



Ability of Ru complexes for ROMP tuned through a combination of phosphines and amines

José L. Silva Sá, Benedito S. Lima-Neto*

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

ARTICLE INFO

Article history:

Received 2 December 2008
Received in revised form 6 February 2009
Accepted 9 February 2009
Available online 25 February 2009

Keywords:

ROMP
Olefin metathesis
Ancillary ligand
Amine–phosphine complexes
Ruthenium

ABSTRACT

Polynorbornene with high molecular weight was obtained via ring opening metathesis polymerization using catalysts derived from $[\text{RuCl}_2(\text{PPh}_2\text{Bz})_2\text{L}]$ (**1** for L = PPh₂Bz; **2** for L = piperidine) type of complexes when in the presence of ethyl diazoacetate in CHCl₃. The polymer precipitated within a few minutes at 50 °C when using **1** with ca. 50% yield ($[\text{NBE}]/[\text{Ru}] = 5000$). Regarding **2**, for either 30 min at 25 °C or 5 min at 50 °C, more than 90% of yields are obtained; and at 50 °C for 30 min a quantitative yield is obtained. The yield and PDI values are sensitive to the $[\text{NBE}]/[\text{Ru}]$ ratio. The reaction of **1** with either isonicotinamide or nicotinamide produces six-coordinated complexes of $[\text{RuCl}_2(\text{PPh}_2\text{Bz})_2(\text{L})_2]$ type, which are almost inactive and produce only small amounts of polymers at 50 °C for 30 min. Thus, we concluded that the novel complexes show very distinct reactivities for ROMP of NBE. This has been rationalized on account of a combination of synergistic effects of the phosphine–amine ancillary ligands.

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1. Introduction

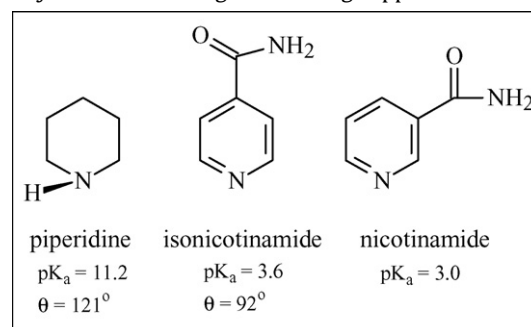
Ring opening metathesis polymerization (ROMP) is a versatile reaction to synthesize macromolecular materials [1–3]. Carbene–metal complexes catalyze this reaction and the ancillary ligands in the coordination sphere define the activities of the complex backbones in the starting and propagating species. These ancillary ligands can provide high reactivity towards olefins under specific reaction conditions [4–9].

Ancillary ligands with different electronic and steric characteristics modify the catalytic process. Polymers with different chemical and physical properties such as molecular mass and PDI can be produced, which can improve the reaction yield. Thus, ancillary ligands are significant means to develop new catalysts to operate under desired conditions.

Our group is currently involved in the development of Ru(II) complexes for ROMP application [10–13], where the main characteristic of these compounds is to show good catalytic activity without requiring special working conditions. Ru(II) complexes are not sensitive to moisture and can be manipulated under air. The carbene catalytic species ($\text{Ru}=\text{CHR}$) are prepared *in situ* from the reaction with ethyl diazoacetate (EDA). Cyclic or acyclic amines and PPh₃ determine the reactivity of these complexes through electronic and steric hindrance balance. For example, $[\text{RuCl}_2(\text{PPh}_3)_3]$ polymerizes norbornene with 63% yield at 50 °C for 5 min, $[\text{NBE}]/[\text{Ru}] = 5000$, whereas $[\text{RuCl}_2(\text{PPh}_3)_2\text{piperidine}]$ promptly synthesizes polynor-

bornene at room temperature with quantitative reaction yield [11]. On the other hand, amine–phosphine hybrid complexes are usually employed as starting hemilabile complex where the amines are replaced at the beginning of the reactions [14,15].

As the influence of the amines have been determinant and absorbing, the present paper reports the application of novel Ru(II) complexes with piperidine, isonicotinamide or nicotinamide when the phosphine is PPh₂Bz. In the early hybrid complexes the phosphine was PPh₃ that is a stronger π -acceptor ligand ($\text{p}K_{\text{a}} = 2.7$) and presents lower cone angle with ($\theta = 145^\circ$) than PPh₂Bz ($\text{p}K_{\text{a}} = 3.6$; $\theta = 152^\circ$). Thus, the purpose is to observe a fine tune in the electronic and steric effects of the phosphines in the reactivity of the metal center. The selected amines are six-ring cyclic molecules that also differ in the electronic character and cone angles (θ), as observed by the $\text{p}K_{\text{a}}$ and θ values, affording to compare their behaviors as ancillary ligands as well the synergetic effects with the phosphine. We chose simple ligands, because they are easy to work with in laboratory and are advantageous for large applications.



* Corresponding author. Tel.: +55 16 33739953; fax: +55 16 33739976.
E-mail address: benedito@iqsc.usp.br (B.S. Lima-Neto).

2. Experimental

2.1. General remarks

All manipulations were performed under an argon atmosphere. All the solvents used were of analytical grade and were distilled from adequate drying agents immediately prior to use. $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, norbornene (NBE), piperidine (pip), nicotinamide (nic), isonicotinamide (isn), benzylidiphenylphosphine (PPh_2Bz) and ethyl diazoacetate (EDA) from Aldrich were used as obtained.

2.2. Synthesis of $[\text{RuCl}_2(\text{PPh}_2\text{Bz})_3]$ (**1**)

PPh_2Bz (5.8 mmol; 1.6 g) was added to a solution of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (0.97 mmol; 0.20 g) in methanol (50 mL) and the resulting solution was refluxed for 4 h. A green precipitate was filtered and washed with methanol, then dried in a vacuum. Yield: 89%. Anal. Calc. for $\text{RuCl}_2\text{C}_{57}\text{H}_{51}\text{P}_3$: C, 68.4; H, 5.1%. Found: C, 68.0; H, 5.1%. FT-IR in Csl: $\nu(\text{Ru}-\text{Cl}) = 319 \text{ cm}^{-1}$; $^{31}\text{P}\{^1\text{H}\}$ NMR in CHCl_3 : 30.9 (t) and 22.5 (d) for a monomeric species; 50.4 (s) and 49.7 (s) ppm for a dimeric species [11,16,17]; -9.1 ppm for free phosphine. EPR: no signal was observed.

2.3. Synthesis of $[\text{RuCl}_2(\text{PPh}_3\text{Bz})_2(\text{pip})]$ (**2**)

Piperidine (19 μL ; 0.20 mmol) was added to the solution of **1** (0.20 g; 0.20 mmol) in CH_2Cl_2 (50 mL) and the resulting solution was stirred at RT for 1 h. Hexane (30 mL) was added and the yellow precipitate was filtered and washed with ethyl ether, then vacuum dried. Yield: 72%. Anal. Calc. $\text{RuCl}_2\text{C}_{43}\text{H}_{45}\text{NP}_2$: C, 63.8; H 5.6; N, 1.7%. Found: C, 63.8; H, 5.8; N, 1.6%. FT-IR in Csl: $\nu(\text{Ru}-\text{Cl}) = 301 \text{ cm}^{-1}$; $\nu(\text{N}-\text{H}; \text{piperidine}) = 2931 \text{ cm}^{-1}$. $^{31}\text{P}\{^1\text{H}\}$ NMR in CHCl_3 : 34.1 (s) and 35.4 (s) ppm for two isomeric species [11]. EPR: no signal was observed.

2.4. Syntheses of $\text{ttr}-[\text{RuCl}_2(\text{PPh}_2\text{Bz})_2\text{L}_2]$, L = nic (**3**) or isn (**4**)

The complexes with nicotinamide (nic) and isonicotinamide (isn) were prepared by adding 0.40 mmol of amine to a solution with 0.20 mmol (0.20 g) of **1** in acetone (50 mL). Each mixture was stirred for 1.5 h under argon at room temperature. The compounds (yellow for nic and orange for isn) were filtered and washed with ethyl ether and then vacuum dried. Anal. Calc. for $\text{RuCl}_2\text{C}_{50}\text{H}_{46}\text{N}_4\text{P}_2\text{O}_2$ (**3**; 68% yield): C, 62.0; H, 4.7; N, 5.8%. Found: C, 61.0; H, 5.0; N, 6.0%. FT-IR in Csl: $\nu(\text{Ru}-\text{Cl}) = 319 \text{ cm}^{-1}$; $\nu(\text{C}=\text{O})$ (nic) = 1679 cm^{-1} ; $\nu(\text{N}-\text{H}; \text{nic}) = 3395 \text{ cm}^{-1}$. $^{31}\text{P}\{^1\text{H}\}$ NMR: 50.1 and -9.0 ppm (free phosphine). EPR: no signal was observed. Anal. Calc. for $\text{RuCl}_2\text{C}_{50}\text{H}_{46}\text{N}_4\text{P}_2\text{O}_2$ (**4**; 77% yield): C, 62.0; H, 4.7; N, 5.8%. Found: C, 62.2; H, 4.7; N, 5.8%. FT-IR in Csl: $\nu(\text{Ru}-\text{Cl}) = 332 \text{ cm}^{-1}$; $\nu(\text{C}=\text{O}; \text{isn}) = 1668 \text{ cm}^{-1}$; $\nu(\text{N}-\text{H}; \text{isn}) = 3378 \text{ cm}^{-1}$. $^{31}\text{P}\{^1\text{H}\}$ NMR: 53.0 ppm; -9.1 ppm (free phosphine). EPR: no signal was observed. Attempts to isolate five coordinated complexes were unsuccessful.

2.5. Instrumentation

Elemental analyses were performed using an EA1110 CHNS-O Carlo Erba Instrument. The EPR measurements were 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 Csl pellets (1:100) on a Bomem FTIR MB 102. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained in CDCl_3 at $25 \pm 0.1^\circ\text{C}$ using a Bruker AC-200 spectrometer. The obtained chemical shifts are reported in ppm relative to 85% H_3PO_4 . Gel permeation chromatography analyses were obtained using a Shimadzu 7725.1 system equipped with a PL gel column (5 m MIXED-C: 30 cm, $\varnothing = 7.5$ mm). The retention times were calibrated with standard monodispersed polystyrene using HPLC-grade CHCl_3 as eluent. PDI is M_w/M_n .

Table 1
ROMP of NBE in the presence of EDA using $[\text{RuCl}_2(\text{PPh}_3\text{Bz})_2\text{L}]$ as precatalysts as a function of temperature and reaction time.

| Entry | L | T ($^\circ\text{C}$) | Time (min) | EDA (μL) | Yield (%) | M_w (10^6) | PDI |
|-----------------|---|------------------------|------------|-----------------------|-----------|------------------|------|
| 1 | PPh_2Bz | 25 | 5 | 3 ^a | NP | | |
| 2 | | 25 | 5 | 5 ^b | NP | | |
| 3 | | 25 | 5 | 7 ^c | NP | | |
| 4 | | 25 | 30 | 3 | <5 | | |
| 5 | | 25 | 30 | 5 | <5 | | |
| 6 | | 25 | 30 | 7 | <1.0 | | |
| 7 | | 50 | 5 | 3 | 50 | 2.4 | 2.74 |
| 8 | | 50 | 5 | 5 | 51 | 1.4 | 2.86 |
| 9 | | 50 | 5 | 7 | 40 | 0.2 | 2.18 |
| 10 | | 50 | 30 | 3 | 50 | 1.7 | 4.72 |
| 11 | | 50 | 30 | 5 | 52 | 1.5 | 6.28 |
| 12 | | 50 | 30 | 7 | 42 | 1.6 | 4.26 |
| 13 | pip | 25 | 5 | 3 | <5 | | |
| 14 | | 25 | 5 | 5 | NP | | |
| 15 | | 25 | 5 | 7 | NP | | |
| 16 | | 25 | 30 | 3 | 92 | 0.2 | 2.22 |
| 17 | | 25 | 30 | 5 | 52 | 0.2 | 2.89 |
| 18 | | 25 | 30 | 7 | 21 | 0.3 | 2.55 |
| 19 | | 50 | 5 | 3 | 94 | 0.5 | 2.32 |
| 20 | | 50 | 5 | 5 | 78 | 0.3 | 3.45 |
| 21 | | 50 | 5 | 7 | 40 | 0.2 | 3.31 |
| 22 | | 50 | 30 | 3 | 100 | 0.2 | 4.32 |
| 23 | | 50 | 30 | 5 | 94 | 0.5 | 4.45 |
| 24 | | 50 | 30 | 7 | 51 | 0.4 | 2.63 |
| 25 ^d | $[\text{RuCl}_2(\text{PPh}_3)_3]$ | 50 | 5 | 5 | 63 | 2.6 | 1.40 |
| 26 ^d | $[\text{RuCl}_2(\text{PPh}_3)_2(\text{pip})]$ | 25 | <1 | 5 | 99 | 0.2 | 1.90 |

$[\text{NBE}]/[\text{Ru}] = 5000$; $[\text{Ru}] = 1.0 \mu\text{mol}$ in 2 mL CHCl_3 ; NP = no polymerization.

^a 28.5 μmol .

^b 47.5 μmol .

^c 66.5 μmol .

^d Ref. [11].

2.6. Polymerization reactions

In a typical ROMP experiment, the metal complex was dissolved in 2 mL of CHCl_3 , followed by adding NBE and ethyl diazoacetate (EDA). The reaction mixture was stirred during different periods of time at 25 or 50 °C in a silicone oil bath. At room temperature, ~5 mL of methanol was added and the precipitated polymer was filtered, washed with methanol and dried at room temperature (RT) before being weighed. The catalytic runs were carried out at least 3 times.

3. Results and discussion

Results for ROMP of NBE using the catalyst precursors $[\text{RuCl}_2(\text{PPh}_2\text{Bz})_2\text{L}]$, L = PPh_2Bz (complex **1**) or pip (complex **2**), in the presence of different amounts of EDA are summarized in Table 1.

The complex **1** does not show good activity at 25 °C up to 30 min (entries 1–6). Nevertheless, the polymer began to precipitate within a few minutes at 50 °C, which was isolated after 5 min (entry 7) with a yield of 50% and PDI over 2. The PDI was larger when the polymer was isolated after 30 min (entry 10).

The complex **2** is reactive at 25 °C with 92% of polynorbornene for 30 min (entry 16). Similar results of yield, M_w and PDI are obtained for 5 min at 50 °C (entry 19). However, for 30 min at 50 °C, a quantitative reaction gives the polymer the same M_w value, but with a larger PDI (entry 22).

The reactions do not occur in the absence of EDA with both complexes **1** and **2**. However, the yield values decrease with an increasing of the EDA concentration under the same reaction conditions (Table 1). In all likelihood, the excess of EDA competes with the olefin of the monomer by the coordination sites on the Ru(II) at the beginning of the reaction and inhibits the ROMP process. A similar behavior was also observed with $[\text{RuCl}_2(\text{PPh}_3)_2\text{pip}]$, which is inactive when increasing the EDA amount from 5 (99% yield) to 50 μL (no polymerization) [11].

When using either complex **1** or **2**, the reaction activity increases with an increasing of the temperature from 25 to 50 °C. However, in the case of **2**, the process occurs at 25 °C for 30 min with a yield of over 90% and the polymer does not precipitate in the course of the reaction. In the case of **1**, the yield is 50% at most and the polymers always precipitate within a few minutes of reaction. It can be regarded that the difference between **1** and **2** is probably the production of the metal–carbene units, and then, the reaction with the olefin for the ROMP reaction to occur, typical of well-defined metathesis catalysts which usually provide an incomplete initiation reaction [1]. This can be rationalized observing the M_w and PDI values. In the case of **1**, activities at 50 °C can be associated with fast polymer productions after producing a few carbene complex units that probably does not occur at 25 °C up to 30 min, followed by fast propagation. This provides long polymer chains (high M_w) that precipitate with large PDIs. In the case of **2**, the enhanced PDIs are also due to the increasing in the propagation rate. However, the initiation is more favorable regarding reaction with complex **1**,

suggesting a more efficient production of the carbene species considering the reactivity at 25 °C and the fact that the polymer does not precipitate (see entries 13 and 16); this means that the polymer is not suddenly produced. It is noteworthy that the M_w results from the reaction with **2** are one order of magnitude smaller than the results with **1**.

When postponing the isolating times, the PDI values increase as a result of the reaction with complex **1** at 50 °C (entries 7–9 and 10–12), without changing the yields that have roughly the same M_w values. This probably takes place due to the occurrence of the intermolecular reactions [1,2]. Active Ru complexes in solution, such as Ru-oligomers, can promote cross-metathesis in the interface solution-material [1]. The reactions with complex **2** also produce polymers with broader PDI at 50 °C when the reaction time is increased. However, in this case, the polymers do not precipitate and the yields increase (entries 19–21 and 22–24). In these cases, it is believed that new catalyst units are produced as a function of time to initiate new polymer chains, providing a decrease in the M_n values.

Considering that **2** differs from **1** by replacing one PPh_2Bz molecule in **1** for pip, the synergistic effect $\text{pip} \xrightarrow{\delta} \text{Ru} \xrightarrow{\pi} \text{olefin}$ increases the olefin activation. Thus, the σ -donor character (estimated by the $\text{p}K_a = 11.2$) combined with the large cone angle ($\theta = 121^\circ$) of the pip in **2** provides better reactivity results than in **1** (Table 1). On the other hand, complex **1** gives the worst results probably because it becomes dimmer in solution, which is broken down at 50 °C. Then, with **1** a fast propagation occurs, since M_w values are large and the polymers precipitate. This fact is strong evidence that the active species from **1** and **2** are different. In the case of **2**, the piperidine molecule is present in the metal coordination sphere.

A comparison between **1** (entry 8) and $[\text{RuCl}_2(\text{PPh}_3)_3]$ (entry 25) shows that the complex with PPh_3 ($\text{p}K_a = 2.7$; $\theta = 145^\circ$) also produces a polymer with long chain (large M_w values), but with a lower PDI value than that synthesized with **1**. The reason for this fact may be a less steric hindrance to approach the monomer in the case of PPh_3 in relation to the more bulky PPh_2Bz . This means that the initiation step is faster, hence making it complete. The steric influence is also observed when compared to the catalytic precursors $[\text{RuCl}_2(\text{PPh}_3)_2\text{pip}]$ and **2**, where the former synthesizes the polymer with similar M_w and PDI values (see entries 17 and 26), but with a better yield for short reaction times.

When the $[\text{NBE}]/[\mathbf{1}]$ ratio is increased from 1000 to 15,000 by increasing the NBE amount, complex **1** provides high yields (Table 2), with quantitative reaction when $[\text{NBE}]/[\mathbf{1}] = 15,000$ (entry 4). When the $[\text{NBE}]/[\mathbf{1}]$ ratio is 1000, polymodal polymer is obtained (entry 1). At higher monomer concentrations, the entropy contribution compensates the enthalpy value [2]. This favors the ROMP reaction, increasing the reaction yield. This fact was observed with similar complexes ($[\text{RuCl}_2(\text{PPh}_3)_3]$, $[\text{RuCl}_2(\text{PPh}_3)_2(\text{sec-BuNH}_2)_2]$, $[\text{RuCl}_2(\text{PPh}_3)_2(\text{NHPPh}_2)_2]$ and $[\text{RuCl}_2(\text{PPh}_3)_2(\text{imidazole})_2]$), when the $[\text{NBE}]/[\text{Ru}]$ ratio changes from 1000 to 5000 [13].

Table 2

ROMP of NBE using $[\text{RuCl}_2(\text{PPh}_3\text{Bz})_2\text{L}]$ as precatalysts as a function of NBE concentration with $[\text{Ru}] = 1.0 \mu\text{mol}$ and 5 μL EDA in 2 mL CHCl_3 ; at 50 °C for 5 min.

| Entry | L | $[\text{NBE}]$ (mol L ⁻¹) | $[\text{NBE}]/[\text{Ru}]$ | Yield (%) | M_w (10 ⁶) | PDI |
|-------|-------------------------|---------------------------------------|----------------------------|-----------|------------------------------|-------------------------------|
| 1 | PPh_2Bz | 0.5 | 1000 | 55 | 0.6; 0.05; 0.02 ^a | 1.71; 1.08; 1.55 ^a |
| 2 | | 2.5 | 5000 | 51 | 1.4 | 2.86 |
| 3 | | 5.0 | 10,000 | 85 | 1.7 | 2.98 |
| 4 | | 7.5 | 15,000 | 100 | 1.5 | 2.41 |
| 5 | pip | 0.5 | 1000 | 37 | 0.3 | 11.3 |
| 6 | | 2.5 | 5000 | 78 | 0.3 | 3.45 |
| 7 | | 5.0 | 10,000 | 52 | 1.0 | 2.57 |
| 8 | | 7.5 | 15,000 | 65 | 0.8 | 2.20 |

^a Trimodal distribution molecular weight.

Table 3
ROMP of NBE using $[\text{RuCl}_2(\text{PPh}_3\text{Bz})_2\text{L}]$ as precatalysts as a function of Ru complex concentration with $[\text{NBE}] = 5.0 \text{ mmol}$; $5 \mu\text{L}$ EDA in 2 mL CHCl_3 ; 50°C ; 5 min .

| Entry | L | Ru (μmol) | $[\text{NBE}]/[\text{Ru}]$ | Yield (%) | M_w (10^6) | PDI |
|-------|-------------------------|------------------------|----------------------------|-----------|------------------------|-------------------------|
| 1 | PPh_2Bz | 2.0 | 2500 | 88 | 0.9 | 4.26 |
| 2 | | 3.0 | 1667 | 100 | 0.6; 0.04 ^a | 1.81; 1.43 ^a |
| 5 | pip | 2.4 | 2083 | 100 | 0.07 | 6.61 |
| 6 | | 3.7 | 1351 | 100 | 0.6 | 12.4 |

^a Bimodal distribution molecular weight.

The yield results do not correlate with the $[\text{NBE}]/[\mathbf{2}]$ ratio by increasing the $[\text{NBE}]$ (entries 5–8). At low $[\text{NBE}]$ ($[\text{NBE}]/[\mathbf{2}] = 1000$), a series of oligomers are produced, attributed to the lack of monomer in the ongoing fast propagation reaction (Table 2; entry 5) [2].

Complex **2** shows a different behavior in relation to the precatalytic **1** when $[\text{NBE}]/[\mathbf{2}] > 5000$, producing polymers with lower yields when compared to $[\text{NBE}]/[\mathbf{2}] = 5000$ value (Table 2). The M_w values are roughly constant with decreasing PDI values, suggesting a reaction without the occurrence of secondary reactions.

Table 3 summarizes the yield and PDI values of polynorbornene obtained at 50°C for 5 min when the $[\text{Ru}]$ is varied while holding the $[\text{NBE}]$. Complex **1** synthesizes polynorbornene with a much better yield, hence increasing the Ru amount. However, the formed polymers show larger PDIs (entries 1–4). With $3.0 \mu\text{mol}$ of **1**, poly-modal polymers are observed with two polymer groups. Complex **2** synthesizes polynorbornene with quantitative yield when using a larger amount of Ru, but the PDI value is also very large.

From the reaction between **1** and the amines nic and isn, six-coordinated complexes are obtained.

The complexes **3**, with nic, and **4**, with isn, do not show good activity at 25°C up to 30 min (Table 4; entries 1–6). At most 12% yield is obtained at 50°C for 30 min with $5 \mu\text{L}$ of EDA (entries 11 and 23; Table 4). The low σ -donor characters and low cone angles of these ligands, different from the piperidine, can be responsible to these results. Thus, the six-coordinated geometric arrangements of these ligands with PPh_2Bz give inert complexes. In spite of the smaller π -acid nature of the isn (isn, $\text{p}K_a = 3.6$; nic, $\text{p}K_a = 3.0$), the smaller cone angle makes complex **4** less active than complex **3**. Recently, it was reported that the activity of Grubbs' catalyst

Table 4
ROMP of NBE in the presence of EDA using $[\text{RuCl}_2(\text{PPh}_3\text{Bz})_2(\text{L})_2]$ as precatalysts as a function of temperature and reaction time.

| Entry | L | T ($^\circ\text{C}$) | Time (min) | Volume EDA (μL) | Yield (%) |
|-------|-----|--------------------------|------------|------------------------------|-----------|
| 1 | nic | 25 | 5 | 3 | NP |
| 2 | | 25 | 5 | 5 | NP |
| 3 | | 25 | 5 | 7 | NP |
| 4 | | 25 | 30 | 3 | NP |
| 5 | | 25 | 30 | 5 | NP |
| 6 | | 25 | 30 | 7 | NP |
| 7 | | 50 | 5 | 3 | 7 |
| 8 | | 50 | 5 | 5 | 7 |
| 9 | | 50 | 5 | 7 | 4 |
| 10 | | 50 | 30 | 3 | 10 |
| 11 | | 50 | 30 | 5 | 12 |
| 12 | | 50 | 30 | 7 | 9 |
| 13 | isn | 25 | 5 | 3 | NP |
| 14 | | 25 | 5 | 5 | NP |
| 15 | | 25 | 5 | 7 | NP |
| 16 | | 25 | 30 | 3 | NP |
| 17 | | 25 | 30 | 5 | NP |
| 18 | | 25 | 30 | 7 | NP |
| 19 | | 50 | 5 | 3 | NP |
| 20 | | 50 | 5 | 5 | NP |
| 21 | | 50 | 5 | 7 | NP |
| 22 | | 50 | 30 | 3 | 5 |
| 23 | | 50 | 30 | 5 | 12 |
| 24 | | 50 | 30 | 7 | 5 |

$[\text{Ru}] = 1.0 \mu\text{mol}$ in 2 mL CHCl_3 ; $[\text{NBE}]/[\text{Ru}] = 5000$; NP = no polymerization.

$[\text{RuCl}_2(\text{PCy}_3)_2(=\text{CHPh})]$ was inhibited when one phosphine was replaced by two N-donor ligands [18], generating six coordinated complexes as occurs in the case of the complexes **3** and **4**. However, six coordinated hybrid complexes with PPh_3 and acyclic amines (NH_2^sBu , NH_2Ph , NHPh_2 and NET_3) were very active for ROMP of NBE [13]. Thus, the fine tune of the electronic and steric effects of the ancillary ligands is a very important key in the development of *in situ* generated metathesis catalysts.

4. Conclusion

Three hybrid amine–phosphine complexes were isolated where each one has two PPh_2Bz molecules, in addition to two chloride ions. The complexes were six-coordinated with either isn or nic and five-coordinated with piperidine. The main difference in the coordination numbers was attributed to steric hindrance, provided by the combination between one phosphine and one or two amines. The reactivities of the complexes for ROMP of NBE were very sensitive to the composition of the metal coordination sphere. The adjustment of the ligands around the metal produced singular effects in the reaction results under the different conditions that they were carried out (reaction time, temperature and concentrations of the reactants). Besides the steric hindrances from the ligands, the synergic electronic balances from the Ru–ligand bonds were also responsible for generating different starting and propagating catalyst species. It is inferred that the *in situ* generated species are different from each other for each starting complex. This is clearly demonstrated by the results obtained with **1** and **2**, as well as in the cases of isn and nic derivative complexes. The propagating species are hybrid amine–phosphine complexes since they produced different results. If the amine leaves the complex, the active species would be similar to the pure phosphine compound, in agreement with early results [10–13].

It is important to observe that large amounts of NBE using small Ru loadings were used in the catalytic runs. This fact represents an elevated reaction ability using the developed precatalysts. Furthermore, our results contribute to the development of alternative catalysts to ROMP as usually stated in the literature [7,9], in addition to the tremendous successes of the *ex situ* generated carbene complexes [2,3].

Acknowledgments

We thank the financial supports from FAPESP (Proc. No. 2006/57757-4), CAPES and CNPq.

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