

## Synthesis of New Iron-Containing Carbon Cages by Reaction of C<sub>60</sub> Fullerene with Ferrocene

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Received April 2, 2003

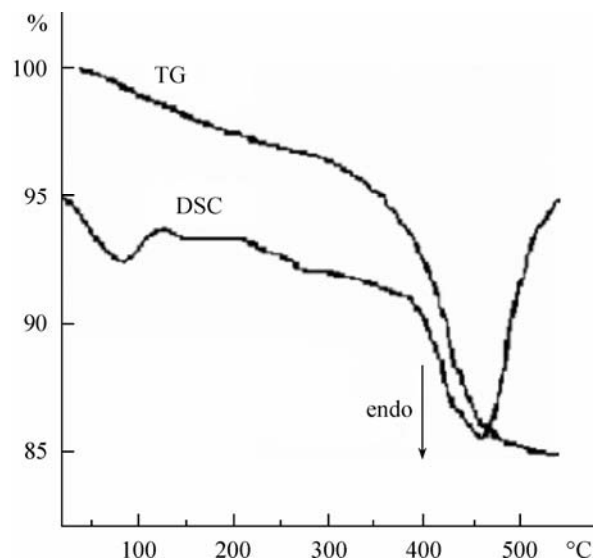
**Abstract**—Reaction of C<sub>60</sub> fullerene with ferrocene in the presence of aluminum chloride and aluminum in an inert atmosphere gave ferrocenyl-substituted fullerene 2C<sub>60</sub>·1.5(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe·3H<sub>2</sub>O. The product is a thermally stable iron-containing carbon cage in which the intersphere cavity is formed by three C<sub>60</sub> polyhedra and is closed by cyclopentadienyl ligands via formation of four carbon–carbon bonds

We previously reported on the chemical synthesis of C<sub>60</sub> fullerene [1] and preparation of C<sub>60</sub>Fe cluster [2]. Taking into account unusual magnetic properties of the cluster, which resemble those of superparamagnetic Co–Cu alloy, in the present work we made an attempt to examine the structure and conditions of formation of its chemical precursor which was obtained by us previously in a poor yield by the Friedel–Crafts reaction of fullerene with ferrocene [2]. The low yield of the ferrocene–fullerene adduct is likely to result from the known low reactivity of C<sub>60</sub> toward electrophilic species, in particular toward ferricinium cation. The latter is unstable, and it decomposes to give a mixture of addition products of cyclopentadiene to fullerene, which is soluble in organic solvents. In order to activate fullerene and prevent decomposition of ferrocene, we performed the reaction in the presence of metallic aluminum. This synthetic technique was proposed previously by Fischer and Hafner for the preparation of bis(η-benzene)chromium [3].

The reaction of fullerene with ferrocene was carried out in dry boiling benzene in the presence of aluminum chloride and metallic aluminum in an inert atmosphere. As a result, we obtained in high yield ferrocenyl-substituted fullerene **I** whose elemental composition corresponded to the formula 2C<sub>60</sub>·1.5(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe·3H<sub>2</sub>O, *M* 1774. Preliminarily, it was found that C<sub>60</sub> is inert toward aluminum chloride (no polymerization or skeletal isomerization of C<sub>60</sub> was observed). Under the

above conditions, no exchange of cyclopentadienyl ligands with benzene occurred: when the reaction was performed in deuterated benzene, the IR spectrum of product **I** contained no C–D absorption.

Compound **I** is a dark brown amorphous powder which is insoluble in organic solvents. This product differs from C<sub>60</sub>(Fc)<sub>2</sub> adducts prepared previously by joint crystallization of fullerene with ferrocene [4] by higher thermal stability. According to the thermo-



**Fig. 1.** Thermogravimetric data for ferrocenyl-substituted fullerene.

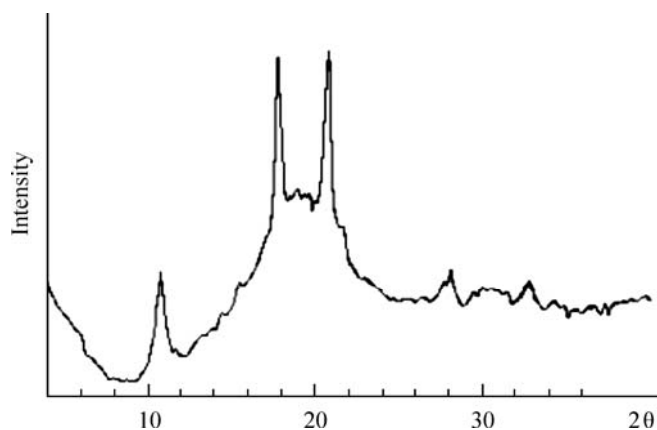
X-Ray diffraction data for ferrocenyl-substituted fullerene

$2\theta$	$\theta$	$\sin\theta$	$\sin^2\theta$	$d, \text{\AA}$	$(hkl)$
10.2	5.1	0.0889	0.0079	8.66	100
10.8	5.4	0.0941	0.0089	8.18	002
17.7	8.85	0.1538	0.0237	5.01	110
20.8	10.4	0.1805	0.0326	4.27	112
21.7	10.85	0.1882	0.0354	4.09	004
28.3	14.1	0.2436	0.0593	3.16	114
31.0	15.5	0.2672	0.0714	2.88	300
32.9	16.45	0.7832	0.0802	2.72	006

gravimetric data (Fig. 1), its decomposition in an inert atmosphere occurs at 350–550°C and is accompanied by a weight loss of 11.2%, which corresponds to elimination of two cyclopentadienyl ligands and three water molecules. The residue has the composition  $C_{60}Fe$  and contains no iron clusters as impurity [2].

The high thermal stability of compound **I** originates from covalent bonding of ferrocene to fullerene. Stretching vibrations of the ferrocene C–H bonds appear in the IR spectrum of **I** at a lower frequency: they give rise to a split band at 2880–2920  $\text{cm}^{-1}$  ( $\Delta\nu = 200 \text{ cm}^{-1}$ ). These frequencies are typical of  $\nu(\text{C–H})$  for dihydrofullerene ( $C_{60}H_2$ ) [5]. The formation of carbon–carbon bonds between the cyclopentadiene fragments of ferrocene and fullerene also follows from the absence of bands from symmetric ring vibrations (1105  $\text{cm}^{-1}$ ) and in-plane C–H bending vibrations (1005  $\text{cm}^{-1}$ ), which are characteristic of unsubstituted ferrocene [6].

X-Ray diffraction study of compound **I** showed (Fig. 2) that insertion of ferrocene into the crystal



**Fig. 2.** X-Ray powder diffraction pattern of ferrocenyl-substituted fullerene.

lattice of fullerene does not distort face-centered cubic structure of the latter [7], as follows from the unit cell parameters of compound **I**, given in table. Therefore, the structure of **I** differs from the structure of  $C_{60}(\text{Fc})_2$  adducts [4] having a triclinic symmetry ( $P1$ ;  $a = 10.094$ ,  $b = 10.528$ ,  $c = 11.306 \text{ \AA}$ ).

In order to elucidate why the face-centered cubic unit cell in **I** is not distorted, we analyzed structural situations in which covalent bonding of ferrocene to fullerene does not change spatial arrangement of the  $C_{60}$  polyhedra. We have found that only one structure meets the above condition. This structure implies that ferrocene molecule occupies the intersphere cavity formed by three  $C_{60}$  polyhedra. Here, each cyclopentadienyl fragment is linked through positions 1 and 3 to two fullerene polyhedra (Fig. 3a, b). Among three fullerene spheres constituting a structural unit of compound **I**, one sphere forms two covalent bonds with the ferrocene fragment. In keeping with the Schlegel representation [5], the addition occurs at the  $C^3$  and  $C^{34}$  atoms of  $C_{60}$  fullerene. The cyclopentadienyl fragments of ferrocene adopt a hindered conformation where one side of the pentagon is parallel to the tangent to that fullerene sphere which is not linked to the given pentagon through a covalent bond and the two other spheres are located at the apices of the five-membered ring. Six hydrogen atoms belonging to the cyclopentadiene rings are located at the centers of the intersphere cavities (canyons), thus creating steric hindrances to insertion of ferrocene into the neighboring cavity in the crystal lattice.

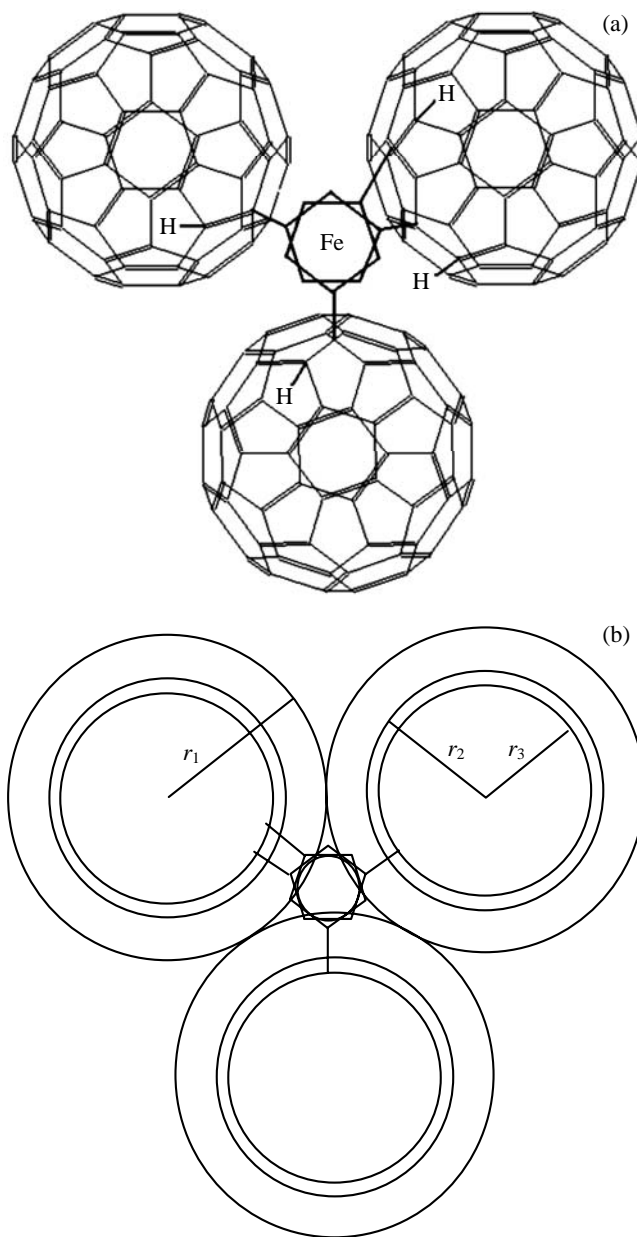
The cyclopentadiene ligands form a cavity, and the iron atom resides at the center of that cavity. As a result, a novel carbon cage is obtained; its horizontal projection is shown in Fig. 3b. It is seen that the three fullerene spheres osculate with each other at a distance corresponding to the van der Waals radius ( $r_1 = 5 \text{ \AA}$ ) and that the cavity thus formed (Fig. 3b) is occupied by the ferrocene pentagons and the circle with a radius of 0.95  $\text{\AA}$  which corresponds to a six-coordinate  $Fe^{2+}$  ion. The circle with a radius of 3.6  $\text{\AA}$  ( $r_2$ ) corresponds to the covalent radius of fullerenes. The fullerene polyhedron may be considered to consist of five annulenes:  $C_5$ ,  $C_{15}$ ,  $C_{20}$ ,  $C_{15}$ , and  $C_5$ . The  $C_5$  and  $C_{15}$  annulenes constitute two corannulene fragments at the poles of the fullerene sphere. The distance between the outer carbon atoms of corannulenes in  $C_{60}$  fullerene is 3.25  $\text{\AA}$ , which is similar to the distance between the cyclopentadienyl ring planes in ferrocene. The circle circumscribing the outer carbon atoms of the corannulene fragments has a radius of 3.2  $\text{\AA}$  ( $r_3$ ). Carbon

atoms located just on that circle are involved in covalent bonding with the ferrocene cyclopentadienyl rings, the length of the carbon–carbon bonds thus formed is  $l = 1.4 \text{ \AA}$  (Fig. 3b).

The above model is characterized by insignificant overlap of the iron electron shells with the fullerene  $\pi$ -system. This model is supported by the Mössbauer spectra recorded at 78 K. The spectrum shown in Fig. 4 (1) contains a quadrupole doublet with a quadrupole coupling (QC) of 2.42 mm/s and an isomer shift (IS) of 0.53 mm/s, which are typical of the state of iron atom in ferrocene. The spectrum of the fullerene–ferrocene complex heated to 350°C (Fig. 4, 2) almost coincides with the spectrum of initial compound **I**, indicating that the latter is thermally stable. The spectrum of a sample heated to 450–500°C (Fig. 4, 3), apart from the ferrocene doublet, displays a second doublet with a quadrupole coupling of 1.2 mm/s and an isomer shift of  $-0.43 \text{ mm/s}$ . These values correspond to the QC and IS values for the iron–fullerene cluster obtained previously [8] by reaction of fullerene radical anion with iron(II) chloride in THF. We can conclude that thermal treatment of compound **I** in an inert atmosphere leads to decomposition of the carbon cage via elimination of cyclopentadiene ligands. The absence of iron clusters in the  $\text{C}_{60}\text{Fe}$  compound thus formed suggests that coordination of iron to the fullerene  $\pi$ -system is more favorable than aggregation to give iron clusters.

It should be noted that the Mössbauer spectrum of the endohedral  $\text{Fe-C}_{60}$  cluster contains one narrow singlet with an isomer shift of  $-0.083 \text{ mm/s}$  [8]. According to the authors, this may be due to strong interaction between the iron atom and carbon matrix. The observed differences in the spectra of **I** and  $\text{Fe-C}_{60}$  indicate essential differences in the character and symmetry of electronic environment therein.

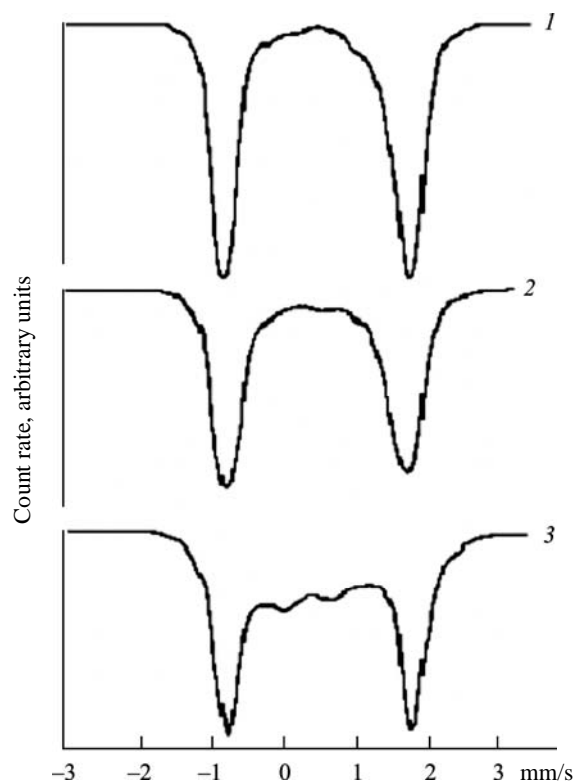
A specific feature of the copolymerization of  $\text{C}_{60}$  with ferrocene in the presence of metallic aluminum is that the product contains no deuterobenzene or benzene, as well as the absence of soluble mono- and bifullerene–ferrocenyl derivatives and initial fullerene. We believe that the first stage of the heterogeneous process gives fullerene–ferrocene clathrate  $\text{C}_{60}(\text{Fc})_2$  [4] which then undergoes radical polymerization initiated by atomic hydrogen. The latter could be formed by reduction with metallic aluminum of hydrogen chloride present in  $\text{AlCl}_3$  as an impurity or of  $\sigma$ -complex **A** which occurs in equilibrium with conjugate acid **B**. The reaction of acid **B** with metallic aluminum



**Fig. 3.** (a) Steric structure of ferrocenyl-substituted fullerene and (b) projection of its molecular model.

could result in reduction of  $\text{H}^+$  to atomic hydrogen via electron transfer from aluminum and reduction of aluminum cation with organometallic compound to give ferrocenyl radical **C** (Scheme 1).

The radical species are formed by a concerted mechanism on the aluminum surface, and (as follows from Scheme 1), aluminum chloride and metallic aluminum catalyze the process. Shift of the equilibrium  $\text{B} \rightleftharpoons \text{C}$  to the right is favored by capture of radical species by fullerene which is known [9] to act as radical trap and by formation of covalent addition



**Fig. 4.** Mössbauer spectra of ferrocenyl-substituted fullerene (recorded at 78 K) (1) without thermal treatment, (2) after heating at 350°C, and (3) after heating at 450–500°C.

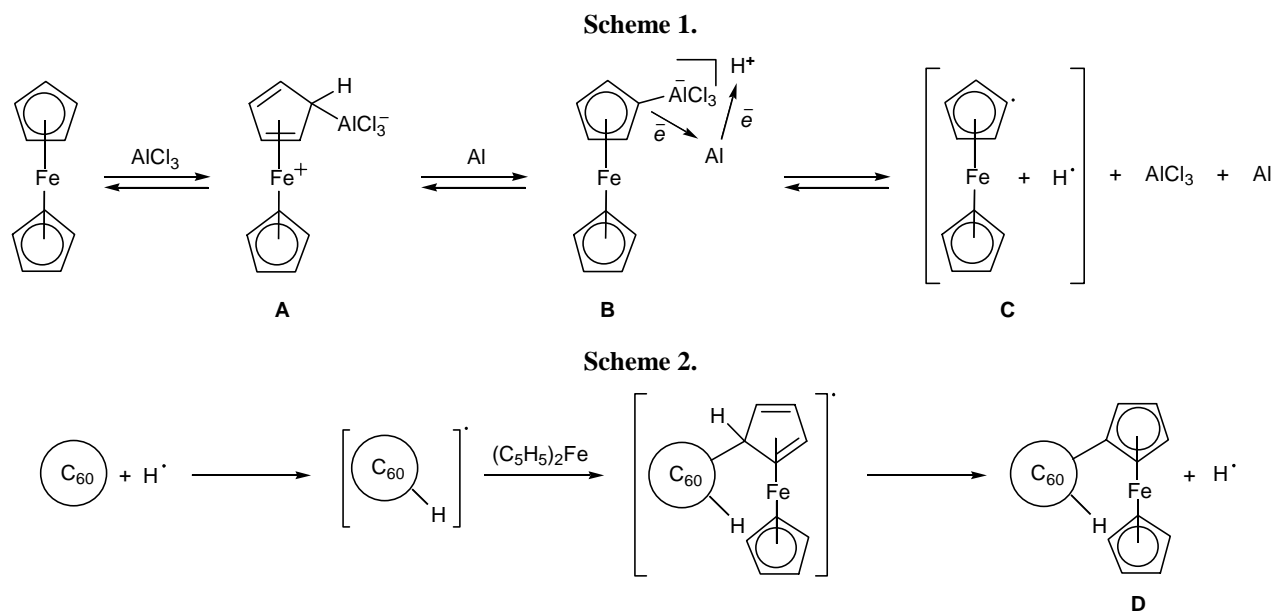
product **D** (Scheme 2). Probably, the reaction in the bulk crystallite is also favored by free rotation of the fullerene polyhedra in the face-centered crystal lattice, which is known [10] to occur at a temperature above

260 K. In this case, addition of radical species to the crystallite surface leads to movement of active centers into the bulk clathrate cage, facilitating the reaction with ferrocene. As a result of consecutive transfer of radical centers from fullerene to cyclopentadienyl fragments, the latter generate atomic hydrogen via  $\beta$ -decomposition, and hydrofullerene radical is formed (Scheme 2). Consecutive addition of fullerene to ferrocene inside the clathrate cage recycles until positions 1 and 3 of the cyclopentadienyl rings in ferrocene (which are spatially optimal for substitution) become involved in covalent bonding. The proposed mechanism is supported by the fact that the reaction in the absence of metallic aluminum leads to decomposition of ferrocene and addition of cyclopentadienyl fragments to fullerene.

## EXPERIMENTAL

The study was performed with the use of an OD-103 Paulik–Erdey derivatograph coupled with a gas-liquid chromatograph, a DRON UM-1 X-ray diffractometer ( $\text{CuK}\alpha$  irradiation, nickel filter), a 50 mCi  $^{57}\text{Co}/\text{RH}$  nuclear X-ray resonance spectrometer, an EXPERT-01T X-ray fluorimeter ( $\text{MgK}\alpha$  irradiation, 1254 eV), and a Specord 75IR spectrometer (the spectra were recorded in KBr).

**Ferrocenyl-substituted fullerene.** A mixture of 360 mg (0.5 mmol) of  $\text{C}_{60}$  fullerene, 360 mg (1.94 mmol) of ferrocene, 360 mg (2.7 mmol) of aluminum chloride, and 100 mg (3.7 mmol) of metallic



aluminum in 20 ml of benzene was heated for 5 h at the boiling point with stirring under argon. The mixture was cooled, 50 ml of ethanol was added, and the precipitate was ground, filtered off, washed with 50 ml of benzene and three 25-ml portions of ethanol, treated on a filter with a solution of iron(III) chloride in 15% hydrochloric acid until gas no longer evolved, washed with water, 25 ml of ethanol, and 10 ml of benzene, and dried for 2 h at 100°C under reduced pressure. Yield 420 mg (94.7%, calculated on the initial fullerene). Found, %: C 91.0, 90.8; H 1.4, 1.3; Fe 4.8, 4.7.  $C_{270}H_{42}Fe_3O_6$ . Calculated, %: C 91.3; H 1.2; Fe 4.7.

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