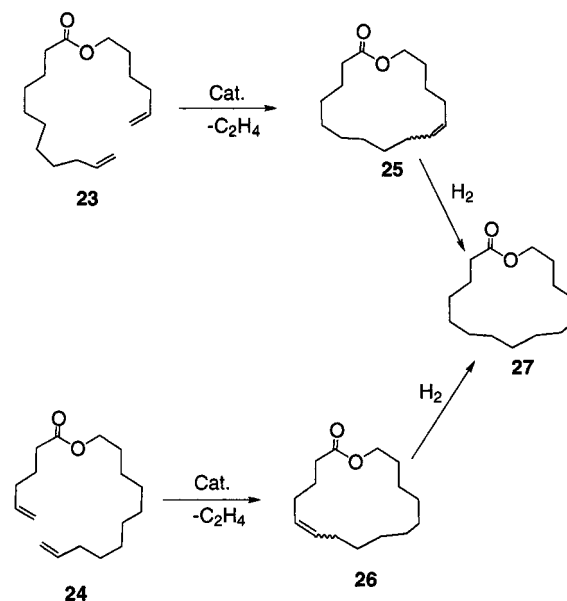
Table 7. RCM of 15[a]
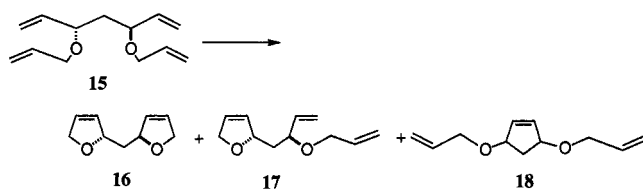
entry	catalyst precursor	cycle	solvent	temp (°C)	time (h)	yield (%)[b]
1[c]	1		C_6H_6	RT	3.0	90 (16)
2	6	1	C_6H_6	RT	2.5	85 (16), 10 (17)
3	6	2	C_6H_6	RT	2.5	10 (16)
4	2		toluene	60	2.0	90 (16)
5	2		CH_2Cl_2	RT	2.0	10 (16), 10 (17)
6	2		CH_2Cl_2	RT	24.0	80 (16)
7	7	1	toluene	60	1.25	92 (16)
8	7	2	toluene	60	1.25	20 (17), 10 (18)
9	3		toluene	60	0.5	90 (16), 8 (17)
10	8	1	toluene	60	1.5	88 (16)
11	8	2	toluene	60	12.0	20 (16)

[a] The catalyst loading is 5 mol %. [b] GC yield, average of two runs. [c] The catalyst loading is 10 mol %.

rings and two carbon−carbon double bonds are formed in the single step. The synthesized polycyclic ethers, which are directly linked, constituted the core motif of *Annonaceous* acetogenins[23] and polyether antibiotics whose pharmacological activities have attracted considerable attention.[24] We report herein results using homogeneous and supported ruthenium catalyst precursors (2, 3, 6−8) in double ring-closing metathesis reactions of acyclic tetraenes 15 and 19. The results are summarized in Tables 7 and 8. Mechanistically, two products are conceivable from the cyclization of the substrates resulting from competition between a single RCM, leading to cycloalkanes 18 and 21 (C-membered ring cyclization), or two RCM reactions, leading to 16 and 20 (tandem two O-membered ring cyclization). RCM of only one O-membered ring gives rise to the formation of 17 and 22.[21] The metathesis reaction of 15 was performed with 5 mol % of the catalyst precursors and afforded the bicyclic compound 16 in good yields in all instances (Table 7, entries 2, 4, 6, 7, 9, 10). The initially formed carbocyclic product 18 was converted to the bicyclic compound 15 over time (Table 7, entries 5, 6). The supported metathesis catalyst precursors 6−8 were very active originally (Table 7, entries 2, 7, 10) but lost

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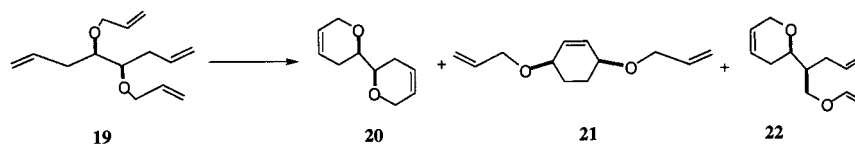(20) (a) Kim, S.-H.; Bowden, N.; Grubbs, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 10801−10802. (b) Kim, S.-H.; Zuercher, W. J.; Bowden, N.; Grubbs, R. H. *J. Org. Chem.* **1996**, *61*, 1073−1081.
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Scheme 3. RCM Leading to the Formation of Exaltolide

their reactivity in the subsequent cycles (Table 7, entries 3, 8, 11). The catalyst precursors 6 and 7 were the only supported catalyst that gave rise to the formation of one O-membered ring-closed product 17 (entries 2 and 8).

Substrate 19 was converted into the bicyclic product 20 in high yields when homogeneous catalyst precursors 1−3 were used (Table 8, entries 2, 5, 8, 13). The carbocycle 21 was formed as well and was converted into the bicyclic product over time (Table 8, entries 1, 2, 6−8). The yield of the reaction using the supported catalyst precursor 6 was much lower than that of its homogeneous counterpart; carbocycle 21 was also produced in this reaction (Table 8, entry 3). Although 7 and 8 showed comparable reactivity to their homogeneous congeners, none of the supported catalyst precursors were reactive in the second cycle (Table 8, entries 3, 4, 11, 12, 14, 15). The monocyclic ether 22, resulting from a single RCM reaction, was formed when using catalyst 6 and supported catalysts 2 and 7 (entries 4, 6, 10, 11).

The RCM reactions involving tetraenes 15 and 19, bearing unsaturated ether functions, produced bicyclic ethers 16 and 20, as major products when catalysts 1, 2, and 3 and the supported catalysts 6, 7, and 8 are used. The previously reported mechanism can explain the formation of polyethers and their monocyclic intermediates.[22]

It has been reported that the catalyst precursors 1, 2, and 5 mediate the formation of medium or large ring systems.[25] To examine the role of the polymer-supported olefin metathesis catalysts in this type of transformation, Exaltolide 27, a musk-odored component of the root oil of *Archangelica officinallis*, used as a valuable perfumery ingredient, was chosen as a target. Ring-closing metathesis of either diene substrate 23 or 24 and subsequent hydrogenation of the product should yield the target molecule 27 (see Scheme 3). The results of the RCM reaction are reported in Table 9. Of the two supported catalyst precursors used in this study, 7 and 8, only the reaction with 8 showed nearly quantitative yield in the first cycle (only one of the *E* or *Z* isomers was obtained); the reaction using catalyst precursor 7

Table 8. RCM of 19[a]

entry	catalyst precursor	cycle	solvent	temp (°C)	time (h)	yield (%)[b]
1[c]	1		C_6H_6	RT	0.5	45 (20), 19 (21)
2	1		C_6H_6	60	6.0	70 (20)
3	6	1	C_6H_6	RT	2.5	58 (20), 30 (21)
4	6	2	C_6H_6	RT	2.5	45 (21), 40 (22)
5	2		toluene	60	1.0	90 (20)
6	2		CH_2Cl_2	RT	1.5	28 (20), 4 (21), 36 (22)
7	2		CH_2Cl_2	RT	2.0	50 (20), 30 (22), 10 (19)
8	2		CH_2Cl_2	RT	12.0	90 (20)
9	7	1	CH_2Cl_2	RT	2.5	10 (20), 80 (19)
10	7	1	CH_2Cl_2	RT	12.0	40 (20), 4 (21), 51 (22),
11	7	1	toluene	60	2.5	90 (20), 10 (22)
12	7	2	toluene	60	3.0	10 (20), 80 (19)
13	3		toluene	60	0.5	90 (20)
14	8	1	toluene	60	1.5	92 (20)
15	8	2	toluene	60	1.0	10 (21), 90 (19)
					12.0	50 (20), 20 (21)

[a] The catalyst loading is 5 mol %. [b] GC yield, average of two runs. [c] The catalyst loading is 10 mol %.

Table 9. Ring-Closing Metathesis of 23[a]
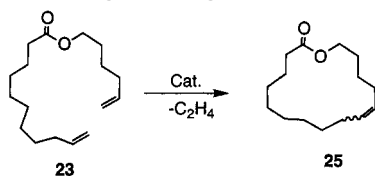
entry	catalyst precursor	cycle	time (h)	yield (%)[b]
1[c]	1		7.0	85
2	2		3.5	87
3	7	1	3.5	50
4	7	2	18.0	10
5	3		1.5	89
6	8	1	1.5	92
7	8	2	5.0	38

[a] All reactions are performed in toluene at 60 °C. [b] GC yield, average of two runs. [c] Reaction was carried out in CH_2Cl_2 at room temperature.

did not go to completion even after 3.5 h (Table 9, entries 3, 6). These catalysts could not be recycled successfully (Table 9, entries 4, 7). It is of note in this example to state that after initial ring closure the reaction can be placed under hydrogen and the hydrogenation to **27** can be efficiently carried out.[26] Compared to the supported catalyst precursors, the homogeneous catalyst precursors **1**−**3** exhibit much better performance (Table 9, entries 1, 2, 5).

It could be noted that when the substrates are oxygen-containing dienes such as **13**, **15**, **19**, and **23**, the polymer-supported catalyst precursors show reduced reactivity in the second catalytic cycle, a phenomenon that was not observed with the nitrogen-containing diene **12**. These results may be interpreted in terms of the reaction between the catalysis-active ruthenium
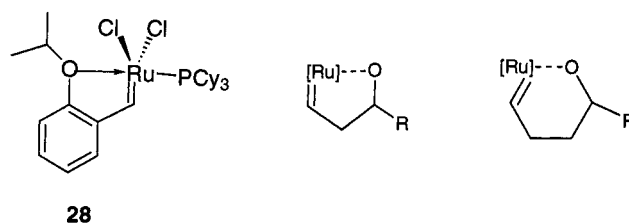

Figure 2. Proposed deactivation mechanism of the Ru catalyst in the RCM of oxygen-containing dienes.

species in the solution and the unreacted substrate that contains an olefinic group and an oxygen donor atom to produce ruthenium carbene complexes similar to Hoveyda's catalyst (**28**)[27] (see Figure 2).[28] The complex thus formed is more stable and less reactive than the initial catalysis-active ruthenium complex and stays in solution instead of attaching back onto the polymer support, thus depleting the active sites in the polymer-supported catalyst precursors and leading to the loss of activity in subsequent cycles.

In all the above RCM experiments initially about 5 mol % of the ruthenium catalysts (**6**, **7**, and **10**, 100 mg; and **8**, 50 mg; 100 mg of **9** corresponds to 1 mol %) have been used. To determine the lowest catalyst loading without significant activity loss, various amounts of the polymer-supported catalyst precursors were tested for their reactivity using **11** as the diene substrate and results are shown in Table 10. These clearly show that in all cases the catalyst loading can be reduced to 12.5 mg without losing significant reactivity (12.5 mg corresponds to 1 mol % ruthenium loading in **6**−**8** and **10** and 0.25 mol % in **9**).

Self-Metathesis Using the Polymer-Supported Catalyst Precursors. An array of complex natural products arises via dimerization through carbon−carbon bond formation.[29] Recently, it has been reported that olefin metathesis (self-metathesis and RCM) provides

(25) (a) Fürstner, A.; Langemann, K. *J. Org. Chem.* **1996**, *61*, 3942−3943. (b) Fürstner, A.; Langemann, K. *Synthesis* **1997**, 792−803. (c) Fürstner, A.; Thiel, O. R.; Ackermann, L.; Schanz, H.-J.; Nolan, S. P. *J. Org. Chem.* **2000**, *65*, 2204−2207.
(26) Examples of such ruthenium tandem catalysis have recently been reported, see for example: Louie, J.; Bielawski, C. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 11312−11313.

(27) Kingsbury, J. S.; Harrity, J. P. A.; Bonitatebus, P. J.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 791−799.
(28) Fürstner, A.; Langermann, K. *Synthesis* **1997**, 792−803.

Table 10. Effect of Catalyst Loading on the RCM of 11

entry	catalyst precursor	yield (%) using 100 mg of polymer	yield (%) using 50 mg of polymer	yield (%) using 25 mg of polymer	yield (%) using 12.5 mg of polymer
1	**6**	95	88	82	79
2	**7**	100	94	72	63
3	**8**		100	97	95
4	**9**	57	55	42	48
5	**10**	95	80	60	40

Table 11. Self-Metathesis Results[a]

X = H, Me, Cl, MeO
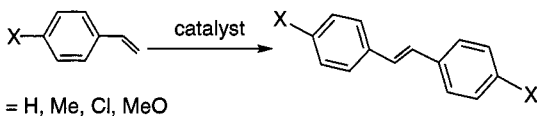
entry	catalyst precursor	X	yield (%)[b]
1	**1**	H	12
		Me	15
		Cl	5
		MeO	16
2	**6**	H	4
		Me	8
		Cl	6
		MeO	8
3	**2**	H	30
		Me	25
		Cl	38
		MeO	14
4	**7**	H	57
		Me	73
		Cl	51
		MeO	24
5	**3**	H	63
		Me	88
		Cl	51
		MeO	16
6	**8**	H	73
		Me	90
		Cl	80
		MeO	44
7[c]	**28**	Cl	26

[a] All reactions are performed with 5 mol % of the catalyst precursor in CH_2Cl_2 at room temperature. The yields were analyzed after 5 h. [b] GC yield, average of two runs. [c] The reaction was performed in toluene at 60 °C. The yield was analyzed after 24 h.

a very efficient method for the assembly of cylindrocyclophanes.[30] This combined with the fact that the homogeneous catalyst precursors are anchored on the polymer support via a simple cross metathesis reaction prompted us to examine the reactivity of the homogeneous olefin metathesis catalyst precursors **1**−**3** and their supported analogues **6**−**8** using a series of substituted styrenes as substrates. The results are summarized in Table 11.

The order of reactivity among the homogeneous catalysts is **3** > **2** > **1**. The same order is observed for their supported analogues: **8** > **7** > **6** with the supported catalyst precursors being more reactive than their homogeneous congeners (see Table 11). High yields

are observed when 4-methylstyrene and 4-cholorostyrene are used as substrates, while self-metathesis for the methoxy-substituted substrate is very poor. Products obtained gave *E* isomers only. We also found that Hoveyda's catalyst **28** is a very poor self-metathesis catalyst (Table 11, entry 7), which could explain the reluctance of the ruthenium-active species in solution to go back onto the polymer support after it has been exposed to an oxygen-containing diene (vide supra).

Mechanism. As we previously reported,[14] we propose that the mechanism involved in the polymer-supported catalyst transformation is a "boomerang" mechanism as first proposed by Barrett and co-workers.[10] In this mechanism, catalyst is released into the solution and takes part in the ring-closing metathesis as in the homogeneous catalysis. The catalytic-active ruthenium species is then recaptured by the vinyl groups of divinylbenzene that are available in abundance (45% of the bulk polymer). Barrett and co-workers have used additives (1-alkenes and triphenylphosphine) to stabilize the ruthenium center in solution.[11] It is believed that the ruthenium methylidene species, which decomposed through a unimolecular process,[31] is at the origin of catalyst death in these "boomerang" polymer-supported systems. A noted difference between the polystyrene and poly-DVB-supported system is the high recovery rate of the poly-DVB system even in the absence of additives. The proposed "boomerang" mechanism is supported by crossover experiment results when a container of virgin DVB has been shown to become impregnated with catalyst when added to reaction mixtures containing DVB-supported catalysts. Barrett and Braddock first conceived of this experiment to provide support for the "boomerang" mechanism.[11] In cases where the catalyst recyclability is poor, the stability of the methylidene species in solution is in question. The substrates showing poor recyclability were selected for their capability of chelating in a fashion illustrated in Figure 2. If chelation occurred, this would render catalyst recovery difficult by DVB under recycling conditions. Most likely the ruthenium species would decompose in solution since accumulated washings do not show a very high level of soluble ruthenium species. Grubbs has stated that "boomerang" catalysts simply act by a slow-release mechanism.[32] In light of the U-tube[11] and crossover experiments performed by us and by the Barrett group, it appears most likely that a "boomerang" mechanism is at play with simple diene substrates. However, in cases where species are unable to be recaptured by the polymer support, the recyclability and further activity are poor. In examples where highly hindered substrates are employed, a slow-release behavior is a more plausible explanation for the observed decrease in catalyst recyclability and efficiency.

We have also studied the effect of phosphine dissociation on the outcome of the reaction. Addition of free PCy_3 inhibits the RCM of diethyl diallymalonate **11** in the presence of polymer-supported catalyst precursor **7** (yield = 100% when no free phosphine is added and plummets to 5% in the presence of 10 mol % of PCy_3). In another experiment the yield of the RCM of dially-

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(30) Smith, A. B., III; Kozmin, S. A.; Adams, C. M.; Paone, D. V. *J. Am. Chem. Soc.* **2000**, *122*, 4984−4985.

(31) Ulman, M.; Grubbs, R. H. *J. Org. Chem.* **1999**, *64*, 7202−7207.
(32) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543−6554.

Scheme 4.   Proposed Dissociative-Boomerang Mechanism
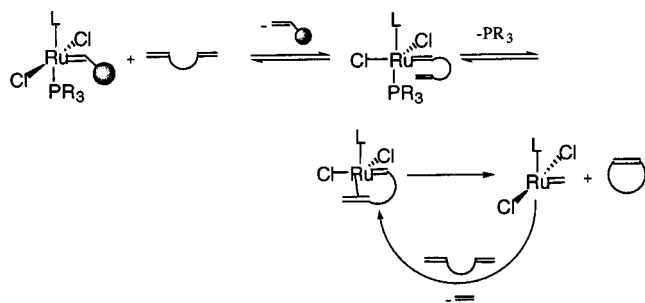
tosylamine **12** jumped to 100% when CuCl was added as a phosphine sponge (see Table 4, entry 8). These results indicate that phosphine dissociation is crucial step in these RCM reactions. The proposed mechanism is depicted in Scheme 4.

Since the supported catalyst is generated by mixing the homogeneous complex and the poly-DVB support, we thought the polymer support could be used as an efficient procedure to "fish out" the ruthenium catalyst from solution, thereby simplifiying the workup procedure. To test this hypothesis, a 10-fold excess (by weight) of poly-DVB was added to catalytic reactions using **2** and **3**. Then the reaction mixture having reached completion was heated for 5 h and subsequently filtered. The isolated poly-DVB support bearing the recovered catalyst was then subjected to an RCM reaction and showed 80% conversion to the desired product. It is noted here that recapture experiments are most efficient with the most active cross metathesis catalysts **7** and **8**. This catalyst recovery−reutilization approach is environmentally more desirable to prior efforts that have focused on destroying the catalyst with additives.[33]

Conclusion. We have developed a simple heterogeneous catalytic system for RCM that is recoverable and recyclable for simple ring-closing substrates. These polymer-supported catalysts display reactivity comparable to that of their homogeneous counterparts, tolerate functional groups, and perform very well with unsubstituted dienes. They perform poorly with substrates that have alternate coordination modes that compete with ruthenium recapture by DVB. In examples where highly hindered substrates are employed, the supported catalysts effectively perform by a slow release of the ruthenium catalyst. The scope and limitations are now better understood, and studies aimed toward the synthesis of more active and more recyclable catalysts are under way.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of dry argon with standard Schlenk tube techniques or in a MBraun glovebox containing less than 1 ppm of oxygen and water. Anhydrous solvents were purchased from Aldrich and used as received. Divinylbenzene (tech. 55%) was purchased from Aldrich and degassed prior to use. Diethyldiallylmalonate (**11**) was purchased from Aldrich, dried over P_2O_5, and vacuum distilled prior to use. Diallytosylamine (**12**),[34] diethyldi(2-methylallyl)malonate (**14**),[35] PCy$_3$Ru(IMes)-

(=CHPh)Cl (**2**),[3] PCy$_3$Ru(SIMes)(=CHPh)Cl$_2$ (**3**),[4] (PCyp$_3$)Ru-(IMes)(=CHCH=C(CH$_3$)$_2$)Cl$_2$[3] (**4**), (PCy$_3$)Ru(IPr)(3-phenylindenylid-1-ene)Cl$_2$ (**5**),[5] 3,5-bisallyloxyhepta-1,6-diene (**15**),[23] 4,5-bisallyloxyocta-1,7-diene (**19**),[29] diene **23**,[24] and Hoveyda's catalyst **28**[7] were prepared according to literature procedures. All other reagents were commercial grade and were used as received without further purification.

The yields of the catalytic reactions were analyzed using a HP 5890 GC with a FID detector and HP-5 column. Thin-layer chromatograms (TLC) and flash chromatography separations were respectively performed on precoated silica gel 60 F254 plates (Merck, 0.25 mm) and on Merck silica gel 60 (230−400 mesh). NMR spectra were recorded on a Oxford 400 MHz spectrometer. Mass spectra were recorded at 70 eV using chemical ionization mode (CI-NH$_3$). IR spectra were recorded as casts on a FT instrument. Elemental analyses were performed by CNRS, Service Central d'Analyse, France. Atomic absorption spectroscopy was performed by Desert Analysis, Tucson, AZ. Experimental synthetic procedures, leading to the isolation of previously unreported complexes, are described below.

Synthesis of Poly-DVB. In the glovebox, AIBN (1.5 wt % of divinylbenzene, 0.066 g), divinylbenzene (tech., 55%, 4.44 g, 5 mL), and toluene (5 mL) were added to a 20 mL scintillation vial, which was sealed with a Teflon-covered screw cap. The vial was then heated to 80 °C for 24 h to give a white insoluble polymer. The vial was opened in the air; the polymer was scraped off the vial and ground to a powder. The solvent was removed in vacuum (yield = 90%).

Synthesis of Polymer-Supported Ruthenium Catalysts 6−10. In the glovebox, poly-DVB (1.0 g), the ruthenium catalysts **1**−**5** (10 wt %, 0.1 g), and toluene (10 mL) were added to a Schlenk flask. The reaction mixture was heated to 50 °C for 5 h and stirred at room temperature for 12 h. The slurry was then filtered on a Schlenk frit, washed with toluene (3 × 10 mL), and dried in vacuo to yield a pale pink solid. Anal. Ru%: **6**, 0.60; **7**, 0.38; **8**, 1.20; **9**, 0.12; **10**, 0.32.

Synthesis of 4,5-Bisacetoxyocta-1,7-diene (13). The starting material, octa-1,7-diene-4,5-diol, was prepared from commercially available 1,3-butadiene diepoxide according to a literature procedure.[28] To a solution of octa-1,7-diene-4,5-diol (500 mg, 3.52 mmol) in dry ether (25 mL) was added dry pyridine (0.86 mL, 10.55 mmol), and the resulting solution was cooled to 0 °C. Acetyl chloride (0.75 mL, 10.55 mmol) was added dropwise, and the reaction mixture was stirred at room temperature for 3 h. The mixture was treated with 1 N HCl (2 × 10 mL), and the organic layer was separated, washed with saturated NaHCO$_3$ (1 × 10 mL) and saturated NaCl (1 × 10 mL), dried over MgSO$_4$, and concentrated. The crude product was purified by column chromatography (pentane/ether, 7/3) to yield the diester (691 mg, 87% yield). ^{1}H NMR (CDCl$_3$): δ 5.71−5.57 (m, 4H), 5.04−4.95 (m, 6H), 2.29−2.21 (m, 4H), 2.01 (s, 6H). ^{13}C NMR (CDCl$_3$): δ 170.2, 132.7, 118.3, 72.5, 35.4, 20.8. IR (neat, cm^{-1}): 2982, 1743, 1373, 1226. MS (DCI/NH$_3$): m/z (MNH$_4^+$) 244.

1,2-Bisacetoxy-4-cyclohexene (22). ^{1}H NMR (CDCl$_3$): δ 5.58−5.54 (m, 2H), 5.09 (dd, J = 3.5, 8.0 Hz, 2H), 2.58 (dd, J = 1.8, 16.0 Hz, 2H), 2.22−2.10 (m, 2H), 2.06 (s, 6H). ^{13}C NMR (CDCl$_3$): δ 170.5, 123.7, 70.0, 30.0, 21.1. IR (neat, cm^{-1}): 2937, 1737, 1370, 1250, 1045. MS (DCI/NH$_3$): m/z (MNH$_4^+$) 216.

General Procedure for Ring-Closing Metathesis. In the glovebox, poly-DVB/Ru catalyst (100 mg (**6**, **7**, **9**, and **10**) and 50 mg (**8**)), solvent (2 mL), and the substrate (1 M solution, 118 μL) were loaded in a Schlenk flask. The reaction mixture was heated under argon to temperatures shown in Tables 2, 4, 5, 6, 7, and 8. Product formation and diene disappearance were monitored by GC analyses.

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Experiments on the Recycling and Reuse of Catalysts 6−10. After the allotted times mentioned in Tables 2, 4, 5, 6, 7, and 8 for each reaction, the polymer-supported catalyst precursors were filtered, washed with the same solvent used in the reactions, and dried in a vacuum. The catalysts were loaded into fresh Schlenk flasks, and a fresh sample of the solvent (2 mL) was then added to each catalyst followed by another aliquot of the substrate (1 M, 118 μL). The extent of reaction was then monitored by GC after the allotted times mentioned in Tables 2 and 4−8. The percentage of the leached ruthenium for each supported catalyst after four cycles was determined by atomic absorption spectroscopy. Anal. Ru%: **6**, 0.033; **7**, 0.009; **8**, 0.020; **9**, 0.0065; **10**, 0.007.