Synthesis and thermal transformations of molecular complexes of bis[tris(trifluoromethyl)germyl]mercury(II) with *o*-quinones

G. A. Abakumov,[a] V. K. Cherkasov,[a]* N. I. Ermolaev,[b] V. I. Nevodchikov,[a] and L. G. Abakumova[a]

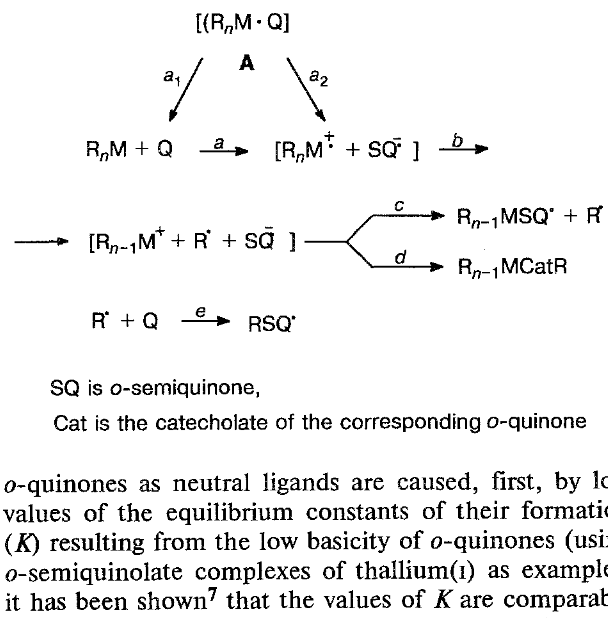
[a]Institute of Organometallic Chemistry, Russian Academy of Sciences,
49 ul. Tropinina, 603600 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831 2) 661 497
[b]Institute of Applied Physics, Russian Academy of Sciences,
603600 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831 2) 365 745

Stable molecular complexes of bis[tris(trifluoromethyl)germyl]mercury(II) $Hg[(CF_3)_3Ge]_2$ (**1**) with *o*-quinones (3,6-di-*tert*-butylbenzoquinone-1,2 (**2**), 3,6-di-*tert*-butyl-4,5-dimethoxybenzoquinone-1,2 (**3**), and 1,4,5,7-tetra-*tert*-butyldibenzo[1,4]dioxin-2,3-dione (**4**)) have been synthesized and characterized by elemental analysis and IR and electronic absorption spectroscopies. Depending on the ratio between the starting reactants, the reactions of *o*-quinones with **1** gave complexes of the composition $R_2Hg \cdot Q$ (**5**, **7**, **9**) or $R_2Hg \cdot Q_2$ (**6**, **8**, **10**), where Q = **2** (**5**, **6**), **3** (**7**, **8**), **4** (**9**, **10**); R = $Ge(CF_3)_3$. According to the spectral data, the molecule of *o*-quinone in $R_2Hg \cdot Q$ acts as a neutral ligand, whereas the second molecule of *o*-quinone in $R_2Hg \cdot Q_2$ is not coordinated to **1**. It has been found by ESR that thermolysis of polycrystalline samples of complexes **6** and **10** involves intermediate formation of radical pairs and finally yields paramagnetic *o*-semiquinone complexes, $SQGe(CF_3)_3$, which are typical products of one-electron oxidation of organometallic compounds by *o*-quinones.

Key words: synthesis; molecular complexes; *o*-quinones; bis[tris(trifluoromethyl)germyl]-mercury(II); thermolysis; one-electron oxidation.

Electron transfer is postulated as the key step of the mechanism of the one-electron oxidation of organometallic compounds (OMC) of nontransition metals by *o*-quinones (Q) (step *a* in Scheme 1).[1] The succeeding steps of this reaction are the fragmentation of the radical cation derived from the OMC (*b*), intracage recombination of the intermediates of the redox process with (*c*) or without (*d*) emergence of free radicals from the solvent "cage," and trapping of the resulting radicals by the second molecule of *o*-quinone (*e*).[1,2] The actual occurrence of steps (*b*—*e*) has been confirmed by the formation of paramagnetic intermediates of oxidation of OMC, *viz*., *o*-semiquinone complexes of metals, which have been detected many times by ESR during various reactions of this sort and also among the final products.[3—6] However, until recently no experimental evidence for the formation of molecular complexes of *o*-quinones with OMC (**A**) as precomplexes in the one-electron oxidation of OMC has been reported. The possibility of the synthesis of these complexes involving nontransition metals is indicated by the fact that reversible formation of complexes of *o*-quinones with thallium(I) *o*-semiquinolate (1 : 1) in a solution was detected by ESR.[7]

Scheme 1



SQ is *o*-semiquinone,
Cat is the catecholate of the corresponding *o*-quinone

The low steady-state concentrations of type **A** complexes of OMC derived from nontransition metals with *o*-quinones as neutral ligands are caused, first, by low values of the equilibrium constants of their formation (K) resulting from the low basicity of *o*-quinones (using *o*-semiquinolate complexes of thallium(I) as examples, it has been shown[7] that the values of K are comparable to the equilibrium constants of the formation of solvate complexes); second, by high rates of the electron transfer in step a_2 in the case of normal OMC, which results from the low potentials of their one-electron oxidation.[8]

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1568—1573, August, 1995.

In the present work we used an oxidation-resistant organobimetallic compound, bis[tris(trifluoromethyl)-germyl]mercury, $Hg[Ge(CF_3)_3]_2$ (**1**), as a model OMC to prepare its molecular complexes with substituted *o*-benzoquinones, *viz.*, 3,6-di-*tert*-butylbenzoquinone-1,2 (**2**), 3,6-di-*tert*-butyl-4,5-dimethoxy-benzoquinone-1,2 (**3**), and 1,4,5,7-tetra-*tert*-butyldibenzo[1,4]dioxin-2,3-dione (**4**), and studied thermal transformations of these complexes by ESR.

Results and Discussion

The complexes were prepared by mixing toluene solutions of stoichiometric quantities of reactants, followed by crystallization of the product by adding hexane. Depending on the stoichiometry chosen, complexes of the composition $R_2Hg \cdot Q$ or $R_2Hg \cdot Q_2$ were isolated.

$R_2Hg \cdot Q$ $R_2Hg \cdot Q$
5, **7**, **9** **6**, **8**, **10**
Q = **2** (**5**, **6**), **3** (**7**, **8**), **4** (**9**, **10**)
R = $Ge(CF_3)_3$

They are readily crystallizing substances, colored red with various tones, and are stable in the crystalline state at temperatures below 0 °C. Their structures have been studied by infrared and electronic absorption spectroscopies.

In the IR spectrum of complex **5**, the absorption band corresponding to C=O stretching vibrations is shifted to lower frequencies (to 1640 cm^{-1}) with respect to the ν_1(CO) = 1665 cm^{-1} and ν_2(CO) = 1685 cm^{-1} frequencies in the IR spectrum of the starting *o*-quinone. The C=O stretching region in the IR spectrum of complex **6** is a superposition of three absorption bands with ν_1(CO) = 1643 cm^{-1}, ν_2(CO) = 1665 cm^{-1}, and ν_3(CO) = 1685 cm^{-1}. The frequency of the first of these practically coincides with ν(CO) in the IR spectrum of complex **5**; the other two bands correspond in frequency to the IR spectrum of pure compound **2**. A similar low-frequency shift is also observed in the IR spectrum of complex **9**: ν(CO) = 1630 cm^{-1} compared to ν_1(CO) = 1660 cm^{-1} and ν_2(CO) = 1675 cm^{-1} in pure **10**. Thus, judging from the data of IR spectroscopy, the quinone molecule in $R_2Hg \cdot Q$ complexes acts as a neutral ligand, while in complexes of the composition $R_2Hg \cdot Q_2$, the second Q molecule is not coordinated to R_2Hg.

In nonpolar solvents (hexane, toluene), the $R_2Hg \cdot Q$ complexes exist in equilibrium with the starting components.

$$R_2Hg \cdot Q \rightleftharpoons R_2Hg + Q \qquad (1)$$

This is indicated by the electronic absorption spectra of their solutions, which are superimpositions of the spectra of the complexes and those of the starting reactants. By adding a fivefold excess of R_2Hg one can almost completely shift equilibrium (1) toward the formation of the complex. At this ratio between the reactants, the electronic absorption spectra differ dramatically from the spectra of the corresponding *o*-quinones. In fact, the spectrum of complex **5** (Fig. 1), instead of the band with λ_{max} = 397 nm (ε = 2830) associated with the long-wave $\pi \rightarrow \pi^*$ transition in the *o*-quinone molecule, exhibits two new bands with λ_{max} = 315 nm (ε = 1300) and λ_{max} = 452 nm (ε = 1745). The spectrum of complex **7** also contains two new bands with λ_{max} = 290 nm (ε = 6000) and λ_{max} = 460 nm (ε = 1650) that are missing from the spectrum of the starting quinone, instead of the band with λ_{max} = 392 nm (ε = 2250).

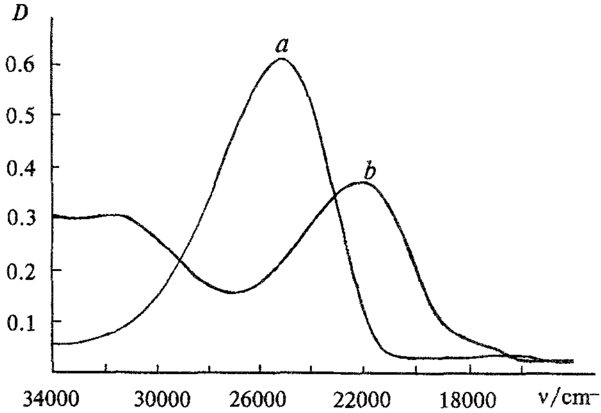
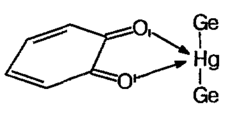


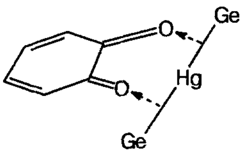
Fig. 1. Electronic absorption spectra of *o*-quinone **2** (*a*) (heptane, C = 2.16 · 10^{-3} *M*, 290 K) and complex **5** (*b*) (heptane, C_2 = 2.16 · 10^{-3} *M*, C_1 = 1.08 · 10^{-2} *M*, 290 K).

The spectral characteristics of complexes **5**, **7**, and **9** obtained are evidence of their "quinone" natures. The C=O stretching frequencies in their IR spectra are only slightly (by 25—50 cm^{-1}) shifted to lower frequencies with respect to those in the spectra of the starting *o*-quinones, thus indicating that the carbonyl functions have been retained in the molecule. The IR spectra of *o*-semiquinone complexes contain no bands corresponding to the ν(C=O) vibrations.[9] The electronic absorption spectra of the resulting complexes also differ from those of the SQ complexes of metals, which contain a typical absorption band in the "red" region (λ_{max} > 700 nm).[10]

The problem of the coordination center and the type of the coordination bond between *o*-quinone and OMC in the complexes under consideration requires additional investigation. In the present work, only some suggestions concerning their structures may be stated based on the spectral data. In these complexes, *o*-quinone may act either as an n-donor, *i.e.*, lend electrons of the n-orbitals of the oxygen atoms for the formation of the coordination bond (complexes with transition metals[11]), or as a π^*-acceptor, *i.e.*, accept the electron charge in the vacant π^*-orbital; this occurs, for example, in charge-transfer complexes with aromatic amines.[12] In the former case, the partner of *o*-quinone must have vacant orbitals, and the resulting complex would be an nv-type complex (**B**), and in the latter case, charge transfer from a σ-orbital of the OMC to the π*-orbital should give a σπ-type complex (**C**).[13]



B



C

The decrease in the stretching frequencies of the C=O bonds in complexes of carbonyl derivatives with OMC is due to the transfer of electron density from n-orbitals of oxygen atoms of the donor molecule to the vacant orbitals of the acceptor molecule.[13] According to this criterion, the $R_2Hg\cdot Q$ complexes studied in this work can be regarded as nv-type complexes. However, from general considerations, one should expect that the ν(CO) stretching frequency would also decrease in the σπ-complexes of *o*-quinones due to the transfer of electron density to the antibonding π*-orbital. It is also quite probable that the complexes under consideration have structure **B** in which both types of interaction, *viz.*, coordination of the unshared electron pairs of *o*-quinone to vacant MO of the OMC molecule and back donation of the electron density from σ-MO of the OMC (the Hg—Ge bond) to the π*-MO of *o*-quinone, are realized. All of the structures discussed are hypothetical. This problem can be unambiguously solved by a planned experiment using X-ray diffraction analysis.

As has been already noted, the data of spectroscopic analysis imply that the second molecule of *o*-quinone incorporated in complexes **6**, **8**, and **10** is not bound to the OMC molecule in solution or in crystals. However, the presence of this molecule has a crucial effect on thermolysis of these complexes determining its direction.

Unlike complex **5**, whose heating *in vacuo* results in its dissociation to give the starting reactants (under atmospheric pressure, it melts at 128 °C, and when the melt is heated further, metallic mercury is liberated, probably due to decomposition of **1**), polycrystalline samples of complex **6** heated either *in vacuo* or under atmospheric pressure turn black at a temperature of ~95 °C, and at higher temperatures they decompose to give metallic mercury and a dark-blue liquid that solidifies on cooling. According to the ESR data, this is the paramagnetic complex $SQGe(CF_3)_3$.

$$R_2Hg\cdot Q \xrightarrow{\Delta} R_2Hg + Q \tag{2}$$

$$R_2Hg\cdot Q_2 \xrightarrow{\Delta} Hg + 2SQGe(CF_3)_3 \tag{3}$$

Crystals of the $R_2Hg\cdot Q$ type complexes cannot be obtained free from minor (less than 0.1 %) quantities of paramagnetic admixtures that can be detected by ESR.

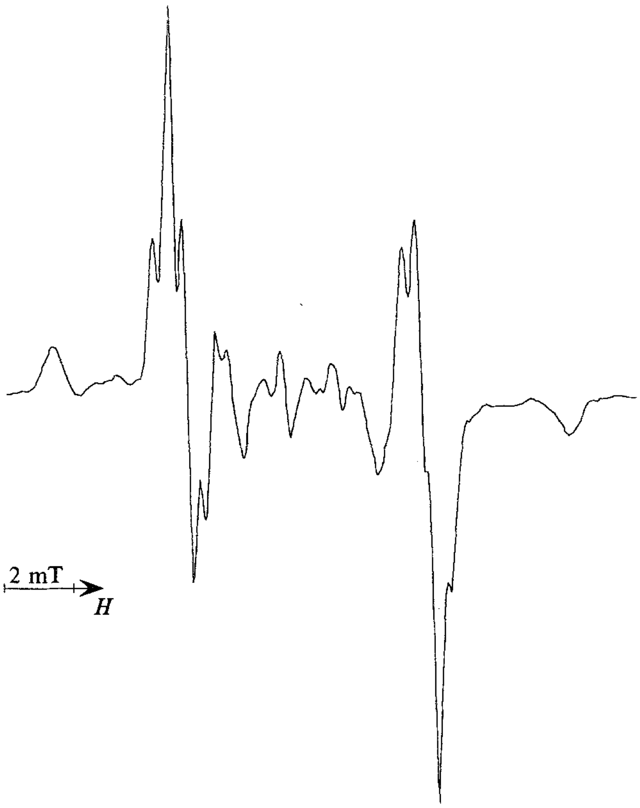


Fig 2. ESR spectrum of the radical pair resulting from thermolysis of a polycrystalline sample of complex **6** (290 K).

The ESR spectra recorded for polycrystalline samples of $R_2Hg\cdot Q_2$ complexes (Fig. 2) are typical of spin triplet states with the axial symmetry of the tensor of dipole interaction.[14] In the case of **6**, $D_\parallel$ = 15 mT, $D_\perp$ = 7.3 mT and for **10** $D_\parallel$ = 10.2 mT, $D_\perp$ = 5.1 mT. At room temperature, the intensity of the ESR spectrum of the biradical gradually increases with time and, along with it, a singlet with g_{eff} = 2.003 appears. The intensity of the singlet increases much more rapidly than that of the signal of the biradical, and finally, the latter becomes entirely covered. The higher the temperature, the more rapidly the evolution of the ESR spectrum occurs. Heating the crystals of complexes of the composition 1 : 1 does not result in the appearance of the signal of the biradical, their ESR spectra exhibit only singlet lines with g_{eff} = 2.003 and ΔH = 1.5 mT during heating.

The compositions and structures of paramagnetic *o*-semiquinone derivatives of germanium, $SQGe(CF_3)_3$ (**11—13**, Q = **2** (**11**), **3** (**12**), or **4** (**13**)) resulting from thermal decomposition of complexes **6**, **8**, and **10** as well as the identity of the products of thermal decomposition of polycrystalline samples and the products of thermolysis in solution were determined by ESR. The ESR spectral pattern obtained for toluene solutions of complexes **5** and **6** at 290 K is shown in Fig. 3. Each of the three components of the triplet (1 : 2 : 1) resulting from the interaction of the unshared electron with the

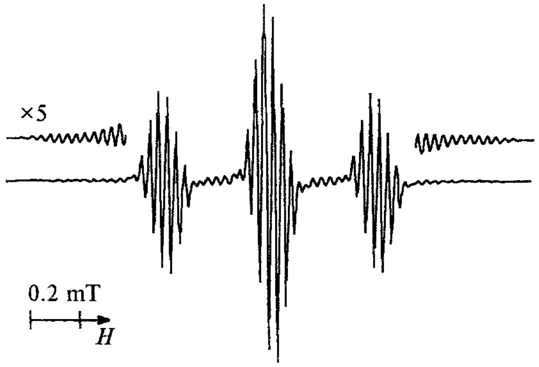


Fig 3. ESR spectrum of *o*-semiquinone complex **11**, the final product of thermolysis of complex **6** (toluene, 290 K).

two protons of the SQ ligand is additionally split into 10 components with a binomial distribution of the intensities in the multiplet (1 : 9 : 36 : 84 : 126 : 126 : 84 : 36 : 9 : 1) corresponding to hyperfine coupling (HFC) of the unpaired electron with nine equivalent nuclei with $S = 1/2$. (The terminal components of the multiplet are not exhibited in the spectrum, due to their low intensities, but the ratio between the intensities of the other components precisely corresponds to the theoretical ratio). One can say with confidence that this multiplet arises due to the HFC of the unpaired electron with the nine equivalent ^{19}F nuclei (100 %, $\mu_N = 2.6273$, $I = 1/2$)[15] of the three trifluoromethyl groups. The ESR spectrum also contains a set of satellite lines caused by interaction of the unpaired electron with the ^{73}Ge magnetic isotope (7.61 %, $\mu_N = -0.87677$, $I = 9/2$).[15] Parameters of the ESR spectra of paramagnetic SQGe(CF$_3$)$_3$ complexes are presented in Table 1.

An identical ESR spectrum appears when the complex is heated in diethyl ether, THF, or another solvent. The intensities of the ESR spectra of both solutions and polycrystalline samples increase with time. This occurs more rapidly, the higher the temperature. In complexes that contain two molecules of *o*-quinone the rate of accumulation of paramagnetic products is much higher than that in complexes of 1 : 1 composition.

Table 1. Parameters of the isotropic ESR spectra of the *o*-semiquinone complexes, SQGe(CF$_3$)$_3$ (toluene, 290 K)

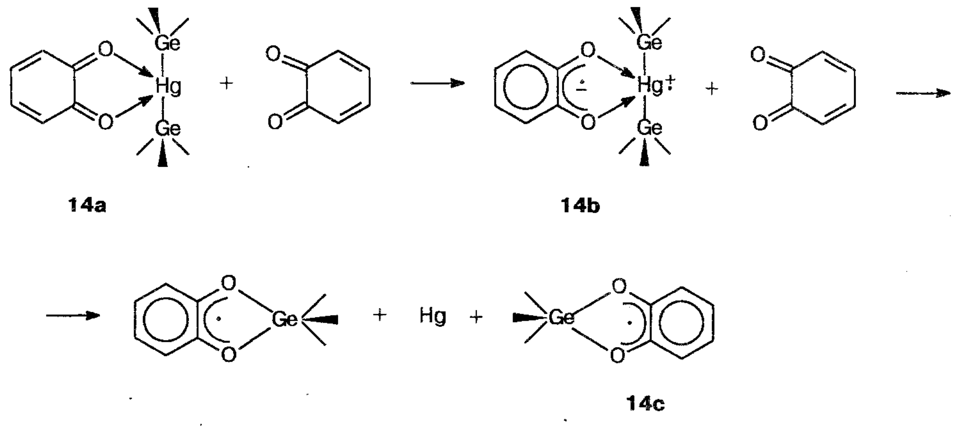
SQGe(CF$_3$)$_3$	g_i	A_i(H) /mT	A_i(^{19}F) /mT	A_i(^{73}Ge) /mT
11	2.0032	0.425 (2 H)	0.032 (9 F)	0.091 (1 Ge)
12	2.0033	0.017 (6 H)	0.035 (9 F)	0.090 (1 Ge)
13	2.0032	—	0.031 (9 F)	—

It should be noted that paramagnetic *o*-semiquinone complexes of tris(trifluoromethyl)germanium possess high thermal stabilities. Their solutions withstand heating to 120 °C with no noticeable changes in the intensity of the ESR signal. In our opinion, transformations of the ESR spectra of the R$_2$Hg · Q$_2$ complexes indicate synchronous local formation of two radical species, related to one another by their origin from one R$_2$Hg molecule in the first step of thermolysis in the crystalline matrix.

$$R_2Hg \cdot Q_2 \xrightarrow{\Delta} [(CF_3)_3GeSQ \cdot Hg \cdot SQGe(CF_3)_3] \qquad (4)$$

The values of r in the radical pairs resulting from thermal transformation of complexes **6** and **10** calculated from the $D_{\|}$ parameter are 7.2 and 8.2 Å, respectively. These values are consistent with the distance between the radical centers in the hypothetical structure (**14c**), whose appearance would be expected from the structure supposed for R$_2$Hg · Q$_2$ complexes (**14a**) (Scheme 2). It is most likely that the primary molecular complex is an nv-type complex with the σπ-type back donation in which one Q molecule is coordinated to the mercury atom. The second Q molecule is incorporated in the crystal lattice as crystal solvate and is located in the immediate vicinity of the R$_2$Hg · Q molecule in the *trans*-position with respect to the first Q molecule, and its carbonyl groups are directed at the Hg—Ge σ-bonds. Thermal excitation results in the transfer of an electron from the group σ-bonding Hg—Ge orbital of molecule **1** to the π*-orbital of the coordinated Q molecule to give a radical-ion pair (**14b**), which is converted into a radical

Scheme 2



pair (**14c**) through fragmentation of the resulting organometallic radical cation to Hg, $^{+}Ge(CF_3)_3$ cation, and $^{\cdot}Ge(CF_3)_3$ radical and subsequent collapse of the cation and the radical with the radical anions of SQ and Q, respectively.

Thus, the results of the present work indicate that molecular complexes of *o*-quinones with OMC can be produced as primary intermediates in the one-electron oxidation of OMC with *o*-quinones.

Experimental

The ESR spectra were recorded on a Bruker ER 200D SRC spectrometer with a standard (ER 4102 ST) or double (ER 4105 DR) resonator (with a working frequency of 9.5 GHz). Temperature control of the samples was carried out using a Bruker ER 4111 VT temperature control unit. IR spectra were recorded on a Specord M-40 spectrometer, and electronic absorption spectra were measured on a Specord M-80 spectrometer.

The 3,6-di-*tert*-butylbenzoquinone-1,2 and 3,6-di-*tert*-butyl-4,5-dimethoxybenzoquinone-1,2 used in the work were synthesized by the known procedures;[16,17] bis[tris(trifluoromethyl)germyl]mercury was prepared by the previously reported procedure.[18] 1,4,5,7-Tetra-*tert*-butyldibenzo[1,4]dioxin-2,3-dione was isolated by column chromatography as one of the by-products in the synthesis of compound **2** (see Ref. 16). Yield 5 %, m.p. 88 °C. Found (%): C, 76.90; H, 8.59. $C_{28}H_{38}O_4$. Calculated (%): C, 76.68; H, 8.73. IR, ν/cm^{-1}: 1660; 1680 (C=O). ^{1}H NMR (CCl_4), δ: 1.29 (s, 1,4-Bu^t); 1.29 (s, 5-Bu^t); 1.31 (s, 7-Bu^t); 6.79 (d, C(8), J = 2.2 Hz); 6.94 (d, C(6)H, J = 2.2 Hz). Solvents of the "pure for analysis" grade were purified by standard procedures.

The complex of bis[tris(trifluoromethyl)germyl]mercury(II) with 3,6-di-*tert*-butylbenzoquinone-1,2 (5). At ambient temperature, a solution of **1** (0.168 g, 0.221 mmol) in 10 mL of toluene was mixed under an argon atmosphere with a solution of *o*-quinone **2** (0.049 g, 0.221 mmol) in 5 mL of toluene. The volume of the reaction mixture was brought to 5 mL, then 15 mL of hexane was added, and the solution was cooled to 0 °C. The resulting light-red crystalline precipitate of **5** was filtered off, washed with cold hexane (2 × 10 mL), and dried *in vacuo* to give 0.205 g (95 %) of complex **5**. Found (%): C, 24.54; H, 2.02. $C_{20}H_{20}O_2F_{18}Ge_2Hg$. Calculated (%): C, 24.50; H, 2.05. M.p. 95 °C.

Complexes **6**—**10** were prepared by a similar procedure. **6**: light-red crystals; yield 93 %. Found (%): C, 34.02; H, 3.53. $C_{34}H_{40}O_4F_{18}Ge_2Hg$. Calculated (%): C, 34.01; H, 3.33. M.p. 128 °C (decomp.). The compositions of complexes **7**—**10** were determined from the data of IR spectroscopy and ESR.

The authors wish to thank M. A. Lopatin for his help in recording the electronic absorption spectra.

This work was carried out with financial support from the Russian Foundation for Basic Research (Project No. 93-03-18369).

References

1. G. A. Abakumov, E. N. Gladyshev, N. S. Vyazankin, G. A. Razuvaev, P. Ya. Bayushkin, and V. A. Muraev, *J. Organomet. Chem.*, 1974, **64**, 327.
2. G. A. Abakumov, in *Kompleksy metallov so svobodnoradikal'nymi ligandami: Metalloorganicheskie soedineniya i svobodnye radikaly* [*Metal Complexes with Free-Radical Ligands: Organometallic Compounds and Free Radicals*], Nauka, Moscow, 1985, 85 (in Russian).
3. G. A. Razuvaev, E. N. Gladyshev, P. Ya. Bayushkin, G. A. Abakumov, and E. S. Klimov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 2762 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1976, **25** (Engl. Transl.)].
4. G. A. Razuvaev, G. A. Abakumov, E. S. Klimov, E. N. Gladyshev, and P. Ya. Bayushkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 1128 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1976, **25** (Engl. Transl.)].
5. E. N. Gladyshev, P. Ya. Bayushkin, G. A. Abakumov, and E. S. Klimov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 176 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1977, **26**, 153 (Engl. Transl.)].
6. G. A. Abakumov, V. I. Nevodchikov, V. K. Cherkasov, and G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, 1978, **242**, 609 [*Dokl. Chem.*, 1978, **242** (Engl. Transl.)].
7. G. A. Abakumov, V. K. Cherkasov, N. O. Druzhkov, V. I. Nevodchikov, V. N. Afanas'ev, and A. N. Korovushkin, *Dokl. Akad. Nauk SSSR*, 1989, **308**, 628 [*Dokl. Chem.*, 1989, **308** (Engl. Transl.)].
8. J. K. Kochi, *Organometallic Mechanisms and Catalysis*, Academic Press, New York, London, 1978, 445.
9. L. G. Abakumova, *VIth European Conf. on Organometallic Chemistry, Abstrs.*, Riga, 1976, 183.
10. A. V. Lobanov, G. A. Abakumov, and G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, 1977, **235**, 824 [*Dokl. Chem.*, 1977, **235** (Engl. Transl.)].
11. C. G. Pierpont and C. W. Lange, *Progress in Inorg. Chem.*, 1994, **41**, 409.
12. G. A. Abakumov, V. I. Nevodchikov, and V. K. Cherkasov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2709 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, 2507 (Engl. Transl.)].
13. E. N. Gur'yanova, I. P. Gol'dshtein, and I. P. Romm, *Donorno-aktseptornaya svyaz'* [*Donor-Acceptor Bond*], Khimiya, Moscow, 1973, 153 pp. (in Russian).
14. J. Werts and J. Bolton, *Teoriya i prakticheskie prilozheniya metoda EPR*, Mir, Moscow, 1975, 245 p [*Theory and Practical Applications of ESR* (Russ. Transl.)].
15. B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. and Radiochem.*, 1970, **13**, 141.
16. N. L. Komissarova, N. S. Belostotskaya, E. V. Dzhuaryan, and V. V. Ershov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, 1380 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1973, **22** (Engl. Transl.)].
17. A. I. Prokof'ev, V. B. Vol'eva, and N. A. Novikova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 2707 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1980, **29**, 1883 (Engl. Transl.)].
18. M. N. Bochkarev, N. L. Ermolaev, G. A. Razuvaev, Yu. K. Grishin, and Yu. A. Ustynyuk, *J. Organomet. Chem.*, 1982, **229**, C1.

Received June 29, 1994;
in revised form March 27, 1995