NJC
Letter

In-situ generated three component ruthenium-based catalyst for ROMP

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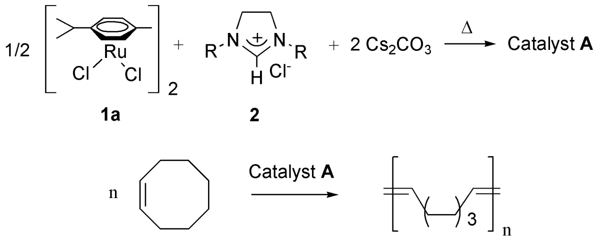
Received (in Montpellier, France) 2nd July 2002, Accepted 14th October 2002
First published as an Advance Article on the web 18th November 2002

The *in-situ* prepared three component system [RuCl$_2$(*p*-cymene)]$_2$/1,3-bis(*R*)-imidazolinium chloride/base (0.5/1/2) catalyses quantitatively the ROMP of cyclooctene at 80 °C for 20 min. After the activation of this catalytic system by preliminary heating at 80 °C in chlorobenzene for 1 h, the resulting catalyst was able to polymerise cyclooctene at room temperature. Other ruthenium sources have also been evaluated in similar *in-situ* prepared systems for ROMP.

Ring opening metathesis polymerisation (ROMP) constitutes an excellent tool to transform cyclic olefins into a variety of linear macromolecules, with regularly displayed double bonds and specific architectures.[1] This is due to the discovery of well-defined single-site alkene metathesis catalysts, such as alkylidene–molybdenum[2] and especially alkylidene–ruthenium catalysts tolerating a large variety of functional groups.[3–11] These ruthenium precatalysts contain a bulky electron-rich ligand and, linked in close proximity to the metal site, an alkylidene,[3,6,7,11] vinylidene,[8] allenylidene,[9] or alkylidyne[10] moiety, or an *in-situ* generated carbene from diazoalkane.[4] The introduction of bulky electron-rich imidazolylidene or imidazolinylidene ligands in ruthenium(II) catalyst precursors has opened a new door toward alkene metathesis and especially has led to the creation of efficient catalysts for ROMP.[6,12,13] These ligands attract interest as their specific geometry, well contrasting with that of bulky phosphines (*e.g.* PCy$_3$), may create or increase activity of the resulting coordinatively unsaturated ruthenium catalytic species.[14]

The straightforward preparation of RuCl$_2$(1,3-imidazolylidene)(arene) has recently been shown by simple reaction of the dinuclear complex [RuCl$_2$(arene)]$_2$ (**1**) with electron rich olefins, sources of non sterically hindered 1,3-imidazolylidene,[15,16] or with a source of bulky imidazolylidene such as a 1,3-bis(mesityl)imidazolium salt in the presence of a base.[17] By contrast, it was recently found that the corresponding reaction of **1** with a bulky non aromatic 1,3-imidazolinium salt in the presence of Cs$_2$CO$_3$ did not lead to the corresponding heterocyclic carbene–ruthenium complex but led to the discovery of a new *in-situ* prepared three component catalyst for alkene metathesis and fine chemistry.[18–21] Indeed, the ruthenium complex [RuCl$_2$(*p*-cymene)]$_2$ (**1a**), the imidazolinium chloride **2a** (R = mesityl) and the base Cs$_2$CO$_3$ in the molar ratio 0.5/1/2, led to the *in-situ* prepared, as yet unidentified catalyst **A** (Scheme 1), which promoted the selective transformation of enynes into conjugated alkenyl cycloalkenes,[18,19] and the ring closing metathesis of dienes in the presence of acetylene.[20,21] This *in-situ* prepared catalyst has not been used profitably in the related ROMP of cyclic olefins. We now wish to report that the combination of the ruthenium source **1a**, an imidazolinium salt **2** and Cs$_2$CO$_3$ leads to an efficient catalyst for high yield ROMP of cyclooctene at 80 °C and at room temperature after preliminary thermal activation of the catalytic system.



Scheme 1 Preparation of catalyst **A**.

The polymerisation of cyclooctene was studied with several types of catalysts based on the same ruthenium source [RuCl$_2$(*p*-cymene)]$_2$ (**1a**), with three different sterically hindered imidazolinium chlorides **2a**, **2b**, and **2c** (Fig. 1) and three different bases Cs$_2$CO$_3$, ^{t}BuOK, and NEt$_3$ in order to give evidence of the influence of the base and of the electron-rich carbene nature. The results are gathered in Table 1. All experiments were performed at 80 °C for 20 min and repeated at least twice. With the 1,3-bis(mesityl)imidazolinium salt **2a**, it was showed that NEt$_3$ inhibits the polymerisation (Table 1, entry 1), ^{t}BuOK gives relatively good yields (80%) with the highest M_n value (35×10^3) (entry 2), whereas Cs$_2$CO$_3$ leads to the best results in term of excellent polymer yield (92%), M_n value (28×10^3) and lower polydispersity (1.3) (entry 3). The nature of caesium carbonate appears to play a specific role, with respect to ^{t}BuOK, even if the M_n value is slightly smaller. Thus, Cs$_2$CO$_3$ not only deprotonates **2a**, but modifies the catalyst in a way that is not yet understood, possibly by substituting the chloride ligand(s) and/or favouring the displacement of *p*-cymene ligand. An experiment with the well established ruthenium ROMP catalyst RuCl$_2$(=CHPh)(PCy$_3$)$_2$[3] (**3**) was carried out under the same conditions for comparison with our catalytic systems (entry 8). It shows that the system **1a**/**2a** with Cs$_2$CO$_3$ (entry 3) gives better yield and

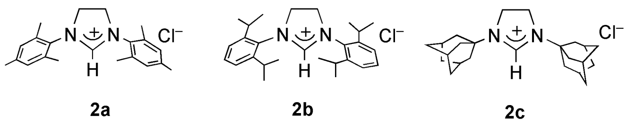


Fig. 1 Imidazolinium chlorides.

DOI: 10.1039/b206423p

Table 1 Cyclooctene polymerisation[a]

Entry	Imidazolinium salt	Base	Yield (%)	$10^{-3} \times M_n$[b]	PDI[c]	% *trans*[d]
1[e]	**2a**	NEt_3	0	—	—	—
2[e]	**2a**	^tBuOK	80	35	1.5	75
3[e]	**2a**	Cs_2CO_3	92	28	1.3	82
4[e]	**2b**	Cs_2CO_3	65	9	1.5	—
5[e]	**2c**	Cs_2CO_3	0	—	—	—
6[f]	**2a**	Cs_2CO_3	85	69	1.4	81
7[f]	**2a**	^tBuOK	50	41	1.3	78
8[e]	**3**		65	70	1.5	—

[a] General conditions: The catalyst was *in-situ* prepared from 7.5×10^{-6} mol of $[RuCl_2(p\text{-cymene})]_2$, 1.5×10^{-5} mol of the imidazolinium chloride, and 3.0×10^{-5} mol of base in 2.5 mL of chlorobenzene. Polymerisation was performed by addition of 4.5×10^{-3} mol of cyclooctene ([monomer]/[Ru] = 300). [b] Determined by GPC in THF *vs.* polystyrene standards. [c] Polydispersity index M_w/M_n. [d] Determined by ^{13}C NMR. [e] 20 min at 80 °C. [f] Activation 1 h at 80 °C and polymerisation 1 h at r. t.

polydispersity than **3** whereas the latter offers a higher M_n value (70×10^3)

The influence of the imidazolinium chlorides with the bulky groups R = mesityl (**2a**), 2,6-bis(isopropyl)phenyl (**2b**), and adamantyl (**2c**) was evaluated using the most favourable base Cs_2CO_3 in the polymerisation of cyclooctene. It is surprising that **2c** inhibits completely the polymerisation (Table 1, entry 5) whereas **2b** leads to moderate yield and molecular weight (entry 4). Thus the combination of **2a** and Cs_2CO_3 appears the best association for cyclooctene polymerisation when **1a** is used as source of the ruthenium (entry 3).

Activation of the ruthenium catalyst

The performance of cyclooctene polymerisation at room temperature remains a challenge, especially for the transformation of functionalised cyclooctene and for application to fragile cyclic olefins. In order to make a step in this direction we considered that in the previous experiments (Table 1), the heating of the ruthenium source **1a** with the *in-situ* generated bulky heterocyclic carbene might initially lead to the displacement of the arene, to generate a coordinatively unsaturated catalytic species of type RuX_2(carbene)(solvent or cyclooctene)$_n$. Indeed, the heating of benzimidazolinium salt with pendent aryl groups in the presence of **1a** and Cs_2CO_3 leads to the coordination of the formed carbene and to the intramolecular displacement of *p*-cymene ligand by the pendent aryl group.[22] Thus, in the absence of cyclooctene, the three component system $[RuCl_2(p\text{-cymene})]_2$/**2a**/$Cs_2CO_3$ (0.5/1/2) was first heated at 80 °C in 2.5 mL of PhCl for 1 h, during which time the solution colour changed from red to brown. After the solution was cooled to room temperature, the cyclooctene was added and the solution was stirred for 1 h at room temperature. Conversion was completed and good yield of polyoctenamer was obtained especially when Cs_2CO_3 was used as a base (Table 1, entry 6) with respect to ^tBuOK (entry 7). Under these conditions the catalyst gives access to high molecular weight $M_n = 69 \times 10^3$ (PDI = 1.4) for a theoretical $M_n = 33 \times 10^3$ thus showing that an average of 50% of ruthenium sites were active. Several efficient ruthenium catalysts successfully performed the ROMP of cyclooctene at room temperature such as the Herrmann catalyst $RuCl_2(=CHPh)\{1,3\text{-bis(mesityl)imidazolylidene}\}_2$ [95% after 1.5 h, $M_n = 266 \times 10^3$, PDI = 1.76],[6] the Grubbs catalyst $RuCl_2(=CHPh)(PCy_3)\{1,3\text{-bis(mesityl)imidazolinylidene}\}$ [total conversion in 30 min],[12] the binuclear Hofmann catalyst $[RuCl(=CHR)\{(^tBu)_2PCH_2P(^tBu)_2\}]_2[OTf]_2$ [95% after 20 min],[7] the Werner carbyne $[RuHCl(\equiv CMe)(OEt_2)(PCy_3)_2]BF_4$ [90% after 3 min],[10] the $RuCl_2$(imidazolylidene)(*p*-cymene) complex under visible light irradiation reported by Noels [99% after 2 h, $M_n = 537 \times 10^3$, PDI = 1.33][13] and the thermally activated allenylidene complex $[RuCl(=C=C=CPh_2)(PCy_3)(p\text{-cymene})][OTf]$. [97% after 10 min, $M_n = 151 \times 10^3$, PDI = 1.7].[23] Although the nature of the catalytic species arising from thermally activated catalyst **A** is not known, this approach to generate a catalyst operating at room temperature has potential for fragile functional cyclic olefins polymerisation.

Table 2 Norbornene polymerisation with *in-situ* generated catalysts from [Ru]/**2a**/Cs_2CO_3[a]

Entry	Ruthenium source	Yield (%)	$10^{-3} \times M_n$[b]	PDI[c]
1	$[RuCl_2(NBD)]_n$	99	12	1.7
2	$[RuCl_2(COD)]_n$	98	14	1.6
3	$RuCl_3{\cdot}xH_2O$	96	46	1.5
4	$RuCl_2(dmso)_4$	98	56	1.6
5	$[RuCl_2(p\text{-cymene})]_2$	97	13	1.5

[a] General conditions: The catalyst was *in-situ* prepared from 1.5×10^{-5} mol of [Ru], 1.5×10^{-5} mol of **2a**, and 3.0×10^{-5} mol of Cs_2CO_3 in 2.5 mL of chlorobenzene. Polymerisation was performed by addition of 4.5×10^{-3} mol of norbornene ([monomer]/[Ru] = 300) for 5 min at 60 °C. [b] Determined by GPC in THF *vs.* polystyrene standards. [c] Polydispersity index M_w/M_n.

Polymerisation based on various ruthenium sources

The present study shows the drastic influence of the nature of both N-heterocyclic carbene and the base. It can be predicted that another ruthenium source should modify significantly the catalyst activity. Thus, the same concept of *in-situ* prepared catalyst was applied to simple easily available ruthenium sources $RuCl_3{\cdot}xH_2O$, $[RuCl_2(NBD)]_n$ (NBD = norbornadiene), $[RuCl_2(COD)]_n$ (COD = 1,5-cyclooctadiene), and $RuCl_2(dmso)_4$ (dmso = dimethylsulfoxide). The previously most active imidazolinium salt **2a** and Cs_2CO_3 were added to the ruthenium precursor in the ratio [Ru]/**2a**/Cs_2CO_3 (1/1/2) to perform the polymerisation of norbornene and cyclooctene. The resulting *in-situ* prepared catalysts were directly used to polymerise 300 equivalents of norbornene (Table 2). The reaction performed at 60 °C in 2.5 mL of PhCl for only 5 min gives in each case complete conversion and $RuCl_3{\cdot}xH_2O$ and especially $RuCl_2(dmso)_4$ lead to high molecular weight with controlled polydispersity (1.5–1.7). A blank test was carried out in the absence of the imidazolinium salt to rule out any erroneous activity and less than 5% of polymer was formed.

The same *in-situ* prepared catalysts were evaluated for cyclooctene polymerisation which requires higher temperature (80 °C). The results are displayed in Table 3. After 20 min at

Table 3 Cyclooctene polymerisation with *in-situ* generated catalysts from [Ru]/**2a**/Cs_2CO_3[a]

Entry	Ruthenium source	Yield (%)	$10^{-3} \times M_n$[b]	PDI[c]
1	$[RuCl_2(NBD)]_n$	20	12	2.7
2	$[RuCl_2(COD)]_n$	30	4	1.1
3	$RuCl_3{\cdot}xH_2O$	48	39	1.5
4	$RuCl_2(dmso)_4$	80	73	1.4

[a] General conditions as in Table 2. Polymerisation was performed for 20 min at 80 °C. [b] Determined by GPC in THF *vs.* polystyrene standards. [c] Polydispersity index M_w/M_n.

80 °C complete conversion was not reached. However, $RuCl_3{\cdot}xH_2O$ and $RuCl_2(dmso)_4$ gave materials with good molecular weights. These results revealed that for cyclooctene polymerisation the use of the ruthenium source $[RuCl_2(p\text{-cymene})]_2$ is the best choice.

The above results show that for cyclooctene polymerisation at both 80 °C or, after thermal activation, at room temperature, the best catalytic system is made from the stable easy available components: $[RuCl_2(p\text{-cymene})]_2$/**2a**/$Cs_2CO_3$. These *in-situ* systems offer potential at the same time to raise hopes for the polymerisation of functional unstrained or fragile cyclic olefins and for the discovery of new catalytic systems by changing the ruthenium source.

Experimental

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Chlorobenzene was dried under P_2O_5 and distilled under argon prior to use. The ruthenium complexes were purchased directly from available commercial sources except **3** which was synthesised according to the literature procedure.[3] The imidazolinium salts were prepared as described in the literature.[24] Norbornene was used as purchased from commercial sources and cyclooctene was distilled from powdered NaOH and stored under argon with 4 Å molecular sieves.

Polymerisation of cycloolefins

Method A. 1.5×10^{-5} mol of [Ru] complex, 1.5×10^{-5} mol of the imidazolinium chloride, and 3.0×10^{-5} mol of the corresponding base were dissolved in 2.5 mL of dry chlorobenzene under argon atmosphere. Freshly distilled monomer (4.5×10^{-3} mol) was added immediately and the suspension was stirred for 20 min at 80 °C. After reaction, the resulting viscous mixture was dissolved with 20 mL of $CHCl_3$ containing 0.1% of 2,6-di-*tert*-butyl-4-methylphenol (BHT) and 0.3 mL of vinyl ether. Then the solution was poured in 200 mL of methanol to precipitate the polymer. The crude product was further purified by using silica gel column chromatography and reprecipitation in MeOH (200 mL, containing 0.1% BHT) to give the polymer as a white solid, which was collected by filtration, dried under vacuum, and characterised by ^{1}H and ^{13}C NMR and GPC calibrated from polystyrene standards.

Method B. 7.5×10^{-6} mol of $[RuCl_2(p\text{-cymene})]_2$ complex, 1.5×10^{-5} mol of the imidazolinium chloride, and 3.0×10^{-5} mol of the corresponding base were dissolved in 2.5 mL of dry PhCl under argon atmosphere. The reaction was heated to 80 °C for 1 h and when the solution had cooled to 20 °C, 4.5×10^{-3} mol of cyclooctene was added and the solution was stirred for 1 h at r.t. The resulting polymer was purified as described in method A.

Acknowledgements

The authors are grateful for support to the European Union within the EU network POLYCAT (UPRN-CT-2000-00010), the COST-Chemistry Program D17 (0003/00), and the Region Bretagne for support within the Regional program PRIR (No. 169 AOC).

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