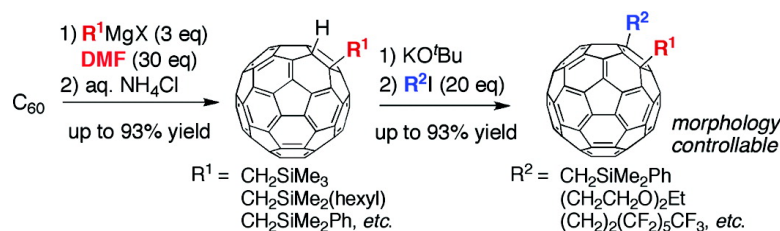


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## Regioselective Synthesis of 1,4-Di(organo)[60]fullerenes through DMF-assisted Monoaddition of Silylmethyl Grignard Reagents and Subsequent Alkylation Reaction

Yutaka Matsuo,<sup>\*,†</sup> Akihiko Iwashita,<sup>‡</sup> Yoko Abe,<sup>†</sup> Chang-Zhi Li,<sup>†</sup> Keiko Matsuo,<sup>‡</sup> Masahiko Hashiguchi,<sup>†</sup> and Eiichi Nakamura<sup>\*,†,‡</sup>

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**Abstract:** Monoaddition of Grignard reagents, in particular tri(organo)silylmethylmagnesium chlorides, to [60]fullerene took place smoothly in the presence of dimethylformamide to produce (organo)(hydro)[60]fullerenes,  $C_{60}R^1H$ , in good yield (up to 93% isolated yield). The hydrofullerene was then deprotonated to generate the corresponding anion,  $C_{60}R^1^-$ , which was then alkylated to obtain  $58\pi$ -electron di(organo)[60]fullerenes,  $C_{60}R^1R^2$ , in good to high yield (up to 93% overall yield). The two-step methodology provides a wide variety of 1,4-di(organo)[60] fullerenes bearing the same or different organic addends on the [60] fullerene core. By changing the addends, one can control the chemical and physical properties of the compounds at the molecular and bulk levels.

### Introduction

The  $58\pi$ -electron [60]fullerene derivatives bearing two organic groups in a 1,2-relative regiochemistry such as PCBM (phenyl C61-butyric acid methyl ester)<sup>1</sup> and fulleropyrrolidines<sup>2</sup> (Chart 1) have found widespread use as n-type organic conductor materials in organic field effect transistor<sup>3</sup> and organic photovoltaic (OPV) applications.<sup>4</sup> This is not only because these molecules retain much of the unique and useful characters of pristine [60]fullerene, such as high electron affinity,<sup>5</sup> small reorganization energy<sup>6</sup> and good charge transporting ability,<sup>7</sup> but also because they possess useful properties unavailable in

the pristine fullerene. The organic addends permit control of the solubility of the materials in a variety of solvents, the molecular ordering in the solid state,<sup>8</sup> and the electronic properties of the fullerene core. The repertoire of the  $58\pi$ -electron fullerene derivatives, however, remains far from ideal. The syntheses of PCBM and fulleropyrrolidines rely on cycloaddition reactions that do not stop after the monoadduct stage and produce multiaddition products that need to be removed by purification.

The 1,4-di(organo)fullerenes shown in Chart 1 are another class of  $58\pi$ -electron fullerene derivatives that deserve attention as potentially more attractive n-type materials than the 1,2-di(organo)fullerenes, such as PCBM and fulleropyrrolidines, because of the much wider structural variations offered. A variety of  $R^1$  and  $R^2$  can be installed to make symmetrical and unsymmetrical derivatives at will. In reality, however, they have never received proper attention perhaps because of the synthetic difficulties. The one-step synthesis of 1,4-bis(trimethylsilylmethyl)[60]fullerene ( $R^1 = R^2 = CH_2SiMe_3$ )<sup>9</sup> starting with  $Me_3SiCH_2MgCl$  has been known for a long time; however, it has given only poor to moderate yields,<sup>9a,10</sup> and the double alkylation of the fullerene dianion  $C_{60}^{2-}$  with a benzylic halide is also not high yielding.<sup>11</sup> Although many monoaddition reactions of the alkyl, aryl, or alkynyl groups,<sup>12–17</sup>

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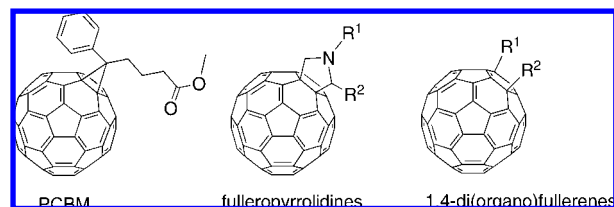
have been reported, systematic investigations for the two-step synthesis of 1,4-di(organo)fullerenes have been seldom performed.<sup>9a,11e,15b,d,e</sup>

Herein we describe how one can achieve excellent yields of the monoaddition of a Grignard reagent to [60]fullerene in the presence of a small amount of dimethylformamide (DMF; 3–10 equiv to the Grignard reagent) and can obtain the 1,4-di(organo)[60]fullerenes in good to excellent overall yield by alkylation of the resulting mono(organo)[60]fullerenes anion with an alkyl halide. The initial addition selectively afforded the monoaddition product, and the subsequent alkylation reaction showed excellent regioselectivity for the location of the organic addends. Using this methodology, we have synthesized a variety of bis(triorganosilylmethyl)fullerenes and examined the chemical and physical properties of the molecules and their bulk materials properties such as solubility, morphology and the LUMO levels through changing the R groups on the side chains—the data so far available for the PCBM and fulleropyrrolidine derivatives.

## Results and Discussion

**Efficient Nucleophilic Addition of DMF-Modified Grignard Reagent to [60]Fullerene to Obtain Mono(organo)[60]fullerenes.** We first examined the monoaddition of a trimethylsilylmethyl Grignard reagent, which has previously been shown to add selectively twice to [60]fullerene in the presence of molecular oxygen.<sup>10</sup> In the absence of oxygen, however, the trimethylsilylmethyl Grignard reagent (3 equiv, in THF) in 1,2-dichlorobenzene produced the desired monoadduct in only 10% yield (HPLC analysis) and gave back most of the [60]fullerene (Table 1, entry 1). This observation is in accordance with what has been known for Grignard reagents in general. We then examined the effects of polar additives. Addition of the large excess of pyridine, which was previously found to be useful for promotion of organocopper addition,<sup>18</sup> improved the yield to some extent (entry 2). We then examined the polar aprotic solvents, DMSO and DMF (30 equiv), and found that they significantly improved

**Chart 1.** [60]Fullerene Derivatives Possessing 58 $\pi$ -Electron Systems



**Table 1.** Effect of the Various Polar Additives<sup>a</sup>

entry	additive (equiv)	yield %	recovery of C <sub>60</sub> %
1	none <sup>b</sup>	10	63
2	pyridine (30)	47	40
3	DMSO (30)	83	14
4	DMF (3)	47	49
5	DMF (10)	86	9
6	DMF (30)	93	7
7	DMF (100)	82	7

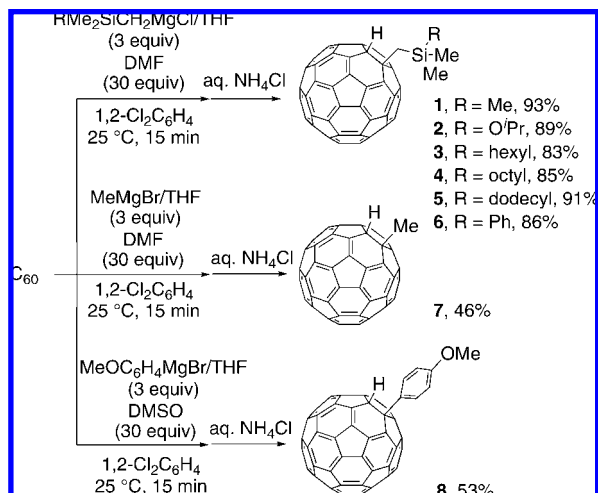
<sup>a</sup> General procedure: A THF solution of Me<sub>3</sub>SiCH<sub>2</sub>MgCl (0.592 M, 0.281 mL, 0.167 mmol) was added to a mixture of C<sub>60</sub> (40.0 mg, 0.0556 mmol) with an additive (1.67 mmol) in 1,2-dichlorobenzene (10 mL). After stirring for 10 min at 25 °C, the reaction was quenched with aqueous NH<sub>4</sub>Cl (0.1 mL) and subjected to HPLC analysis (Buckyprep column) using C<sub>60</sub>Ph<sub>5</sub>H (0.66 mM, 5  $\mu$ L) as an internal standard. <sup>b</sup> Note that this system contains some THF, originating from the Grignard reagent.

the yields (entries 3 and 6). Thus, the reaction of [60]fullerene with 3 equiv of Me<sub>3</sub>SiCH<sub>2</sub>MgCl in the presence of 3 equiv of DMF improved the yield to 47% (entry 4), 10 equiv to 86% (entry 5) and 30 equiv of DMF in 1,2-dichlorobenzene for 10 min at 25 °C to 93% yield (entry 6). In these reactions, the purple color of the solution of [60]fullerene immediately changed to dark green upon addition of Grignard reagent, suggesting that the Grignard addition is very rapid. Further addition of DMF (100 equiv) resulted in a slightly decreased yield, possibly because of a reaction with the Grignard reagent (entry 7). The present reaction condition reproducibly produced a variety of monoadducts (see the next paragraph) in up to 93% isolated yield in a short reaction time (5 to 15 min), and represents a significant improvement over the 39% isolated yield reported previously by Nagashima.<sup>9a,19</sup> The reaction was also carried out with similar efficiency on a two- to six-gram scale (Experimental Section and Supporting Information).

The utility of the silylmethyl addends was previously demonstrated for the design of new fullerene mesogens,<sup>8b,d</sup> in that the silicon atom allows the installation of a variety of organic addends on the side chain. Thus, a variety of substituted

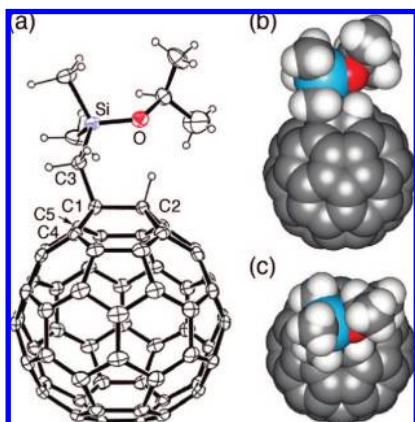
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- (19) We repeated the Nagashima's protocol a few times (using a THF suspension of C<sub>60</sub> and three portions of the trimethylsilylmethyl Grignard reagent added over 5 h), and found that the control of the reaction is very difficult. It is because fullerene was completely insoluble (as is well known) and the whole reaction mixture remained to be a suspension. Although the THF-soluble part of the reaction was quite clean and contained much of the mono-adduct (60% HPLC area ratio), the whole reaction mixture contained 23% of the mono-adduct, 26% of C<sub>60</sub>, and 27% of a dimer, (Me<sub>3</sub>SiCH<sub>2</sub>)<sub>2</sub>C<sub>60</sub>-C<sub>60</sub>(CH<sub>2</sub>SiMe<sub>3</sub>) (HPLC area ratios). See Supporting Information for the details of this control experiment.

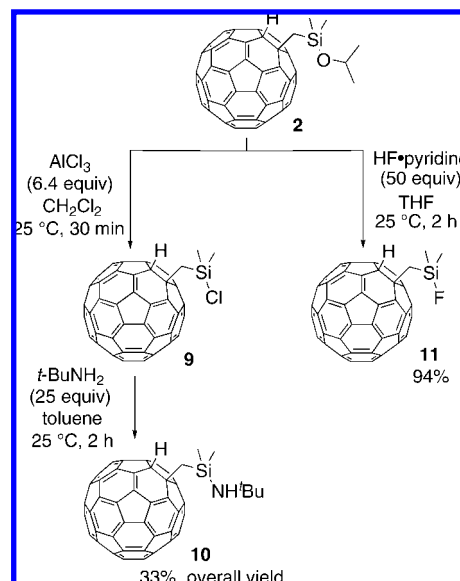
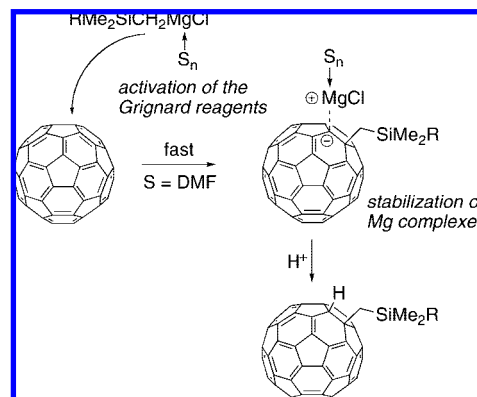
**Scheme 1.** Scope of the Polar Additive-Mediated Mono-Addition Reaction

silylmethyl Grignard reagents, (*i*-PrO)Me<sub>2</sub>SiCH<sub>2</sub>MgCl, (C<sub>6</sub>H<sub>13</sub>)Me<sub>2</sub>SiCH<sub>2</sub>MgCl, (C<sub>8</sub>H<sub>17</sub>)Me<sub>2</sub>SiCH<sub>2</sub>MgCl, (C<sub>12</sub>H<sub>25</sub>)Me<sub>2</sub>SiCH<sub>2</sub>MgCl, and PhMe<sub>2</sub>SiCH<sub>2</sub>MgCl were used to install adducts onto the [60]fullerene core under the DMF conditions to produce the corresponding monoadducts **2–6** in high isolated yields (Scheme 1).<sup>20</sup> The reaction of methyl, longer *n*-alkyl (data not shown), and aryl Grignard reagents also took place rapidly, giving the desired monoadducts **7** and **8** in a synthetically viable yield of about 50%. In the synthesis of **8**, DMSO gave slightly better yield than DMF. Without DMF or DMSO, these reactions were too slow to be practically useful.

Characterization of these monoadducts was achieved by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, high-resolution mass spectrometry (HRMS), and combustion analysis. In the <sup>1</sup>H NMR spectra, the signal due to the hydrogen atom directly connected to the fullerene core appeared at around 6.5 ppm for all compounds. The <sup>13</sup>C NMR spectrum exhibited 30 signals for the C<sub>60</sub> moieties in the aromatic region (135–158 ppm, quaternary carbons). X-ray crystallographic analysis was performed for the isopropoxy compound **2** using single crystals obtained by slow evaporation of a CS<sub>2</sub> solution (Figure 1). One interesting feature of the structure of **2** is the direction of the isopropoxy group on



**Figure 1.** Crystal structure of **2**. (a) ORTEP diagrams with 30% probability level ellipsoids. (b) CPK models. Selected bond lengths: C1–C2 = 1.581(4), C1–C4 = 1.531(4), C1–C5 = 1.532(4), C1–C3 = 1.574(4), C3–Si = 1.883(4), and C2⋯O = 3.18 Å. Selected angles: C2–C1–C3 = 110.0(3), C3–C1–C4 = 112.5(3), C3–C1–C5 = 111.3(2), and C3–Si–O = 104.81(14)°.

**Scheme 2.** Nucleophilic Substitution Reactions of the Isopropoxy Group**Scheme 3.** Coordination of DMF to Magnesium Atom

the silylmethyl group. The oxygen atom of the isopropoxy group is located close to the hydrogen atom on the fullerene core as if there is a hydrogen bond between the oxygen and the acidic hydrogen atom (vide infra) attached to the fullerene core. The distance between the oxygen atom and the C2 carbon atom is 3.18 Å, which is short enough to expect the formation of a C–H⋯O hydrogen bond.<sup>21</sup> Chemical shift of the C<sub>60</sub>-H signal in the <sup>1</sup>H NMR spectrum ( $\delta$  6.82) supports this consideration. The value is obviously lower field shifted than other silylmethylfullerenes **1** and **3–6** ( $\delta$  6.39–6.45) and the methylfullerene **6** ( $\delta$  6.40).

The mono(silylmethyl)[60]fullerenes provide interesting opportunities for derivatization to a variety of compounds, as reported by Nagashima et al.<sup>9b</sup> For instance, resubstitution of the isopropoxy group of **2** by a chlorine group through treatment with AlCl<sub>3</sub> provided a silyl chloride **9**,<sup>9b,22</sup> which can be converted to a silyl amide by treatment with *t*-BuNH<sub>2</sub> in 33%

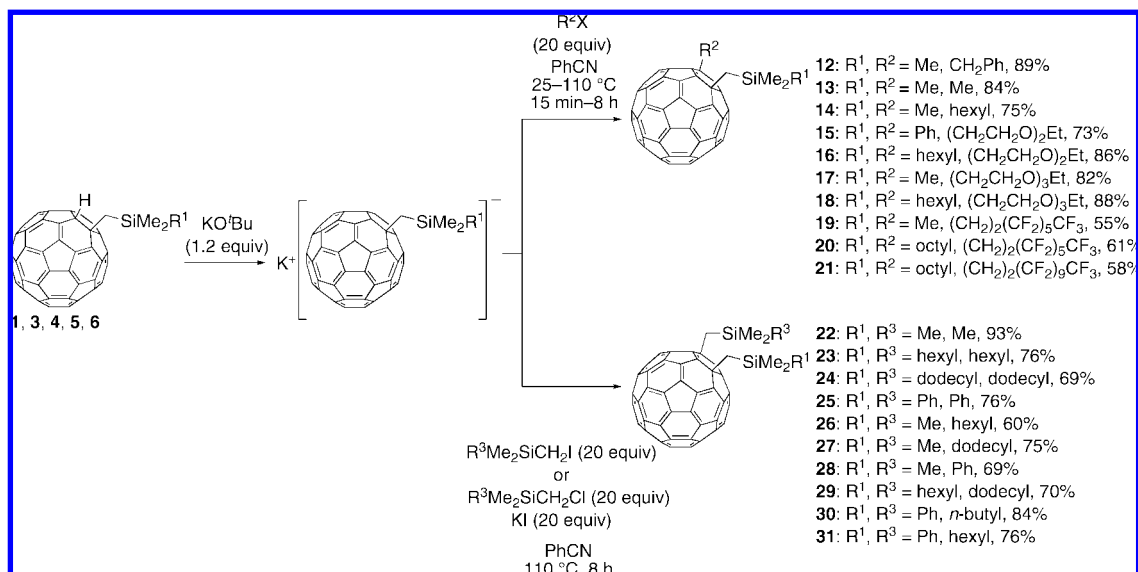
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(22) Note that products strongly depend on the solvent. The reaction of **2** with AlCl<sub>3</sub> in toluene afforded a double hydroarylated product, C<sub>60</sub>(CH<sub>2</sub>SiMe<sub>2</sub>O*i*-Pr)(C<sub>6</sub>H<sub>4</sub>Me)<sub>2</sub>H<sub>2</sub>. See ref 16a.



Scheme 4. Synthesis of Various Di(organo)[60]fullerenes



total yield from **2** (Scheme 2) and to other silicon compounds.<sup>23</sup> Fluorosilane **11** was obtained, as an air-stable compound in 94% isolated yield, directly from **2** by treatment with HF·pyridine.

Given the fact that even 1 equiv of DMF is quite effective and the effect saturated after addition of more than 10 equiv, that is, 3.3 equiv to the Grignard reagent, (Table 1, entries 4–7), we can conclude that the effect of added DMF is less likely to be the result of the polarity of DMF but is more likely to be a consequence of coordination to the magnesium atom (Scheme 3). One probable effect of DMF is the enhancement of the nucleophilicity of the Grignard reagent.<sup>24,25</sup> We can also speculate that DMF stabilizes the magnesium intermediate and protects it from a second addition of nucleophiles to monoalkyl-[60]fullerene anions.<sup>26</sup> Further discussion of the DMF effect needs more detailed mechanistic studies.

**Conversion of Mono(organo)[60]fullerenes to Di(organo)-[60]fullerenes.** The mono(silylmethyl) adducts **1–6** serve as a platform for the synthesis of a library of fullerene derivatives bearing diverse organic groups. The hydrogen atom attached to the fullerene core can be readily deprotonated with KOtBu in benzonitrile at room temperature, and the resulting anion can be alkylated with an alkyl halide (Scheme 4).<sup>27–29</sup> Upon base treatment, the color of the solution changed immediately from red to dark green, and gradually changed to dark red after treatment of the anion with benzyl bromide. After 15 min reaction, HPLC analysis (chart given in Supporting Information) and MS measurement indicated the formation of a di(organo)-[60]fullerene,  $\text{C}_{60}(\text{CH}_2\text{SiMe}_3)(\text{CH}_2\text{Ph})$  (**12**) in 89% yield (Table 2, entry 1). The reaction was regioselective to give exclusively

Table 2. Detailed Reaction Conditions in the Synthesis of Di-Adducts 12–31

entry	substrate	electrophile	temp/°C	product	yield/% <sup>a</sup>
1	<b>1</b>	PhCH <sub>2</sub> Br	25	<b>12</b>	89
2	<b>1</b>	MeI	25	<b>13</b>	84
3	<b>1</b>	C <sub>6</sub> H <sub>12</sub> Br	25	<b>14</b>	75
4	<b>6</b>	Et(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> I	110	<b>15</b>	73
5	<b>3</b>	Et(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> I	110	<b>16</b>	86
6	<b>1</b>	Et(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> I	110	<b>17</b>	82
7	<b>3</b>	Et(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> I	110	<b>18</b>	88
8	<b>1</b>	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>5</sub> (CH <sub>2</sub> ) <sub>2</sub> I	110	<b>19</b>	55
9	<b>4</b>	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>5</sub> (CH <sub>2</sub> ) <sub>2</sub> I	110	<b>20</b>	61
10	<b>4</b>	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>9</sub> (CH <sub>2</sub> ) <sub>2</sub> I	80	<b>21</b>	58
11	<b>1</b>	Me <sub>3</sub> SiCH <sub>2</sub> I	80	<b>22</b>	93
12	<b>3</b>	C <sub>6</sub> H <sub>13</sub> Me <sub>2</sub> SiCH <sub>2</sub> Cl <sup>b</sup>	110	<b>23</b>	76
13	<b>5</b>	C <sub>12</sub> H <sub>25</sub> Me <sub>2</sub> SiCH <sub>2</sub> Cl <sup>b</sup>	110	<b>24</b>	69
14	<b>6</b>	PhMe <sub>2</sub> SiCH <sub>2</sub> Cl <sup>b</sup>	110	<b>25</b>	76
15	<b>1</b>	C <sub>6</sub> H <sub>13</sub> Me <sub>2</sub> SiCH <sub>2</sub> Cl <sup>b</sup>	110	<b>26</b>	60
16	<b>1</b>	C <sub>12</sub> H <sub>25</sub> Me <sub>2</sub> SiCH <sub>2</sub> Cl <sup>b</sup>	110	<b>27</b>	75
17	<b>1</b>	PhMe <sub>2</sub> SiCH <sub>2</sub> Cl <sup>b</sup>	110	<b>28</b>	69
18	<b>3</b>	C <sub>12</sub> H <sub>25</sub> Me <sub>2</sub> SiCH <sub>2</sub> Cl <sup>b</sup>	110	<b>29</b>	70
19	<b>6</b>	C <sub>4</sub> H <sub>9</sub> Me <sub>2</sub> SiCH <sub>2</sub> Cl <sup>b</sup>	110	<b>30</b>	84
20	<b>6</b>	C <sub>6</sub> H <sub>13</sub> Me <sub>2</sub> SiCH <sub>2</sub> Cl <sup>b</sup>	110	<b>31</b>	76

<sup>a</sup> Isolated yield. <sup>b</sup> In the presence of a stoichiometric amount of potassium iodide.

the desired 1,4-di(organo)[60]fullerenes and did not give any sizable amounts of other regioisomers.

The UV–vis spectrum of compound **12** exhibited a broad absorption at 443 nm characteristic of 1,4-adducts of [60]fullerene, rather than a sharp peak around 430 nm characteristic of substituted 1,2-dihydrofullerenes.<sup>15b,30</sup> The <sup>13</sup>C NMR spectrum of **12** showed 58 signals resulting from the 58 sp<sup>2</sup>-carbon atoms of the fullerene core in the aromatic region, reflecting the C<sub>1</sub> symmetric structure of the product. Iodomethane and 1-bromohexane also reacted with fullerene anions and slowly produced the corresponding diadducts **13** and **14** in high yield (entries 2 and 3). Heating at 80 °C was effective in accelerating the reaction in the case of unreactive 1-bromohexane. Similarly, a variety of diadducts **15** to **21** were synthesized by the reaction

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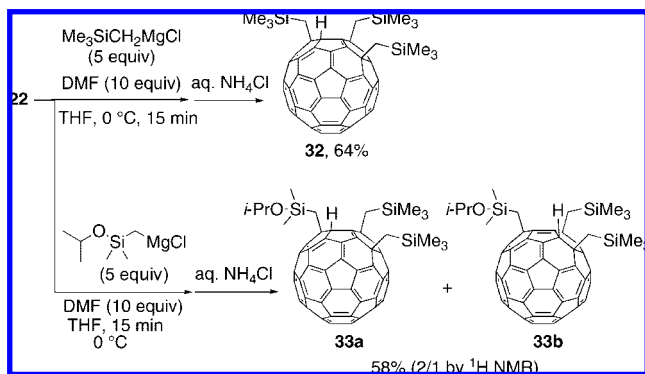
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## Scheme 5. Synthesis of Tri(organo)[60]fullerenes



with diethoxyethylidide, triethoxyethylidide, tridecafluoro-8-iodooctane, and nonadecafluoro-11-iodoundecane as shown in Table 2 (entries 4–10). The yields of the perfluorinated derivatives were moderate because of side product formation. One side product identified by HPLC is a dimer  $\text{C}_{60}\text{R}-\text{C}_{60}\text{R}$ . The dimer formation suggests the formation of a radical  $\text{C}_{60}\text{R}\cdot$  intermediate, which may have produced various other side products yet to be identified. The introduction of perfluorinated carbon chains can change the electronic properties of the fullerene core (vide infra).

Introduction of a trimethylsilylmethyl group needed heating at  $80\text{ }^\circ\text{C}$  for 8 h, to obtain the desired symmetrical diadduct **22** in 93% yield (entry 11). Various diadducts with two identical or different silylmethyl groups, **23** to **31**, were synthesized in a similar manner (entries 12–20). Synthetically speaking, alkyl chlorides are the preferred alkylating agents because of their ready availability. Thus, we employed dimethylalkylsilylmethyl chloride for the reaction through in situ conversion into dimethylalkylsilylmethyl iodide in the presence of potassium iodide (entries 12–20).

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for symmetric diadducts (**22**, **23**, **24**, **25**) and asymmetric diadducts (**26**, **27**, **28**, **29**, **30**, **31**) were in good agreement with  $\text{C}_s$  and  $\text{C}_1$  symmetric structures, respectively. Both types of compounds show good solubility in various organic solvents, such as toluene, THF, and chloroform. In particular, the asymmetric compounds are more readily soluble in organic solvents. For example, **25** is soluble in toluene, THF and chloroform only up to 2 wt% concentration, but **28** is soluble in these solvents to over 10 wt% concentration. The solubility of compounds is an issue of utmost importance when we consider the practical utilities of these compounds.

The di(organo)[60]fullerenes can be converted further to tri(organo)[60]fullerenes (Scheme 5). Although we previously reported the basic methodology,<sup>10,31</sup> we have now found that DMF assists the addition of the third group to obtain tris(trimethylsilylmethyl)[60]fullerene in better yields. For instance, the addition of trimethylsilylmethylmagnesium chloride to **22** took place quickly at  $0\text{ }^\circ\text{C}$  in the presence of DMF (10 equiv) to give the triadduct  $\text{C}_{60}(\text{CH}_2\text{SiMe}_3)_3\text{H}$  (**32**) in 64% yield. Reaction of the isopropyl dimethylsilylmethyl group gave  $\text{C}_{60}(\text{CH}_2\text{SiMe}_3)_2(\text{CH}_2\text{SiMe}_2\text{O}^i\text{Pr})\text{H}$  (**33**) under the same conditions.

The selective introduction of the third addend has a precedent<sup>31a</sup> and the mechanism behind such high regio-

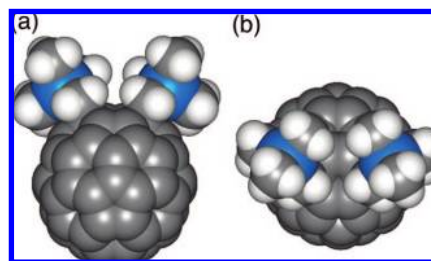


Figure 2. Crystal structure of **22**. (a) Side view of CPK model. (b) Top view of CPK model.

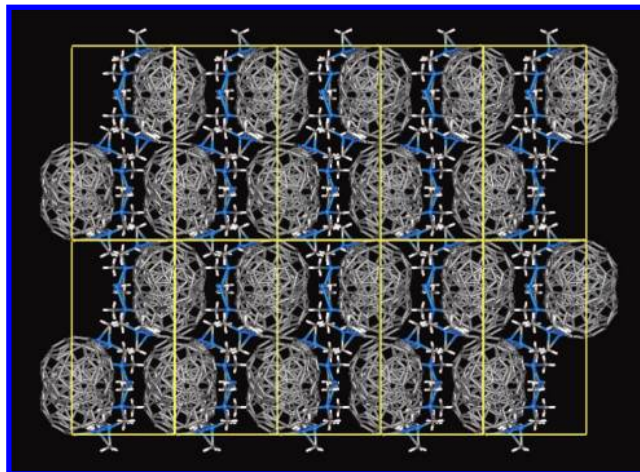


Figure 3. Crystal packing of **22**. View along the C axis. The crystal is monoclinic, space group =  $P2_1/c$  (No. 14),  $a = 10.2560(6)\text{ \AA}$ ,  $b = 19.2380(10)\text{ \AA}$ ,  $c = 19.9820(14)\text{ \AA}$ ,  $\beta = 98.016(4)^\circ$ , and  $V = 3904.0(4)\text{ \AA}^3$ .

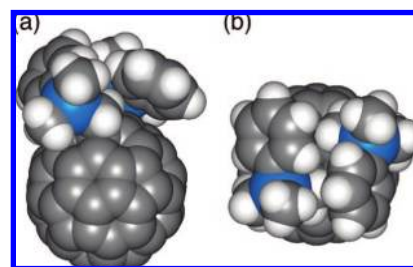


Figure 4. Crystal structure of **25**. (a) Side view of CPK model. (b) Top view of CPK model.

lectivity has been discussed in relation to the regioselectivity of the selective penta-addition of organocopper reagents to [60]fullerene.<sup>32</sup> These triadducts **33** may serve for the synthesis of pendant-type bidentate ligands<sup>33</sup> that can achieve  $\eta^5$ -fullereneindenyl<sup>34,35</sup> and silanoxide- coordination to a single metal atom (Cf. Figure 1).

**X-Ray Crystal Structural Studies of Di(organo)[60]fullerenes.** Single crystal X-ray analysis of the di(organo)[60]fullerenes **22** and **25** was performed (Figures 2–5). Both crystals were obtained with slow diffusion of ethanol that was put on  $\text{CS}_2$  solutions of the compounds. In the crystal of **22**, two trimeth-

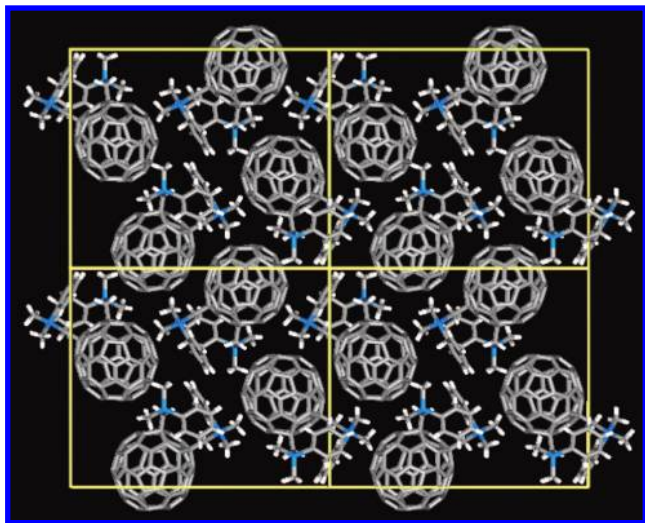
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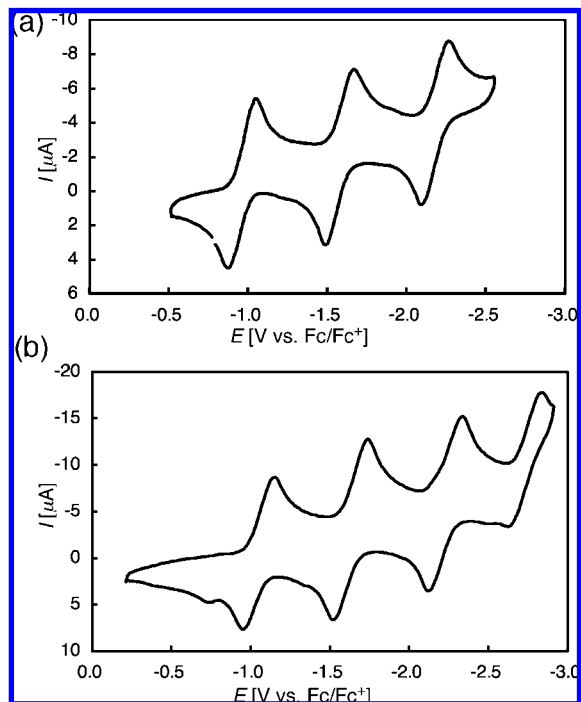


**Figure 5.** Crystal packing of **25**. View along the A axis. The crystal is monoclinic, space group =  $P2_1/n$  (No. 14),  $a = 10.3603(2)$  Å,  $b = 19.0203(4)$  Å,  $c = 22.6651(5)$  Å,  $\beta = 97.1369(11)^\circ$ , and  $V = 4431.68(16)$  Å<sup>3</sup>.

ylsilylmethyl groups are located in a 1,4-position and spatially oriented in a  $C_s$ -symmetric fashion. The packing diagram reveals a layered structure containing sheet structures composed of the [60]fullerene cores. The close packing of fullerene molecules within the layer suggests potential application in thin-film devices such as a [60]fullerene-based organic field effect transistor.<sup>36</sup> In the crystal of **25**, on the other hand, the two dimethylphenylsilylmethyl groups point in opposite directions to minimize the molecular volume. In the crystal packing of this compound, no apparent layered structure was observed. Such structural information will contribute to the design of crystal and liquid crystal structures,<sup>8</sup> and the properties of the organic device applications containing these compounds. We note in passing that the crystals did not contain any solvent molecules.

**Substituent Effects on the Electronic Properties of the Fullerenes.** We noted above that the solubility of the compounds can be modified by changing the substituents. An equally important question is whether or not we can change the electronic properties of the compounds by changing the substituents. It was unclear whether or not the substituents attached through the silylmethyl linkage would exert much of an electronic effect on the fullerene core, and hence we examined cyclic voltammograms in THF at room temperature. The cyclic voltammograms of **21** and **25** are shown in Figure 6a and b, respectively, as typical examples. The voltammograms exhibited three reversible waves on reduction, which can be assigned to the formation of their monoanion, dianion, and trianion, respectively. All diadducts listed in Table 2 are electrochemically stable up to the three-electron reduction, while other 1,2- and 1,4-diadducts in the literatures is known to show multiple reductions.<sup>11c,e</sup> The values of their reversible half-wave potentials ( $E_{1/2}^{\text{red}1}$ ,  $E_{1/2}^{\text{red}2}$ , and  $E_{1/2}^{\text{red}3}$ ) and estimated LUMO levels<sup>37</sup>

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**Figure 6.** Electrochemical properties of the di(organo)[60] fullerenes. (a) Cyclic voltammogram of **21**. (b) Cyclic voltammogram of **25**. Measurements were performed in a 0.5 mM (for **21**) and 0.4 mM (for **25**) THF solution containing  $\text{Bu}_4\text{N}^+\text{ClO}_4^-$  (0.1 M) as a supporting electrolyte at 25 °C with a scan rate of 0.1  $\text{Vs}^{-1}$ .

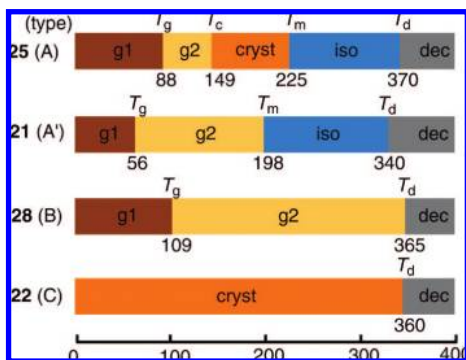
**Table 3.** Reduction Potentials for the Di(organo)[60]fullerenes and PCBM<sup>a</sup>

compound	$E_{1/2}^{\text{red}1}/\text{V}$	$E_{1/2}^{\text{red}2}/\text{V}$	$E_{1/2}^{\text{red}3}/\text{V}$	LUMO level/eV <sup>b</sup>
<b>15</b>	-1.03	-1.65	-2.28	-3.77
<b>18</b>	-1.04	-1.63	-2.23	-3.76
<b>21</b>	-0.96	-1.58	-2.17	-3.84
<b>23</b>	-1.04	-1.68	-2.33	-3.76
<b>24</b>	-1.03	-1.66	-2.29	-3.77
<b>25</b>	-1.06	-1.63	-2.23	-3.74
<b>26</b>	-1.03	-1.68	-2.32	-3.77
<b>27</b>	-1.03	-1.66	-2.30	-3.77
<b>28</b>	-1.03	-1.62	-2.22	-3.77
<b>29</b>	-1.04	-1.66	-2.29	-3.76
<b>31</b>	-1.05	-1.66	-2.28	-3.75
PCBM	-1.00	-1.59	-2.19	-3.80

<sup>a</sup> Potential in volts vs ferrocene/ferrocenium measured with cyclic voltammetry in THF containing  $\text{Bu}_4\text{N}^+\text{ClO}_4^-$  (0.1 M) as a supporting electrolyte. Glassy-carbon, platinum wire, and Ag/Ag<sup>+</sup> electrodes were used as working, counter, and reference electrodes, respectively.  
<sup>b</sup> Values from the vacuum level were estimated using the following equation; LUMO level =  $-(E_{1/2}^{\text{red}1} + 4.8)$ .<sup>37</sup>

of diadducts with PCBM as a reference are listed in Table 3. All compounds show the first reduction potentials being slightly more negative than -1.00 V (up to -1.06 V for **25**), except that the fluoros alkyl chain functionalized **21** has an  $E_{1/2}^{\text{red}1}$  of -0.96 V. This difference of  $E_{1/2}^{\text{red}1}$  indicates that attachment of  $\text{CF}_3(\text{CF}_2)_5$  and  $\text{CF}_3(\text{CF}_2)_9$  to the fullerene  $\text{sp}^3$ -carbon atom lower the LUMO level from the average value of ca. -3.74 eV (e.g., **25**) to -3.84 eV (**21**) in spite of the fact that the fluoros groups are connected by a long  $\text{CH}_2\text{SiCH}_2\text{CH}_2$  unit to the fullerene core. We consider that the inductive effect of the fluoros groups is so large that the presence of the three  $\text{sp}^3$ -hybridized carbon atoms between the fluoros group and the fullerene  $\pi$ -system still permits the transmission of the inductive effect.





**Figure 7.** Thermal properties of diadducts.  $T_g$ : glass transition temperature.  $T_c$ : crystallization temperature.  $T_m$ : melting temperature.  $T_d$ : decomposition temperature. Parentheses denote the types of the morphology, for instance, A', no  $T_c$ ; B, no  $T_m$ ; C, crystal until decomposition. The original data are tabulated in Supporting Information.

**Temperature-Dependent Morphology Change of Di(organo)-[60]fullerenes.** The bulk properties of the fullerene diadducts and their temperature dependence are the important factors to be considered for their application to organic electronics. We therefore carried out differential scanning calorimetry (DSC), thermogravimetry-differential thermal analysis (TG-DTA), and powder X-ray diffraction analysis (XRD) of some representative compounds. All analyses were performed using samples that were reprecipitated by addition of methanol into toluene or chloroform solution of the compounds. The results of DSC analysis and TG-DTA are summarized in Figure 7 (all data given in Table S1, Supporting Information). Thermal stability is the first important issue, and all compounds listed in Figure 7 and Table S1 (Supporting Information) were thermally stable until around 350 °C, a temperature suitable for organic electronics applications. Their glass transition temperatures ranged from 7 to 109 °C.

Another important aspect is the morphology, which we can control by careful choice of the two side chains attached to the fullerene core. The observed crystallization and melting behaviors of the compounds can be categorized into three kinds, A-C in Figure 7. One class is quasi-crystalline compounds (i.e., **21**, **23**, **24**, **25**, **26**, and **27**). On the XRD analysis, all compounds in this category showed a crystalline pattern at 20 °C and then only a halo pattern on reaching the melting temperature. This category is divided into two types, compounds that show crystallization peaks on the DSC analysis before melting temperature (i.e., **23**, **25**, and **26**; type A) and compounds that do not show such crystallization behavior during the heating process (i.e., **21**, **24**, and **27**; type A'), depending on the length of their side chains. The former compounds have rather shorter alkyl chains (i.e., the Me, C<sub>6</sub>H<sub>13</sub>, and Ph groups), and thus exhibit relatively high melting temperatures of over 200 °C. The latter compounds bear long alkyl chains and melt at lower temperature before crystallization.

The compounds categorized into type A thus show crystallization and melting during the heating process, but do not exhibit recrystallization during the cooling process. For example, compound **25** showed one exothermic peak due to crystallization at 149 °C on the first heating run. An optical microscopic analysis indicated that this sample contains both amorphous solid and microcrystals at room temperature (data not shown) and that the amorphous part changed to the crystalline state on heating. Then this compound displayed an endothermic peak due to melting at 225 °C also on the first heating. In the cooling

process, no apparent peak was detected. These results indicate that the amorphous form of the compound was retained throughout the cooling process to afford a noncrystalline solid at low temperature. For this class of compounds, we can therefore obtain both crystalline and noncrystalline solids by changing the thermal processing procedure.

The second class consists noncrystalline compounds (i.e., **28**, **30**, and **31**; type B; for these, only a halo pattern was observed on the XRD analysis, see Supporting Information), which do not show any crystallization tendency under any of the conditions that we examined. It is noteworthy that these compounds bear both aromatic and aliphatic substituents on their two side chains, which could give them an amorphous nature.

The third class is a crystalline compound (i.e., **22**, type C) that has a symmetric structure having the same short side chain (i.e., Me groups). The dimethyl compound is just crystalline, and it did not show any transition until its decomposition at 360 °C. This preliminary investigation of the structure/morphology relationship provides useful pieces of basic information for the design of materials for thin-film-based organic electronic devices.

## Conclusion

In conclusion, we have developed a simple and quick method for the synthesis of a variety of mono(organo)[60]fullerenes, C<sub>60</sub>R<sup>1</sup>H, which can then be converted selectively to 1,4-di(organo)[60]fullerenes, C<sub>60</sub>R<sup>1</sup>R<sup>2</sup>. The method is particularly useful for the introduction of silylmethyl groups, which can bear a variety of organic groups on the silicon atom. The use of DMF allows the first monoaddition to take place selectively in excellent yield, making this first synthetic step simple and effective. The second step includes alkylation with an alkyl halide, which takes place regioselectively to give a 1,4-diadduct as the exclusive product. Overall, the synthesis requires simple starting materials, Grignard reagents, alkyl halides, DMF and solvents, dichlorobenzene and benzonitrile. The synthesis is regioselective enough not to require extensive purification procedures. This is an advantage over the synthesis of the well-known PCBM family of compounds, which requires removal of multiple adducts.

The presence of the silicon group in the side chain is the key feature of the diorgano compounds reported here, because we can readily install functional groups on the silicon atom either after the addition (Scheme 1) or before the addition (various examples in Tables 1 and 2). This flexibility in the synthesis allowed us to investigate the effects of the organic addends on the solubility, the stability, the electronic properties and the morphologies that are important in electronics applications of these compounds. Thus, the high solubility of some compounds is ideal for device fabrication using the wet process. The tuning of the LUMO level should also be useful because fullerene molecules are used widely as electron transporting materials in OPV applications. The diverse thermal behaviors of the diadducts as investigated by DSC, TG-DTA, XRD, and X-ray crystallographic analyses suggest that the bulk morphology of these compounds can be modified by the proper choice of substituents.

We have carried out some preliminary studies on the electronic properties of the compounds. For instance, the electron mobility of **25** as an amorphous thin film has an acceptable value of ca.  $1 \times 10^{-4}$ , in comparison with that of PCBM ( $5 \times$



$10^{-5}$ ) under the same measurement method (SCLC,<sup>38</sup> space charge limited current). With these encouraging data combined with the versatility of the present synthetic methodology in hand, we are currently studying the potential of the compounds in organic electronics applications and conducting mechanistic studies so that we can understand the effect of DMF to improve the reaction further.

## Experimental Section

**General Considerations.** All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk technique or a glovebox 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  $\times$  250 mm). Preparative HPLC was performed on a Buckyprep column (20 mm ID  $\times$  250 mm) using toluene/2-isopropanol (10/0 - 4/6) as eluent (flow rate 5–15 mL/min, detected at 350 nm with an UV spectrophotometric detector, Shimadzu SPD-6A) and an RP-FULLERENE column (Nomura Chemical, 20 mm ID  $\times$  250 mm) using toluene/acetonitrile (7/3 - 4/6) as eluent (flow rate 5–12 mL/min, detected at 350 nm with an UV spectrophotometric detector, Shimadzu SPD-6A). Flash silica gel column chromatography was performed on silica gel 60N (Kanto Chemical, spherical and neutral, 140–325 mesh) Gel permeation column chromatography was performed on a Japan Analytical Industry LC-9201 (eluent: toluene) with JAIGEL 2H and 3H polystyrene column. NMR spectra were measured with a JEOL EX-400 (400 MHz) or a JEOL ECA-500 (500 MHz) spectrometer. Spectra are reported in parts per million from internal tetramethylsilane ( $\delta$  0.00 ppm) for <sup>1</sup>H NMR, from solvent carbon (e.g.,  $\delta$  77.00 ppm for chloroform) for <sup>13</sup>C NMR. High-resolution mass spectra were measured by APCI using a time-of-flight mass analyzer on a JEOL JMS-T100LC (AccuTOF) spectrometer.

Cyclic voltammetry (CV) was performed using HOKUTO DENKO HZ-5000 voltammetric analyzer. All 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<sup>+</sup> 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<sup>+</sup>.

Differential scanning calorimetry (DSC) was performed on a NETZSCH thermal analyzer (DSC 204/F1). Samples (~5 mg) were placed in aluminum pans and heated at 10 °C/min, under N<sub>2</sub> gas.

**Typical Example of a Large-Scale Synthesis of the Monoadduct: 1-(Dimethylphenylsilylmethyl)-1,9-dihydro(C<sub>60</sub>-I<sub>h</sub>)[5,6]fullerene, C<sub>60</sub>(CH<sub>2</sub>SiMe<sub>2</sub>Ph)H (6).** To a solution of C<sub>60</sub> (2.00 g, 2.78 mmol) in 1,2-dichlorobenzene (500 mL) containing *N,N*-dimethylformamide (6.45 mL, 83.3 mmol) was added a THF solution of PhMe<sub>2</sub>SiCH<sub>2</sub>MgCl (9.80 mL, 0.850 M, 8.33 mmol) at 25 °C. Color of the solution immediately changed from purple to dark green. After stirring for 10 min, saturated aqueous NH<sub>4</sub>Cl solution (1.0 mL) was added to terminate the reaction. The resulting dark red solution was subjected to vacuum distillation to remove 1,2-dichlorobenzene. The residue containing a small amount of 1,2-dichlorobenzene (ca. 0.5–3 mL) was dissolved in toluene (200 mL), and passed through a pad of silica gel to remove magnesium salts. The toluene solution was concentrated to obtain a solution (ca. 5–10 mL) containing the product, which was reprecipitated by addition of methanol (ca. 100–200 mL) to obtain brown powder. Purification of the product was carried out with preparative HPLC separation (Buckyprep column, eluent: toluene/2-propanol = 7/3) to obtain the title compound (1.99 g, 2.28 mmol, 82% isolated yield,

analytically pure). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  0.89 (s, 6H, SiCH<sub>3</sub>), 3.16 (s, 2H, CH<sub>2</sub>), 6.39 (s, 1H, C<sub>60</sub>H), 7.44–7.46 (m, 3H, Ph), 7.88–7.90 (m, 2H, Ph); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  -0.75 (2C, SiCH<sub>3</sub>), 38.03 (1C, CH<sub>2</sub>), 61.57 (1C, C<sub>60</sub>H), 62.23 (1C, C<sub>60</sub>CH<sub>2</sub>), 128.19 (2C, Ph), 129.68 (1C, Ph), 134.16 (2C, Ph), 134.89 (2C, C<sub>60</sub>), 136.57 (2C, C<sub>60</sub>), 138.22 (1C, Ph), 140.05 (2C, C<sub>60</sub>), 140.20 (2C, C<sub>60</sub>), 141.63 (2C, C<sub>60</sub>), 141.64 (2C, C<sub>60</sub>), 141.94 (2C, C<sub>60</sub>), 141.97 (2C, C<sub>60</sub>), 142.03 (2C, C<sub>60</sub>), 142.06 (2C, C<sub>60</sub>), 142.54 (2C+2C, C<sub>60</sub>), 143.27 (2C, C<sub>60</sub>), 144.66 (2C, C<sub>60</sub>), 144.71 (2C, C<sub>60</sub>), 145.28 (2C, C<sub>60</sub>), 145.36 (2C, C<sub>60</sub>), 145.39 (2C+2C, C<sub>60</sub>), 145.64 (2C, C<sub>60</sub>), 145.88 (2C, C<sub>60</sub>), 146.18 (2C, C<sub>60</sub>), 146.22 (2C, C<sub>60</sub>), 146.30 (2C, C<sub>60</sub>), 146.41 (2C, C<sub>60</sub>), 149.92 (2C, C<sub>60</sub>), 147.35 (1C, C<sub>60</sub>), 147.49 (1C, C<sub>60</sub>), 154.05 (2C, C<sub>60</sub>), 157.86 (2C, C<sub>60</sub>); APCI-HRMS (-): *m/z* calcd for C<sub>69</sub>H<sub>13</sub>Si (M - H<sup>+</sup>), 869.0787; found, 869.0743.

**Typical Example of Large-Scale Synthesis of the Diadduct: 1,7-Bis(dimethylphenylsilylmethyl)-1,7-dihydro(C<sub>60</sub>-I<sub>h</sub>)[5,6]fullerene, C<sub>60</sub>(CH<sub>2</sub>SiMe<sub>2</sub>Ph)<sub>2</sub> (25).** To a solution of 6 (1.02 g, 1.17 mmol) in benzonitrile was added a THF solution of KO<sup>t</sup>Bu (1.41 mL, 1.0 M, 1.41 mmol) at 25 °C. A dark green solution of potassium salt of C<sub>60</sub>(CH<sub>2</sub>SiMe<sub>2</sub>Ph)<sup>-</sup> was obtained immediately. After stirring for 10 min, PhMe<sub>2</sub>SiCH<sub>2</sub>Cl (4.23 mL, 23.4 mmol) and potassium iodide were added to the solution. Then, the reaction mixture was stirred for 17 h at 110 °C. The resulting dark red solution was treated with 1.0 mL of saturated aqueous NH<sub>4</sub>Cl solution, and then vacuum distillation was performed to remove benzonitrile. The residue containing a small amount of benzonitrile (ca. 0.5–2 mL) was dissolved in toluene (100 mL), and passed through a pad of silica gel to remove potassium salts. The toluene solution was concentrated to obtain a solution (ca. 2–5 mL) containing the product, which was reprecipitated by addition of methanol (ca. 50–100 mL) to obtain dark brown powder. Purification of the product was performed by silica gel column chromatography (eluent: CS<sub>2</sub>/hexane = 1/1 to 1/5) or preparative HPLC separation (Buckyprep column, eluent: toluene/2-propanol = 7/3) to obtain analytically pure product 25 (0.906 g, 0.889 mmol, 76% isolated yield) as black crystals. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>):  $\delta$  0.67 (s, 6H, SiCH<sub>3</sub>), 0.68 (s, 6H, SiCH<sub>3</sub>), 2.63 (d, 2H, <sup>2</sup>J = 14.6 Hz, CH<sub>2</sub>), 2.77 (d, 2H, <sup>2</sup>J = 14.9 Hz, CH<sub>2</sub>), 7.37–7.38 (m, 6H, Ph), 7.69–7.71 (m, 4H, Ph); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>):  $\delta$  -0.98 (2C, SiCH<sub>3</sub>), -0.92 (2C, SiCH<sub>3</sub>), 32.56 (2C, CH<sub>2</sub>), 55.70 (2C, C<sub>60</sub>CH<sub>2</sub>), 127.89 (4C, Ph), 129.40 (4C, Ph), 133.94 (4C, Ph), 138.14 (2C, C<sub>60</sub>), 138.18 (2C, C<sub>60</sub>), 138.54 (1C, C<sub>60</sub>), 141.56 (2C, C<sub>60</sub>), 141.80 (1C, C<sub>60</sub>), 142.21 (2C, C<sub>60</sub>), 142.39 (2C, C<sub>60</sub>), 142.53 (2C, C<sub>60</sub>), 142.72 (2C, C<sub>60</sub>), 142.97 (2C, C<sub>60</sub>), 143.10 (2C, C<sub>60</sub>), 143.30 (2C, C<sub>60</sub>), 143.46 (2C, C<sub>60</sub>), 143.83 (2C, C<sub>60</sub>), 144.08 (2C, C<sub>60</sub>), 144.11 (2C, C<sub>60</sub>), 144.32 (2C, C<sub>60</sub>), 144.56 (2C, C<sub>60</sub>), 144.67 (2C, C<sub>60</sub>), 144.74 (2C, C<sub>60</sub>), 144.93 (2C, C<sub>60</sub>), 145.29 (2C, C<sub>60</sub>), 146.65 (2C, C<sub>60</sub>), 146.80 (2C, C<sub>60</sub>), 146.96 (2C, C<sub>60</sub>), 147.04 (2C, C<sub>60</sub>), 147.22 (2C, C<sub>60</sub>), 147.74 (2C, C<sub>60</sub>), 148.40 (2C, C<sub>60</sub>), 153.24 (2C, C<sub>60</sub>), 157.33 (2C, C<sub>60</sub>); Anal. calcd for C<sub>78</sub>H<sub>26</sub>Si<sub>2</sub>: C, 91.92; H, 2.57. Found: C, 91.76; H, 2.78.

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**Supporting Information Available:** Procedure of the synthesis of all compounds in the text, procedure for the scale up synthesis of 6, HPLC data in the synthesis of 22, details for the attempted reaction in a THF suspension, DSC data of 22, 23, 25, 27 and 30, powder XRD data of 22, 23, 27, and 30, and X-ray crystallographic data of 2, 22, and 25. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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