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Development of easily accessible ruthenium-based catalysts for metathesis polymerization using 4-X-pyridines as ancillary ligands

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Abstract

Complexes of the type $[RuCl_2(PPh_3)_2(N^{III})_2]$, where N^{III} = 4-X-pyridines [X = $C(O)NH_2$(isonicotinamide), H (pyridine), CH_3 (4-picoline) or NH_2 (4-amino-pyridine)] were investigated for catalysis of norbornene via ring-opening metathesis polymerization (ROMP). The results show that the yields are greater than 70% in $CHCl_3$ when [NBE]/[Ru] = 3000 ($M_n \sim 10^4$ to 10^5 and $M_w/M_n \sim 1.2$–2.0) at 50 ± 1 °C for 5 min. Considering the complex with isonicotinamide under similar conditions but for [NBE]/[Ru] = 5000, the yield reaches 94% of isolated polymer with $M_w/M_n = 1.2$. The behavior of the amine complexes were observed by $^{31}P\{^1H\}$ and ^1H NMR analyses leading to the conclusion that a five-coordinated diamine–monophosphine complex is the active initiator. This 16-electron complex becomes inert when N^{III} is a good σ-donor ligand, such as pyridine, 4-picoline or 4-amino-pyridine. Consequently, there is a decrease in catalytic activity since the subsequent step represents the exit of an amine ligand in order that the ROMP reaction can occur successfully.

Keywords: ROMP; Norbornene; Norbornadiene; Ruthenium; Ancillary ligands; Amine–phosphine complex

1. Introduction

Very recently, the ability of the five-coordinated complex, $[RuCl_2(PPh_3)_2(piperidine)]$, in promoting ring-opening metathesis polymerization (ROMP, Scheme 1) of norbornene and norbornadiene was investigated by observing their high catalytic activity compared to the precursor $[RuCl_2(PPh_3)_3]$ [1]. It was concluded that this high catalytic activity occurs because the new complex does not undergo dimerization as does its precursor.

In the framework of a systematic study to develop catalytic ROMP systems that are resistance to moisture and air under mild condition, this paper shows the results obtained with the six-coordinated complexes of type $[RuCl_2(PPh_3)_2(N^{III})_2]$, where N^{III} denotes 4-X-pyridines: X = $C(O)NH_2$ (isonicotinamide; pK_a = 3.6), H (pyridine; pK_a = 5.2), CH_3 (4-picoline; pK_a = 6.0) or NH_2 (4-amino-pyridine; pK_a = 9.2). These selected ligands show different electronic nature while maintaining their steric effect.

The growing interest in the development of new polymers formed from ROMP has stimulated researchers to search new catalysts for this reaction [2]. In this context, the present paper aims at contributing in the development of such catalysts by using N-cyclic or N-acyclic amine as ancillary ligands. It is well known that the ligand nature can have profound and largely unpredictable effects on the catalytic activity of the coordination complexes and present results strongly support this fact.

Several amine–phosphine complexes have been synthesized from $[RuCl_2(PPh_3)_3]$ or similar complexes [3], but catalytic processes with these types of compounds have not been widely investigated. Some other authors have improved the catalytic activity of $[RuCl_2(PPh_3)_3]$ using N-donor ligands as additives [4]. It is, however, understand here that this represents an in situ formation of an amine–phosphine complex.

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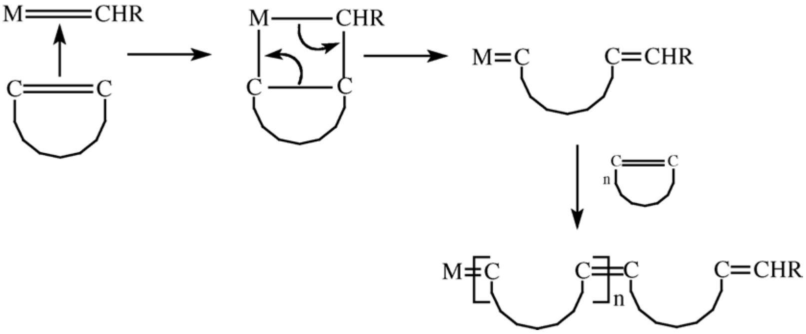

Scheme 1.

2. Experimental

2.1. General remarks

All manipulations were carried out under argon. All solvents used were of analytical grade and were distilled from appropriate drying agents immediately prior to use: $RuCl_3 \cdot xH_2O$ from Stream, norbornene (NBE) from Across, pyridine (py), 4-picoline (4-pic), isonicotinamide (isn) and 4-amino-piridine (4-Apy) from Merck and ethyldiazoacetate (EDA), norbornadiene (NBdiene) and PPh_3 from Aldrich were used as archived. The $[RuCl_2(PPh_3)_3]$ complex was prepared as indicated in literature [5] and its purity checked by satisfactory elemental analysis and spectroscopic examination ($^{31}P\{^1H\}$ and ^1H NMR and FTIR).

2.2. Synthesis of $[RuCl_2(PPh_3)_2(N^{III})_2]$

The complex $[RuCl_2(PPh_3)_2(N^{III})_2]$ where N^{III} = pyridine (py) or 4-picoline (4-pic) was prepared as described in literature with little modification [3]; a 1.23 mmol of amine was added to a 0.47 mmol of a solution of $[RuCl_2(PPh_3)_3]$ in acetone (50 mL) and the mixture refluxed for 3 h under argon. The solution was then reduced up to 5 mL under vacuum. The resulting yellow solid was filtered, washed with ether and methanol and then dried in vacuum. Anal. Calc. for $[RuCl_2(PPh_3)_2(py)_2]$: C, 64.64; H, 4.72; N, 3.28. Found: C, 64.03; H, 4.90; N, 3.46 (70% yield). Anal. Calc. for $[RuCl_2(PPh_3)_2(4\text{-pic})_2]$: C, 65.31; H, 5.02; N, 3.17. Found: C, 65.01; H, 5.17; N, 3.42 (65% yield). The complexes with isonicotinamide (isn) or 4-aminopyridine (4-Apy) were prepared by adding 1.23 mmol of amine to a solution of 0.47 mmol of $[RuCl_2(PPh_3)_3]$ in acetone (25 mL) and the mixture stirred under argon at room temperature for 1:30 h. An orange (for isn) and a gray (for 4-Apy) compounds were precipitated in solution. The solid was washed with ether and dried in vacuum. Anal. Calc. for $[RuCl_2(PPh_3)_2(isn)_2]$: C, 61.28; H, 4.50; N, 5.96. Found: C, 61.20; H, 4,38; N, 6.00 (83% yield). Anal. Calc. for $[RuCl_2(PPh_3)_2(4\text{-Apy})_2]$: C, 61.40; H, 4.90; N, 6.50. Found: C, 61.27; H, 5.00; N, 6.70 (68% yield). All these complexes were EPR silent.

2.3. Instrumentation

Elemental analyses were carried out by 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. UV–visible spectra were measured in a Varian Cary 5G spectrophotometer using quartz cuvettes (10 mm). The ^1H and $^{31}P\{^1H\}$ NMR spectra were obtained in a $CDCl_3$ solution at 25.0 ± 0.1 °C using a Bruker AC-200 spectrometer equipped with a probe operating at 200.13 and 81.015 MHz, respectively. Chemical shifts are herein reported in ppm relative to the frequency of tetramethylsilane or 85% H_3PO_4. The molecular weight (M_n) and molecular weight distribution (M_w/M_n) was obtained by gel-permeation chromatography analyses obtained on a Shimadzu 77251 spectrometer system equipped with a PL gel column (5 μm mixed-C: 30 cm, Ø = 7.5 mm). The retention time was calibrated with respect to 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 is dissolved in 2 mL of $CHCl_3$ and a certain amount of monomer and 5.4 μmol of ethyldiazoacetate are later added. In the present study, the reaction mixture was maintained at 50 ± 1 °C for different periods of time in a silicone oil bath. At room temperature, 5 mL of methanol was added and the precipitated polymer filtered, washed with methanol and dried in vacuum before being weighed.

3. Results and discussion

3.1. Catalytic activity of $[RuCl_2(PPh_3)_2(N^{III})_2]$ complexes

Experiments with different amounts of the monomer were carried out in order to determine the optimal monomer concentration for the polymerization reaction. A [NBE]/[Ru] molar ratio of 3000 was obtained for either N^{III} = py or

4-pic with the isolated polymer reaching 67% ($M_n = 4.2 \times 10^4$; $M_w/M_n = 1.3$) or 70% yield ($M_n = 4.3 \times 10^4$; $M_w/M_n = 1.3$), respectively, at 50 ± 1 °C for 5 min. In either case, the polymer was shown to be bimodal, the yields showing a decrease in the range of 3000–5000, which is likely to occur if k_i is higher than k_p. A better [NBE]/[Ru] molar ratio of 5000 was found for either N^{III} = isn or 4-Apy with the isolated polymer reaching 98% ($M_n = 1.7 \times 10^5$; $M_w/M_n = 1.5$) or 63% ($M_n = 1.9 \times 10^5$; $M_w/M_n = 1.8$), respectively, under similar conditions. In the latter cases, a polymer with unimodal distribution was obtained. These complexes were shown to be inactive in ROMP of norbornene and norbornadiene at room temperature (24–26 °C) when a similar molar ratio is used.

The polymerization reactions were investigated at 50 ± 1 °C as a function of time (Fig. 1). For N^{III} = py or 4-pic, an increase of 20% in the reaction yield was observed. With 4-Apy, the yield showed a slight decreased, while with isn, the yield remained constant through out the reaction. In all cases, similar increases in the values of M_n of the order of 10^5 were observed. The M_w/M_n values ranged between 1.2 and 2.4 with an average value of 1.7. In the case of isn derivative complex, the reaction is almost quantitative with M_w/M_n decreasing up to 1.2. Comparing these results and those of the second-generation Grubbs catalysts [6], the activity of the vinylidene are shown to be much lower, with a much broader molecular weight distribution.

The catalyst lifetime was also investigated by carrying out a ROMP experiment with a 2-day aged solution that was kept under argon at room temperature. An appropriate volume of the solution was taken and mixed with a monomer solution at 50 ± 1 °C followed by the addition of EDA. The catalyst activity reached 80% with py ($M_n = 6.7 \times 10^4$; $M_w/M_n = 1.7$), 81% with 4-pic ($M_n = 7.1 \times 10^4$; $M_w/M_n = 1.7$), 81% with isn ($M_n = 1.5 \times 10^5$; $M_w/M_n = 1.8$) and 50% with 4-Apy ($M_n = 4.4 \times 10^5$; $M_w/M_n = 1.8$). These results show that the complexes do not lose their ROMP-activity in solution.

The living nature of the polymerization reactions when the amine–phosphine ruthenium complexes are used as starting material is demonstrated in the M_n and M_w/M_n versus [NBE]/[Ru] molar ratio curves where an increase in the molecular weights, with the addition of monomer, is observed in each case (Fig. 2). For 4-pic complex, a very good linear relationship between the molecular weights and the molar ratio is observed with a fairly narrow

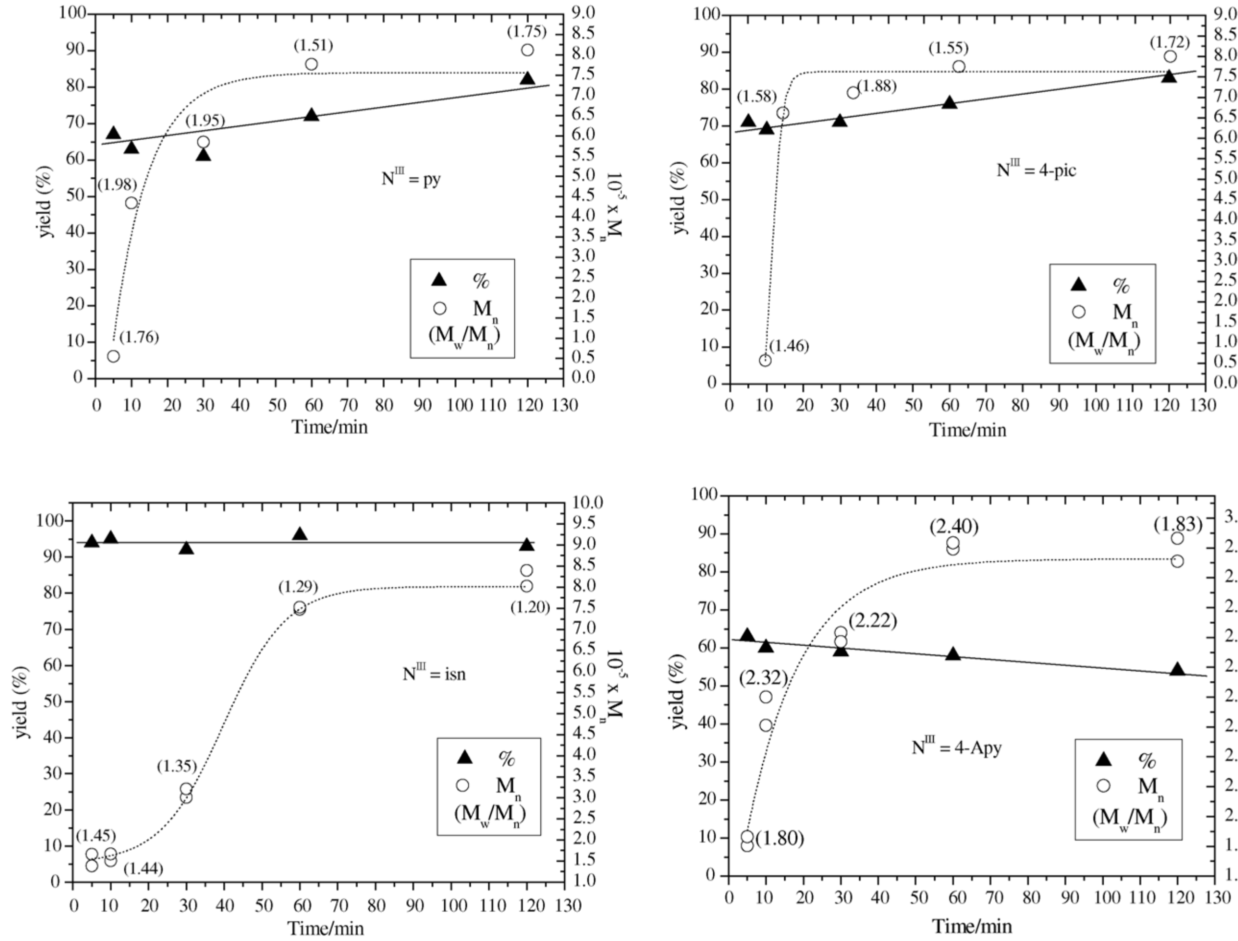

Fig. 1. Plots of yield, M_n and M_w/M_n as a function of polymerization time for ROMP norbornene with $[RuCl_2(PPh_3)_2(N^{III})_2]$ complexes in $CHCl_3$ at 50.0 ± 1.0 °C; [Ru] = 1.2 μmol; [NBE]/[Ru] = 3000 for N^{III} = py and 4-pic and 5000 for L = isn and 4-Apy; 5 μL of EDA.

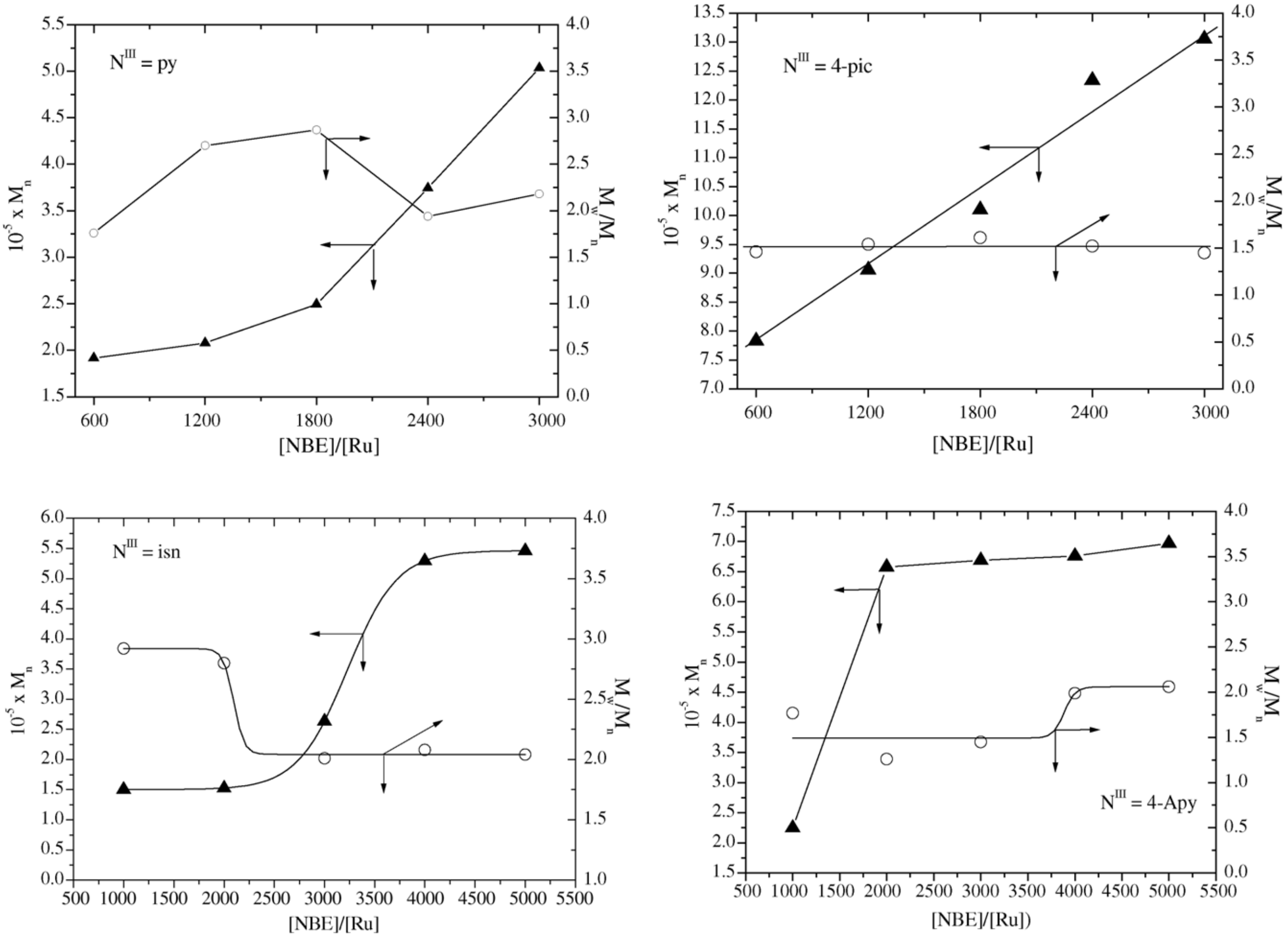

Fig. 2. Plot of M_n (▲) and M_w/M_n (O) for polynorbornene as a function of [NBE]/[Ru] molar ratio with $[RuCl_2(PPh_3)_2(N^{III})_2]$ solutions in $CHCl_3$ at 50 ± 1 °C for 5 min; 5 μL of EDA.

molecular weight distribution, which remained constant. This clearly indicates that the polymer chains are increasing in uniformity.

The complexes are completely ROMP-inactive in the absence of EDA. Reactions carried out in presence of different amounts of EDA showed that the yield of the polymer is directly proportional to the molar ration of EDA up to 5 μL ([EDA]/[Ru] = 48) (Table 1). For volumes of EDA higher than 5 μL, the yield decreases up to 50 μL. This, probably, occurs because the increase in the EDA concentration results in a competition between the monomer and EDA for the metal center and thus, poisoning the system. Other research studies confirm these observations, showing that the degree of polymerization is dependent on the amounts of diazo compound [7].

The py- and 4-pic derivative complexes are active for ROMP of norbornadiene yielding 16 and 18%, respectively, at 50 ± 1 °C during 5 min, but the polymers are shown to be insoluble in $CHCl_3$. The complexes with isn and 4-Apy have so far been shown to be inactive for ROMP of norbornadiene under similar conditions.

The ROMP reaction did not occur in the presence of either excess of PPh_3 or amines. This was also true when the Cl^- ligands were replaced by $OSO_2CF_3^-$ (using $AgSO_3CF_3$), indicating that π-donor ligands are necessary in the coordination metal sphere, as has been earlier reported [8].

An important advantage of these systems is that choosing the time, molar ratio of monomer and amounts of carbene can control the degree of polymerization.

Similar complexes from reactions of $[RuCl_2(PPh_3)_3]$ with 2,6-lutidine and 2-picoline have proved unsuccessful so far. The coordination of the amine is presumably unfavorable because of steric hindrance. However, it is believed that the presence of large amines in the coordination metal center sphere could improve the catalytic results in a way similar to that observed when PPh_3 was substituted for PCy_3 using $[RuCl_2(phosphine)_2(CHR)]$ [2]. Further, a different behavior was observed when piperidine was used as ancillary ligand in $[RuCl_2(PPh_3)_2(amine)_x]$, which is larger than pyridine [1].

3.2. Characterization of the complexes in solution

The six-coordinated nature of the synthesized complexes is supported by the satisfactory analytical results, which are in good agreement with the assigned formulation. The

Table 1
Influence of [EDA]/[Ru] molar ratio on the polymerization of norbornene at 50 ± 1 °C for 5 min; [NBE]/[Ru] = 3000 for py and 4-pic or 5000 for isn and 4-Apy complexes

V_{EDA} (μL) (n_{EDA}/n_{Ru})	$[RuCl_2(PPh_3)_2(py)_2]$			$[RuCl_2(PPh_3)_2(4\text{-pic})_2]$			$[RuCl_2(PPh_3)_2(isn)_2]$			$[RuCl_2(PPh_3)_2(4\text{-Apy})_2]$		
	Yield (%)	$M_n \times 10^{-4}$	M_w/M_n	Yield (%)	$M_n \times 10^{-4}$	M_w/M_n	Yield (%)	$M_n \times 10^{-4}$	M_w/M_n	Yield (%)	$M_n \times 10^{-4}$	M_w/M_n
1 (9.5)	44	0.44	9.61	31	0.71	8.04	90	18.25	1.95	28	11.1	2.05
2 (19)	50	0.44	8.70	38	0.36	9.70	91	4.69	2.51	38	2.0	1.98
3 (29)	54	6.53[a]	1.29	47	4.91[a]	1.28	93	4.51	2.44	45	1.12	2.03
		0.12	2.18		0.11	2.13						
4 (38)	62	6.37[a]	1.31	59	5.68[a]	1.41	87	5.90	1.87	61	9.5	1.85
		0.3	2.07		0.11	2.02						
5 (48)	67	4.17[a]	1.32	70	4.34[a]	1.31	94	16.60	1.49	63	19.0	2.51
		0.21	1.89		0.11	1.90						
10 (95)	55	5.97[a]	1.17	58	0.27	6.52	23	5.54[a]	1.64	56	5.13[a]	1.63
		0.12	2.21					0.093	1.85		0.08	1.13
20 (190)	36	0.15	3.87	44	2.69[a]	1.32	20	6.01[a]	1.49	32	7.04[a]	2.10
					0.10	1.77		0.10	2.01		0.15	1.14
30 (285)	31	3.11[a]	1.44	21	2.62[a]	1.26	15	4.55[a]	1.39	18	8.25[a]	1.87
		0.10	1.54		0.11	1.77		0.11	1.98		0.09	1.57
40 (380)	26	0.29	24.37	10	2.59[a]	1.27	9	5.47 [a]	1.26	15	7.16[a]	2.22
					0.11	1.79		0.11	2.16		0.17	1.17
50 (475)	20	0.32	9.59	7	3.25[a]	1.38	5	5.62 [a]	1.43	13	4.07	2.10
					0.10	1.73		0.09	2.03			

[a] Bimodal polymer.

absence of any signal in the EPR spectra of the complexes suggests a low spin d^6 ruthenium metal center.

In addition to analytical results, the presence of Cl^- ligands in the isolated compound seems to be confirmed by the typical Ru–Cl stretch bands in the vibrational spectra observed in the range 350–300 cm^{-1}. However, it is difficult to say if the two Cl^- ligands are positioned in a *trans*- (one band) or *cis*- (two bands) configuration relative to each other because of the set of weak bands in the neighborhood. On the other hand, the solid state isomerism is not very important at this moment since we are dealing with kinetically labile octahedral complexes and the resulting complex can be a sterochemically nonrigid molecule in the ROMP mechanism reaction as will be discussed later.

The electronic spectrum of these complexes in $CHCl_3$ changes continuously up to approximately 12 h (Fig. 3). The $t_{1/2}$ values are, respectively, 16 h ($k_{obs} = 1.2 \times 10^{-5}\ s^{-1}$) and 15 h ($k_{obs} = 1.3 \times 10^{-5}\ s^{-1}$) for complexes with py and 4-pic at 25.0 ± 0.1 °C. For the pyridine complex, the $t_{1/2}$ value at 50.0 ± 0.1 °C is 3.7 min ($k_{obs} = 3.1 \pm 10^{-3}\ s^{-1}$). For the isn derivative complex, the electronic spectrum is also shown to change continuously up to approximately 12 h at 25.0 ± 0.1 °C, however, two consecutive reactions with $t_{1/2}$ values of 3.24 min ($k_{obs} = 3.6 \times 10^{-3}\ s^{-1}$) and 1.21 h ($k_{obs} = 1.6 \times 10^{-4}\ s^{-1}$) are observed (Fig. 4).

The analyses of $^{31}P\{^1H\}$ NMR show a sharp peak at 37.2 ppm in the case of N^{III} = py and a new sharp peak emerges at 28.3 ppm for 12 h (Fig. 5). A peak, which is attributed to free phosphine, appears simultaneously at –4.7 ppm [9]. This is a clear indication of the release of PPh_3, suggesting the formation of a five-coordinated complex since the medium is a typical non-coordinated solvent. A similar behavior is observed with 4-pic including the peak values.

For the complex with isn, the first $^{31}P\{^1H\}$ NMR spectrum also shows a peak at low field (35.7 ppm), which disappears with time. This peak disappears simultaneously with another peak at high field (31.1 ppm), which increases as a function of time. The presence of free PPh_3 is also observed (−5.0 ppm). It seems that a five-coordinated complex is also formed in this case.

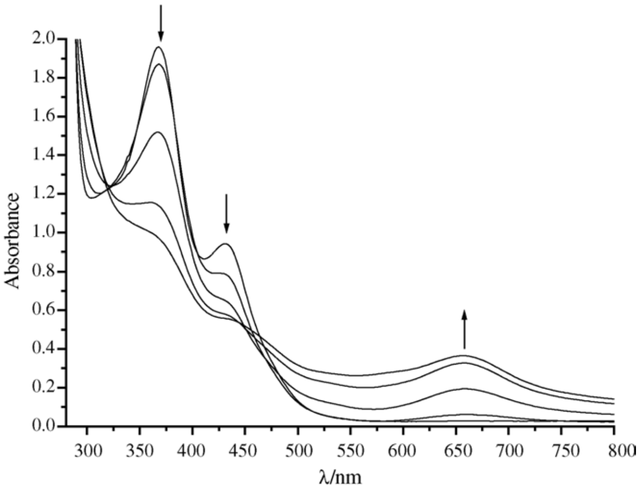

Fig. 3. UV–visible spectra as a function of time for $[RuCl_2(PPh_3)_2(py)_2]$; [Ru] = 1.0×10^{-4} mol L^{-1} in $CHCl_3$ at 25.0 ± 0.1 °C; total time of 12 h.

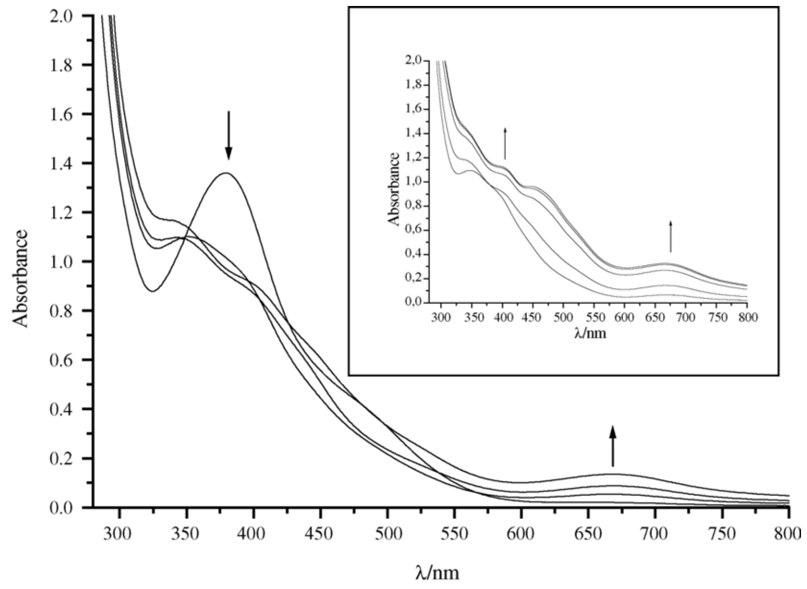

Fig. 4. UV–visible spectra as a function of time for $[RuCl_2(PPh_3)_2(isn)_2]$; $[Ru] = 1.0 \times 10^{-4}$ mol L^{-1} in $CHCl_3$ at 25.0 ± 0.1 °C; total time of 12 h (first 40 min in the main frame).

For the 4-Apy complex, the solubility is limited in $CHCl_3$ making it difficulty to observe its behavior when $^{31}P\{^1H\}$ NMR is used.

Comparing the behavior of the pyridine and isonicotinamide complexes, it seems that a faster release of PPh_3 occurs in the case of isn complex. Thus, despite the fact the isn is more π-acid, the starting material used with this ligand is more proper for this type of catalysis reaction. If a five-coordinated complex is rapidly obtained, a second open-position can also be reach rapidly where at least two closed position are necessary for reaction to occur completely.

The ^1H NMR spectra (Fig. 6) show signals of free PPh_3 [7.80–7.40 ppm (*meta*) and 6.77–6.64 ppm (*ortho* and *para*) ranges] in addition to coordinated PPh_3 [7.78–7.39 ppm (*meta*) and 6.57–6.46 ppm (*ortho* and *para*) ranges] in the case of py complex. The amine peaks are detected in the ranges of 8.80–8.67 ppm (*ortho*), 7.20–7.04 ppm (*para*) and 7.00–6.80 ppm (*meta*) in the case of coordinated py. Similar ranges are observed in the case of 4-pic complex. New peaks which may be attributed to the coordinated PPh_3 at intervals of 6.64–6.45 ppm or 6.36–6.28 ppm for the complexes with py or 4-pic, respectively, appears with time. News peaks at intervals of 6.82–6.72 ppm (*meta*) and 6.61–6.49 ppm (*meta*) that are attributed to coordinated py and 4-pic, respectively, also appear. No peaks that could be attributed to free amines are observed. Thus, these news peaks confirm the formation of a five-coordinated complex with two amines and one-coordinated PPh_3. This arrangement is also confirmed by the release of PPh_3 detected by $^{31}P\{^1H\}$ NMR as already discussed. In the case of the isn complex, no spectral variation

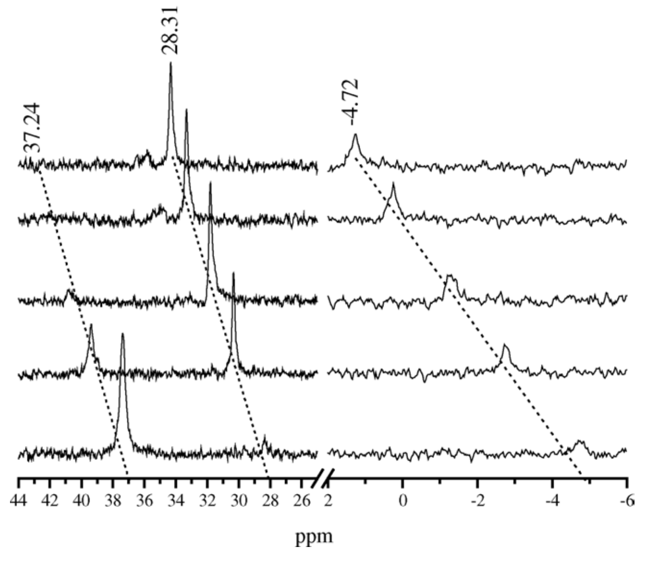

Fig. 5. $^{31}P\{^1H\}$ NMR spectra as a function of time for $[RuCl_2(PPh_3)_2(py)_2]$ in $CDCl_3/CHCl_3$ at 25.0 ± 0.1 °C; total time of 12 h.

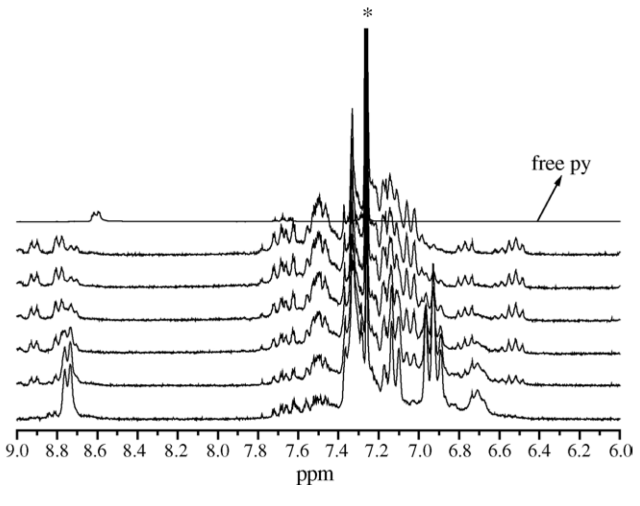

Fig. 6. ^1H NMR spectra as a function of time for $[RuCl_2(PPh_3)_2(py)_2]$ in $CDCl_3$ at 25.0 ± 0.1 °C (*, $CHCl_3$); total time of 12 h.

is observed in a period of 48 h. This is because the spectral changes must have already occurred during this time.

In all the above-mentioned cases, a five intermediated coordinated complex is formed in solution since a PPh_3 molecule undergoes dissociation at 25.0 ± 0.1 °C. The difference in the catalytic behavior is how fast this process occurs. Considering the $t_{1/2}$ values, it can be observed that in the case of isn for instance, this process is faster than with py. The dissociation of PPh_3 in the case of py takes place at a similar time at 50 ± 1 °C as that of the isn complex. Thus, the formation of the five-coordinated complex occurs first followed by the additional release of other ligands in the presence of EDA and substrate. The second ligand that dissociates is an amine since free PPh_3 signal is detected in a pos-ROMP solution. This leads us to think that if the 16-electron five-coordinated complex were electronically stabilized with two good σ-donor ligands like py, 4-pic or 4-Apy, the intermediate complex would be more kinetically inert than the complex with isn because this ligand behaves as a moderate π-acceptor ligand. In any case, the five-coordinated intermediate is a stable complex in solution up to 120 min, ready to initiate the catalysis reaction as observed in Fig. 2. Furthermore, the fact that the reaction does not occur in the presence of either PPh_3 or amine supports the dissociation of one phosphine and amine from the coordination sphere, resulting in the $\{RuCl_2(PPh_3)(\text{-}N^{III})\}$ moiety complex as the ROMP-active species.

4. Conclusion

This investigation clearly demonstrates that amines, when coordinated to Ru(II) complex in the presence of EDA, act as good ancillary ligands in the polymerization of norbornene. Although the reactivity is less pronounced than that of the corresponding piperidine complex [1], the amines studied can be used as an alternative to ancillary ligands. The resulting complexes can be used for practical purposes due to several reasons; the amines are readily available from commercial products, the production of polymers or the degree of polymerization can be controlled by choosing the reaction time, molar ratio of monomer/metal and amounts of carbene and the corresponding polydispersity is comparable to that of a well-established olefin metathesis. Furthermore, it has been demonstrated that amine–phosphine complexes are better starting material than $[RuCl_2(PPh_3)_3]$, its precursor [1].

Another advantage of these systems is that the polymerization can be carried out in air or with anhydrous solvents, a condition which is not feasible for must molybdenum, tungsten and others ruthenium catalysts [2].

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