Notes

Haloalkane C−X Bond Activation by a Ruthenium(II) Complex: X-ray Characterization of a Ruthenium(III) Intermediate Species in the Atom Transfer Radical Polymerization of Methyl Methacrylate

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*Summary: The binuclear Ru(II) N_2-bridged complex [{$RuCl_2$(NN′N)}$_2$(μ-N_2)] (**1**; NN′N = 2,6-bis[(dimethylamino)methyl]pyridine) promotes the atom transfer radical polymerization (ATRP) of methyl methacrylate under mild conditions. The intermediate paramagnetic Ru(III) species mer-[$RuCl_3$(NN′N)] (**2**) has been isolated and characterized by X-ray diffraction methods. The reaction of **1** with CH_2Cl_2 gives the dichloromethyl Ru(II) complex [RuCl($CHCl_2$)(NN′N)] (**3**).*

Introduction

Mononuclear Ru(II) complexes are known to be good catalyst precursors for the addition of poly(haloalkanes) to olefins.[1−3] Ruthenium-catalyzed inter- or intramolecular processes of this type have allowed the synthesis of many natural products with important biological activity.[2] When this reaction is carried out in a stoichiometric manner, it leads to 1:1 adduct formation (the Kharasch reaction).[1] In contrast, when an excess of alkene is used, a polymerization reaction can take place.[3] According to detailed mechanistic studies of these so-called atom transfer radical polymerization (ATRP) reactions, the key step involves the formation of a transient radical intermediate and a more stable (persistent) radical, i.e., a Ru(III) complex.[4] It has been proposed that the reactive radical is confined within the coordination sphere of the Ru(III) species.[4a,b,d] However, the characterization of the persistent radical species, either in solution or in the solid state, has proven to be difficult and, as far as we are aware, no solid-state structures of such species have been determined previously.[3,4]

In a recent study, we have described the synthesis and structural characterization of neutral and cationic ruthenium(II) complexes which contain the terdentate ligand 2,6-bis[(dimethylamino)methyl]pyridine (NN′N).[5] These complexes have been shown to be good catalyst precursors for the cycloalkylation of aromatic amines with diols,[6] as well as for the ring-opening metathesis polymerization of norbornene derivatives.[7]

We report herein the use of the binuclear ruthenium(II) N_2-bridged complex [{$RuCl_2$(η^3-NN′N)}$_2$(μ-N_2)] (**1**; Scheme 1)[5] as promoter for the polymerization of methyl methacrylate.

Results and Discussion

Complex **1** promotes the radical polymerization of methyl methacrylate (MMA) in the presence of CCl_4. The polydispersity indexes of the polymers so obtained

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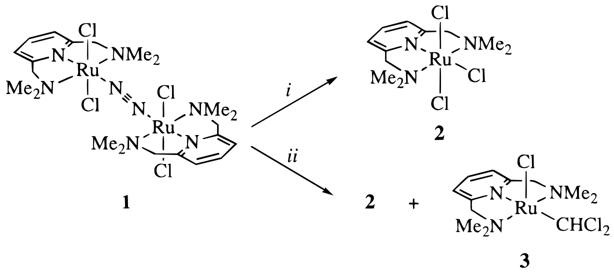
Scheme 1[a]



[a] Legend: (*i*) CCl_4, room temperature, 30 min; (*ii*) CH_2Cl_2, reflux temperature, 24 h.

range between 1.41 and 1.63. These values are in accordance with previously reported results for reactions following ATRP-type mechanisms.[3] The ruthenium(III) derivative *mer*-[$RuCl_3$(NN′N)] (**2**) precipitates in the course of the polymerization process. The precipitation of **2** is accompanied by a decrease in the polymerization activity, resulting in activities and conversions for our system being lower in comparison with those of other ATRP catalysts previously reported.[3]

To increase our knowledge about our catalytic system, the reaction of **1** with CCl_4 was carried out. Treatment of compound **1** with an excess of CCl_4 at room temperature results in the formation of an orange precipitate, subsequently identified as *mer*-[$RuCl_3$(NN′N)] (**2**; Scheme 1), and a colorless solution. GC-MS analysis of this solution shows the formation of C_2Cl_6 as the only detected new organic product. The formation of C_2Cl_6, which presumably arises from the coupling of two $CCl_3^•$ radical fragments, has been observed previously in this type of process.[4b] Compound **2** was found to be quite insoluble in common organic solvents, being only slightly soluble in CH_2Cl_2. The ^1H NMR spectrum of **2** (CD_2Cl_2) does not show any of the characteristic peaks associated with the benzylic protons and with the methyl groups of the terdentate ligand, pointing to the presence of paramagnetic species.

Crystals suitable for an X-ray crystal structure determination were grown from a solution of this complex in CH_2Cl_2/benzene. A molecular plot is depicted in Figure 1, with a selection of bond lengths and angles listed in the figure caption. The Ru atom is hexacoordinated in a distorted-octahedral ligand environment, with the three N-donor fragments in a meridional configuration. The molecule possesses no mirror planes, because of the nonplanarity of the NN′N ligand. Additionally, there is an interplanar angle of 14.0(3)° between the pyridine ring and the N(1)−Ru−N(3) plane, which also breaks the mirror symmetry. Bond lengths and angles are typical when compared with those of related structures.[5,8] Full structural details can be found in the Supporting Information.

All these data suggest that, in the MMA polymerization process, complex **1** reacts with CCl_4 to give two radicals, $CCl_3^•$ and complex **2** (Scheme 2, eq 1). The reaction of $CCl_3^•$ with MMA gives a radical monomer which subsequently adds MMA to give the radical polymeric chains **P**$^•$ (Scheme 2, eq 2). As the coupling of two such radical polymers would result in a neutral

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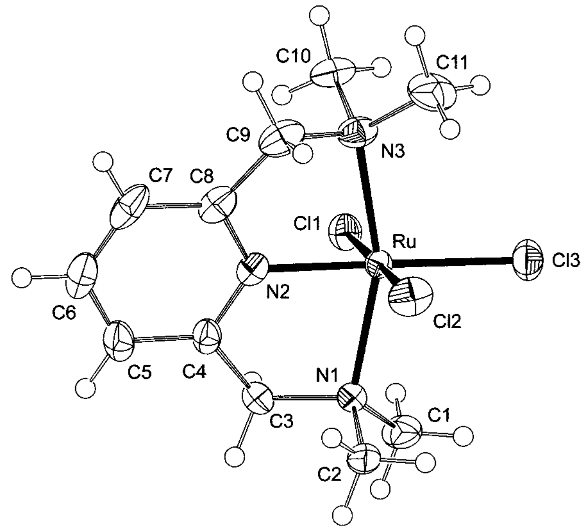
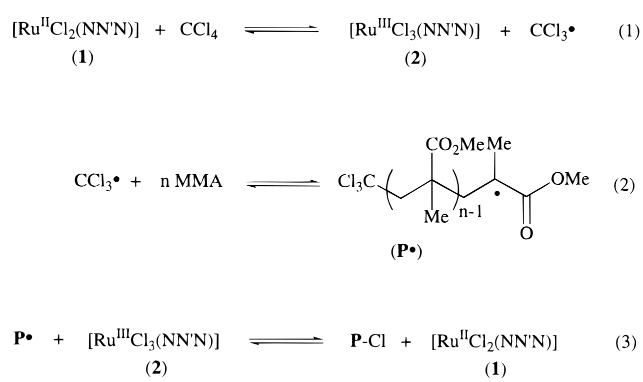


Figure 1. Molecular structure of compound **2**. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å), angles (deg), and torsion angles (deg): Ru−Cl(1) = 2.3614(9), Ru−Cl(2) = 2.3727(10), Ru−Cl(3) = 2.3673(11), Ru−N(1) = 2.175(3), Ru−N(2) = 1.991(3), Ru−N(3) = 2.175(3); Cl(1)−Ru−Cl(2) = 179.35(4), Cl(2)−Ru−Cl(3) = 90.68(4), Cl(1)−Ru−N(1) = 86.09(8), Cl(1)−Ru−N(3) = 93.10(9), Cl(2)−Ru−N(1) = 93.64(8), Cl(2)−Ru−N(3) = 86.95(9), Cl(3)−Ru−N(2) = 178.96(9); N(1)−C(3)−C(4)−N(2) = 28.2(4), N(2)−C(8)−C(9)−N(3) = 28.2(5).

Scheme 2



polymeric molecule, this would reduce the number of radicals in solution and the polymerization activity. A way to create new radicals would be by regenerating complex **1** from **2**. This would occur by coupling of a radical polymer **P**$^•$ with **2** (Scheme 2, eq 3). The fact that complex **2** precipitates suggests that the process shown in eq 3 is quite inefficient, and this explains why the precipitation of **2** is accompanied by a decrease of the polymerization activity.

Previously reported, detailed mechanistic studies of this type of polymerization reaction confirm its radical nature and eliminate the possibility of a mechanism involving oxidative addition of CCl_4 to the Ru(II) complex.[4b] Similar polymerization reactions of MMA using [$RuCl_2(PPh_3)_3$] as catalyst precursor have been recently reported by Sawamoto and co-workers,[3] although, in this case, the presence of methylbis(2,6-di-*tert*-butylphenoxide)aluminum, $MeAl(ODBP)_2$, was found to be necessary for the polymerization reaction to take place.[3a]

Compound **2** could also be obtained by treatment of **1** with different chlorinated solvents, e.g., $CHCl_3$, CH_2Cl_2, and CH_2ClCH_2Cl. When $CHCl_3$ and CH_2ClCH_2Cl are used, the only detected ruthenium-containing complex is **2**. In contrast, when **1** is refluxed for 24 h in CH_2Cl_2, the formation of **2**, together with a new 16-electron Ru(II) derivative, i.e., [RuCl($CHCl_2$)(NN′N)] (**3**; Scheme 1), is observed. The ^{1}H NMR spectrum of **3** shows the resonances of the diastereotopic CH_2 and NMe_2 groups of the terdentate ligand as doublets (δ 5.35 and 3.47) and singlets (δ 2.72 and 2.58), respectively, suggesting the absence of a molecular symmetry plane as well as rigid Ru−N coordination of both amine substituents. The hydrogen atom of the haloalkane fragment appears as a singlet at δ 6.95, while the C atom of this fragment appears at δ 90.8. These NMR data are in accordance with those reported previously for similar dichloromethyl complexes of rhodium[9] and, together with the data obtained from APT and HETCOR experiments on **3**, strongly support the structure proposed for **3** in Scheme 1. Complex **3** appeared to be stable in $CHCl_3$ or CH_2Cl_2 solutions at room temperature for several hours. The formation of unsaturated 16-electron complexes of Ru containing pincer ligands is not rare and has been observed previously.[5,8a,10] However, other structural possibilities, such as the formation of dimeric species, are also possible and cannot be discarded, since FAB-MS investigations did not allow us to clearly distinguish between these two options. Coordination of CH_2Cl_2 to Ru centers[11] and similar reactions involving the activation of C−Cl bonds of CH_2Cl_2 by Ru complexes have been reported.[12]

Conclusions

The present work contributes to knowledge on the catalytic pathway of ruthenium-promoted ATRP-type processes, confirming the intermediacy of a persistent radical in these reactions (a Ru(III) species). This result corroborates earlier mechanistic studies on ATRP processes,[3,4] although it cannot exclude the intermediacy of additional active species during the polymerization process.

Experimental Section

General Considerations. Solvents were dried over sodium benzophenone ketyl (Et_2O, THF, hydrocarbons) or CaH_2 (CH_2Cl_2, $ClCH_2CH_2Cl$, $CHCl_3$) and distilled under a nitrogen atmosphere prior to use. Unless otherwise stated, the reactions were performed under an atmosphere of nitrogen at room temperature. All reagents were obtained from commercial sources and were used without further purification. Complex **1** was prepared as described previously.[5] ^{1}H (200.133 and 300.103 MHz) and $^{13}C\{^1H\}$ (50.323 and 75.453 MHz) NMR spectra were recorded at room temperature with either a Bruker AC-200 or a AC-300 instrument, using $SiMe_4$ as internal standard (δ_H or δ_C 0.00). Fast atom bombardment mass spectra (FAB-MS) were obtained from the Analytical Chemical Department of Utrecht University on two different machines: (1) a JEOL JMS SX/SX 102A four-sector mass spectrometer, operated at 10 kV accelerating voltage and equipped with a JEOL MS-FAB 10 D FAB gun operated at a 5 mA emission current, producing a beam of 6 keV of xenon atoms and (2) a JEOL JMS AX 505 spectrometer, operated at 3 kV accelerating voltage and equipped with a JEOL MS-FAB 10 D FAB gun operated at a 10 mA emission current, producing a beam of 6 keV of xenon atoms. Nitrobenzyl alcohol was used as matrix. Data acquisition and processing were accomplished using JEOL Complement software. Microanalyses were obtained from H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, (Germany).

Synthesis of 2. A solution of **1** in CCl_4 was stirred at room temperature for 30 min, resulting in the formation of an orange precipitate. The solid was collected and washed with diethyl ether (2 × 10 mL) to give **2** as an orange solid (90% isolated yield). Anal. Calcd for $C_{11}H_{19}Cl_3N_3Ru$: C, 32.97; H, 4.78; N, 10.49. Found: C, 33.11; H, 4.97; N, 10.33.

Synthesis of 3. Complex **1** was stirred in CH_2Cl_2 at reflux temperature for 24 h, where upon the color of the solution changed from orange to red and an orange solid precipitated. The solid was filtered off and subsequently identified as complex **2** (70% isolated yield). The remaining solution was evaporated to dryness and the solid residue washed with pentane (2 × 10 mL) to afford **3** as an orange solid (20% isolated yield). *^{1}H NMR data* (300.113 MHz, CD_2Cl_2; δ): 2.58 (s, 6 H, NMe_2), 2.72 (s, 6 H, NMe_2), 3.47 (d, J = 15.0 Hz, 2 H, CH_2), 5.35 (d, J = 15.0 Hz, 2 H, CH_2), 7.64 (d, J = 8.2 Hz, 2 H, Ar H), 8.04 (t, J = 8.2 Hz, 1 H, Ar H), NN′N ligand; 6.95 (s, 1 H, CHCl$_2$) ppm. *$^{13}C\{^1H\}$ NMR data* (75.453 MHz, CD_2Cl_2; δ): 51.3 (NMe_2), 54.5 (NMe_2), 74.0 (CH$_2$), 120.9 (m-C), 139.0 (p-C), 159.2 (o-C), NN′N ligand; 90.8 (CHCl$_2$) ppm. Anal. Calcd for $C_{12}H_{20}Cl_3N_3Ru$: C, 34.83; H, 4.87; N, 10.16. Found: C, 34.64; H, 4.81; N, 10.03.

Polymerization Reactions. A typical polymerization reaction proceeds as follows: 100 mg (0.132 mmol) of **1** and 10 mL (93 mmol) of methyl methacrylate were dissolved in 100 mL of benzene, and 50 μL (0.528 mmol) of CCl_4 was added. The mixture was stirred at reflux temperature for 1 h. The brownish gel formed was poured into vigorously stirred methanol to give a brown precipitate. The MeOH-soluble fraction contains unreacted monomer as well as soluble low-molecular-weight oligomers. The solid was redissolved in THF, the solution was filtered, and precipitation was induced with methanol to give a white solid. This solid was dried under reduced pressure to afford 3.0 g (32%) of PMMA (conversion based on isolated polymer). The polymers were analyzed by GPC using THF as a solvent and polystyrene standards. TON (mol of monomer converted × (mol catalyst)$^{-1}$): 227−311. Molecular weight distributions (M_n; monomodal): 6700−10 100. Polydispersity indexes (PDI = M_w/M_n): 1.41−1.63.

Crystal and Refinement Data for 2. A red crystal (0.58 × 0.25 × 0.03 mm^3) obtained by layering hexane on a solution of the complex in dichloromethane/benzene was used for the X-ray diffraction study. Crystal data: formula $C_{11}H_{19}Cl_3N_3Ru$; M_w = 400.71; a = 7.002(2) Å, b = 15.3892(18) Å, c = 14.322(4) Å; β = 105.975(17)°; V = 1483.7(6) Å^3; monoclinic, space group $P2_1/c$, Z = 4; temperature 150 K; Enraf-Nonius CAD4T diffractometer with rotating anode (Mo Kα, λ = 0.710 73 Å); $\omega/2\theta$ scans; 11 471 measured reflections, 3395 unique reflections; 163 parameters; R1(F, observed reflections) = 0.0341; wR2(F^2, all reflections) = 0.0762; structure solution

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with Patterson methods (DIRDIF-97);[13] structure refinement with SHELXL-97[14] against F^2. Non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were refined as rigid groups. Structure graphics, checking for higher symmetry and absorption correction (DELABS, 0.56−0.86 transmission range), were performed with the program PLATON.[15]

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Supporting Information Available: Tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and H atom coordinates for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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