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Notes

Highly Selective Metathesis of 1-Octene in Ionic Liquids

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Summary: The self-metathesis of 1-octene to form 7-tetradecene catalyzed by ruthenium carbene complexes at low concentrations (0.02 mol %) was investigated in ionic liquids as reaction media and as additives. The study showed that the ionic liquid has a significant effect on the selectivity of the metathesis of 1-octene, with conversion to product of greater than 95% being obtained and selectivities of over 98% being realized. The outcomes of the reactions compared well with those performed under solventless conditions, showing improved conversions and selectivities.

1. Introduction

Ionic liquids represent a new class of solvents that has received growing attention in both industry and academia. Their remarkable properties, such as negligible vapor pressure and variable physicochemical characteristics, allowing tailoring of the ionic liquids according to the needs of the reaction, have led to their application instead of conventional organic solvents. Many transition metal-catalyzed reactions, including olefin metathesis, have been performed in ionic liquids.[1] Cross- and self-metathesis of olefins were first studied in 1995 in acidic chloroaluminate ionic liquids ([bmim][AlCl$_3$/EtAlCl$_2$]) using W(OAr)$_2$Cl$_4$ complexes.[2] More recently, imidazolium-appended carbene ligands have also been used in ring-closing and cross-metathesis reactions carried out in ionic liquids.[3] Much of the research performed using ionic liquids with ruthenium carbene complexes for olefin metathesis has focused on ring-closing metathesis (RCM) and ring-opening metathesis polymerization (ROMP), and not much research has been carried out on the metathesis of linear olefins in ionic liquids.

The development of well-defined ruthenium alkylidene catalyst systems (Figure 1) has led to the olefin metathesis reaction being extensively investigated, and it has become a powerful tool in synthetic organic chemistry. Many ruthenium carbene complexes are air- and moisture-stable and are tolerant of a wide variety of functional groups, enhancing their appeal and usefulness in synthesis.[4]

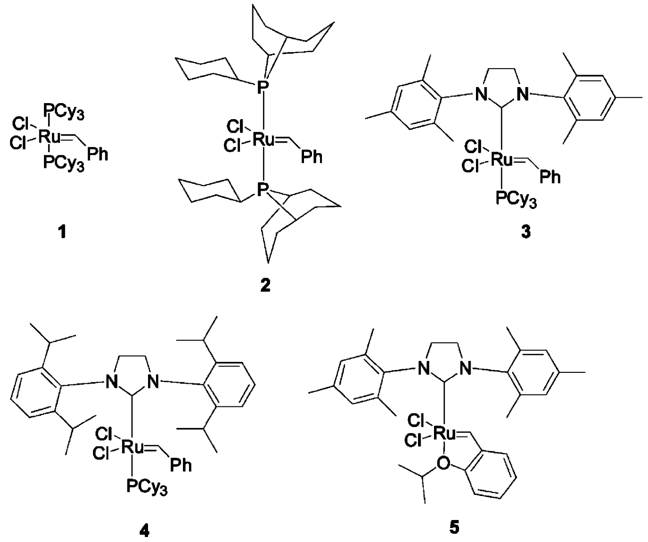

Figure 1. Ru catalysts for olefin metathesis.

The first-generation Grubbs catalyst **1** has been studied as a catalyst for the metathesis of 1-octene, but is less stable than the second-generation Grubbs catalyst.[5] PhobCat [Cl$_2$(Phoban-Cy)$_2$Ru═CHPh] (**2**) is a catalyst developed at Sasol Technology (South Africa) and has shown excellent selectivity and enhanced catalyst stability during olefin metathesis.[6] The second-generation Grubbs catalysts[7] **3** and **4** and the Grubbs−Hoveyda[8] catalyst **5** show good activity, although isomerization seems to be a drawback.[9]

In the present work, the viability of performing self-metathesis of 1-octene in ionic liquids using these well-known ruthenium carbene complexes was investigated. This study focused on ionic liquids based on imidazolium-type cations with varied anions (Figure 2). One of the prime intentions of this study was to achieve high conversions and selectivities for the primary metathesis product 7-tetradecene. When considering chemistry for commercial application, even a few percent increase in conversion and selectivity becomes important. It will become

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(1) Welton, T. *Coord. Chem. Rev.* **2004**, *248*, 2459.

(2) Chauvin, Y.; Olivier-Bourbigou, H. *Chemtech* **1995**, 26.

(3) Clavier, H.; Audic, N.; Guillemin, J.-C.; Mauduit, M. *J. Organomet. Chem.* **2005**, *690*, 3585.

(4) Trnka, T.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18.

(5) Dinger, M. B.; Mol, J. C. *Adv. Synth. Catal.* **2002**, *344*, 671.

(6) Forman, G. S.; McConell, A. E.; Hanton, M. J.; Slawin, A. M. Z.; Tooze, R. P.; Janse van Rensburg, W.; Meyer, W. H.; Dwyer, C.; Kirk, M. M.; Serfontein, D. W. *Organometallics* **2004**, *23*, 4824.

(7) (a) Buijsman, R. C.; van Vuuren, E.; Sterrenburg, J. G. *Org. Lett.* **2001**, *3*, 3785. (b) Csihony, S.; Fischmeister, C.; Bruneau, C.; Horvath, I. T.; Dixneuf, P. H. *New J. Chem.* **2002**, *26*, 1667.

(8) Audic, N.; Clavier, H.; Maudit, M.; Guillemin, J. *J. Am. Chem. Soc.* **2003**, *125*, 9248.

(9) (a) Bourgeois, D.; Pancrazi, A.; Nolan, S. P.; Prunet, J. *J. Organomet. Chem.* **2002**, *643*, 247. (b) van Schalkwyk, C.; Vosloo, H. C. M.; Botha, J. M. *J. Mol. Catal.* **2002**, *3668*, 1.

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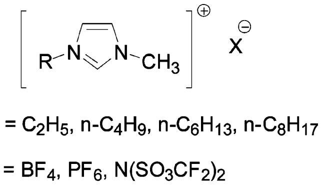

Figure 2. Imidazolium-type ionic liquids.

Table 1. Conversion of 1-Octene and Selectivity toward 7-Tetradecene[a]

entry	solvent	catalyst	conversion of 1-octene	selectivity toward 7-tetradecene
1	solventless	**3**	99	70
2	[bmim][PF_6]	**3**	98	95
3	solventless	**4**	99	67
4	[edmim][$N(SO_2CF_3)_2$]	**4**	99	94

[a] Catalyst **3** or **4** (0.01 mol %), 16 mL of 1-octene (olefin:Ru 8446:1), 6 mL of IL (no IL with solventless reaction), 60 °C.

clear in this paper that we have established conditions under which such increases are obtainable.

2. Results and Discussion

The influence of ionic liquids was investigated for the self-metathesis of 1-octene using ruthenium carbene complexes and compared to the solventless reaction reaction. In many instances, the ruthenium carbene complexes were found to undergo deactivation during the metathesis reaction in both the solventless and ionic liquid reactions.

The first-generation Grubbs catalyst showed a slightly lower activity (33% conversion of 1-octene) at 40 °C in ionic liquids compared to the solventless reaction (37% conversion of 1-octene). Good selectivity (99% for 7-tetradecene) was achieved in both instances. Significant leaching of the catalyst was observed in all ionic liquids tested, and approximately 72% of the Ru was found to have leached into the organic phase, as determined by ICP OES analysis.

PhobCat showed a lower activity compared to the Grubbs catalyst but was active for a longer period of time in both ionic liquids and the solventless reaction. Similar high activity (90% conversion of 1-octene) and excellent selectivity (>99%) were achieved in the ionic liquids and the solventless reactions. PhobCat also showed significant leaching into the organic phase, and no beneficial effect of ionic liquid presence was observed.

The second-generation Grubbs catalyst showed good activity for olefin metathesis, although selectivity is known to be a problem.[10] Catalysts **3** and **4** were used in solventless and ionic liquid (IL) reactions at 60 °C, and the results, after reaction times of 5 h, are shown in Table 1. The lack of selectivity demonstrated in the solventless reactions was ascribable to secondary metathesis product (SMP) formation, such as double-bond isomerization in the product. In contrast, the IL medium showed a distinct inhibition of the formation of SMPs.

The Grubbs–Hoveyda catalyst showed good solubility in ILs with concomitant lower leaching into the organic layer (<2% of the catalyst leached into the organic layer as determined by ICP OES analysis thereof) and was more extensively investigated as a catalyst for the self-metathesis of 1-octene in ILs. Here, 1-butyl-3-methylimidazolium (bmim)-based ILs were employed for the first set of reactions, in conjunction with various anions, in the self-metathesis of 1-octene (Table 2, entries 1–4). The bmim BF_4 IL and the solventless reaction performed the best in this set of reactions. Since the bmim $N(SO_2CF_3)_2$ (bmim BTI) performed relatively poorly, it was anticipated that ILs involving the BTI counterion would best display the effects that changes to the cation would have on the outcome of the reaction. Therefore, ILs in which the alkyl group was changed were tested next.

Table 2. Grubbs–Hoveyda Catalyst Performance after 5 h Reaction Time at 40 °C[a]

entry	solvent	conversion of 1-octene	selectivity toward 7-tetradecene
1	solventless	93	91
2	[bmim][BF_4]	92	95
3	[bmim][PF_6]	80	99
4	[bmim][$N(SO_2CF_3)_2$]	47	98
5	[emim][$N(SO_2CF_3)_2$]	90	98
6	[hmim][$N(SO_2CF_3)_2$]	13	99
7	[edmim][$N(SO_2CF_3)_2$]	92	97
8	[bdmim][$N(SO_2CF_3)_2$]	91	98
9	[odmim][$N(SO_2CF_3)_2$]	41	99

[a] Grubbs–Hoveyda (12.5 mg, 0.02 mol %), 16 mL of 1-octene (olefin: Ru = 4987:1), 2 mL of IL (no IL with solventless reaction), 40 °C.

Table 3. Use of [edmim][$N(SO_2CF_3)_2$] as an Additive[a]

entry	solvent	conversion of 1-octene	selectivity toward 7-tetradecene
1	solventless	93	91
2	5 equiv [edmim][$N(SO_2CF_3)_2$]	93	97
3	10 equiv [edmim][$N(SO_2CF_3)_2$]	96	98
4	50 equiv [edmim][$N(SO_2CF_3)_2$]	97	95
5	2 mL [edmim][$N(SO_2CF_3)_2$]	92	97

[a] Grubbs–Hoveyda (12.5 mg, 0.02 mol %), 16 mL of 1-octene (olefin: Ru = 4987:1), x equiv of IL (Ru:IL = 1:x) (with solventless reaction, add no IL), 40 °C.

It is clear from the data shown in Table 2, entries 4–6, that longer chain lengths tended to inhibit the reaction, leading to lower conversions to the 7-tetradecene product, while a shorter chain length substantially elevated the activity of the catalyst in the IL to one similar to the solventless reaction, at higher selectivities for the desired product. Reactions performed in 2-functionalized ILs (entries 7–9) were found to be less sensitive to the length of the alkyl group: both the ethyl and butyl imidazolium ionic liquids were suitable for this reaction, also showing enhanced selectivities over the solventless reaction.

The enhanced selectivities of the reactions as carried out in ionic liquids are believed to be due to a lack of solubility of the metathesis product in the polar ionic medium, which would limit contact of that compound with the catalyst. This was confirmed by solubility studies (7-tetradecene in various ILs) independent of the present work by our group. Additionally, it is possible that the nature of the catalyst changes in the IL (accounting for the enhanced conversions and selectivities), the most likely change of which would be by counterion exchange in the presence of a large excess of the IL counterion.

One of the ILs was used as an additive to the solventless reaction, rather than as cosolvents forming separate layers, and the results of this interesting aspect of the study are detailed in Table 3. Here, [edmim][$N(SO_2CF_3)_2$] was used as the additive, since this IL demonstrated superior results in the two-phase systems, and the results show a clear beneficial effect in terms of conversion and selectivity of these reactions in the presence of small amounts of that solvent.

Some halogenated ILs (100 equiv) were added to 1-octene, and the effect on the Grubbs–Hoveyda catalyst was investigated

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[10] (a) Hong, S. H.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2004**, *126*, 7414. (b) Lehman, S. E., Jr.; Schwendeman, J. E.; O'Donnell, P. M.; Wagener, K. B. *Inorg. Chim. Acta* **2003**, *345*, 190.

Table 4. Use of Halide-Based Ionic Solids at 40 °C[a]

entry	solvent	conversion of 1-octene	selectivity toward 7-tetradecene
1	solventless	93	91
2	100 equiv [emim][Cl]	95	98
3	100 equiv [emim][Br]	91	98
4	100 equiv [edmim][Br]	95	91

[a] Grubbs−Hoveyda (12.5 mg, 0.02 mol %), 16 mL of 1-octene (olefin: Ru = 4987:1), 100 equiv of IL (Ru:IL = 1:100) (no IL with solventless reaction), 40 °C.

Table 5. Recycling of the Grubbs−Hoveyda Catalyst in [edmim][N(SO_2CF_3)$_2$]

entry	time of each cycle	conversion of 1-octene	selectivity toward 7-tetradecene
1[a]	20 min	59	98
	40 min	51	98
2[b]	20 min	79	98
	40 min	69	95

[a] Grubbs−Hoveyda (12.5 mg, 0.02 mol %), 16 mL of 1-octene (olefin: Ru = 4987:1), 2 mL of IL, 40 °C. [b] Grubbs−Hoveyda (7.5 mg, 0.01 mol %), 16 mL of 1-octene (olefin:Ru = 8446:1), 2 mL of IL, 40 °C.

at 40 °C (Table 4). Once again, an enhancement over the solventless reaction was observed in all cases, with respect to yield and/or selectivity, indicating improvements to catalyst stability and inhibition of secondary reactions.

Some recycling experiments were carried out to establish if the IL-dissolved catalyst would be recycled. To this end, the organic layer of a standard reaction using the Grubbs−Hoveyda catalyst and [edmim][N(SO_2CF_3)$_2$] was withdrawn from the reaction mixture after a period of 20 min and analyzed (Table 5). A second aliquot of 1-octene was added to the IL layer, the reaction of which was allowed to proceed for 20 min, after which the organic layer was withdrawn from the reaction vessel. The results given in the table clearly demonstrate that the catalyst, via the IL layer, is recyclable, retaining activity and selectivity for product through two catalyst cycles and for two different catalyst loadings.

3. Conclusion

The first-generation Grubbs catalyst underwent rapid deactivation in both the ILs and the solventless reactions, and both PhobCat and the first-generation Grubbs catalyst showed substantial leaching into the organic layer. The second-generation Grubbs catalyst showed significant SMP formation in the solventless reaction, which was substantially inhibited when using ionic liquids as solvents. This improved yields and selectivities. The Grubbs−Hoveyda catalyst show enhanced selectivity in the self-metathesis of 1-octene in all cases in the presence of ionic liquids, the effect of which was also manifested even when using only small amounts of the ionic liquid in question. Overall, the use of ionic liquids in the metathesis reaction improved not only the conversion (>95% in many instances) of the reaction but also the selectivity (>98% at very high conversions) toward the primary product. Additionally, the use of these solvents also allowed easy recovery/recycling of the catalyst.

4. Experimental Section

All experiments were performed using standard Schlenk techniques under an atmosphere of argon. A biphasic reaction mixture was obtained in all cases when 1-octene was used with ionic liquids.

4.1. Materials. Commercially sourced 1-octene was passed through neutral alumina and stored under argon. Ionic liquids were synthesized according to literature procedures.[11] The ruthenium carbene complexes were used as received.

4.2. Catalytic Experiments. Reactions were performed in 100 mL three-necked round-bottomed flasks equipped with a magnetic stirrer bar and reflux condenser. A bubbler connected to the outlet of the condenser allowed the escape of evolved ethylene and excess argon pressure. In a typical experiment, 0.02 mol % of the catalyst was dissolved in 2 mL of the ionic liquid followed by the addition of 1-octene (16 mL). The resulting reaction mixture was stirred while purging with argon to flush off ethylene formed. The progress of the metathesis reaction was monitored by sampling through a septum at regular time intervals. Samples were immediately quenched with 2 drops of *tert*-butylhydroperoxide (TBHP) to deactivate the catalyst. The samples were analyzed by GC, and the reaction products were identified by GC/MS. A 50 m PONA column of 0.2 mm internal diameter and 0.5 μm film thickness with a temperature limit of 320 °C was utilized. A flame ionization detector was used for detection of reaction components with helium as the carrier gas.

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[11] Wilkes, J. S.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1992**, 965.