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The ring size of cyclic amines as relevant feature in the activity of Ru-based complexes for ROMP

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The novel complex [$RuCl_2(PPh_3)_2$(pyrrolidine)] presented a square pyramidal (SQP) type geometry, with the amine in the apical position and *trans*-positioned phosphines. There was activity for ROMP of norbornene (NBE) under either air or inert atmosphere of argon at 25 °C. Saturation profile-fitting describes the curves of yields as a function of time (5 - 120 min) under either atmosphere. The results were sensitive to the solution volume in the range of 2 - 8 mL of $CHCl_3$, mainly under air. Quantitative yields under argon for 120 min at any solution volume were obtained. The order of magnitude of 10^3 - 10^5 g mol^{-1} for M_w and PDI values ranging from 1.6 to 3.5 were measured by SEC. In the most of the cases, the ratios of yields from the runs under argon and air were close to the unit, indicating an insignificant loss of reactivity of the active species in the presence of molecular oxygen from the air. A parent complex with diethylamine, but with trigonal bipyramidal (TBP) type geometry, was inactive for ROMP. The activity in these types of complexes were compared with already reported Ru-amine-based complexes in terms of electronic effects, with an additional discussion involving the synergism in the novel *ttt*-[$RuCl_2(PPh_3)_2$(perhydroazepine)(isonicotinamide)] complex.

Introduction

The production of unsaturated polymers has increased with the development of transition metal complexes for Ring Opening Metathesis Polymerization (ROMP).[1-3] This process occurs via a carbene-metal complex (M=CHR) (Fig. 1), different from an alkyl-metal complex as in Ziegler-Natta type polymerization.[1, 4-6] The initiation occurs via coordination of acyclic olefin to produce a metallocyclobutane intermediate from a [2π+2π] interaction with the M=CHR initial moiety. As a consequence, a novel carbene-metal complex, with the first monomeric unit, is generated in the medium, able to advance continuously on the propagation step where other cyclic olefins are coordinated, activated and polymerized.[1, 4]

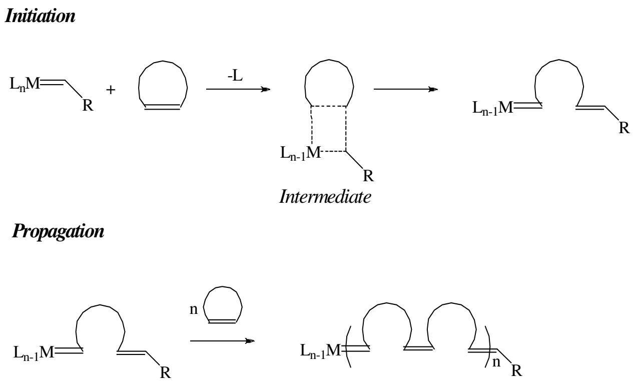


Fig. 1 - ROMP mechanism illustration.

Transition metal complexes that act as complexes for ROMP are driven through electronic and steric effects from the ancillary ligands.[1, 6-8] The tuning provided by these ligands has been the key to the development of novel complexes. Yields and characteristics of the polymers are very influenced by the nature of the ancillary ligands, because they can alter the initiation and propagation steps in the polymerization process.[9]

In recognition of the widespread importance of ROMP, many complexes have emerged over the years to produce new polymers, as well as to revise synthetic routes.[10, 11] In our research group, ROMP has been studied from novel non-carbene Ru-based complexes, where the catalytic species is produced *in situ* from reaction with ethyl diazoacetate.[12-17] Many of these compounds have presented good activity, forming polymers and copolymers in high yields, with different thermal and morphological characteristics. An advantage associated with these types of complexes is the conditions of storage and manipulation. In some cases, activity under air atmosphere has been observed. For example, complexes of the type [$RuCl_2(PPh_3)_2$(amine)], with perhydroazepine (***1***) or piperidine (***2***), quantitatively produced polymers from norbornene (NBE) and norbornadiene (NBD) at room temperature for 1 - 5 min, with [monomer]/[Ru] = 10,000.[12, 16] Both cyclic amines are σ-donor molecules with rings differing in one CH_2 unit. On the other hand, the polyNBE yield decreased from 63 to 19% (5 min; 50 ºC) when using a complex with the non-π-acceptor imidazole ligand, *ttt*-[$RuCl_2(PPh_3)_2$(imidazole)$_2$], compared with their synthesis precursor [$RuCl_2(PPh_3)_3$]; where *ttt* means a full *trans*-positioned ligands from isomeric structure.[13] However, 94% of polyNBE was obtained with the complex *ttt*-[$RuCl_2(PPh_3)_2$(isonicotinamide)$_2$] under similar conditions, where the isonicotinamide is a π-acceptor ligand (pK_a 3.5).[13] Although the imidazole and isonicotinamide ligands present similar cone angles, the π-acceptor nature of the isonicotinamide provoked a *trans*-effect in the coordination sphere, increasing the lability in the starting complex in the respective complex, favoring ROMP.[13] From these results, the electronic nature of the amine is a determinate feature for the catalyst activity.

In this paper, we studied the catalysis of parent complexes of the type [$RuCl_2(PPh_3)_2$(amine)], where the amine is pyrrolidine (***3***) or diethylamine (***4***) (Fig. 2). The goal is to observe the ring size influence, discussing the σ-donor ability and steric hindrance, obtaining resources to compare the results with those obtained with the complexes ***1*** and ***2***.[12, 16] Furthermore, to have an additional gain in the discussion, it was necessary to observe the influence of a π-acceptor amine in the coordination sphere to better understand the electronic forces in the activity in this type of complex. In this sense, the complex *ttt*-[$RuCl_2(PPh_3)_2$(perhydroazepine)(isonicotinamide)] was obtained (***5***).

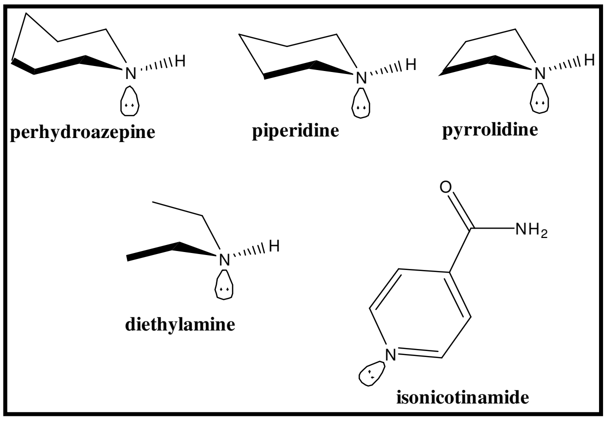


Fig. 2 - Amines structures.

Experimental

General remarks

Syntheses of the complexes and polymerization reaction in inert atmosphere were performed under argon atmosphere. All the solvents were analytical grade. Ruthenium(III) chloride hydrate ($RuCl_3{\cdot}xH_2O$), isonicotinamide, perhydroazepine (hexamethylene imine), triphenylphosphine (PPh_3), pyrrolidine, diethylamine, norbornene (NBE), norbornadiene (NBD) and ethyl diazoacetate (EDA) from Aldrich were used as achieved. Other commercially available reagents were used without further purification. The complexes [$RuCl_2(PPh_3)_2$(perhydroazepine)] (*1*) and [$RuCl_2(PPh_3)_2$(piperidine)] (*2*) were obtained following the literature,[12, 16] as well as [$RuCl_2(PPh_3)_3$].[18]

Syntheses of the complexes

[$RuCl_2(PPh_3)_2$pyrrolidine] (*3*): Pyrrolidine (3.1 mmol; 260 μL) was added into a solution of [$RuCl_2(PPh_3)_3$] (1.0 mmol; 1.0 g) in acetone (30 mL). The resulting mixture was stirred at room temperature for 1.5 h. The green precipitate was filtered, washed with diethyl ether and dried in a vacuum. *Yield:* 54%. *Elemental Analysis* for $RuCl_2P_2C_{40}H_{39}N$ *Calculated:* C, 62.57; H, 5.08; N, 1.82%; *Experimental:* C, 62.43; H, 5.18; N, 1.82%. *FTIR* in CsI: υ_{Ru-Cl} = 320 cm^{-1}, υ_{N-H} = 3,232 cm^{-1}. *EPR:* no signal was observed. ^{31}P NMR {^1H} ($CDCl_3$): δ (ppm) = 62.6 (s), 50.5 and 45.8 (dd), 45.3 (s), 30.1 (s) and -4.5 (s).

[$RuCl_2(PPh_3)$(diethylamine)] (*4*): Diethylamine (0.94 mmol; 97 μL) was added into a solution of [$RuCl_2(PPh_3)_3$] (0.31 mmol; 0.3 g) in dichloromethane (10 mL). The resulting mixture was stirred at room temperature for 2 h. Cold hexane was added and a green precipitate was filtered, washed with diethyl ether and dried in a vacuum. *Yield:* 48%. *Elemental Analysis* for $RuCl_2P_2C_{40}H_{41}N$ *Calculated*: C, 62.4; H, 5.3; N, 1.8%; *Experimental:* C, 58.8; H, 5.0; N, 1.4%. *FTIR* in CsI: υ_{Ru-Cl} = 322 cm^{-1}, υ_{N-H} = 3,135 cm^{-1}. *EPR:* g = 2.21 and 1.86. ^{31}P NMR {^1H} ($CDCl_3$): δ (ppm) = 45.4 (s), 29.7 (s) and -4.9 (s).

[$RuCl_2(PPh_3)$(perhydroazepine)(isonicotinamide)] (*5*): Isonicotinamide (1.26 mmol; 154 mg) was added into a solution of [$RuCl_2(PPh_3)_2$(perhydroazepine)] *(1)* (1.25 mmol; 1.0 g) in acetone (30 mL). The resulting mixture was stirred at room temperature for

1.0 h. The brown precipitate was filtered, washed with diethyl ether and dried in a vacuum. *Yield:* 88%. *Elemental Analysis* for $RuCl_2P_1C_{48}H_{48}N_2$ *Calculated:* C, 56.29; H, 5.20; N, 6.49%; *Experimental:* C, 54.81; H, 5.18; N, 6.54%. *FTIR* in CsI: υ_{Ru-Cl} = 314 cm^{-1}, υ_{N-H} = 3,266 cm^{-1}. *EPR:* no signal was observed. $^{31}P\ \{^1H\}$ NMR ($CDCl_3$): δ (ppm) = 30.1 (s), 27.6 (s) and -4.5 (s).

Polymerization

In a typical ROMP experiment, the Ru-based complex (1.0 mg) was dissolved in a volume of $CHCl_3$ (2.0, 4.0, 6.0 or 8.0 mL) either under argon or air atmosphere. NBE was added to the reaction solution, followed by adding 5.0 µL of ethyl diazoaetate (EDA). The molar ratio [monomer]/[Ru] was 5,000. The polymerization was performed for different periods of time (5, 30, 60 or 120 min) at 25 ± 1 ºC in a silicone oil bath. At 25 ºC, 20 mL of methanol was added and the precipitated polymer was filtered, washed with methanol and dried in a vacuum before being weighed. The experiments were carried out at least twice and the listed values are the arithmetic averages.

Characterization

Elemental analyses were performed using an EA1110 CHNS-O Carlo Erba Instrument.

FTIR spectra were obtained in CsI pellets (1:100) on a Bomem FTIR MB 102.

All NMR analyses were performed using a Bruker DRX-400 of 9.4 T. The $^{31}P\{^1H\}$ NMR spectra were obtained in $CDCl_3$ at 25.0 ± 0.1 °C. Chemical shifts were reported in ppm relative to a high frequency of TMS. The complexes (40 mg) were dissolved in $CDCl_3$ that was previously degassed via Tygon® tube (~ 600 µL) into the NMR tube. For experiments performed in presence of PPh_3, the molar ratio was $[PPh_3]/[Ru] = 50$. For $^{13}C\{^1H\}$ NMR analyses of the polymers, 150 mg of polymer was dissolved in 10 mL of $CHCl_3$, and an aliquot (300 µL) was added into the NMR tube with $CDCl_3$.

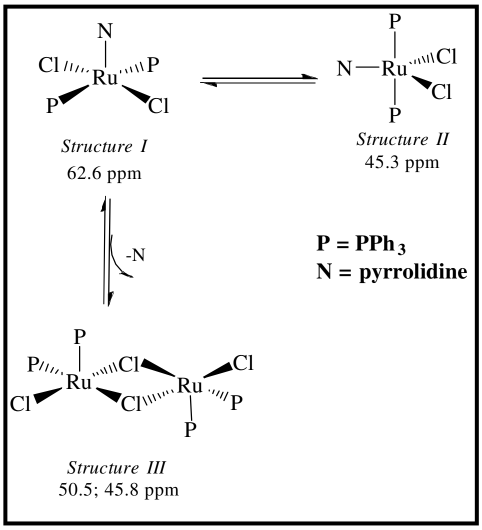
Electronic paramagnetic resonance (EPR) X-band/~9.85 GHz (Bruker EMX plus) measurements were carried out in a rectangular cavity with 100 kHz magnetic field modulation and 4 G of modulation amplitude at 77 K.

Size exclusion chromatography (SEC) analyses were obtained using a Shimadzu Prominence LC system equipped with a LC-20AD pump, a DGU-20A5 degasser, a CBM-20A communication modulo, a CTO-20A oven and a RID-10A detector, connected with a PL gel column (5 m MIXED-C: 30 cm, Ø = 7.5 mm). The retention time was calibrated with standard monodispersed polystyrene using HPLC-grade $CHCl_3$ as an eluent. PDI (polydispersity index) is M_w/M_n. 50 mg of polymer was dissolved in 10 mL $CHCl_3$, filtered and injected (>20 µL).

Results and discussion

Characterization of complexes *3*, *4* and *5*

The ^{31}P NMR spectrum of ***3*** (Fig. 1S) in $CDCl_3$ showed peaks at 62.6 and 45.3 ppm that are concordant with two isomeric species that coexist in the solution, as already observed with the complexes of the type $[RuCl_2(PPh_3)_2(amine)]$.[12, 16] The first peak refers to a square pyramidal (SQP) type geometry with two PPh_3 *trans*-positioned in the equatorial plane, while the peak at 45.3 refers to a trigonal bipyramid (TBP) type geometry with two PPh_3 *trans*-positioned in the axial plane (Scheme 1). In both cases, the Cl^- ions are *trans*-positioned according to the FTIR analyses. The double doublet at 50 and 45 ppm (J = 33.5 Hz) is probably originated from dimeric species formed from amine discoordination (Scheme 1 - Structure III), similar to the observed when ***1*** is in solution.[16]



Scheme 1 - Possible structures of ***3*** in $CDCl_3$.

Peaks at -4.5 and 30.1 ppm are assigned to free and oxidized phosphine, respectively,[19, 20] probably from full discoordination of PPh_3 molecules from the starting complex. It was not possible to observe a peak that could be associated with a complex with only one PPh_3 ligand, such as a dimer with only one amine, as observed in the case of ***1***.[16]

When ***3*** was dissolved in solution of PPh_3, the ^{31}P NMR spectrum (Fig. 2S) showed a strong peak associated with the SQP-geometry (Scheme 1 - Strucure I), indicating that other species were suppressed.[16] This suggests that SQP-geometry is the main starting complex.

^{31}P NMR spectrum of complex ***4*** (Fig. 3S) showed a peak at 45.4 ppm relative to a TBP-geometry species; peaks at 29.6 and -4.9 ppm are free and oxidized phosphine. It was not possible to observe a peak at *ca.* 60 ppm, typical of the SQP-geometry, as observed in the spectra of complexes ***1***, ***2*** and ***3***, even in the presence of PPh_3. The EPR spectrum of ***4*** presented signs that can be associated with a d^6 Ru^{II} electronic distribution in a TBP field, in agreement with the geometry proposed from the ^{31}P NMR spectrum.[21-23]

^{31}PNMR spectrum of ***5*** in $CDCl_3$ shows a peak at 27.6 ppm (Fig. 4S). This suggests a PPh_3 molecule *trans*-positioned to the π-receptor isonicotinamide, with the perhydroazepine in the axial axis of a SQP-geometry; the Cl^- ions are *trans*-positioned in the basal SQP-geometry, according to FTIR analyses. Peaks at −4.5 and 30.1 ppm were assigned to free and oxidized phosphine.

Catalytic activity

Complex ***3*** produced polyNBE under different conditions at 25 °C (Table 1). The yield increased as a function of the reaction time under argon, with quantitative yields for 120 min independent of the volume of solvent. Runs for 5 min were sensitive to solvent volume. A profile of the results is shown in Fig. 3A.

Polymer M_w values were higher (*ca.* 10^5 g mol^{-1}) when the runs with ***3*** were carried out either in 4 or 6 mL for different times. Low M_w values in the runs with 2 mL of solvent were associated with the fast gelation of the solution, which avoided the chain growth.[24] ROMP reactions are generally disfavored in small mole number of the reagent.[1] Large volumes reduce the solution gelation, permitting the reaction to occur without the interference of medium volume. This results in high yields of polymers with long chains. For example, quantitative yield (100%) resulted from a run with 16 mL for 12 h under argon, with M_w of 2.3×10^6 g mol^{-1} and PDI of 2.5. However, a linear correlation between time and solution volume cannot be taken as a rule, considering the experiment with 23 mL for 24 h, under similar conditions, which resulted in 100% yield, M_w of 3.6×10^4 g $mol^{-1}$and PDI of 2.6.

Similar complexes with perhydroazepine (***1***) and piperidine (***2***) showed quantitative yields of polyNBE at 25 °C for less than 5 min.[12, 16] As pyrrolidine is expected to present lower σ-donor characteristic than the perhydroazepine and piperidine ligand, it is possible that a fall in the initiation speed occurs by decreasing the synergism amina→Ru→olefin; the olefin π*-orbital will be inefficiently saturated.[12, 16] However, the propagation step seems to be more efficient when compared with ***1***, as evidenced by M_w values, but are similar to those observed with ***2***.[12, 16] The electronic nature of the pyrrolidine seems to have greater influence than the steric hindrance on the activity of ***3***.

The PDI average value of polyNBE synthesized with ***3*** is 2.6 (Table 1). In general, PDI value increases as a function of solution volume in all the cases. For 5, 30 and 120 min with 2 mL of solvent, PDI of 1.7 on average is observed. In spite of unclear behavior, the PDI values of polyNBE synthesized with ***3*** are lower than those observed with ***1*** and higher than those observed with ***2***. Probably, there is a difference in the propagation step, which is more controlled in the case of ***2*** and ***3***.[12, 16]

Under air, 63% of polyNBE was obtained with ***2*** mL of solvent for 5 min (Fig. 3B). Increasing the time to 120 min resulted in *ca.* 80% yield. Increasing the solution volume, the yield decreased for any reaction time, and the M_w values were lower than the observed under argon atmosphere; 10^3 g mol^{-1} in most of the cases (Table 1).

The difference in the yields with ***3*** from different atmospheres can be associated with the occurrence of an oxidation process, without a clear trend in the M_w and PDI values. However, when comparing the yields from runs in argon and in air atmosphere, the $yield_{argon}/yield_{air}$ ratio is close to 1.0. It is believed that better $yield_{argon}/yield_{air}$ values with ***3***, as compared with ***1***, occur because of the resistant to the reaction with O_2, where the $Ru^{II} \rightarrow Ru^{III}$ oxidation process should be less pronounced in ***3***, because the pyrrolidine is less σ-donor. It is believed that the oxidized specie coexist in solution with the main catalytic specie, however, this one is inactive or at least has low activity in the catalysis because the Ru→olefine (π-electron transference) is impaired, since, Ru(III) is electronic poorer than Ru(II).

Table 1. Yield, Mw, PDI values and $\text{yield}_{\text{argon}}/\text{yield}_{\text{air}}$ ratio of polyNBE with ***3*** in different $CHCl_3$ volumes, reaction times and atmosphere reaction at 25 °C; and $\text{yield}_{\text{argon}}/\text{yield}_{\text{air}}$ ratio with ***1***

		Under argon			Under air			$\frac{\text{yield}_{\text{argon}}}{\text{yield}_{\text{air}}}$	
Time (min)	$CHCl_3$ volume (mL)	Yield (%)	M_w (10^5) (g mol^{-1})	PDI	Yield (%)	M_w (10^5) (g mol^{-1})	PDI	with ***3***	whit ***1******
5	2	68	0.014	1.6	63	0.9; 0.2	3.4; 3.2	1.1	1.5
5	4	61	1.5	3.3	53	0.9	3.5	1.2	2.2
5	6	40	4.6	2.8	51	1.6	2.9	0.8	3.3
5	8	36	0.88	2.9	35	2.4; 0.013	5.4; 1.7	1.0	10
30	2	76	0.7	1.7	82	0.6	3.0	1.0	1.3
30	4	84	2.0	2.9	78	0.02	2.8	1.1	1.8
30	6	74	6.6	2.4	70	0.01	1.9	1.1	2.4
30	8	79	0.3	2.8	55	0.13	3.0	1.4	10
60	2	76	0.1	2.8	83	0.02	2.3	0.9	1.2
60	4	88	3.7	2.6	85	0.02	2.0	1.0	1.4
60	6	83	6.0	2.5	69	0.5	1.8	1.2	2.2
60	8	76	0.1	3.6	63	2.4	3.7	1.2	4
120	2	100	4.8	1.8	82	4.9	3.4	1.2	1.0
120	4	100	4.4	2.6	79	0.04	2.8	1.3	1.0
120	6	100	1.2	2.8	63	0.03	2.7	1.6	1.2
120	8	100	0.2	2.3	53	0.04	2.9	1.9	1.7

* From data in reference [16]

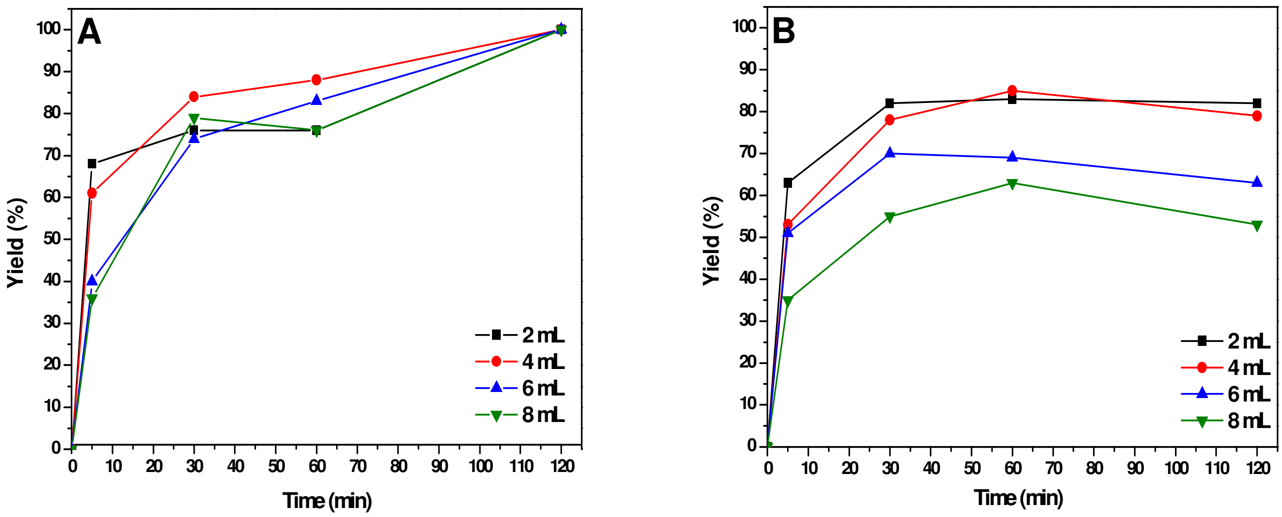


Fig. 3 - Yield percentage of polyNBE synthesized with ***3*** in different $CHCl_3$ volumes and reaction times, performed either under argon (A) or air (B)

Catalytic runs with ***4*** showed low yields (*ca.* 16%) for any reaction time (5 or 120 min), even at 40 °C. Probably, the TBP-geometry of this complex does not facilitate the coordination of EDA to produce the carbene-Ru moiety in the induction period, followed by coordination of the monomer to initiate ROMP. Species from SQP-geometry is accredited to be the active species that reacts with the EDA, as observed with ***1*** and ***2***. This structure permits that the EDA and the monomer coordinate to metal center in a *cis* geometry rearrangement to provide the occurrence of the metallocyclobutane.[12, 16]

Table 2 shows yield, PDI and M_w values of polyNBE obtained with ***5***. Under argon, the yields are lower than 58%, but they increase as a function of the reaction time. On the other hand, the M_w values are in order of 10^5 g $mol^{-1}$for any time and solution volume, with PDI value of 2.0 on average. The low yield of polymer with ***5***, as compared with ***1***, can be attributed to the π-acceptor proprieties of the isonicotinamide ligand, delocalizing the electronic density as observed from the ^{31}P NMR spectrum (^{31}P NMR: 27.6 ppm at ***5***; 61.5 ppm at ***1***). This π-acceptor ligand can disfavor the Ru→olefin electronic transfer which interferes in the polymerization processes. However, this electronic transit can favor a more controlled propagation step, because M_w values are higher than those observed with ***1***.[14]

Yields of polyNBE with ***5*** are lower under air atmosphere than under argon (Table 2). For 5 min, polymer formation is not observed; and for 30 min, some polyNBE is synthesized with 4 mL of solvent (yield < 5%). The best yields were *ca.* 30% with ***2*** mL of solution for 60 and 120 min. The yield$_{argon}$/yield$_{air}$ ratio decreases when the solvent volume increases, reaching 1.5 with 8 mL for 120 min. Polymodal mass distribution is observed in most of the cases.

Table 2. Yield, M_w, PDI values and yield$_{argon}$/yield$_{air}$ ratio of polyNBE with ***5*** in different $CHCl_3$ volumes, reaction times and atmosphere reaction at 25 °C

Under argon					Under air			
Time (min)	$CHCl_3$ volume (mL)	Yield (%)	M_w (10^5) (g mol^{-1})	PDI	Yield (%)	M_w (10^5) (g mol^{-1})	PDI	$\frac{\text{yield}_{argon}}{\text{yield}_{air}}$
5	2	<10	-	-	NP	-	-	-
5	4	12	-	-	NP	-	-	-
5	6	<5	-	-	NP	-	-	-
5	8	<5	-	-	NP	-	-	-
30	2	<10	-	-	NP	-	-	-
30	4	45	0.9	2.1	<5	-	-	-
30	6	34	1.1	2.2	<5	-	-	-
30	8	33	1.0	2.1	<10	-	-	-
60	2	41	1.4	2.0	12	0.9	3.5	3.4
60	4	50	1.4	2.0	23	1.3;0.6	2.2;1.8	2.2
60	6	35	1.1	2.1	22	1.4;0.6	3.4;1.8	1.6
60	8	37	0.9	2.0	18	1.2;0.5	2.4;2.0	2.0
120	2	38	1.2	1.8	23	1.0;0.6	2.4;1.4	1.6
120	4	57	1.3	1.9	35	1.3;0.5	2.3;1.6	1.6
120	6	58	0.9	2.1	34	1.9;0.7	3.4;2.0	1.7
120	8	45	1.3	2.0	30	1.8;0.6	2.4;2.1	1.5

Characterization of the polymers

The σ_c values obtained from ^{13}C NMR spectra (Fig. 5S) of polyNBE synthesized with ***3*** and ***5*** are shown in the Table 3.

When comparing σ_c values for polyNBE synthesized with ***1***[16] and ***3*,** lower values for ***3*** are observed, indicating that more *trans*-polyNBE is formed. This suggests that the results obtained with ***3*** are due to the smaller cone angle of the pyrrolidine relative to the perhydroazepine ligand. Thus, ***3*** can permit the "twist" of the monomer with more efficiency, favoring the formation of the *trans* conformation of groups around a C=C double bond of the polymer. The absence of steric hindrance produced 100% of *trans*-polyNBE in ROMP with $RuCl_3$.[25] In the case of ***5***, the σ_c value of 0.45 on average shows that the cone angle of isonicotinamide ($\theta = 92°$) did not influence the stereochemistry of polyNBE compared with ***1***.

From the literature[26, 27], polyNBE obtained with Ru-based complexes with high content *cis* is indicative that propagating species is rapid. Consequently, low *cis* content is indicative of propagating species with low reactivity. This can be observed when analyzing the results from ***1*** and ***3***. The complex ***1*** presents high *cis* content and, as already discussed, probably due to an efficient propagate step. Whereas ***3*** presents low *cis* content, probably because the propagation step is more controlled.

With ***5***, the M_w and PDI results suggest a slow propagation step. However, low reactivity is indicative of a slow and inefficient initiation step that appears to influence the *cis* content.[26, 27]

Table 3. σ_c values for polyNBE synthesized with either ***3*** or ***5*** for 5 or 120 min in 2 mL $CHCl_3$ under argon atmosphere at 25 °C

		Complex ***3***		Complex ***5***	
Assignments	Chemical shifts (ppm)	σ_c^1 (5 min)	σ_c^2 (120 min)	σ_c^3 (5 min)	σ_c^4 (120 min)
$C^{1,4}$ - ct	38.43	0.3	0.3	0.5	0.44
$C^{1,4}$ - cc	38.67				
$C^{1,4}$ - tt	43.14				
$C^{1,4}$ - tc	43.42				
$C^{5,6}$ - tt	32.24	0.35	0.35	0.45	0.45
$C^{5,6}$ - tc	32.39				
$C^{5,6}$ - ct	32.94				
$C^{5,6}$ - cc	33.13				
C^7 - tt	41.38	*	*	0.53	0.42
C^7 – ct; tc	42.11				
C^7 - cc	42.77				
$C^{2,3}$ - t	133.05	0.31	0.32	0.44	0.42
$C^{2,3}$ - c	133.9				

*ND

Conclusions

The complex $[RuCl_2(PPh_3)_2(pyrrolidine)]$ (***3***) presented activity for ROMP of norbornene (NBE) under either air or inert atmosphere of argon at 25 °C, as observed with the complexes ***1*** and ***2***. These three complexes present SQP-geometries, different from the TBP-geometry of the complex with diethylamine (***4***), which was inactive for ROMP. This suggests that the cyclic amines in the apical position of the SQP-geometry provoke less steric hindrance which provides prompt reactivity for ROMP. Reactivity in these types of complexes in terms of electronic effects corroborates the starting geometric arrangements. The expected high σ-donor characteristic of perhydroazepine favors better yields with ***1***, but produce polymers with low M_w values and large PDI due to inefficient propagation-initiation balance. Complex ***3*** presented better yields when the polymerizations were performed in air atmosphere compared with ***1***. This can be associated with better controlled propagation where the metallic center is always coordinated with norbornene. Fast propagation from ***1*** can provoke a vacancy in the coordination sphere due to a higher ring size, which can react with O_2 dissolved in the solution.

An additional discussion involving the electronic synergism in the novel *ttt*-$[RuCl_2(PPh_3)_2(perhydroazepine)(isonicotinamide)]$ complex revealed the power of controlling the propagation rate by a π-acceptor ligand.

From these studies, three features must be observed when selecting this type of complex to act as a complex for ROMP: the amine σ-donor electronic proprieties, the presence of a π-acceptor amine in the metal coordination sphere, and the complex geometry type. When a less σ-donor amine is the ancillary ligand, the propagation step is more controlled with efficient initiation. When a π-acceptor amine participates as ancillary ligand concomitant with an σ-donor amine, the propagation step is also more controlled, but the initiation step is less efficient. Finally, an acyclic amine can disable the structure of the complex for ROMP.

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Notes

†Electronic Supplementary Information (ESI) available: ^{31}P NMR spectra of complexes ***3***, ***4*** and ***5***; ^{31}P NMR spectra of complex ***3*** in PPh_3 presence; ^{13}C NMR spectra of polyNBE with ***3*** and ***5***.

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