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Organometallic complex catalysis in water
II. [☆] Water soluble organoruthenium(IV) catalysts for the emulsion polymerization of norbornene

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Abstract

The bis(allyl)ruthenium complexes $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(OH_2)(O_2CCH_3)]^+BF_4^-$ (**2**) and $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(OH_2)(O_3SCF_3)_2]$ (**3b**) were obtained by reaction of the dimeric chloro-bridged bis(allyl)ruthenium complex $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ with the corresponding silver or sodium salts and their structure was determined by NMR and IR spectroscopy. Compounds **2** and **3b** are water soluble and prove to be very active single component catalysts for the emulsion polymerization of norbornene. The polymerization only takes place by ring opening of the monomer. The high *cis* selectivity of 85–90% is unusual for ruthenium-based catalysts for the ring-opening polymerization of strained cyclo-olefins. The polymers thus produced have very high molecular weights ($M_n \approx 1.5 \times 10^6$ g mol^{-1}) with a monomodal distribution and with polydispersities ranging from 2.0 to 2.5.

Keywords: Emulsion polymerization; Norbornene; Ring opening; Water-soluble organometallic catalysts

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1. Introduction

The emulsion polymerization of organic monomers using organometallic compounds as initiators is an area that has experienced only minimal growth in the parts. One main reason for this is the slow development of water soluble organometallic catalysts. However, mechanistic and kinetic investigations of the organometallic-initiated emulsion polymerization can be advanced through understanding of catalytic structure reactivity relationships and kinetics in micelles.

In 1965, Rinehardt and Smith [2] described the first successful emulsion polymerization of norbornene with iridium and ruthenium halide catalysts used in conjunction with a suitable reducing agent. These systems, however, gave low yields of polymers (typically less than 10%) which had principal *trans* configuration of double bonds in the backbone.

Ruthenium(II) complexes, such as $Ru(OH_2)_6(tos)_2$ (tos = *p*-toluenesulfonate), have recently been shown to be good catalysts for the ring-opening metathesis polymerization of 7-oxanorbornene derivatives in aqueous media [3].

Our interest has been foccused on the synthesis and catalytic properties of ruthenium complexes of the 4^+ metal oxidation state. The monomeric bis(allyl)-ruthenium(IV) complex $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})LCl_2]$ ($L = SbPh_3$ or $P(OPh)_3$] [1] polymerizes the ring-opening polymerization of norbornene in organic solvents with high activity and a *cis* selectivity up to 30% which is higher than that of many other ruthenium-based catalysts for the polymerization of strained cyclo-olefins [4–7].

Two water-soluble allyl complexes of ruthenium in a high oxidation state have recently been reported in the literature [8,9]. In this paper the synthesis of water soluble bis(allyl)ruthenium(IV) complexes and their use as pre-catalysts for the emulsion polymerization of norbornene is described.

2. Results and discussion

Complexes **1** and **3a** were obtained by reaction of the dimeric chloro-bridged bis(allyl)ruthenium(IV) complex

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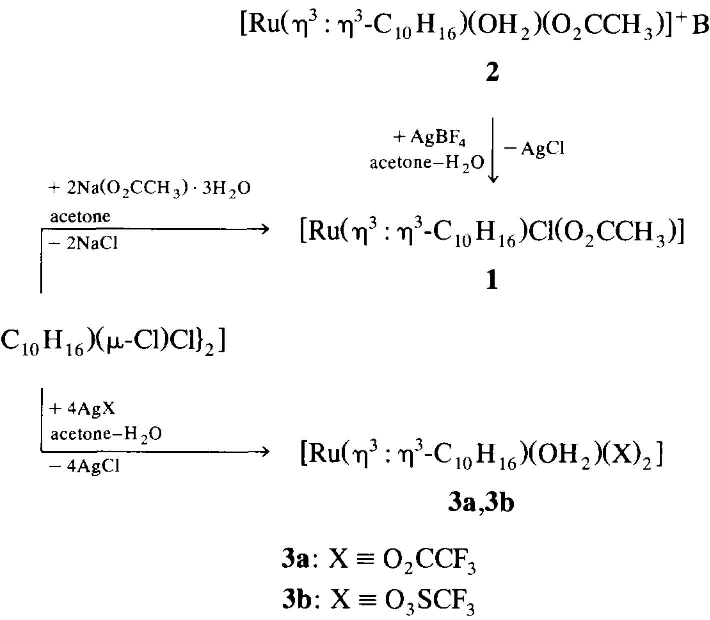


Fig. 1. Formation of the bis(allyl)ruthenium(IV) compounds $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(O_2CCH_3)]$ (**1**) $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(OH_2)(O_2CCH_3)]^+$ BF_4^- (**2**), $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(OH_2)(O_2CCF_3)_2]$ (**3a**) and $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(OH_2)(O_3SCF_3)_2]$ (**3b**).

[10] with 2 mol equivalents of sodium acetate in acetone for **1** and for **3a** with 4 mol equivalents of silver trifluoroacetate in an acetone–water mixture (Fig. 1).

The orange–yellow compound **3a** is stable in air and decomposes at 130–135 °C under a nitrogen atmosphere to a brown residue. Compound **3a** dissolves in acetone, methylene chloride, chloroform and diethyl ether but it is insoluble in water.

By reaction of **1** with 1 mol equivalent silver terafluoroborate in an acetone–water mixture the cationic bis(allyl)ruthenium(IV) complex **2** is obtained with a 80% yield. The orange-brown complex **2** is stable in air, decomposes at 125–130 °C under nitrogen to a dark-brown residue and is soluble in acetone and in water.

Complex **3b** is prepared by reaction of 4 mol equivalents of silver trifluormethansulfonate with $[\{Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ in an acetone–water mixture with a 70% yield. The orange-red compound **3b** is hygroscopic. Under a nitrogen atmosphere, **3b** is changed to an orange–red oil at 45–50 °C which decomposes at 115–120 °C to a dark-brown residue. Compound **3b** is very soluble in acetone and in water. Nitrogen-saturated water solutions of **2** and **3b** are stable for some weeks at room temperature.

The IR spectra of **1** and **2** (Table 1) both display strong bands at 1521 and 1463 cm^{-1}, and 1519 and 1463 cm^{-1}, assignable to $\nu_{asym}(OCO)$ and $\nu_{sym}(OCO)$ respectively [10]: A $\Delta\nu(=\nu_{asym}-\nu_{sym})$ value of 58 for **1** and 56 for **2** clearly indicate a chelate mode of coordination for the carboxylato ligand [11].

Furthermore **2** displays a strong broad band at 3424 cm^{-1} assignable to $\nu(OH)$ and indicative of hydrogen bonding in the solid state, as well as an additional very strong broad band at 1084 cm^{-1} for the non-coordinating BF_4^- anion [12].

Compounds **3a** and **3b** both display in the IR spectra a strong broad band at 3385 cm^{-1} and 3320 cm^{-1} respectively, assignable to $\nu(OH)$. The trifluoracetate

Table 1
Selected IR data for **1–3b**

Compound	IR absorption (cm^{-1})				
	$\nu_{asym}(OCO)$	$\nu_{sym}(OCO)$	$\Delta\nu$	$\nu(OH_2)$	Other
1 $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(O_2CCH_3)]$ [a]	1521 s	1463 vs	58	—	—
2 $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(OH_2)(O_2CCH_3)]^+BF_4^-$	1519 s	1463 vs	56	3424 s(br)	1084 vs(br) ($\nu(BF_4^-)$)
3a $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(OH_2)(O_2CCF_3)_2]$ [a]	1706 vs, 1674 vs	1422 m	252–284	3385 s(br)	1193 vs, 1145 vs ($\nu(CF_3)$)
3b $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(OH_2)(O_3SCF_3)_2]$	—	—	—	3320 s(br)	1248 vs(br) ($\nu_{asym}(SO_3)$ [b]), 1031 vs ($\nu_{sym}(SO_3)$ [c]), 1169 s(br) ($\nu(CF_3)$)

[a] In agreement with the literature [10].
[b] Two shoulders.
[c] One shoulder.

ligand of **3a** give ν(CF) bands at 1193 and 1145 cm^{-1}, ν_{asym}(OCO) at 1706 and 1674 cm^{-1} and ν_{sym}(OCO) at 1422 cm^{-1}. The much larger value of $\Delta\nu$ (252–284 cm^{-1}) is suggestive of a monodendate mode of coordination [11]. The trifluormethanesulfonate ligand of **3b** give ν(CF) bands at 1169 cm^{-1}, $\nu_{asym}(SO_3)$ with two shoulders at 1248 cm^{-1}, and $\nu_{sym}(SO_3)$ with one shoulder at 1031 cm^{-1} [13].

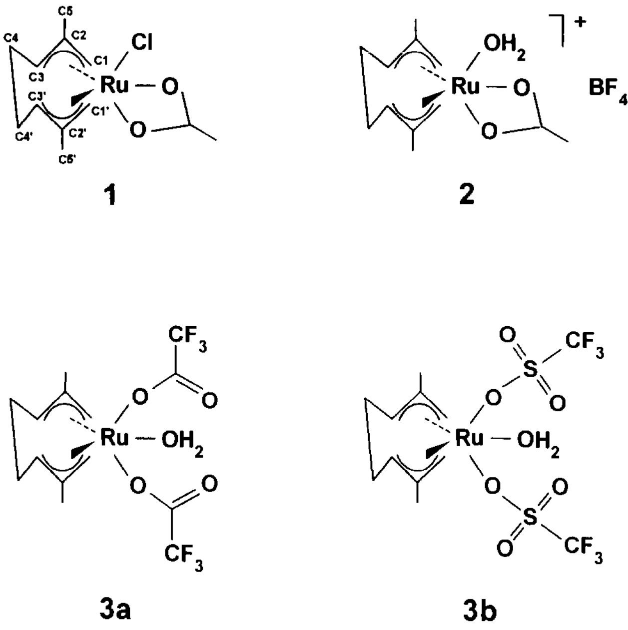
2.1. NMR spectroscopy characterization

The proton NMR spectra of **1** and **3a** are in agreement with those in the literature [10] (Table 2). The influence of various solvents ($CDCl_3$ and acetone-d_6) is unimportant.

The spectrum of the cationic complex **2** displays a pattern of $\eta^3:\eta^3$-$C_{10}H_{16}$ resonances closely analogous to those for **1**. The terminal allylic protons of the 2.7-dimethylocta-2.6-diene-1.8-diyl ligand give rise to four equally intense singlet signals. The two internal allylic protons resonate as two equally intense multiplets and the four ethylenic protons exhibit a broad multiplet, while the methyl substituents exhibit two equal resonances of relative intensity 3. This indicates that the two axial sites of the pentagonal bipyramidal complex are inequivalent (Fig. 2). A further singlet resonance is due to the acetate methyl group and the coordinating water molecule resonates as a sharp singlet resonance. The chemical shift of acetate methyl group is in agreement with that found for **1**.

In the ^{13}C NMR spectra of **1** and **2** recorded in acetone-d_6 and $CDCl_3$ no influence of the solvent was observed (Table 3). In confirming the proton NMR observations, both complexes show identical patterns with ten resonances of the 2.7-dimethylocta-2.6-diene-1.8-diyl ligand rather than the five observed for **3a** and **3b** and two resonances of the carboxylate ligand. In the ^{13}C NMR spectra of **2** the C2 resonances of the allyl group coordinating at the ruthenium are shifted to a low field compared with those for **1**. This is an expression of the stronger acceptor effect of the metal at the allyl group and is consistent with the cationic character of **2**.

The ^1H NMR spectrum of **3b** displays half the number of $\eta^3:\eta^3$-$C_{10}H_{16}$ resonances of **1** and **2** but is closely analogous to those for **3a**. The spectrum exhibits one resonance of relative intensity 3 for the methyl group and five equally intense resonances attributable to



1 **2** **3a** **3b**

Fig. 2. Schematic representation of **1**–**3b** with atom numbers.

Table 2
^1H NMR data for **1**–**3b** recorded at 298 K (for **1** and **3a** see [10])

Compound	δ (ppm) (J_{H-H} (Hz))				
	Terminal allyl	Internal allyl	Ethylenic	$-CH_3$	Ligand
1 $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(O_2CCH_3)]$ [a]	5.29(s, 1H), 4.65(s, 1H)	4.08(m, 1H)	2.48–2.64(m, 4H)	2.24(s, 3H)	1.79(s, 3H, $-CH_3$)
	4.43(s, 1H), 3.52(s, 1H)	3.47(m, 1H)		2.12(s, 3H)	
$[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(O_2CCH_3)]$ [b]	5.49(s, 1H), 4.63(s, 1H)	4.19(m, 1H)	2.50–2.60(m, 4H)	2.28(s, 3H)	1.83(s, 3H, $-CH_3$)
	4.61(s, 1H), 3.55(s, 1H)	3.49(m, 1H)		2.11(s, 3H)	
2 $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})OH_2(O_2CCH_3)]^+BF_4^-$ [a]	5.81(s, 1H), 5.37(s, 1H)	4.47(m, 1H)	3.05(m, 2H)	2.24(s, 3H)	1.81(s, 3H, $-CH_3$)
	4.67(s, 1H), 3.74(s, 1H)	4.35(m, 1H)	2.84(m, 2H)	2.20(s, 3H)	7.08(s, 2H, OH_2)
$[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})OH_2(O_2CCH_3)]^+BF_4^-$ [c]	5.44(s, 1H), 5.24(s, 1H)	4.13(m, 1H)	2.80(m, 2H)	2.06(s, 3H)	1.96(s, 3H, $-CH_3$)
	4.25(s, 1H), 3.80(s, 1H)	4.07(m, 1H)	2.50(m, 2H)	2.03(s, 3H)	—
3a $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})OH_2(O_2CCF_3)_2]$ [b]	5.67(s, 2H), 4.22(s, 2H)	4.42(m, 2H)	3.07(m, 2H)	2.11(s, 6H)	7.13(s, 2H, OH_2)
			2.46(m, 2H)		
3b $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})OH_2(O_3SCF_3)_2]$ [a]	5.99(s, 2H), 4.17(s, 2H)	4.87(m, 2H)	3.27(m, 2H)	2.39(s, 6H)	7.12(s, 2H, OH_2)
			2.74(m, 2H)		
$[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})OH_2(O_3SCF_3)_2]$ [c]	5.46(s, 2H), 4.18(s, 2H)	4.33(m, 2H)	2.96(m, 2H)	2.11(s, 6H)	—
			2.61(m, 2H)		

[a] Solvent, acetone-d_6.
[b] Solvent, $CDCl_3$.
[c] Solvent, D_2O.

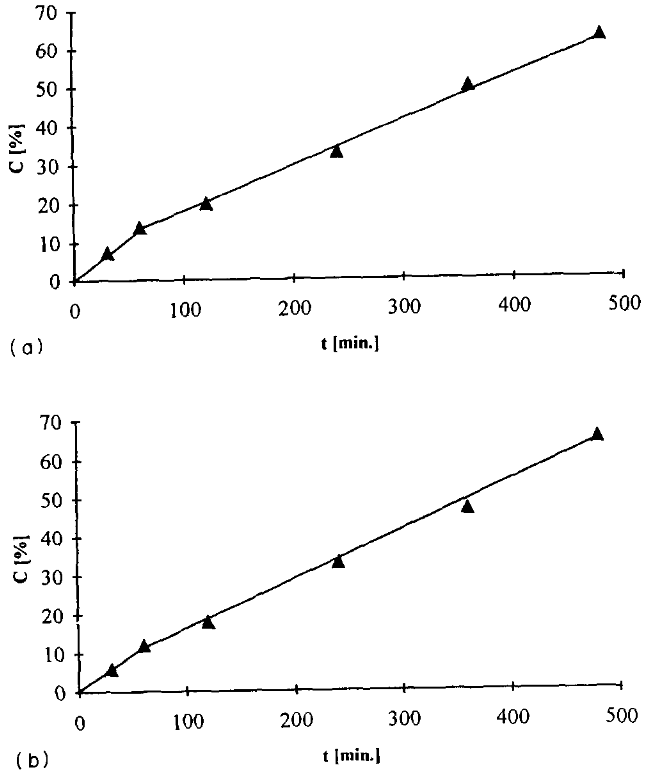


Fig. 3. Conversion-time diagram of catalysis with **2** (above) and **3b** (below) (conditions: [NB] = 2.8 M; [Ru] = 4.6×10^{-3} M; [NB]:[Ru] = 600; emulsifier: $c = 0.08$ M; $T = 60$ °C).

the five types of proton of the 2.7-dimethylocta-2.6-diene-1.8-diyl ligand (Table 2). This implies that there is *C*2 symmetry with equivalent axial sites on the trigonal bipyramid as shown in the crystal structures of $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(SbPh_3)]$ [1] and **3a** [10] (see also Fig. 2). Furthermore the chelating mode of the trifluormethylsulfonate group is monodendate in conformity with the IR investigations. The water ligand occurs as a sharp singlet resonance just as in **3a**.

The proton NMR data are confirmed by the ^{13}C NMR spectra of **3a** and **3b** (Table 3). Both compounds exhibit five resonances for the 2.7-dimethylocta-2.6-diene-1.8-diyl ligand with identical shifts and half the number of resonances of **1** and **2**. The carboxylate ligand exhibits two resonances, a quartet at 166.0 ppm for the carbonyl C atom and a quartet at 113.2 ppm for the CF_3 group. The CF_3 group of the trifluormethanesulfonate ligand resonates as a quartet at 121.1 ppm.

The ^1H NMR spectra of **2** and **3b** recorded in D_2O exhibit no change in patterns and only a small change in chemical shifts. The H_2O peak disappears and the D_2O signal is significantly broadened. This is an indication of an exchange of H_2O and D_2O.

2.2. Results of catalysis

Complexes **2** and **3b** catalyze the ring-opening polymerization in an aqueous emulsion with the same high activity. For technical details of polymerization see Section 4. Fig. 3 shows the conversion time diagrams of the polymerization using **2** and **3b** as catalysts.

Under the given reaction conditions the conversion increases linearly in two periods with increasing reaction time. In a first period up to 60 min, both complexes show turn-over numbers (TONs) of about 100 (mol PNB) $(\text{mol Ru})^{-1}$ h^{-1} (PNB ≡ precipitated polynorbornene). In the further course of polymerization up to 480 min the TONs decrease at a constant level of about 50 (mol PNB) $(\text{mol Ru})^{-1}$ h^{-1}.

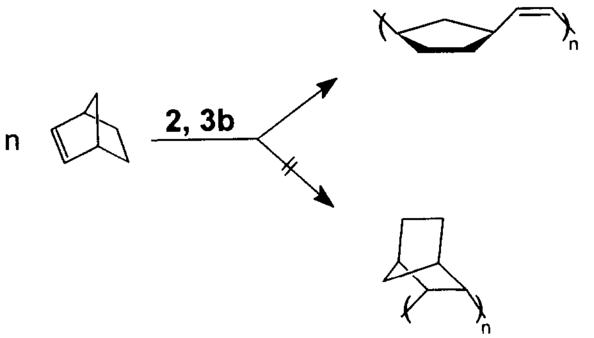
The given TONs are related to the total concentration of ruthenium $[Ru]_{tot}$. It must be taken into consideration that, during the catalysis, only a small amount of $[Ru]_{tot}$ is active into the micelles, similar to radical-initiated emulsion polymerization [14]. Therefore the TONs related to $[Ru]_{act}$, are essentially higher.

Table 3
^{13}C NMR data for **1–3b** recorded at 298 K

Compound	δ (ppm)					
	C(1)/C(1′)	C(2)/C(2′)	C(3)/C(3′)	C(4)/C(4′)	C(5)/C(5′)	Ligand
1 $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(O_2CCH_3)]$ [a]	84.9/85.2	118.3/124.5	93.2/93.7	32.0/33.7	18.1/18.5	$-CO_2$ 189.2 $-CH_3$ 24.0
$[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(O_2CCH_3)]$ [b]	84.9/85.3	118.1/123.5	92.2/92.9	31.5/33.2	18.1/18.4	$-CO_2$ 189.6 $-CH_3$ 24.1
2 $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(OH_2)(O_2CCH_3)]^+ BF_4^-$ [a]	82.9/85.8	126.8/133.2	101.7/103.4	36.1/34.1	18.1/18.6	$-CO_2$ 192.3 $-CH_3$ 23.8
3a $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(OH_2)(O_2CCF_3)_2]$ [b]	85.9	133.4	98.9	36.8	18.8	$-CO_2$ 166.0(q) $^2J_{C-F}$ = 37.7 Hz $-CF_3$ 113.2(q) C–F = 288.6 Hz
3b $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})(OH_2)(O_3SCF_3)_2]$ [a]	85.0	133.6	97.9	36.3	18.5	$-CF_3$ 121.1(q) J_{C-F} = 321.7 Hz

[a] Solvent, acetone-d_6.
[b] Solvent, $CDCl_3$.

Compounds **2** and **3b** catalyze only the ring-opening polymerization of norbornene:



(1)

The quantitative determination of unsaturation by integration of ^{1}H NMR spectra showed that the polymers contained about 100% of ring-opened units and no bicyclo[2.2.1]hept-2.3-ylene units.

The high *cis* selectivity of the catalysts **2** and **3b** of 85–90% (^{1}H NMR (CDCl$_3$, 250.133 MHz) δ 5.32 (olefin-H, *trans*), 5.19 (olefin-H, *cis*) ppm; ^{13}C NMR (CDCl$_3$, 62.896 MHz) δ 133.0 (olefin-C, *trans*), 133.9 (olefin-C, *cis*) ppm) is remarkable and unusual for ruthenium-based catalysts for ring-opening polymerization of norbornene. Such catalysts are *trans* catalysts with *trans* selectivities of about 90% [4–7].

The number-averaged molecular weights M_n of the polymers produced with **2** amount to about 5×10^5 g mol^{-1}, while the polymers obtained with **3b** have $M_n \approx 1.5 \times 10^6$ g mol^{-1}. The molecular weight distribution of all polymers is monomodal and the polydispersities range from 2.0 to 2.5. The maximum M_n corresponding to a polymerization degree $\bar{n} \approx 16\,000$ has already been reached at a polymerization time of 30 min. This means that the initial rate of polymerization is on the order at least 550 equivalents min^{-1}. An initiation phase as described by Novak and Grubbs [3] for the emulsion polymerization of 7-oxanorbornene derivatives using Ru(OH$_2$)$_6$(tos)$_2$ as catalyst could not be observed. While the conversion increases with increasing reaction time, M_n remains unchanged. All polymers thus produced show a Schultz–Flory distribution.

3. Conclusions

For the first time, water soluble bis(allyl)ruthenium(IV) complexes were prepared, which prove to be single-component catalysts for the ring-opening polymerization of norbornene in aqueous emulsion. The polymers can be made in a quantity of some grams by this method.

The structural variation in the prepared ruthenium(IV) complexes is the key to a systematic study of catalytic structure–reactivity relationship for emulsion polymerization. Moreover new dimensions of application will be opened up for the emulsion polymerization by the use of structural variable complex catalysts compared with the usual radical initiator systems. Finally the use of water is an attractive advantage in contrast with the homogeneous catalysis in organic solvents.

4. Experimental details

All reactions and manipulations were carried out under a nitrogen atmosphere. The solvents were distilled from calcium hydride or Na–benzophenone under nitrogen and stored over molecular sieves. Acetone was not dried, only distilled. Norbornene (Merck) was distilled from calcium hydride under nitrogen prior to use. Water was distilled under nitrogen and emulsifier (sodium dodecylbenzenesulfonate (Aldrich)) was added to obtain a 2.7 wt.% solution. Ruthenium trichloride hydrate was obtained from Degussa AG. The silver salts (AgBF$_4$, Ag(O$_2$CCF$_3$) and Ag(O$_3$SCF$_3$)), Na(O$_2$CCH$_3$) $\cdot$ 3H$_2$O and isoprene were obtained from Fluka. The compound [{Ru(η^3 : η^3-C$_{10}$H$_{16}$)(μ-Cl)Cl}$_2$] was prepared by published literature methods [15].

Elemental analysis were performed in the Microanalytical Laboratory of our institute (M. Barth).

NMR spectra were obtained on a JEOL JMN-GX 400 and a Bruker AC 250 spectrometer and IR spectra were recorded with a Perkin–Elmer 1640 FT-IR instrument.

4.1. Preparations

4.1.1. [{Ru(η^3 : η^3-C$_{10}$H$_{16}$)Cl(O$_2$CCH$_3$)] (1) [10]

To a suspension of [{Ru(η^3 : η^3-C$_{10}$H$_{16}$)(μ-Cl)Cl}$_2$] (0.48 g, 7.8×10^{-4} mol) in 10 cm^3 of acetone, Na(O$_2$CCH$_3$) $\cdot$ 3H$_2$O (0.22 g, 1.6×10^{-3} mol) was added and the mixture stirred for 12 h. The resulting orange–red solution was filtered through Celite to remove the precipitate of AgCl. The solution was evaporated to about one quarter volume and diethyl ether was added to precipitate the product as orange crystals which were isolated by filtration, washed with diethyl ether and dried in vacuo. The yield was 0.33 g (1.0×10^{-3} mol, 65%).

Elemental Anal. Found: C, 43.53; H, 5.78; Ru, 31.0. C$_{12}$H$_{19}$ClO$_2$Ru Calc.: C, 43.44; H, 5.73; Ru, 30.5%.

4.1.2. [{Ru(η^3 : η^3-C$_{10}$H$_{16}$)(OH$_2$)(O$_2$CCH$_3$)]$^+$ BF$_4^-$ (2)

To a solution of **1** (0.28 g, 8.6×10^{-4} mol) in a mixture of 5 cm^3 of acetone and 0.1 cm^3 of distilled water was added AgBF$_4$ (0.17 g, 8.6×10^{-4} mol). This mixture was stirred for 1 h and the resulting orange–brown solution was filtered through Celite to remove the precipitate of AgCl. After evaporation the solvent diethyl ether was added and the product precipitated in form of an orange–red powder which was isolated by filtration, washed with diethyl ether and dried in vacuo. The yield was 0.27 g (6.8×10^{-4} mol, 80%).

Elemental Anal. Found: C, 35.46; H, 5.29; Ru, 25.0. $C_{12}H_{21}BF_4O_3Ru$ Calc.: C, 35.91; H, 5.24; Ru, 25.2%.

4.1.3 [{Ru($\eta^3:\eta^3$-$C_{10}H_{16}$)(OH_2)(O_2CCF_3)$_2$] (3a) [10]

The compound [{Ru($\eta^3:\eta^3$-$C_{10}H_{16}$)(μ-Cl)Cl}$_2$] (0.41 g, 6.6×10^{-4} mol) was suspended in a mixture of 15 cm^3 of acetone and 0.3 cm^3 of distilled water. $Ag(O_2CCF_3)$ (0.58 g, 2.6×10^{-3} mol) was added and the mixture stirred for 24 h. After filtration through Celite to remove the precipitate of AgCl the solution was evaporated to dryness. The orange–yellow residue was washed with 2×5 cm^3 pentane and dried in vacuo. The yield was 0.42 g (8.7×10^{-4} mol, 66%).

Elemental Anal. Found: C, 35.32; H, 3.72; Ru, 20.9. $C_{14}H_{18}F_6O_5Ru$ calc.: C, 34.93; H, 3.74; Ru, 21.0%.

4.1.4. [{Ru($\eta^3:\eta^3$-$C_{10}H_{16}$)(OH_2)(O_3SCF_3)$_2$] (3b)

The compound [{Ru($\eta^3:\eta^3$-$C_{10}H_{16}$)(μ-Cl)Cl}$_2$] (0.58 g, 9.4×10^{-4} mol) was suspended in a mixture of 15 cm^3 of acetone and 0.3 cm^3 of distilled water. $Ag(O_3SCF_3)$ (0.96 g, 3.7×10^{-3} mol) was added and the mixture stirred for 24 h. The resulting orange solution was filtered through Celite to remove the precipitate of AgCl. The solvent was evaporated and the residue was an orange–red oil which was washed with 2×5 cm^3 pentane and next with 5 cm^3 diethyl ether; it was then evaporated to dryness to give an orange–red powder. The yield was 0.72 g (1.3×10^{-3} mol, 70%).

Elemental Anal. Found: C, 25.99; H, 3.34; Ru, 17.6. $C_{12}H_{18}F_6O_7RuS_2$ Calc.: C, 26.04; H, 3.25; Ru, 18.3%.

4.2. Polymerization procedure

In a typical polymerization run the catalyst ((2–3) $\times$ 10^{-5} mol) was put in a Schlenk tube with a thermostable cover, a central neck and a side arm, which was connected with a vacuum–nitrogen system. Then 5 cm^3 of a water solution of 2.7 wt.% emulsifier (1.36 g or sodium dodecylbenzenesulfonate per 50 cm^3 of distilled water) was introduced into the Schlenk tube (0.25 g of C_7H_{11} per 1 g of H_2O). Finally, freshly distilled norbornene (1.3 g, 1.4×10^{-2} mol) was placed into the Schlenk tube to give a C_7H_{11} to catalyst molecular ratio of 600. Then the mixture was thermostated to 60 °C ± 0.1 and stirred at 1000 c min^{-1}.

The polymerization was terminated by pouring the reaction mixture into an excess of methanol (30 cm^3) with a small amount of di-*tert*-butyl-*p*-cresole as antioxidant. The polymers were obtained after drying as white amorphous powders.

4.3. Molecular weight determination

Molecular weights were determined by gel permeation chromatography (GPC) with a Waters 717 by using linear Waters 10681 Ultrastyragel column. The RI detector was a Waters 410 instrument. As the mobile phase tetrahydrofuran was used with a flow rate of 0.5 cm^3 min^{-1}. The measurement temperature was 25 °C.

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