

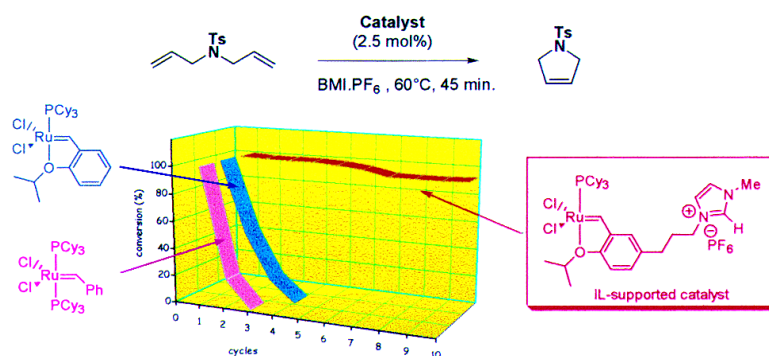
Communication

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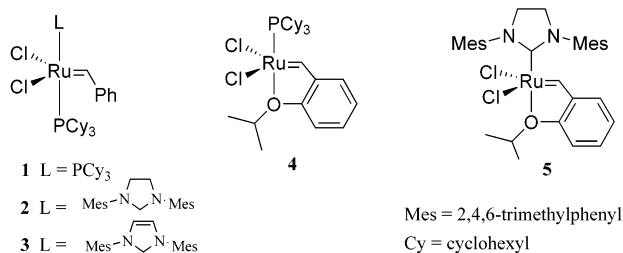
An Ionic Liquid-Supported Ruthenium Carbene Complex: A Robust and Recyclable Catalyst for Ring-Closing Olefin Metathesis in Ionic Liquids

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Ring-closing metathesis (RCM)¹ 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**² 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,³ and various strategies were employed to recover and reuse the catalyst for the RCM reaction.⁴

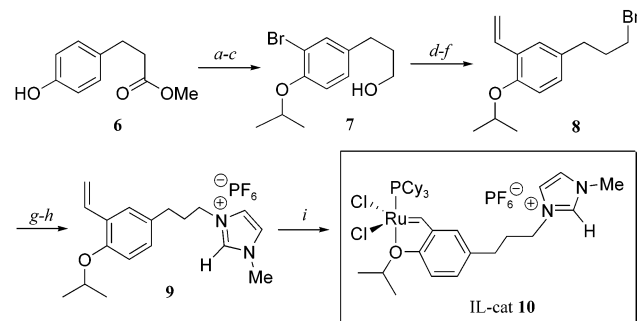
Ionic liquids (IL) are a new class of solvents⁵ which present interesting properties such as nonvolatility, high stability, and easy recyclability. Because these solvents are immiscible with many organic solvents, it was very attractive to perform RCM and attempt to recover and recycle the ionic liquid layer containing the Ru catalyst after a simple extraction of the product. Pioneers of using this strategy, Buijsman and co-workers,^{6a} have reported that the Grubbs's Ru catalyst precursor **1** dissolved in 1-butyl-3-methylimidazolium hexafluorophosphate (BMI·PF₆)⁷ 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^{6b} have described RCM performed by ruthenium allenylidene salts in BMI·PF₆, 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.⁸ 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·PF₆.

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**^a



^a Reaction conditions: (a) 2.2 equiv NaH, 2.2 equiv *i*-PrI, DMF, THF, rt, 90%. (b) 1.05 equiv Br₂, 0.04 equiv HOAc, CH₂Cl₂, rt, 98%. (c) 1 equiv LiAlH₄, THF, 0 °C, 95%. (d) 1.5 equiv Bu₃SnCHCH₂, 3 mol % Pd(PPh₃)₄, toluene, 110 °C, 75%. (e) 1.5 equiv Et₃N, CH₂Cl₂, 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) HPF₆, H₂O, 0 °C, 87% overall for two steps. (i) 1.5 equiv **1**, 1.25 equiv CuCl, CH₂Cl₂, 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 HPF₆, afforded the desired hexafluorophosphate imidazolium salt **9**, which was purified by silica gel chromatography. Following Hoveyda's method^{4c} 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 CH₂Cl₂/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 preformed solution of 2.5 mol % IL catalyst **10** in BMI·PF₆. 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·PF₆ 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·PF₆ solution and accomplished the ninth run after 3

Table 1. Comparative Recycling and Reuse in BMI-PF₆ of IL Catalyst **10** and Catalysts **1** and **4** in the RCM of Diene **11**

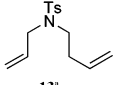
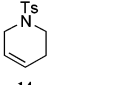
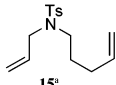
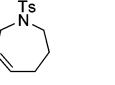
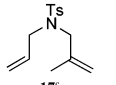
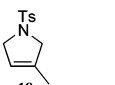
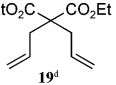
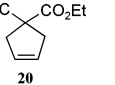
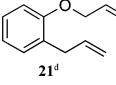
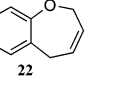
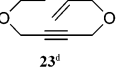
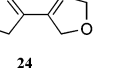
catalyst	cycle (% conv. ^a)									
	1	2	3	4	5	6	7	8	9	10 ^b
10	>98	>98	>98	>98	>98	96	92	92	92	95
1	>98	20	—	—	—	—	—	—	—	—
4	>98	40	20	—	—	—	—	—	—	—

^a Determined by ¹H NMR spectroscopy analysis. ^b **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-PF₆ (23 wt % at 26°C)⁹ 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-PF₆ solvent could be recovered by treatment with black carbon^{6b} and reused with a new loading of catalyst.

Having established the recyclability and reuse of IL catalyst **10** in BMI-PF₆, 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.(%) ^b
		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

^a **10** (2.5 mol %), BMI-PF₆ (0.2M), 60 °C, 45 min. ^b Determined by ¹H NMR spectroscopic analysis. ^c **10** (5 mol %), BMI-PF₆ (0.2 M), 60 °C, 4 h. ^d **10** (2.5 mol %), BMI-PF₆ (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-PF₆ 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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