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Facile method for the synthesis of ruthenacarboranes, diamagnetic 3,3-[$Ph_2P(CH_2)_nPPh_2$]-3-H-3-Cl-*closo*-3,1,2-$RuC_2B_9H_{11}$ (n = 3 or 4) and paramagnetic 3,3-[$Ph_2P(CH_2)_nPPh_2$]-3-Cl-*closo*-3,1,2-$RuC_2B_9H_{11}$ (n = 2 or 3), as efficient initiators of controlled radical polymerization of vinyl monomers

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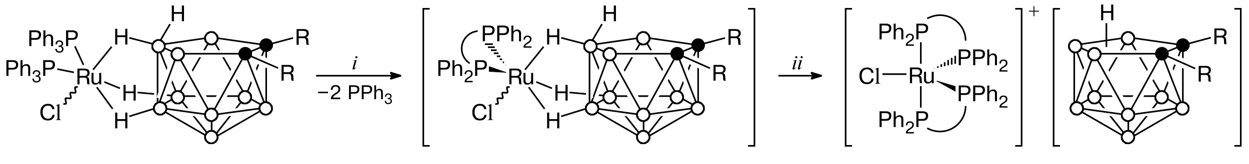
A facile preparative procedure was developed for the synthesis of 17- and 18-electron *closo*-(diphosphine)ruthenacarborane complexes. This method is based on the replacement of PPh_3 ligands with bis(diphenylphosphino)alkanes $Ph_2P(CH_2)_nPPh_2$ (n = 2—4) in ruthenacarborane 3,3-$(PPh_3)_2$-3-Cl-3-H-*closo*-3,1,2-$RuC_2B_9H_{11}$. The resulting complexes exhibit high activity in controlled radical polymerization of vinyl monomers.

Key words: bis(diphenylphosphino)alkanes, ruthenium carborane complexes, synthesis, controlled radical polymerization, vinyl monomers.

Recently,[1—3] we have demonstrated that the replacement of PPh_3 ligands in three-bridge *exo-nido*-ruthenacarboranes 5,6,10-{$Cl(Ph_3P)_2Ru$}-[5,6,10-(μ-H)$_3$-10-H-7,8-R_2-*exo-nido*-7,8-$C_2B_9H_8$] (R = H (**1**) or Me (**2**)) with chelating diphosphine ligands affords either diamagnetic (18-electron) or paramagnetic (17-electron) chelate *closo*-(diphosphine)ruthenacarboranes depending on the reaction conditions. This method proved to be rather efficient for the synthesis of certain *closo*-ruthenacarboranes, for example, with 1,4-bis(diphenylphosphino)butane (dppb) (see Ref. 2) or chiral (–)-2,4-bis(diphenylphosphino)pentane (bdpp).[1,3] The synthesis of chelate *closo* complexes with the use of diphosphinoalkanes having a shorter unbranched aliphatic chain according to this scheme is complicated by the formation of the by-products $[RuCl(Ph_2P(CH_2)_nPPh_2)_2]^+$[7,8-$R_2$-7,8-*nido*-$C_2B_9H_{10}$]$^-$ (see Ref. 4) *via* the cleavage of B—H...Ru coordination bonds in *exo-nido*-(diphosphine)ruthenacarboranes that are generated in the first step in the presence of an excess of diphosphine (Scheme 1).

Diamagnetic and paramagnetic *closo*-(diphosphine)ruthenacarboranes are of interest not only for the chemistry of metallacarboranes but also for the synthesis of narrow-disperse macromolecules based on vinyl monomers. In

Scheme 1



1, **2**

R = H (**1**), Me (**2**)

$Ph_2P\frown PPh_2 = Ph_2P(CH_2)_nPPh_2$, n = 2, 3

i. $Ph_2P(CH_2)_nPPh_2$, C_6H_6; *ii*. $Ph_2P(CH_2)_nPPh_2$.

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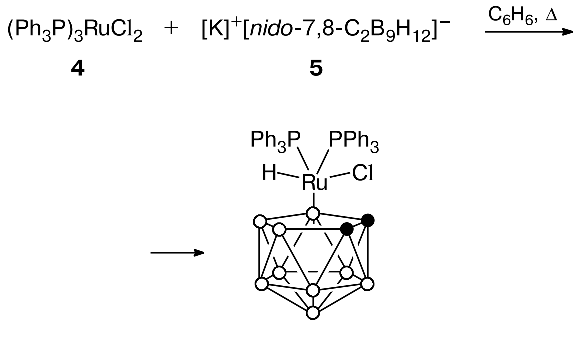
polymerization of the latter, such ruthenacarboranes serve as initiators and regulators[5] of atom transfer radical polymerization (ATRP).[6,7] In this connection, it was important to develop a more versatile procedure for the synthesis of diphosphine *closo* complexes, which is not complicated by the formation of by-products.

In the present study, we examined the direct ligand exchange in the reaction of the *closo* complex 3,3-$(PPh_3)_2$-3-Cl-3-H-*closo*-3,1,2-$RuC_2B_9H_{11}$ (**3**) with bis(diphenylphosphino)alkanes $Ph_2P(CH_2)_nPPh_3$ (n = 2—4). As a result, we succeeded not only in extending a series of known 17- and 18-electron *closo*-(diphosphine)ruthenacarboranes but also in developing a new efficient initiator of controlled radical polymerization of methyl methacrylate (MMA) and styrene.

Results and Discussion

The starting *closo* complex **3** has been synthesized earlier by two methods: (1) according to a scheme[8] involving the reaction of the $[NHMe_3]^+$[*nido*-7,8-$C_2B_9H_{12}]^-$ salt with the $(PPh_3)_3RuHCl \cdot PhMe$ complex to form dihydride metallacarborane 3,3-$(PPh_3)_2$-3,3-$(H)_2$-*closo*-3,1,2-$RuC_2B_9H_{11}$, whose treatment with gaseous HCl afforded complex **3** in 40% yield and (2) by the thermal *exo-nido* → *closo* rearrangement of complex **1**,[9] which, in turn, was prepared by the reaction of 16-electron $(PPh_3)_3RuCl_2$ (**4**) with the *nido*-dicarbaundecaborate salt $[K]^+$[*nido*-7,8-$C_2B_9H_{10}]^-$ (**5**) in an Et_2O—THF mixture[10] or benzene at 22 °C.[5] In the present study, we substantially modified the latter method by using the one-pot thermal reaction of complex **4** with an insignificant excess of salt **5** in benzene to prepare *closo* complex **3** (Scheme 2). This reaction under argon gave the target product **3** (after purification on a silica gel column and crystallization) in 51% yield. The structure of complex **3** was confirmed by IR and ^1H, $^{31}P\{^1H\}$, and $^{11}B/^{11}B\{^1H\}$ NMR spectra, which were completely identical to the spectroscopic data for the authentic sample.[9]

Scheme 2



3

Table 1. Selected geometric parameters of molecule **3**

Bond	*d*/Å	Bond angle	ω/deg
Ru(3)—P(1)	2.3756(5)	P(1)—Ru(3)—P(2)	103.665(19)
Ru(3)—P(2)	2.3757(5)	P(1)—Ru(3)—Cl(1)	84.871(18)
Ru(3)—Cl(1)	2.4284(5)	P(2)—Ru(3)—Cl(1)	87.729(19)
Ru(3)—H(3M)	1.40(3)	P(1)—Ru(3)—H(3M)	73.4(11)
Ru(3)—C(1)	2.257(2)	P(2)—Ru(3)—H(3M)	69.9(11)
Ru(3)—C(2)	2.226(2)	Cl(1)—Ru(3)—H(3M)	143.5(11)
Ru(3)—B(4)	2.316(2)	C(13)—P(1)—C(19)	104.24(10)
Ru(3)—B(7)	2.242(2)	C(13)—P(1)—C(25)	100.15(10)
Ru(3)—B(8)	2.281(2)	C(25)—P(1)—C(19)	103.63(10)
P(1)—C(13)	1.835(2)	C(13)—P(1)—Ru(3)	119.09(7)
P(1)—C(19)	1.847(2)	C(19)—P(1)—Ru(3)	110.89(7)
P(1)—C(25)	1.838(2)	C(25)—P(1)—Ru(3)	116.94(7)
P(2)—C(31)	1.841(2)	C(37)—P(2)—C(31)	97.32(10)
P(2)—C(37)	1.837(2)	C(43)—P(2)—C(31)	104.84(10)
P(2)—C(43)	1.826(2)	C(43)—P(2)—C(37)	104.43(10)
C(1)—C(2)	1.624(3)	C(31)—P(2)—Ru(3)	123.57(7)
		C(37)—P(2)—Ru(3)	117.11(7)
		C(43)—P(2)—Ru(3)	107.53(7)

In addition, we performed repeated single-crystal X-ray diffraction study of *closo* complex **3**, because the principal X-ray diffraction data published in the brief communication[9] were lost and are missing from the Cambridge Structural Database. In the present study, we performed X-ray diffraction analysis of monosolvate $\mathbf{3} \cdot CH_2Cl_2$. The molecular structure of this complex is shown in Fig. 1. Selected bond lengths and bond angles of **3** are given in Table 1.

The positions of all hydrogen atoms, including the hydride ligand at the metal atom (Ru—H, 1.40(3) Å), in complex **3** were located. The metal atom is almost symmetrically coordinated to the open C_2B_3 face of *nido*-carborane so that the Ru—C (2.257(2) and 2.226(2) Å) and Ru—B (2.242(2)—2.316(2) Å) distances vary only slightly, the shift of the metal atom from the center of the plane toward the boron or carbon atoms being virtually absent. The Ru...C_2B_3 distance is 1.721 Å. The bond lengths between the Ru atom and the other ligands (Ru—P(1), 2.3756(5) Å; Ru—P(2), 2.3757(5) Å) and the Ru—Cl bond length (2.4284(5) Å) are similar to the corresponding parameters in structurally related *closo*-ruthenacarboranes, for example, in the neutral complex 1,1-$(PPh_3)_2$-1-Cl-1-H-*closo*-1,2,3-$RuC_2B_4H_6$ (Ru—P, 2.3653 and 2.3773 Å; Ru—Cl, 2.4311 Å)[11] and the anionic complex [3,3-$(PPh_3)_2$-3-Cl-*closo*-3,1,2,-$RuC_2B_9H_{11}]^-[Et_4N]^+$ (Ru—P, 2.346 and 2.344 Å; Ru—Cl, 2.452 Å).[12] The conformation of the ruthenium-containing group $RuHCl(PPh_3)_2$ relative to the pentagonal C_2B_3 plane of the *nido*-carborane ligand is of interest. The Ru—H bond exactly projects onto the B(8)—H bond (P(3)—Ru—B(8)—H(8) torsion angle is 15°), the B(8)—H(8)...H—Ru distance being very short (2.02 Å), which might result from the unique through-space inter-

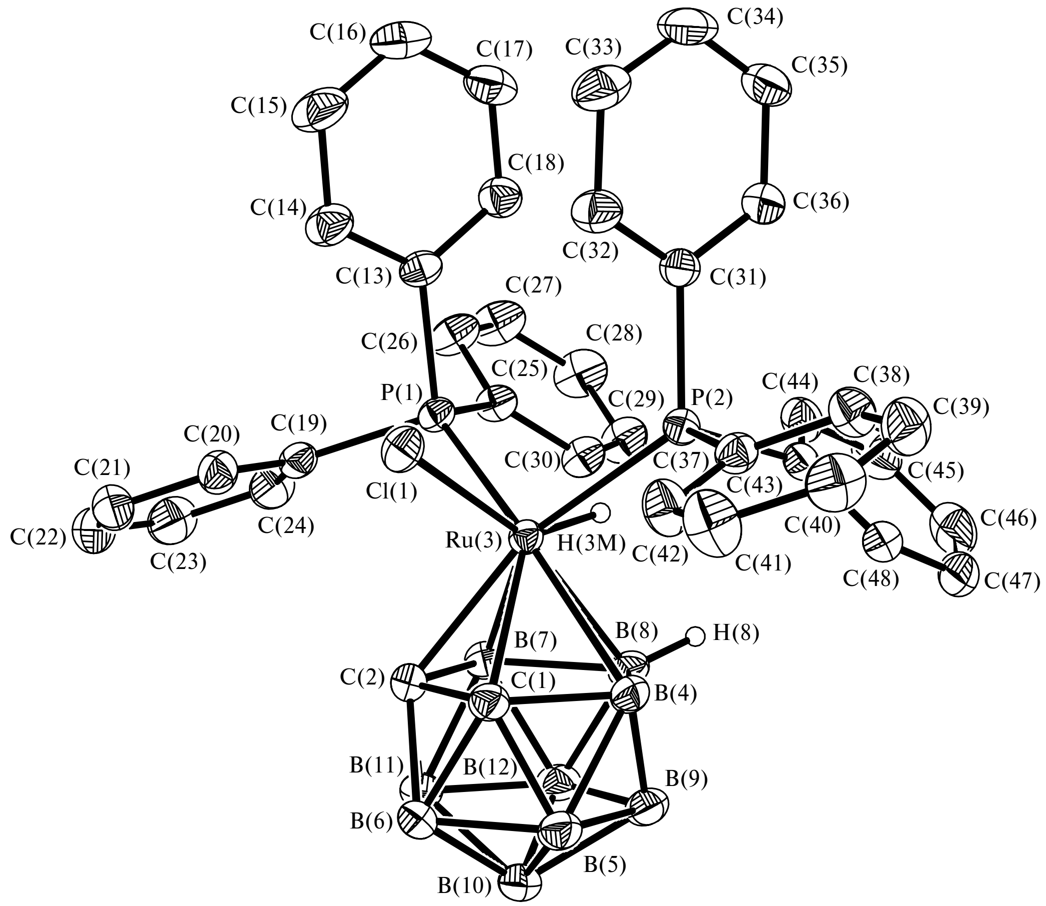
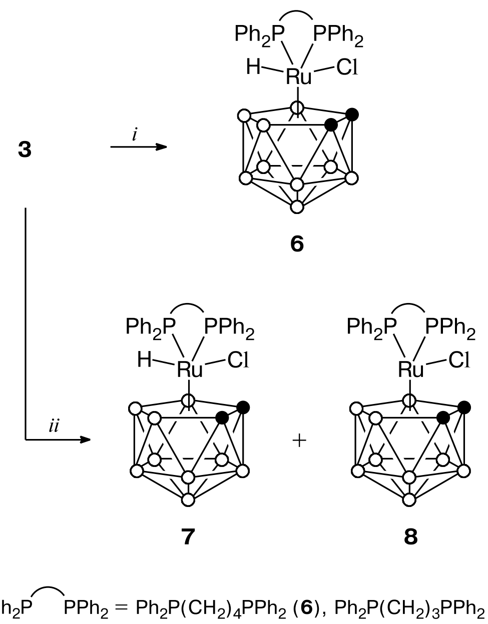


Fig. 1. Molecular structure of complex **3**.

action between these two hydrogen atoms. As a consequence, the spin-spin coupling constant $^3J(H^{Ru},H^8)$ = 10.3 Hz in the ^1H NMR spectrum of this complex is unusually large.[9]

From the chemical standpoint, *closo*-ruthenacarborane complex **3** proved to be a rather convenient and active reagent. It was found that the reaction of **3** with a 10% excess of 1,4-bis(diphenylphosphino)butane (dppb) or 1,3-bis(diphenylphosphino)propane (dppp) in benzene is accomplished by the replacement of the PPh_3 ligands by diphosphines already at room temperature. However, under these conditions the formation of the target products in both reactions occurs very slowly (in the reaction with dppb, the 100% conversion of **3** is attained within 3 days; in the reaction with dppp, within 6 days). In the former case, the replacement affords exclusively the 18-electron complex 3,3-($Ph_2P(CH_2)_4PPh_2$)-3-H-3-Cl-*closo*-3,1,2-$RuC_2B_9H_{11}$ (**6**) in 86% yield. In the latter case, the reaction produces a mixture of the 18- and 17-electron complexes 3,3-($Ph_2P(CH_2)_3PPh_2$)-3-H-3-Cl-*closo*-3,1,2-$RuC_2B_9H_{11}$ (**7**) and 3,3-($Ph_2P(CH_2)_3PPh_2$)-3-Cl-*closo*-3,1,2-$RuC_2B_9H_{11}$ (**8**) in a ratio of 6.7 : 1 in a total yield of ~90% (Scheme 3). Earlier, we have synthesized[2] an analogous mixture of complexes **7** and **8** by the reaction of

Scheme 3



= $Ph_2P(CH_2)_4PPh_2$ (**6**), $Ph_2P(CH_2)_3PPh_2$ (**7**, **8**)

Reagents and conditions: *i*. $Ph_2P(CH_2)_4PPh_2$, C_6H_6, 80 °C, 1 h; *ii*. $Ph_2P(CH_2)_3PPh_2$, C_6H_6, 80 °C, 2 h.

exo-nido complex **1** with dppp, and this mixture has been separated into individual compounds by TLC. The structures of these complexes were established by ^{1}H and ^{31}P{^{1}H} NMR or ESR spectroscopy.

It was found that heating of complex **3** with dppb or dppp in benzene substantially accelerates the replacement of the PPh_3 ligands by diphosphines (reactions were completed within 1 and 2 h, respectively). However, the reaction of **3** with dppb at high temperature produces diamagnetic complex **6** in a somewhat lower yield (70%). The reaction of **3** with dppp affords a mixture of compounds **7** and **8** with paramagnetic complex **8** predominating. A separate experiment demonstrated that refluxing of a mixture of approximately equal amounts of **7** and **8** in benzene for 6 h afforded predominantly paramagnetic complex **8** (according to HPLC data, the **8** : **7** ratio was 98 : 2). In the case of the favorable formation of one product, chromatographic (TLC) monitoring of this reaction presents substantial difficulty because of the close values of R_f for complexes **7** and **8** (0.35 and 0.31, respectively). It is also impossible to perform ^{1}H or ^{31}P{^{1}H} NMR monitoring in the case of a predominance of paramagnetic complex **8** in the reaction mixture. Hence, we monitored the reaction of **3** with dppp by HPLC on a silica gel column with the use of a 4 : 1 *n*-hexane—CH_2Cl_2 mixture as the eluent. The clear separation of the chromatographic peaks corresponding to complexes **7** and **8** (Fig. 2) allowed us to rather precisely determine the ratio of products **7** and **8** in the final mixture (see above) and estimate the purity of paramagnetic complex **8**.

It was found that the reaction of *closo*-complex **3** with a 10% excess of bis(diphenylphosphino)ethane (dppe) produces the 17-electron paramagnetic complex 3,3-($PPh_2CH_2CH_2PPh_2$)-3-Cl-*closo*-3,1,2-$RuC_2B_9H_{11}$ (**9**) in 35% yield (Scheme 4) both on heating in benzene (2 h) and at room temperature (54 h). However, the formation of target product **9** in both reactions was accompanied by the formation of an insignificant amount of the yellow diamagnetic carborane-containing ruthenium complex (**10**). We failed to establish the exact structure of the latter complex in spite of the ^{1}H and ^{31}P{^{1}H} NMR spectroscopic data (see the Experimental section).

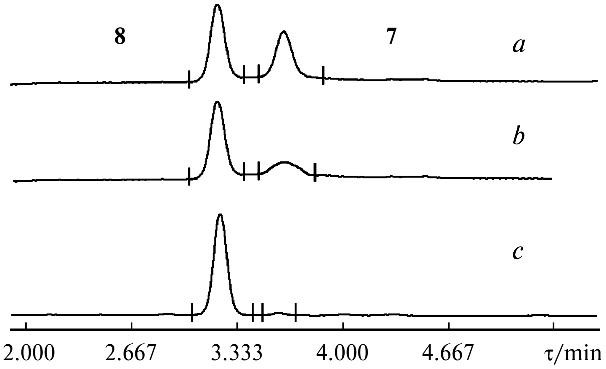
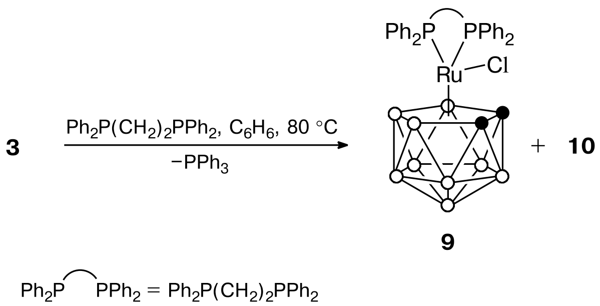


Fig. 2. Chromatographic (HPLC) separation of complexes **7** and **8** on a Separon SGX column (150×3 mm) packed with silica gel 5 μ with the use of a 4 : 1 *n*-hexane—CH_2Cl_2 mixture as the eluent: (*a*) a mixture of complexes **7** and **8** (41 : 59) prepared by the reaction of **3** with dppp at 80 °C for 2 h and isolated by silica gel column chromatography; (*b*) thermolysis products of a mixture of complexes **7** and **8** (starting ratio was 41 : 59) after refluxing in benzene for 2 h; (*c*) the final thermolysis products of a mixture of complexes **7** and **8** (2 : 98) after refluxing in benzene for 6 h.

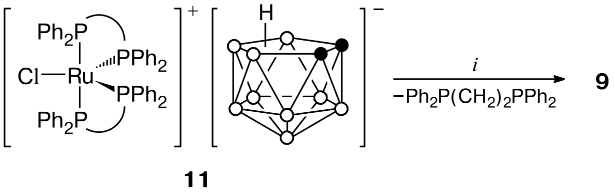
Scheme 4



Note: **10** is diamagnetic ruthenacarborane with unknown structure.

Paramagnetic complex **9** can also be synthesized starting from the ionic complex $[RuCl(dppe)_2]^+$[7,8-*nido*-$C_2B_9H_{12}]^-$ (**11**), which has been prepared earlier[4] as the only product by replacing the PPh_3 ligands in *exo-nido*-ruthenacarborane **1** by dppe. In a dilute CH_2Cl_2 solution, one of the dppe ligands in complex **11** undergoes slow dissociation with the concomitant formation of *closo* complex **9**. After 7 days, the latter was isolated by silica gel column chromatography in 24% yield (Scheme 5).

Scheme 5



Reagents and conditions: *i*. CH_2Cl_2, 7 days.

The structures of diamagnetic and paramagnetic complexes **3** and **6—8** synthesized in the present study were confirmed by comparing their ^{1}H, ^{31}P{^{1}H}, and ^{11}B/^{11}B{^{1}H} NMR and ESR spectra with the spectra of the samples prepared earlier. The composition and structure of new paramagnetic complex **9** was established by elemental analysis, ESR spectroscopy (Fig. 3), and X-ray

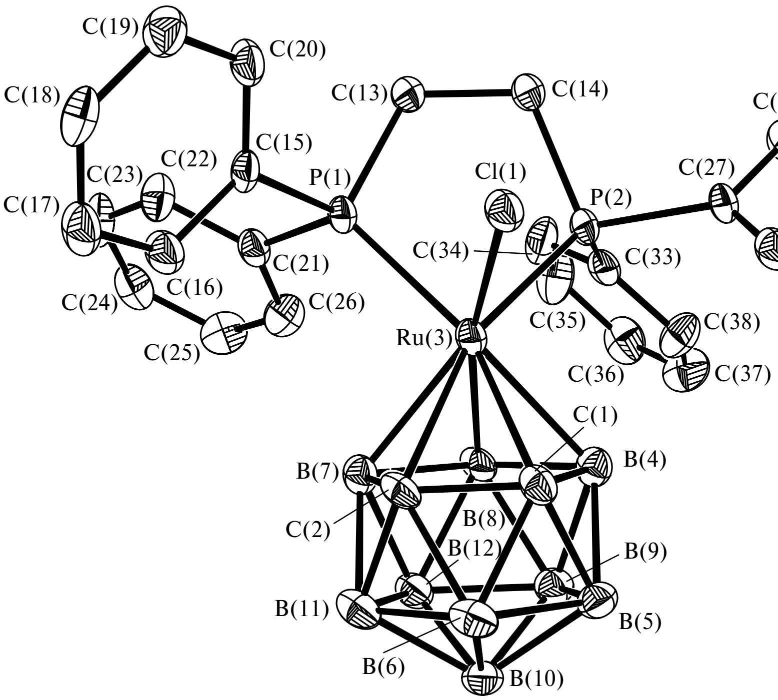


Fig. 3. ESR spectrum of complex **9**.

diffraction (Fig. 4). The ESR spectrum of low-spin d^5 complex **9** has a rhombic nature with three distinct g factors, $g_1 = 2.253$, $g_2 = 2.108$, and $g_3 = 1.998$.

The molecular structure of complex **9** established by X-ray diffraction is shown in Fig. 4. Selected geometric parameters are given in Table 2. The Ru atom has a pseudooctahedral configuration and is bound to two phosphorus atoms of the dppe ligand (Ru—P, 2.345(1) and 2.325(1) Å), the chlorine ligand (Ru—Cl, 2.381(1) Å), and the *nido*-carborane ligand (Ru—C, 2.237(4) and 2.261(4) Å; Ru—B(4), Ru—B(7), and Ru—B(8), 2.235(5)—2.256(5) Å). Taking into account that the carborane ligand in molecule **9** is doubly charged (2^-), whereas the chlorine ligand is singly charged (1^-), the formal oxidation state of the Ru atom is +3 and this atom has 17 electrons, which is confirmed by the ESR spectrum. It should be noted that, as in other known 17-electron *closo*-ruthenacarboranes,**[1,3,5]** the general tendency toward a shortening of the Ru—Cl bond by ~0.1 Å compared to 18-electron analogs is retained in complex **9**.

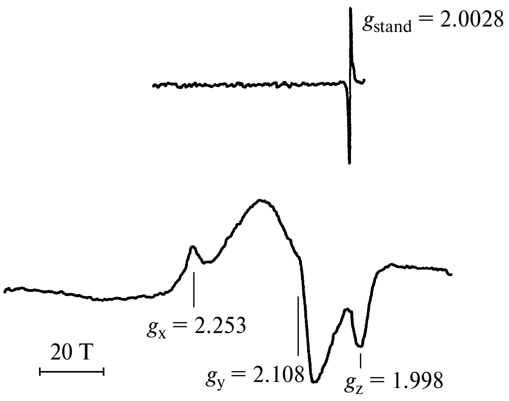


Fig. 4. Molecular structure of complex **9**.

Table 2. Selected geometric parameters of molecule **9**

Bond	d/Å	Bond angle	ω/deg
Ru(3)—P(1)	2.3448(11)	P(2)—Ru(3)—P(1)	82.02(4)
Ru(3)—P(2)	2.3249(11)	P(2)—Ru(3)—Cl(1)	86.61(4)
Ru(3)—Cl(1)	2.3809(11)	P(1)—Ru(3)—Cl(1)	88.49(4)
Ru(3)—C(1)	2.237(4)	C(15)—P(1)—C(13)	108.25(19)
Ru(3)—C(2)	2.261(4)	C(15)—P(1)—C(21)	102.54(18)
Ru(3)—B(4)	2.235(5)	C(21)—P(1)—C(13)	101.81(19)
Ru(3)—B(7)	2.243(5)	C(13)—P(1)—Ru(3)	111.29(13)
Ru(3)—B(8)	2.256(5)	C(15)—P(1)—Ru(3)	107.65(13)
P(1)—C(13)	1.863(4)	C(21)—P(1)—Ru(3)	124.23(14)
P(1)—C(15)	1.831(4)	C(27)—P(2)—C(14)	102.93(19)
P(1)—C(21)	1.833(4)	C(33)—P(2)—C(14)	107.49(19)
P(2)—C(14)	1.842(4)	C(33)—P(2)—C(27)	101.69(19)
P(2)—C(27)	1.831(4)	C(14)—P(2)—Ru(3)	108.41(13)
P(2)—C(33)	1.829(4)	C(27)—P(2)—Ru(3)	118.21(14)
C(1)—C(2)	1.611(6)	C(33)—P(2)—Ru(3)	116.85(13)
C(13)—C(14)	1.536(6)	C(14)—C(13)—P(1)	112.5(3)
		C(13)—C(14)—P(2)	112.2(3)

In continuation of studies on catalytic activity of diamagnetic and paramagnetic phosphine-substituted *closo-* and *exo-nido*-ruthenacarboranes,**[5]** we tested new paramagnetic complex **9** as a catalyst for the controlled radical polymerization of methyl methacrylate (MMA) and styrene according to the ATRP [6] and reverse ATRP [7] mechanisms.

Our experiments demonstrated that ruthenium carborane complex **9** is an efficient co-initiator of the controlled synthesis of macromolecules. For example, in the presence of CCl_4 and complex **9**, the conversion of styrene into polystyrene at 90 °C was higher than 91% (after 69 h). The average molecular weight (M_n) is 19630, and the polydispersity of the resulting macromolecules (M_w/M_n) is 1.56. The polydispersity is somewhat larger than the analogous parameters for the ideal living polymerization[6,7] but is substantially lower than those obtained in the synthesis of polystyrene under conditions of classical radical polymerization ($M_w/M_n > 2$).

Complex **9** is more active compared to analogous cyclopentadienyl derivatives of ruthenium, for example, $[RuCl(Cp^*)(PPh_3)_2]$ or $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$, which have been proposed[13—15] for the controlled synthesis of macromolecules in the living polymer chain mode. These ruthenium complexes are efficient only in combination with additives of co-catalysts, in particular, of aluminum alkoxides, the polymerization rate in the presence of these compounds being very low and the deep conversion (~90%) being attained only within 400—600 h. In addition, taking into account the weight, the yield, and the polydispersity coefficient of polystyrene, complex **9** is nowadays the most efficient catalyst precursor among metallacarboranes tested in the controlled radical polymerization of styrene.[16,17]

The polydispersity coefficients in polymerization of MMA according to the ATRP mechanism in the presence of complex **9** and CCl_4 as the co-initiator are much lower (M_w/M_n is at most 1.23) than those observed in the synthesis of polystyrene under analogous conditions.

Polymerization in the presence of metal complex catalysts with the use of azoisobutyronitrile (AIBN) instead of CCl_4 as the co-initiator occurs according to the reverse ATRP mechanism. In this case, the average molecular weight of poly(methyl methacrylate) (PMMA) ($M_n = 45870$) and the polydispersity ($M_w/M_n = 1.43$) of samples are substantially larger. The observed deterioration of the molecular-weight characteristics in the presence of AIBN is undoubtedly associated with thermal decomposition of the latter and related noncontrolled radical polymerization occurring in parallel with the synthesis of macromolecules in the living polymer chain mode.

A comparison of the polydispersity coefficients of PMMA samples synthesized according to the ATRP mechanism with the use of ruthenacarborane **9** ($M_w/M_n = 1.23$) and diamagnetic ruthenium complexes **3** and **6** (M_w/M_n are 1.62 and 1.25, respectively[5]) and the paramagnetic *o*-cycloboronated analog of these complexes, $[3\text{-}Cl\text{-}3,3\text{-}Ph_2PMe_3PPh\text{-}o\text{-}C_6H_4\}\text{-}1,2\text{-}Me_2\text{-}closo\text{-}3,1,2\text{-}RuC_2B_9H_{10}]$, for which M_w/M_n is 1.37,[5] indicates that binding of phosphine ligands by methylene bridges is the most substantial factor responsible for the formation of narrow-disperse macromolecules in polymerization processes. Apparently, the electronic configuration of the metal atom in this series of compounds has no noticeable effect on the molecular-weight characteristics of the resulting macromolecules.

Experimental

The phosphine/diphosphine replacement reactions of complex **3** were carried out under argon in anhydrous solvents, which were prepared according to standard procedures. A new one-pot method was developed for the synthesis of complex **3**. The reaction products were isolated by column chromatography with the use of silica gel (Merck, 230—400 mesh). Commercial phosphines were used (Strem Chemicals and Aldrich-Chemie). The NMR spectra were recorded on Bruker AMX-400 (400.13 MHz for ^1H, 161.98 MHz for ^{31}P, and 128.3 MHz for ^{11}B) and Bruker Avance^{TM}300 (300.13 MHz for ^1H) spectrometers. The ESR spectra of complexes **8** and **9** were measured on a Varian E-12A radiospectrometer. The mixture of complexes **7** and **8** was analyzed on a Separon SGX column (150×3 mm, silica gel 5 μ) equipped with an UV detector (254 nm). Elemental analysis was carried out in out in the Laboratory of Microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences.

Synthesis of 3,3-bis(triphenylphosphine)-3-chloro-3-hydrido-3,1,2-*closo*-dicarbollylruthenium (3). A mixture of complex **4** (0.5 g, 0.52 mmol) and the potassium salt of *nido*-7,8-dicarbaundecaborate **5** (0.11 g, 0.63 mmol) in anhydrous benzene (120 mL) was heated for 3 h with magnetic stirring at 75—78 °C (mixture was prevented from boiling) and argon was bubbled directly through the solution. Then the reaction temperature was raised with stirring to the boiling point of the solvent, the major portion of the latter being distilled off under argon to ~8—10 mL. After cooling, the residue was purified by a silica gel column chromatography, the product being eluted under a pressure of argon with a 5 : 1 benzene—*n*-hexane mixture. The first green fraction consisting of a mixture of PPh_3 and complex **3** was collected separately. After repeated chromatography of this fraction under the same conditions, complex **3** was obtained in a yield of 0.03 g. The major amount of complex **3** as dark-yellow crystals (0.18 g) was obtained from the second fraction, which was diluted (after elution from the column) with an equal volume of *n*-hexane and crystallized at 0—2 °C for 15 h. The total yield of complex **3** was 0.21 g (51%). Elution from the chromatographic column with benzene afforded the third orange fraction containing 0.02 g of *exo-nido* complex **1**.

Synthesis of 3-chloro-3,3-(1,4-diphenylphosphinobutane)-3-hydrido-3,1,2-*closo*-dicarbollylruthenium (6). *A.* A solution of complex **3** (0.04 g, 0.05 mmol) and dppb (0.025 g, 0.06 mmol) in benzene (12 mL) was stirred at room temperature for 72 h. The solvent was evaporated *in vacuo*. The residue was chromatographed on a silica gel column, and yellow-orange *closo* complex **6** was eluted with a 1 : 1 benzene—*n*-hexane mixture. After recrystallization from an *n*-hexane—CH_2Cl_2 mixture, the yield of complex **6** was 0.03 g (86%). The ^1H and $^{31}P\{^1H\}$ NMR spectroscopic data for complex **6** were completely identical to the spectroscopic data of the sample prepared earlier.[2]

B. A solution of complex **1** (0.05 g, 0.06 mmol) and diphosphine **3** (0.03 g, 0.07 mmol) in benzene (12 mL) was stirred at 80 °C for 1 h. The mixture was concentrated *in vacuo*. The residue was chromatographed on a silica gel column, complex **6** being eluted with a 1 : 1 benzene—*n*-hexane mixture. Then the mixture was concentrated. After recrystallization from a CH_2Cl_2—*n*-hexane mixture, complex **6** was obtained in a yield of 0.03 g (70%). The ^1H and $^{31}P\{^1H\}$ NMR spectroscopic data for complex **6** were completely identical to those for the sample prepared earlier.[2]

Synthesis of the complexes 3-chloro-3,3-(1,3-diphenylphosphinopropane)-3-hydrido-3,1,2-*closo*-dicarbollylruthenium (7) and 3-chloro-3,3-(1,3-diphenylphosphinopropane)-3,1,2-*closo*-dicarbollylruthenium (8). ***A.*** A solution of complex **1** (0.05 g, 0.06 mmol) and dppp (0.03 g, 0.07 mmol) in benzene (8 mL) was stirred at room temperature for 144 h. The solvent was evaporated *in vacuo*. The residue was chromatographed on a silica gel column, the orange band consisting of complexes **7** and **8** being eluted with a 1 : 1 benzene—*n*-hexane mixture. The resulting fraction was concentrated, after which a mixture of complexes **7** and **8** was obtained in a yield of 0.04 g (90%). A comparison of R_f for complexes **7** ($R_f = 0.31$) and **8** ($R_f = 0.35$) with R_f for the samples prepared earlier[2] provided evidence for the identity of these compounds. The percentage of the products in the mixture determined by HPLC were as follows: 87% of complex **7** and 13% of complex **8**.

B. A solution of complex **3** (0.04 g, 0.050 mmol) and dppp (0.021 g, 0.050 mmol) in benzene (10 mL) was refluxed with stirring for 3 h until diamagnetic complex **7** disappeared from the reaction mixture. The course of the reaction was monitored by HPLC. The solvent was evaporated *in vacuo*. The residue was chromatographed on a silica gel column, complex **8** being eluted with a 1 : 1 benzene—*n*-hexane mixture. The yield of paramagnetic complex **8** was 0.017 g (49%).

C. A mixture of complexes **7** and **8** (0.02 g, ~0.029 mmol; which was prepared in a ratio of ~1 : 1 by heating complex **3** with dppp in benzene for 1.5 h) was dissolved in benzene (10 mL), and the mixture was refluxed with stirring for 6 h. The course of the reaction was monitored by HPLC, and heating was terminated when diamagnetic complex **7** was completely consumed. The solvent was evaporated *in vacuo*. The residue was chromatographed on a silica gel column, complex **8** being eluted with benzene. After evaporation of the solvent and crystallization from a 3 : 1 CH_2Cl_2—*n*-hexane mixture, the yield of **8** was 0.013 g (66%). The ESR spectroscopic data (CH_2Cl_2, $g_{stand} = 2.003$, $T = 77$ K) for complex **8** are identical to those for the sample of complex **8** synthesized earlier.[2]

Synthesis of 3-chloro-3,3-(1,2-diphenylphosphinoethane)-3,1,2-*closo*-dicarbollylruthenium (9) and complex 10. ***A.*** A solution of complex **3** (0.17 g, 0.214 mmol) and dppe (0.085 g, 0.214 mmol) in benzene (20 mL) was refluxed with stirring for 2 h. The solvent was evaporated *in vacuo*. The residue was chromatographed on a silica gel column, orange complex **9** being eluted with a 2 : 1 benzene—*n*-hexane mixture. After recrystallization from a 3 : 1 CH_2Cl_2—*n*-hexane mixture, the yield of complex **9** was 0.05 g (35%). Complex 9. Found (%): C, 49.70; H, 5.01; B, 14.15. $C_{28}H_{35}B_9ClP_2Ru$. Calculated (%): C, 50.40; H, 5.25; B, 14.58. ESR (CH_2Cl_2, $g_{stand} = 2.003$, $T = 77$K): $g_1 = 2.253$; $g_2 = 2.108$; $g_3 = 1.998$). Diamagnetic complex **10** (0.02 g) was the next elution product. The structure of the latter was not established in the present study. Complex 10. ^1H NMR (C_6D_6), δ: 7.70, 7.60, 7.38, 7.11, 6.98, and 6.78 (all m, 20 H, Ph); 2.63, 2.25, 2.14, and 2.01 (all m, 1 H each, CH_2CH_2); 2.59 and 1.31 (both br.s, 1 H each, CH carb.). $^{31}P\{^1H\}$ NMR (C_6D_6), δ: 62.8 (d, 2 P, $J_{P,P} = 31.5$ Hz); 35.9 (m, 1 P); 10.75 (d, 1 P, $J_{P,P} = 31.5$ Hz). $^{11}B\{^1H\}$ NMR (C_6D_6), δ: −3.0 and −6.2 (both br, 1 B); −12.2 (v.br, 5 B); −24.6 (v.br, 2 B).

B. A solution of complex **3** (0.045 g, 0.056 mmol) and dppe (0.025 g, 0.056 mmol) in benzene (10 mL) was stirred at room temperature for 2.5 days. The reaction mixture was worked up analogously to method *A*. The yield of complex **9** was 0.015 g (35%). The amount of complex **10** generated under these conditions was insignificant (<0.005 g).

C. Complex **11** (0.2 g, 0.19 mmol) was placed in a flask filled with argon, and anhydrous CH_2Cl_2 (75 mL) was added. The dark-red solution was stirred for 7 days until the starting complex completely disappeared. The course of the reaction was monitored by TLC using a 3 : 1 CH_2Cl_2—*n*-hexane mixture as the eluent. The mixture was concentrated *in vacuo* to 5—7 mL and chromatographed on a silica gel column, complex **9** being eluted with a 3 : 1 CH_2Cl_2—*n*-hexane mixture. After evaporation and recrystallization, the yield of compound **9** was 0.03 g (24%). The ESR spectroscopic data for complex **9** are identical to those of the sample prepared according to the method *A*.

X-ray diffraction study of complexes 3 and 9. Crystallographic data and details of the structure refinement for compounds **3** and **9** are given in Table 3. Experimental data sets were collected on a Bruker SMART 1000 diffractometer equipped with an area detector (graphite monochromator, λ(Mo-Kα) = 0.71073 Å,

Table 3. Crystallographic data and details of structure refinement for compounds **3** and **9**

Parameter*	3	9
Molecular weight	879.39	667.31
Space group	$P2_1/n$	$P\bar{1}$
T/K	293(2)	120(2)
a/Å	12.8963(2)	10.170(2)
b/Å	22.6214(3)	11.517(2)
c/Å	14.8518(2)	15.452(3)
α/deg		70.383(3)
β/deg	105.573(1)	75.303(3)
γ/deg		64.880(3)
V/Å^3	4173.7(1)	1530.4(5)
Z	4	2
d_{calc}/g cm^{-3}	1.399	1.448
μ/cm^{-1}	6.74	7.24
$2\theta_{max}$/deg	58	54
Number of independent reflections	11048	6633
R_{int}	0.0349	0.0384
R_1 (based on F for reflections with $I > 2\sigma(I)$)	0.0351 (7779)	0.0553 (5476)
wR_2 (based on F^2 for all reflections)	0.0820	0.1327
Number of parameters im refinement	518	370
GOOF	0.992	0.991

* The molecular formulas are $C_{38}H_{42}B_9ClP_2Ru \cdot CH_2Cl_2$ (**3**) and $C_{28}H_{35}B_9ClP_2Ru$ (**9**).

ω-scanning technique). The structures were solved by direct methods and refined by the full-matrix least-squares method against F^2_{hkl} with anisotropic displacement parameters for all nonhydrogen atoms. The hydrogen atom of the hydride ligand in complex **3** and the hydrogen atoms of the carborane ligands in both complexes were located in difference electron density maps. The other hydrogen atoms were placed in geometrically calculated positions. All calculations were carried out on a personal computer with the use of the SHELXTL program package.[18] Complete tables of the atomic coordinates, bond lengths, bond angles, and anisotropic displacement parameters were deposited with the Cambridge Structural Database.

Synthesis of polymers with the use of ruthenium carborane complexes. Methyl methacrylate and styrene were washed with a 10% aqueous NaOH solution to remove the inhibitor and then with distilled water to remove the residual alkali to neutral pH and dried over calcium chloride. Purification was performed by vacuum distillation, and the fraction with the boiling point of 38 °C (15 Torr) (MMA) and 48 °C (20 Torr) (styrene), respectively, was collected.[19]

Polymerization according to the ATRP mechanism was performed with the use of CCl_4 as the initiator. Azoisobutyronitrile (AIBN) was used as the initiator of polymerization according to the reverse ATRP mechanism. The samples were prepared as follows: the monomer and precise amounts of the initiator (0.0625 to 0.25 mol.% of AIBN or CCl_4, respectively) and the catalyst (0.125 mol.% of ruthenacarborane) were placed in glass ampoules and deaerated three times by refreezing the ampoules in liquid nitrogen. Polymerization was performed at a residual pressure of 1.3 Pa. Polymerization was monitored under isothermic conditions by the weight method. The ampoule was placed in a thermostat for a strictly specified time, after which the ampoule was withdrawn and refrozen in liquid nitrogen to terminate polymerization. The resulting polymer was precipitated into petroleum ether. The polymer was purified from residues of the monomer, the initiator, and the catalyst by reprecipitation of the PMMA and polystyrene samples from chloroform. Then the samples of the polymers were dried *in vacuo* to a constant weight, and the degree of conversion was calculated.

Analysis of the molecular-weight characteristics of polymers. The molecular weights and the molecular-weight distributions of PMMA and polystyrene were determined by GPC on a Knauer instrument (Germany) equipped with a linear column (Phenomenex, USA) with the use of an RI Detektor K-2301 differential refractometer as the detector and chloroform as the eluent. Narrow-disperse polystyrene standards were used for calibration. The average molecular weights determined from the calibration against polystyrene samples were converted to the weights of the MMA polymers according to the standard formulas for PMMA.[20]

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