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Photochemical Functionalization of C_{60} with Cyclosilanes and Cyclogermane

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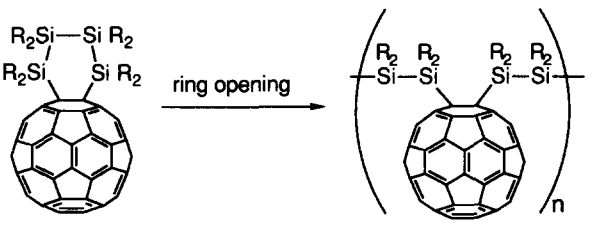
Key Words: *fullerene, disilacyclobutene, cyclotetrasilane, cyclotetragermane*
Abstract: *The photochemical reaction of 3,4-benzo-1,2-disilacyclobutene **1** with C_{60} afforded stable 1:1 adduct **2** with C_{2v} symmetry. The photochemical reaction of cyclotetrasilane **4a** with C_{60} afforded adducts **5a** and **6a**, the latter was obtained from a rearrangement of the cyclotetrasilane unit. Similarly, cyclotetragermane **4c**, gave **5c** and the rearranged product **6c**. In the case of cyclotetrasilane **4b**, only the rearranged product **6b** was obtained in high yield. The structures of all compounds were determined by spectroscopic methods, including ^{29}Si-^{1}H HMBC hetero nuclear shift correlation experiments.*

INTRODUCTION

Since the development of a gram-scale synthesis of C_{60}[1], the chemical functionalization of this new allotropic form of carbon has attracted much interest and led to fascinating results.[2-6] One promising approach in this direction is photochemical derivatizations; recently, we reported the photochemical addition of cyclic-disilanes to C_{60}.[7] Related to these results, we applied a similar conversion to other cyclosilanes (3,4-benzo-1,2-disilacyclobutene **1**, cyclotetrasilane **4a**, **4b**) and cyclogermane (cyclotetragermane **4c**). Wang and West reported that fullerene-doped polysilane displays enhanced photoconductivity.[8] Fullerene-bonded polysilane derivatives might be expected to show higher photoconductivity. Among the attractive targets are the fullerene-bonded polysilanes (Scheme 1). Fullerene-silicon derivatives bearing Si-Si and Ge-Ge rings (**5** and **6**), whose thermal or catalyzed ring opening may be expected to provide fullerene-substituted polysilanes and polygermanes.[9]

Scheme 1

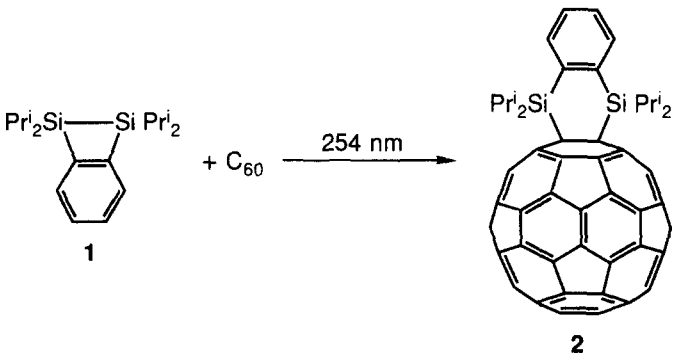


RESULTS AND DISCUSSION

Photochemical reaction of 3,4-benzo-1,1,2,2-tetraisopropyl-1,2-disilacyclobutene **1** *with* C_{60}

Irradiation of a solution of disilacyclobutene **1** and C_{60} in toluene with a low-pressure mercury lamp (254 nm) for 2h gave unidentified complex mixture (complete consumption of C_{60}). However, irradiation of a solution of disilacyclobutene **1** and C_{60} in toluene-*t*-BuOH mixed solvent with a low-pressure mercury lamp for 6h followed by purification by means of gel-permeation chromatography afforded brown adduct **2** in 14% yield (based on unreacted C_{60}, Scheme 2).

Scheme 2



1 **2**

The FAB mass spectrum of **2** exhibits one peak at *m/z* 1024-1027 ($C_{78}H_{32}Si_2$, M^+, molecular cluster ion), as well as one for C_{60} at *m/z* 720-723.

For isopropyl group with two diastereotropic methyl groups, two quartets at δ 19.94 and 20.15 as well as one doublet at 14.74 ppm appear in the ^{13}C NMR spectrum. The corresponding methyl and methine protons resonate at δ 1.14 (d, 12H, *J* = 7.4Hz), 1.40 (d, 12H, *J* = 7.4Hz) and 2.17 (sept, 4H, *J* = 7.4Hz) in the ^1H NMR spectrum.

One AA'BB' pattern appear at δ 7.58 (dd, 2H, *J* = 5.7, 3.5Hz) and 8.03 (dd, 2H, *J* = 5.7, 3.5Hz) in the ^1H NMR spectrum and two doublets at 128.81 and 136.12 ppm in the ^{13}C NMR spectrum.

The ^{13}C NMR spectrum of **2** shows 17 signals for the C_{60} skeleton, of which four correspond to two carbon atoms and 13 correspond to four carbon atoms: one at δ = 63.93 and the remainder between δ = 130 and 160 (Figure 1).

This is the appropriate number and ratio of peak intensities for a C_{60} adduct of C_{2v} symmetry.[10] The ^{13}C NMR signal at δ = 63.93 strongly supports 1, 2-addition (6-6 closed, Scheme 2).

The mechanistic pathway for the formation of **2** and effect of *t*-BuOH are not clear at the present time. The formation of adduct **2** did not occur under the irradiation of a high-pressure mercury lamp (> 300 nm), which indicate that diradical **3** formed by the initial Si-Si bond cleavage might be trapped with C_{60} to afford adduct **2** (Scheme 3).

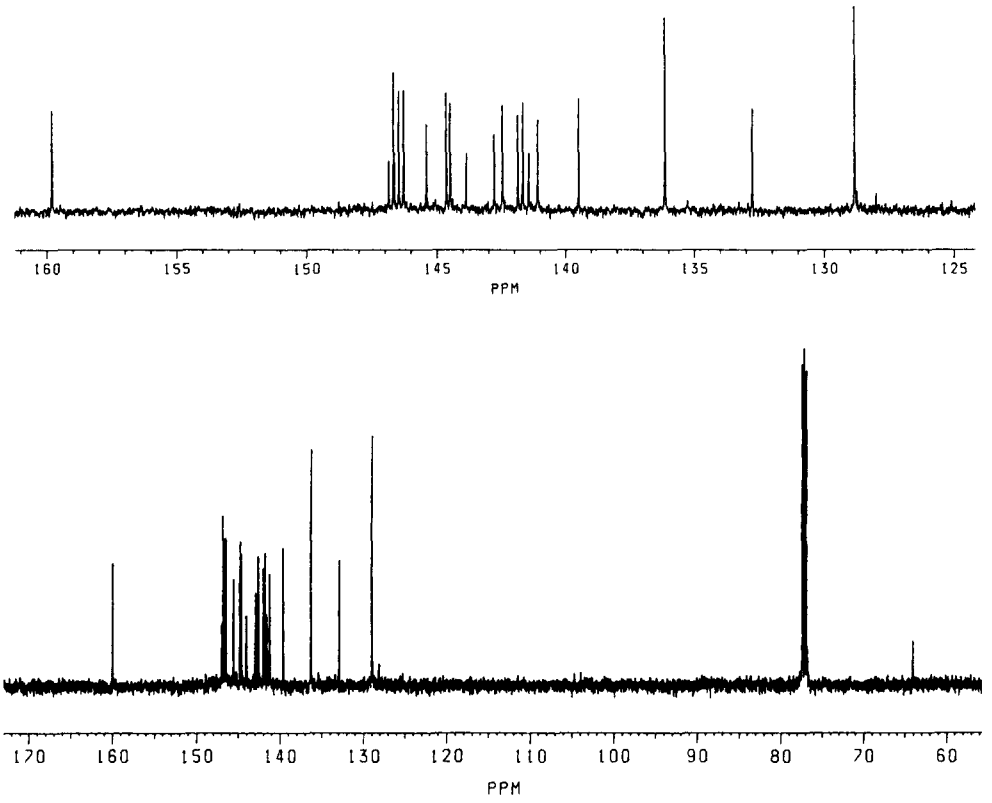
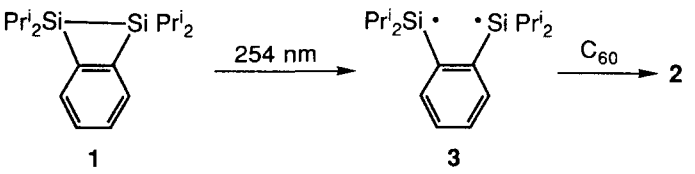


Figure 1. ^{13}C NMR spectrum (125 MHz, 1:1 CS_2-$CDCl_3$) of **2**

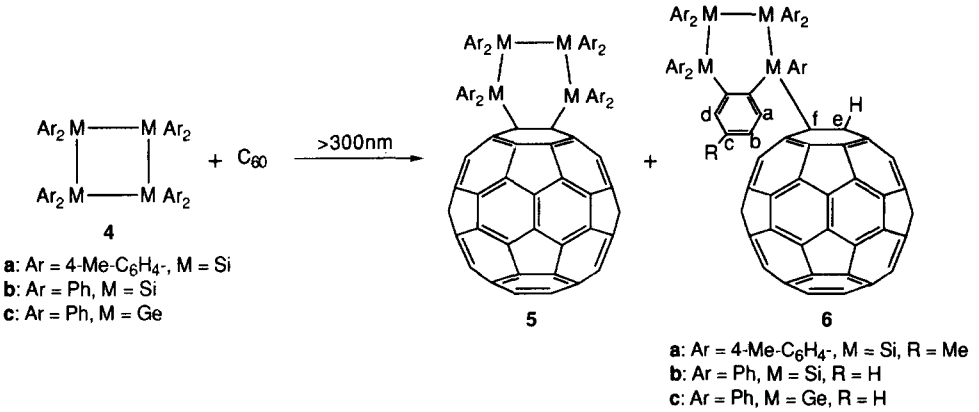
Scheme 3



*Photochemical reactions of cyclotetrasilanes **4a**, **4b** and cyclotetragermane **4c** with C_{60}*

Irradiation of a solution of cyclotetrasilane **4a** and C_{60} in toluene with a high-pressure mercury lamp ($\lambda >$ 300 nm) for 6 h under argon atmosphere, followed by purification by means of gel-permeation chromatography afforded brown adducts **5a** and **6a** in 13% and 46% yields, respectively (based on unreacted C_{60}, Scheme 4). Under identical conditions, only **6b** was obtained from **4b** in 87 % yield.

Scheme 4



4

a: Ar = 4-Me-C_6H_4-, M = Si
b: Ar = Ph, M = Si
c: Ar = Ph, M = Ge

5

6

a: Ar = 4-Me-C_6H_4-, M = Si, R = Me
b: Ar = Ph, M = Si, R = H
c: Ar = Ph, M = Ge, R = H

The FAB mass spectrum of **5a** exhibits one peak at *m/z* 1560-1563 ($C_{116}H_{56}Si_4$, M^+, molecular cluster ion), as well as one for C_{60} at *m/z* 720-723.

The ^{13}C NMR spectrum of **5a** displays 38 signals for all quaternary carbon. Of the 38, one fullerene carbon atom resonates at 62.18 ppm. The signals of all other carbons appear in the region between δ 125-165 ppm. The ^1H NMR spectrum of **5a** displays 4 methyl signals and 4 pairs of AB quartets, supporting *Cs* symmetry for the molecule. The ^{29}Si NMR spectrum of **5a** shows two peaks at -22.25 and -11.34 ppm which are assigned to the silicon atoms of **5a**.

Symmetry arguments support the following possibilities: (i) a 5,6-ring junction or 1,4-addition to the C_{60} with ring inversion (in the case of a 5,6-ring junction or 1,4-addition on the C_{60} with frozen conformer; observation of 60 signals for C_{60} carbon would have to be expected) (ii) a 6-6-ring junction on the C_{60} with a frozen conformer (no ring inversion).[7a] To obtain further information concerning the structure of **5a**, ^1H NMR measurement was carried out at a variable temperature. A chemical shift change of the *p*-tolyl groups, reflecting a conformational change of the molecule, was observed (Figure 2).[11] From these findings, a 6, 6-ring junction on the C_{60} with a frozen conformer is most probable for **5a**.

The FAB mass spectrum of **6a** exhibits one peak at *m/z* 1560-1563 ($C_{116}H_{56}Si_4$, M^+, molecular cluster ion), as well as one for C_{60} at *m/z* 720-723.

The ^{13}C NMR spectrum of **6a** displays 64 signals for all quaternary carbon which indicates the absence of any symmetry element in this molecule. Of the 64, one fullerene carbon atom resonates at 60.35 ppm. The signals of all other carbons appear in the region between 125-160 ppm.

The partial structure of the fragment annulated to the C_{60} moiety derives from the NMR spectroscopic properties for **6a**: For *one 4-methyl-o-phenylene group*, three doublets at δ 129.24 (C^b), 139.92 (C^a), and 141.36 (C^d) appear in the ^{13}C NMR spectrum. As evidenced by homo- (^1H-^1H) and hetero-nuclear (^1H-^{13}C) shift correlation (COSY) experiments, the corresponding methine protons resonate at 7.56 (H^b), 9.13 (H^a) and 7.66 (H^d) ppm, and one methyl signal appears in the ^1H NMR spectrum.

The other *seven 4-Me-C_6H_4- groups* give rise to 14 doublet in the ^{13}C NMR spectrum, 13 doublets (overlapping might obscure one signal) and 7 methyl signals in the ^1H NMR spectrum.

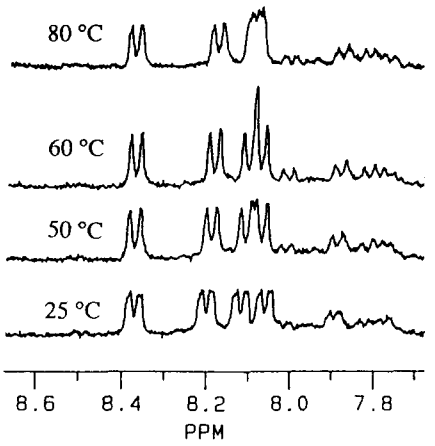


Figure 2. Variable temperature ^{1}H NMR spectrum (300 MHz, toluene-d_8) of **5a** which shows only four pair of doublet at ortho-position.

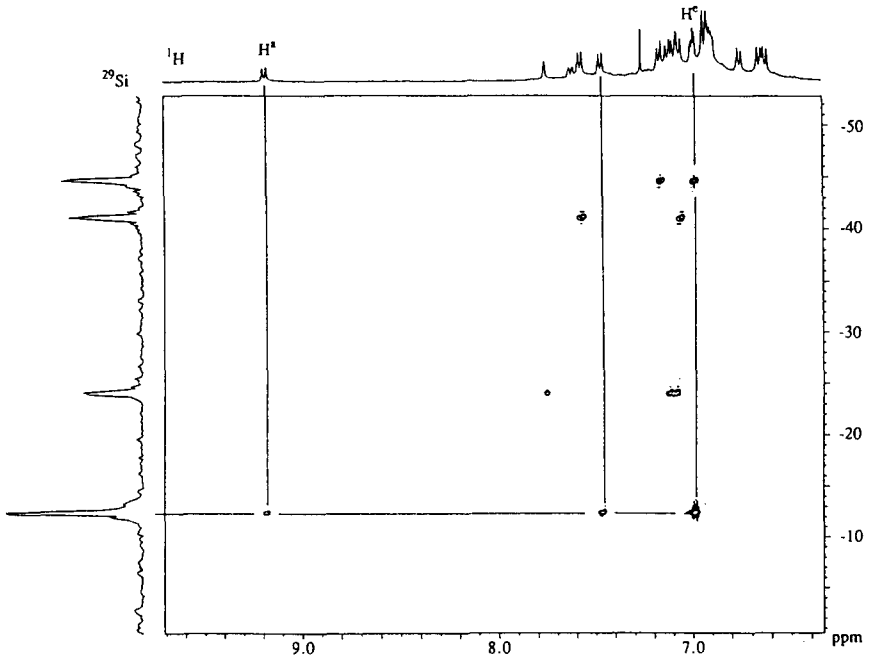


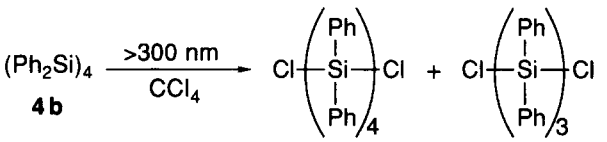
Figure 3. ^{1}H-^{29}Si HMBC spectrum of **6a**

The presence of *one hydrogen connected to* C_{60} is deduced from one doublet at 60.35 (C^e) ppm in the ^{13}C NMR and one singlet at δ 6.91 (H^e) in the ^1H NMR spectrum, respectively. The ^{29}Si NMR spectrum of **6a** shows four peaks at -44.83, -41.26, -24.30, and -12.66 ppm which are assigned to the silicon atoms of **6a**. The connectivities between these structural elements were determined by ^{29}Si-^1H HMBC experiment.[7c] It was shown that the silicon resonance at -12.66 ppm correlated to both H^a and H^e methyne proton signals (Figure 3).

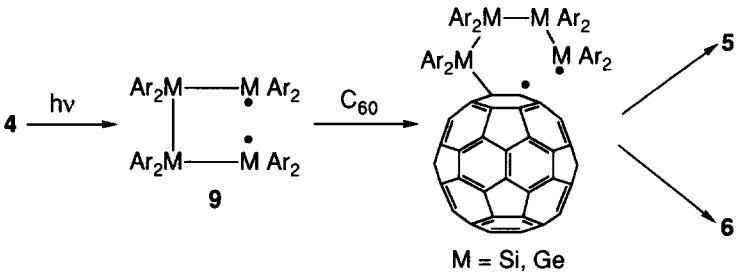
Regarding the addition pattern of the fullerene moiety, a 6,6-ring junction of the tetrasilacyclohexane fragment is most probable. In the case of a 5,6-junction, formation of two diastereomeric adducts would have to be expected.[12,13] The possibility of 1,4-addition can be eliminated by ^{13}C-^1H COLOC (Correlation Spectroscopy via Long-range Coupling). It was shown that the proton resonance at 6.91 ppm (H^e) correlates to C^f quaternary carbon on the C_{60}.

In order to obtain information concerning the mechanistic pathway for the formation of **5** and **6**, we carried out the photochemical reaction (λ > 300 nm) of **4b** in the presence of CCl_4 to give 1,4-dichloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane (**7b**) and 1,3-dichloro-1,1,2,2,3,3-hexaphenyltrisilane (**8b**) in 37 % and 31 % yield, respectively (Scheme 5). Under identical photolytic condition, adduct **5a** did not convert to **6a** in a control experiment. These findings indicate that biradical (**9**) might be involved in the course of the reaction (Scheme 6).

Scheme 5



Scheme 6



In the case of cyclotetragermane **4c**, products **5c** (43%) and **6c** (37%, based on unreacted C_{60}) were obtained. The structures of the adducts **5b**, **5c**, and **6c** were determined in similar manner by use of one and two dimensional NMR techniques; for details.

Further investigations on the synthesis of fullerene-bonded polysilane derivatives are in progress.

Experimental

General remarks and materials

Cyclotetrasilane **4a**[14b], **4b**[14a] and cyclotetragermane **4c**[15] were prepared according to literature procedures. C_{60} was obtained by GPC purification of the toluene extract of fullerene soot. ^1H, ^{13}C and ^{29}Si NMR spectra were obtained from Bruker AM500, AC400, AC300 and MSL400 instruments. Mass spectral data were obtained on JEOL JMS SX102A and JEOL HX110/110 tandem mass spectrometers. Gel permeation chromatography (GPC) was performed on a LC 908 instrument (Japan Analytical Industry Co. Ltd) with a series of Jaigel 1H and 2H columns and toluene as eluent. The solutions were irradiated in pyrex tubes (of 60 mL) by a high-pressure mercury lamp. All solvents, and reagents were purified according to standard procedures.

Preparation of 1,2-bis(diisopropylsilyl)benzene

To a mixture of Mg (6.73 g, 0.28 mol) and i-Pr_2SiHCl (46.0 g, 0.31 mol) in 40 mL of THF, was added a solution of o-dibromobenzene (26.9 g, 0.12 mol) in THF 60 mL, during 2.5 h with keeping a gentle refluxing under argon atmosphere. After the addition, the reaction mixture was refluxed for 2.5 h. The mixture was hydrolyzed with water and organic layer was extracted with ether. The residue was purified by column chromatography (9.26 g, 29%).

colorless oil; ^1H NMR (400 MHz, C_6D_6) δ 1.09 (d, 12H, J = 7.2Hz), 1.19 (d, 12H, J = 7.2Hz), 1.30 (sept, 4H, J = 7.2Hz), 4.63 (t, 2H), 7.22 (dd, 2H, J = 3.4, 5.5Hz), 7.54 (dd, 2H, J = 3.4, 5.5Hz); ^{13}C NMR (100 MHz, C_6D_6) δ 12.0 (d), 19.2 (q), 19.4 (q), 128.2 (d), 135.8 (d), 142.3 (s); Anal. Calcd for $C_{18}H_{34}Si_2$: C, 70.51; H, 11.18. Found: C, 70.72; H, 11.03.

Preparation of 1,2-bis(chlorodiisopropylsilyl)benzene

To a 111 mg (0.62 mmol) of $PdCl_2$, was added 5.43 g (17.8 mmol) of 1,2-bis(diisopropylsilyl)benzene in 15 mL of CCl_4. After the stirring of the mixture at 77 °C for 76 h, the catalyst was filtered off under argon flow, 5.16 g (76%) of product was obtained by distillation using Kugelrohr.

colorless oil; bp 121-126 °C/4 Torr (Kugelrohr); ^1H NMR (90 MHz, C_6D_6) δ 0.96 (d, 12H, J = 7.2Hz), 1.17 (d, 12H, J = 7.2Hz), 1.65 (sept, 4H, J = 7.2Hz), 7.13 (dd, 2H, J = 3.3, 5.7Hz), 7.86 (dd, 2H, J = 3.5, 5.7Hz); ^{13}C NMR (100 MHz, C_6D_6) δ 17.0 (d), 17.8 (q), 18.2 (q), 128.7 (d), 136.3 (d), 140.1 (s); Anal. Calcd for $C_{18}H_{32}Cl_2Si_2$: C, 57.57; H, 8.59. Found: C, 57.27; H, 8.30.

Preparation of 3,4-benzo-1,1,2,2-tetraisopropyl-1,2-disilacyclobutene (1)

To a 0.75 g (32.8 mmol) of Na, was added 5.16 g (13.6 mmol) of 1,2-bis(diisopropylsilyl)benzene in 10 mL of toluene. After the stirring of the mixture at 110 °C for 13 h, all solid was filtered off under argon flow. 4.03 g (97%) of **1** was obtained.

1: colorless oil; ^1H NMR (500 MHz, C_6D_6) δ 1.20 (d, 12H, J = 7.3Hz), 1.26 (d, 12H, J = 7.3Hz), 1.41 (sept, 4H, J = 7.3), 7.27 (dd, 2H, J = 3.2, 5.3Hz), 7.51 (dd, 2H, J = 3.2, 5.3Hz); ^{13}C NMR (125 MHz, C_6D_6) δ 14.2 (d), 20.0 (q), 20.1 (q), 129.2 (d), 132.8 (d), 155.9 (s); HRMS Calcd for $C_{18}H_{32}Si_2$: 304.2043. Found: 304.2025; UV(*n*-hexane) λ_{max}/nm(ε): 214 (17000).

Photochemical reaction of ***1*** *with* C_{60}

Irradiation of a solution of 3,4-benzo-1,2-disilacyclobutene **1** (42.2 mg, 139 μmol) and C_{60} (100 mg, 139 μmol) in toluene (120 mL)-*t*-BuOH (2.5 mL) mixed solvent with a low-pressure mercury lamp (254 nm) for 6 h followed by purification by means of gel-permeation chromatography afforded brown adduct **2** in 0.012 g (14% yield, based on unreacted C_{60}) and 40.0 mg of unreacted C_{60}.

2: brown solid, $(C_{18}H_{32}Si_2)C_{60}$ (FAB MS, m/z 1024-1027); ^{1}H NMR (500 MHz, 1:1 $CDCl_3$-CS_2) δ 1.14 (d, 12H, *J* = 7.4Hz), 1.40 (d, 12H, *J* = 7.4Hz), 2.17 (sept, 4H, *J* = 7.4), 7.58 (dd, 2H, *J* = 3.5, 5.7Hz), 8.03 (dd, 2H, *J* = 3.5, 5.7Hz); ^{13}C NMR (125MHz, C_6D_6): δ (number of quarternary carbons) δ 14.74 (d), 19.94 (q), 20.15 (q), 63.93 (2), 128.81 (d), 132.74 (4), 136.12 (d), 139.47 (4), 141.07 (4), 141.42 (2), 141.64 (4), 141.84 (4), 142.44 (4), 142.76 (2), 143.85 (2), 144.47 (4), 144.61 (4), 145.38 (4), 146.26 (4), 146.44 (4), 146.65 (4), 146.84 (2), 159.79 (4).

Photochemical reaction of ***4a-4c*** *with* C_{60}

Irradiation of a solution of 70.1 mg (83.3 μmol) of **4a** and 60.0 mg (83.3 μmol) of C_{60} in 60 mL of toluene with a high-pressure mercury lamp (> 300 nm) for 6 h followed by purification by means of recycling gel-permeation chromatography afforded **5a** (0.010 g, 13% based on unreacted C_{60}), **6a** (0.035 g, 46% based on unreacted C_{60}). Under identical conditions only **5b** was obtained from **4b** (0.117 g, 87% based on unreacted C_{60}). In the case of cyclotetragermane **4c**, also to give **5c** (0.035 g, 43% based on unreacted C_{60}) and **4c** (0.030 g, 37% based on unreacted C_{60}).

5a: $(C_{56}H_{56}Si_4)C_{60}$ (FAB MS, m/z 1560-1564 M^++1 cluster); ^{1}H NMR (500MHz, 1:1 $CDCl_3$-CS_2): δ 2.21 (s, 6H, Si-C_6H_4Me), 2.25 (s, 6H, Si-C_6H_4Me), 2.30 (s, 6H, Si-C_6H_4Me), 2.32 (s, 6H, Si-C_6H_4Me), 2.230 (s, 3H, Si-C_6H_4Me), 2.233 (s, 3H, Si-C_6H_4Me), 2.26 (s, 3H, Si-C_6H_4Me), 2.40 (s, 3H, Si-C_6H_4Me), 6.76 (d, 4H, *J* = 7.7 Hz), 6.87 (d, 4H, *J* = 7.7 Hz), 6.92 (d, 4H, *J* = 7.7 Hz), 6.98 (d, 4H, *J* = 7.7 Hz), 7.33 (d, 4H, *J* = 7.7 Hz), 7.37 (d, 4H, *J* = 7.7 Hz), 7.45 (d, 4H, *J* = 7.7 Hz), 7.62 (d, 4H, *J* = 7.7 Hz); ^{13}C NMR (126MHz, $CDCl_3$): δ (number of quaternaly carbons) 62.18 (2), 127.35 (2), 128.65 (2), 132.94 (4), 136.67 (2), 139.21 (2), 139.49 (2), 139.62 (4), 140.14 (1), 140.41 (2), 141.43 (2), 141.62 (2), 141.91 (1), 142.00 (2), 142.03 (1), 142.85 (2), 142.98 (2), 143.31 (2), 143.36 (2), 143.51 (2), 144.48 (2), 144.52 (2), 144.56 (2), 144.70 (2), 144.92 (2), 145.02 (2), 145.23 (2), 145.26 (2), 145.71 (2), 146.11 (1), 147.14 (2), 147.50 (2), 148.11 (2), 148.55 (2), 148.64 (2), 151.02 (2), 151.20 (2), 165.03 (2), side chain: δ 21.54 (q), 21.60 (q), 21.63 (q, two carbon), 128.31 (d), 128.34 (d), 128.53 (d), 128.58 (d); ^{29}Si NMR (400 MHz, 1:1 $CDCl_3$-CS_2): δ -22.25, -11.34.

6a: $(C_{56}H_{56}Si_4)C_{60}$ (FAB MS, m/z 1560-1564 M^++1 cluster); ^{1}H NMR (500MHz, 1:1 $CDCl_3$-CS_2): δ 2.02 (s, 3H, Si-C_6H_4Me), 2.16 (s, 3H, Si-C_6H_4Me), 2.19 (s, 3H, Si-C_6H_4Me), 2.22 (s, 3H, Si-C_6H_4Me), 2.230 (s, 3H, Si-C_6H_4Me), 2.233 (s, 3H, Si-C_6H_4Me), 2.26 (s, 3H, Si-C_6H_4Me), 2.40 (s, 3H, Si-C_6H_4Me), 6.53 (d, 2H, *J* = 7.6 Hz), 6.57 (d, 2H, *J* = 7.6Hz), 6.68 (d, 2H, *J* = 7.6Hz), 6.81 (d, 2H, *J* = 7.6Hz), 6.83 (d, 2H, *J* = 7.6Hz), 6.85 (d, 4H, *J* = 7.6Hz), 6.90 (d, 2H, *J* = 7.6Hz), 6.91 (s, 1H), 6.99 (d, 2H, *J* = 7.6Hz), 7.00 (d, 2H, *J* = 7.6Hz), 7.03 (d, 2H, *J* = 7.6), 7.08 (d, 2H, *J* = 7.6Hz), 7.38 (d, 2H, *J* = 7.6Hz), 7.49 (d, 2H, *J* = 7.6Hz), 7.56 (d, 1H, *J* = 7.8Hz, H^b), 7.66 (s, 1H, H^d), 9.13 (d, 1H, *J* = 7.8Hz, H^a); ^{13}C NMR (126MHz, 1:1 $CDCl_3$-CS_2): δ (number of quaternaly carbons) 127.24 (1), 129.52 (1), 130.08 (1), 136.32 (1), 137.52 (1), 138.15 (1), 138.18 (1), 138.36 (1), 138.43 (1), 138.52 (1), 138.99 (1), 139.14 (1), 139.26 (1), 139.43 (1), 139.45 (1), 139.54 (1), 140.51 (1), 141.16 (1), 141.17 (1), 141.27 (1), 141.39 (1),

141.60 (1), 141.63 (1), 141.68 (1), 141.72 (1), 141.75 (1), 141.78 (1), 142.26 (1), 142.29 (1), 142.32 (1), 142.35 (1), 142.96 (1), 143.23 (1), 143.28 (1), 144.25 (1), 144.39 (1), 144.45 (1), 144.52 (2), 144.58 (1), 144.85 (1), 145.13 (1), 145.18 (2), 145.26 (2), 145.86 (1), 145.87 (1), 145.95 (1), 145.97 (1), 146.01 (1), 146.04 (1), 146.07 (1), 146.12 (2), 146.20 (1), 146.23 (1), 146.52 (1), 147.05 (1), 147.37 (2), 147.48 (1), 148.27 (1), 153.26 (1), 155.08 (1), 156.61 (1), 157.67 (1), side chain: δ 60.35 (d, C^e), 63.02 (s, C^f), 128.04 (d), 128.17 (d), 128.26 (d), 128.35 (d), 128.58 (d), 128.61 (d), 128.68 (d), 129.24 (d, C^b), 136.44 (d), 136.71 (d), 136.78 (d), 137.42 (d), 137.68 (d), 137.70 (d), 138.32 (d), 139.92 (d, C^a), 141.36 (d, C^d); ^{29}Si NMR (400 MHz, 1:1 $CDCl_3$-CS_2): δ -44.83, -41.26, -24.30, -12.66.

6b: $(C_{48}H_{40}Si_4)C_{60}$ (FAB MS, m/z 1448-1451 M^++1 cluster); ^1H NMR (500MHz, 1:1 $CDCl_3$-CS_2): δ 6.7-7.3 (m, 31H, Si-Ph), 6.96 (s, 1H, H^e), 7.54 (d, 2H *J* = 7.3Hz, Si-Ph), 7.61 (t, 1H *J* = 7.6Hz, H^c), 7.65 (d, 2H *J* = 7.0Hz, Si-Ph), 7.79 (t, 1H, *J* = 7.6Hz, H^b), 7.87 (d, 1H, *J* = 7.6Hz, H^d) 9.30 (d, 1H, *J* = 7.6Hz, H^a); ^{13}C NMR (126MHz, 1:1 $CDCl_3$-CS_2): δ (number of quaternaly carbons) 130.06 (1), 130.95 (1), 131.96 (1), 132.54 (1), 133.01 (1), 134.47 (1), 135.22 (1), 135.47 (1), 135.55 (1), 135.70 (1), 135.98 (1), 139.12 (1), 139.35 (1), 139.58 (1), 140.54 (1), 141.00 (1), 141.03 (1), 141.12 (1), 141.25 (1), 141.30 (1), 141.41 (1), 141.47 (1), 141.52 (1), 141.54 (1), 141.63 (1), 141.65 (1), 141.85 (1), 142.18 (2), 142.21 (1), 142.25 (1), 143.10 (1), 143.13 (1), 144.20 (1), 144.31 (1), 144.33 (1), 144.34 (1), 144.37 (2), 144.80 (1), 145.03 (1), 145.07 (1), 145.09 (1), 145.13 (2), 145.27 (1), 145.75 (1), 145.78 (1), 145.86 (2), 145.94 (2), 145.98 (1), 146.00 (1), 146.07 (1), 146.11 (1), 146.43 (1), 146.88 (1), 146.99 (1), 147.04 (2), 147.90 (1), 152.74 (1), 154.30 (1), 155.91 (1), 156.83 (1), side chain: δ 60.11 (d, C^e), 62.32 (s, C^f), 127.24 (d, Si-Ph), 127.39 (d, Si-Ph), 127.42 (d, Si-Ph), 127.57 (d, Si-Ph), 127.62 (d, Si-Ph), 127.80 (d, Si-Ph), 127.83 (d, Si-Ph), 128.16 (d, Si-Ph), 128.48 (d, C^b), 128.71 (d, Si-Ph), 128.76 (d, Si-Ph), 128.85 (d, Si-Ph), 128.93 (d, Si-Ph), 128.95 (d, Si-Ph), 129.43 (d, C^c), 129.59 (d, Si-Ph), 136.26 (d, Si-Ph), 136.43 (d, Si-Ph), 136.58 (d, Si-Ph), 137.15 (d, Si-Ph), 137.29 (d, Si-Ph), 137.52 (d, Si-Ph), 138.00 (d, Si-Ph), 139.55 (d, C^a), 140.88 (d, C^d); ^{29}Si NMR (300 MHz, 1:1 $CDCl_3$-CS_2): δ -44.32, -41.79, -24.08, -13.68.

5c: ^1H NMR (500MHz, 1:1 $CDCl_3$-CS_2): δ 6.96 (t, 2H, *J* = 7.6Hz), 7.06 (t, 4H, *J* = 7.6Hz), 7.10 (t, 2H, *J* = 7.6Hz), 7.14 (t, 1H, *J* = 7.6Hz), 7.21 (t, 2H, *J* = 7.6Hz), 7.24 (t, 1H, *J* = 7.6Hz), 7.26 (d, 2H, *J* = 7.6Hz), 7.45 (d, 2H, *J* = 7.6Hz), 7.53 (d, 4H, *J* = 7.6 Hz); ^{13}C NMR (126MHz, 1:4 C_6D_6-CS_2): δ (number of quaternaly carbons) 64.13 (2), 134.70 (2), 135.82 (2), 136.61 (2), 136.77 (2), 137.64 (2), 140.66 (2), 140.90 (2), 141.20 (1), 142.07 (1), 142.28 (1), 142.38 (2), 142.51 (2), 143.34 (4), 143.45 (2), 143.77 (2), 143.80 (2), 144.08 (2), 144.86 (2), 145.00 (2), 145.26 (2), 145.34 (2), 145.44 (2), 145.49 (2), 145.53 (2), 145.56 (2), 146.32 (1), 147.47 (2), 147.89 (2), 148.44 (2), 148.50 (2), 148.85 (2), 150.02 (2), 150.85 (2), 164.56 (2), side chain: δ 128.34 (d), 128.35 (d), 128.70 (d), 128.78 (d), 129.15 (d), 129.21 (d), 129.52 (d), 129.78 (d), 137.02 (d, three carbons), 137.28 (d).

6c: $(C_{48}H_{40}Ge_4)C_{60}$ (FAB MS, m/z 1622-1635 M^++1 cluster); ^1H NMR (500MHz, 1:1 $CDCl_3$-CS_2): δ 6.8-7.3 (m, 31H, Si-Ph), 7.01 (s, 1H, H^e), 7.49 (d, 2H *J* = 6.9Hz, Ge-Ph), 7.53 (t, 1H *J* = 7.6Hz, H^c), 7.55 (d, 2H *J* = 6.9Hz, Si-Ph), 7.70 (t, 1H, *J* = 7.6Hz, H^b), 7.73 (d, 1H, *J* = 7.6Hz, H^d) 9.00 (d, 1H, *J* = 7.6Hz, H^a); ^{13}C NMR (126MHz, 1:1 $CDCl_3$-CS_2): δ (number of quaternaly carbons) 134.06 (1), 134.34 (1), 134.60 (1), 135.11 (1), 135.45 (1), 135.71 (1), 135.77 (1), 136.18 (1), 137.15 (1), 138.10 (1), 138.45 (1), 139.69 (1), 139.70 (1), 139.73 (1), 139.85 (1), 140.90 (1), 141.24 (1), 141.34 (1), 141.37 (2), 141.57 (1), 141.59 (1), 141.77 (1), 141.78 (1), 142.06 (1), 142.13 (1), 142.32 (2), 142.35 (2), 142.96 (2), 143.31 (1), 143.36 (1), 144.27 (1), 144.34 (1), 144.45 (1), 144.48 (1), 144.59 (1), 144.68 (1), 145.09 (1), 145.18 (1), 145.20

(1), 145.29 (1), 145.33 (3), 145.88 (1), 146.03 (2), 146.07 (1), 146.12 (2), 146.20 (1), 146.27 (1), 146.33 (1), 146.61 (1), 146.80 (1), 147.16 (1), 147.28 (1), 147.36 (1), 147.42 (1), 147.53 (1), 152.97 (1), 154.52 (1), 156.73 (1), 157.13 (1), side chain: δ 60.13 (d, C^e), 64.44 (s, C^f), 127.89 (d), 127.98 (d), 128.00 (d), 128.09 (d), 128.16 (d), 128.17 (d), 128.37 (d), 128.50 (d), 128.56 (d), 128.65 (d), 128.73 (d), 128.75 (d, C^b), 129.21 (d), 129.51 (d, C^c), 135.39 (d), 135.58 (d), 135.68 (d), 136.11 (d), 136.30 (d), 136.36 (d), 136.69 (d), 138.81 (d, C^a), 139.54 (d, C^d).

*Photochemical reaction of **4b** in the presence of CCl_4*

Irradiation of a solution of 500 mg (0.687 mmol) of cyclotetrasilane **4b** in 50 mL of toluene and 5 mL of CCl_4 mixed solvent with a high-pressure mercury lamp (> 300 nm) for 30 min followed by purification by means of gel-permeation chromatography (toluene as a solvent) afforded **7b** (0.204 g, 27%) and **8b** (0.130 g, 31%).

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