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Allenylidene-ruthenium-arene precatalyst for ring opening metathesis polymerisation (ROMP)

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Dedicated to professor Pascual Royo on the occasion of his 65th birthday

Abstract

The ruthenium allenylidene complex [RuCl(=C=C=CPh$_2$)(PCy$_3$)(*p*-cymene)][OTf] constitutes an excellent precatalyst for the ROMP at room temperature of norbornene ($M_n = 198 \times 10^3$, PDI = 1.8) and cyclooctene ($M_n = 143 \times 10^3$, PDI = 1.9). The activation of the precatalyst by initial heating (25 min, 60 °C) generates a catalytic species that operates at room temperature to produce in 10 min 90% of polyoctenamer ($M_n = 151 \times 10^3$, PDI = 1.7).

Keywords: Ruthenium catalyst; Allenylidene; ROMP; Polymerisation; Cyclic olefins

1. Introduction

The ring opening metathesis polymerisation (ROMP) of cyclic olefins constitutes an excellent method to synthesise linear polymers with regularly disposed CH=CH double bonds [1–3] that can be functionalised or hydrogenated [4,5]. It has also the potential to polymerise functional cyclic olefins when function tolerant catalysts are found [6,7]. The ROMP of cyclic olefins has made a tremendous profit of the discovery of well-defined ruthenium-alkylidene precatalysts for alkene metathesis for fine chemistry such as the Grubbs RuCl$_2$(=CHR)(PCy$_3$)L [8,9] and Noels RuCl$_2$(L)(*p*-cymene)–N$_2$CHSiMe$_3$ complexes [6,7,10] (L = PCy$_3$, imidazolinylidene). Recently, a new type of alkene metathesis precatalysts, the ionic 18 electron ruthenium allenylidene complexes [RuCl(=C=C=CAr$_2$)(PCy$_3$)(*p*-cymene)][X] [11] have shown to promote ring closing metathesis (RCM) of dienes [11–13] as well as cyclisation with skeleton rearrangement of enynes [13–15]. However, their potential in ROMP has not been evaluated in spite of the possible recovery or recycling of the catalyst [16]. Furthermore, a few ruthenium allenylidene complexes have been shown to be active in alkene metathesis [17–20]. Now we report the first uses of ionic allenylidene-ruthenium catalyst in ROMP and we show the efficient polymerisation of cyclooctene under mild conditions.

2. Results and discussion

Two types of ruthenium-allenylidene precatalysts have been studied, the in-situ prepared catalyst **A** and the isolated catalyst **B**. The catalyst **A** is simply made by reaction of [RuCl(PCy$_3$)(*p*-cymene)][OTf], arising from the treatment of RuCl$_2$(PCy$_3$)(*p*-cymene) with AgOTf, with 1.1 equivalent of propargyl alcohol HC≡C–C(OH)Ph$_2$ in chlorobenzene for 15 min at room temperature, and *used as such* in polymerisation. The catalyst **B** is prepared by reaction of the same ruthenium precursor with the 1,1-diphenylpropargyl alcohol in

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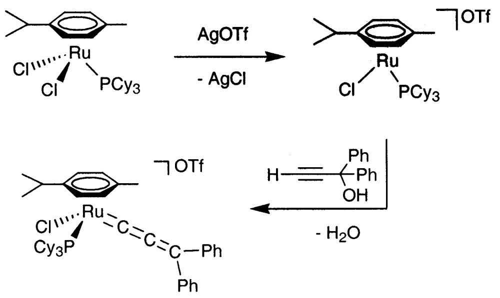


Scheme 1.

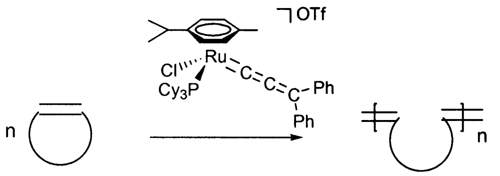
dichloromethane but isolated by precipitation in diethylether [11] (Scheme 1).

2.1. Norbornene polymerisation

The polymerisation of norbornene was first attempted with catalysts **A** and **B** (Scheme 2). The polymerisation of 4.5 × 10^{-3} mol of norbornene with 1.5 × 10^{-5} mol of in-situ prepared catalyst **A** in 35 ml of PhCl at 60 °C led to partial conversion (Table 1, entry 1). However, complete conversion and high yield of polymer, but with high polydispersity, were obtained at 60 °C when 1 ml of carbene precursor $N_2CHSiMe_3$ (0.1 M) was used (Table 1, entry 2). The same polymerisation can be achieved more efficiently at room temperature when a 14 times more concentrated solution of pure catalyst **B** was used (Table 1, entry 3). The latter conditions seem appropriate for generating high molecular weight ($M_n = 198 \times 10^3$) with lower polydispersity (1.8).

2.2. Cyclooctene polymerisation

The polymerisation of unstrained olefins such as cyclooctene is usually more difficult to perform. Catalyst **A** promotes the polymerisation of cyclooctene at room temperature provided that UV irradiation is used for 2 h (Table 2, entries 1 and 2). By contrast, when polymerisation is performed by catalyst **B** with larger cyclooctene-ruthenium ratio (1000), 15 h at room temperature are necessary to produce similar polymer ($M_n = 143 \times 10^3$, PDI = 1.9). It is noteworthy that at 80 °C, quantitative polymerisation is reached after 5 min only (Table 2, entry 4). At this temperature, catalyst **B** appears very efficient but not every molecule of complex is active. Indeed, high molecular weight can be obtained ($M_n = 267 \times 10^3$ vs. theoretical $M_n = 110 \times 10^3$) showing that only an average of 41% of ruthenium species promote the polymerisation. Under these conditions, catalyst **B** allows the formation of high molecular weight with low polydispersity (1.4). The above results shows that the ionic precatalyst **B** is much more active than the neutral and ionic ruthenium-allenylidenes, containing DMSO ligands $RuCl_2(=C=C=CAr_2)(PCy_3)_2(DMSO)$ and $[RuCl(=C=C=CPh_2)(PCy_3)(DMSO)_2][OTf]$ [17].



Scheme 2.

2.3. Activation of ruthenium-allenylidene catalyst

It was observed that the 18 electron catalyst **B** releases the arene ligand on heating to produce coordinatively unsaturated active species [11,14]. The preliminary displacement of arene was attempted. Another form of 'activated' catalyst, catalyst **C**, was obtained by heating the precatalyst **B** in chlorobenzene in the absence of cyclooctene. Thus, 3 × 10^{-5} mol of precatalyst **B** in 2.5 ml of PhCl was heated under inert atmosphere for 25 min at 60 °C. The solution colour changed from violet to brown and, after the solution had cooled down to 20 °C, 4.5 × 10^{-3} mol of cyclooctene was added. After 10 min at room temperature, 97% of polymer was formed (Table 2, entry 5). The thermal activation of precatalyst **B** generates a new catalytic species (**C**), of which the structure is still unknown, as it allows the cyclooctene polymerisation at room temperature in a very short time.

The above ROMP experiments show that $[RuCl(=C=C=CPh_2)(PCy_3)(p\text{-cymene})][OTf]$ is an excellent precatalyst for the cyclooctene polymerisation either at 80 °C or at room temperature after activation.

3. 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 Ar prior to use. The starting complex $[RuCl(PCy_3)(p\text{-cymene})][OTf]$ was synthesised as described in the literature [11]. Norbornene was used as purchased from comercial sources and cyclooctene was distilled from powdered NaOH and stored under Ar with 4 Å molecular sieves.

3.1. Preparation of catalyst A

An orange solution of 11 mg (1.5 × 10^{-5} mol) of $[RuCl(PCy_3)(p\text{-cymene})][OTf]$ in 35 or 5 ml of PhCl was treated with 3.5 mg (1.7 × 10^{-5} mol) of the 1,1-diphenylpropargyl alcohol $HC{\equiv}C{-}C(OH)Ph_2$. The violet resulting solution was kept stirring for 15 min at room temperature before the addition of the corresponding monomer.

Table 1
Norbornene polymerisation with precatalysts **A** and **B**

Catalyst	Ratio [a]	Conditions	Yield (%)	$10^{-3} \times M_n$ [b]	PDI [c]	% cis [d]
A	300 [e]	4 h 60 °C [f]	35	175	2.7	19
A + $N_2CHSiMe_3$ [g]	300 [e]	4 h 60 °C [f]	90	92	3.4	27
B	1000 [h]	5 min r.t. [i]	90	198	1.8	25

[a] Molecular norbornene/catalyst.
[b] Determined by GPC in THF vs. polystyrene standards.
[c] Polydispersity index M_w/M_n.
[d] Determined by ^{1}H-NMR.
[e] 1.5×10^{-5} mol of ruthenium catalyst.
[f] 35 ml of PhCl.
[g] 0.1 mmol of $N_2CHSiMe_3$.
[h] 4.5×10^{-6} mol of ruthenium catalyst.
[i] 2.5 ml of PhCl.

3.2. Preparation of catalyst **B**

This catalyst was prepared as described in literature [11].

3.3. Preparation of catalyst **C**

A violet solution of 26 mg (3×10^{-5} mol) of precatalyst [RuCl(=C=C=CPh$_2$)(PCy$_3$)(*p*-cymene)][OTf] in 2.5 ml of PhCl was heated under inert atmosphere for 25 min at 60 °C. The solution colour changed from violet to brown, and after the solution had cooled down to 20 °C, cyclooctene was added.

3.4. Polymerisation of cycloolefins

The corresponding amount of catalyst **A**, **B** or **C** and 4.5×10^{-3} mol of the corresponding monomer were dissolved in freshly distilled PhCl and the solution was stirred at the desired temperature. After the 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 MeOH to precipitate the polymer. The crude product was further purified using silica gel column chromatography using $CHCl_3$ containing 0.1% of BHT as eluent. The solution was poured into a vigorously stirred 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.

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Table 2
Cyclooctene polymerisation with precatalysts **A**, **B**, and **C**

Catalyst	Ratio [a]	Conditions	Yield (%)	$10^{-3} \times M_n$ [b]	PDI [c]	% cis [d]
A	150 [e]	2 h r.t. [f]	12	–	–	–
A	150 [e]	r.t./UV [g]	99	143	1.8	–
B	1000 [h]	15 h r.t. [i]	95	143	1.9	27
B	1000 [h]	5 min 80 °C [i]	90	267	1.4	22
C	150 [e]	10 min r.t. [j]	97	151	1.7	–

[a] Molecular ratio cyclooctene/catalyst.
[b] Determined by GPC in THF vs. polystyrene standards.
[c] Polydispersity index M_w/M_n.
[d] Determined by ^{13}C-NMR.
[e] 3×10^{-5} mol of ruthenium catalyst.
[f] 5 ml of PhCl.
[g] 5 ml PhCl, 2 h r.t. + 2 h r.t./UV.
[h] 4.5×10^{-6} mol of ruthenium catalyst.
[i] 2.5 ml PhCl.
[j] Prepared by heating of **B** in 2.5 ml of PhCl for 25 min at 60 °C.

References

[1] R.R. Schrock, Acc. Chem. Res. 23 (1990) 158.
[2] R.M. Buchmeiser, Chem. Rev. 100 (2000) 1565.
[3] A. Fürstner, Angew. Chem. Int. Ed. Engl. 39 (2000) 3013.
[4] C.W. Bielawski, J. Louie, R.H. Grubbs, J. Am. Chem. Soc. 122 (2000) 12872.
[5] S.D. Drouin, F. Zamanian, D.E. Fogg, Organometallics 20 (2001) 5495.
[6] A.W. Stumpf, E. Saive, A. Demonceau, A.F. Noels, J. Chem. Soc. Chem. Commun. (1995) 1127.
[7] A. Demonceau, A.W. Stumpf, E. Saive, A.F. Noels, Macromolecules 30 (1997) 3127.
[8] P. Schwab, R.H. Grubbs, J.W. Ziller, J. Am. Chem. Soc. 118 (1996) 100.
[9] C.W. Bielawski, R.H. Grubbs, Angew. Chem. Int. Ed. Engl. 39 (2000) 2903.
[10] L. Delaude, A. Demonceau, A.F. Noels, Chem. Commun. (2001) 986.
[11] A. Fürstner, M. Liebl, C.W. Lehmann, M. Piquet, R. Kunz, C. Bruneau, D. Touchard, P.H. Dixneuf, Chem. Eur. J. 6 (2000) 1847.
[12] A. Fürstner, M. Picquet, C. Bruneau, P.H. Dixneuf, Chem. Commun. (1998) 1315.
[13] M. Picquet, D. Touchard, C. Bruneau, P.H. Dixneuf, New J. Chem. (1999) 141.
[14] M. Picquet, C. Bruneau, P.H. Dixneuf, Chem. Commun. (1998) 2249.
[15] D. Sémeril, J. Le Nôtre, C. Bruneau, P.H. Dixneuf, A.F. Kolomiets, S.N. Osipov, New J. Chem. 1 (2001) 16.
[16] D. Sémeril, H. Olivier-Bourbigou, C. Bruneau, P.H. Dixneuf, Chem. Commun. (2002) 146.
[17] I. Alaoui-Abdallaoui, D. Sémeril, P.H. Dixneuf, J. Mol. Catal. A: Chem. 182–183 (2002) 577.
[18] M. Saoud, A. Romerosa, M. Peruzzini, Organometallics 19 (2000) 4005.
[19] S. Jung, D. Brandt, H. Werner, New J. Chem. (2001) 1101.
[20] H.-J. Schanz, L. Jafarpour, E.D. Stevens, S.P. Nolan, Organometallics 18 (1999) 5187.