

## Radical functionalization of [60]fullerene and its derivatives initiated by the $\cdot\text{C}(\text{CF}_3)_2\text{C}_6\text{H}_4\text{F}$ radical

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It was found that the 2-(*p*-fluorophenyl)hexafluoroisopropyl radical produced by thermal dissociation of the Polishchuk dimer  $[\text{C}(\text{CF}_3)_2\text{C}_6\text{H}_4\text{F}]_2$  can withdraw, under mild conditions, the H atom from the methyl group of toluene and mesitylene to form the corresponding radicals, whose addition to [60]fullerene occurs more selectively than in the case of photochemical production of these radicals. Dynamics of the step-by-step multiaddition of the radicals to  $\text{C}_{60}$  was studied by ESR. It was found that the addition of benzyl radicals affords adducts containing from 3 to 5 benzyl groups, whereas no spin-adducts with five addends were observed for more bulky 3,5-dimethylphenylmethyl radicals. The interaction of 3,5-dimethylphenylmethyl radicals with the metal complexes  $(\eta^2\text{-C}_{60})[\text{IrH}(\text{CO})(\text{PPh}_3)_2]$  and  $(\eta^2\text{-C}_{60})[\text{Pd}(\text{PPh}_3)_2]$  was studied for the first time. It was shown that the palladium derivative undergoes only demetallation. In the case of the Ir complex, up to 3 radicals add to the fullerene ligand in the same hemisphere where the transition metal is coordinated. The reaction rates are ~5 times lower than those for  $\text{C}_{60}$ . The ability of 2-(*p*-fluorophenyl)hexafluoroisopropyl radicals to dehydrogenate  $\text{C}_{60}\text{H}_{36}$  was found.

**Key words:** ESR, fullerene, radical functionalization, spin adducts.

The ability of fullerenes to add many free radicals<sup>1–5</sup> due to a big number of weakly conjugated double bonds in their molecules is one of the characteristic reactions of these compounds. The structure of radical adducts formed depends on the radical nature.<sup>3</sup> For example, the addition of benzyl radicals to fullerene results in stable radicals of allylic and cyclopentadienyl types,<sup>2</sup> which can be synthons for the preparation of metal complexes with  $\eta^1$ -,  $\eta^3$ -, and  $\eta^5$ -coordination. The possibility of formation of  $\text{C}_{60}$  complexes with the metal coordination at the cyclopentadienyl fragment of fullerene has been shown in Ref. 6. However, the method applied presently for the generation and addition of radicals to fullerenes is not a selective and preparative procedure because it gives a mixture of fullerenes containing from 1 to 20 radicals. Perhaps, this is related to the photoexcitation of fullerene itself during generation of radical species, which favors polyaddition. In addition, irradiation initiates oligomerization of the fullerene itself and the products of its radical functionalization, resulting in a decrease in the target products. Therefore, search for other, not photochemical, methods of radical generation is needed. From this viewpoint, the Polishchuk dimer<sup>7,8</sup>  $[\text{C}(\text{CF}_3)_2\text{C}_6\text{H}_4\text{F}]_2$  (**1**), which can dissociate to

form  $p\text{-FC}_6\text{H}_4(\text{CF}_3)_2\text{C}\cdot$  radicals (**2**) even at room temperature, is of interest.

In this work, dimer **1** was used for the initiation of mesitylene and radical functionalization of fullerene  $\text{C}_{60}$  and its organometallic derivatives, as well as for dehydrogenation of  $\text{C}_{60}\text{H}_{36}$ .

### Experimental

The reaction was carried out in a tube of the resonator cavity of an ESR spectrometer. A saturated solution of fullerene in benzene, toluene, or mesitylene and dimer **1** were loaded into the tube. The fullerene : **1** ratio was 1 : 10 for arylmethylation of  $\text{C}_{60}$  and 1 : 8 for phenylmethylation of metallofullerenes. For dehydrogenation of polyhydrofullerene,  $\text{C}_{60}\text{H}_{36}$  and **1** in a ratio of 1 : 2 were loaded into the tube.

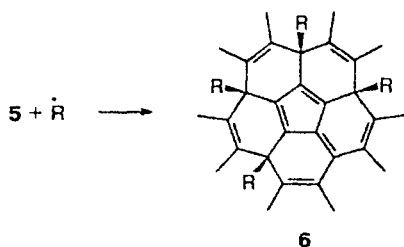
ESR spectra were recorded on a Varian E-12A spectrometer. Samples were thermostatted using an electron controller (Unipan). Electron impact mass spectra in a mass range from 50 to 1000 a.m.u. were obtained on a Kratos MS890 spectrometer with an ionizing electron energy of 70 eV and a temperature of the ionization chamber of 300 °C (the reaction mixture was supported away from the solution on the end of a quartz needle inserted into a direct-inlet plunger, and after the solvent was evaporated, the plunger was introduced into the mass spectrometer).

## Results and Discussion

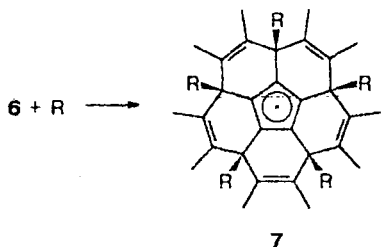
Radical **2** formed from dimer **1** does not add to  $C_{60}$  during the reaction either in the absence of a solvent (below 430 K) or in a saturated benzene solution (350 K) of compound **2**. In both cases, the ESR spectra exhibit only a signal of radical **2** with the characteristic hyperfine coupling (HFC) of an unpaired electron with nuclei of fluorine and hydrogen atoms.<sup>7</sup> Fullerene  $C_{60}$  does not interact with radical **2**, most likely, because of steric hindrances of the radical center.

A different situation is observed in dissociation of dimer **1** ( $10^{-2}$  mol  $L^{-1}$ ) in a saturated toluene solution of  $C_{60}$ . When the reaction mixture is heated to 340 K, a stable radical with the  $g$  factor (2.0021) characteristic of the spin adduct of the benzyl radical with  $C_{60}$  appears in the ESR spectra (Fig. 1). Taking into account that radical **3** is unstable and dimerizes without photoexcitation, we can assume that the stable radical detected has an allylic structure (**5**) (Scheme 1).

This assumption agrees with the further dynamics of radical addition. After 20-min heating, an increase in the intensity of the ESR signal corresponding to radical **5** ceases, and 4 min later, the intensity of the signal begins to decrease. This can be related to the addition of the fourth benzyl radical and formation of adduct **6**.



After 8 min, an increase in the intensity of the ESR signal starts again and ceases after consumption of dimer **1**. This may indicate the addition of the fifth benzyl radical to form the fullereryl radical of cyclopentadienyl type **7** (the parameters of the ESR spectra of **5** and **7** are the same).



Temperature increase to 380 K again results in a decrease in the intensity of the ESR signal, which is presumably associated with the decomposition of the cyclopentadienyl radical. The kinetic parameters of this reaction were found:  $k_{380} = 9.33 \cdot 10^{-4} s^{-1}$ ,  $k_{400} = 27 \cdot 10^{-4} s^{-1}$ ,  $k_{420} = 45 \cdot 10^{-4} s^{-1}$ , and  $E_a = 12$  kcal  $mol^{-1}$ .

Scheme 1

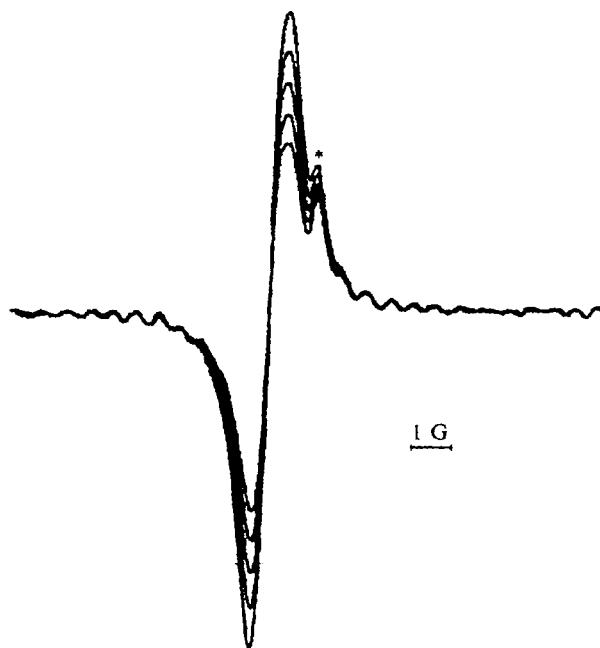
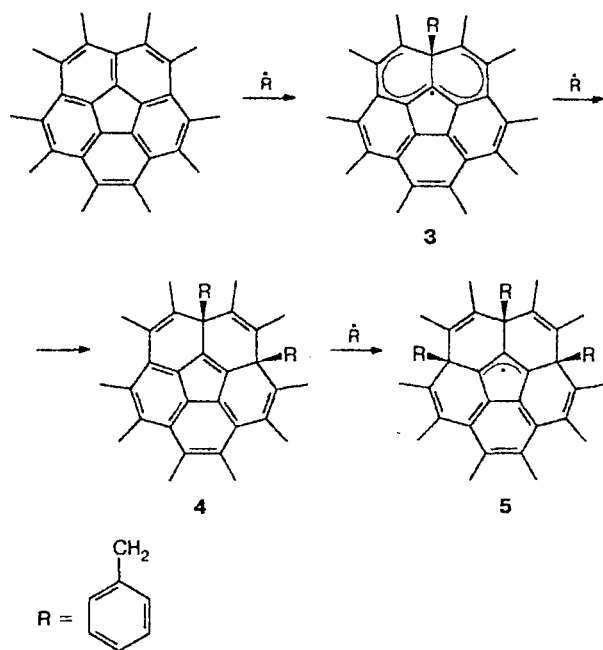


Fig. 1. ESR spectra of the fullereryl radical in a saturated toluene solution of  $C_{60}$  containing  $10^{-2}$  mol  $L^{-1}$  of dimer **1** at 300 K recorded after 132 s. The signal from defects of the quartz Dewar tube is marked by the asterisk.

After evaporation of the solvent in this sample, its mass spectrum exhibits three groups of peaks of ions with  $m/z$  808–814, 899–906, and 991–996, corre-

sponding to products containing 1, 2, and 3 benzyl radicals, respectively. Since the range of the mass spectrometer is restricted by a mass of  $\sim 1000$  amu, we were able to detect only ions of products with a number of benzyl complexing agents not higher than three. Analysis of the ratio of peak intensities by the SCIPE program,<sup>9</sup> which calculates the elemental composition of ions, shows that the mass spectra contain ions corresponding to hydrogenation and dehydrogenation products along with molecular ions corresponding to benzyl adducts. They can form due to both fragmentation under electron impact and ionization of the corresponding products appearing in the reaction course; however, the nature of these ions was not studied.

Functionalization of  $C_{60}$  by benzyl radicals during photolysis of *tert*-butyl peroxide ( $10^{-3}$  mol  $L^{-1}$ ) in a saturated toluene solution of  $C_{60}$  within the 220–300 K range results in the formation of several stable spin adducts, but the stepped character of their accumulation was not observed. This is related, most likely, to a high rate of addition of the radicals during their photochemical generation, which does not allow one to monitor stages of their successive addition, according to the known data.<sup>2</sup>

The use of *tert*-butylbenzene instead of toluene does not lead to the formation of any spin adducts (340–400 K). This is related, most likely, to a higher energy of the C–H bond in the methyl group of *tert*-butylbenzene ( $\sim 95$  kcal  $mol^{-1}$ ) as compared to toluene (83 kcal  $mol^{-1}$ ), which prevents the generation of the  $\cdot CH_2CMe_2Ph$  radical under the action of dimer 1.

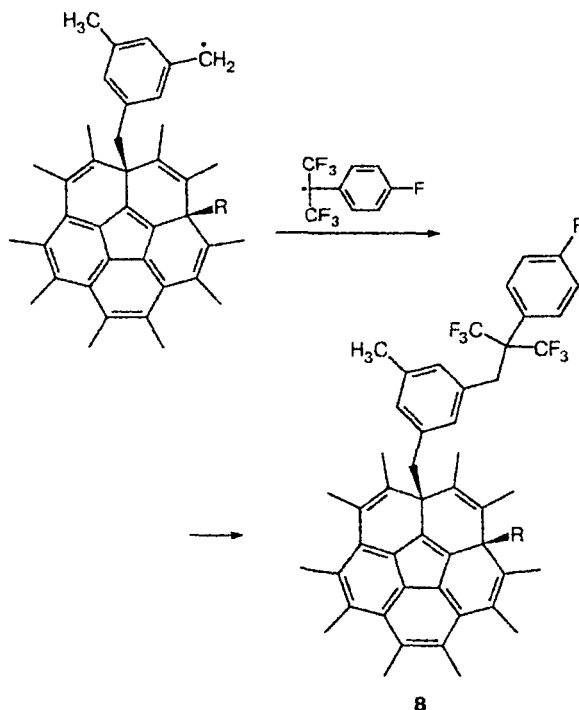
By contrast, the addition of benzyl radicals to fullerene in a solution of mesitylene with a lower energy of the C–H bond (75 kcal  $mol^{-1}$ ) than that of toluene occurs easily: the ESR signal of the stable fullerenyl radical of the allylic type and an increase in its intensity in a saturated mesitylene solution of  $C_{60}$  containing  $10^{-2}$  mol  $L^{-1}$  of dimer 1 was observed already at 300 K.

As for toluene, the ESR signal of the fullerenyl radical of the allylic type reached a maximum after 20 min and disappeared almost completely, which is most likely associated with the addition of the fourth 3,5-dimethylphenylmethyl radical. The fifth radical does not add, probably, due to steric hindrances related to its larger volume as compared to that of the benzyl radical.

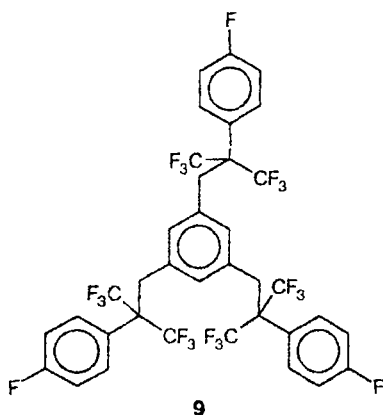
The mass spectrum of the concentrated reaction mixture contains peaks of ions with  $m/z$  839 and 958, corresponding to products of addition of one and two 3,5-dimethylphenylmethyl radicals to  $C_{60}$ . Because of a low intensity of these peaks we cannot draw a dependable conclusion on the presence of the desired products in the reaction mixture from the data of the mass spectra. This can be due to two reasons. First, the reaction of  $C_{60}$  with mesitylene initiated by radical 2 proceeds, probably, more deeply than the similar reac-

tion with toluene because of a higher reactivity of mesitylene, and polyaddition products (–4) are mainly formed. The masses of molecular ions of the latter are beyond detection limits. In addition, the products should possess a lower volatility than the corresponding benzyl derivatives. This explains why the spectrum contains not even residual ions that should form when similar molecular ions lose one or several 2,3-dimethylphenylmethyl groups. Second, addition of mesityl radicals to  $C_{60}$  can be impeded by secondary processes associated with the addition of radicals 2 at free methyl groups of mesityl in mesitylfullerene adducts. This possibility is shown in Scheme 2 for the formation of adduct 8. Such products should have a high molecular mass and a low volatility and can hardly be observed by electron impact mass spectrometry.

Scheme 2



In our opinion, the possibility of similar reactions is the result of the fact that the mass spectrum of the concentrated reaction mixture after the reaction of  $C_{60}$  with mesitylene in the presence of dimer 1 contains peaks of ions with  $m/z$  851, 833, and 813 that are  $[M - H]^+$ ,  $[M - F]^+$ ,  $[M - F - HF]^+$ , and/or  $[M - H - F_2]^+$  ions of the product (9) of recombination of three radicals 2 with radicals formed successively during elimination of hydrogen atoms from three methyl groups of the mesityl fragment:

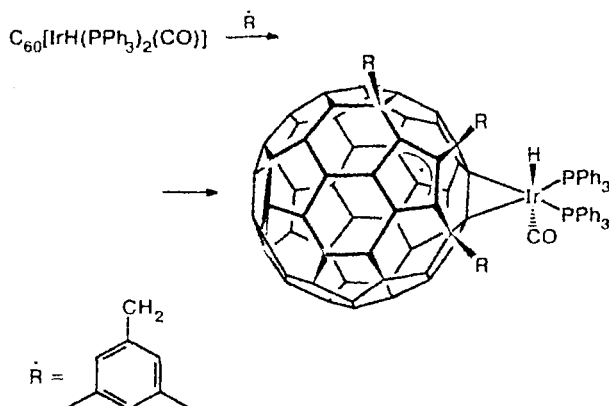


We also detected the peaks of ions with  $m/z$  607, 589, 569 and 363, 345, 325, corresponding, most likely, to similar recombination products with two and one radical **2**.

Mild conditions, under which we observed the addition of 3,5-dimethylphenylmethyl radicals to  $C_{60}$ , make it possible to study radical addition to thermally unstable fullerene derivatives, such as metal complexes, and to estimate a relative rate of this reaction as compared to that with  $C_{60}$ .

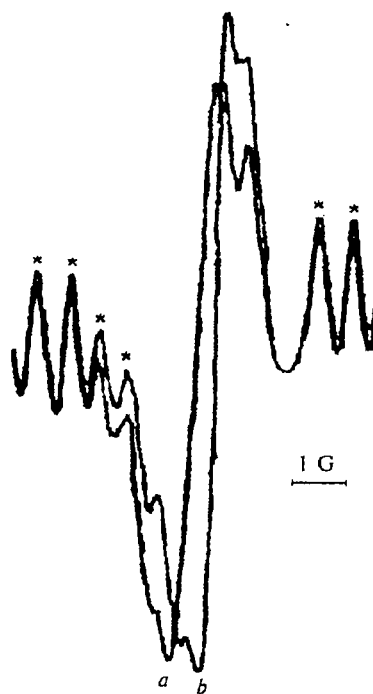
We studied the radical addition of 3,5-dimethylphenylmethylene radicals to the  $(\eta^2-C_{60})[IrH(CO)(PPh_3)_2]$  complex<sup>10</sup> and established that when the reaction is carried out under the same conditions as that with  $C_{60}$  (at the same ratio of reactants), the intensity of the ESR signal of the spin adduct is ~5 times lower than the intensity of the signal from the spin adduct of 3,5-dimethylphenylmethyl radicals with  $C_{60}$ . Only when the concentration of metal complexes in a mesitylene solution is increased fivefold as compared to that of  $C_{60}$ , we detected a similar picture of accumulation of adducts. It follows from this that the addition of such an organometallic group as  $IrH(CO)(PPh_3)_2$  to fullerene decreases

Scheme 3



the rate of interaction of 3,5-dimethylphenylmethyl radicals with substituted fullerene. The value of the  $g$  factor ( $g = 2.0028$ ) of the metal-containing fullerenyl radical obtained differs from the  $g$  factor of spin adducts of 3,5-dimethylphenylmethyl radicals with  $C_{60}$  (2.0021). This difference is most likely related to the addition of 3,5-dimethylphenylmethylene radicals to the same hemisphere to which the metallogroup is bound and to the interaction of an unpaired electron with the metal atom<sup>11</sup> (Scheme 3).

In fact, heating of the metal-containing fullerenyl radical for 6 min to the temperature of decomposition of the metal complex (370 K) results in the shift of the line of the ESR spectrum and a change in the  $g$  factor to the value characteristic of the spin adduct of  $C_{60}$  (Fig. 2).



**Fig. 2.** ESR spectra of the metal-containing fullerenyl radical in mesitylene at 300 K (*a*) and demetallated fullerenyl radical during heating at 370 K for 6 min (*b*). The components of the ESR-spectrum of radical **2** are marked by the asterisks.



**Fig. 3.** ESR spectrum of the paramagnetic product of radical dehydrogenation of  $C_{60}H_{36}$  at 300 K.

The interaction of mesityl radicals with the  $(\eta^2\text{-C}_{60})[\text{Pd}(\text{PPh}_3)_2]$  complex<sup>12</sup> occurs in a different way. Formation of spin adducts is not observed at 300 K for 10 min, and spin adducts with  $g = 2.0020$  characteristic of those of  $\text{C}_{60}$  are detected only at 320 K for 6 min. It can be assumed that in the case of the palladium complex, the induction period is related to its demetallation due to the addition of the 3,5-dimethylphenylmethyl radical to the metal atom.

As shown above, radical **2** does not eliminate the H atom from methyl groups at the tertiary carbon atom, for which the bond energy is  $\sim 95 \text{ kcal mol}^{-1}$ ; however, this process occurs easily in toluene ( $83 \text{ kcal mol}^{-1}$ ) and mesitylene ( $\sim 75 \text{ kcal mol}^{-1}$ ).<sup>13</sup> Taking into account this fact, it was of interest to study the possibility of elimination of the H atom by radical **2** from hydrocarbon  $\text{C}_{60}\text{H}_{36}$ ,<sup>14</sup> estimate the energy of the C—H bond in this compound, and detect radicals that formed. Experiments were carried out in a benzene solution containing  $\text{C}_{60}\text{H}_{36}$  and dimer **1** at 330 K. After 4 min, a relatively broad singlet (16 G) with  $g = 2.0022$  appears in the ESR spectrum. It can be assumed that this signal belongs to the hydrofullerenyl radical of cyclopentadienyl type with additional HFC with remote H atoms, resulting in broadening of a quadruplet (Fig. 3).

Dehydrogenation of  $\text{C}_{60}\text{H}_{36}$  (4 min) is accompanied by the appearance of a brown color (the initial solution is colorless). Heating of a benzene solution of  $\text{C}_{60}\text{H}_{36}$  containing no dimer **1** does not result in the appearance of ESR signals and a change in the color of the solution. It follows from the data obtained that radical **2** eliminates the hydrogen atom from  $\text{C}_{60}\text{H}_{36}$ , and the energy of the C—H bond in this compound is relatively low ( $\leq 83 \text{ kcal mol}^{-1}$ ), which agrees with the results of calculations<sup>13</sup> ( $60 \text{ kcal mol}^{-1}$ ).

Thus, the use of the  $\cdot\text{C}(\text{CF}_3)_2\text{C}_6\text{H}_4\text{F}$  radical for the generation of benzyl or 3,5-dimethylphenylmethyl radicals makes it possible to perform stepped addition of free radicals to fullerenes and its derivatives, which provides new challenges for preparative chemistry.

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