Catalysis Communications 49 (2014) 43–46

Contents lists available at ScienceDirect

Catalysis Communications

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

Short Communication

Thermally stable pseudo-third-generation Grubbs ruthenium catalysts with pyridine–phosphinimine ligand

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ARTICLE INFO

Article history:
Received 5 November 2013
Received in revised form 30 January 2014
Accepted 31 January 2014
Available online 8 February 2014

Keywords:
Thermally stable
Ruthenium-based catalyst
Olefin metathesis
RCM
ROMP

ABSTRACT

The ligand precursors 2-$(R_3P{=}N)CH_2-Py$ (R = Ph(**1a**), Cy(**2a**)) were prepared from reaction of pyridine azide with various phosphine ligands. Reaction of **1a** or **2a** with $RuCl_2({=}CHPh)(Py)_2(H_2IMes)$ (Py = pyridine) afforded the ruthenium alkylidene complex $RuCl_2({=}CHPh)(Py-CH_2-(N{=}PR_3))(H_2IMes)$ (R = Ph(**1**), Cy(**2**)). Both catalysts showed good thermal stability and latent behavior toward RCM and ROMP reactions.

1. Introduction

Olefin metathesis has become a very useful synthetic method not only for organic synthesis but also for polymer, pharmaceutical, and industrial chemistry [1–4]. A significant number of ruthenium olefin metathesis catalysts have been developed which include the Grubbs first-generation catalyst $RuCl_2({=}CHPh)(PCy_3)_2$ (**A**), second-generation catalyst $RuCl_2({=}CHPh)(PCy_3)(SIMes)$ (**B**) and third-generation catalyst $RuCl_2({=}CHPh)(Py)_2(SIMes)$ (**C**, Py = pyridine) (Fig. 1) [5–7]. A significant number of modification to the first and second generation Grubbs catalysts have been developed to give a subtle balance between stability and activity [8]. In some cases, the catalysts were substituted by various types of ligands such as amines [9,10] and carbenes [11–17] which can reduce the initiation time [9,10], increase stability and activity [10,11], and enhance selectivity [12,13]. However, modification of third-generation Grubbs catalyst is relatively rare [7a,18,22].

On the other hand, latent catalysts that show little or no activity under normal conditions have been investigated by several research groups [19–28] owing to the advantage of mixing monomer solutions directly with a catalyst that is unreactive in ambient conditions. Moreover, latent metathesis catalysts can be activated by a variety of irritators, including heat [21,22], acid [23], light [24–27] and others [28].

In seeking to develop pseudo-third-generation Grubbs latent olefin metathesis catalysts with good thermal stability, we have examined a series of ruthenium based catalysts containing pyridine–phosphinimine ligands. As we know, the phosphinimine ligands have exhibited good thermal stability in olefin polymerization [29,30] which are readily prepared, and in addition, the ligands exhibited a convenient ^{31}P NMR spectroscopic characterization. Furthermore, the phosphinimine ligands are amenable to substituent modification for tuning of both the electronic and steric characteristics [29,30]. Herein, we report the synthesis of new ruthenium alkylidene species which contains pyridine–phosphinimine bidentate ligands.

2. Experimental

2.1. Instruments and reagents

All experiments were carried out under a nitrogen atmosphere in a Braun drybox unless otherwise specified. All solvents were distilled prior to use. The solvents for reaction were distilled to remove water over Na, CaH_2 or K_2CO_3. Anhydrous grade solvents were transferred into a bottle containing molecular sieves under a nitrogen stream in the drybox, and were used without further purification. All NMR experiments were carried out on a Bruker Avance 500 spectrometer using $CDCl_3$, DMSO-d_6 or C_6D_6 as the solvent with tetramethylsilane as the internal standard (^{31}P NMR with 85% H_3PO_4 as the internal standard). Chemical shift values (δ) are given in parts per million. Elemental analyses were determined on a Vario EL III elemental analyzer. HRMS data was obtained on an FTICR–MS instrument (IonSpec 7.0 T) or Agilent 6520 ESI-TOF MS instrument. The melting points were determined on an X-4 binocular microscope melting point apparatus (Beijing Tech. Instruments Co., Beijing, China) and are uncorrected.

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http://dx.doi.org/10.1016/j.catcom.2014.01.033

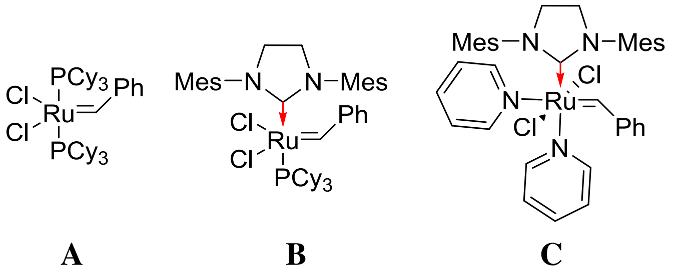


Fig. 1. Grubbs first-, second- and third-generation catalysts.

2.2. Preparation of ruthenium catalyst

2.2.1. $(H_2IMes)(Py-CH_2N{=}PPh_3)Cl_2Ru{=}CHPh$ (1)

A mixture of (2-pyridyl) − CH_2 − N═PPh_3 (86 mg, 0.235 mmol) and toluene (5 mL) was slowly added to a stirred solution of (H_2IMes) Cl_2Ru═CHPh(Py)$_2$ (100 mg, 0.138 mmol) in toluene (10 mL). Then the mixture was heated to 65 °C for 7 h and then cooled. The solvent was removed under vacuum to give the red–brown solid. The crude product was washed with hexane to obtain the product **1** (97 mg, 75% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 19.55 (s, 1H, Ru═CH), 8.24 (s, 1H, Py), 7.98 (d, 1H, Py, $J = 5$ Hz), 7.78–7.14 (m, 24H, Ph), 6.90 (d, 1H, Py, $J = 5$ Hz), 6.49 (t, 1H, Py, $J = 5$ Hz), 4.48 (d, 2H, CH_2, $J = 15$ Hz), 3.92 (d, 4H, $-CH_2-CH_2-$, $J = 75$ Hz), 2.68–2.35 (m, 18H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 219.45, 161.28, 153.73, 153.26, 148.06, 138.93–128.45, 122.17, 121.08, 120.29, 51.95, 51.01, 48.79, and 21.07–18.60. ^{31}P NMR (202 MHz, $CDCl_3$): δ 29.55 (s, PPh_3). HRMS (ESI-TOF) m/z: calcd for $C_{52}H_{54}Cl_2N_4PRu$ 937.2507; found: 937.2495.

2.2.2. $(H_2IMes)(Py-CH_2N{=}PCy_3)Cl_2Ru{=}CHPh$ (2)

Compound **2** was prepared in the same method as compound **1**. This compound was obtained as a dark brown solid (97 mg, 74% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 18.32 (s, 1H, Ru═CH), 9.03 (d, 1H, Py, $J = 5$ Hz), 8.72 (s, 1H, Py), 8.42-7.01 (m, 9H, Ph), 6.51 (d, 1H, Py, $J = 5$ Hz), 6.34 (d, 1H, Py, $J = 10$ Hz), 4.32 (d, 2H, CH_2, $J = 10$ Hz), 4.09 (d, 4H, $-CH_2-CH_2-$, $J = 20$Hz), 2.87–2.61 (m, 18H, CH_3), 2.54–1.03 (m, 33H, PCy_3). ^{13}C NMR (126 MHz, CDCl3) δ 221.7, 158.7, 156.2, 151.8, 147.4, 138.1, 137.3, 136.9, 133.9, 130.0, 128.6, 127.8, 127.5, 124.8, 122.2, 120.2, 77.4, 77.1, 76.8, 53.6, 53.1, 47.3, 44.8, 31.7, 31.3, 25.0, 21.0, 20.0, 17.8, and 16.6. ^{31}P NMR (202 MHz, $CDCl_3$): δ 56.63 (s, PCy_3). HRMS (ESI-TOF) m/z: calcd for $C_{52}H_{72}Cl_2N_4PRu$ 955.3915; found: 955.3836.

2.3. General procedure for olefin metathesis [31]

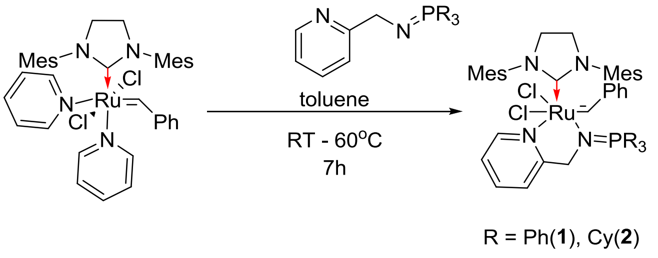
An NMR tube with a screw-cap septum top was charged inside a glovebox with catalyst stock solution (0.016 M, 100 μL, 1.60 μmol, 2.0 mol%) and CDCl3 (0.75 mL). The sample was equilibrated at 30 °C in the NMR probe before diethyl 2,2-diallyl malonate (19.3 μL, 19.2 mg, 0.080 mmol, 0.1 M) was added via syringe. The conversion to product was determined by comparing the ratio of the integrals of the methylene protons in the starting material, δ 2.61 (dt), with those in the product, δ 2.98 (s).

3. Results and discussion

Inspired by the results that replacement of PCy_3 with an NHC can enhance stability and activity of the Grubbs catalyst [6], we envisioned bidentate ligands which featured one phosphinimine ligands together with one weakly binding donor pyridine ligands that might be suited for modification of the Grubbs third generation catalyst. With these concepts in mind, the ligand precursors $C_6H_4NCH_2$-N═PR_3 (R = Ph(**1a**), Cy(**2a**),) were readily prepared using an equimolar mixture of 2-substituted pyridines azides and a PR_3(R = Ph(**1a**), Cy(**2a**)) in DMF, and the resulting white solids [30] were isolated in high yields (Scheme 1). The ^{1}H NMR spectra of ligands **1a**–**2a** showed the expected resonances with ^{31}P NMR resonances around 12.3 ppm for *N*-(2-pyridyl)triphenyl-iminophosphorane. Treatment of ligand **1a** or **2a** with 1 equiv of $RuCl_2$(═CHPh)(Py)$_2$(H_2IMes) in toluene produced an immediate color change from green to dark brown, and compound **1** was isolated in 78% yield as a microcrystalline dark brown solid. The ^{1}H NMR spectrum of **1** revealed a singlet at 19.56 ppm which integrated to a single proton and could be assigned to the Ru═CH fragment. The corresponding carbon signal for this Ru═CH fragment was also observed in the ^{13}C NMR spectrum (see ESI). Subsequently, the thermal stability of compounds **1** and **2** were investigated. At room temperature, the solution of compounds **1** and **2** in $CDCl_3$ showed no decomposition by NMR spectroscopy over 2 days. More remarkably, both compounds could be heated in $CDCl_3$ at 60 °C for 6 h with no decomposition, and catalyst **1** showed slight decomposition after 10 h even at 100 °C in toluene (see ESI).

This observed catalyst stability was promising for applications in latent metathesis chemistry. With the new catalysts in hand, the utility of compounds **1** and **2** as metathesis catalysts was assessed employing standard metathesis tests [31]. In ring closing metathesis reaction, firstly we chose diethyl 2,2-diallyl malonate as a substrate. Both catalysts showed less than 5% conversion of diethyl 2,2-diallyl malonate after 30 min at 25 °C (Table 1, entry 1). The reaction was subsequently heated at 60 °C for 30 min, and the conversion reached 100% by catalyst **1** and 88% by catalyst **2** respectively (Table 1, entries 2 and 5). To gain more information about the kinetic profiles of the catalysts **1** and **2** for RCM by the temperature, we measured the progress of the RCM reaction of diethyl 2,2-diallyl malonate by using Grubbs third-generation catalyst (**G3**), catalysts **1** and **2** at different temperatures (Figs. 2 and 3). Interestingly, Grubbs third-generation catalyst (**C**) showed no rate-dependence of temperature in RCM of diethyl 2,2-diallyl malonate, while catalysts **1** and **2** did. Overall catalysts **1** and **2** showed faster initiation and increased reaction rates at high temperature (Figs. 2 and 3). These results clearly showed catalysts **1** and **2** possessed the good latent behavior toward ring-closing metathesis of diethyl 2,2-diallyl malonate. To further examine the latency of the catalyst in metathesis of more demanding compounds, tri- or tetrasubstituted olefins were attempted (Table 1). Increasing the steric effect of the substrate by using diethyl 2-allyl-2-(2-methylallyl)malonate also gave satisfied results. The RCM of diethyl 2-allyl-2-(2-methylallyl)malonate afforded 100% (30 min, catalyst **1**) and 83% (480 min, catalyst **2**) conversion at 60 °C. The even more challenging substrate diethyl 2,2-bis(2-methylallyl) malonate gave only 10% conversion at 60 °C after 480 min by catalysts **1** and **2**, and no further conversion was observed within another 2 days of monitoring. In order to investigate the latent behavior in cross metathesis reaction, furthermore, the cross metathesis of allyl benzene and *cis*-1,4-diacetoxy-2-butene was tested; however, very low catalytic reactivity was observed for catalysts **1** and **2** even at 60 °C after 12 h.

Toward the goal of developing a practical latent metathesis catalyst for ROMP applications, catalysts **1** and **2** were tested for polymerization of cyclooctadiene (COD) in chloroform (Table 2). In contrast to RCM reactions, 0.1 mol% of **1** initiated the ROMP of COD (0.5 M in chloroform)



Scheme 1. Synthetic route for catalysts **1** and **2**.