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Deoxygenation of Some α-Dicarbonyl Compounds by Tris(diethylamino)phosphine in the Presence of Fullerene C_{60}

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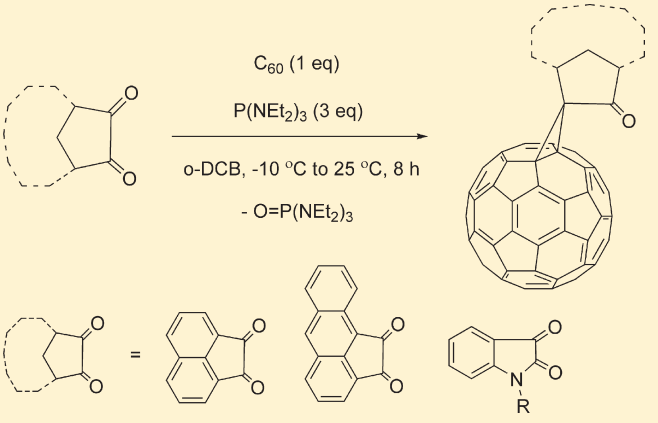
Supporting Information

ABSTRACT: The reactions of such cyclic α-diketones as acenaphthenequinone, aceanthrenequinone, and N-alkylisatins, with hexaethyltriaminophosphine in the presence of the fullerene C_{60}, lead to the formation of methanofullerene derivatives under mild conditions. This process proceeds via deoxygenation of the dicarbonyl compound by the P(III) derivative and is likely to involve the intermediate formation of α-ketocarbenes. The structure of some methanofullerenes has been confirmed by NMR and XRD. The electrochemical behavior of the methanofullerenes was also investigated.



INTRODUCTION

The deoxygenation of organic compounds by trivalent phosphorus compounds is a widely used process in organic chemistry.[1,2] For example, it is known that compounds having nitrogen−oxygen or oxygen−oxygen bonds can be deoxygenated fully or partially by trialkyl or triaryl phosphites.[3−9] The three-component reaction of *o*-nitrobenzaldehyde with aniline derivatives in the presence of the triethyl phosphite leading to various 2-arylindazoles may also be considered as such a processes.[10] Sulfoxides can also be transformed to the corresponding sulfides under the action of triphenyl or trimethyl phosphites, although tris(trimethylsilyl) phosphite is a more effective reagent for the sulfoxide deoxygenation.[11−13] Phosphine oxides can be reduced by using the $HSiCl_3/PPh_3$ system to the tertiary phosphines.[14]

Among a great variety of the deoxygenation reactions, those of carbonyl compounds with trivalent phosphorus derivatives can be considered as a separate class. They have been used in the synthesis of a variety of organic compounds including biologically active ones. For example, the interactions of trialkyl phosphites or sodium diethyl phosphite with some oxiranes or benzaldehyde derivatives lead to the formation of olefins such as ethylenes or stilbenes in moderate yields.[15,16] 2,2′-Diformylbiphenyl and its derivatives undergo an intramolecular cyclization with tris(dimethylamino)phosphine to give the corresponding epoxides.[17] The deoxygenation of some 1,3-dicarbonyl compounds (cyclic anhydrides or acids thioanhydrides) is supposed to proceed through the formation of carbenes.[18,19] A number of publications deal with the reactions of aroyl- and heteroaroylphosphonates with the trialkyl phosphites. These reactions proceed under mild conditions and are also presumed to involve anionic intermediates or carbene intermediates which undergo intramolecular insertion into multiple bond or intermolecular reactions.[20−26] However, there is no unambiguous proof of carbenes formation in the deoxygenation reaction of organic compounds under the action of phosphorus(III) derivatives.

The above-mentioned reactions are well studied, but at the same time there are only two articles[16,27] devoted to the deoxygenation of α-dicarbonyl compounds by phosphorus(III) reagents. Here we report new results concerning the reaction of cyclic α-diketones, such as acenaphthenequinone, aceanthrenequinone, and *N*-alkylisatins, with tris(diethylamino)phosphine in the presence of the fullerene C_{60} as a third component to confirm the structure of the possible carbene intermediates. Fullerene is known to be a remarkable trap of carbenes preparing by various methods, methanofullerenes forming as a result of these processes.[28,29] The latest investigations show that the

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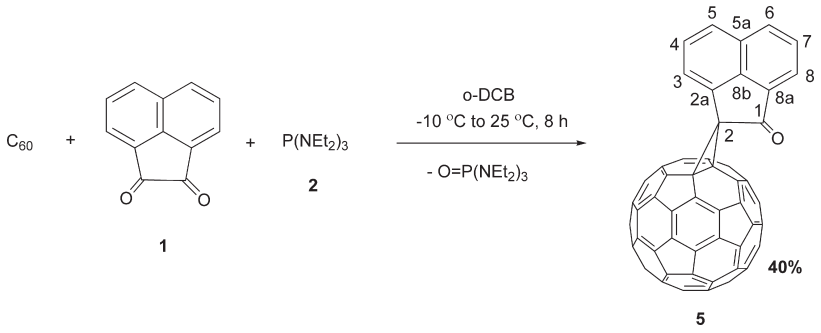
Scheme 1. Synthesis of Methanofullerene 5 via Three-Component Reaction



methanofullerenes are prospective pharmacophores, antioxidants, and reagents for photodynamic therapy.[29−35]

RESULTS AND DISCUSSION

Information about the reactions of *o*-quinones with P(III) reagents is rather limited. It has been shown that the reaction of 2-R_2N-2,5-dimethyl-1,3,2-diazaphospholanes with acenaphthenequinone **1** leads to an oligomer with undefined structure.[36] To investigate the influence of the nature of the substituent at phosphorus in this reaction, we took hexaethyltriaminophosphine **2** instead of the diazaphospholane. As a result, 1,1′-bis(acenaphthen-1-ylidene)-2,2′-dione was obtained.[37] Furthermore, we have established that the reactions of the aminophosphine **2** with *N*-acetyl- and *N*-1-(3′,5′-di-*tert*-butyl-4′-hydroxybenzyl)isatin (**3** and **4**, respectively) led to the isatin dimerization product as well as for quinone **1**.[38] We concluded that carbenes had been generated from the dicarbonyl compounds **1**, **3**, and **4** under the action of phosphine **2**. To provide support for this hypothesis, we attempted to use alkenes such as trichloroethylene, hex-1-ene, and some enamines to trap the proposed carbene intermediate. However, our attempts failed. On the other hand, we were successful at trapping the intermediate by using of the fullerene C_{60} in the two-component system of acenaphthenequinone **1** and aminophosphine **2**. Methanofullerene **5** was obtained as a result of this three-component reaction (Scheme 1).[39]

It is well-known that cycloaddition to the fullerene sphere can lead to the formation of the various monoadducts, namely, [6,6]- and [5,6]methanofullerenes or [6,6]- and [5,6] homofullerenes.[28,29] [5,6]Methanofullerenes and [5,6]homofullerenes are supposed to form by the dipolarophile cycloaddition of an addend to a C═C bond on the fullerene sphere. A pathway to the [6,6]-opened adducts is not clear at the present time. As for [6,6]-methanofullerenes, the most probable pathway for their formation is thought to be via generation of the carbene from an addend. The physical data for four fullerene isomers are in many ways similar and the plausible determination of an adduct structure from this information is a nontrivial task.[40] To determine the structure of methanofullerene **5** we have obtained its IR, UV, NMR, and mass confirmed by XRD.

These results, which were published as brief reports,[37−39] allowed us to conclude that the reactions of the hexaalkyltriaminophosphines with dicarbonyl compounds are likely to pass through carbene intermediates. To determine the affect of the structure of the dicarbonyl compound's aromatic fragments on the regiochemistry of the reaction we have explored the reactions of the aminophosphine **2** with 1,2-naphthoquinone **6**, acenaphthenequinone **7**, 1-methylisatin **8**, 1-allylisatin **9**, 1-acetylisatin **3**, and 1-(3′,5′-di-*tert*-butyl-4′-hydroxybenzyl)isatin **4** in the presence of the fullerene C_{60}.

The addition of the fullerene was achieved in the following way: the phosphine **2** was added to the mixture of the α-diketone with the fullerene C_{60} in *o*-dichlorobenzene (*o*-DCB) at −10 °C. The temperature was gradually increased to 20−25 °C over 8 h. The separation of the reaction products by the column chromatography on silica gel gave unreacted fullerene, fullerene monoadducts, and nonseparated polyadduct mixtures.

The reaction of 1,2-naphthoquinone **6** with aminophosphine **2** and fullerene does not lead to the formation of any fullerene adducts. Only the initial fullerene was isolated by column chromatography from the reaction mixture in quantitative yield. Attempts to reveal any fullerene products by HPLC failed. It should be noted that 1,2-naphthoquinone **6** reacts with aminophosphine **2** to form 2-hydroxy-4-[tris(diethylamino)phosphonium]naphthyl-1-ate.[41]

Two fractions were obtained after the separation of the reaction components in the three-component system of acenaphthenequinone **7**, hexaethyltriaminophosphine **2**, and fullerene C_{60}. The first fraction contained unreacted fullerene. The ^{13}C NMR, IR, and UV−vis spectroscopy data show that both unreacted fullerene and 2-(3′-cyclopropa[1″,9″](C$_{60}$-I_h)-[5,6]fulleren-3′-yl}-1-acenaphthenone **10** were present in the second fraction. Unfortunately, the attempted separation of these compounds by repeated column chromatography failed. On the one hand, this fact may be connected with a similar adsorption activity of the fullerene and compound **10**. On the other hand, the fullerene and compound **10** could have formed a molecular complex (Scheme 2). The fullerene is known to form complexes with polycyclic compounds.[42]

To try to separate compound **10** and C_{60} *p*-Bu^t-calix[8]arene **11** was added to the second fraction, resulting in the complex **12** precipitating (Scheme 2).

After separation and drying in vacuo, this complex had a mustard color. Elemental analysis and the IR spectroscopic data showed that complex **12** was the known 1:1 molecular complex of C_{60} with compound **11**.[43] Bands for the bonds in both the fullerene and the calixarene **11** were shown in the IR spectrum of the complex **12**. Meanwhile, a slight shift of the C_{60} vibrational mode at 528, 578, 1184, 1429 cm^{-1} and some bands of the calixarene **11** at 729, 782, 876, 1485, 2960 cm^{-1} was observed in the IR spectrum of **12** as compared with the pure C_{60} (525, 577,

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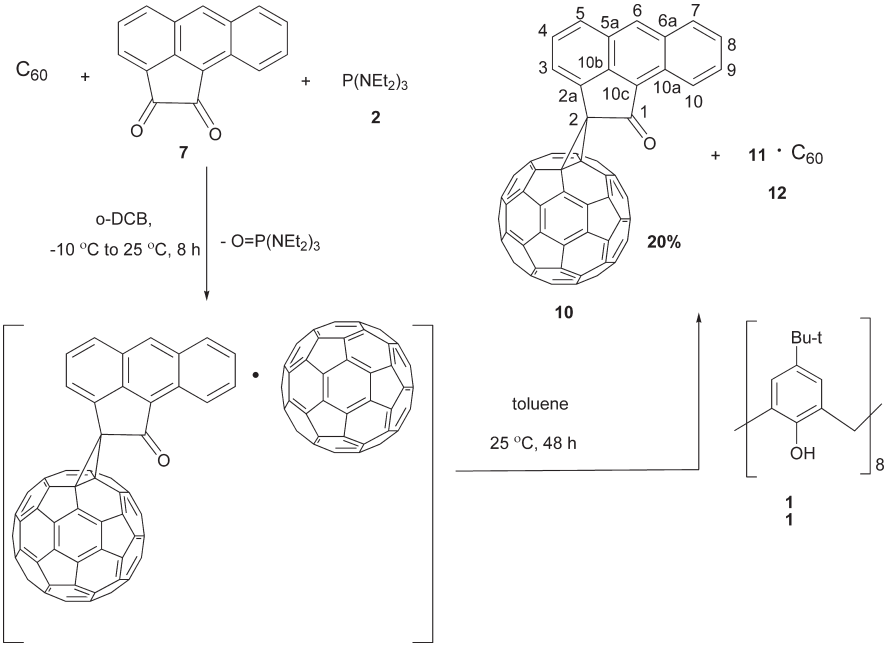
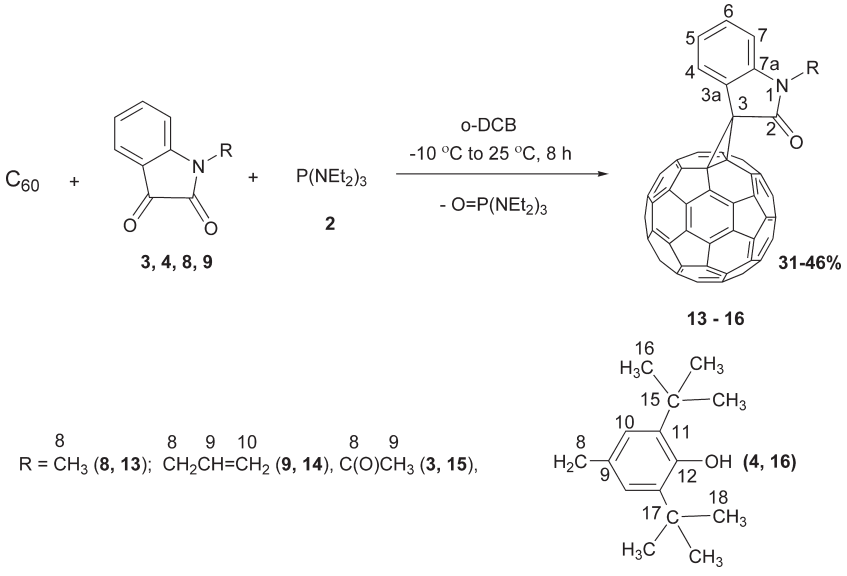
Scheme 2. Synthesis of Compound 10 in Detail



Scheme 3. Novel Indolin-2-one-Containing Methanofullerenes



1181, 1427 cm^{-1}) and calixarene **11** (728, 784, 874, 1487, 2957 cm^{-1}). In addition, the bands of the calixarene **11** had lost their intensity and had broadened in the spectrum of the complex **12**. These data are in good agreement with those reported previously.[43] Complex **12** breaks down to the fullerene C_{60} in $CDCl_3$, which precipitated as a black sediment and was identified by IR spectroscopy. Only fullerene bands were found in the IR spectrum.

The methanofullerene **10** was obtained by repeated column chromatography of the filtrate after separation of the complex **12**. The yield of **10** was 20% with respect to the starting fullerene. The mass spectrum of the methanofullerene **10** contains the molecular ion peak at m/z 937 and a peak for its degradation product $[M^{+} - CO]$ (calcd for $C_{75}H_8$ 909, found 908). The IR and ^1H NMR spectroscopic data for the methanofullerene **10** prove that the structure of the aceanthrene fragment remains unchanged. The IR spectrum of this compound showed a band at 527 cm^{-1} which is characteristic for organofullerenes. There is both a narrow low-intensity band at λ_{max} 433 nm characteristic for [6,6]-closed fullerene structures[28] and a band for the aceanthrene fragment at 405 nm in the UV spectrum.

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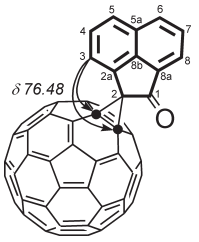

Figure 1. Structure of **5** with the principal HMBC correlations from the protons of the acenaphthenone moiety (in gray-bold) to the fullerene carbons.

The methanofullerenes **13**−**16** were isolated by column chromatography on silica gel from the reaction mixtures of isatins **3**, **4**, **8**, and **9** and phosphine **2** in the presence of the fullerene C_{60} (Scheme 3). The yields of compounds **13**−**16** are within 30−35%. UV, IR, and NMR spectroscopies confirmed their structure. The composition was established by MALDI-TOF mass spectrometry.

The mass spectra of compounds **13**−**16** show the molecular ion peaks at *m*/*z* 866, 892, 894, and 1070 correspondingly. The IR spectra include both a band characteristic for the fullerene sphere at 526−527 cm^{-1} and bands for the addends (**13**: 1724, 1611, 1468, 1372, 1344, 742 cm^{-1}; **14**: 1721, 1609, 1464, 1354, 987, 920, 743 cm^{-1}; **15**: 1773, 1745, 1713, 1608, 1552, 1460, 1378, 1336, 1307, 1265, 1212, 1166, 1095, 1039, 981, 749, 598 cm^{-1}; **16**: 3438, 2955, 2922, 2864, 1722, 1636, 1611, 1466, 1431, 1356, 1236,1186, 1157, 1112, 744 cm^{-1}). A narrow low-intensity band at λ_{max} 430−427 nm characteristic of the [6,6]-closed fullerene structures was observed in the UV spectra of these compounds. The UV spectra of compounds **13**−**16** show a broad band at λ_{max} 500 nm which is a superposition of both bands of the fullerene sphere and ones of the indolinone fragment.

Finally, the structures of the methanofullerenes **5**, **10**, and **13**−**16** were determined by NMR. In addition, an XRD analysis was carried out for compounds **5** and **13**.

Thus, the reactions of quinones **1** and **7** and isatins **3**, **4**, **8**, and **9** with aminophosphine **2** in the presence of the fullerene go through the formation of [6,6]-closed fullerene adducts, methanofullerenes **5**, **10**, and **13**−**16**. 1,2-Naphthoquinone **6**, in contrast, does not enter into such a three-component reaction. This compound also behaves unusually in the reaction with aminophosphine **2**.[41] Whereas quinone **1** and isatins **3** and **4** give the ketocarbene dimerization products, naphthoquinone **6** undergoes phosphorylation at the four position of the naphthalene fragment. This is likely to be related to the peculiarity of the naphthoquinone's electronic structure which easy turns into the aromatic dihydroxynaphthalene system. The formation of similar aromatic compounds is impossible for derivatives **1**, **3**, **4**, and **7**−**9**. These compounds are likely to give the ketocarbenes under the action of aminophosphine **2**, which easily add to the fullerene.

Electron transfer from the phosphine **2** to the α-diketone is most likely to occur to give the ion-radical pair **A** (Scheme 4, example for isatins). Then this pair generates carbene **B** step by step with the elimination of the hexaethyltriamidophosphate. These carbenes then undergo dimerization in the absence of the fullerene or add to C═C bond of the fullerene to form methanofullerenes in three-component reactions.

NMR Studies of Compounds 5, 10, and 13−16. The complete structure elucidation of compounds **5**, **10**, and **13**−**16** was carried out by a variety of correlation NMR methods (COSY $^1H-^1H$, HSQC $^1H-^{13}C$, HMBC $^1H-^{13}C$, see the Supporting Information).[44] For example, for **5** from the 2D COSY spectrum two spin systems of protons can be easily assigned in the heterocyclic moiety. Then all hydrogenated carbons can be determined from the 2D HSQC spectrum. Finally, from HMBC correlations all carbons of the acenaphthenone fragment can be unequivocally assigned (Figure 1).

In the ^{13}C NMR spectra of **5** there are 28 peaks in the range 138−147 ppm corresponding to the fullerene moiety (21 signals with 2C intensity, 4 lines with 1C, and 3 signals with 4C). There is also one peak (76.48 ppm) with an intensity corresponding to two carbons and having four-bond scalar HMBC connectivity from the H^3 proton of the acenaphthenone (8.56 ppm). Thus, the fullerene sphere is of the closed type and the cycloaddition has occurred to the C═C bond.

For the methanofullerene **10** there are 44 peaks in ^{13}C NMR spectra from which the 16 signals were exactly assigned to the carbons of aceanthrene fragment by a variety of 2D NMR correlation techniques. The fullerene sphere of **10** is characterized by signals, whose number and intensity (22 signals with the intensity 2C, three signals with 4C and four signals corresponding to 1C) indicate C_s symmetry of the sphere. Thus, the sp^3-carbon of the C_{60} cage appeared at 76.6 ppm corresponding to the [6,6]-type of addend linkage.

For compounds **13**−**16** the addend nuclei (up to C^3) were unambiguously assigned by a variety of 2D NMR correlation methods. For example, for **13** the NOE between N-CH_3 and H^7 allows a direct assignment of all protons in the "benzo" fragment. HMBC correlations between the CH_3 protons and the C═O (C^2, 169.09 ppm) and between the H4 and sp^3 carbon

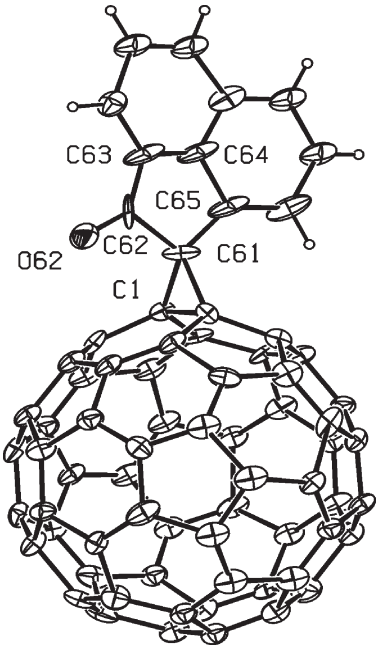

Figure 2. ORTEP view of the molecular structure of compound **5**. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented by circles of arbitrary size. Carbon disulfide molecules are omitted for clarity. Selected bonds lengths (Å): C(1)−C(61) 1.51(1), C(1)−C(2) 1.63(1), C(2)−C(61) 1.59(1), C(62)−O(62) 1.17(1), C(62)−C(63) 1.32(1), C(62)−C(61) 1.65(1), C(63)−C(64) 1.398(8), C(61)−C(65) 1.48(1) Å.

(C^3, 42.08 ppm) led us to conclude that for **13** the addend linkage to the fullerene sphere is in the C^3 position and not at C^2. An almost perfect correlation of the calculated (GIAO B3LYP/6-31G(d)//HF/6-31G)[45−48] versus experimental ^{13}C chemical shifts (R^2 = 0.998, see the Supporting Information) provides additional support for the validity of the above conclusion about the structure. The same is also true for compounds **14**−**16**. The number of peaks observed for compounds **14**−**16** in the range 138−146 ppm is due to the 58 sp^2-carbons of the C_{60} sphere, consistent with the C_s symmetry of their molecular structures. Moreover, the C_{60} cage sp^3carbons resonate at 75.1−75.4 ppm in these compounds, thus proving the [6,6]-type of the addend linkage.

Crystal Structures of 5 and 13. Crystals of **5** were obtained by a slow evaporation of the compound from a carbon disulfide solution. The structure was studied by the XRD analysis, which showed that compound **5** forms a 1:2 inclusion complex with carbon disulfide molecules. It should be noted that the methanofullerene **5** molecule has noncrystallographic C_s symmetry but loses it in the crystal and is located at a general position; the molecular structure and selected bonds lengths are shown in Figure 2.

The aromatic acenaphthene fragment of the methanofullerene **5** appears planar within the experimental error. The dihedral angles between the cyclopropane C(1)−C(61)−C(2) plane and the planes of the two six-membered rings of the fullerene fragment are 64.7° and 66.3°.

The supramolecular structure of the methanofullerene **5** in the crystal is determined mainly by the interplay of two type of π-electronic interactions: fullerene···fullerene and fullerene··· aromatic substituents.

Interactions between aromatic-ring systems of the methanofullerene **5** molecules result in continuous zigzag chain formation along the *0a* crystallographic axis in the crystal with two alternating distances between the fullerene centroids of 10.11 and 10.04 Å (Figure 3, a), and the angle between the centroids of three fullerene fragments is 83.74°. The fullerene molecules are assembled in zigzag chains due to $\pi-\pi$ interactions of the six-membered rings "face to face"; the shortest distances between the

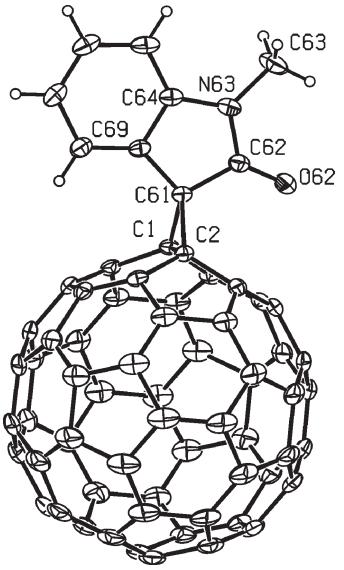

Figure 4. ORTEP view of the molecular structure of methanofullerene **13**. Displacement ellipsoids are drawn at the 30% probability level. Chloroform molecule is omitted for clarity. Selected bonds lengths (Å): C(1)−C(61) 1.526(3), C(1)−C(2) 1.589(3), C(2)−C(61) 1.540(3), C(61)−C(69) 1.492(3), C(61)−C(62) 1.516(3), C(62)−O(62) 1.215(3), C(62)−N(63) 1.358(3), C(63)−N(63) 1.443(3), C(64)−C(65) 1.389(3), C(64)−N(63) 1.395(3), C(64)−C(69) 1.400(3) Å.

planes of aromatic rings of the neighboring fullerenes are 3.32 and 3.37 Å.

The presence of a large aromatic substituent at the fullerene core and solvent molecules in the crystal hinders the fullerene··· fullerene interactions and leads to the obligatory participation of the substituents in the π-electronic interactions. As a result, each methanofullerene **5** molecule additionally participate in the four π-interactions between aromatic substituents and fullerene fragments (the distances between interacting planes are 3.11 and 3.23 Å) and the one $\pi-\pi$ interaction between aromatic substituents of two neighboring fullerenes with the shortest distances

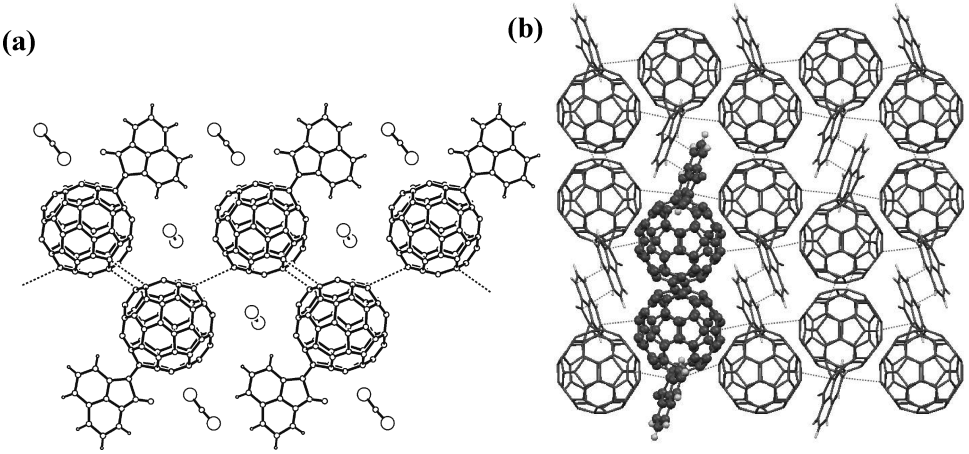

Figure 3. (a) Zigzag fullerene arrangement in the crystal of **5**, view along *0a* axis. Dashed lines indicate the fullerene···fullerene interactions. (b) View along *0b* axis on the honeycomb-like arrangement of the methanofullerene molecules in the crystal of **5**. The solvent molecules are omitted for clarity. Dashed lines indicate the all type of π-electronic interactions. The solvent molecules are distributed between 1 and 3 fullerene molecules in zigzag chains and in the cavities of the honeycomb-like supramolecular structure in such a manner that close contacts between them are not detected. Such types of mutual arrangement of the molecules in the crystal of **5** lead to a high packing coefficient (73.3%).

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between interacting planes 3.48 Å. These contacts link the zigzag chains into a three-dimensional honeycomb-like networks with pseudocavities arranged along the *0a* crystallographic axis in the crystal (Figure 3, b).

The crystals of **13** were obtained by the evaporation of a chloroform solution as an inclusion compound with the solvent chloroform molecule in a 1:1 stoichiometry. The molecules with C_s-symmetry are located in the general position of the monoclinic unit cell, and the chloroform molecule is disordered over 2 positions with relative occupancies 0.6: 0.4. The planarity of cyclic fragment in the molecule (standard deviation within 0.02(1) Å, Figure 4) is caused by the lack of large substituents in the 'benzo' fragment of the bicyclic moiety. The dihedral angles between the cyclopropane ring plane and the planes of two six-membered cycles of fullerene fragment are 64.9° and 64.3°.

The quality of the experiments allowed us to analyze the distributions of the bonds lengths in the fullerene cores of both molecules, methanofullerenes **5** and **13** (Figure 5). It is interesting to note that there is an averaging of the bond lengths in molecule **5**, but for **13**, despite the rather wide range of bonds lengths, the most typical are those corresponding to the carbon−carbon bonds in 5-membered cycles (1.45−1.46 Å) and 6-membered cycles (1.37−1.39 Å). This result can be considered as unambiguous proof of the cyclic substituent's influence on a fullerene fragment in the methanofullerene **13** molecule.

In the crystal, the methanofullerene **13** molecules are linked with chloroform molecules by C−H···O-intermolecular interaction between hydrogen H(70) of the solvent molecule and the oxygen O(62) of the carboxyl group. The parameters of the interaction are: distance H(70)···O(62) 2.32 Å, angle C(70)−H(70)···O(62) 149.07°.

Each methanofullerene **13** molecule is in a hexagonal environment in the crystal but participates in the fullerene···fullerene interactions only with five neighboring fullerene fragments. The corresponding packing diagram, which shows the intermolecular interactions, is presented in Figure 6.

These interactions form continuous goffered layers parallel to the *0bc* plane in crystal, the distances between the fullerene centroids are in the range of 10.07−10.15 Å. There are $\pi\cdots\pi$ interactions between the 5-membered aromatic rings (5/5 interactions, distance between the centers of interacting rings is 3.89 Å), 5- and 6-membered rings (5/6 interactions, distance between the centers is 3.88 Å and the dihedral angle is 19.33°), and 6-membered rings (6/6 interactions with distance 4.09 Å and dihedral angle 18.08°). The goffered layers are surrounded by the aromatic substituents and solvent molecules. The absence of the fullerene···fullerene interactions with the sixth molecule in a hexagonal environment can be explaned by a steric factors and the participation of this molecule in $\pi\cdots\pi$-interactions between the aromatic substituents of two molecules of the neighboring layers. Owing to such a type of π-electronic interaction and fullerene···aromatic substituents interactions the goffered layers are linked in a three-dimensional network.

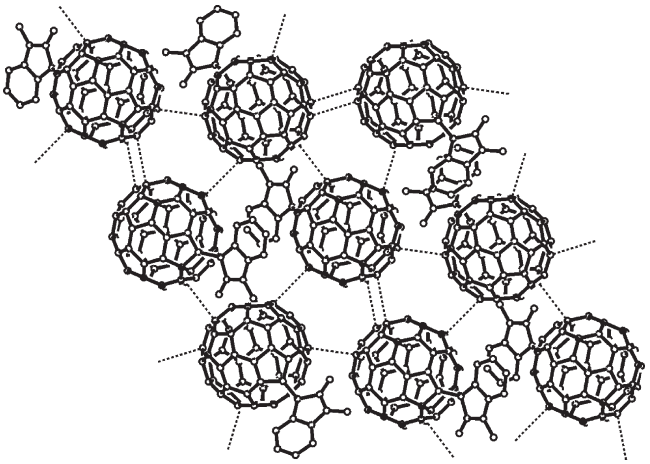

Figure 6. Monolayer fullerene arrangement in the crystal of **13**; the view along the *0a*-axis. H atoms and chloroform molecules are omitted for clarity. Dashed lines indicate the fullerene···fullerene interactions.

Table 1. Peak Potentials (E_p^{red}) and Currents (I_p^{red}, μA) on the CV Curves of C_{60} and Compounds 1, 5, 7−10, 13, and 14[a]

		E_p^{red} V /(I_p^{red}, μA)			
compd	conc, M	C_1	C_2	C_3	C_4
C_{60}	5.0×10^{-3}	−0.83 (4.2)	−1.24 (3.8)	−1.70 (3.9)	−2.16 (3.9)
1	1.7×10^{-3}	−1.22 (11.3)	−1.92 (8.0)		
5	1.7×10^{-3}	−0.90 (3.0)	−1.22 (2.3)	−1.41 (1.8)	−1.84 (1.8)
7	1.7×10^{-3}	−1.20 (6.4)	−1.82 (2.8)	−2.02 (2.8)	−2.24 (2.8)
10	1.0×10^{-3}	−0.88 (2.0)	−1.22 (2.0)	−1.40 (1.5)	−1.82 (1.1)
8	6.7×10^{-3}	−1.35 (10.5)	−2.02 (8.8)		
13	1.0×10^{-3}	−0.89 (1.9)	−1.22 (2.0)	−1.43 (1.0)	−1.85 (0.9)
9	5.7×10^{-3}	−1.31 (9.8)	−1.99 (7.0)		
14	1.0×10^{-3}	−0.90 (2.1)	−1.24 (1.8)	−1.44 (1.5)	−1.88 (1.2)

[a] Supporting electrolyte, 0.1 M Bu_4NBF_4; cathode, glassy carbon (GC) (S_{work} = 3.14 mm^2); reference electrode, Ag/0.01 M $AgNO_3$ in MeCN; scan rate, V_{pot} = 50 mV s^{-1}.

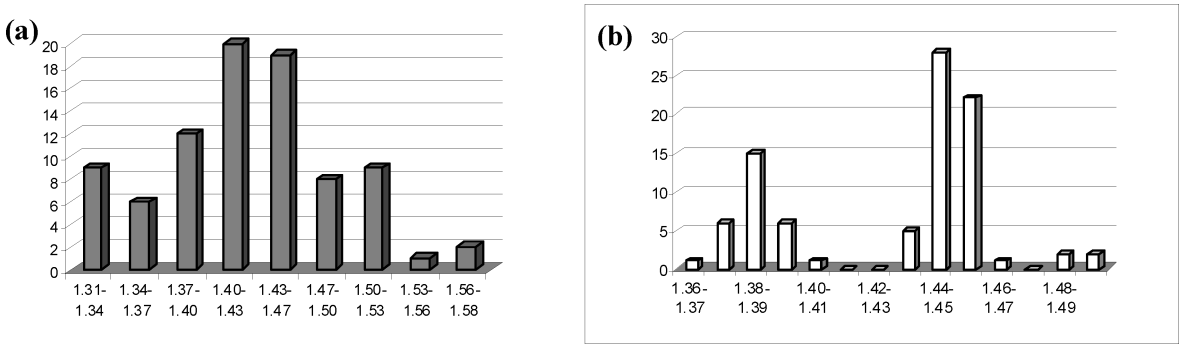

Figure 5. Bond lengths distribution in the fullerene fragments of (a) methanofullerene **5** and (b) methanofullerene **13** molecules.

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Electrochemical Study of 1, 5, 7−10, 13, 14, and C_{60}. Practical properties of the methanofullerenes, including their biological activity, are connected generally with the ability to accept electrons and form radicals. The electrochemical reduction of the methanofullerenes **5**, **10**, **13**, and **14** and also the starting quinones **1** and **7**, isatins **8** and **9**, and fullerene C_{60} was studied by cyclic voltammetry (CV).

The results of electrochemical study of the methanofullerenes **5**, **10**, **13**, and **14**, as well as comparative data for C_{60}, starting quinones **1** and **7**, and isatins **8** and **9**, are shown in Table 1. Four classical reversible one-electron reduction peaks are observed on the CV curve of the fullerene C_{60}. The reduction of the quinones **1** and **7** is a reversible process which is realized as two reversible one-electron transfer steps. The first electron transfer of the compounds **1** and **7** is observed at the same potential range as the second reduction peak of free C_{60} molecule (Table 1).

The electrochemical behavior of the isatins **8** and **9** at cathodic potentials is also characterized as two reversible one-electron processes which are negatively shifted with respect to the values of the electroreduction of the quinones **1** and **7** (−1.35 and −1.31 V versus Ag/0.01 M $AgNO_3$ in MeCN). The electroreduction of the methanofullerenes **5**, **10**, **13**, and **14** proceeds as the reversible transfer of four electrons displaying four reversible peaks on the CV curves (Table 1). A comparison of the potentials and of the peak's currents for C_{60}, the quinones **1** and **7**, the isatins **8** and **9**, and the methanofullerenes **5**, **10**, **13**, and **14** shows that the first step of the methanofullerene reduction (C_1) involves an electron transfer onto fullerene sphere. At the same time, the second peak of the reduction (C_2) and the other cathodic peaks (C_3 and C_4) that appeared on the CV curve of the methanofullerenes **5**, **10**, **13**, and **14** correspond to the reduction of both the fullerene sphere and attached polycyclic addend. A comparison of the reduction potentials demonstrates that the first reduction peaks of all methanofullerenes are shifted on 50−70 mV to the cathodic region as compared with that of free C_{60}. It could be a result of the fullerene sphere electrophilicity decreasing due to the opening of one C=C bond.[49] It should be noted that reversibility of the electrochemical reduction process allows us to conclude that the methanofullerenes **5**, **10**, **13**, and **14** are stable on the cyclic voltammetry time scale.

CONCLUSION

Involvement of the fullerene in the reaction with phosphine **2** and a variety of α-diketones mentioned above has allowed us to make an unambiguous conclusion about the intermediate formation of carbenes in the deoxygenation reaction of the organic compounds under the action of the phosphorus(III) derivatives. New polycyclic methanofullerenes **5**, **10**, and **13**−**16** were obtained in these three-component reactions. NMR and XRD data confirm the [6,6]-type of addend linkage and the carbene addition regiochemistry. It should be also noted that the investigated reaction is the first example of useful application of the deoxygenation methodology in the synthesis of the methanofullerenes.

EXPERIMENTAL SECTION

The quinones **1** and **7** were purchased from a commercial supplier. Isatins **3**, **4**, **8**, and **9** were prepared as described previously.[50] IR spectra were recorded in KBr pellets. UV spectra were recorded in CH_2Cl_2. ^1H and ^{13}C NMR spectra were recorded at room temperature (~20 °C) in deuterated chloroform ($CDCl_3$) on 600 and 400 MHz spectrometers equipped with a pulsed gradient unit capable of producing magnetic field pulse gradients in the *z*-direction of 56 G·cm^{-1}. Chemical shifts are reported on the δ (ppm) scale and are relative to the residual ^1H and ^{13}C signal of $CHCl_3$ in the $CDCl_3$.

In CV studies, a stationary glassy carbon (GC) disk electrode with a working surface of 3.14 mm^2 was used as the working electrode. The CV curves were recorded in the three-electrode type electrochemical cell in *o*-DCB/MeCN (3: 1 by volume) solution in the presence of Bu_4NBF_4 (0.1 M) and X−Y two-coordinate recorder with a potential sweep rate of 50 mV s^{-1}. Silver electrode Ag/$AgNO_3$ (0.01 M solution in MeCN) was served as the reference electrodes ($E°(Fc/Fc^+)$ = +0.20 V). A Pt wire with a diameter of 1 mm served as the auxiliary electrode. Measurements were carried out under thermostatic conditions (20 °C) in a nitrogen atmosphere.

COMPUTATIONAL METHODS

Chemical shifts of **13** were determined within the DFT framework using a hybrid exchange-correlation functional, B3LYP, at the 6-31G(d) level as implemented in Gaussian 98.[51] Full geometry optimizations were performed at the ab initio RHF/6-31G level. All data were referred to TMS (^1H and ^{13}C) chemical shifts that were calculated under the same conditions.

The XRD analysis for the crystals of compounds **5** and **13** were collected at 296 K using graphite-monochromated Mo Kα (λ 0.71073 Å) radiation. Data were corrected for the absorption effect using the SADABS program.[52] The structures were solved by direct methods and refined by the full-matrix least-squares method using SHELXTL[53] and WinGX[54] programs. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in idealized positions and refined by using the riding model. Data collections: images were indexed, integrates, and scaled using the APEX2[55] data reduction package. All figures were created using PLATON.[56]

Crystallographic data (excluding structure factors) for the structures **5** and **13** in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 772639-772640. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

2-(3-Cyclopropa[1,9](C$_{60}$-*I*$_h$)[5,6]fulleren-3-yl)-1-acenaphthenone (5).[39]. Hexaethyltriaminophosphine **2** (0.093 g, 0.375 mmol) was added dropwise to a mixture of acenaphthenequinone **1** (0.023 g, 0.126 mmol) and C_{60} (0.090 g, 0.125 mmol) in anhydrous *o*-dichlorobenzene (40 cm^3) at −10 °C. The mixture was stirred for 8 h at −10 °C, after which time the temperature was allowed to warm to 25 °C. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using mixture of the toluene and petroleum ether 85:15 as eluent to give unreacted C_{60} (0,027 g, 30%) and a fraction containing a mixture of the methanofullerene **5** and polyproducts. The methanofullerene **5** (0.044 g, 40%) was obtained by repeated column chromatography: ν_{max} (KBr)/cm^{-1} 1723, 1625, 1420, 1229, 1026, 774, 713, 526; λ_{max} (CH_2Cl_2)/nm 258, 329, 438 (ribbon), 504, 690; ^1H NMR (600.13 MHz; mixture of CS_2 and $CDCl_3$) δ 7.81 (1H, dd, *J* 7.4 and 7.8, C(4)H), 7.93 (1H, dd, *J* 7.4 and 7.0, C(7)H), 8.07 (1H, d, *J* 8.2, C(5)H), 8.23 (1H, d, *J* 7.0, C(8)H), 8.28 (1H, d, *J* 8.2, C(6)H), 8.56 (1H, d, *J* 7.0, C(3)H); ^{13}C NMR (150.94 MHz; mixture of CS_2 and $CDCl_3$) δ 47.73 (C(2)), 121.54 (C(3)), 122.30 (C(8)), 125.78 (C(5)), 128.20 (C(7)), 128.60 (C(4)), 130.41 (C(5a)), 131.79 (C(6)), 131.92 (C(8a)), 135.21 (C(2a)), 141.27 (C(8b)), 193.15 (C(1)), fullerene moiety: 76.48 (2C), 138.52 (2C), 140.74 (2C), 141.11 (2C), 141.25 (2C), 141.42 (2C), 141.83 (2C), 141.94 (2C), 142.02 (2C), 142.58 (2C), 142.75 (2C), 142.81 (2C), 142.83 (1C), 142.94 (1C), 143.37 (2C), 143.51 (2C), 143.91 (2C), 144.04 (1C), 144.15 (2C), 144.29 (2C), 144.43 (4C), 144.45

(2C), 144.50 (2C), 144.66 (4C), 144.77 (1C), 144.91 (2C), 144.96 (4C), 145.25 (2C), 146.17 (2C); MS MS (MALDI) m/z calcd for $C_{72}H_6O$ 886, found 886.

2-(3-Cyclopropa[1,9](C$_{60}$-*I*$_h$)[5,6]fulleren-3-yl)-1-acenanthrenone (10). Hexaethyltriaminophosphine **2** (0.093 g, 0.376 mmol) was added dropwise to a mixture of aceanthrenequinone **7** (0.029 g, 0.125 mmol) and C_{60} (0.090 g, 0.125 mmol) in anhydrous *o*-dichlorobenzene (40 cm^3) at −10 °C. The mixture was stirred for 8 h at −10 °C, after which time the temperature was allowed to warm to 25 °C. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using mixture of the toluene and petroleum ether 85:15 as eluent to give unreacted C_{60} (0.036 g, 40%), the fraction containing the methanofullerenes **10** and C_{60}, and the fraction containing the mixture of the polyadducts. The *p*-Bu^t-calix[8]arene **11** was added to the fraction containing the methanofullerenes **10** and C_{60}, and the precipitate **12** occurred immediately. The methanofullerene **10** (0.024 g, 20%) was obtained by column chromatography of the filtrate after separation of the complex **12**. The data for the methanofullerene **10**: ν_{max} (KBr)/cm^{-1} 1731, 1700, 1458, 1425, 1155 1107, 1079, 737, 7670, 527; λ_{max} (CH_2Cl_2)/nm 258, 329, 405, 433 (ribbon), 517, 590, 610; ^{1}H NMR (600.13 MHz; mixture of CS_2 and $CDCl_3$) δ 7.71 (2H, m, C(4,8)H), 7.82 (1H, dd, J 7.2, C(9)H), 8.13 (1H, d, J 8.9, C(5)H), 8.23 (1H, d, J 8.5, C(7)H) 8.53 (1H, d, J 7.0, C(3)H), 8.79 (1H, s, C(6)H), 9.34 (1H, d, J 8.5, C(10)H); ^{13}C NMR (150.94 MHz; mixture of CS_2 and $CDCl_3$) δ 47.39 (C(2)), 121.14 (C(3)), 122.62 (C(10)), 124.67 (C(10b)), 125.37 (C(5)), 126.95 (C(8)), 127.95 (C(5a)), 128.14 (C(4)), 128.74 (C(10a)), 129.11 (C(7)), 129.70 (C(9)), 132.06 (C(6)), 133.29 (C(6a)), 135.23 (C(2a)), 142.98 (C(10c)), 193.94 (C(1)), fullerene moiety: 76.61 (2C), 138.67 (2C), 140.86 (2C), 141.21 (2C), 141.26 (2C), 141.56 (2C), 141.85 (2C), 142.06 (2C), 142.13 (2C), 142.70 (2C), 142.88 (2C), 142.95 (2C), 143.06 (1C), 143.47 (2C), 143.63 (2C), 144.02 (2C), 144.15 (1C), 144.27 (2C), 144.42 (2C), 144.56 (5C), 144.62 (2C), 144.81 (2C), 144.90 (4C), 144.97 (1C), 145.02 (2C), 145.08 (4C), 145.37 (2C), 145.28 (2C); MS MS (MALDI) m/z calcd for $C_{76}H_8O$ 937, found 937. Anal. Calcd for $C_{76}H_8O$: C, 97.44; H, 0.85. Found: C, 96.94; H, 0.83.

Data for complex **12**: ν_{max} (KBr)/cm^{-1} 528, 578, 729, 782, 876, 1118, 1184, 1203, 1248, 1293, 1362, 1429, 1452, 1485, 1603, 2868, 2960. Anal. Calcd for $C_{148}H_{112}O_8$: C, 88.06, H, 5.57. Found: C, 89.26, H, 5.59.

1-Methyl-3-(3-cyclopropa[1,9](C$_{60}$-*I*$_h$)[5,6]fulleren-3-yl)indolin-2-one (13). Hexaethyltriaminophosphine **2** (0.120 g, 0.480 mmol) was added dropwise to a mixture of the isatin **8** (0.020 g, 0.124 mmol) and C_{60} (0.100 g, 0.138 mmol) in anhydrous *o*-dichlorobenzene (40 cm^3) at −10 °C. The mixture was stirred for 8 h at −10 °C, after which time the temperature was allowed to rise to 25 °C. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using a mixture of toluene and petroleum ether 7:2 as eluent to give unreacted C_{60} (0.014 g, 14%), the methanofullerene **13** (0.044 g, 37%), and a polyadducts mixture: ν_{max} (KBr)/cm^{-1} 1724, 1611, 1468, 1322, 1344, 772, 527; λ_{max} (CH_2Cl_2)/nm 430 (ribbon), 500, 720; ^{1}H NMR (600.13 MHz; mixture of CS_2 and $CDCl_3$) δ 3.57 (3H, s, C(8)H$_3$), 7.17 (1H, d, J 7.9, C(7)H), 7.26 (1H, m, C(5)H), 7.55 (1H, dd, J 7.9 and J 7.5, C(6)H), 8.32 (1H, d, J 7.7, C(4)H); ^{13}C NMR (150.94 MHz; mixture of CS_2 and $CDCl_3$) δ 26.64 (C(8)), 42.08 (C(3)), 108.53 (C(7)), 122.66 (C(5)), 123.78 (C(4)), 125.01 (C(3a)), 129.43 (C(6)), 143.50 (C(7a)), 169.09 (C(2)), fullerene moiety: 75.18 (2C), 138.79 (2C), 140.90 (2C), 141.24 (2C), 141.32 (2C), 141.48 (2C), 142.10 (4C), 142.14 (2C), 142.73 (2C), 142.90 (2C), 142.98 (2C), 143.04 (2C), 143.66 (2C), 143.71 (1C), 144.05 (3C), 144.14 (1C), 144.32 (2C), 144.44 (2C), 144.66 (6C), 144.88 (2C), 144.93 (1C), 144.96 (2C), 145.08 (4C), 145.10 (2C), 145.13 (2C), 145.36 (2C), 145.42 (2C); MS MS (MALDI) m/z calcd for $C_{69}H_7NO$ 866, found 866. Anal. Calcd for $C_{69}H_7NO$: C, 95.73, H, 0.81, N, 1.62. Found: C, 95.21, H, 0.80, N, 1.91.

1-Allyl-3-(3-cyclopropa[1,9](C$_{60}$-*I*$_h$)[5,6]fulleren-3-yl)indolin-2-one (14). Hexaethyltriaminophosphine **2** (0.100 g, 0.400 mmol) was added dropwise to a mixture of the isatin **9** (0.025 g, 0.130 mmol) and C_{60} (0.090 g, 0.125 mmol) in anhydrous *o*-dichlorobenzene (40 cm^3) at −10 °C. The mixture was stirred for 8 h at −10 °C, after which time the temperature was allowed to 25 °C. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using a mixture of toluene and petroleum ether 7:2 as the eluent to give unreacted C_{60} (0.006 g, 7%), the methanofullerene **14** (0.036 g, 32%), and the polyadduct mixture: ν_{max} (KBr)/cm^{-1} 1721, 1609, 1464, 1354, 987, 920, 743; λ_{max} (CH_2Cl_2)/nm 430 (ribbon), 500, 714; ^{1}H NMR (600.13 MHz; mixture of CS_2 and $CDCl_3$) δ 4.69 (2H, d, J 5.3, C(8)H$_2$), 5.41 and 5.53 (2H, d, J 17.2 and 10.6, C(10)H$_2$), 6.14−6.06 (1H, m, C(9)H), 7.20 (1H, d, J 7.9, C(7)H), 7.26 (1H, m, C(5)H), 7.52 (1H, dd, J 7.9 and J 7.6, C(6)H), 8.34 (1H, d, J 7.6, C(4)H); ^{13}C NMR (150.94 MHz; mixture of CS_2 and $CDCl_3$) δ 42.05 C(3)), 43.24 (C(8)), 109.56 (C(7)), 118.57 (C(10)), 122.71 (C(5)), 123.91 (C(4)), 125.09 (C(3a)), 129.37 (C(6)), 131.28 (C(9)), 142.83 (C(7a)), 169.13 (C(2)), fullerene moiety: 75.29 (2C), 138.92 (2C), 140.98 (2C), 141.30 (2C), 141.43 (2C), 141.57 (2C), 142.13 (2C), 142.18 (2C), 142.22 (2C), 142.80 (2C), 142.99 (2C), 143.04 (2C), 143.07 (2C), 143.12 (2C), 143.57 (2C), 143.75 (2C), 144.14 (4C), 144.23 (1C), 144.41 (1C), 144.53 (2C), 144.75 (5C), 145.00 (4C), 145.05 (1C), 145.17 (2C), 145.20 (2C), 145.23 (2C), 145.46 (4C); MS MS (MALDI) m/z calcd for $C_{71}H_9NO$ 892, found 892. Anal. Calcd for $C_{71}H_9NO$: C, 95.63; H, 1.01; N, 1.57. Found: C, 95.14,; H, 0.71; N, 1.95.

1-Acetyl-3-(3-cyclopropa[1,9](C$_{60}$-*I*$_h$)[5,6]fulleren-3-yl)indolin-2-one (15). Hexaethyltriaminophosphine **2** (0.110 g, 0.450 mmol) was added dropwise to a mixture of the isatin **3** (0.020 g, 0.160 mmol) and C_{60} (0.100 g, 0.140 mmol) in anhydrous *o*-dichlorobenzene (40 cm^3) at −10 °C. The mixture was stirred for 8 h at −10 °C, after which the temperature was allowed to rise to 25 °C. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using a mixture of toluene and petroleum ether 8:2 as eluent to give unreacted C_{60} (0.0160 g, 16%), the methanofullerene **15** (0.038 g, 31%), and the polyadducts mixture: ν_{max} (KBr)/cm^{-1} 1773, 1745, 1713, 1608, 1552, 1460, 1378, 1336, 1307, 1265, 1212, 1166, 1095, 1039, 981, 749, 598, 527; λ_{max} (CH_2Cl_2)/nm 432 (ribbon), 496, 702; ^{1}H NMR (600.13 MHz; mixture of CS_2 and $CDCl_3$) δ 2.91 (3H, s, C(9)H), 7.41 (1H, dd, J 7.8 and 7.8, C(5)H), 7.59 (1H, dd, J 7.8 and 8.3, C(6)H), 8.41 (1H, d, J 7.8, C(4)H), 8.62 (1H, d, J 8.3, C(7)H); ^{13}C NMR (150.94 MHz; mixture of CS_2 and $CDCl_3$) δ 26.88 (C(9)), 41.90 (C(3)), 116.74 (C(7)), 122.93 (C(4)), 124.24 (C(3a)), 125.00 (C(5)), 129.68 (C(6)), 140.03 (C(7a)), 169.27 (C(8)), 169.42 (C(2)), fullerene moiety: 75.11 (2C), 138.96 (2C), 140.80 (2C), 140.90 (2C), 141.18 (4C), 141.97 (4C), 142.06 (2C), 142.63 (2C), 142.78 (4C), 142.89 (4C), 143.18 (2C), 143.33 (1C), 143.52 (2C), 143.88 (3C), 144.32 (6C), 144.59 (8C), 144.86 (2C), 144.98 (4C), 145.04 (4C); MS MS (MALDI) m/z calcd for $C_{70}H_7NO_2$ 894, found 894. Anal. Calcd for $C_{70}H_7NO_2$: C, 94.07; H, 0.78; N, 1.57. Found: C, 93.60; H, 0.53; N, 1.82.

1-(3′,5′-Di-*tert*-butyl-4′-hydroxybenzyl)-3-(3″-cyclopropa[1‴,9‴](C$_{60}$-*I*$_h$)[5,6]fulleren-3″-yl)indolin-2-one (16). Hexaethyltriaminophosphine **2** (0.100 g, 0.400 mmol) was added dropwise to a mixture of the isatin **4** (0.050 g, 0.136 mmol) and C_{60} (0.100 g, 0.138 mmol) in anhydrous *o*-dichlorobenzene (40 cm^3) at −10 °C. The mixture was stirred for 8 h at −10 °C, after which time the temperature was allowed to warm to 25 °C. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using mixture of the toluene and petroleum ether 8:2 as eluent to give unreacted C_{60} (0.013 g, 13%), the methanofullerene **16** (0.069 g,

46%), and a polyadducts mixture: ν_{max} (KBr)/cm^{-1} 3438, 2955, 2922, 2864, 1722, 1636, 1611, 1466, 1431, 1356, 1236,1186, 1157, 1112, 744, 526; λ_{max} (CH_2Cl_2)/nm 427 (ribbon), 494, 687; ^{1}H NMR (400 MHz; mixture of CS_2 and $CDCl_3$) δ 1.45 (18H, s, C(16−18)H and C(20−22)H), 5.13 (2H, s, C(8)H), 5.20 (1H, s, C(12)OH), 7.23 (1H, d, J 7.4, C(7)H), 7.24 (1H, dd, J 7.8 and 7.4, C(5)H), 7.35 (2H, s, C(10)H and C(14H), 7.50 (1H, dd, J 7.4 and 7.4, C(6)H), 8.34 (1H, d, J 7.8, C(4)H); ^{13}C NMR (100 MHz; mixture of CS_2 and $CDCl_3$) δ 30.18 (C(16−18), C(20−22), 34.23 (C(15), C(19)), 42.30 (C(3)), 44.66 (C(8)), 109.91 (C(7)), 122.58 (C(5)), 123.84 (C(4)), 124.74 (C(9), C(10), C(14)), 125.15 (C(3a)), 129.28 (C(6)), 136.23 (C(11), C(13)), 143.12 (C(7a)), 153.49 (C(12)), 169.52 (C(2)), fullerene moiety: 75.38 (2C), 138.91 (2C), 140.96 (2C), 141.29 (2C), 141.44 (2C), 141.60 (2C), 142.18 (2C), 142.22 (4C), 142.83 (2C), 142.98 (2C), 143.06 (2C), 143.29 (2C), 143.56 (2C), 143.76 (2C), 144.14 (2C), 144.18 (2C), 144.24 (1C), 144.38 (2C), 144.53 (2C), 144.72 (2C), 144.73 (2C), 144.76 (2C), 144.97 (2C), 145.05 (3C), 145.16 (2C), 145.18 (2C), 145.22 (2C), 145.48 (2C), 145.57 (2C); MS MS (MALDI) m/z calcd for $C_{83}H_{27}NO_2$ 1070, found 1070. Anal. Calcd for $C_{83}H_{27}NO_2$: C, 93.18, H, 2.52, N, 1.31. Found: C, 92.68, H, 2.24, N, 1.68.

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H and ^{13}C NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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