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A Scalable Synthesis of Methano[60]fullerene and Congeners by the Oxidative Cyclopropanation Reaction of Silylmethylfullerene

Ying Zhang, Yutaka Matsuo,* Chang-Zhi Li, Hideyuki Tanaka, and Eiichi Nakamura*

Department of Chemistry, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

S *Supporting Information*

ABSTRACT: 1,2-Dihydromethano[60]fullerene and its congeners have attracted much interest, but they have been synthesized only in very low yields because of several insurmountable problems. A new three-stage synthesis involving addition of a silylmethylmagnesium chloride to [60]- and [70]fullerene and oxidation of the anionic intermediate with $CuCl_2$ afforded the methano[60]- and methano[70]fullerenes in 90% and 70% overall yield, respectively. The reaction with 1,4-diorgano[60]fullerene also proceeded smoothly to give a diastereomerically pure 56-π-electron fullerene that has a higher LUMO level than the parent fullerene and gave a higher open-circuit voltage and better power conversion efficiency when fabricated into an organic photovoltaic device.

Because [60]fullerene is widely employed in the development of organic photovoltaic (OPV) devices,[1] the control of its electronic state and morphology by addition of organic addends to the fullerene core has become a very important issue.[2,3] For instance, an increasing number of addends can reduce the π-conjugation length, raise the LUMO level,[4] and hence increase the open-circuit voltage (V_{OC}) of the OPV device, which is beneficial for device performance.[5−7] However, the addends inevitably change the crystal packing, typically reduce the fullerene−fullerene contact distance, and may also reduce the carrier mobility. As the most stable and the smallest 1,2-disubstitution available for fullerene modification, cyclopropanation is ideal for reducing the conjugation length with minimal structural perturbation.[8] Thus, 1,2-dihydromethano[60]fullerene[9] ($C_{61}H_2$, **1**) and its congeners[10] have been synthesized since 1993, typically through 1,3-dipolar cycloaddition of diazomethane[9,10b] or by the use of diiodomethane[10c,d] as the one-carbon source. Because of polyaddition of the methylene group,[10c,d] formation of fulleroid isomers,[9,10b] and incomplete reaction,[10c,d] the product yields are very low without exception, making them unusable for practical applications. We report herein a new three-stage route to the 58-π-electron methanofullerene **1** (Scheme 1), which we carried out on a gram scale in 85% overall yield. The best reported yield of **1** is only 30−40% (70% yield of for $C_{71}H_2$ as opposed a previously reported 4% yield; see Scheme 2).[10] The reaction is also applicable to the regiocontrolled synthesis of 56-π-electron methanofullerenes **11a**, **11b**, and **14** (see Scheme 3). The key step is the regioselective monoaddition of a silylmethyl Grignard reagent to [60]- or 1,4-di(organo)[60]fullerenes under our previously reported conditions[11,12] followed by an oxidative C−C bond-formation reaction in the presence of a base and $CuCl_2$. The installation of a methano group raised the LUMO level of the parent fullerene, caused no significant change in the crystal packing, rigidified the crystal structure, and improved the power conversion efficiency (PCE) of OPV devices.

We synthesized the 58-π-electron methanofullerene **1** via two routes (Scheme 1). We first prepared silylmethylfullerene **2** in 89−93% yield by addition of ^{i}PrOMe$_2$SiCH$_2$MgCl in the presence of *N*,*N*-dimethylformamide (DMF).[12] This was converted to dark-green potassium complex **3** at 25 °C, which was then heated together with $CuCl_2$ (4 equiv) at 100 °C for 12 h to give the purple compound **1** in 79% isolated yield after silica gel chromatography (CS_2 as eluent). Although a precise mechanism has not yet been elucidated, we believe that the reaction involves the cyclization of a γ-silyl cation generated by Cu(II) oxidation of anion **3**. The reaction may have a kinship to a Cu(II)-catalyzed multiple C−C bond formation that may involve a related species.[13] Because the chromatographic behavior of the silylmethyl intermediate **2** was very different from those of both the starting fullerene and the methanofullerene, the methanofullerene was easily obtained in a pure state.

We also synthesized **1** (Scheme 1, bottom) using a higher-yielding, two-step route via fullerene dimer **4**, which was obtained in 100% yield as an inseparable diastereomeric mixture by oxidation of **3** with *N*-chlorosuccinimide (NCS) or I_2.[14] Heating dimer **4** in *o*-dichlorobenzene (ODCB) at 100 °C for 4 h with $CuCl_2$ afforded **1** in quantitative yield. Filtration through silica gel afforded a purple product that showed spectral properties identical with those reported for **1** (mass, *m*/*z* 734.02; ^{1}H NMR, 3.93 ppm).[9]

The latter method was readily amenable to scale-up. Thus, to a mixture of dimethylisopropoxysilylmethyl[60]fullerene dimer **4** (1.00 g, 0.59 mmol) and $CuCl_2$ (316 mg, 2.35 mmol) was added ODCB (0.5 L). After the dark reaction mixture was stirred for 4 h at 100 °C, MeOH (10 mL) was added, and the dark solution was filtered through a silica gel pad eluted with CS_2. The volatiles were removed by rotary evaporation, and the residue was suspended in methanol; after filtration, the methanofullerene was obtained as a brown powder (0.82 g, 95% purity by HPLC analysis).

The synthesis was extended to the cyclopropanation of [70]fullerene (Scheme 2). ^{i}PrOMe$_2$SiCH$_2$MgCl was added to the fullerene in the presence of DMF at 25 °C to obtain a mixture of 1,2-isomer **5** and 5,6-isomer **6** in an approximate ratio of 2.5:1. Treatment of the mixture with ^{t}BuOK and then with $CuCl_2$ at 100 °C for 12 h afforded a 2.5:1 mixture of 1,2-dihydromethano[70]fullerene **7** and 5,6-dihydromethano[70]fullerene **8**[10b] in a combined yield of 93% (70% from [70]fullerene).

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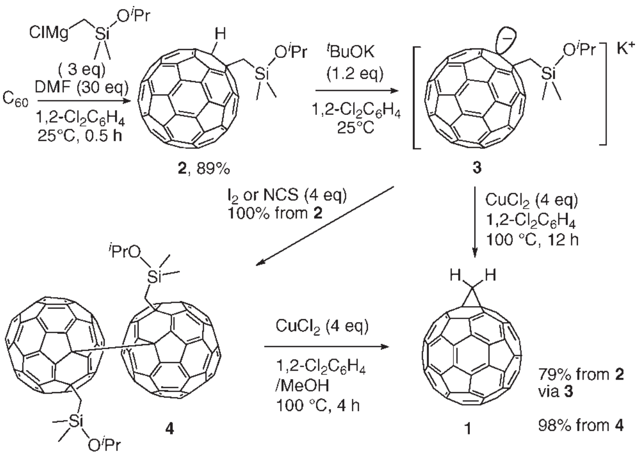
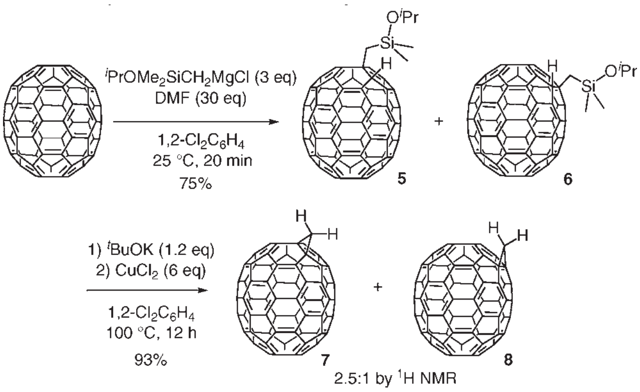
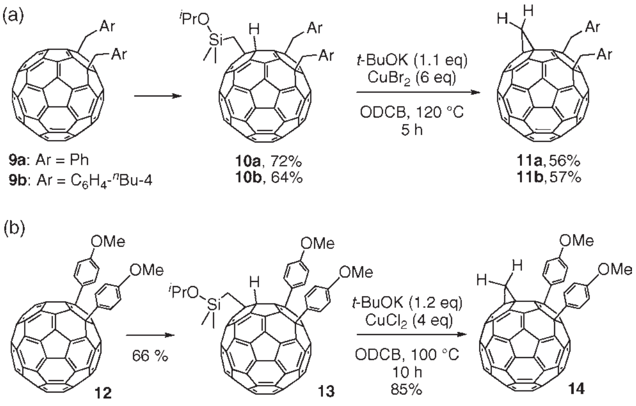
Scheme 1. Synthesis of 1,2-Dihydromethano[60]fullerene (1) from Silylmethylfullerene and Its Dimer



Scheme 2. Synthesis of 1,2- and 5,6-Dihydromethano[70]fullerene



Scheme 3. Synthesis of the 56-π-Electron Methanofullerene Derivatives



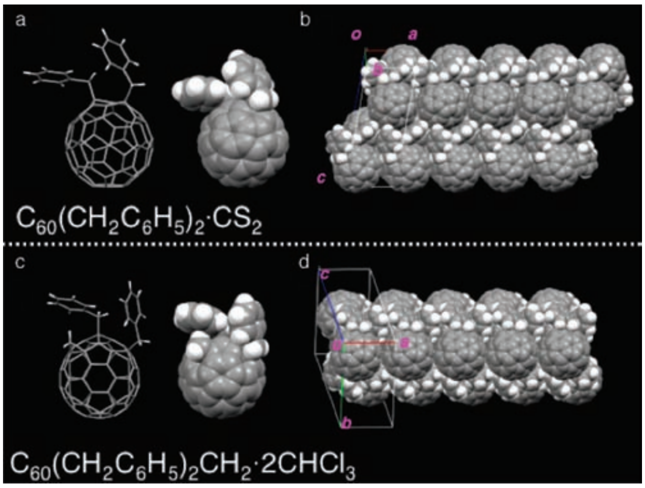


Figure 1. Crystal structures of **9a**·CS_2 and **11a**·$CHCl_3$: (a) side view of **9a**; (b) crystal packing in **9a** along the *a* axis; (c) side view of **11a**; (d) crystal packing in **11a** along the *a* axis. Solvent molecules have been omitted for clarity.

Table 1. Reduction Potentials and LUMO Levels for Fullerene Derivatives[a]

Ar	$E_{1/2}^{\text{red}}$ (V vs Fc/Fc$^+$)			
	E_1	E_2	E_3	LUMO level (eV)[b]
C_{60}	−1.10	−1.49	−1.94	−3.70
1	−1.21	−1.62	−2.13	−3.59
9a	−1.19	−1.60	−2.09	−3.61
11a	−1.33	−1.68	–	−3.47
9b	−1.20	−1.61	−2.10	−3.60
11b	−1.33	−1.68	−2.35	−3.47
12	−1.15	−1.53	−2.01	−3.65
14	−1.29	−1.64	−2.30	−3.51

[a] Potentials in V vs a ferrocene/ferrocenium (Fc/Fc$^+$) couple were measured by cyclic voltammetry in 1,2-$Cl_2C_6H_4$ solution containing $Bu_4N^+PF_6^-$ (0.1 M) as a supporting electrolyte at 25 °C with a scan rate of 0.05 V/s. Glassy carbon, platinum wire, and Ag/Ag$^+$ electrodes were used as the working, counter, and reference electrodes, respectively. [b] Estimated using the following equation:[17] LUMO level = $-(4.8 + E_{1/2}^{\text{red1}})$ eV.

We next demonstrated the regioselective cyclopropanation of 1,4-diorgano[60]fullerenes. Thus, the synthesis of 56-π-electron compound **11** from C_{60} was achieved through a three-step operation on a gram scale using inexpensive reagents (Scheme 3). First, 1,4-bisbenzyl adducts **9a** and **9b** were obtained from fullerene dianion using K/$PhCH_2Br$ (**9a**, 61% yield; **9b**, 52% yield).[15] The regioselectivity of the cyclopropanation was secured by the high regioselectivity of the monoaddition[11,12] of ^{i}PrOMe$_2$SiCH$_2$MgCl to **9a** and **9b**. Finally, the $CuBr_2$ oxidation of the anions of **10** afforded methanofullerenes **11** in ~60% yield. Similarly, methanofullerene **14** was also synthesized in 56% overall yield from 1,4-diarylfullerene adduct **12**.[16]

X-ray crystallographic analyses of single crystals of **9a** containing CS_2 and **11a** containing $CHCl_3$ indicated that the added methano group in the latter indeed did not much affect either the conformation of the benzyl side chains or the crystal packing. Thus, the side orientations in the **9a**·CS_2 and **11a**·2$CHCl_3$ cocrystals illustrated in Figure 1a,c are almost identical to each other. In addition, the crystal parameters of the **9a**·CS_2 and **11a**·2$CHCl_3$ cocrystals (including the minimum fullerene—fullerene center-to-center distances) are similar to each other (see the Supporting Information for details).

Table 2. Comparison of 9b and 11b in p−n and BHJ Photovoltaic Cells

device type	fullerene	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
small-molecule p−n[a]	**9b**[b]	3.2	0.59	0.53	1.0
	11b[b]	4.3	0.77	0.57	1.9
polymer BHJ[c]	**9b**	4.8	0.69	0.49	1.6
	11b	7.1	0.82	0.58	3.4

[a] The general device structure was ITO/PEDOT:PSS/BP/fullerene/NBphen/Al. PCEs were derived from the equation PCE = $(J_{SC} \cdot V_{OC} \cdot \mathrm{FF})/P_0$, where P_0 is the incident light intensity (=100 mW/cm^2). [b] For the n layer, 0.7 wt % **9b** in toluene or 0.7 wt % **11b** in 1:1 CS_2/chlorobenzene was spin-coated onto the BP p layer. [c] The general device structure was ITO/PEDOT:PSS/P3HT:fullerene (1:1)/Ca (20 nm)/Al (130 nm).

A comparison of the thermotropic properties of **9** vs **11** as studied by differential scanning calorimetry measurements showed that the methanofullerene compounds **11a** and **11b** in the solid state exhibit thermal behavior similar to that of **9a** and **9b**, but the phase transition temperatures are shifted consistently by ∼45 °C. We therefore consider that the methanofullerene molecules **11a** and **11b** in crystals are less mobile than **9a** and **9b** (see the Supporting Information for details).

The LUMOs of the 56-π-electron methanofullerene compounds **11a**, **11b**, and **14** (as estimated by cyclic voltammetry measurements) were found to be consistently higher than those of the correponding 58-π-electron 1,4-diorganofullerenes by as much 0.14 V, as opposed to 0.11 V found for the parent compound **1** (Table 1). Methanofullerenes **1**, **11b**, and **14** underwent reversible three-electron reduction, as does pristine C_{60}, while **11a** underwent two-electron reduction.

In agreement with the higher LUMO, the V_{OC} values of OPV devices using a methanofullerene were also found to be higher than that of the device using the parent fullerene (Table 2). First, we examined the performance of a p−n heterojunction, small-molecule OPV device using tetrabenzoporphyrin (BP) as an electron donor and a fullerene as an electron acceptor.[2] A device using **9b** as the acceptor performed with a 1.0% PCE, while the one using methanofullerene **11b** performed much better (1.9%). The short-circuit current density (J_{SC}) increased by 1.1 mA/cm^2 and the V_{OC} value by as much as 0.18 V, while the fill factor (FF) remained essentially the same. We may surmise that the higher LUMO level of **11b** contributes to the improvement of V_{OC}. We also fabricated a polymer fullerene bulk heterojunction (BHJ) OPV device[18] by using poly(3-hexylthiophene) (P3HT) as the donor. The device using **11b** as the acceptor showed a PCE of 3.4% with a V_{OC} of 0.82 V, while the one using **9b** showed a PCE of 1.6% with a V_{OC} of 0.69 V. The V_{OC} of 0.82 V is substantially higher than the value obtained for a BHJ device using phenyl-C_{61}-butyric acid methyl ester (PCBM) (0.58 V).[19]

In summary, we have described a new method for the synthesis of 58-π-electron dihydromethanofullerenes and 56-π-electron congeners that was made possible by the discovery of a new type of oxidative C−C bond formation on the surface of a fullerene core. Unlike the previously reported low-yielding methods, the present method is efficient and scalable and can introduce a methylene group regioselectively even onto an organofullerene because of the high regioselectivity of the first step in the synthesis. We also found that introduction of the methylene group raises the LUMO level and the J_{SC} and V_{OC} values, thereby increasing the PCE, as demonstrated for methanofullerene **11b**. It is very important to note that **11b** is a regioisomerically pure 56-π-electron molecule, as opposed to the popularly used 56-π-electron fullerenes (e.g., bis-PCBM)[6] that are produced as a mixture of structural isomers and cannot form a well-defined packing in the solid state. Obviously, each isomer has a different electronic state, and the density of states of the isomer mixture in the solid state would be broadened. We therefore expect that the methanofullerenes will provide the organoelectronic community with a novel tool for increasing the performance of OPV and related devices.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Synthetic procedures and characterization for methanofullerene derivatives, their electrochemical and thermotropic properties, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

matsuo@chem.s.u-tokyo.ac.jp; nakamura@chem.s.u-tokyo.ac.jp

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