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Journal of Molecular Catalysis A: Chemical 268 (2007) 127–133
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
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Ionic imidazolium containing ruthenium complexes and olefin metathesis in ionic liquids

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Received 8 November 2006; received in revised form 7 December 2006; accepted 10 December 2006
Available online 15 December 2006

Abstract

The preparation of two ionic Hoveyda's type catalysts with an ionic chain, containing an imidazolium salt tag link to the *ortho* oxygen atom (**11**) and to the *meta*-position (**12**) of the styrenylidene ligand is presented. The catalysts are evaluated in ionic liquid medium: the 1-butyl-3-methyl and 1-butyl-2,3-dimethyl imidazolium salts $(bmim)^+X^-$ ($X = PF_6^-$, NTf_2^- (bistrifluoromethylsulfonimide)) for RCM of *N*,*N*-diallyltosylamide and dimethyldiallylmalonate. The catalysts show good activity for the first cycle with moderate recyclability.

Keywords: Alkene metathesis; Ruthenium-alkylidene; Ionic liquids; Imidazolium salts; Ionic catalysts

1. Introduction

Alkene metathesis [1] has recently dramatically improved synthetic approaches leading to multifunctional natural products [2], supramolecular molecular materials [3], or polymer preparation [4]. This is due to the discovery of efficient, highly functional group tolerant ruthenium catalysts such as $RuCl_2(=CHR)(PCy_3)_2$ **1** by Grubbs and co-workers [5], $RuCl_2(=CHPh)(PCy_3)(IMes)$ **2** [6,7] and $RuCl_2(=CHPh)(PCy_3)(ImesH_2)$ **3** [8] by Nolan and Grubbs. A tremendous interest now arises for the search of reusable molecular ruthenium catalysts. The creation of chelating *ortho*-isopropyloxybenzylidene-ruthenium catalysts **4** [9] and **5** [10] by Hoveyda, and then the modified catalysts by Wakamatsu and Blechert **6** [11] and Grela et al. **7** [12] (Fig. 1) have shown, beside high catalytic activity and high stability, the ability to be recycled in alkene metathesis reaction [9b,10a,13].

Ionic liquids are suitable non-volatile solvents for organic and organometallic reactions and they offer opportunities for metal catalyzed reactions, especially of industrial importance [14]. Initial attempts to perform alkene metathesis catalysis with neutral complexes **1–3** have shown the feasibility of the reaction in ionic liquids for both RCM [15] and cross-metathesis [16] reactions but with moderate recyclability. Several successful examples of recyclability for olefin metathesis in ionic liquids have been performed, first using intrinsically ionic catalysts precursors such as ionic allenylidene-ruthenium precursors **8** [17] and then Hoveyda type catalysts carrying an ionic fragment such as catalysts **9** [18] or **10** [19] (Fig. 2).

Both catalysts **9** and **10** show excellent abilities to be recycled without critical loss of activity over 10 cycles in RCM reactions. It was of interest to evaluate other possibilities of grafting an ionic tag to the chelating ligand of the Hoveyda catalyst **4** involving short step number synthesis.

We report here the synthesis of two ionic Hoveyda and Blechert's type catalysts with potential for alkene metathesis in ionic media: the first with an imidazolium linked to the *ortho* oxygen atom of a benzylidene ligand **11**, the second with an imidazolium group attached at the *ortho* position of the isopropoxy group **12** (Fig. 3).

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doi:10.1016/j.molcata.2006.12.016

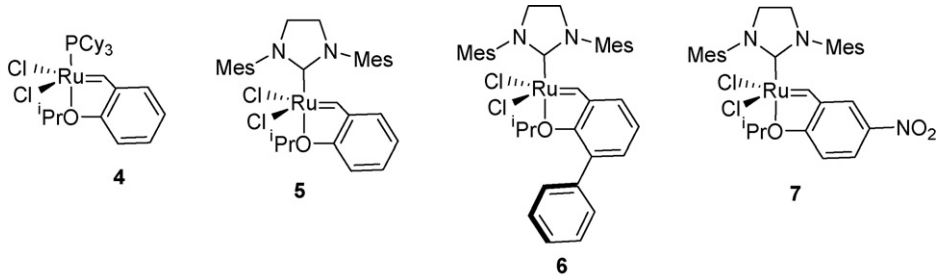


Fig. 1. Selected chelating alkylidene-ruthenium based olefin metathesis catalysts.

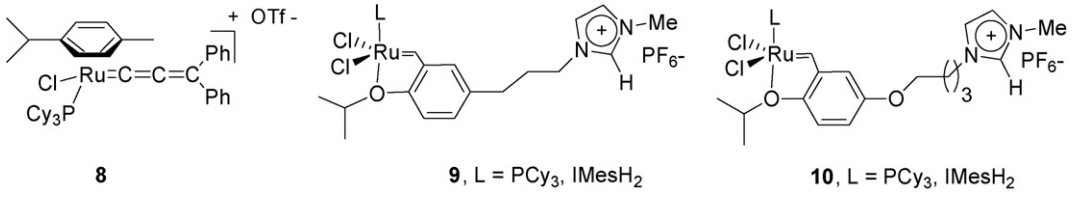


Fig. 2. Examples of ionic ruthenium catalysts operating in ionic liquids.

2. Experimental

Organic reactions were performed in air, excepted the Wittig reactions, the organometallic and catalytic reactions were performed under an argon atmosphere. ^{1}H, ^{31}P, ^{19}F and ^{13}C spectra were recorded on a BRUKER DPX 200 (200 MHz) and a BRUKER AM 300 WB (300 MHz). Chemical shifts are given in ppm. Elemental Analysis and High Resolution Mass Spectrometry were performed by the Centre Régional de Mesures Physiques de l'Ouest, Université de Rennes. Diethyl ether and THF were distilled over sodium and benzophenone, toluene over sodium, heptane over calcium hydride and dichloromethane was distilled over phosphorous pentoxide. Compoud **16** was synthesised according to the Blechert procedure [20]. The ionic liquid [bmim][PF_6] was synthesised by classical anion metathesis from [bmim][Cl] purchased from Solvionic, [bdmim][NTf_2] was provided by IFP.

2.1. General procedure for the RCM reactions in ionic liquids

In a dried schlenck tube under an argon atmosphere were introduced 2 mL of ionic liquid and the catalyst. After complete dissolution, 0.1 g of substrate was introduced and the reaction stirred under the appropriate conditions (see article). The organic products were extracted twice with 5 mL of distillated heptane. The remaining reaction mixture was dried under vacuum for 1 h at r.t. and loaded with fresh substrate (0.1 g) to start a new run.

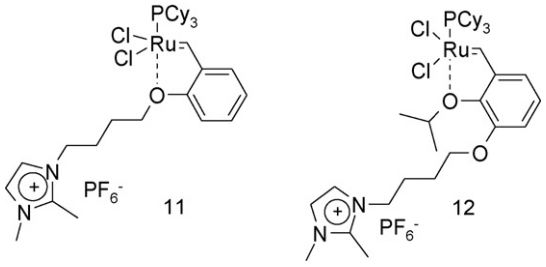


Fig. 3. Ruthenium catalysts with an ionic imidazolium branch.

2.2. Synthesis of 2-(4-bromo-butoxy)-benzaldehyde **13**

A solution of salicylaldehyde (2.44 g, 20 mmol, 1 equiv.), dibromobutane (27 g, 125 mmol, 6.2 equiv.) and K_2CO_3 (4.14 g, 30 mmol, 1.5 equiv.) in DMF (40 mL) was stirred overnight at 60 °C. To this solution was added diethyl ether (100 mL) and the resulting mixture was washed four times with distilled water (100 mL). Trap-to-trap distillation was used to remove most of the solvents. The dibromobutane excess was also recovered by distillation. The residual oil was purified by silica-gel chromatography (heptane–Et_2O, 90:10 to 75:25) and dried *in vacuo* to give 3.5 g of a light yellowish oil (70% yield).

^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.89–2.14 (m, 4H, CH_2), 3.46 (t, $J = 6.2$ Hz, 2H, CH_2Br), 4.08 (t, $J = 5.8$ Hz, 2H, CH_2O), 6.97 (m, 2H, C*H*ar.), 7.49 (ddd, $J = 8.4$ Hz, $J = 7.4$ Hz, $J = 1.9$ Hz, 1H, C*H*ar.), 7.78 (dd, $J = 7.4$ Hz, $J = 1.9$ Hz, 1H, C*H*ar.), 10.45 (s, 1H, C*H*O).

^{13}C NMR (75.46 MHz, $CDCl_3$) δ: 28.1 (*C*H_2), 29.8 (*C*H_2), 33.7 (*C*H_2), 67.8 (*C*H_2), 112.9 (*C*Har.), 121.2 (*C*Har.), 125.2 (*C*ar.), 128.7 (*C*Har.), 136.4 (*C*Har.), 161.6 (*C*ar.), 190.0 (*C*O).

HRMS: *m/z* calcd. for $C_{10}H_{12}OBr$: 227.0071; found: 227.0084.

Anal. calc. for $C_{11}H_{13}O_2Br$: C, 51.38; H, 5.10; found: C, 51.22; H, 5.17.

2.3. Synthesis of 1-(4-iodo-butoxy)-2-vinyl-benzene **14**

To a suspension of triphenylmethylphosphonium iodide (7.07 g, 17.5 mmol, 1.5 equiv.) in diethyl ether (40 mL) was added dropwise a solution of *n*BuLi (1.6 M in hexane, 10 mL, 16 mmol, 1.36 equiv.). The mixture was stirred for 30 min at room temperature. The solution became orange and a solid pre-

cipitated. To this mixture was added dropwise a solution of aldehyde **13** (3 g, 11.7 mmol, 1 equiv.) in diethyl ether (20 mL). The mixture was stirred for 1 h and 30 min at room temperature and then filtrated. The solid was washed with Et_2O and the combined organic solutions were concentrated and purified by filtration on a short plug of silica-gel with Et_2O as the eluant. The solution was concentrated and dried *in vacuo* to give 2.46 g of a colorless oil (72% yield). According to ^{1}H NMR the product is composed of a 85%/15% mixture of iodo- and bromo-compounds, respectively.

^{1}H NMR (200.131 MHz, $CDCl_3$) δ: 1.91–2.20 (m, 4H, CH_2), 3.31 (t, J = 6.7 Hz, 1.7H, CH_2–I), 3.54 (t, J = 6.4 Hz, 0.3H, CH_2–Br), 4.05 (t, J = 5.6 Hz, 2H, CH_2–O), 5.26 (dd, J = 11.2 Hz, J = 1.5 Hz, 1H, CH=CH_2), 5.74 (dd, J = 17.8 Hz, J = 1.5 Hz, 1H, CH=CH_2), 7.50–6.81 (m, 5H, CH=CH_2, CH arom.).

^{13}C NMR (75.46 MHz, $CDCl_3$) δ: 7.1 (CH_2I), 30.6 (CH_2), 30.7 (CH_2), 67.4 (OCH_2), 112.2 (CH), 114.9 (=CH_2), 121.2 (CH), 126.9 (CH), 129.3(CH), 132.0 (CH).

A set of signals corresponding to the bromo-derivative was observed at: 28.4, 30.0, 34.0, and 67.58 ppm.

HRMS: *m*/*z* calcd. for $C_{12}H_{15}OI$: 302.0167; found: 302.0166.

Anal. Found: C, 49.14; H, 5.16 corresponding to $C_{12}H_{15}OI_{0.81}Br_{0.19}$.

2.4. Synthesis of 2,3-dimethyl-1-[4-(2-vinyl-phenoxy)-butyl]-imidazolium hexafluorophosphate ***15***

A solution of **14** (592 mg, 1.96 mmol, 1 equiv.) and 1,2-dimethylimidazole (392 mg, 4.07 mmol, 2 equiv.) in toluene (6 mL) was stirred for 3 days at 80 °C. After cooling, heptane (10 mL) was added to completely precipitate the salt. The solvent was removed using a filtrating cannula and the solid dried *in vacuo*. It was then dissolved in 20 mL of water and a solution of KPF_6 (433 mg, 2.35 mmol, 1.2 equiv.) in 10 mL of water was added followed by 15 mL of dichloromethane. The reaction mixture was stirred for 1 h at room temperature. The organic layer was washed three times with water (15 mL) and concentrated. The residue was taken up in a small amount of acetone, and then dried *in vacuo* to give 813 mg of a white solid (100% yield).

^{1}H NMR (300 MHz, acetone-d_6) δ: 1.90–1.96 (m, 2H, CH_2–CH_2–CH_2), 2.06–2.11 (m, 2H, CH_2–CH_2–CH_2), 2.75 (s, 3H, CCH_3), 3.90 (s, 3H, NCH_3), 4.09 (t, J = 6.0 Hz, 2H, CH_2–O), 4.37 (t, J = 7.5 Hz, 2H, CH_2–N), 5.24 (dd, J = 11.1 Hz, J = 1.5 Hz, 1H, CH=CH_2), 5.79 (dd, J = 18.0 Hz, J = 1.5 Hz, 1H, CH=CH_2), 6.91–7.00 (m, 3H, CHar.), 7.06 (dd, J = 18.0 Hz, J = 11.1 Hz), 7.51–7.59 (m, 3H, CHar., CHimid.).

^{13}C NMR (75.46 MHz, CD_2Cl_2) δ: 8.8 (CCH_3), 25.9 (CH_2), 26.5 (CH_2), 34.6 (NCH_3), 47.9 (NCH_2), 67.3 (OCH_2), 112.2 (CH), 113.72(=CH_2), 120.7 (CH), 120.9 (CH), 122.5 (CH), 126.2 (CH), 126.3 (CCH=CH_2), 129.1 (CH), 131.7 (CH=CH_2), 144.7 (CCH_3), 156.1 (COCH_2).

HRMS: *m*/*z* calcd. for $C_{17}H_{23}N_2O$: 271.1810; found: 271.1810.

Anal. calc. for $C_{17}H_{23}F_6N_2OP$: C, 49.04; H, 5.57; N, 6.73; found: C, 49.51; H, 5.76; N, 6.61.

2.5. Synthesis of 3-(4-bromo-butoxy)-2-isopropoxy-benzaldehyde ***17***

A solution of aldehyde **16** (660 mg, 3.66 mmol, 1 equiv.), dibromobutane (8 g, 36.6 mmol, 10 equiv.) and K_2CO_3 (1.16 g, 8.4 mmol, 2.3 equiv.) in DMF (20 mL) was stirred for 24 h at 50 °C. Trap-to-trap distillation was used to remove most of solvents. To this solution was added diethyl ether (100 mL) and the resulting mixture was washed four times with distilled water (100 mL). After concentration, the residual oil was purified by silica-gel chromatography (heptane–Et_2O, 80:20 to 70:30) and dried *in vacuo* to give 915 mg of a colorless oil (80% yield).

^{1}H NMR (200.131 MHz, $CDCl_3$) δ: 1.36 (d, J = 5.2 Hz, 6H, CH_3–CH), 2.09 (m, 4H, CH_2–CH_2–CH_2–CH_2), 3.54 (t, J = 5.8 Hz, 2H, CH_2–Br), 4.08 (t, J = 5.6 Hz, 2H, CH_2–O), 4.64 (sept., J = 5.6 Hz, 1 Hz, 1H, CH_3–CH), 7.05–7.2 (m, 2H, CHar.), 7.4–7.5 (m, 1H, CHar.), 10.48 (s, 1H, CH=O).

^{13}C NMR (75.46 MHz, $CDCl_3$) δ: 22.7 (CH_3), 28.3 (CH_2), 29.9 (CH_2), 33.7 (CH_2), 68.3 (CH_2), 76.7 (CH), 119.3 (CHar.) 119.5 (CHar.), 124.1 (CHar.), 131.4 (Car.), 152.9 (Car.), 163.8 (Car.), 191.3 (C=O).

HRMS: *m*/*z* calcd. for $C_{14}H_{19}O_3Br$: 314.0517; found: 314.0548.

Anal. calc. for $C_{14}H_{19}O_3Br$: C, 53.35; H 6.08; found: C 53.57; H 5.97.

2.6. Synthesis of 1-(4-iodo-butoxy)-2-isopropoxy-3-vinyl-benzene ***18***

A solution of NaH (95%, 108 mg, 4.28 mmol, 1.9 equiv.) and triphenylmethylphosphonium iodide (1.725 g, 4.27 mmol, 1.9 equiv.) in THF (20 mL) was stirred at 65 °C for 2 h. To this solution was added dropwise a solution of **17** (692 mg, 2.20 mmol) in Et_2O (10 mL) at room temperature. The mixture was refluxed for 30 min. Solvent evaporation followed by purification on silica-gel chromatography (heptane–Et_2O, 80:20) afforded 573 mg of **18** as a colorless oil (73% yield). According to ^{1}H NMR the product is composed of a 90%/10% mixture of iodo- and bromo-compounds, respectively.

^{1}H NMR (200.131 MHz, $CDCl_3$) δ: 1.32 (d, J = 6.2 Hz, 6H, CH_3–CH), 1.9–2.15 (m, 4H, CH_2–CH_2–CH_2–CH_2), 3.30 (t, J = 6.7 Hz, 1.8H, CH_2–I), 3.53 (t, J = 6.7 Hz, 0.2H, CH_2–Br), 4.02 (t, J = 5.6 Hz, 2H, CH_2–O), 4.45 (sept., J = 6.2 Hz, 1H, CH_3–CH), 5.28 (dd, J = 11.1 Hz, J = 1.4 Hz, 1H, CH=CH_2 *cis*), 5.73 (dd, J = 17.9 Hz, J = 1.4 Hz, 1H, CH=CH_2 *trans*), 6.75–7.3 (m, 4H, CH=CH_2, CH arom.).

^{13}C NMR (50.33 MHz, $CDCl_3$) δ: 6.9 (CH_2I), 23.0 (CH(CH_3)$_2$), 30.6 (CH_2), 30.7 (CH_2), 67.69 (OCH_2), 75.8 (CH(CH$_3$)$_2$), 113.0 (CH), 114.8 (=CH_2), 118.2 (CH), 123.8(CH), 132.6 (C CH=CH_2), 133.7 (C CH=CH_2), 145.2 (CO CH(CH_3)$_2$), 152.8 (COCH_2).

HRMS: *m*/*z* calcd. for pour $C_{15}H_{21}O_2I$: 360.0586; found: 360.0554.

Anal. found: C 51.22, H 5.95. $C_{15}H_{21}O_2Br_{0.10}I_{0.90}$ fits with C 50.67, H 5.95.

2.7. Synthesis of 1-[4-(2-isopropoxy-3-vinyl-phenoxy)-butyl]-2,3-dimethyl-imidazolium hexafluorophosphate **19**

A solution of **18** (378 mg, 1.05 mmol, 1 equiv.) and 1,2-dimethylimidazole (230 mg, 2.38 mmol, 2.25 equiv.) in toluene (4 mL) was stirred for 48 h at 80 °C. After cooling, heptane (10 mL) was added to completely precipitate the salt. The solvent was removed using a filtrating cannula and the solid dried *in vacuo*. It was then dissolved in 20 mL of water and a solution of KPF_6 (433 mg, 2.35 mmol, 1.2 equiv.) in 10 mL of water was added followed by 15 mL of dichloromethane. The reaction mixture was stirred for 1 h at room temperature. The organic layer was washed three times with water (15 mL) and concentrated. The residue was taken up in a small amount of acetone, and then dried *in vacuo* to give 481 mg of a white solid (100% yield).

^{1}H NMR (300.08 MHz, $CDCl_3$) δ: 1.24 (d, J = 6.3 Hz, 6H, CH(CH_3)$_2$), 1.79–1.98 (m, 4H, CH_2), 2.50 (s, 3H, CH_3), 3.68 (s, 3H, CH_3), 3.95 (t, J = 5.7 Hz, 2H, OCH_2), 4.07 (t, J = 7.2 Hz, 2H, NCH_2), 4.36 (sept., J = 6.0 Hz, 1H, CH(CH$_3$)$_2$), 5.24 (d, J = 11.4 Hz, 1H, CH=CH_2), 5.69 (d, J = 18.0 Hz, 1H, CH=CH_2), 6.78 (d, J = 8.1 Hz, 1H, CH), 6.92–7.20 (m, 5H, CH).

^{13}C NMR (75.46 MHz, $CDCl_3$) δ: 9.0 (CCH$_3$), 22.50 (CH(CH_3)$_2$), 25.9 (CH_2), 26.5 (CH_2), 34.9 (NCH_3), 48.2 (NCH_2), 67.6 (OCH_2), 75.6 (CH(CH$_3$)$_2$), 112.7 (CH), 114.6 (=CH_2), 117.7 (CH), 120.8 (CH), 122.4 (CH), 123.7 (CH), 131.9 (CH=CH$_2$), 132.6 (C CH=CH$_2$), 143.9 (CCH$_3$), 144.5 (CO CH(CH_3)$_2$), 152.3 (COCH$_2$).

^{31}P {^{1}H} NMR (81.019 MHz, $CDCl_3$) δ: −143.0 (sept., J = 708 Hz).

HRMS: cm/z calcd. for $C_{20}H_{29}N_2O_2$: 329.2229; found: 329.2223.

Anal. calc. for $C_{20}H_{29}F_6N_2O_2P$: C 50.63, H 6.16 N 5.90; found: C 51.00, H 6.31, N 5.69.

2.8. Synthesis of ionic catalyst **11**

A solution of **1** (251 mg, 0.30 mmol, 1 equiv.), **15** (100 mg, 0.37 mmol, 1.2 equiv.) and CuCl (30 mg, 0.3 mmol, 1 equiv.) in dichloromethane (8 mL) was stirred for 2 h at 40 °C. After cooling to room temperature, the solution was concentrated to 2 mL and precipitated in heptane (30 mL) under vigorous stirring. The precipitate was filtrated off, taken up in 10 mL of acetone and filtrated. Acetone was evaporated and the solid was washed with Et_2O (10 mL) to give 186 mg of a brown powder (91% yield).

^{1}H NMR (200.131 MHz, $CDCl_3$) δ: 1.0–2.5 (m, 37H, CH_2), 2.56 (s, 3H, CH_3), 3.69 (s, 3H, CH_3), 4.06 (s, 2H, OCH_2), 4.68 (s, 2H, NCH_2), 7.0–7.8 (m, 6H, CHar. and CHimid.), 17.39 (d, J = 4.6 Hz, 1H, Ru=CH).

^{13}C NMR (75.475 MHz, CD_3COCD_3) δ: 8.9 (CCH$_3$), 25.9 (CH_2), 26.1 (CH_2), 26.2 (CH_2), 27.4 (d, J_{PC} = 10.6 Hz, CH_2), 29.9 (CH_2) 34.8 (NCH_3), 35.3 (d, J_{PC} = 25.4 Hz, PCH), 47.9 (NCH_2), 70.1 (OCH_2), 113.1 (CH), 121.1 (CH), 122.1 (CH), 122.7 (CH), 123.6 (CH), 129.8 (CH), 143.6(C), 144.9 (C), 154.5 (C), 275.7 (CRu).

^{31}P NMR (81.02 MHz, $CDCl_3$) δ: 61.60 (s), −143.24 (sept., J = 712 Hz).

HRMS: m/z calcd. for $C_{34}H_{54}Cl_2N_2OPRu$: 709.2394; found: 709.2398.

Anal. calc. for $C_{34}H_{54}Cl_2F_6N_2OP_2Ru$: C 47.77, H 5.74; found: C 47.94, H 5.49.

2.9. Synthesis of ionic catalyst **12**

A solution of **1** (268 mg, 0.32 mmol, 1 equiv.), **19** (139 mg, 0.42 mmol, 1.3 equiv.) and CuCl (32 mg, 0.32 mmol, 1 equiv.) in dichloromethane (10 mL) was stirred for 2 h at 40 °C. After cooling to room temperature, the solution was concentrated to 2 mL and purified by silica-gel chromatography (dichloromethane–acetone, 1:1) to give 153 mg of a brown powder (56% yield).

^{1}H NMR (300.08 MHz, CD_3COCD_3) δ: 1.2–2.5 (m, 43H, CH_2), 2.85 (s, 3H), 3.98 (s, 3H), 4.28 (t, 6.1 Hz, 2H, OCH_2), 4.48 (t, 6.8 Hz, 2H, NCH_2), 6.18 (m, 1H, OCH(CH$_3$)$_2$), 7.12 (m, 1H, CH), 7.45 (m, 2H, CH), 7.79 (dd, J = 13.2, 2.0 Hz, 2H, CH), 17.46 (d, J = 5.0 Hz, 1H, Ru = CH).

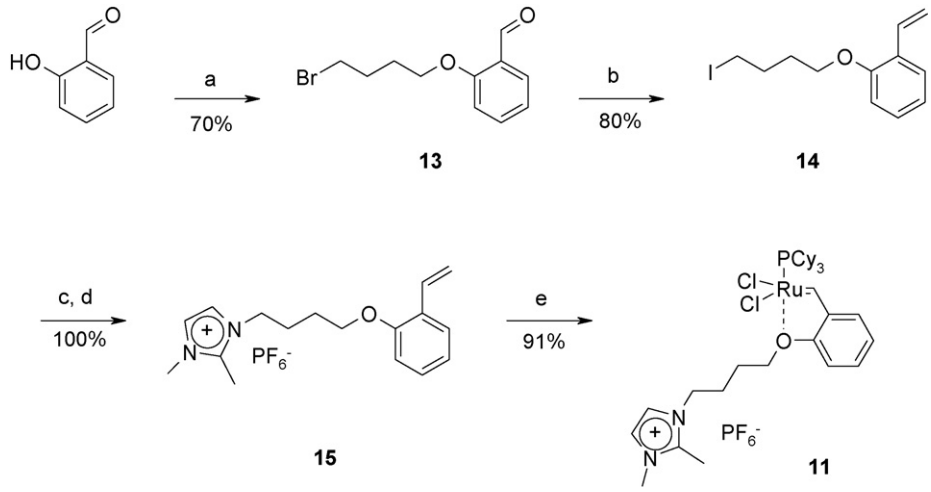
^{13}C NMR (50.33 MHz, CD_3COCD_3) δ: 9.5 (CCH$_3$), 22.6 (CH(CH_3)$_2$), 26.4 (CH_2), 26.6 (CH_2), 27.3 (CH_2), 28.0 (d, J_{PC} = 10.8 Hz, CH_2), 30.3 (s, CH_2), 35.22 (NCH_3), 35.3 (d, J_{PC} = 25.6 Hz, PCH), 48.4 (NCH_2), 69.4 (OCH_2), 80.8 (CH(CH$_3$)$_2$), 115.8 (CH), 116.3 (CH), 121.5 (CH), 123.2 (CH), 124.4 (CH), 140.9 (C), 145.4 (C), 147.1 (C), 149.7 (C), 280.4 (d, J_{PC} = 14.1 Hz).

^{31}P NMR (81.01 MHz, CD_3COCD_3) δ: 59.20 (s), −143.02 (sept., J = 708 Hz). HRMS: m/z calcd. for $C_{37}H_{60}Cl_2N_2O_2PRu$: 767.2813; found: 767.2818. Anal. calc. for $C_{37}H_{60}Cl_2F_6N_2O_2P_2Ru$: C 46.33, H 6.45; found: C 46.36, H 6.29.

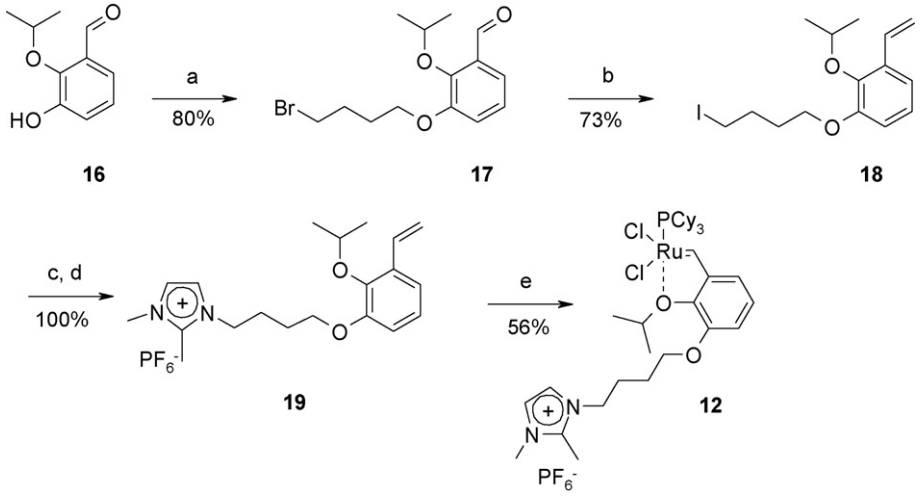
3. Results and discussion

The design of **11** was motivated by the fact that the imidazolium moiety being far from the oxygen atom should not modify too much, by electronic and steric effects, the Hoveyda's catalyst and catalytic activity in ionic liquids. Furthermore, the synthesis of **11** was performed in only five steps from the commercially available and cheap salicylaldehyde as the starting material (Scheme 1).

The first step consists in the phenol etherification with an excess (6 equiv.) of 1,4-dibromobutane to ensure the monosubstitution of the dibrominated reagent affording the brominated ether **13** in 70% yield. The dibromobutane excess can be recovered by distillation of the crude product and reused in subsequent reactions. Conversion of the aldehyde into the styrene derivative is accomplished by a Wittig reaction in diethyl ether during which we observed the partial substitution of the bromide by an iodide. Substitution of iodide by 1,2-dimethylimidazole precipitates the imidazolium salt in toluene. The raw product treated with an aqueous solution of KPF_6 leads to precipitation of the corresponding hexafluorophosphate salt **15** with a quantitative yield. The last step consists in a ligand metathesis in the pres-



Scheme 1. (a) K_2CO_3, 1,4-dibromobutane (6 equiv.), DMF, 60 °C, 20 h. (b) $Ph_3PCH_3{}^+I^-$, *n*BuLi, Et_2O, r.t. (c) 1,2-Dimethylimidazole, toluene, 80 °C, 3 days. (d) KPF_6, H_2O, r.t. 1 h. (e) **1**, CuCl, CH_2Cl_2, 40 °C, 2 h.



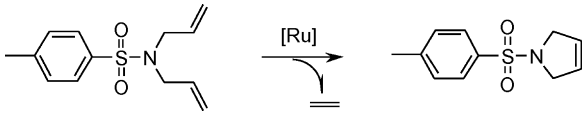
Scheme 2. (a) K_2CO_3, 1,4-dibromobutane (10 equiv.), DMF, 50 °C, 20 h. (b) $Ph_3PCH_3{}^+I^-$, NaH, THF. (c) 1,2-Dimethylimidazole, toluene, 80 °C, 48 h. (d) KPF_6, H_2O, r.t., 1 h. (e) **1**, CuCl, CH_2Cl_2, 40 °C, 2 h.

ence of CuCl as a phosphine scavenger according to the Hoveyda procedure [10a] to afford the desired ionic complex **11** in 91% yield.

According to the same approach the ionic complex **12** preparation was motivated by two observations: (i) as observed by Hoveyda and co-workers [9b], the presence of the isopropoxy substituent in the coordinating ether is expected to ensure higher activity and stability and (ii) according to Wakamatsu and Blechert [11], an increase of the steric hindrance at the *ortho* position of the isopropoxy group should improve the catalytic activity. Thus, starting from the aldehyde **16** [20], the ionic complex **12** was prepared in five steps with an overall yield of 33% as depicted in Scheme 2.

The catalytic activity of **11** and **12** was investigated for the RCM of *N*,*N*-diallyltosylamide (Table 1). Two 1-butyl-3-methyl imidazolium (bmim) based ionic liquids (PF_6^- and bistrifluoromethylsulfonimide NTf_2^- anions) were used in order to observe the possible influence of the counter anion on the reaction outcome since the ruthenium coordination by the NTf_2^- anion has recently been shown [21]. Both complexes were found to be totally soluble in ionic liquid media. After each cycle, the reaction products were extracted with heptane, and a new load of substrate was added. In both cases, the RCM reaction took

Table 1
RCM of *N*,*N*-diallyltosylamide with catalyst **11** and **12** in [bmim][X^-]



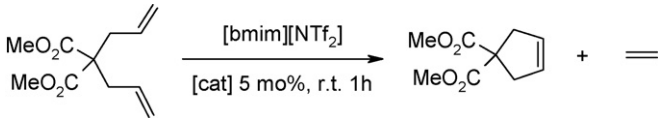
Catalyst	Ionic liquid anion	Run (conversion wt%)[a]		
		1	2	3
11[b]	NTf_2^-	90	89	75
11[b]	PF_6^-	90	85	60
12[c]	PF_6^-	89	77	46

[a] Determined by GC/MS.
[b] 2.5 mol% of **11**, 60 °C, 45 min.
[c] 2.5 mol% of **12** in [bdmim][PF_6], r.t., 45 min.

place under mild conditions (60 °C, 45 min) affording 90% of the RCM product. A slight activity decrease with the number of cycles was observed and the benefit of using the NTf_2^- *versus* PF_6^- anion was not important (Table 1).

The same level of catalytic activity was reached with catalyst **11** at 60 °C and **12** at room temperature thus showing the beneficial effect of the steric congestion on the benzylidene ligand. This is in agreement with the report of Blechert on the role of the substituents of the aryl moiety over initiation kinetics [22], as an increase of the steric bulk at the *meta*-position of the benzylidene ligand weakens the Ru–O bond, resulting in a faster initiation but a slower reformation of the complex. This phenomena is also visible in the catalyst synthesis, since the yield observed in the final step is lower with the bulky styrenyl ether, 56% for **12** *versus* 91% for **11**. Thus, it is reasonable to postulate that catalyst **12** has a fast initiation step, producing active species and affording the best conversion on the first cycle, however, the reformation of the initial complex being more difficult, this catalyst is not easily recyclable.

Catalysts **11** and **12** have also been used in the RCM of dimethyldiallylmalonate. The reaction is slower than that of bisallyltosylamide. Mild conditions and short reaction time have been selected not to reach complete reaction, in order to evaluate and compare the catalyst activity and recyclability with regard to the reference catalysts **1**, **3** and **4** (Scheme 3).



Scheme 3. RCM reaction of dimethyl diallylmalonate in [bmim][NTf_2].

Table 2
Recycling and reuse of ionic ruthenium catalysts **11** and **12** in [bmim][NTf_2]

	Cycle (conversion wt%[a])			
	1	2	3	4
1	4	0	–	–
3	35	10	–	–
4	31	11	5	–
11	24	22	22	16
12	53	39	23	8

5 mol% of catalyst, r.t., 1 h.
[a] Determined by GC/MS.

The results clearly show that the neutral catalysts **1**, **3** and **4** are not appropriate for olefin metathesis in ionic liquid media. The catalyst **12** displays a much better activity than **11** on the initial run but this is to the detriment of recyclability. Indeed the catalytic activity of **12** decreases slowly with the number of catalytic cycles whereas **11** maintains an almost constant activity over the four first cycles (Table 2).

4. Conclusion

Two new ionic olefin metathesis ruthenium complexes, designed to operate in ionic liquid media, have been synthesised *via* a five step sequence. These catalysts operate in ionic liquids [bmim][X] or [bdmim][X] with good activity in the first cycle with respect to catalyst **1**–**4**. Their synthesis is more straightforward than that of catalysts **9** and **10**. They lead to good activity for the first cycle but they offer moderate recycling properties with regard to these catalysts. The activity of **11** reveals that attachment at the *ortho* oxygen is responsible for a slow initiation. Catalyst **12** presents a good initiation but is less recoverable likely due to a difficult recoordination of the ligand.

Acknowledgements

The authors are grateful to Valentin Poirier a 3rd year student, the CNRS and the Institut Français du Pétrole for financial support. We also thank the Centre Régional de Mesures Physiques de l'Ouest, University of Rennes, for HRMS measurements and elemental analysis.

References

[1] (a) R.H. Grubbs (Ed.), Handbook of Metathesis, vol. 1–3, Wiley-VCH, Weinheim, 2003;
(b) S.J. Connon, S. Blechert, in: P.H. Dixneuf, C. Bruneau (Eds.), Ruthenium Catalysts and Fine chemistry, vol. 11, Springer, 2004, p. 93;
(c) A. Fürstner, Angew. Chem., Int. Ed. Engl. 39 (2000) 3012.
[2] (a) K.C. Nicolaou, P.G. Bulger, D. Sarlah, Angew. Chem. Int. Ed. 44 (2005) 4490;
(b) S.J. Connon, S. Blechert, Angew. Chem. Int. Ed. 42 (2003) 1900.
[3] (a) A.J. Nawara, T. Shima, F. Hampet, J.A. Gladysz, J. Am. Chem. Soc. 128 (2006) 4962;
(b) A.F.M. Kilbiner, S.J. Cantrill, A.W. Waltman, M.W. Day, R.H. Grubbs, Angew. Chem. Int. Ed. 42 (2003) 3281;
(c) D.G. Hamilton, N. Feeder, S.J. Teat, J.K.M. Sanders, New J. Chem. (1998) 1019;
(d) B. Mohr, J.-P. Sauvage, R.H. Grubbs, M. Weck, Angew. Chem. Int. Ed. 36 (1997) 1308.
[4] (a) M.R. Buchmeiser, Chem. Rev. 100 (2000) 1565;
(b) J.E. Schwendeman, A. Cameron Church, K.B. Wagener, Adv. Synth., Catal. 344 (2002) 597.
[5] (a) S.T. Nguyen, L.K. Johnson, R.H. Grubbs, J.W. Ziller, J. Am. Chem. Soc. 114 (1992) 3974;
(b) P. Schwab, M.B. France, J.W. Ziller, R.H. Grubbs, Angew. Chem. Int. Ed. 34 (1995) 2039.
[6] J. Huang, S.P. Nolan, J.L. Petersen, J. Am. Chem. Soc. 121 (1999) 2674.
[7] (a) M. Scholl, T.M. Trnka, J.P. Morgan, R.H. Grubbs, Tetrahedron Lett. 40 (1999) 2247;
(b) T. Weskamp, F.J. Kohl, W. Hieringer, D. Gleich, W.A. Herrmann, Angew. Chem., Int. Ed. 38 (1999) 2416.
[8] M. Scholl, S. Ding, C.W. Lee, R.H. Grubbs, Org. Lett. 1 (1999) 953.
[9] (a) J.P.A. Harrity, D.S. La, D.R. Cefalo, M.S. Visser, A.H. Hoveyda, J. Am. Chem. Soc. 120 (1998) 2343;
(b) J.S. Kingsbury, J.P.A. Harrity, P.J. Bonitatebus, A.H. Hoveyda, J. Am. Chem. Soc. 121 (1999) 791.
[10] (a) S.B. Garber, J.S. Kingsbury, B.L. Gray, A.H. Hoveyda, J. Am. Chem. Soc. 122 (2000) 8168;
(b) S. Gessler, S. Randl, S. Blechert, Tetrahedron Lett. 41 (2000) 9973.
[11] H. Wakamatsu, S. Blechert, Angew. Chem. Int. Ed. 41 (2002) 2403.
[12] K. Grela, S. Harutyunyan, A. Michrowska, Angew. Chem. Int. Ed. 41 (2002) 4038.
[13] A. Michrowska, L. Gulajski, K. Grela, Chem. Commun. (2006) 841.
[14] (a) Y. Chauvin, H. Olivier-Bourbigou, Chem. Tech. 9 (1995) 26;
(b) H. Olivier-Bourbigou, L. Magna, J. Mol. Catal. A: Chem. 182 (2002) 419;
(c) D. Zhao, M. Wu, Y. Kou, E. Min, Catal. Today 74 (2002) 157;

(d) T. Welton, Coord. Chem. Rev. 248 (2004) 2459.
[15] (a) R.C. Buijsman, E. van Vuuren, J.G. Sterrenburg, Org. Lett. 3 (2001) 3785;
(b) K.J. Mayo, E.H. Nearhoof, J.J. Kiddle, Org. Lett. 9 (2002) 1567.
[16] (a) X. Ding, X. Lu, B. Hui, Z. Chen, M. Xiao, B. Guo, W. Tang, Tetrahedron Lett. 47 (2006) 2921;
(b) D.B.G. Williams, M. Ajam, A. Ranwell, Organometallics 25 (2006) 3088.
[17] (a) D. Sémeril, H. Olivier-Bourbigou, C. Bruneau, P.H. Dixneuf, Chem. Commun. (2002) 146;
(b) Sz. Csihony, C. Fischmeister, C. Bruneau, I.T. Horváth, P.H. Dixneuf, New J. Chem. 26 (2002) 1667.
[18] (a) N. Audic, H. Clavier, M. Mauduit, J.-C. Guillemin, J. Am. Chem. Soc. 125 (2003) 9248;
(b) H. Clavier, N. Audic, M. Mauduit, J.-C. Guillemin, Chem. Commun. (2004) 2282;
(c) H. Clavier, N. Audic, J.C. Guillemin, M. Mauduit, J. Organomet. Chem. 690 (2005) 3585.
[19] Q. Yao, Y. Zhang, Angew. Chem. Int. Ed. 42 (2003) 3395;
Q. Yao, M. Sheets, J. Organomet. Chem. 690 (2005) 3577.
[20] S.J. Connon, A.M. Dunne, S. Blechert, Angew. Chem. Int. Ed. 41 (2002) 3835.
[21] D.B. Williams, M.E. Stoll, B.L. Scott, D.A. Costa, W.J. Oldham, Chem. Commun. (2005) 1438.
[22] M. Zaja, S.J. Connon, A.M. Dune, M. Rivard, N. Buschmann, J. Jinicek, S. Blechert, Tetrahedron 59 (2003) 6545.