

Polymerization of Styrene and Methyl Methacrylate Mediated by Ruthenium(II) and Osmium(II) Cyclometalated Complexes with Bidentate Ligands.

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Transition-metal-catalyzed living radical polymerization or ATRP has progressed tremendously since the first reports in 1995¹ and nowadays it is a versatile method for synthesis of well-defined (co)polymer structures.² Various complexes based on different transition metals have been successfully applied for the purpose^{2,3}, but copper compounds occupy a leading position as active and versatile catalysts which are able to mediate polymerizations of many vinyl monomers in a living fashion. The Ru(II) systems are less frequently employed and still not so well developed for this kind of polymerization as compared with those of Cu-based, though the Ru(II) complexes play a prominent role in closely related atom transfer radical addition reactions.⁴ Most of the Ru(II)- complexes used so far for ATRP are neutral compounds which contain phosphine and chloride ligands.⁵ However coordinational chemistry of ruthenium is exceptionally rich and vast variety of Ru(II)-based catalytic systems can be designed by a proper choices of ligand environment that makes Ru-systems very promising candidates for development of new family of ATRP catalysts.

Here we would like to report application and comparative analysis of new series of cyclometalated based on phenylpyridine Ru(II) and Os(II) complexes with bidentate ligands of general formula $[Mt(o-C_6H_4-2-py)(LL)_2]PF_6$, where Mt is Ru or Os, and LL is bipyridine (bpy) and its derivatives or phenanthroline (phen) correspondingly, as catalysts for radical polymerization of styrene (St) and methyl methacrylate (MMA).

The polymerizations were conducted in bulk and solution (anisole 50% v/v) under N₂ at 100°C for St and 60-80° C for (MMA) in the presence of Al(O*i*Pr)₃ and without it using the standard $[M]_0/[In]_0/[Cat]_0 = 200/1/1$ molar ratio. 1-phenylethyl bromide (PEB) and ethyl 2-bromoisobutyrate (EBiB), were used as initiator.

Structures of the complexes are shown in the Figure 1. All the five complexes, **1- 5**, used in the study are coordinatively saturated ionic compounds, have the same number of coordinating atoms (one carbon and five nitrogen atoms) and do not contain chloride or phosphine ligands. The only difference between the ruthenium complexes, **1 – 4**, lies in diimine ligands. When switching from phen (**1**) and bpy (**2**) to

Me₂bpy (**3**) and then to *t*-Bu₂bpy (**4**) the complex becomes slightly bulkier and electronic differences are also introduced.

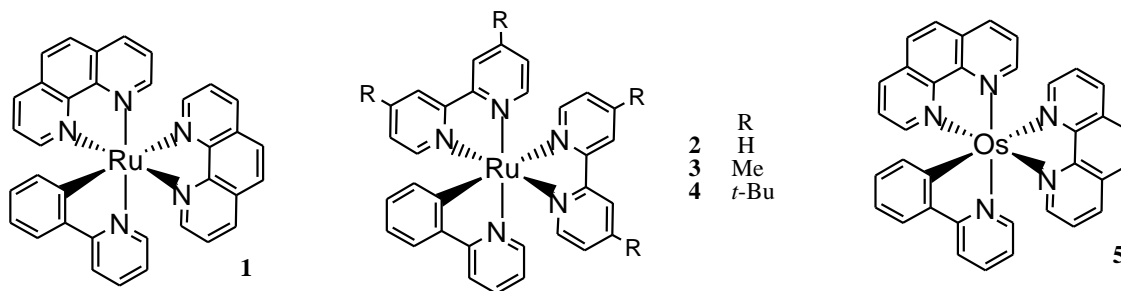


Figure 1. Structures of the complexes.

The Ru^{II}/Ru^{III} reduction potentials of **1** and **2** are equal (543 mV and 540 mV in MeCN vs Ag/AgCl respectively), while the electron-donating groups of the *t*-Bu₂Bpy and Me₂Bpy ligands induced a significant decrease of the redox potentials to 436 and 441 mV (MeCN vs Ag/AgCl) respectively. Though reducing powers of the complexes **3** and **4** with substituted bpy ligands are very similar, *t*-Bu substituent is significantly bulkier. The Os complex **5** is a structural analogue of the Ru complex **1**, but its redox potential is equal to 310 mV (MeCN vs Ag/AgCl). Thus we are able to compare catalytic performance of the complexes of very similar structures depending on their reducing power as well as influence of substituent volume. All the complexes were exceptionally stable in air and can be used in the polymerizations without precautions.

The four Ru compounds turned out to be very active catalysts for polymerization of St.; high conversions were reached in 6 – 10 h depending on the catalyst and reaction conditions (Table 1 and Figure 2). Under the conditions employed activity of the complexes was high enough to mediate the polymerization without any additives, however the use of Al(O^{*i*}Pr)₃ increased the polymerization rate and improved the control over the molecular weights. Comparative analysis of the St polymerizations conducted by complexes **1** and **2** showed that the polymerization mediated by **1**, the complex with two phen ligands, was faster, better controlled and much less affected by the Al additive and the initiator nature than the polymerization mediated by **2**, the complex with two bpy ligands (Table 1).

In order to verify the influence of the reducing power of the catalysts a comparative study of the solution polymerization of St mediated by all four Ru complexes under the same conditions was performed. The results are shown in Figure 2. All complexes demonstrated good catalytic performance: molecular weights grew linearly with conversions and were very close to the calculated values, values of M_w/M_n (PDIs) were satisfactorily narrow. Nevertheless PDIs were notably broader for the polymers

obtained with complexes **3** and **4** with the substituted bpy ligands than for the PSt synthesized with **1** and **2**.

Table 1. Polymerization of St in bulk at 100° C mediated by **1** and **2**.

Cat.	Initiator		Time (h)	Conv (%)	$M_{n, GPC} \times 10^{-3}$	$M_{n, th} \times 10^{-3}$	PDI
1	PEB	<i>a</i>	8	57	8.8	11.8	1.27
		<i>b</i>	6	57	7.4	11.8	1.22
1	EBiB	<i>a</i>	8	60	10.1	12.5	1.36
		<i>b</i>	5	66	14.7	13.7	1.23
2	PEB	<i>a</i>	10	35	11.1	7.3	1.48
		<i>b</i>	8	66	9.7	13.7	1.30
2	EBiB	<i>a</i>	6	34	8.7	7.1	1.47
		<i>b</i>	5	58	10.0	12.0	1.20

a [St]₀: [Ru]₀: [In]₀ = 200:1:1 (without Al(O*i*Pr)₃); *b* [St]₀: [Ru]₀: [In]₀: [Al]₀ = 200:1:1:1.

It is worthy noting that again, as in the case of the bulk polymerization, no correlation between the activity and reducing power of the catalysts was found. Thus rates of polymerizations mediated by **2** and **3** were very similar despite of more than 100 mV lower redox potential of **3**. Meanwhile the polymerization mediated by **4** with the bulkiest ligand was faster than those mediated by **2** and **3** though the redox potentials of **3** and **4** are almost equal. Interestingly that the highest rate together with the best level of control was observed again for the polymerization mediated by **1** and this is regardless of its high redox potential. The complex **1** was able to conduct the St polymerization with good control even at the catalyst initiator ratio = 0.1.

Surprisingly, the Os complex **5**, a very stable compound possessing the lowest redox potential, more than 200 mV lower than that of **1**, was not able to mediate polymerization of St. Only traces of the polymer were detected after 30 h of the reaction in bulk under the standard conditions without Al(O*i*Pr)₃.

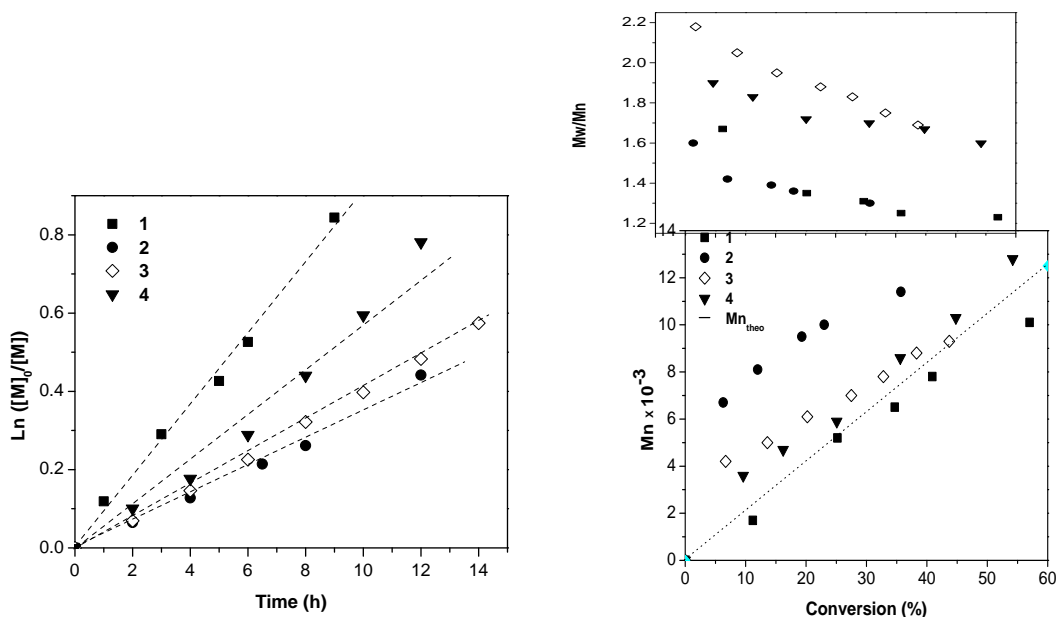


Figure 2. Kinetic plots and evolution of the molecular weights for St polymerization mediated by complexes **1** – **4**.

The complexes **1** and **2** were applied for polymerization of MMA as well. However at 100° C polymerizations of MMA mediated by both of them were very poorly controlled. The level of controlled was significantly improved decreasing the temperature, but the catalysts, particularly **1**, had very limited solubility in MMA and anisole at lower temperatures. The optimal conditions for living polymerization of MMA are under investigation in our group now.

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