Letter

New two component catalytic system for ROMP of cycloolefins: ruthenium(methallyl)$_2$(diphosphine)/imidazolinium salt

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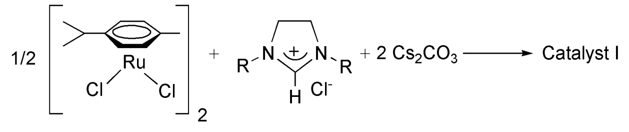
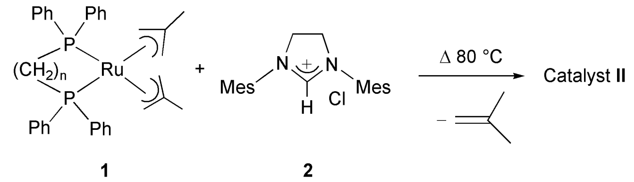
A new *in-situ* generated catalytic system for the ROMP of cycloalkenes is prepared by combination of Ru(methallyl)$_2$ {Ph$_2$P(CH$_2$)$_n$PPh$_2$} (n = 1, 2, 4, 6) and a bulky 1,3-bis(2,4,6-trimethylphenyl)imidazolinium salt. Cyclooctene is polymerised at 80 °C for 20 min in 75–88% yield or at room temperature, after the activation of this catalytic system by preliminary heating at 80 °C in chlorobenzene.

Ring opening metathesis polymerisation (ROMP) has become a useful tool for the synthesis of macrocycles and polymers that have CH=CH bonds and functional groups regularly distributed.[1–3] Over the last decade, ruthenium-based catalysts for alkene metathesis have tremendously contributed to the development of polymer chemistry *via* the ROMP process. In particular, the alkylidene complexes RuCl$_2$(=CHR)(PCy$_3$)$_2$[4,5] have played a key role and their catalytic activity has been recently increased by the replacement of a hindered phosphine by a more electron-donating and bulky N-heterocyclic carbene ligand, such as 1,3-bis(R)imidazol-2-ylidene.[6–12] Excellent catalytic performance in ROMP was also found by electron-rich and hindered chelating diphosphine–ruthenium complexes with an alkylidene moiety [RuCl(=CHR)(^{t}Bu$_2$PCH$_2$-P^{t}Bu$_2$)]$_2$[OTf]$_2$[13,14] or RuCl$_2$(=CHPh){R$_2$P(CH$_2$)$_n$PR$_2$}.[15] It is noteworthy that the precursors Ru{η^3-methallyl}$_2${Cy$_2$-P(CH$_2$)$_n$PCy$_2$} were able to perform the norbornene polymerisation at room temperature in modest yield, but without the initial help of an alkylidene ligand or reagent initiator.[16] These observations motivated the search for new efficient ROMP initiators from readily available simple ruthenium–diphosphine precursors associated with an electron releasing bulky heterocyclic carbene.

The possibility to *in-situ* generate catalytic systems from readily available and stable reagents is an important challenge. A simple three component *in-situ* generated catalyst for alkene metathesis, based on a stable source of ruthenium species [RuCl$_2$(arene)]$_2$, a precursor of hindered electron-donating carbene, the 1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride, and Cs$_2$CO$_3$ (catalyst **I**), has recently been reported (Scheme 1).[17,18] We now present a new ROMP initiator, easily made by the *in-situ* combination of two components, Ru{η^3-CH$_2$C(CH$_3$)=CH$_2$}$_2${Ph$_2$P(CH$_2$)$_n$PPh$_2$} (**1**) and 1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride (**2**) (1:1), (catalyst **II**, Scheme 2), able to perform both norbornene and cyclooctene polymerisation. The precursor **1**, directly obtained from the commercial complex Ru{η^3-CH$_2$C(CH$_3$)=CH$_2$}$_2$(cyclooctadiene) **3**,[19] possesses allyl groups that are expected to promote the generation of the carbene by protonation with **2** and thus replace the use of an additional base.[20]



Scheme 1



Scheme 2

The initial study of the ROMP of norbornene revealed the catalytic activity of the system based on the complexes Ru{η^3-CH$_2$C(CH$_3$)=CH$_2$}$_2${Ph$_2$P(CH$_2$)$_n$PPh$_2$} {n = 1 (**1a**), 2 (**1b**), 4 (**1c**), 6 (**1d**)} and the imidazolinium salt (**2**) (1:1). The catalytic system in chlorobenzene was loaded with 300 equiv. of norbornene and heated at 80 °C. Only 2 min were necessary for the polymerisation of norbornene in quantitative yield for the four precursors **1a**–**d** (M_n = 308–636 × 10^3) with relatively low polydispersity (PDI = 1.3–1.7) (Table 1, entries 3–6). It is noteworthy that the variation of the alkyl bridge of the chelating diphosphine ligand has a strong influence on the polymer average molar mass. In particular the shortest bridges (**1a**–**b**) led to high M_n values. It was checked that the presence of the imidazolinium salt is essential as with the complex **1c** alone a slight amount of polymer (5%) was obtained after 24 h at 80 °C (Table 1, entry 1), by contrast to the electron-rich precursor Ru(η^3-methallyl)$_2${Cy$_2$P(CH$_2$)$_n$PCy$_2$} (25 h at rt,

Table 1 ROMP of norbornene by *in-situ* prepared precursors[a]

Entry	Catalyst precursor	Conditions	Yield (%)	$10^{-3} \times M_n$[b]	PDI[c]
1	**1c**	24 h 80 °C	5	153	2.0
2	**1c** + **2** + Cs$_2$CO$_3$	2 min 80 °C	97	275	1.7
3	**1a** + **2**	2 min 80 °C	99	610	1.3
4	**1b** + **2**	2 min 80 °C	99	636	1.3
5	**1c** + **2**	2 min 80 °C	98	308	1.7
6	**1d** + **2**	2 min 80 °C	99	374	1.5

[a] General conditions: the catalyst was *in-situ* prepared from 1.5 × 10^{-5} mol of **1**, 1.5 × 10^{-5} mol of **2**, (and 3.0 × 10^{-5} of Cs$_2$CO$_3$ for entry 2) in 2.5 mL of chlorobenzene ([monomer]/[Ru] = 300). [b] Determined by GPC in THF *vs.* polystyrene standards. [c] Polydispersity index M_w/M_n.

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Table 2 ROMP of cyclooctene by *in-situ* prepared precursors[a]

Entry	Catalyst precursor	[monomer]/[ruthenium]	Yield (%)	$10^{-3} \times M_n$[b]	PDI[b]	% *cis*[c]
1	**1c** + **2** + Cs$_2$CO$_3$	300	73	182	1.8	45
2	**1a** + **2**	300	78	518	1.3	45
3	**1b** + **2**	300	75	542	1.3	43
4	**1c** + **2**	300	88	358	1.6	40
5	**1d** + **2**	300	80	354	1.4	45
6	**1c** + **2**	600	85	330	1.4	—
7	**1c** + **2**	900	80	314	1.5	—
8	**1c** + **2**	1200	82	343	1.5	44
9	**3** + **2**	300	60	112	1.9	42
10	**4** + **2** + Cs$_2$CO$_3$	300	92	28	1.3	18

[a] Polymerisation at 80 °C for 20 min. [b] See details in Table 1. [c] Determined by ^{13}C NMR.

16–61% yield, $M_n = 210\text{–}380 \times 10^3$).[16] This shows the profitable effect of the carbene ligand associated with a less electron-rich ruthenium–diphosphine precursor. The presence of Cs$_2$CO$_3$ did not significantly modify the ROMP activity of the two component system (Table 1, compare entries 2 and 5).

The new initiators based on **1** and **2** were evaluated for the more difficult to perform polymerisation of cyclooctene. The polymerisation reactions were carried out at 80 °C and after 20 min a gel was formed from which polyoctenamers were obtained in 75 to 88% yields (Table 2, entries 2–5). It is noteworthy that the short alkyl bridging chains (n = 1, 2, **1a**–**b**) resulted in high M_n values whereas longer bridges (n = 4, 6, **1c**–**d**) gave lower M_n values. Thus, the selection of the diphosphine constitutes an easy way to control the molecular weight by contrast to catalyst **I**.[21] The presence of the base Cs$_2$CO$_3$ is not required as it gives even lower yield and M_n value (Table 2, compare entries 1 and 4).

The system Ru(methallyl)$_2$(cyclooctadiene) (**3**), the precursor of complexes **1**, with **2** is also active for ROMP of cyclooctene but with much lower activity (Table 2, entry 9) and shows the beneficial role of the diphosphine ligand. However, the two component catalyst **II** is less active than the Grubbs catalyst RuCl$_2$(=CHR)(PCy$_3$){=C$\overline{\text{N(2,4,6-trimethylphenyl)CH}_2\text{CH}_2\text{N}}$-(2,4,6-trimethylphenyl)} ([monomer]/[initiator] = 10.000, 30 min rt, insoluble)[8] but allows higher molecular weights to be obtained than the three component system [RuCl$_2$(*p*-cymene)]$_2$ (**4**)/**2**/Cs$_2$CO$_3$ (Table 2, entry 10).[21]

The generation of the initiator (catalyst **II**) can be explained by the presence of η^3-allyl ligands, that are easily released as isobutene on protonation of complex **1** with the imidazolinium salt leading to a carbene ligand (Scheme 2). Indeed, it is now established that imidazolinium salts can be deprotonated by the weak base Cs$_2$CO$_3$, in the presence of [RuCl$_2$(*p*-cymene)]$_2$, to afford Ru(imidazol-2-ylidene)Cl$_2$(arene).[22] The reaction between **1c** and **2** was monitored by ^{1}H and ^{31}P NMR in a mixture of PhCl and CDCl$_3$ and after 20 min at 80 °C up to 90% of cyclooctene was polymerised. The ^{31}P NMR spectrum showed that 90% of the starting material **1c** (45.4 ppm) remained unreacted and a new signal appeared at 50.7 ppm showing that only a small amount of the complex had reacted with the imidazolinium salt. Indeed, the comparison between the theoretical (33×10^3) and experimental (358×10^3) M_n values indicates that only 9% of ruthenium sites have initiated polymerisation. When the monomer/ruthenium ratio is increased from 600 to 1200, by decreasing the catalyst amount, it does not result in an important change of the M_n values (Table 2, entries 6–8). This demonstrates the low percentage in the formation of the initiator species but its very high activity.

It appeared that all the potential of the system was not developed in 20 min at 80 °C, thus a previous activation of the system **1c**/**2** was attempted in the absence of cycloolefin by heating the mixture **1c**/**2** (1:1) in chlorobenzene for 2 h at 80 °C. To the resulting solution at room temperature was added freshly distilled cyclooctene and the suspension was stirred for 2 h. Polymerisation took place at 23 °C and the polyoctenamer was isolated in 50–62% yield (Table 3).

Table 3 ROMP of cyclooctene at room temperature[a]

Entry	Catalyst precursor	Yield (%)	$10^{-3} \times M_n$[b]	PDI[b]	% *cis*[b]
1	**1a** + **2**	58	365	1.8	42
2	**1b** + **2**	50	415	1.6	38
3	**1c** + **2**	60	353	1.5	35
4	**1d** + **2**	62	253	1.4	40

[a] Conditions: 2 h 80 °C before addition of cyclooctene, 2 h rt. [b] See details in Tables 1 and 2.

The above results show that the addition of one equiv. of the imidazolinium chloride **2** to the easily accessible and stable bis(allyl)ruthenium–diphosphine complex **1** significantly promotes the cyclooctene polymerisation with high molecular weight. The action of a base is no longer necessary, probably due to the presence of allyl groups. This system shows potential for the ROMP of functional cyclic alkenes at room temperature and for fine chemistry. Studies focusing on the characterisation of catalytic species are currently under way.

Experimental

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Chlorobenzene was dried over P$_2$O$_5$ and distilled under argon prior to use. The ruthenium complex **3** was obtained directly from available commercial sources. Complexes **1a**–**d**[19] and the imidazolinium salts[23] were synthesised according to the literature. Norbornene was used as received from commercial sources. Cyclooctene was distilled from powdered NaOH and stored under argon over 4 Å molecular sieves.

Polymerisation of cycloolefins

Method A. 1.5×10^{-5} mol of ruthenium complex (**1**) and 1.5×10^{-5} mol of the 1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride (**2**) were mixed in 2.5 mL of dry PhCl under argon atmosphere. Freshly distilled monomer (4.5×10^{-3} mol) was added immediately and the suspension was stirred at the desired temperature. 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 ethyl vinyl ether. The solution was poured in 300 mL of methanol to precipitate the polymer, which was collected by filtration, dried under vacuum, and characterised by ^{1}H and ^{13}C NMR. Average molecular weights were determined using GPC calibrated with polystyrene standards.

Method B. 1.5×10^{-5} mol of **1** and 1.5×10^{-5} mol of **2** were dissolved in 2.5 mL of dry PhCl under argon atmosphere. The reaction was heated to 80 °C for 2 h and when the solution had cooled down to 23 °C, 4.5×10^{-3} mol of cyclooctene was added and the solution was stirred for 2 h at rt. The resulting polymer was purified as described in method A.

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References

1 M. R. Buchmeiser, *Chem. Rev.*, 2000, **100**, 1565.
2 A. Fürstner, *Angew. Chem., Int. Ed.*, 2000, **39**, 3012.
3 T. M. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, 2001, **34**, 18.
4 S. T. Nguyen, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1993, **115**, 9858.
5 P. Schwab, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1996, **118**, 100.
6 T. Weskamp, W. C. Schattenmann, M. Spiegler and W. A. Herrmann, *Angew. Chem., Int. Ed.*, 1998, **37**, 2490.
7 J. Huang, H.-J. Schanz, E. D. Stevens and S. P. Nolan, *Organometallics*, 1999, **18**, 5375.
8 C. W. Bielawski and R. H. Grubbs, *Angew. Chem., Int. Ed.*, 2000, **39**, 2903.
9 S. B. Garber, J. S. Kingsbury, B. L. Gray and A. H. Hoveyda, *J. Am. Chem. Soc.*, 2000, **122**, 8168.
10 S. Gessler, S. Randl and S. Blechert, *Tetrahedron Lett.*, 2000, **41**, 9973.
11 A. Fürstner, O. R. Thiel and C. W. Lehmann, *Organometallics*, 2002, **21**, 331.
12 H. Wakamatsu and S. Blechert, *Angew. Chem., Int. Ed.*, 2002, **41**, 2403.
13 S. M. Hansen, M. A. O. Volland, F. Rominger, F. Eisenträger and P. Hofmann, *Angew. Chem., Int. Ed.*, 1999, **38**, 1273.
14 M. A. O. Volland, C. Adlhart, C. A. Kiener, P. Chen and P. Hofmann, *Chem. Eur. J.*, 2001, **7**, 4621.
15 D. Amoroso and D. E. Fogg, *Macromolecules*, 2000, **33**, 2815.
16 C. Six, K. Beck, A. Wegner and W. Leitner, *Organometallics*, 2000, **19**, 4639.
17 D. Sémeril, M. Cléran, C. Bruneau and P. H. Dixneuf, *Adv. Synth. Catal.*, 2001, **343**, 184.
18 D. Sémeril, C. Bruneau and P. H. Dixneuf, *Helv. Chim. Acta*, 2001, **84**, 3335.
19 J. Höfer, H. Doucet, C. Bruneau and P. H. Dixneuf, *Tetrahedron Lett.*, 1991, **32**, 7409.
20 D. S. McGuiness, K. J. Cavell, B. F. Yates, B. W. Skelton and A. H. White, *J. Am. Chem. Soc.*, 2001, **123**, 8317.
21 R. Castarlenas, I. Alaoui-Abdallaoui, D. Sémeril, B. Mernari, S. Guesmi and P. H. Dixneuf, *New J. Chem.* , in press (DOI: 10.1039/b206423p).
22 B. Çetinkaya and I. Özdemir, personal communication.
23 A. J. Arduengo, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall and M. Unverzagt, *Tetrahedron*, 1999, **55**, 14 523.