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# Regioselective synthesis of tetra(aryl)-mono(silylmethyl)[60]fullerenes and derivatization to methanofullerene compound

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Dedicated to Professor Gilbert Stork on the occasion of his 90th birthday

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ABSTRACT

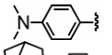
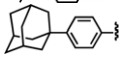
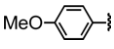
A method for the facile synthesis of tetraaryl-trimethylsilylmethyl-hydro[60]fullerenes, $C_{60}Ar_4(CH_2SiMeR)H$, has been developed in which readily prepared anionic mono(silylmethyl) fullerene is subjected to reaction conditions for organocopper-mediated multiple addition. Penta(organo)fullerene derivatives bearing different substituents and diverse functionality were synthesized in moderate to good yield under simple and mild reaction conditions. Further organic and organometallic transformations of these fullerenes allowed us to synthesize transition-metal complexes and a new methanofullerene derivative, 1,9-methano-6,12,15,18-tetraphenyl[60]fullerene, $C_{60}Ph_4(CH_2)$.



## 1. Introduction

Functionalization of fullerene has led to numerous derivatives[1] that exhibit a surprising diversity of new properties that would otherwise be unavailable, for example, unique biochemical activity,[2] photoelectric function,[3] self-assembly capability,[4] and metal complexation properties.[5] To achieve selective multiple addition to fullerene in high overall yield, one must control not only the number of organic addends but also the regioselectivity of the addition. As we have reported previously, the pentaaddition of an arylcopper reagent to $C_{60}$ is a good example of a reaction that exclusively produces pentaarylated $C_{60}R_5H$ in high yield.[6] We have been interested for some time in the multiple addition of different organic groups, for instance, the addition of a phenylcopper reagent to 1,4-dibenzylated $C_{60}$ to synthesize $C_{60}Ph_3(benzyl)_2H$[7] and the copper-mediated addition of alkylzinc reagents to synthesize $C_{60}Ph_4(C_4H_7O)H$.[8] In the present study, we demonstrate that heterogeneous pentaaddition is a promising approach to considerably expanding the repertoire of available fullerene derivatives; herein, we report efficient syntheses of tetra(aryl)-mono(silylmethyl)[60]fullerene, $C_{60}Ar_4(CH_2SiMeR)H$ (Eq. 1 and Table 1), which accomplished by reacting an anionic mono(silylmethyl) fullerene with an organocopper reagent to synthesize the multiple addition product regioselectively. The anionic intermediate can be readily prepared in up to 93% yield through addition of $RMe_2SiCH_2MgCl$ to $C_{60}$ in the presence of DMF.[9] This has proved to be a practical strategy not only for selectively introducing a diverse set of aryl and silylmethyl groups to $C_{60}$, but also for elaborating the products into

**Table 1**
Synthesis of $C_{60}Ar_4(CH_2SiMeR)H$ (**1**) (Eq. 1)

| Entry | ArMgBr | $RMe_2SiCH_2MgCl$ | Conditions | **1** | Yield (%) |
|---|---|---|---|---|---|
| 1 |  | $Me_3SiCH_2MgCl$ | 45 °C/6 h | **1a** | 71 |
| 2 |  | $PhMe_2SiCH_2MgCl$ | 45 °C/5 h | **1b** | 78 |
| 3 |  | $^iPrOMe_2SiCH_2MgCl$ | 45 °C/5.5 h | **1c** | 72 |
| 4 |  | $Me_3SiCH_2MgCl$ | 45 °C/13.5 h | **1d** | 81 |
| 5 |  | $Me_3SiCH_2MgCl$ | 45 °C/26 h[a] | **1e** | 53 |
| 6 |  | *n*-Octyl$Me_2SiCH_2MgCl$ | 50 °C/6 h | **1f** | 73 |

[a] Reaction performed in the presence of 15 equiv ArMgBr.

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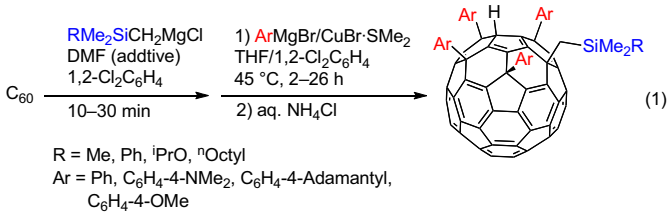
a variety of new compounds through organic and organometallic transformations of the silylmethyl moiety and the cyclopentadienyl moiety.




## 2. Results and discussion

We first examined the synthesis of tetraphenyl-trimethylsilylmethyl-hydro[60]fullerenes, $C_{60}Ph_4(CH_2SiMe_3)H$. A solution of anionic mono(silylmethyl) fullerene was prepared by adding $Me_3SiCH_2MgCl$ to $C_{60}$ in the presence of DMF.[9] This solution was then added to a solution of organocopper reagent prepared from PhMgBr and $CuBr\cdot SMe_2$ at room temperature. As monitored by HPLC, the reaction proceeded smoothly to completion ($C_{60}$ completely consumed) under stirring for 6 h at 45 °C to produce $C_{60}Ph_4(CH_2SiMe_3)H$ as the major product in 71% isolated yield (Table 1, entry 1).[10] The reaction after 2 h at 45 °C, however, was incomplete and produced $C_{60}(CH_2SiMe_3)H$ in 32% HPLC yield, and $C_{60}Ph_4(CH_2SiMe_3)H$ in 13% HPLC yield, along with various intermediate products.

This straightforward method can selectively introduce aryl and silylmethyl groups onto $C_{60}$. The reaction produced $C_{60}Ar_4(CH_2SiMeR)H$ (**1**) in moderate to good yield, and could be applied to a wide array of aryl and silylmethyl Grignard reagents (Table 1, entries 1–6). A molecular model of the tetra(4-adamantylphenyl) derivative, $C_{60}(C_6H_4\text{-}4\text{-}admantyl)_4[CH_2SiMe_3]H$ (**1e**), suggested an intriguing molecular structure composed of a π-rich bottom face and an entirely aliphatic top face.

The product $C_{60}Ar_4(CH_2SiMeR)H$ (**1**) was characterized by $^1H$, $^{13}C$ NMR, and APCI–HRMS. Three isomers differing in the position of the Cp proton could not be separated and three proton signals were detected by $^1H$ NMR. X-ray analysis of a dark-red single crystal of compound **1d** revealed a *quasi*-$C_s$ symmetrical molecular structure, $C_{60}(C_6H_4\text{-}4\text{-}NMe_2)_4(CH_2SiMe_3)H$ (Fig. 1).[11] The cavity created by the one silyl and four aryl addends can be clearly seen in Fig. 1b.

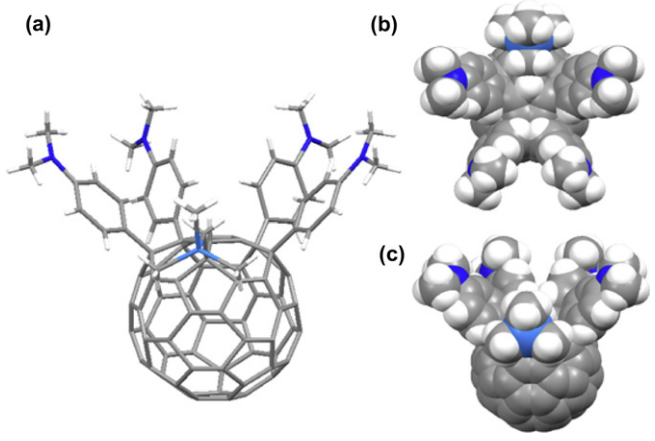
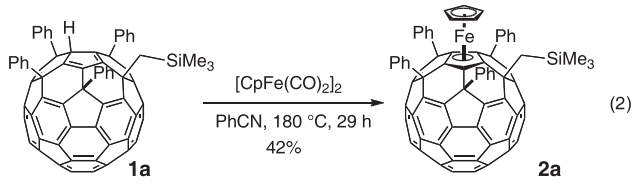



**Fig. 1.** Single-crystal structure of **1d**. (a) Capped stick model. (b) Top view of space-filling model. (c) Side view of space-filling model.

The reactivity of cyclopentadiene with these compounds is illustrated by the smooth conversion of **1a** to the corresponding iron complex (**2a**), in 42% isolated yield through heating in the presence of $[CpFe(CO)_2]_2$ in PhCN at 180 °C for 29 h (Eq. 2).[12]




X-ray crystallographic analysis of compound **2a** revealed a *quasi*-$C_s$ symmetrical structure (Fig. 2). The average bond length between the iron atom and the carbon atoms of the Cp ring was 2.054 Å and that between the iron atom and the carbon atoms of the fullerene cyclopentadienide was 2.076 Å. These values are similar to those found in $C_1$-symmetric $Fe[C_{60}Ph_4(C_4H_7O)]Cp$ and $C_{5v}$-symmetric bucky ferrocene $Fe(C_{60}Ph_5)Cp$. The Cp ring rotates about the Cp–Fe–$C_{60}$ axis faster than the NMR time scale. The cyclopentadienide in the fullerene core has $C_s$ symmetry as shown by three $^{13}C$ singlets at δ 91.94, 93.02, and 97.01 due to the five $sp^3$ carbons, while the Cp ring exhibits only one proton (δ=3.38) and carbon (δ=72.16) singlet.

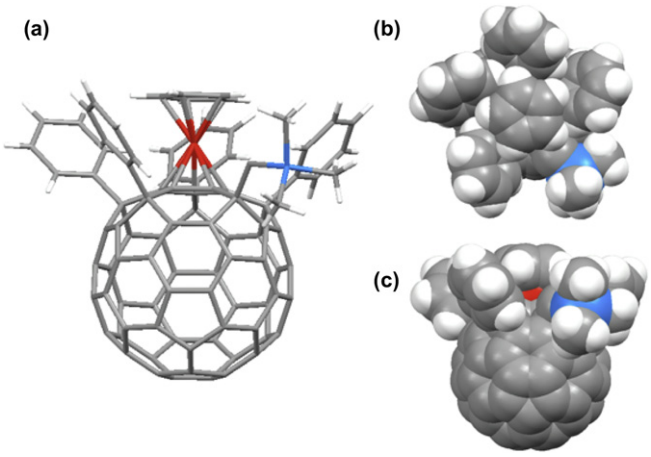



**Fig. 2.** Single-crystal structure of **2a**. (a) Capped stick model. (b) Top view of space-filling model. (c) Side view of space-filling model.

Cyclic voltammetry was carried out in THF containing tetrabutylammonium perchlorate as a supporting electrolyte. Bucky ferrocene **2a** exhibited a reversible one-electron oxidation wave at 0.39 V ($E^{ox}_{1/2}$) and two-step, one-electron reduction waves at −1.43 V ($^1E^{red}_{1/2}$) and −2.04 V ($^2E^{red}_{1/2}$) versus $Fc/Fc^+$ (Fig. 3). The difference of one addend between **2a** and $Fe(C_{60}Ph_5)Cp$ ($E^{ox}_{1/2}$, 0.50 V)[12e] decreased the oxidation potential by 0.11 V, which can be ascribed to the stronger electron-donating effect of the trimethylsilylmethyl group compared with the phenyl group.

Selective chemical modification of the isopropoxy silylmethyl group in $C_{60}Ph_4[CH_2SiMe_2(O^iPr)]H$ (**1c**) enabled access to several interesting new fullerene derivatives (Eq. 2). For instance, silanol derivative **3** was obtained in 91% yield through hydrolysis of the corresponding chlorosilane intermediate.[13] This hydrolysis reaction was carried out by simply stirring the isopropoxy silyl compound in THF with 10 equiv of 35% aq HCl at 50 °C for 2 h and then treating the reaction mixture with satd $NaHCO_3$. Alternatively, nucleophilic substitution of the silyl chloride with $^iPrNH_2$ gave the corresponding silyl amide derivative (**4**).

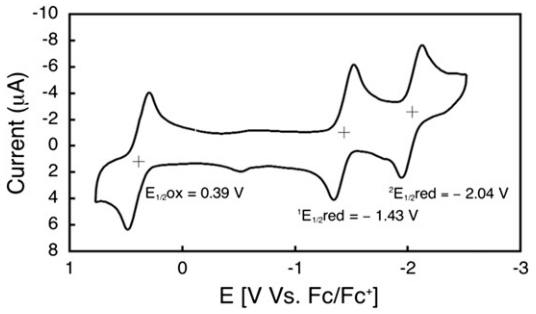
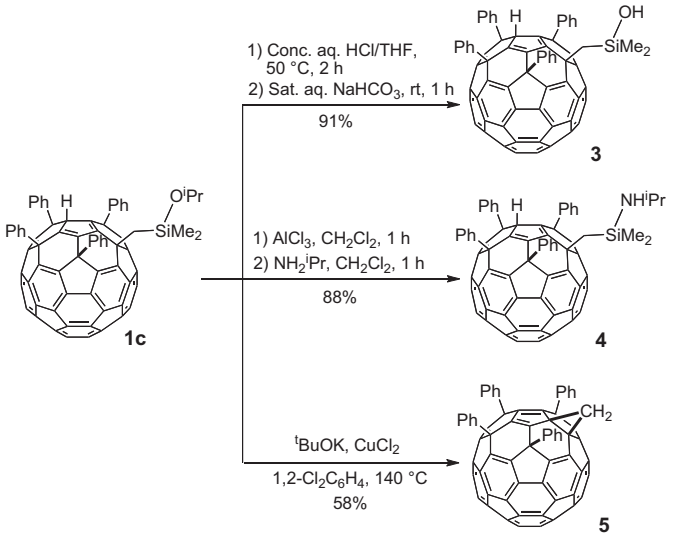



**Fig. 3.** Cyclic voltammogram of **2a** in THF containing tetrabutylammonium perchlorate as supporting electrolyte (vs $Fc/Fc^{+}$).

Cu(II)-promoted conversion of the silylmethyl fullerene into methanofullerene[14] converted **1c** into a new type of methanofullerene. Treatment of **1c** with *t*-BuOK (1.5 equiv)[15] in *ortho*-dichlorobenzene followed by heating in the presence of $CuCl_2$ (6 equiv) enabled **5** to be prepared in 58% isolated yield (Scheme 1). The structure of **5** was confirmed by X-ray crystallographic analysis (Fig. 4).




**Scheme 1.** Conversion of the $^{i}$PrO group of **1c** to other functional fullerene derivatives.

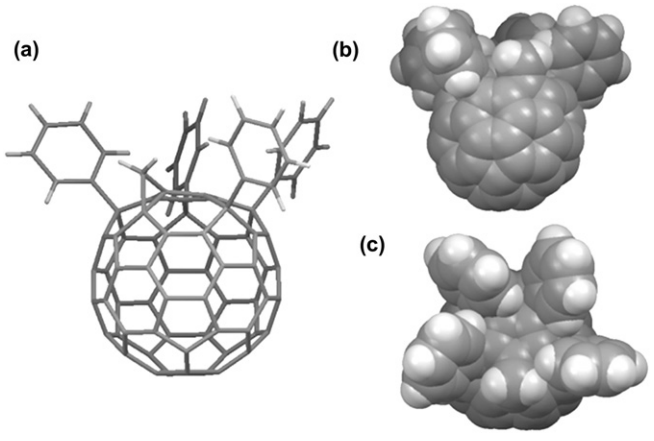



**Fig. 4.** Single-crystal structure of **5**. (a) Capped stick model. (b) Top view of space-filling model. (c) Side view of space-filling model.

In summary, we have developed a method for the facile synthesis of mono(silylmethyl)-tetra(aryl)[60]fullerene, $C_{60}Ar_4(CH_2SiMeR)H$, in which a readily prepared anionic mono(silylmethyl) fullerene is subjected to reaction conditions for organocopper-mediated multiple addition. Subsequent organic and organometallic transformations of these fullerenes enabled access to transition-metal complexes and new fullerene derivatives.

## 3. Experimental

### 3.1. General

All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk technique under an argon or nitrogen atmosphere. HPLC analyses were performed on a Shimadzu LC-10A system equipped with SPD-M10A diode array detector and a Buckyprep column (Nacalai Tesque Inc., 4.6 mm ID×250 mm). Preparative HPLC was performed on a Buckyprep column (20 mm ID×250 mm) using toluene/2-isopropanol (7/3 to 4/6) as eluent (flow rate 5–15 ml/min, detected at 350 nm with an UV spectrophotometric detector, Shimadzu SPD-6A). Flash silica gel column chromatography was performed on silica gel 60 N (Kanto, spherical and neutral, 140–325 mesh) as described by Still.[16] Gel permeation column chromatography was performed on a Japan Analytical Industry LC-9201 (eluent: toluene) with JAIGEL 2*H* and 3*H* polystyrene column. NMR spectra were measured with a JEOL ECA-500 (500 MHz) spectrometer. Spectra are reported in parts per million from internal tetramethylsilane ($\delta$ 0.00 ppm) for $^{1}$H NMR, from solvent carbon (e.g., $\delta$ 77.00 ppm for chloroform) for $^{13}$C NMR. High-resolution mass spectra were measured by APCI using a time-of-flight mass analyzer on a JEOL JMS-T100LC (AccuTOF) spectrometer. $Me_3SiCH_2MgCl$, $PhMe_2SiCH_2MgCl$, $(^{i}PrO)Me_2SiCH_2SiMgCl$, and $(C_8H_{17})Me_2SiCH_2SiMgCl$ were prepared according to the literatures,[17] and titrated before use. Other materials were purchased from Tokyo Chemical Industry Co., Sigma–Aldrich Co., Kanto Chemical Co., Inc., Wako Pure Chemical Industries, or other commercial suppliers and used after appropriate purification.

### 3.2. General procedure for the synthesis of tetraaryl-trimethylsilylmethyl-hydro[60]fullerenes (1a–f)

To a solution of $C_{60}$ (72 mg, 0.10 mmol) in 1,2-dichlorobenzene (10 mL) containing *N*,*N*-dimethylformamide (0.23 mL, 3 mmol) was added the THF solution of $RMe_2SiCH_2MgCl$ (0.30 mmol) at room temperature. After stirring for 10–30 min, the resulting dark-green solution was transferred by a cannula to the slurry of organocopper reagent, which was prepared by mixing ArMgBr (1.5 mmol) to $CuBr{\cdot}SMe_2$ (245 mg, 1.2 mmol) in THF (5 mL) for ca. 20 min. The combined mixture was stirred at 45 °C until $C_{60}$ disappeared as monitored by HPLC (Also, the color of resulting mixture changes from dark green to brown). The reaction was then quenched with 0.10 mL satd aq $NH_4Cl$ solution, and dilute with degassed toluene (ca. 10 mL). Then, the mixture was filtered through a pad of silica gel and concentrated under reduced pressure. The residue was purified with silica gel column or preparative HPLC separation (Buckyprep 20 mm ID×250 mm) to give desired compound as a red solid. Three isomers (i.e., 6,9,13,15-tetraaryl-18-trimethylsilylmethyl-1-hydro[60]fullerene, 6,13,15,18-tetraaryl-9-trimethylsilylmethyl-1-hydro[60]fullerene, and 9,13,15,18-tetraaryl-6-trimethylsilylmethyl-1-hydro[60]fullerene)[18] differing in the position of the Cp proton could not be separated.

*3.2.1. $C_{60}(H)(C_6H_5)_4[CH_2SiMe_3]$ (**1a**).* Synthesis of **1a** was performed according to the general procedure at 45 °C for 6 h. The concentrated residue was purified with silica gel column chromatography (eluent: first $CS_2$/hexane=5/1, then $CS_2$) to give

compound **1a** (79.3 mg, 71% yield, 94% purity) as a red solid. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ −0.04 (s, 5H, $SiCH_3$), 0.17 (s, 4H, $SiCH_3$), 1.75–2.04 (m, 2H, $CH_2$), 4.94, 5.16, 5.17 (s, 1H, $C_{60}H$, three signals due to isomers), 7.10–7.27 (m, 5H, Ar–*H*), 7.32–7.62 (m, 10H, Ar–*H*), 7.76–8.00 (m, 5H, Ar–*H*); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 0.69, 1.18, 1.25, 29.79, 29.86, 53.70, 54.29, 55.74, 59.34, 59.49, 59.61, 59.66, 61.30, 61.66, 61.77, 62.72, 63.32, 128.02, 128.19, 128.22, 128.29, 128.32, 128.42, 128.44, 128.47, 128.51, 128.57, 128.72, 128.82, 128.89, 129.22, 129.30, 129.46, 129.53, 129.59, 129.63, 129.67, 129.83, 140.17, 140.45, 140.49, 140.56, 140.64, 140.82, 143.55, 143.71, 143.74, 143.83, 144.17, 144.31, 144.44, 144.48, 144.58, 144.68, 144.71, 144.74, 144.76, 144.80, 144.89, 144.93, 144.99, 145.05, 145.31, 145.34, 145.74, 145.84, 145.87, 146.02, 146.22, 146.32, 146.36, 146.40, 146.43, 146.45, 146.58, 146.62, 146.65, 146.76, 146.82, 147.08, 147.21, 147.56, 147.62, 147.70, 147.76, 147.80, 147.86, 147.89, 148.30, 148.34, 148.44, 148.65, 148.68, 148.72, 148.75, 148.79, 148.81, 148.89, 148.92, 149.02, 149.10, 149.15, 149.32, 149.37, 149.39, 149.42, 149.46, 149.80, 149.84, 151.05, 151.98, 152.33, 152.53, 152.72, 153.16, 154.12, 154.32, 154.41, 157.04, 157.27, 157.70, 157.85, 159.88; APCI–HRMS (−): *m*/*z* calcd for $C_{88}H_{32}Si$ ($M-H^+$), 1115.2195; found, 1115.2200.

*3.2.2. $C_{60}(H)(C_6H_5)_4[CH_2SiMe_2Ph]$ (**1b**).* Synthesis of **1b** was performed according to the general procedure at 45 °C for 5 h. The concentrated residue was purified with preparative HPLC separation (toluene/2-isopropanol=7/3, flow rate 10 ml/min) to give compound **1b** (92 mg, 78% yield, 94% purity) as a red solid. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.07–0.22 (m, 6H, $SiCH_3$), 1.80–2.12 (m, 2H, $CH_2$), 4.70, 4.89, 4.90 (s, 1H, $C_{60}H$, three singlet due to isomers), 6.84–7.02 (m, 8H, Ar–*H*), 7.03–7.24 (m, 12H, Ar–*H*), 7.29–7.69 (m, 5H, Ar–*H*). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ −1.37, −1.22, −1.18, −0.96, 28.03, 28.28, 52.76, 53.34, 54.80, 58.46, 58.54, 58.71, 58.74, 58.86, 58.93, 60.55, 60.87, 60.93, 61.04, 62.02, 62.61, 65.31, 127.50, 127.54, 127.59, 127.68, 127.73, 127.75, 127.88, 128.00, 128.10, 128.16, 128.55, 128.60, 128.76, 128.87, 128.89, 128.94, 128.96, 129.01, 129.15, 129.21, 133.68, 133.82, 137.96, 138.00, 138.07, 139.42, 139.72, 139.74, 139.81, 139.91, 140.09, 140.10, 140.16, 142.51, 143.00, 143.07, 143.20, 143.42, 143.61, 143.62, 143.82, 143.84, 143.93, 143.97, 144.00, 144.02, 144.06, 144.14, 144.18, 144.24, 144.27, 144.29, 144.42, 144.53, 144.86, 145.05, 145.23, 145.48, 145.50, 145.57, 145.63, 145.68, 145.71, 145.87, 145.96, 145.98, 146.13, 146.78, 146.93, 146.99, 147.02, 147.04, 147.09, 147.12, 147.54, 147.57, 147.61, 147.69, 147.94, 147.96, 147.99, 148.01, 148.03, 148.16, 148.22, 148.52, 148.55, 148.57, 148.59, 148.64, 148.66, 148.68, 148.70, 148.95, 150.52, 151.04, 151.27, 151.63, 151.77, 151.97, 152.31, 152.34, 152.93, 153.42, 153.55, 153.60, 155.85, 156.13, 156.33, 156.93, 158.89; APCI–HRMS (−): *m*/*z* calcd for $C_{93}H_{34}Si$ ($M-H^+$), 1177.2357; found, 1177.2347.

*3.2.3. $C_{60}(H)(C_6H_5)_4[CH_2SiMe_2(O^iPr)]$ (**1c**).* Synthesis of **1c** was performed according to the general procedure at 45 °C for 5.5 h. The concentrated residue was purified with preparative HPLC separation (toluene/2-isopropanol=65/35, flow rate 10 ml/min) to give compound **1c** (106 mg, 72% yield, 99% purity) as a red solid. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.07–0.22 (m, 6H, $SiCH_3$), 0.89–1.05 (m, 6H, $CH_3$), 1.80–2.12 (m, 2H, $CH_2$), 3.76–4.94 (m, 1H, CH), 4.96, 5.15 (s, 1H, $C_{60}H$, two signals due to isomers), 7.10–7.53 (m, 12H, Ar–*H*), 7.62–7.63 (m, 2H, Ar–*H*), 7.78–8.00 (m, 6H, Ar–*H*); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 0.67, 0.78, 0.85, 1.03, 1.31, 25.44, 25.51, 25.54, 25.69, 28.81, 52.02, 52.68, 54.04, 58.46, 58.68, 58.81, 58.90, 58.96, 60.58, 60.97, 61.07, 62.05, 62.61, 65.11, 65.24, 65.31, 127.53, 127.60, 127.69, 127.72, 127.79, 127.83, 128.04, 128.10, 128.53, 128.59, 128.76, 128.82, 128.89, 128.94, 128.96, 129.,14, 139.48, 139.78, 139.88, 140.00, 143.12, 143.39, 143.67, 143.80, 143.87, 143.95, 143.99, 144.02, 144.05, 144.11, 144.20, 144.24, 144.35, 144.51, 145.15, 145.25, 145.32, 145.52, 145.62, 145.66, 145.73, 145.99, 146.07, 146.88, 147.12, 147.17, 147.63, 147.72, 147.74, 147.96, 148.02, 148.05, 148.08, 148.19, 148.27, 148.33, 148.40, 148.60, 148.65, 148.69, 148.76, 153.67, 156.57, 156.66, 156.98, 157.08, 158.90; APCI–HRMS (−): *m*/*z* calcd for $C_{90}H_{36}OSi$ ($M-H^+$), 1159.2463; found, 1159.2475.

*3.2.4. $C_{60}(H)(C_6H_4\text{-}4\text{-}NMe_2)_4[CH_2SiMe_3]$ (**1d**).* Synthesis of **1d** was performed according to the general procedure at 45 °C for 13.5 h. The concentrated residue was purified with preparative HPLC separation (toluene/2-isopropanol=70/30, flow rate 10 ml/min) to give compound **1d** (120 mg, 81% yield, 96% purity) as red solid. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ −0.11–0.22 (m, 9H, $SiCH_3$), 1.54–2.03 (m, 2H, $CH_2$), 2.83–3.03 (m, 24H, $N(CH_3)_2$), 4.84, 5.08, 5.10 (s, 1H, $C_{60}H$, three signals due to isomers), 6.52–6.65 (m, 4H, Ar–H), 6.71–6.90 (m, 4H, Ar–H), 7.40–7.50 (m, 3H, Ar–H), 7.62–7.90 (m, 5H, Ar–H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ −0.01, 0.39, 40.79 (br), 52.90, 53.53, 54.56, 54.94, 57.55, 57.96, 58.12, 58.18, 58.25, 58.30, 60.30, 62.02, 113.04 (br), 125.28, 128.21, 128.45, 128.55, 128.61, 128.79, 128.91, 129.02, 129.16, 141.81, 142.65, 142.83, 143.24, 143.53, 143.84, 143.87, 143.94, 143.96, 144.01, 144.05, 144.10, 144.19, 144.26, 144.45, 144.59, 144.64, 144.92, 145.26, 145.31, 145.47, 145.61, 145.70, 145.78, 145.85, 146.00, 146.19, 146.27, 146.39, 146.71, 146.82, 146.92, 146.97, 147.04, 147.10, 147.12, 147.49, 147.61, 147.67, 147.88, 147.91, 147.93, 147.97, 148.08, 148.13, 148.20, 148.24, 148.26, 148.30, 148.32, 148.35, 148.40, 148.45, 148.51, 148.58, 148.60, 148.64, 148.69, 149.19, 149.39, 149.75, 156.64; APCI–HRMS (−): *m*/*z* calcd for $C_{96}H_{52}SiN_4$ ($M-H^+$), 1287.3883; found, 1287.3886.

*3.2.5. $C_{60}(H)(C_6H_4\text{-}4\text{-}Admantyl)_4[CH_2SiMe_3]$ (**1e**).* Synthesis of **1e** was performed according to the general procedure by using 15 equiv 4-Admantyl phenyl magnesium bromide at 45 °C for 26 h as monitored by HPLC. The concentrated residue was purified with preparative HPLC separation (toluene/2-isopropanol=70/30, flow rate 10 ml/min) to give compound **1e** (88 mg, 53% yield, 99% purity) as a red solid. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.11–0.22 (m, 9H, $SiCH_3$), 1.62–2.15 (m, 62H, C*H* and $CH_2$), 4.94, 5.10, 5.22 (s, 1H, $C_{60}H$, three signals due to isomers), 7.06–7.24 (m, 8H, Ar–*H*), 7.28–7.36 (m, 4H, Ar–*H*), 7.37–7.48 (m, 2H, Ar–*H*), 7.50–7.90 (m, 2H, Ar–*H*); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 0.34, 0.64, 21.44, 28.89, 35.87, 35.93, 35.99, 36.03–36.82, 43.05, 43.11–43.24, 53.53, 54.56, 55.14, 58.37, 58.58, 60.72, 125.04, 125.28, 125.29, 125.36, 125.54, 127.37, 127.42, 127.59, 127.62, 127.76, 127.99, 128.06, 128.09, 128.20, 129.01, 138.72, 140.64, 142.93, 143.98, 144.08, 144.21, 144.30, 144.52, 145.59, 145.63, 145.73, 145.94, 146.34, 146.81, 147.05, 147.08, 147.54, 147.69, 147.91, 147.96, 148.15, 148.21, 148.24, 148.33, 148.44, 148.52, 148.62, 148.63, 148.66, 148.69, 150.19, 150.33, 150.64, 150.67, 151.96, 152.50, 157.11; APCI–MS (−): *m*/*z* 1287.4; APCI–MS, APCI–HRMS calcd for $C_{128}H_{88}Si$ ($M-H^+$), 1651.6582; found, 1651.6578.

*3.2.6. $C_{60}(H)(C_6H_4\text{-}4\text{-}OMe)_4[CH_2SiMe_2(n\text{-}C_8H_{17})]$ (**1f**).* Synthesis of **1f** was performed according to the general procedure at 45 °C for 6 h. The concentrated residue was purified with preparative HPLC separation (toluene/2-isopropanol=70/30, flow rate 10 ml/min) to give compound **1f** (98 mg, 73% yield, 99% purity) as a red solid. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ −0.04 (m, 3H, $SiCH_3$), 0.09 (m, 3H, $SiCH_3$), 0.84–0.88 (m, 5H, $SiCH_2$ and $CH_3$), 1.09–1.18 (m, 13H, $CH_2$), 1.73–2.06 (m, 2H, $CH_2Si$), 3.75–3.88 (m, 12H, $OCH_3$), 4.92, 5.10, 5.16 (s, 1H, $C_{60}H$, three signals due to isomers), 6.68–7.00 (m, 8H, Ar–*H*), 7.26 (m, H, Ar–*H*), 7.28–7.88 (m, 7H, Ar–*H*); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ −1.36, −1.29, −1.14, −1.05, 14.12, 16.28, 16.54, 22.64, 23.53, 23.78, 29.15, 29.21, 29.24, 29.29, 31.91, 33.47, 33.56, 54.98, 55.30, 55.39, 55.41, 55.43, 57.90, 58.20, 59.95, 62.16, 62.66, 113.95, 113.99, 114.05, 114.13, 114.17, 114.26, 114.35, 114.43, 114.47, 116.00, 128.68, 128.77, 128.87, 128.90, 129.02, 129.08, 129.15, 129.20, 129.29, 129.35, 131.63, 131.91, 131.98, 132.14, 132.25, 132.30, 138.17, 138.44, 140.32, 142.73, 142.93, 142.97, 143.05, 143.38, 143.54, 143.62, 143.68, 143.79, 143.86, 143.91, 143.95, 144.05, 144.15, 144.23, 144.28, 144.43, 144.49, 144.63, 145.00, 145.03, 145.28, 145.44, 145.53, 145.61, 145.67, 145.80, 145.87, 145.97, 146.08, 146.36, 146.48, 146.80, 146.85, 146.92, 146.99, 147.04, 147.06, 147.11, 147.12, 147.56, 147.66, 147.68, 147.71, 147.91, 147.98, 148.00,

148.04, 148.09, 148.11, 148.14, 148.20, 148.23, 148.26, 148.26, 148.32, 148.34, 148.50, 148.53, 148.55, 148.62, 148.65, 148.68, 148.71, 148.95, 149.08, 150.64, 151.50, 151.88, 152.07, 152.22, 152.55, 153.82, 154.08, 156.09, 156.50, 157.00, 157.32, 158.50, 158.65, 158.76, 158.89, 158.91, 158.98, 159.10, 159.11; APCI–MS (−): *m*/*z* ($M-H^+$) 1334.4; APCI–HRMS calcd for $C_{99}H_{54}O_4Si$ ($M-H^+$), 1333.3719; found, 1333.3730.

### 3.3. Synthesis of (6,9,12,15-tetraphenyl-18-trimethylsilylmethyl[60]fullerenyl)iron cyclopentadienide, Fe[$C_{60}(C_6H_5)_4(CH_2SiMe_3)$]($C_5H_5$) (2a)

To a 25-mL round bottomed flask equipped with a condenser was charged with **1a** (50 mg, 0.045 mmol) and $[Fe(C_5H_5)(CO)_2]_2$ (63.4 mg, 0.18 mmol). The reaction vessel was flushed with nitrogen, and then benzonitrile (5 mL) was added. After stirring at 180 °C for 29 h, benzonitrile was removed by distillation at 70 °C under vacuum. The residue was purified with a silica gel column using $CS_2$ as an eluent, and preparative HPLC separation (toluene/2-isopropanol=55/45, flow rate 10 ml/min) to give compound **2a** (23 mg, 42% yield) as a red solid. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.24 (s, 9H, Si$CH_3$), 2.54 (s, 2H, $CH_2$Si), 3.38 (s, 5H, $C_5H_5$), 7.47 (t, *J*=7.5 Hz, 4H, Ar–*H*), 7.95 (d, *J*=7.5 Hz, 4H, Ar–*H*), 8.07 (d, *J*=7.5 Hz, 4H, Ar–*H*); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 0.64 (Si$CH_3$), 34.39 ($CH_2$Si), 52.47, 58.42, 72.16 ($C_5H_5$), 91.74, 93.02, 97.01, 152.28, 127.50, 127.68, 127.83, 128.20, 128.85, 129.02, 129.09, 137.86, 142.74, 143.04, 143.07, 143.10, 143.12, 143.22, 143.72, 144.04, 144.11, 144.17, 144.53, 147.34, 147.42, 147.44, 148.13, 148.15, 148.18, 148.21, 148.39, 148.42, 148.47, 152.23, 152.65, 152.86, 153.39, 154.44; APCI–MS (−): *m*/*z* ($M-H^+$); APCI–HRMS calcd for $C_{93}FeH_{36}Si$ ($M-H^+$), 1235.1857; found, 1235.1797.

### 3.4. Synthesis of tetraphenyl-[hydroxy(dimethyl)silylmethyl]-hydro[60]fullerene, $C_{60}(C_6H_5)_4[CH_2SiMe_2OH]$ (3)

A mixture of compound **1c** (150 mg, 0.129 mmol), aq HCl (1.29 mmol), and THF (10 mL) was stirred at 50 °C for 2 h. The resulting solution was then extracted with toluene/water. The organic phase was separated and concentrated to ca. 5 mL of volume. To the resulting solution satd aq $NaHCO_3$ (5 mL)/THF (5 mL) was added and subjected to Ar babbling for 5 min. After stirring for 1 h, the suspension was extracted with toluene/water. The organic layer was collected, dried by anhydrous $Na_2SO_4$, and concentrated to a small volume. Precipitation by addition of *n*-hexane afforded compound **3** (131 mg, 91% yield, 92% purity) as a red solid. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.03–0.21 (m, 6H, Si$CH_3$), 1.85–2.12 (m, 2H, $CH_2$), 5.12, 5.18, 5.19 (s, 1H, $C_{60}H$, three signals due to isomers), 7.12–7.57 (m, 12H, Ar–*H*), 7.62–7.64 (m, 2H, Ar–*H*), 7.81–8.00 (m, 6H, Ar–*H*); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 0.95, 1.26, 1.69, 1.84, 1.87, 29.88, 52.00, 52.82, 54.09, 58.62, 58.80, 58.82, 58.97, 60.63, 60.85, 60.97, 61.08, 61.93, 62.11, 62.72, 125.28, 127.10, 127.27, 127.36, 127.50, 127.54, 127.56, 127.62, 127.73, 127.81, 127.86, 127.92, 128.00, 128.13, 128.21, 128.28, 128.54, 128.61, 128.79, 128.91, 128.94, 129.02, 129.07, 137.86, 139.39, 139.62, 139.64, 139.70, 139.77, 140.05, 140.39, 142.92, 143.05, 143.84, 144.02, 144.04, 144.07, 144.10, 144.20, 144.22, 144.28, 144.38, 145.58, 145.65, 145.68, 146.39, 147.03, 147.07, 147.13, 147.18, 147.77, 148.00, 148.02, 148.09, 148.20, 148.24, 148.34, 148.65, 148.69, 148.73, 148.75, 150.59, 151.04, 151.26, 151.63, 151.78, 151.95, 152.05, 152.43, 152.49, 153.11, 153.33, 153.68, 154.83, 156.28, 156.39, 156.45, 156.97, 157.24, 158.37; APCI–HRMS (−): *m*/*z* calcd for $C_{87}H_{30}OSi$ ($M-H^+$),1117.1993; found, 1117.1988.

### 3.5. Synthesis of tetraphenyl-{(2-propylamino)(dimethyl)silylmethyl}-1-hydro[60]fullerene $C_{60}(C_6H_5)_4[CH_2SiMe_2NH^iPr]$ (4)

To the $CH_2Cl_2$ solution of **1c** (50 mg, 0.043 mmol) was added a suspension of $AlCl_3$ (37.0 mg, 0.276 mmol) in 5 mL $CH_2Cl_2$. After stirring at room temperature for 1 h, $^i$PrNH$_2$ (1.08 mmol, 64.0 mg) was added, and the mixture was stirred for 1 h. The concentrated residue was precipitated with MeCN. Purification with a silica gel column by eluting with $CS_2$/toluene gave **4** (44 mg, 88% yield). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 0.06–0.08 (m, 4H, Si$CH_3$), 0.18 (s, 1H, Si$CH_3$), 0.21 (s, 1H, Si$CH_3$), 0.88–1.04 (m, 6H, $CH_3$), 1.79–2.10 (m, 2H, $CH_2$), 3.78–3.91 (m, 1H, C*H*), 4.95, 5.12, 5.14 (s, 1H, $C_{60}H$, three signals due to isomers), 7.10–7.51 (m, 12H, Ar–*H*), 7.61–7.64 (m, 1H, Ar–*H*), 7.77–7.88 (m, 4H, Ar–*H*), 7.98–8.00 (m, 1H, Ar–*H*); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 0.92, 1.00, 1.04, 1.10, 1.26, 2.72, 25.70, 25.77, 25.80, 25.94, 29.04, 52.27, 52.92, 54.29, 58.70, 58.92, 59.06, 59.15, 59.21, 60.83, 61.21, 61.32, 62.31, 62.85, 65.36, 65.49, 65.55, 127.30, 1127.39, 127.55, 127.72, 127.78, 127.85, 127.93, 127.97, 128.04, 128.08, 128.29, 128.34, 128.42, 128.77, 128.85, 129.01, 129.08, 129.15, 129.19, 129.22, 129.38, 139.73, 140.05, 140.12, 140.16, 140.43, 142.95, 143.63, 144.05, 144.12, 144.14, 144.20, 144.24, 144.26, 144.28, 144.36, 144.43, 144.44, 144.49, 144.59, 144.66, 144.76, 144.86, 145.39, 145.49, 145.57, 145.60, 145.77, 145.87, 145.90, 145.98, 146.13, 146.17, 146.24, 146.32, 146.63, 146.77, 147.12, 147.25, 147.36, 147.42, 147.74, 147.88, 147.96, 147.99, 148.21, 148.30, 148.33, 148.36, 148.43, 148.52, 148.55, 148.58, 148.65, 148.85, 148.90, 148.94, 149.00, 149.10, 149.37, 150.64, 151.16, 151.50, 151.86, 152.07, 152.21, 152.28, 152.62, 152.67, 153.58, 153.92, 154.29, 156.19, 156.71, 156.82, 157.26, 157.33, 159.18; APCI–HRMS (−): *m*/*z* calcd for $C_{90}H_{37}SiN$ ($M^-$), 1159.2695; found, 1159.2742.

### 3.6. Synthesis of 1,9-methano-6,12,15,18-tetraphenyl[60]fullerene, $C_{60}(C_6H_5)_4(CH_2)$ (5)

To the suspension of **1c** (20 mg, 0.017 mmol) and $CuCl_2$ (13.9 mg, 0.103 mmol) in *ortho*-dichlorobenzene (3 mL) was added a THF solution of *t*-BuOK (26 μL, 0.026 mmol, 1 M). After stirring at 140 °C for 19 h, the mixture was stirred further at 160 °C for 69 h. The concentrated residue was purified with a silica gel column by eluting with $CS_2$ to give compound **5** (10 mg, 58% yield, 99% purity by HPLC). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 3.44 (s, 2H, $CH_2$), 7.27–7.36 (m, 12H, Ar–*H*), 7.62 (d, *J*=6 Hz, 4H, Ar–*H*), 7.78 (d, *J*=6 Hz, 4H, Ar–*H*); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 33.33, 51.72, 57.21, 59.29, 127.48, 127.68, 127.84, 128.31, 128.58, 128.92, 128.97, 139.31, 139.86, 143.26, 143.91, 144.05, 144.08, 144.48, 144.96, 145.26, 145.33, 145.56, 146.72, 146.85, 146.87, 147.15, 147.24, 147.34, 147.59, 147.79, 148.16, 148.89, 149.12, 151.06, 151.09, 155.06; APCI–HRMS (−): *m*/*z* calcd for $C_{85}H_{22}$ ($M^-$), 1042.1722; found, 1042.1715.

### 3.7. Electrochemical properties of compound 2a

Cyclic voltammetry (CV) was performed using HOKUTO DENKO HZ-5000 voltammetric analyzer. Measurements were carried out in a one-compartment cell under Ar gas, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and an $Ag/Ag^+$ reference electrode. Measurements were performed in THF solution containing tetrabutylammonium perchlorate (0.1 M) as a supporting electrolyte at 25 °C with a scan rate of 0.1 V/s. All potentials were corrected against $Fc/Fc^+$.

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### Supplementary data

Supplementary data includes CIF files for **1d**, **2a**, and **5**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.09.125.

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10. Regioselectivity is controlled by the first addend, which makes peripheral carbon atoms more reactive with structural distortion to determine the positions for the second, third, fourth, and fifth organic addends.
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