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Unusual Rearrangement in the Photochemical Addition of Bis(alkylidene)disilacyclobutanes to C_{60}

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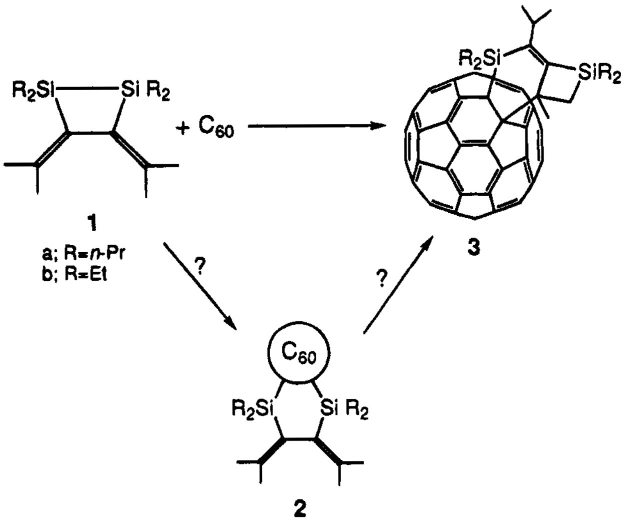
Summary: The photochemical reaction of bis(alkylidene)-disilacyclobutanes ***1a,b*** *with C_{60} afforded the stable 1:1 adducts* ***3a,b****, resulting from an unexpected rearrangement of the disilacyclobutane unit. The structures of* ***3a,b*** *were determined by spectroscopic methods, including $^{29}Si-^{1}H$ HMBC hetero nuclear shift correlation experiments.*

Since the development of the gram-scale synthesis of C_{60}[1-3] the chemical functionalization of this new allotropic form of carbon has attracted much interest and led to fascinating results.[4-7] One promising approach in this direction is photochemical derivatization;[8,9] recently, we reported a photoinduced [3 + 2] cycloaddition of a disilirane to C_{60} which resulted in the formation of a 1,3-disilolane.[10] On the basis of this result it might be anticipated that the similar conversion of bis(alkylidene)disilacyclobutanes **1** should yield the corresponding C_{60} annulated disilacyclohexane derivatives **2** (Scheme 1). Instead, adducts **3** resulting from an unexpected rearrangement of the disilacyclobutane moiety are obtained.

Irradiation of a solution of 21.0 mg (62.4 μmol) of disilacyclobutane[11] **1a** and 30.0 mg (41.6 μmol) of C_{60} in 30 mL of toluene with a high-pressure mercury lamp (filter: λ < 300 nm) for 24 h followed by purification by means of gel-permeation chromatography afforded the brown adduct **3a**[12] in 61% yield. Under identical conditions **3b**[13] was obtained from **1b** in 52% yield.

Scheme 1



The FAB mass spectrum of **3a** exhibits one peak at *m/z* 1056–1059 ($C_{80}H_{40}Si_2$, $M^+ + 1$ cluster), as well as one for C_{60} at *m/z* 720–723.

The UV–vis absorption of **3a** is virtually identical with that of C_{60} except for subtle differences in the area between 190 and 700 nm.[12]

The C_{60} unit of **3a** displays 52 resonances in the ^{13}C NMR spectrum, which indicates the absence of any symmetry element in this molecule. One signal has a relative intensity of 4, two signals have a relative intensity of 3, and one signal has a relative intensity of 2; thus, the number of carbon atoms sums up to 60. While two fullerene carbon atoms resonate at 63.99 (C^i)

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(12) $(C_{20}H_{40}Si_2)C_{60}$ (FAB MS, *m/z* 1056–1059): UV-vis (hexane) λ_{max} 210, 255, 347, 389, 416, 508, 633, 661 nm; ^1H NMR (500 MHz, C_6D_6) δ 0.8–1.8 (Si–$(CH_2)_2CH_3$), 0.93 (t, 3H, J = 7.2 Hz, Si–$(CH_2)_2CH_3$), 1.01 (t, 3H, J = 7.3 Hz, Si–$(CH_2)_2CH_3$), 1.10 (t, 3H, J = 7.2 Hz, Si–$(CH_2)_2CH_3$), 1.17 (t, 3H, J = 7.2 Hz, Si–$(CH_2)_2CH_3$), 1.32 (d, 3H, J = 6.8 Hz, $H^{a'}$), 1.33 (d, 3H, J = 6.8 Hz, H^a), 1.45 (d, 1H, J = 15.5 Hz, H^f), 2.48 (s, 3H, H^g), 2.87 (sep, 1H, J = 6.8 Hz, H^b), 3.16 (d, 1H, J = 15.5 Hz, H^f); ^{13}C NMR (126 MHz, C_6D_6) δ (number of carbon atoms on C_{60}) 132.71 (1), 134.79 (1), 135.37 (1), 136.30 (1), 138.46 (1), 139.28 (1), 139.83 (1), 140.86 (1), 141.42 (1), 141.47 (1), 141.75 (3), 141.90 (1), 142.24 (1), 142.39 (1), 142.57 (1), 142.71 (2), 142.93 (1), 143.22 (1), 143.24 (3), 143.30 (1), 143.56 (1), 144.14 (1), 144.20 (1), 144.47 (1), 144.81 (1), 144.86 (1), 145.10 (1), 145.24 (1), 145.50 (1), 145.59 (1), 145.64 (1), 145.74 (1), 146.05 (1), 146.12 (1), 146.25 (1), 146.30 (1), 146.61 (1), 146.63 (1), 146.65 (1), 146.68 (1), 146.89 (4), 147.10 (1), 147.21 (1), 147.26 (1), 147.96 (1), 149.83 (1), 157.53 (1), 157.83 (1), 160.49 (1), 161.81 (1), side chain δ 18.19 (t, Si–$(CH_2)_2CH_3$), 18.50 (q, two carbon, Si–$(CH_2)_2CH_3$), 18.55 (t, Si–$(CH_2)_2CH_3$), 18.74 (q, Si–$(CH_2)_2CH_3$), 18.81 (t, Si–$(CH_2)_2CH_3$), 18.95 (t, Si–$(CH_2)_2CH_3$), 18.97 (q, Si–$(CH_2)_2CH_3$), 19.59 (t, Si–$(CH_2)_2CH_3$), 19.73 (t, Si–$(CH_2)_2CH_3$), 20.05 (t, Si–$(CH_2)_2CH_3$), 23.41 (q, C^a), 23.52 (t, Si–$(CH_2)_2CH_3$), 24.00 (q, $C^{a'}$), 25.34 (t, C^f), 34.32 (q, C^g), 36.08 (d, C^b), 54.64 (s, C^e), 63.99 (s, C^i), 77.50 (s, C^h), 157.14 (s, C^c), 170.65 (s, C^d); ^{29}Si NMR (400 MHz, C_6D_6) δ −14.30, 4.20.

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and 77.50 (C^h) ppm, the signals of the other 50 all appear in the region between δ 130 and 165 ppm.

The partial structure of the fragment annulated to the C_{60} moiety is derived from the following NMR spectroscopic properties.

For *one isopropyl group with two diastereotropic methyl groups* two quartets at δ 23.52 (C^a) and 24.00 ($C^{a'}$) as well as one doublet at 36.08 (C^b) appear in the ^{13}C NMR spectrum. As evidenced by homo- ($^1H-^1H$) and heteronuclear ($^1H-^{13}C$) shift correlation (COSY) experiments the corresponding methyl and methine protons resonate at δ 1.33 (H^a), 1.32 ($H^{a'}$), and 2.87 (H^b) in the ^1H NMR spectrum.

A methylene group gives rise to a triplet at δ 25.34 in the ^{13}C NMR spectrum and two doublets with a rather large shift difference at δ 1.45 (H^f) and 3.16 ($H^{f'}$) in the ^1H NMR spectrum. The presence of *one isolated C–C double bond* is deduced from two singlets at δ 157.14 (C^c) and 170.65 (C^d) in the ^{13}C NMR spectrum. Furthermore, the signals of *one methyl group* are observed at 34.32 (C^g) and 2.48 (H^g) ppm, respectively, in the ^{13}C NMR and ^1H NMR spectra as well as a resonance of *one quaternary carbon* at δ 54.64 (C^e).

The connectivities between these structural elements were determined by $^{13}C-^1H$ COLOC (correlation spectroscopy via long-range coupling) and $^{13}C-^1H$ HMBC (^1H-detected multiple-bond heteronuclear multiple quantum coherence) experiments (Figure 1a). It was shown that one olefinic carbon atom (C^c) is bonded to carbon C^b of the isopropyl group, while the other olefinic carbon (C^d) is attached to the quaternary carbon (C^e). Furthermore, the latter is connected to the methyl (CH_3^g) and methylene (CH_2^f) groups, as well as to carbon C^h of the C_{60} unit.

However, since from such shift correlation experiments it is not possible to exclude the presence of bonds, there are eight possible structures **3**–**10** which are in agreement with these data (Figure 1b). Of those, **9** can be excluded, since the silicon atom of the silacyclopropene ring should give a ^{29}Si NMR resonance between −100 and −80 ppm,[14] while only two signals at 4.20 and −14.30 ppm were detected.

Moreover, upon irradiation of the H^a,$H^{a'}$-methyl and H^b methine proton resonances of the isopropyl group strong NOE enhancements of 12–19% and 17–27%, respectively, are observed for the signals of four Si-*n*-Pr methyl groups. Clearly, this indicates that the isopropyl group is flanked by the two di-*n*-propylsilyl units; of the structures depicted in Figure 1b, this is only the case for structures **3** and **6**.

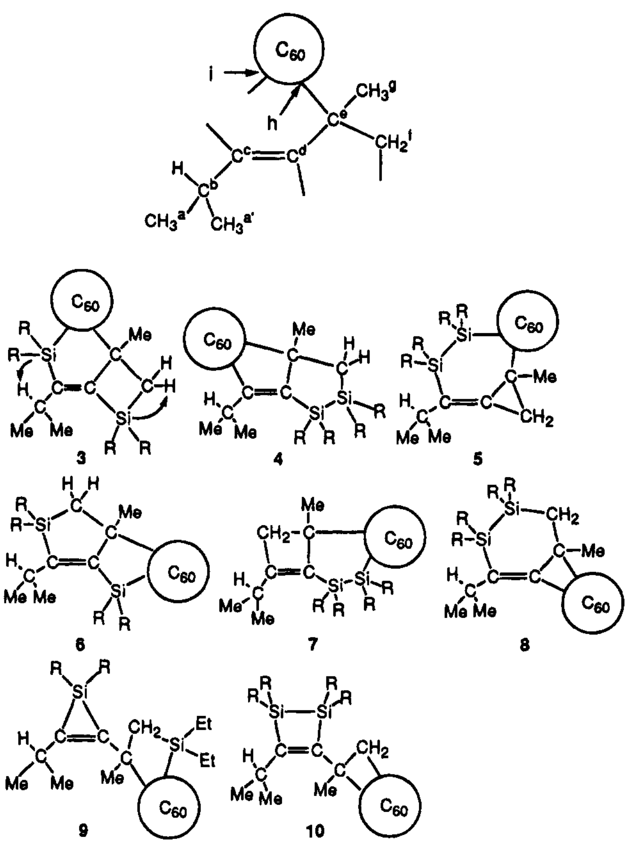

Figure 1. (a, top) Connectivities derived from $^1H-^1H$ homo- and $^1H-^{13}C$ heteronuclear shift correlation experiments. (b, bottom) The eight possible isomers derived from the substructure depicted in (a). The arrows in structure **3** indicate the observed $^{29}Si-^1H$ couplings.

In order to distinguish between those two alternatives, it was essential to obtain information concerning the bonding situation at the silicon atoms. To attain this target, we developed a pulse sequence for a $^{29}Si-^1H$ HMBC experiment, which permits a $^{29}Si-^1H$ shift correlation over two and/or three bonds (Figure 2).[15] Besides cross-peaks between the signals of the silicon atoms and the *n*-propyl methylene protons, the spectrum uncovers couplings between the silicon resonance at −14.3 ppm and the H^b isopropyl methine proton resonance over three bonds as well as between the Si resonance at 4.20 ppm and both H^f and $H^{f'}$ methylene proton signals over two bonds. The connectivity requirements derived from this experiment are only met in structure **3**.

With regard to the addition pattern of the fullerene moiety a 6,6-ring junction of the silabutene fragment is most probable.[16] In the case of a 5,6- or 1,4-

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(13) UV–vis (hexane): λ_{max} 210, 255, 327, 392, 417, 510, 632, 658 nm. ^1H NMR (500 MHz, C_6D_6): δ 0.8–1.6 (Si–Et proton), 1.27 (d, 3H, J = 6.9 Hz, $H^{a'}$), 1.30 (d, 3H, J = 6.9 Hz, H^a), 1.38 (d, 1H, J = 15.5 Hz, H^f), 2.39 (s, 3H, H^g), 2.82 (sept, 1H, J = 6.9 Hz, H^b), 3.09 (d, 1H, J = 15.5 Hz, $H^{f'}$). ^{13}C NMR (126 MHz, C_6D_6): δ (number of carbon atoms on C_{60}) 132.73 (1), 134.76 (1), 135.33 (1), 136.18 (1), 138.43 (1), 139.32 (1), 139.79 (1), 140.87 (1), 141.40 (1), 141.48 (1), 141.74 (1), 141.88 (1), 142.24 (1), 142.40 (1), 142.57 (1), 142.70 (3), 142.91 (1), 143.21 (3), 143.23 (1), 143.28 (1), 143.55 (1), 144.12 (1), 144.21 (1), 144.46 (1), 144.79 (2), 145.10 (1), 145.24 (1), 145.50 (1), 145.59 (1), 145.62 (1), 145.73 (1), 146.04 (1), 146.12 (1), 146.25 (1), 146.30 (1), 146.62 (3), 146.68 (1), 146.86 (1), 146.90 (4), 147.09 (1), 147.21 (1), 147.25 (1), 147.94 (1), 149.79 (1), 157.64 (1), 157.78 (1), 160.33 (1), 161.69 (1); side chain δ 7.96 (t, Si–CH_2CH_3), 8.07 (q, Si–CH_2CH_3), 8.40 (t, Si–CH_2CH_3), 8.43 (q, Si–CH_2CH_3), 8.67 (t, Si–CH_2CH_3), 8.83 (q, Si–CH_2CH_3), 9.80 (q, Si–CH_2CH_3), 12.20 (t, Si–CH_2CH_3), 23.32 (q, C^a), 23.84 (q, $C^{a'}$), 24.47 (t, C^f), 34.06 (q, C^g), 36.16 (d, C^b), 54.24 (s, C^e), 63.96 (s, C^i), 77.50 (s, C^h), 157.22 (s, C^c), 170.05 (s, C^d). ^{29}Si NMR (400 MHz, C_6D_6): δ −11.47, 8.12.

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(15) Spectra were recorded on a Bruker MSL-400 (400.13 and 79.46 MHz for ^1H and ^{29}Si, respectively) at 30 °C: **3a** and **3b**, 20 mg in 1.5 mL of C_6D_6, 5 mm sample tube. The probe head used in this experiment was a Bruker VSP 10 mm normal BB probe head. Pulse sequence:

$$\begin{array}{lllllll} ^1H, & D0-90°-\tau_1- & -\tau_2- & -\Delta-180°-\Delta- & -(FID) \\ ^{29}Si, & 90° & 90° & & 90° \end{array}$$

D0 = 2 s; $\tau_1 = (1/2J_{Si-H})^{single\ bond} = 1/280$ s; $\tau_2 = (1/2J_{Si-H})^{long\ range} = 1/16$ s; Δ = incremental delay; DS = 8; NS = 32; 16-phase cycle. The necessary experimental time was 10 h. While our work was in progress a $^{119}Sn-^1H$ HMBC experiment was reported; cf.: Kayser, F.; Biesemans, M.; Bouâlam, M.; Tiekink, E. R. T.; Khloufi, A. E.; Meunier-Piret, J.; Bouhdid, A.; Jurkschat, K.; Gielen, M.; Willem, R. *Organometallics* **1994**, *13*, 1098.

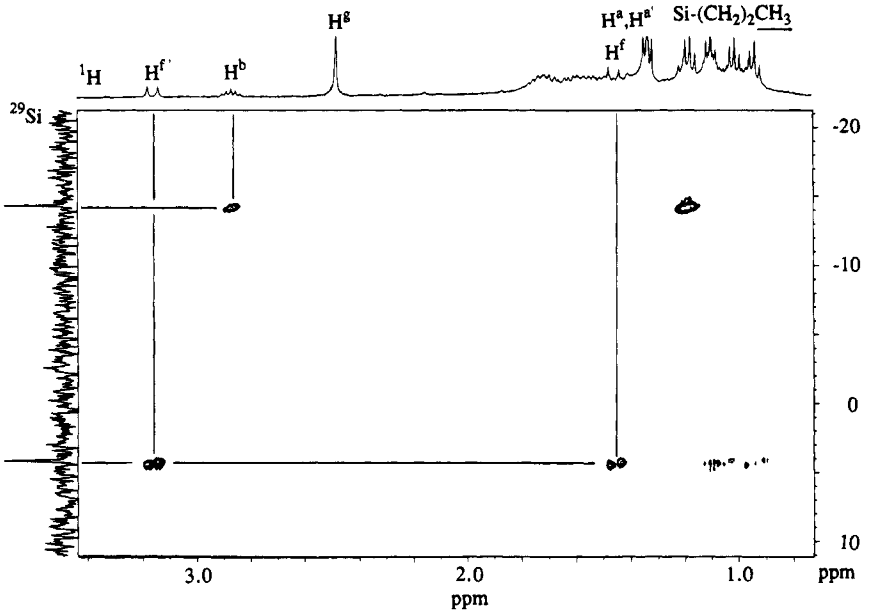

Figure 2. $^{29}Si-^{1}H$ HMBC NMR spectrum of **3a**.

junction—the two possible alternatives—in each case the formation of two diastereomeric adducts would have to be expected.[17,18]

The structure of adduct **3b** was determined in a similar manner by use of one- and two-dimensional NMR techniques; for details cf. the supplementary material.

The mechanistic pathway for the formation of **3** is not clear at the present time. However, since 5 equiv of rubrene, a well-established triplet quencher, completely inhibits the reaction between **1a,b** and C_{60} and, furthermore, the disilacyclobutanes **1a,b** are stable under the reaction conditions, triplet excited C_{60} might be involved in the course of the reaction. Alternatively, the initially formed **2** might rearrange to **3** under the applied photolytic conditions.[19] Further investigations to clarify the mechanistic origin of **3** are in progress.

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Supplementary Material Available: Detailed NMR spectra for **3a** and **3b** (11 pages). Ordering information is given on any current masthead page.

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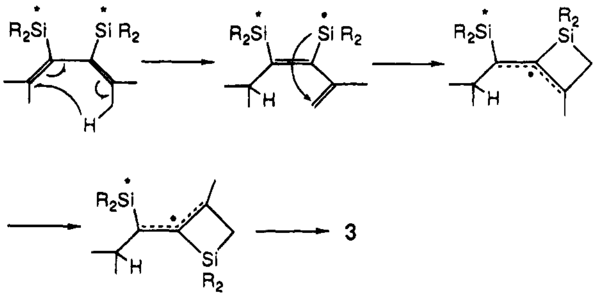
[19] A possible mechanism for the formation of the disila fragment of **3a,b** is



• : radical or bond to C_{60}