

Piperidine as ancillary ligand in the novel $[\text{RuCl}_2(\text{PPh}_3)_2(\text{piperidine})]$ complex for metathesis polymerization of norbornene and norbornadiene

José Milton E. Matos, Benedito S. Lima-Neto*

Instituto de Química de São Carlos, Universidade de São Paulo, CP 780, CEP 13560-970, São Carlos, SP, Brasil

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Abstract

Reaction between $[\text{RuCl}_2(\text{PPh}_3)_3]$ and piperidine (pip) gives the novel $[\text{RuCl}_2(\text{PPh}_3)_2(\text{pip})]$ complex, which quantitatively polymerizes norbornene (NBE) via ring opening metathesis polymerization for less than 1 min at RT, in the presence of 5 μL of ethyldiazoacetate. An M_w/M_n value of 1.05 is obtained if amounts of norbornene are added in several batches up to the $[\text{NBE}]/[\text{Ru}] = 5.000$. Norbornadiene is polymerized with 48% yield for 5 min at RT. The precursor complex gives only 63% of polynorbornene and 6% of polynorbornadiene for 5 min at 50 °C. $^{31}\text{P}\{^1\text{H}\}$ NMR analyses indicate that the new complex does not undergo dimerization in solution as it occurs in the case of the precursor complex. It is proposed that the presence of the piperidine is appropriated in enhancing the rate of reaction and controlling the ruthenium metathesis catalysis via a highly active five-coordinated mononuclear Ru(II) complex.

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1. Introduction

The development of olefin metathesis catalyzed by transition metals experienced an increase in the 1990s after the discovery of the well-defined Grubbs carbene–phosphine complexes [1,2], $[\text{RuCl}_2(\text{PR}_3)_2(=\text{CRR}')]_2$, which have been appropriate for synthesis of new formulations [2]. Besides the importance of the presence of the carbene in the starting catalyst for the initiation of the reaction, the phosphine ligands also play a role as an additional key ligand when dealing with ring opening metathesis polymerization (ROMP) [3]. Phosphine ligands are not only important for the initiation but also for the propagation process [1]. Thus, the properties of the polymers depend on the ligands coordinated to the metal center not directly engaged in reaction. These ligands are well known as ancillary ligands.

The most commonly used ancillary ligands are the phosphines where they tuning the substitution lability of metal complexes via a systematic variation of their steric and electronic properties [4,5].

Besides phosphines, amine ligands can also drive the activity of metals by controlling the electronic density or steric effects in the coordination metal sphere [6]. Despite their importance, these ligands are not widely explored in homogeneous catalysis.

With this in mind, the present study is one in a series that reports the synthesis of novel Ru(II) complexes simultaneously coordinated to PPh_3 and amine (L), with very rapid quantitative application to norbornene (NBE) and norbornadiene ROMP under room temperature. Here, L denotes piperidine, and the usefulness of the complex is ascertained by observing the influence of the ligand piperidine in relation to its precursor, $[\text{RuCl}_2(\text{PPh}_3)_3]$, containing only phosphines as ancillary ligands.

Furthermore, this paper studies the synthesis of ROMP active complexes that are not sensitive to moisture as opposed to

* Corresponding author. Tel.: +55 16 3373 9953; fax: +55 16 3373 9976.
E-mail address: benedito@iqsc.usp.br (B.S. Lima-Neto).

carbene-catalysts that are very active but sensitive to moisture [1,2]. Moreover, a close study of the existing literature on this topic shows that a non-carbene ROMP catalyst appropriate for fast and living reaction with significant quantitative yield, high M_n value and narrow molecular weight distribution is rare.

2. Experimental

2.1. General remarks

Unless otherwise cited, all manipulations were carried out under argon. All the solvents used were of analytical grade and distilled from the appropriate drying agents immediately prior to use. Other commercially available reagents were purified by standard procedure or used without further purification. $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ from Stream, norbornene from Across, piperidine from Merck and ethyldiazoacetate, PPh_3 and norbornadiene (NBdiene) from Aldrich were used as achieved. The $[\text{RuCl}_2(\text{PPh}_3)_3]$ complex was prepared by method cited in literature and its purity was checked by satisfactory elemental analysis and spectroscopic ($^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR and FTIR) examination [7,8].

2.2. Synthesis of $[\text{RuCl}_2(\text{PPh}_3)_2(\text{pip})]$

Piperidine (0.12 mL; 1.23 mmol) was added to a solution of $[\text{RuCl}_2(\text{PPh}_3)_3]$ (0.40 g; 0.47 mmol) in acetone (25 mL) and a dark green solution was stirred at RT for 1 h. The resultant compound, a green precipitated, was then filtered and washed with methanol and ethyl ether, then dried in a vacuum. The analytical data for $\text{RuCl}_2\text{P}_2\text{NC}_{41}\text{H}_{41}$ is 63.08% C, 5.16% H and 1.79% N; found: 63.01% C, 5.05% H and 1.69% N. FTIR in CsI: $\nu_{\text{Ru-Cl}} = 338$ and 310 cm^{-1} , $\nu_{\text{N-H}}$ (piperidine) = 3223 cm^{-1} . EPR: no signal was observed. Yield: 0.31 g (65%).

Several attempts to obtain the crystal have so far been unsuccessful.

2.3. Instrumentation

Elemental analyses were done using an EA 1110 CHNS-O Carlo Erba Instrument. EPR was carried out at 77 K using a Bruker ESP 300C apparatus (X-band) equipped with a TE102 cavity and HP 52152A frequency counter. IR spectra were obtained in CsI pellets on a Bomem FTIR MB 102. ^1H and

$^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained in CDCl_3 solution at $25.0 \pm 0.1\text{ }^\circ\text{C}$ using a Bruker AC-200 spectrometer equipped with a probe operating at 200.13 and 81.015 MHz, respectively. The obtained chemical shifts are reported in ppm relative to high frequency of tetramethylsilane or 85% H_3PO_4 . Gel permeation chromatography analysis was obtained on a Shimadzu 77251 spectrometer system equipped with a PL gel column (5 μm MIXED-C: 30 cm, $\varnothing = 7.5\text{ mm}$). The retention time was calibrated with a standard monodispersed polystyrene using HPLC-grade CHCl_3 as eluent.

2.4. Polymerization reactions

In a typical ROMP experiment, a 1.27 μmol of metal complex was dissolved in 2 mL of CHCl_3 and a certain amount of monomer was added so that the molar ratio $[\text{monomer}]/[\text{Ru}]$ is 5.000, after which 5.4 μmol of ethyldiazoacetate (EDA) was added. The molar ratios were maintained unless where cited otherwise. The reaction mixture was stirred for different periods of time at room temperature ($\text{RT} = 24\text{--}26\text{ }^\circ\text{C}$ or at $50 \pm 1\text{ }^\circ\text{C}$) in silicone oil bath. At room temperature, 5 mL of methanol was added and the precipitated polymer was filtered, washed with methanol and dried in vacuum before being weighed.

3. Results and discussion

3.1. Polymerization reactions

It was observed that in the presence of 5 μL of EDA, the complex with piperidine showed unusual catalytic activity with very short reaction time at room temperature contrary to the complex with three PPh_3 molecules. Table 1 shows the data for the polymerization of norbornene and norbornadiene with $[\text{RuCl}_2(\text{PPh}_3)_2\text{L}]$, where L = piperidine or PPh_3 . It must be highlighted that for L = PPh_3 , better yields were achieved only at $50\text{ }^\circ\text{C}$ for 5 min.

The activity of the novel complex was sensitive to amount of the monomer in the medium. On addition of a fresh feed of monomer to the reaction mixture up to a point where nearly all monomer of the previous batch was consumed (5 min), the values of the M_n increased up to 2.000, then a saturation profile was obtained up to 5.000 (Fig. 1). After 25 min (five batches), the polymer was isolated and more than 99% of the all monomer feed had been converted. The final polymer

Table 1
ROMP of norbornene (NBE) or norbornadiene (NBdiene) catalyzed by $[\text{RuCl}_2(\text{PPh}_3)_2(\text{L})]$ in CHCl_3 ; 5 μL EDA

Complex	Monomer	[mon]/[Ru]	Temperature ($^\circ\text{C}$)	Reaction time (min)	Yield (%)	M_n	M_n/M_w	trans (%)
L = pip	NBE	2.000	RT	<1	>99	2.2×10^6	1.14	58
	NBE	5.000	RT	5 batches (25 min)	>99	2.6×10^6	1.05	59
	NBE	5.000	RT	<1	>99	1.2×10^5	1.90	59
	NBdiene	5.000	RT	5	48	5.3×10^3	3.40	60
L = PPh_3	NBE	5.000	50	5	63	1.9×10^6	1.40	59
	NBdiene	5.000	50	5	6	3.4×10^3	3.53	61

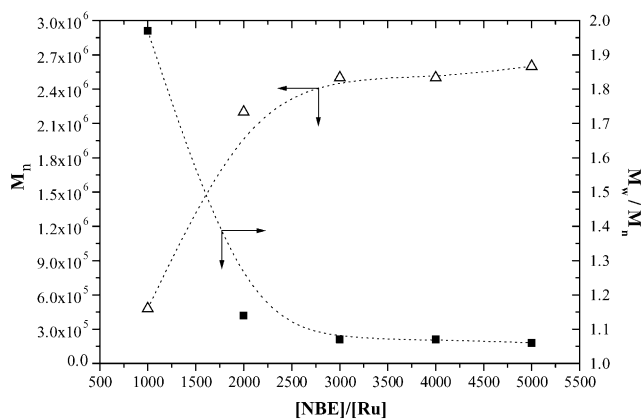


Fig. 1. M_n and M_w/M_n values as a function of [NBE]/[Ru] molar ratio for polynorbornene monitored by GPC using $[\text{RuCl}_2(\text{PPh}_3)_2(\text{pip})]$ in CHCl_3 at RT; 5 μL of EDA.

showed a unimodal GPC chromatogram and a narrow polydispersity index ($M_w/M_n = 1.05$). Comparing the M_n and M_w/M_n values, it is interesting to observe that the M_w/M_n curve reaches saturation at values close to the unity, indicating that the polymer chains are uniform at the end. Constant values of M_n above 2.000 mol of [NBE]/[Ru] indicate that the polymer chain is not increasing at all. Thus, one would conclude that the added monomer is mainly polymerized in the smaller chains, characterizing the living nature of the process, since all the monomer feed had been consumed. It is also possible to say that the complex is very active when the reaction is started with less amounts of monomer which allows more metal complex units interact with it. Starting with high amounts of monomer, the fast polymer reaction leads to precipitation of the polymer resulting in a high M_w/M_n value. A comparison of the narrow M_w/M_n value with that obtained when the same amount of monomer was added at once supports the fact that the initiation and propagation steps are rapid. High M_w/M_n values of norbornadiene were expected since there is a possible formation of cross-polymer with very active catalyst [1].

It was also observed that the carbene content has a large influence on the activity of the complex with piperidine tested for norbornene at amounts between 5 and 50 μL of EDA (Fig. 2). A substantial increase in the activity occurred followed by a drop and then a total loss of activity. Experiments with 20 and 50 μL of EDA under flux of argon gave similar results (70 and 5%, respectively), suggesting that the poisoning of the catalyst is not due to the coordination of N_2 from the excess of EDA on the Ru(II) metal center.

In the absence of EDA, the complex with piperidine was also active with a polynorbornene yield of 55% at RT for 12 h. In this case, the polymer showed a bimodal molecular weight distribution, with 42% of polymer being of low molecular weight ($M_n = 1.0 \times 10^3$ and $M_w/M_n = 2.7$), and 58% of a higher molecular weight material with a narrower molecular weight distribution ($M_n = 1.2 \times 10^5$ and $M_w/M_n = 1.6$).

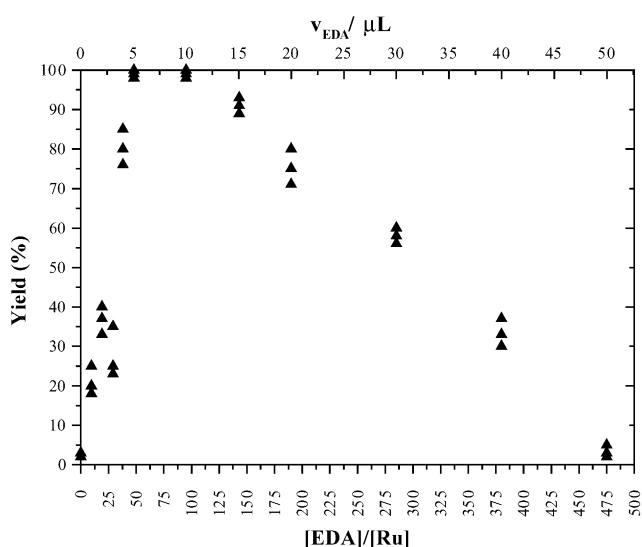


Fig. 2. Polynorbornene yield obtained as a function of [EDA]/[Ru] molar ratio using $[\text{RuCl}_2(\text{PPh}_3)_2(\text{pip})]$ in CHCl_3 at RT; [NBE]/[Ru] = 5.000.

The catalyst lifetime was investigated by carrying out a ROMP experiment as a function of time. One chloroform solution of catalyst was continuously kept under argon at room temperature and then an appropriate volume of the solution was taken off and mixed with the monomer, followed by the additions of EDA. After 1 day of aging the solution, the catalyst activity was observed to drop to 75% yield and remained constant over a period of 1 month (Fig. 3). In a similar experiment, it was observed that $[\text{RuCl}_2(\text{PPh}_3)_2(\text{pip})]$ is sensitive to the O_2 from the air, its activity dropping to 50%. In this case, the resulting polymer showed a bimodal molecular weight distribution with a very high M_w/M_n value. A similar behavior in activity under air was observed for norbornadiene (Fig. 3).

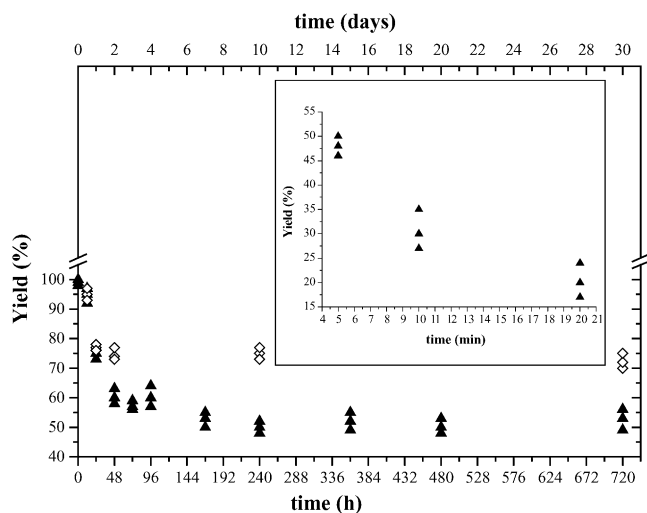
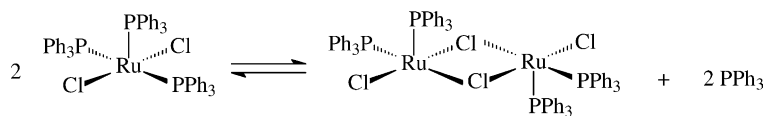


Fig. 3. Yield as a function of time for the ROMP of norbornene and norbornadiene (in prominence) in absence (\diamond) or presence of air (\blacktriangle), using $[\text{RuCl}_2(\text{PPh}_3)_2(\text{pip})]$ in CHCl_3 at RT; [monomer]/[Ru] = 5.000, 5 μL EDA.



Scheme 1.

The ROMP reaction did not occur in the presence of either excess PPh_3 or piperidine. This was also the case when the Cl^- ligands were replaced by $\text{OSO}_2\text{CF}_3^-$ (using AgSO_3CF_3), indicating the necessity of the presence of π -donor ligands, as reported in literature [9].

3.2. Characterization of the complex and mechanism reaction

The five-coordinated nature of the new complex is supported by the satisfactory analytical results that are in good agreement with the assigned formulation. The absence of a signal in the EPR spectrum of the complex suggests the presence of the +2 oxidation state of ruthenium. Typical vibration bands in the IR spectrum confirm the presences of Cl^- and piperidine in the isolated compound (vide experimental section). Two $\nu_{\text{Ru}-\text{Cl}}$ bands indicate that the two Cl^- ligands are not *trans*-positioned to each other.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the piperidine complex in CDCl_3 consists of two sharp peaks at 62.7 and 45.0 ppm (Fig. 4). The low field resonance disappears for 5.5 h, leaving the high field signal. No evidence of free PPh_3 or OPPh_3 was found for up to 11 h. This behavior seems to be different from that of the parent $[\text{RuCl}_2(\text{PPh}_3)_3]$ complex, which acts as a dimeric complex in solution and the release of phosphine is detected in the solution, as illustrated in Scheme 1 [8]. This results lead to the conclusion that the complex with piperidine does not form binuclear complex but exists as a mononuclear in solution. Single sharp peaks indicate that two phosphine are equivalents [10]. Thus, from the NMR data, the five-coordinated piperidine complex probably exists as two isomeric arrangements as illustrated in Fig. 5,

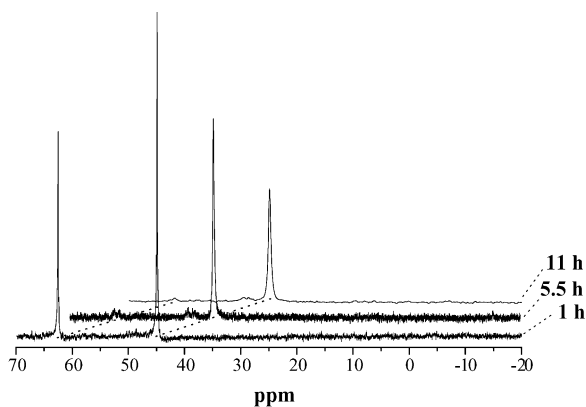


Fig. 4. Changes in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $[\text{RuCl}_2(\text{PPh}_3)_2(\text{pip})]$ in CDCl_3 at different time.

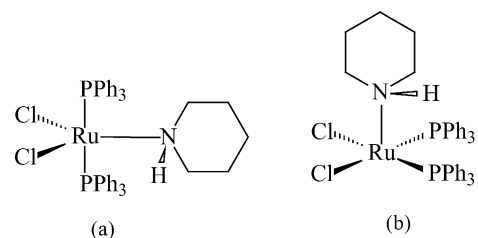


Fig. 5. Two possible isomeric arrangements of $[\text{RuCl}_2(\text{PPh}_3)_2(\text{pip})]$: (a) trigonal bipyramidal shape and (b) square pyramidal shape.

where the square pyramidal isomer seems more stable in solution (peak at higher field). This fact is in accordance with literature [8]. Two $\nu_{\text{Ru}-\text{Cl}}$ bands in the IR spectrum support the *cis*-positioned Cl^- ligands in these two possible structures.

The presence of a vacant sixth position on the ruthenium center allows the coordination of a ligand, poisoning the catalyst as observed in the presence of either PPh_3 or piperidine. Otherwise, this open position allows the start of the ROMP reaction. On the other hand, rearrangement to a more stable isomer in solution is consistent with the fact that the aged solution is less active (Fig. 3).

The resonance at 45.0 ppm in the $^{31}\text{P}\{^1\text{H}\}$ spectrum disappeared for 24 h when the solution was exposed to air. In this study, a signal was observed at -4.7 ppm, which is typical of free PPh_3 . This signal was simultaneously converted to OPPh_3 whose spectrum is a sharp resonance at 29.4 ppm. It was shown that this former resonance value could be experimentally obtained by addition of PPh_3 to the solution, which is in agreement with literature [8].

When the solution was exposed to air, the ^1H NMR spectrum also indicated that coordinated PPh_3 were not really present, suggesting $\text{Ru}-\text{PPh}_3$ complex had been decomposed. Although the catalyst lost the phosphine ligands, it remained active (Fig. 3), suggesting the importance of the piperidine piperidine being coordinated. Hence, it can be inferred that the complex with piperidine keeps this ligand coordinated in solution under argon and that one PPh_3 molecule is dissociated in presence of monomer and EDA, while other PPh_3 molecule remains coordinated.

4. Conclusion

The high activity of the new catalysts is attributed to the retention, in solution, of the mononuclear character of the started five-coordinated complex as well as the increase

of electron density of the metal center via the presence of an electron-donating nitrogen compound in its coordination sphere. This is only possible because piperidine is bulky ($\theta = 121^\circ$) and electron rich ($pK_a = 11.2$). Hence, its nature shows a great influence on the catalytic activity of the complex, which seems to be a good option as an ancillary ligand to be explored in homogeneous catalysis.

The different yields and energetic condition when using the precursor complex support the fact that the new complex is more active. The precursor forms a dimeric specie in solution with square pyramidal moieties, becoming more inert; i.e., the arrangements and dissociation of ligands from the coordination metal sphere to promote reaction with EDA and monomer is slower.

Few papers have discussed bulky and basic amines as additives to improve radical polymerization with $[\text{RuCl}_2(\text{PPh}_3)_3]$ as starting material [11]. These papers have proposed the existence of coordination of these ligands to the metal center. The present paper supports these observations, but in addition, it tests for metathesis polymerization. Furthermore, the first studies have demonstrated that 1,5-cyclooctene is also polymerized in the presence of the new complex under mild conditions.

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