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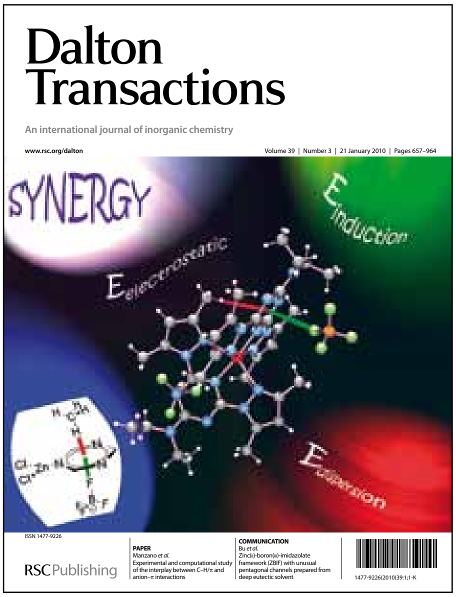

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ARTICLE TYPE

Ruthenium-based complexes containing benzimidazolium tag covalently connected to *N*-heterocyclic carbene ligands: environmentally friendly catalysts for olefin metathesis transformations

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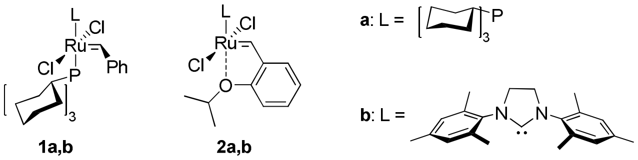
Two Ruthenium-based pre-catalysts containing ionic tag covalently connected to a *N*-heterocyclic carbene (NHC) ligand are reported. These novel complexes, bearing a polar benzimidazolium group, are air-stable and can be easily prepared from commercially available reagents. The quaternary benzimidazolium tag allows efficient separation of ruthenium wastes from the metathesis product after reaction. Application in several olefin metathesis transformations leads to desired products of high purity, which exhibit as low ruthenium contamination levels as 1 ppm after simple filtration through a pad of silica gel.

Introduction

In the past two decades, olefin metathesis has become an ineluctable powerful tool for synthetic organic chemistry[1]. Among the different metal-based complexes enabling to catalyse this transformation, homogeneous ruthenium pre-catalyst such as Grubbs **1a**,**b**[2] and Hoveyda–Grubbs **2a**,**b**[3] have widely contributed to the intensive use of this technology to make valuable molecules[4] (Scheme 1).



Scheme 1 Selected ruthenium precatalysts for alkene metathesis

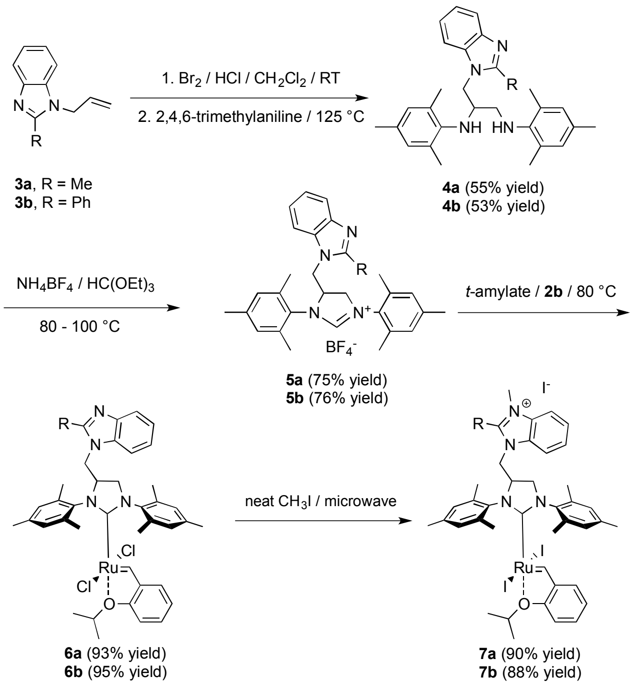
On the other hand, ruthenium-based complexes share common liability of all homogeneous transition metal-catalysed reactions, which is difficult separation of toxic metal side products[5]. Indeed, considering a catalytic process that involves 5 mol % of Ru pre-catalyst loading, the ruthenium content in the final product exceeds 2000 ppm[6] after purification by silica gel chromatography. As olefin metathesis reaction is commonly used in pharmaceutical processes and production of fine chemicals, ruthenium concentration levels have to be drastically decreased below 5 ppm[5]. To solve this issue and decrease ruthenium wastes, water extraction, scavengers[7], supported phosphines[8] or treatment with activated charcoal in combination with few cycles of chromatography[9] were proposed. However, the efficiency of these removal protocols remains moderate, giving around 100 to 1200 ppm of ruthenium contamination in the best cases. Other concepts based on catalysts immobilisation on various supports were also studied with more or less success.[10] Among them, strategies involving the introduction of polar or non-polar tags on phosphine[11], pyridine[12] or benzylidene[13] ligands showed promising results. Nevertheless, all these tag containing pre-catalysts operate on leaving ligands and active dichlororuthenium methylene species are logically disconnected from the support leading to the undesired Ru-leaching. Therefore, introduction of a tag to non-dissociative *N*-heterocyclic carbene ligand[14] (NHC) in second generation of Hoveyda type catalysts **2b** should allow enhanced separation and recovering of metathesis catalyst. This should promise environmentally friendly metathesis process with low ruthenium contamination. Surprisingly, only few examples of introduction of ionic tag on this ancillary ligand were reported[15]. In continuation of our program to develop ‘greener’ metathesis complexes, we report herein a new class of stable ruthenium homogeneous pre-catalysts that contain a *N*-methyl benzimidazolium tag covalently connected to the NHC fragment.

Results and discussion

Synthesis of ionically-tagged NHC ligand precursors and their related Ru-complexes

The general routes to *N*-heterocyclic carbene ligands (NHC) synthesis are well established[16]. However, as the NHC ligand precursor is intrinsically an (di)azolium function, the introduction of an additional ionic group is difficult to manage in a synthetic manner. Indeed, generation of the free carbene ligand requires strong bases (KHMDS for instance) that are incompatible with the presence of the spectator ionic tag. Irreversible side-reactions could occur such as the tag loss or, in some cases, the formation of corresponding bis-carbene species when the spectator ionic tag is an imidazolium function. Furthermore, certain reactions involved to build the heterocyclic framework of NHC precursors require generally the use of strong reducing reagents ($LiAlH_4$) or hard nucleophiles (Grignard and organozinc reagents) that are also incompatible with the ionic tag spectator. Taking in consideration all these problematic issues, we decided to develop a more suitable synthetic pathway providing the targeted ionically-tagged NHC based Ru-complexes. As depicted in the scheme 2, we started from the costless *N*-allyl benzimidazoles **3a-b**. The bromination under acidic conditions followed by the direct substitution using an excess of mesitylamine gave the desired diamines **4a-b** in 53% and 55% of yield respectively[17]. Subsequent treatment with ethylorthoformate in the presence of NH$_4$BF$_4$ yielded the NHC ligand precursors **5a-b** in 75% and 76%. The deprotonation of the imidazolium proton with potassium *t*-amylate in toluene followed by the addition of Hoveyda complex **2a** afforded the corresponding benzimidazole-grafted pre-catalysts **6a-b** in excellent isolated yields of 90 and 95%, respectively. Any attempts of quarternization with alkyl bromides, chlorides, tosylates and sultones up to 200°C under conventional heating or microwave conditions were unsuccessful. Hopefully, microwave irradiation of catalysts **6a-b** in neat methyl iodide at 120 °C led to the desired pre-catalysts **7a-b** in very good isolated yields (90% and 88%, respectively). However, this process resulted in a halogen exchange at ruthenium centre from dichloride to diodide, as witnessed the shift of benzylidene protons of 16.43 and 16.25 ppm for catalysts **6a-b** to 15.50 and 15.45 ppm for catalysts **7a-b**, respectively[18a]. It is well established that halides and more generally various anionic ligands are labile in solution, and these complexes undergo anionic ligand exchange even in non-protic media at room temperature [18b]. Apparently, elevated temperatures facilitate this exchange. All attempts to optimize the quarternization conditions to prevent the halogen exchange afforded inseparable mixture of dichloro, chloroiodo and diodo ruthenium complexes.

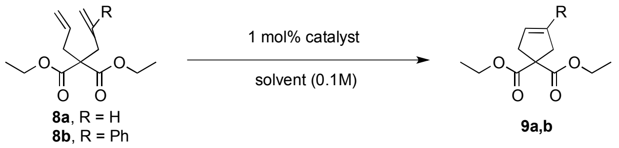
Therefore we decided to use stable diodide complexes **7a** and **7b**.



Scheme 2 Synthesis of desired complexes **7a-b**

Catalytic Performances

To compare relative activities of pre-catalysts **2b**, **6a-b** and **7a-b**, the ring-closing metathesis (RCM) of diallyl malonate (DEDAM) **8a** and diethyl-methallylallyl malonate (DEMAM) **8b** were investigated. As depicted in figure 1, RCM of **8a** performed under standard conditions (CH$_2$Cl$_2$ at 0.1M, 30 °C, 1 mol%)[19] showed that both the rate of metathesis reaction and the conversion were slightly lower for all new tagged-complexes, compared to the non-modified Hoveyda complex **2b**. Similar trends were also observed during the RCM of **8b** performed at 60 °C (figure 2). Considering the complexes **6a-b**, we suspect the presence of the free tertiary amine of the benzimidazole unit that is susceptible to chelate the Ru-active species. For the pre-catalysts **7a-b**, the lower reactivity is probably due to the presence of diodo anionic ligands that minimizes the catalytic performance of the resulting I$_2$(NHC)Ru-methylene species compared to their parent Cl$_2$(NHC)Ru-methylene counterparts[20].



Scheme 3 RCM reaction of DEDAM **8a** and DEMAM **8b**

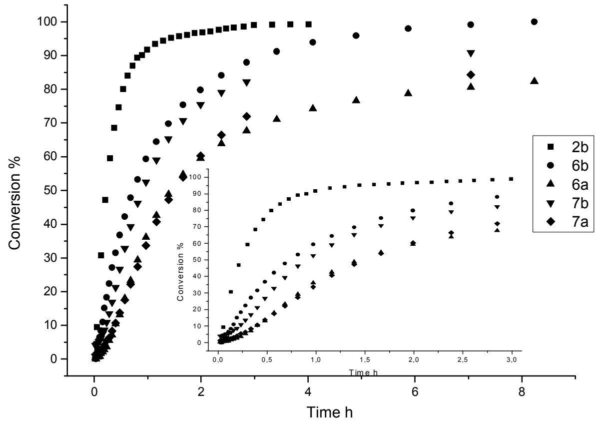


Figure 1 Kinetic profile of RCM of DEDAM **8a**, 1 mol % catalyst, CD$_2$Cl$_2$ (0.1M), 30 °C

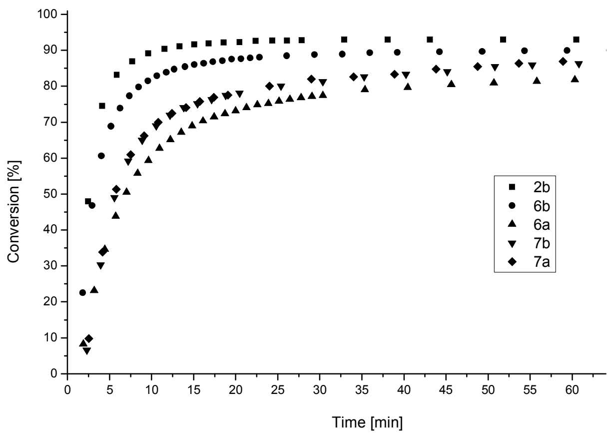
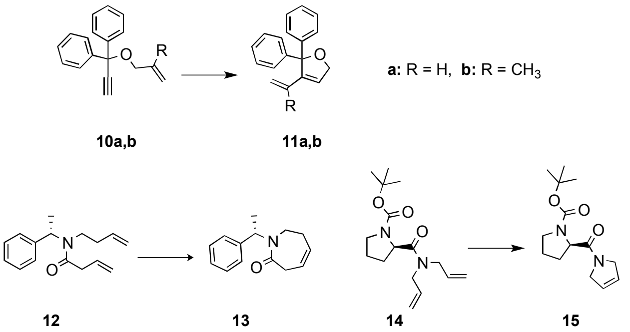
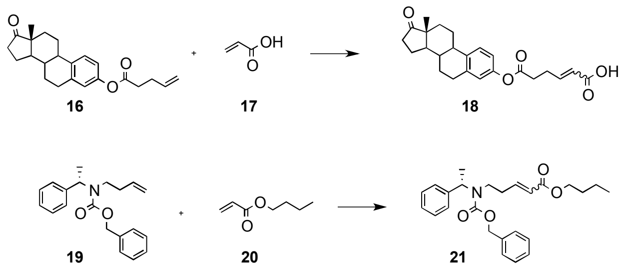


Figure 2 Kinetic profile of RCM of Diethyl 2-allyl-2-methallylmalonate **8b**, 1 mol % catalyst, toluene-D8 (0.1M), 60°C

To further compare catalysts **7a-b** and evaluate the possibility to remove easily residual Ru-wastes from the product, various olefin metathesis transformations were investigated. We selected ring-closing or enyne metathesis reactions involving substrates **10a-b**, **12**, **14** (Scheme 4) and cross-metathesis reactions involving olefins **16** and **19** (Scheme 5). Results are summarized in Table 1.



Scheme 4 Selected enyne and ring-closing metathesis reactions



Scheme 5 Selected cross-metathesis reactions

For enyne metathesis, the less-hindered substrate **10a** gave full conversion with 1 mol% loading of catalyst after 12 h at 80°C under conventional heating or after 30 min at 120°C using microwave irradiation. On the other side, despite the use of 5 mol % of **7a-b** in refluxing toluene over 24 h, only the starting-material **10b** was recovered. It should be noted, that this substrate is particularly difficult even for the most active catalysts [21]. Regarding RCM reactions, substrates **12** and **14** were tested. Cyclization proceeds smoothly with 1 mol% of catalysts at 40°C for 12h, affording respectively the corresponding metathesis products **13** and **15** in 87 to 95% of isolated yields.

Table 1 Representative metathesis reactions

Substrate[a]	**Catalyst**	**Loading** (mol%)	**Conditions**	**Conv.**[b]**/Yield**[c] (%)
10a	**7a**	1	12 h, 80 °C	98/95
	7a	1	0.5 h, 123 °C[d]	99/95
	7b	1	12 h, 80 °C	98/95
	7b	1	0.25 h, 123 °C[d]	93/89
10b	**7a**	5	24 h, 110 °C	0/96[e]
	7b	5	24 h, 110 °C	0/95[e]
12	**7a**	1	12 h, 40 °C	92/87
	7b	1	12 h, 40 °C	99/94
14	**7a**	1	12 h, 40 °C	94/90
	7b	1	12 h, 40 °C	99/95
16 + 4eq. **17**	**7a**	5	12 h, 80 °C	95/90[f]
	7b	5	12 h, 80 °C	98/93[g]
19 + 4eq. **20**	**7a**	5	12 h, 80 °C	97/90[h]
	7b	5	12 h, 80 °C	99/93[i]

[a] 1 mmol, toluene (0.1M). [b] Conversion monitored by ^{1}H NMR spectroscopy. [c] Isolated yields. [d] Microwave irradiation, 300 W. [e] Starting material recovered. [f] *E*/*Z* ratio= 3.5/1 [g] *E*/*Z* ratio= 3.7/1 [h] *E*/*Z* ratio= 2.4/1 [i] *E*/*Z* ratio= 2.7/1

Regarding Cross-metathesis transformation, the steroid like substrate **16** and functionalised-homoallyl amine **19** were reacted at 80°C in toluene over 12h with acrylic acid **17** and *n*-butylacrylate **20**, respectively. To obtain conversions >95% and excellent isolated yields (90-93%) in desired cross-metathesis products **18** and **21**, a catalyst loading of 5 mol% and 4 equivalents of electron-deficient olefin partners were necessary.

Ruthenium contamination in metathesis products

In order to remove the residual Ru-wastes, the reaction mixture was deposited on dry silica (2 g per 0.0025 mmol of catalyst used) and the metathesis product was eluted with appropriate solvent (Figure 3). The ruthenium content in selected metathesis products was quantified by ICPMS analyses[22] (table 2).

Table 2 Residual Ru content in selected products[a]

Product	**Catalyst**	**Loading** (mol%)	**Eluent**[b]	**Ru content** (ppm)[c]
11a	**7a**	1	Toluene	6.2
13	**7b**	1	cHex/EA 2/1	5.6
15	**7a**	1	cHex/EA 1/1	196
18	**7a**	5	EA	30
21	**7b**	5	Toluene	<1

[a] Reaction mixture filtrated through pad of silica (2g per 0.0025 mmol of catalyst) [b] EA = Ethyl Acetate, cHex = Cyclohexane [c] Determined by ICP-MS analysis[22].

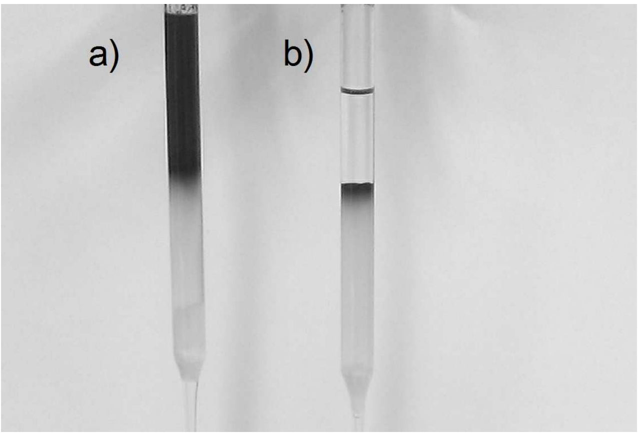


Figure 3 Separation of residual Ru catalyst/side products: a) deposition of reaction mixture on silica b) elution of product

As expected, the presence of highly polar *N*-methyl benzimidazolium tags on the NHC ancillary ligand in catalysts **7a-b** allowed very efficient separation of residual ruthenium side products as low as 1 ppm (product **21**). To obtain good separation and residual Ru content as low as possible, the choice of the eluent appears crucial but remains closely dependent on the nature of the organic product. Toluene, ethyl acetate (EA) or mixtures of cyclohexane/EA are tolerated. Remarkably, metathesis products **11**, **13** and **21** were isolated in excellent purity, containing only few ppm traces of metallic ruthenium. However, application of such flash-chromatography protocol for certain highly polar products such as **15** appeared more problematic despite the reduction of the eluent polarity (cyclohexane/EA 1/1; 196 ppm). On contrary, while pure ethyl acetate was necessary for recovering efficiently the lipidic product **21**, the filtration protocol remained suitable as the ruthenium content was drastically reduced down to 30 ppm.

Conclusions

Two new Hoveyda-type complexes bearing *N*-methyl benzimidazolium tag covalently connected to the NHC ligand were synthetized and fully characterized. The involved strategy using the quaternarisation of tertiary amine directly on the Ru-complex opens a promising way to generate new class of ionic-tag containing metal-NHC complexes. The catalysts **7a-b** were efficient for RCM, cross- and enyne metathesis of moderately hindered substrates. Nevertheless, they exhibited low activity towards sterically hindered olefins. In order to reach more efficient catalysts, further optimizations of the key quarternisation reaction on Ru-complex to avoid exchange of anionic co-ligand from chloride to iodide are currently underway. Moreover, thanks to the covalent grafting of highly polar benzimidazolium tag, easy and highly efficient separation of ruthenium wastes from the metathesis product through the simple filtration over small quantity of SiO_2 allowed decreasing residual metal concentration as low as 1 ppm. Therefore, compared to other Ru-removal protocols[23], ionic-tagged complexes **7a-b** might prove suitable olefin metathesis catalysts for pharmaceutical and other technologically advanced applications demanding low Ru content.

Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental procedures, characterization data and ^1H and ^{13}C NMR spectra for all previously unreported compounds.]. See DOI: 10.1039/b000000x/

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