Study of paramagnetic iron and ruthenium metallacarboranes using cyclic voltammetry and matrix-activated laser desorption/ionization time-of-flight spectrometry*

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The complex investigation of paramagnetic (17-electron) iron and ruthenium *closo*-metallacarboranes with chelate diphosphine ligands 3,3-($Ph_2P(CH)_nPPh_2$)-3-Cl-*closo*-3,1,2-$MC_2B_9H_{11}$ (M = Fe, n = 2, 3; Ru, n = 4), *o*-phenylenecycloboronated 3-Cl-3,3,8-[$Ph_2P(CH)_nPPh$-µ-(C_6H_4-*o*)]-1,2-R_2-*closo*-3,1,2-$RuC_2B_9H_{10}$ (n = 3, 4; R = H or Me), and bis(*o*-cycloboronated) 3-Cl-3,3,7,8-[$Ph_2P(CH)_nP$-µ-C_6H_4-*o*)$_2$]-*closo*-3,1,2-$RuC_2B_9H_9$ (n = 4, 5) was performed using cyclic voltammetry and matrix-activated laser desorption/ionization time-of-flight (MALDI-TOF) spectrometry. Some diamagnetic iron and ruthenium *exo*—*nido*- and *commo*-complexes were studied using the same methods. A relationship between the redox potentials of the metallacarborane complexes and their stability and transformations under the MALDI-TOF conditions was established.

Key words: ruthenacarboranes, ferracarboranes, MALDI-TOF, cyclic voltammetry.

The studies of ferrocene derivatives Fe(C_5H_4X)-($C_5H_{5-n}Y_n$) (X = Br, PR_2; Y = C_6H_5) by matrix-activated laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry and cyclic voltammetry (CV) showed[1] that similar redox transformations occur in the liquid and gas phases. In the present work, this complex approach based on a combination of the indicated methods was used for the study of 17-electron iron and ruthenium *closo*-metallacarboranes. Note that it is usually difficult to identify and study paramagnetic metallacarborane clusters because of a restricted range of efficient physicochemical methods of analysis: ESR[2] and X-ray diffraction analysis.[3] The latter is most objective for the establishment of the structures of the complexes in the solid state, but requires high-quality single crystals, which is difficult to accomplish in practice.

In this work, we studied in detail the recently synthesized[4] carborane iron complexes with diphosphine ligands 1—3 by CV and MALDI-TOF. It has previously been established[4] that diamagnetic complex 1 undergoes the reversible redox transformation at the potential

$E_{1/2}$ = 0.32 V (*vs* Ag/Ag$^+$ as a reference pseudo-electrode) corresponding to the transformation of Fe^{II} into Fe^{III}. The value obtained for the redox potential (E_{redox}) of *commo*-complex 1 indicates that its oxidation is more difficult than that of ferrocene, which makes it possible to recommend this compound for use as an internal standard in electrochemical studies along with ferrocene. Note that there is no signal corresponding to the reduction of complex 1 in the cathodic region of the CV curve in the potential range from 0 to −1.2 V (*vs* Ag/Ag$^+$).

Unlike the reversible oxidation of complex 1 (see Ref. 4), paramagnetic (17-electron) trivalent complex 2 exhibits stages of irreversible oxidation corresponding, most likely, to the oxidation of iron to Fe^{IV} at E = 990 mV and the reduction to Fe^{II} at E = −620 mV (Fig. 1). The anodic peak at a potential of 90 mV corresponds to the reversible oxidation of the decomposition products of complex 2 formed by its irreversible reduction. Similar CV curves show the behavior of 17-electron complex 3. The electrochemical properties of compounds 1—3 were earlier presented in more detail.[4]

Paramagnetic *closo*-ruthenacarboranes with diphosphine ligands 4—9 are structural analogs of iron complexes 2 and 3 and are applied as catalysts of controlled radical polymerization of vinyl monomers *via* the atom

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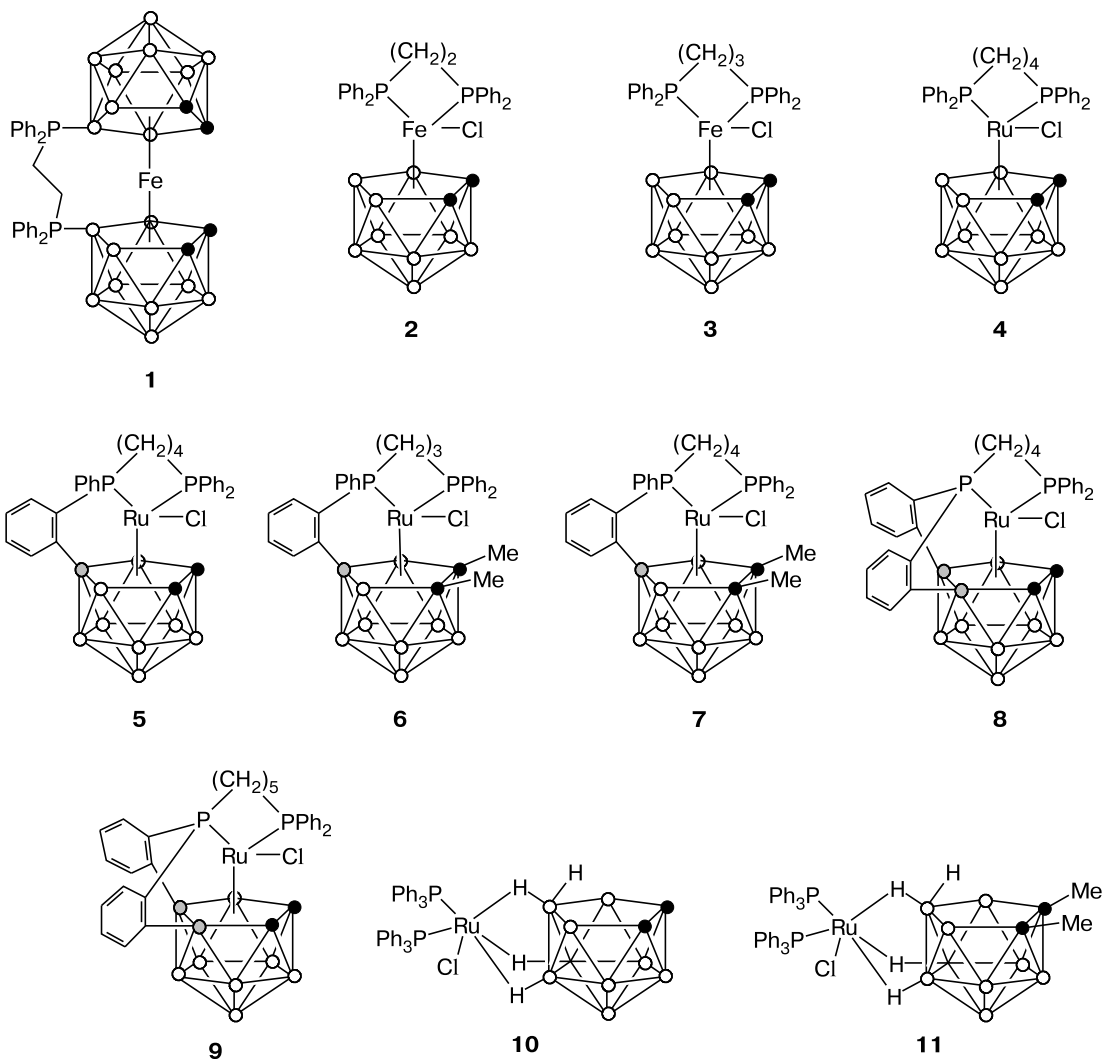
transfer radical polymerization (ATRP).[5—9] It is known[10—12] that the key reaction of this transformation is the oxidative addition of the halogen atom from the alkyl halide initia-
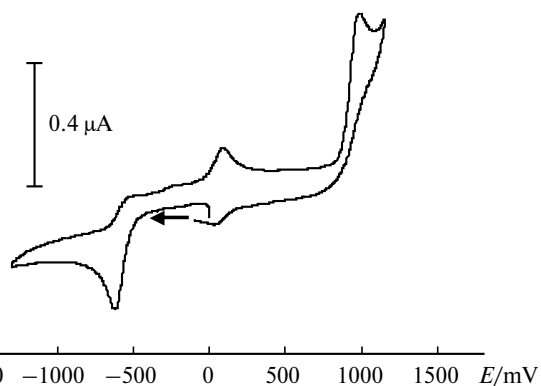

Fig. 1. Cyclic voltammogram of complex **2** in 1,2-dichloro-ethane solution (T = 25 °C, concentration of the complex C = 0.003 mol L^{-1}, supporting electrolyte 0.2 M Bu$_4$NPF$_6$, sweep rate 100 mV s^{-1}).

tor to a transition metal complex accompanied by an increase in the oxidation state of the metal. Therefore, the determination of the values of potentials E_{redox} of the catalysts is important for the evaluation of their efficiency. The earlier CV study of complexes **4—9** showed[13] that all compounds of the *closo*-structure are reduced to stable anions. The value of the potential at which the ruthenium compounds are reduced is by 0.4—0.5 V lower than those of the iron complexes. In this work, we determined the oxidation potentials of the indicated compounds to Ru^{IV} and analyzed the dependence of the reversibility of the oxidation process on their structure. The CV curves of ruthenium complexes **4—7** in a 1,2-dichloroethane solution are presented in Fig. 2. The irreversible oxidative electron transfer corresponding to the transition Ru^{III} → Ru^{IV} in the region E = 600—900 mV, which is by 0.1—0.2 V lower than those for the ferracarborane analogs, is observed for all complexes. As follows from the data presented in Table 1, the values of potentials of the transformations of the ruthenium complexes on the electrode depend
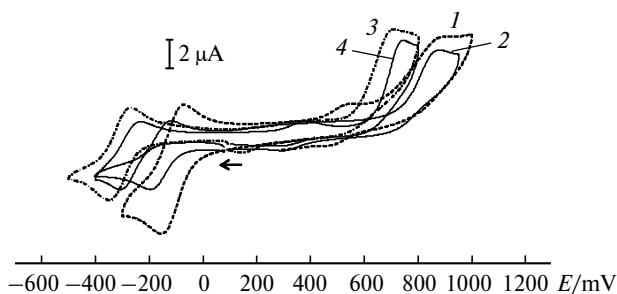
Fig. 2. Cyclic voltammograms of complexes **4**—**7** (curves *1*—*4*, respectively) in 1,2-dichloroethane solution ($T = 25$ °C, concentration of the complexes $C = 0.003$ mol L^{-1}, supporting electrolyte 0.2 M Bu$_4$NPF$_6$, sweep rate 100 mV s^{-1}).

Fig. 3. Cyclic voltammograms of complexes **5** (curve *1*) and **8** (curve *2*) in 1,2-dichloroethane solution ($T = 25$ °C, concentration of the complexes $C = 0.003$ mol L^{-1}, supporting electrolyte 0.2 M Bu$_4$NPF$_6$, sweep rate 100 mV s^{-1}).

on the structures of both the diphosphine and carborane ligands of the studied compounds. The example of compounds **6** and **7** shows that the elongation of the methylene chain in the diphosphine ligand increases the reduction potential. A comparison of the oxidation potentials of compounds **5** and **7** indicates that the presence of substituents in the carborane ligand decreases, on the contrary, the value of reduction potential. This can be explained by the electron-donating effect of the methyl groups at the cluster carbon atoms. The formation in the molecule of an additional bond between the carborane and diphosphine ligands of compound **5** decreases the oxidation potential compared to that of noncyclic analog **4**.

Table 1. Oxidation and reduction potentials of the studied metallacarboranes[a]

Complex	Transition				
	$M^{II} \rightarrow M^{III}$				$M^{III} \rightarrow M^{IV}$
	$E_{p,a}/B$	$E_{p,c}/B$	E^0/B^b	I_a/I_c	$E_{p,a}/V$
1[c]	0.36	0.28	0.32	1.0	—
2[c]	−0.62	—	—	—	0.990
3[c]	−0.61	—	—	—	0.920
4	−0.074	−0.155	−0.115	1.0	0.898
5	−0.120	−0.197	−0.159	1.0	0.879
6	−0.270	−0.351	−0.311	1.0	0.707
7	−0.235	−0.306	−0.270	1.0	0.744
8[d]	−0.178	−0.248	−0.213	0.9	0.807
9[d]	−0.102	−0.171	−0.137	1.0	0.813
Ferrocene[e]	0.236	0.156	0.196	1.0	—

[a] The values of potentials are presented *vs* Ag/Ag$^+$, $E_{p,c}$ is the cathodic peak potential, and I_a/I_c is the ratio of the anodic and cathodic peak currents.
[b] $E^0 = (E_{p,a} + E_{p,c})/2$.
[c] Data of Ref. 4.
[d] The values of $E_{p,c}$, E^0, and I_a/I_c for the transition $M^{III} \rightarrow M^{IV}$ were obtained only for complexes **8** (0.731, 0.769, and 1.0) and **9** (0.728, 0.771, and 1.1).
[e] Data of Ref. 1.

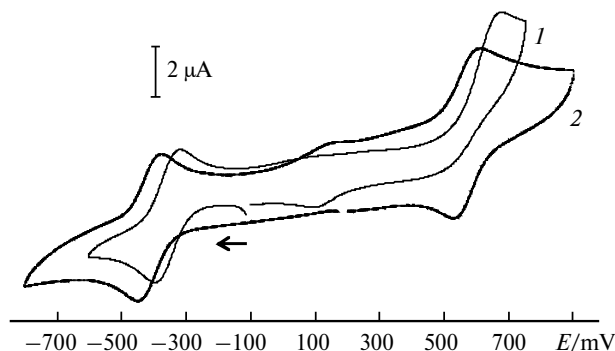An interesting structural feature of complexes **8** and **9** is the presence of two *ortho*-phenylenecycloboronated fragments in the molecule. The CV study of these compounds showed that the formation of the second cyclic bond results in a higher shift of the reduction potential of $Ru^{III} \rightarrow Ru^{II}$ to the cathodic region and also in the reversible transformation of Ru^{III} into Ru^{IV} (Fig. 3). Therefore, the formation of the second covalent bond between the carborane and diphosphine ligands stabilizes the ruthenium complexes in the oxidation state Ru^{IV}.

exo—*nido*-Ruthenacarboranes **10** and **11** are the Ru^{II} compounds that are irreversibly oxidized at a potential higher than 0.4 V (Fig. 4). The presented voltammograms of these complexes exhibit three consecutive peaks (the values of potentials are given in Table 2). The potentials of the first ($E^1_{p,a}$) and second ($E^2_{p,a}$) oxidation peaks of compounds **10** and **11** differ, whereas the positions of their third peak ($E^3_{p,a}$) coincide. This is due, most likely, to the fact that the oxidation of the product formed by the irreversible oxidation of complexes **10** and **11** corresponds to the third peak. Note that no reduction signals are observed in the voltammograms in the cathodic region (to −1.3 V).

When analyzing the metallacarboranes by the MALDI-TOF method, we used *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), whose main advantages are the weak polarity, tolerance to organometallic compounds, and possibility to work at a low power of laser irradiation, which minimizes fragmentation.[1,14—18]

The main signal in the mass spectrum of compound **1** obtained in the positive ion mode is the intense signal with $m/z = 717.3$ Da corresponding to the molecular cation (Fig. 5) and representing a set of ten lines with different intensities due to the isotope pattern of the boron and ruthenium atoms. The number of lines, their relative intensity, and absolute values of m/z are well consistent with the theoretically calculated distribution for the molecular cation. As for the ferrocene derivatives,[1] the mass spec-
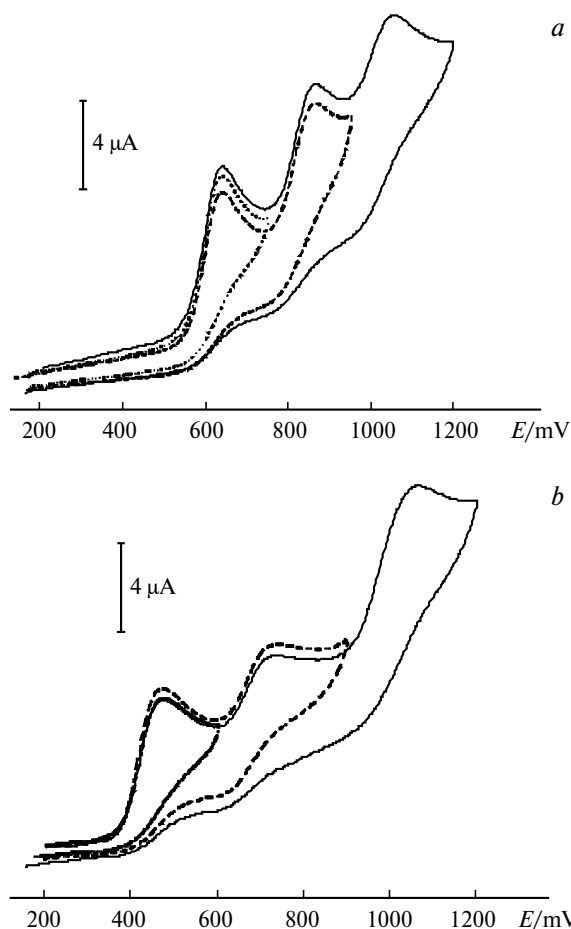
Fig. 4. Cyclic voltammograms of complexes **10** (*a*) and **11** (*b*) in 1,2-dichloroethane solution (*T* = 25 °C, concentration of the complexes *C* = 0.003 mol L^{-1}, supporting electrolyte 0.2 *M* Bu$_4$NPF$_6$, sweep rate 100 mV s^{-1}).

trum of complex **1** obtained in the negative ion mode is significantly less informative. The main signal in this spectrum is the signal from the molecular anion of the matrix with *m/z* = 250.1 Da, whereas the signal from the molecular anion [**1**]$^-$ is absent.

Thus, the signal of the molecular cation is observed and the signal of the molecular anion is absent in the mass spectrum of complex **1** capable of reversible electrooxidizing. This indicates that complex **1** is oxidized to the molecular cation in both the gas and liquid phases. At the same time, the formation of the molecular anion is energetically unfavorable under the laser activation conditions.

Table 2. Results of the electrochemical study of *exo—nido*-ruthenacarboranes (*E*$_{p,a}$/V)*

Complex	$E^1_{p,a}$	$E^2_{p,a}$	$E^3_{p,a}$
10	0.64	0.87	1.06
11	0.48	0.74	1.07

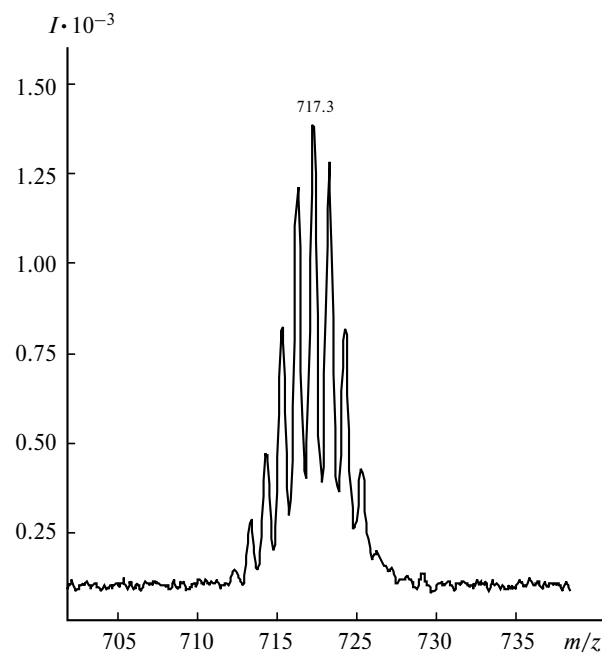* The values of potentials are given *vs* Ag/Ag$^+$.

Fig. 5. Fragment of the mass spectrum of compound **1** detected in the positive ion mode. Matrix is DCTB; *I* is intensity (arb. units).

As established above, paramagnetic *closo*-ferracarborane complexes **2** and **3** are not characterized by reversible electrochemical reactions. The mass spectral analysis showed that these compounds cannot form stable molecular ions that can be detected by the MALDI-TOF method. The spectra of these complexes contain a series of signals corresponding to the products of fragmentation of their molecular ions. Based on the mass spectral data, we can assume the fragmentation mechanism and attribute it to the reactivity of the complexes. The spectra of complex **2** detected in the negative ion mode (Fig. 6, *a*) exhibit intense signals with *m/z* = 321.2 Da corresponding to the [Fe(C$_2$B$_9$H$_{11}$)$_2$]$^-$ anion. The signal with *m/z* = 224.0 corresponding to the anionic species [FeC$_2$B$_9$H$_{11}$Cl]$^-$ should also be emphasized. The signals from the fragmentation products [Fe(dppe)C$_2$B$_9$H$_{11}$]$^+$ (dppe is ethylenebis-(diphenylphosphine)) and [Fe(dppp)C$_2$B$_9$H$_{11}$]$^+$ (dppp is 1,3-bis(diphenylphosphino)propane) with *m/z* = 587.0 and 601.1 Da, respectively, are observed in the spectra detected in the positive ion mode for paramagnetic complexes **2** and **3**. For complex **2**, the signal from [FeCl(dppe)]$^+$ with *m/z* = 488.9 Da is additionally observed (see Fig. 6, *b*). Thus, the results of the analysis indicate that the molecular ions of the paramagnetic iron complexes are unstable and easily undergo fragmentation in the gas phase with the ejection of the ligands bound to the metal. This conclusion also confirms the instability of the oxidized and reduced forms of complexes **2** and **3** observed in electrochemical experiments.[4]

In spite of similar structures of *closo*-ferracarboranes **2** and **3** and their ruthenium-containing analogs **4—9**, the
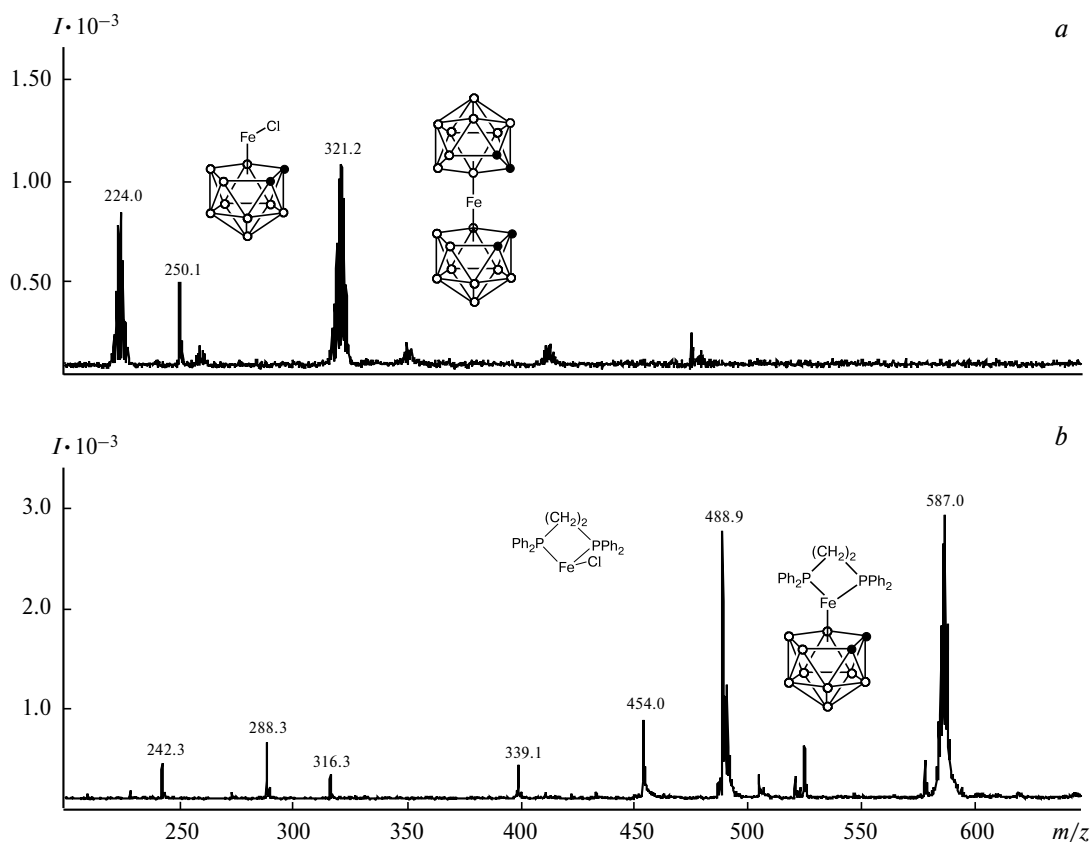
Fig. 6. Mass spectra of paramagnetic *closo*-ferracarborane **2** detected in the negative (*a*) and positive (*b*) ion modes. Matrix is DCTB; *I* is intensity (arb. units).

mass spectra of these compounds differ significantly. The fragments of the mass spectra of compound **5** obtained in the detection modes of ions with unlike signs are presented in Fig. 7. In the spectrum detected in the negative ion mode (Fig. 7, *a*), the most intense is the signal ($m/z = 694.3$ Da) of the molecular anion formed upon electron capturing by the 17-electron complex. The signal consists of 15 lines with the intensity completely identical to the theoretically calculated isotope pattern. Note that the distribution determined by the boron, chlorine, and ruthenium atoms, which have several stable isotopes, makes it possible to unambiguously identify the signals from the ruthenacarborane clusters against the background of possible impurities and fragmentation products. Similar mass spectra were also obtained for other *closo*-ruthenacarboranes **4** and **6**—**8**; the results of MALDI-TOF studies of these complexes were discussed in detail.[19] Unlike the iron-containing analogs, the paramagnetic ruthenium complexes are capable of forming stable molecular anions both in the gas phase (in the MALDI-TOF source) and upon the reduction on the electrode.

The mass spectrum of complex **5** detected in the positive ion mode contains no signal of the molecular cation (see Fig. 7, *b*). The most intense signal ($m/z = 658.3$ Da) corresponding to the fragmentation ion formed from the

molecular ion by halogen atom detachment. The probable structure of the fragmentation product was established by comparing the isotope pattern of this ion observed in the spectrum with the theoretically predicted one. The absolute values of m/z of the peaks in the spectrum were also taken into account. Thus, unlike the stable 18-electron anions, the corresponding Ru[IV] cations are unstable and easily decompose in both the solution (CV method) and mass spectrometer.

The mass spectra obtained for complexes **8** and **9** in the negative ion mode (Fig. 8, *a*) contain intense signals of molecular anions ($m/z = 691.3$ and 706.1 Da), which agree with the theoretically calculated isotope distribution. The mass spectrum of compound **8** differs from the spectrum presented for complex **5** (see Fig. 7, *a*) only by the shift of the molecular anion signal by two units toward smaller masses, which corresponds to the detachment of two hydrogen atoms upon the formation of bis(*ortho*-phenylenecycloboronated) complex **8**. The analysis of the latter in the positive ion mode shows the fragmentation product and also an intense signal of the molecular cation (see Fig. 8, *b*), which was absent from the spectra of compounds **4**—**7**.

The mass spectrum of compound **9** also contains signals from the molecular cation ($m/z = 706.2$ Da) and fragmentation product ($m/z = 670.2$ Da). Thus, the for-
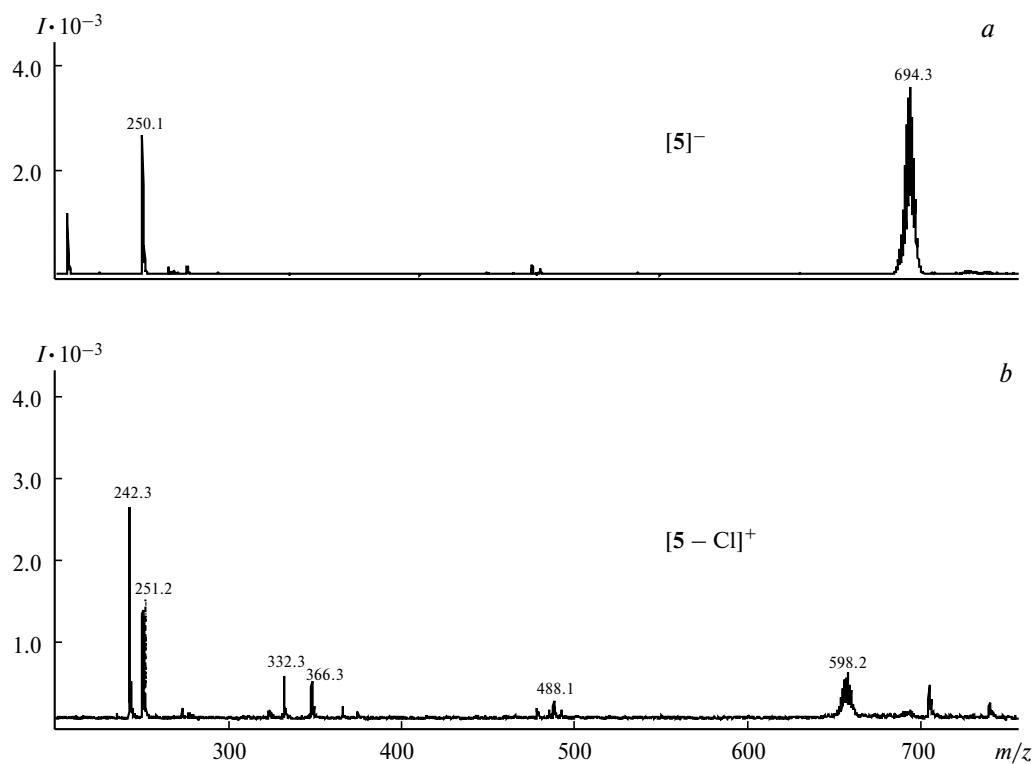
Fig. 7. Mass spectra of paramagnetic *closo*-ruthenacarborane **5** detected in the negative (*a*) and positive (*b*) ion modes. Matrix is DCTB; *I* is intensity (arb. units).
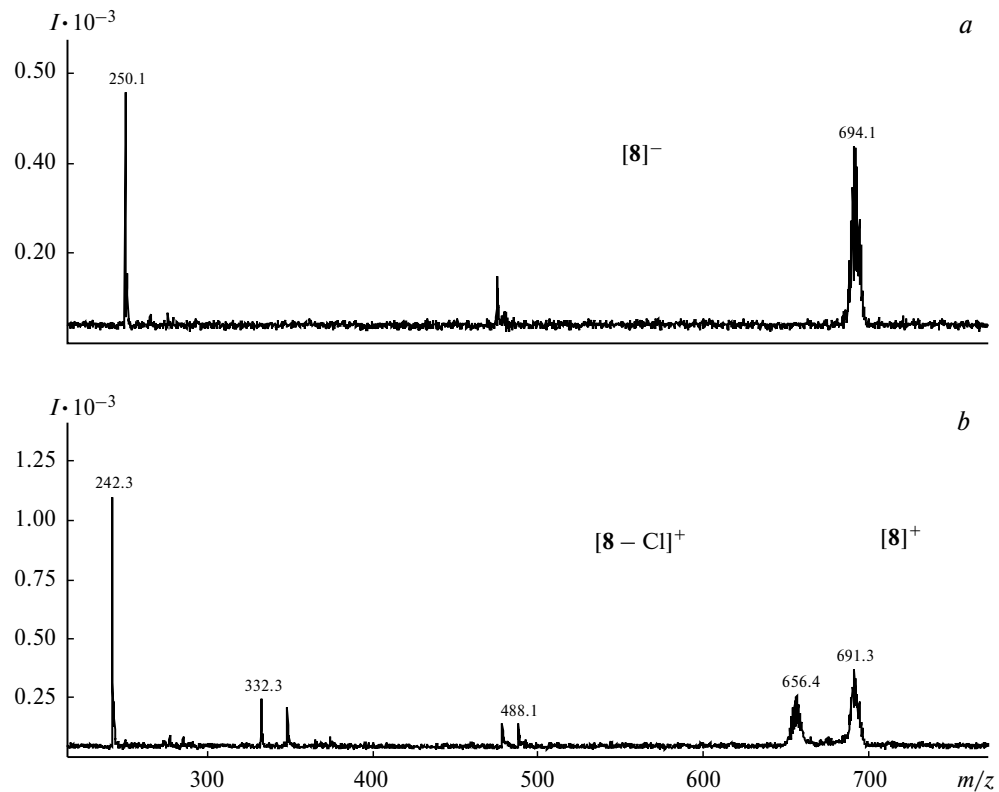

Fig. 8. Mass spectra of paramagnetic *closo*-ruthenacarborane **8** detected in the negative (*a*) and positive (*b*) ion modes. Matrix is DCTB; *I* is intensity (arb. units).

mation of the second *ortho*-phenylenecycloboronated fragment in the ruthenacarborane molecule makes the molecular cations stable. This is manifested in both the mass spectra and reversibility of electrochemical oxidation.

It was established by the CV method that *exo—nido*-ruthenacarboranes **10** and **11** are irreversibly oxidized on the electrode, and the mass spectrometric analysis made it possible to determine the nature of formed particles. The mass spectrum of compound **10** is shown in Fig. 9. As should be expected (taking into account the results of electrochemical studies), the signals of the molecular ions of both signs are absent and the fragmentation peaks are observed, in particular, the peak of the dicarba-*nido*-undecaborate anion with m/z = 134 Da and the peaks of cations containing the ruthenium atom and their adducts with the matrix (see Fig. 9). The presented mass spectra indicate that in the gas phase, under the MALDI-TOF conditions, *exo—nido*-ruthenacarboranes **10** and **11** dissociate with the cleavage of the two-electron three-center B—H···Ru bonds. This affords the corresponding $\{C_2B_9\}$ monoanions and Ru^{III} cations that can give stable adducts with the molecules of the matrix used for the transition of the substance to the gas phase. Perhaps, a similar dissociation process also occurs in solution: the formed particles containing the ruthenium atom enter the oxidation

Table 3. Comparison of the behavior of the metallacarborane clusters under the conditions of mass spectrometric and electrochemical analyses

Com-pound	Reversibility of electrochemical processes		Presence of signal of molecular ion in mass spectrum	
	Ox	Red	Cat	An
1	+	−	+	−
2—3	−	−	−	−
4—7	−	+	−	+
8—9	+	+	+	+
10—11	−	−	−	−
Ferrocene*	+	−	+	−

Note. Ox is oxidation, Red is reduction, Cat is the positive ion mode, An is the negative ion mode, + indicates the reversible process/signal is observed, and − indicates the irreversible process/no signal. * Data of Ref. 1.

reactions on the working electrode, which is detected as several consecutive peaks.

The generalized results of studying the metallacarboranes clusters under the MALDI-TOF and CV conditions are presented in Table 3. An analysis of the obtained data
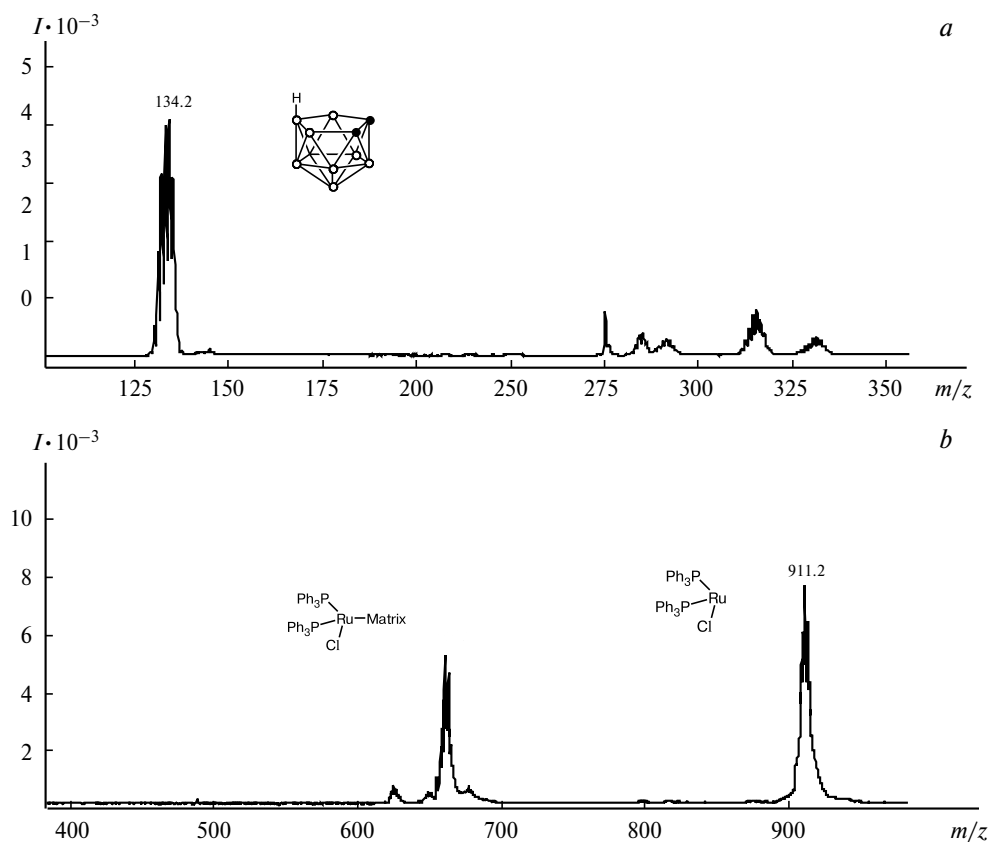

Fig. 9. Mass spectra of *exo—nido*-ruthenacarborane **10** detected in the negative (*a*) and positive (*b*) ion modes. Matrix is DCTB; *I* is intensity (arb. units).

shows that the complexes capable of reversible electro-chemical oxidizing give stable fragmentation ions in the mass spectra detected in the positive ion mode, whereas signals of molecular anions can be observed in the spectra for the reversibly reducible molecules.

Thus, a relationship between the one-electron redox transformations that occur in the liquid and gas phases is observed for the paramagnetic metallacarborane systems, and tandem use of MALDI-TOF and CV makes it possible to obtain an important additional information on the structures and reactivities of the metallacarborane complexes.

Experimental

Prior to electrochemical studies, acetonitrile and 1,2-dichloroethane were distilled above calcium hydride in argon. The ruthenium and iron carborane complexes of the *closo*-structure were synthesized using earlier published procedures.[4—9] The syntheses of *exo—nido*-ruthenacarboranes **10** and **11** were published previously.[20]

Voltammetric studies were carried out in an inert atmosphere in a three-electrode cell using an IPC-Pro potentiostat. The disc platinum working electrode ($d = 1$ mm) was used. A platinum wire, whose surface area considerably exceeded the working surface area of the indicatory electrode, served as an auxiliary electrode. The reference electrode was a silver wire immersed in a solution of $AgNO_3$ + Bu_4NPF_6 in acetonitrile separated from the cell with a porous glass membrane.[21] All potentials were measured *vs* this electrode. Tetrabutylammonium hexafluorophosphate (Acros Organics) served as a supporting electrolyte.

The metal complex compounds were examined in the linear mode on a Bruker Microflex LT instrument equipped with a nitrogen laser (wavelength 337.1 nm). Cesium iodide (clusters $(CsI)_nCs^+$) or sodium trifluoroacetate $(CF_3CO_2Na)_nCF_3CO_2^-$ were used for the calibration of the mass spectrometer. The calibration dependence was approximated by the third-power polynomial. The experimental data were processed and the theoretical isotope distribution was calculated using the Bruker Compass flex Series 1.3 program package. *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile served as a matrix. Samples were prepared by mixing in a microcell of a solution (5 μL) of the studied substance (10 mg mL^{-1} in CH_2Cl_2) and a solution (5 μL) of a solution of the matrix (20 mg mL^{-1} in THF). The obtained solution (2 μL) was deposited on the stainless steel support and analyzed.

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