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Novel ruthenium(II) and (III) carborane complexes with diphosphine ligands and their application in radical polymerization*

I. D. Grishin,* N. A. Knyazeva, and A. M. Penkal′

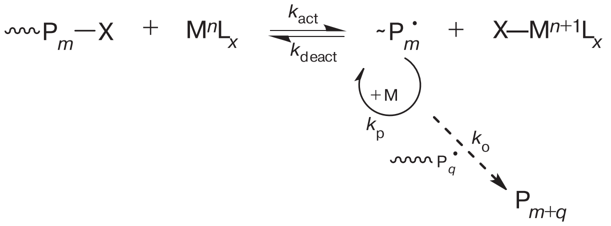
N. I. Lobachevsky National Reseach State University of Nizhny Novgorod,
23 prosp. Gagarina, 603950 Nizhny Novgorod, Russian Federation.
Fax: +7 (831) 462 3550. E-mail: grishin_i@ichem.unn.ru

Ruthenium(II) and (III) carborane complexes containing XantPhos as a ligand were synthesized for the first time. It was shown that the reaction of the known complex *exo*-5,6,10-[Cl(Ph_3P)$_2$Ru]-5,6,10-(μ-H)$_3$-10-*H*-*nido*-7,8-$C_2B_9H_8$ with a 10% molar excess of XantPhos in benzene at 80 °C leads to a new *closo*-ruthenacarborane 3-Cl-3,3-[$\varkappa^2$-XantPhos]-*closo*-3,1,2-$RuC_2B_9H_{11}$, which can be easily converted to the corresponding acetonitrile complex 3-CH_3CN-3,3-[$\varkappa^2$-XantPhos]-*closo*-3,1,2-$RuC_2B_9H_{11}$ by the reaction with isopropylamine in a dichloromethane—acetonitrile solvent mixture at 40 °C. These compounds, as well as previously synthesized ruthenium(II) carborane complexes, were used as a basis for new catalyst systems allowing to conduct controlled radical polymerization at high rates even at low catalyst loading. The specific features of methyl methacrylate polymerization under the action of the indicated catalyst systems were considered and the mechanism of the process was investigated.

Key words: methyl methacrylate, XantPhos, ruthenacarboranes, amines, controlled radical polymerization, MALDI mass spectrometry.

Atom transfer radical polymerization (ATRP) is a powerful tool for preparing homo- and copolymers with specified molecular weight characteristics, architecture, and properties.[1—8] This process is based on the reversible transfer of a halogen atom between a polymer chain and a transition metal complex, which is accompanied by single electron transfer and a change in the oxidation state of the metal (Scheme 1).

Scheme 1



The ATRP is distinguished by the procedural simplicity of implementation, as well as by a large library of monomers and initiators, which can be used to obtain macromolecules with a desired architecture. In contrast to two other known methods of controlled radical polymerization, namely, stable free-radical polymerization[9—12] and RAFT,[13,14] which require the introduction of stoichiometric amounts of regulating agents with respect to the initiator, ATRP in some cases allows the synthesis of macromolecules using metal complex catalysts at concentrations at the level of parts per million (ppm), thereby significantly reducing the cost of polymer production.[1]

Despite the fact that by now quite a number of catalyst systems for carrying out ATRP have been proposed, the development of new catalysts characterized by higher efficiency and stability under conditions of the process remains an important issue. According to modern concepts of the process of controlled radical polymerization,[1,2] a transition metal complex acting as a catalyst should be capable of reversible addition of a halogen atom, which is accompanied by the expansion of the coordination sphere and a change in the oxidation state of the metal (see Scheme 1). In this case, in order to avoid decomposition of the complex during polymerization, the metal atom must be strongly bonded to the ligands. Among the compounds meeting these requirements, we should mention the ruthenium carborane clusters.[15—17] The ability of this metal to form stable compounds in the oxidation states +2 and +3 in combination with the presence of a carborane ligand characterized by a double negative charge and spatial aromaticity with a delocalized electron density make ruthenacarboranes of various structures good candidates for the role of catalysts for the processes under

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consideration. The good stability of complexes with carborane ligands under conditions of polymerization allows the process to be carried out up to the high conversions of monomers.[18,19] It should be noted that metallacarboranes are successfully used as catalysts for cycloaddition reactions,[20] reduction of ketimines,[21,22] reductive amination,[23] metathesis,[24] and radical addition.[25]

As it is known,[8,26] the catalytic activity of a transition metal complex in the processes of organic synthesis and polymerization largely depends on the ligand environment. At the same time, even a seemingly insignificant change in the structure of a compound often leads to significant changes in its properties and catalytic activity. Previous studies on the use of ruthenium carborane complexes with diphosphine ligands in ATRP showed that the process control efficiency increases with an increase in the number of methylene units in the diphosphine chain and the ligand bite angle.[19,27] Therefore, the ligands with large bite angles should be considered as building blocks for the development of more efficient ATRP catalysts.

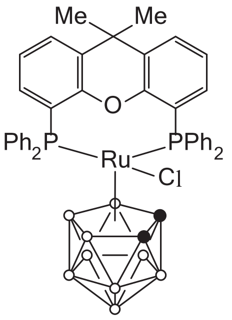
An example of the ligand meeting this criterion is XantPhos.[26,28] Complexes of transition metals with XantPhos are actively used in the catalysis of a wide range of processes of organic synthesis, which include hydrogenation,[29] cross-coupling,[30] dehydrogenation,[31] and dehydropolymerization[32] of aminoboranes and many other reactions.[28]

Recent studies of the catalytic activity of ruthenium(II) complexes in controlled radical polymerization showed that complexes with labile acetonitrile ligands are a promising catalysts for this process.[33] They are characterized by higher activity compared to their neutral chlorine-containing counterparts. Similar results were obtained in the study of the catalytic activity of ruthenium(II) cyclometallated derivatives.[34] Taking into account the foregoing, it is logical to suppose that new ruthenium(II) carborane complexes with nitrile ligands can be promising catalysts for atom transfer polymerization.[35,36]

In the present work, we obtained new ruthenium carborane complexes **1** and **2** with XantPhos as a chelating ligand and investigated the possibility of their use in the radical polymerization of methyl methacrylate (MMA). Besides, we carried out a comparative analysis of their catalytic activity in the synthesis of polymers with the activity of the known ruthenium phosphine complex **3** with XantPhos, as well as of the recently synthesized ruthenium carborane complexes **4—7** with diphenylphosphinobutane and nitrile ligands.

Results and Discussion

The main precursor for the synthesis of a wide range of ruthenium complexes is the well-known tris(triphenylphosphine)ruthenium dichloride.[37] The reaction of this compound with XantPhos leads to the substitution of two triphenylphosphine ligands[38] and the formation of complex **3**. An attempt to obtain a carborane complex of ruthenium with the XantPhos ligand by the reaction of complex **3** with $[K]^+[nido\text{-}7,8\text{-}C_2B_9H_{12}]^-$ in benzene according to the procedure used for obtaining derivatives of 1,4-(diphenylphosphino)butane (dppb)[39] was unsuccessful. This can be explained by the fact that, unlike dppb, XantPhos occupies three equatorial positions in the coordination sphere of ruthenium due to the presence of an oxygen



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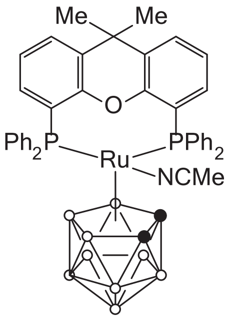

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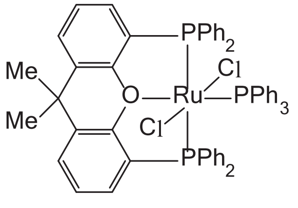

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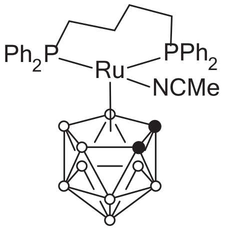

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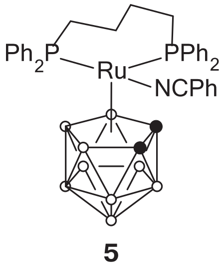

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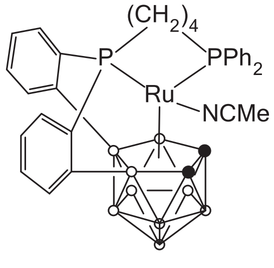

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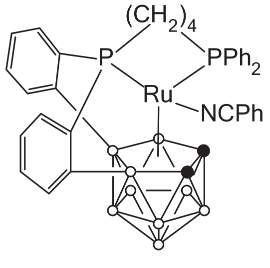

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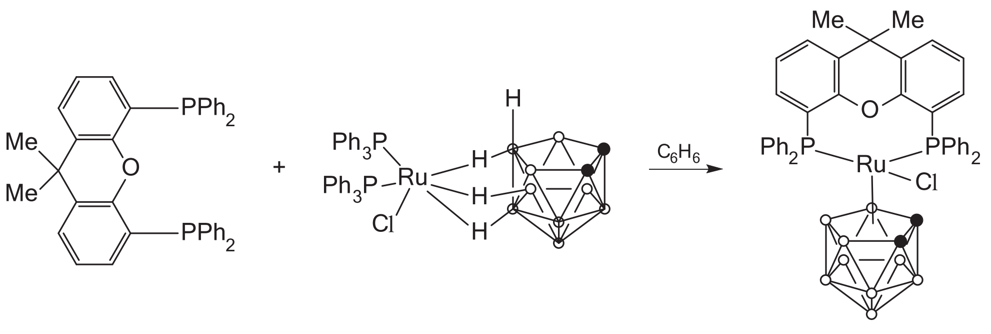
Scheme 2



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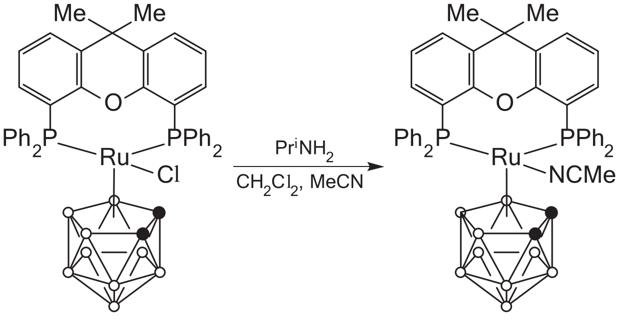
atom. This structure makes it impossible to form a bond with the carborane ligand, since this requires two vacant equatorial and one axial sites in the coordination sphere.

The reaction of the known[40] *exo-nido*-complex, *exo*-5,6,10-[Cl(Ph$_3$P)$_2$Ru]-5,6,10-(μ-H)$_3$-10-*H*-*nido*-7,8-C$_2$B$_9$H$_8$, with a 10% molar excess of XantPhos in benzene at 80 °C allowed us to isolate a new *closo*-ruthenacarborane complex, 3-Cl-3,3-[ϰ^2-XantPhos]-*closo*-3,1,2-Ru-C$_2$B$_9$H$_{11}$ (**1**), as a dark red crystalline substances in 43% yield (Scheme 2). The EPR results showed that complex **1** is a paramagnetic ruthenacarborane. The anisotropic spectrum recorded in a solid matrix (dichloromethane—toluene) contains three components with g_1 = 2.502, g_2 = 2.049, g_3 = 1.942. The spectrum pattern is typical of ruthenium complexes containing the metal in a pseudo-octahedral environment, and the values of g factor are very close to those for the previously investigated paramagnetic *closo*-ruthenacarboranes with chelate diphosphine ligands,[27,39] The MALDI mass spectrum of compound **1** recorded in the negative mode contains a peak from the molecular anion in the form of an envelope centered at m/z = 847.4 Da typical of such compounds and completely corresponding to the calculated isotope pattern. According to the results of previous studies,[41] the presence of an abundant peak from the molecular anion in the mass spectrum is typical of *closo* metallacarboranes characterized by a strong bond between the metal and the η^5-coordinated dicarbollide ligand, which suggests a *closo* structure for compound **1**.

The reduction of complex **1** with isopropylamine at 40 °C in a mixture of dichloromethane—acetonitrile according to the known procedure[34,35] allowed us to obtain complex **2** as a yellow crystalline substance (Scheme 3). Unlike its precursor, complex **2** is diamagnetic. The ^{31}P NMR spectrum contains one signal at δ 35.21, indicating the equivalence of the phosphorus atoms coordinated to ruthenium. The ^{1}H NMR spectrum exhibits the signals for the protons of the phenyl rings and the xanthene core, the protons at the carbon atoms of the carborane basket, as well as three singlets for the methyl groups of the ligand and the coordinated acetonitrile molecule. From the ^{1}H NMR spectroscopy data, it follows that the methyl groups of the XantPhos ligand are nonequivalent.

Scheme 3

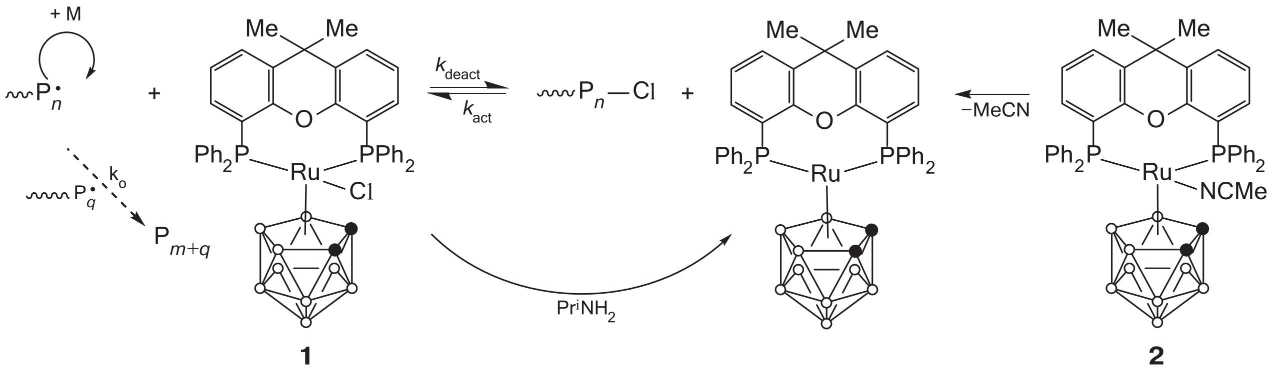


1 **2**

Polymerization of MMA in the presence of complexes of ruthenium with XantPhos as a ligand. The new ruthenacarborane complexes **1** and **2**, as well as their precursor **3**, were investigated as a basis of the catalyst system for the radical polymerization of MMA. It should be noted that, despite the aforementioned widespread use of ruthenium derivatives with XantPhos as ligands in catalysis of various processes of organic synthesis,[28] the possibility of their use in radical polymerization has not been previously studied.

According to modern theoretical concepts of ATRP, the process is the most efficiently carried out in the presence of agents reducing the catalyst (Activators Generated by Electron Transfer, AGET) (Scheme 4).[42] Tin(II) compounds,[43] ascorbic acid, glucose,[44] as well as aliphatic amines,[45] are successfully used as such compounds. The reducing agent is an integral part of high performance catalyst systems to carry out AGET ATRP, since it can significantly increase the rate of the process and improve control over it when catalysts are used in extremely small amounts. We used this methodology to assess the catalytic activity of complexes of ruthenium with XantPhos. Iso-

Scheme 4



propylamine was used as a reducing agent, while carbon tetrachloride was the initiator of polymerization. These reducing agent and initiator were successfully tested by us earlier in polymerization of methacrylic monomers in the presence of ruthenacarboranes.[18,19,45]

The results of our experiments showed that the system based on complex **3** can be used to initiate polymerization of MMA. However, the data obtained evidence that the process proceeds in an uncontrolled mode, leading to the formation of polymers with molecular weights significantly exceeding the theoretically calculated values and high polydispersity coefficients (Table 1). From the kinetic dependence shown in Fig. 1, it follows that at the initial stages of polymerization, its rate is comparable to that observed in the presence of identical amounts of compounds **1** and **2** in the polymerization system, but then a pronounced gel effect and acceleration of the process are observed.

In contrast, the use of ruthenacarboranes **1** and **2** as catalysts under similar conditions allows one to achieve a higher degree of control over the process. The considered compounds (**1** and **2**) have a similar structure and differ from each other by the presence of an acetonitrile or chlorine ligand. As noted above, the ruthenium atom in complex **2** is in the formal oxidation state +2, while complex **1** is a compound of the trivalent metal. Similar to the previously studied complexes with dppb ligand,[36] complexes **1** and **2** can readily interconvert in the course of redox reactions. Complex **2** is readily formed upon reduction of compound **1** with amines in the dichloromethane—acetonitrile solvent mixture. In turn, the reaction of complex **2** with carbon tetrachloride or hydrogen chloride leads to the formation of compound **1** in quantitative yield.

As follows from the kinetic curves shown in Fig. 1, the polymerization of MMA in the presence of complexes **1** and **2** proceeds at comparable rates, but has a different character. The linear dependence of the logarithm of the ratio of the monomer initial to the current concentration $\ln([M]_0/[M])$ on time, which indicates a constant number of active centers, is observed only for the complex of trivalent ruthenium **1**. In the case of its divalent analog **2**, this dependence is not linear. The process proceeds at

Table 1. Results of experiments on polymerization of MMA at T = 80 °C in the presence of ruthenacarborane complexes **1**—**3**, carbon tetrachloride, and isopropylamine ($[MMA] : [CCl_4] : [Ru] : [Pr^iNH_2] = 10000 : 25 : 1 : 4$)

Complex	t/h	Conversion (%)	$M_n \cdot 10^{-3}$	$M_w \cdot 10^{-3}$	M_w/M_n	$M_n \cdot 10^{-3}$ (theor.)*
1	1.2	2.1	7.4	11.5	1.56	0.8
	4.4	6.8	7.6	12.0	1.58	2.7
	12.6	15.5	8.6	13.0	1.56	6.2
	29.3	32.1	10.5	16.0	1.51	12.8
2	1.2	11.9	7.5	12.0	1.61	4.8
	4.4	23.2	10.7	17.4	1.63	9.3
	13.6	29.4	11.9	19.0	1.61	11.8
	30.0	36.7	14.0	22.0	1.58	14.7
3	1.2	2.5	150	590	2.50	0.9
	4.2	7.1	190	640	2.96	2.8
	8.0	12.5	215	705	3.05	5.0
	18.9	95.3	352	920	3.83	38.1

* The theoretical value of the number average molecular weight (M_n) at a given conversion calculated on the assumption that one molecule of initiator gives one polymer chain.

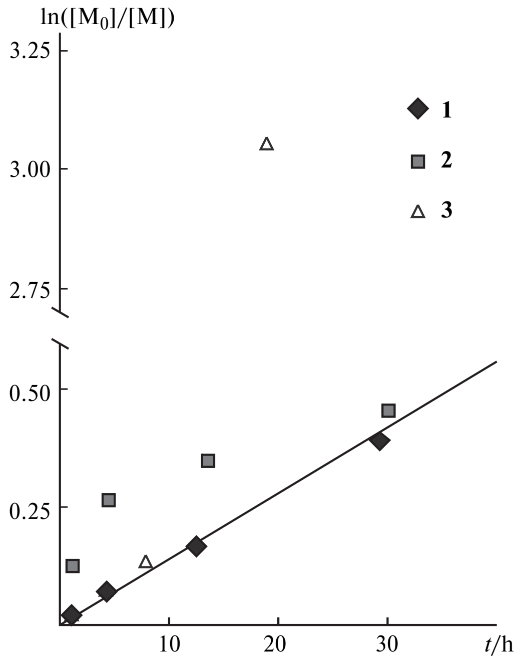


Fig. 1. Kinetic curves for bulk polymerization of MMA at 80 °C in the presence of complexes **1—3** ([MMA] : [CCl_4] : [Ru] : : [Pr^iNH_2] = 10000 : 25 : 1 : 4).

a high initial rate, and then it gradually slows down. The noted kinetic features correlate with the plausible mechanism of AGET ATRP for the process of MMA polymerization. The reversible nature of the process is due to the transfer of a halogen atom between the ruthenium(II) complex and the dormant polymer chain (see Schemes 1 and 4). When a ruthenium complex in the lower oxidation state is introduced into the system, quite a large number of active centers are formed at the initial moment of time due to the interaction with the initiator, which leads to rapid polymerization. As the process develops, a metal complex in the higher oxidation state accumulates in the system due to the side process of irreversible chain termination, which enters into the reversible chain termination reaction, while the concentration of the complex in the lower oxidation state, reinitiating polymerization, decreases. This slows down the process. When a trivalent ruthenium complex is used as the starting compound, the formation of a real catalyst of the process occurs due to the reaction with isopropylamine (see Scheme 4). In this case, there is no large amount of activator in the system at the initial moment of time, which determines the stationary concentration of chains already at the initial stage of the process.

As follows from the data presented in Table 1, the course of polymerization in the presence of complexes **1** and **2** is accompanied by an increase in the number average molecular weight of the polymer and a decrease in the polydispersity coefficient, which is typical of the controlled radical polymerization. Note that the use of chlorine-containing complex **1** makes it possible to obtain polymers with a narrower molecular weight distribution. This fact is logically explained by the lower chain termination at the initial stage of polymerization.

Despite the noted increase in the rate of the process for complexes of divalent ruthenium in comparison with their trivalent analogs, on the whole, the polymerization of MMA under these conditions is rather slow. The highest conversion of the monomer in 30 h does not exceed 40%, which is unacceptable for practical application. In order to increase the rate of polymerization, we proposed to increase the concentration of isopropylamine as an activator and a reducing agent, which converts the catalyst into the active form.

Carrying out the polymerization at a [complex] : [amine] ratio of 1 : 40 led to a significant increase in the rate of polymerization, which made it possible to increase the conversion to more than 90% within a quite short for controlled processes period of time (about two to three hours).

As follows from the presented kinetic dependences of MMA polymerization (Fig. 2, *a*, *1*), a linear dependence of the logarithm of the ratio of the monomer initial concentration to the current one on time is observed at the initial stages of the process. The polymerization is accompanied by an increase in the molecular weight of the samples with an increase in conversion. The molecular weights of the obtained polymers slightly exceed the theoretically calculated values. At the same time, the molecular weight distribution is unimodal and rather narrow, with the polydispersity coefficient (M_w/M_n) decreasing as the monomer conversion increases. At a high conversion, we observed acceleration of the polymerization process and broadening of the molecular weight distribution. Apparently, this is due to the increase in the viscosity of the system, leading to a loss of control over the process.

In order to reduce the viscosity at a high degree of conversion, 25 vol.% of toluene was added to the system as a solvent. In this case, for a more accurate dosage of the initiator we prepared a 0.1 *M* solution of carbon tetrachloride in toluene, which was directly introduced into the polymerization system. We successfully used this procedure of polymerization earlier in the study of the catalytic activity of ruthenium carborane complexes.[18,19] Carrying out the polymerization under the indicated conditions leads to a slight decrease in the polymerization rate, but allows one to achieve a higher degree of control over the process. It was found that the polymerization under such conditions is accompanied by an increase in the molecular weight of the polymer and a decrease in the polydispersity coefficient of the samples as the degree of monomer conversion increases. It should be noted that the process also accelerates at high degrees of conversion, however, it does not lead to undesirable broadening of the molecular weight distribution of the polymer.

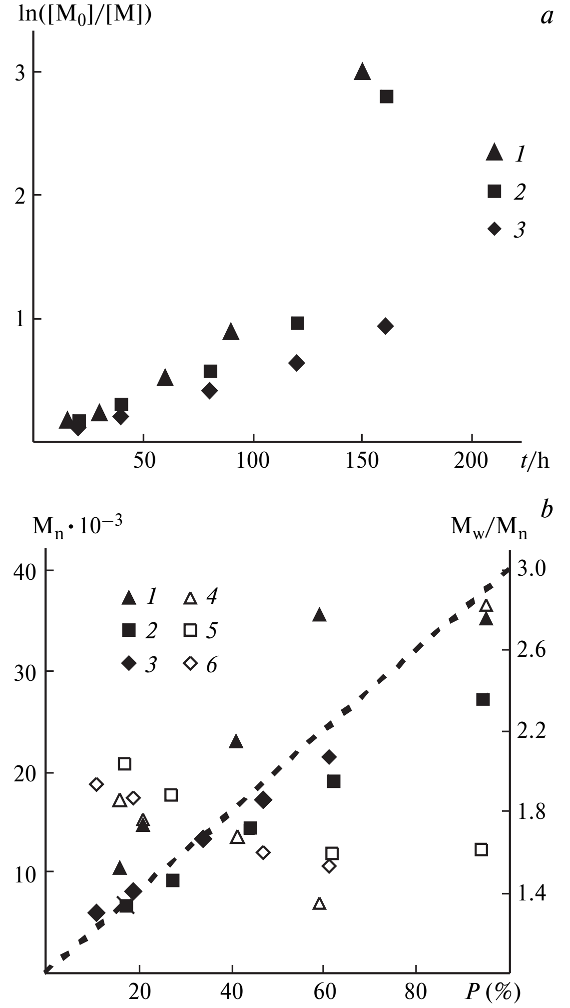


Fig. 2. Kinetic dependencies (*a*), as well as dependences of the molecular weight (M_n, *1—3*) and polydispersity coefficients (M_w, *4—6*), on conversion *P* (*b*) for the polymerization of MMA under the action of systems based on complexes **2** (*1*, *2*, *4*, *5*) and **1** (*3*, *6*) in bulk (*1*, *4*) and in the presence of 25 vol.% of toluene (*2*, *3*, *5*, *6*) (T = 80 °C, [MMA] : [CCl_4] : [Ru] : [Pr^iNH_2] = = 10000 : 25 : 1 : 40; the dashed line corresponds to the theoretically calculated value of the molecular weight).

The polymerization of MMA in the presence of complex **1** under similar conditions also proceeds under control. Note that, in this case the rate of polymerization is somewhat lower than the process occurring in the presence of complex **2**. This may also be related to the necessity of primary activation of compound **1** by its reduction with an amine to the corresponding derivative of divalent ruthenium.

The controlled character of the polymerization is confirmed by the analysis of end groups of the synthesized polymethyl methacrylate (PMMA) by MALDI TOF mass spectrometry. As an example, Fig. 3 shows the mass spectrum of PMMA obtained in the presence of complex **1**. The spectrum clearly shows the main series of signals, which corresponds to living chains with a CCl_3 group at the head of the chain, a chlorine atom at its end, and a sodium cation acting as an ionizing agent. The second, less strong series of signals corresponds to dead chains formed as a result of disproportionation of radicals or elimination of the HCl molecule and containing a hydrogen atom or a double bond at the chain terminus. A comparison of the signal intensities allows us to conclude that the proportion of living chains is no less than 90%. This is an indication of a controlled process. The mass spectra recorded for polymers obtained in the presence of complex **2** and complexes **6**, **7** have a similar pattern.

Polymerization of MMA in the presence of systems based on complexes of ruthenium(II) with diphosphinobutane and nitrile ligands. The data obtained show that the use of ruthenium(II) complexes in the catalysis of polymerization allows one to achieve a higher rate of the process in comparison with the use of their trivalent analogs. Taking this fact into account, we investigated the process of polymerization of MMA in the presence of the recently obtained ruthenium(II) *closo*-carborane complexes **4—7** with nitrile ligands. Compounds **4** and **5** contain an unsubstituted dppb ligand, while complexes **6** and **7** are the *ortho*-phenylenecycloboronated derivatives which have covalent bonds between the diphosphine and the carborane ligands in their structure. Such compounds, known in the series of ruthenium[18,39] and iron[46] metallacarboranes, are formed at high temperatures and are characterized by higher thermal stability, which makes them attractive for use in catalysis.

The kinetic curves of MMA polymerization shown in Fig. 4 are similar to those for the previously considered cases with complexes **1** and **2** (see Fig. 2). In this case, a linear dependence is observed at the initial stages of the process, indicating a constant number of the active centers, as well as an acceleration of the process at higher degrees of conversion. It is noteworthy that the nature of the coordinated nitrile does not affect the rate of the process. The presence of an *ortho*-phenylenecycloboronated fragment in the metallacarborane structure leads to a slight decrease in the rate of the process, but significantly improves the degree of control over it.

When compounds **4** and **5** are used as catalysts, the formation of a polymer with a molecular weight of more than 10,000 is observed already at the initial degrees of conversion, which significantly exceeds the theoretically calculated values. The further course of the process is accompanied by a slight increase in the molecular weight, with the polydispersity coefficients of the obtained samples exceeding the value of 2.0, which does not allow one to consider the process as being controlled. The molecular weight characteristics of the samples synthesized in the presence of compounds **4** and **5** are practically identical, which, like the kinetic curves of MMA polymerization described above (see Fig. 4), indicates that the process is not affected by the nitrile ligand nature.

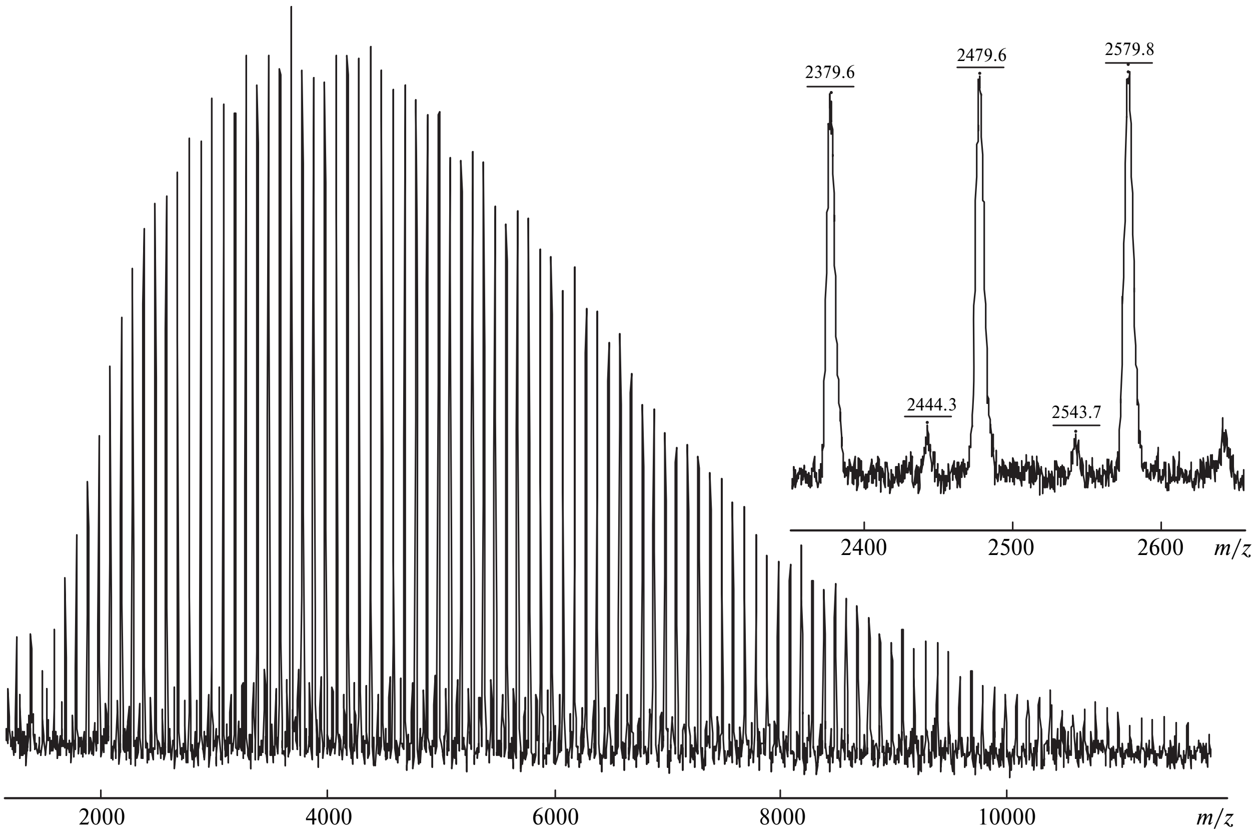


Fig. 3. MALDI TOF mass spectrum of the PMMA sample obtained in the presence of a catalyst system based on complex **1** at 80 °C ([MMA] : [CCl_4] : [Ru] : [Pr^iNH_2] = 10000 : 25 : 1 : 40).

The polymers obtained in the presence of the systems based on complexes **6** and **7** are characterized by narrower curves of molecular weight distribution, the width of which in addition decreases during the process (Fig. 5, *b*). In this case, the polymerization is characterized by a linear increase in the molecular weights of the samples and the conversion, as well as by a good agreement of these parameters with the theoretically calculated values, which is typical of the processes of controlled synthesis of polymers.[5—8]

The MALDI mass spectra of the obtained samples have a structure similar to that shown in Fig. 3 and confirm a controlled course of the process. The MALDI spectrum clearly exhibits the main series of the signals, which corresponds to the living chains with a CCl_3 group at the head of the chain and a chlorine atom at its terminus.

To sum up, the carried out experiments showed that ruthenium(II) carborane complexes with labile nitrile ligands are promising catalysts for controlled synthesis of polymers, which make it possible to carry out radical polymerization of MMA to deep degrees of conversion within a fairly short time and with low concentrations of metal complexes. The results of our work in combination with the data of previous studies on the use of systems based on ruthenacarboranes[45,47] and amines in radical polymerization allow us to conclude that the nature of polymerization and molecular weight characteristics of the obtained samples practically do not depend on the form in which the catalyst is introduced into the system:

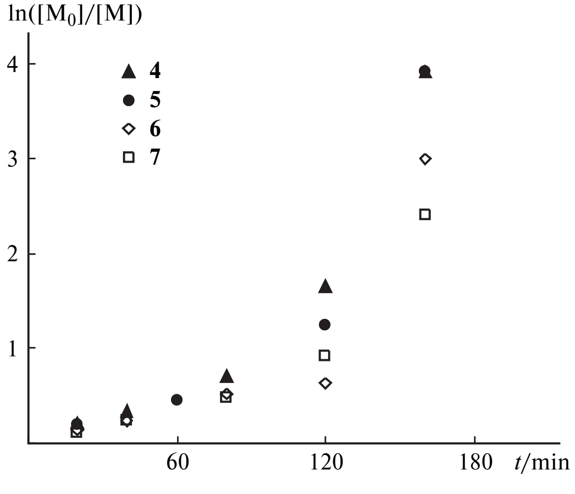


Fig. 4. Kinetic dependencies of polymerization of MMA at 80 °C under the action of catalyst systems based on complexes **4—7** in the presence of 25 vol.% of toluene ([MMA] : [CCl_4] : [Ru] : [Pr^iNH_2] = 10000 : 25 : 1 : 40).

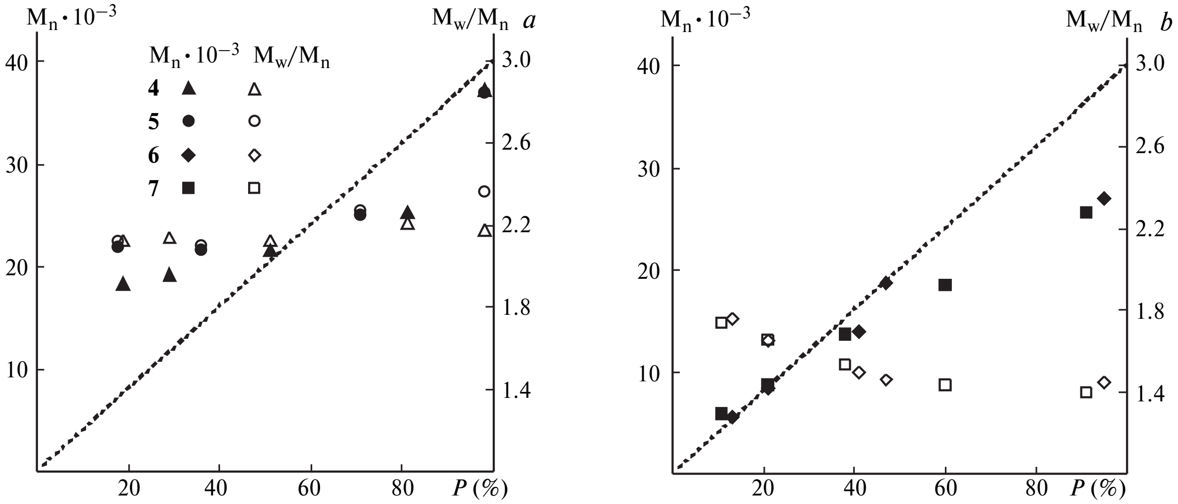


Fig. 5. Dependences of the molecular weight characteristics of the obtained polymers on the conversion in polymerization of MMA under the action of systems based on complexes **4**, **5** (*a*) and **6**, **7** (*b*) in the presence of 25 vol.% of toluene ($T = 80$ °C, [MMA] : : [CCl_4] : [Ru] : [Pr^iNH_2] = 10000 : 25 : 1 : 40; the dashed line corresponds to the theoretically calculated value of the molecular weight).

in the form of a 17-electron chlorine-containing complex or its 18-electron analog containing a stabilizing nitrile or triphenylphosphine ligand. As shown in Scheme 4, under the process conditions, both forms form 16-electron species which are directly involved in the abstraction of the halogen atom from the initiator or a dormant chain. Note that the nature of the stabilizing ligand (benzonitrile, acetonitrile, or phosphine) has no principal effect on the course of the process either.

At the same time, an increase in the amount of amine as a polymerization activator from 4 : 1 to 40 : 1 relative to metallacarborane leads to a significant increase in the rate of the process, making it possible to achieve deep conversions within several hours, which is important from the point of view of practical application of the proposed systems.

The structure of the stabilizing chelate phosphine ligand, which is part of the metallacarborane, significantly affects the molecular weight characteristics of the samples obtained in its presence. The use of complexes with *ortho*-phenylenecycloboronated fragments makes it possible to achieve a better degree of control over the process compared to their non-boronated counterparts, which was also observed by us earlier in the study of chlorine-containing ruthenacarboranes in catalysis and can be explained by the higher stability of the former. At the same time, the use of complexes with XantPhos, which do not contain *ortho*-phenylenecycloboronated fragments, makes it possible to achieve significantly better control over polymerization compared to similar derivatives of 1,4-bis(diphenylphosphino)butane. This fact indicates a higher stability of these compounds and allows one to consider the XantPhos-type diphosphine ligands as convenient building blocks for the development of new highly efficient ruthenacarborane catalysts of polymerization, as well as for other processes.

Experimental

The solvents used in the synthesis were dried over appropriate agents and distilled under argon. Their physicochemical constants corresponded to the literature data. Ruthenium catalysts of polymerization were synthesized under argon atmosphere. The starting complex *exo*-5,6,10-[Cl(Ph_3P)$_2$Ru]-5,6,10-(μ-H)$_3$-10-*H*-*nido*-7,8-$C_2B_9H_8$[37] and compounds **3**,[30] **4**—**7**[27,28] were obtained according to previously described procedures. Isolation of products by column chromatography and their purification by recrystallization were carried out in air. Chromatography was carried out on Macherey-Nagel silica gel (230—400 mesh). The purity of the obtained metallacarboranes was confirmed by HPLC (Kromasil 60—5CN column 250×4.6 mm, eluent CH_2Cl_2—*n*-hexane, 1 : 3; flow rate 1 mL min^{-1}) on a Knauer Smartline chromatograph with a diode array UV detector. ^1H, ^{31}P, and ^{11}B NMR spectra were recorded on an Agilent DD2 NMR 400NB spectrometer in deuterated dichloromethane. Anisotropic EPR spectra were recorded in a frozen matrix of a CH_2Cl_2—toluene mixture at 150 K on a Bruker-EMX radio spectrometer (operating frequency ~9.75 GHz). IR spectra were recorded on an Infralum FT spectrometer. Analysis of metal complexes and polymers by MALDI time-of-flight mass spectrometry was carried out in a linear mode on a Bruker Microflex LT instrument, using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malonitrile (DCTB) as a matrix by applying solutions onto a stainless steel substrate. In the analysis of polymers, sodium trifluoroacetate was used as an ionizing agent. The molecular weight characteristics of polymers were determined by gel permeation chromatography in a THF solution according to PMMA standards on a Knauer instrument with a cascade of two columns (Phenomenex, Phenogel with pore size 10^3 and 10^5 Å), using a RI Detektor K- 2301 differential refractometer and a UV Detektor K-2501 UV detector.

Synthesis of 3,3-XantPhos-3-Cl-*closo*-3,1,2-Ru$C_2B_9H_{11}$ (1). The complex *exo*-5,6,10-[Cl(Ph_3P)$_2$Ru]-5,6,10-(μ-H)$_3$-10-*H*-*nido*-7,8-$C_2B_9H_8$ (110 mg, 0.137 mmol) and XantPhos (87 mg, 0.151 mmol) were placed into a flask. The flask with the contents was degassed three times and then filled with argon. After that, benzene distilled in an argon atmosphere (15 mL) was added to the reaction mixture. The process was carried out for 3 h at 80 °C. After completion of the reaction, the mixture was chromatographed on a column with silica gel, using benzene as an eluent. A bright red band was eluted. Then the solvent was evaporated *in vacuo* to a volume of about 2 mL, after which hexane (20 mL) was added and the solution was left to crystallize for 12 h. The analytically pure product (50.8 mg, 43.5%) was obtained. MALDI MS (*m*/*z*): 847.4 $[M]^-$ (distribution from nine B atoms and one Cl atom; m/z_{theor} = 847.2). EPR ($C_6H_5CH_3$—CH_2Cl_2, 150 K): $g_1 = 2.502$, $g_2 = 2.049$, $g_3 = 1.942$. IR (KBr), ν/cm^{-1}: 2574 ($\nu_{\text{(B—H)}}$).

Synthesis of 3,3-XantPhos-3-NCMe-*closo*-3,1,2-$RuC_2B_9H_{11}$ (2). The complex **1** (24 mg, 0.024 mmol) was placed into a Schlenk tube, followed by the addition of dichloromethane (2 mL), acetonitrile (2 mL), and isopropylamine (120 μL). The flask with the contents was degassed three times to a residual pressure of about 1.3 Pa by freezing in liquid nitrogen and evacuating the solvent, after which it was filled with argon. The reaction proceeded during 2.5 h at ~20 °C. After the end of the process, the mixture was chromatographed on a column with silica gel. A bright yellow band was eluted, using hexane—ethyl acetate as an eluent. The solvent was evaporated *in vacuo*. The recrystallization from hot acetonitrile gave the analytically pure product (10.5 mg, 44%). MALDI MS (*m*/*z*): 853.3 $[M]^+$ (distribution from nine B atoms; m/z_{theor} = 853.3). ^{1}H NMR (CD_2Cl_2, 25 °C), δ: 6.73—7.62 (m, 26 H, Ph+XantPhos); 2.47 (s, 3 H, CH_3); 1.93 (s, 3 H, CH_3CN); 1.69 (s, 3 H, CH_3); 1.53 (br.s, 2 H, $C_{\text{carb}}H$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C), δ: 35.21. $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 25 °C), δ: –25.3 (3 B), –11.3 (4 B), –5.48 (1 B), –0.43 (1 B). IR (KBr), ν/cm^{-1}: 2542 ($\nu_{\text{(B—H)}}$), 2254 ($\nu_{\text{(C≡N)}}$).

Reaction of complex 2 with hydrogen chloride. Complex **2** (12.4 mg, 0.015 mmol) was placed into a Schlenk tube, followed by the addition of dichloromethane (2 mL). The flask with the contents was degassed three times by freezing in liquid nitrogen and filled with argon, after which concentrated hydrochloric acid (2.5 μL, 0.03 mmol of HCl) was added using a micropipette. The reaction mixture was stirred for 1 h at 35 °C. After completion of the reaction, the mixture was chromatographed on a column with silica gel, using a mixture of benzene—hexane as an eluent. A bright red band was eluted. The solvent was evaporated *in vacuo*. Recrystallization from hexane gave the product (11 mg, 89%) identified by HPLC as complex **1**.

Reaction of complex 2 with carbon tetrachloride. Complex **2** (10 mg, 0.012 mmol) was placed into a flask, which was degassed three times and filled with argon. Benzene (4 mL) and CCl_4 (40 μL) distilled under argon were added to complex **2**. The reaction mixture was stirred for 1 h at 35 °C. After completion of the reaction, the mixture was chromatographed on a column with silica gel, using benzene—hexane as an eluent, to obtain complex **1** (8.2 mg, 83%).

Polymerization procedure. Calculated amounts of the monomer, initiator (CCl_4), isopropylamine, and ruthenium complex were placed in a round-bottom flask. The thus prepared mixture was poured into glass ampoules (1 mL each) and deoxygenated by degassing three times in liquid nitrogen to a residual pressure below 1.3 Pa. The ampoules were sealed and placed in a thermostat heated to 80 °C for a specified time. To terminate the polymerization, the ampoule with the reaction mixture was frozen. The resulting solution of a polymer was diluted with dichloromethane and precipitated into excess petroleum ether. Then the polymer was dissolved in dichloromethane, precipitated into petroleum ether, filtered, and vacuum dried to a constant weight.

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