

**Comparative Study of the Catalytic Activity of the Complexes;
Ru(Cp*)Cl(PAr₃)₂, [Ar = -C₆H₅ (1) and 4-CF₃-C₆H₄ (2)] in the Styrene
Polymerization by ATRP.**

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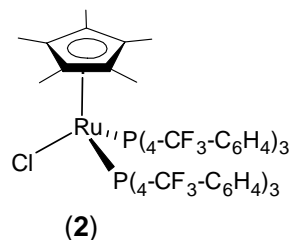
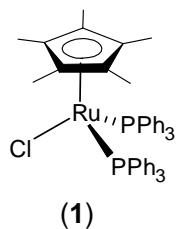
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Abstract: The styrene polymerization by Atom Transfer Radical Polymerization was conducted independently with two iso-structural complexes as catalysts; Ru(Cp*)Cl(PPh₃)₂, (1) and Ru(Cp*)ClP[(4-CF₃-C₆H₄)₃]₂ (2), in order to evaluate the electronic properties of the ligands [triphenylphosphine vs tris(*p*-trifluoromethylphenyl)phosphine] over the rate and the control of the polymerization. The kinetic data for polymerization carried out with catalyst 1 and ethyl 2-bromopropionate as initiator in toluene at 90°C, show that molecular weights grow linearly with conversion with an average initiation efficiency of 0.77 ($f = M_{n(th)} / M_{n(GPC)}$). On the other hand, the molecular weights obtained in the kinetic study with complex 2 as catalyst, grow with conversion but show a marked deviation below the theoretical molecular weights. This behavior was explained by the gradual irreversible oxidation of the catalyst 2 as observed by ³¹P-NMR analysis where the signal assigned to complex 2 gradually disappears as a function of polymerization time.

Catalyst 1 promotes the polymerization with a rate of polymerization (R_p) higher than that obtained with catalyst 2; this is in agreement with the better electron donating properties of PPh₃ versus P(4-CF₃-C₆H₄)₃.

Introduction: Half sandwich organometallic complexes containing transition metal from the eighth group (Fe¹ and Ru²) have demonstrated to be an important group of catalysts in the polymerization of vinyl monomers by ATRP. The reversible oxid-reduction to one electron that these complexes experiment in its catalytic action in the control radical polymerization, promotes the establishment of dynamic equilibrium between active and dormant species, with equilibrium constant ($K_{ATRP} = k_{act}/k_{deact}$) that principally depends on the catalyst nature.³ The ancillary ligands commonly used in these kind of complexes are; η⁵-cyclopentadienyl (Cp), η⁵-pentamethylcyclopentadienyl (Cp*), η⁵-indenyl (Ind) and η⁶-arene. The others ligands that complete the coordination sphere in these complexes are; alkyl and aryl phosphynes, some arsines, and halogen atoms (typically Cl or Br). The catalytic properties of the complexes can be modulated varying the basicity and steric volume of phosphynes.⁴ In this sense, in the present communication we report the comparative study of the catalytic activity of the complexes 1 and 2 in the styrene polymerization by ATP.



Experimental section: Synthesis of complex **1**. We follow the reported method by Heinekey.⁵ In a 100 mL round flask equipped with a Teflon stopcock, complex $[\text{Cp}^*\text{RuCl}_2]_n$ (500 mg, 1.62 mmol) and PPh_3 (4.3 g, 16.3 mmol, 10 equiv.) were charged in dry EtOH (40 mL). The reaction flask was stirred at reflux temperature for 24 h. After that, the powder was filtered through a frit, and the solid washed with EtOH (2 x 5 mL) and Et_2O (3 x 5 mL). Drying under vacuum yielded the product as a yellow powder (1.16 g, 90 % yield). $^1\text{H-NMR}$ (300 MHz, CDCl_3 ; r.t.; δ = ppm): 1.02, (t, $^4J=1.5\text{Hz}$, 15H, Cp^*); 6.9-7.5, (m, 30H, Ar); $^{31}\text{P-NMR}$ (121.4 MHz, CDCl_3 , r.t.): 40.1(s).

Synthesis of complex **2**. In a 100 mL round flask equipped with a Teflon stopcock, complex $[\text{Cp}^*\text{RuCl}]_4$ (202 mg, 0.186 mmol) and $\text{P}(4\text{-CF}_3\text{-C}_6\text{H}_4)_3$ (687 mg, 1.47 mmol, 8 equiv.) were charged in dry THF (10 mL). The reaction flask was stirred at room temperature for 15 minutes, next the powder was filtered through a frit, and the solid washed with THF/pentane (3 x 5 mL). Drying under vacuum yielded the product as a yellow light powder (675 mg, 75 % yield). $^1\text{H-NMR}$ (300 MHz, CD_2Cl_2 , r.t.). 7.2-7.8 (b, 24 H, Ar), 1.02 (s, 15H, Cp^*), $^{13}\text{C-NMR}$ (75.5 MHz, CD_2Cl_2 , r.t.). 142.6 (s b, *Cipso*), 136.9 (s ancho, *Corto*), 127.6 (s b, *Cpara*), 133 (c, $^2J_{\text{C-F}}=33\text{ Hz}$, *Cmeta*), 126 (c, $^1J_{\text{C-F}}=275\text{ Hz}$, CF_3), 92.9(s, Cp^*), 11 (s, Cp^*). $^{31}\text{P-NMR}$ (121.6 MHz, CD_2Cl_2 , r.t.). 42.6 (s).

Styrene homo-polymerization with **1** and **2** as catalysts: A 50 mL Schlenk tube was charged with 4.63 mL (40.2 mmol) of styrene and 1.35 mL of toluene, the tube was fitted with a rubber septum and degassed by three cycles vacuum/argon. Next, 25.7 μL (0.198 mmol) of ethyl-2-bromopropionate (EtBrP) were added via syringe. Five samples of 1 mL of this solution were transferred via syringe into individual Schlenk tubes equipped with a Teflon stopcock, that were previously charged with 13.5 mg (17 μmol) of complex **1** or 20.5 mg (17 μmol) in the case of complex **2**. While maintained under an inert atmosphere, each tube was attached to the vacuum line, “freeze-pump-thaw” degassed once, and sealed under vacuum. The tubes were placed in an oil bath at 90°C. At time intervals, the tubes were removed from the oil bath and cooled with water ice. Afterwards, the individual tubes were opened and about 1 mL of chloroform was added to dissolve the polymer. At this point, the corresponding conversion was determined by $^1\text{H-NMR}$. Afterwards, each polymer solution was precipitated in methanol (100 to 150 mL). The white product was filtered through a frit, washed with methanol and subsequently vacuum-dried overnight. The polymers were analyzed by $^1\text{H-NMR}$ and GPC.

Results and discussion: The kinetic polymerizations of St with **1** or **2** as catalysts, were conducted under the same conditions of concentration and temperature in order to compare the catalytic activity between two complexes. In the figure 1a), we compare the rate of polymerization inferred from the k_p^{app} 's values. The R_p obtained with **1** was higher than that obtained with complex **2**, this result is in agreement with the better electron donating properties of PPh_3 versus $\text{P}(4\text{-CF}_3\text{-C}_6\text{H}_4)_3$ causing that catalyst **1** has higher electron density and is more active than **2**.

With regard to the control obtained in the growth of molecular weights, in the figure 1b), we observe that M_n 's generated with complex **1** grow linearly with monomer conversion and close to the theoretical molecular weights ($M_{n(\text{th})}$), with initiation efficiency of average 0.77 ($f = M_{n(\text{th})} / M_{n(\text{GPC})}$). The IPD's obtained were narrow, (1.10 a 1.11) suggesting a fast interchange between active and dormant species.

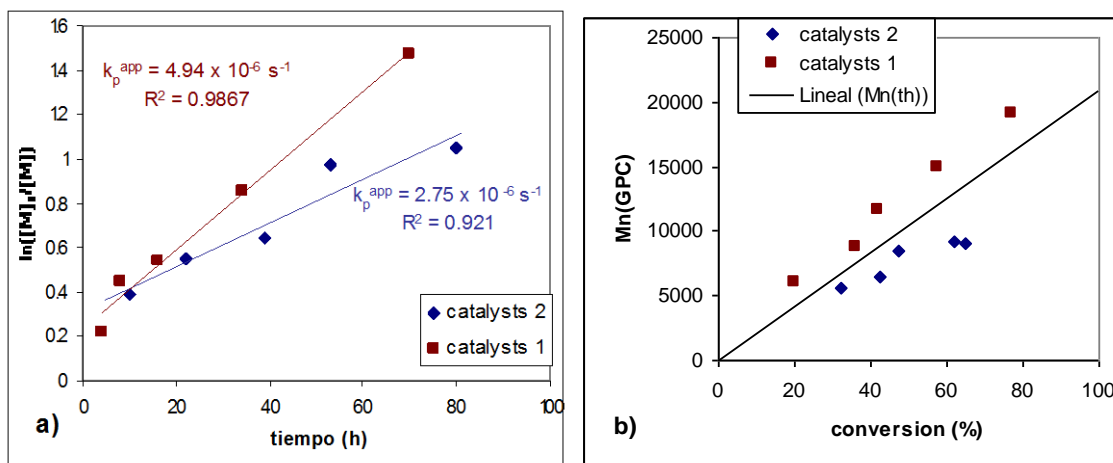


Figure 1. a) Semilogarithmic kinetic plot and b), dependence of M_n upon of monomer conversion for in toluene ATRP of St at 90°C, with complexes **1** and **2** as catalysts. $[St]_0=6.7\text{M}$, $[EtBrP]_0=33\text{mM}$, $[1]_0=[2]_0=17\text{mM}$.

The M_n 's obtained in the kinetics with catalysts **2**, figure 1b), grow with conversion but with a marked deviation below the $M_{n(th)}$'s. This tendency was explained proposing that catalysts **2** undergo the gradually and irreversible oxidation to a Ru(III) complex; $ClBrRu(Cp^*)(P(4-CF_3-C_6H_4)_3)$ (**3**), that is paramagnetic and does not show signal by ^{31}P -NMR, figure 2. The existence of chain transfer (CT) to monomer or to solvent was eliminated as the cause of M_n 's deviation, because their corresponding CT constants are low.⁶

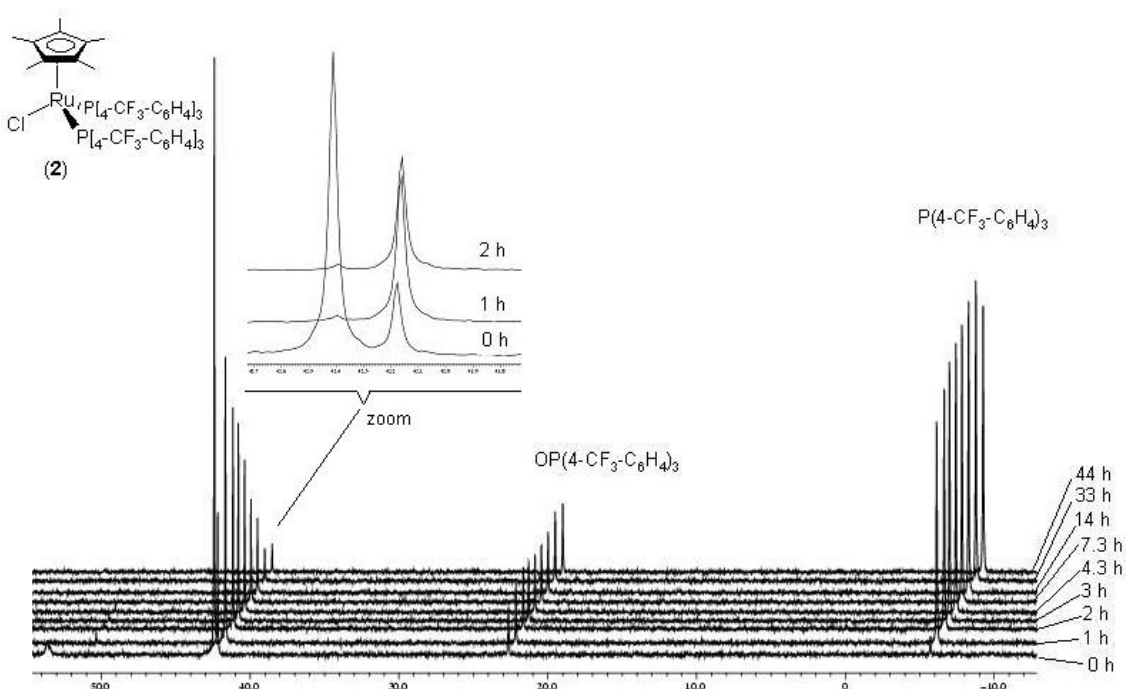


Figure 2. ^{31}P -NMR spectra for in C_6D_6 ATRP of St at 90°C. The kinetic polymerization was conducted in an NMR tube sealed under vacuum. $[St]_0=3.3 \text{ M}$, $[EtBrP]_0=22.7 \text{ mM}$, $[2]_0=8.97 \text{ mM}$. The first spectrum (0 h) was collected before heating.

As it is also observed from figure 2, the signal corresponding to complex **2** gradually disappears generating as only detectable products; free phosphine (signal around -5

ppm) and phosphine oxide (signal at 22.4 ppm), the latter present as contaminant from the beginning of the kinetics.

The IPD's values (1.14 to 1.20) obtained in the kinetics with complex **2** were wide compared with those obtained with complex **1**; this as a consequence of oxidation of catalysts **2** during the polymerization.

The zoom region in around 42 ppm, figure 2, shows the presence of two signals. One of them corresponds to complex **2** (42.4 ppm), and the other one (42.2 ppm) was assigned to the new complex $\text{Ru}(\text{Cp}^*)\text{Cl}(\eta^2\text{-CH}_2=\text{CHPh})(\text{P}(4\text{-CF}_3\text{-C}_6\text{H}_4)_3)$ (**4**), where one equivalent of styrene has replaced one of $\text{P}(4\text{-CF}_3\text{-C}_6\text{H}_4)_3$ in the complex **2**.

Conclusions: We found that catalyst **1** was more active than catalyst **2** in the ATRP of styrene under the same polymerization condition, this as a consequence of the better electron donating properties of PPh_3 compared to $\text{P}(4\text{-CF}_3\text{-C}_6\text{H}_4)_3$. In the case of polymerization conducted with complex **2** it suffers gradual irreversible oxidation that provokes lost in the control of polymerization.

Acknowledges: The authors thanks the financial support from CIQA (F70632). Villa Hernández also thanks to CIQA for his graduate studies fellowship.

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