An ionic liquid-tagged second generation Hoveyda–Grubbs ruthenium carbene complex as highly reactive and recyclable catalyst for ring-closing metathesis of di-, tri- and tetrasubstituted dienes

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Abstract

A second generation Hoveyda–Grubbs ruthenium carbene complex bearing an ionic liquid tag was prepared and shown to be a highly reactive catalyst for the ring-closing metathesis of di-, tri- and tetrasubstituted diene and enyne substrates in minimally ionic solvent systems ([Bmim]PF_6/CH_2Cl_2, 1:9–1:1 v/v). Both the catalyst and the ionic liquid can be conveniently recycled and repeatedly reused (up to 17 cycles) with only a very slight loss of activity. The ionic liquid tag is crucial to the high level of recyclability of the catalyst since the original second generation Grubbs and Hoveyda–Grubbs catalysts rapidly lose their activity when recycled in the ionic liquid layer.
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1. Introduction

The advent of well-defined Ru carbene catalysts, most notably, the Grubbs-type Ru benzylidenes **1** [1a] and **2** [1b], and the closely related Ru complex **3** [1c,1d], has fueled the widespread application of olefin metathesis [2] (Fig. 1). Another significant advance in this area is the discovery by Hoveyda and co-workers of the Ru catalysts **4** [3a] and **5** [3b] that bear an isopropoxy ether ligand tethered to the benzylidene group. The unique bidentate nature of this ligand renders catalysts **4** and **5** a number of interesting and useful properties [3d]. For example, both **4** and **5** exhibit enhanced stability compared to catalysts **1** and **2**, allowing them to be retrieved from the crude reaction mixture by silica gel chromatography. These catalysts also show reactivity profiles different from those of **4** and **5**. The robustness and recyclability of **4** and **5** provide an excellent opportunity for the development of immobilized and supported Ru catalysts for olefin metathesis [4]. Our contribution in this field includes the synthesis and catalytic application of the air stable poly(ethylene glycol) monomethyl ether (MeO-PEG)-bound first generation Ru catalyst **6** [5a], the more reactive poly(ethylene glycol) (PEG)-bound second generation Ru catalyst **7** [5b], and the poly(fluoroalkyl acrylate)-bound second generation Ru complex **8** [6] (Fig. 2). We have established that the soluble polymer-bound catalysts **6** and **7** are highly reactive toward the ring-closing metathesis (RCM) of various diene and enyne substrates, and in

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Fig. 1. Ru catalysts for olefin metathesis.
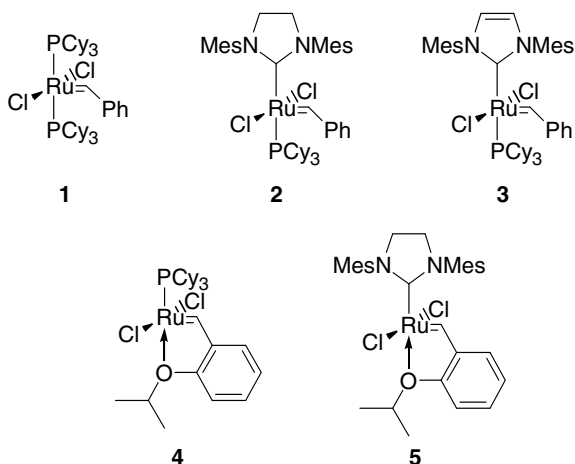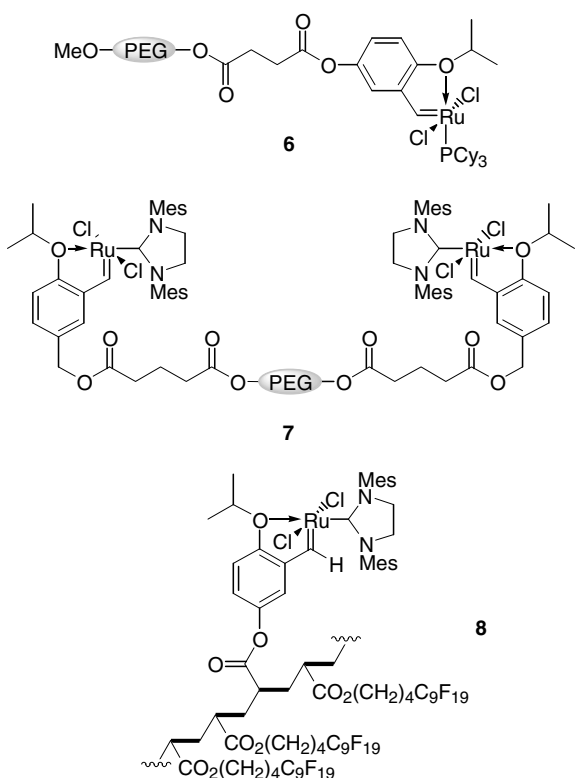

Fig. 2. Soluble polymer bound and fluorous Ru catalysts.

Fig. 3. Ionic liquid-tagged Ru catalysts.

in minimally fluorous solvent systems and can be readily separated from the reaction mixture by fluorous extraction with FC-72 [7,8] and repeatedly reused.

The recently emerged room-temperature ionic liquids have gained increasing popularity as innovative and environmentally benign reaction media, and as new vehicles for the immobilization of transition metal-based catalysts [9]. This new concept of catalyst immobilization and recycling has also been applied to several Ru-catalyzed olefin metathesis reactions [10]. Although the olefin metathesis reactions generally proceed smoothly if an appropriate ionic liquid is chosen as the solvent, the recovered catalysts in the ionic liquid layer rapidly lose their activity in subsequent runs. We have recently reported that both the first generation Grubbs catalyst **1** and the more stable and recyclable catalyst **4** experienced poor recyclability when the room-temperature ionic liquid 1-butyl-3-methylimidazolium hexafluoro phosphate [Bmim]PF$_6$ was used to immobilize these catalysts [11]. This is attributed to the inherently poor recyclability in the case of catalyst **1**, and for the recyclable catalyst **4**, its poor retention in the ionic liquid phase, and hence significant leaching during extraction of the reaction product with diethyl ether. To solve this problem, a designer ionic liquid tag is attached to the isopropoxy styrenyl ligand and the resulting catalyst **9** (Fig. 3) was found to exhibit an extremely high level of recyclability in RCM reactions that lead to the formation of disubstituted cyclic olefins. We now wish to report on our extension of this strategy to the second generation Ru catalyst **5**. The ionic liquid-bound second generation Ru catalyst **10** maintains a high level of activity similar to that of **5** but can be conveniently recycled and repeatedly reused in the RCM of a wide variety of di-, tri-, and even tetrasubstituted diene and enyne substrates. A similar concept was used, independently, by Mauduit and co-workers in the development of the ionic liquid supported-Ru catalysts **11** [4p] and **12** [4q].

the case of catalyst **7**, cross metathesis (CM) and ring-opening/cross metathesis (RO-CM). Meanwhile, these catalysts can be conveniently recycled by precipitation with diethyl ether and repeatedly reused without significant loss of their activity, demonstrating the practical advantage of using a soluble polymer to immobilize Ru catalysts. The air stable fluorous Ru carbene complex **8** was shown to be highly reactive in effecting the RCM of a broad spectrum of diene and enyne substrates
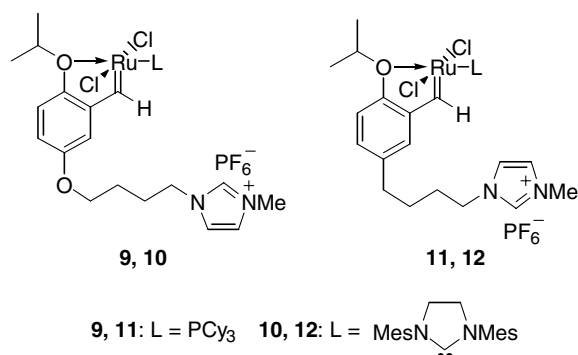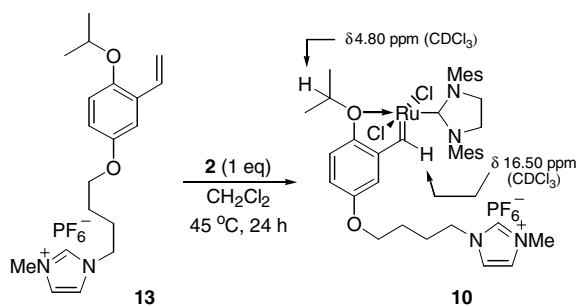
Scheme 1. Synthesis of the ionic liquid-tagged Ru catalyst 10.

2. Result and discussion

The ionic liquid-tagged Ru catalyst 10 was assembled by treatment of the functionalized ionic liquid 13 [11] with an equimolar amount of the second generation Grubbs catalyst 2 in CH_2Cl_2 at 45 °C as shown in Scheme 1. After removal of the volatiles under vacuum, ^{1}H NMR (CDCl_3, 500 MHz) spectroscopic analysis revealed a conversion of greater than 90% of the styrene ligand. The formation 10 was indicated by its characteristic carbene signal at δ 16.50 ppm, which is the only carbene peak observed, as well as the methine proton peak at δ 4.80 ppm of the Ru-bound isopropoxy ligand. The structural assignment was secured by comparison with ^{1}H NMR data of the original Hoveyda–Grubbs' catalyst 5 (δ 16.56 ppm of Ru = CHPh and 4.90 ppm of OCHMe_2) [3b] and those of the PEG-bound catalyst 7 [5b] and the fluorous Ru catalyst 8 [6]. Ionic liquid

[Bmim]PF_6 was then added to the crude reaction mixture followed by washing of the ionic liquid layer with anhydrous ether to remove the released PCy_3 ligand.

The activity and recyclability of 10 was initially evaluated with the RCM of test dienes 14–16 as shown in Table 1. The reactions were performed in a homogeneous mixture of [Bmim]PF_6 and CH_2Cl_2 (1:9 v/v) as the solvent [12,13] and in the presence of 1 mol% of catalyst 10 [14] at 45 °C. Under these conditions, diethyl diallylmalonate 14 underwent RCM quantitatively after 1 h as revealed by ^{1}H NMR spectroscopy. Separation of the reaction product simply involves concentration of the reaction mixture under vacuum followed by extraction of the ionic liquid layer with diethyl ether [15]. The ionic liquid layer was then used for a second run of the RCM. As shown by the data in Table 1, the recycled catalyst in the ionic liquid layer remained highly reactive, even after 10 runs of recycling and reuse. This high level of recyclability was also established with the RCM of both dienes 15 and 16.

Since an advantage of the second generation Ru catalysts such as 2, 3 and 5 that bear a nucleophilic N-heterocyclic carbene ligand is their increased activity relative to that of the first generation catalysts 1 and 4, we next examined the performance and recyclability of 10 in the RCM of trisubstituted dienes by using 20 as the test substrate [5b,6]. It can be seen from Table 2 that diene 20 cyclized cleanly to give the trisubstituted cyclic olefin 21 in the presence of 2 mol% of 10. Both the ionic liquid and the catalyst were recycled and used for a total of six runs with only a very slight drop in its

Table 1
Reactivity and recyclability of the ionic liquid-tagged Ru catalyst 10 in the RCM of disubstuted dienes[a]

14 → 17[b]

Cycle	1	2	3	4	5	6	7	8	9	10
% Conv[c]	>98	≫98	98	98	96	94	92	92	92	90

15 → 18[b]

Cycle	1	2	3	4	5	6	7	8	9	10
% Conv[c]	>98	>98	>98	>96	>98	98	98	96	97	96
Cycle	11	12	13	14	15	16	17			
% Conv[c]	95	95	94	94	93	93	90			

16 → 19[d]

Cycle	1	2	3	4	5	6	7	8	9	10
% Conv[c]	97	98	97	98	96	97	96	96	93	89

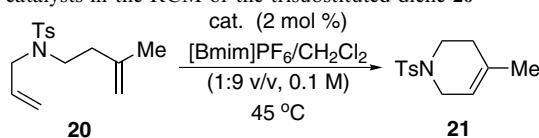[a] All reactions were performed with 1.0 mmol of the diene substrates in the solvent system [Bmim]PF_6/CH_2Cl_2 (1:9 v/v, 5 mL) at 45 °C under an Ar atmosphere.
[b] Reactions were run for 1 h.
[c] Determined by 500 MHz ^{1}H NMR spectroscopy.
[d] Reactions were run for 1.5 h.

Table 2
Reactivity and recyclability of different Ru catalysts in the RCM of the trisubstituted diene **20**[a]

Cat. **10**	Cycle	1	2	3	4	5	6
	Time (h)	2	2	2	2	2	2
	% Conv.[b]	96	96	95	93	91	90
Cat. **2**	Cycle	1	2	3	4	–	–
	Time (h)	2	2	2	4		
	% Conv.[b]	98	76	38	20		
Cat. **5**	Cycle	1	2	3	4	–	–
	Time (h)	2	2	2	4		
	% Conv.[b]	97	52	34	12		

[a] All reactions were performed with 0.5 mmol of the diene.
[b] Determined by 500 MHz ^{1}H NMR spectroscopy.

activity. In contrast, the un-tagged Ru catalysts **2** and **5** rapidly lost their activity in the second and subsequent runs, pointing to a limitation of using [Bmim]PF$_6$ as an ionic liquid medium to effectively immobilize the catalysts. Therefore, the ligand modification via phase tagging in catalyst **10** plays a crucial role in maintaining its high level of recyclability.

Having established the recyclability and reusability of **10**, we next examined its performance in the RCM of a variety of tri- and tetrasubstituted diene and enyne substrates leading to the formation of various carbocyclic and heterocyclic olefins (Table 3). To test the scope of catalyst **10** in the formation of trisubstituted cyclic olefins, a single batch of the catalyst (2 mol%) was used in the RCM of seven substrates in a consecutive manner. In the first run, the sulfone-tethered enyne **22** [6,16] underwent RCM uneventfully to give in high yield the conjugate diene **23** after 5 h at 45 °C. (Table 3, catalyst batch **A**, cycle 1). The recycled ionic layer was then used in the RCM of the trisubstituted dienes **24**, **26**, **28**, **30**, **32**, and **34**. At the end of each reaction, the catalyst/ionic liquid was recovered and subsequently reused in the reaction of another substrate for an appropriate period of reaction time that was chosen based on our previous experience with these dienes using the fluorous catalyst **8** [6]. All reactions proceeded smoothly and gave the corresponding cyclic olefin products all in excellent yield (catalyst batch **A**, cycles 2–7). Finally, the reactivity of **10** in the RCM of tetrasubstituted dienes was examined using sulfonamide **36** as a test substrate [5b,6]. In the presence of 4 mol% of **10**, the tetrasubstituted cyclic olefin **37** was formed in high yield after 16 h (catalyst batch **B**, cycle 1). The recovered catalyst was used in a second run of this demanding metathesis reaction and essentially similar reactivity was observed (catalyst batch **B**, cycle 2). Remarkably, the catalyst remained fully active

even after being used for an extended period of time as tested by its performance in the RCM of diene **20** (catalyst batch **B**, cycle 3), further attesting to the superb stability and recyclability of catalyst **10**.
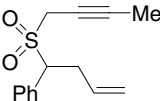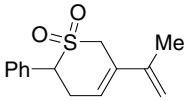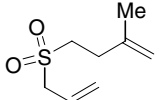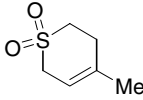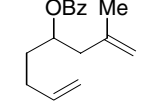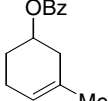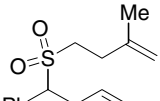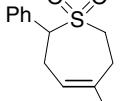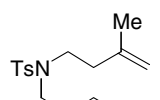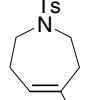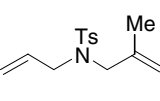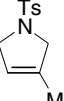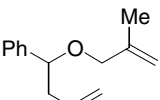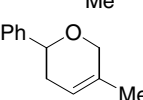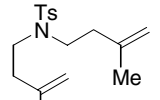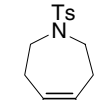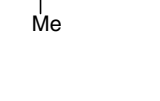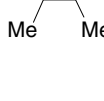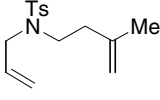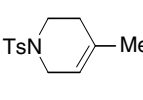
In conclusion, we have shown that the readily assembled ionic liquid-tagged Ru carbene complex **10** is a highly efficient catalyst for the RCM of di-, tri- and tetrasubstituted diene and enyne substrates in minimally ionic solvent systems, with the combined advantage of high reactivity and a high level of recyclability and reusability. Both the catalyst and the ionic liquid can be conveniently recycled and repeatedly reused with only a very slight loss of activity. Given the growing interest in the development of catalyst systems suitable for organic transformations in ionic liquid and the widespread application of olefin metathesis in organic synthesis, catalyst **10** should prove to be of unique utility in both areas.

3. Experimental

3.1. General

Unless otherwise noted, all reactions were performed under an atmosphere of dry Ar with oven-dried glassware and anhydrous solvents. CH$_2$Cl$_2$ was dried over CaH$_2$ and distilled prior to use. Diethyl ether was distilled from sodium/benzophenone under a nitrogen atmosphere. Catalyst **2** [1b] was obtained from Strem and was used as received. The ionic liquid [Bmim]PF$_6$ was purchased from Acros and used as received. ^{1}H NMR spectra were acquired in CDCl$_3$ at 500 MHz. Diethyl diallylmalonate **14** was purchased from Aldrich. Diene **15** [5,6,11] was prepared from diallylamine and *p*-toluenesulfonyl chloride in the presence of Et$_3$N in

Table 3
Reactivity and recyclability of the ionic liquid-tagged Ru catalyst **10** in the RCM of tri- and tetrasubstuted enyne and diene substrates[a]

catalyst batch	Cycle	Substrate		Product		Conditions	%conv.[b] (% yield)[c]
A (2 mol % Ru)	1		22		23	45 °C, 5 h	78(75)
	2		24		25	45 °C, 1.5 h	>98(96)
	3		26		27	45 °C, 1.5 h	91(90)
	4		28		29	45 °C, 3 h	>98(98)
	5		30		31	45 °C, 1.5 h	98(96)
	6		32		33	45 °C, 3 h	94(92)
	7		34		35	45 °C, 1.5 h	93(92)
B (4 mol % Ru)	1		36		37	45 °C, 16 h	79(77)
	2		36		37	45 °C, 16 h	78(76)
	3 (2 mol % Ru)		20		21	45 °C, 2 h	93(91)

[a] Reactions were performed with 0.5 mmol of the substrates in [Bmim]PF$_6$/CH$_2$Cl$_2$ (1:9 v/v, 5 mL) for all cycles of catalyst batch **A** and 0.25 mmol of diene **36** in [Bmim]PF$_6$/CH$_2$Cl$_2$ (1:1 v/v, 1 mL) for cycles 1 and 2 of catalyst batch **B**, and 0.50 mmol of diene **20** in [Bmim]PF$_6$/CH$_2$Cl$_2$ (1:9 v/v, 5 mL) for cycle 3 of catalyst batch **B**.
[b] Determined by 500 MHz ^{1}H NMR spectroscopy.
[c] Isolated yield after purification by silica gel chromatography.

CH$_2$Cl$_2$. Diene **16** [5,11] was synthesized from *N*-allyl-*p*-toluenesulfonamide by alkylation with 5-bromo-1-pentene in the presence of NaH in DMF. Diene **34** was prepared according to literature [17]. All other diene substrates are known materials and were prepared according to published procedures [6,16]. All products reported in Tables 1–3 are known compounds and were reported previously [5,6,11,16].

3.2. Immobilization of Ru catalyst 2 in the ionic liquid [Bmim]PF₆: general procedure for the synthesis of the ionic liquid-tagged Ru carbene complex 10, reactivity and recyclability of 10 in the RCM of dienes 14–16

Preparation of **10**: general procedure: A 10 mL flask was charged with a solution of the ionic liquid-tagged ligand **13** (4.6 mg, 0.010 mmol) and the Grubbs catalyst **2** (8.4 mg, 0.010 mmol) in CH_2Cl_2 (4 mL). The reaction mixture was heated to 45 °C (bath temperature) for 24 h. After cooling to rt, the solvent and volatiles were removed under vacuum. ¹H NMR spectroscopic analysis indicated a greater than 90% conversion of the styrene ligand and the formation of **10** as evidenced by the upfield shift of the methine peak in $OCHMe_2$, δ 4.80 ppm (septet, 1H, $J = 6.0$ Hz) and the characteristic carbene signal at δ 16.50 ppm. The ionic liquid [Bmim]-PF_6 (0.5 mL) was added and the crude reaction mixture thoroughly washed with ether (4×5 mL) to remove the released PCy_3 ligand. The ionic liquid layer was then dried under vacuum for 1 h before use.

RCM of **14**: general procedure for product isolation and catalyst recycling. To a flask containing catalyst **10** (0.01 mmol) in [Bmim]PF₆ (0.5 mL), prepared according to the general procedure, was added a solution of diene **14** (24 µL, 25 mg, 1.0 mmol) in CH_2Cl_2 (4.5 mL). The reaction mixture was heated to 45 °C for 1 h. After cooling to rt, the reaction mixture was concentrated under vacuum to remove the CH_2Cl_2 cosolvent and extracted with ether (3×5 mL). The combined ether extracts were concentrated to dryness in vacuo. Examination of the crude reaction product by ¹H NMR spectroscopy revealed complete conversion of **14** and the clean formation of the cyclized product **17**. The ionic lquid layer was dried on the vacuum line prior to its reuse. A second run of the RCM of **14** using the recycled catalyst and ionic liquid was conducted in exactly the same way as described for the first cycle. This reaction was repeated for eight more cycles, each time using the catalyst and ionic liquid recovered from a previous cycle. The results are listed in Table 1.

Another two batches of catalyst **10** were prepared and used in the RCM of dienes **15** and **16**, respectively. A total of 17 cycles for diene **15** and ten cycles for diene **16** were performed according to the general procedures as described for the RCM of diene **14**. The results are listed in Table 1.

3.3. Reactivity and recyclability of catalysts 10, 2 and 5 in the RCM of Diene 20

The RCM of diene **20** [6] (140 mg,0.5 mmol) was performed with a new batch of catalyst **10** (0.01 mmol), prepared according to the general procedure, in[Bmim]PF₆ (0.5 mL)/CH_2Cl_2 (4.5 mL) at 45 °C for 2 h for a total of six cycles. At the end of each cycle, the ionic liquid layer

was recycled from the crude reaction mixture according to the general procedures and subsequently reused for the next cycle. The crude reaction product was analyzed by ¹H NMR spectroscopy to determine the conversion of diene **20** to the cyclized product **21** [6]. The results are listed in Table 2. The same reaction was repeated in the presence of catalysts **2** and **5** [3b], respectively, for a total of four cycles (2 h for the first three cycles and 4 h for cycle 4) for each catalyst. The results with catalysts **2** and **5** are listed in Table 2.

3.4. Sequential use of catalyst 10 in the RCM of different substrates

3.4.1. Catalyst batch A, cycle 1

Enyne **22** [16] (124 mg,0.5 mmol) and catalyst **10** (0.01 mmol), prepared according to the general procedure, in[Bmim]PF₆ (0.5 mL)/CH_2Cl_2 (4.5 mL) were heated at 45 °C for 5 h. After cooling to rt, the crude reaction product was separated from the ionic liquid layer following the general procedure. Analysis of the crude product mixture by ¹H NMR spectroscopy revealed a 78:22 ratio between the RCM product **23** and enyne **22**. Purification by flash column chromatography (hexanes/CH_2Cl_2, 1:1 v/v) gave 93 mg (75%) of the known cyclic sulfone **23** [6,16].

3.4.2. Catalyst batch A, cycle 2

The catalyst and ionic liquid recycled from the RCM of **22** (cycle 1) was used in the RCM of **24** [6] (86 mg, 0.50 mmol) under identical conditions to those of **22** except that the reaction mixture was heated at 45 °C for 1.5 h. After separation of the ionic liquid layer according to the general procedure, the crude product mixture was analyzed by ¹H NMR spectroscopy which revealed complete conversion of **24** and clean formation of the cyclized product **25**. Purification by flash column chromatography (hexanes/CH_2Cl_2, 1:3 v/v) gave 70 mg (96%) of the known cyclic sulfone **25** [6,18].

3.4.3. Catalyst batch A, cycle 3

The catalyst and ionic liquid recycled from the RCM of **24** (cycle 2) was used in the RCM of **26** [6] (122 mg, 0.50 mmol) under identical conditions to these of **24**. After separation of the ionic liquid layer according to the general procedure, the crude product mixture was analyzed by ¹H NMR spectroscopy which revealed a 91:9 ratio between the RCM product **27** and diene **26**. Purification by flash column chromatography (hexanes/EtOAc, 20:1 v/v) gave 97 mg (90%) of the known compound **27** [6].

3.4.4. Catalyst batch A, cycle 4

The catalyst and ionic liquid recycled from the RCM of **26** (cycle 3) was used in the RCM of **28** [6] (132 mg, 0.50 mmol) under identical conditions to these of **24**

except that the reaction mixture was heated at 45 °C for 3 h. After separation of the ionic liquid layer according to the general procedure, the crude product mixture was analyzed by ^{1}H NMR spectroscopy which revealed complete conversion of **28** and clean formation of the cyclized product **29**. Purification by flash column chromatography (hexanes/CH$_2$Cl$_2$, 1:2 v/v) gave 116 mg (98%) of the known cyclic sulfone **29** [6].

3.4.5. Catalyst batch A, cycle 5

The catalyst and ionic liquid recycled from the RCM of **28** (cycle 4) was used in the RCM of **30** [6] (147 mg, 0.50 mmol) under identical conditions to these of **24**. After separation of the ionic liquid layer according to the general procedure, the crude product mixture was analyzed by ^{1}H NMR spectroscopy which revealed a 98:2 ratio between the RCM product **31** and diene **30**. Purification by flash column chromatography (hexanes/EtOAc, 6:1 v/v) gave 127 mg (96%) of the known compound cyclic sulfonamide **31** [6].

3.4.6. Catalyst batch A, cycle 6

The catalyst and ionic liquid recycled from the RCM of **30** (cycle 5) was used in the RCM of **32** [6] (133 mg, 0.50 mmol) under identical conditions to these of **28**. After separation of the ionic liquid layer according to the general procedure, the crude product mixture was analyzed by ^{1}H NMR spectroscopy which revealed a 94:6 ratio between the RCM product **33** and diene **32**. Purification by flash column chromatography (hexanes/EtOAc, 8:1 v/v) gave 109 mg (92%) of the known compound cyclic sulfonamide **33** [6,17a].

3.4.7. Catalyst batch A, cycle 7

The catalyst and ionic liquid recycled from the RCM of **32** (cycle 6) was used in the RCM of **34** [17b] (101 mg, 0.50 mmol) under identical conditions to these of **24**. After separation of the ionic liquid layer according to the general procedure, the crude product mixture was analyzed by ^{1}H NMR spectroscopy which revealed a 93:7 ratio between the RCM product **35** and diene **34**. Purification by flash column chromatography (hexanes/CH$_2$Cl$_2$, 4:1 v/v) gave 80 mg (92%) of the known cyclic ether**35** [6,19].

3.4.8. Catalyst batch B, cycles 1 and 2

Tetrasubstituted diene **36** [6] (77 mg,0.25 mmol) and catalyst **10** (0.01 mmol), prepared according to the general procedure, in 0.5 mL [Bmim]PF$_6$ and 0.5 mL CH$_2$Cl$_2$ were heated at 45 °C for 16 h. After cooling to rt, the crude reaction product was separated from the ionic liquid layer following the general procedure. Analysis of the crude reaction product by ^{1}H NMR spectroscopy revealed a 79:21 ratio between the RCM product **37** and diene **36**.Purification by flash column chromatography (hexanes/EtOAc, 12:1 v/v) gave 54 mg

(77%) of the known cyclic sulfonamide **37** [6]. This reaction was repeated for another run using the catalyst and ionic liquid recovered from the first run. The result is listed in Table 3.

3.4.9. Catalyst batch B, cycle 3

The catalyst and ionic liquid recycled from the RCM of **36** (cycle 2) was used in the RCM of **20** [6] (140 mg, 0.50 mmol) in 4.5 mL CH$_2$Cl$_2$. The reaction was run for 2 h at 45 °C. After separation of the ionic liquid layer according to the general procedure, the crude product mixture was analyzed by ^{1}H NMR spectroscopy which revealed a 93:7 ratio between the RCM product **21** and diene **20**. Purification by flash column chromatography (hexanes/EtOAc, 5:1 v/v) gave 114 mg (91%) of the known cyclic sulfonamide **21** [6,20].

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[13] A heterogeneous solvent system consisting of [Bmim]PF$_6$ and toluene was used by Mauduit and coworkers in the recycling and reuse of catalyst **12**, see [4q].

[14] The loading of **10** was estimated based on full conversion of the styrene ligand of **13**. Therefore, the estimated value represents only an upper limit of the actual amount of the catalyst, which should be slightly lower due to the presence of a small amount of free ligand that remained unreacted (less than 10% as revealed by 500 MHz ^{1}H NMR spectroscopy).

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