FULL PAPERS

Metathesis of 1-Octene in Ionic Liquids and Other Solvents: Effects of Substrate Solubility, Solvent Polarity and Impurities

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Abstract: With the self-metathesis of 1-octene to 7-tetradecene catalyzed by Grubbs 1st generation [benzylidene-bis(tricyclohexylphosphine)dichlororuthenium, (**1**)] precursor at low concentrations (0.02 mol%) as basis, the effects of the solubility of the substrate in ionic liquids, the solvent polarity, as well as the influence of various impurities stemming from the preparation of ionic liquids have been investigated. The solubility of the substrate in the ionic liquid has little effect on the conversion, and the reaction is not mass-transfer limited. While a higher polarity of an organic solvent increases the rate, it is independent of the polarity excerted by the cation of an ionic liquid. Of paramount importance for reproducible results is the purity of ionic liquids. An extensive study shows that catalyst deactivation by impurities increases in the order of water < halide < 1-methylimidazole. In the presence of water or 1-methylimidazole impurities, the Grubbs-Hoveyda precursor (**3**) is superior to both the 1st (**1**) and 2nd (**2**) generation Grubbs complexes. Under impurity-free conditions or in the presence of chloride, the performance of **2** is equivalent to that of **3**.

Keywords: Grubbs' catalysts; HPLC; ionic liquids; 1-octene solubility; olefin metathesis; purity

Introduction

Although ionic liquids have been investigated as solvents in many transition metal-catalyzed reactions[1] and are beginning to be applied in industrial processes,[2,3] relatively little attention has been paid to the metathesis of olefins. Cross- and self-metathesis was first studied in 1995,[4] with $W(OAr)_2Cl_4$ complexes dissolved in Lewis acidic 1-butyl-3-methylimidazolium chloride/$AlCl_3$/$EtAlCl_2$ ionic liquids. Both the active catalyst and ionic liquid can be recycled several times.[4] Other precursors, such as tungsten(VI) chloride and sodium perrhenate, give fast isomerization of 1-hexene, yielding mainly 4-octene, albeit with low yields and at high catalyst concentrations.[5] Better results are obtained using ruthenium-based precursors, leading to a patent on ring-closing metathesis or polymerization of α,ω-unsaturated dialkenes in ionic liquids.[6] Grubbs 1st and 2nd generation, and ruthenium allenylidene catalyst precursors have been investigated in detail in ring-closing metathesis.[7–17] Many of these reactions feature high selectivities and high reaction rates in the first run, which then decrease upon recycling due to catalyst leaching or deactivation. However, attachment of an "ionic liquid tag" to catalyst ligands hugely improves the recyclability of the system.[12–15]

Interestingly, neither of these nor most other studies involving transition metal catalysts attach any importance to the purity of the ionic liquid used as solvent, although it is known that impurities such as water, amines or halides, stemming from the preparation of the ionic liquid, affect the reaction outcome, especially if transition metal catalysts are used.[4,18–31] In this sense, the conclusions drawn from this present study are certainly transferable to other catalytic reactions.

In general, self-metathesis proceeds under mild conditions, which allows for the controlled manipulation of the carbon number of an alkene feed. We have now chosen 1-octene as a test substrate example, and studied its self-metathesis reaction in various

ionic liquids using the 1st generation Grubbs catalyst precursor (**1**, Scheme 1). In order to show the validity of the conclusions for other catalysts, the study was
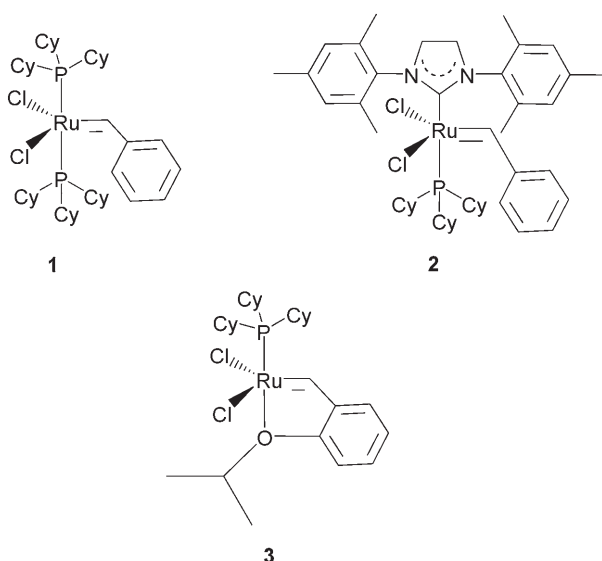
Scheme 1. 1st (**1**) and 2nd (**2**) generation Grubbs, and Grubbs-Hoveyda (**3**) catalyst precursors.

extended to the 2nd generation (**2**) and Grubbs-Hoveyda (**3**) precursors. It is known that the 1st generation precursor is generally less stable than the more sophisticated 2nd generation, Grubbs-Hoveyda or Ru-allenylidene precursors.[32,33] However, they are also five to six times more expensive than the 1st generation complex type, and only a comprehensive economical balance will reveal which precursor is more profitable. While the use of expensive catalysts may be acceptable in the fine chemical or pharmaceutical sector, this aspect becomes more important if a large-scale petrochemical product with small profit margins is concerned.

The 1st generation Grubbs catalyst has been well-studied[32] in the metathesis of 1-octene. In the absence of solvent, the activity of the catalyst is largely independent of the reaction temperature (between 20 and 80 °C). A maximum turnover frequency (TOF) of 8640 h^{-1} at 22 °C, using ppm-level catalyst concentrations, is reported.[32]

Intriguing results observed during a preliminary study led to an extensive investigation of the influence of solvent polarity, the solubility of the educt, and the effect of strongly coordinating impurities present in the ionic liquids. These impurities impact on the catalysts themselves and the results should apply to other examples of metathesis as well.

Results and Discussion

Preliminary 1-Octene Metathesis Study using 1 as Catalyst Precursor

During preliminary experiments with Grubbs 1st generation catalyst precursor **1**, we found that higher turnover frequencies are achieved at lower catalyst concentrations in neat 1-octene (see Supporting Information), which can be assigned to an increased rate of bimolecular decomposition of the catalyst at higher catalyst concentrations.[34] Therefore, 0.02 mol% (1.22×10^{-3} mol L^{-1} octene) catalyst (**1**) precursor concentration was chosen since the corresponding amount of catalyst can be weighed out without introducing too large an error, while giving reasonably good turnover frequencies. Previous investigations have used this catalyst precursor at much higher concentrations; e.g., Buijsman et al.[8] found that 5 mol% catalyst precursor leads to optimal results in a ring-closing metathesis. In addition, we noted that a biphasic reaction mixture resulted when 1-octene was added to any of the ionic liquids discussed here, while a homogeneous reaction mixture is formed with organic solvents (*vide infra*) or in solvent-free modus. The results of our initial studies of the metathetic reaction (Scheme 2) are shown in Table 1.

Interestingly, the reaction occurs *in* the ionic liquid only; no catalytic activity of the organic top phase was observed after separation of the biphasic reaction mixture. Leaching did occur, as indicated by the brownish tint of the organic phase. This means that the decomposition product(s) of the catalyst is/are selectively leached into the top-phase. Optimization of
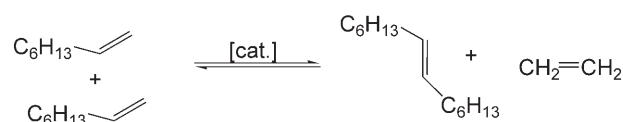
Scheme 2. Metathesis of 1-octene to 7-tetradecene in the presence of a catalyst.

Table 1. Conversion of 1-octene to 7-tetradecene in dependence of two series of ionic liquid homologues.

Ionic Liquid	Conversion [%][a]	Halide [wt. %]	Water [wt. %]
[C$_4$mim][BF$_4$]	30.3	0.044	0.253
[C$_6$mim][BF$_4$]	40.9	0.109	0.072
[C$_8$mim][BF$_4$]	26.4	0.269	0.119
[C$_8$dmim][BF$_4$]	2.0	0.223	0.218
[C$_4$py][BF$_4$]	25.4	<0.035	0.190
[C$_6$py][BF$_4$]	53.0	0.177	0.102
[C$_8$py][BF$_4$]	43.8	0.512	0.204

[a] *Reaction conditions:* room temperature, 4 h, 0.02 mol% catalyst precursor 1, ionic liquid:1-octene = 1:1 (vol/vol).

the catalyst's longevity and affinity for the ionic liquid phase is a subject of our future research. In order to determine the influence of the nature of the ionic liquid, we carried out reactions in tetrafluoroborate-based ionic liquids featuring either 1-alkyl-3-methyl-imidazolium or *N*-alkylpyridinium cations with varying alkyl substituents. Significant trends were observed on increasing the alkyl chain on the cation of the ionic liquids: both, 1-alkyl-3-methylimidazolium- and *N*-alkylpyridinium-based tetrafluoroborate ionic liquids gave higher conversions for the hexyl derivatives than either the butyl- or octyl-substituted ones.

In Table 1, the amounts of water and halide impurity are specified. It becomes obvious that the conversions observed do not directly relate to the water or halide contamination. In order to be able to fully explain the phenomena observed, we investigated not only the solubility of the substrate in ionic liquids – we reasoned that higher solubility would result in higher conversion – but also other characteristics of the ionic liquids, as well as the role played by contaminants.

Solubility of 1-Octene in Ionic Liquids

Very little solubility data for alkene substrates in ionic liquids are available at present in the literature,[35–37] and therefore the solubility of 1-octene in ionic liquids was determined by gas chromatography (see Supporting Information). For ionic liquids based on the same cation the solubility increases the order of $[BF_4]^- < [PF_6]^- < [OTf]^- < [BTI]^-$ ([OTf]$^-$ = trifluoro-methylsulfonate and [BTI]$^-$ = bis[trifluoromethanesulfonyl]imide).

For a given anion, lengthening of the alkyl chain on the cation leads to a higher solubility of 1-octene. *N*-Alkylpyridinium-based ionic liquids seem to possess similar solubilities as 1-alkyl-3-methylimidazolium melts with the same alkyl substituent. Literature data

of the solubilities for 1-hexene[36] and 1-octene[37] are in good agreement, with 1-hexene being, as expected, slightly better soluble than 1-octene.

Unfortunately, it was difficult to determine the solubility of 7-tetradecene, which is generally very low in the ionic liquids used in this study, except for [C$_8$py]-[BTI] (4.3 mol%). As this is one of the more "lipophilic" ionic liquids, we assume the solubilities of 7-tetradecene in the other ionic liquids to be well below 4 mol%. The lower solubility of the product is of advantage for the metathesis reaction design, since the product is expelled from the ionic liquid, and can thus be easily separated from the reaction mixture.

Therefore, the trends observed in our preliminary investigation (Table 1) are not related to the solubility of 1-octene in the ionic liquids: a steady increase in conversion upon lengthening of the alkyl substituent would be anticipated if the reaction was solubility- and, therefore, mass transfer-controlled.

However, the fact that the hexyl-derivatives perform better than both the butyl- and the octyl-derivative is reminiscent of the trends reported in a polarity study of various ionic liquids carried out by Carmichael et al.,[38] where the hexyl-derivative had a higher polarity than either the shorter or longer substituted homologue, although theoretically, an increase in the length of the alkyl chain should lead to decreased polarity.

Thus, experiments were carried out in organic solvents of various polarities in an attempt to elucidate the source of this phenomenon.

Effect of the Solvent Polarity on the Metathesis of 1-Octene

Several solvents were chosen to correlate the conversions obtained to two constants (the relative permittivity and the molecular dipole moment) used to quantify polarity (Table 2). It should be noted that

Table 2. Conversion and TOF of the metathesis of 1-octene to 7-tetradecene in various solvents, and correlation to solvent polarity.

Entry	Solvent	Conversion[a] [%]	TOF [h^{-1}]	Rel. Permittivity[b]	Mol. Dipole Moment[c]
1	neat[d]	48.2	630		
2	neat[e]	41.1	1230		
3	chloroform	66.7	875	4.81	1.04
4	toluene	27.1	355	2.43	0.38
5	xylene (mix)	26.0	340	2.40	0.31
6	*n*-hexane	22.2	290	1.89	0.00
7	tetrahydrofuran	5.2	70	7.47	1.69

[a] *Reaction conditions:* room temperature, 4 h, 0.02 mol% catalyst **1** (6.10×10^{-4} mol L^{-1} octene + solvent), solvent:1-octene = 1:1 (vol/vol).
[b] Formerly known as dielectric constant, at 20 °C.[39]
[c] In the gas phase (in Debye).[39]
[d] In the absence of solvent, i.e., at 1.22×10^{-3} mol L^{-1} catalyst precursor.
[e] At 6.10×10^{-4} mol L^{-1} catalyst precursor.

unlike with ionic liquids, 1-octene is mutually miscible with all investigated molecular solvents, thus yielding homogeneous reaction mixtures.

In Table 2, entries 1 and 2, the conversions and TOFs obtained in the absence of any solvent are shown. Entry 1 refers to experiments conducted in 5 mL of 1-octene in order to allow for comparison relating to the relative catalyst:1-octene ratio in the ionic liquid experiments, while for entry 2, 10 mL of 1-octene were used to simulate the effect of extra solvent. As discussed above, a reduction of the overall catalyst concentration effectively increases the efficiency of the catalyst, probably due to reduced catalyst decomposition.[34] Neither of the investigated organic solvents added to the reaction mixture improves the efficiency of the catalyst. Nevertheless, distinct differences are obvious: with the exception of tetrahydrofuran, the conversions correlate well with both the dipole moment and the relative permittivity. While the reaction carried out with chloroform gave good conversions, less polar solvents, such as toluene, xylene and *n*-hexane, reduce the rate markedly. Similar effects have been previously observed.[40] The large inhibitory effect of tetrahydrofuran may be linked to potential strong binding of the excess solvent to the catalytically active site.

We hasten to mention that neither molecular solvents nor ionic liquids are necessary to carry out the reaction. In general, the use of a solvent can only be justified if it brings about an increase of reaction rate, selectivity, control of exotherms, or if catalyst recycling is facilitated. A recent energy balance as part of a life-cycle assessment has shown that more than six recycle runs are necessary before the use of an ionic liquid can be justified in this particular reaction. The energy required for the manufacture of the ionic liquid has to recovered by the advantages a biphasic system offers in terms of facile product separation.[41]

Effect of the Purity of the Ionic Liquid on the Metathesis of 1-Octene

The strong inhibiting effect of tetrahydrofuran as well as the results reported in Table 1 led us to reconsider impurities that are potentially strong-coordinating and which may deactivate the catalyst in the experiments with ionic liquids. From their preparative methodology, we anticipated halide impurities, and water could be present due to the hygroscopic properties of the ionic liquids.[42] Both of these impurities had been determined in the preliminary study, albeit with a relatively high detection limit for halide impurities (0.035 and 0.080 wt.% for chloride and bromide, respectively, see Table 1). Also, the effects observed can not be directly correlated with impurity concentrations.

We, therefore, included the determination of 1-methylimidazole (residual starting material from ionic liquid preparation) in an extended study of the effects of the water, chloride and imine content in ionic liquids.

The effect of residual halide from the ionic liquid synthesis on the reaction outcome was investigated by adding known amounts of $[C_6mim]Cl$ to catalysis-grade $[C_4mim][BF_4]$. Figure 1 shows that the initial re-
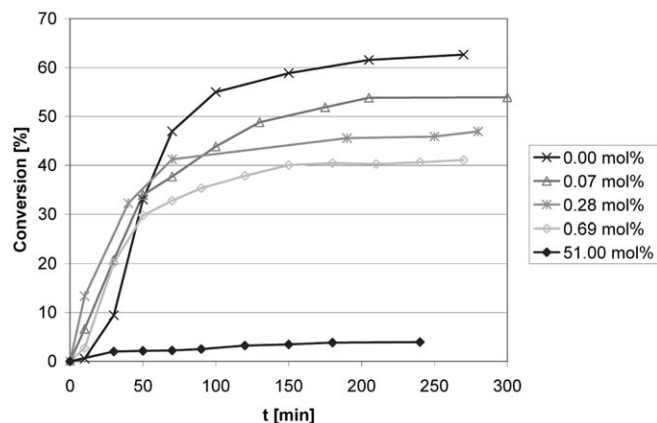
Figure 1. Influence of added increments of chloride ($[C_6mim]Cl$) to pure $[C_4mim][BF_4]$ on the conversion of the metathesis of 1-octene at room temperature as a function of time.

action rates are not severely influenced by the presence of chloride, at least not at concentrations between 0.00 and 0.69 mol% in the ionic liquid. Table 3 shows that the latter value corresponds to a molar ratio of 23 (chloride:catalyst precursor **1**), indicating that the relative stability of the catalyst to halide is comparatively high. A further increase of the chloride content suppresses conversion, and at 51.00 mol% of chloride with respect to the ionic liquid, the catalytic activity is almost quantitatively inhibited. No reaction is observed in pure $[C_6mim]Cl$.

In a similar fashion, the effect of water in an ionic liquid was investigated by adding known quantities of water to catalysis-grade $[C_2mim][BF_4]$ (Figure 2). This impurity shows a less pronounced effect, and even at 88.44 mol% water with respect to the ionic liquid (corresponding to a ratio of water:catalyst precursor of about 4500), the catalytic activity is reduced by only 40%.

Surprisingly, the catalytic activity is most sensitive to the addition of 1-methylimidazole to catalysis-grade $[C_4mim][BF_4]$ (Figure 3), and the presence of a mere 0.18 mol% with respect to ionic liquid leads to a decrease in turn-over frequency by factor 11, although this corresponds to only a six-fold excess of 1-methylimidazole over catalyst precursor! In fact, this imine is so potent in its inhibitory role towards the

Table 3. Dependence of type and concentration of deliberately added impurity on the TOF.[a]

Ionic Liquid	"Impurity"	Ratio Impurity/Catalyst	Mol % Impurity (rel. IL)	Wt. % Impurity (rel. IL)	TOF [h^{-1}]
[C$_4$mim][BF$_4$]	[C$_6$mim]Cl	0	0.00	< 0.001	825
		2	0.07	0.01	710
		11	0.28	0.04	590
		23	0.69	0.11	525
		1720	51.00	8.00	65
[C$_2$mim][BF$_4$]	H$_2$O	12	0.24	0.02	850
		104	2.04	0.19	825
		4494	88.44	8.05	525
		7913	168.26	15.32	390
[C$_4$mim][BF$_4$]	1-methylimidazole	0	0.00	0.00	825
		2	0.06	0.02	600
		4	0.12	0.04	175
		6	0.18	0.06	75

[a] *Reaction conditions:* room temperature, 4 h, 0.02 mol % catalyst precursor **1**, ionic liquid:1-octene = 1:1 (vol./vol.).
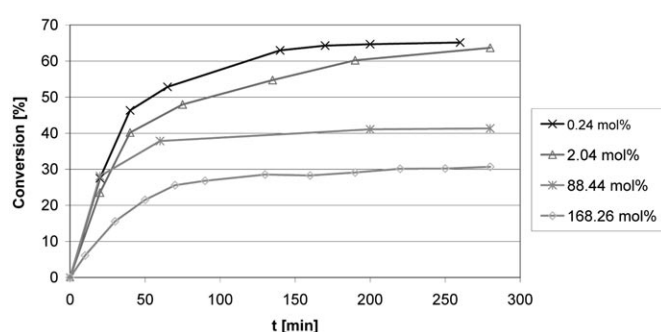
Figure 2. Influence of added increments of water to pure [C$_2$mim][BF$_4$] on the conversion of the metathesis of 1-octene at room temperature as a function of time.
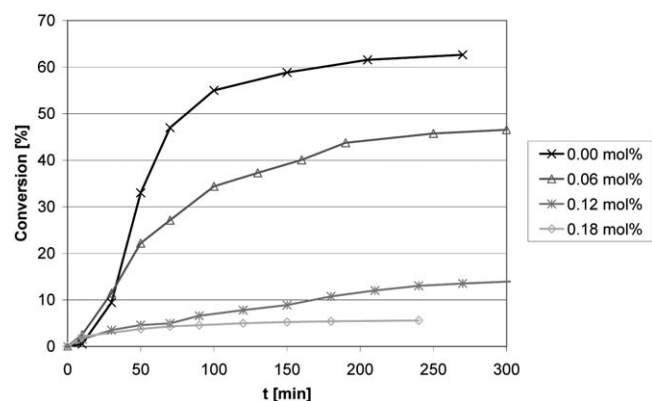
Figure 3. Influence of added increments of 1-methylimidazole to pure [C$_4$mim][BF$_4$] on the conversion of the metathesis of 1-octene at room temperature as a function of time.

catalyst that, even at concentrations at the detection limit of our currently best HPLC method (0.025 wt. % for 1-methylimidazole), an effect is clearly visible.

A Performance Comparison of Other Ruthenium-Based Catalyst Precursors

The effect of impurities on the performance of metathesis catalysts was investigated by including the 2nd generation (**2**) Grubbs, and the Grubbs-Hoveyda (**3**) catalyst precursors. Experiments were conducted at impurity levels at which previously a pronounced effect on the catalyst activity had been detected, i.e., 0.28 mol % chloride, 88 mol % water or 0.12 mol % 1-methylimidazole, respectively. Table 4 shows that in the absence of any impurity, the performance of **2** and **3** is virtually similar and much better than that of

Table 4. Dependence of type of deliberately added impurity on the performance of various metathesis catalyst precursors.[a]

"Impurity"	Catalyst precursor	Mol % Impurity (rel. IL)	Conv. [mol %] at 2 h	4 h
pure	1st generation (**1**)	< l.o.d.[b]	55.8	60.2
	2nd generation (**2**)	< l.o.d.	75.0	83.4
	Grubbs-Hoveyda (**3**)	< l.o.d.	73.3	86.5
[C$_6$mim]Cl	**1**	0.28	43.0	45.8
	2	0.28	48.0	71.3
	3	0.28	47.4	74.0
H$_2$O	**1**	88.44	40.0	41.0
	2	88.44	28.7	44.8
	3	88.44	60.3	69.1
1-methylimidazole	**1**	0.12	7.8	13.0
	2	0.12	5.2	5.3
	3	0.12	38.0	39.0

[a] *Reaction conditions:* room temperature, 0.02 mol % catalyst precursor, ionic liquid:1-octene = 1:1 (vol/vol).
[b] l.o.d. = limit of detection.

1. However, in the presence of halide impurity, all precursors exhibit a reduced rate of reaction. Again, **2** and **3** show similar reaction profiles and are less susceptible to chloride poisoning than **1**.

Contrary hereto the 2nd generation Grubbs catalyst **2** is even less effective than **1** in the presence of either water or 1-methylimidazole impurity. Overall, although still significantly negatively influenced, precursor **3** is much less affected than either **1** or **2** by the presence of any of the three impurities chloride, water or 1-methylimidazole.

Final Remarks

Further investigations with **1** showed that similar TOFs can in fact be achieved in sufficiently pure $[C_npy][BF_4]$, $[C_nmim][BF_4]$ and $[C_ndmim][BF_4]$ ($n = 4$, 6, 8), i.e., irrespective of the solubility of 1-octene. Comparison of the TOFs obtained in neat 1-octene (1230 and 630 h^{-1}, at 6.10×10^{-4} and 1.22×10^{-3} mol L^{-1} catalyst, respectively, see Table 2) and in pure ionic liquids (850 h^{-1}) shows that the latter lies between the two reactions performed in the absence of any solvent. Considering that the active catalyst resides only in the ionic liquid phase where its relative concentration is comparable to entry 1 in Table 2, the TOF obtained in ionic liquids is high. This observation possibly points to an improved catalyst activity and stability in the ionic liquid.

In pure ionic liquids, no isomerization was observed. However, the chromatograms of reaction mixtures in which either chloride, water or 1-methylimidazole was deliberately added showed signals corresponding to 2- and 3-octene which increased over the duration of the experiment to about 5%. This is not surprising since the decomposed ruthenium catalyst is known to act as an efficient double-bond isomerization catalyst.[34,40]

Conclusions

Our investigations, based on the metathesis 1-octene in ionic liquids, have shown that transition-metal catalysis in such solvents is extremely sensitive to the three impurities halide, water and imines such as 1-methylimidazole. While the former can be accumulated by absorption of moisture from the atmosphere or wet feedstock, all three may stem from the preparation of the ionic liquid itself. The effect of traces of water or halides on both the physico-chemical properties and reaction out-come has been recognized in the literature,[4,18–31,42,43] but, to the best of our knowledge, no systematic study, particularly including the effect of imine impurity, has been previously undertaken. This impurity, however, has a pronounced effect on the rate of ruthenium-catalyzed metathesis of 1-octene. The detection limit of the HPLC method is too high for the concentrations at which 1-methylimidazole is effective as a catalyst poison, and better analytical methods need to be developed.

The study has shown that the catalyst precursors **2** and **3** are also affected to various degrees by the impurities investigated, and we anticipate that other transition-metal catalysts would exhibit similar behavior in the presence of these impurities. It is, therefore, of utmost importance that authors, as well as manufacturers of ionic liquids, determine the purity of the ionic liquids used. More sensitive as well as time- and cost-effective analytical methods are presently being developed and evaluated in our laboratories. These results, although not directly transferable to other types of catalysis than metathesis, indicate an approach that should be considered for other catalytic cycles as well.

In general, the use of ionic liquids leads to good conversions at very low catalyst loadings (0.02 mol%) and under mild conditions. Although biphasic, no mass-transfer limitations have been observed, and the cation-dependent polarity and solubility plays, if at all, a subordinate role in the conversion. Compared to molecular solvents such as chloroform, using ionic liquids allows for the reaction to be carried out in a biphasic reaction mode, thus facilitating solvent-product separation. In the case of **1**, decomposition of the catalyst occurs in both classes of solvents, and the decomposition product can be efficiently removed from the product using a method described by Cho and Kim.[44] Interestingly, the high TOF obtained in pure ionic liquids when compared to organic solvents at similar catalyst concentrations indicate an improved catalyst stability and activity. Further investigations are in process to elucidate this aspect.

Experimental Section

General Remarks

Pure ionic liquids (for catalysis, Fluka) were used as supplied. Product specification: $[C_4mim][BF_4]$: water < 200 ppm, halogens < 10 ppm. $[C_2mim][BF_4]$: water < 200 ppm, halogens < 10 ppm.

All other ionic liquids were prepared according to known procedures[45] from the corresponding halide precursor ($[C_4mim]Cl$, $[C_8mim]Cl$, $[C_8dmim]Cl$, $[C_4py]Cl$, $[mC_4py]Cl$, $[C_8py]Cl$, $[C_6mim]Br$, $[C_6py]Br$, where $[C_nmim]$, $[C_ndmim]$, $[C_npy]$ and $[mC_npy]$ stand for 1-alkyl-3-methylimidazolium, 1-alkyl-2,3-dimethylimidazolium, N-alkylpyridinium and 4-methyl-N-alkylpyridinium, respectively, and n = number of carbons of the alkyl substituent), sodium tetrafluoroborate, hexafluorophosphoric acid, trifluoromethanesulfonic acid (H[OTf]), and lithium bis(trifluoromethanesulfonyl)imide (Li[BTI]).

1-Octene (Riedel-deHaën) was distilled twice from KOH to destroy peroxide impurities, degassed and stored under nitrogen to reduce oxygenates to a minimum.

The 1st generation Grubbs catalyst precursor [benzylidene-bis(tricyclohexylphosphine) dichlororuthenium (**1**)], 2nd generation Grubbs catalyst precursor {benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro-(tricyclohexylphosphine)ruthenium (**2**)} and Grubbs-Hoveyda precursor [dichloro(o-isopropoxyphenylmethylene)(tricyclohexylphosphine) ruthenium (**3**)] were used as received from Aldrich. All organic solvents used were distilled prior to use.

Conversions were determined by gas chromatography. GC-details: Hewlett–Packard 5890 GC, PONA column, initial temp. 100 °C, heating rate 4 °C min⁻¹ to 300 °C, injector temp.: 250 °C, detector temp. 300 °C (FID). DELSI NELMAG GC, OV-1 (equivalent to SPB-1) column, isothermal run (180 °C), injector temp.: 220 °C, detector temp 220 °C (FID). Varian CP-3800 GC, HP5 column, initial temp. 60 °C, heating rate 10 °C min⁻¹ to 100 °C, injector temp.: 250 °C, detector temp.: 300 °C (FID).

No correction factors were taken into account, as there is no change in functionalization in both the product and starting material. The AUC thus reflects the respective weight percentage. Both, the retention times of 1-octene and the 7-tetradecene were determined by comparison to a pure sample and NMR spectroscopy. Conversions are given as the molar percentage of 1-octene converted to 7-tetradecene.

Preliminary Study of the Metathesis of 1-Octene in Ionic Liquids and Organic Solvents

1-Octene (5 mL, $M_r = 112.22$ g mol⁻¹; $\rho = 0.715$ g mL⁻¹; 0.0319 mol) was transferred into a Schlenk flask containing 5 mg catalyst precursor (**1**) ($M_r = 823.0$ g mol⁻¹, 0.02 mol %) and 5 mL of either the ionic liquid or organic solvent. The reactions were carried out at room-temperature and determined after 4 h reaction time. The organic phase was analyzed as described above. Due to the low solubilities of both 1-octene and 7-tetradecene, their concentration in the ionic liquid phase was not taken into account for the conversion studies. Experiments were performed twice and agreed within 5 %.

Purity of Ionic Liquids

The purities of the ionic liquids used were determined by Karl-Fischer titration (water), Volhard titration (halides) and HPLC (1-methylimidazole). Experimental details are available in the Supporting Information.

Influence of Chloride

Due to the high hygroscopicity of [C₆mim]Cl (specification: < 0.17 wt. % 1-methylimidazole, 0.01 wt. % water), a standard solution (0.0617 g [C₆mim]Cl in 10 mL chloroform) was prepared. In 5 g [C₄mim][BF₄] (for catalysis, Fluka), increments of the standard solution (0, 0.5, 2, and 5 mL) were dissolved, and chloroform removed on a rotary evaporator. In the case of the sample with the highest chloride content, 2.286 g [C₆mim]Cl was directly dissolved in [C₄mim][BF₄]. 5 mL 1-octene and 6 mg of the catalyst precursor were added. The progress of the reaction was determined by taking samples of the upper phase at appropriate times, dilution with diethyl ether and analysis by GC.

Due to the high purity of the ionic liquid used, the chloride content of the blank sample was not taken into account.

Influence of Water

6 g [C₂mim][BF₄] (for catalysis, Fluka) and 5 mL 1-octene were transferred into a Schlenk flask. Before adding 5 mg of the catalyst precursor, either none, 10, 500, or 900 μL water was added using Eppendorf pipettes. The progress of the reaction was determined by taking samples of the upper phase at appropriate times, dilution with diethyl ether and analysis by GC. Due to the absorption of water from the atmosphere into the ionic liquid, the water content of the blank sample was determined (0.022 wt. %) and taken into account for the calculations.

Influence of 1-Methylimidazole

5 g [C₄mim][BF₄] (for catalysis, Fluka) and 5 mL 1-octene were transferred into a Schlenk flask. Before adding 5 mg of the catalyst precursor, either none, 1, 2 or 3 μL 1-methylimidazole was added using a GC-syringe. The progress of the reaction was followed by taking samples of the upper phase at appropriate times, dilution with diethyl ether and analysis by GC.

Acknowledgements

References

[1] T. Welton, *Coord. Chem. Rev.* **2004**, *248*, 2459–2477.

[2] B. Weyershausen, K. Lehmann, *Green Chem.* **2005**, *7*, 15–19.

[3] M. Freemantle, *Chem. & Eng. News* **2003**, *81*, 9.

[4] Y. Chauvin, H. Olivier-Bourbigou, *Chemtech* **1995**, *26*, 26–30.

[5] A. V. Vasnev, A. A. Greish, L. M. Kustov, *Mendeleev Commun.* **2004**, 59–61.

[6] M. Jautelat, C. Guertler, Metathese in Gegenwart ionischer Flüssigkeiten, European Patent EP1035093, **2000**.

[7] P. Schwab, M. B. France, J. W. Ziller, R. H. Grubbs, *Angew. Chem. Int. Ed.* **1995**, *34*, 2039–2041.

[8] R. C. Buijsman, E. van Vuuren, J. G. Sterrenburg, *Org. Lett.* **2001**, *3*, 3785–3787.

[9] K. G. Mayo, E. H. Nearhoof, J. J. Kiddle, *Org. Lett.* **2002**, *4*, 1567–1570.

[10] D. Semeril, H. Oliver-Bourbigou, C. Bruneau, P. H. Dixneuf, *Chem. Commun.* **2002**, 146–147.

[11] S. Csihony, C. Fischmeister, C. Bruneau, I. T. Horvath, P. H. Dixneuf, *New J. Chem.* **2002**, *26*, 1667–1670.

[12] Q. W. Yao, Y. L. Zhang, *Angew. Chem. Int. Ed.* **2003**, *42*, 3395–3398.

[13] N. Audic, H. Clavier, M. Mauduit, J. C. Guillemin, *J. Am. Chem. Soc.* **2003**, *125*, 9248–9249.

[14] Q. Yao, M. Sheet, *J. Organometal. Chem.* **2005**, *690*, 3577–3584.

[15] H. Clavier, N. Audic, J. C. Guillemin, M. Mauduit, *J. Organometal. Chem.* **2005**, *690*, 3585–3599.

[16] V. Martinez, J. C. Blais, G. Bravic, D. Astruc, *Organometal.* **2004**, *23*, 861–874.

[17] H. Clavier, L. Boulanger, N. Audic, L. Toupet, M. Mauduit, J. C. Guillemin, *Chem. Commun.* **2004**, 1224–1225.

[18] Y. Chauvin, L. Mussmann, H. Olivier, *Angew. Chem. Int. Ed.* **1996**, *34*, 2698–2700.

[19] P. A. Z. Suarez, J. E. L. Dullius, S. Einloft, R. F. de Souza, J. Dupont, *Inorg. Chim. Acta* **1997**, *255*, 207–209.

[20] A. L. Monteiro, F. K. Zinn, R. F. De Souza, J. Dupont, *Tetrahedron: Asymmetry* **1997**, *8*, 177–179.

[21] P. J. Dyson, D. J. Ellis, D. G. Parker, T. Welton, *Chem. Commun.* **1999**, 25–26.

[22] B. Ellis, W. Keim, P. Wasserscheid, *Chem. Commun.* **1999**, 1049–1049.

[23] A. J. Carmichael, M. J. Earle, J. D. Holbrey, P. B. McCormac, K. R. Seddon, *Org. Lett.* **1999**, *1*, 997–1000.

[24] P. J. Dyson, D. J. Ellis, R. Lincoln, K. Russel, P. J. Smith, T. Welton, *Electrochem. Soc., Proc.* **2000**, *99–141*, 161–168.

[25] C. E. Song, E. J. Roh, *Chem. Commun.* **2000**, 837–838.

[26] V. Gallo, P. Mastrorilli, C. F. Nobile, G. Romanazzi, G. P. Suranna, *J. Chem. Soc., Dalton Trans.* **2002**, 4339–4342.

[27] K. R. Seddon, A. Stark, *Green Chem.* **2002**, *4*, 119–123.

[28] R. A. Sheldon, R. Madeira Lau, M. J. Sorgedrager, F. van Rantwijk, K. R. Seddon, *Green Chem.* **2002**, *4*, 147–151.

[29] G. S. Owens, M. M. Abu-Omar, in: *Ionic Liquids- Industrial Applications for Green Chemistry*; (Eds.: R. D. Rogers, K. R. Seddon), ACS, Washington, DC, **2002**, Vol. 818, p. 321–333.

[30] R. F. de Souza, V. Rech, J. Dupont, *Adv. Synth. Catal.* **2002**, *344*, 153–155.

[31] M. A. Klingshirn, G. A. Broker, J. D. Holbrey, K. H. Shaughnessy, R. D. Rogers, *Chem. Commun.* **2002**, 1394–1395.

[32] M. B. Dinger, J. C. Mol, *Adv. Synth. Catal.* **2002**, *344*, 671–677.

[33] S. J. Connon, S. Blechert, *Angew. Chem. Int. Ed.* **2003**, *42*, 1900–1923.

[34] M. Ulmann, R. H. Grubbs, *J. Org. Chem.* **1999**, *64*, 7202–7207.

[35] P. Wasserscheid, C. M. Gordon, C. Hilgers, M. J. Muldoon, I. R. Dunkin, *Chem. Commun.* **2001**, 1186–1187.

[36] F. Favre, H. Olivier-Bourbigou, D. Commereuc, L. Saussine, *Chem. Commun.* **2001**, 1360–1361.

[37] C. C. Brasse, U. Englert, A. Salzer, H. Waffenschmidt, P. Wasserscheid, *Organometallics* **2000**, *19*, 3818–3823.

[38] A. J. Carmichael, K. R. Seddon, *J. Phys. Org. Chem.* **2000**, *13*, 591–595.

[39] J.-L. M. Abboud, R. Notario, *Pure Appl. Chem.* **1999**, *71*, 645–718.

[40] W. Buchowicz, J. C. Mol, *J. Mol. Catal. A: Chem.* **1999**, *148*, 97–103.

[41] D. Kralisch, A. Stark, S. Körsten, G. Kreisel, B. Ondruschka, *Green Chem.* **2005**, 7, 301–309.

[42] K. R. Seddon, A. Stark, M. J. Torres, *Pure Appl. Chem.* **2000**, *72*, 2275–2287.

[43] H. L. Ngo, K. LeCompte, L. Hargens, A. B. McEwen, *Thermochim. Acta* **2000**, *357*, 97–102.

[44] J. H. Cho, B. M. Kim, *Org. Lett.* **2003**, *5*, 531–533.

[45] J. S. Wilkes, M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.* **1992**, 965–967.