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Ionically Tagged Ru–Alkylidenes for Metathesis Reactions under Biphasic Liquid–Liquid Conditions

Benjamin Autenrieth,[a] Felix Willig,[a] Dominik Pursley,[a] Stefan Naumann,[a] and Michael R. Buchmeiser*[a, b]

The synthesis of the novel ionic Ru–alkylidenes $[Ru[(4\text{-}CO_2)(1\text{-}CH_3)Py^+)]_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)][OTf^-]_2$ (**1**, $IMesH_2 = 1,3$-dimesitylimidazolin-2-ylidene, Py = pyridine, OTf^- = triflate) and $[RuCl[(4\text{-}CO_2)(1\text{-}CH_3)Py^+)](IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)][OTf^-]$ (**2**) is reported. Catalysts **1** and **2** were successfully used in various metathesis reactions under biphasic liquid–liquid conditions using 1-butyl-2,3-dimethylimidazolium tetrafluoroborate and heptane as liquid phases. Ruthenium leaching into the heptane phase was very low ($<0.4\,\%$), translating into Ru contamination of the products between 0.3 and 2.5 ppm. Both **1** and **2** exhibited comparable reactivity in organic solvents and under biphasic conditions. Catalyst **1** and **2** were also successfully used in the continuous metathesis of methyl oleate and 1,7-octadiene under supported liquid–liquid conditions. Finally, the disproportionation of the monocarboxylato monochloro substituted Ru–alkylidene **2** was traced by ^1H NMR analysis at 40 °C, thereby demonstrating the formation of complex **1** and the neutral complex $[RuCl_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)]$.

Introduction

Olefin metathesis reactions have gained a strong position in organic synthesis and have found widespread application in the creation of carbon–carbon bonds.[1–4] Especially for the preparation of pharmaceutically active compounds it is, however, essential to reduce heavy-metal contamination of the products to an unobjectionable low degree, a task that is hard to accomplish through homogeneous catalysis and that entails a costly purification process. Many efforts have been put on the heterogenization of primarily homogeneous metathesis catalysts. A multitude of examples exist in which ruthenium- and molybdenum-based complexes are immobilized on different support materials and are successfully used in various metathesis reactions.[5–15] In these reactions, metal contamination of the products could be reduced to a respectable extent. However, the heterogenization step is often relatively complex and recycling of the support material is restricted or not possible. This, in turn, makes the entire catalytic process simply uneconomical, and, therefore, metathesis with supported, well-defined catalysts did not find entry to key-step syntheses on an industrial scale.

Ionic liquids are promising solvents for catalysis including metathesis[16–23] because they do not only dissolve a wide range of substrates and catalysts, but also form biphasic systems with a series of standard organic solvents. Recently, we reported on the development of the dicationic Ru–alkylidene complex $[Ru(DMF)_3(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)^{2+}][(BF_4^-)_2]$ ($IMesH_2 = 1,3$-dimesitylimidazolin-2-ylidene; for a general structure of dicationic Ru–alkylidenes, see structure A in Figure 1), with which we verified the feasibility of a concept for conducting continuous metathesis reactions under supported biphasic liquid–liquid conditions.[24] Thereby, the decisive factor has been the tendency of the compound to immobilize selectively within an ionic liquid phase, a task that cannot be accomplished with neutral Ru–alkylidene complexes.[25,26] Owing to its electrophilic character, the charged Ru–alkylidene complex exhibited high reactivity towards electron-rich carbon–carbon multiple bonds, however, coordinating moieties such as, for example, ester groups, coordinate to the Ru center as well.[27] This in turn led to a decrease in reactivity, which could be compensated by increasing the reaction temperature. The main reason for the sensitivity of catalysts of type A towards coordinating moieties is that the positive charge is located directly at the Ru center (Figure 1).[28,29] Nevertheless, performing continuous metathesis reactions under biphasic conditions with high yields at low temperatures is certainly desirable. On that account, this report deals with the development of ionically tagged Ru–alkylidene complexes that meet these requirements.

There are few Ru–alkylidene complexes that have ionically tagged alkylidene moieties (type B, Figure 1).[30–39] Irrespective of their activity, the loss of the alkylidene ligand during the

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[a] *B. Autenrieth, F. Willig, D. Pursley, S. Naumann, Prof. M. R. Buchmeiser*
Lehrstuhl für Makromolekulare Stoffe und Faserchemie
Institut für Polymerchemie, Universität Stuttgart
Pfaffenwaldring 55, 70569 Stuttgart (Germany)
Fax: (+49) 0711-685-64050
E-mail: michael.buchmeiser@ipoc.uni-stuttgart.de

[b] *Prof. M. R. Buchmeiser*
Institut für Textilchemie und Chemiefasern (ITCF) Denkendorf
Körschtalstr. 26, 73770 Denkendorf (Germany)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201300199. It contains NMR spectra of $[(1\text{-}CH_3)(4\text{-}CO_2K)Py^+][BF_4^-]$, of complexes **1** and **2** and of the corresponding precursors as well as of the disproportionation of complex **2** at 80 °C (Figure S1–S9). Kinetics for the RCM of 1,7-octadiene and N,N-diallyltrifluoroacetamide promoted by **1** (Figure S10) and GC–MS data for the RCM reactions (Figure S11–S14) are also provided.

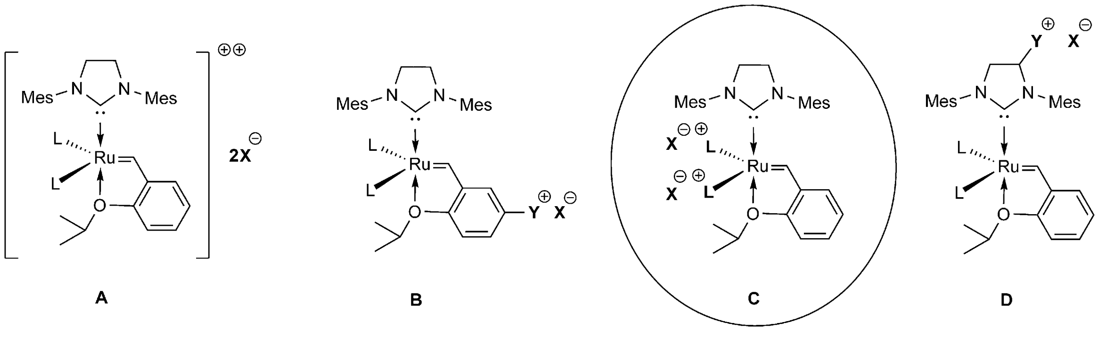


Figure 1. Possibilities for introducing an ionic charge to Grubbs–Hoveyda-type Ru–alkylidene complexes. A) ionic Ru center; B) ionically tagged benzylidene ligand; C) ligands with ionic functionalities; D) Ionically tagged NHC ligand.

first catalytic cycle and the poor "boomerang" effect of the corresponding styrene derivative[40] represent a serious drawback, particularly under biphasic liquid–liquid conditions, under which the neutral Ru–alkylidene intermediates would immediately be transferred to the second organic phase. Under these conditions, such a complex bearing an ionically tagged alkylidene ligand would completely lose its charge and thus its tendency to immobilize selectively within a (supported) ionic liquid phase. Therefore, our focus was on creating active metathesis catalysts with a permanent ionic charge by introducing charged ligands. One way to introduce an ionic charge to a Ru–alkylidene complex is the use of ionically tagged N-heterocyclic carbene (NHC) ligands (Type D, Figure 1).[41–43] Herein, we substituted both chloride ligands in the parent second-generation Grubbs–Hoveyda catalyst $[RuCl_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)]$ (**GH**) by ligands with ionic functionalities (Figure 1, Type C). These ligands will not demerge during the metathesis reaction and, depending on their electronic nature, the reactivity of the catalyst can be further adjusted. Moreover, derivatives of Grubbs and **GH** catalysts possessing electron-withdrawing ligands, for example, perfluorocarboxylates or pseudohalides, are known to have high activity resulting from the high polarization of the Ru–alkylidene moiety.[5,44–48] In the following, the preparation of the novel ionic Ru–alkylidenes $[Ru[(4\text{-}CO_2)(1\text{-}CH_3)Py^+)]_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)]_2$ (**1**, Py = pyridine, OTf^- = triflate) and $[RuCl[(4\text{-}CO_2)(1\text{-}CH_3)Py^+)](IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)][OTf^-]$ (**2**) possessing ionic carboxylate ligands and their use in various metathesis reactions under both homogeneous and biphasic conditions, including supported liquid-phase ones, is reported.

Experimental Section

Materials and characterization

Unless noted otherwise, all preparations were performed in a glovebox (LabMaster 130, MBraun; Garching, Germany) or by standard Schlenk techniques under an N_2 atmosphere. CH_2Cl_2, THF, diethyl ether and pentane were purchased from J. T. Baker (Devender, Netherlands) and were dried using an MBraun SPS-800 solvent purification system. Starting materials were purchased from Aldrich (Schnelldorf, Germany), TCI Europe (Zwijndrecht, Belgium) and ABCR (Karlsruhe, Germany) and used without any further purification. The initiators $[RuCl(CF_3SO_3)(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)]$ and $[Ru(CF_3SO_3)_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)]$ were prepared as described in the literature.[5]

NMR spectra were recorded on a Bruker Avance III 400 spectrometer in the indicated solvent at 25 °C and are listed in parts per million (ppm) downfield from tetramethylsilane as internal standard. GC–MS data were obtained by using an Agilent Technologies 5975C inert MSD with triple-axis detector, a 7693 autosampler, and a 7890 A GC system equipped with an SPB-5 fused silica column (34.13 m × 0.25 mm × 0.25 μm film thickness). The injection temperature was set to 150 °C. The column temperature ramped from 45 to 250 °C within 8 min, and was then held for a further five minutes. The column flow was $1.05\ mL\,min^{-1}$. IR spectra were measured on a Bruker IFS 28 using ATR technology using either NaCl cuvettes or KBr pellets.

Synthesis of $[(1\text{-}CH_3)(4\text{-}CO_2K)Py^+][BF_4^-]$: To an aqueous solution of 4-carboxy-1-methylpyridinium chloride (500 mg, 2.88 mmol), KOH (162 mg, 2.88 mmol) was added and the mixture was stirred for 15 min at RT. Then, an aqueous solution of $AgBF_4$ (561 mg, 2.88 mmol) was added dropwise and stirring was continued for another 2 h. The white precipitate of AgCl was filtered off and the solvent was removed in vacuo. The salt obtained was treated with anhydrous THF to remove traces of water and was then dried in vacuo. Yield: 725 mg (2.76 mmol, 96 %). ^1H NMR (400.13 MHz, D_2O): $\delta = 8.84$ (d, $J = 6.5$ Hz, 2 H), 8.24 (d, $J = 6.5$ Hz, 2 H), 4.41 ppm (s, 3 H); ^{13}C NMR (100.61 MHz, D_2O): $\delta = 169.0$, 152.2, 145.7, 126.5, 47.9 ppm; ^{19}F NMR (376.50 MHz, D_2O): $\delta = -150.5$ ppm; IR (KBr): $\tilde{\nu} = 3444$ (b), 3106 (m), 3037 (s), 1633 (s), 1602 (m), 1560 (s), 1456 (m), 1360 (s), 1285 (m), 1182 (m), 1030 (m), 899 (m), 879 (m), 858 (s), 783 (vs), 687 (s), 613 (s), 521 (s), 459 cm^{-1} (m).

Synthesis of $[Ru[(4\text{-}CO_2)(1\text{-}CH_3)Py^+)]_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)][OTf^-]_2$ (**1**): A solution of $[Ru(CF_3SO_3)_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)]$ (200 mg, 0.23 mmol) in CH_2Cl_2 (5 mL) was added to a suspension of $[(1\text{-}CH_3)(4\text{-}CO_2K)Py^+][BF_4^-]$ (129 mg, 0.49 mmol) in CH_2Cl_2 (10 mL). A color change to dark red was observed and stirring was continued for 2 h at RT. The mixture was then passed through a pad of celite and the solvent was removed in vacuo. The target compound was obtained as a dark red solid (216 mg, 0.19 mmol, 82 %). ^1H NMR (400.13 MHz, CD_2Cl_2): $\delta = 18.23$ (s, 1 H), 8.80 (d, $J = 6.5$ Hz, 4 H), 8.01 (d, $J = 6.7$ Hz, 4 H), 7.52 (d, $J = 5.9$ Hz, 1 H), 7.46 (t, $J = 8.7$ Hz, 1 H), 7.12 (t, $J = 7.3$ Hz, 1 H), 6.83 (s, 4 H), 6.73 (d, $J = 8.3$ Hz, 1 H), 4.66–4.56 (m, 1 H), 4.47 (s, 6 H), 4.00 (s, 4 H), 2.32 (s, 12 H), 2.14 (s, 6 H), 0.94 ppm (d, $J = 6.2$ Hz, 6 H); ^{13}C NMR (100.61 MHz, CD_2Cl_2): $\delta = 309.7$, 202.2, 166.0, 154.9, 147.1, 145.9, 143.5, 138.8, 137.8, 136.9, 130.8, 130.1, 127.6, 123.9, 123.6, 123.0, 119.8, 112.8, 75.3, 52.8, 49.2, 21.5, 21.1, 18.7 ppm; ^{19}F NMR

(376.50 MHz, CD_2Cl_2): $\delta = -78.9$ ppm; IR (KBr): $\tilde{\nu} = 3452$ (b), 3107 (m), 3046 (m), 2960 (m), 2913 (m), 2850 (m), 1946 (m), 1722 (m), 1637 (s), 1571 (m), 1479 (m), 1398 (m), 1301 (m), 1257 (s), 1138 (m), 1091 (m), 1026 (s), 926 (m), 852 (m), 795 (m), 769 (m), 681 (m), 638 (vs), 571 (s), 515 (s), 467 (m), 420 cm^{-1} (m); elemental analysis (%) calcd. for $C_{47}H_{53}F_6N_4O_{11}RuS_2$ ($M_r = 1129.13$ g mol^{-1}): C 50.00, H 4.73, N 4.98; found: C 49.98, H 4.75, N 5.16.

Synthesis of $[RuCl[(4\text{-}CO_2)(1\text{-}CH_3)Py^+)](IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)][OTf^-]$ (**2**): A solution of $[RuCl(CF_3SO_3)(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)]$ (200 mg, 0.27 mmol) in CH_2Cl_2 (5 mL) was quickly added to a suspension of $[(1\text{-}CH_3)(4\text{-}CO_2K)Py^+][BF_4^-]$ (71 mg, 0.27 mmol) in CH_2Cl_2 (15 mL). A color change from green to red was observed and stirring was continued for 1 h at RT. The precipitate was removed by filtering the reaction mixture through a pad of celite. After solvent removal, **2** was obtained as a red powder, which was redissolved in CH_2Cl_2 (3 mL) and precipitated in diethyl ether (15 mL). Yield: 210 mg, 0.24 mmol, 89%. ^1H NMR (400.13 MHz, CD_2Cl_2): $\delta = 17.18$ (s, 1H), 8.79 (d, $J = 6.5$ Hz, 2H), 8.02 (d, $J = 6.7$ Hz, 2H), 7.47–7.42 (m, 1H), 7.24 (s, 2H), 7.07 (s, 2H), 7.06–7.02 (m, 1H), 6.99–6.93 (m, 1H), 6.73 (d, $J = 8.3$ Hz, 1H), 4.78–4.69 (m, 1H), 4.47 (s, 3H), 4.16–4.08 (m, 4H), 2.55 (s, 6H), 2.49 (s, 6H), 2.12 (s, 6H), 1.30 (d, $J = 6.1$ Hz, 3H), 0.91 ppm (d, $J = 6.1$ Hz, 3H); ^{13}C NMR (100.61 MHz, CD_2Cl_2): $\delta = 304.4$, 208.7, 162.6, 151.9, 147.1, 144.6, 142.8, 138.7, 138.0, 136.5, 134.6, 130.3, 129.1, 128.9, 128.6, 126.5, 126.3, 121.8, 121.5, 112.3, 111.5, 73.9, 50.7, 47.9, 29.3, 20.1, 20.0, 18.1, 17.6 ppm; ^{19}F NMR (376.50 MHz, CD_2Cl_2): $\delta = -79.0$ ppm; IR (KBr): $\tilde{\nu} = 3417$ (vb), 2955 (m), 29113 (m), 2846 (m), 2353 (vs), 1643 (vs), 1574 (m), 1471 (s), 1381 (m), 1319 (m), 1265 (vs), 1149 (s), 1097 (m), 1026 (s), 926 (m), 845 (m), 791 (m), 665 (m), 633 (s), 571 cm^{-1} (m); elemental analysis (%) calcd. for $C_{39}H_{45}F_3N_3O_6RuS$ ($M_r = 877.37$ g mol^{-1}): C 53.39, H 5.17, N 4.79; found: C 53.59, H 5.17, N 4.77.

Metathesis under biphasic conditions

1 (2.5 mg, 2.2 μmol) was dissolved in 1-butyl-2,3-dimethylimidazolium tetrafluoroborate, $[BDMIM^+][BF_4^-]$, (200 mg) and the solution was heated to 40 °C. Then a solution of the substrate (0.1–4.4 mmol) in heptane (2 mL) was added and the biphasic system was stirred vigorously (600 rpm) for 12 h. Reactions were quenched by adding ethyl vinyl ether (1 mL). After removing the nonpolar phase, the ionic-liquid phase was extracted extensively with diethyl ether (3×1 mL; stirring for 20 min at 600 rpm). The organic phases were combined and subjected to GC–MS analysis to determine conversion.

Metathesis under biphasic conditions using monolith--supported ionic liquids

Metathesis reactions under supported ionic liquid phase (SILP) conditions were performed under air, comparable to a method published earlier.[24] The loaded monolithic support was placed inside a Merck L-5025 column thermostat and warmed to 45 °C. Using a syringe pump (WPT, Aladdin-1000), the substrate (1,7-octadiene and methyl oleate as neat reactants) was flushed through the monolith at a flow rate of 0.1 mL min^{-1}. The eluent was collected and subjected to GC–MS analysis to determine conversion. Used SILP phases were removed by subsequent flushing with methanol (5 mL) and CH_2Cl_2 (5 mL). The thus cleaned monolithic support was again recharged with catalyst dissolved in $[BDMIM^+][BF_4^-]$ and used for further catalysis.

Ru measurements

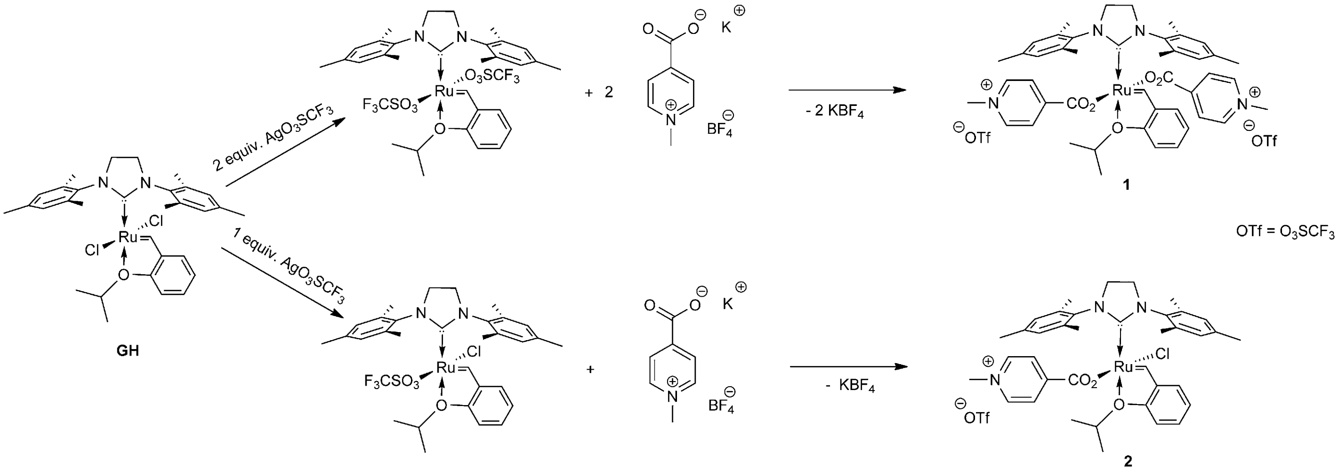
The Ru content was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, $\lambda = 240.272$ nm, ion line, back ground lines at $\lambda_1 = 240.254$ nm and $\lambda_2 = 240.295$ nm) using a Spectro Arcos device (Ametek GmbH; Meerbusch, Germany). Standardization was carried out with Ru standards containing 0.1, 0.5, 1.0, 2.5, and 5 ppm of Ru. The Ru content of both the support and the product fraction was determined by dissolving 100 mg samples in aqua regia.

Results and Discussion

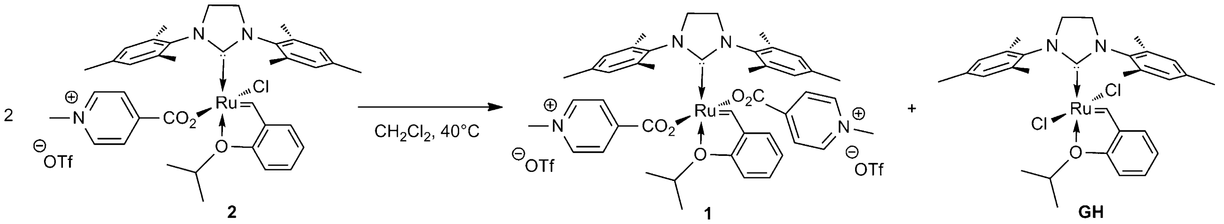
Catalyst Preparation

As outlined above, the primary objective was to create an ionically tagged, Ru–alkylidene complex for metathesis reactions under biphasic conditions, which would retain the ionic charge throughout the entire metathesis reaction and be more active at lower temperatures towards substrates bearing coordinating functionalities than $[Ru(DMF)_3(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)^{2+}][(BF_4^-)_2]$.[24,27] Such an ionically tagged metathesis catalyst would selectively dissolve in an ionic liquid but not in the second non-polar liquid transport phase, e.g., heptane, which should allow for low metal contamination of the products. For this purpose, the bis-ionically tagged catalyst $[Ru[(4\text{-}CO_2)(1\text{-}CH_3)Py^+)]_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)][OTf^-]_2$ (**1**) was prepared in 82% isolated yield and was obtained as a red solid by adding two equivalents of $[(1\text{-}CH_3)(4\text{-}CO_2K)Py^+][BF_4^-]$ to the modified Grubbs–Hoveyda type catalyst $[Ru(CF_3SO_3)_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)]$ (Scheme 1). Typically, silver salts were used to replace the chlorides in the Grubbs-Hoveyda type complex $[RuCl_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)]$ by the desired ligands. As the very poor solubility of the pyridinium salt used in the synthesis described herein did not allow for the preparation of highly pure silver salts, we decided to use the corresponding potassium salts to substitute the more weakly bound triflate ligands in the complex $[Ru(CF_3SO_3)_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)]$ instead (Scheme 1).

In an analogous manner, the ionic monocarboxylato monochloro Ru–alkylidene $[RuCl[(4\text{-}CO_2)(1\text{-}CH_3)Py^+)](IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)][OTf^-]$ (**2**) was prepared in 89% isolated yield by adding one equivalent of $[(1\text{-}CH_3)(4\text{-}CO_2K)Py^+][BF_4^-]$ to $[RuCl(CF_3SO_3)(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)]$ (Scheme 1). This catalyst **2** can be expected to be more active than the bis-ionic Ru–alkylidene **1**. Thus, compared to the pyridinium carboxylate ligand, the chloride is more electron withdrawing and should therefore lead to a more polarized Ru=C bond than in **1**. The absence of a signal for BF_4^- in the ^{19}F NMR spectrum implies its substitution by the triflate (OTf^-, $CF_3SO_3^-$) ligand, which now acts as the counter ion. Thus, solely the signal for OTf^- was observed, whereas BF_4^- was detected in the precipitate of KBF_4 that formed during the reaction in CH_2Cl_2. After removal of the potassium tetrafluoroborate, the product was precipitated in diethyl ether. The fact that complex **2** was obtained as a pure compound is remarkable because monocarboxylato-monochloro-Ru–alkylidenes are known to undergo fast ligand scrambling, and thereby disproportionate into the



Scheme 1. Syntheses of the ionic Ru complexes **1** and **2**.



Scheme 2. Disproportionation reaction of the monocarboxylate complex **2** in CH_2Cl_2.

corresponding biscarboxylate and bischloride species (Scheme 2).[5,12,49] For compound **2**, which can be obtained in a pure form, the disproportionation rate, however, was relatively low at ambient temperature. After 24 h in solution, only 8 % of the biscarboxylate complex **1** and the **GH** complex could be detected by NMR spectroscopy. However, at 40 °C, a temperature typical for many metathesis reactions, the disproportionation proceeded more rapidly (Figure 2).

As could be followed by ^1H NMR analysis, disproportionation was first detected after 2 h at 40 °C. Besides the signal for the alkylidene proton of **2** at $\delta = 17.13$ ppm (CD_2Cl_2), the signals for the alkylidene protons of **1** at $\delta = 18.16$ ppm and of **GH** at $\delta = 16.45$ ppm appeared (Figure 2). After 8 h in solution at 40 °C, the biscarboxylate complex **1** and bischloride complex **GH** amounted to 38 %, an equilibrium concentration, which did not change any further (Figure 3). At 80 °C, the disproportionation reaction proceeded more rapidly and 40 % of the initial amount of complex **2** disproportionated within 30 min. As the ratio between **1** and **GH** was about 1:1 at lower temperature, it decreased to 1:5 at 80 °C, suggesting significant decomposition of **1** at this temperature (see the Supporting Information, Figure S9).

Homogeneous metathesis reactions using 1 and 2 in organic solvents

To screen activities and to compare them with that of [Ru-$(DMF)_3(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)^{2+}][(BF_4^-)_2]$, initiators **1** and **2** were subjected to ring-closing metathesis (RCM) reactions of various dienes in CH_2Cl_2 at $T = 40$ °C, as well as in $C_2H_4Cl_2$ at $T = 70$ °C. 1,7-Octadiene, diethyl diallyl malonate (DEDAM), diethyl di(methallyl) malonate (DEMAM), *tert*-butyl-*N*,*N*-diallyl carbamate (TBDC), *N*,*N*-diallylacetamide, and *N*,*N*-diallyltrifluoroace-

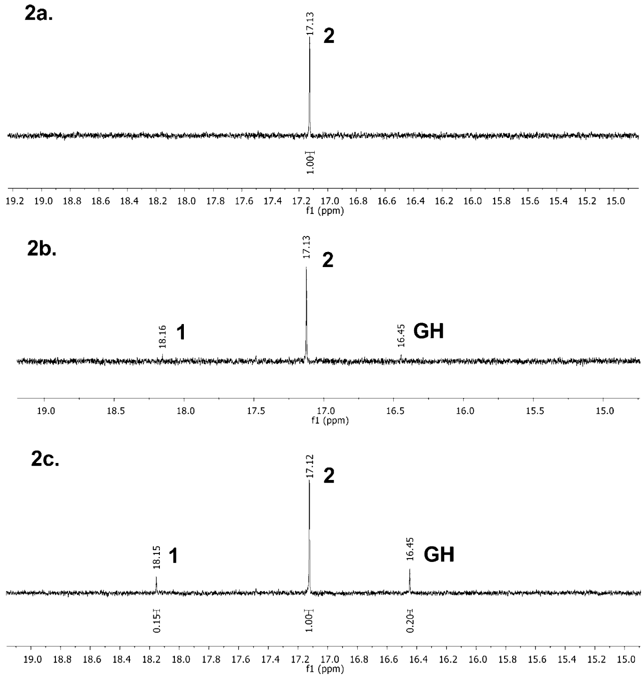


Figure 2. Disproportionation of **2** at 40 °C in CD_2Cl_2. ^1H NMR spectra a) after 1 h in CD_2Cl_2 at 40 °C; b) after 2 h in CD_2Cl_2 at 40 °C, and c) after 24 h in CD_2Cl_2 at 40 °C.

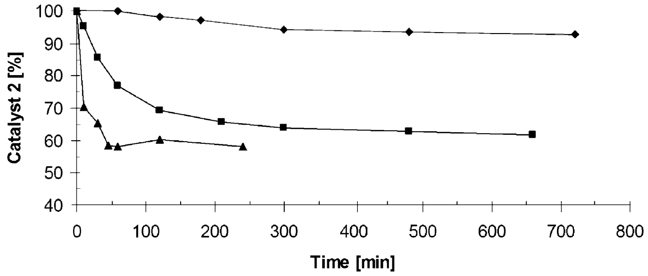


Figure 3. Disproportionation of catalyst **2** in solution at different temperatures: Room temperature (◆); 40 °C (■); 80°C (▲).

tamide (DAFA) served as substrates. In addition, the self-metathesis reaction of methyl oleate was examined (Table 1).

The reaction kinetics for the RCM of 1,7-octadiene and DAFA promoted by **1** at 40 °C and 70 °C, respectively, are given in Figure S10. In the RCM of 1,7-octadiene, a maximum turnover number (TON) of approximately 500 was obtained at both temperatures (Table 1). As expected, the reaction rate was significantly higher at 70 °C. The same was observed for the RCM of DAFA, for which final TONs of 400 and 550, respectively, were found. For all substrates listed in Table 1, the maximum TONs did not increase to a large extend with increasing temperature, though the reactions proceeded more rapidly. These findings indicate that complex **1** exhibited, a priori, a certain reactivity towards diverse olefins, which is primarily not limited by decomposition at elevated temperature. The fact that **1**, in contrast to $[Ru(DMF)_3(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)^{2+}][(BF_4^-)_2]$,[24] was active already at low temperatures suggests that reactivity is not affected by substrates with coordinating moieties. Notably, **2** allowed for substantial TONs of 60 in the RCM of DEMAM.

Table 1. Metathesis reactions in organic solvents promoted by catalysts **1** and **2**.

Substrate	Catalyst [mol %]	Solvent	*T* [°C]	TON[a]
DEDAM	**1** [0.1]	CH_2Cl_2	40	380
		$C_2H_4Cl_2$	70	400
	2 [0.05]	CH_2Cl_2	40	>2000
TBDC	**1** [0.1]	CH_2Cl_2	40	150
		$C_2H_4Cl_2$	70	200
	2 [0.05]	CH_2Cl_2	40	1000
1,7-octadiene	**1** [0.1]	CH_2Cl_2	40	500
		$C_2H_4Cl_2$	70	550
	2 [0.05]	CH_2Cl_2	40	>2000
DAFA	**1** [0.1]	CH_2Cl_2	40	400
		$C_2H_4Cl_2$	70	550
	2 [0.05]	CH_2Cl_2	40	1300
N,N-diallylacetamide	**1** [0.1]	CH_2Cl_2	40	300
		$C_2H_4Cl_2$	70	360
	2 [0.1]	CH_2Cl_2	40	300
DEMAM	**1** [1.0]	CH_2Cl_2	40	30
		$C_2H_4Cl_2$	70	30
	2 [1.0]	CH_2Cl_2	40	60
methyl oleate	**1** [0.05]	CH_2Cl_2	40	700
		$C_2H_4Cl_2$	70	850
		toluene	100	800
	2 [0.05]	CH_2Cl_2	40	1300

[a] turnover number determined by GC–MS. Reaction time: 3 h. Definitions: DEDAM = diethyl diallyl malonate; TBDC = *tert*-butyl-*N,N*-diallyl carbamate; DAFA = *N,N*-diallyltrifluoroacetamide; DEMAM = diethyl di-(methallyl) malonate.

In the self-metathesis of methyl oleate with **1** as the catalyst, a final TON of 700 was obtained at 40 °C (Table 1). In this reaction, alongside the *E*-isomer, only the primary metathesis products were observed. If conducting the reaction at 70 °C, conversion slightly increased but, again, the *E*-isomer remained. As methyl oleate isomerizes already at room temperature,[24] this process competes with the metathesis reaction. At higher temperature, self-metathesis predominates. Conducting the reaction at 100 °C gave a TON of 800, if considering exclusively the formation of primary metathesis products. The reaction proceeded faster than at 70 °C, although at this temperature selectivity decreased, that is, products resulting from secondary metathesis processes were observed as well. These compounds amounted to about 10 % of the total product fraction.

For most reactions, much higher conversions were obtained if the monocarboxylato-chloro complex **2** was used instead of **1**, which was attributed to a stronger polarization of the Ru–alkylidene.[47] As outlined above, this complex slowly disproportionates if it is dissolved in CH_2Cl_2, thereby generating the neutral complex **GH** (Scheme 2, Figure 1). Therefore, it is not possible to claim, without restrictions, that the high conversions are solely caused by the defined species **2**. The difficulty that the active species at reaction conditions might not be identical to the one initially used may generally arise for all Grubbs-Hoveyda type initiators bearing mixed anionic ligands and caution should be taken in interpreting the results.[49,50] However, in view of a reaction time of 3 h and the slow propensity of **2** to disproportionate (see above), the TONs observed for **2** at 40 °C can, at least to a major extent, be attributed to **2** and not to the **GH** complex, which forms only slowly upon disproportionation.

Metathesis reactions under biphasic conditions (ionic liquid/organic solvent) using catalysts 1 and 2

The RCM of DAFA, DEDAM, 1,7-octadiene, and *tert*-butyl *N,N*-diallyl carbamate as well as the self-metathesis of methyl oleate were performed under biphasic conditions by using $[BDMIM^+][BF_4^-]$ as ionic liquid phase and either neat reactants or heptane as the second liquid phase. Despite the comparably small amount of ionic liquid and the large amount of polar substrate, which both favor the transfer of catalyst into the nonpolar phase, a low catalyst leaching of $\leq 0.4\%$ into the product phase was observed for all reactions if using the bis-ionically tagged complex **1** (Table 2). This leaching translated into Ru contamination of < 2.5 ppm in the products. Notably, for reactions with low conversions the Ru leaching was below the detection limit of ICP–OES and was, therefore, reported as 0 %.

Table 2. Metathesis reactions under biphasic conditions ([BDMIM$^+$][BF$_4^-$])/heptane) using **1** and **2**. $T=40\,^\circ$C.

Substrate	Catalyst [mol %]	TON[a]	Ruthenium leaching[b] [%]	 contamination [ppm]
DAFA[c]	**1** [0.1]	400	0.04	0.4
	2 [0.05]	1300	0.17	0.9
DEDAM[d]	**1** [0.1]	700	0.13	1.3
	2 [0.05]	1800	0.27	1.4
1,7-octadiene[e]	**1** [0.1]	500	0.03	0.3
	2 [0.05]	> 2000	0.12	0.6
TBDC	**1** [0.2]	100	0	0
	2 [0.1]	500	0.24	2.4
methyl oleate[f]	**1** [0.05]	560	0.22	1.1
	2 [0.05]	940	0.35	1.8

[a] Determined by GC–MS after 12 h. [b] Percentage of initial Ru (catalyst) loading. [c] Heptane as the second liquid phase; ionic liquid (0.1 g), heptane (2.0 g), DAFA (0.2 g). [d] Heptane as the second liquid phase; ionic liquid (0.1 g), heptane (2.0 g), DEDAM (0.25 g). [e] Neat; ionic liquid (0.1 g), 1,7-octadiene (0.1 g). [f] Neat; ionic liquid (0.1 g), methyl oleate (0.5 g). Definitions: DAFA = *N,N*-diallyltrifluoroacetamide; DEDAM = diethyl diallyl malonate; TBDC = *tert*-butyl-*N,N*-diallyl carbamate.

The TONs observed for **1** under biphasic conditions were in the same range as those determined for reactions in solution (Table 2, Table 1). In the RCM of DEDAM under biphasic conditions, TONs up to 700 were obtained, exceeding those observed in an organic solvent. Owing to the low polarity of 1,7-octadiene and its immiscibility with the ionic liquid phase, its RCM reaction was performed without the use of another liquid transport phase. Catalyst leaching for this reaction was negligible (0.03 %) and a TON of 500 was obtained, which was within the same range than as in CH_2Cl_2 at 40 °C. Only the formation of cyclohexene and no isomerization products were observed at this temperature.

In the self-metathesis of methyl oleate catalyzed by **1**, a TON of 560 was obtained if the reaction was performed under biphasic conditions. Again, for this reaction the TON was similar to that determined in solution. As in solution, reaction monitoring by GC–MS under biphasic conditions again revealed the selective formation of the two desired cross-metathesis products as well as isomerization of the *Z*-double bond in the substrate molecule.

Likewise, much higher conversion was achieved if the mono-ionic initiator **2** was used under biphasic conditions than in solution. Ru leaching was low ($\leq$ 0.35 %), and TONs were similar to those obtained in solution for that particular catalyst.

RCM of 1,7-octadiene and self-metathesis of methyl oleate promoted by 1 and 2 under biphasic conditions using monolith-supported ionic liquids

As catalysts **1** and **2** displayed similar reactivities in homogeneous as well as in biphasic metathesis, we decided to perform the self-metathesis of methyl oleate as well as the RCM of 1,7-octadiene in a continuous manner. Inspired by the work of Wasserscheid et al.,[51–53] we recently published a method to perform continuous metathesis under biphasic liquid–liquid conditions using a monolith-supported ionic liquid phase (SILP),[24] which was herein applied to the bis-ionic catalyst **1** as well as to the mono-ionic complex **2**. For these purposes, ring-opening metathesis polymerization (ROMP) derived polymeric monoliths were prepared and surface grafted with norborn-5-en-2-ylmethyl-*N,N,N*-trimethylammonium tetrafluoroborate. The ionic liquid, that is, [BDMIM$^+$][BF$_4^-$], containing, for example, catalyst **1** was then immobilized on the surface of the monolith. Importantly, our concept enabled continuous product formation, simply by cycling reactants through a monolithic support containing a suitable catalyst dissolved in an ionic liquid. The fact that a biphasic liquid/liquid system was used expands the range of potentially accessible substrates. Owing to their low polarity, methyl oleate and 1,7-octadiene were both used as neat reactants. Reactions were performed at 40 °C, and at 80 °C if catalyst **1** was used. Reactions catalyzed by complex **2** were performed at 40 °C. For the self-metathesis of methyl oleate, at 40 °C a TON of 500, similar to that obtained under biphasic conditions, was observed for catalyst **1** (Table 3, see Table 2). Catalyst leaching was only 0.08 % of the initial amount of initiator. As the reaction proceeded slowly at this temperature, it was required to cycle the reactant through the supported catalyst, which, in turn, demonstrated its stability during a prolonged period of time. An increase in temperature to 80 °C accelerated the reaction; maximum conversion was already obtained after 60 min, and concomitantly, ruthenium leaching slightly increased to 0.24 %. The same trend was observed in the RCM of 1,7-octadiene, an increase in reaction temperature from 40 °C to 80 °C resulted in a fivefold shorter reaction time if using the dicationic complex **1**. Catalyst contamination of the product phase was low in this case, too (0.2 %).

Table 3. Metathesis reactions under continuous monolith-supported liquid–liquid conditions using **1** and **2**.

Substrate	Flow rate [mL min^{-1}]	Catalyst [mol %]	T [°C]	t[a] [min]	TON	Ruthenium leaching[b] [%]	 contamination [ppm]
methyl oleate	0.1	**1** [0.1]	40	240	500	0.08	0.8
	0.1	**1** [0.1]	80	60	600	0.24	2.4
	0.1	**2** [0.1]	40	100	800	0.22	2.2
1,7-octadiene	0.1	**1** [0.1]	40	100	550	0.11	1.1
	0.1	**1** [0.1]	80	20	550	0.20	2.0
	0.1	**2** [0.05]	40	35	1450	0.43	2.2

[a] Time until maximum TON was reached, cyclization of the substrates was required. The volume of the column used was 1.66 mL.[24] The total porosity of the monolith was 80%. Catalysts **1** and **2** (3 mg) were dissolved in 100 mg [BDMIM$^+$][BF$_4^-$], respectively. [b] Based on the initial amount of catalyst.

Again, for reactions under supported biphasic conditions, much higher conversion was achieved if the monoionic initiator **2** was used (Table 3), as was observed for reactions in one organic solvent (Table 1) and under biphasic conditions (Table 2). TONs were comparable to the ones obtained under biphasic conditions for catalyst **2** and the Ru leaching was low ($\leq$0.43 %). Maximum conversion was obtained within only 100 min for the self-metathesis of methyl oleate and within 35 min in the case of the RCM of 1,7-octadiene. The reactions were performed at 40 °C to minimize the influence of the disproportionation reaction, which is more pronounced at elevated temperatures. No isomerization reactions were observed and both catalysts yielded solely products resulting from primary metathesis.

Conclusions

Two novel ionic Ru–alkylidene complexes, [Ru[(4-CO$_2$)(1-CH$_3$)Py$^+$)]$_2$(IMesH$_2$)(=CH-2-(2-PrO)-C$_6$H$_4$)][OTf$^-$]$_2$ (**1**) and [RuCl[(4-CO$_2$)(1-CH$_3$)Py$^+$)](IMesH$_2$)(=CH-2-(2-PrO)-C$_6$H$_4$)][OTf$^-$] (**2**), were synthesized from [Ru(CF$_3$SO$_3$)$_2$(IMesH$_2$)(=CH-2-(2-PrO)-C$_6$H$_4$)] and [RuCl(CF$_3$SO$_3$)(IMesH$_2$)(=CH-2-(2-PrO)-C$_6$H$_4$)], respectively, and were used in various RCM reactions in solution as well as under biphasic liquid–liquid conditions. Catalysts **1** and **2** were also used in the continuous metathesis of methyl oleate and 1,7-octadiene under supported liquid–liquid conditions. Both catalysts could be successfully immobilized within an ionic liquid phase, as illustrated by the low Ru leaching ($\leq$0.4 %). Compared to the dicationic complex [Ru(DMF)$_3$(IMesH$_2$)(=CH-2-(2-PrO)-C$_6$H$_4$)$^{2+}$][(BF$_4$$^-$)$_2$], which required elevated reaction temperatures to be active, **1** and **2** are metathesis-active for a variety of substrates at low temperatures. Clearly, the use of ionic ligands preserved the catalytic activity for substrates with coordinating functionalities. At the same time it also guaranteed for an effective and permanent immobilization within a polar stationary phase, that is, an ionic liquid. **1** and **2** exhibited comparable reactivity if performing the reactions either in solution or under biphasic conditions. An increase in temperature considerably accelerated the reaction, yet it was not leading to significantly higher TONs. Complex **2**, possessing one chloride and one ionic carboxylate ligand, exhibited an increased activity compared to complex **1**. In solution, the disproportionation reaction of this compound was traced by means of ^{1}H NMR spectroscopy at elevated temperatures, whereby the bis-ionic species **1** and the neutral complex [RuCl$_2$(IMesH$_2$)(=CH-2-(2-PrO)-C$_6$H$_4$)] formed. This finding illustrates an intermolecular anionic ligand exchange with Grubbs–Hoveyda type initiators bearing mixed anionic ligands.

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Keywords: biphasic catalysis · heterogeneous catalysis · ionic liquids · metathesis · ruthenium

[1] R. H. Grubbs, *Handbook of Metathesis, 1st ed.* (Ed.: R. H. Grubbs), Wiley-VCH, Weinheim, Germany, **2003**.
[2] R. R. Schrock, *Chem. Rev.* **2009**, *109*, 3211 – 3226.
[3] Y. Vidavsky, A. Anaby, G. N. Lemcoff, *Dalton Trans.* **2012**, *41*, 32 – 43.
[4] X. Wu, M. Tamm, *Beilstein J. Org. Chem.* **2011**, *7*, 82 – 93.
[5] J. O. Krause, O. Nuyken, K. Wurst, M. R. Buchmeiser, *Chem. Eur. J.* **2004**, *10*, 777 – 784.
[6] J. O. Krause, S. Lubbad, O. Nuyken, M. R. Buchmeiser, *Adv. Synth. Catal.* **2003**, *345*, 996 – 1004.
[7] J. O. Krause, S. Lubbad, O. Nuyken, M. R. Buchmeiser, *Macromol. Rapid Commun.* **2003**, *24*, 875 – 878.
[8] M. Mayr, D. Wang, R. Kröll, N. Schuler, S. Prühs, A. Fürstner, M. R. Buchmeiser, *Adv. Synth. Catal.* **2005**, *347*, 484 – 492.
[9] M. Mayr, B. Mayr, M. R. Buchmeiser, *Angew. Chem.* **2001**, *113*, 3957 – 3960; *Angew. Chem. Int. Ed.* **2001**, *40*, 3839 – 3842.
[10] *Polymeric Materials in Organic Synthesis and Catalysis, 1st ed.* (Ed.: M. R. Buchmeiser), Wiley-VCH, Weinheim, Germany, **2003**.
[11] S. Xie, F. Svec, *Biotechnol. Bioeng.* **1999**, *62*, 30 – 35.
[12] M. R. Buchmeiser, *Chem. Rev.* **2009**, *109*, 303 – 321.
[13] S. C. Schürer, S. Gessler, N. Buschmann, S. Blechert, *Angew. Chem.* **2000**, *112*, 4062 – 4065; *Angew. Chem. Int. Ed.* **2000**, *39*, 3898 – 3901.
[14] J. S. Kingsbury, S. B. Garber, J. M. Giftos, B. L. Gray, M. M. Okamoto, J. T. Fourkas, A. H. Hoveyda, *Angew. Chem.* **2001**, *113*, 4381 – 4386; *Angew. Chem. Int. Ed.* **2001**, *40*, 4251 – 4256.
[15] F. Sinner, M. R. Buchmeiser, *Angew. Chem.* **2000**, *112*, 1491 – 1494; *Angew. Chem. Int. Ed.* **2000**, *39*, 1433 – 1436.
[16] V. I. Pârvulescu, C. Hardacre, *Chem. Rev.* **2007**, *107*, 2615 – 2665.
[17] T. Welton, *Chem. Rev.* **1999**, *99*, 2071 – 2084.
[18] H. Olivier-Bourbigou, L. Magna, D. Morvan, *Appl. Catal. A* **2010**, *373*, 1 – 56.
[19] P. Sledz, M. Mauduit, K. Grela, *Chem. Soc. Rev.* **2008**, *37*, 2433 – 2442.
[20] P. Wasserscheid, *Chem. Unserer Zeit* **2003**, *37*, 52 – 63.
[21] P. Wasserscheid, W. Keim, *Angew. Chem.* **2000**, *112*, 3926 – 3945; *Angew. Chem. Int. Ed.* **2000**, *39*, 3772 – 3789.
[22] P. Wasserscheid, T. Welton in *Ionic Liquids in Synthesis* (Ed.: P. Wasserscheid, T. Welton), Wiley-VCH, Weinheim, Germany, **2002**.
[23] Y. S. Vygodskii, A. S. Shaplov, E. I. Lozinskaya, O. A. Filippov, E. A. Shubina, R. Bandari, M. R. Buchmeiser, *Macromolecules* **2006**, *39*, 7821 – 7830.
[24] B. Autenrieth, W. Frey, M. R. Buchmeiser, *Chem. Eur. J.* **2012**, *18*, 14069 – 14078.
[25] J. H. Kim, B. Y. Park, S.-W. Chen, S.-g. Lee, *Eur. J. Org. Chem.* **2009**, 2239 – 2242.
[26] R. C. Buijsman, E. van Vuuren, J. G. Sterrenburg, *Org. Lett.* **2001**, *3*, 3785 – 3787.
[27] B. Autenrieth, E. B. Anderson, D. Wang, M. R. Buchmeiser, *Macromol. Chem. Phys.* **2013**, *214*, 33 – 40.
[28] O. Songis, A. M. Slawin, C. S. Cazin, *Chem. Commun.* **2012**, *48*, 1266 – 1268.
[29] M. S. Sanford, L. M. Henling, R. H. Grubbs, *Organometallics* **1998**, *17*, 5384 – 5389.
[30] Q. Yao, M. Sheets, *J. Organomet. Chem.* **2005**, *690*, 3577 – 3584.
[31] J. B. Binder, I. A. Guzei, R. T. Raines, *Adv. Synth. Catal.* **2007**, *349*, 395 – 404.
[32] E. Borré, M. Rouen, I. Laurent, M. Magrez, F. Caijo, C. Crevisy, W. Solodenko, L. Toupet, R. Frankfurter, C. Vogt, A. Kirschning, M. Mauduit, *Chem. Eur. J.* **2012**, *18*, 16369 – 16382.
[33] S. W. Chen, J. H. Kim, K. Y. Ryu, W. W. Lee, J. Hong, *Tetrahedron* **2009**, *65*, 3397 – 3403.
[34] H. Clavier, N. Audic, J.-C. Guillemin, M. Mauduit, *J. Organomet. Chem.* **2005**, *690*, 3585 – 3599.
[35] C. Thurier, C. Fischmeister, C. Bruneau, H. Olivier-Bourbigou, P. H. Dixneuf, *J. Mol. Catal. A* **2007**, *268*, 127 – 133.
[36] Q. Yao, Y. Zhang, *Angew. Chem.* **2003**, *115*, 3517 – 3520; *Angew. Chem. Int. Ed.* **2003**, *42*, 3395 – 3398.
[37] G. Liu, H. He, J. Wang, *Adv. Synth. Catal.* **2009**, *351*, 1610 – 1620.
[38] X. Ding, X. Lv, B. Hui, Z. Chen, M. Xiao, B. Guo, W. Tang, *Tetrahedron Lett.* **2006**, *47*, 2921 – 2924.
[39] N. Audic, H. Clavier, M. Mauduit, J.-C. Guillemin, *J. Am. Chem. Soc.* **2003**, *125*, 9248 – 9249.
[40] T. Vorfalt, K.-J. Wannowius, H. Plenio, *Angew. Chem.* **2010**, *122*, 5665 – 5668; *Angew. Chem. Int. Ed.* **2010**, *49*, 5533 – 5536.

[41] D. M. Lynn, B. Mohr, R. H. Grubbs, L. M. Henling, M. W. Day, *J. Am. Chem. Soc.* **2000**, *122*, 6601 – 6609.
[42] K. Skowerski, C. Wierzbicka, G. Szczepaniak, L. Gulajski, M. Bieniek, K. Grela, *Green Chem.* **2012**, *14*, 3264 – 3268.
[43] K. Skowerski, G. Szczepaniak, C. Wierzbicka, L. Gulajski, M. Bieniek, K. Grela, *Catal. Sci. Technol.* **2012**, *2*, 2424 – 2427.
[44] J. O. Krause, M. T. Zarka, U. Anders, R. Weberskirch, O. Nuyken, M. R. Buchmeiser, *Angew. Chem.* **2003**, *115*, 6147 – 6151; *Angew. Chem. Int. Ed.* **2003**, *42*, 5965 – 5969.
[45] J. O. Krause, O. Nuyken, M. R. Buchmeiser, *Chem. Eur. J.* **2004**, *10*, 2029 – 2035.
[46] T. S. Halbach, S. Mix, D. Fischer, S. Maechling, J. O. Krause, C. Sievers, S. Blechert, O. Nuyken, M. R. Buchmeiser, *J. Org. Chem.* **2005**, *70*, 4687 – 4694.
[47] S. Naumov, M. R. Buchmeiser, *Organometallics* **2012**, *31*, 847 – 856.
[48] B. F. Straub, *Adv. Synth. Catal.* **2007**, *349*, 204 – 214.
[49] K. Tanaka, V. P. Böhm, D. Chadwick, M. Roeper, D. C. Braddock, *Organometallics* **2006**, *25*, 5696 – 5698.
[50] G. Occhipinti, F. R. Hansen, K. W. Törnroos, V. R. Jensen, *J. Am. Chem. Soc.* **2013**, *135*, 3331 – 3334.
[51] A. Riisager, R. Fehrmann, M. Haumann, P. Wasserscheid, *Eur. J. Inorg. Chem.* **2006**, 695 – 706.
[52] A. Riisager, R. Fehrmann, M. Haumann, P. Wasserscheid, *Top. Catal.* **2006**, *40*, 91 – 102.
[53] P. Wasserscheid, *J. Ind. Eng. Chem.* **2007**, *13*, 325 – 338.

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B. Autenrieth, F. Willig, D. Pursley,
S. Naumann, M. R. Buchmeiser*

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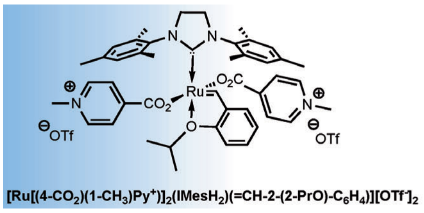
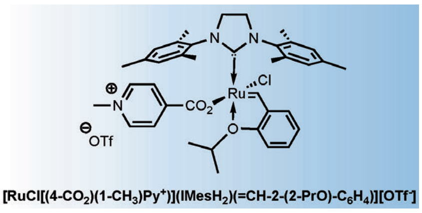
Ionically Tagged Ru–Alkylidenes for Metathesis Reactions under Biphasic Liquid–Liquid Conditions



$[Ru[(4\text{-}CO_2)(1\text{-}CH_3)Py^+)]_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)][OTf^-]_2$



$[RuCl[(4\text{-}CO_2)(1\text{-}CH_3)Py^+)](IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)][OTf^-]$

Perfect for ionic liquids: Two new ionically tagged Ru–alkylidene complexes have been synthesized and successfully applied to various metathesis reactions under biphasic liquid–liquid conditions. Both catalysts have also performed well under supported liquid–liquid conditions.