DOI: 10.1002/adsc.200505318

A Bimetallic Ruthenium Complex as a Catalyst Precursor for the Atom Transfer Radical Polymerization of Methacrylates at Ambient Temperature

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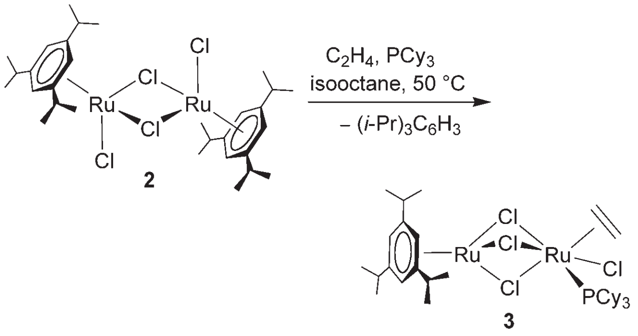
Received: August 12, 2005; Accepted: December 22, 2005

Abstract: The bimetallic ruthenium complex [(1,3,5-*i*-$Pr_3C_6H_3$)Ru(μ-Cl)$_3$RuCl(C_2H_4)(PCy_3)] has been synthesized by reaction of [(1,3,5-*i*-$Pr_3C_6H_3$)$RuCl_2$)]$_2$ with one equivalent of PCy_3 in the presence of ethylene. It can be used as a catalyst precursor for the controlled atom transfer radical polymerization of methacrylates at 35 °C. The resulting polymers show low polydispersities.

Keywords: acrylates; bimetallic complex; polymerization; radical reaction; ruthenium

Starting with seminal publications in the mid 1990s,[1] transition metal-catalyzed atom transfer radical polymerizations (ATRP) have become ubiquitous in modern macromolecular chemistry.[2] For most applications, Cu(I) complexes with amine-based ligands are used as the catalysts.[3] Nevertheless, there are a number of other transition metals which are known to catalyze ATRP reactions.[2] Among those, ruthenium complexes are of special interest because some of them were found to display very high activities.[4,5]

In continuation of our efforts to develop new catalysts for ruthenium-catalyzed radical reactions,[5a,6] we have recently described the homobimetallic complex [(cymene)Ru(μ-Cl)$_3$RuCl(C_2H_4)(PCy_3)] (**1**).[7] This complex shows an outstanding catalytic activity in atom transfer radical addition (ATRA) reactions. Since ATRP and ATRA are mechanistically closely related,[2] we were interested to see whether complex **1** can also be used for the controlled polymerization of acrylates. Unfortunately, complex **1** showed a very limited solubility in the monomer-toluene starting mixtures. We therefore investigated possibilities to increase the solubility of complex **1**. A modification of the π-ligand appeared to be a suitable strategy because the catalytically relevant $RuCl_2(C_2H_4)(PCy_3)$ fragment would not be directly affected. Consequently, the well-soluble dimer [(1,3,5-*i*-$Pr_3C_6H_3$)$RuCl_2$]$_2$ (**2**)[8] was chosen as the starting material. When a solution of complex **2** in isooctane was heated to 50 °C with one equivalent of PCy_3 in the presence of an atmosphere of ethylene, the desired bimetallic complex **3** was formed (Scheme 1). The product precipitates from solution and can be isolated by filtration (yield: 90%).



Scheme 1. Synthesis of the bimetallic complex **3**.

The new complex was comprehensively characterized by ^1H and ^{13}C NMR spectroscopy, elemental analysis and single-crystal X-ray crystallography. The ^{13}C NMR spectrum of **3** in CD_2Cl_2 showed two signals of equal intensity for the methyl groups of the *i*-$Pr_3C_6H_3$ π-ligand. This can be explained by the fact that complex **3** is chiral and configurationally stable on the NMR time scale. The methyl groups are thus diastereotopic. In the ^1H NMR spectrum, however, the difference between the two CH_3 groups was not resolved and only one doublet was observed at $\delta = 1.39$ ppm. In order to avoid partial dissociation of the labile ethylene ligand, all spectra were recorded under an atmosphere of C_2H_4.

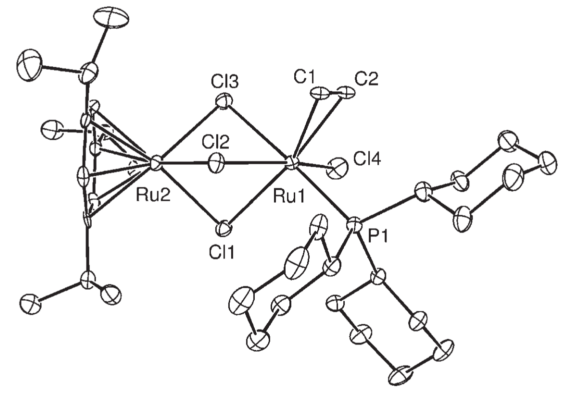


Figure 1. ORTEP[11] representation of the molecular structure of **3** in the crystal. The hydrogen atoms are not shown for clarity. Selected bond length [Å] and angles [°]: Ru1–Cl1 2.5349(9), Ru1–Cl2 2.4630(10), Ru1–Cl3 2.5322(9), Ru1–P1 2.3192(9), Ru1–Cl4 2.3892(10), Ru1–C1 2.218(3), Ru1–C2 2.166(3), C1–C2 1.367(5), Ru2–Cl1 2.4409(9), Ru2–Cl2 2.4178(8), Ru2–Cl3 2.4397(9); P1–Ru1–Cl3 177.22(3), P1–Ru1–Cl4 89.50(3), P1–Ru1–Cl1 99.16(3).

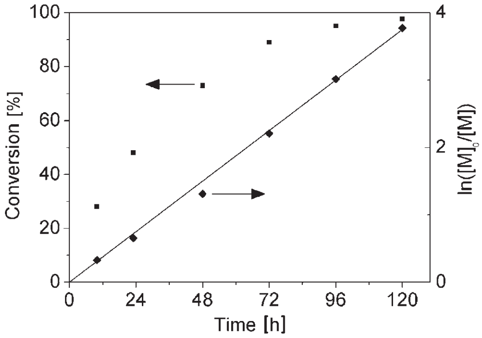


Figure 2. Time dependence of the conversion and of $\ln([M]_0/[M])$ for the living radical polymerizations of MMA with catalyst **3**. The reactions were performed in toluene at 35 °C with a catalyst/initiator/MMA ratio of 1:2:800.

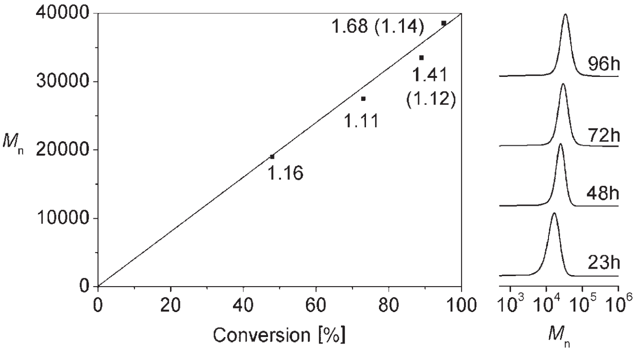


Figure 3. The molecular weights and the molecular weight distributions of the PMMA polymers. Reaction conditions: **3**/initiator/MMA = 1:2:800, toluene, 35 °C.

Analysis of complex **3** by X-ray crystallography confirmed the expected dinuclear structure with three chloro bridges (Figure 1).[9,10] Overall, the structure is similar to what was observed for the (cymene)Ru complex **1**.[7] The Ru–Cl bond lengths of the bridging chloro ligands (2.42–2.53 Å) are larger than the Ru–Cl bond distance found for the terminal chloro ligand [Ru1–Cl4 = 2.3892(10) Å]. The bond distances between the ethylene carbon atoms and the ruthenium atom [Ru1–C1 = 2.218(3), Ru1–C2 = 2.166(3) Å] as well as the carbon-carbon distance of the coordinated olefin [C1–C2 = 1.367(5) Å] are within the expected range.

To evaluate the ability of complex **3** to catalyze ATRP reactions, we first investigated the polymerization of methyl methacrylate (MMA) in toluene using a catalyst/initiator/substrate ratio of 1:2:800. Contrary to what was observed for **1**, complex **3** was well soluble in this monomer-solvent mixture. The polymerization was carried out at a temperature of 35 °C and ethyl 2-bromo-2-methylpropionate was employed as the initiator.[12] The plot of $\ln([M]_0/[M])$ versus time (Figure 2) follows a linear relationship, which is typical for a controlled polymerization. Furthermore, a linear evolution of M_n as a function of conversion was observed (Figure 3). The observed molecular weights agreed well with the calculated values and the polydispersities were very low. Unfortunately, longer reaction times lead to a small amount of polymers with a higher molecular weight (less than 4%) (Figure 4). If these polymers were included in the calculation, a final PDI of 1.68 was obtained. Focusing on the main polymer peak, however, a polydispersity of 1.14 was recorded. A radical mechanism was supported by the tacticity of the polymer (rr:rm:mm = 64:29:7) and by the fact that the addition of 5 equivalents of galvinoxyl (relative to initiator) blocked the reaction completely.

Other methacrylates such as ethyl methacrylate (EMA), isobornyl methacrylate (IBMA) and *t*-butyl methacrylate (*t*-BuMA) were successfully polymerized at 35 °C as well (Table 1). For PEMA and P-*t*-BuMA, very low polydispersities of 1.15 and 1.14 were obtained. For polymerizations with isobornyl methacrylate, on the other hand, a significantly broader molecular weight distribution of PDI = 2.46 was found (Figure 5). The two acrylates tested, butyl acrylate (BuA) and *t*-butyl acrylate (*t*-BuA), gave very low conversions (Table 1).

Regarding the mechanism, is seems likely that, in a first step, the ethylene ligand is cleaved off. The resulting unsaturated Ru complex is then able to reversibly abstract a halogen atom from the initiator or subsequently from the growing polymer end. This mechanism is supported by the fact that the ethylene ligand in the structurally related complex **1** can be replaced by a halogen atom as evidenced by the isolation of the mixed valence Ru(II)-Ru(III) complex [(cymene)Ru(μ-Cl)$_3$RuCl$_2$(PCy$_3$)].[7]

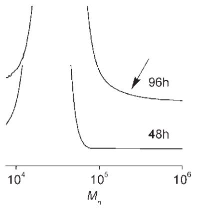


Figure 4. The molecular weight distributions of the PMMA polymers after 48 and 96 h highlighting the small amounts of polymers with a higher molecular weight.

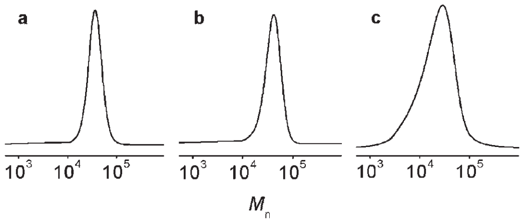


Figure 5. Molecular weight distributions of the polymers obtained after 96 h with the monomers ethyl methacrylate (**a**), *t*-butyl methacrylate (**b**) and isobornyl methacrylate (**c**). Reaction conditions: **3**/initiator/monomer = 1:2:800, toluene, 35 °C.

Table 1. ATRP of acrylates catalyzed by complex **3**.

Monomer	Yield [%]	M_n[a]	PDI
MMA	95	38500	1.68 (1.14)[b]
EMA	93	40500	1.15
IBMA	89	40000	2.46
t-BuMA	88	47000	1.14
BuA	2	–	–
t-BuA	12	–	–

[a] All values are based on PMMA calibrations.
[b] The value for the major peak is given in brackets.

In summary, we have demonstrated that complex **3** can be used to efficiently catalyze the ATRP of methacrylates at a temperature of only 35 °C without the need of an additive such as Al(O-*i*-Pr)$_3$.[13] It should be noted that ruthenium-catalyzed polymerizations of methacrylates are generally performed at temperatures of around 80–85 °C and that there are only a few Ru catalysts which allow one to work under milder conditions.[4,5] The hydride complex $[RuH_2(PPh_3)_4]$, for example, was reported to catalyze the controlled polymerization of MMA at 30 °C but significantly higher catalyst concentrations (MMA/Ru = 200:1) and reaction times (300 h) were required.[14,15] Complex **3** thus ranges among the most active ruthenium catalysts for ATRP reactions described so far.

Experimental Section

Synthesis of Complex 3

A mixture of [(1,3,5-*i*-$Pr_3C_6H_3$)$RuCl_2$]$_2$ (**2**) (100 mg, 133 μmol) and tricyclohexylphosphine (37.3 mg, 133 μmol) in isooctane (20 ml) was heated for 48 h to 50 °C under an atmosphere of ethylene. Upon cooling to room temperature, the product precipitated in form of an orange powder, which was filtered and washed with hexane; yield: 103 mg (90%). ^{1}H NMR (400 MHz, $CD_2Cl_2+C_2H_4$): δ = 1.23–1.26 (m, 9H, PCy_3), 1.39 [d, ^{3}J = 7 Hz, 18H, $CH(C\mathit{H}_3)_2$], 1.49–2.01 (m, 24H, PCy_3), 2.97 [sept, ^{3}J = 7 Hz, 3H, $C\mathit{H}(CH_3)_2$], 3.53 (m, 2H, C_2H_4), 3.97 (m, 2H, C_2H_4), 5.39 (s, 3H, CH, arene); ^{13}C NMR (101 MHz, $CD_2Cl_2+C_2H_4$): δ = 23.50, 23.77 (s, CH_3, *i*-Pr), 28.08 (s, PCy_3), 29.32–29.50 (m, PCy_3), 30.62 (m, PCy_3), 32.96 (s, CH, *i*-Pr), 37.10 (d, J_{PC} = 21 Hz, PCy_3), 61.65 (d, J_{PC} = 2 Hz, C_2H_4), 76.35 (s, CH, arene), 104.46 (s, C, arene); ^{31}P NMR (162 MHz, $CD_2Cl_2+C_2H_4$): δ = 43.29 (s); anal. calcd. (%) for $C_{35}H_{61}Cl_4Ru_2P$: C 49.06, H 7.18; found: C 49.06, H 7.14.

Typical Polymerization Procedure

Complex **3** (5.0 mg, 5.8 μmol) was placed in a Schlenk tube containing a magnetic stirrer. The monomer and a solution of the initiator ethyl 2-bromo-2-methylpropionate in toluene (0.1 M) were added so that the molar ratio catalyst/initiator/monomer was 1:2:800. *n*-Octane was added as the internal standard for GC measurements. The mixture was placed into a thermostatted oil bath at 35 °C, which was shielded from light. After a given period of time, the reaction mixture was diluted with THF (2 mL) and the product was precipitated with hexane (10 mL), isolated and dried in vacuum. All substrates and solvents were dried and freshly distilled and handled under an atmosphere of dry dinitrogen. The molecular weights and molecular weight distributions of the polymers were determined by gel permeation chromatography using PMMA standards.

Acknowledgements

This work was supported by a postdoctoral fellowship from the Ministère de la Culture, de l'Enseignement Supérieur et de la Recherche, Luxembourg (M. H.) and by the Swiss National Science Foundation. We thank Prof. Harm-Anton Klok, EPFL, for his support with the GPC measurements.

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