Heterobimetallic ruthenium(II) and palladium(II) complexes as bifunctional catalysts to obtain functionalized polymers via coupling of Heck and ROMP reactions

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Resumo/Abstract (Helvética, tam. 12)

RESUMO - Novos complexos heterobimetalicos de rutenio e paladio (Ru-PdCl e Ru-PdPh) [foram sintetizados e caracterizados por espectroscopias FTIR, UV-Vis, 1H, 13C{1H} e 31P{1H} NMR, voltametria cíclica, espectrometria de massa e métodos DFT. A atividade catalítica de Ru-PdCl e Ru-PdPh na reação de Heck de norbornadieno (NBD) e um haleto de arila (PhX) foi avaliada utilizando sob diferentes temperaturas, solventes e bases em função do tempo. Ambos os complexos foram capazes de fornecer uma conversão com valores chegando a 98 %, usando iodo benzeno e trietilamina em DMF por 3 horas. A ROMP de norborneno (NBE) usando Ru-PdCl e Ru-PdPh na presença trimetilsilildiazometano como iniciado foram avaliados em função do tempo usando [NBE]/[Iniciador]/[Ru] = 5000/28/1 a 50 °C produzindo bons rendimentos de poliNBE, chegando a 44% e 80% para Ru-PdCl e Ru-PdPh, respectivamente.

*Palavras-chave: Catalisadores multifuncionais, acoplamento, olefina funcionalizada.*

ABSTRACT - New heterobimetallic complexes of ruthenium and palladium (Ru-PdCl and Ru-PdPh) were synthesized and characterized by FTIR, UV-Vis, 1H, 13C{1H}, and 31P{1H} NMR spectroscopies, cyclic voltammetry, mass spectrometry, and DFT methods. The catalytic activity of Ru-PdCl and Ru-PdPh in the Heck reaction of norbornadiene (NBD) and an aryl halide (PhX) was evaluated using different temperatures, solvents, and bases over time. Both complexes were able to provide a conversion with values reaching 98%, using iodobenzene and triethylamine in DMF for 3 hours. The ring opening metathesis polymerization (ROMP) of norbornene (NBE) using Ru-PdCl and Ru-PdPh in the presence of trimethylsilyldiazomethane as an initiator were evaluated over time using [NBE]/[Initiator]/[Ru] = 5000/28/1 at 50 °C, producing good yields of polyNBE, reaching 44% and 80% for Ru-PdCl and Ru-PdPh, respectively.

*Keywords: Multifunctional catalysts; catalysis; coupling, functionalized olefin.*

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## Introdução

Several couplings using different polymerization methods have been developed to obtain copolymers by sequentially adding monomers through a living polymerization [1-3]. However, this strategy has some disadvantages, including the need to protect intermediates, transformation steps, and the use of various catalysts and initiators in the reaction medium [3]. Therefore, using multifunctional catalysts capable of mediating reactions with different mechanisms offers many advantages compared to the classical method of synthesizing functionalized polymers and block copolymers. This approach enables the combination of incompatible monomers into a macromolecule without requiring intervention during polymerization, which provides new opportunities for designing new materials [3-5].

The coupling between aryl halides and olefins, catalyzed by palladium, was independently discovered by Heck and Mizoroki and is considered one of the most significant carbon-carbon coupling reactions. It finds wide application in synthetic chemistry, including polymer synthesis, due to its high selectivity and tolerance for a large number of functional groups [6-7]. This reaction can be used for the functionalization of olefinic monomers with applications in ROMP, leading to the production of polymers with functional groups that can provide specific characteristics and applications different from conventional ones[8-10].

The Heck reaction is one of the primary synthetic procedures catalyzed by palladium, which involves the insertion of vinyl or aryl halides into alkenes to produce new alkenes (Scheme 3). The mechanism proposed by Heck for the neutral palladium catalyst involves the presence of a palladium(0) species. This complex is typically generated in situ, followed by an oxidative addition of Pd(0) to form an aryl or alkenyl palladium(II) complex, which is the key step in the process. Subsequently, a molecule of alkene coordinates to the Pd(II) species formed, leading to a cis insertion of the alkene. A β-elimination of the palladium(II) hydride occurs, and the active Pd(0) species is regenerated through a reaction between the palladium hydride and a base, continuing the catalytic cycle [11].

Norbornene and its derivatives are very attractive chemicals as versatile starting compounds of functionalized materials for not only academic research but also industrial use. One of the industrial usages is in the manufacture of highly transparent polymers for optical, because of their high transparency, negative birefringence, negative dispersion, and high heat-resistance properties.

Ring opening metathesis polymerization (ROMP) has emerged as one of the most successful synthetic techniques for the preparation of polymers with predetermined molecular weights, narrow molecular weight distributions, and high degrees of chain end functionalities [1-4]. Thus, ROMP has enabled ready access to well-defined polymers for numerous applications in diverse areas including drug delivery [5,6], electronic materials [7,8], vegetable oils functionalization [9,10], self-healing [11,12] and nanostructures [13,14]. The mechanism of the ROMP reaction involves an alkylidene catalyst and is identical to the mechanism of olefin metathesis with three important steps. In the initiation stage, the transition metal alkylidene complex coordinates to one cyclic olefin and subsequently forms a 4-membered metallacyclobutane intermediate through [2+2]-cycloaddition. The resulting complex retains almost the same reactivity toward cyclic olefins as it grows longer with every repetition of the first step. The continuous consumption of cyclic olefins during chain growth is identified as the propagation step. The polymerization is terminated when the monomer is totally depleted or when the transition metal is deactivated or removed [15,16].

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## Experimental

*Synthesis of the bimetallic complex Ru-PdCl.*

An oven‐dried 50 mL Schlenk flask equipped with a magnetic stirring bar and capped with a rubber septum containing 0.1 g (0.22 mmol) of the [{RuCl2(*p*‐cymene)(piperidine-NH2)] and 0.19 g (0.22 mmol) of the [PdCl2(PPh3)2] was purged of air by applying three vacuum/nitrogen cycles before the addition of 24 μL (0.22 mmol) of salicylaldehyde in 15 mL of CH2Cl2. The reaction mixture was stirred for 12 hr at room temperature. Finally, the solvent was evaporated under vacuum till dryness. The orange precipitate was washed with petroleum ether (20 ml) and dried under vacuum. Yield: 88%.

FTIR: ν(Ru-Cl) = 305 and 290 cm−1; ν(N-H) = 3261 cm−1; ν(C-H) = 3080 - 3010 cm-1; ν(C=C) 1625 - 1430 cm-1.  1H NMR (CDCl3, 400.13 MHz): δ(ppm) = 7.90-7.30 (m, 19H, CH2), δ(ppm) = 5.20-4.95 (d, 4H, CH2), δ(ppm) = 2.90-1.02 (m, 16H, CH3). 31P{1H} NMR (CDCl3, 161.98 MHz, δ): 24.17 (s).



**Figure 1.** Synthesis of the **Ru-PdCl** complex.

*Synthesis of the bimetallic complex Ru-PdPh.*

An oven‐dried 50 mL Schlenk flask equipped with a magnetic stirring bar and capped with a rubber septum containing 0.10 g (0.22 mmol) of the [{RuCl2(*p*‐cymene)(piperidine-NH2)] and 0.18 g (0.22 mmol) of the [PdBr(Ph)(PPh3)2] was purged of air by applying three vacuum/nitrogen cycles before the addition of 24 μL (0.22 mmol) of salicylaldehyde in 15 mL of CH2Cl2. The reaction mixture was stirred for 12 hr at room temperature. Finally, the solvent was evaporated under vacuum till dryness. The orange precipitate was washed with petroleum ether (20 ml) and dried under vacuum. Yield: 88%.

FTIR: ν(Ru-Cl) = 305 and 290 cm−1; ν(N-H) = 3261 cm−1; ν(C-H) = 3080 - 3010 cm-1; ν(C=C) 1625 - 1430 cm-1.  1H NMR (CDCl3, 400.13 MHz): δ(ppm) = 7.90-7.30 (m, 19H, CH2), δ(ppm) = 5.20-4.95 (d, 4H, CH2), δ(ppm) = 2.90-1.02 (m, 16H, CH3). 31P{1H} NMR (CDCl3, 161.98 MHz, δ): 24.17 (s).



**Figure 2.** Synthesis of the **Ru-PdPh** complex.

*Reductive Heck of NBD.*

In an oven-dried round bottom flask under an atmosphere of nitrogen at room temperature were placed complex (0.0005 mmol) and solvent (3 mL). After stirring, the aryl bromide (5.0 mmol), olefinic substrate (10 mmol) and base (6.0 mmol) were introduced into the reaction flask. The reaction mixture was heated until the desired temperature for the required reaction time under an atmosphere of nitrogen. At the end of the reaction, the reaction mixture was cooled to room temperature, diluted with EtOAc (20 mL), washed with diluted HCl and water. The combined organic layer was dried over anhydrous MgSO4 and stripped off the solvent under reduced pressure. The residue was subjected to column chromatography on silica gel using ethyl acetate and hexane mixtures to afford the Reductive-Heck product in high purity. The products were characterized by 1H NMR analysis.



**Figure 3.** Synthesis of functionalized norbornene.

*ROMP of NBE.*

A 50 mL round-bottom flask equipped with a magnetic stirring bar and capped with a two-way stopcock was charged with the norbornene (NBE) and 2-phenyl-5-norbornene (NBE-Ph), degassed CHCl3 (2 mL) and 1.1 µmol of complex was added under a nitrogen atmosphere. The solution was stirred for a few minutes at room temperature and then in an oil bath thermostated at 50 °C, followed by addition of 5 µL of ethyl diazoacetate (EDA) ([EDA]/[Ru] = 28). The molar ratio [monomer]/[Ru] was 5000 and the reaction mixture was stirred for 10, 20, 30, 40, 50 or 60 min. At room temperature, 10 mL of methanol was added to the reaction flask and the polymer was filtered, washed with methanol. The precipitated polymer was filtered, dried in a vacuum oven at 40 °C up to constant weight, and characterized by GPC in THF using a polystyrene calibration.

## Resultados e Discussão

The **Ru-PdCl** and **Ru-PdPh** complexes were synthetized according to the procedure described in the literature.

The full spectroscopic characterization consisting of FTIR, multinuclear NMR (1H, 31P{1H}) and UV-Vis, was carried out for both complexes. The FTIR spectra of **Ru-PdCl** and **Ru-PdPh** (Fig. S) contain a characteristic υ(C=N) stretching vibration at 1590 cm-1 and υ(P−C) stretching vibration at 1090 cm−1, confirming the coordination of palladium complex to the metal center of ruthenium giving complexes **Ru-PdCl** and **Ru-PdPh**. Two bands observed around 345 and 310 cm−1 were attributed to ν(Ru–Cl) asymmetric and symmetric stretching vibrations, respectively, suggesting two cis-positioned Cl‑ ligands in the complex **3**.

In the 1H NMR spectra of complexes **Ru-PdCl** and **Ru-PdPh**, a series of multiplet resonances were observed in the range δ = 7.84 to 7.05 ppm correspond to the 18 aromatic protons in PPh3 and the aryl ligand in for the complex **Ru-PdPh**, also are observed in the range δ = 1.05 to 2.8 ppm correspond to the 10 aliphatic protons in *p*-cymene and the fragment amine. Two distinct doublets are observed from δ = 5.24 to 4.95 ppm, corresponding to the 4 inequivalent protons in the *p*-cymene ring, due to the asymmetry at the ruthenium center in the complexes. In the 13C{1H} NMR spectra, all the chemical shifts are observed in the expected regions.The 31P{1H} NMR spectra for complexes **Ru-PdCl** and **Ru-PdPh** showed one single resonance signal at 23.6 and 24.3 ppm, respectively, in their spectra, indicative of phosphine coordination to palladium center with the field shifted as single resonance signal corresponding to Ru-Pd-P coordination.

*Reductive Heck*

To get our desired compound, 2-phenyl-5-norbornene, reductive Mizoroki-Heck reaction between 2,5-norbornadiene and arylbenzene catalyzed by **Ru-PdCl** or **Ru-PdPh** were performed in different conditions.

To evaluate the efficiency of the bimetallic complexes, preliminary studies in the reaction of norbornene with arylbenzene under the reductive conditions (Et3N, HCO2H) showed that the palladium center present in the complex structure were efficient providing phenylnorbornene as a single product in high yields (Table 1 and 2).

Solvent screening revealed that DMSO was the choice for gaining high yield albeit reaction can also be performed in other solvent. Base is another important parameter in palladium-catalyzed hydroarylation reaction.

**Tabela 1.** Table 4. Heck reaction using Ru-PdCl complex.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | **PhX** | **Base** | **Solvent** | **Time (h)** | **Conv. (%)** |
| **1** | PhBr | Et3N | DMF | 2 | 87,5 |
| **2** | PhI | Et3N | DMF | 2 | 97,8 |
| **3** | PhI | Et3N | DMSO | 2 | 93,0 |
| **4** | PhI | Et3N | DMF | 1 | 96,3 |
| **5** | PhI | CsCO3 | DMF | 2 | 96,0 |
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**Tabela 2.** Heck reaction using Ru-PdPh complex.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | **PhX** | **Base** | **Solvent** | **Tim (h)** | **Conv (%)** |
| 1 | PhBr | Et3N | DMF | 2 | 77,3 |
| 2 | PhBr | Et3N | DMSO | 2 | 55,0 |
| 3 | PhI | Et3N | DMF | 2 | 74,1 |
| 4 | PhI | Et3N | DMF | 3 | 98,6 |
| 5 | PhI | Et3N | DMF | 1 | 69,4 |
| 6 | PhI | Et3N | Toluene | 2 | 62,4 |
| 71 | PhI | Et3N | DMF | 2 | 49,5 |
| 8 | PhI | CsCO3 | DMF | 2 | 96,4 |
| 9 | PhI | Et3N | DMSO | 2 | 69,5 |
| 10 | PhBr | CsCO3 | DMF | 2 | 79,7 |

1 Temperature of 60 °C.

*ROMP reactions*

In order to assess the catalytic efficiency of the **Ru-PdCl** and **Ru-PdPh** complexes, ring-opening metathesis polymerization (ROMP) of norbornene (NBE) was performed in CHCl3 at 50 °C with a [NBE]/[Ru]=5000 ratio and using [Initiator]/[Ru]= 28 (31-34).

The increase in time (10–60 min) afforded good yields of polyNBE, reaching 44 % and 80 % of conversion with 60 min at 50 °C for **Ru-PdCl** and **Ru-PdPh**, respectively. At lower temperatures, the catalysts did not show good catalytic activity. This behavior can be attributed to an increased production of the Ru-carbene species in the initiation reaction because of the higher temperature.



**Figura 4.** Dependence of yield, for ROMP of norbornene using **Ru-PdCl** and **Ru-PdPh** as a function of time at 50 °C. Conditions: [NBE]/[Ru] = 5000; [Initiator]/[Ru] = 28; CHCl3 as solvent.

The molecular weights (Mn) and polydispersity value (Ð) as a function of time were studied using GPC analyses, in which a slight increase of the Mn values could be observed in the beginning of the polymerization, followed by an abrupt increase after 30 min with moderate Ð. In general, polymers synthesized using **Ru-PdPh** showed higher Mn values (2.6 × 105 g·mol−1) and narrower molecular weight distribution (Ð = 1.66) in 60 min than those synthesized with **mono-Ru** (1.5 × 105 g·mol−1 and 1.86 for Mn and Ð, respectively).

The temperature study was carried out with the aim of evaluating its influence as a parameter in the ROMP reaction. The reaction was monitored by varying the temperature from 15 - 35 °C with intervals of 5 °C between each experiment using **Ru-PdPh** (Figure 5). The data obtained from this experiment can determine the kinetic dependence of the reaction with temperature from the formation of the active species (Ru=C), which can be significant for discussions related to ROMP reactions when the active metal carbene species is generated in situ.

**Figure 5.** First-order rate plots were used to determine the total kinetic rate constant, kobs, for the ROMP reaction of NBE with **Ru-PdPh**, [NBE]/[Initiator]/[Ru] = 100/5/1, in CHCl3.

Activation parameters (Ea, ΔH‡, ΔS‡, ΔG‡) were then determined for this process. Based on the values of kapp and considering its dependence on reaction temperature, according to the Arrhenius equation, the graph in Figure 6 can be used to determine the activation energy (Ea). The data follow a linear relationship, and the calculated activation energy is 26,5 kJ mol-1.

 **Figure 6.** Arrhenius plot (ln(kobs) versus 1000/T). Estimation of activation energy for ROMP reaction; [NBE]/[Initiator]/[Ru] = 10/5/1, in CHCl3.

The thermodynamic parameters of the transition state such as activation entropy (ΔS‡) and activation enthalpy (ΔH‡) were determined using the Eyring equation. From Figure 7, -ln(kobs/T) as a function of 1000/T, the values of ΔH ‡ and ΔS ‡ can be calculated from the slope and intercept, respectively. The graphs show a linear behavior, and the calculated thermodynamic parameters are Δ H ‡ = 5,44 KJ.mol-1 and ΔS ‡ = -19,74 KJ.mol-1.K-1.

 **Figure 7.** Eyring plot (-ln(kapp/T) versus 1/T) for the estimation of activation energy and thermodynamic parameters of the transition state for the ROMP reaction; [NBE]/[EDA]/[Ru] = 10/5/1, in CHCl3.

The value of ΔS‡ is negative and supports the proposed associative mechanism, as expected for a bimolecular step. This negative value may also reflect the restriction of the reactants' movement relative to the transition state during polymerization, which allows for greater flexibility of the activated complex and the progression of the reaction over time.

## Conclusões

The new **Ru-PdCl** and **Ru-PdPh** complexes were successfully synthesized and characterized by FT-IR, UV–Vis, 1H, 13C{1H}, and 31P{1H} NMR spectroscopy, MALDI-TOF, and DFT. The catalytic activity of Ru-PdCl and Ru-PdPh in the Heck reaction of norbornadiene (NBD) and an aryl halide (PhX) was evaluated using different temperatures, solvents, and bases over time. Both complexes were able to provide a conversion with values reaching 98%, using iodobenzene and triethylamine in DMF for 3 hours. **Ru-PdCl** and **Ru-PdPh** were active for ROMP of NBE at 50 °C with [NBE]/[Ru] ratio of 5000 in the presence of trimethylsilyl diazomethane ([Initiator]/[Ru] = 28) for 10–60 min. The complex **Ru-PdPh** exhibited better performance in ROMP, which is associated to the greater Pd fragment−Ru fragment−olefin synergism, providing an electron-rich ruthenium center, reaching 80 % yield of polyNBE in 60 min.

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