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Synthesis of 3′*H*-Cyclopropa[1,9](C_{60}-I_h)[5,6]fullerenes from 2′-Aryl-1′,1′-dimethyl-2′,5′-dihydro-1′*H*-pyrrolo[3′,4′:1,9]-(C_{60}-I_h)[5,6]fulleren-1-ium Iodides

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Abstract—New 1′,1′-dimethyl-2′,5′-dihydro-1′*H*-pyrrolo[3′,4′:1,9](C_{60}-I_h)[5,6]fulleren-1-ium iodides containing different aryl groups in position *2* of the pyrrolidine ring have been synthesized. Their reactions with bis(toluene)chromine afforded the corresponding 3′-aryl-3′*H*-cyclopropa[1,9](C_{60}-I_h)[5,6]fullerenes.

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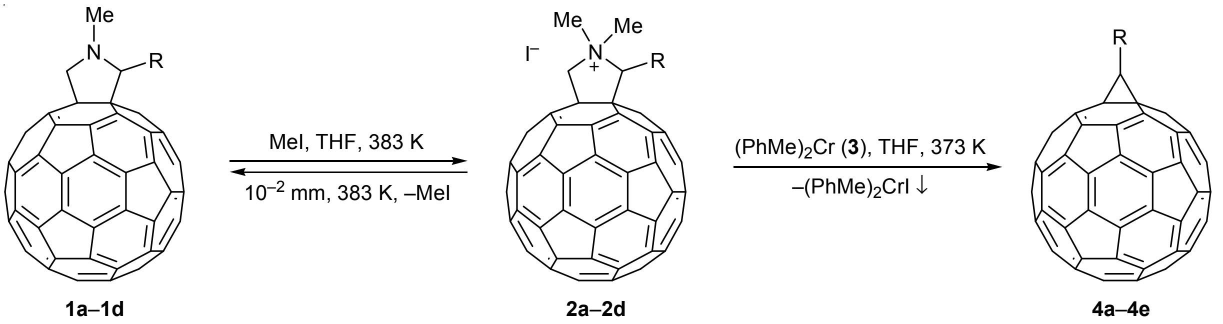
Pyrrolidine- [1] and cyclopropane-fused fullerenes [2] are well studied C_{60} derivatives [3]. Salt-like pyrrolidinofullerenes, fulleropyrrolidinium iodides, attract attention of researchers in the fields of biology [4–8] and design of solar energy conversion devices [9–11]. Up to now, several tens of such compounds have been reported, but there are very scarce data on their reactions with strong electron donors. We have synthesized new pyrrolidinofullerenes **1a**–**1d** and fulleropyrrolidinium iodides **2a**–**2d** with various aryl substituents in position *2* of the pyrrolidine ring and studied their reaction with bisarene chromium complexes with the goal of obtaining new cyclopropafullerenes.

Iodides **2a**–**2d** reacted with bis(toluene)chromium(0) (**3**) in the presence of THF to give new cyclopropafullerenes **4a**–**4e** (Scheme 1). The yields of **4a** and **4c**–**4e** ranged from 20 to 30%, while the yield of **4b** was as low as ~8% due to simultaneous reduction of the nitro group with formation of an appreciable amount of **4e**. Taking into account that $Bu_4N^+Br^-$ failed to react with complex **3** under analogous conditions, we presumed that the presence of an electron-

Scheme 1.



$$\mathbf{4a}\text{–}\mathbf{4c},\ \mathbf{4e},\ \mathbf{1a}\text{–}\mathbf{1c}\ \underset{\text{Cu(OAc)}_2,\ \text{THF}}{\overset{\mathbf{3},\ \text{PhMe}}{\rightleftarrows}}\ \underbrace{[\mathbf{4a}]^{\dot{-}}[\mathbf{3}]^{+\cdot}\text{–}[\mathbf{4c}]^{\dot{-}}[\mathbf{3}]^{+\cdot}}_{\mathbf{5a}\text{–}\mathbf{5c}},\ \underbrace{[\mathbf{4e}]^{\dot{-}}[\mathbf{3}]^{+\cdot}}_{\mathbf{5e}},\ \underbrace{[\mathbf{1a}]^{\dot{-}}[\mathbf{3}]^{+\cdot}\text{–}[\mathbf{1c}]^{\dot{-}}[\mathbf{3}]^{+\cdot}}_{\mathbf{6a}\text{–}\mathbf{6c}}$$

R = 3,5-*t*-Bu_2-4-HOC_6H_2 (**a**), 3-Br-5-EtO-4-$MeOC_6H_2$ (**b**), 4-MeO-3-MeOC(O)$CH_2OC_6H_3$ (**c**), 3,4-$(MeO)_2$-5-$O_2NC_6H_2$ (**d**), 3-H_2N-4,5-$(MeO)_2C_6H_2$ (**e**).

deficient fullerene is a necessary condition for the reaction to occur. In the first step, complex **3** is oxidized to the corresponding radical cation which precipitates from the reaction mixture as iodide. Further heating leads to the formation of radical anions $[\mathbf{4a}]^{\dot{-}}$–$[\mathbf{4c}]^{\dot{-}}$ and $[\mathbf{4e}]^{\dot{-}}$, as follows from the presence in the near-infrared spectra of absorption bands typical of radical ion salts **5a–5c** and **5e** prepared from fullerenes **4a–4c** and **4e** and complex **3** and stable in THF at 373 K. Treatment of the reaction solutions with $Cu(OAc)_2$ at 293 K, as well as of salts **5a–5c** and **5e** afforded fullerenes **4a–4c** and **4e**. Iodides **2a–2d** decomposed at 423 K with quantitative formation of initial neutral fullerenes **1a–1d** and methyl iodide. Radical ion salts **6a–6c** derived from **1a–1c** and **3** reacted with MeI in THF at 373 K to give mixture of polyaddition products among which no fullerenes **4a–4c** were detected. Thus, 3′-aryl-3′*H*-cyclopropa[1,9](C_{60}-I_h)[5,6]fullerenes can be synthesized from 2′-aryl-1′-methyl-2′,5′-dihydro-1′*H*-pyrrolo[3′,4′:1,9](C_{60}-I_h)[5,6]fullerenes through the corresponding *N*,*N*-dimethylpyrrolidinium iodides.

EXPERIMENTAL

The ESR spectra were recorded in THF at 293 K on a Bruker EMX instrument. The ^1H NMR spectra were recorded in $CDCl_3$ at 293 K on a Bruker DPX-400 spectrometer using tetramethylsilane as internal standard. The electronic absorption spectra were measured on a Perkin Elmer Lambda 25 spectrophotometer. The chromium content of the isolated compounds was calculated from the amount of Cr_2O_3 residue after combustion.

All experiments with fullerenes **4a–4e** and fullerides **5a–5c**, **5e**, and **6a–6c** were carried out in evacuated ampules with protection from atmospheric oxygen and moisture. The solvents were purified and dried according to standard procedures, followed by degassing via triple freeze–thaw cycles under reduced pressure. Thermal decomposition of iodides **2a–2d** was carried out in evacuated (to 10^{-2} mm) sealed glassware. Volatile products were trapped in a receiver cooled with liquid nitrogen.

Fullerenes **1a–1d** were synthesized from sarcosine and 3,5-di-*tert*-butyl-4-hydroxy-, 5-bromo-3-ethoxy-4-methoxy-, 4-methoxy-3-(2-methoxy-2-oxoethoxy)-, or 3,4-dimethoxy-5-nitrobenzaldehyde in chlorobenzene at 463 K in a sealed ampule according to modified procedure [1]. The mixture was evaporated under reduced pressure, and the residue was washed with acetone, dried under reduced pressure, and purified by silica gel chromatography. The first fraction contained unreacted C_{60}, and the target product was isolated from the second fraction.

2,6-Di-*tert*-butyl-4-(1′-methyl-2′,5′-dihydro-1′*H*-pyrrolo[3′,4′:1,9](C_{60}-I_h)[5,6]fulleren-2′-yl)phenol (1a). Eluent decalin–benzene (4:1). UV spectrum (decalin), λ_{max}, nm: 256, 310, 326, 431, 639, 671, 693, 705. ^1H NMR spectrum (C_6D_6), δ, ppm: 1.36 s (18H, *t*-Bu), 2.60 s (3H, NCH_3), 3.83 d (1H, 5′-H, *J* = 9.54 Hz), 4.49 d (1H, 5′-H, *J* = 9.29 Hz), 4.70 s (1H, 2′-H), 4.96 s (1H, OH), 7.75 br.s (2H, H_{arom}).

2′-(5-Bromo-3-ethoxy-4-methoxyphenyl)-1′-methyl-2′,5′-dihydro-1′*H*-pyrrolo[3′,4′:1,9]-(C_{60}-I_h)[5,6]fullerene (1b). Eluent toluene. UV spectrum (decalin), λ_{max}, nm: 208, 258, 327, 429, 483, 659, 681, 693. ^1H NMR spectrum, δ, ppm: 1.41 t (3H, OCH_2CH_3, *J* = 7.027 Hz), 3.25 s (3H, NCH_3), 3.92 s (3H, OCH_3), 4.32 m (2H, OCH_2), 4.69 s (1H, 2′-H), 5.58 s (2H, 5′-H), 7.38 s (1H, H_{arom}), 8.49 s (1H, H_{arom}).

Methyl 2-[2-methoxy-5-(1′-methyl-2′,5′-dihydro-1′*H*-pyrrolo[3′,4′:1,9](C_{60}-I_h)[5,6]fulleren-2′-yl)-phenoxy]acetate (1c). Eluent toluene–acetone (57:1). UV spectrum (decalin), λ_{max}, nm: 210, 256, 310, 328, 431, 638, 669, 692, 704. ^1H NMR spectrum, δ, ppm: 2.84 s (3H, NCH_3), 3.78 s (3H, $COOCH_3$), 3.91 s (3H, OCH_3), 4.28 s (1H, 2′-H), 4.70 s (2H, OCH_2COO), 4.95 s (2H, 5′-H), 6.84 m (1H, H_{arom}), 7.43 m (2H, H_{arom}).

2′-(3,4-Dimethoxy-5-nitrophenyl)-1′-methyl-2′,5′-dihydro-1′*H*-pyrrolo[3′,4′:1,9](C_{60}-I_h)[5,6]-fullerene (1d). Eluent toluene. UV spectrum (decalin), λ_{max}, nm: 211, 256, 311, 324, 430, 635, 667, 689, 701. ^1H NMR spectrum, δ, ppm: at 293 K: 2.85 s (3H, NCH_3), 3.95 s (3H, OCH_3), 4.00 s (3H, OCH_3), 4.32 d (1H, 5′-H, *J* = 9.05 Hz), 4.98 s (1H, 2′-H), 5.04 d (1H, 5′-H, *J* = 7.78 Hz), 7.76 br.s (2H, H_{arom}); at 323 K: 2.86 s (3H, NCH_3), 3.94 br.s (3H, OCH_3), 3.99 s (3H, OCH_3), 4.33 d (1H, 5′-H, *J* = 9.79 Hz), 4.98 s (1H, 2′-H), 5.05 d (1H, 5′-H, *J* = 9.74 Hz), 7.77 s (2H, H_{arom}).

Compounds 2a–2d (*general procedure*). Iodides **2a–2d** were synthesized in ~50% yield according to modified procedure [8]. Fullerenes **1a–1d** are poorly soluble in chloroform; therefore, the reaction was carried out in THF. A solution of 0.2 mmol of **1a–1d** and 2 mL (32.8 mmol) of methyl iodide in 50 mL of THF was heated for 72 h at 373 K in a sealed degassed ampule. The solvent was removed by decanting, and the light brown residue was washed with THF (2 × 5 mL) and toluene (2 × 10 mL) and dried under reduced pressure (10^{-2} mm) at 313 K. Compounds **2a**–**2d** were isolated as brown powders insoluble in toluene and poorly soluble in THF.

2′-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-1′,1′-dimethyl-2′,5′-dihydro-1′*H*-pyrrolo[3′,4′:1,9](C_{60}-I_h)-[5,6]fulleren-1′-ium iodide (2a). UV spectrum (THF): λ_{max} 430 nm.

2′-(5-Bromo-3-ethoxy-4-methoxyphenyl)-1′,1′-dimethyl-2′,5′-dihydro-1′*H*-pyrrolo[3′,4′:1,9]-(C_{60}-I_h)[5,6]fulleren-1′-ium iodide (2b). UV spectrum (THF): λ_{max} 429 nm.

2′-[4-Methoxy-3-(2-methoxy-2-oxoethoxy)-phenyl]-1′,1′-dimethyl-2′,5′-dihydro-1′*H*-pyrrolo-[3′,4′:1,9](C_{60}-I_h)[5,6]fulleren-1′-ium iodide (2c). UV spectrum (THF): λ_{max} 429 nm.

2′-(3,4-Dimethoxy-5-nitrophenyl)-1′,1′-dimethyl-2′,5′-dihydro-1′*H*-pyrrolo[3′,4′:1,9](C_{60}-I_h)[5,6]-fulleren-1′-ium iodide (2d). UV spectrum (THF): λ_{max} 428 nm.

Compounds 4a–4d (*general procedure*). A solution of complex **3** in THF was added in small portions with vigorous stirring at 293 K to a suspension of 0.2 mmol of iodide **2a**–**2d** in 40 mL of THF until complete dissolution. The resulting red transparent solution was stirred for 20 min, and a yellow solid separated. The liquid phase was separated by decanting and heated for 5 h at 373 K in a sealed ampule. The mixture was cooled to 293 K, excess $Cu(OAc)_2$ was added, the mixture was stirred for 2 h, the solvent was removed, and the residue was dried under reduced pressure and extracted with toluene. The extract was filtered and evaporated, and the residue was washed with acetone, dried under reduced pressure, and purified by silica gel chromatography. A red fraction was collected, the solvent was removed, and the residue was washed with acetone and dried under reduced pressure, The product was a brown powder.

2,6-Di-*tert*-butyl-4-(3′*H*-cyclopropa[1,9](C_{60}-I_h)-[5,6]fulleren-3′-yl)phenol (4a). Eluent decalin, first fraction. UV spectrum (decalin), λ_{max}, nm: 205, 260, 327, 431, 494, 665, 687, 698. ^{1}H NMR spectrum, δ, ppm: 1.53 s (18H, *t*-Bu), 5.35 s (1H, OH), 5.38 s (1H, 3′-H), 7.76 s (2H, H_{arom}).

3′-(5-Bromo-3-ethoxy-4-methoxyphenyl)-3′*H*-cyclopropa[1,9](C_{60}-I_h)[5,6]fullerene (4b). Eluent toluene, first fraction. UV spectrum (decalin), λ_{max}, nm: 209, 260, 328, 430, 491, 662, 684, 695. ^{1}H NMR spectrum, δ, ppm: 1.50 t (3H, $OCH_2C\mathbf{H}_3$, J = 7.03 Hz), 3.98 s (3H, OCH_3), 4.20 q (2H, OCH_2, J = 7.03 Hz), 5.30 s (1H, 3′-H), 7.44 s (1H, H_{arom}), 7.72 s (1H, H_{arom}).

Methyl 2-[2-methoxy-5-(3′*H*-cyclopropa[1,9]-(C_{60}-I_h)[5,6]fulleren-3′-yl)phenoxy]acetate (4c). Eluent toluene–acetone (143 : 1), first fraction. UV spectrum (decalin), λ_{max}, nm: 207, 259, 327, 430, 493, 664, 685, 696. ^{1}H NMR spectrum, δ, ppm: 3.85 s (3H, OCH_3), 4.01 s (3H, $COOCH_3$), 4.80 s (2H, OCH_2COO), 5.36 s (1H, 3′-H), 6.97 m (1H, H_{arom}), 7.49 m (2H, H_{arom}).

3′-(3,4-Dimethoxy-5-nitrophenyl)-3′*H*-cyclopropa[1,9](C_{60}-I_h)[5,6]fullerene (4d). Eluent toluene, first fraction. UV spectrum (decalin), λ_{max}, nm: 208, 258, 327, 429, 483, 659, 681, 693. ^{1}H NMR spectrum, δ, ppm: 4.05 s (3H, OCH_3), 4.10 s (3H, OCH_3), 5.32 s (1H, 3′-H), 7.71 m (1H, H_{arom}), 7.96 s (1H, H_{arom}).

2,3-Dimethoxy-5-(3′*H*-cyclopropa[1,9](C_{60}-I_h)-[5,6]fulleren-3′-yl)aniline (4e). Eluent toluene, third fraction. UV spectrum (decalin), λ_{max}, nm: 211, 260, 327, 429, 479, 665, 687, 698. ^{1}H NMR spectrum, δ, ppm: 3.93 s (3H, OCH_3), 3.96 s (3H, OCH_3), 4.04 s (2H, NH_2), 5.31 s (1H, 4′-H), 6.91 s (1H, H_{arom}), 6.98 s (1H, H_{arom}).

Compounds 5a–5c, 5e, and 6a–6c (*general procedure*). Fullerene **1a**–**1c**, **4a**–**4c**, or **4e**, 0.1 mmol, was dissolved in 30 mL of toluene, 5 equiv of complex **3** was added, and the mixture was stirred for 20 min. The liquid phase was separated by decanting, and the residue was washed with toluene (2 × 10 mL) and dried under reduced pressure (10^{-2} mm) at 303 K. The products were isolated as brown powders insoluble in hexane, poorly soluble in toluene, and readily soluble in THF.

Bis(toluene)chromium(I) 3′-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3′*H*-cyclopropa[1,9](C_{60}-I_h)[5,6]-fullerenelide (5a). Near-IR spectrum (THF), λ_{max}, nm: 569, 827, 1026. ESR spectrum: g_1 = 1.99927 ($\mathbf{4a}^{-\cdot}$), g_2 = 1.98646 ($\mathbf{3}^{+\cdot}$). Found, %: Cr 4.36. $C_{89}H_{38}CrO$. Calculated, %: Cr 4.43.

Bis(toluene)chromium(I) 3′-(5-bromo-3-ethoxy-4-methoxyphenyl)-3′*H*-cyclopropa[1,9](C_{60}-I_h)[5,6]-fullerenelide (5b). Near-IR spectrum (THF), λ_{max}, nm: 569, 828, 1027. ESR spectrum: g_1 = 1.99970 ($\mathbf{4b}^{-\cdot}$), g_2 = 1.98638 ($\mathbf{3}^{+\cdot}$). Found, %: Cr 4.27. $C_{84}H_{27}BrCrO_2$. Calculated, %: Cr 4.34.

Bis(toluene)chromium(I) 3′-[4-methoxy-3-(2-methoxy-2-oxoethoxy)phenyl]-3′*H*-cyclopropa[1,9]-(C_{60}-I_h)[5,6]fullerenelide (5c). Near-IR spectrum

(THF), λ_{max}, nm: 568, 825, 1026. ESR spectrum: g_1 = 1.99983 ($\mathbf{4c}^{\dot{-}}$), g_2 = 1.98654 ($\mathbf{3}^{+\cdot}$). Found, %: Cr 4.40. $C_{85}H_{28}CrO_4$. Calculated, %: Cr 4.47.

Bis(toluene)chromium(I) 3′-(5-amino-3,4-dimethoxyphenyl)-3′*H*-cyclopropa[1,9](C_{60}-I_h)[5,6]fullerenelide (5e). Near-IR spectrum (THF), λ_{max}, nm: 565, 824, 1025. ESR spectrum: g_1 = 1.99962 ($\mathbf{4e}^{\dot{-}}$), g_2 = 1.98635 ($\mathbf{3}^{+\cdot}$). Found, %: Cr 4.57. $C_{83}H_{27}CrNO_2$. Calculated, %: Cr 4.64.

Bis(toluene)chromium(I) 2′-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1′-methyl-2′,5′-dihydro-1′*H*-pyrrolo[3′,4′:1,9](C_{60}-I_h)[5,6]fullerenelide (6a). Near-IR spectrum (THF), λ_{max}, nm: 571, 764, 991, 1001. ESR spectrum: g_1 = 1.99981 ($\mathbf{1a}^{\dot{-}}$), g_2 = 1.98693 ($\mathbf{3}^{+\cdot}$). Found, %: Cr 4.21. $C_{91}H_{43}CrNO$. Calculated, %: Cr 4.27.

Bis(toluene)chromium(I) 2′-(5-bromo-3-ethoxy-4-methoxyphenyl)-1′-methyl-2′,5′-dihydro-1′*H*-pyrrolo[3′,4′:1,9](C_{60}-I_h)[5,6]fullerenelide (6b). Near-IR spectrum (THF), λ_{max}, nm: 565, 774, 992, 1003. ESR spectrum: g_1 = 1.99961 ($\mathbf{1b}^{\dot{-}}$), g_2 = 1.98651 ($\mathbf{3}^{+\cdot}$). Found, %: Cr 4.10. $C_{86}H_{32}BrCrNO_2$. Calculated, %: Cr 4.17.

Bis(toluene)chromium(I) 2′-[4-methoxy-3-(2-methoxy-2-oxoethoxy)phenyl]-1′-methyl-2′,5′-dihydro-1′*H*-pyrrolo[3′,4′:1,9](C_{60}-I_h)[5,6]fullerenelide (6c). Near-IR spectrum (THF), λ_{max}, nm: 568, 772, 991, 1002. ESR spectrum: g_1 = 1.99982 ($\mathbf{1c}^{\dot{-}}$), g_2 = 1.98667 ($\mathbf{3}^{+\cdot}$). Found, %: Cr 4.22. $C_{87}H_{33}CrNO_4$. Calculated, %: Cr 4.31.

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