

Supporting Information

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

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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 μ mol, 15 eq) was added to a suspension of CuBr·SMe₂ (176 mg, 847 μ 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 μ mol) in 5 mL of 1,2-Cl₂C₆H₄, 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. NH₄Cl. 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 ¹H NMR analysis

indicated the ratio of **2a:2b:2c** is 25:65:10. Analytical sample was obtained by GPC (CHCl₃) purification: ¹H NMR (400 MHz, CDCl₃) 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 (PhCH₂)₂Ph₃HC₆₀·(CHCl₃)_{0.9} (C_{92.9}H_{30.9}Cl_{2.7}): C, 89.79; H, 2.78. Found: C, 90.05; H, 3.08.

K⁺[(PhCH₂)₂Ph₃C₆₀]⁻ (3). To a dark red solution of **2** (16.2 mg, 14.6 μmol) in 0.550 mL of degassed THF-*d*₈ 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. N₂ temperature under a reduced pressure and subjected to the NMR measurements: ¹H NMR (THF-*d*₈, 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); ¹³C NMR (THF-*d*₈, 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-Cl₂C₆H₄ 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. NH₄Cl 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. ¹H NMR analysis indicated the ratio of **4a**:**4b** is 62: 38. Analytical sample was obtained by GPC (CHCl₃) purification: ¹H NMR (CDCl₃, 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⁺); FAB-MS m/z 982 (MH⁺); Anal. Calcd for C₈₀H₂₀, C 97.95; H, 2.05. Found: C 97.66; H, 2.34.

K⁺[(PhCH₂)₂PhC₆₀]⁻ (5). To a solution of **4** (5.2 mg, 5.3 μmol) in 0.55 mL of degassed THF-*d*₈ 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: ¹H NMR (THF-*d*₈, 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.