Synthesis of a new RuII/NiII heterobimetallic complex as a bifunctional catalyst for mechanistically distinct polymerization reactions - Romp and addition polymerization.

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Resumo/Abstract

RESUMO - Com a necessidade de novos materiais poliméricos que pudessem satisfazer os avanços das tecnologias, a busca por polímeros com propriedades e arquiteturas sofisticadas tem se tornado cada vez mais atrativa. Os catalisadores heterobimetálicos vêm ganhando grande ascensão nos últimos anos devido suas multifuncionalidades em catálise, bem como o sinergismo mecanistico que tais sistemas podem proporcionar1. Nesse trabalho, foi desenvolvido um catalisador heterobimetálico de rutênio(II) e níquel(II) [RuCl2(6-p-cymene)][(-Schiff-pip)Ni(Aryl-NBE)(PPh3)] (Ru-Ni) e sua atividade catalítica foi avaliada em reações de polimerização de ROMP e adição utilizando o norborneno (NBE) como monômero. Ru-Ni demonstrou-se ativo para as polimerizações de abertura de anel via metátese (ROMP), alcançando um rendimento de 40% a 50 °C, utilizando uma razão molar [NBE]/[Ru] = 5000, 3 L de EDA e um tempo de reação de 60 minutos. O complexo heterobimetálico também apresentou-se ativo frente a reações de polimerização de NBE via adição, usando o metilaluminoxano (MAO) como cocatalisador, obtendo um rendimento de 92% utilizando a razão molar [Al]/[Ni] = 2500 a 30°C, com um TOF (turnover frequence) de 6,96.

*Palavras-chave: Complexo bimetálico, catalisador bifuncional, ROMP, polimerização via adição, norborneno.*

ABSTRACT - With the need for new polymeric materials that could satisfy the advances in technology, the search for polymers with sophisticated properties and architectures has become increasingly attractive. Heterobimetallic catalysts have been gaining great ascension in recent years due to their multifunctionality in catalysis, as well as the mechanistic synergism that such systems can provide. In this work, a ruthenium(II) and nickel(II) heterobimetallic catalyst [RuCl2(6-*p*-cymene)][(-Schiff-pip)Ni(Aryl-NBE)(PPh3)] (Ru- Ni) was sinthetized and its catalytic activity was evaluated in ROMP and addition polymerization reactions using norbornene (NBE) as monomer. Ru-Ni was shown to be active for metathesis ring opening polymerizations (ROMP), reaching a yield of 40% at 50 °C, using a molar ratio [NBE]/[Ru] = 5000, 3L of EDA and a reaction time of 60 minutes. The heterobimetallic complex was also active against NBE polymerization reactions via addition, using methylaluminoxane (MAO) as cocatalyst, obtaining a yield of 92% using the molar ratio [Al]/[Ni] = 2500 at 30°C, with a TOF (turnover frequency) of 6.96.

*Keywords: Bimetallic complex, bifunctional catalyst, ROMP, polymerization via addition, norbornene.*

## Introduction

The use of heterobimetallic complexes has become an interesting research topic in recent years, especially regarding their use as catalysts in the field of catalysis. The recurrent synergism between the metal centers present leads to an increase in the catalytic potential. Furthermore, these systems become even more interesting due do to their greater selectivity when detected to monometallic systems 1.

Schiff bases are functional groups commonly used as a bridge between transition metals of heterobimetallic complexes,2,3 their p-\* orbitals have low energy and are easily occupied, so the possibility of forming bonds by back donation leads to a consequent increase of the stability of the metallic centers.4 Furthermore, thanks to the easy structural modification of the Schiff bases, in centers such as NiII it is possible to have greater control of the steric and electronic effects 5.

Significant advances in the use of metals in the addition polymerization reaction occurred in the search for more efficient catalysts. In particular, nickel catalysts have become very attractive due to their high catalytic activity, possibility of controlling the microstructure of the growing polymer and low oxophilicity, thus being able to polymerize polar monomers6. Many nickel complexes are known as privileged catalysts for alkene reactions, such as oligomerization or reductive coupling. These catalysts readily donate d-electrons to π-acceptors, so olefin binding is easily activated. Another important factor that makes them competitive is the great versatility and availability of synthesis of these complexes, expanding the possibility of modulating the reactivity and selectivity of the catalysts7.

Among the various metals used as catalysts in ROMP reactions, ruthenium is a particularly attractive choice due to its easy accessibility to a wide number of metal complexes with many different ligands, its affordable cost, and the wide range of accessible oxidation states ( 2 a +8). RuII catalysts are highly selective against functionalized substrates in metathesis reactions, given their electronic preferences for olefins, as the RuII ion is a good π-donor of electrons with a low spin 4*d*π6 configuration. This characteristic makes RuII complexes an excellent option for the development of catalysts for ROMP reactions.

In this work, a novel bimetallic complex was designed to contain a RuII metal center with activity in ROMP reactions and a NiII center for addition polymerizations. Thus, a new catalyst with the potential to mediate incompatible polymerization reactions was sought, since within the search carried out, no heterobimetallic catalyst ever developed was effective in the tandem catalysis of ROMP reactions and addition polymerization.

## Experimental

*General Procedures*

The monometallic ruthenium complex, [RuCl2(*η*6-*p*-cymene)((4-methylamino)-piperidine)] (**Mono-Ru)**, was reported other times and its route of synthesis was performed according to the literature2. Solvent used in each synthesis was previously dried in a Vigreux distillation column and the purity of the reagents used can be found in Table 1.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Reagent | M.M. (g/mol) | Structure/Formula | Purity | Origin |
| Norbornene | 94,15 |  | 99 % | Sigma |
| ethyldiazoacetate (EDA) | 114,10 |  | 99% | Sigma |
| Tetrabutylammonium Hexafluorophosphate (TBAPF6) | 387.43 |  | 98 % | Sigma |
| 4-(aminomethyl)piperidine | 114,19 |  | 96% | Sigma |
| 5-norbornene-2-carboxylic acid | 138,07 |  | >98% | Sigma |
| Triphenylphosphine | 262,29 | PPh3 | >95,0% | Sigma |
| n-butyllithium | 64,06 |  | 2,5 M | Sigma |
| Salicylaldehyde | 112,12 |  | 98% | Sigma |
| Methylaluminoxane | - | [(CH3)0,95(*n*-C8)H­17]0,05AlO]n | 7% | Sigma |

*Synthesis of the NBE-Aryl-Br*

1 mL of 5-norbornene-2-carboxylic acid (8.1 mmol;), 1.17 g of N,N'-dicyclohexylcarbodiimide (DCC; 8.1 mmol) were added in a 200 mL flask containing a solution of 0.928 g of 4-bromophenol (5.4 mmol and 1.97 g of 4-(dimethylamino)pyridine (DMAP; 16.2 mmol; 3 equiv.) in 20 mL of acetonitrile. The mixture was stirred under reflux temperature (80 °C) for 24 h. After the reaction, the mixture was filtered to remove the white solid. Then the solution was evaporated and the brownish solid was dissolved in 25 mL of diethyl ether, and washed sequentially with 1 molar hydrochloric acid, saturated sodium bicarbonate solution and a saturated NaCl solution. Finally, the organic phase was separated evaporated, the crude solid was then isolated and purified by column chromatography to obtain an oil. The yield obtained was of 60%.

*Synthesis of the complex [Ni(PPh3)2(Aryl-NBE)Br] (****Mono-Ni****)*

In a 100 mL Schlenk flask containing ~1 g of Ni(PPh3)4 (0,9 mmol) previously synthetized following the procedure already reported, a solution of dried THF (20 mL) and 1,31 g NBE-Aryl-Br (4,5 mmol) was added and the system remained under stirring for 4 hours.2 The resulted solution was kept under 25 °C for 12 h, then 30 mL of pentane were added to force precipitation. The precipitate was filtered via cannula and washed with small portions of THF (4 × 5 mL). The yield obtained was of 30% considering the previous step. 8

*Synthesis of the bimetallic complex Ni(II)-Ru(II) [RuCl2(6-p-cymene)][(-Schiff-pip)Ni(Aryl-NBE)(PPh3)] (****Ru-Ni****)*

The reaction to obtain **Ru-Ni** was conducted using each reactants in 1 eqv. Thus, 15 mL of previously dried and deaired DCM were added to a 100 mL Schlenk containing 0,2 g (0.228 mmol) of **Mono-Ni** and 96 mg (0.228 mmol) of [RuCl2(η6-*p*-cymene)((4-methylamino)-piperidine)], followed by the addition of 25.7 L of salicylaldehyde (0.23mmol). The system was maintained under magnetic stirring for 12 hours. The reaction volume was reduced to approximately 5 mL by a positive flow of N2(g). After the reaction, 20 mL of pentane was added to the mixture. The liquid was removed by filtration via cannula under an inert atmosphere, then the complex was washed with diethyl ether (3 x 5 mL), dried under vacuum, and isolated, obtaining an yield of 70%.

Results and discussion

*Characterization of the NBE-Aryl-Br*

NBE-Aryl-Br was characterized by 1H NMR in CDCl3 (Figure 1). The hydrogens present on aromatic ring (CHAr) were identified as two doublets in the region of 6.50 and 8.00 ppm. The =CH hydrogens from cycloalkene undergoes to an anisotropic effect, appearing between 6.29 ppm (1H, =CH, J = 5.7 Hz) and 6.00 ppm (1H, =CH, J = 5.8 Hz) as two double doublets. Methine hydrogens bonded directly to the allenic carbons of the cycloalkene were identified between 3.00 and 3.50 ppm. Finally, the methylene hydrogens of the cycloalkene appear as overlapping signals, between 1.00 and 2.50 ppm.



**Figure 1.** 1H NMR spectrum of NBE-Aryl-Br in CDCl3.

*Characterization of the [Ni(PPh3)2(Aryl-NBE)Br] complex (****Mono-Ni****)*

**Mono-Ni** was initially characterized by 31P{1H} using (CD3)2SO as solvent and the spectrum is shown on Figure 2. According to the spectrum, a well-defined singlet at 22.54 ppm was observed, confirming the presence of the coordinated triphenylphosphines. Furthermore, the singlet also suggests that both triphenylphosphines are equivalent, in a trans configuration (Figure 2).



**Figure 2.** 31P{1H} NMR Spectrum of **Mono-Ni** in (CD3)2SO.

**Mono-Ni** had its electrochemical behavior evaluated by cyclic voltammetry using a scan rate of 100 mV.s1, potential window from 0.9 to 2.0 V, [Ni] = 1.0 mmol L1 and using [*n*-Bu4NPF6] as support electrolyte. The cyclic voltammogram in Figure 3 shows an oxidation process at 1.55 V referring to the irreversible process for the NiII/III couple redox.



**Figure 3.** Cyclic voltammogram of **Mono-Ni** in CH2Cl2. Scan rate of 100 mV.s1; potential window ranging from 0.9 to 2.0 V; [Ni] = 1.0 mmol L1; supporting electrolyte [n-Bu4NPF6] = 0.1 mol L1.

*Characterization of the bimetallic complex* *[RuCl2(6-p-cymene)][(-Schiff-pip)Ni(Aryl-NBE)(PPh3)] (****Ru-Ni****)*

**Ru-Ni** had its absorption spectrum recorded in CH2Cl2 at 25 °C between 200 to 800 nm, which was compared to the spectra of its precursors (Figure 4.) The spectra of the complexes showed intense absorption bands in the region of 228-230 nm attributed to the and n  intraligand transitions of the amine and/or *p*-cymene in the ruthenium compounds, and to the PPh3 ligand or NBE-Aryl-Br, in the case of the nickel complex. A smaller band is observed at 323 nm for complexes **Mono-Ru** and **Ru-Ni** referring to the MLCT transitions 9. A MLCT band at 409 nm present in complex **Mono-Ru** was also observed with a hypsochromic shift of 24 nm (390 nm) in the spectrum of the complex of interest (**Ru-Ni**). These changes in the spectral profile, when compared to the others, suggest that there was the formation of a new species from the change in the coordination sphere of the precursor.



**Figure 4.** Comparison of absorption spectra in the UV-Vis region for in CH2Cl2 at 25 °C; [Ru] = 0.1 mmol L-1.

According to the 31P{1H} NMR spectrum of the sample, a well-defined singlet at 21.79 ppm can be observed, confirming the presence of the phosphine ligand in the metallic center. Furthermore, the presence of a single signal, with a smaller chemical shift in relation to **Mono-Ni** (Figure 5), suggests that there was a change in the sphere of coordination of the nickel center.



**Figure 5.** 31P{1H} NMR spectrum of **Ru-Ni** in (CD3)2SO.

From the analysis of cyclic voltammetry, it was possible to identify two oxidation processes. The first one at 1.19 was attributed to the interconversion of the RuII/III redox couple 2. The second process appeared at 1.37 V, assigned to the NiII/III redox pair. When compared to the monometallic Ni complex (**Mono-Ni**), it is possible to observe a shift to lower potentials, suggesting that electrons are more accessible in the bimetallic species (Figure 6).

**Figure 6.** Cyclic voltammogram of **Ru-Ni** in CH2Cl2. Scan rate of 100 mV.s1; potential window ranging from 0.0 to 2.0 V; [Ru] = 1.0 mmol L1; supporting electrolyte [n-Bu4NPF6] = 0.1 mol L1.

*Ring opening metathesis polymerization - ROMP*

**Ru-Ni** had its catalytic activity evaluated in ROMP reactions of norbornene in the ratio of [NBE]/[Ru] = 5000/1, using 3 L of EDA, temperatures of 25 and 50 ºC and with a time variation of 10 to 60 min using CHCl3 as solvent (Figure 7). The yields obtained in 60 min were around 35 and 40% at temperatures of 25 and 50 °C, respectively.



**Figure 7.** Yield dependency (numbers entered into bars) for norbornene ROMP using **Ru-Ni** as a function of time at 25 and 50 °C. Conditions: [NBE]/[Ru] = 5000/1; EDA = 5 µl; CHCl3 as solvent.

For both conditions, the molecular weight and polydispersity index (Ð) of the polymers obtained were monitored by SEC. It was possible to observe an increase of the molecular weight with the increasing of the time (Table 2), which is expected in longer reaction times, reaching 8.80x105 and 3.70x105 Da in 60 min of reaction at 25 and 50 °C, respectively. When analyzing the Ð obtained, a decrease in longer times is observed for both temperatures. As the ROMP reactions require some time for every complex available in the system to react with the EDA to form the active species, it is plausible that the Ð decrease over time, due to the greater homogeneity of the chains.

**Table 2.** Polymerization data via ROMP using **Ru-Ni** as catalyst.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Entry** | **Time (min)** | **T (ºC)** | **Mn (×103) (g.mol−1)** | **Ð** |
| 1 | 10 | 25 | 125 | 2,3 |
| 2 | 20 | 178 | 2,1 |
| 3 | 30 | 265 | 2,2 |
| 4 | 40 | 564 | 2,3 |
| 5 | 50 | 856 | 1,5 |
| 6 | 60 | 880 | 1,5 |
| 7 | 10 | 50 | 152 | 2,9 |
| 8 | 20 | 202 | 2,6 |
| 9 | 30 | 217 | 2,8 |
| 10 | 40 | 210 | 2,6 |
| 11 | 50 | 323 | 2,4 |
| 12 | 60 | 370 | 2,3 |

*Polymerization via addition of norbornene*

Addition polymerization reactions were performed using **Ru-Ni** (2.5 mol), MAO as cocatalyst in different Al/[Ni] ratios, NBE as monomer, and toluene as solvent in 15 min at different temperatures (Table 3).

Initially, the polymerization was carried out in the absence of MAO at 30 °C (entry 1) and no polymer formation was observed, demonstrating that the polymerization does not occur without the addition of the cocatalyst. It was possible to observe that the Al/[Ni] ratio exerted great influence, since higher amounts of MAO caused an increase in the yields. of the obtained polymers (entries 2-5). However, when increasing the [Al]/[Ni] ratio to 3000 (entry 6), there was a drop in the yield, indicating that great excess of Al/[Ni] ratios can deactivate the catalytic species. In this sense, the best Al/[Ni] ratio found was 2500 (entry 5), reaching yields around 90%. The effect of temperature was evaluated conducting the reactions at 60 and 90 °C (entries 7 and 8). It was noted that the temperature variation did not influence the yields obtained in these conditions, since a significant variation in the mass of the polymers was not observed.

**Table 3.** Addition polymerization data using **Ru-Ni** as catalyst.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Entry** | **[Al]/[Ni]** | **T (ºC)** | **Yield (%)** | **Activityb** |
| 1 | 0 | 30 | 0 | --- |
| 2 | 1000 | 30 | 45 | 3,36 |
| 3 | 1500 | 30 | 53 | 4,00 |
| 4 | 2000 | 30 | 52 | 3,90 |
| 5 | 2500 | 30 | 90 | 6,80 |
| 6 | 3000 | 30 | 49 | 3,66 |
| 7 | 2500 | 60 | 88 | 6,60 |
| 8 | 2500 | 90 | 92 | 6,96 |

aReaction conditions: [Ni] = 2.5 mol, [NBE]/[Ni] = 20,000, VTotal = 10 mL and 15 min of reaction. b106 gmol1 Ni. h1.

## Conclusion

NBE-Aryl-Br, [Ni(PPh3)2(Ph-NBE)Br] (**Mono-Ni**), and [Br(PPh3)Ni(N,O)-Ru(*p*-cymene)pip] (**Ru-Ni**) were synthetized and further characterized. Complexes **Mono-Ni** and **Ru-Ni** showed irreversible behavior for the cyclic voltammetry analysis. **Mono-Ni** presented an oxidation potential at 1.55 V associated with the redox pair NiII/III, while **Ru-Ni** showed two oxidation potentials at 1.19 and 1.37 V, referring to the RuII/III and NiII/III pairs, respectively. **Ru-Ni** showed to be active for ROMP reactions at 25 50 °C, reaching values of 35 and 40% of yield, respectively. Furthermore, **Ru-Ni** was also able to polymerize norbornene via addition polymerization, showing good results, with 92% of yield using a ratio of [Al]/[Ni] = 2500, 2.5 μmol of catalyst at 90 ºC. In this way, **Ru-Ni** showed a dual catalytic behavior in ROMP and polymerization via addition of NBE.

## Acknowledgment

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