

# Olefin self-cross-metathesis catalyzed by the second-generation Grubbs carbene complex in room temperature ionic liquids

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**Abstract**—Olefin self-cross-metathesis (CM) reactions catalyzed by the second-generation Grubbs carbene complex have been compared in dichloromethane and two kinds of selected room temperature ionic liquids (RTILs). Both the catalyst and the ionic liquids could be simply recovered and reused for at least four cycles just with a little drop in activity. Significant enhancements in the reactivity, yield and reaction rate were achieved.

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In the past decade, olefin metathesis catalyzed by ruthenium carbene complexes has played an important role in the formation of carbon–carbon double bond.<sup>1</sup> Owing to the development of well-defined homogeneous catalysts, most remarkably, the Grubbs-type ruthenium alkylidene **1**<sup>2</sup> (Cy = cyclohexyl) and **2**<sup>3</sup> (Mes = mesityl = 2,4,6-trimethylphenyl), and closely related ruthenium complex **3**,<sup>4</sup> more attention than ever before has been paid to olefin metathesis. However, there exist two major disadvantages in these catalysts mentioned above. One is their poor recyclability and the other is the difficulty to remove the ruthenium residue from the final products.<sup>5</sup> Hoveyda and co-workers developed Ru catalyst **4**<sup>6</sup> and **5**<sup>7</sup> (Fig. 1), making big improvements in activity, stability and recyclability.

For both the environmental and economical viewpoints, this kind of catalysts has become increasingly important. Moreover, the recently emerged room temperature ionic liquids (RTILs) have been successfully introduced to some transition-metal-catalyzed chemical reactions instead of conventional organic solvents,<sup>8</sup> which makes the process more compatible to the environment and economical due to their unique physical and chemical properties such as non-volatility, excellent thermal sta-

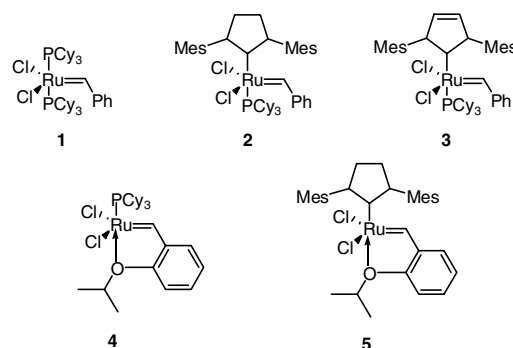
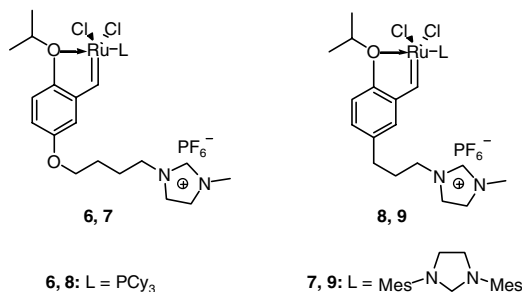


Figure 1. Ru catalysts for olefin metathesis.

bility, the ease of recovery and good ability to dissolve many kinds of organometallic compounds. Recently, Yao and his group have developed the ionic liquids supported-Grubbs catalysts **6**<sup>9</sup> and **7**<sup>10</sup> which showed high level of activity and recyclability in olefin ring-closing metathesis (RCM). A similar concept was adopted by Mauduit and co-workers in the development of the ionic liquid supported-Ru catalysts **8**<sup>11</sup> and **9**<sup>12</sup> (Fig. 2). However, to date, most work has been focused on RCM<sup>13</sup> and ring-opening metathesis (ROM) in RTILs.<sup>14</sup> Very few publications concerning self-cross metathesis (CM) in RTILs have been reported. In this study, we have investigated the activity and recyclability of catalyst **2** for self-cross-metathesis reaction of some terminal olefins in two kinds of most frequently used ionic

**Keywords:** Olefin cross-metathesis; Ru-catalyst; Ionic liquids.

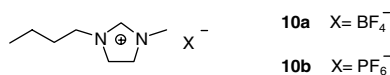
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**Figure 2.** Imidazolium-tagged Ru catalysts.

liquids, 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF<sub>4</sub>) **10a** and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF<sub>6</sub>) **10b** (Fig. 3).

The activity and recyclability of **2** in ionic liquids were initially evaluated with the CM of the test styrene **11**. All the reactions were performed with 1 mmol of **11** in different solvents (3 mL) and in the presence of 2.5 mol % of catalyst **2** at 45 °C for 3 h under nitrogen (Table 1). The progress of the reaction was followed by TLC. Isolation of the reaction products was simply accomplished by extracting the ionic liquids layer with anhydrous diethyl ether. The ionic liquids containing the catalyst **2** was then recovered by evaporating the solvent under vacuum and reused for several cycles without obvious loss of their activity. As shown in Table 1, yields of products in ionic liquids were approximately equal to that obtained in dichloromethane (DCM) in the



**Figure 3.**

**Table 1.** Comparative activity and recyclability of **2** for CM of styrene in different solvents<sup>a</sup>

Entry	Solvent	Cycle	Yield (%) <sup>b</sup>
1 <sup>c</sup>	DCM	1	81
2	<b>10a</b>	1	74
		2	61
		3	54
		4	48
3	<b>10b</b>	1	85
		2	82
		3	79
		4	75

<sup>a</sup> All reactions were performed with 1 mmol of styrene in the solvent system (3 mL) and in the presence of 2.5 mol % of catalyst **2** at 45 °C for 3 h under a nitrogen atmosphere.

<sup>b</sup> Isolated yield after extraction with dimethyl ether followed by purification by silica gel column chromatography, and only *E*-isomers were obtained in all cases.

<sup>c</sup> DCM was evaporated after 4 h and product was obtained using silica gel column chromatography.

first cycle. Nevertheless, ionic liquids containing catalyst **2** could be recovered and reused for at least four cycles with a little drop in activity. These studies clearly indicated that **10b** (entry 3) was the best solvent, giving better recyclability of catalyst **2**. Meanwhile, we speculated that the gradually lowering isolation yields (entries 2 and 3) were probably caused by the decomposition of catalyst and by extraction of the catalyst to the organic phase,<sup>15</sup> as the light brown color of the dimethyl ether layer showed. So our speculation was proved from the following two aspects. At first, we chose petroleum ether as the extracting solvent with lower polarity in the light of the properties of our products. Fortunately, we made a little but satisfactory improvement in reducing catalyst leaching. Subsequently, reaction time and temperature were optimized (Table 2). Higher temperature and longer reaction time had negative effects on the catalyst recycling, owing to the thermal decomposition of Ru catalyst.<sup>16</sup> Having established the recyclability and reuse of **2**, we next examined its performance in the CM of several different terminal olefins (Table 3).<sup>17</sup> The substrate *p*-methylstyrene **13** was easily converted into the product **14** with a satisfactory isolated yield for up to four cycles even under milder conditions (entry 1) compared with those used for the metathesis of styrene. However, the substrates **15**, **17** and **19** were checked under more drastic conditions: longer heating time (from 4 h at room temperature to 12 h at 50 °C) and the larger amount of catalyst (from 2 to 5 mol %). Poor or even no formation of the expected products was observed in the first cycle (entries 3–6). These results showed the limitation of catalytic activity of catalyst **2**. Nevertheless, as shown by the good yields obtained in successive cycles with more active substrate **13**, the recovered [BMIM]PF<sub>6</sub> containing catalyst **2** still remained highly efficient (entry 3: cycle 2 and entry 4: cycle 2) with an exception of **21** and **23** (entry 5: cycle 2 and entry 6; cycle 2). There are some possible explanations for these phenomena. For acrylonitrile, it has an electron deficient double bond showing low reactivity with catalysts of this kind.<sup>18</sup> As for the substrate  $\alpha$ -methylstyrene with a bulky methyl substitution directly on the double bond greatly hindered the metathesis.<sup>19</sup> In the case of substrates **21** and **23**, a 14 e<sup>-</sup> ruthenium catalytic species **24** produced during the reaction<sup>20</sup> (Scheme 1), would preferentially accept the unshared electron pair of nitrogen atom instead of electrons of the  $\pi$  bond, leading to the loss of the activity of catalyst

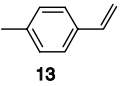
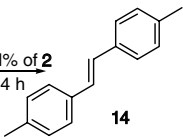
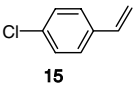
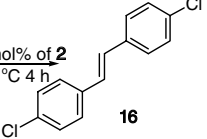


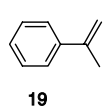
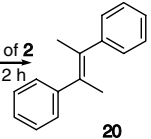
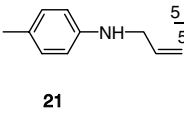
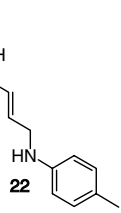
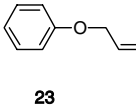
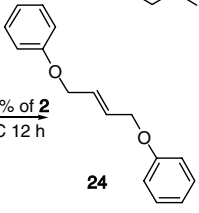
**Table 2.** Optimization of the reaction<sup>a</sup>

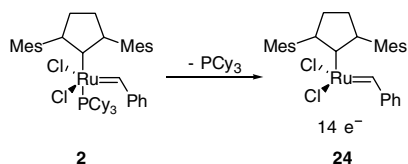
Entry	Temp (°C)	Time (h)	Cycle (% yield) <sup>b</sup>			
			1	2	3	4
1	rt	4	82	81	79	70
2	50	2	83	76	69	64
3	50	4	85	72	65	59
4	70	2	87	69	61	50
5	70	4	86	65	58	47

<sup>a</sup> All reactions were performed using **11** (1 mmol) in the **10b** (3 mL) containing 2.5 mol % of **2**.

<sup>b</sup> Isolated yield after extraction with petroleum ether followed by purification by silica gel column chromatography and only *E*-isomers were obtained in all cases.

**Table 3.** CM of different substrates catalyzed by **2** in [BMIM]PF<sub>6</sub><sup>a</sup>

Entry	Substrate	Conditions	Product	Cycle	Yield (%) <sup>b</sup>
1		2 mol% of <b>2</b> RT 4 h		1	89
				2	84
				3	80
				4	75
2		3 mol% of <b>2</b> 50 °C 4 h		1	81
				2	79
				3	75
				4	63
3		5 mol% of <b>2</b> 50 °C 12 h		1	15
				2 <sup>c</sup>	64
4		5 mol% of <b>2</b> 50 °C 12 h		1	0
				2 <sup>c</sup>	75
5		5 mol% of <b>2</b> 50 °C 12 h		1	0
				2 <sup>c</sup>	0
6		5 mol% of <b>2</b> 50 °C 12 h		1	0
				2 <sup>c</sup>	0

<sup>a</sup> All reactions were performed under N<sub>2</sub>.<sup>b</sup> Isolated yield after extraction with petroleum ether followed by purification by silica gel column chromatography and only *E*-isomers were obtained in all cases.<sup>c</sup> Reactions were performed with **13**.**Scheme 1.**

**2.**<sup>21</sup> When loading the most active substrate **13** to the recovered ionic liquid, no desired product appeared.

In summary, we have reported that ionic liquids acted as powerful media for CM showing great advantages over traditional organic solvent. Convenient catalysts recycling, as well as acceleration of reaction rate were

achieved. Most important, the process was friendly to the environment according to the conception of ‘green’ chemistry. The study of the second-generation Hoveyda–Grubbs catalyst **5** with broad functional groups tolerance and ease of use for highly electron deficient olefins of CM is currently underway in our laboratory and these results will be reported in due course.

### Acknowledgements

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- Some descriptions about catalyst leaching were also reported in Refs. 9, 10 and 12. Evaporation of dimethyl ether from the organic phase gave a crude reaction mixture and TLC showed styrene had completely converted. The crude reaction mixture was then dissolved in CH<sub>2</sub>Cl<sub>2</sub> and recharged another portion of *p*-methylstyrene **13**. After heating the mixture to 45 °C for 4 h, the product **14** could be observed. The experiment was the direct

evidence, which indicated a part of catalyst was extracted into dimethyl ether.

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  17. General procedure for CM reactions in [BMIM]PF<sub>6</sub>: A 25 mL three-necked round-bottom flask was charged with [BMIM]PF<sub>6</sub> (3 mL) and catalyst 2 followed by being degassed for three times with nitrogen. The mixture was stirred for half an hour to afford completion dissolution of the catalyst. The substrate (1 mmol, *c* = 0.3 M) was then introduced. The reaction mixture was stirred under indicated conditions and the whole process was monitored by TLC. Upon the completion, the resulting mixture was extracted with dry petroleum ether (4 × 3 mL) and then the evaporating solvent gave the crude product. The crude product was purified by silica gel column chromatography using petroleum ether (60–90 °C) as the eluent, affording the satisfactory product. The ionic liquids layer was dried on the vacuum line before the use for next cycles. All products listed in Tables 1–3 are known compounds.
- spectral data for selected compounds: **12**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.11 (2H, s, –CH=CH–), 7.25 (2H, t, *J* = 7.5 Hz, ArH), 7.36 (4H, t, *J* = 8.0 Hz, ArH), 7.52 (4H, d, *J* = 10.5 Hz, ArH); Anal. Calcd for C<sub>14</sub>H<sub>12</sub>: C, 93.29; H, 6.71. Found: C, 93.44; H, 7.10. Compound **14**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 2.37 (6H, s, 2CH<sub>3</sub>), 7.04 (2H, s, –CH=CH–), 7.16 (4H, d, *J* = 8.0 Hz, ArH), 7.40 (4H, d, *J* = 8.1 Hz, ArH); Calcd for C<sub>16</sub>H<sub>16</sub>: C, 92.26; H, 7.74. Found: C, 92.22; H, 8.07. Compound **16**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.02 (2H, s, –CH=CH–), 7.33 (4H, d, *J* = 9.0 Hz, ArH), 7.43 (4H, d, *J* = 10.0 Hz, ArH); Anal. Calcd for C<sub>14</sub>H<sub>10</sub>Cl<sub>2</sub>: C, 67.49; H, 4.05. Found: C, 67.70; H, 3.86.
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