Efficient catalytic systems based on paramagnetic *closo*-ruthenacarboranes for the controlled synthesis of polymers*

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Novel catalytic systems were proposed for controlled radical polymerization of vinyl monomers. These systems are based on the paramagnetic (17-electron) *closo*-complex, namely, 3,3-(dppb)-3-Cl-*closo*-3,1,2-$RuC_2B_9H_{11}$ (**1**, dppb is 1,4-bis(diphenylphosphino)butane) and its mono(*P*-phenylene)- and di(*P*,*P*-*ortho*-phenylene)cycloboronated derivatives, namely, [3-Cl-3,3,8-{$Ph_2P(CH_2)_4PPh$-μ-(C_6H_4-*o*)}-1,2-R_2-*closo*-3,1,2-$RuC_2B_9H_n$] (R = H, *n* = 10 (**2**); R = Me, *n* = 8 (**3**)) and [3-Cl-3,3,7,8-{$Ph_2P(CH_2)_4P$-μ-(C_6H_4-*o*)$_2$}-*closo*-3,1,2-$RuC_2B_9H_9$] (**4**). With the polymerization of methyl methacrylate as an example, the effect of the steric hindrances in complexes **1**—**4** on the synthesis and molecular-weight characteristics of the resulting polymers was analyzed. In the presence of aliphatic amines, the polymerization rate increases substantially and the catalyst concentration can be lowered without losing control of the process. The structure of 17-electron complex **3** in the solid state and its paramagnetic nature were confirmed by X-ray diffraction and ESR spectroscopy.

Key words: controlled radical polymerization, poly(methyl methacrylate), paramagnetic *closo*-ruthenacarboranes, 1,4-bis(diphenylphosphino)butane, *tert*-butylamine, X-ray diffraction analysis, ESR spectroscopy, MALDI-TOF mass spectrometry.

Preparation of polymers with desired molecular-weight characteristics, which largely influence their physicochemical properties, is a key problem of synthetic polymer chemistry. At present, the most efficient tool for its solution is controlled radical polymerization (CRP).[1—6] The CRP concept allows step-by-step chain propagation, thus opening up wide scope for macromolecular design (including the synthesis of block copolymers and nanosized polymer structures).

Various methods and approaches are currently used for CRP implementation. Among them, reversible inhibition with nitroxyl radicals is best studied.[3,7,8] Degenerate chain transfer agents[4,9—11] and systems based on transition metal complexes,[1,2,12—14] which can regulate free-radical polymerization by reversible transfer of a halogen atom, are also very efficient. The latter approach (atom transfer radical polymerization, ATRP) has been most actively developed in the last few years.

The ATRP process, which follows the atom transfer mechanism, can be catalyzed by systems based on complexes of ruthenium,[2,13,15—17] copper,[1,18,19] iron,[20,21] osmium,[18] and some other transition metals. According to modern theoretical concepts, efficient catalysts for ATRP reactions should rapidly and reversibly transfer the terminal halogen atom from a dormant polymer chain to the metal atom, which depends on the electron density at the metal center.[12—14]

Examples of such catalysts include ruthenium complexes with dicarbollyl η^5-{C_2B_9} ligands, which can act as electron donors and stabilize metals in their high oxidation states.[22] Earlier,[23—25] it has been noted that these complexes are highly efficient in atom transfer radical polymerization of a wide range of vinylic monomers and

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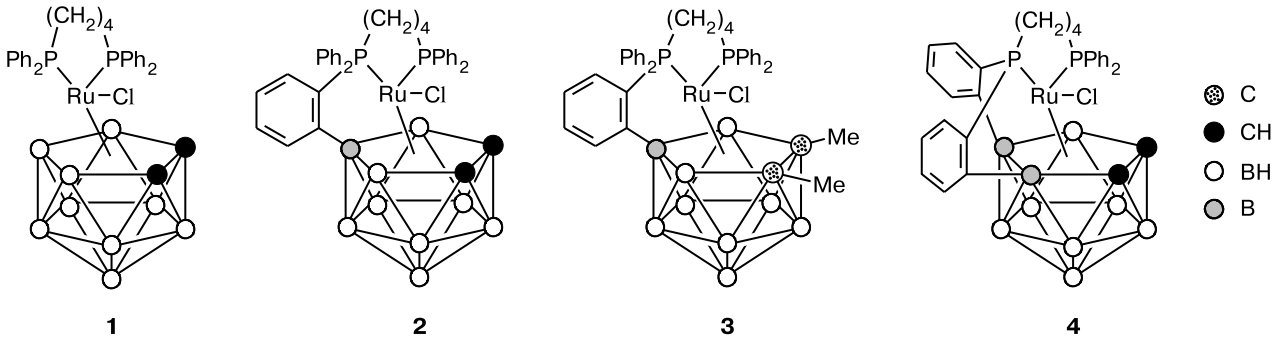


1 **2** **3** **4**

found that the catalytic activity of *closo*- or *exo-nido*-ruthenacarboranes in the ATRP process largely depends on both the ligand environment and oxidation state of the ruthenium atom.[24]

In the present work, we propose a number of paramagnetic (17-electron) carborane complexes of Ru^{III} (**1**—**4**) as promising catalysts for controlled radical polymerization.

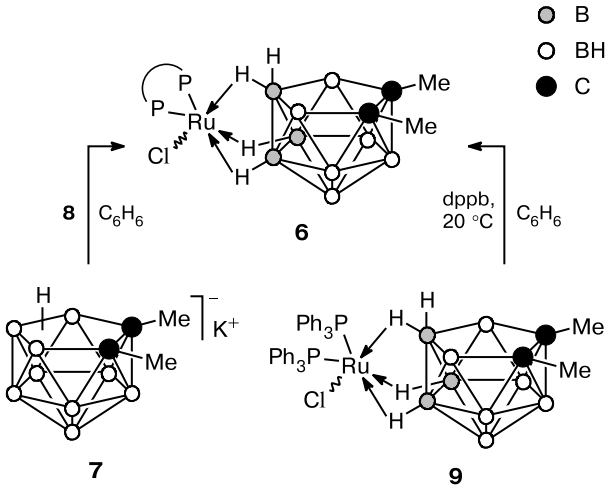
Results and Discussion

Synthesis of paramagnetic *closo*-ruthenacarboranes 1—4. Recently,[26] we have described the synthesis of paramagnetic *closo*-ruthenacarboranes **1** and **2** from the diamagnetic 18-electron complex 3,3-(dppb)-3-H-3-Cl-*closo*-3,1,2-$RuC_2B_9H_{11}$ (**5**) in boiling benzene in the presence of CCl_4 as a radical initiator; thermolysis of complex **1** in toluene at 95 °C also yields complex **2**. Di(*P*,*P*-*ortho*-phenylene)cycloboronated complex **4** can be obtained by thermolysis of complex **1** or **2** under more drastic conditions (toluene, 110 °C);[26] its structure has been confirmed by X-ray diffraction.

Thermolysis was also used for the synthesis of the paramagnetic mono(*P*-*ortho*-phenylene)cycloboronated complex [3-Cl-3,3,8-{$Ph_2P(CH_2)_4PPh$-μ-(C_6H_4-*o*)}-1,2-$(CH_3)_2$-*closo*-3,1,2-$RuC_2B_9H_8$] (**3**); however, the starting reagent was *exo*-5,6,7-[RuCl-($Ph_2P(CH_2)_4PPh_2$)]-5,6,10-(μ-H_3)-10-H-7,8-$(CH_3)_2$-*nido*-7,8-$C_2B_9H_6$ (**6**) with an *exo-nido*-structure. Complex **6** as a mixture of isomers (see below) can be prepared in two ways: here we employed a direct reaction[27] of K[7,8-$(CH_3)_2$-*nido*-7,8-$C_2B_9H_{10}$] (**7**) with $Cl_2Ru(PPh_3)$-(dppb) (**8**) (81% yield); earlier,[28] the PPh_3 ligands in the known C,C′-dimethylated complex *exo*-5,6,7-[$RuCl(PPh_3)_2$)]-5,6,10-(μ-H_3)-10-H-7,8-$(CH_3)_2$-*nido*-7,8-$C_2B_9H_6$ (**9**)[29] were replaced by dppb (Scheme 1).

Complex **6** was characterized by ^1H and $^{31}P\{^1H\}$ NMR spectra; its composition was confirmed by elemental analysis data (see Experimental). The ^1H NMR spectrum of complex **6** shows high-field multiplets for the B—H...Ru bonds of the symmetric (s) and asymmetric isomers (as) (s : as ≈ 2 : 1) and a signal for the bridging "extra"-H atom

Scheme 1



from both isomers. Because complex **6** is extremely poorly soluble even in CD_2Cl_2 and the low-intensity multiplets for the dppb ligand are superimposed, we failed to assign them to the s- and as-isomers of the complex. The $^{31}P\{^1H\}$ NMR spectrum of complex **6** is more informative: it contains a distinct signal at δ 54.5 (s-isomer) and two weaker signals at δ 58.5 and 50.5 (as-isomer).

Like other C,C′-disubstituted ruthenium *exo-nido*-complexes,[27,30] complex **6** in hot benzene does not undergo isomerization into the corresponding 18-electron *closo*-product 3,3-(dppb)-3-H-3-Cl-1,2-$(CH_3)_2$-*closo*-3,1,2-$RuC_2B_9H_9$. However, when heated in toluene at 95—97 °C, complex **6** eliminates the hydride ligand to give paramagnetic complex **3**, which was isolated from the reaction mixture as the only metal-containing compound in 34% yield.

The structure and geometry of complex **3** in the solid state were determined by X-ray diffraction (its molecular structure is shown in Fig. 1; selected bond lengths and bond angles are listed in Table 1).

The Ru atom in structure **3** has a pseudooctahedral 17-electron configuration; its formal oxidation state is +3. Its hexacoordinate state involving the doubly charged (2–)

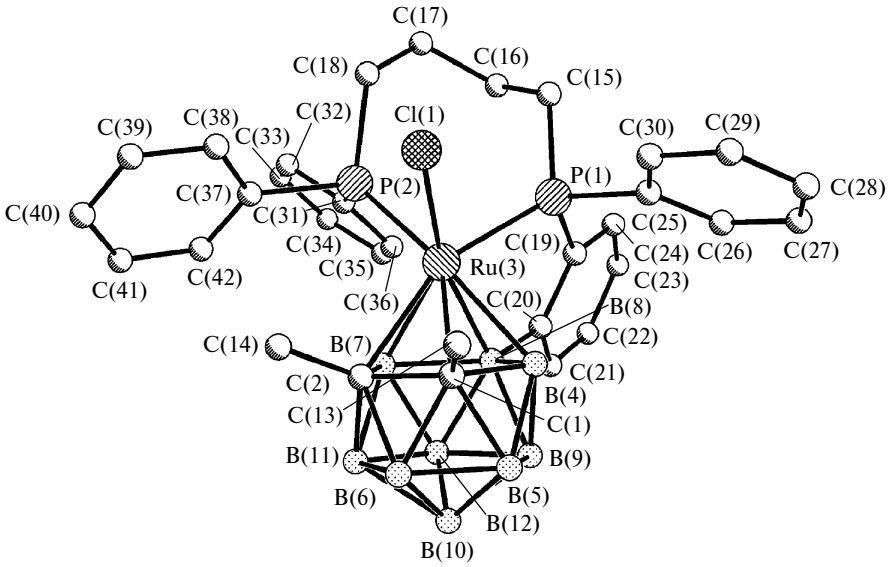


Fig. 1. Molecular structure of complex **3**.

dicarbollide dianion, the singly charged (1–) chloride anion, and the neutral diphosphine ligand agrees well with this conclusion. The distinctive feature of structure **3** is the mono(*P-ortho*-phenylene)cycloboronated diphosphine ligand coordinated to the metal atom in a bidentate fashion. The presence of bridging *ortho*-cycloboronated fragment in complex **3** accounts for the observed difference in the Ru—P(1) and Ru—P(2) bond lengths (2.3114(12) Å and 2.4043(11) Å, respectively). In turn, the electron deficiency of the metal makes the Ru—Cl bond appreciably shorter (2.3897(11) Å); note that this bond in complex **4** is also shortened: 2.3853 and 2.3723 Å for two independent structures.[26] In structurally similar 18-electron *closo*-ruthenacarboranes, the Ru—Cl bond is substantially longer: 2.4284 Å in the neutral complex 3,3-$(PPh_3)_2$-3-H-3-Cl-*closo*-3,1,2-$RuC_2B_9H_{11}$[31] and 2.515 Å and 2.452 Å in the anionic complexes $[3,3\text{-}L_2\text{-}3\text{-}Cl\text{-}3,1,2\text{-}RuC_2B_9H_{11}]^-$ $[Cat]^+$ (L = PPh_3, Cat = Et_4N[32] and L = CO, Cat = = $Au(PPh_3)_2$,[33] respectively). At the same time, the distance between the Ru atom and the pentagonal plane C_2B_3 of the carborane ligand are sufficiently close in all these complexes.

The paramagnetic nature of complex **3** was confirmed by its ESR spectrum recorded in the CH_2Cl_2—toluene matrix at 150 K (Fig. 2). The anisotropic ESR spectrum of complex **3** shows a rhombic symmetry of the *g* tensor, which is typical of ruthenium complexes with the pseudo-octahedral configuration of the metal atom.[34,35] The values of three components of the *g* factor are very close to those for carborane-unsubstituted complex **2** (g_1 = 2.385, g_2 = = 2.095, and g_3 = 1.972)[26] also containing the *ortho*-cycloboronated bridge. This fact suggests that the configuration of the metal atom in complex **3** is virtually unaffected by the presence of the substituents in the carborane ligand.

Comparison of the catalytic activities of paramagnetic complexes 1—4 in the controlled synthesis of poly(methyl methacrylate). According to preliminary data,[26] paramagnetic complexes **1**, **2**, and **4** in combination with CCl_4 are

Table 1. Selected geometrical parameters in structure **3**

Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
Ru(3)—P(1)	2.3114(12)	Ru(3)—B(4)	2.242(5)	B(8)—Ru(3)—P(1)	80.40(13)
Ru(3)—P(2)	2.4043(11)	Ru(3)—B(7)	2.209(5)	P(1)—Ru(3)—P(2)	91.10(4)
Ru(3)—Cl(1)	2.3897(11)	Ru(3)—B(8)	2.232(5)	P(1)—Ru(3)—Cl(1)	91.34(4)
Ru(3)—C(1)	2.306(4)	P(2)—C(18)	1.841(5)	C(20)—C(19)—P(1)	114.10(3)
P(1)—C(15)	1.822(5)	P(2)—C(31)	1.834(4)	C(18)—P(2)—Ru(3)	116.61(15)
P(1)—C(19)	1.822(4)	P(2)—C(37)	1.833(4)	C(15)—P(1)—Ru(3)	122.22(16)
P(1)—C(25)	1.831(4)	C(16)—C(17)	1.521(6)	P(2)—Ru(3)—Cl(1)	85.74(4)
C(1)—C(2)	1.632(6)	C(17)—C(18)	1.541(6)	C(18)—C(19)—B(8)	119.10(4)
C(15)—C(16)	1.538(6)	C(1)—C(13)	1.522(6)		
C(20)—B(8)	1.581(7)	C(2)—C(14)	1.508(6)		
Ru(3)—C(2)	2.320(4)				

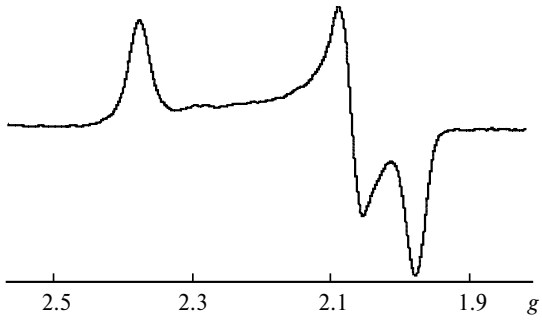


Fig. 2. Anisotropic ESR spectrum of complex **3** in the toluene—CH_2Cl_2 matrix at 150 K; $g_1 = 2.376$, $g_2 = 2.070$, $g_3 = 1.978$.

catalytically more active than 18-electron diamagnetic complex **5** in the controlled synthesis of poly(methyl methacrylate) (PMMA); the resulting polymers have low polydispersity indices (M_w/M_n = 1.15—1.17). Our present comparative study revealed that paramagnetic complexes **1**, **2**, and **4** in the bulk polymerization of methyl methacrylate (MMA) at 80 °C are also superior to complex **3** containing the C,C′-dimethylated ligand. For instance, the polydispersity index of PMMA obtained in the presence of complex **3** is 1.36, while M_w/M_n = 1.15 for its unsubstituted analog **2** (Table 2). Undoubtedly, this effect is due to the spatial shielding of the central metal atom by two methyl groups of the ligand, which precludes the approach of a growing macroradical and the reversible activation/deactivation of growing polymer chains.

It should be noted that complex **2** is the most stable in solution among all the complexes under consideration at both room and elevated temperatures, as well as in the presence of free radicals in the system. For this reason, we used this paramagnetic *closo*-ruthenacarborane for a more detailed kinetic study of the ATRP process with the polymerization of MMA as an example.

We found out that the bulk polymerization of MMA in the presence of complex **2** and CCl_4 as a radical initiator proceeds uniformly without autoacceleration (Fig. 3, *a*), which is a specific feature of ATRP processes.[1,2,5] However, the monomer conversion *P* under these conditions does not exceed 70% in 200 h. The molecular weight of polymer samples increases linearly with *P* (Fig. 3, *b*), which also confirms the controlled mode of the polymerization process.[12,13] The polydispersity indices of the PMMA samples are nearly 1.2 and shows a decline as *P* increases. Interestingly, the molecular weights of the PMMA samples monotonically increase from zero, as in a controlled process characterized by simultaneous stepwise propagation of all polymer chains.

To confirm the controlled mode of the polymerization, we carried out postpolymerization of MMA in the presence of complex **2** on a macroinitiator prepared with the use of the same catalyst (Fig. 4, *a*). We found that the

Table 2. Polymerization of MMA in the presence of CCl_4 and ruthenacarboranes **1**—**4***

Complex	Conversion (%)	M_n	M_w	M_w/M_n
1**	66.8	18800	21900	1.17
2**	58.4	15700	18000	1.15
3	53.3	23000	31200	1.36
4**	62.4	14700	17000	1.16

* Conditions: the concentrations of the *closo*-ruthenacarboranes and CCl_4 are 0.125 and 0.25 mol.%, respectively; 80 °C, 80 h.
** The data from Ref. 26.

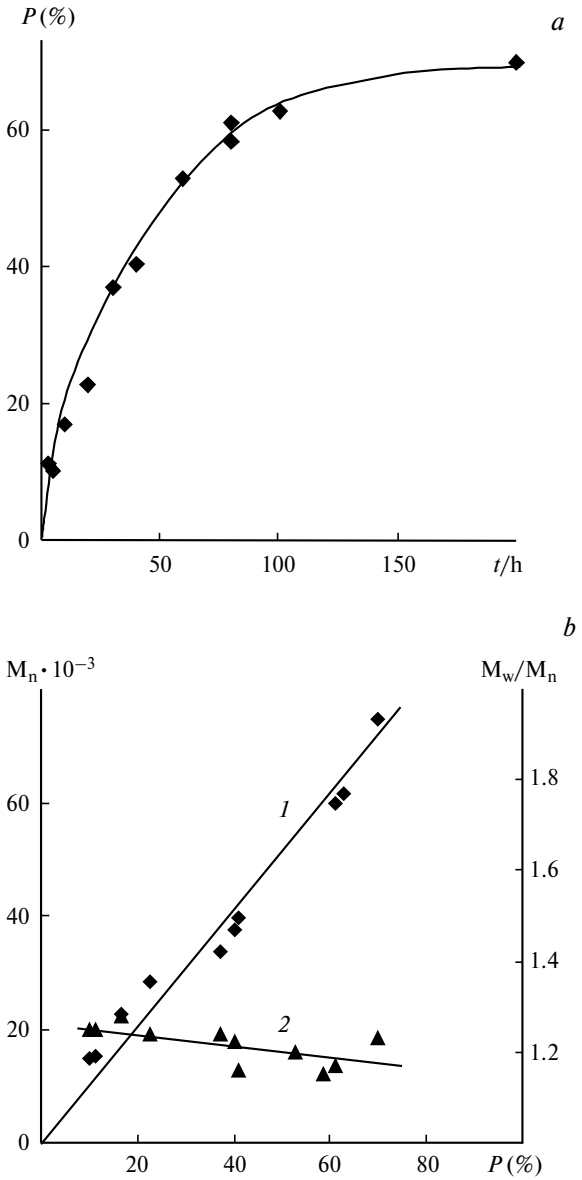


Fig. 3. Polymerization of MMA in the presence of complex **2** (0.125 mol.%) and CCl_4 (0.25 mol.%) at 80 °C: (*a*) the plot of the conversion *P vs.* the polymerization time *t*; (*b*) the plots of M_n (*1*) and the polydispersity index (*2*) *vs.* the conversion *P*.

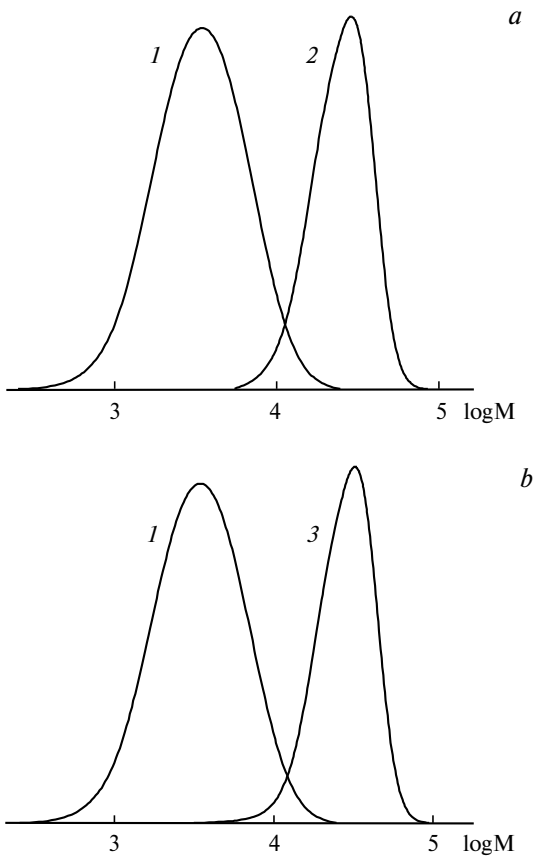


Fig. 4. Shifts of the molecular weight distribution curves of the polymer samples subjected to postpolymerization (*a*) and block copolymerization (*b*): prepolymer (*1*) (macroinitiator), postpolymer (*2*), and block copolymer (3).

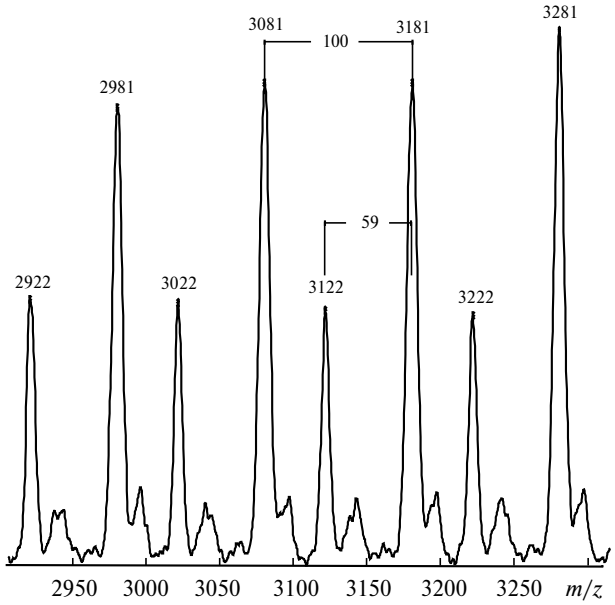


Fig. 5. Fragment of the mass spectrum of PMMA obtained at 80 °C in the presence of complex **2** and CCl_4.

postpolymerization increases the molecular weight of PMMA. For instance, starting from a macroinitiator with M_n = 3000 and M_w/M_n = 1.50, we obtained a postpolymer with M_n = 25 600 and M_w/M_n = 1.17. As noted above, the narrowing of the molecular weight distribution (MWD) is characteristic just of "living" polymerization processes.[1,5] Replacement of MMA at the second step of the process by a different monomer (butyl methacrylate) led to the formation of a block copolymer. The distinct shift of the MWD curve to the higher molecular weights and the low polydispersity index of the resulting block copolymer suggests few "dead" chains and the rapid initiation of the postpolymerization (Fig. 4, *b*).

Another solid piece of evidence for the controlled mode of the polymerization in the presence of paramagnetic *closo*-ruthenacarboranes emerged from a MALDI-TOF MS study of the polymers obtained (Fig. 5). The spectrum shows two series of peaks spaced at 100 Da, which corresponds to the molecular weight of MMA. The absolute values of the molecular weights of the observed peaks agree well with the theoretically calculated ones. Under the assumption that the polymerization of MMA under these conditions indeed follows the atom transfer mechanism, the mass of the fragmentation ion should consists of the mass of the CCl_3 group in the "head" of the macromolecule, the mass of the Cl atom at the second end of a dormant chain, the mass of the monomer units, and the mass of the sodium cation used for ionization of the polymer. For instance, the molecular weight of a macromolecule consisting of 30 monomer units will be

$$3 \cdot 35.5 + 12 + 30 \cdot 100.1 + 35.5 + 23 = 3180.$$

The spectrum shows a peak at m/z = 3181, which corresponds to the weight calculated above. The second series of peaks differs from the first one by 59 Da. This difference agrees well with the average (with allowance for the ratio of Cl isotopes) molecular mass of NaCl (58.5). Thus, laser-excited macromolecules eliminate the terminal Cl atom, which is usually observed for polymers obtained by atom transfer polymerization.[36] The presence of the terminal halogen atom in macromolecules confirms that the polymerization process generally follows the ATRP mechanism and agrees with the proven possibility of using the polymers obtained as macroinitiators.

To propose an accurate mechanism for the polymerization of MMA in the presence of complex **2** and CCl_4, we found it essential to determine the structure of the ruthenium catalyst isolated from the reaction mixture. For this purpose, the mother liquor left after the precipitation of PMMA and containing the ruthenium complex was distilled *in vacuo* at ≤30 °C. Column chromatography of the solid residue on silica gel followed by its crystallization from CH_2Cl_2—*n*-hexane gave a red crystalline solid.

According to TLC data and the ESR spectrum (the anisotropic spectrum with $g_1 = 2.385$, $g_2 = 2.097$, and $g_3 = 1.974$), the solid is the starting complex **2**. Therefore, this complex is an actual catalyst for the "living" chain polymerization of MMA.

Controlled free-radical polymerization in the presence of transition metal complexes has a serious drawback limiting its commercial use: the resulting polymers are contaminated with the catalyst and should be additionally purified. This negative effect can be reduced by, *e.g.*, development of catalytic systems that could take an efficient control of the process when used in small amounts. The use of less amounts of the catalyst is of both ecological and economic importance because expensive metal-containing materials can thus be spared.

It is known that aliphatic amines are efficient promoters of ruthenium complexes and substantially increases the rate of controlled radical polymerization.[18,25,37] Indeed, our experiments showed that addition of Bu^tNH_2 as a cocatalyst for complex **2** increases the polymerization rate without losing control of the process (Fig. 6).

The polymerization of MMA in the presence of the catalytic system **2**—Bu^tNH_2 proceeds rapidly and uniformly with a high MMA conversion *P*. With an increase in *P*, the molecular weights of PMMA samples increase and their polydispersity indices decrease. This system provides a much higher (by an order of magnitude) polymerization rate and a narrow MWD of the resulting polymer ($M_w/M_n < 1.2$).

Addition of amines as promoters to paramagnetic carborane complexes of Ru^{III} allows controlled polymerization even when the concentration of the catalyst is low-

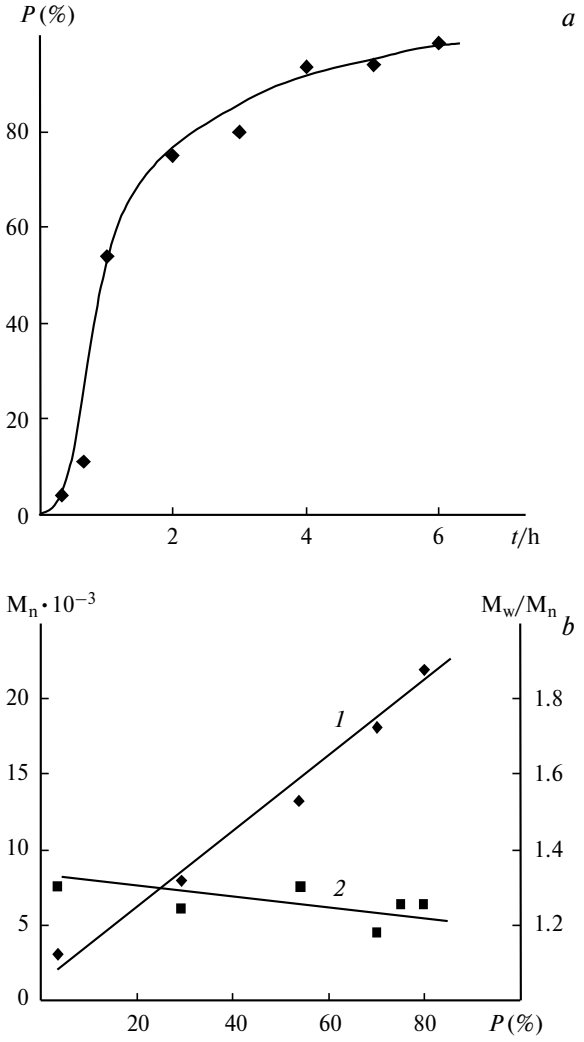


Fig. 6. Polymerization of MMA in the presence of complex **2** (0.125 mol.%), CCl_4 (0.25 mol.%), and Bu^tNH_2 (0.05 mol.%) at 80 °C: (*a*) the plot of the conversion *P vs.* the polymerization time *t*; (*b*) the plots of M_n (*1*) and the polydispersity index (*2*) *vs.* the conversion *P*.

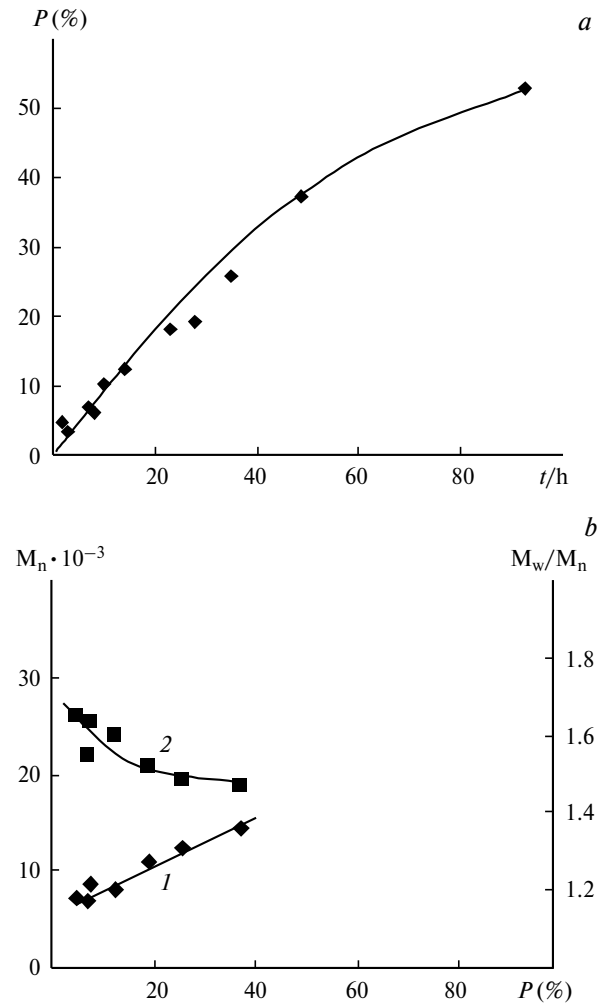


Fig. 7. Polymerization of MMA in the presence of complex **2** (0.012 mol.%), CCl_4 (0.25 mol.%), and Bu^tNH_2 (0.05 mol.%) at 80 °C: (*a*) the plot of the conversion *P vs.* the polymerization time *t*; (*b*) the plots of M_n (*1*) and the polydispersity index (*2*) *vs.* the conversion *P*.

ered by an order of magnitude (0.0125 mol.%), although this decreases the polymerization rate. For instance, the MMA conversion in the case of catalyst **2** did not exceed 60% in 100 h (Fig. 7, *a*). At the same time, the polydispersity index of the polymer obtained under these conditions is 1.3—1.6 (Fig. 7, *b*). As noted above, the decrease in the polydispersity index and the increase in the molecular weight of PMMA with an increase in *P* is characteristic of "living" chain polymerization processes.

The MMA polymerization rate at low concentrations of the catalyst can be increased by using the amine in a concentration of 0.5 mol.% (Fig. 8). It can be seen in Fig. 8 that at this concentration of the amine, the controlled synthesis of PMMA proceeds with a nearly 100% conversion of the monomer in 25 h and the resulting polymers have sufficiently narrow MWD ($M_w/M_n \approx 1.3$). The molecular weight of the polymer increases linearly with *P*, which suggests step-by-step chain propagation.

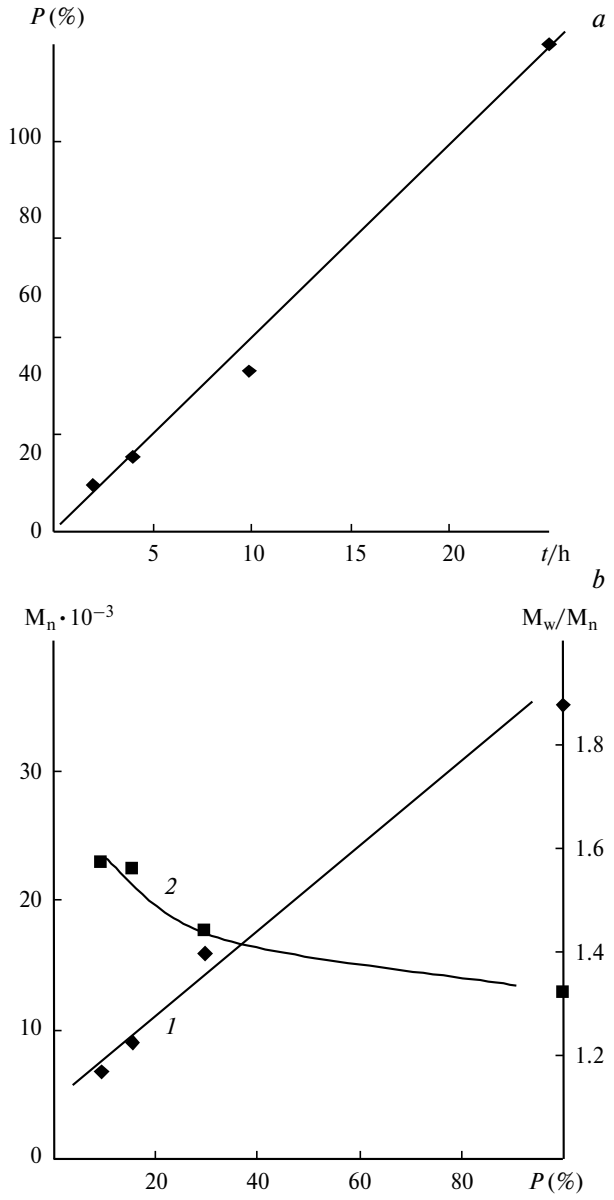


Fig. 8. Polymerization of MMA in the presence of complex **2** (0.012 mol.%) and Bu^tNH_2 (0.5 mol.%): (a) the plot of the conversion *P vs.* the polymerization time *t*; (*b*) the plots of M_n (*1*) and the polydispersity index (*2*) *vs.* the conversion *P*.

The following conclusions can be drawn from our experimental data: (a) the paramagnetic *closo*-metallacarborane complexes of Ru^{III} under study are efficient catalysts for the Atom Transfer Radical Polymerization of MMA; (b) the steric hindrances presented by the substituents at the carbon atoms in the *nido*-$\{C_2B_9\}$ ligand negatively affect the controlled polymerization; (c) addition of amines (*e.g.*, Bu^tNH_2) substantially increases the rate of MMA polymerization without losing control of this process.

Catalytic systems containing paramagnetic *closo*-ruthenacarboranes and amines can successfully be used in ATRP even at concentrations of the Ru^{III} catalyst at a level of several one-hundredths percent.

Experimental

closo- and *exo-nido*-Ruthenacarboranes were obtained under argon in anhydrous solvents prepared according standard procedures.[38,39] Products were isolated and purified by column chromatography on ACROS silica gel (0.035—0.070 mm). The anisotropic ESR spectrum of complex **3** was recorded in the frozen CH_2Cl_2—toluene matrix at 150 K on a Bruker-EMX radio spectrometer (~9.75 GHz). The *g* factors are referenced to diphenylpicrylhydrazyl ($g = 2.0037$). Elemental analysis of novel complexes was carried out at the Microanalysis Laboratory of the A. N. Nesmeyanov Institute of Organoelement Compounds (Russian Academy of Sciences).

Synthesis of *exo*-chloro[1′,4′-bis(diphenylphosphino)butane]-*nido*-[7,8-dimethyl-10-hydro-7,8-dicarbaundecaborane-5,6,10-tris(hydrido)]ruthenium (6, a mixture of symmetric (s) and asymmetric isomers (as)). ***A.*** A mixture of complex **8** (0.1 g, 0.117 mmol)[40] and the K^+ salt **7** (0.025 g, 0.125 mmol) in benzene (10 mL) was stirred at 22 °C for 3.5 h until the dark green solution turned yellowish orange with partial precipitation of poorly soluble complex **6** as a powder. The reaction mixture was concentrated *in vacuo*, dissolved in CH_2Cl_2 (50 mL), and filtered through a folded paper filter. The solution was concentrated by half, diluted with *n*-hexane, and chromatographed on silica gel with CH_2Cl_2—*n*-hexane as an eluent. The collected yellowish orange fraction was concentrated and dried *in vacuo* to give analytically pure complex **6** (0.068 g, 81%) as a yellow powder; the ratio of s- and as-isomers was 2 : 1. Found (%): C, 52.84; H, 5.94; P, 8.50. $C_{32}H_{44}B_9ClP_2Ru$. Calculated (%): C, 53.06; H, 6.08; P, 8.56. ^{1}H NMR (600.22 MHz, CD_2Cl_2), δ: 7.85—7.20 (m, Ph, s + as); 3.56, 3.42, 3.35, 2.46, 2.40, 2.03, 1.97, 1.50 (all br.m, $Ph_2PCH_2CH_2CH_2CH_2PPh_2$, s + as); 1.45 (s, CH_3, as); 1.41 (s, CH_3, s + as); −1.07 (m, H_{extra}, s); −1.51 (q**, H_{extra}, as); −3.54, −6.03 (both m, as); −4.23 (m, s); −15.72 (m, as); −17.22 (m, s); the assignment of the signals to the s- and as-

* Virtual.

isomers of complex **6** was performed only for the signals in the hydride range and for the Me substituents in the carborane. $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2), δ: 57.8, 52.2 (both br.m, as); 53.9 (br.s, s).

B. A solution of dppb (0.02 g, 0.05 mmol) in C_6H_6 (10 mL) was added to a suspension of *exo-nido*-complex **9** (0.035 g, 0.04 mmol) in C_6H_6 (10 mL). The reaction mixture was stirred with a magnetic stirring bar at room temperature for 24 h until the starting complex was consumed completely (TLC, CH_2Cl_2—*n*-hexane (1 : 1)). The solvent was removed *in vacuo*. The yellowish orange powdery residue was dissolved in CH_2Cl_2 (~30 mL) and chromatographed on silica gel with CH_2Cl_2—*n*-hexane (1 : 1) as an eluent. The product obtained was crystallized from CH_2Cl_2—*n*-hexane (1 : 1) to give complex **6** (0.025 g, 86%) consisting of s- and as-isomers in a ratio of 2.5 : 1 ($^{31}P\{^1H\}$ NMR).

Synthesis of 3-chloro-1,2-dimethyl-3,3-{[1′,1′,6′-triphenyl-6′-(6′,8-μ-(*ortho*-phenylene)]-1′,6′-diphosphahexane}-*closo*-3,1,2-dicarbollylruthenium (3). A solution of *exo-nido*-complex **6** (0.07 g, 0.01 mmol) in freshly distilled toluene (15 mL) was heated in an inert atmosphere at 95—97 °C for 8 h until the starting complex was consumed completely (monitoring by TLC). The solvent was removed *in vacuo*. The residue was chromatographed on silica gel with benzene—*n*-hexane (2 : 1) as an eluent. The collected dark red fraction was concentrated and the residue was recrystallized from CH_2Cl_2—*n*-hexane. The yield of analytically pure complex **3** was 0.024 g (34%). Found (%): C, 50.74; H, 5.60. $C_{32}H_{41}B_9ClP_2Ru \cdot 0.5CH_2Cl_2$. Calculated (%): C, 51.10; H, 5.50. ESR (toluene—CH_2Cl_2, 150 K, g_{stand} = = 2.0037): g_1 = 2.376, g_2 = 2.070, g_3 = 1.978. The purity of complex **3** was additionally confirmed by HPLC (Separon SGX column, CH_2Cl_2—*n*-hexane (1 : 3)). The chromatogram showed a single peak with a retention time of 2.08 min.

Polymerization of MMA was carried out in sealed glass tubes. Methyl methacrylate was pretreated with 10% aqueous NaOH to remove the inhibitor, washed with distilled water to a neutral reaction, dried over anhydrous $CaCl_2$, and distilled *in vacuo*. A fraction with b.p. 38 °C (15 Torr)[41] was collected. When the concentration of the catalyst was 0.125 mol.%, precise amounts of the Ru^{III} complex, MMA, and 0.1 *M* CCl_4 in toluene were placed in each tube. The tubes were frozen in liquid nitrogen, degassed three times to a residual pressure of about 1.3 Pa, and sealed. Polymerization was carried out at a strictly fixed temperature (80 °C) for a given period of time. To interrupt the polymerization, the tubes were frozen and the polymer obtained was precipitated with light petroleum. To purify the polymer from the residual amounts of the monomer, the promoter, and the catalyst, the PMMA samples were dissolved in $CHCl_3$, precipitated with light petroleum twice, and dried *in vacuo* to a constant weight. Then the monomer conversion was calculated. When polymerization was carried out in the presence of Bu^tNH_2, the amine was preliminarily dissolved in the monomer and added to the system in a dosed amount. When the concentration of the catalyst was 0.013 mol.%, the components of the system (catalyst, monomer, amine, and promoter) were mixed in a separate flask. The resulting mixtures were placed in glass tubes, the tubes were sealed, and the polymerization was initiated.

Analysis of PMMA samples. The molecular weight (MW) and molecular weight distribution (MWD) of the polymers obtained were determined by gel permeation chromatography on a Knauer setup with a two-column cascade (Phenomenex Phenogel, pore size 10^3—10^5 Å) and an RI Detektor K-2301 differential refractometer as a detector. Tetrahydrofuran was used as an eluent. The setup was calibrated against narrow-distributed standards based on PMMA. Chromatograms were interpreted with the ChomGate program. The polymers were also examined by MALDI-TOF mass spectrometry on a Bruker Microflex LT instrument in the linear mode. *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) was employed as a matrix. PMMA samples were prepared as follows. Equal volumes of a solution of PMMA (10 mg mL^{-1}) in THF and a solution of DCTB in THF (20 mg mL^{-1}) were mixed and then sodium trifluoroacetate was added. The resulting solution (1 μL) was applied to a stainless steel target plate and irradiated for recording a MALDI-TOF spectrum.

X-ray diffraction study of complex 3. The crystals of complex **3** ($C_{32}H_{41}B_9ClP_2Ru \cdot 0.5C_6H_{14}$, M = 764.48) are orthorhombic, space group *Pbca*; at 100 K, a = 17.373(2) Å, b = 14.155(1) Å, c = 30.711(3) Å, V = 7552(1) Å^3, Z = 8, d_{calc} = 1.345 g cm^{-3}, μ(Mo-Kα) = 5.96 cm^{-1}. The crystals were obtained by slow evaporation of a solution of complex **3** in benzene—hexane. The intensities of 91 868 reflections (7384 independent reflections, R_{int} = 0.1665) were measured on a Bruker SMART APEX II diffractometer with an area detector[42] (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, ω scan mode, $2\theta_{max}$ = 52°, T = 100 K). An absorption correction was applied semiempirically with the SADABS program.[43] The structure was solved by the direct methods and refined anisotropically (for all non-hydrogen atoms) by the full-matrix least-squares method on F^2_{hkl}. The hydrogen atoms of the carborane fragment were located from difference electron-density maps; the other H atoms were located geometrically. All the hydrogen atoms were refined using a riding model. Final residuals are R_1 = 0.0439 (on F_{hkl} for 4422 reflections with $I > 2\sigma(I)$), wR_2 = 0.1143, and S = 1.009 (on F^2_{hkl} for all independent reflections). All PC-assisted calculations were performed with the SHELXTL program package.[44] Comprehensive tables of the atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters have been deposited with the Cambridge Crystallographic Data Center.

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