

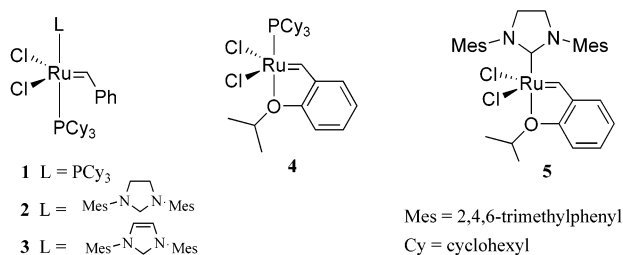
# An Ionic Liquid-Supported Ruthenium Carbene Complex: A Robust and Recyclable Catalyst for Ring-Closing Olefin Metathesis in Ionic Liquids

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Ring-closing metathesis (RCM)<sup>1</sup> is a powerful method to generate heterocyclic and macrocyclic motifs present in many natural products. Several well-defined homogeneous ruthenium carbene complexes such as **1–5**<sup>2</sup> are efficient catalyst precursors, are air and moisture stable, and are extremely tolerant toward different organic functional groups.



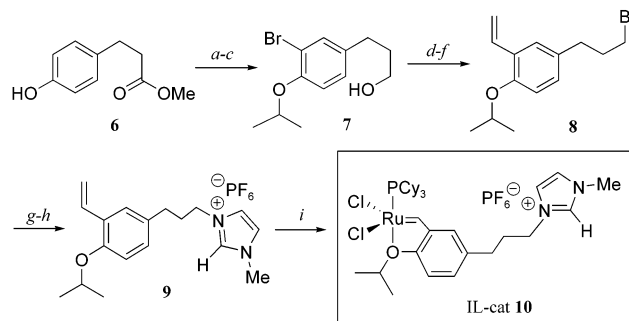
The concept of recoverable and recyclable catalysts has become extremely important from both the environmental and economical points of view,<sup>3</sup> and various strategies were employed to recover and reuse the catalyst for the RCM reaction.<sup>4</sup>

Ionic liquids (IL) are a new class of solvents<sup>5</sup> which present interesting properties such as nonvolatility, high stability, and easy recyclability. Because these solvents are immiscible with many organic solvents, it was very attractive to perform RCM and attempt to recover and recycle the ionic liquid layer containing the Ru catalyst after a simple extraction of the product. Pioneers of using this strategy, Buijsman and co-workers,<sup>6a</sup> have reported that the Grubbs's Ru catalyst precursor **1** dissolved in 1-butyl-3-methylimidazolium hexafluorophosphate (BMI·PF<sub>6</sub>)<sup>7</sup> promoted the RCM of several dienes for at least three cycles. However low conversion was obtained at the last cycle caused by extraction of the catalyst to the organic phase. More recently, Dixneuf and co-workers<sup>6b</sup> have described RCM performed by ruthenium allenylidene salts in BMI·PF<sub>6</sub>, but the catalyst proved to be efficient only for the first two cycles due to the slow decomposition of the catalytic system.

During the development of the biphasic Rh-catalyzed hydroformylation in IL, several research groups have clearly demonstrated that cationic ligands were especially suitable to avoid catalyst leaching from the ionic liquid layer.<sup>8</sup> In light of these results, we thought that application of this strategy for RCM in IL by introduction of an ionic liquid pattern (as an alkyl imidazolium salt) directly bound to the ligand should avoid the problem of catalyst leaching. Moreover, the resulting ionic catalyst should be completely soluble in IL and would allow the RCM reaction to be carried out under standard homogeneous conditions.

Herein, we report the synthesis of an alkyl imidazolium salt-supported ruthenium catalyst **10** (i.e. IL catalyst **10**) and its use and recycling in BMI·PF<sub>6</sub>.

The route for the synthesis of the ruthenium IL catalyst **10** is illustrated in Scheme 1. Starting from the commercially available

**Scheme 1.** Synthesis of IL Catalyst **10**<sup>a</sup>

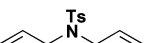
<sup>a</sup> Reaction conditions: (a) 2.2 equiv NaH, 2.2 equiv *i*-PrI, DMF, THF, rt, 90%. (b) 1.05 equiv Br<sub>2</sub>, 0.04 equiv HOAc, CH<sub>2</sub>Cl<sub>2</sub>, rt, 98%. (c) 1 equiv LiAlH<sub>4</sub>, THF, 0 °C, 95%. (d) 1.5 equiv Bu<sub>3</sub>SnCHCH<sub>2</sub>, 3 mol % Pd(PPh<sub>3</sub>)<sub>4</sub>, toluene, 110 °C, 75%. (e) 1.5 equiv Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C to rt. (f) 2 equiv LiBr, THF, DMF, rt, 74% overall for two steps. (g) 2 equiv 1-methylimidazole, toluene 110 °C. (h) HPF<sub>6</sub>, H<sub>2</sub>O, 0 °C, 87% overall for two steps. (i) 1.5 equiv **1**, 1.25 equiv CuCl, CH<sub>2</sub>Cl<sub>2</sub>, rt, 78%.

methyl-3(4-hydroxyphenyl)propionate **6**, etherification of the phenol group with isopropyl iodide, followed by bromination of the aromatic ring and reduction of the ester group afforded **7** in 84% yield. Introduction of the vinyl group was accomplished by a Pd-catalyzed Stille coupling in 75% yield. Alkylation of 1-methylimidazole with the bromine **8**, followed by anion exchange in water with HPF<sub>6</sub>, afforded the desired hexafluorophosphate imidazolium salt **9**, which was purified by silica gel chromatography. Following Hoveyda's method<sup>4c</sup> for the incorporation of the Ru center, the imidazolium styrenyl ether ligand **9** was treated with a slight excess of Grubbs's catalyst **1** in the presence of CuCl. Removal of excess of **1** by a simple filtration in acetone followed by a crystallization in a 1/1 CH<sub>2</sub>Cl<sub>2</sub>/pentane mixture afforded pure IL catalyst **10** (checked by elementary analysis) in 78% yield as an air-stable brown powder.

The *N,N*-diallyltosylamide **11** was directly added into a pre-formed solution of 2.5 mol % IL catalyst **10** in BMI·PF<sub>6</sub>. Complete formation of the cyclic olefin **12** was obtained after heating at 60 °C for 45 min, and no cross-metathesis product has been observed (Table 1). Importantly, isolation of the pure product was easily accomplished by extraction with toluene, and the IL solution containing IL-cat **10** was reused for the next cycle of metathesis. Excellent conversions were obtained for up to nine consecutive cycles of recycling and reuse. We have also tested the Grubbs's catalyst **1** and Hoveyda's catalyst **4** diluted in BMI·PF<sub>6</sub> under the same conditions of recycling and reuse (Table 1). After the second cycle, low conversion was obtained caused by extraction of the catalyst to the organic phase. These results show the importance of attaching an imidazolium ionic liquid pattern to the catalyst to avoid its leaching from the IL phase.

We have investigated the chemical stability of the IL catalyst **10** in BMI·PF<sub>6</sub> solution and accomplished the ninth run after 3

**Table 1.** Comparative Recycling and Reuse in BMI-PF<sub>6</sub> of IL Catalyst **10** and Catalysts **1** and **4** in the RCM of Diene **11**




**11**

**Catalyst**  
(2.5 mol%)

BMI.PF<sub>6</sub> (c = 0.2M)

60°C, 45 min.



**12**

catalyst	cycle (% conv. <sup>a</sup> )									
	1	2	3	4	5	6	7	8	9	10 <sup>b</sup>
<b>10</b>	>98	>98	>98	>98	>98	96	92	92	92	95
<b>1</b>	>98	20	—	—	—	—	—	—	—	—
<b>4</b>	>98	40	20	—	—	—	—	—	—	—

<sup>a</sup> Determined by <sup>1</sup>H NMR spectroscopy analysis. <sup>b</sup> **13** as starting material.

months. A similarly high conversion was obtained, showing that IL catalyst remains active. Moreover, this recycled catalyst solution was used for the metathesis of a second substrate **13** (cycle 10) to lead to the cyclized product **14** with 95% conversion, but the crude NMR spectrum showed a contamination by small amounts (<5%) of compound **12**, product of the previous reaction. This contamination can be explained by the partial miscibility of toluene in BMI-PF<sub>6</sub> (23 wt % at 26°C)<sup>9</sup> which keeps small amounts of product in the ionic liquid phase. At last, importantly, when the IL catalyst **10** lost its activity after repeated use, the BMI-PF<sub>6</sub> solvent could be recovered by treatment with black carbon<sup>6b</sup> and reused with a new loading of catalyst.

Having established the recyclability and reuse of IL catalyst **10** in BMI-PF<sub>6</sub>, we tried several RCM reactions with other substrates (Table 2). Ring-closing metathesis of **13** has afforded the six-membered ring **14** in quantitative conversion for each of six consecutive cycles.

**Table 2.** Recyclability of IL-cat **10** in Various RCM Reactions

Substrate	Product	Cycle	Conv. (%) <sup>b</sup>
		1	>98
		2	>98
		3	>98
		4	>98
		1	>98
		2	>98
		3	>98
		4	96
		1	92
		2	92
		3	73
		1	98
		2	98
		3	90
		4	74
		1	94
		2	78
		3	48
		1	>98
		2	>98
		3	92
		4	69

<sup>a</sup> **10** (2.5 mol %), BMI-PF<sub>6</sub> (0.2M), 60 °C, 45 min. <sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopic analysis. <sup>c</sup> **10** (5 mol %), BMI-PF<sub>6</sub> (0.2 M), 60 °C, 4 h. <sup>d</sup> **10** (2.5 mol %), BMI-PF<sub>6</sub> (0.2M), 60 °C, 2 h.

In the case of the seven membered ring **16**, quantitative conversion in up to three cycles was obtained to reach 80% conversion after the seventh cycle. However, with the sterically

demanding olefin **17**, we used more drastic conditions (5 mol % of IL catalyst **10**, at 60°C over 4 h). Although conversions of 92% were obtained for the first two cycles, they decreased dramatically to reach 73% after the third cycle due to the decomposition of the catalyst after repeated heating. Concerning the oxygen-containing dienes such as **19**, **21**, and **23**, the IL catalyst proved to be efficient only for the first two cycles. We attribute this to the slow but competing decomposition of the catalytic system where a stable oxygen-ligated ruthenium carbene complex can be formed due to the presence of oxygen's substrate. These limitations of IL catalyst **10** led us to develop a more efficient IL catalyst, based on complex **5**, to promote efficient RCM with trisubstituted or oxygen-containing olefins. Its preparation is underway in our laboratory. In summary, we have developed an ionic liquid-supported catalyst for olefin metathesis carried out in IL. The IL catalyst has shown high activity with a remarkable recyclability and can be stored in BMI-PF<sub>6</sub> several months without loss of activity.

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**Supporting Information Available:** Experimental details and analytical data for the work described (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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# Ring-closing metathesis in biphasic BMI·PF<sub>6</sub> ionic liquid/toluene medium: a powerful recyclable and environmentally friendly process†

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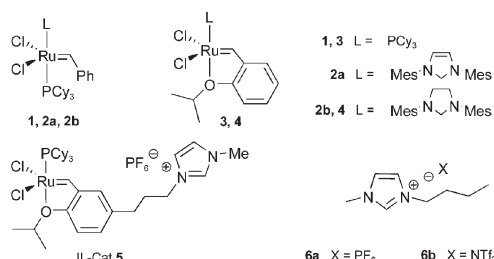
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Biphasic BMI·PF<sub>6</sub>/toluene solvent is a remarkably suitable and clean medium for performing olefin metathesis with a new 2nd generation ionic liquid supported-ruthenium catalyst: high levels of recyclability and reusability combined with a high reactivity were obtained with a variety of di- or tri-substituted and/or oxygen-containing dienes, and very low residual ruthenium levels were detected (1 to 22 ppm) in the products.

Olefin metathesis<sup>1</sup> has received considerable attention in synthetic organic chemistry since the development of well-defined homogeneous ruthenium carbene complexes **1**<sup>2</sup> and **2**,<sup>3</sup> which are easy to handle and extremely tolerant towards different functional groups. However, the major disadvantages of the use of these homogeneous catalysts are their poor recyclability and the difficulty of removing the ruthenium waste from the product. Hoveyda and co-workers have achieved spectacular improvements by the development of recyclable catalysts **3**<sup>4a</sup> and **4**<sup>4b</sup> based on a “release–return” olefin metathesis mechanism. This concept of recoverable and recyclable transition-metal-based catalysts has become extremely important from both an environmental and economic viewpoint and various strategies have been employed for their immobilization on different supports.<sup>5</sup>



Because of their interesting properties such as ease of reuse, non-volatility and good ability to dissolve many kinds of organic and organometallic compounds, Room Temperature Ionic Liquids (RTILs) are promising candidates to replace volatile solvents traditionally used in organic chemistry.<sup>6</sup> In order to develop a more environmentally friendly RCM process in these new clean media, we<sup>7</sup> and others<sup>8</sup> have recently immobilised the ruthenium catalyst **3** in 1-butyl-3-methylimidazolium hexafluorophosphate (BMI·PF<sub>6</sub>) **6a** by anchoring an imidazolium tag on the styrenyl ligand. Our first generation of ionic liquid-supported ruthenium complex **5** has been extremely suitable for performing RCM in BMI·PF<sub>6</sub> for various diene substrates and can be used several times. However, in the case of sterically demanding olefins **9**, because harsher conditions were necessary to complete the RCM reaction, our IL-catalyst **5** proved to be efficient only for the first two cycles. The rapid thermal decomposition of the catalyst system led us to develop a more efficient IL-catalyst, based on the well-defined ruthenium complexes **4** bearing an *N*-heterocyclic carbene (NHC) ligand, which promoted remarkable thermal stability and better

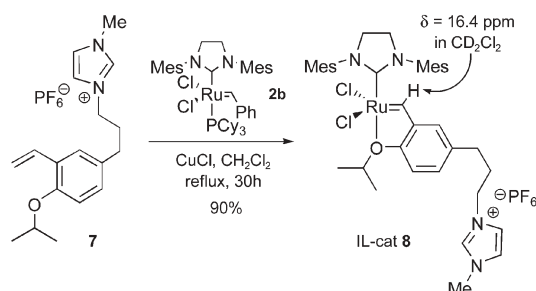
general activity.<sup>3</sup> Herein, we report the synthesis of the IL-phosphine free *N*-heterocyclic carbene complex **8** and its use in a biphasic BMI·PF<sub>6</sub>/toluene medium.

The ruthenium IL-catalyst **8** was easily obtained from the 2nd generation Grubbs' catalyst **2b** by a simple exchange of the styrene group following the procedure described by Hoveyda and co-workers<sup>4</sup> (Scheme 1). The hexafluorophosphate imidazolium styrenyl ether ligand **7** was treated with a slight excess of **2b** in the presence of CuCl. After a crystallisation in a toluene/dichloromethane mixture, pure IL-catalyst **8** was isolated in 90% yield as an air stable green powder.

We have investigated the activity of IL-catalyst **8** in RTILs in the ring closing metathesis of the trisubstituted diene **9**, as shown in Table 1. Although high conversions were obtained for the first three cycles in BMI·PF<sub>6</sub> solvent at 60 °C, they decreased rapidly to 16% at the fifth cycle (entry 1). At 40 °C (entry 2), only 76% conversion was obtained after the first run due to the high viscosity of BMI·PF<sub>6</sub> at this temperature, which led to reduced catalyst mobility. Replacement of BMI·PF<sub>6</sub> solvent by less viscous RTILs, such as BMI·NTf<sub>2</sub> **6b**, increased the recyclability of the catalyst. However, because of the partial miscibility of toluene in BMI·NTf<sub>2</sub>, product extraction proved complicated.

To overcome these problems, a volume of toluene was added in the IL medium and the RCM reaction performed under biphasic conditions. With a 50/50 (v/v) BMI·PF<sub>6</sub>/toluene mixture, a 63% conversion was achieved after the sixth run. By increasing the volume of toluene (25/75 BMI·PF<sub>6</sub>/toluene), we improved considerably the recycling and reuse of the catalyst. Because the IL-catalyst **8** is a recyclable catalyst based on a “release–return” olefin metathesis mechanism<sup>4b</sup>, we assume that, during reaction, the ligand–ruthenium bond is cleaved, allowing the 14-electron ruthenium catalytic specie to reside preferentially in the toluene phase. Once the substrate has been consumed, this active complex returns to the BMI·PF<sub>6</sub> by reattachment to the styrenyl ether ligand **7**. In this way, the RCM reaction with IL-catalyst **8** is even feasible at room temperature in a 25/75 BMI·PF<sub>6</sub>/toluene mixture. Thus, a higher level of recyclability (8 cycles) was obtained when the metathesis reaction was carried out at 25 °C (entry 5) and excellent conversions were obtained with an equal length of time (3 h).

Additionally, one major problem in the use of the olefin metathesis reactions (especially in the production of biologically

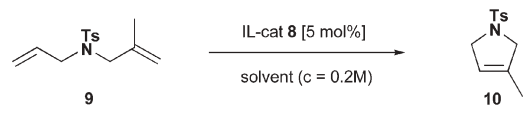


**Scheme 1** Synthesis of the 2nd generation ionic liquid immobilised ruthenium complex **8**.

† Electronic supplementary information (ESI) available: experimental details. See <http://www.rsc.org/suppdata/cc/b4/b407964g/>



**Table 1** Optimisation in the RCM of trisubstituted diene **9** with the IL-catalyst **8** and ruthenium contaminant level in cyclised product **10**



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Entry	Solvent	Conditions	Cycle/conversion (%) <sup>a</sup>							
			1	2	3	4	5	6	7	8
1	BMI·PF <sub>6</sub>	60 °C, 3 h	>98	97	91	68	16	—	—	—
2	BMI·PF <sub>6</sub>	40 °C, 4 h	76	—	—	—	—	—	—	—
3	BMI·NTf <sub>2</sub>	40 °C, 4 h	>98	>98	91	89	74	50	—	—
4	BMI·PF <sub>6</sub> /toluene 50/50	40 °C, 3 h	>98	>98	>98	96	85	63	—	—
5	BMI·PF <sub>6</sub> /toluene 25/75 Ru residue (ppm) <sup>b</sup>	25 °C, 3 h	>98	>98	>98	>98	>98	>98	95	95
			16.9	5.4	1.6	3.3	1.2	22	5.7	2.3

<sup>a</sup> Determined by <sup>1</sup>H NMR (400 MHz). <sup>b</sup> Determined by ICP-MS spectroscopic analysis.

active compounds) is the toxic ruthenium waste, which is very difficult to remove from the product (even after repeated purification by silica gel column chromatography). Several research groups have developed efficient methods for removal of ruthenium by-products<sup>9</sup> and the residual ruthenium levels have been reduced, in the best case, to 200–400 ppm of products. In our work, after each cycle using IL-catalyst **8** in the above biphasic approach, the residual ruthenium levels were determined. ICP-MS spectroscopic analysis of RCM product **10**, obtained employing optimum reaction and recycling conditions (entry 3), revealed very low residual ruthenium levels (between 1.2 to 22 ppm). The average value over eight cycles (7.3 ppm) is approximately an order of magnitude lower than the best previously reported methods.<sup>9b-d</sup>

Having established the recyclability and reuse of IL-catalyst **8**, we evaluated its activity in the RCM of several diene substrates at room temperature or at 40 °C (Table 2). Excellent conversions were obtained in all cases (entries 1 to 6) for up to eight cycles. As an example, we also measured the residual ruthenium level for the first run of diethyl diallylmalonate **11** and only 2.5 ppm were detected in the cyclised product **12**. Finally, to examine the scope of IL-catalyst **8**, we focused on its performance with the tetra-substituted dienes **21** and **23**, which are known to be extremely difficult substrates. The IL-catalyst proved to be efficient only for the first run for **21**, and inactive for **23** (entries 7 and 8), showing the limitation of the catalyst activity. Nevertheless, remarkably, as shown by the excellent conversions observed in successive runs with the disubstituted diene **17**, the recovered catalyst still remained highly active, attesting to the stability and the high level of recyclability of IL-cat **8** in the BMI·PF<sub>6</sub>/toluene medium at higher temperature.

In summary, we have developed a powerful recyclable IL-phosphine free *N*-heterocyclic carbene ruthenium complex to perform metathesis reactions in a BMI·PF<sub>6</sub>/toluene biphasic medium. High level of recyclability and reusability combined with a high reactivity were obtained for the RCM of several substrates including tri-substituted and/or oxygen-containing dienes. The low residual ruthenium levels in the RCM products promote this environmentally friendly RCM process in synthesis. A study of its use in cross-metathesis reaction is under way in our laboratory and will be reported in due course.

**Table 2** Activity and recyclability of IL-catalyst **9** in the RCM of various dienes

Entry	Substrate	Product	Conditions	Cycle/conversion (%) <sup>a</sup>			
1			<b>[2.5 mol%]</b> 25 °C, 3 h	1	>98	5	>98
				2	>98	6	>98
				3	>98	7	95
				4	>98	8	95
2			<b>[2.5 mol%]</b> 40 °C, 6 h	1	>98	5	>98
				2	>98	6	>98
				3	>98	7	83
				4	>98	8	33
3			<b>[2.5 mol%]</b> 25 °C, 3 h	1	>98	5	>98
				2	>98	6	94
				3	>98	7	81
				4	>98	8	36
5			<b>[2 mol%]</b> 25 °C, 3 h	1	>98	5	>98
				2	>98	6	>98
				3	>98	7	96
				4	>98	8	94
6			<b>[2 mol%]</b> 25 °C, 3 h	1	>98	5	>98
				2	>98	6	>98
				3	>98	7	94
				4	>98	8	92
7			<b>[5 mol%]</b> 60 °C, 7 h	1	65		
				2	0		
				3 <sup>b</sup>	<b>94</b>		
				4 <sup>b</sup>	<b>90</b>		
8			<b>[5 mol%]</b> 60 °C, 24 h	1	0		
				2 <sup>b</sup>	<b>&gt;98</b>		
				3 <sup>b</sup>	<b>&gt;98</b>		

<sup>a</sup> Determined by <sup>1</sup>H NMR spectroscopic analysis at 400 MHz.

<sup>b</sup> Reaction performed with **17** at 25 °C for 3 h.

## Notes and references

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# Olefin metathesis in room temperature ionic liquids using imidazolium-tagged ruthenium complexes

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## Abstract

New recyclable imidazolium-tagged ruthenium catalysts have been developed to perform olefin metathesis in room temperature ionic liquids (RTILs). High level of recyclability combined with a high reactivity were obtained in the ring-closing metathesis (RCM) of a variety of di- or tri-substituted and/or oxygen-containing dienes. Extremely low residual ruthenium levels were detected in the RCM products (average of 7.3 ppm per run). Several examples of olefin cross-metathesis (CM) have been also studied.  
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**Keywords:** Supported catalysts; Olefin metathesis; Ionic liquid

## 1. Introduction

In the past decade, room temperature ionic liquids (RTILs) [1,2] have received a growing attention from both academia and industry. Due to their interesting properties such as negligible vapour pressure and ease of reuse, RTILs are interesting candidates to replace volatile solvents traditionally used in the chemical industry. Moreover, RTILs present three major advantages compared to their traditional counterparts: (1) Their good ability to solvate both polar and non-polar species allowing the dissolution of a wide range of organic, inorganic and organometallic compounds. (2) Their good thermal stability over a large temperature range (up to 250 °C). (3) Their modular immiscibility with many usual organic solvents allowing an easier extraction of the organic products. On the other hand, the main disadvantage of these new solvents is certainly their high viscosities at room temperature that are often more than

one hundred more important than those of water or any classical organic solvent. This involves a dramatic slowing down of the solutions homogenization and therefore a decrease in the reactivity of the dissolved reagents and/or catalysts. However, fortunately, at higher temperature, the viscosity decreases significantly allowing the desired homogenous conditions. Recent improvements have been achieved to reduce the RTIL viscosity by using new bulky counter-anions and/or by modifying the cations backbone. RTILs became thus ideal solvents for the transformations involving organometallics and requiring high temperatures in most cases. During the last decade, many reactions have been revisited in these clean media without significant loss of yields and sometimes with an improvement of the chemo- or the regioselectivity (see Fig. 1).

Olefin metathesis [3,4] has gained considerable attention in synthetic organic chemistry since the development of well-defined homogeneous ruthenium carbene complexes **2** [5] and **3–4** [6,7], which are easy to handle in air and tolerant towards a large variety of functional groups. This tremendous improvement led in the last decade to the achievement of many new syntheses of

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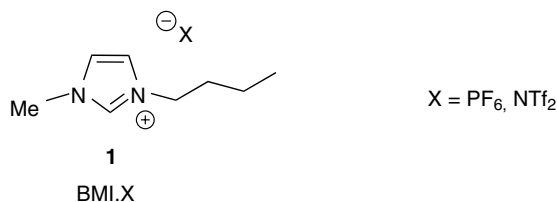


Fig. 1.

natural organic molecules often allowing shorter synthetic pathways. However, because they are homogeneous catalysts, two important disadvantages are usually associated with their use: (1) their poor recyclability and (2) the difficulty to remove the ruthenium waste from the final products. Hoveyda and co-workers have contributed a lot to the improvement of the recycling aspect through the development of boomerang catalysts **5** [8a] and **6** [8b] based on a “release-and-return” olefin metathesis mechanism. This concept of recoverable and recyclable transition metal-based catalysts has become extremely important from both an environmental and an economic viewpoint [9] and various strategies have been employed for the immobilization of such catalysts on different supports [10] (see Fig. 2).

In order to develop a more environmentally friendly olefin metathesis process in RTILs [11], we have recently immobilized the ruthenium catalysts **8** [12] and **9** [13] in the 1-butyl-3-methylimidazolium hexafluorophosphate (BMI·PF<sub>6</sub>) **1**. In a pioneering work, Buisjmann and co-workers [11a] had observed that the Grubbs’ catalyst **2** dissolved in BMI·PF<sub>6</sub> promoted the RCM of several dienes for at least three cycles. Nevertheless, low conversions were progressively obtained due to the extraction of the catalyst to the organic phase during the recuperation of the RCM products. Introduction of an imidazolium pattern directly bound to Hoveyda’s boomerang catalyst appeared to us as a possible answer to this leaching problem. The resulting ionic catalyst, completely soluble in the BMI·PF<sub>6</sub> layer, would allow the RCM reaction to be carried out under standard homogeneous conditions.

Herein, we report an overview of the efficiency of these imidazolium-tagged ruthenium complexes **8** and

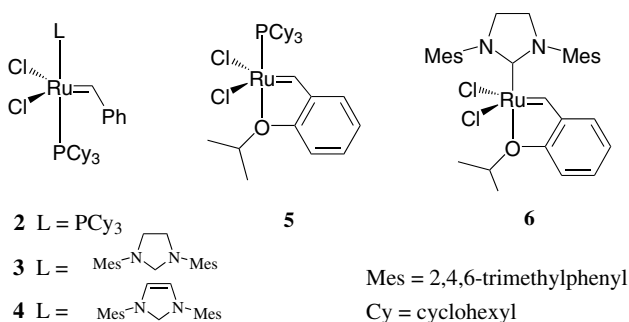


Fig. 2.

**9** in the RCM and CM reactions performed in BMI·PF<sub>6</sub> under monophasic or biphasic conditions. Several studies have been carried out on the recyclability of the modified catalysts and on the kinetic effects of the catalyst loading and the imidazolium-ligand **7** loading for the RCM metathesis. The level of ruthenium contaminant in the final metathesis products was also checked by ICP-MS measurements (see Fig. 3).

## 2. Results and discussion

### 2.1. Synthesis of the imidazolium-tagged styrenyl ether ligand **7**

The synthetic route to the imidazolium-bound ligand **7** is illustrated in Scheme 1. Inspired by the strategy developed by Hoveyda for the immobilization of its boomerang Ru-complex **5** on a silicon-based support [8b], we started the synthesis from the commercially available methyl-3-(4-hydroxyphenyl)propionate **10** (Scheme 1).

Etherification of the phenol group with isopropyl iodide was achieved in 90% yield using sodium hydride in DMF/THF mixture. Selective *ortho*-bromination of the aromatic ring gave the bromophenol ether **11** in 98% yield. Reduction of the ester group with LiAlH<sub>4</sub> followed by Pd-catalyzed Stille coupling to introduce the vinyl group afforded the corresponding styrenyl ether **12** in 71% overall yield. The alcohol function was then converted to the corresponding bromide **13** via a standard nucleophilic substitution performed by treatment of LiBr on the mesylate intermediate in 74% overall

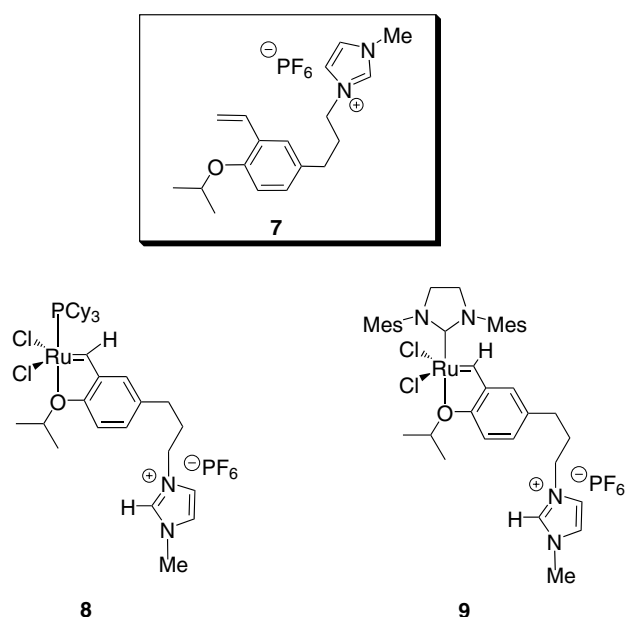
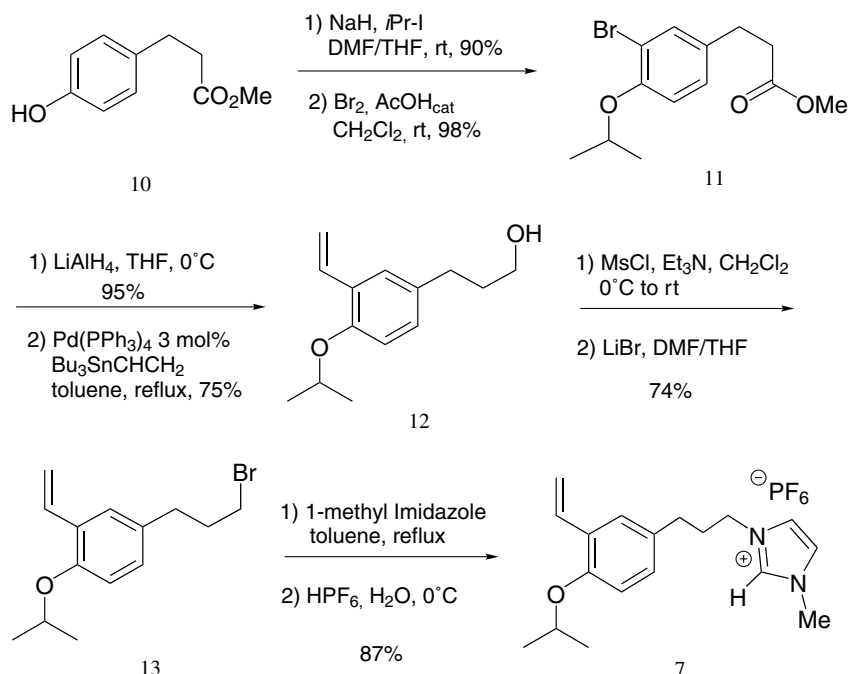


Fig. 3. Imidazolium-tagged ligand and complexes.

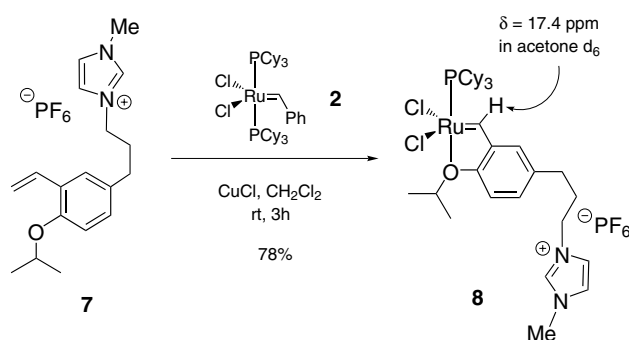


Scheme 1. Synthesis of imidazolium-tagged ligand 7.

yield. Alkylation of 1-methylimidazole by the alkyl bromide **13** allowed the introduction of the desired imidazolium tag on the styrenyl ether ligand. Finally, the anion exchange is accomplished by treatment of the bromide salt with an aqueous HPF<sub>6</sub> solution to afford the expected imidazolium hexafluorophosphate salt **7** in high yield after purification by silica gel chromatography (87% overall in two steps). Two points have to be mentioned concerning the last steps of this synthesis. Firstly, better yields and minimum waste were obtained when the anion metathesis was performed with KPF<sub>6</sub> instead of the aqueous HPF<sub>6</sub> solution. This is due to the fact that commercially available HPF<sub>6</sub> solutions are generally polluted by the presence of non-negligible amounts of fluorhydric acid. Secondly, purification of the imidazolium styrenyl ether salt **7** was crucial to remove eventual traces of styrene dimer, which could decrease the yield of the ruthenium complex formation.

## 2.2. First generation of imidazolium-tagged ruthenium complex 8

Following Hoveyda's method [8a] for the incorporation of the Ru center, the imidazolium styrenyl ether ligand **7** was treated with a slight excess of Grubbs' catalyst **2** in the presence of CuCl (Scheme 2). Removal of the excess of **2** by a simple filtration in acetone followed by a crystallisation in a 1/1 CH<sub>2</sub>Cl<sub>2</sub>/pentane mixture afforded pure imidazolium-tagged ruthenium complex **8** (checked by elementary analysis) in 78% yield as an air-stable brown powder.



Scheme 2. Synthesis of the imidazolium-tagged ruthenium complex 8.

The potential of this new ruthenium complex in the RCM reaction performed in BMI · PF<sub>6</sub> was then evaluated. *N,N*-Diallyltosylamide **14** was chosen as substrate for the reference reaction. Diene **14** was directly added into a preformed solution of 2.5 mol% of complex **8** in BMI · PF<sub>6</sub>. Complete formation of the cyclic olefin **15** was obtained after heating at 60 °C for 45 min and no cross-metathesis product was observed by NMR analysis (Table 1). Importantly, isolation of the pure product was easily accomplished by extraction with toluene and the BMI · PF<sub>6</sub> layer containing the complex **8** was reused with a new loading of substrate. Excellent conversions were obtained for up to nine consecutive cycles of recycling and reuse.

In order to establish a comparison, the recycling and reuse of Grubbs' catalyst **2** and Hoveyda's catalyst **5** under the same reaction conditions were checked (Table 1). After the second cycle, low conversions were obtained in



Comparative recycling and reuse between the imidazolium-tagged complex **8** and the catalysts **2** and **5** in BMI · PF<sub>6</sub>

<sup>a</sup> Determined by <sup>1</sup>H NMR spectroscopic analysis at 400 MHz. <sup>b</sup> **16** as substrate

both cases caused by the extraction of the catalyst to the organic phase, as the brown coloration of the toluene layer clearly showed. These results show the importance to attach an imidazolium tag to the boomerang catalyst to avoid its leaching from the BMI · PF<sub>6</sub> phase.

The chemical stability of complex **8** in solution in BMI · PF<sub>6</sub> was then investigated. The ninth run was accomplished three months after the eighth one (the catalyst in BMI · PF<sub>6</sub> being stored under N<sub>2</sub> atmosphere) and a similarly high conversion was obtained showing that the catalyst was still active. Moreover, the same catalyst solution was used for the RCM reaction of a second substrate **16** (cycle 10) to lead to the cyclic product **17** with 95% conversion. Nevertheless, the NMR spectrum of the crude product showed a slight contamination by the compound **15** (<5%) formed during the previous reaction. This can be explained by the partial miscibility of toluene in BMI · PF<sub>6</sub> (23 wt% at 26 °C) [14] that involves the retention of small amounts of organic compounds in the ionic liquid phase.

Having established the recyclability of the imidazolium-tagged complex **8** in  $\text{BMI} \cdot \text{PF}_6$ , other substrates were tested in order to afford different size of ring (Table 2). The six-membered ring **17** was achieved in a quantitative conversion for each of the six consecutive cycles to finally reach 92% at the eighth cycle (entry 1). Similar results were obtained in the formation of the seven-

### Recyclability of imidazolium-tagged complex **8** in the RCM reactions of substrates **16** and **18**

<sup>a</sup> Determined by <sup>1</sup>H NMR spectroscopic analysis at 400 MHz.

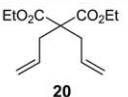
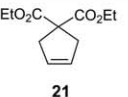
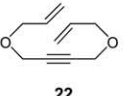
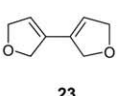
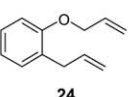
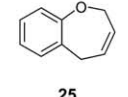
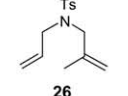
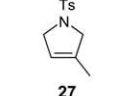
membered ring **19** with quantitative conversion up to three cycles to reach 80% of conversion after the seventh and last cycle (entry 2).

Lastly, in order to generalize the use of our complex **1** in  $\text{BMI} \cdot \text{PF}_6$ , the oxygen-containing substrates **20**, **22** and **24** and the sterically demanding olefin **26** were screened (Table 3). These substrates, known to be problematic in RCM, were tested under more drastic conditions: longer heating time (from 45 min to 2 h or 4 h) or/and a more important catalyst loading (from 2.5 to 5 mol%). Whereas good to excellent conversions were obtained for all the first runs, the recycling of the complex was quite disappointing compared to the previous results. Indeed, concerning the oxygen-containing dienes (entries 1–3), the catalytic system proved to be efficient only for the first two cycles. This behaviour was attributed to a slow but competing decomposition of the catalytic species involving the formation of stable and unproductive oxygen-ligated ruthenium carbene complexes which can be a fortiori extracted to the organic phase.

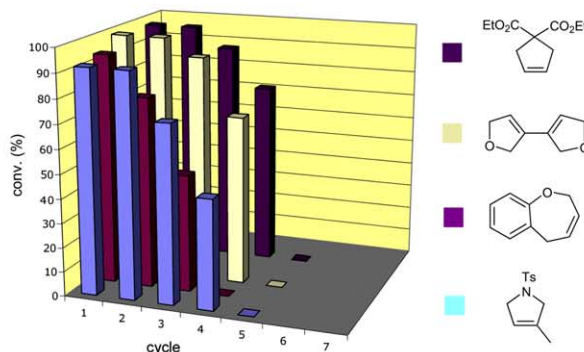
In the case of the tri-substituted diene **26**, although conversions of 92% were obtained for the first two cycles, they decreased dramatically to reach 73% after the third cycle and 45% for the last cycle. Because a longer time was necessary to complete the metathesis reaction and to form the cyclic product **27**, the negative effects of the thermal decomposition of the Ru-catalyst were observed as early as the third cycle. This thermal degradation of imidazolium-tagged complex **8** led us



Table 3  
Recycling of imidazolium-tagged catalyst **8** in BMI · PF<sub>6</sub> medium: scope and limitations

Entry	Substrate	Conditions	Product	Cycle (% conv.) <sup>a</sup>			
				1	2	3	4
1		<b>8</b> (2.5 mol%), 60°C, 2h		98	98	90	74
2		<b>8</b> (2.5 mol%), 60°C, 2h		>98	>98	92	69
3		<b>8</b> (2.5 mol%), 60°C, 2h		94	78	48	
4		<b>8</b> (5 mol%), 60°C, 4h		92	92	73	45

<sup>a</sup> Determined by <sup>1</sup>H NMR spectroscopic analysis at 400 MHz.



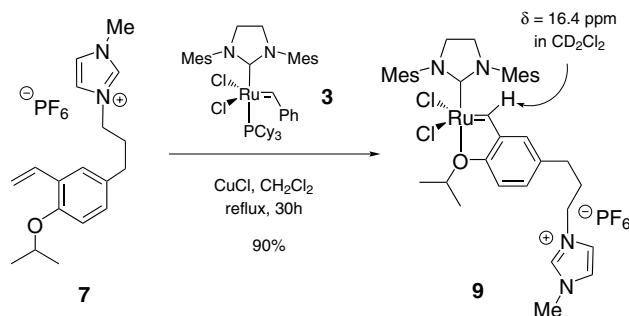
to develop a more efficient complex, based on the second generation of ruthenium complexes **6** bearing an electron-rich and sterically demanding *N*-heterocyclic carbene (NHC) ligand, able to promote efficient RCM in more drastic conditions.

Indeed, NHC-complexes are known to possess an exceptional catalytic activity [15] associated to a better thermal stability than complexes containing phosphine units, allowing to perform many synthetic transformations in harsher conditions. Imidazolium-tagged NHC-complex **9** was therefore synthesized and its activity in BMI · PF<sub>6</sub> medium was investigated.

### 2.3. Second generation of imidazolium-tagged ruthenium complex **9**

The imidazolium-tagged ruthenium catalyst **9** was readily obtained from the second generation Grubbs' catalyst **3** by a simple exchange of the styrenyl group following the procedure described by Hoveyda and co-workers [6a] (Scheme 3). The imidazolium-bound styrenyl ether ligand **7** was treated with a slight excess of **3** in the presence of CuCl. After refluxing 30 h in dichloromethane followed by a crystallisation in a toluene/dichloromethane mixture, the resulting catalyst **9** was isolated in a pure form in 90% yield as an air stable green powder.

To control the efficiency and the thermal stability of this new generation of imidazolium-tagged NHC–Ru complex **9** in harsher conditions, the ring-closing metathesis of the tri-substituted diene **26** was investi-

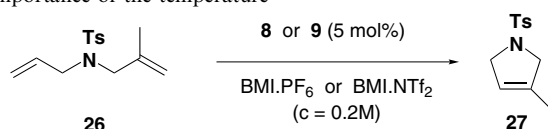


Scheme 3. Synthesis of the second-generation imidazolium-tagged ruthenium complex **9**.

gated in BMI · PF<sub>6</sub> as solvent. As shown in Table 4, whereas high conversions were obtained for the first three cycles at 60 °C over 4 h, a rapid decrease until 16% at the fifth cycle was observed (entry 1). As expected, this second generation of catalyst had a longer lifetime than the first generation; nevertheless, the improvement in the recycling was very slight. We thus decided to perform the RCM reaction at lower temperature (40 °C, entry 2), but only 76% of conversion was observed in the first run. The main reason of this lower reactivity is due to the high viscosity of the ionic liquid at this temperature that promotes the reduction of the catalyst mobility. Replacement of BMI · PF<sub>6</sub> by the less viscous BMI.NTf<sub>2</sub> improved significantly the recyclability of the catalyst. However, product extraction became more complicated due to the partial miscibility of toluene in BMI.NTf<sub>2</sub> (40 wt%) [14] involving several

Table 4

Optimization of the reaction conditions: importance of the temperature



Entry	Catalyst	Solvent	Conditions	Cycle (% conv.) <sup>a</sup>						
				1	2	3	4	5	6	7
1	8	BMI · PF <sub>6</sub>	60 °C, 4 h	92	92	73	45	–	–	–
2	9	BMI · PF <sub>6</sub>	60 °C, 4 h	>98	97	91	68	16	–	–
3	9	BMI · PF <sub>6</sub>	40 °C, 4 h	76	–	–	–	–	–	–
4	9	BMI · NTf <sub>2</sub>	40 °C, 4 h	>98	>98	91	89	74	50	–

<sup>a</sup> Determined by <sup>1</sup>H NMR spectroscopic analysis at 400 MHz.

washing to recover the final cyclic product. Changing the extraction solvent did not improve the final recovery step even when using a more adapted solvent such as diethylether. Indeed, a preliminary study realized with the imidazolium-tagged complex **8** had shown that the use of oxygenated solvents had a dramatic negative effect on the recycling.

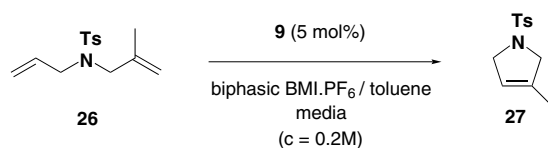
To overcome the problem related to the BMI · PF<sub>6</sub> viscosity, the behaviour of catalyst **9** under biphasic conditions was investigated. Indeed, due to the “release-and-return” mechanism of the olefin metathesis reactions catalysed by Hoveyda’s complex, imidazolium-tagged complex **9** appeared to be very suitable for a use in an ionic liquid/organic solvent biphasic mixture. A closer look to the mechanism [8] shows that during the reaction, the ionic styrenyl ether ligand **7** is separated from the metallic centre, allowing the 14-electrons ruthenium catalytic specie to reside preferentially in the organic phase. Once the substrate is consumed, this active catalytic specie returns to the BMI · PF<sub>6</sub> phase by reattachment to the imidazolium-tagged styrenyl ether ligand **7**. In order to simplify the extraction procedures, toluene was chosen to play the role of immiscible organic solvent. Thus, a volume of toluene was added in the BMI · PF<sub>6</sub> medium and the RCM reaction was performed at 40 °C. As shown in Table 5, with a 50/50 (v/v) BMI · PF<sub>6</sub>/toluene mixture (entry 2), the recycling and reuse of the supported catalyst **9** at 40 °C was considerably improved to reach 63% of conversion for the sixth run. When increasing the volume of toluene (25/75: BMI · PF<sub>6</sub>/toluene), in spite of a reaction time reduced to 3 h, even better results were obtained with a conversion of 88% for the eighth cycle (entry 3). Moreover, in this biphasic medium, the problems related to the BMI · PF<sub>6</sub> viscosity do no longer exist and the RCM is even feasible at room temperature in a 25/75 BMI · PF<sub>6</sub>/toluene mixture. Thus, a higher level of recyclability (8 cycles) was obtained when the metathesis reaction was carried out at 25 °C (entry 4) and excel-

lent conversions were obtained with an equal reaction time (3 h) to reach 95% of conversion in the last cycle (the overall turnover frequency is around 6.6 mol h<sup>-1</sup>).

Additionally, another advantage in the use of a biphasic medium is certainly the ease to follow the advancement of the reaction by TCL or NMR analyses. It is also important to note that before each new loading of substrate, the eventual remaining toluene was completely removed under vacuum from the ionic liquid. However, it was observed that the BMI · PF<sub>6</sub> viscosity was becoming less important after several cycles. This is probably due to the formation of a liquid clathrate between the BMI · PF<sub>6</sub> and the aromatic solvent. As recently reported by Rodgers and co-workers [16], a toluene inclusion in the BMI · PF<sub>6</sub> phase was observed leading to the formation of a specific liquid clathrate (with a 1:0.8 ratio of IL to organic in the lower, IL-rich phase of the liquid clathrate biphasic systems). On the light of this result, we have slightly changed the procedure in the preparation of the catalytic biphasic batch system. Before adding the catalyst and the toluene phase to perform the RCM reaction, the ionic liquid is washed several times with toluene to form the desired clathrate where the dissolution of our imidazolium-tagged complex **9** is improved.

Having established the best media for the recyclability and the reuse of the second generation of imidazolium-tagged complex **9**, we next focused on the determination of the ruthenium contaminant level in the metathesis products. Indeed, the main disadvantage usually related to the use of the homogeneous Ru-complexes is the difficulty to remove the toxic ruthenium waste from the product even after repeated purification by silica gel column chromatography. Overcoming the problem of ruthenium leaching into the reaction mixture became crucial, especially in the pharmaceutical industry where biologically active compounds are produced. Several research groups have developed efficient methods for the removal of ruthenium by-products [17] and

Table 5

RCM in a biphasic BMI · PF<sub>6</sub>/toluene mixture: optimization of the catalyst recycling

Entry	Solvent	Conditions	Cycle (% conv.) <sup>a</sup>							
			1	2	3	4	5	6	7	8
1	BMI · PF <sub>6</sub>	40 °C, 4 h	76	—	—	—	—	—	—	—
2	BMI · PF <sub>6</sub> /toluene 50/50	40 °C, 4 h	>98	>98	>98	96	85	63	—	—
3	BMI · PF <sub>6</sub> /toluene 25/75	40 °C, 3 h	>98	>98	>98	97	94	93	90	88
4	BMI · PF <sub>6</sub> /toluene 25/75	25 °C, 3 h	>98	>98	>98	>98	>98 >98	95	95	—

<sup>a</sup> Determined by <sup>1</sup>H NMR spectroscopic analysis at 400 MHz.

the residual ruthenium levels have been reduced, in the best cases, to 200–40 ppm. In order to validate that the use of our complex **9** in a biphasic BMI · PF<sub>6</sub>/toluene media is a clean RCM process, the residual ruthenium levels were determined in the final product **27** after each cycle using 5 mol% of supported catalyst **9**.

As shown in Table 6, extremely low residual ruthenium levels (between 1.2 and 22 ppm) were revealed by ICP-MS analysis. The average value over eight cycles (7.3 ppm) is unprecedented low in the area of homogeneous catalysis, approximately an order of magnitude lower than the best previously reported methods [17b–17d].

Finally, in order to optimize the catalytic process in this new biphasic medium, attempts have been made to reduce the catalyst loading and to check if the presence of an excess of ionic ligand **7** in the reaction mixture could allow an improvement of the catalyst's recycling. A kinetic study involving the loading of the catalyst **9** and the ionic ligand **7** has therefore been carried out for the RCM reaction of *N,N*-diallyltosylamide **14**.

As shown in Scheme 4, reduction of the catalyst loading from 2 to 1 mol% caused a logical increase of the reaction time (3 h 30 instead of 2 h at 25 °C), as well as a dramatic negative effect on the recycling (only 49% of conversion for the fourth cycle, entry 2). To overcome this problem, imidazolium-tagged styrenyl ether ligand **7** (1 mol%) was added to the reaction mixture. Unfortunately, the presence of the ligand **7** did not allow any significant improvement of the recycling, but led to a dramatic lowering of the catalytic activity (20 h instead of 3 h 30 at 25 °C, entry 3). The reaction time was diminished to 3 h when the reaction was performed at 40 °C, and thus a better recycling was obtained (entry 4). Nevertheless, these new conditions are less efficient than the use of 2 mol% of catalyst at 25 °C, where high levels of recyclability were observed (entry 1).

In order to generalize the use of the efficient catalyst **9** under these biphasic conditions, a survey of the RCM

scope at room temperature or at 40 °C has been undertaken (Table 7). Excellent conversions were obtained in all cases (entries 1–4) for up to six cycles. Remarkably, these good results of recycling also include the sterically hindered oxygenated diene **28** for which a reaction time of 6 h at 40 °C is necessary to assure a complete conversion. Nevertheless, a decrease of the catalytic activity was observed during the eighth cycle for dienes **28** and **30**. Concerning the residual ruthenium levels at the end of these reactions, as an example, an analysis by ICP-MS of the crude product **21** after the first run (entry 1) revealed a low value of only 2.5 ppm.

Finally, to study the limitation in the recycling of the supported catalyst **9**, we next focussed on its performance in the RCM of diallyl-ether **32** and tetra-substituted dienes **34** and **36**, which are known to be extremely problematic substrates. In the case of substrate **32** (Table 8, entry 1), although the first two runs performed with a quantitative yield, only 40% of conversion was observed for the last cycle probably because of the competitive formation of stable oxygen-ligated ruthenium carbene complexes, which are extracted from the ionic liquid phase.

Concerning the tetra-substituted diene **36**, no formation of product **37** was observed despite the use of harsher conditions (entry 2: cycle 1, 60 °C over one day). This result, caused by the poor reactivity of the complex **9** against this highly hindered substrate, clearly shows the limitation of our supported catalyst. Nevertheless, as shown by the complete conversions obtained in the two following runs performed with the more reactive *N,N*-diallyltosylamine **14** (entry 2: cycles 2 and 3), catalyst **9** still remained remarkably active, attesting its thermal stability in the BMI · PF<sub>6</sub>/toluene medium even after extended heating at high temperature.

This phenomenon was less important with the catalytic batch used for the dienes **34** (entry 3), in spite of the presence of 5 mol% of complex. Indeed, conversely to the preceding batch, only 65% of conversion was

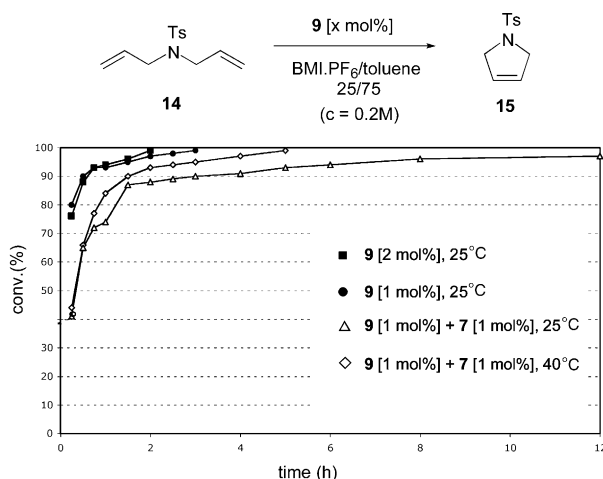
Table 6  
Ruthenium contaminant level in the cyclized product **27**

Cycle	1	2	3	4	5	6	7	8
Conv. (%) <sup>a</sup>	>98	>98	>98	>98	>98	>98	95	95
Ru residue (ppm) <sup>b</sup>	16.9	5.4	1.6	3.3	1.2	22	5.7	2.3

<sup>a</sup> Determined by <sup>1</sup>H NMR spectroscopic analysis at 400 MHz.

<sup>b</sup> Determined by ICP-MS spectroscopic analysis.

observed for the first run and no conversion at all for the second run. After two new successive loadings of the more reactive *N,N*-diallyltosylamine **14**, 94% and 90% of product **15** were obtained for the third and the fourth run respectively (entry 3: cycles 3 and 4). However, 10 h were necessary to obtain such levels of conversion. A possible explanation of this significant decrease of reactivity could be that the catalytic cycle during the first run with the diene **34** is unachieved involving the decomposition (or more probably the extraction) of the major



entry	conditions	additive	cycle / conv.(%) <sup>a</sup>						
			1	2	3	4	5	6	7
1	<b>9</b> [2 mol%] 25°C, 2h30	none	>98	>98	>98	>98	>98	>98	96
2	<b>9</b> [1 mol%] 25°C, 3h30	none	>98	97	92	49	--	--	--
3	<b>9</b> [1 mol%] 25°C, 20h	<b>7</b> [1 mol%]	>98	>98	87	75	--	--	--
4	<b>9</b> [1 mol%] 40°C, 3h	<b>7</b> [1 mol%]	>98	>98	>98	97	94	73	23

<sup>a</sup> Determined by <sup>1</sup>H NMR (400 MHz).

Scheme 4. Kinetic study of the RCM reaction of diene **14** with complex **9** under biphasic conditions (BMI · PF<sub>6</sub>/toluene: 25/75).

part of the 5 mol% catalyst. Thus, only a few mol% (and may be only traces) still remain active for the following runs to react with the more reactive diallylamine **14** but with a longer reaction time.

#### 2.4. Activity and recyclability of imidazolium-tagged Ru-complex **9** in olefins cross-metathesis

Olefin cross-metathesis (CM) [18] is not yet readily used in the academic research area compared to the RCM reaction. Nevertheless, the recent development of more active and thermally robust second-generation ruthenium catalysts is currently putting important emphasis on this reaction. Recent works [19] in the CM field have shown that the second generation of the Hoveyda–Grubbs boomerang catalyst **6** presented a better activity and selectivity than the second generation of Grubbs' catalyst **3**. For this reason and in order to extend the use of our environmentally friendly second-generation imidazolium-tagged catalyst **9**, its performance was screened in the range of CM reactions. Moreover, to date, very few publications concerning the use of supported and/or recyclable catalysts for the CM reaction have been reported in the literature.

The CM reaction between the olefin **38** and a range of electron deficient olefins was then studied in similar reaction conditions than the ones described by Blechert and co-workers [20]. As shown in Table 9, the CM reaction involving the methylacrylate **39** performed well with 5 mol% of catalyst **9** in a BMI · PF<sub>6</sub>/toluene (20/80) mixture at room temperature and the expected product **40** was obtained with 80% isolated yield after purification by silica gel chromatography (instead of 87% as reported by Blechert).

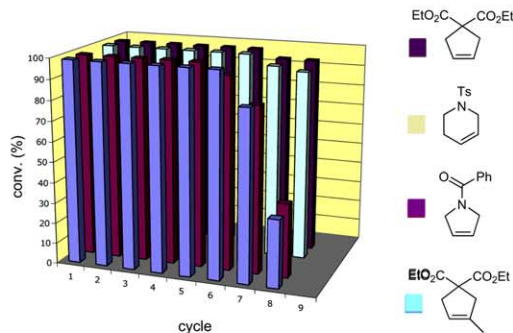
Whereas similar isolated yield was obtained for the second cycle, results decreased in the two following runs to finally reach 40% yield for the fifth cycle. This rapid decrease of reactivity in the CM reaction can be explained by the difficult re-anchoring of the active catalytic specie to the cationic imidazolium-tagged ligand **7**. The main reason is probably due to the large excess of methylacrylate (two equivalents) in the reaction mixture, which provoke a competitive metathesis reaction against the styrenyl ether ligand **7**. Resolving this problem by using only one equivalent of electron deficient olefin is strictly impossible because the excess is necessary to avoid the formation of the self-cross metathesis by-product. Using a strategy developed by Barrett and co-workers [17d] to improve the recycling of its polystyrene-supported ruthenium catalyst, 25 mol% of 1,7-octadiene were then used as additive at the end of the CM reaction. Indeed, this additive, more reactive than the methylacrylate olefin, is able to promote a competitive RCM reaction and should allow an improvement of the re-anchoring process. Unfortunately,



Table 7

Activity and recyclability of complex **9** with a range of dienes under biphasic conditions (BMI · PF<sub>6</sub>/toluene: 25/75)

Entry	Substrate	Conditions	Product	Cycle (% conv.) <sup>a</sup>							
				1	2	3	4	5	6	7	8
1		<b>9</b> (2.5 mol%) 25°C, 3h		>98	>98	>98	>98	>98	>98	95	95
2		<b>9</b> (2.5 mol%) 40°C, 6h		>98	>98	>98	>98	>98	>98	83	33
3		<b>9</b> (2.5 mol%) 25°C, 3h		>98	>98	>98	>98	>98	94	81	36
4		<b>9</b> (2 mol%) 25°C, 3h		>98	>98	>98	>98	>98	>98	94	92

<sup>a</sup> Determined by <sup>1</sup>H NMR spectroscopic analysis at 400 MHz.

whereas good isolated yields are obtained until the third run, they decrease rapidly in the next runs to reach 31% (entry 2).

Table 8

Recycling of imidazolium-tagged catalyst **9** in BMI · PF<sub>6</sub>/toluene (25/75) medium: scope and limitations

Entry	Cycle	Substrate	Conditions	Product	Conv. (%) <sup>a</sup>
1	1		<b>9</b> (2 mol%) 40°C, 8h		>98
	2				>98
	3				90
	4				40
2	1		<b>9</b> (2.5 mol%) 60°C, 24h		0
	2		25°C, 3h		>98
	3				>98
3	1		<b>9</b> (5 mol%) 60°C, 7h		65
	2				0
	3		25°C, 10h		94
	4				90

<sup>a</sup> Determined by <sup>1</sup>H NMR spectroscopic analysis at 400 MHz.

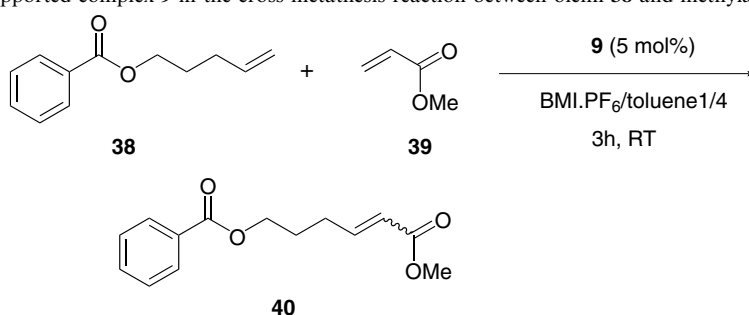
Despite these poor results, we have also screened the activity and the recyclability of the catalyst **9** in the CM reaction between olefin **38** and a few electron deficient olefins: methylvinylketone, acrolein and *N,N*-dimethylacrylamide. The results are summarized in the Table 10. In the case of methylvinylketone, the isolated yields were good only in the first two cycles to decrease dramatically to 35% in the last run. Whereas with acrolein 32% of isolated yield was obtained as early as the second run, only the self-cross-metathesis by-product was formed with 44% yield with the *N,N*-dimethylacrylamide.


Finally, cross-metathesis between the methylvinylketone and the chiral homoallyl-amine **41** derived from the commercially available enantiopure  $\alpha$ -methylbezyll-amine was studied (Table 11). Similar results of recycling were observed under standard conditions (entry 1). Using other conditions (BMI · PF<sub>6</sub>/CH<sub>2</sub>Cl<sub>2</sub> as solvent) developed by Yao and Zhang [10j] with its imidazolium-tagged ruthenium catalyst, the CM reaction performed with a better isolated yield to reach 94% but no improvement in the recycling was observed (entry 2).

### 3. Conclusion

This work reports the development of an imidazolium-tagged styrenyl ether ligand that led to efficient ionic boomerang catalysts to perform metathesis reactions in ionic liquids. Whereas a high level of recyclability

Table 9

Activity and recyclability of supported complex **9** in the cross-metathesis reaction between olefin **38** and methylacrylate **39**

Entry	Cycle	Additive before extraction	Isolated Yield (%)	E/Z
1	1	none	80	>20/1
	2		82	>20/1
	3		70	>20/1
	4		70	>20/1
	5		40	>20/1
2	1	 25 mol% 1h, RT	76	>20/1
	2		82	>20/1
	3		80	>20/1
	4		52	>20/1
	5		31	>20/1

combined with a high reactivity were obtained with the first generation catalyst **8**, the second generation of *N*-heterocyclic carbene ruthenium complex **9** appeared to be more suitable to perform ring-closing metathesis reactions of less reactive substrates in harsher conditions. Moreover the use of a biphasic BMI · PF<sub>6</sub>/toluene medium increased considerably the recycling of the catalyst and extremely low residual ruthenium levels were detected by ICP-MS in the final products. Olefins cross-metathesis with this environmentally friendly process was also studied. Although excellent activities were observed in the first runs, the recyclability levels were very low. This limitation led us to develop a new imidazolium-tagged ligand containing a NHC unit in order to obtain a more efficient and recyclable catalyst. These results will be reported in due course.

## 4. Experimental





### 4.1. General

<sup>1</sup>H (400 MHz), <sup>13</sup>C (100 MHz), <sup>31</sup>P (162 MHz) and <sup>19</sup>F (36.5 MHz) NMR spectra were recorded on a Bruker ARX400 spectrometer with complete proton decou-

pling for nucleus other than <sup>1</sup>H. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl<sub>3</sub>, <sup>1</sup>H: δ 7.27 ppm, <sup>13</sup>C: δ 77.0 ppm, CD<sub>2</sub>Cl<sub>2</sub>, <sup>1</sup>H: δ 5.31 ppm, <sup>13</sup>C: δ 53.7 ppm and (CD<sub>3</sub>)<sub>2</sub>CO: <sup>1</sup>H: δ 2.05 ppm, <sup>13</sup>C: δ 205.1 ppm). Data are reported as follows: chemical shift (δ) in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, sept = septuplet, br = broad, m = multiplet), coupling constants (Hz), integration and attribution. High-resolution mass spectra (HRMS) were recorded at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO), Université de Rennes 1 on a Micromass ZABSpecTOF instrument. Elemental analyses were also performed at the CRMPO.

### 4.2. Materials

All non-aqueous reactions were performed under an argon atmosphere using oven-dried glassware. Toluene was distilled from sodium metal under nitrogen. Tetrahydrofuran and diethyl ether were distilled from sodium metal/benzophenone ketyl under nitrogen. Dichloromethane and triethylamine were distilled from calcium hydride under nitrogen. Dimethylformamide was distilled from phosphorous pentoxide under vacuum and

Entry	 EWG	Cycle	Isolated Yield (%)	E/Z
1		1	88	>20/1
		2	87	>20/1
		3	35	>20/1
2		1	92	>20/1
		2	32	>20/1
3		1	0 (44 % in self cross)	

Entry	Conditions	Cycle	Isolated yield (%)	<i>E/Z</i>
1	BMI · PF <sub>6</sub> /toluene 1/4	1	80	>20/1
2	RT, 6 h	2	25	>20/1
	BMI · PF <sub>6</sub> /CH <sub>2</sub> Cl <sub>2</sub> 1/9	1	94	>20/1
	40 °C, 3 h	2	4	>20/1

and solvents were obtained from commercial sources and used without further purification. Analytical TLC were performed on Merck silica gel 60F<sub>254</sub> plates, and visualized under UV-light. Chromatographic purifications were performed on a column with 230–400 mesh silica gel (Merck 9385) using the indicated solvent system.

To a suspension of sodium hydride (1.27 g, 31.8 mmol, 1.1 equiv) in dry tetrahydrofuran (80 ml) was added at 0 °C a solution of methyl-3-(4-hydroxyphenyl)-propionate **10** (5.2 g, 28.9 mmol) in dry tetrahydrofuran (80 ml). After gas evolution, dry dimethylformamide (80 ml) and isopropyl bromide (3.2 ml, 31.8 mmol, 1.1 equiv) were syringed into the reaction mixture. The resulting mixture was stirred at room temperature for 2 h. Sodium hydride (1.27 g, 31.8 mmol, 1.1 equiv) and isopropyl bromide (3.2 ml, 31.8 mmol, 1.1 equiv) were added into the reaction mixture followed by a stirring of 2 h to complete the reaction. The mixture was concentrated under vacuum and ethyl acetate (100 ml) was added. The organic layer was washed four times with a saturated solution of sodium hydrogenocarbonate and one time with brine, dried over magnesium sulfate, filtered and concentrated. Purification by silica gel chromatography (pentane/ethyl acetate, 8/2) afforded the desired product as a colorless oil (5.76 g, 26.0 mmol, 90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm): 1.34 (d, *J*(H,H) = 6.1 Hz, 6H, 2CH<sub>3</sub>), 2.62 (t, *J*(H,H) = 7.9 Hz, 2H, CH<sub>2</sub>), 2.90 (t, *J*(H,H) = 7.9 Hz, 2H, CH<sub>2</sub>), 3.69 (s, 3H, CH<sub>3</sub>), 4.52 (sept, *J*(H,H) = 6.1 Hz, 1H, CH), 6.83 (d, *J*(H,H) = 8.7 Hz, 2H, 2CH<sub>ar</sub>), 7.11 (d, *J*(H,H) = 8.7 Hz, 2H, 2CH<sub>ar</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm): 22.5 (2C), 30.5, 36.4, 52.0, 70.2, 116.3 (2C), 129.6 (2C), 132.8, 156.8, 173.8. HRMS (EI) calcd for C<sub>13</sub>H<sub>18</sub>O<sub>3</sub>: 222.1256, found: 222.1250.

To a solution of 3-(4-isopropoxy-phenyl)-propionic acid methyl ester (3.53 g, 15.9 mmol) in dry dichloromethane (80 ml) was added acetic acid (36  $\mu$ L, 0.64 mmol, 0.04 equiv). Bromine (860  $\mu$ L, 16.7 mmol, 1.05 equiv) was then slowly added dropwise at room temperature, forming a red solution. Over the course of 1.5 h the mixture gradually turned pale yellow. The reaction was then quenched with a saturated sodium thiosulfate solution (20 ml). After dilution with water, the organic layer was separated. The aqueous layer was extracted with diethyl ether. The combined organic layers were dried over magnesium sulfate, filtrated and concentrated to a colorless oil (4.7 g, 15.6 mmol, 98%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 1.36 (d,  $J(\text{H,H}) = 6.1$  Hz, 6H, 2 $\text{CH}_3$ ), 2.59 (t,  $J(\text{H,H}) = 7.9$  Hz, 2H,  $\text{CH}_2$ ), 2.67 (s, 3H,  $\text{CH}_3$ ), 2.86 (t,  $J(\text{H,H}) = 7.9$  Hz,

2H, CH<sub>2</sub>), 4.50 (sept,  $J(\text{H,H}) = 6.1$  Hz, 1H, CH), 6.83 (d,  $J(\text{H,H}) = 8.4$  Hz, 1H, CH<sub>ar</sub>), 7.06 (dd,  $J(\text{H,H}) = 2.0$  and 8.4 Hz, 1H, CH<sub>ar</sub>), 7.38 (d,  $J(\text{H,H}) = 2.0$  Hz, 1H, CH<sub>ar</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 22.5 (2C), 30.1, 36.1, 52.0, 72.6, 114.1, 116.4, 128.5, 133.5, 134.7, 153.4, 173.5. HRMS (EI) calcd for C<sub>13</sub>H<sub>17</sub>O<sub>3</sub>Br: 300.0361, found: 300.0348.

#### 4.2.3. 3-(3-Bromo-4-isopropoxy-phenyl)-propan-1-ol

To a solution of 3-(3-bromo-4-isopropoxy-phenyl)-propionic acid methyl ester (4.37 g, 14.5 mmol) in dry tetrahydrofuran (200 ml) was added, at 0 °C, lithium aluminum hydride (551 mg, 14.5 mmol, 1 equiv). The mixture was stirred for 45 min, at 0 °C. The reaction was then quenched with water (550  $\mu$ L), NaOH 15% in water (550  $\mu$ L) and water (1.65 ml). The mixture was filtrated on a plug of celite and the cake was washed with dichloromethane and hot tetrahydrofuran. The organic layer was evaporated off under vacuum, diluted with dichloromethane, washed with brine, dried over magnesium sulfate and concentrated. A purification by silica gel chromatography using pentane/ethyl acetate (8/2) as the eluent afforded the desired product as a colorless oil (3.76 g, 13.8 mmol, 95%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 1.37 (d,  $J(\text{H,H}) = 6.1$  Hz, 6H, 2CH<sub>3</sub>), 1.83 (tt,  $J(\text{H,H}) = 6.4$  and 7.4 Hz, 2H, CH<sub>2</sub>), 1.88 (s, br, 1H, OH), 2.62 (t,  $J(\text{H,H}) = 7.4$  Hz, 2H, CH<sub>2</sub>), 3.65 (t,  $J(\text{H,H}) = 6.4$  Hz, 2H, CH<sub>2</sub>), 4.50 (sept,  $J(\text{H,H}) = 6.1$  Hz, 1H, CH), 6.85 (d,  $J(\text{H,H}) = 8.4$  Hz, 1H, CH<sub>ar</sub>), 7.06 (dd,  $J(\text{H,H}) = 2.0$  and 8.4 Hz, 1H, CH<sub>ar</sub>), 7.38 (d,  $J(\text{H,H}) = 2.0$  Hz, 1H, CH<sub>ar</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 22.0 (2C), 30.7, 34.0, 61.8, 72.3, 113.6, 116.1, 128.1, 133.1, 135.7, 152.6. HRMS (EI) calcd for C<sub>12</sub>H<sub>17</sub>O<sub>2</sub>Br: 272.0412, found: 272.0404.

#### 4.2.4. 3-(4-Isopropoxy-3-vinyl-phenyl)-propan-1-ol (**12**)

A Schlenk flask was charged with dry toluene (30 ml) and tetrakis(triphenylphosphine)palladium (292 mg, 0.25 mmol, 0.05 equiv). The mixture was degassed and 3-(3-bromo-4-isopropoxy-phenyl)-propan-1-ol (1.25 g, 4.58 mmol) diluted in dry toluene (5 ml) was added dropwise through a syringe. The resulting mixture was stirred 15 min before adding tributylvinylstannane (2.2 ml, 6.87 mmol, 1.5 equiv). The flask was heated at 110 °C overnight. After cooling to room temperature, the mixture was filtrated on a plug of celite and the cake was washed with diethyl ether. The solvent was evaporated off under vacuum and a purification by silica gel chromatography using pentane/ethyl acetate (8/2) as the eluent afforded the desired product as a colorless oil (910 mg, 4.17 mmol, 91%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 1.37 (d,  $J(\text{H,H}) = 6.1$  Hz, 6H, 2CH<sub>3</sub>), 1.89 (tt,  $J(\text{H,H}) = 6.4$  and 7.4 Hz, 2H, CH<sub>2</sub>), 2.00 (s, br, 1H, OH), 2.67 (t,  $J(\text{H,H}) = 7.4$  Hz, 2H, CH<sub>2</sub>), 3.68 (t,  $J(\text{H,H}) = 6.4$  Hz, 2H, CH<sub>2</sub>), 4.51 (sept,

$J(\text{H,H}) = 6.1$  Hz, 1H, CH), 5.25 (d,  $J(\text{H,H}) = 11.2$  Hz, 1H, CH<sub>2</sub>), 5.76 (d,  $J(\text{H,H}) = 17.8$  Hz, 1H, CH<sub>2</sub>), 6.83 (d,  $J(\text{H,H}) = 8.4$  Hz, 1H, CH<sub>ar</sub>), 7.04–7.11 (m, 2H, CH and CH<sub>ar</sub>), 7.34 (d,  $J(\text{H,H}) = 2.0$  Hz, 1H, CH<sub>ar</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 22.7 (2C), 31.7, 34.8, 62.6, 71.5, 114.2, 115.0, 126.8, 128.2, 129.0, 132.4, 134.3, 153.8. HRMS (EI) calcd for C<sub>14</sub>H<sub>20</sub>O<sub>2</sub>: 220.1463, found: 220.1456.

#### 4.2.5. Methanesulfonic acid 3-(4-isopropoxy-3-vinyl-phenyl)-propyl ester

To a solution of 3-(4-isopropoxy-3-vinyl-phenyl)-propan-1-ol (1.21 g, 5.51 mmol) and triethylamine (1.15 ml, 8.27 mmol, 1.2 equiv) in dry dichloromethane (30 ml) was added, at 0 °C, methanesulfonyl chloride (640  $\mu$ L, 8.27 mmol, 1.5 equiv). The reaction mixture was stirred for 3.5 h at room temperature before diluting with dichloromethane. The organic phase was washed four times with a 5% citric acid solution, dried over sodium sulfate and concentrated to a yellow oil. The product was used without further purification in the following reaction. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 1.36 (d,  $J(\text{H,H}) = 5.8$  Hz, 6H, 2CH<sub>3</sub>), 2.08 (tt,  $J(\text{H,H}) = 6.0$  and 7.6 Hz, 2H, CH<sub>2</sub>), 2.71 (t,  $J(\text{H,H}) = 7.6$  Hz, 2H, CH<sub>2</sub>), 3.02 (s, 3H, CH<sub>3</sub>), 4.25 (t,  $J(\text{H,H}) = 6.0$  Hz, 2H, CH<sub>2</sub>), 4.52 (sept,  $J(\text{H,H}) = 5.8$  Hz, 1H, CH), 5.38 (dd,  $J(\text{H,H}) = 1.5$  and 11.2 Hz, 1H, CH<sub>2</sub>), 5.75 (dd,  $J(\text{H,H}) = 1.3$  and 17.8 Hz, 1H, CH<sub>2</sub>), 6.84 (d,  $J(\text{H,H}) = 8.4$  Hz, 1H, CH<sub>ar</sub>), 7.05 (m, 2H, CH and CH<sub>ar</sub>), 7.30 (m, 1H, CH<sub>ar</sub>).

#### 4.2.6. 4-(3-Bromo-propyl)-1-isopropoxy-2-vinyl-benzene (**13**)

To a crude mixture of methanesulfonic acid 3-(4-isopropoxy-3-vinyl-phenyl)-propyl ester (1.64 g, 5.5 mmol) in tetrahydrofuran (20 ml) and dimethylformamide (8 ml) was added lithium bromide (960 mg, 11 mmol, 2 equiv) in one portion. The mixture was stirred overnight at room temperature. After evaporation of the solvent, the residue was diluted in ethyl acetate. The organic layer was washed three times with a saturated sodium hydrogenocarbonate solution then with brine, dried over magnesium sulfate, filtrated and concentrated. A purification by silica gel chromatography using pentane/ethyl acetate (98/2) as the eluent afforded the desired product as a colorless oil (1.16 g, 4.1 mmol, 74% (two steps)). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 1.38 (d,  $J(\text{H,H}) = 6.1$  Hz, 6H, 2CH<sub>3</sub>), 2.18 (tt,  $J(\text{H,H}) = 6.6$  and 7.3 Hz, 2H, CH<sub>2</sub>), 2.75 (t,  $J(\text{H,H}) = 7.3$  Hz, 2H, CH<sub>2</sub>), 3.43 (t,  $J(\text{H,H}) = 6.6$  Hz, 2H, CH<sub>2</sub>), 4.53 (sept,  $J(\text{H,H}) = 6.1$  Hz, 1H, CH), 5.27 (dd,  $J(\text{H,H}) = 1.5$  and 11.2 Hz, 1H, CH<sub>2</sub>), 5.77 (dd,  $J = 1.5$  and 17.8 Hz, 1H, CH<sub>2</sub>), 6.85 (d,  $J(\text{H,H}) = 8.4$  Hz, 1H, CH<sub>ar</sub>), 7.07 (m, 2H, CH and CH<sub>ar</sub>), 7.31 (m, 1H, CH<sub>ar</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 22.7 (2C), 33.5, 33.7, 34.8, 71.4, 113.9, 114.4,



126.5, 127.7, 128.5, 132.4, 133.7, 153.6. HRMS (EI) calcd for  $C_{14}H_{19}OBr$ : 282.0619, found: 282.0610.

#### 4.2.7. 1-[3-(4-Isopropoxy-3-vinyl-phenyl)-propyl]-3-methyl-3H-imidazol-1-ium hexafluorophosphate (7)

A 10 ml round bottomed flask equipped with a condenser was charged with 4-(3-bromo-propyl)-1-isopropoxy-2-vinyl-benzene **13** (1.1 g, 3.9 mmol), methyl-imidazole (623  $\mu$ L, 7.8 mmol, 2 equiv) and dry toluene (3.9 ml). The mixture was stirred overnight at 100 °C then the solvent was evaporated off. The residue was dissolved in distilled water (30 ml). Hexafluorophosphoric acid (10 ml, 60% in water) was slowly added dropwise. After 10 min stirring, dichloromethane and brine were added. The organic phase was washed with brine until to reach a neutral pH, dried over magnesium sulfate, filtrated and concentrated. A purification by silica gel chromatography using dichloromethane/acetone (3/1) as the eluent afforded the desired product as a colorless oil (1.47 g, 3.41 mmol, 87% (two steps)).  $^1H$  NMR (400 MHz,  $(CD_3)_2CO$ ):  $\delta$  (ppm): 1.29 (d,  $J(H,H) = 6.1$  Hz, 6H,  $2CH_3$ ), 2.09 (tt,  $J(H,H) = 7.4$  Hz, 2H,  $CH_2$ ), 2.56 (t,  $J(H,H) = 7.4$  Hz, 2H,  $CH_2$ ), 3.77 (s, 3H,  $CH_3$ ), 4.09 (t,  $J(H,H) = 7.2$  Hz, 2H,  $CH_2$ ), 4.46 (sept,  $J(H,H) = 6.0$  Hz, 1H, CH), 5.19 (d,  $J(H,H) = 11.4$  Hz, 1H,  $CH_2$ ), 5.75 (d,  $J(H,H) = 17.8$  Hz, 1H,  $CH_2$ ), 6.78 (d,  $J(H,H) = 8.4$  Hz, 1H,  $CH_{ar}$ ), 6.98 (m, 2H, CH and  $CH_{ar}$ ), 7.17 (m, 2H,  $2CH$ ), 7.25 (m, 1H,  $CH_{ar}$ ), 8.28 (s, 1H, CH).  $^{13}C$  NMR (100 MHz,  $(CD_3)_2CO$ ):  $\delta$  (ppm): 21.1 (2C), 30.3, 30.4, 35.0, 48.5, 70.0, 113.2, 113.6, 121.0 (2C), 122.5, 125.1, 126.6, 127.7, 130.9, 134.6, 152.6.  $^{19}F$  NMR (376 MHz,  $(CD_3)_2CO$ ):  $\delta$  (ppm): -72.3 (d,  $J(F,P) = 712.8$  Hz, 6F,  $PF_6$ ).  $^{31}P$  NMR (162 MHz,  $(CD_3)_2CO$ ):  $\delta$  (ppm): -143.1 (sept,  $J(P,F) = 712.8$  Hz, 1P,  $PF_6$ ). HRMS (FAB) calcd for  $C^{+}$ :  $C_{18}H_{25}N_2O$ : 285.1967, found: 285.1957.

#### 4.2.8. Ionic liquid-supported catalyst (8)

In a Schlenk apparatus were introduced copper (I) chloride (49 mg, 0.5 mmol, 1.25 equiv) and Grubbs catalyst **2** (494 mg, 0.6 mmol, 1.5 equiv). Three degassing (vacuum/argon) were performed and the 1-[3-(4-Isopropoxy-3-vinyl-phenyl)-propyl]-3-methyl-3H-imidazol-1-ium hexafluorophosphate **7** (172 mg, 0.4 mmol) in solution in dry dichloromethane (8 ml) was syringed into the reaction mixture. The resulting solution was again degassed three times and stirred for 3 h at room temperature. The solvent was evaporated off under vacuum, the residue was dissolved in dry acetone (8 ml). The excess of **2** was removed by filtration and washed with acetone (8 ml). After concentration, the catalyst was precipitated in a 1/1 pentane/dichloromethane mixture (8 ml), filtrated, washed with the same mixture (8 ml) and dried under vacuum to afford a brown solid (270 mg, 0.31 mmol, 78%).  $^1H$  NMR (400 MHz,  $(CD_3)_2CO$ ):  $\delta$  (ppm): 1.30 (m, 11H,  $2CH_3$  and  $PCy_3$ ),

1.70–1.90 (m, 23H,  $PCy_3$ ), 2.40 (m, 5H,  $CH_2$  and  $PCy_3$ ), 2.90 (m, 4H,  $CH_2$  and  $PCy_3$ ), 4.01 (s, 3H,  $CH_3$ ), 4.50 (t,  $J(H,H) = 7.0$  Hz, 2H,  $CH_2$ ), 5.37 (sept,  $J(H,H) = 7.7$  Hz, 1H, CH), 7.28 (d,  $J(H,H) = 7.9$  Hz, 1H,  $CH_{ar}$ ), 7.62 (d,  $J(H,H) = 8.6$  Hz, 1H,  $CH_{ar}$ ), 7.68 (m, 2H,  $2CH$ ), 7.81 (m, 1H,  $CH_{ar}$ ), 9.00 (s, 1H, CH), 17.39 (d,  $J(H,H) = 4.9$  Hz, 1H, Ru = CH).  $^{13}C$  NMR (100 MHz,  $(CD_3)_2CO$ ):  $\delta$  (ppm): 22.1, 22.4, 26.4 (3C), 27.9 (d,  $J(C,P) = 9.9$  Hz, 6C), 28.7 (6C), 29.5, 31.2, 33.6 (d,  $J(C,P) = 21.2$  Hz, 3C), 36.1, 46.8, 69.9, 113.6, 122.4 (2C), 124.3, 131.4, 137.2, 137.5, 143.3, 146.9.  $^{19}F$  NMR (376 MHz,  $(CD_3)_2CO$ ):  $\delta$  (ppm): -72.9 (d,  $J(F,P) = 708.0$  Hz, 6F,  $PF_6$ ).  $^{31}P$  NMR (162 MHz,  $(CD_3)_2CO$ ):  $\delta$  (ppm): -143.0 (sept,  $J(P,F) = 708$  Hz, 1P,  $PF_6$ ), 60.3 (s, 1P,  $PCy_3$ ). HRMS (FAB) calcd for  $C^{+}$ :  $C_{35}H_{56}N_2OCl_2PRu$ : 723.2551, found: 723.2556. Elemental analysis calcd for  $C_{35}H_{56}N_2OF_6Cl_2P_2Ru$ : C, 48.39; H, 6.50; N, 3.22; found: C, 48.14; H, 6.57; N, 3.37.

#### 4.2.9. Ionic liquid-supported catalyst (9)

In a Schlenk flask, 1-[3-(4-isopropoxy-3-vinyl-phenyl)-propyl]-3-methyl-3H-imidazol-1-ium hexafluorophosphate **7** (159 mg, 0.37 mmol) was diluted in dry dichloromethane (37 ml). Copper (I) chloride (73 mg, 0.74 mmol) and Grubbs' catalyst **3** (494 mg, 0.6 mmol, 1.5 equiv) were introduced. The resulting solution was degassed three times (vacuum/argon) and stirred for 30 h at reflux. The solvent was evaporated under vacuum, the residue was dissolved in dry acetone (10 ml) and the insoluble materials were removed by filtration and washed with acetone ( $2 \times 5$  ml). The filtrate was evaporated under vacuum and then solubilised in the minimum amount of dichloromethane. The same amount of toluene was added and the solution was cooled at -10 °C over 10 h. The resulting green crystals were filtered and washed with cold toluene and dried under vacuum to afford a green powder (228 mg, 90%).  $^1H$  NMR (400 MHz,  $CD_2Cl_2$ ):  $\delta$  (ppm): 1.19 (d,  $J(H,H) = 1.7$  Hz, 6H,  $2CH_3$ ), 2.15 (quint,  $J(H,H) = 6.8$  Hz, 2H,  $CH_2$ ), 2.41 (s, 18H,  $6CH_3$ ), 2.76 (t,  $J(H,H) = 6.8$  Hz, 2H,  $CH_2$ ), 3.67 (s, 3H,  $CH_3$ ), 4.13 (m, 6H,  $3CH_2$ ), 4.81 (sept,  $J(H,H) = 6.2$  Hz, 1H, CH), 6.59 (d,  $J(H,H) = 1.7$  Hz, 1H,  $CH_{ar}$ ), 6.74 (d,  $J(H,H) = 8.5$  Hz, 1H,  $CH_{ar}$ ), 7.07 (s, 3H,  $3CH_{ar}$ ), 7.17 (m, 2H,  $2CH$ ), 7.38 (dd,  $J(H,H) = 1.7$  and 8.5 Hz, 1H,  $CH_{ar}$ ), 8.25 (s, 1H, CH), 16.45 (s, 1H, Ru = CH).  $^{13}C$  NMR (100 MHz,  $CD_2Cl_2$ ):  $\delta$  (ppm): 21.1 (6C), 21.4 (2C), 30.8, 31.6, 36.8, 50.3, 51.8 (2C), 75.6, 113.3, 121.4, 121.9, 124.0, 125.5, 128.4 (4C), 129.2 (2C), 129.5 (4C), 133.8, 136.5, 139.1, 145.2 (2C), 150.8, 210.2, 295.2 (q,  $J(C,Ru) = 27.2$  Hz, 1C).  $^{19}F$  NMR (376 MHz,  $CD_2Cl_2$ ):  $\delta$  (ppm): -72.8 (d,  $J(F,P) = 711$  Hz, 6F,  $PF_6$ ).  $^{31}P$  NMR (162 MHz,  $CD_2Cl_2$ ):  $\delta$  (ppm): -143.1 (sept,  $J(P,F) = 711$  Hz, 1P,  $PF_6$ ). HRMS (FAB) calcd for  $C^{+}$ : 749.2327, found:

749.2321. Elemental analysis calcd for  $C_{38}H_{49}Cl_2F_6N_4OPRu$ : C, 51.01; H, 5.52; N, 6.26; found: C, 50.92; H, 5.50; N, 5.77.

#### 4.3. General procedure for RCM reactions in ionic liquid

BMI · PF<sub>6</sub> (5 ml) was introduced in a Schlenk flask and dried 2 h under vacuum at 70 °C. The ionic liquid-supported catalyst was added and the mixture was stirred until the catalyst was dissolved. The diene (1 mmol,  $c = 0.2$  M) was then introduced into the reaction mixture and heated at the desired temperature during the indicated time. At the end of the reaction, the mixture was cooled and the cyclized product was obtained by extraction with dry toluene ( $4 \times 10$  ml). The solvent was evaporated and the crude product purified by flash chromatography using pentane/ethyl acetate (9/1) as the eluent. The conversion rate was determined by <sup>1</sup>H NMR spectroscopy on the crude product. The BMI · PF<sub>6</sub> phase containing the IL-catalyst was dried under vacuum before its reuse with a new addition of diene.

#### 4.4. General procedure for RCM reactions in BMI · PF<sub>6</sub>/toluene (25/75)

BMI · PF<sub>6</sub> (1.25 ml) was introduced into a Schlenk flask and dried for 2 h under vacuum at 70 °C then washed with dry toluene ( $3 \times 10$  ml). The ionic liquid-catalyst was added and the mixture was stirred for 1 h at room temperature under vacuum to afford a complete dissolution of the catalyst. The diene (1 mmol,  $c = 0.2$  M) was then introduced followed by dry toluene (3.75 ml) and the reaction mixture was stirred at the indicated temperature. The progress of the reaction could be followed by <sup>1</sup>H NMR or by TLC. The product was extracted from the reaction mixture with dry toluene ( $4 \times 10$  ml). The combined toluene extracts layers were evaporated to afford the crude product. The conversion rate was examined by 400 MHz <sup>1</sup>H NMR spectroscopy.

#### 4.5. General procedure for CM reactions in BMI · PF<sub>6</sub>/toluene (20/80)

BMI · PF<sub>6</sub> (0.50 ml) was introduced into a Schlenk flask and dried for 2 h under vacuum at 70 °C then washed with dry toluene ( $3 \times 5$  ml). The ionic liquid-catalyst was added and the mixture was stirred for 1 h at room temperature under vacuum to afford a complete dissolution of the catalyst. The diene (0.5 mmol,  $c = 0.2$  M) was then introduced followed by dry toluene (2 ml) and the electron-deficient olefin (1 mmol, 2 equiv.). The reaction mixture was stirred at room temperature. The progress of the reaction could be followed by TLC. The product was extracted from the reaction mixture with dry toluene ( $4 \times 5$  ml). The combined tolu-

ene extracts layers were evaporated to afford the crude product. The product was purified by silica gel chromatography using pentane/ethyl acetate (9/1) as the eluent afforded the desired product.

#### 4.6. Procedure to recover the BMI · PF<sub>6</sub>

The ionic liquid BMI · PF<sub>6</sub> containing the decomposed IL-catalyst (5 ml) was dissolved in 10 ml of dichloroethane. Black carbon (500 mg) was added and the resulting mixture was refluxed for 12 h. The mixture was cooled to room temperature and then filtered onto a plug of celite. The solvent was removed to afford the pure BMI · PF<sub>6</sub> as a colorless oil which was finally dried for 4 h at 70 °C under vacuum. This recovered BMI · PF<sub>6</sub> was used in a RCM reaction with a new loading of IL-catalyst and substrate without loss of performance compared to the fresh one.

#### 4.7. Procedure for ICP-MS measurement

All samples were prepared by weighing 5 mg of the crude compound (that was previously filtered through a slim bed of silica gel in order to remove BMI · PF<sub>6</sub> traces) and then adding 10 ml of 0.12 M hydrochloric acid in glacial acetic acid. The analyses were performed on a PE Instrument Elan 6000 Inductive Coupled Plasma Mass Spectrometer (ICP-MS) using <sup>99</sup>Ru and <sup>101</sup>Ru isotopes, which are not interfered by molybdenum oxide. All samples were diluted 10 times in ultra pure water. The Ru level was determined by comparison with a standard Ru sample (10 µg/mL). The analyses have been realised by UT2A Company, France (<http://www.univ-pau.fr/ut2a>).

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