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Letters to the Editor

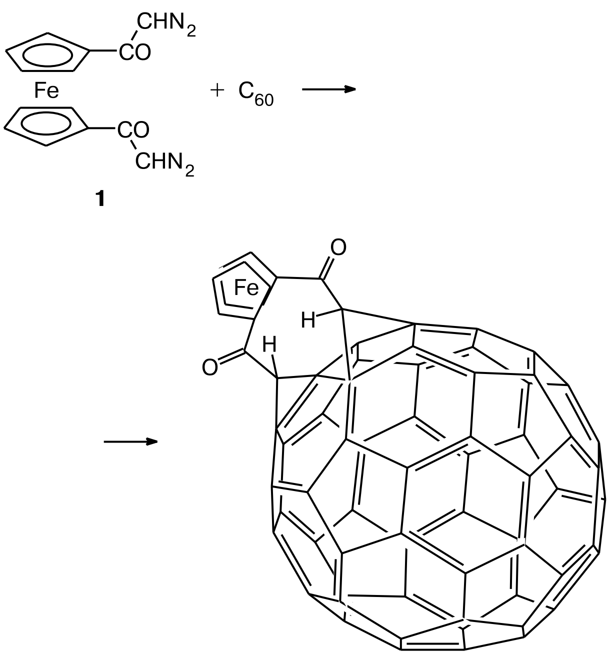
Reaction of 1,1´-bis(diazoacetyl)ferrocene with C_{60} fullerene: synthesis of conformationally rigid fullerene—ferrocene *ansa*-derivative

V. I. Sokolov, T. V. Potolokova, M. N. Nefedova, and A. S. Peregudov*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: sokol@ineos.ac.ru

Compounds whose molecules combine both metallocene and fullerene moieties have been of increasing interest in connection with prospects for fabrication of a "molecular wire" with charge transfer from the former to the latter fragment. A number of synthetic approaches to such compounds have been proposed.[1,2] In particular, we have developed a synthetic route involving the use of the diazoacetyl derivatives of cymantrene and ferrocene in the reaction with C_{60}.[3,4] In this work we report on the reaction of C_{60} with heteroannular 1,1´-bis(diazoacetyl)ferrocene **1** (Scheme 1), which has been briefly outlined earlier.[5] The proposed structure of product **2** follows from the rather informative IR, UV, ^{1}H NMR, and ^{13}C NMR spectra. All the H and C nuclei in both cyclopentadienyl rings of the ferrocenyl moiety were found to be different, which proves their nonequivalence in compound **2**.

Scheme 1



2

Previously unknown 1,1´-bis(diazoacetyl)ferrocene (**1**) was obtained from 1,1´-ferrocenedicarboxylic acid chloride and diazomethane in ether following a standard procedure. After chromatography the yield of pure **1** was 28%, m.p. 125 °C. Found (%): C, 52.20; H, 3.11; N, 17.35. $C_{14}H_{10}FeN_4O_2$. Calculated (%): C, 52.20; H, 3.13; N, 17.39. IR spectrum, ν/cm^{-1}: 1620 (CO); 2110 (N_2). ^{1}H NMR ($CDCl_3$), δ: 5.50 (s, 2 H, CH); 4.75, 4.66 (both m, 4 H, C_5H_4).

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The noncatalyzed reaction* of compound **1** with C_{60} fullerene (1 : 1) was carried out in boiling toluene (110 °C) with stirring in argon atmosphere until complete disappearance of diazoketone (6.5 h); the purple reaction mixture turned brown. The solvent was removed *in vacuo* and the residue was dissolved in CS_2 and chromatographed on a column with SiO_2. Elution with a 1 : 1 toluene—hexane mixture gave first the unreacted C_{60} and then product **2** in a 26% yield with respect to the consumed C_{60}. IR spectrum (CS_2), ν(CO)/cm^{-1}: 1673 and 1735. UV spectrum (toluene), λ_{max}/nm: 318, 365, 443, 549, 716. Mass spectrum (MALDI-TOF, 9-nitroanthracene as the matrix), *m/z*: 720 [C_{60}], 989 [M]$^+$, 1006 [M$^+$ + O]. ^{1}H NMR (400 MHz, CS_2—acetone-d_6, 10 : 1), δ: 5.933 (s, 1 H); 5.463, 5.191, 5.075, 4.945, 4.928, 4.848, 4.775, 4.677 (all m, 1 H); 4.354 (s, 1 H). ^{13}C NMR (100 MHz, CS_2—acetone-d_6, 10 : 1), δ: 198.11 (CO), 196.25 (CO), 78.57, 78.30, 76.91 (C_{ipso}); 76.82, 76.63 (C_{ipso}); 74.84, 74.75, 74.57, 72.26, 70.66, 62.35, 53.87, 50.38, 49.69. The chemical shifts of the ferrocene fragment lie in the range δ 70—79. The chemical shifts of atoms of the fullerene cage (δ 130—148) are not reported.

The mass spectrum indicates that the ratio of the fullerene and ferrocene is 1 : 1. A marked distinction between two CO—CH spacers attached to the fullerene cage should be emphasized. The low-frequency band of the carbonyl group (1673 cm^{-1}) is in excellent agreement with the methanofullerene structure of the major adduct obtained from C_{60} and $FcCOCHN_2$ (1680 cm^{-1}),[4] whereas the other band (1735 cm^{-1}) should most likely be assigned to the fulleroid fragment of the molecule; no literature data on such structures (acylfulleroids) are available. The C nuclei of the carbonyl groups are different in the ^{13}C NMR spectrum. A maximum at 443 nm in the UV spectrum is characteristic of the (6 : 6) methanofullerene fragment.[6] The δ region occupied by ten proton resonances is bounded by the signals of the methine protons, CH—CO, with the chemical shifts lying in the intervals characteristic of the CH group in methanofullerene (δ 5.93) and fulleroid (isomer with a proton located above a hexagon) — δ 4.35 (see Ref. 4). The remaining eight resonances originate from the H_α and H_β protons of the two cyclopentadienyl rings. Nonequivalence of these and eight C atoms of the same rings points to simultaneous attachment of both C_5H_4 rings of the ferrocene moiety to the fullerene cage and to the formation of a rigid structure with no symmetry elements and significantly distorted geometry. Taken altogether, these data assure ourselves that both carbenoid fragments of the diazo groups did add to the same fullerene cage but the additions occurred in different manner, at the (6 : 6) and (6 : 5) junctions. This resulted in the nearly rigid *ansa*-structure, which is unprecedented in fullerene chemistry.

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* No fullerene derivatives were detected among products of the reaction carried out in the presence of $Rh_2(OAc)_4$.