RuII/PdII heterobimetallic complexes as multifunctional catalysts for mechanistically distinct reactions: Heck, ROMP and vinyl polymerization of norbornene

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 **Resumo/Abstract**

RESUMO - Os complexos heterobimetálicos surgiram como uma ferramenta versátil no desenvolvimento de novos catalisadores multifuncionais para acoplar diferentes mecanismos de polimerização, através de uma catálise dual. Neste trabalho, novos complexos baseados em complexos heterobimetálicos combinando um centro metálico de Ru com o Pd, foram desenvolvidos como pré- catalisadores para diferentes mecanismos de polimerização: ROMP e polimerização vinílica do norborneno e para reações de Heck. Os complexos [Pd(4-aminopiridina)(tsc)] foram sintetizados a partir da reação dos respectivos ligantes tiosemicarbazona, e 4- aminopiridina na presença de Et3N. Os complexos heterobimetálicos do tipo [RuCl2(*p*-cimeno)(-4-aminopiridina)Pd(tsc)] foram sintetizados a partir da reação equimolar entre [RuCl2(*p*-cimeno)]2 e os respectivos complexos de paládio. Os complexos sintetizados foram caracterizados por RMN de 1H. Os testes iniciais em reações de Heck do norbornadieno (NBD) demonstraram- se promossires. Conversões quantitativas foram alcançadas para o complexo Pd-1 quando as razões molares de [Cat.]/[PhI]/[NBD]

= 1/418/1344 foram empregadas a 120 ºC durante 16h.

*Palavras-chave: Catalisador multifuncional, paládio, rutênio, catálise dual.*

ABSTRACT - The heterobimetallic complexes have emerged as a versatile tool in the development of new multifunctional catalysts to couple different polymerization mechanisms through a dual catalysis. In this work, new complexes based on heterobimetallic complexes combining a Ru metal center to Pd, were developed as pre catalysts for different polymerization mechanisms: ROMP and vinyl polymerization of norbornene and for Heck reaction. The Pd monometallic complexes [Pd(4-aminopyridine)(tsc)] were synthesized from the reaction of the respective thiosemicarbazone ligands, and 4-aminopyridine in the presence of Et3N.

The heterobimetallic complexes of the type [RuCl2(*p*-cymene)(-4-aminopyridine)Pd(tsc)] were synthesized from the equimolar reaction between [RuCl2(*p*-cymene)]2 and the respective palladium complexes. The synthesized complexes were characterized by 1H NMR. Initial tests on Heck reactions of norbornadiene (NBD) proved to be successful. Quantitative conversions were achieved for Pd- 1 complex when molar ratios of [Cat.]/[PhI]/[NBD] = 1/418/1344 were employed at 120°C for 16h.

*Keywords: Multifunctional catalyst, palladium, ruthenium, dual catalysis.*

# Introduction

The use of a multifunctional catalyst presents many advantages compared to the classical methods for the synthesis of block copolymers, from the combination of mechanistically incompatible monomers. Dual catalysts also have two or more different active sites capable of simultaneously initiating polymerization mechanisms independently and selectively. Therefore, the synthetic possibilities for obtaining differentiated polymeric materials are extremely wide from the use of different derivatives of norbornene. Polynorbornenes can be designed for different applications from the use of different substituents in the monomeric units, generating different compositions in the polymers.

Monometallic complexes based on palladium and ruthenium are effective catalysts for a wide range of transformations. To increase the range of catalytic reactions, numerous studies involving heterobimetallic complexes associating Ru(II) and Pd(II) fragments have already been reported [1-3]. The present work describes the synthesis and

characterization of a new series of heterobimetallic complexes based on Ru(II) and Pd(II) and their monometallic palladium fragments for Heck reaction of NBD and ROMP and vinyl polymerization of Ph-NBE (Figure 1).

**Fig. 1.** The Ru-Pd heterobimetallic complexes and their monometallic palladium fragments.

# Experimental



*1.1 Ligands synthesis*

To a solution of diacetylmonoxime (8.0 mmol) in a 2:3 mixture of EtOH:H2O (10 mL) an equimolar amount of thiosemicarbazide in EtOH (10 mL) was added. Afterwards,

0.5 mL of acetic acid was added to catalyze the reaction. The reaction mixture was refluxed and stirred for 4 h. Then, the colorless precipitate was filtered, washed with *n*-hexane and dried under reduced pressure. The solid was recrystallized from ethanol.

*2.2 Monometallic palladium complexes synthesis*

To a solution of [PdCl2(MeCN)2] (0.1 mmol, 25.8 mg) in MeCN (2 mL), one equivalents of L1, L2 or L3 (0.1 mmol) was added. After 30 min of stirring at room temperature 4-aminopyridine (0.1 mmol) and 3 drops of Et3N was added. After 4 h of stirring at room temperature, the precipitate formed was filtered off, washed with MeCN and n-hexane in sequence and dried under reduced pressure. The orange solids products were obtained.

*2.3. Heterobimetallic complexes synthesis*

Pd-1 Pd-2 or Pd-3 (0.570 mmol) and [RuCl2(*p*- cymene)]2 (0.570 mmol) were added to a system containing dichloromethane. The mixture was stirred at RT for 12 h and filtered. The dark orange powder was washed with dichloromethane and dried under vacuum for 2 h.

*2.4 Heck reactions*

In a typical procedure for Heck reaction a mixture of 20 µmol of the complex, Ph-I (96 µL, 0.8607 mmol), norbornene (262.5 mg, 2.7878 mmol), Et3N (390 µL, 2.798 mmol) and formic acid (84 µL 2.226 mmol). in DMSO (5 mL) were maintained under stirring and temperature (60- 120 ºC) for 16h. To the resulting solution was added 5 mL of water, and the mixture was extracted with pentane (3 x 10 mL). The organic phase was dried with MgSO4 and subsequently filtered. The solvent was reduced under reduced pressure to generate the products with high yield values.

compared to related palladium complexes.

In this work, the Heck reaction is used in order to insert different substituent groups in the substrate for later application in polymerization reactions (Figure 2). The catalytic behavior of monometallic and heterobimetallic complexes in Heck reactions are presented in Table 1.

 



**Fig. 2.** Heck reactions of norbornadiene.

The HCOOH/Et3N system was used as a hydride source to favor the reducing conditions in an efficient system, as previously reported [4]. As the temperature increased to 120°C, quantitative conversions were obtained (Entries 1-3, Table 1). Catalyst concentration also had a significant effect on catalysis, with the decrease from 18.0 to 2.0 mmol.L− promoting a substantial decrease in the conversion value to 28% (Entry 4, Table 1). Although the catalytic activity of the heterobimetallic complexes is relatively lower compared to the monometallic analogues, the Ru-Pd-3 complex showed efficient catalytic activity with 97% of conversion. The 1H NMR spectra of Ph-NBE indicate the formation of the product from the hydroarylation reaction.

**Table 1**. Catalytic hydroarylation of norbornadiene.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Entry** | **Cat.** | **Conc. Cat.****(mmol.L-1)** | **T (ºC)** | **Conv.****(%)*b*** |
| **1** | Pd-1 | 18,0 | 60 | 35 |
| **2** | Pd-1 | 18,0 | 90 | 55 |
| **3** | Pd-1 | 18,0 | 120 | 100 |
| **4** | Pd-1 | 2,0 | 120 | 28 |
| **5** | Pd-1 | 18,0 | 120 | 73 |
| **6*e*** | Pd-1 | 18,0 | 120 | 100 |
| **7** | Pd-2 | 18,0 | 120 | 92 |
| **8** | Pd-3 | 18,0 | 120 | 100 |
| **9** | Ru-Pd-1 | 18,0 | 120 | 87 |
| **10** | Ru-Pd-1 | 18,0 | 90 | 39 |
| **11** | Ru-Pd-1 | 2,0 | 90 | 44 |
| **12*e*** | Ru-Pd-1 | 18,0 | 120 | 98 |
| **13** | Ru-Pd-2 | 18,0 | 120 | 93 |
|  **14**  | Ru-Pd-3  | 18,0  | 120  | 95  |

# Results and Discussion

The 1H NMR spectra of the palladium monometallic exhibit peaks in the 1.80−2.75 ppm range as doublets assigned to the CH3 hydrogen groups from TSC ligands. The spectrum of the complex Pd-3 shows additional signs in the 6,62−7,99 ppm range assigned to the phenyl substituent. The presence of the 4-aminopyridine ligand in the complexes formed is observed from the multiplets around 8.00 and 6.80 ppm characteristic of the aromatic ring and from the singlet at 6.50 ppm from the two hydrogen atoms from the primary amine. The spectra of the heterobimetallic complexes show the presence of the Pd and Ru centers, confirming the obtaining of the heterobimetallic structures of interest. The presence of signals assigned to the TSCs ligands coordinated to the Pd center can be observed between 1.82 and 2.81 ppm. The signals of *p*-cymene group from Ru center were observed in the range 1.20−2.85 ppm and 5.80 ppm. The coordination of the 4-aminopyridine to the Ru metal center was confirmed by the displacement of the −NH2 group,

# Conclusion

Palladium monometallic complexes and heterobimetallic complexes were synthesized and characterized by 1H NMR. The monometallic and heterobimetallic systems are efficient in Heck reactions, reaching quantitative conversion values.

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