

Study of initiation mechanism of the polymerization of vinyl monomers catalyzed by cyclometalated ruthenium(II) complexes.

Maria-Ortencia González^{1*}, L. Alexandrova¹, R. Le Lagadec²,

^{1*} Departamento de Reología, Instituto de Investigaciones en Materiales, Circuito exterior s/n C.U. Apdo. postal 70-360 Delegación Coyoacán, 04510 México D.F.

² Departamento de Química Inorgánica, Instituto de Química, Circuito exterior s/n C.U. Apdo. postal 70-360 Delegación Coyoacán, 04510 México D.F.

E-mail: matza10@hotmail.com

Atom transfer radical polymerization (ATRP) is one of the most effective methods for precision polymer synthesis in controlled/living radical polymerization. Our research group has developed synthetic routes for the preparation of new cyclometalated-ruthenium(II) complexes, which have been applied successfully in ATRP. For the research of catalytic systems based on cyclometalated-ruthenium(II) complexes it is necessary to study the mechanism of initiation. We performed a series of studies involving the interaction of ruthenium species with a variety of initiators, monomers and additives to different reaction conditions and characterized the obtained products.

Introduction.

ATRP allows to obtain polymers of controlled architecture and molecular weights with narrow polydispersities. The key reaction here is a reversible one-electron redox homolitical halogen abstraction by a transition metal catalyst form a halogen containing initiation, typically an alkyl halide.

Different transition-metal complexes have been applied as catalysts in ATRP [1]. The major success was achieved by copper and ruthenium compounds. Recently, our research group has developed synthetic routes for the preparation of new cyclometalated-ruthenium(II) [2].

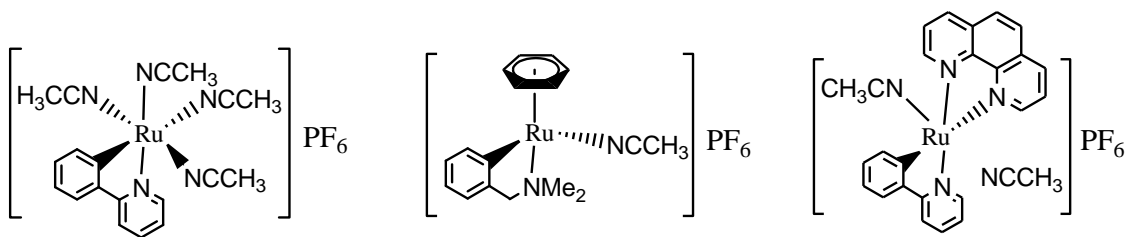


Figure 1. Some cyclometalated ruthenium(II) complexes.

Introduction of the metal-carbon σ -bond makes the complexes more robust and at the same time allows to reduce their redox potential. Some of the complexes demonstrate high lability of the acetonitrile ligands under certain conditions and thus, species with much lower redox potentials have been generated. These complexes have been applied successfully in controlled/living radical polymerization of styrene (St), methyl metacrylate (MMA) and buthyl acrylate (BA) [3]. However in order to develop an initiation system of high activity, understanding the mechanism is a crucial point.

Up to now the initiation mechanism in ATRP process has been studied for copper complexes. This mechanism is not applicable for ruthenium derivatives due to the difference in structure and electronic properties. Thus, we performed a series of studies involving the interaction of cyclometalated ruthenium species with a variety of initiators, monomers and additives at different reaction conditions and characterized the obtained products.

Experimental Section.

Materials. The monomers MMA and St were distilled under reduced pressure and kept under nitrogen, the others reagents and solvents were used as received from Aldrich Chem. Co. The synthesis and characterization of $[\text{Ru}(\text{NCMe})_4(\text{Phpy})]\text{PF}_6$ and $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{NCMe})(\text{dmba})]\text{PF}_6$ catalysts were detailed in the reference [2].

Procedures. We performed a series of studies involving the interaction of cyclometalated ruthenium(II) species with a variety of initiators (CCl_4 and $(\text{CH}_3)_2\text{C}(\text{Br})\text{CO}_2\text{C}_2\text{H}_5$), monomers (St and MMA) and additives ($\text{Al}(\text{OiPr})_3$) at different reaction conditions and characterized the obtained products. The reactions were conducted in solution using the Schlenk techniques at 80°C and at room temperature for 18 h. The resulting solution was evaporated to dryness and the residue purified by column chromatography on neutral Al_2O_3 (CH_2Cl_2 as diluent). The yellow fraction was collected, evaporated under vacuum and analyzed by ^1H -NMR, IR and M/S.

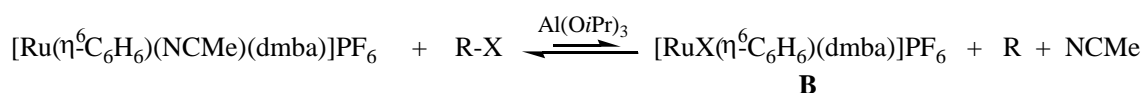
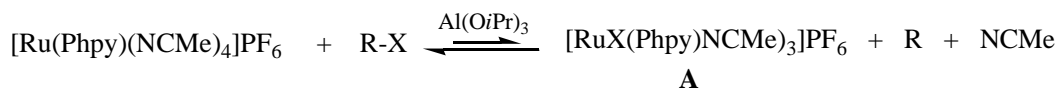
Also, these reactions were also carried out in NMR sealed tubes using as solvents toluene- d_8 and acetone- d_6 (solvents in which the polymerization is carried out) in the NMR equipment to 80°C and 50°C respectively and the reactions were monitored (by ^1H -NMR) every 5 minutes for 3 h.

Finally, the polymerizations reactions were conducted in solution, using the Schlenk technique at 100°C for 6 h. The Ru complexes and the $\text{Al}(\text{OiPr})_3$ were degassed under vacuum and purged with nitrogen. Then the monomer was added and the mixture was

stirred 15 min until a homogeneous solution. Finally the initiator was added to the mixture. After this the Schlenk tube was submerged in an oil bath previously heated to 100°C.

Results and Discussion.

Reactions were carried out hoping to isolate intermediate species A, B, as shown below:



At this first stage of the project, we could not isolate and characterize different products to the promoters, the cyclometalated ruthenium(II) complexes. The organometallic species bearing a Ru-X (ruthenium-halogen) bond is not very stable due to rapid, reversible interchange reaction between active and inactive species, so if this species is formed during the reaction it should be difficult to isolate.

In the reactions that were realized using the RMN equipment, it was noted the formation of the polymer during the reaction.

Based on the general mechanism for ATRP systems that are carrying out a reversible redox process $\text{Ru}^{\text{II}} / \text{Ru}^{\text{III}}$ and the formation of a metal-halide bond as an intermediate specie, the polymerization reactions of St were conducted in solution using a compound $[\text{Ru}(\text{phpy})_2(\text{bpy})]\text{PF}_6$ and a compound with Ru-Cl bond $(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}(\text{dmba})$, which were synthesized using the techniques reported in the literature [4,5].

Tabla 1. Results of the reactions made with $\text{RuCl}(\eta^6\text{-C}_6\text{H}_6)(\text{dmba}) + \text{Al}(\text{OiPr})_3 + \text{R-X} + \text{St}$

Reacción	Conversión (%)	$M_{n\text{Teo}}$	$M_{n\text{GPC}}$	PDI
1	80	16700	18800	1.62
2	78	16600	16900	1.65
3	74	15400	14900	1.40
4	71	14800	14500	1.35

Tabla 2. Dates of $[\text{Ru}(\text{phpy})_2(\text{bpy})]\text{PF}_6 + \text{R-X} + \text{Al}(\text{OiPr})_3 + \text{St}$

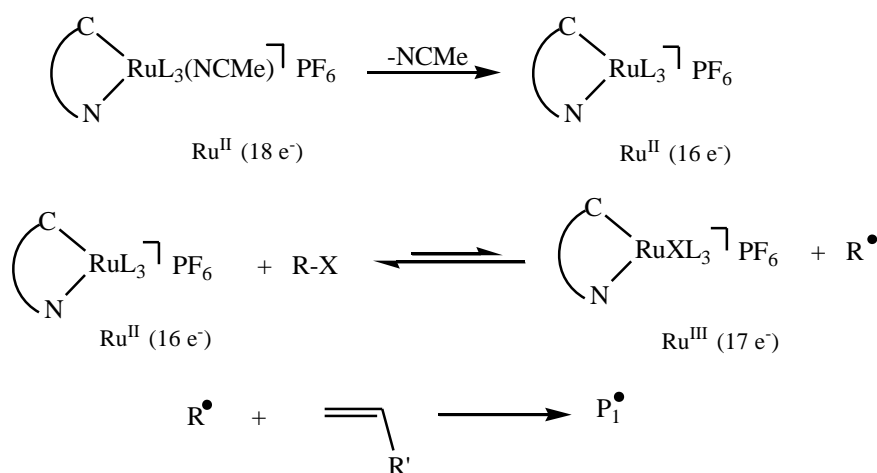
Reacción	Conversión (%)	$M_{n\text{Teo}}$	$M_{n\text{GPC}}$	PDI
1	17	3500	7300	1.21
2	14	2900	5700	1.32
3	11	2200	2100	1.26

With this, we see the role played by the of ruthenium(III) species and the importance of the Ru-Cl bond in the polymerization process.

Conclusions.

Based on the results and discussion we proposed a displacement of a labile ligand, forming a ruthenium(II) species of 16 electrons with a vacant site. Subsequently, the carbon-halogen bond of the initiator (R-X) is activated by the transition-metal complex in the oxidation state II generating a alkyl radical (R[•]) and a metal compound in higher oxidation state (Ru^{III} specie with 17 electrons). The metal center is experiencing a reversible redox reaction via interactions with halogen terminals.

INITIACIÓN



Where $\text{L}_3 = (\text{NCMe})_3, \eta^6\text{-C}_6\text{H}_6$

Figure 2. Proposed mechanism of the initiation of the polymerization catalized by cyclometalated ruthenium(II) complexes .

References.

- 1) K. Matyjaszewski, J. Xia, *Chem. Rev.* **2001**, *101*, 2921.
- 2) a) S. Fernandez, M. Pfeffer, V. Ritleng, C. Sirlin, *Organometallics*, **1999**, *18*, 2390, b) A. Ryabov, R. Le Lagadec, H. Estevez, L. Alexandrova, A. Fisher, M. Pfeffer *Inorg. Chem.* **2005**, *44*, 1626.
- 3) (a) F. Díaz Camacho, R. Le Lagadec, A. D. Ryabov, L. Alexandrova, *J. Pol. Sc. Part A*, **2008**, *46*, 4193 ; (b) F. Diaz Camacho, S. L. Morales, R. Le Lagadec, L. Alexandrova, *Macromol. Symp.* **2006**, *242*, 25.

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- 4) C.L Hendrikus., M. Pfeffer, J. P. Sutter, *Organometallics*, **1993**, 12, 4464.
 - 5) H. Estevez, *Tesis: Síntesis de metalociclos de rutenio (II) y (III) para la bioelectrocatalisis*, UNAM, **2004**, 38.