

## Supporting Information

### Stepwise Synthesis of Fullerene Cyclopentadienide $R_5C_{60}^-$ and Indenide $R_3C_{60}^-$ . An Approach to Fully Unsymmetrically Substituted Derivatives

Masaya Sawamura,\* Motoki Togano, Kazuhiro Suzuki, Atsushi Hirai, Hitoshi Iikura, and Eiichi Nakamura\*

*Department of Chemistry, The University of Tokyo, Bunkyo-ku, Tokyo 113-0033*

**Mixture of 1,4-dibenzyl-11,15,30-triphenyl-1,3,4,11,15,30-hexahydro[60]fullerene (2a), 1,4-dibenzyl-11,15,30-triphenyl-1,4,11,13,15,30-hexahydro[60]fullerene (2b) and 1,4-dibenzyl-11,15,30-triphenyl-1,2,4,11,15,30-hexahydro[60]fullerene (2c).** A solution of PhMgBr in THF (0.89M, 0.951 mL, 847  $\mu$ mol, 15 eq) was added to a suspension of CuBr·SMe<sub>2</sub> (176 mg, 847  $\mu$ mol, 15 eq) in 5 mL of degassed THF at 23 °C. To this suspension was added a degassed solution of 1,4-dibenzyl-1,4-dihydro[60]fullerene (**1**) (51.0 mg 56.5 mmol) in 5 mL of 1,2-Cl<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, and the mixture was stirred for 2 h at 23 °C. Resulting brownish-green suspension was quenched with 0.2 mL of degassed sat. aq. NH<sub>4</sub>Cl. The resulting brown suspension was filtered through a pad of silica gel and evaporated. The residue was subjected to HPLC purification (Bucky Prep, Nacalai Tesque Co., 350 nm, toluene/2-propanol = 7/3). Fractions containing **2** were collected and concentrated to a small volume. Precipitated by the addition of MeOH afforded 53.7 mg (86%) of **2** as an orange solid. The <sup>1</sup>H NMR analysis

indicated the ratio of **2a**:**2b**:**2c** is 25:65:10. Analytical sample was obtained by GPC (CHCl<sub>3</sub>) purification: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.71 (d, *J* = 13.0 Hz, 1H, PhCHH, **2b**), 2.89 (d, *J* = 13.2 Hz, 1H, PhCHH, **2a**), 2.96 (d, *J* = 13.0 Hz, 1H, PhCHH, **2b**), 3.10 (d, *J* = 13.2 Hz, 1H, PhCHH, **2a**), 3.23 (d, *J* = 13.2 Hz, 2H, PhcHH, **2c**), 3.40 (d, *J* = 13.2 Hz, 1H, PhCHH, **2b**), 3.48 (d, *J* = 13.2 Hz, 1H+2H, PhCHH, **2a** and **2c**), 3.50 (d, *J* = 13.2 Hz, 1H, PhCHH, **2a**), 3.55 (d, *J* = 13.0 Hz, 1H, PhCHH, **2b**), 4.66 (s, 1H, Cp-H, **2b**), 5.14 (s, 1H, Cp-H, **2a**), 5.24 (s, 1H, Cp-H, **2c**), 7.00-7.68 and 7.83-8.05 (m, 25H+25H+25H, aromatic, **2a**+**2b**+**2c**); Anal. Calcd for (PhCH<sub>2</sub>)<sub>2</sub>Ph<sub>3</sub>HC<sub>60</sub>·(CHCl<sub>3</sub>)<sub>0.9</sub> (C<sub>92.9</sub>H<sub>30.9</sub>Cl<sub>2.7</sub>): C, 89.79; H, 2.78. Found: C, 90.05; H, 3.08.

**K<sup>+</sup>[(PhCH<sub>2</sub>)<sub>2</sub>Ph<sub>3</sub>C<sub>60</sub>]<sup>-</sup> (3).** To a dark red solution of **2** (16.2 mg, 14.6 μmol) in 0.550 mL of degassed THF-*d*<sub>8</sub> in an NMR tube was added 18.0 μL of *t*-BuOK solution (1.0M in THF, 18.0 μmol) under a nitrogen atmosphere. Color of the solution became darken immediately, indicating the formation of cyclopentadienyl anion. Then NMR tube was sealed at liq. N<sub>2</sub> temperature under a reduced pressure and subjected to the NMR measurements: <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 400MHz) δ 3.34 (d, 2H, *J* = 13.1 Hz, PhCHH), 3.66 (d, 2H, *J* = 13.1 Hz, PhCHH), 6.98 (t, *J* = 7.3 Hz, 2H, aromatic), 7.03 (deformed d, *J* ≈ 5.1 Hz, 3H, aromatic), 7.11 (t, *J* = 7.6 Hz, 4H, aromatic), 7.17 (t, *J* = 7.7 Hz, 2H, aromatic), 7.28 (deformed t, 8H, aromatic), 7.84-7.88 (m, 2H, aromatic), 8.25 (deformed d, *J* ≈ 7.7, 4H, aromatic); <sup>13</sup>C NMR (THF-*d*<sub>8</sub>, 100MHz) δ 50.74 (2C), 60.66 (2C), 62.09 (2C), 62.42 (1C), 125.80 (1C), 126.14 (2C), 126.16 (2C), 127.84 (2C), 127.96 (2C), 127.98 (4C), 128.27 (4C), 128.99 (1C), 129.13 (4C), 129.22 (2C), 129.95 (2C), 131.52 (4C), 140.96 (3C), 142.68 (2C), 142.71 (2C), 142.84 (4C), 142.92 (2C), 146.19 (2C),

146.24 (1C), 146.37 (2C), 146.74 (1C), 146.87 (2C), 146.88 (2C), 146.89 (2C), 147.09 (4C), 147.19 (2C), 148.82 (2C), 148.83 (2C), 148.98 (2C), 149.02 (2C), 149.25 (2C), 149.29 (2C), 149.59 (2C), 159.26 (2C), 159.61 (2C), 159.75 (2C), 160.29 (2C), 160.31 (2C).

**Mixture of 1,4-dibenzyl-11-phenyl-1,4,11,12-tetrahydro[60]fullerene**

**(4a) and 1,4-dibenzyl-11-phenyl-1,3,4,11-tetrahydro[60]fullerene (4b).** A solution of 1,4-dibenzyl-1,4,-dihydro[60]fullerene (1.00 g, 1.11 mmol) in 300 mL of 1,2-Cl<sub>2</sub>C<sub>6</sub>H<sub>4</sub> was degassed under a reduced pressure at 22 °C over 20 min. To this solution was added PhMgBr in THF (0.89M, 4.49 mL, 4.00 mmol, 3.6 eq) at 22 °C. The mixture was stirred for 2.5 h at this temperature. After quenching by 1.0 mL of degassed sat. NH<sub>4</sub>Cl aqueous solution, the mixture was filtered through a pad of silica gel and evaporated. The residue was subjected to HPLC purification (Bucky Prep. 350 nm, toluene/2-propanol = 7/3). Fractions containing **4** were collected and concentrated to a small volume. Precipitation by the addition of MeOH afforded 783 mg (72%) of **4** as a brown solid. <sup>1</sup>H NMR analysis indicated the ratio of **4a:4b** is 62: 38. Analytical sample was obtained by GPC (CHCl<sub>3</sub>) purification: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz) δ 3.20 (d, *J* = 13.2 Hz, 1H, PhCHH, **4b**), 3.28 (d, *J* = 13.2 Hz, 1H, PhCHH, **4b**), 3.29 (d, *J* = 13.2 Hz, 1H, PhCHH, **4a**), 3.32 (d, *J* = 13.2 Hz, 1H, PhCHH, **4a**), 3.48 (d, *J* = 13.2 Hz, 1H, PhCHH, **4a**), 3.69 (d, *J* = 13.2 Hz, 1H, PhCHH, **4b**), 3.77 (d, *J* = 13.2 Hz, 1H, PhCHH, **4b**), 3.85 (d, *J* = 13.2 Hz, 1H, PhCHH, **4a**), 5.22 (s, 1H, indenyl-H, **4b**), 5.65 (s, 1H, indenyl-H, **4a**), 7.13-7.64 (m, 13H+13H, aromatic, **4a+4b**), 8.04-8.08 (m, 2H, aromatic, **4a**), 8.11-8.14 (m, 2H, aromatic, **4b**); APCI-MS m/z 981

(M<sup>+</sup>); FAB-MS m/z 982 (MH<sup>+</sup>); Anal. Calcd for C<sub>80</sub>H<sub>20</sub>, C 97.95; H, 2.05. Found: C 97.66; H, 2.34.

**K<sup>+</sup>[(PhCH<sub>2</sub>)<sub>2</sub>PhC<sub>60</sub>]<sup>-</sup> (5).** To a solution of **4** (5.2 mg, 5.3 μmol) in 0.55 mL of degassed THF-*d*<sub>8</sub> in an NMR tube was added 7.0 μL of *t*-BuOK solution (1.0M in THF, 7.0 μmol) under an argon atmosphere. A color of the solution changed immediately from dark brown to dark green, indicating the formation of indenyl anion: <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 400 MHz) δ 3.73 (d, *J* = 12.6 Hz, 1H, PhCHH), 4.10 (d, *J* = 12.6 Hz, 1H, PhCHH), 7.05-7.32 (m, 7H, aromatic), 7.41-7.50 (m, 4H, aromatic), 7.52-7.56 (m, 2H, aromatic), 8.29-8.34 (m, 2H, aromatic). Signals for two methylene protons were overlapped with that of THF.