Journal of Molecular Catalysis A: Chemical 394 (2014) 198–204

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Editor's choice paper

Room temperature polymerization of norbornene with a hydride-bridged dinuclear ruthenium complex system

Jinsen Chen, Xun Chen, Congzhi Zhu, Jin Zhu *

Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, State Key Laboratory of Coordination Chemistry, Nanjing National Laboratory of Microstructures, Nanjing University, 22 Hankou Road, Nanjing 210093, Jiangsu, China

ARTICLE INFO

Article history:
Received 19 April 2014
Received in revised form 9 July 2014
Accepted 12 July 2014
Available online 22 July 2014

Keywords:
Ring-opening metathesis polymerization
Hydride-bridged dinuclear ruthenium complex
Amine borane adduct

ABSTRACT

A two-component system, $[Ru(p\text{-cymene})Cl_2]_2$ (**C1**)/$BH_3{\bullet}NMe_3$, allows for the catalytic ring-opening metathesis polymerization (ROMP) of norbornene at 60 °C. A hydride-bridged complex isolated from the two-component system, $[RuCl(p\text{-cymene})]_2(\mu\text{-H})(\mu\text{-Cl})$ (**C2**), is also active in the ROMP reaction, albeit at a reduced rate. Abstraction of one chloride ligand from **C2**, by the reaction with 1 equiv of either $AgPF_6$ or $AgSbF_6$, leads to the generation of either $[\{Ru(p\text{-cymene})\}_2(\mu\text{-H})(\mu\text{-Cl})_2]PF_6$ (**C3**) or $[\{Ru(p\text{-cymene})\}_2(\mu\text{-H})(\mu\text{-Cl})_2]SbF_6$ (**C4**) and further reduction of ROMP activity. Importantly, a reaction of **C2** with 2 equiv each of $AgSbF_6$ and $BH_3{\bullet}NMe_3$ provides the ability to achieve room temperature ROMP of norbornene. Various hydride-bridged dinuclear ruthenium complexes have been observed in the room temperature system based on ^1H NMR analysis. An independent synthesis of a complex mixture containing $[\{Ru(p\text{-cymene})\}_2(\mu\text{-H})_3]PF_6$ (**C5**) and a single-component complex $[\{Ru(\eta^6\text{-}C_6Me_6)\}_2(\mu\text{-H})_3]PF_6$ (**C6**) rules out the catalytic capacity of this tri-μ-hydrido species. A di-μ-hydrido complex, $[\{Ru(p\text{-cymene})\}_2(\mu\text{-H})_2(\mu\text{-Cl})]PF_6$ (**C7**), is therefore postulated to act as the ROMP reaction center at room temperature.

1. Introduction

Ring opening metathesis polymerization (ROMP) has emerged as an important tool for the preparation of architecturally unique macromolecules from cyclic olefins [1–11]. A wide variety of catalytic systems, ranging from simple metal salts to highly sophisticated alkylidene complexes, have been used for the achievement of this synthetically useful transformation. Among all metals, ruthenium-based complexes are thought to be more stable toward air and moisture and are more tolerant of polar functional groups [1,5,12,13]. Therefore, tremendous efforts have been directed toward the understanding of reactivity patterns on ruthenium-based systems [14–17]. In this regard, Grubbs catalysts represent the ultimate in terms of activity, but they are not cost effective. Therefore, alternative catalyst precursors that are more readily accessible have been and are still being actively developed. For example, one representative dinuclear complex is $[RuCl_2(p\text{-cymene})]_2$, from which mononuclear complexes can be facilely generated through the addition of appropriate ligands. These di- and mononuclear complexes can be used for the in situ generation of active catalytic centers, i.e., alkylidene complexes, by reaction with cyclic alkenes, diazo compounds, alkynes, etc [18–24]. A three-legged piano stool structure, $RuCl_2(p\text{-cymene})(PR_3)$, which can be obtained simply by adding a phosphine ligand to $[RuCl_2(p\text{-cymene})]_2$, is active for the ROMP of norbornene [18,20]. The carbene species is presumably generated by the reaction between $RuCl_2(p\text{-cymene})(PR_3)$ and norbornene. For a better norbornene ROMP reactivity, $RuCl_2(p\text{-cymene})(PR_3)$ and $[RuCl_2(p\text{-cymene})]_2$ can also be directly activated by (trimethylsilyl)diazomethane (TMSD) [18]. Another type of ROMP catalysts are ruthenium arene complexes bearing N-heterocyclic carbene (NHC) ligand, $RuCl_2(p\text{-cymene})(NHC)$, which show good thermally induced or photoinduced ROMP activity [22,24,25]. In addition, a ruthenium allenylidene complex containing carbene species shows ROMP activity [26,27]. In spite of tremendous advances in this field, further developments are in demand for the creation of uniquely structured non-Grubbs catalysts for the polymerization of norbornene at room temperature.

Herein, we wish to report on the development of a series of catalytic systems, afforded by Ru complexes and amine borane adducts, for the ROMP of norbornene. In particular, a two-component system, $[Ru(p\text{-cymene})Cl_2]_2$ (**C1**)/$BH_3{\bullet}NMe_3$, can be used for the ROMP of norbornene at 60 °C. Structural modification of a key complex isolated from the two-component mixture, $[RuCl(p\text{-cymene})]_2(\mu\text{-H})(\mu\text{-Cl})$ (**C2**), through the abstraction of chloride ligand and incorporation of hydride bridge ultimately

---

* Corresponding author. Tel.: +86 2583686291; fax: +86 2583317761.
E-mail address: jinz@nju.edu.cn (J. Zhu).

http://dx.doi.org/10.1016/j.molcata.2014.07.019

leads to the elaboration of a system with room temperature ROMP activity. The hydride ligand is critical based on its high trans effect (for ligand dissociation) and the ability to generate carbene species through plausible migratory insertion and α-elimination steps. This catalytic system bearing hydride ligand could be an alternative for the well-defined Ru-based initiators which rules out the need for installation of complex ancillary ligands like phosphine or NHC or *O*-Ligand in the coordination sphere or the need for activation with diazo compounds in search of novel catalytically active species.

2. Experimental

2.1. General

All reactions were carried out under an inert atmosphere of either nitrogen or argon using standard Schlenk technique or glovebox. $[RuCl_2(p\text{-cymene})]_2$ (**C1**) was obtained from Alfa Aesar and used without further purification. All other reagents were purchased from either Acros Organics, Sigma-Aldrich, or Alfa Aesar Chemicals and used without further purification unless otherwise noted. Hexane, toluene, and THF were distilled over Na/benzophenone. CH_2Cl_2, $CHCl_3$, chlorobenzene, and 1,4-dioxane were distilled over calcium hydride. Preparative thin-layer chromatography (TLC) was carried out on glass plates ($25 \times 15 \times 0.25\,cm^3$) coated with silica gel G (10–40 μm). ^1H NMR spectra were recorded at 400 MHz on a Bruker AC 400 spectrometer. ^{13}C NMR spectra were obtained at 125 MHz on a Bruker AC 500 spectrometer. ^{11}B spectra were recorded on a Bruker AC 400 operating at 128.38 MHz and were referenced to neat $BF3{\bullet}Et_2O$ as the external standard. Chemical shifts are reported in parts per million (ppm) with reference to solvent residual nuclei in deuterated solvents. Molecular weights and polydispersity indices were measured using a Shimadzu pump coupled to a Shimadzu UV detector with THF as the eluent and a flow rate of 1 mL/min on American Polymer Standards column set (100, 1000, 100,000 Å, linear mixed bed). All gel permeation chromatography (GPC) curves were calibrated against poly(styrene) standards. *Mw*, *Mn*, and PDI represent the weight-averaged molecular weight, number-averaged molecular weight, and polydispersity index (*Mw*/*Mn*), respectively. The polymer microstructures were determined by comparison of their ^1H and ^{13}C NMR spectra with those reported in the literature.

2.2. Synthesis of **C2**

A 5 mL $CHCl_3$ solution of $BH_3{\bullet}NMe_3$ (15 mg, 0.2 mmol) was added to a flask containing **C1** (120 mg, 0.2 mmol). The mixture was allowed to react under stirring at room temperature for 20 min. Volatiles were removed in vacuo, and the residue was subjected to TLC separation using ethyl acetate/petroleum ether (3:2 v/v) as the eluent. The complex was obtained from the major band as a deep red solid (90% yield) and the NMR spectra correspond to what has been described previously (Figs. S1 and S2) [28].

2.3. General procedure for ROMP

To a solution of the catalyst **C2** (6 mg, 0.001 mmol) in the desired solvent (4 mL) under nitrogen was added the exact amount of norbornene (188 mg, 0.5 M). The solution was stirred at 60 °C for different periods of time. To stop the polymerization reaction, 100 μL of ethyl vinyl ether in 20 mL of $CHCl_3$ was added to the resulting mixture. After being allowed to react for 20 min, the solution was slowly poured into methanol (500 mL) under vigorous stirring. The synthesized polymer was precipitated and dried in vacuum overnight. For other catalytic systems, a similar procedure was adopted.

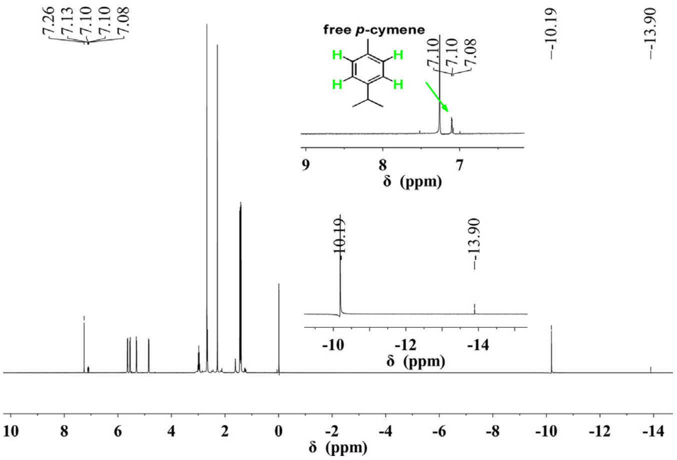
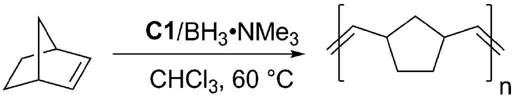


Fig. 1. ^1H NMR of the reaction mixture of $[Ru(p\text{-cymene})Cl_2]_2$ (**C1**), $BH_3{\bullet}NMe_3$, and norbornene at 60 °C in $CHCl_3$.

3. Results and discussion

3.1. $C1/BH_3{\bullet}NMe_3$ catalytic system

We started the investigation of the feasibility of employing **C1**/$BH_3{\bullet}NMe_3$ for the ROMP reaction of norbornene in a variety of solvents ($CHCl_3$, 1,4-dioxane, THF, chlorobenzene, toluene) (entries 1–5, Table 1). $CHCl_3$ was identified to be the best medium, and in this solvent, the two-component system allowed for 98% conversion of monomer to polymer (determined by the ratio of ^1H NMR signal of the olefinic protons of the polymer to the monomer) with a isolated polymer yield of 89% at 60 °C within 10 min (Eq. (1)). Control experiments (Fig. S3) confirmed the requirement of both complex **C1** and $BH_3{\bullet}NMe_3$ for the ROMP of norbornene. With the catalytic system in hands, we next examined whether structural variation on the amine part of the adduct could affect the ROMP reactivity. Both primary and secondary amines, $(CH_3)_3CNH_2$ and $NHMe_2$ (entries 6 and 7, Table 1), could be used for the substitution of NMe_3 giving polymer yields of 78% and 80%, respectively (with *Mns* of 194.2 and 176.9 × 10^3 g/mol). A preference for the trans configuration in the poly(norbornene) product was found based on ^1H NMR analysis (as determined from the ^1H NMR signal of the olefinic protons, see Fig. S4) [29].



(1)

Studies by other groups have shown that release of the arene ligand of Ru-arene complexes is crucial for the generation of catalytically active species [21,30,31]. De-coordination or partial de-coordination of *p*-cymene ligand has been reported by Noels and other groups [18,29]. A multiplet peak at δ 7.10 (Fig. 1) was identified on ^1H NMR after a 60 °C reaction between complex **C1**, $BH_3{\bullet}NMe_3$ and norbornene was performed. To test whether the multiplet peak was derived from free, non-ligated *p*-cymene, 10 μL of pure *p*-cymene was added to the reaction mixture. Indeed, the addition of pure *p*-cymene led to a significant increase of the peak intensity at δ 7.10, thus confirming the true identity of the species. The peak could be integrated to ~2.5% of the ligated *p*-cymeme in solution, which might indicate that the fraction of active Ru species was low. An attempt at tracing the alkylidene Ru (δ 13–20) species by NMR instead allowed the identification of a singlet peak at high filed (δ −10.19) (Fig. 1).

From the position of the peak we speculated that some type of Ru-hydride complex was formed. In addition, the color of the