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Ionic imidazolium containing ruthenium complexes and olefin metathesis in ionic liquids

Cyril Thurier [a], Cédric Fischmeister [a], Christian Bruneau [a],
Hélène Olivier-Bourbigou [b], Pierre H. Dixneuf [a,*]

[a] *Laboratoire Catalyse et Organométalliques, Institut Sciences Chimiques de Rennes,*
UMR 6226 CNRS-Université de Rennes, Campus de Beaulieu, 35042 Rennes, France
[b] *IFP-Lyon, BP3, 69390 Vernaison, France*

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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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[*] Corresponding author.

E-mail addresses: Helene.olivier-bourbigou@ifp.fr (H. Olivier-Bourbigou), pierre.dixneuf@univ-rennes1.fr (P.H. Dixneuf).

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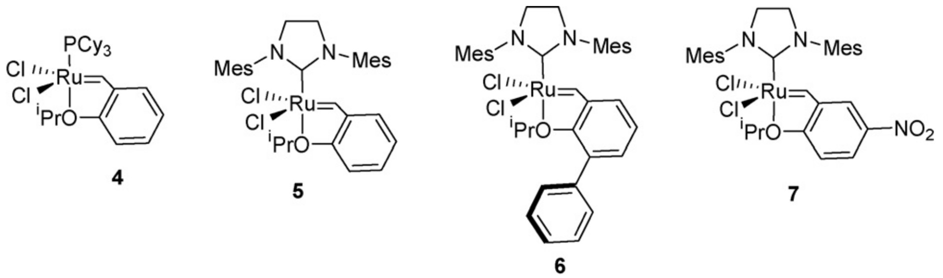

Fig. 1. Selected chelating alkylidene-ruthenium based olefin metathesis catalysts.

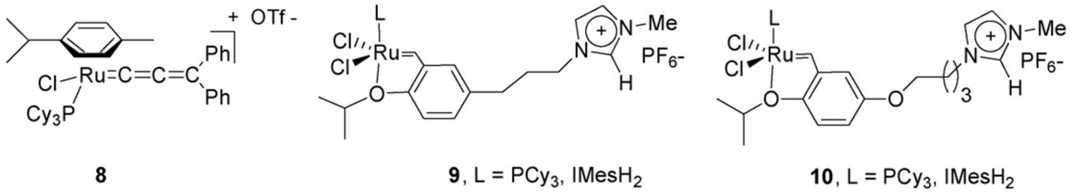

Fig. 2. Examples of ionic ruthenium catalysts operating in ionic liquids.

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.

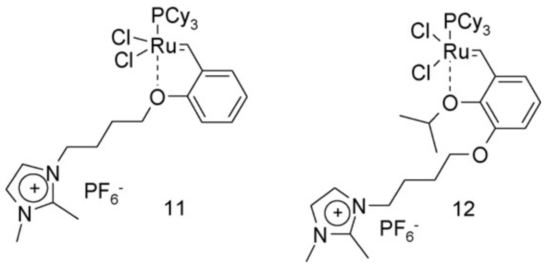

Fig. 3. Ruthenium catalysts with an ionic imidazolium branch.

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$_2$CO$_3$ (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$_2$O, 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$_2$Br: 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-