Supporting Information

Synthesis of Ferrocene/hydrofullerene Hybrid and Functionalized Bucky Ferrocenes

Motoki Toganoh, Yutaka Matsuo and Eiichi Nakamura*
Department of Chemistry, The University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan
e-mail: nakamura@chem.s.u-tokyo.ac.jp

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1. Experimental Section

General. All reactions were carried out in an oven-dried reaction vessel under argon or nitrogen and were analyzed by HPLC (column: Buckyprep, 4.6 x 250 mm, Nacalai tesque; flow rate: 1.0 mL/min; eluent: toluene/2-propanol = 7/3; detector: SPD-M10Avp, Shimadzu). The isolated yields were calculated on the basis of the starting fullerene compounds. All ^{1}H NMR spectra were measured at 400 MHz (JEOL EX-400), and ^{13}C NMR spectra at 100 MHz. Spectra are reported in part per million from internal tetramethylsilane (δ 0.00 ppm) for ^{1}H NMR and from solvent carbon (e.g. δ 77.00 ppm for chloroform) for ^{13}C NMR. IR spectra were recorded on Applied Systems Inc., REACT IR 1000 as powder on a diamond probe, or on a JASCO IR-420 instrument as a KBr disk; absorptions are reported in cm^{-1}. Mass spectra were measured with Waters ZQ2000 (APCI mode) equipped with a Buckyprep column. High resolution mass spectra were recorded on JEOL JMS-T100LC instrument. Preparative HPLC was performed on a Buckyprep column (20 x 250 mm) using toluene/2-propanol = 7/3, 6/4 or 5/5 as eluent (flow rate 20 mL/min, detected at 350 nm with an UV spectrophotometric detector, Shimadzu SPD-6A).

Solvents and Materials. All commercially available reagents were distilled or recrystallized before use unless otherwise noted. PhCN was distilled under reduced pressure from P_2O_5 and stored under nitrogen. The use of molecular sieves should be avoided, since the reaction became irreproducible. The water content of the solvent was determined with a Karl-Fischer Moisture Titrator (MK-210, Kyoto Electronics Company) to be less than 30 ppm. $[Fe(C_5H_5)(CO)_2]_2$ and TBAOH (1M in MeOH) were purchased from Acros Organics and used as received.

Synthesis of (η^5-cyclopentadienyl)[(1,2,3,4,5-η)-9,12,15,18-tetrahydro(C_{60}-I_h)[5,6]fulleren-1(*6H*)-yl]iron(II) <$Fe(C_{60}H_5)(C_5H_5)$ (1)>.

C_{60} (19.9 mg, 27.6 μmol, 1.00 equiv) and $[Fe(C_5H_5)(CO)_2]_2$ (51.7 mg, 146 μmol, 5.29 equiv) in PhCN (2.00 mL) was degassed under reduced pressure (~0.3 mmHg) over 30 min at 0 °C and the resulting mixture was stirred at 160 °C for 22 h. The reaction mixture was diluted with 8 mL of toluene/2-propanol = 7/3, filtered with a pad of Celite and subjected to preparative HPLC separation. A collected fraction was concentrated to dryness and dried under reduced pressure to give $Fe(C_{60}H_5)(C_5H_5)$ (**1**) as a brown solid (5.9 mg, 25% yield). ^{1}H NMR (CS_2, 400 MHz) δ 4.94 (s, 5H, C_5H_5), 5.42 (s, 5H, $C_{60}H_5$); ^{13}C NMR (CS_2, 100 MHz) δ 45.39 (d, $^1J_{CH}$ = 143 Hz, 5C), 71.11 (5C), 85.32 (5C), 143.91 (10C), 145.68 (10C), 147.13 (5C), 148.48 (10C), 148.50 (5C), 151.85 (10C); HRMS (APCI+) calcd for $C_{65}H_{11}{}^{56}Fe$ ($M+H^+$): 847.0210, found: 847.0206.

Synthesis of [(1,2,3,4,5-η)-6,9-dibenzyl-9,12,15,18-tetrahydro(C_{60}-I_h)[5,6]fulleren-1(*6H*)-yl](η^5-cyclopentadienyl)iron(II) <$Fe[C_{60}(PhCH_2)_2H_3](C_5H_5)$ (5)>.

$C_{60}(PhCH_2)_2$ (**3**, 100 mg, 111 μmol, 1.00 equiv) and $[Fe(C_5H_5)(CO)_2]_2$ (378 mg, 1.07 mmol, 9.64 equiv) in PhCN (20.0 mL) was degassed under reduced pressure (~0.3 mmHg) at 0 °C for 40 min and the resulting mixture was heated at 160 °C for 90 h. The reaction mixture was concentrated to dryness under reduced pressure and the residue was subjected to preparative HPLC separation. Collected fractions were concentrated to dryness and dried under reduced pressure to give **5** as an orange solid (50.3 mg, 44% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.34 (d, *J* = 13.0 Hz, 2H, PhCH*H*), 4.39 (d, *J* = 13.0 Hz, 2H, PhCH*H*), 5.11 (s, 5H, C_5H_5), 5.48 (d, *J* = 2.4 Hz, 1H, $C_{60}H$), 5.52 (d, *J* = 2.4 Hz, 2H, $C_{60}H$), 7.46-7.62 (m, 10H, Ph); ^{13}C NMR (CS_2, 100 MHz) δ 45.08 (2C), 45.39 (1C), 51.03 (2C), 56.02 (2C), 70.56 (5C), 83.39 (1C), 85.19 (2C), 93.48 (2C), 127.44 (2C), 128.61 (4C), 130.62 (4C), 136.92 (2C), 142.81 (2C), 143.08 (2C), 143.63 (2C), 143.82 (2C), 143.97 (2C), 144.70 (2C), 145.08 (2C), 145.59 (2C), 145.71 (2C), 145.72 (2C), 147.00 (2C), 147.04 (2C), 147.08 (1C), 148.11 (2C), 148.19 (2C), 148.23 (2C), 148.27 (2C), 148.29 (2C), 148.40 (2C+1C), 148.46 (2C), 150.64 (2C), 151.38 (2C), 151.79 (2C), 153.35 (2C), 153.37 (2C); HRMS (APCI+) calcd for $C_{79}H_{22}{}^{56}Fe$ (M^+): 1026.1071, found: 1026.1110.

Synthesis of [(1,2,3,4,5-η)-6,9-dibenzyl-12-phenyl-9,12,15,18-tetrahydro(C_{60}-I_h)[5,6]fulleren-1(*6H*)-yl](η^5-cyclopentadienyl)iron(II) <Fe[$C_{60}(PhCH_2)_2PhH_2$](C_5H_5) (6)>.

$C_{60}(PhCH_2)_2PhH$ (**4**, 101 mg, 103 μmol, 1.00 equiv) and $[Fe(C_5H_5)(CO)_2]_2$ (37.0 mg, 104 μmol, 1.01 equiv) in PhCN(20.0 mL) was degassed under reduced pressure (~0.3 mmHg) at 0 °C for 30 min and the resulting mixture was stirred at 160°C for 14 h. The reaction mixture was concentrated to dryness under reduced pressure. Purification of the product was performed by preparative HPLC. Collected fractions were concentrated to a small volume and precipitated with methanol. Precipitates were collected by filtration, washed with methanol and dried under reduced pressure to give 5 as an orange solid (93.5 mg, 82% yield). IR (KBr disk) 3085 (w), 3060 (w), 3027 (w), 2959 (w), 2918 (m), 2850 (w), 1494 (s), 1454 (s), 1418 (m), 1384 (m), 1286 (w), 1261 (s), 1236 (w), 1198 (w), 1177 (w), 1156 (w), 1106 (s), 1030 (m), 908 (w), 822 (m), 804 (m), 767 (w), 744 (w), 723 (w), 698 (s), 674 (w), 551 (m), 508 (m); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.06 (s, 2H, PhCH_2), 4.07 (d, J = 13.2 Hz, 1H, PhCH*H*), 4.20 (d, J = 13.2 Hz, 1H, PhCH*H*), 4.33 (s, 5H, C_5H_5), 5.26 (d, J = 2.8 Hz, 1H, C_{60}H), 5.42 (d, J = 2.8 Hz, 1H, C_{60}H), 7.26-7.39 (m, 8H, Ph), 7.48-7.54 (m, 3H, Ph), 7.70 (t, J = 7.8 HZ, 2H, Ph), 8.16 (dd, J = 0.8, 8.0 Hz, 2H, Ph); ^{13}C NMR (CS_2, 100 MHz) δ 45.09 (d, $^1J_{CH}$ = 142 Hz, 1C), 45.39 (d, $^1J_{CH}$ = 142 Hz, 1C), 50.16 (t, $^1J_{CH}$ = 131 Hz, 1C), 51.09 (t, $^1J_{CH}$ = 131 Hz, 1C), 55.98 (1C), 56.02 (1C), 58.58 (1C), 70.57 (5C), 83.67 (1C), 84.03 (1C), 92.11 (1C), 93.75 (1C), 94.33 (1C), 127.40 (1C), 127.51 (1C), 127.80 (1C), 127.90 (2C), 128.57 (2C), 128.68 (2C), 129.21 (2C), 130.56 (2C), 130.59 (2C), 136.81 (1C), 136.97 (1C), 142.76 (1C), 142.84 (1C), 142.94 (1C), 143.08 (1C), 143.34 (1C), 143.55 (1C), 143.65 (1C), 143.66 (1C), 143.70 (1C), 143.88 (1C), 143.89 (1C), 144.18 (1C), 144.59 (1C), 144.69 (1C), 144.90 (1C), 144.94 (1C), 145.06 (1C), 145.58 (1C+1C), 145.80 (1C), 145.82 (1C), 146.97 (1C), 147.05 (1C+1C), 147.13 (1C), 147.26 (1C), 148.08 (1C), 148.11 (1C+1C), 148.12 (1C), 148.16 (1C), 148.22 (1C+1C+1C), 148.23 (1C), 148.28 (1C), 148.39 (1C), 148.42 (1C), 148.45 (1C), 148.46 (1C), 148.50 (1C), 150.62 (1C), 150.84 (1C), 151.27 (1C), 151.56 (1C), 151.93 (1C), 152.95 (1C), 153.11 (1C), 153.43 (1C), 153.83 (1C), 153.87 (1C); Anal. Calcd for **6**: C, 92.56; H, 2.38. Found: C, 92.44; H. 2.63; HRMS (APCI+) calcd for $C_{85}H_{26}{}^{56}Fe$ (M^+): 1102.1384, found: 1102.1396.

Synthesis of [(1,2,3,4,5-η)-6,9-dibenzyl-12-phenyl-(9,12,15,18-tetrahydro(C_{60}-I_h)[5,6]fulleren-1(*6H*)-yl][η^5-(1,3-bis(trimethlysilyl))cyclopentadienyl]iron(II) <Fe[$C_{60}(PhCH_2)_2PhH_2$][(1,3-$Me_3Si)_2C_5H_3$] (7)>.

A mixture of $C_{60}(PhCH_2)_2PhH$ (**4**, 19.7 mg, 20.1 mmol, 1.00 equiv) and $[Fe(C_5(1,3\text{-}Me_3Si)_2H_3)(CO)_2]_2$ (13.2 mg, 20.5 mmol, 1.02 equiv) in PhCN (4.0 mL) was degassed under reduced pressure (~0.3 mmHg) at 0 °C for 30 min and the resulting mixture was stirred at 160 °C for 24 h. The resulting reaction mixture was diluted with toluene/2-propanol=1/1

and filtered through a pad of Celite. The filtrate was subjected into preparative HPLC separation. The collected fractions were concentrated to dryness and dried under reduced pressure to give $Fe[C_{60}(PhCH_2)_2PhH_2][(1,3\text{-}Me_3Si)_2C_5H_3]$ (**7**) as a red solid (13.2 mg, 53% yield). ^{1}H NMR (CS_2, 400 MHz) δ 0.58 (s, 9H, Me_3Si), 0.83 (s, 9H, Me_3Si), 3.53 (s, 1H, Cp*H*), 4.20 (d, *J* = 13.2 Hz, 1H, PhCH*H*), 4.36 (d, *J* = 13.2 Hz, 1H, PhCH*H*), 4.40 (d, *J* = 13.2 Hz, 1H, PhCH*H*), 4.47 (d, *J* = 13.2 Hz, 1H, PhCH*H*), 4.63 (s, 1H+1H, Cp*H*), 5.52 (d, *J* = 2.6 Hz, 1H, C_{60}H), 5.65 (d, *J* = 2.6 Hz, 1H, C_{60}H), 7.44-7.81 (m, 10H, Ph), 7.81 (t, *J* = 7.5 Hz, 1H, Ph), 7.96 (t, *J* = 7.5 Hz, 2H, Ph), 8.40 (d, *J* = 7.5 Hz, 2H, Ph); ^{13}C NMR (CS_2, 100 MHz) δ 0.87 (3C), 1.38 (3C), 45.39 (1C), 45.76 (1C), 51.63 (1C), 51.70 (1C), 55.34 (1C), 55.70 (1C), 58.62 (1C), 77.54 (1C), 77.60 (1C), 77.97 (1C), 78.67 (1C), 80.66 (1C), 82.43 (1C), 83.08 (1C), 93.11 (1C), 94.02 (1C), 5.77 (1C), 127.43 (1C), 127.63 (1C), 127.83 (1C), 128.14 (2C), 128.64 (2C), 128.80 (2C), 129.27 (2C), 130.55 (2C), 130.65 (2C), 136.68 (1C), 136.80 (1C), 142.87 (1C), 142.93 (1C), 143.07 (1C), 143.08 (1C), 143.38 (1C), 143.56 (1C), 143.61 (1C), 143.72 (1C), 143.83 (1C), 143.96 (1C), 144.02 (1C), 144.20 (1C), 144.58 (1C), 144.66 (1C), 144.78 (1C), 145.04 (1C), 145.08 (1C), 145.46 (1C), 145.72 (1C), 145.73 (1C), 147.02 (1C), 147.07 (1C), 147.11 (1C), 147.18 (1C), 147.22 (1C), 147.28 (1C), 148.16 (1C), 148.18 (1C), 148.21 (1C), 148.22 (1C), 148.24 (1C), 148.28 (1C), 148.30 (1C), 148.32 (1C), 148.37 (1C), 148.43 (1C), 148.45 (1C), 148.47 (1C), 148.52 (1C), 158.56 (1C), 148.58 (1C), 150.10 (1C), 150.48 (1C), 150.97 (1C), 151.21 (1C), 151.43 (1C), 152.59 (1C), 152.79 (1C), 153.33 (1C), 153.62 (1C), 153.88 (1C); HRMS (APCI+) calcd for $C_{91}H_{42}{}^{56}Fe^{28}Si_2$ (M^+): 1246.2174, found: 1246.2141.

Deprotonation of 6.

To a solution of **6** (2.1 mg, 1.9 μmol) in PhCN-d_5 (0.60 mL) in an NMR tube was added a solution of tetrabutylammonium hydroxide in MeOH (1.0 M, 6.0 μl, 3.2 equiv) at 21 °C under nitrogen. The color of the solution changed from orange to dark brown within a few seconds. This sample was directly used for NMR analysis. ^{1}H NMR (PhCN-d_5, 400 MHz)δ 4.40 (d, *J* = 13.0 Hz, 1H, PhCH*H*), 4.53 (d, *J* = 13.0 Hz, 1H, PhCH*H*), 4.74 (d, *J* = 13.0 Hz, 1H, PhCH*H*), 4.75 (d, *J* = 13.0 Hz, 1H, PhCH*H*), 5.26 (s, 5H, Cp), 7.91 (d, *J* = 7.4 Hz, 2H, Ph), 8.09 (d, *J* = 7.8 Hz, 2H, Ph), 8.72 (d, *J* = 7.8 Hz, 2H, Ph) [Signals of the other aromatic protons overlapped with those of the solvent.].

cf. The ^{1}H NMR spectrum of **4** in PhCN-d_5: ^{1}H NMR (PhCN-d_5, 400MHz) δ 4.29 (d, *J* = 13.2 Hz, 1H, PhCH*H*), 4.33 (d, *J* = 13.4 Hz, 1H, PhCH*H*), 4.37 (d, *J* = 13.4 Hz, 1H, PhCH*H*), 4.39 (d, *J* = 13.2 Hz, 1H, PhCH*H*), 4.58 (s, 5H, Cp), 5.48 (d, *J* = 2.6 Hz, 1H, C_{60}H), 5.55 (d, *J* = 2.6 Hz, 1H, C_{60}H), 7.79 (d, *J* = 7.2 Hz, 2H, Ph), 7.88 (t, *J* = 7.8 Hz, 2H, Ph), 8.32 (dd, *J* = 0.8, 8.2 Hz, 2H, Ph) [Signals of the other aromatic protons overlapped with those of the solvent.].

Typical procedures of alkylation of 6.

A solution of tetrabutylammonium hydroxide (1.0 M in MeOH, 3.1 equiv) was added to a solution of $Fe[C_{60}(PhCH_2)_2PhH_2](C_5H_5)$ (**6**, 1.0 equiv) at room temperature (21~26 °C). A color of the resulting solution changed from orange to dark red at a moment. After 5 min, the mixture was treated with alkyl halide (RX, 5 to 40 equiv, depending on RX), resulting change of color from dark red to brown. HPLC analysis indicated the full consumption of the starting material within 10 minutes. Then the mixture was diluted with 8 mL of toluene/2-propanol = 1/1, filtered with a pad of alumina and subjected to preparative HPLC separation. A collected fraction was concentrated to dryness and dried under reduced pressure to give a di-alkylated product $Fe[(C_{60}(PhCH_2)_2PhR_2](C_5H_5)$.

Synthesis of [(1,2,3,4,5-η)-6,9-dibenzy-12,15-dimethyl-18-phenyl-9,12,15,18-tetrahydro(C_{60}-I_h)[5,6]fulleren-1(*6H*)-yl](η^5-cyclopentadienyl)iron(II) <$Fe[C_{60}(PhCH_2)_2Me_2Ph](C_5H_5)$ (8)>.

The procedures (RX = MeI) described above was performed to obtain **8**. Yield: 81%; ^{1}H NMR (CS_2, 400 MHz) δ 1.86 (s, 3H, Me), 1.97 (s, 3H, Me), 3.26 (d, *J* = 12.8 Hz, 1H, PhCH*H*), 3.32 (d, *J* = 13.2 Hz, 1H, PhCH*H*), 3.33 (d, *J* = 12.8 Hz, 1H, PhCH*H*), 3.59 (1H, PhCH*H*) [This signal overlaps with the signal due to the Cp moiety.], 3.62 (s, 5H, Cp), 6.44-6.59 (m, 8H, Ph), 6.70 (d, *J* = 7.0 Hz, 2H, Ph), 6.78 (t, *J* = 7.4 Hz, 1H, Ph), 6.96 (t, *J* = 7.6 Hz, 2H, Ph), 7.46 (d, *J* = 7.3 Hz, 2H, Ph); ^{13}C NMR (CS_2, 100 MHz) δ 29.27 (1C), 29.82 (1C), 49.93 (1C), 50.38 (1C), 50.44 (1C), 51.08 (1C), 55.65 (1C), 55.78 (1C), 58.58 (1C), 69.50 (5C), 91.15 (1C), 91.21 (1C), 92.11 (1C), 92.17 (1C), 93.22 (1C), 127.18 (1C), 127.32 (1C), 127.59 (1C), 128.23 (2C), 128.35 (2C), 128.48 (2C), 128.94 (2C), 130.36 (2C), 130.40 (2C), 136.51 (1C), 136.60 (1C), 142.55 (1C), 142.56 (1C), 142.62 (1C), 142.64 (1C), 143.09 (1C), 143.10 (1C), 143.26 (1C), 143.31 (1C), 143.37 (1C), 143.38 (1C), 143.60 (1C), 143.76 (1C+1C), 143.81 (1C+1C), 144.07 (1C), 144.16 (1C), 144.43 (1C), 144.75 (1C), 144.83 (1C), 144.99 (1C), 146.75 (1C), 146.837 (1C), 146.842 (1C), 146.98 (1C), 147.03 (1C), 147.70 (1C), 147.74 (1C), 147.76 (1C), 147.77 (1C), 147.79 (1C), 147.82 (1C), 147.90 (1C+1C), 147.95 (1C), 148.00 (1C), 148.10 (1C), 148.16 (1C), 148.24 (1C), 148.25 (1C), 148.29 (1C), 151.88 (1C), 152.04 (1C), 152.11 (1C), 152.35 (1C), 152.41 (1C), 152.94 (1C), 153.87 (1C), 154.63 (1C), 154.80 (1C), 155.02 (1C); HRMS (APCI+) calcd for $C_{87}H_{30}{}^{56}Fe$ (M^+): 1130.1697, found: 1130.1708.

Synthesis of [(1,2,3,4,5-η)-6,9-diallyl-12,15-dibenzyl-18-phenyl-9,12,15,18-tetrahydro(C_{60}-I_h)[5,6]fulleren-1(*6H*)-yl](η^5-cyclopentadienyl)iron(II) <$Fe[C_{60}(allyl)_2(PhCH_2)_2Ph](C_5H_5)$ (9)>.

The procedures (RX = allyl bromide) described above was performed to obtain **9**. Yield: 77%; ^{1}H NMR (CS_2, 400 MHz) δ 2.80 (d, *J* = 7.0 Hz, 2H, H_2C=CH-CH_2), 2.81 (dd, *J* =

6.5, 13.8 Hz, 1H, H_2C=CH-CH*H*), 3.03 (dd, *J* = 7.7, 13.8 Hz, 1H, H_2C=CH-CH*H*), 3.27 (d, *J* = 13.0 Hz, 1H, PhCH*H*), 3.32 (d, *J* = 13.0 Hz, 1H, PhCH*H*), 3.33 (d, *J* = 13.2 Hz, 1H, PhCH*H*), 3.602 (s, 2H, CpH), 3.603 (s, 2H, CpH), 3.604 (s, 1H, CpH), 3.61 (d, *J* = 13.2 Hz, 1H, PhCH*H*), 4.62 (d, *J* = 10.0 Hz, 2H, H*H*C=CH-CH_2), 4.68 (d, *J* = 17.0 Hz, 1H, H*H*C=CH-CH_2), 4.72 (d, *J* = 16.8 Hz, 1H, H *H*C=CH-CH_2), 5.62-5.74 (m, 2H, H_2C=C*H*-CH_2), 6.42-6.58 (m, 8H, Ph), 6.69 (d, *J* = 7.0 Hz, 2H, Ph), 6.78 (t, *J* = 7.4 Hz, 1H, Ph), 6.97 (t, *J* = 7.8 Hz, 2H, Ph), 7.44 (d, *J* = 7.8 Hz, 2H, Ph); ^{13}C NMR (CS_2, 100 MHz) δ 47.36 (1C), 48.04 (1C), 49.96 (1C), 50.98 (1C), 54.48 (1C), 54.60 (1C), 55.65 (1C), 55.72 (1C), 58.51 (1C), 69.78 (5C), 90.88 (1C), 91.28 (1C), 91.38 (1C), 92.37 (1C), 93.20 (1C), 119.32 (1C), 119.37 (1C), 127.21 (1C), 127.34 (1C), 127.65 (1C), 128.20 (2C), 128.33 (2C), 128.47 (2C), 128.94 (2C), 130.37 (2C), 130.40 (2C), 134.24 (1C), 134.52 (1C), 136.45 (1C), 136.53 (1C), 142.54 (1C), 142.58 (1C), 142.63 (1C), 142.65 (1C), 142.92 (1C+1C), 143.00 (1C+1C), 143.11 (1C), 143.12 (1C), 143.56 (1C), 143.58 (1C), 143.80 (1C), 144.36 (1C+1C), 144.49 (1C), 144.58 (1C), 144.68 (1C), 144.71 (1C), 144.73 (1C), 144.97 (1C), 146.75 (1C), 146.85 (1C), 146. 90 (1C), 146.98 (1C), 147.03 (1C), 147.70 (1C), 147.75 (1C), 147.78 (1C+1C+1C), 147.86 (1C+1C+1C), 147.88 (1C), 147.92 (1C), 148.12 (1C), 148.17 (1C), 148.25 (1C+1C), 148.30 (1C), 151.85 (1C), 152.06 (1C), 152.22 (1C), 152.24 (1C), 152.30 (1C), 152.55 (1C), 152.70 (1C+1C), 152.87 (1C), 153.08 (1C); HRMS (APCI+) calcd for $C_{91}H_{35}{}^{56}Fe$ ($M+H^+$): 1183.2088, found: 1183.2046.

Synthesis of [(1,2,3,4,5-*η*)-6,9,12,15-tetrabenzyl-18-phenyl-9,12,15,18-tetrahydro(C_{60}-*I*$_h$)[5,6]fulleren-1(*6H*)-yl](*η*^{5}-cyclopentadienyl)iron(II) <Fe[C_{60}($PhCH_2$)$_4$Ph](C_5H_5) (10)>.

The procedures (RX = $PhCH_2Br$) described above was performed to obtain **10**. Yield; 60%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.18 (d, *J* = 13.2 Hz, 2H, PhCH*H*), 4.20 (d, *J* = 13.2 Hz, 2H, PhCH*H*), 4.24 (d, *J* = 13.2 Hz, 2H, PhCH*H*), 4.49 (d, *J* = 13.2 Hz, 2H, PhCH*H*), 4.54 (s, 5H, C_5H_5), 7.28-7.47 (m, 16H, Ph), 7.52-7.62 (m, 5H, Ph), 7.80 (t, *J* = 7.8 Hz, 2H, Ph), 8.43 (d, *J* = 7.2 Hz, 2H, Ph); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 49.61 (2C), 50.82 (2C), 55.54 (2C), 55.61 (2C), 58.59 (1C), 69.42 (5C), 91.25 (2C), 92.21 (2C), 93.05 (1C), 126.97 (2C), 127.05 (2C), 127.49, 128.04 (2C), 128.15 (4C), 128.21 (4C), 128.81 (2C), 130.13 (4C), 130.17 (4C), 136.51 (2C), 136.58 (2C), 142.19 (2C), 142.22 (2C), 142.24 (2C), 142.25 (2C), 142.69 (2C), 143.37 (2C), 143.87 (1C), 144.19 (2C), 144.40 (2C), 144.52 (2C), 144.83 (2C), 146.56 (2C), 146.58 (1C), 146.75 (2C), 147.425 (2C), 147.434 (2C), 147.44 (2C), 147.49 (2C+2C), 147.79 (1C), 147.87 (2C), 147.99 (2C), 151.60 (2C), 152.02 (2C), 152.24 (2C), 152.38 (2C), 152.80 (2C); HRMS (APCI+) calcd for $C_{99}H_{38}{}^{56}Fe$ (M^+): 1282.2323, found: 1282.2280.

Synthesis of [(1,2,3,4,5-*η*)-6,9-dibenzy-12,15-bis((3-etoxycarbonyl)propyl)-18-phenyl-

9,12,15,18-tetrahydro(C_{60}-I_h)[5,6]fulleren-1(*6H*)-yl](η^5-cyclopentadienyl)iron(II) <Fe[C_{60}($PhCH_2$)$_2$($EtOOCCH_2CH_2CH_2$)$_2$Ph](C_5H_5) (11)>.

The procedures (RX = $EtOOCCH_2CH_2CH_2Br$) described above was performed to obtain **11**. Yield: 64%. When the same reaction using **6** (1.0 mg, 0.91 μmol), TBAOH (3.1 eq, 3.1 μL, 1M solution of MeOH), and $EtOOCCH_2CH_2CH_2I$ (5.0 eq, 1.1 mg, 4.5 μmol) was performed, product **11** was obtained in 79% yield (0.95 mg, 0.71 μmol). ^{1}H NMR (CS_2, 400 MHz) δ 0.60 (t, *J* = 7.2 Hz, 3H, C*H*$_3$CH$_2$OCO), 0.64 (t, *J* = 7.0 Hz, 3H, C*H*$_3$CH$_2$OCO), 1.55-1.76 (m, 4H, CH_2), 1.79-2.17 (m, 7H, CH_2), 2.45 (dt, *J* = 4.8, 12.8 Hz, 1H, CH*H*), 3.29 (s, 2H, PhC*H*$_2$), 3.32 (d, *J* = 13.0 Hz, 1H, PhCH*H*), 3.44 (q, *J* = 7.2 Hz, 2H, CH$_3$C*H*$_2$OCO), 3.51 (q, *J* = 7.2 Hz, 2H, CH$_3$C*H*$_2$OCO), 3.55 (s, 5H, Cp), 3.59 (d, *J* = 13.0 Hz, 1H, PhCH*H*), 6.43-6.59 (m, 8H, Ph), 6.70 (d, *J* = 7.0 Hz, 2H, Ph), 6.76 (t, *J* = 7.5 Hz, 1H, Ph), 6.97 (t, *J* = 7.8 Hz, 2H, Ph), 7.44 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (CS_2, 100 MHz) δ 15.10 (1C), 15.13 (1C), 23.88 (1C), 24.24 (1C), 34.17 (1C), 34.34 (1C), 41.97 (1C), 42.61 (1C), 49.88 (1C), 50.85 (1C), 54.43 (1C), 54.51 (1C), 55.76 (1C), 55.77 (1C), 58.63 (1C), 60.44 (1C), 60.46 (1C), 69.82 (5C), 91.18 (1C), 91.60 (1C), 91.76 (1C), 9207 (1C), 93.02 (1C), 127.11 (1C), 127.30 (1C), 127.49 (1C), 128.28 (2C), 128.41 (2C), 128.46 (2C), 129.08 (2C), 130.43 (2C), 130.47 (2C), 136.60 (1C), 136.66 (1C), 142.55 (1C), 142.57 (1C), 142.61 (1C), 142.65 (1C), 143.00 (1C), 143.01 (1C), 143.05 (1C), 143.09 (1C), 143.12 (1C), 143.13 (1C), 143.66 (1C), 143.69 (1C), 143.73 (1C), 144.33 (1C), 144.46 (1C), 144.61 (1C), 144.63 (1C), 144.72 (1C), 144.75 (1C), 144.84 (1C), 145.04 (1C), 146.78 (1C), 146.87 (1C), 146.91 (1C), 147.02 (1C), 147.06 (1C), 147.72 (1C), 147.77 (1C), 147.79 (1C), 147.80 (1C), 147.81 (1C), 147.87 (1C), 147.88 (1C+1C), 147.90 (1C), 147.92 (1C), 148.14 (1C), 148.16 (1C), 148.23 (1C), 148.28 (1C), 148.32 (1C), 152.17 (1C), 152.22 (1C), 152.28 (1C), 152.38 (1C), 152.43 (1C), 152.78 (1C), 152.98 (1C), 153.05 (1C), 153.29 (1C), 153.38 (1C), 171.60 (1C), 171.80 (1C); HRMS (APCI+) calcd for $C_{97}H_{46}{}^{56}Fe^{16}O_4$ (M^+): 1330.2746, found: 1330.2697.

Synthesis of [(1,2,3,4,5-η)-6,9-dibenzy12-phenyl-15,18-bis(4-phthalimidobutyl)-9,12,15,18-tetrahydro(C_{60}-I_h)[5,6]fulleren-1(*6H*)-yl](η^5-cyclopentadienyl)iron(II) <Fe[C_{60}($PhCH_2$)$_2$Ph(C_6H_4(CO)$_2$N$CH_2CH_2CH_2CH_2$)$_2$](C_5H_5) (12)>.

The procedures (RX = $C_6H_4(CO)_2NCH_2CH_2CH_2CH_2Br$) described above was performed to obtain **12**. Yield: 70%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.05-2.20 (m, 8H, butyl), 2.80-3.10 (m, 4H, butyl), 3.80-3.95 (m, 4H, butyl), 4.05-4.20 (m, 4H, CH_2Ph), 4.40 (s, 5H, Cp), 7.20-7.40 (m, 7H, Ph), 7.52 (m, 4H, Ph), 7.70 (m, 2H, C_6H_4), 7.73 (m, 2H, Ph), 7.74 (m, 2H, C_6H_4), 7.79 (m, 2H, C_6H_4), 7.86 (m, 2H, C_6H_4), 8.21 (d, 2H, *o*-Ph); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.97 (1C), 25.05 (1C), 29.08 (1C), 29.35 (1C), 37.51 (1C), 37.67 (1C), 42.17 (1C), 42.73 (1C), 49.65 (1C), 50.51 (1C), 54.51 (1C), 54.57 (1C), 55.60 (1C), 55.62 (1C), 58.57 (1C), 69.50 (5C), 91.32 (1C), 91.80 (1C), 92.00 (1C), 92.16 (1C), 92.89 (1C), 123.28

(2C), 123.32 (2C), 126.97 (1C), 127.21 (1C), 127.55 (1C), 128.15 (2C), 128.18 (2C), 128.40 (2C), 128.95 (2C), 130.40 (2C), 130.45 (1C), 130.51 (2C), 132.04 (2C), 132.12 (2C), 133.96 (2C), 133.99 (2C), 136.90 (2C), 142.44 (1C), 142.46 (1C), 142.48 (2C), 142.80 (1C), 142.82 (1C), 142.84 (1C), 142.93 (1C), 143.00 (1C), 143.69 (1C), 143.77 (1C), 143.96 (1C), 144.53 (1C), 144.62 (1C), 144.70 (1C), 144.71 (1C), 144.78 (1C), 144.91 (1C), 144.96 (1C), 145.16 (1C), 146.87 (1C), 146.95 (1C), 146.97 (1C), 147.07 (1C), 147.13 (1C), 147.75 (1C), 147.78 (1C), 147.79 (1C), 147.81 (1C), 147.83 (1C), 147.85 (1C), 147.92 (1C+1C+1C), 148.01 (1C), 148.10 (1C), 148.15 (1C), 148.23 (1C), 148.26 (1C), 148.30 (1C), 152.24 (1C), 152.31 (1C), 152.50 (1C), 152.57 (1C), 152.71 (1C), 152.94 (1C), 153.15 (1C), 153.24 (1C), 153.34 (1C), 153.43 (1C), 168.44 (2C), 168.50 (2C); HRMS (APCI+) calcd for $C_{95}H_{60}{}^{56}Fe^{16}O_{10}$ (M^+): 1504.2964, found: 1504.2922.

Synthesis of [(1,2,3,4,5-η)-6,9,12,15,18-pentabenzyl-9,12,15,18-tetrahydro(C_{60}-I_h)[5,6]fulleren-1(*6H*)-yl](η^5-cyclopentadienyl)iron(II) <Fe[C_{60}($PhCH_2$)$_5$](C_5H_5) (13)>.

A solution of tetrabutylammonium hydroxide (1.0 M in MeOH, 6.8 equiv) was added to a solution of Fe($C_{60}H_5$)(C_5H_5) (**1**, 1.0 equiv) at room temperature (21~26 °C). A color of the resulting solution changed from orange to dark red at a moment. After 5 min, the mixture was treated with benzyl bromide (286 equiv), resulting change of color from dark red to brown. HPLC analysis indicated the full consumption of the starting material within 10 minutes. Then the mixture was diluted with 8 mL of toluene/2-propanol = 1/1, filtered with a pad of alumina and subjected to preparative HPLC separation. A collected fraction was concentrated to dryness and dried under reduced pressure to give a penta-alkylated product Fe[(C_{60}($PhCH_2$)$_5$](C_5H_5) (**13**) in 47% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.30 (s, 10H, CH_2), 5.16 (s, 5H, Cp), 7.30 (t, 5H, *p*-Ph), 7.34 (t, 10H, *m*-Ph), 7.30 (d, 10H, *o*-Ph); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 50.90 (5C), 55.76 (5C), 69.45 (10C), 92.12 (5C), 127.14 (5C), 128.32 (10C), 130.30 (10C), 136.67 (5C), 142.31 (10C), 144.55 (10C), 146.63 (5C), 147.46 (10C), 147.96 (5C), 152.28 (10C); HRMS (APCI+) calcd for $C_{100}H_{40}{}^{56}Fe$ (M^+): 1296.2479, found: 1296.2477.

Synthesis of [(1,2,3,4,5-η)-6,9,12,15,18-penta(3-etoxycarbonyl)propyl-9,12,15,18-tetrahydro(C_{60}-I_h)[5,6]fulleren-1(*6H*)-yl](η^5-cyclopentadienyl)iron(II) <Fe[C_{60}($EtOOCCH_2CH_2CH_2$)$_5$](C_5H_5) (14)>.

The procedure described for **13** was performed to obtain **14**. Complex **14** was prepared from **1** (1.5 mg, 0.0018 mmol) and $ICH_2CH_2CH_2COOEt$ (60 mg, 0.246 mmol) in PhCN (2.0 mL). Yield: 1.5 mg (1.0 mmol, 58%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.29 (t, 10H, OCH_2CH_3), 2.32 (m, 10H, $C_{60}CH_2CH_2CH_2$), 2.59 (t, 10H, $C_{60}CH_2CH_2CH_2$), 2.74 (m, 10H, $C_{60}CH_2CH_2CH_2$), 4.19 (q, 10H, OCH_2CH_3), 4.77 (s, 5H, Cp). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.47 (OCH_2CH_3), 23.72 ($C_{60}CH_2CH_2CH_2$), 34.67 ($C_{60}CH_2CH_2CH_2$), 42.68 ($C_{60}CH_2CH_2CH_2$), 54.46 (C_{60}(sp^3)),

60.60 (O*C*H_2CH_3), 69.54 (Cp), 91.86 (FCp), 143.02 (C_{60}), 144.84 (C_{60}), 147.22 (C_{60}), 148.10 (C_{60}), 148.41 (C_{60}), 153.28 (C_{60}), 173.24 (COO); HRMS (APCI+) calcd for $C_{95}H_{60}{}^{56}Fe^{16}O_{10}$ (M^+): 1416.3539, found: 1416.3551.

Synthesis of [(1,2,3,4,5-*η*)-6,9,12,15-tetrabenzyl-18-phenyl-9,12,15,18-tetrahydro(C_{60}-I_h)[5,6]fulleren-1(*6H*)-yl](tricarbonyl)rhenium(I) <Re[C_{60}($PhCH_2$)$_4$Ph](CO)$_3$ (15)>.

To a solution of Re[C_{60}($PhCH_2$)$_2$$PhH_2$](CO)$_3$ (9.6 mg, 7.7 μmol, 1.0 equiv) in PhCN (2.0 mL) was added a solution of tetrabutylammonium hydroxide in methanol (1.0 M, 18.4 μl, 2.4 equiv) at 22 °C. A color of the solution changed from orange to dark red at a moment, indicating generation of a dianion species. After 10 min, the mixture was treated with $PhCH_2Br$ (25.0 μl, 27 equiv) and the color of the reaction mixture immediately changed from dark red to brown. HPLC analysis indicated the full consumption of the starting material after 8 minutes. Then the mixture was diluted with 8 mL of toluene/2-propanol = 7/3, filtered with a pad of alumina and subjected to preparative HPLC separation. A collected fraction was concentrated to dryness and dried under reduced pressure to give **15** as an orange solid (5.3 mg, 48% yield). IR (powder) 2968 (w), 2933 (w), 2024 (s), 1940 (m), 1927 (m), 1494 (w), 1456 (w), 749 (m), 697 (s), 686 (m); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.79 (d, *J* = 12.8 Hz, 2H, PhCH*H*), 3.82 (d, *J* = 13.6 Hz, 2H, PhCH*H*), 3.84 (d, *J* = 12.8 Hz, 2H, PhCH*H*), 4.14 (d, *J* = 13.6 Hz, 2H, PhCH*H*), 7.21-7.74 (m, 23H, Ph), 8.19 (d, *J* = 7.6 Hz, 2H, Ph); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 51.91 (2C), 52.43 (2C), 55.87 (2C), 55.95 (2C), 58.74 (1C), 109.90 (2C), 110.75 (2C), 112.97 (1C), 127.26 (2C), 127.33 (2C), 127.51 (2C), 128.17 (4C), 128.22 (4C), 128.85 (2C), 129.32 (2C), 130.37 (4C), 130.40 (4C), 131.90 (2C), 132.49 (1C), 135.94 (2C), 135.99 (2C), 142.75 (2C), 142.81 (2C+2C), 143.21 (2C), 143.32 (2C), 143.40 (1C), 144.02 (2C), 144.05 (2C), 144.17 (2C), 144.50 (2C), 146.47 (2C), 146.49 (1C), 146.62 (2C), 147.43 (2C), 147.47 (2C+2C), 147.49 (2C), 147.52 (2C), 148.26 (2C), 148.36 (2C), 149.71 (2C), 149.94 (2C), 150.15 (2C), 150.39 (2C), 150.43 (2C), 192.33 (3C); HRMS (APCI+) calcd for $C_{97}H_{33}{}^{187}ReO_3$ (M^+): 1432.1987, found: 1432.1922.

Synthesis of [(1,2,3,4,5-*η*)-6,9-dibenzyl-12-phenyl-15,18-bis(4-phthalimidobutyl)-9,12,15,18-tetrahydro(C_{60}-I_h)[5,6]fulleren-1(*6H*)-yl](tricarbonyl)rhenium(I) <Re[C_{60}($PhCH_2$)$_2$Ph(C_6H_4(CO)$_2$$NCH_2CH_2CH_2CH_2$)$_2$](CO)$_3$ (16)>.

To a solution of Re[C_{60}($PhCH_2$)$_2$$PhH_2$](CO)$_3$ (9.6 mg, 7.7 μmol, 1.0 equiv) in PhCN (2.0 mL) was added a solution of tetrabutylammonium hydroxide in methanol (1.0 M, 18.4 μl, 2.4 equiv) at 22 °C. A color of the solution changed from orange to dark red at a moment, indicating generation of a dianion species. After 10 min, the mixture was added *N*-(4-bromobutyl)phthalimide (54.3 mg, 0.193 mmol, 25 equiv) and heated at 80 °C for 30 min. Color of the reaction mixture immediately changed from dark red to brown. HPLC analysis

indicated the full consumption of the starting material. Then the mixture was diluted with 8 mL of toluene/2-propanol = 7/3, filtered with a pad of silica and subjected to preparative HPLC separation. A collected fraction was concentrated to dryness and dried under reduced pressure to give **16** as an orange solid (9.3 mg, 73% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.95-2.10 (m, 8H, butyl), 2.45-2.70 (m, 4H, butyl), 3.76-3.83 (m, 4H, butyl), 3.81 (d, 1H, CH_2Ph), 3.83 (s, 2H, CH_2Ph), 4.09 (d, 1H, CH_2Ph), 7.28-7.65 (m, 18H, Ph), 7.68-7.72 (m, 4H, C_6H_4), 7.79-7.84 (m, 4H, C_6H_4), 7.99 (d, 2H, *o*-Ph); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.04 (1C), 25.53 (1C), 28.81 (1C), 29.06 (1C), 37.44 (1C), 37.58 (1C), 44.58 (1C), 44.81 (1C), 51.95 (1C), 52.02 (1C), 54.94 (1C), 55.27 (1C), 55.96 (1C), 56.10 (1C), 58.81 (1C), 109.44 (1C), 110.23 (1C), 110.44 (1C), 112.18 (1C), 112.93 (1C), 123.21 (4C), 127.33 (1C), 127.45 (1C), 127.63 (2C), 128.16 (2C), 128.25 (1C), 128.34 (2C), 129.41 (2C), 130.54 (2C), 130.79 (2C), 132.05 (4C), 133.82 (1C), 133.86 (4C), 136.20 (1C), 136.22 (1C), 142.92 (1C), 142.95 (1C), 143.00 (1C), 143.07 (1C), 143.34 (1C+1C), 143.36 (1C), 143.45 (1C), 143.51 (1C), 143.57 (1C), 144.29 (1C+1C+1C), 144.32 (1C+1C), 144.47 (1C+1C+1C), 144.57 (1C+1C), 146.75 (1C), 146.82 (1C+1C), 146.90 (1C), 146.92 (1C), 147.68 (1C), 147.81 (1C+1C), 147.86 (1C+1C), 148.50 (1C+1C), 148.56 (1C+1C), 148.61 (1C), 150.22 (1C), 150.28 (1C), 150.35 (1C), 150.47 (1C), 150.59 (1C), 150.92 (1C), 150.96 (1C+1C), 151.00 (1C), 151.01 (1C), 168.26 (2C), 168.31 (2C), 192.53 (3C); HRMS (APCI+) calcd for $C_{107}H_{44}N_2O_7{}^{187}Re$ (M^+): 1653.2678, found: 1653.2644.

2. ^{1}H NMR Spectra of 6 and Deprotonated Products

$Fe[C_{60}(PhCH_2)_2PhH_2](C_5H_5)$ in PhCN-d_5