# Homolytic Reactive Mass Spectrometry of Fullerenes: Interaction of $C_{60}$ and $C_{70}$ with Organo- and Organoelement Mercurials in the Electron Impact Ion Source of a Mass Spectrometer; EPR, CIDEP, and MS Studies of Several Analogous Reactions of $C_{60}$ Performed in Solution

**Yury I. Lyakhovetsky,* Elena A. Shilova, Vasily V. Bashilov, Viatcheslav I. Sokolov, Yuri S. Nekrasov, and Boris L. Tumanskii*,[†]**

*A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences, 28 Vavilov Str, 119991 GSP-1 Moscow V-334, Russia*

*Received: June 29, 2009; Revised Manuscript Received: September 30, 2009*

Interaction of $C_{60}$ with organo- and organoelement mercurials ($CF_3HgBr$, PhHgBr, *p*-$CH_3C_6H_4HgBr$, *p*-$CH_3OC_6H_4HgCl$, $CF_3HgPh$, $Ph_2Hg$, (*o*-carborane-9-yl)$_2$Hg, (*m*-carborane-9-yl)$_2$Hg, (*p*-carborane-9-yl)$_2$Hg, and (*m*-carborane-9-yl)HgCl) in the ionization chamber (IC) of the electron impact (EI) ion source of a mass spectrometer at 250−300 °C results in the transfer of the corresponding organic or organoelement radicals from the mercurials to the fullerene. Some of the processes are accompanied by hydrogen addition. $C_{70}$ reacts with $Ph_2Hg$ and (*o*-carborane-9-yl)$_2$Hg at 300 °C in a similar fashion. A homolytic reaction path is considered for the reactions. It suggests both the thermal and EI initiated homolytic dissociation of the mercurials to the intermediate organic or organoelement radicals followed by their interaction with the fullerenes at the metallic walls of the IC. When EI is involved, the dissociation is supposed to occur via superexcited states (the excited states with the electronic excitation energies higher than the first ionization potentials) of the mercury reagents, with possible contribution of the process proceeding via their molecular ions. In line with the results obtained in the IC, $C_{60}$ reacts with $Ph_2Hg$ and (*o*-carborane-9-yl)$_2$Hg under UV-irradiation in benzene and toluene solutions to furnish phenyl and carboranyl derivatives of the fullerene, respectively, some also containing the acquired hydrogen atoms. EPR monitoring of the processes has shown the formation of phenylfullerenyl and *o*-carborane-9-yl-fullerenyl radicals. *g*-Factors and hyperfine coupling (hfc) constants with $^{10}B$, $^{11}B$, and $^{13}C$ nuclei of both the latter and *m*-carborane-9-yl-fullerenyl radical formed in the reaction of $C_{60}$ with (*m*-carborane-9-yl)$_2$Hg have been determined by the special EPR studies. The unusually great chemically induced dynamic electron polarization (CIDEP) of the latter radical where even the $^{13}C$ satellite lines are polarized has been observed and is discussed in terms of both radical-triplet-pair and radical-pair mechanisms. The similar CIDEP effect is also intrinsic to the *o*-carborane-9-yl-fullerenyl radical obtained under the same conditions. The analogous transfer of the carboranyl radicals from (*o*-carborane-9-yl)$_2$Hg to $C_{60}$ occurs when their mixture is boiled in $^tBuPh$ for 10−15 h.

## 1. Introduction

Ions registered in mass spectrometers can stimulate the search for methods for the synthesis of the corresponding compounds. The most striking examples of it are $C_{60}$ and $C_{70}$. Their molecular ions were first found in the Smalley source of a mass spectrometer,[1] and the intensive 5-year investigations followed allowed developing methods for the synthesis of the species in bulk amounts.[2,3] The aforesaid relates in full measure to the results of the reactive mass spectrometry of fullerenes (reactions of fullerenes with other species occurring within the ionization chamber (IC) of a mass spectrometer and their mass spectral monitoring). Those can supply chemists with valuable information as to what fullerene reactions can be successfully implemented in a “flask” or chemical reactor and what methods would be suitable for this purpose. Since mass spectrometry did much in the discovery of this class of compounds, it is no wonder that reactions of fullerenes in reactors attached to mass spectrometers[4−8] or ones occurring immediately in mass spectrometers have been studied by several research groups. These latter include processes occurring in the chemical ionization (CI) plasma[9−15] and ion/molecule reactions performed and monitored by Fourier-transform ion cyclotron resonance mass spectral (FTMS) technique or by application of other mass spectral methods, such as “selected-ion flow tube” (SIFT),[16] in combination with ion-generating techniques. Both FTMS and SIFT modes allow one to get fullerene ions and collide them with the neutral molecules of other reactants or conversely.[17−31] However, besides the ion/molecule reactions, other types of processes can occur in an IC or its walls, particularly radical ones, provided the partial pressures of the reactants are sufficient.[32,33] McEwen and co-workers were the first who observed addition of alkyl groups to $C_{60}$ under conditions of negative CI with methane as a reagent gas. They proposed a radical scheme of the processes and provided some evidence in favor of it. According to the scheme, alkyl radicals were formed in the methane CI plasma and reacted further with $C_{60}$ adsorbed at the walls of an IC. The paramagnetic species were stabilized by acquiring hydrogen atoms or the next alkyl radicals, and the products were vaporized from the surface to be

---

* Corresponding authors. Yu. I. Lyakhovetsky. E-mail: yulyakh@ineos.ac.ru. B. L. Tumanskii. E-mail: tboris@tx.technion.ac.il.

[†] Present address: Shulich Faculty of Chemistry, Technion-Israel Institute of Technology, Haifa 3200, Israel.

10.1021/jp906058q CCC: $40.75

registered after electron attachment.[33] In our earlier papers, we reported that the reactions of $C_{60}$ and $C_{70}$ with perfluorocompounds—the Scherer radical (perfluorodiisopropylethylmethyl, $C_9F_{19}^•$), a mixture of perfluorononenes, $\beta$-fluorosulphatotetrafluoroethyldiheptafluoroisopropylmethyl radical ($C_9F_{18}OSO_2F^•$), mercury(II) trifluoroacetate, and with ketones $Me_2CO$, MeCOPh, $Bu_2CO$, and MeCOBn—proceeded in the electron impact (EI) ion source of a mass spectrometer and resulted in the transfer of the $CF_3$ and corresponding alkyl (phenyl) radicals from the reactant to the fullerenes, respectively. A homolytic reaction mechanism close to the above one was suggested, and findings in its favor were given.[34] Noteworthy, it is the homolytic reactions that can be transferred more easily from an IC to solution since they are less dependent on the solvent. Actually, $C_{60}$ was shown to react with the Scherer radical and acetophenone in solution (the latter reaction occurred under UV irradiation) adding $CF_3$, $CH_3$, and Ph radicals, respectively.[34a,c,35]

To find other examples indicating that the reactive mass spectrometry, especially a homolytic one, can serve as a tool for predicting the reactivity of fullerenes in solution, we have studied, in the present work, the behavior of organo- and organoelement mercurials RHgX in an IC under EI in the presence of $C_{60}$ or $C_{70}$. The results obtained have been compared with those of several reactions between the same reagents in solution. It should be added that the reactive mass spectrometry of fullerenes as a test for their reactivity in a flask or chemical reactor possesses some advantages: (i) the reactions require only tiny amounts of reagents, (ii) the experiments can be completed rather quickly, and (iii) products are identified in the course of the runs.

## 2. Experimental Section

**2.1. Reagents and Solvents.** $C_{60}$ (99.98%) was purchased from a producer in Nizhnii Novgorod (Russia). $C_{70}$ was both of the same origin and prepared by Roger Taylor and co-workers at the University of Sussex (Brighton, England). The fullerenes were used without additional purification. Diphenylmercury(II) (**1**) was prepared by the reaction of PhMgBr and $HgCl_2$ in ether under argon according to the procedure of D'Ans et al.:[36] mp 125 °C (from ethanol); EI ionization mass spectrum (EI-MS) $m/z$ of the maximal intensity ion in each isotope cluster, 356 ($M^{+•}$), 279 ($[M - Ph]^+$), 154 ($[C_6H_5]_2^{+•}$), 153 ($C_6H_5C_6H_4^{+•}$), 152 ($[C_6H_4)_2]^{+•}$), 202 ($Hg^+$), 77 ($Ph^+$). Trifluoromethylmercury(II) bromide (**2**) was obtained from $CF_3HgOCOCF_3$ in water via $CF_3HgOH$ according to the procedure described by Seythert et al.:[37] mp 88−90 °C; EI-MS $m/z$ 350 ($M^{+•}$), 331 ($[M - F]^+$), 281 ($[M - CF_3]^+$), 271 ($[M - Br]^+$), 202 ($Hg^+$), 101 ($Hg^{2+}$), 69 ($CF_3^+$). Trifluoromethylphenylmercury(II) (**3**) and phenylmercury(II) bromide (**4**) were synthesized by interaction of equimolar amounts of species **1** and **2** in benzene.[37] Compound **3**: mp 140−143 °C, EI ionization mass spectrum is depicted in Figure 1a. Compound **4**: mp 275 °C, EI-MS $m/z$ 358 ($M^{+•}$), 281 ($[M - Ph]^+$), 279 ($[M - Br]^+$), 202 ($Hg^+$). Samples of bis(*o*-, *m*-, *p*-carborane-9-yl)mercury(II) (**5a**,**b**,**c**) and (*m*-carborane-9-yl)mercury(II) chloride (**6**) were kindly provided by Dr. V. Kampel. The EI ionization mass spectrum of **5b** is presented in Figure 1b. The mass spectra of **5a** and **5c** were similar. The mass spectrum of **6** $m/z$: 379 ($M^{+•}$), {344, 343} ($[M - Cl]^+$), 237 ($HgCl^+$), 202 ($Hg^+$), 178 ($m\text{-}C_2H_2B_{10}H_9Cl^{+•}$), 143 ($m\text{-}C_2H_2B_{10}H_9^+$). The spectrum also showed a low-intensity cluster of peaks with the maximal intensity peak at $m/z$ 487 attributed to $M^{+•}$ of **5b**, the compound being probably formed, at least partly, due to disproportionation of **6** in the IC at 270 °C. *p*-Tolylmercury(II) bromide (**7**) was obtained according to the protocol of Hilpert and Grüttner:[38] mp 239−240 °C, EI-MS $m/z$ 372 ($M^{+•}$), 293 ($[M - Br]^+$), 281 ($HgBr^+$), 202 ($Hg^+$), 101 ($Hg^{2+}$) 91 ($C_7H_7^+$), 89 ($C_7H_5^+$), 65 ($C_5H_5^+$), 63 ($C_5H_3^+$). Two low-abundant peak clusters (with respect to that containing the 372 u ion peak) corresponding to the molecular ions of $CH_3C_6H_4HgCl$ and $CH_3C_6H_4HgI$ (the maximal intensity peaks at $m/z$ 328 and 420, respectively) were present in the spectrum. The compounds may not be intrinsic to the sample but formed due to halogen exchange, occurring in the IC at 270 °C, with iodine and chlorine containing species adsorbed at the metallic surface of the IC.[39] A sample of *p*-anisylmercury(II) chloride (**8**) used had a mp of 248 °C and EI ionization mass spectrum $m/z$: 344 ($M^{+•}$), 329 ($[M - CH_3]^+$), 309 ($[M - Cl]^+$), 301 ($[M - CH_3CO]^+$), 237 ($HgCl^+$), 142 ($CH_3OC_6H_4Cl^{+•}$), 107 ($CH_3OC_6H_4^+$), 99 ($C_5H_4Cl^+$), 92 ($OC_6H_4^{+•}$), 77, 64, 63. The spectrum also contained two low intensity peak clusters with the maximal intensity peaks at $m/z$ 388 and 436, respectively, which were attributed to the molecular ions of $CH_3OC_6H_4HgBr$ and $CH_3OC_6H_4HgI$. Again, these compounds could be formed, at least partly, owing to the halogen exchange reactions occurring at the IC surface.

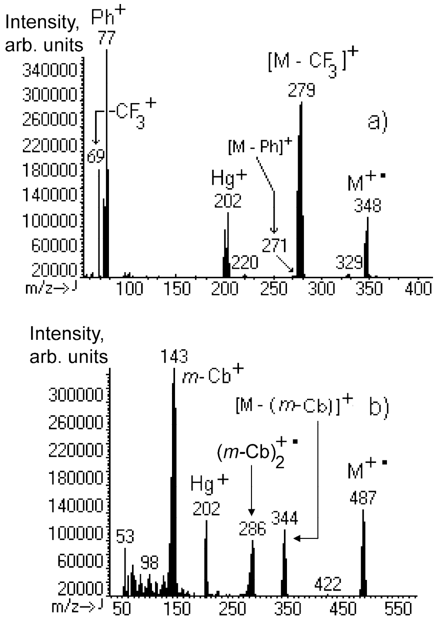


**Figure 1.** EI ionization mass spectra of (a) $CF_3HgPh$ (**3**) and (b) ($m\text{-}C_2H_2B_{10}H_9)_2Hg$ (**5b**). *m*-Cb stands for *m*-carborane-9-yl. The spectra displayed were recorded at the energy of ionizing electrons 70 eV and the IC temperature 200 °C.

Commercial grade benzene, toluene, and *t*-butylbenzene were distilled in argon prior to the experiments.

**2.2. Technique and Methods.** EI ionization mass spectra for species **1**−**8** and the reaction mixtures of the reactions in solvents were obtained on a Kratos MS890a instrument at 70 eV and the IC temperatures of 200−300 °C. The general protocol for the reactions in the IC of the mass spectrometer was described in ref 34a as procedure B. The EPR monitoring of photochemical reactions "a" and "c" (see below) was conducted with a Varian E-12A EPR spectrometer. The measurements of EPR characteristics of *m*-carborane-9-yl-fullerenyl and *o*-carborane-9-yl-fullerenyl radicals (**9** and **10**, respectively) formed in the course of the photochemical reactions between $C_{60}$ and mercurials **5b** and **5a**, respectively, and the CIDEP experiments were made on a Bruker EMX-10/12 X-band ($\nu = 9.3$ GHz) digital EPR spectrometer equipped with a Bruker $N_2$-temperature controller.

***a. Interaction of $C_{60}$ with Mercurial* 5a *under UV Irradiation.*** $C_{60}$ (5.0 mg, 6.9 × $10^{-3}$ mmol) was dissolved in 2 mL of freshly distilled toluene. Compound **5a** (17 mg, 3.5 × $10^{-2}$ mmol) was placed into a quartz ampule, and 1 mL of the fullerene solution was added to it. A small sample of the mixture for MS analysis was transferred by a capillary to a glass ampule, which was soldered. The content of the quartz ampule was degassed by a triple freeze−thaw procedure, and the ampule was filled with moisture- and air-free argon and placed into the resonator of the EPR spectrometer. No signals from radicals were detected. The ampule was then irradiated by the unfiltered focused light of a high-pressure mercury lamp DRSH-1000 (1000 W). The EPR spectra showed a signal with a *g*-factor of 2.0023 from paramagnetic carboranyl-containing derivatives of the fullerene as a quadruplet due to the unpaired electron hyperfine couplings to $^{11}$B nuclei. From time to time, the ampule was taken from the resonator and the content agitated. The samples for MS analysis were taken after the irradiation periods of 10, 22, 34, 44, and 60 min. To reveal the couplings with $^{10}$B nuclei and determine the hfc constants, the EPR spectrum after 60 min of irradiation was recorded on a higher sensitivity level. The mass spectra for all samples, including one taken before irradiation, showed peaks corresponding to carboranyl-containing derivatives of $C_{60}$, the intensities of these peaks for the samples after irradiation being, however, pronouncedly higher than those for the sample taken before irradiation.

The analogous reaction was performed with 3.4 mg (7.0 × $10^{-3}$ mmol) of **5a** and 0.2 mL of the fullerene solution (6.9 × $10^{-4}$ mmol of $C_{60}$). A drop of the reaction mixture taken after 60 min of irradiation was chromatographed on a Silufol plate using a mixture of hexane/toluene (4: 1) as eluent and $I_2$ as a developer. A brown spot remained at the start point, and two spots with $R_f$ 0.47 and 0.51 were developed ($R_f$ of **5a** and $C_{60}$ were 0.47 and 0.54, respectively). The reaction mixture was applied onto a large Silufol plate and chromatographed with the above eluent. A part of the plate with compound **5a** and $C_{60}$ was cut off, and the remaining one was turned 90° and chromatographed with toluene. The mass spectrum of the eluted products displayed peaks due to fullerene derivatives containing one and two carboranyl moieties (the peaks grouping around ones at *m*/*z* 864 and 1008). The 487 u ion and the other ions of its isotope cluster ($M^{+•}$ of **5a**) were virtually absent in the spectrum indicating that the above fullerene derivatives could not be formed due to the reaction occurring in the IC.

***b. Thermal Reaction of $C_{60}$ with Compound* 5b.** A reflux condenser was connected to a flask with compound **5b** (2.4 mg, 4.9 × $10^{-3}$ mmol). The air was replaced by argon. This procedure was repeated twice, *t*-butylbenzene (2 mL) added, and the content agitated. Argon was bubbled through it via a capillary for 25 min. $C_{60}$ (3.1 mg, 4.3 × $10^{-3}$ mmol) was then added, and the mixture was again bubbled by argon for 25 min. A small sample was taken for MS. A slow argon flow over the reflux condenser was then maintained. The reaction mixture was refluxed for 5 h and cooled to room temperature. The flask was wrapped up by black paper and left overnight. A brown film was scraped down from the flask walls, and the reaction mixture was bubbled by argon, refluxed another 5 h, and left overnight. On the next day, argon was bubbled through the mixture, a sample for MS taken, and the same amount of **5b** added. Argon was again bubbled, and the reaction mixture was refluxed for an additional 5 h followed by taking the sample. All three samples contained products of carboranyl radical additions to the fullerene, the monoadduct prevailing significantly. The integrated peak intensities of the ion group due to it (859−869 u) derived from the spectrum obtained by peak-summarizing over magnetic scans increased in a row—before heating/10 h reflux/15 h reflux as 1:1.29:1.65. It should be noted that the intensities of the main signals significantly exceeded the dynamic range of the instrument. That means the real increase along the row should be greater. To eliminate errors that may have been due to a possible increase in the amounts of samples introduced in the mass spectrometer, the integrated intensities were normalized to those of the $[C_{60} - C_{10}]^{+•}$ ion. The later ones were chosen since they were less than the intensities for the monoadduct, while those of $C_{60}{}^{+•}$ were greater. The ratios for the samples taken before, after 10 h, and 15 h heating proved to be 1.47 ± 0.12 (SD), 2.13 ± 0.02, and 1.79 ± 0.05. A decrease in the last value as compared with the second one can be caused by the above-mentioned fact that the normalizing intensities were lower than the product ones. The magnitudes presented indicate that the samples taken after heating contained carbonyl derivatives of $C_{60}$, though some amounts of them were formed during the MS analysis.

***c. Photochemical Reaction of $C_{60}$ with Mercurial* 1.** To $C_{60}$ (3.0 mg, 4.2 × $10^{-3}$ mmol) was added benzene (2 mL) freshly distilled over Na. The mixture was stirred and left overnight. The solution acquired magenta color, but the fullerene dissolved incompletely, ca. a third of the solid remaining. An amount of 0.2 mL of the suspension was added to species **1** (1.0 mg, 2.8 × $10^{-3}$ mmol) placed in a quartz ampule. The content of the ampule was degassed by a triple freeze−thaw procedure, filled with argon, and placed into the resonator of the EPR spectrometer. The ampule was irradiated by the focused unfiltered light of the DRSH-1000 lamp for 45 min. The solution acquired light-brown color (the brown color is characteristic of aryl and alkylderivatives of $C_{60}$), and the EPR spectrum displayed a small broadened (line width ~1 G) signal of a radical with *g*-factor of 2.0023. A sample from the reaction mixture was subjected to MS, the mass spectrum showing peaks of ions due to the addition of one and two phenyl radicals to the fullerene. The same ions were detected for the control mixture not subjected to irradiation. However, the integrated intensity of the corresponding peak groups (at *m*/*z* 796−801 and 872−878) from the spectrum obtained by peak-summarizing over magnetic scans exceeded the analogous value for the control by a factor of 1.9. The ratio of analogous integrated intensities for the $C_{60}{}^{+•}$ ion (720−725 u) turned out to be 0.86, indicating that the above increase could not be caused by an increase in the quantity of the analyte introduced into the mass spectrometer.

***d. Determination of Characteristics of Radicals* 9 *and* 10 *and CIDEP Studies.*** Ampules with a saturated toluene solution of $C_{60}$ contained either **5b** or **5a** (the molar ratio of the fullerene to **5b** or **5a** = 10:1) were degassed by 20-fold freeze−thaw procedures, and their contents were photolyzed in the cavity of the Bruker EPR spectrometer using a high-pressure mercury lamp (1 kW; ARC lamp power supply, model 69920), the output of which was focused onto the sample with a quartz lens and filtered through distilled water to remove infrared radiation.

The EPR spectra were recorded at microwave power 0.5 mW, 100 kHz magnetic field modulation of 0.7 G amplitude, sweep time 671.1 s, conversion time 81.9 msec, time constant 1310 msec, and receiver gain 5 × $10^4$. The digital field resolution was 8192 points per spectrum allowing all hyperfine splittings to be measured directly with accuracy better than 0.1 G. The spectra processing and simulation were performed with the Bruker WIN-EPR and SimFonia Software. The *g*-factor values were determined using 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) as a reference (*g* = 2.0058).

## 3. Results and Discussion

**3.1. Interactions of $C_{60}$ and $C_{70}$ with RHgX in the Ionization Chamber (IC) of a Mass Spectrometer.** Figure 1 displays EI ionization mass spectra of trifluoromethylphenylmercury(II) (**3**) and bis(*m*-carborane-9-yl)mercury(II) (**5b**). The loss of $CF_3$ and $m$-$C_2H_2B_{10}H_9$ radicals, respectively, is clearly seen. In the case of compound **3**, the peak of the $CF_3{}^{202}Hg^+$ ion with *m/z* 271 formed due to the elimination of the phenyl radical from the molecular ion is of a very low intensity. The other process $PhHg^+$ (279 u) $\rightarrow$ $Ph^\bullet + Hg^+$ (202 u) (both intensive ions are present in the spectrum) that formally could furnish the phenyl radicals is forbidden according to the even-electron rule. Thus, it can occur only to a negligible extent. However, a peak at *m/z* 69 due to the $CF_3{}^+$ cation formed from the molecular ion is present in the spectrum. This indicates that fragmentation $CF_3HgPh^{+\bullet} \rightarrow CF_3{}^+ + HgPh^\bullet \rightarrow Hg + Ph^\bullet$ can furnish the phenyl radicals. At the same time, both radicals $R^\bullet$ and $X^\bullet$ are eliminated from the molecular radical cations of all other RHgX compounds examined: $Ph_2Hg$ (**1**), $CF_3HgBr$ (**2**), PhHgBr (**4**), (*o*-carborane-9-yl)$_2$Hg (**5a**), (*p*-carborane-9-yl)$_2$Hg (**5c**), (*m*-carborane-9-yl)HgCl (**6**), $p$-$CH_3C_6H_4HgBr$ (**7**), and $p$-$CH_3OC_6H_4HgCl$ (**8**) (see the respective mass spectra in the Experimental Section and ref 40). The radicals may also be generated due to the decomposition of the molecular ions via the routes analogous to above that for $M^{+\bullet}$ of **3**. Some of the molecular ions $RHgX^{+\bullet}$ produce radical cations $RX^{+\bullet}$ that can further decompose affording radicals. Besides, organomercurials RHgX are capable, in principle, of dissociation at high temperatures to give the corresponding radical $R^\bullet$, some such as **1**, below 300 °C, the reaction, however, being very slow in this temperature region.[40,41] On the other hand, it can be accelerated by the stainless steel walls of an IC and catalytic amounts of various metal-containing compounds that ought to be present at the surface of the IC if a mass spectrometer is permanently used for analysis of organometallic species (and it is in our case).[40] As to *closo*-carborane-9-yl-mercury(II) derivatives **5a**–**c** and **6**, they may decompose effectively even in the gas phase since the "B–Hg" bond is significantly weaker than the "Ph-Hg" one and thus should be inclined to thermal homolytic dissociation to a greater extent.

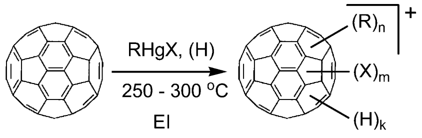
All the foregoing indicates that compounds **1**–**8** producing active radicals under EI ought to be suitable reactants for interaction with fullerenes in an IC or, in other words, for the "homolytic reactive mass spectrometry of fullerenes".

In fact, $C_{60}$ reacted with these species in an IC with the transfer of the corresponding organic or organoelement radicals from the latter to the former (Scheme 1).

The results of the reactions are exemplified below by EI ionization mass spectra recorded in the course of the reactions between $C_{60}$ and compounds **5a**–**c** carried out in the IC at 270 °C (Figure 2).

Scheme 1 involves hydrogen addition to some products, especially paramagnetic ones, as it was observed earlier for the reactions of $C_{60}$ with the Scherer radical, mercury(II) trifluoroacetate, a mixture of perfluoronones, radical $C_9F_{18}SO_2F^\bullet$, and ketones in an IC.[34] Table 1 indicates that it is also intrinsic to the reactions between $C_{60}$ and compounds **5b**,**c** and **6**. It presents the first ionic group of the reaction products in the "spectra of ions" (trios composed of the formulas of ions, their average masses, and the integrated peak abundances of ions of all isotopic combinations constituting the formulas). The spectra of ions of this group for the reactions have been calculated by the program AELITA[42,43] based on the spectra obtained by peak-summarizing over magnetic scans. They have then been averaged over several runs. The ion intensities from Table 1 display that the main recorded products of the reactions are those containing a hydrogen atom attached to the fullerene core.

**SCHEME 1**



| Reactant | R | X | n | m |
|---|---|---|---|---|
| **1** | Ph | Ph | n + m = 1 - 5 with traces of 6 - 8 | |
| **2** | $CF_3$ | Br | 1, 2 | - |
| **3** | $CF_3$ | Ph | 1, 2 | - |
| | | | - | 1, 2 |
| **4** | Ph | Br | 1 | - |
| **5a** | $o$-$C_2H_2B_{10}H_9$ | $o$-$C_2H_2B_{10}H_9$ | n + m = 1 | |
| **5b** | $m$-$C_2H_2B_{10}H_9$ | $m$-$C_2H_2B_{10}H_9$ | n + m = 1 | |
| **5c** | $p$-$C_2H_2B_{10}H_9$ | $p$-$C_2H_2B_{10}H_9$ | n + m = 1, 2 | |
| **6** | $m$-$C_2H_2B_{10}H_9$ | Cl | 1 | - |
| **7** | $p$-$CH_3C_6H_4$ | Br | 1, 2 | - |
| **8** | $p$-$CH_3OC_6H_4$ | Cl | 1 | - |

Another example is provided by Figure 3 and Table 2 illustrating the reaction between $C_{60}$ and $Ph_2Hg$ (**1**). Since the products are wholly organic in this case and thus the contributions from $^{13}C$- and, to a very small extent, $^2H$-containing ions to the intensities of product ions only count, another calculation method has been used. It involves the consecutive subtraction of the above contributions calculated with the help of the program SCIPE[44] taking the first peak of each group as the

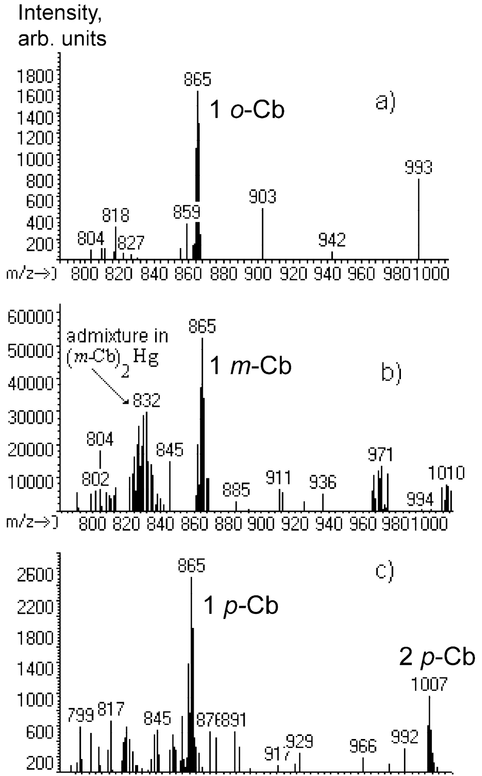


**Figure 2.** EI ionization mass spectra in the high mass region recorded during the reactions of $C_{60}$, in an IC at 70 eV and 270 °C, with (a) bis(*o*-carborane-9-yl)mercury(II) (**5a**), (b) bis(*m*-carborane-9-yl)mercury(II) (**5b**), and (c) bis(*p*-carborane-9-yl)mercury(II) (**5c**). *m*-, *o*-, and *p*-Cb stand for *m*-, *o*-, and *p*-carborane-9-yl, respectively, and together with the numerals at the peaks for the numbers of the corresponding radicals attached to the fullerene core.

**TABLE 1: Distribution of the Ion Intensities ($I_{rel}$) in the First Ion Group of the Products in the Spectra of Ions Derived from Mass Spectra Recorded in the Course of the Reactions between $C_{60}$ and Carboranylmercurials 5b,c and 6 in the IC[a]**

| reactant | ion, [.. .]$^+$ | average mass, u | $I_{rel}$, %[b] |
|---|---|---|---|
| **5b** | $H_2C_{60}B_{10}H_9$-*m*-$C_2H_2$ | 865.88 | 9 |
| | $HC_{60}B_{10}H_9$-*m*-$C_2H_2$ | 864.88 | 53 |
| | $(C_{60}B_{10}$-*m*-$C_2)H_{10}$ | 862.86 | 38 |
| **5c** | $H_3C_{60}B_{10}H_9$-*p*-$C_2H_2$ | 866.89 | 4 |
| | $HC_{60}B_{10}H_9$-*p*-$C_2H_2$ | 864.88 | 55 |
| | $(C_{60}B_{10}$-*p*-$C_2)H_{11}$ | 863.87 | 38 |
| | $(C_{60}B_{10}$-*p*-$C_2)H_{10}$ | 862.86 | 2 |
| | $(C_{60}B_{10}$-*p*-$C_2)H_8$ | 860.84 | 1 |
| **6** | $HC_{60}B_{10}H_9$-*m*-$C_2H_2$ | 864.88 | 70 |
| | $(C_{60}B_{10}$-*m*-$C_2)H_{11}$ | 863.87 | 22 |
| | $(C_{60}B_{10}$-*m*-$C_2)$ $H_8$ | 860.84 | 8 |

[a] The calculations were also made for the reaction with compound **5a** and the second ion group of the products from the reaction with compound **5c**. However, the pronounced scatter of the results of the runs was observed. This occurred probably because of insufficient intensities of the corresponding ion peaks so that the background ones contributed significantly to the intensities. That is the reason why we have not included these data in the table. [b] Normalized to 100% total for each reaction.

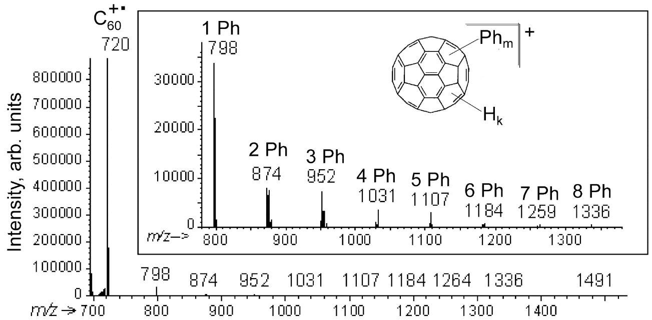


**Figure 3.** High mass region mass spectrum recorded during the reaction of $C_{60}$ with $Ph_2Hg$ (**1**) in an IC at 70 eV and 270 °C (for simplicity of the spectrum, the background peaks are omitted).

starting one. As in the previous cases, the summarized single magnetic scan spectra have been treated.

Again, ions with hydrogen atoms attained have high peak intensities in the spectra, though $C_{60}Ph_2^{+\bullet}$ dominates in the second group. The latter can be easily explained in terms of a homolytic reaction mechanism.

Earlier, we reported several facts evidencing that the hydrogen atoms present in products from the reactions between $C_{60}$ and some perfluoroorganic compounds in an IC were mainly provided by hydrogen-containing compounds adsorbed at the metal surface of the IC.[34a] This finds support in the present study since some products from the reaction of $C_{60}$ with compound **2** contain hydrogen atoms, whereas **2** itself lacks them. All this is not surprising since the experiments were made with a mass spectrometer constantly used for the analysis of organic- and organoelement compounds and its IC had to be contaminated with them. However, when $C_{60}$ was reacted with hexadeuteroacetone, some products obtained had deuterium atoms attached to the fullerene core.[45] This indicates that reagents themselves can provide hydrogen if they contain hydrogen atoms.

Thus, both sources, hydrogen-containing compounds adsorbed at the IC surface and mercurials themselves, especially **5a**,**b** and **6**−**8** amenable to homolytic hydrogen abstraction, could provide those hydrogen atoms that added to the fullerene core in the course of the reactions considered.

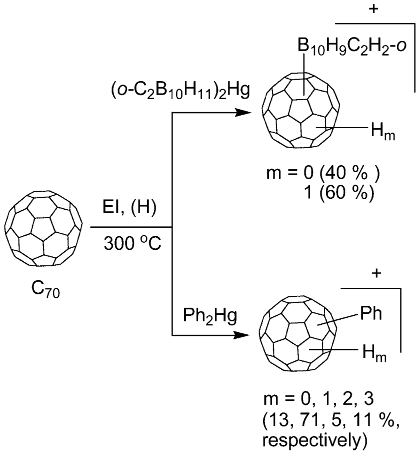
Since compounds **5a**−**c** are isomers, an obvious question to be considered is whether the results of the reactions of $C_{60}$ with them in the IC depend on the isomer reacted, besides the certainty that isomeric products were formed. In fact, only one difference in the results was revealed: in the case of **5c**, we reliably found products of double addition of the *p*-carboranyl radicals to $C_{60}$ (see Figure 2c). The ratio of the integrated intensity of their ion peaks at *m*/*z* 1002−1014 to that of the monoadduct (peaks at *m*/*z* 859−870) derived from the spectrum obtained by peak-summarizing over magnetic scans is 8% ± 1% (SD). At the same time, we failed to register the respective products with assurance in the cases of isomers **5a** and **5b**. This can not be, however, due to properties intrinsic to the last two reactions, but since the corresponding products may be less volatile, their molecular ions are less stable, even owing to some technical reasons. Taking into account such a low value of the relative intensity and the above uncertainties, one can consider the specificity of the reaction with **5c** as insignificant.

**TABLE 2: Abundances ($I_{rel}$)[a] in the Monoisotopic ($^{12}C$, $^1H$) Mass Spectra of the First Three Groups of the Products from the Reaction between $C_{60}$ and $Ph_2Hg$ (1) in the IC**

| group no. | nominal mass, u | ion, [.. .]$^+$ | $I_{rel, \%}$ |
|---|---|---|---|
| I | 796 | $C_{60}C_6H_4$ | 4 |
| | 797 | $C_{60}Ph$ | 13 |
| | 798 | $HC_{60}Ph$ | 83 |
| | 799 | - | 0 |
| II | 873 | $C_6H_4C_{60}Ph$ | 11 |
| | 874 | $C_{60}Ph_2$ | 54 |
| | 875 | - | 3[b] |
| | 876 | $H_2C_{60}Ph_2$ | 25 |
| | 877 | - | 0 |
| | 878 | $H_4C_{60}Ph_2$ | 7 |
| III | 950 | $C_6H_4C_{60}Ph_2$ | 9 |
| | 951 | $C_{60}Ph_3$ | 19 |
| | 952 | $HC_{60}Ph_3$ | 43 |
| | 953 | $H_2C_{60}Ph_3$ | 9 |
| | 954 | $H_3C_{60}Ph_3$ | 20 |
| | 955 | - | 0 |

[a] Normalized to the integral intensity of the corresponding ion group and averaged over several runs. [b] The ion is not specified since mass spectra of $C_{60}$ recorded under conditions when the molecular ion peak intensities fell within the dynamic interval of the instrument and treated in a similar manner showed the calculation error to be ≤3%.

**SCHEME 2**

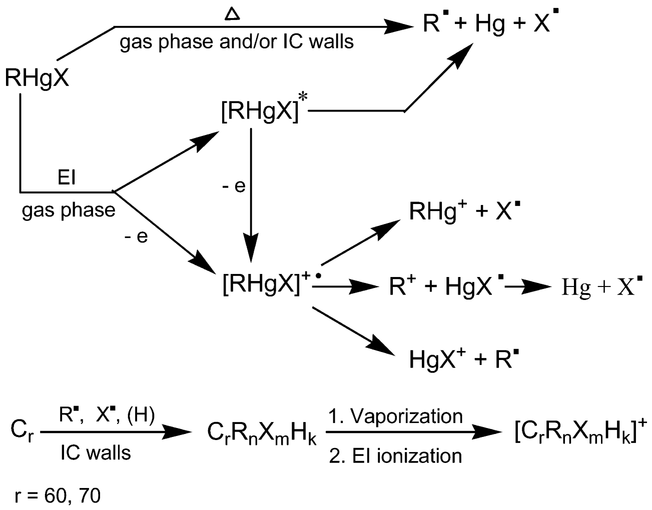


$C_{70}$ reacted in the IC with compounds **5a** and **1** similarly to $C_{60}$. The results of the reactions and calculations of the spectra of ions by the AELITA program, averaged over two runs for each reagent, are presented in Scheme 2.

At the beginning of the paragraph, we have indicated that the reactions discussed can in principle be EI and thermally initiated. In our earlier works, we showed that the reactions of $C_{60}$ in an IC with the Scherer radical ($C_9F_{19}^{\bullet}$) and radical $C_9F_{18}SO_2F^{\bullet}$ were initiated though mostly by EI, but the thermal reaction occurred as well. On the contrary, EI was necessary for the reactions of the fullerene with a mixture of isomeric perfluorononenes $C_9F_{18}$ or acetone to proceed. For revealing these facts, special procedures including ones "with the filament switched off" were developed and employed.[34a,c] In the present work, we used one of these methods slightly modified. $C_{60}$ was applied onto the outer surface of a capillary ampule, a dot of compound **1** placed inside it, and the ampule inserted into an IC. The experiments were made in pairs; viz., the first run was carried out with the filament switched off, then the probe with the ampule extracted from the instrument, and the filament switched on that allowed registering the products evaporating from the surface of the IC. This was followed by the second run in which the filament was turned on in the course of the entire experiment except for the time required for the removal of the probe. In both cases, the summarized ion currents due to products with masses 796−801 u registered after the extraction of the probe were computed, and the ratio of the first value to the second one was obtained. The experimental pair was duplicated, and the ratios were averaged to give a value of 0.294 ± 0.017 (SD). The magnitude obtained indicates that the process was EI activated by ca. 70%, while a thermal reaction was responsible for the remaining ca. 30%.

The mechanistic investigations of the reactions in an IC between $C_{60}$ and the above-mentioned perfluororadicals, perfluorononenes, and acetone counted in favor of the fact that the process involved the formation of active radicals from the second reactants that further reacted with the fullerene at the surface of the IC. The experiments with $C_{60}$ and acetone effected by a procedure with the potential of the repelling electrode relative to the IC cage set to zero showed that the positive ions were not involved in the process.[34a,c] The same proved to be valid for the reaction of $C_{60}$ with PhCOH.[45] Since the participation of the negative ions seems highly improbable, this suggests that the intermediate methyl (phenyl) radicals should have been formed via the homolytic dissociation of acetone (benzaldehyde) molecules being in a superexcited state (the state with electronic excitation energy higher that the first ionization potential).[46] However, this statement can be invalid (or incompletely valid) for some organo- and organoelement mercury compounds since their first ionization potentials (IPs) can be lower than those of acetone and benzaldehyde. For example, the following IP values (in electronvolts) were reported for mercurial **1**: 9.4 ± 02 measured by an EI method,[47a] 9.03 (the first vertical IP) determined by photoelectron spectroscopy (PE),[47b] and 8.30 ± 0.03 obtained by means of photoionization (PI).[47c] At the same time, the IP values are 9.92 ± 0.04[47d] and 9.71 ± 0.03[47e] (EI), 9.71 ± 0.02 (PE),[47f] and 9.69 ± 0.01 (PI)[47g] for acetone; and 9.82 ± 0.04[47d] and 9.74 (EI),[47h] 9.71 (PE),[47i] and 9.51 ± 0.02 (PI),[47g] for benzaldehyde. Thus, the IP values for mercurial **1** measured by all three methods are less than those for acetone and benzaldehyde. Since the reactions discussed occur under EI and the ionization is governed by the Franck−Condon principle, it is better to compare the vertical IP values determined by EI (EI-IP) or PE (PE-IP). The gaps between the EI-IP value for **1** and those for acetone and benzaldehyde are less than the corresponding gaps of PE-IP ones. However, the EI-IP of **1** reported seems to be too high since the difference between it and the IP measured by PI (PI-IP), 1.1 eV, is too great and the EI-IP of $Hg(CH_3)_2$ that lacks benzene ring $\pi$-orbitals determined by the same EI method, 8.90 ± 0.2,[47j] is lower, with the difference between it and the PI-IP, 9.10 ± 0.05, being reasonable.[47k]

**SCHEME 3**



To the best of our knowledge, no EI-IP value has been reported for compound **4**, but its PE-IP value is 8.77 ± 0.05,[47l] which is also lower than the foregoing EI-IP and PE-IP values for acetone and benzaldehyde.

Thus, one cannot exclude the possibility that the competition between the superexcited states and molecular ions of these mercurials generated by EI resulted in enhanced relative amounts of the latter as compared with those for acetone or benzaldehyde. In other words, the homolytic dissociation of the molecular ions of some organo- and organoelement mercurials could provide the radicals in quantities sufficient for the reactions to proceed.

Taking into account all of the preceding, Scheme 3 of the discussed processes seems plausible.

According to Scheme 3, the reaction begins with the generation of active intermediate radicals $R^{\bullet}$ and $X^{\bullet}$ occurring thermally and/or under EI. The thermal process can proceed in the gas phase and/or at the surface of an IC. When EI is involved, the gas-phase homolytic dissociation of the reactant can occur via a superexcited state and the preliminary formed molecular ion. The radicals generated further react with the fullerenes adsorbed at the IC walls, the paramagnetic species obtained being stabilized by the addition of the second radicals or abstracting hydrogen atoms from the reactant or a hydrogen-containing compound adsorbed on the surface of the IC. All such products vaporize from the surface to be registered after EI ionization. If X = Hal (Cl, Br), the halogen-containing products cannot be registered since they are known to be unstable under EI.[48] However, one cannot exclude a certain contribution to the process from the reaction occurring wholly in the gas phase.

**3.2. Reactions of $C_{60}$ with Bis(*o*-, *m*-carborane-9-yl)mercury(II) (5a,b) and Diphenylmercury(II) (1) in Solution.** The above results of the homolytic reactive mass spectrometry of $C_{60}$, when the second reactants were organo- and organoelement mercurials, indicated that one could try to implement the analogous reactions of $C_{60}$, trifluoromethylation, arylation, and carboranylation of the fullerene, with suitable reagents of this

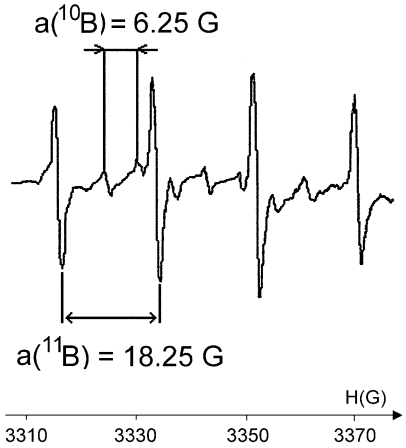


**Figure 4.** EPR spectrum of the reaction mixture of $C_{60}$ and mercurial **5a** in toluene solution recorded at 293 K under UV irradiation (in 1 h from the beginning). The lines in the spectrum are slightly broadened due to the presence of mono- and polycarboranylated paramagnetic derivatives of $C_{60}$; thus the hfc constants depicted [$a(^{11}B)$ and $a(^{10}B)$] are averaged ones (for more detailed characteristics of *o*-carboranylfullerenyl radical and its polarization, see below).

type in solution. The EI initiated reactions contributed significantly to the processes in the IC, as shown by the example of mercurial **1**. That suggested the use of UV irradiation in the quartz region, as the simplest substitute for the irradiation with electrons, in order to initiate these reactions in solution. It is especially so, since organomercurials are known to undergo the homolytic decomposition producing the corresponding organic radicals when UV irradiated in solution.[40] This was reported to be valid for carboranylmercurials **5a**−**c**.[49]

A mixture of $C_{60}$ and compound **5a** at a molar ratio of 1:10.1 in toluene solution was irradiated with unfiltered focused light of a high-pressure mercury lamp DRSH-1000 (1000 W) directly in the resonator of a Varian E-12A EPR spectrometer. The reaction was monitored by EPR and MS; namely, the EPR spectra were recorded and samples for MS taken before and after 10, 22, 44, and 60 min irradiation. No signal was recorded in the first spectrum, while signals from carboranylfullerenyl radicals with a *g*-factor of 2.0023 were found in the last four spectra (Figure 4). On the contrary, ion peaks of products of carboranyl radical additions to the fullerene were registered for all samples subjected to MS including the first (control) one, taken before irradiation (a spectrum obtained after 1 h of irradiation is given in Figure 5). However, the intensities of the peaks for the samples taken in the course of the irradiation were more than an order of magnitude greater than those for the first sample. Moreover, in the second run the final reaction mixture was subjected to TLC that allowed us to remove $C_{60}$ and compound **5a** from the products. The EI ionization mass spectrum of the isolated mixture of products showed the same peaks as before. From this, one can conclude that the bulk of the products was formed during the photolysis, though a small contribution to the spectra of crude reaction mixtures came from the reaction occurring directly in the mass spectrometer.

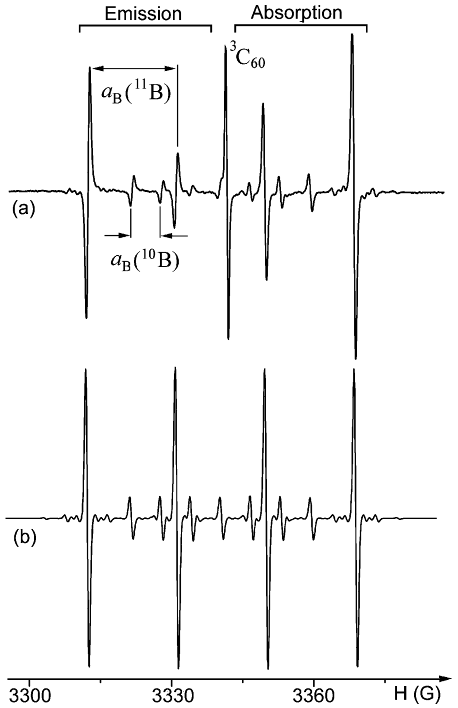


**Figure 6.** (a) EPR spectrum of a **5b**-containing saturated toluene solution of $C_{60}$ (molar ratio $C_{60}$:**5b** = 10:1) under UV irradiation at 250 K. (b) Simulated EPR spectrum of radical **9**.

The Figure 5 spectrum and the other magnetic scan spectra in this analysis were obtained with relatively high both sensitivity level of the instrument and quantity of the sample introduced into it. This was done to catch the peaks corresponding to products of polyaddition of the carboranyl radicals. In the case of the monoaddition product, however, it caused the multiplets due to the isotope- and hydrogen-containing ions to merge into singlets (see Figure 5, the peak at *m*/*z* 864). It

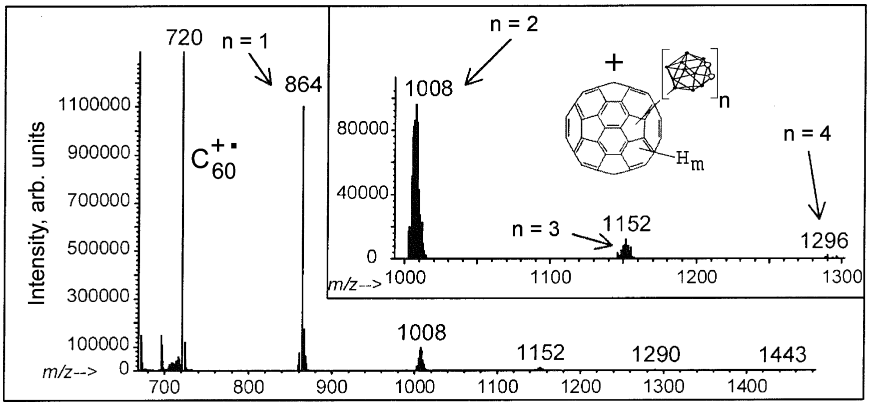
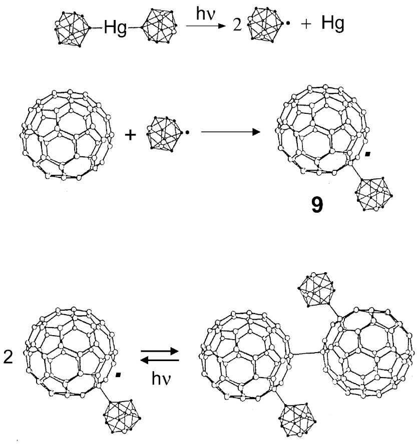


**Figure 5.** EI ionization mass spectrum in the high mass region of the reaction mixture of $C_{60}$ and mercurial **5a** in toluene solution after 1 h of UV irradiation. For the better quality of the spectrum, especially in the inset, the background peaks are deleted. Also, the hydrogen atoms in the carboranyl moieties are not shown.

**SCHEME 4**



excluded the possibility to calculate the spectrum of ions from these data by the aforesaid method and thus to reveal hydrogen-containing ions. To get the resolved peaks with the intensities falling within the dynamic interval of the instrument, the analysis was repeated with less sensitivity and amount of the sample. The treatment of the summarized over 43 magnetic scans spectrum by the AELITA program package produced values of the relative intensities (in percentage of the total intensity of the group) of 36 and 64 for $C_{60}C_2B_{10}H_{11}^+$ (863.87 u) and $HC_{60}B_{10}H_9C_2H_2^{+\bullet}$ (864.88 u), respectively. Thus, the main peak in this ion group turns out to be one due to monohydro-*o*-carborane-9-yl-[60]fullerene. This indicates that hydrogen addition takes place. The sources of hydrogen atoms appear to be the solvent (toluene) and/or the mercury reagent itself. However, some hydrogen attainment, especially by paramagnetic species present in the reaction mixture, could occur, as we have shown above, in the course of the MS analysis. Moreover, carboranylfullerenyl radicals formed during the reaction produce the corresponding dimers (see below). When the reaction mixture is introduced in a mass spectrometer, they should decompose in the IC returning the corresponding radicals. These can acquire hydrogen atoms, abstracting them from hydrogen-containing compounds adsorbed at the metallic walls of the IC and/or from **5a** present in the sample.

The reactions of $C_{60}$ and $C_{70}$ with compound **5b** performed in toluene solution under UV irradiation were reported earlier by some of us.[50,51] In the first case, *m*-carborane-9-yl-[60]fullerenyl radical (**9**) was registered, which underwent reversible dimerization with the rate constant of ca. $10^6$ l mol$^{-1}$ sec$^{-1}$ at 0 °C and $\Delta H$ ca. −10 kcal mol$^{-1}$. The longer irradiation (30 min) of a toluene solution of $C_{60}$ containing excess **5b** resulted in multiple additions of the carboranyl radicals to the fullerene.

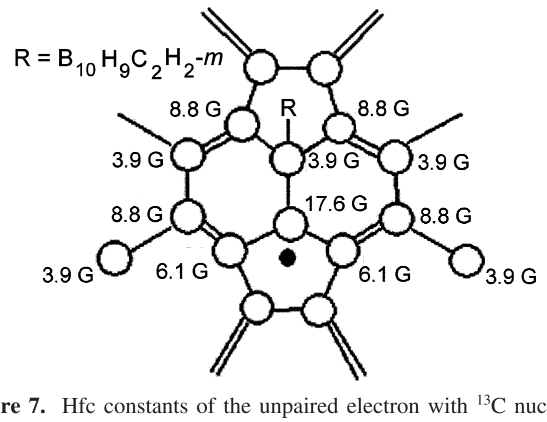


**Figure 7.** Hfc constants of the unpaired electron with $^{13}C$ nuclei of the $C_{60}$ framework in radical **9**.

**SCHEME 5**

1) Radical-triplet-pair mechanism

$^3C_{60} + m\text{-}H_2C_2H_9B_{10}\overset{\bullet}{C}_{60} \longrightarrow C_{60} + m\text{-}H_2C_2H_9B_{10}\overset{\bullet}{C}_{60}{}^*$

2) Radical-pair mechanism

$^3[m\text{-}H_2C_2H_9B_{10}\overset{\bullet}{C}_{60}]_2 \longrightarrow 2\ m\text{-}H_2C_2H_9B_{10}\overset{\bullet}{C}_{60}{}^*$

* - indicates that the unpaired electron in the radical is polarized

In the present work, to get more detailed information on the radical formed and the processes occurring, the study has been prolonged with the use of a Bruker EMX-10/12 EPR spectrometer. UV irradiation of a saturated toluene solution of $C_{60}$ containing compound **5b** in a molar ratio $C_{60}$:**5b** = 10:1 within the cavity of the instrument with unfiltered focused light of a high-pressure mercury arc lamp (1000 W) leads to the appearance of an intensive spectrum ($g = 2.0022$) (Figure 6) consistent with radical **9** formed according to Scheme 4.

The spectrum exhibits hyperfine couplings (hfc) of the unpaired electron with the magnetic nucleus of a $^{10}B$ atom and that of a $^{11}B$ atom: $a(^{10}B) = 6.23$ G, seven lines [$^{10}B$: average natural abundance 19.8%,[43] $I = 3$], $a(^{11}B) = 18.54$ G, four lines [$^{11}B$: average natural abundance 80.2%,[43] $I = 3/2$], and with several carbon nuclei of the $C_{60}$ framework [$a_C(1^{13}C) = 17.6$ G; $a_C(4^{13}C) = 8.8$ G; $a_C(2^{13}C) = 6.1$ G; $a_C(4^{13}C) = 3.9$ G] (Figure 7). The constants similar to those given in Figure 7 were observed for the hfc of the unpaired electron with $^{13}C$ nuclei of alkyl-, silyl-, and phosphorylfullerenyl radicals.[52−54] Besides, a signal with $g = 2.00135$ is present in the spectrum and assigned to $^3C_{60}$, the lowest triplet state of $C_{60}$.[55]

At 250 K, when the UV light has been turned off, a fast decrease in the intensity of the EPR signal of **9** ($\tau_{1/2} < 0.1$ s) due to dimerization of radical **9** has been observed, with its increase up to the primary value upon the irradiation resumption.

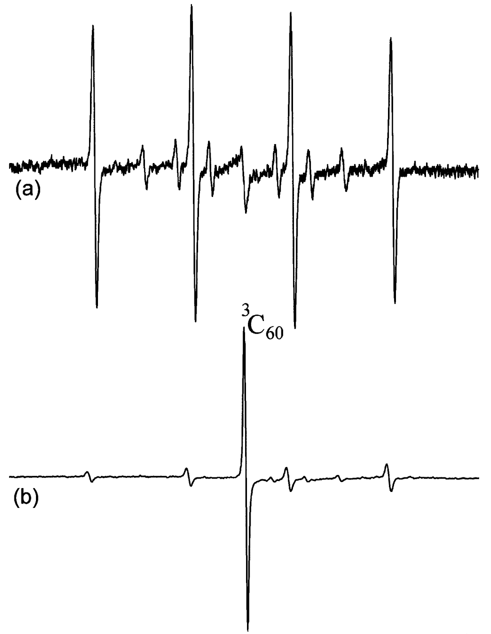


**Figure 8.** EPR spectrum of a **5b**-containing saturated toluene solution of $C_{60}$ (molar ratio $C_{60}$:**5b** = 10:1) under UV irradiation: (a) at 380 K and (b) at 200 K.

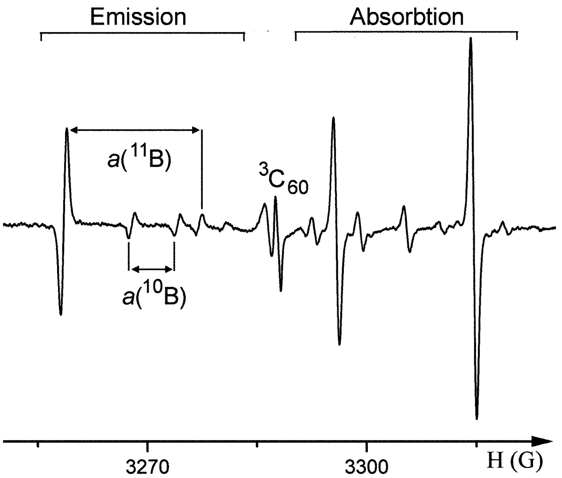


**Figure 9.** EPR spectrum of a saturated toluene solution of $C_{60}$ containing $(o\text{-}C_2H_2B_{10}H_9)_2Hg$ (**5a**) (molar ratio $C_{60}$:**5a** = 10:1) under UV irradiation at 250 K.

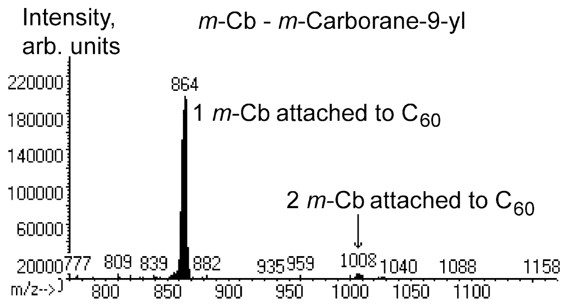


**Figure 10.** EI ionization mass spectrum in the high mass region of the reaction mixture of $C_{60}$ and compound **5b** in $^t$BuPh after 15 h reflux.

These findings indicate that the photodissociation contributes significantly to the overall process of the dissociation of the dimer at this temperature.

A fascinating feature of this EPR spectrum appears to be the fact that all low-field lines have a phase corresponding to emission (*E*), while the high-field ones correspond to absorption (*A*). This spectral pattern is an example of manifestation of the unprecedented strong chemically induced dynamic electron polarization (CIDEP). For the first time, even the polarization of the $^{13}C$ satellite lines has been observed. The CIDEP effects for other radical adducts of fullerenes were reported and discussed in terms of radical-triplet-pair and radical-pair mechanisms.[56] Obviously, the CIDEP of radical **9** originates due to the same reasons, with the triplet state $^3C_{60}$ likely participating (Scheme 5). However, a question to be considered is: what caused such a strong CIDEP in a radical formed due to addition of boron-centered one to $C_{60}$? Evidently, it resulted from several "successful" properties of radical **9** such as long-time spin−lattice relaxation, photochemical stability (irradiation with unfiltered UV light of a 1000 W mercury lamp does not lead to its degradation), and relatively high values of hyperfine interaction of the unpaired electron with the $^{10}B$ and $^{11}B$ nuclei.

We have elucidated that three factors are essential to achieve the maximal CIDEP effect: (i) very accurate vacuumization of the sample to remove the traces of oxygen; (ii) great excess of $C_{60}$ relative to mercurial **5b**, and (iii) temperature of the reaction of 250−260 K. CIDEP has not been observed at 380 K (Figure 8a) because of the temperature-activated dissociation of dimer $m\text{-}H_2C_2H_9B_{10}C_{60}\text{-}C_{60}B_{10}H_9C_2H_2\text{-}m$ and the faster spin−lattice relaxations in radical **9** and $^3C_{60}$ occurring at this temperature. The viscosity of toluene is greater at 200 K so that the rates of both processes responsible for polarization decrease. As a result, the CIDEP falls significantly, the emission (reverse-phase effect) being absent, and the signal from $^3C_{60}$ dominates in the spectrum (Figure 8b).

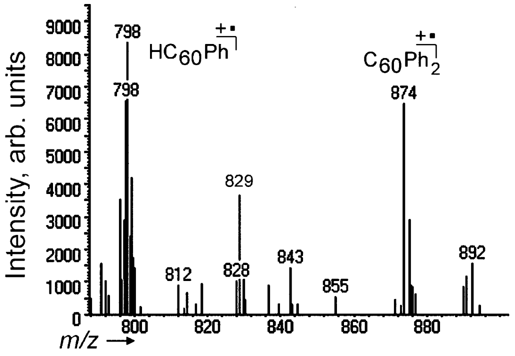


**Figure 11.** Part of the EI ionization mass spectrum in the high mass region of the sample from the reaction mixture of $C_{60}$ and **1** in benzene solution after 45 min of UV irradiation.

**TABLE 3: Distribution of Ion Peak Abundances ($I_{rel}$), Normalized to 100% Total of Each Group, for Two Groups of the Products in the Spectrum of Ions (AELITA) and Monoisotopic ($^{12}C$, $^1H$) Mass Spectrum (SCIPE, Repeated Use)[a] of the Reaction Mixture of $C_{60}$ and Mercurial 1 in Benzene Solution after 45 min of UV Irradiation**

| | | | $I_{rel}$, % | |
|---|---|---|---|---|
| | | | method | |
| group no. | nominal mass, u | ion, [.. .]$^+$ | A | S[b] |
| | 796 | $C_{60}C_6H_4$ | 14 | 14 |
| I | 797 | $C_{60}Ph$ | 13 | 12 |
| | 798 | $HC_{60}Ph$ | 73 | 74 |
| | 872 | $C_6H_4C_{60}C_6H_4$ | 10 | 12 |
| | 873 | $C_6H_4C_{60}Ph$ | 6 | 7 |
| II | 874 | $C_{60}Ph_2$ | 65 | 62 |
| | 875 | $HC_{60}Ph_2$ | 9 | 10 |
| | 876 | $H_2C_{60}Ph_2$ | 9 | 9 |

[a] Both spectra have been derived from that obtained by summarizing 67 single magnetic scan mass spectra. [b] "A" stands for AELITA and "S" for SCIPE.

Experiments on the Bruker spectrometer have also revealed the following characteristics of the analogous spin adduct formed in the reaction of $C_{60}$ with *o*-carboranylmercurial **5a**: $g = 2.0022$, $a_B(^{10}B) = 6.23$ G; $a_B(^{11}B) = 18.51$ G, $a_C(1^{13}C) = 17.8$ G; $a_C(4^{13}C) = 8.7$ G; $a_C(2^{13}C) = 6.0$ G; $a_C(4^{13}C) = 3.83$ G. The CIDEP effect similar to that described above has been observed (Figure 9).

Since experiments in an IC showed the possibility of the thermal reactions between organomercurials and fullerenes in it by way of the example of $C_{60}$ and $Ph_2Hg$ (**1**), we have examined the possibility to implement such a reaction in solution. We decided on the reaction between $C_{60}$ and **5b**—the bond $Hg{-}B_{10}H_9C_2H_2$ should be inclined to thermally activate homolytic dissociation more than the Hg−Ph one since the carboranyl radicals forming in the process are more stable than phenyl ones. In fact, $C_{60}$ reacted with **5b** in $^t$BuPh solution under reflux to yield carboranylated derivatives (Figure 10).

The treatment of the summarized over 83 magnetic scans spectrum by means of the program AELITA yielded the following relative ion intensities, normalized to 100% total of the first product group, in the spectrum of ions: $C_{60}C_2B_{10}H_{10}^{+\bullet}$ (862.86 u) 23%, $C_{60}C_2B_{10}H_{11}^{+}$ (863.87 u) 0%, $HC_{60}C_2H_2B_{10}H_9^{+\bullet}$

(864.88 u) 61%, $H_2C_{60}C_2H_2B_{10}H_9^+$ (865.88 u) 16%.[57] These values indicate that the main product in the first group (and, apparently, among all registered) turns out to be monohydro-*m*-carborane-9-yl-[60]fullerene. The source of hydrogen atoms appears to be the solvent (and, probably, **5b** itself), but hydrogen partly can be acquired during the MS analysis, as we have shown above, especially since the reaction itself partly proceeded immediately within the IC in the course of the analysis (see Experimental Section).

Analogous results were obtained for the photochemical reaction of $C_{60}$ with $Ph_2Hg$ (**1**). The process was monitored by EPR and MS. A small broadened singlet with *g*-factor = 2.0023 appeared in the EPR spectra when the reagents in benzene solution were irradiated by a quartz region UV light. The signal can be attributed to paramagnetic phenyl derivatives of $C_{60}$. Figure 11 depicts a mass spectrum of the sample taken from the reaction mixture after 45 min of the irradiation. The ion peaks due to fullerene derivatives containing one and two phenyl groups are clearly seen. Though these peaks are present in the control spectra of the unirradiated reaction mixture, as it occurred with the product peaks in the case of experiments with $C_{60}$ and **5a** (cf. above), their integrated intensity in the summarized over magnetic scans spectrum is nearly twice as large as that in the control (see Experimental Section). Most probably, the peaks in the control spectra arose owing to the reaction between $C_{60}$ and **1** which occurred in the IC.

Both methods described above, the AELITA program and the iteratively used SCIPE program, have been employed for examining the possibility of hydrogen addition to the fullerene core to occur in the course of the reaction. They gave similar results indicating that the hydrogen addition also took place in this case (Table 3). The source of the hydrogen atom appears to be the solvent (benzene) or crystallization solvent in the $C_{60}$ sample (toluene). Since dimers of phenylfullerenyl radicals had to be present in the reaction mixture and decompose in the IC heated at 300 °C recovering the radicals, the hydrogen addition could partly occur in the IC.

## 4. Conclusions

All organo- and organoelement mercurials examined are capable of transferring the respective organic or organoelement radicals to $C_{60}$ while reacting with the latter in the ionization chamber (IC) of the EI ion source of a mass spectrometer heated at 250−300 °C. No differences that would be significant have been revealed between the results of the reactions of $C_{60}$ with isomeric bis(*o*-, *m*-, *p*-carborane-9-yl)mercurials. By way of the examples of $Ph_2Hg$ and (*o*-carborane-9-yl)$_2$Hg, it has been shown that these reactions are also intrinsic to $C_{70}$. The most plausible scheme of the reactions involves the formation of active organic or organoelement radicals from the reactants due to EI or thermal activation of the reactant molecules followed by the dissociation. When EI is involved, the dissociation may proceed via superexcited states. However, the reaction pathway involving the ionization of the molecules to the molecular ions and their further dissociation providing the radicals can also contribute to the overall process. The radicals formed react with the fullerenes at the metal walls of the IC to give the corresponding fullerene derivatives. The radical centers in paramagnetic species are capped with the next radicals or hydrogen atoms abstracted from hydrogen-containing compounds, including the mercury(II) reagents, adsorbed at the IC surface. The products vaporize from the surface to be registered after EI ionization. To some extent, the analogous process can occur totally in the gas phase.

$Ph_2Hg$, (*o*-carborane-9-yl)$_2$Hg, and (*m*-carborane-9-yl)$_2$Hg are capable of entering the same reaction with $C_{60}$ in solution activated by UV irradiation. The last named compound reacts with the fullerene in a similar fashion under reflux in *t*-butylbenzene. In the UV light activated reactions, EPR studies have exhibited the formation of the corresponding (phenyl-, *o*-carboranyl-, and *m*-carboranylfullerenyl) radicals, and the characteristics of the two last named radicals, including hfc constants for the unpaired electron coupling with $^{13}C$ nuclei of the $C_{60}$ cage, have been determined. The unusually high CIDEP effects for these last radicals that first revealed polarization of the $^{13}C$-sutellites have been observed and explained in terms of radical-$^3C_{60}$ and radical-pair mechanisms. Parameters that allow obtaining the maximal CIDEP in such radicals are specified.

In general, these findings provide additional evidence, to ones already obtained from the reactions of some perfluoroorganics and ketones with $C_{60}$, in favor of the fact that the results of the homolytic reactive mass spectrometry can serve as a quick and efficient tool for elucidating what reactions of fullerenes can be implemented in solution or solid phase/state and by what means.

**Acknowledgment.** The financial support for this study from RFBR (grants # 99-0333067 & 03-0332695) and MSIT RF (grants # 40.012.1.1.1147 & 41.002.1.1.1405) is gratefully acknowledged. The authors are also thankful to Dr. V. Kampel for providing them with samples of *o*-, *m*-, and *p*-carboranylmercurials and the late Prof. R. Taylor for $C_{70}$.

**Supporting Information Available:** EI ionization mass spectra recorded in the course of the reactions of $C_{60}$ in an IC with: $CF_3HgBr$ (**2**, Figure S1), $CF_3HgPh$ (**3**, Figure S2), PhHgBr (**4**, Figure S3), *m*-$C_2H_2B_{10}H_9HgCl$ (**6**, Figure S4), *p*-$CH_3C_6H_4HgBr$ (**7**, Figure S5), *p*-$CH_3OC_6H_4HgCl$ (**8**, Figure S6), and $C_{70}$ with (*o*-$C_2H_2B_{10}H_9$)$_2$Hg (**5a**, Figure S7), and $Ph_2Hg$ (**1**, Figure S8). This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature (London)* **1985**, *318*, 162.

(2) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature (London)* **1990**, *347*, 354.

(3) Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1423.

(4) Han, K.-L.; Lu, R.-C.; Lin, H.; Gallogy, E. B.; Jackson, W. M. *Chem. Phys. Lett.* **1995**, *243*, 29.

(5) Boltalina, O. V.; Borschevskii, A. Ya.; Sidorov, L. N.; Street, J. M.; Taylor, R. *Chem. Commun.* **1996**, 529.

(6) Boltalina, O. V.; Lukonin, A. Yu.; Pavlovich, V. K.; Sidorov, L. N.; Taylor, R.; Abdul-Sada, A. K. *Fullerene Sci. Technol.* **1998**, *6*, 469.

(7) Chilingarov, N. S.; Nikitin, A. V.; Rau, J. V.; Sidorov, L. N. *Fullerene Sci. Technol.* **1998**, *6*, 577.

(8) Boltalina, O. V.; Goryunkov, A. A.; Markov, V. Yu.; Ioffe, I. N.; Sidorov, L. N. *Int. J. Mass. Spectrom.* **2003**, *228*, 807.

(9) McElvany, S. W.; Callahan, J. H. *J. Phys. Chem.* **1991**, *95*, 6186.

(10) McElvany, S. W.; Ross, M. M. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 268.

(11) Liu, Z.; Hao, G.; Wang, H.; Hu, W.; Guo, X.; Ma, G.; Ma, D.; Liu, S. *Wuli Huaxue Huebao* **1995**, *11*, 751. [*Chem. Abstr.*, **1995**, *123*, 169042j].

(12) Dunsch, L.; Kirbach, U.; Klostermann, K. *J. Mol. Struct.* **1995**, *348*, 381.

(13) Sun, D.; Liu, Zi.; Liu, Zh.; Guo, X.; Hao, C.; Xu, W.; Liu., S. *Fullerene Sci. Technol.* **1997**, *5*, 1461.

(14) Ren, X.-Y.; Liu, Z.-Y.; Zhu, T.-Q.; Wen, X.-H.; Guo, X.-H. *J. Mol. Struct. (Theochem)* **2003**, *664−665*, 247.

(15) Ren, X.-Y.; Liu, Z.-Y.; Guo, X.-H. *J. Mol. Struct. (Theochem)* **2004**, *686*, 43.

(16) This technique is used by Bohme and co-workers who have completed, by application of it, a large number of works on ion/molecule reactions of fullerenes. Most of them are covered by Cronert's review (see

ref 28). We give in the references only recent ones and earlier ones that were not included in the review.

(17) Sanderlin, L. S.; Paulino, J. A.; Chow, J.; Kahr, B.; Ben-Amotz, D; Squires, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 5489.

(18) Roth, L. M.; Huang, Y.; Schwedler, J. T.; Cassady, C. J.; Ben-Amotz, D.; Kahr, B.; Freiser, B. S. *J. Am. Chem. Soc.* **1991**, *113*, 6298.

(19) Huang, Y.; Freiser, B. S. *J. Am. Chem. Soc.* **1991**, *113*, 9418.

(20) Jiao, Q.; Huang, Y.; Lee, S. A.; Cord, J. R.; Freiser, B. S. *J. Am. Chem. Soc.* **1992**, *114*, 2726.

(21) Wan, Z.; Cristian, J. F.; Anderson, S. L. *Phys. Rev. Lett.* **1992**, *69*, 1352.

(22) Kan, S. Z.; Byun, Y. G.; Freiser, B. S. *J. Am. Chem. Soc.* **1995**, *117*, 1177.

(23) Bazir Y. J.; Anderson S. L. *Int. J. Mass Spectrom.* **1999**, *185/186/187*, 603.

(24) (a) Welling, M.; Schuessler, H.; Thompson R. I.; Walther H. *In Fullerenes. Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, M. S., Ruoff, R. S., Eds.; The Electrochemical Society, Inc.: Pennington, NJ, USA, 1997; Vol. 4(97−14), p 751; (b) Bohme, D. K. ibid, p 763; (c) McElvany, S. W.; Holliman, C. L. ibid, p 772.

(25) Milburn, R. K.; Hopkinson, A. C.; Sun, J.; Bohme, D. K. *J. Phys. Chem. A* **1999**, *103*, 7528.

(26) Ling, Y.; Bohme, D. K. *Eur. J. Mass Spectrom.* **1999**, *5*, 471.

(27) Petrie, S.; Bohme, D. K *Astrophys. J.* **2000**, *540*, 869.

(28) Cronert, S. *Chem. Rev.* **2001**, *101*, 329.

(29) Blagojevic, V.; Petrie, S.; Bohme, D. K. *Int. J. Mass Spectrom.* **2004**, *233*, 33.

(30) Koyanagi, G. K.; Xu, J.; Bohme, D. K. *Chem. Phys. Lett.* **2008**, *450*, 228.

(31) Bohme, D. K. *Can. J. Chem.* **2008**, *86*, 177.

(32) (a) McEwen, C. N.; Rudat, M. A. *J. Am. Chem. Soc.* **1979**, *101*, 6470. (b) McEwen, C. N.; Rudat, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 4343.

(33) McEwen, C. N.; McKay, R. G.; Larson, B. S. *J. Am. Chem. Soc.* **1992**, *114*, 4412.

(34) (a) Lyakhovsetsky, Yu.I.; Shilova, E. A.; Tumanskii, B. L.; Usatov, A. V.; Avetysian, E. A.; Sterlin, S. R.; Pleshkova, A. P.; Novikov, Yu. N.; Nekrasov, Yu. S.; Taylor, R. *Fullerene Sci. Technol.* **1999**, *7*, 263. (b) Lyakhovetsky, Yu.I.; Bashilov, V. V.; Efanova, T. V; Shilova, E. A.; Sokolov, V. I.; Nekrasov, Yu. S. *Fullerenes, Nanotubes, Carbon Nanostruct.* **2009**, *17*, 85. (c) Shilova, E. A.; Lyakhovetsky, Yu.I.; Tumanskii, B. L.; Belokon', A. I.; Nekrasov, Yu. S. *Mendeleev Commun.* **1999**, 176.

(35) Darwish, A. D.; Abdul-Sada, A. K.; Avent, A. G.; Lyakhovetsky, Yu.; Shilova, E. A.; Taylor, R. *Org. Biomol. Chem.* **2003**, *1*, 3102.

(36) D'Ans, J.; Zimmer, H.; Bergmann, H. *Chem. Ber.* **1952**, *85*, 583.

(37) Seyferth, D.; Hopper, S. P.; Murphy, G. J. *J. Organomet. Chem.* **1972**, *46*, 201.

(38) Hilpert, S.; Grüttner, G. *Ber.* **1915**, *48*, 906.

(39) Zagorevskii, D. V.; Mikeladze, M. Sh.; Nekrasov, Yu. S.; Lependina, O. L *Org. Mass Spectrom.* **1989**, *24*, 86.

(40) Wardell, J. L. Mercury. *Comprehensive Organometallic Chemistry. The synthesis, Reactions and Structures of Organometallic Compounds*; Wilkinson, G., Ed.; Pergamon Press: Oxford, New York, Toronto, Sydney, Paris, Frankfurt, 1982; Vol. 2, p 863.

(41) Razuvaev, G. A.; Petukhov, G. G.; Kudryavtsev, L. F.; Shubenko, M, A. *Zh. Obsch. Khim.* **1963**, *23*, 2764.

(42) Sukharev, Y. N.; Nekrasov, Y. S. *Org. Mass. Spectrom.* **1976**, *11*, 1232.

(43) The natural abundance ratio for the boron isotopes $^{11}$B/$^{10}$B varies within the limits of 3.77 and 4.42 (average values 4.06 or 19.8 and 80.2% of $^{10}$B and $^{11}$B, respectively).[58] In the calculations by the AELITA program, the value of 4.06 is employed. It is highly improbable that the qualitative picture of the calculation results can change at any other ratio from the above segment. For example, the simulation of peak intensity distribution for the $HC_{60}B_{10}H_9C_2H_2^{+\bullet}$ ion carried out with the use of the program SCIPE for the ends of the segment showed that in both cases the most intensive peak proved to be that of the 865 u ion in spite of the fact that the adjacent peaks were of close intensities.

(44) Sukharev, Yu.N.; Sizoi, V. F.; Nekrasov, Yu. S. *Org. Mass. Spectrom.* **1981**, *16*, 23.

(45) Lyakhovetsky, Yu. I. Unpublished results.

(46) Makarov, V. I.; Polak, L. S. *Khim. Vys. Energ.* **1970**, *4*, 3. [*High Energy Chem.* **1970**, *4*, 1 (Eng. Transl.)].

(47) (a) Glockling, F.; Irwin, J. G.; Morrison, R. J.; Sweeny, J. J. *Inorg. Chim. Acta* **1976**, *19*, 267. (b) Furlani, C.; Piancastelli, M. N.; Cauletti, C.; Faticanti, F.; Ortaggi, G. *J. Electron Spectrosc. Relat. Phenom.* **1981**, *22*, 309. (c) Rodionov, A. N.; Potapov, V. K.; Rogozhin, K. L. *Khim. Vys. Energ.* **1973**, *7*, 278. [*High Energy Chem.* **1973**, *7*, 249 (Eng. Transl.)]. (d) Morrison, J. D.; Nicholson, A. J. C. *J. Chem. Phys.* **1952**, *20*, 1021. (e) Mouvier, G.; Hernandez, R. *Org. Mass. Spectrom.* **1975**, *10*, 958. (f) Young, V. Y.; Cheng, K. L. *J. Chem. Phys.* **1976**, *65*, 3187. (g) Watanabe, K. *J. Chem. Phys.* **1957**, *26*, 542. (h) Benoit, F. *Org. Mass Spectrom.* **1973**, *7*, 1407. (i) Gal, J.-F.; Geribaldi, S.; Pfister-Guillouso, G.; Morris, D. G. *J. Chem. Soc., Perkin Trans. 2* **1985**, 103. (j) Hobrock, B. G.; Kiser, R. W. *J. Phys. Chem.* **1962**, *66*, 155. (k) Distefano, G.; Dibeller, V. N. *Int. J. Mass Spectrom. Ion Phys.* **1970**, *4*, 59. (l) Baidin, V. N.; Timoshenko, M. M.; Chizhov, Yu.V. *J. Organomet. Chem.* **1985**, *292*, 55.

(48) Taylor, R. *Lecture Notes on Fullerene Chemistry. A Handbook for Chemists*; Imperial College Press: London, 1999; p 99.

(49) Tumanskii, B. L.; Kampel', V. Ts.; Solodovnikov, S. P.; Bregadze, V. I.; Godovikov, N. N. *Izv. AN SSSR, Ser. Khim.* **1985**, 2644. [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Russ. Chem. Bull.*) **1985**, *34*, 2450 (Engl. Transl.)].

(50) Tumanskii, B. L.; Bashilov, V. V.; Solodovnikov, S. P.; Bubnov, N. N.; Sokolov, V. I. *Izv. Acad. Nauk, Ser. Khim.* **1995**, 1840.[*Russ. Chem. Bull.* **1995**, *44*, 1771 (Engl. Transl.)].

(51) Tumanskii, B.; Kalina, O. *Radical Reactions of Fullerenes and Their Derivatives. Developments in Fullerene Studies, 2*; Kluwer Academic Publishers: Dodrecht, the Netherlands, 2001; pp 62−63.

(52) (a) Morton, J. R.; Preston, K. F.; Krusic, P. J.; Wasserman, E. *J. Chem., Soc., Perkin Trans. 2* **1992**, 1425. (b) Keizer, P. N.; Morton, J. R.; Preston, K. F.; Krusic, P. J. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1041.

(53) Tumanskii, B. L.; Tsikalova, M. V.; Gasanov, R.; Usatov, A. V.; Martynova, E. V.; Sabirov, A. R.; Stankevich, I. V.; Novikov, Yu. N. Identification features for the free radical adducts of organometallic fullerene derivatives. In *Fullerene Research Advances*, 1st ed.; Kramer, C. N., Ed.; Nova Science Pub. Inc., 2007; p 117.

(54) (a) Tumanskii, B. L. *Izv. Akad. Nauk, Ser. Khim.* **1996**, 2396. [*Russ. Chem. Bull.* **1996**, *45*, 2267 (Engl. Transl.)]. (b) Tumanskii, B. L.; Bashilov, V. V.; Shaposhnikova, E. N.; Solodovnikov, S. P.; Bubnov, N. N.; Sokolov, V. I. *Izv. Acad. Nauk, Ser. Khim.* **1996**, 2679. [*Russ. Chem. Bull.* **1996**, *45*, 2538 (Engl. Transl.)].

(55) Closs, G. L.; Gautam, P.; Zhang, D.; Krusic, P. J.; Hill, S. A.; Wasserman, E. *J. Phys. Chem.* **1992**, *96*, 5228.

(56) (a) Klemt, R.; Roduner, E.; Fischer, H. *Chem. Phys. Lett.* **1994**, *229*, 524. (b) Morton, J. R.; Preston, K. F. *Chem. Phys. Lett.* **1996**, *255*, 15. (c) Koptyug, I. V.; Goloshevsky, A. G.; Zavarine, I. S.; Turro, N. J.; Krusic, P. J. *J. Phys. Chem. A* **2000**, *104*, 5726.

(57) The computation was fulfilled using data of 10 h reaction since the product ion intensities in the mass spectra of the 15 h reaction mixture exceeded the dynamic interval of the instrument in the experiments reported.

(58) Vasyukova, N. I.; Nekrasov, Yu. S.; Sukharev, Yu. N.; Mazunov, V. A.; Sergeev, Yu. L. *Izv. AN SSSR, Ser. Khim.* **1985**, 1337. [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Russ. Chem. Bull.*) **1985**, *34*, 1223 (Engl. Transl.)].

JP906058Q