# DMSO Molecule as Ancillary Ligand in Ru-Based Catalysts for Ring Opening Metathesis Polymerization

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A polimerização *via* metátese por abertura de anel (ROMP) de norborneno (NBE) ocorre em presença do complexo *fac*-[RuCl$_2$(S-DMSO)$_3$(O-DMSO)] e etildiazoacetato (5 μL), onde DMSO é dimetilsulfóxido coordenado pelo átomo de enxofre ou de oxigênio. O rendimento é 62% (PDI = 1,64) à temperatura ambiente por 5 min e 88% (PDI = 1,93) a 50 °C por 30 min, com [NBE]/[Ru] = 516 em CHCl$_3$. Na presença de NBu$_4$ClO$_4$ o rendimento é 90% (PDI = 1,64) à temperatura ambiente por 5 min. O complexo é praticamente inativo quando uma ou duas moléculas de DMSO são substituídas por piridina, imidazol, 2-metil-imidazol ou benzoimidazol. A formação *in situ* da espécie catalítica e os comportamentos das moléculas de DMSO como ligantes ancilares nas reatividades dos complexos de Ru$^{II}$ são discutidas nesse trabalho.

The ring-opening metathesis polymerization (ROMP) of norbornene (NBE) occurs in the presence of the *fac*-[RuCl$_2$(S-DMSO)$_3$(O-DMSO)] complex and ethyldiazoacetate (5 μL), where DMSO is S- or O-bonded dimethylsulfoxide. The yield is 62% (PDI = 1.64) at room temperature for 5 min and 88% (PDI = 1.93) at 50 °C for 30 min, with [NBE]/[Ru] = 516 in CHCl$_3$. The yield is 90% (PDI = 1.64) in the presence of NBu$_4$ClO$_4$ at room temperature for 5 min. The complex is practically inactive when one or two molecules of DMSO are replaced by pyridine, imidazole, 2-methyl-imidazole or benzimidazole. The *in situ* formation of the catalytic species and the behavior of the DMSO molecules as ancillary ligands in the reactivity of the Ru$^{II}$ complexes are discussed.

**Kewords:** olefin metathesis, ROMP, ancillary ligand, ruthenium, DMSO

## Introduction

Over the last 15 years, olefin metathesis has been widely applied in organic and polymer synthesis.[1-5]

The significance of this process for so many purposes was recognized by The Nobel Foundation and the researchers, Yves Chauvin (Institut Francais du Petrole, France), Robert H. Grubbs (California Institute of Technology, USA) and Richard R. Schrock (Massachusetts Institute of Technology, USA) were awarded the Nobel Prize for Chemistry in 2005 "for the development of the metathesis method in organic synthesis".[6] Grubbs and Schrock develop well-defined metal-carbene catalysts for the reaction, following the mechanistic proposal suggested by Chauvin. Whereas Grubbs mainly works with Ru, Schrock mainly works with Mo and W.

Ru-based compounds are user-friendly catalysts for many olefin metathesis processes because they are resistant towards many basic functional groups.[1-3,5,7]

Besides the self-electronic nature of the metal center in the metal-carbene complex, the electronic and steric effects of the ancillary ligands can provide catalysts which are able to promote high-efficiency alkene metathesis.[1,2,6,7] Typically, phosphines, esters, amines and N-heterocyclic carbenes have been tested as ancillary ligands.

Thus, the combination of metal and ligands can provide powerful catalysts for olefin metathesis.

While the novel Grubbs and Schrock carbene-type catalysts are well established, there is a claim for cheaper and more robust industrial type catalysts considering large-scale applications.[2,7-9] For this type of procedure,

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the carbene catalyst would be generated *in-situ* from precatalysts used as starting compounds.

The development of precatalysts is also based on the influence of the ancillary ligands on the metal center as occurs in the cases with metal-carbene catalysts. An important key in the use of non-carbene type catalysts as starting compounds is the beginning metal reactivity considering the *in-situ* formation of the catalyst itself.

With this in mind, we have worked to discover new $Ru^{II}$-based precatalysts for ring-opening metathesis polymerization (ROMP) of cyclic olefins (Scheme 1), with the purpose of establishing strategies for syntheses of precatalyst compounds capable of working in mild conditions of temperature and resistant to air (meaning $O_2$) and moisture, which would be cheaper for industrial processes.[10] In addition, these compounds could be stored and handled without large restriction to air, moisture, light and warmth, which are typical tropical conditions.
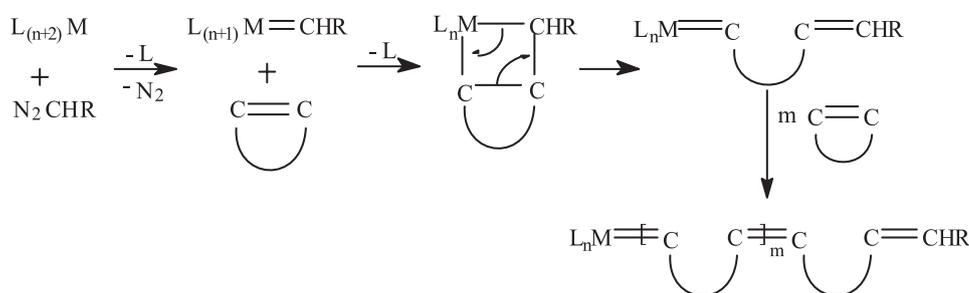
The *fac*-[RuCl$_2$(S-DMSO)$_3$(O-DMSO)] complex is neither atmospheric air nor moisture sensitive and easy to handle and fulfill the requirements discussed above.[11,12]

In general, an interesting feature of sulfoxide molecules is the ambidentate nature.[13] Both metal-S-bonded and metal-O-bonded complexes are isolated with dimethylsulfoxide (DMSO) as a ligand.[13] The linkage isomers with S- and O-bonded complexes depend on the oxidation state of the metal and the electronic and steric properties of the sulfoxide, as well as the other coordinated ligands.[13] The metal-S-bonded mode is usual with "soft" metal centers, such as low spin $d^6$ $Ru^{II}$ complexes, where $d_\pi$ back-bonding is observed.[13]
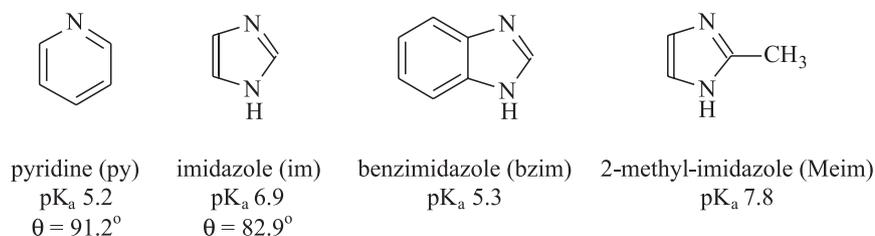
In *fac*-[RuCl$_2$(S-DMSO)$_3$(O-DMSO)], the O-DMSO molecule is axial and it is more labile than the other S-bonded ligands.[13] This complex experiences an easy ligand substitution reaction and is a starting material for new complexes with phosphine, CO, NO and amine ligands, for example.[12,13]

The complex *fac*-[RuCl$_2$(S-DMSO)$_3$(O-DMSO)] was evaluated as a catalyst precursor for 1-hexene hydrogenation with successful results.[14] It is well known that in this type of process at least two labile positions are necessary to make the reaction happen, as for olefin metathesis (Scheme 1). Thus, this complex with DMSO can be an alternative catalyst for ROMP application under mild conditions, where the DMSO molecules would be ancillary ligands. In addition, this complex can be an alternative to the ill-defined $Ru^{III}$ salts employed in industry[9] as it behaves as a well-defined $Ru^{II}$ coordination complex. Indeed, the DMSO molecule was already tested in the Ru-based ROMP precatalyst where the *fac*-[RuCl$_2$(S-DMSO)$_3$(O-DMSO)] complex was a precursor for the syntheses of Ru-allenylidene complexes of type [RuCl$_2$(=C=C=CR$_2$)(PCy$_3$)$_n$(DMSO)$_m$] and RuCl(=C=C=CR$_2$)(PCy$_3$)$_n$(DMSO)$_m$] (triflate).[15] However, the article did not mention the role of DMSO in the reactivity of the complexes.

In this work, considering that in the course of our research with $Ru^{II}$ complexes, we found a beneficial effect of the combination of usual amines and phosphines as ancillary ligands,[10] the activities of the complexes *fac*-[RuCl$_2$(S-DMSO)$_3$(O-DMSO)] and [RuCl$_2$(S-DMSO)$_{4-x}$(N)$_x$] derivatives were investigated for ROMP of norbornene (NBE), where N = pyridine, imidazole, benzimidazole



**Scheme 1**



pyridine (py)            imidazole (im)       benzimidazole (bzim)    2-methyl-imidazole (Meim)
pK$_a$ 5.2                 pK$_a$ 6.9                  pK$_a$ 5.3                      pK$_a$ 7.8
θ = 91.2°                 θ = 82.9°

**Scheme 2**

or 2-methyl-imidazole (Scheme 2). In these complexes there are also combinations of σ-donor and π-receptor ligands. Different reactant concentrations, reaction time and temperature were examined, using ethyldiazoacetate (EDA) as a starting source of carbene. The formation of the *in situ* active catalytic species was discussed in each case, emphasizing the behavior of the DMSO molecule as an ancillary ligand.

## Experimental

### General remarks

All the handling was carried out under argon atmosphere. Ruthenium trichloride, $NBu_4ClO_4$, pyridine (py), imidazole (im), 2-methyl-imidazole (Meim), benzimidazole (bzim) and ethyldiazoacetate (EDA; $N_2CHCOOCH_2CH_3$) from Aldrich, norbornene (NBE) from Across and silver triflate from Strem were used without further purification. Analytical grade solvents were freshly distilled prior to use. CHN analyses were performed on an EA 1110 CHNS-O Carlo Erba Instrument. IR spectra were obtained on a BOMEM FTIR MB 102 SERIES spectrometer with samples dispersed in CsI pellets or 0.1 mm liquid cell (NaCl windows). ^{1}H NMR spectra were recorded on a Bruker AC 200 spectrometer ($CDCl_3$). All spectra were run at room temperature (RT) with residual proton as an internal standard. Electronic spectra were obtained in a quartz cell (1.00 cm) on a Lambda 40 Perkin-Elmer UV-Vis spectrophotometer equipped with a Pettier thermostat. The molecular weights ($M_w$; $M_n$) and the polydispersity index (PDI = $M_w/M_n$) of the polymers were determined by gel permeation chromatography at room temperature using a Shimadzu 77251 system equipped with two serial placed columns (PLgel 5 μm MIXED-C: 30 cm, $\varnothing$ = 7.5 mm). The retention times were calibrated with standard monodispersed polystyrene using HPLC-grade $CHCl_3$ as an eluent.

### Syntheses of the complexes

The complexes were prepared according to the literature procedures: *fac*-[RuCl_2(S-DMSO)_3(O-DMSO)] (Anal. Calc.: C, 19.83, H, 4.99; Found: C, 19.80, H, 4.79%); *fac*-[RuCl_2(S-DMSO)_3(py)] (Anal. Calc.: C, 27.21; H, 4.77; N, 2.88; Found: C, 27.09; H, 4.81; N, 2.70%); *fac*-[RuCl_2(S-DMSO)_3(im)] (Anal. Calc.: C, 22.79; H, 4.68; N, 5.91; Found: C, 22.85; H, 4.32; N, 6.23%); *cis,cis,cis*-[RuCl_2(S-DMSO)_2(im)_2] (Anal. Calc.: C, 25.86; H, 4.34; N, 12.06; Found: C, 26.15; H, 4.24; N, 11.94%); *cis,cis,cis*-[RuCl_2(S-DMSO)_2(Meim)_2] (Anal. Calc.: C, 29.79; H, 4.91; N, 11.38; Found: C, 29.36; H, 4.44; N, 11.41%); *cis,cis,cis*-[RuCl_2(S-DMSO)_2(bzim)_2] (Anal. Calc.: C, 38.30; H, 4.25; N, 9.92. Found: C, 38.72; H, 4.23; N, 9.99%).[16]

### Polymerization procedures

In a typical experiment with *fac*-[RuCl_2(S-DMSO)_3(O-DMSO)], 100 mg of NBE (1.2 mmol) and 5 μL of EDA (5.4 μmol) were added to a solution of the complex (2.1 μmol) in $CHCl_3$ (2.5 mL). The reaction mixture was maintained at room temperature (RT; 24 ± 1 ºC) or 50 ºC (silicone oil bath; ± 1 ºC) for 5 min. Methanol was added to the cooled solution and the precipitated polymer was filtered, washed with methanol and dried under ambient conditions. The polymerization yields were determined gravimetrically. The catalytic runs were repeated at least 3-6 times. Errors associated with weighting of NBE or isolating and drying the polymer explain the variations in yields. The polymer was not produced when the reaction was carried out in absence of Ru complex either at RT or 50 ºC for 90 min.

In experiments as a function of time, the reactions were quenched with methanol. In experiments as a function of the EDA molar ratio, the reactions were initiated with different volumes of EDA, maintaining both the complex and NBE concentrations constant. In experiments as a function of [NBE]/[Ru] molar ratio, different weights of monomer were used in order to maintain the complex concentration constant.

Polymerization reactions in the presence of excess $NBu_4ClO_4$, NaCl, DMSO or amines were carried out with 100 μmol of each compound added to the complex solutions (2.1 μmol in 2.5 mL $CHCl_3$). The mixtures were stirred at RT for 30 min. Then, typical polymerization procedures were carried out.

Substitution reaction of $Cl^-$ ion by triflate ion was obtained with a fresh Ru solution (2.1 μmol in 2.5 mL $CHCl_3$) in the presence of 2 μmol of $AgCF_3SO_3$ at RT for 10 min. The produced AgCl was filtered off and the resulting solution was used for polymerization tests.

## Results and Discussion

### Catalytic experiments

In order to propose a route and the cause for ROMP of NBE with the Ru-DMSO complexes, a number of reactions were carried out.

The results as a function of EDA volume and [NBE]/[Ru] molar ratio at RT with *fac*-[RuCl_2(S-DMSO)_3(O-DMSO)] as starting material are summarized in Table 1.

Whereas the polymerization reaction did not occur in the absence of EDA at RT for 90 min (Table 1; entry 1),

**Table 1.** Influence of EDA volume, [NBE]/[Ru] molar ratio and reaction time on the ROMP of NBE with *fac*-[RuCl$_2$(S-DMSO)$_3$(O-DMSO)] at RT

| Entry | EDA volume / µL (µmol) | [NBE]/[Ru] | time / min | Yield / % | *trans*-content / % |
|---|---|---|---|---|---|
| 1 | 0 | 516 | 5 | 0 | |
| 2 | 1 (9.5) | 516 | 5 | 21 ± 3 | |
| 3 | 2 (19) | 516 | 5 | 44 ± 4 | |
| 4 | 3 (28.5) | 516 | 5 | 51 ± 3 | 56 |
| 5 | 4 (38) | 516 | 5 | 54 ± 3 | 56 |
| 6 | 5 (47.5) | 516 | 5 | 62 ± 6 | 61 |
| 7 | 10 (95) | 516 | 5 | 58 ± 8 | 53 |
| 8 | 15 (143) | 516 | 5 | 59 ± 4 | 56 |
| 9 | 20 (190) | 516 | 5 | 53 ± 4 | 54 |
| 10 | 5 | 1031 | 5 | 71 ± 2 | 57 |
| 11 | 5 | 1547 | 5 | 73 ± 8 | 56 |
| 12 | 5 | 2062 | 5 | 78 ± 4 | 56 |
| 13 | 5 | 2578 | 5 | 79 ± 8 | 56 |
| 14 | 5 | 3094 | 5 | 83 ± 1 | 52 |
| 15 | 5 | 5156 | 5 | 81 ± 3 | 50 |
| 16 | 5 | 516 | 10 | 60 ± 7 | 51 |
| 17 | 5 | 516 | 20 | 68 ± 6 | 52 |
| 18 | 5 | 516 | 30 | 71 ± 7 | 53 |
| 19 | 5 | 516 | 60 | 80 ± 6 | 55 |
| 20 | 5 | 516 | 120 | 83 ± 7 | 57 |

2.1 µmol of Ru in 2.5 mL of CHCl$_3$.

polymers were isolated when the reactions were carried out in the presence of EDA at RT for 5 min (Table 1; entries 2-9). Similar behavior was observed for [RuCl(µ-Cl)(η$^3$: η$^3$-C$_{10}$H$_{16}$)]$_2$ when 2 µL of EDA were necessary to initiate the reaction with NBE.[17] In the present case, the dependence of the yield on the EDA volume becomes relatively constant over 5 µL with *ca.* 60% yield, as suggested from the saturation profile observed in the plot of reaction yield *versus* EDA volume (Figure 1). This behavior is different from early experiments with five-coordinated [RuCl$_2$(PPh$_3$)$_2$(amine)] complexes where the reactivity decreased with 5-7 µL of EDA.[15] The difference is associated to excessive coordination of EDA molecules in the case of the five-coordinated complexes, inhibiting the formation of the catalysts. In the present case, where the complex is six-coordinated, a substitution reaction via a dissociative nature mechanism is expected to occur.

The dependence of the yield on the [NBE]/[Ru] molar ratio with 5 µL of EDA increased up to the value of 3,000 with *ca.* 80% yield at RT for 5 min (Table 1; entries 6 and 10-15). The polymerization behavior also showed a saturation mechanism profile (Figure 1). The increase in the activity when increases [NBE]/[Ru] ration is in agreement with the fact that the most favorable conditions for a
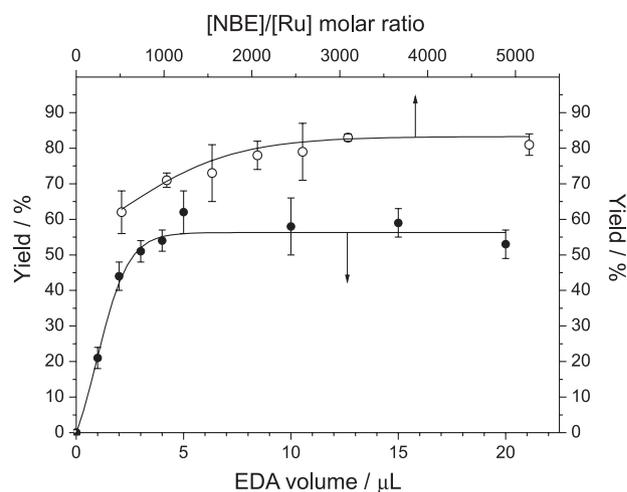


**Figure 1.** Plots of yields for ROMP of NBE with *cis*-[RuCl$_2$(S-DMSO)$_3$(O-DMSO)] *versus* EDA volume ([NBE]/[Ru] = 516) and [NBE]/[Ru] molar ratio (5 µL of EDA) at RT for 5 min; 2.1 µmol of Ru in CHCl$_3$.

successful ROMP reaction is to use the highest monomer concentration at the lowest temperature possible in order to decrease the entropic penalty.[1]

Experiments as a function of time and temperature with 5 µL of EDA and [NBE]/[Ru] = 516 are shown in Tables 1 and 2. Whereas the reaction yield rose over 80% when

**Table 2.** Influence of temperature and reaction time on the ROMP of NBE with [RuCl$_2$(S-DMSO)$_x$(L)$_y$] type complexes in absence or presence of NBu$_4$ClO$_4$

| Entry | L ligand (x;y) | NBu$_4$ClO$_4$ 146 μmol | T / °C | time / min | Yield / % | *trans*-content / % | M$_w$ (×10$^4$) | PDI |
|---|---|---|---|---|---|---|---|---|
| 1 | O-DMSO (3;1) | absent | RT | 5 | 62 ± 6 | 61 | 14 | 1.64 |
| 2 | | absent | 50 | 5 | 65 ± 4 | 62 | 9.3 | 1.70 |
| 3 | | absent | 50 | 30 | 88 ± 9 | 60 | 9.1 | 1.93 |
| 4 | | present | RT | 5 | 90 ± 8 | 56 | 11 | 1.64 |
| 5 | | present | 50 | 30 | 94 ± 4 | 63 | 8.9 | 2.12 |
| 6 | py (3;1) | absent | RT | 5 | 8 ± 1 | 59 | | |
| 7 | | absent | 50 | 5 | 63 ± 6 | 59 | 8.4 | 1.68 |
| 8 | | absent | 50 | 30 | 62 ± 4 | 58 | 8.0 | 1.74 |
| 9 | | present | RT | 5 | 8 ± 2 | | | |
| 10 | | present | 50 | 30 | 60 ± 1 | 59 | 6.1 | 1.85 |
| 11 | im (3;1) | absent | RT | 5 | < 1 | | | |
| 12 | | absent | 50 | 5 | < 1 | | | |
| 13 | | absent | 50 | 30 | 8 ± 3 | | | |
| 14 | | present | RT | 5 | 0 | | | |
| 15 | im (2;2) | absent | RT | 5 | 0 | | | |
| 16 | | absent | 50 | 5 | < 1 | | | |
| 17 | | absent | 50 | 30 | < 1 | | | |
| 18 | | present | RT | 5 | 0 | | | |
| 19 | Meim (2;2) | absent | RT | 5 | < 1 | | | |
| 20 | | absent | 50 | 5 | < 1 | | | |
| 21 | | absent | 50 | 30 | 42 | 45 | | |
| 22 | | present | RT | 5 | 0 | | | |
| 23 | bzim (2;2)* | absent | RT | 5 | 0 | | | |
| 24 | | absent | 50 | 5 | < 1 | | | |
| 25 | | absent | 50 | 30 | 5 | | | |
| 26 | | present | RT | 5 | 0 | | | |

1 mg of Ru (*ca.* 2 μmol) in 2.5 mL CHCl$_3$; 1.2 mmol of NBE ([NBE]/[Ru] *ca.* 500); 5 μL of EDA; *10% DMF/CHCl$_3$.

increasing the reaction time up to 60 min at RT (Table 1; entries 6 and 16-20; Figure 2), the yields were similar (62-65%) either at RT or 50 °C for 5 min (Table 2; entries 1-2). However, an almost quantitative conversion at 50 °C for 30 min was observed (Table 2; entry 3).

The Ru catalytic activity is inhibited when in the presence of DMSO (RT for 5 min; 5 μL EDA), but it is roughly the same in the presence of Cl$^-$ ions with 55% yield. These experiments support the fact that the Cl$^-$ ligands are not involved in the replacement process of ligands for the *in situ* formation of the catalyst, contrary to DMSO. In addition, this could suggest a participation of Cl$^-$ ligands in the reactivity of the catalyst. A proof of this is that the ROMP reaction does not occur under similar conditions when the Cl$^-$ ions are replaced by triflate in the starting Ru-DMSO complex. A different behavior was observed for [Ru(=CPh)(OC$_6$F$_5$)$_2$(py) (IMes)] which occurs in the absence of halide.[18]



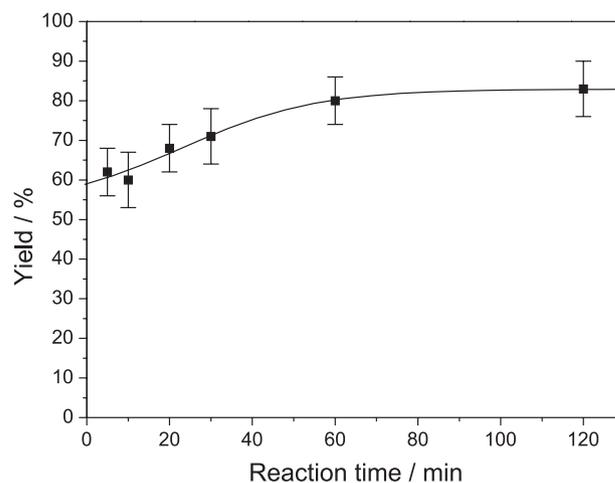**Figure 2.** Plot of yield for ROMP of NBE with *cis*-[RuCl$_2$(S-DMSO)$_2$(O-DMSO)] *versus* reaction time at RT for 5 min; 5 μL of EDA, [NBE]/[Ru] = 516, 2.1 μmol of Ru in CHCl$_3$.

The experiments as a function of initial reactant concentrations, time and temperature and in the presence either of DMSO or Cl⁻ ion suggest that the catalyst formation is kinetically dependent on the DMSO labilization. Thus, in an attempt to accelerate this step, some experiments were carried out in the presence of $NBu_4ClO_4$, as a promoter, considering that the DMSO molecule could be associated with cations in solution and to weaken some Ru-DMSO bonds.[13,19] The result was 90% yield in the presence of $NBu_4ClO_4$ at RT for 5 min (Table 2; entry 4), which is *ca.* 50% higher than in the absence of salt. A similar result was observed at 50 ºC for 30 min (Table 2; entry 5). Hence, this confirms the idea to improve the complex reactivity where there are probable interactions between DMSO and $NBu_4ClO_4$.

On the other hand, in most of the cases, the amounts of isolated polymer were very low when the reactions were carried out with amine derivative complexes either at RT or 50 ºC for 5 or 30 min, even in the presence of $NBu_4ClO_4$ (Table 2). Better results (*ca.* 60%) were obtained in the case of the complex with pyridine at 50 ºC either for 5 or 30 min (Table 2). However, the reactions were inhibited in the presence of pyridine or DMSO, or replacing the Cl⁻ by triflate ions, at 50 ºC for 30 min. The activities were maintained in the presence of Cl⁻ ions under similar conditions. Then, these results suggest that the py and DMSO molecules leave the metal coordination sphere so that the ROMP can take place. In the case with Meim, the reaction occurs with 42% of isolated polymer at 50 ºC for 30 min and $NBu_4ClO_4$ does not change the results.

Experiments carried out under air at RT for 5 min resulted in similar yields (59%). This is in accordance with the expectation that the complex is quite stable towards air during the catalytic process.

When performing the ROMP reaction with a Ru-DMSO complex solution aged for 24 h at RT under argon, a similar activity as a fresh solution was obtained with 55% yield at RT for 5 min, demonstrating stability of the complex in $CHCl_3$.

The GPC data shows $M_w$ values of *ca.* $10^5$ and PDI values of 1.6-1.7 for the polyNBEs obtained with *fac*-$[RuCl_2(S-DMSO)_3(O-DMSO)]$ either in the absence or presence of $NBu_4ClO_4$ with [NBE]/[Ru] = 516 and 5 μL of EDA (Table 2). When the temperature is increased to 50 ºC, the PDI values are *ca.* 2. This can be attributed to an increased production of the Ru-carbene species in the initiation reaction because of the higher temperature. However, some degree of intermolecular chain-transfer reaction cannot be ruled out, considering the increase in the yield followed by a rise in the molecular weight distribution without increasing the $M_n$.[1,20]

The results from ¹H NMR pointed out polymers with 51-61% content in the *trans* form (Tables 1 and 2).

*Mechanism considerations*

The replacement of two adjacent ligands from the Ru coordination sphere is expected as the present complexes are six-coordinated. Thus, substitution reactions with EDA and NBE must occur to obtain success in the metathesis polymerization.

The electronic spectrum of the *fac*-$[RuCl_2(S-DMSO)_3(O-DMSO)]$ complex in $CHCl_3$ does not change for 48 h at RT in the absence or presence of NBE (Figure 3). This suggests that the complex does not undergo dissociation of coordinated ligands and it does not react with NBE in the absence of EDA. A different electronic spectrum is immediately observed when adding EDA to the fresh Ru solution in the absence and presence of NBE. The change is very fast when NBE is present and the solution becomes viscous, consequently suggesting the occurrence of a polymerization process. It is possible to infer that the catalysis process initiates through the formation of the carbene-complex from EDA, followed by a reaction with NBE.
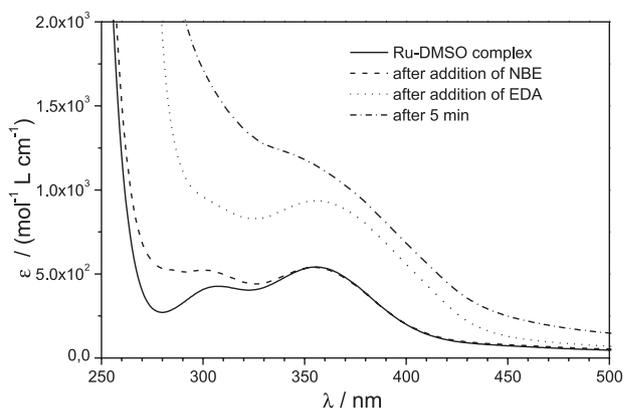


**Figure 3.** UV-Visible spectra of *cis*-$[RuCl_2(S-DMSO)_3(O-DMSO)]$ upon addition of NBE and EDA; [Ru] = 0.80 mmol L⁻¹ in $CHCl_3$ at RT.

The ¹H NMR spectrum of the $[RuCl_2(S-DMSO)_3(O-DMSO)]$ complex after reacting with EDA showed an increase in the signal at 2.57 ppm, attributed to the hydrogen atoms of the methyl group in the free DMSO.[21] A signal at 2.68 ppm, attributed to protons from the O-DMSO molecule, does not change. It is known that the axial O-DMSO ligand undergoes an easy replacement because of the soft chemical behavior of the Ru^{II} ion.[12,13] This can provide the formation of the carbene complex in this coordination position, justifying the presence of the free DMSO in solution. In addition, isomerization of the S-DMSO *trans*-bonded to the

O-DMSO can occur when it reacts with EDA, as occurs in syntheses of many DMSO-Ru$^{II}$-[π-acceptor] complexes.[13] It can justify the non-changing in the O-DMSO $^1$H NMR signal. This isomerization is induced by a high π-electron competition between S-DMSO and the π-acceptor carbene ligand which is *trans*-positioned for some moments. It implies that the carbene ligand shows a higher *trans* effect than the S-DMSO, explaining the isomerization from S- to O-DMSO in the complex. Thus, it is possible to suggest that the reaction initiates with the formation of the carbene complex replacing the O-bonded DMSO, with concomitant *trans*-isomerization S- to O-DMSO. It is followed by coordination of the olefin from the NBE that replaces an equatorial S-DMSO. In this process, higher yield values are obtained when increasing the reaction time or in the presence of salt (Table 2; entries 1). In the latter case, the O atom from the equatorial S-DMSO molecule can interact with NBu$_4^+$ cation by an electrostatic interaction.[19] This enables the axial S-DMSO ligand to leave so that the formation of the carbene complex can take place.

The $^1$H NMR signals at 2.71 and in the range of 3.3-3.6 ppm in the spectrum of a solution polyNBE generated *in situ* confirm the presence of both O- and S-DMSO molecules. Thus, both O- and S-DMSO molecules are present in the catalyst in the reaction of ROMP of NBE, working as ancillary ligands.

With these data, the reaction mechanism for the formation of the carbene-complex in the initiation process can be illustrated in Scheme 3.

The O-DMSO substitution which provides the carbene complex can be visualized by analyzing the behavior of the fully S-bonded mono-amine derivative complexes which failed to ROMP (Table 2). Crystal data for L = NH$_3$ show an axial-amine structure *trans*-positioned to S-DMSO.[22] This suggests a similar structure for the current complexes with one amine. For L = py, the better yields were only obtained at 50 ºC either for 5 or 30 min which are the same results using the *fac*-[RuCl$_2$(S-DMSO)$_3$(O-DMSO)] complex for 5 min at RT. At RT, the yield with py-complex is very low. Consequently, the *in situ* formation of the catalyst probably occurs from the dissociation of the pyridine at 50 ºC with the formation of the carbene-complex. This is different from the O-DMSO complex, which is more labile and reacts at RT. The fact that the yield is not affected when NBu$_4$ClO$_4$ is present in the pyridine-complex solution, contrary to the case with *fac*-[RuCl$_2$(S-DMSO)$_3$(O-DMSO)], confirms that the salt has no effect on the carbene-complex formation. The salt does not affect the exit of the pyridine when increasing the temperature. Thus, salt takes only the second step of the mechanism with *fac*-[RuCl$_2$(S-DMSO)$_3$(O-DMSO)]. It means that the carbene complex formation occurs in the absence or presence of salt. Therefore, the salt allows the second DMSO molecule to leave. A similar result suggests that the catalyst moiety complex is the same when the reaction is initiated either with the *fac*-[RuCl$_2$(S-DMSO)$_3$(O-DMSO)] or pyridine derivative complex. The higher PDI values in the experiments at 50 ºC in the absence or presence of salt can be a result of an increase in the $k_i$ relative to $k_p$, as suggested in the literature (see Table 2).[1,20]

The other amine complexes are also inert to the carbene complex formation and the salt does not promote the reaction. Following the interaction between the NBu$_4^+$
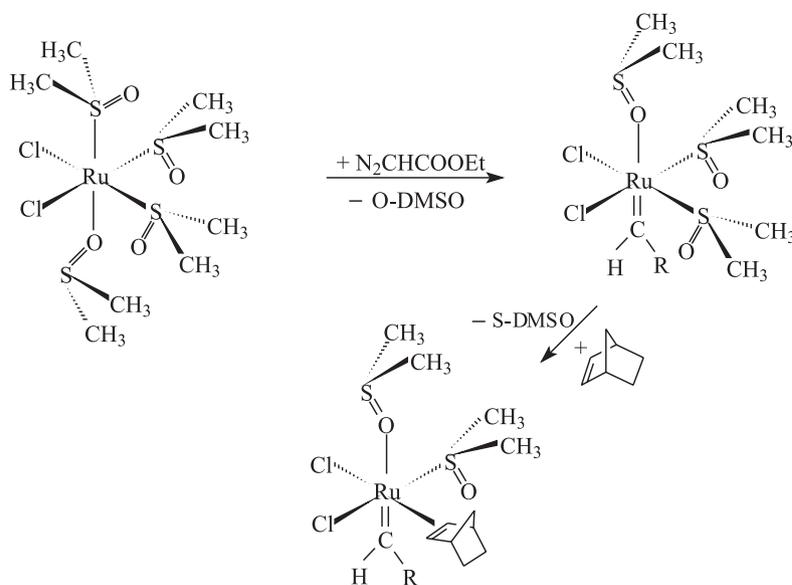


**Scheme 3**

cation with the oxygen atom from S-DMSO molecule,[19] it can be proposed that the NBu$_4^+$ cations, in fact, interact with the oxygen atom of the equatorial S-DMSO molecule by electrostatic interaction. This provides a fast substitution of the axial S-bonded DMSO molecule in *fac*-[RuCl$_2$(S-DMSO)$_3$(O-DMSO)] at room temperature with better yields, without affecting the PDI.

The presence of the O-DMSO molecule in the *fac*-[RuCl$_2$(S-DMSO)$_3$(O-DMSO)] complex and its absence in the amine type complex, when the complexes are in solution, can be observed from the FTIR experiments. The infrared spectra of the *fac*-[RuCl$_2$(S-DMSO)$_3$(O-DMSO)] complex in CH$_2$Cl$_2$ shows typical $\nu_{S=O}$ (S-DMSO), $\nu_{S=O}$ (O-DMSO), $\nu_{Ru-S}$ (S-DMSO) and $\nu_{Ru-O}$ (O-DMSO) bands, in agreement with those in the solid state spectra.[12,13,16] In the case of the amine complexes, both $\nu_{S=O}$ (O-DMSO) and $\nu_{Ru-O}$ (O-DMSO) bands are not observed. It suggests that the complexes are S-DM*SO* types, as expected.[13,16] Furthermore, they do not undergo isomerization when in solution. It can be supposed that the amines block the production of the carbene, resulting in inert complexes to ROMP.

The imidazole ligand, which is a better σ-donor than pyridine considering the pK$_a$ values, makes the complex less active than the pyridine derivative complex (Table 2; entries 11-14).

If a second amine molecule replaces another DMSO molecule, the resulting complexes are also inert to ROMP. Then, no successful reactions are obtained with complexes with two coordinated amines (Table 2; entries 15-26).

The complex with two Meim shows activity at 50 ºC. Perhaps this activity is associated to the hindrance of the methyl group. In the case of bzim, the complex was only soluble in 10% DMF/CHCl$_3$ and the presence of DMF can poison the complex activity.

The Cl$^-$ ions are not discoordinated in the course of the polymerization process considering the same yield results when in the presence of NaCl. In counterpart, the presence of Cl$^-$ ions are important for the process considering that the reaction failed to occur under specified conditions when they were substituted by triflate ion. Thus, it can be expected that the π-donor Cl$^-$ ligands also perform the role of the ancillary ligand, as known in the literature.[23]

The best activity of the pyridine derivative at 50 ºC for either 5 or 30 min can be attributed to temperature dependence where the salt can take the second reaction step.

## Conclusions

The *fac*-[RuCl$_2$(S-DMSO)$_3$(O-DMSO)] complex behaves as a precatalyst for the ROMP of NBE in mild conditions, with {RuCl$_2$(S-DMSO)(O-DMSO)} a moiety

complex as the active species. Both O- and S-DMSO molecules provide ancillary effects for this catalytic process. The presence of an N-heterocyclic inhibits the production of the active catalytic species due to its interaction with the Ru$^{II}$ metal center which makes the formation of the carbene complex difficult. This is contrary to many amine-phosphine Ru$^{II}$ complexes where the presence of amines enhanced the reactivity in relation to the pure phosphine complexes.[10] The system with *fac*-[RuCl$_2$(S-DMSO)$_3$(O-DMSO)] is versatile, as it does not require operating conditions with extreme absence of humidity and O$_2$.

## Acknowledgments

## Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br, as PDF file.

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