Ruthenium carborane complexes in the controlled radical polymerization of methyl methacrylate

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New initiators based on *closo-* and *exo-nido-*ruthenacarboranes with phosphine and diphosphine ligands were proposed as chain growth regulators. They allow conducting the controlled synthesis of poly(methyl methacrylate) under radical initiation conditions.

Key words: ruthenium carborane complexes, methyl methacrylate, controlled radical polymerization.

The controlled synthesis of macromolecules opens up broad prospects for controlling the chain growth under radical initiation conditions.^{1,2} A substantial drawback of radical polymerization is the high reactivity of the radical species, which actively participate not only in the chain growth, but also in side reactions, for example, disproportionation, dimerization, and chain transfer, which finally results in high polydispersity of the polymers and makes the process uncontrolled.³ The so-called Atom Transfer Radical Polymerization (ATRP), first accomplished in 1995 in the synthesis of polyolefins, is now the most efficient method for the targeted control of the elementary steps of radical polymerization.^{4,5} This approach is actually based on the Kharasch reaction, discovered in 1945,⁶ in which alkyl halides act as sources of carboncentered radicals in the presence of transition metal complexes where the oxidation state of the metal can easily and reversibly change (Scheme 1).

The possibility of fast and reversible redox transformations of the metal and the presence of a halogen atom bound to the metal atom are necessary conditions for the high activity of metal complexes in this type of processes.⁷ Currently, ATRP is carried out using various transition metal complexes, including copper,⁸ nickel,⁹ iron,¹⁰ rhodium,¹¹ molybdenum,¹² palladium,¹³ and ruthenium.^{14–16} Examples of using metallacarborane catalysts with charge-compensating phosphorus-¹⁷ or sulfur-containing^{18,19} substituents at the carborane cage ligand in this process and in the Kharasch reaction are known. As shown already in the first experiments, Ru^{II} carborane complexes exhibit the highest activity among all





Bimolecular termination

 M^n is a transition metal in the oxidation state *n*; X, Y = Cl or Br; L is the organic ligand

known ruthenium catalysts used in the reaction of styrene and methyl methacrylate (MMA) with CCl₄ (Kharasch reaction) (with $3-H-3,3-(PPh_3)_2-8-S(Et)Ph-3,1,2-RuC_2B_9H_{10}$ used as the catalyst, the turnover number is 1800 and 1500 per hour, respectively, at 40 °C).¹⁸

This communication describes the use of classical *closo*- and *exo-nido*-ruthenacarboranes **1**–**5**, containing readily available non-substituted or dimethyl-substituted carborane ligands as regulators of the radical polymerization of MMA. The general principles of the ATRP catalysts²⁰ are fulfilled, in particular, for complexes **1**–**5** where the ruthenium atom can easily change its oxidation state; in addition, each complex contains a halogen atom bound to the Ru atom.

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Results and Discussion

18-Electron complexes 1–4 were synthesized according to published methods.^{21–23} *exo-nido*-Ruthenacarboranes 1 and 2 were obtained from the K⁺ salts of *nido*-dicarbaundecaborates $[nido-7, 8-R_2-7, 8-C_2B_9H_{10}]^-K^+$ (R = H, Me) and Ru(PPh₃)₃Cl₂ by a known but slightly modified procedure,²¹ in which the THF—ether binary mixture used previously as the solvent was replaced by benzene. Complex 3 was synthesized by the thermal *exo-nido*→*closo*-rearrangement of ruthenacarborane 1 in benzene,²² and complex 4 was obtained by the reaction of ruthenacarborane 1 with 1,4-bis(diphenylphosphino)butane (dppb) in benzene at room temperature.²³



The paramagnetic *o*-cycloborated *closo*-ruthenacarborane **5** was prepared on heating of ruthenacarborane **2** with a 10% excess of 1,3-bis(diphenylphosphino)propane (dppp) in toluene (Scheme 2). Complex **5**, formed together with the known cationic complex [RuCl(Ph₂P(CH₂)₃PPh₂)₂]⁺[*nido*-7,8-Me₂-7,8-C₂B₉H₁₀]⁻ (**6**),²⁴ was isolated from the reaction mixture in 64% yield by column chromatography on silica gel (see Experimental).

The structure of **5** was established using X-ray diffraction and ESR data, and its composition was confirmed by elemental analysis. The molecular structure of **5** is shown in Fig. 1, while selected bond lengths and angles are summarized in Table 1. According to X-ray diffraction data,

Scheme 2



the Ru atom in complex 5 is coordinated to the doubly charged (2-) {C₂B₉} ligand, neutral diphosphine, and singly charged (1-) chloride ligand. Thus, the six-coordinate Ru atom has a formal oxidation state +3 and a deficient 17-electron configuration. The paramagnetic nature of complex 5 is also confirmed by the ESR spectrum (see Experimental). An interesting feature of compound 5 is the presence of *o*-phenylcycloboronated diphosphine ligand. Note that in the series of *closo*-metallacarborane complexes of transition metals, this is only the second²⁵ structurally characterized complex of this type. The presence of an o-cycloboronated fragment in the complex accounts for the observed differences in the Ru-P(1)(2.306(4) Å) and Ru-P(2) (2.369(4) Å) bond lengths. Attention is also attracted by the substantially shortened Ru-Cl bond length (2.375(1) Å). In 18-electron *closo*-ruthenacarboranes having a similar structure, the Ru-Cl distance is much longer, for example, in neutral complex 3 (Ru-Cl, 2.429 Å)²² or in the an-

Table 1. Selected geometric parameters of molecule 5

Bond	d/Å	Angle	ω/deg
Ru(3) - P(1)	2.306(4)	B(8) - Ru(3) - P(1)	80.8(3)
Ru(3) - P(2)	2.369(4)	P(1) - Ru(3) - P(2)	85.66(13)
Ru(3)-Cl(1)	2.375(3)	P(1) - Ru(3) - Cl(1)	91.35(12)
Ru(3) - C(1)	2.319(1)	P(2) - Ru(3) - Cl(1)	86.06(12)
Ru(3)-C(2)	2.316(1)	C(15) - P(1) - Ru(3)	120.5(3)
Ru(3) - B(4)	2.245(1)	C(18) - P(1) - Ru(3)	105.8(4)
Ru(3) - B(7)	2.203(1)	C(17) - P(2) - Ru(3)	113.5(4)
Ru(3) - B(8)	2.223(1)	C(16) - C(15) - P(1)	117.1(7)
P(1) - C(15)	1.827(1)	C(15)-C(16)-C(17)	112.0(8)
P(1) - C(18)	1.829(1)	C(16) - C(17) - P(2)	112.4(7)
P(1)-C(24)	1.812(1)	C(19) - C(18) - P(1)	113.0(8)
P(2)-C(17)	1.829(1)	C(18) - C(19) - B(8)	119.3(8)
P(2)-C(30)	1.836(1)		
P(2)-C(36)	1.833(1)		
C(1) - C(2)	1.635(1)		
C(15)-C(16)	1.498(1)		
C(16)-C(17)	1.537(1)		
C(18) - C(19)	1.419(1)		



Fig. 1. Molecular structure of complex 5.

ionic complexes $[3,3-L_2-3-Cl-3,1,2-RuC_2B_9H_{11}]^{-}[Cat]^+$ (L = PPh₃, Cat = Et₄N, Ru-Cl, 2.515 Å;²⁶ L = CO, Cat = Au(PPh₃)₂, Ru-Cl, 2.452 Å).²⁷ The distances from the ruthenium atom to the C₂B₃ pentagonal plane of the carborane ligand are similar in all of these compounds.

We found that ruthenium carborane complexes 1-5 actively initiate polymerization of methyl methacrylate in the presence of CCl₄; in some cases, the degree of monomer conversion is close to 100% (Table 2).

As follows from the obtained data (see Table 2), 18-electron ruthenium(11) *exo-nido*-complexes (compounds **1** and **2**) are the best choice as regards the degree of conversion and initiation efficiency; with these com-

Com- plex	z	q	t _p /h	Conver- sion (%)	$M_{ m w}$	M _n	$M_{\rm w}/M_{\rm n}$
1	II	18e	45.4	94.0	83500	53500	1.56
2	Π	18e	80.3	98.5	100200	51800	1.93
3	IV	18e	45.4	87.8	58900	36200	1.62
4	IV	18e	110	82.7	33600	26800	1.25
5	III	17e	114	70.0	57400	41900	1.37

Table 2. Polymerization of MMA catalyzed by ruthenacarboranes

Note. Conditions: ruthenacarborane concentration, 0.125 mol.%; temperature, 80 °C, initiator, CCl_4 (0.25 mol.%). *z* is the oxidation number, *q* is the electron environment, t_p is the polymerization time, M_w is the weight average molecular weight, M_n is the number average molecular weight, M_w/M_n is the polydispersity coefficient.

pounds, the monomer conversion exceeds 90%. The resulting polymers have rather high molecular weights $(M_n > 50$ thousand) and a polydispersity of <2.

When focusing on the synthesis of narrow-polydispersity macromolecules, of most interest are ruthenacarborane complexes 3-5 of the closo-structure. If they are used in the synthesis of poly(methyl methacrylate) (PMMA), the polydispersity of the sample is in a range of 1.25 - 1.62(see Table 2), which corresponds to the basic parameters of living radical polymerization.^{1-3,20} However, MMA polymerization involving the ruthenium closo-complexes proceeds at a much lower rate than that with exo-nido-complexes, reaches a much lower limiting conversion, and gives a polymer with a lower molecular weight (see Table 2). All the proposed diamagnetic closo-ruthenacarboranes exceed in activity related ruthenium cyclopentadienyl derivatives, for example, $RuCl(Cp^*)(PPh_3)_2$, which can also control the molecular-mass characteristics of the polymers. These compounds are mainly used for the synthesis of PMMA together with co-catalysts, in particular, aluminum alkoxides, because the rate of polymerization in the presence of these compounds without additives is low and a high degree of conversion ($\sim 90\%$) is attained only after 300–600 h (see Refs 7, 28, and 29).

Comparison of the polydispersity of PMMA synthesized in the presence of complex **3** and compounds **4**, **5** indicates that binding of phosphine ligands by methylene fragments creates favorable steric conditions for control of the polymer chain growth by the ruthenacarborane molecule, which finally results in a narrow-polydispersity polymer with $M_w/M_n \le 1.25$ in the case of complex 4. The samples of PMMA obtained in the presence of diphosphine-substituted complexes, diamagnetic 4 and paramagnetic 5, show only slight differences in polydispersity coefficients (see Table 2).

The very similar polydispersities of the polymer samples obtained with complexes 1 and 3 having different structures are due, in our opinion, to a rearrangement of the *exo-nido* complex 1 into *closo* complex 3, which readily occurs in benzene at 80 °C.²² This rearrangement does not take place in the case of sterically more hindered dimethyl-substituted *exo-nido*-complex 2 (see Ref. 22), in whose presence a polymer with a greater polydispersity coefficient is formed ($M_w/M_n \le 1.93$). This fact indicates that the chain growth step and the formation of macro-molecular characteristics of PMMA samples are affected by both steric and structural features of the catalysts.

Complexes 1 and 3 are also active in the polymerization of MMA according to the ATRP mechanism in the presence of other radical initiators, for example, ethyl 2-bromoisobutyrate (MMA : initiator : catalyst = 1: 0.25: 0.125). The relatively low (<1.85) polydispersity values for PMMA are retained.*

Thus, this study has shown that ruthenium complexes with carborane ligands are efficient catalysts for controlled ATRP synthesis of PMMA. The complexes with *closo*-structure are more efficient regulators of the molecular mass characteristics of the polymers than *exo-nido*-ruthenacarboranes.

Experimental

Complexes 1-4, $^{21-23}$ 5, and 6 were synthesized under argon using anhydrous solvents prepared by standard procedures. The products were isolated and purified by column chromatography using silica gel Merck (230–400 mesh). Commercial diphosphines dppp and dppb (Strem Chemicals) were used. The ESR spectrum of complex 5 was recorded on a Varian E-12A radiospectrometer. Elemental analysis of complex 5 was performed at the laboratory of microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds.

Synthesis of 3-chloro-1,2-dimethyl-3,3-{[1['],1[']-diphenyl-5[']phenyl-5[']-(5['],8- μ -(*o*-phenylene)]-1['],5[']-diphosphapentane}*closo*-3,1,2-dicarbollylruthenium (5) and 1['],3[']-bis(diphenylphosphinopropane)chlororuthenium(1)-7,8-dimethyl-7,8-dicarba*nido*-undecaborate (6). Complex 2 (0.36 g, 0.44 mmol) was added to a solution of dppp (0.2 g, 0.48 mmol) in toluene (20 mL) and the reaction mixture was refluxed for 2.5 h with stirring using a magnetic stirrer. The solvent was evaporated *in vacuo*, the residue was chromatographed on a column with silica gel, the major reaction product (complex 5) being eluted with a n-C₆H₁₂-CH₂Cl₂ mixture (1 : 1). The yield of 5 was 64%. The second reaction product was eluted from the column by more polar CH₂Cl₂, which was removed *in vacuo* to give 0.05 g (11%) of complex **6**. The data of ¹H, ³¹P{¹H}, and ¹¹B NMR spectra of complex **6** fully coincided with the published data,²⁴ which indicates that these compounds are identical. **Complex 5**. Found (%): C, 48.73; H, 4.79; B, 12.07. C₃₁H₃₀P₂B₉ClRu · CH₂Cl₂. Calculated (%): C, 48.50; H, 5.18; B, 12.28. ESR (CH₂Cl₂, $g_{\text{stand}} = 2.0023$, T = 77 K): $g_{\text{av}} = 2.1096$.

X-Ray diffraction study of 5. The crystals of $5 \cdot 3C_6H_6$ are triclinic, $C_{49}H_{57}B_9ClP_2Ru$, M = 940.77, space group $P\overline{1}$, at 173 K a = 10.131(9), b = 10.232(11), c = 26.14(3) Å, $\alpha = 80.90(3), \beta = 84.16(4), \gamma = 61.17(3)^{\circ}, V = 2343(4) \text{ Å}^3, Z = 2,$ $d_{calc} = 1.335 \text{ g cm}^{-3}, \ \mu(\text{Mo-K}\alpha) = 4.95 \text{ cm}^{-1}$ (no absorption correction was applied). The intensities of 8478 reflections (7996 independent reflections, $R_{int} = 0.071$) were measured on a Syntex P21 diffractometer (graphite monochromator, λ (Mo-K α) = 0.71073 Å, $\theta/2\theta$ scan mode, $2\theta_{max} = 50^{\circ}$). The structure was solved by the direct method and refined by the full-matrix least-squares method on F^2_{hkl} with anisotropic thermal parameters for all nonhydrogen atoms. The structure contains three solvating benzene molecules, one of which is disordered. The hydrogen atoms of the carborane ligand were located from the difference synthesis and included in the final refinement with fixed coordinates. The other hydrogen atoms were placed into geometrically calculated positions and included in the refinement in the riding model. The final R-factors $R_1 = 0.099$ (refinement on F_{hkl} for 5492 reflections with $I > 2\sigma(I)$), $wR_2 = 0.226$ and S = 1.019 (refinement on F_{hkl}^2 for all independent reflections). All calculations were carried out on a personal computer using the SHELXTL software.30 The full tables of atom coordinates, bond lengths, bond angles, and anisotropic thermal parameters were deposited with the Cambridge Structural Database.

Polymerization of MMA. The physicochemical parameters of the solvents correspond to published data.³¹ Methyl meth-acrylate was purified by vacuum distillation to collect the fraction with b.p. 38 °C (15 Torr).³²

Carbon tetrachloride was used in the ATRP as the initiator. The samples were prepared as follows: the monomer and exact portions of the initiator and the catalyst (ruthenacarboranes) were placed in glass tubes, and degassed three times. The tubes were frozen in liquid nitrogen and polymerization was carried out at a residual pressure of 1.3 Pa. The polymerization kinetics was monitored under isothermal conditions by the weighing method. The tube was place in a thermostat for a strictly specified period of time. After that, the tube was taken out and frozen in liquid nitrogen to terminate polymerization. The resulting polymer was precipitated by petroleum ether, reprecipitated from a chloroform solution, and dried *in vacuo* to a constant weight, and the degree of conversion was calculated.

Analysis of poly(methyl methacrylate). The molecular weight and the molecular weight distribution of PMMA were determined by GPC on a Knauer setup with a linear column (Phenomenex, USA). A RI Detektor K-2301 differential refractometer was used ad the detector. Chloroform was used as the eluent. Narrow-polydispersity polystyrene samples were used for calibration. The average molecular weights were converted from calibration against polystyrene samples to the polymers under study using standard formulas for PMMA.³³

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