

Atom-Transfer Radical Addition Reactions Catalyzed by RuCp* Complexes: A Mechanistic Study

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Abstract: Kinetic and spectroscopic analyses were performed to gain information about the mechanism of atomtransfer radical reactions catalyzed by the complexes [RuCl₂Cp*(PPh₃)] and [RuClCp*(PPh₃)₂] (Cp* = pentamethylcyclopentadienyl), in the presence and in the absence of the reducing agent magnesium. The reactions of styrene with ethyl trichloroacetate, ethyl dichloroacetate, or dichloroacetonitrile were used as test reactions. The results show that for substrates with high in-

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trinsic reactivity, such as ethyl trichloroacetate, the oxidation state of the catalyst in the resting state is +3, and that the reaction is zero-order with respect to the halogenated compound. Furthermore, the kinetic data suggest that the metal catalyst is not directly involved in the rate-limiting step of the reaction.

Introduction

The atom-transfer radical addition (ATRA) of halogenated compounds to olefins represents a versatile C–C coupling reaction with many applications in organic synthesis.^[1] The first investigations about ATRA reactions were performed by Kharasch and his group in the 1940s.^[2] Three decades later it was discovered that [RuCl₂(PPh₃)₃] is able to catalyze this type of reaction.^[3] Meanwhile, many transition-metal complexes are known to promote inter- and intramolecular ATRA reactions.^[1] The highest activities are typically found for copper^[1,4] and ruthenium^[1,5-7] catalysts.

One of the best catalysts described so far is the half-sandwich complex $[RuCl_2Cp^*(PPh_3)]$ (1; $Cp^* = pentamethylcy$ clopentadienyl).^[6,7] Turnover numbers (TONs) of more than1000 have been achieved for different substrate combina-

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tions. An additional advantage from a practical point of view is the fact that complex **1** is not air-sensitive and is easy to make. Complex **1** has been used in combination with either AIBN (AIBN = azobisisobutyronitrile)^[6] or powdered magnesium^[7] as the co-catalyst (Scheme 1). The co-catalyst



Scheme 1. Intra- and intermolecular ATRA reactions of halogenated compounds and olefins are efficiently catalyzed by the ruthenium complex **1** in combination with AIBN or Mg.

is believed to have a twofold role: it activates the Ru^{III} catalyst by reduction to a Ru^{II} complex, and it helps to avoid an accumulation of Ru^{III} complexes due to termination reactions of carbon-centered radicals.

In view of the substantial efforts to optimize the performance of Ru-based ATRA catalysts,^[5-7] it is surprising that there are hardly any mechanistic studies on this process apart from some early kinetic investigations with the firstgeneration catalyst $[RuCl_2(PPh_3)_3]$.^[8] The work reported below aims to fill this gap. We will demonstrate that the

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highly active $[RuCl_2Cp^*(PPh_3)]$ –Mg catalyst system behaves in a markedly different way from the "classical" catalyst $[RuCl_2(PPh_3)_3]$. Furthermore, we will provide evidence that the Ru catalyst is not directly involved in the rate-limiting step of ATRA reactions with highly active substrates such as ethyl trichloroacetate.

Results and Discussion

Our interest in exploring the mechanism of RuCp*-catalyzed ATRA reactions was triggered by the following unusual observation: ethyl dichloroacetate and ethyl trichloroacetate both underwent ATRA reactions with styrene, with the former reacting faster under similar conditions (Scheme 2a and b). However, if both substrates were used in parallel, only the ATRA product of ethyl trichloroacetate was formed, whereas ethyl dichloroacetate was not consumed at all (Scheme 2c).



Scheme 2. Ru-catalyzed ATRA reactions of ethyl trichloroacetate and ethyl dichloroacetate with styrene. The selectivity observed in the competition reaction c) is in contrast to the reactivity of the substrates a) and b).

To explain these results, we first investigated the time course of the reaction of ethyl trichloroacetate and ethyl dichloroacetate with styrene in more detail. The reactions were performed with four different catalyst systems: the Ru^{III} complex **1** (0.5 mol%) in the absence and in the presence of an excess of Mg, and the Ru^{II} complex [RuClCp*-(PPh₃)₂] (**2**, 0.5 mol%) in the absence and in the presence of an excess of Mg (Scheme 3).

The time courses for the 2×4 reactions are shown in Figures 1 and 2. Depicted are the yields of the reactions. The values for the conversion (styrene consumption) are slightly higher, but the differences are below 3%. The reactions



Scheme 3. Reactions of ethyl trichloroacetate and ethyl dichloroacetate with styrene catalyzed by a) the Ru^{II} complex 1 with Mg, b) the Ru^{II} complex 2 with Mg, c) the Ru^{II} complex 2 without Mg, and d) the Ru^{III} complex 1 without Mg.



Figure 1. Reactions of ethyl dichloroacetate with styrene catalyzed by the Ru^{III} complex 1 with Mg (•), by the Ru^{II} complex 2 with Mg (•), by the Ru^{III} complex 2 without Mg (•), and by the Ru^{III} complex 1 without Mg (•). Reaction conditions: [ethyl dichloroacetate]=100 mM, [styrene]= 100 mM, [Ru]=0.5 mM, [Mg]=100 mg (4.1 mmol), toluene (1000 μ L), 35 °C. The data represent averaged values of two independent experiments. The yields were determined by GC using mesitylene as an internal standard.

with ethyl dichloroacetate (Figure 1) were consistently faster than the reactions with ethyl trichloroacetate (Figure 2). This reactivity order is surprising in view of the fact that homolytic C–Cl bond cleavage is easier for the trichloroester. There was no significant difference between reactions catalyzed by 1+Mg or by 2+Mg. Apparently, the catalyst precursors 1 and 2 were rapidly converted to the same active species (see below). Reactions with the Ru^{II} catalyst 2 without the reducing agent Mg were considerably slower. The beneficial effect of Mg was in line with what was observed previously.^[7] When the Ru^{III} complex 1 was used without Mg, no product was detected for reactions with ethyl dichloroacetate. The ATRA of ethyl trichloroacetate, how-



Figure 2. Reactions of ethyl trichloroacetate with styrene catalyzed by the Ru^{III} complex 1 with Mg (\bullet), by the Ru^{II} complex 2 with Mg (\blacktriangle), by the Ru^{II} complex 2 without Mg (\blacksquare), and by the Ru^{III} complex 1 without Mg (*). Reaction conditions: [ethyl trichloroacetate]=100 mm, [styrene]=100 mм, [Ru]=0.5 mм, [Mg]=100 mg (4.1 mmol), toluene (1000 µL), 35 °C. The data represent averaged values of two independent experiments. The yields were determined by GC using mesitylene as an internal standard.

ever, proceeded slowly to give a yield of 1.2% after 40 min. This unexpected catalytic activity, although not very high, continues for long periods of time, affording a yield of 69% after a reaction time of eleven days. Both substrates, that is, styrene and ethyl trichloroacetate, could potentially form radicals by thermal or photochemical activation. These radicals would be able to reduce the Ru^{III} complex 1 and start the ATRA reaction. The following observations suggest that a substrate-induced activation of 1 is not an important contribution under our reaction conditions: a reduction of complex 1 with styryl radicals can be excluded because we would observe ATRA adducts for ethyl trichloroacetate and for ethyl dichloroacetate, which is not the case. The reduction of complex 1 by radicals derived from ethyl trichloroacetate also seems unlikely. The Ru^{II}-catalyzed ATRA of ethyl trichloroacetate and styrene without Mg is not very efficient, and only very low turnover numbers were achieved (Figure 2). The observed yield of 69% (TON=138) with complex 1 could only be explained if we assume a repetitive activation of Ru^{III} complexes by the halogenated substrate. However, we were not able to detect any decomposition of ethyl trichloroacetate in reactions with styrene without Ru (analysis by GC after six days). The homolytic C-Cl bond cleavage of ethyl trichloroacetate thus seems to be negligible under our reaction conditions.

Subsequently, we examined the time course of the reaction of styrene with an equimolar amount of ethyl trichloroacetate and ethyl dichloroacetate. For this experiment we used the Ru^{III} catalyst **1** (0.5 mol%) in conjunction with Mg. There was zero conversion of the dichloroester as long as there was trichloroester in the reaction mixture (see Supporting Information). However, once the trichloroester was completely consumed, the reaction of the dichloroester with styrene started. These results suggested that the trichloroester was able to monopolize the catalyst completely.

To examine whether such effects can also be observed for other substrate combinations, we performed competition experiments of di- and trichloroesters with dichloroacetonitrile. By itself, dichloroacetonitrile was found to be less reactive than ethyl dichloroacetate, but more reactive than ethyl trichloroacetate (see Supporting Information). In competition experiments, dichloroacetonitrile blocked the reaction dichloroacetate with styrene ethyl completely (Scheme 4a). However, when equimolar amounts of ethyl trichloroacetate and dichloroacetonitrile were used, the ATRA reaction of the nitrile was slowed down but not

blocked completely (Scheme 4b; for details see Supporting

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Scheme 4. Ru-catalyzed ATRA competition reactions of ethyl trichloroacetate or ethyl dichloroacetate and dichloroacetonitrile with styrene.

The competition experiments show that ethyl trichloroacetate and dichloroacetonitrile are both able to block the ATRA reaction of ethyl dichloroacetate and styrene. This can be explained by assuming the following scenario: ethyl trichloroacetate and dichloroacetonitrile react rapidly with the catalytically active Ru^{II} complex to give an intermediate, which is then slowly transformed into the product. The catalyst in the resting state, however, is not able to react with ethyl dichloroacetate, prohibiting its conversion.

If the reaction of the Ru catalyst with ethyl trichloroacetate is fast in comparison to the rate-limiting step, then the reaction order with respect to this substrate should be zero. This was confirmed by kinetic experiments with 0.25, 0.50, 1.00, 1.50, or 2.00 equivalents of ethyl trichloroacetate with respect to a fixed amount of styrene, using 0.5 mol% of complex 1 in the presence of Mg. The rates of product formation (and the rates of styrene consumption) were very similar for the five reactions (see Supporting Information). A related behavior was observed for dichloroacetonitrile: when ATRA reactions were performed with variable nitrile concentrations, a constant reaction rate was obtained for dichloroacetonitrile concentrations of 0.1 M or higher (see Supporting Information). However, decreasing the substrate concentration below 0.1 M resulted in a slightly decreased re-

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action rate. The zero-order rate dependence with respect to the chlorinated substrates is in contrast to what was found for the first-generation catalyst $[RuCl_2(PPh_3)_3]$: for addition reactions of CCl_4 to 1-octene, a first-order dependence of the rate on the CCl_4 concentration was observed.^[8]

Reactions with a variable concentration of styrene (12.5, 25, 37.5, 50, or 100 mM) and a fixed amount of ethyl trichloroacetate (100 mM) revealed a linear dependence of the initial reaction rate on the olefin concentration (see Supporting Information). However, for higher styrene concentrations (150 or 200 mM) a deviation from a linear relationship was observed. This saturation behavior could be explained by the increased formation of polymeric side products at high styrene concentrations. Indeed, the plot for the rate of styrene consumption versus initial styrene concentration is linear even at higher styrene concentrations (see Supporting Information).

The influence of the catalyst loading was studied as well. Reactions with 0.125, 0.25, 0.50, 0.75, or 1.00 mol% of complex **1** showed that the reaction rate increased with an apparent reaction order of 1/3 with respect to the Ru concentration. It should be noted that the kinetic analysis is complicated by the fact that the catalyst was a mixture of a soluble Ru complex and the insoluble magnesium powder. A large excess of Mg was used with respect to the Ru catalyst, but the total amount of Mg was still crucial. This was evidenced by control experiments with Ru complex **1** (1 µmol, 1 mol% with respect to styrene) and Mg (0.8 or 4.1 mmol). The latter reaction was approximately twice as fast as the former. This indicated that the reaction rate was controlled by the amount of the homogeneous catalyst *and* the amount of the heterogeneous co-catalyst.

To learn more about the catalyst in the resting state, we performed in situ UV/Vis measurements of reactions catalyzed by the Ru^{II} complex **2** in the absence of Mg. The only colored species in solution were the Ru complexes. Importantly, the spectrum of the Ru^{III} complex **1** was clearly distinguishable from that of the Ru^{II} complex **2**. An oxidation of **2** into **1** can therefore be followed by UV/Vis spectroscopy.^[9] The results of these experiments are shown in Figures 3 and 4.

For reactions between ethyl trichloroacetate, styrene, and 0.5 mol% of complex 2 in toluene, the UV/Vis spectrum recorded after 2 min at room temperature was nearly identical to that of a solution of the pure complex 1 (Figure 3). This suggested that the dominant Ru species in reactions with ethyl trichloroacetate was the Ru^{III} complex 1. This was further substantiated by stoichoimetric reactions of complex 2: upon addition of only ten equivalents of ethyl trichloroacetate, an instantaneous and quantitative oxidation to the Ru^{III} complex **1** occurred, as shown by UV/Vis spectroscopy. In this context, a recent study by Matyjaszewski et al. is of interest. They have shown that complex 2 in conjunction with AIBN is a potent catalyst for atom transfer radical polymerization reactions.^[10] It was postulated that complex 2 is reversibly oxidized to give a 19e⁻ complex of the formula [RuXClCp*(PPh₃)₂] (X=Br, Cl). Our UV/Vis studies sug-



Figure 3. UV/Vis spectra of three different solutions: a toluene solution containing ethyl trichloroacetate, styrene, and complex **2** recorded 2 min after mixing (dotted line); a toluene solution containing styrene, ethyl trichloroacetate, and complex **1** (dashed line); a toluene solution containing styrene and complex **2** (solid line). Concentrations: [ethyl trichloroacetate]=100 mM, [styrene]=100 mM, [Ru]=0.5 mM.



Figure 4. UV/Vis spectra of three different solutions: a toluene solution containing ethyl dichloroacetate, styrene, and complex 2 recorded 2 min after mixing (dotted line); a toluene solution containing styrene, ethyl dichloroacetate, and complex 1 (dashed line); a toluene solution containing styrene and complex 2 (solid line). Concentrations: [ethyl dichloroacetate] = 100 mM, [styrene] = 100 mM, [Ru] = 0.5 mM.

gest that the oxidation product of **2** is more likely to be the $17e^{-}$ complex [RuXClCp*(PPh₃)].

The UV/Vis spectrum of a solution containing ethyl dichloroacetate instead of ethyl trichloroacetate was in agreement with the presence of a mixture of complexes **1** and **2** (Figure 4). Further evidence for a partial oxidation of **2** to **1** was obtained by recording spectra of solutions containing complex **2** and different concentrations of ethyl dichloroacetate. The spectra gradually changed from that of pure **2** to that of complex **1**, with a clear isosbestic point at 411 nm (see Supporting Information). From the UV/Vis spectra it can be concluded that the resting state for Mg-free reactions with ethyl trichloroacetate is the Ru^{III} complex **1**. For ethyl dichloroacetate, on the other hand, we observe a mixture of the Ru^{II} complex **2** and the Ru^{III} complex **1**.

Additional information about the nature of the Ru complexes and possible radical intermediates formed under catalytic conditions was obtained by electron spin resonance (ESR) spectroscopy. For this study only ethyl trichloroacetate was used, as the data suggested that this substrate reacted to a greater extent with complex **2**. Preliminary studies

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RuCp*-catalyzed ATRA of ethyl trichloroacetate to styrene (Scheme 5). In the first step (shown in purple) the Ru^{III}

complex 1 is reduced by Mg to a Ru^{II} complex. We have no

experimental data for the structure of this complex, but the

showed that the room-temperature ESR spectra displayed a broad, non-resolved signal centered at g=2.175, with a line width of ≈ 280 G. In contrast, much better-resolved ESR spectra were observed for frozen solutions. Therefore, we focused on low-temperature

ESR studies performed at 20 K. For comparison, we first recorded the ESR spectrum of the Ru^{III} complex 1. Ethyl trichloroacetate and styrene were added to the solution to imitate the reaction conditions (the substrates were not expected to react with complex 1 to a significant extent). The recorded trace showed a well-resolved three-line spectrum characteristic of a paramagnetic ruthenium d⁵ complex of low spin S = 1/2 with distorted octahedral symmetry (Figure 5, top).^[11] The corresponding g-factor values for the observed peaks were: $g_x =$ 2.501, $g_v = 2.067$, and $g_z = 1.946$. The average g-factor value for Cl₃CCO₂Et k_2 k_2 k_4 k_5 k_5

Scheme 5. Proposed mechanism for the RuCp*-catalyzed ATRA of ethyl trichloroacetate to styrene.

these three peaks, $\langle g \rangle = [g_x^2/3 + g_y^2/3 + g_z^2/3]^{1/2}$, is 2.184, which is also close to the *g*-factor value observed at room temperature for a non-resolved ESR spectrum.

Subsequently, we recorded the ESR spectra of reaction mixtures containing styrene, ethyl trichloroacetate, and the Ru^{II} complex **2**. Two experimental procedures were used: in one case, the sample was allowed to react for 40 min at room temperature, and then the sample was frozen rapidly. Alternatively, the sample was frozen directly after mixing the reagents. In both cases the ESR spectra were very similar to that obtained for complex **1**, indicating that rapid and quantitative oxidation of the Ru^{II} complex **2** had occurred (Figure 5, bottom).

Based on all of the above-mentioned experiments we would like to propose the following mechanism for the



Figure 5. X-band ESR spectra of a frozen toluene solution (20 K) of complex **1** (top) and of a rapidly frozen mixture of complex **2** (1 mM), styrene (200 mM), and ethyl trichloroacetate (200 mM) in toluene (bottom).

 $16e^{-}$ complex [RuClCp*(PPh₃)] (3) seems to be a plausible candidate. It should be noted that previous attempts to make complex 3 on a preparative scale have failed.^[12] However, a structurally related complex with a sterically demanding cyclopentadienyl ligand has recently been characterized crystallographically.^[13] For reactions with the catalyst precursor 2, the active intermediate 3 can be accessed by loss of one phosphine ligand. The Ru^{II} complex 3 starts the main catalytic cycle (Scheme 5, blue) by rapidly reacting with ethyl trichloroacetate to give complex 1 along with the radical 'CCl₂CO₂Et. Chloro-atom transfer reactions of this kind are known to be reversible, but the equilibrium in this case is completely on the side of the Ru^{III} complex $(k_2 \gg$ k_{-2}). The subsequent coupling between 'CCl₂CO₂Et and styrene (k_3) is the rate-limiting step of the reaction. This assumption is supported by the UV/Vis and ESR experiments, which show that complex 1 is the resting state of the reaction. It also explains the observation that ethyl trichloroacetate is able to monopolize the catalyst in competition experiments with ethyl dichloroacetate. The latter substrate is expected to react more slowly with the active Ru^{II} complex 3 because of its lower intrinsic reactivity. In the resting state, on the other hand, the Ru complex 1 is not able to activate ethyl dichloroacetate. The main product of the reaction is formed in a chloro-atom transfer between complex 1 and the benzyl radical. The equilibrium of this reversible reaction is expected to be on the side of Ru^{II} complex ($k_4 >$ k_{-4}).^[9] The following control experiment provided evidence that the last chloro-atom transfer step is not rate-determining: reactions between ethyl dichloroacetate^[14] and styrene were performed with 0.5 mol% of the Ru^{II} complex 2 with-

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out Mg. The reaction rate would be expected to increase with addition of the Ru^{III} complex **1** if step 4 was crucial for the overall rate, but no such increase was observed.

For reactions between ethyl trichloroacetate and styrene, a second catalytic pathway (Scheme 5, red) seems to be operational next to the main catalytic cycle (Scheme 5, blue). This was concluded from the results of reactions with the Ru^{III} catalyst **1** without Mg, which showed a slow but steady formation of the ATRA product (see above). It seems plausible to invoke a Ru^{IV} complex as a catalytic intermediate, but attempts to characterize a catalytically relevant Ru^{IV} species have so far not been successful.

Along with the productive catalytic pathways, there are two reactions which give low but detectable amounts of side products. First, the carbon radical ' CCl_2CO_2Et can undergo a homocoupling to give the dimer (CCl_2CO_2Et)₂ (small amounts were detected by GC–MS). This termination reaction is not as likely for the less stable benzyl radical, but the latter can react with styrene to give oligomers and polymers.

It is expected that a mechanism similar to that described in Scheme 5 is operational for the ATRA reaction of ethyl dichloroacetate and styrene. One important difference is that the equilibrium for the first chloro-atom transfer reaction is not completely on the side of Ru^{III} complex **1** $(k_2 \cong k_{-2})$. Furthermore, the catalytic Ru^{III/IV} pathway (Scheme 5, shown in red) is not relevant for ethyl dichloroacetate, presumably because of the lower oxidizing power of this substrate compared to ethyl trichloroacetate.

Conclusion

Kinetic and spectroscopic analysis have been performed to gain information about the mechanism of atom-transfer radical reactions (ATRA) catalyzed by the complexes [RuCl₂Cp*(PPh₃)] and [RuClCp*(PPh₃)₂] in the presence and in the absence of the reducing agent magnesium. The ATRA reactions of styrene with ethyl trichloroacetate, ethyl dichloroacetate, or dichloroacetonitrile were used as test reactions. The results show that for substrates with high intrinsic reactivity such as ethyl trichloroacetate or dichloroacetonitrile, the oxidation state of the catalyst in the resting state is +3, and that the reaction is zero-order with respect to the halogenated compound. This is in contrast to what is observed for less active catalysts such as [RuCl₂(PPh₃)₃], which show a first-order dependence of the reaction rate on the chlorinated substrate. Furthermore, the kinetic data suggest that the metal catalyst is not directly involved in the ratelimiting step of the reaction. An important consequence of this finding is that it will not be possible to make a faster catalyst for the ATRA reaction of ethyl trichloroacetate or dichloroacetonitrile and styrene, at least under reaction conditions similar to those described above. This should not imply that it is not worthwhile to search for better ATRA catalysts. First of all, for substrates with a lower intrinsic reactivity (more stable carbon-halogen bonds), the first chloro-atom transfer step may easily become rate-limiting. In this case, the nature of the catalyst will be important. Secondly, a better catalyst could also be a more stable catalyst, which gives rise to higher turnover numbers, or a more selective catalyst, which gives low amounts of side products. However, the fact that the rate-limiting step of ATRA reactions can be metal-independent should be considered for future studies, even more so as it is common practice to test new catalysts with intrinsically active substrates such as CCl_4 .^[5]

Another interesting finding of our study is the observation that a Ru^{III} complex such as **1** can be catalytically active without prior reduction. In this case, the ATRA reactions could be mediated by a Ru^{III}/Ru^{IV} redox couple, but further investigations are needed to verify this point. Under normal reaction conditions, the contribution of this second catalytic cycle is expected to be small. However, it is conceivable that other Ru^{III} or Os^{III} complexes will display a higher propensity to catalyze ATRA reactions through this alternative pathway. Investigations along these lines are currently being performed in our laboratory.

Experimental Section

General: The complexes $[RuCl_2Cp^*(PPh_3)]$ (1)^[15] and $[RuClCp^*(PPh_3)_2]$ (2)^[16] were prepared according to literature procedures. Mg powder (>99%) was purchased from Fluka, and was agitated by means of a stirring bar under an atmosphere of dry dinitrogen for 10 days before use. All ATRA reactions were performed in a glove box under an atmosphere of dinitrogen. The solvents and the commercially available substrates were distilled from appropriate drying agents and stored under nitrogen. GC measurements were made on a Varian Chrompack CP-3380 apparatus (Chrompack CP-SIL8CB column; 30 m; 250 µm) coupled to a FID detector. UV/Vis measurements were made on a Perkin–Elmer Lambda 40 UV/Vis spectrometer.

General procedure for the ATRA of chlorinated esters or of dichloroacetonitrile to styrene: Complex 1 or 2 (400 μ L of a 1.25 mM stock solution in toluene) was added to a 1.5 mL vial that contained Mg (100 mg; if Mg was used for the reaction). The total volume was increased to 900 μ L with toluene and the resulting mixture was stirred at 35 °C for 10 min. The reaction was then initiated by addition of a freshly prepared stock solution containing styrene, the chlorinated compound, and mesitylene as an internal standard (100 μ L; final concentrations: [styrene]=100 mM; [chlorinated compound]=100 mM; [internal standard]=10 mM). The solution was stirred at 35 °C and samples (25 μ L) were removed at given times from the reaction mixtures, diluted with non-deoxygenated acetone (500 μ L), and analyzed by GC.

UV/Vis measurements: Samples (450 $\mu L)$ of the corresponding reaction mixtures were removed two minutes after adding the substrate and were transferred to a quartz cuvette of 0.5 mm thickness, which was tightly closed. The UV/Vis spectra of the reaction mixtures were recorded and compared with standards of complexes 1 and 2 of the same Ru concentration.

ESR measurements: The ESR spectra were recorded at low temperature (20 K) using an ESR spectrometer, Model E540 EleXys (Bruker BioSpin GmbH, Karlsruhe, Germany), operating in the microwave X-band, equipped with a cylindrical TE₀₁₁ high-Q cavity, model ER 4122SHQE, and a continuous-flow helium cryostat, Model ESR900, from Oxford Instruments (Abington, UK). The Instrumental settings of Bruker EleXys spectrometer were: microwave frequency: \approx 9.402 GHz; microwave power: 0.2 mW; scan time: 336 s; modulation frequency: 100 kHz; modulation amplitude: 5 G; time constant: 20.5 ms; gain: 50 dB; single scan of 2000 G. Samples (800 µL) of the corresponding reaction mixtures were

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removed immediately after thorough mixing of the reagents, and the solutions were transferred into 4 mm OD/3.0 mm ID quartz ESR tubes, from Wilmad–Labglass (Buena, NJ, USA). The samples were quenched in liquid nitrogen and stored at 77 K. To acquire the ESR spectra, the samples were transferred quickly to the precooled cavity of the ESR spectrometer (\approx 50 K). Alternatively, the solutions were transferred into 2.4 mm OD/2.0 mm ID quartz capillary tubes, which were subsequently put into the 4 mm OD/3.0 mm ID quartz ESR tube before freezing.

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