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Alkene metathesis catalysis in ionic liquids with ruthenium allenylidene salts

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Ring closing metathesis of dienes in 1-butyl-3-methylimidazolium salts in the presence of ruthenium allenylidene salts as catalyst is described.

Metal-catalysed olefin metathesis has become a powerful method in organic synthesis and polymer science as illustrated by useful applications discovered during the last five years.[1,2] This is mainly due to the performance of efficient neutral alkylidene molybdenum[3] and ruthenium[4] catalysts in organic solvents for the production of functional alkenes,[5] medium size rings and macrocycles,[6] and polymers.[7] The recent discovery of well-defined ruthenium allenylidene salts $[LnRu{=}C{=}C{=}CAr_2]^+X^-$ as alkene metathesis catalyst precursors[8,9] provided impetus to study the possibility of performing alkene metathesis in ionic liquids. Indeed, since the first uses of ionic liquids in catalysis reported in 1990 by Chauvin *et al.*[10] for propene dimerisation and by Wilkes *et al.*[11] for ethylene polymerisation, a number of transition metal-catalyzed reactions in ionic solvents have been found.[12]

We report here the first example of a metathesis reaction performed in ionic liquids in the presence of ruthenium allenylidene salt catalysts:[13] the ring closing reaction of a diallylamide in 1-butyl-3-methylimidazolium salts [bmim][X] and biphasic media containing one ionic salt and an organic phase.

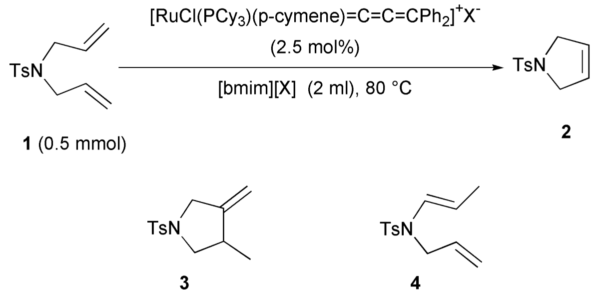
The first efficient catalytic RCM transformation of non conjugated dienes in organic solvent in the presence of a well-defined 18 electron ruthenium salt $[RuCl({=}C{=}C{=}CPh_2)(PCy_3)(p\text{-cymene})][X]$ was shown to be dramatically dependent on the nature of the counter anion X^- of the catalyst.[9] This observation led us to investigate the catalytic transformation of the diene **1** with complexes $[RuCl({=}C{=}C{=}CPh_2)(PCy_3)(p\text{-cymene})][X]$ **I** (X = PF_6), **II** (X = BF_4) and **III** (X = TfO) as catalyst precursors in different [1-butyl-3-methylimidazolium][X] ionic liquids.

The treatment of 0.5 mmol of diallyltosylamide **1** at 80 °C for 5 h in 2 ml of a 1-butyl-3-methylimidazolium salt ([bmim][X]) in the presence of 2.5 mol% of a precatalyst $[RuCl({=}C{=}C{=}CPh_2)(PCy_3)(p\text{-cymene})][X]$[8,9] led to the transformation of **1** and the formation of *N*-tosyldihydropyrrole **2** together with the cycloisomerisation and isomerisation by-products **3** and **4** (Scheme 1, Table 1).

The results shown in Table 1 (entries 1–4) confirm that the RCM reaction is possible in ionic liquids with a ruthenium allenylidene salt as catalyst. However, the reaction, which is slower in ionic solvent than in toluene, lacks selectivity with the systems **II**–[bmim][BF_4] and **III**–[bmim][BF_4], as it was the case in toluene when the reaction was performed with the catalyst **II** containing BF_4^- as counter anion.[9] These experiments show that the catalytic RCM transformation strongly depends on the nature of the counter anion of the ionic salt. This is consistent with a rapid anion exchange between the ionic solvent and the initial ruthenium precursor.

As the triflate salt **III** appeared to be the most active and selective precursor for the olefin metathesis in [bmim][PF_6] (entry 4), the reaction was attempted with the same triflate counter anion in both the catalyst and the ionic salt, and after 2.5 h at 80 °C the complete conversion of **1** was obtained with a very high selectivity in **2** (97%) (entry 5). The reaction could also be performed at room temperature and after 18 h at 20 °C in [bmim][TfO], diallyltosylamide **1** was converted to 100% of **2** in the presence of 2.5 mol% of **III** (entry 6). Thus, the best choice for the performance of a fast and selective metathesis reaction in ionic solvent is the triflate ruthenium precursor **III** in [bmim][TfO].

However, for practical applications, due to the slow decomposition of the catalyst **III** in the presence of water difficult to remove from [bmim][TfO], we have developed a more convenient system by using **III** in [bmim][PF_6]. As the organic product was extracted with toluene, a biphasic system with toluene and an ionic salt was studied to ensure a rapid and complete conversion of the substrate. The catalyst precursor **III** was first generated just before use by treatment of 17 mg (0.025 mmol) of $[RuCl(PCy_3)(p\text{-cymene})][TfO]$ with 5 mg (0.025 mmol) of 1,1-diphenylprop-2-yn-1-ol at room temperature for



Scheme 1

Table 1 Catalytic transformation of the diene **1**: combined influences of the catalyst precursor and the ionic salt[a]

Entry	Catalyst precursor	Solvent	Time (h)	Conversion	**1**[c]	**2**[c]	**3**[c]	**4**[c]
1	[A][PF_6] **I**	[bmim][PF_6]	5	65	35	58	5	2
2	[A][BF_4] **II**	[bmim][BF_4]	6	75	25	37	30	8
3	[A][TfO] **III**	[bmim][BF_4]	5	60	40	23	31	6
4	[A][TfO] **III**	[bmim][PF_6]	5	85	15	83	2	
5	[A][TfO] **III**	[bmim][TfO]	2.5	100		97	3	
6	[A][TfO] **III**	[bmim][TfO]	18[b]	100		100		

[a] General conditions: **1** (0.5 mmol), catalyst (2.5 mol%), [bmim][X] salt 2 ml, 80 °C, then the products are extracted with 3 × 5 ml of toluene. [A][PF_6] = $[RuCl({=}C{=}C{=}CPh_2)(PCy_3)(p\text{-cymene})][PF_6]$ **I**, [A][BF_4] = $[RuCl({=}C{=}C{=}CPh_2)(PCy_3)(p\text{-cymene})][BF_4]$ **II**, [A][TfO] = $[RuCl({=}C{=}C{=}CPh_2)(PCy_3)(p\text{-cymene})][TfO]$ **III**, [b] Performed at rt. [c] Relative ratios of **1**, **2**, **3** and **4**.

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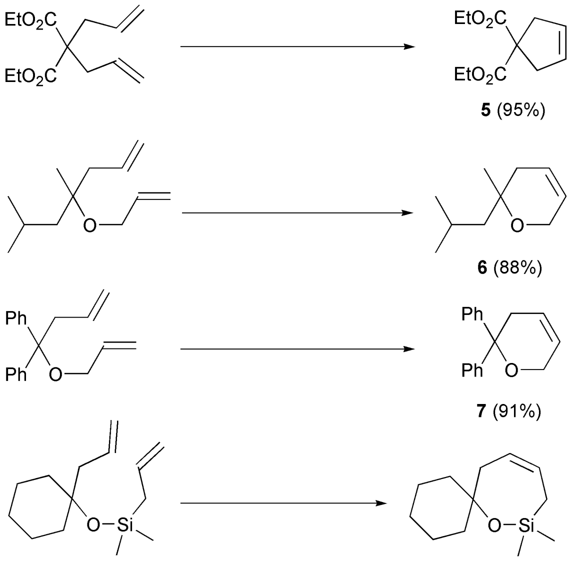
15 min in 1 ml of toluene. Then, 1 ml of [bmim][PF_6] (50 mmol) was added to the mixture. The ionic liquid rapidly turned violet and the toluene phase became colourless, which indicated that the ruthenium allenylidene salt was preferentially dissolved in the ionic phase. The addition of 0.5 mmol of various dienes to this catalytic system prepared *in situ* followed by heating at 80 °C made possible the preparation of cyclic compounds resulting from ring closing metathesis, which were collected in the organic phase and extracted from the ionic liquid with toluene. Thus, the 5-membered cyclopentene **5** was obtained in 95% yield after 6 h from diethyl diallylmalonate, the 6-membered rings **6** and **7** were isolated in 88 and 91% yield after 3.5 h of reaction from the corresponding allyl homoallyl ethers, and the 7-membered siloxane ring **8** was produced in 93% yield after 4 h (Scheme 2).

The possibility of recycling the catalyst arising from **III** in [bmim][TfO] without organic solvent at 20 °C was attempted. The first metathesis experiment with **1** gave 100% of **2** after 18 h of reaction. After extraction of the reaction products from the ionic liquid with toluene, a second loading of **1** (0.5 mmol) was added to the ionic liquid containing the ruthenium species formed during the first run. After 18 h of reaction at room temperature a similar extraction treatment afforded **2** in 86% isolated yield. The third loading of **1** under the same reaction conditions led to only 33% of **2**. The catalyst proved to be efficient for the first two consecutive runs but the third run resulted in a markedly lower conversion. This is due to the slow decomposition of the catalytic system, which was also observed after two days in organic solvent. Indeed, it is known that imidazolium salts featuring a proton at carbon 2 can protonate metals and give metal–aminocarbene species.[14] The good yield of **2** (86%) obtained after 2 cycles (36 h of reaction) suggests that other ionic liquids able to stabilize the catalytic species more efficiently should increase the reactivity and allow more cycles within 2 days.



Scheme 2

However, the ionic liquid itself could be reused many times if it was cleaned up after each reaction by treatment with black carbon at 80 °C for 16 h in 1,2-dichloroethane and then engaged in the reaction with a new loading of catalyst and substrate.

The above results show that the metathesis of dienes can be performed in ionic liquids with ruthenium allenylidene salts as catalyst precursors, when the anions are correctly chosen. These results open new possibilities for the design of catalysts in the salt state, and also to favour the formation of ionic intermediates in a catalytic cycle.

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