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Intramolecular Rearrangements of Silenes. 3.[†] From 2,5-Bis(1-methyl-1-silacyclobut-1-yl)-*p*-xylene to 1,2,4,5-Tetrahydro-1,1,4,4-tetramethyl-1,4-disiladicyclobuta-[*a*,*d*]benzene. The First Silacyclobutene Diannelated [*a*,*d*]Benzene[‡]

L. E. Gusel'nikov,* V. V. Volkova, E. N. Buravtseva, and A. S. Redchin

Laboratory of Organosilicon Chemistry, Topchiev Institute of Petrochemical Syntheses of the Russian Academy of Sciences, 29 Leninsky Prospect, Moscow 117912, Russia

N. Auner,* B. Herrschaft, B. Solouki, and G. Tsantes

Institut für Anorganische Chemie, Johann Wolfgang Goethe-Universität, Marie-Curie-Strasse 11, 60439 Frankfurt am Main, Germany

Y. E. Ovchinnikov, S. A. Pogozhikh, and F. M. Dolgushin

Nesmeyanov Institute of Organo-Element Compounds, Russian Academy of Science, 28 Vavilova Str., Moscow 117813, Russia

V. V. Negrebetsky

Russian State Medical University, 1 Ostrovityanova Str., Moscow 117869, Russia

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Low-pressure pyrolysis of 2,5-bis(1,1-dimethyl-1-silacyclobut-1-yl)-*p*-xylene (**1**) results in the formation of 1,2,4,5-tetrahydro-1,1,4,4-tetramethyl-1,4-disiladicyclobuta[*a*,*d*]benzene (**2**), here named as the butterfly compound and representing the first silacyclobutene diannelated [*a*,*d*]benzene. Both compounds, **1** and **2**, were characterized by NMR, IR, and MS methods; furthermore, the molecular structures were determined by single-crystal X-ray diffraction analysis. Density functional and ab initio calculations prove that the difference in the benzene carbon−carbon bond lengths in **2** results primarily from substituent effects and is not caused by ring strain effects. Forming strongly bent silicon−carbon bonds, silicon decreases the amount of strain in the model compounds, in the 1-silacyclobut-2-ene **10** by 8.3 kcal/mol and in the 1,4-disiladicyclobuta[*a*,*d*]benzene **15** by 19.0 kcal mol^{-1}, compared to the analogous hydrocarbons. The total strain energy is additive, depending on the number of annelated rings. The photoelectron spectrum of the butterfly compound exhibits three isolated bands at low energy. The ground state of the radical cation $\tilde{\mathrm{X}}(^2\mathrm{A_g})$ at 8.15 eV and the first exited state $\tilde{A}(^2\mathrm{A_g})$ at 8.7 eV arises from π-electron ionization at the benzene molecule center. The calculated values with 8.35 and 8.82 eV are in agreement with the experimental vertical ionization energies.

Introduction

The aryl-substituted silacyclobutane [2 + 2] cycloreversion reaction, causing a "transient arylsilene rearrangement", has been developed as a versatile tool for the synthesis of a variety of benzo-condensed small- and medium-sized silacycles. The gas-phase thermal decomposition of silacyclobutanes has been of long-standing interest, since it was historically the first method to produce silenes as reactive intermediates.[2,3a] The landmark paper by Gusel'nikov and Flowers[3b,c] demonstrated that dimethylsilacyclobutane decomposes thermally to 1,1-dimethylsilene and ethene. This was the start of numerous investigations on the thermal decomposition of silacyclobutanes.[2] Early work of Grobe et al.[4] claimed that the gas-phase pyrolysis of phenyl-substituted silacyclobutanes led to the formation of the corresponding transient silenes, which reacted to form 1,3-disilacyclobutanes by head-to-tail dimerization and products resulting from competitive intramolecular rearrangements. Further investigations on the thermally induced [2 + 2] cycloreversion reaction of aryl-substituted silacyclobutanes showed silene-based rear-

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* To whom correspondence should be addressed. L.E.G.: e-mail, guselnikov@iname.com; fax +7 095 2302224. N.A.: e-mail, Auner@chemie.uni-frankfurt.de; fax, +49 69 798 29188.

[†] For part 2, see ref 1a.

[‡] First reported at the 30th Organosilicon Symposium, 1997; see ref 1b.

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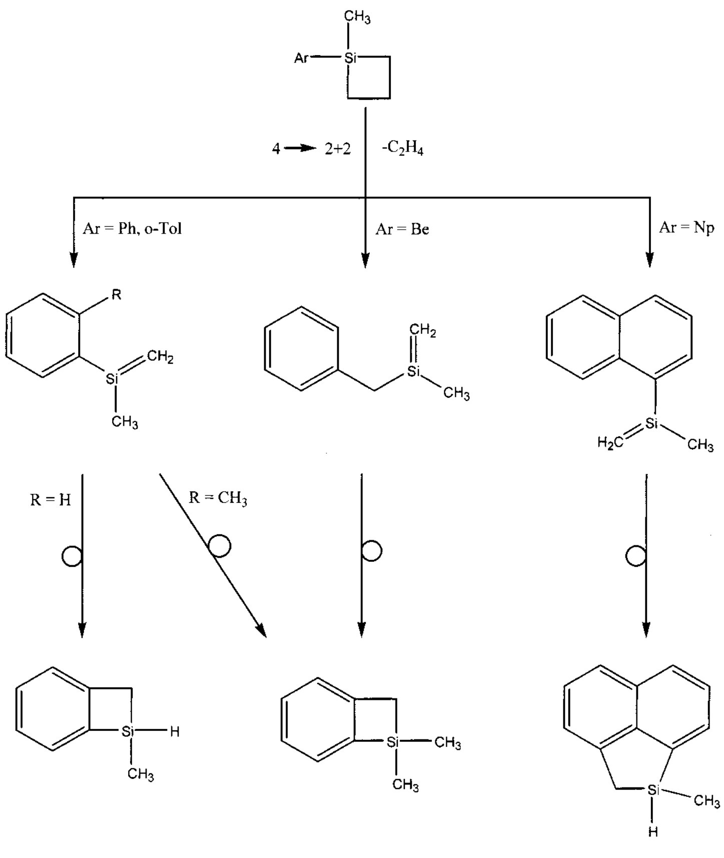
Scheme 1



rangements to give benzo-condensed small- and medium-sized silacycles. Recently we reported on the gas-phase pyrolyses of 1-phenyl-, 1-*o*-tolyl-, 1-benzyl-, and 1-naphthyl-1-methyl 1-substituted silacyclobutanes, yielding 3,4-benzo-1-silacyclobutanes and 1-methyl-1-silaacenaphthene[1b,5] (Scheme 1).

In this paper we report the pyrolysis of 2,5-bis(1-methyl-1-silacyclobut-1-yl)-*p*-xylene (**1**), which gives the novel butterfly compound 1,2,4,5-tetrahydro-1,1,4,4-tetramethyl-1,4-disiladicyclobuta[*a*,*d*]benzene[1b] (**2**) (Scheme 2); this compound represents a new class of small-ring-annelated benzenes having *two* silacyclobutene moieties annelated to the benzene nucleus. In addition, compound **2** may serve as a potential precursor for the generation of the hitherto unknown silasemiquinone intermediates and as a promising monomer for ring-opening polymerization.

Results and Discussion

2,5-Bis(1-methyl-1-silacyclobut-1-yl)-*p*-xylene (**1**) was prepared by starting from 2,5-dibromo-*p*-xylene and 1-chloro-1-methyl-1-silacyclobutane by Grignard reaction according to Scheme 3.

Details of the X-ray crystal structure determination[6] of **1** is given in the Experimental Section. In the solid state molecules of **1** pile up to form stacks along [010] at 120 K with the normal vector of the benzene subunit pointing not exactly along the crystallographic *b* axis of the unit cell. All intermolecular contact distances are in the range of van der Waals distances; therefore, no intermolecular π-interactions can be deduced.

The centrosymmetric molecule (Figure 1) exhibits the structural features of both the unsaturated carbacycles and the saturated silacycles. Bond distances and angles of the 1,4-dimethylbenzene-2,5-diyl subunit lie in the usual range for aromatic hydrocarbons in the solid state. The 1-methyl-1-silacyclobut-1-yl substituent shows a folded conformation with nearly ideal local mirror symmetry. The silicon atom exhibits strong deviations

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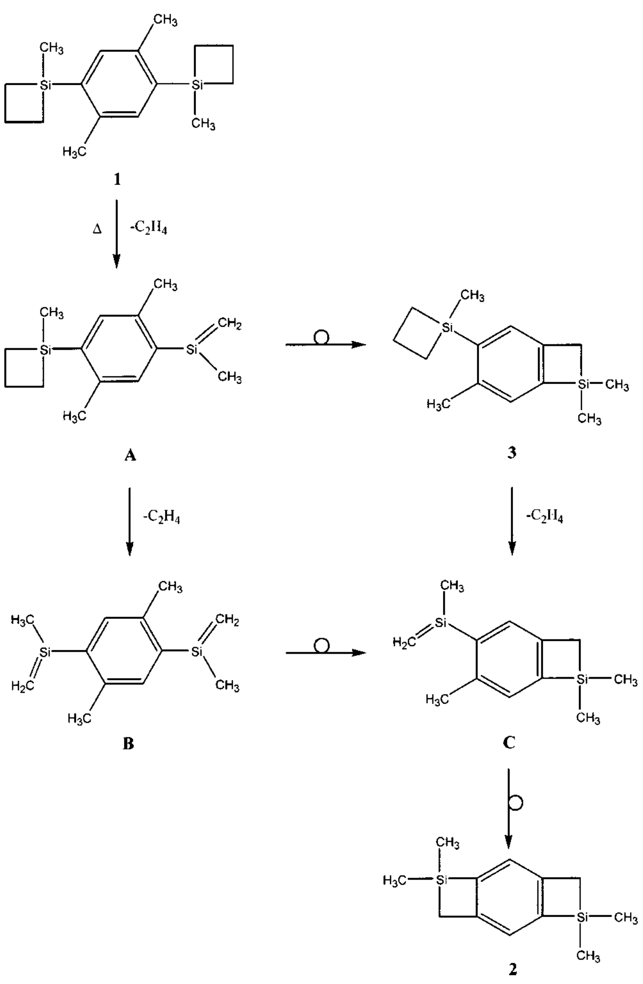
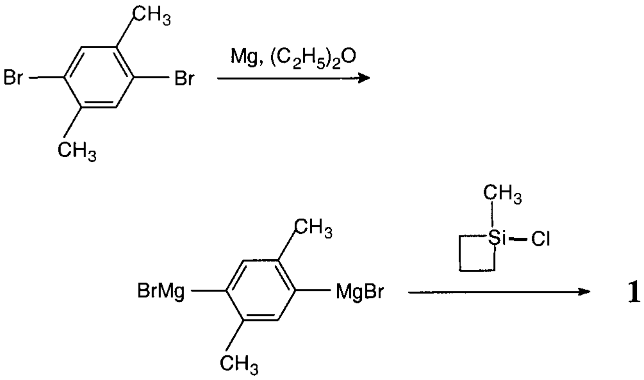
(6) X-ray structure determination of compounds **1** and **2** were first performed at 293 K (Supporting Information) by Y. E. Ovchinnikov, S. A. Pogozhikh, and F. M. Dolgushin, Nesmeyanov Institute of Organo-Element Compounds, Russian Academy of Science, Moscow.

Scheme 2



Scheme 3



from tetrahedral symmetry with two bond angles of 118° and 120° and one of 80°. The silicon−carbon bond lengths are not affected by this distortion and are in the normal range for saturated silahydrocarbons. The geometry of the ring has a puckered conformation with a dihedral Si8C10C16/Si8C15C16 angle of 158.60(4)° observed in **1** at 120 K. At room temperature (293 K) no substantial changes in the molecular packing or the molecular geometry could be observed.

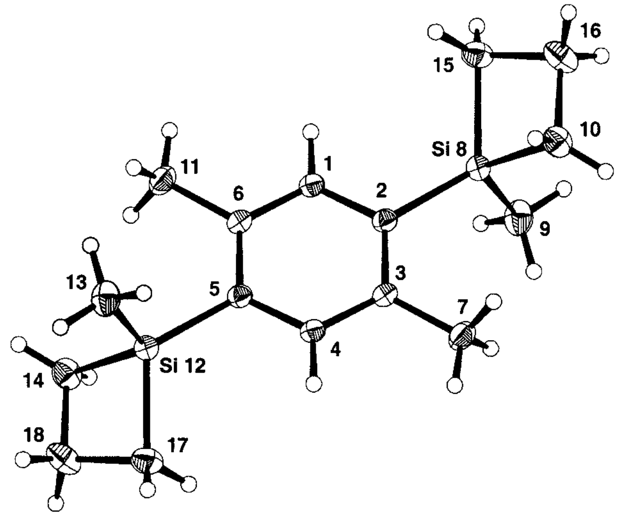


Figure 1. Molecular structure of 2,5-bis(1-methyl-1-silacyclobut-1-yl)-*p*-xylene (**1**). The numbering was chosen in accordance with Figure 2 and the theoretical part. Selected bond distances at 120 K (Å): Si8−C2 = 1.8708(9), Si8−C10 = 1.878(1), Si8−C15 = 1.883(1), C2−C3 = 1.409(1), C3−C4 = 1.396(1), C10−C16 = 1.563(1), C15−C16 = 1.562(1).

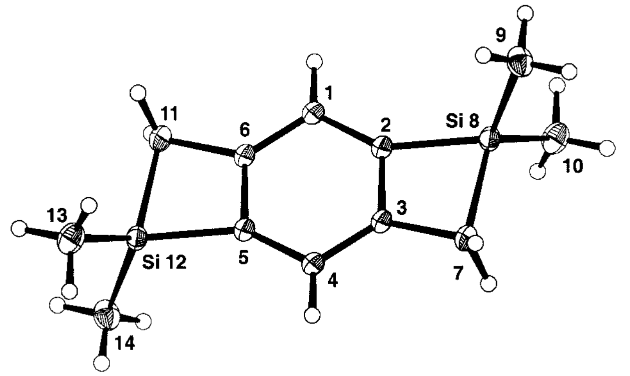


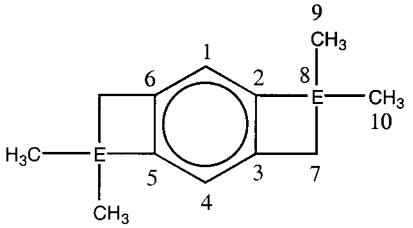
Figure 2. Molecular structure of 1,2,4,5-tetrahydro-1,1,4,4-tetramethyl-1,4-disiladicyclobuta[*a*,*d*]benzene (**2**). The numbering of atoms is in accordance with the theoretical part. Selected bond distances at 100 K (Å): Si8−C2 = 1.8657(8), Si8−C7 = 1.8996(8), Si8−C9 = 1.8586(9), Si8−C10 = 1.8571(9), C1−C2 = 1.3943(9), C2−C3 = 1.4154(9), C3−C7 = 1.5242(10).

Low-Pressure Pyrolysis (LPP) of 1: Isolation and Characterization of 2. The LPP of silacyclobutane **1** was performed in the range of 670−690 °C and at 5 × 10^{-2} Torr. As the main pyrolysis product resulting from silacyclobutane **1**, butterfly compound **2** was isolated as a crystalline solid. Details of the pyrolysis conditions, the spectroscopic characterization, and the experimental details of the X-ray single-crystal structure determination of **2** are given in the Experimental Section. Crystals from different batches appear in two polymorphs. The structure of the $P2_1/n$ polymorph was determined at room temperature, and for the $I2/a$ polymorph, the data collection was carried out at 100 K. A phase transition upon cooling could not be observed.

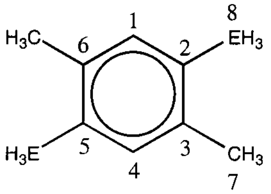
At 100 K, as can be seen from Figure 2, the centrosymmetric molecule shows the silacyclobutene moieties condensed to the aromatic ring, resulting in an almost planar arrangement with only the silicon-bonded methyl substituents situated above and below the molecular plane (Figure 2).

The benzo[*a*,*d*] annelated silacycles are planar within the available accuracy at 100 K, and the carbon−carbon bond lengths of the aromatic ring are in the usual range

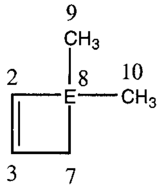
Chart 1



2, E=Si
2a, E=C



4, E=Si
4a, E=C



5, E=Si
5a, E=C

for aromatic hydrocarbons in the solid state. Consequently, the silacycles cannot be interpreted as intrinsic silacyclobutene: the bond length C2−C3 (1.4154(9) Å) is much shorter than the corresponding bond length C10−C16 in **1** at 1.563(1) Å but is clearly longer than in a free silacyclobutene with 1.35 Å.[7] The remaining bond lengths of the silacycle are in good agreement with standard values. The molecules are piled up as rods running along [100] with intermolecular distances exceeding π-interaction limits. At room temperature the different polymorph of **2** is almost planar as well and shows only minor differences in the molecular geometry. The final difference electron density map[8] in the least-squares plane of **2** at 100 K proves that the silicon−carbon bonds are clearly displaced outward the internuclear axes, whereas the benzene moiety does not show this phenomenon at all.

Theoretical Study. Two effects of the two [*a*,*d*] annelated silicon-containing four-membered rings on the geometry of the benzene ring in **2** might be anticipated. Pure substituent effects must be distinguished from ring strain effects, resulting from the annelation of the two silacyclobutene moieties. To differentiate between those, the molecular structures of **2** and model compounds **4** and **5** (Chart 1) have been optimized employing density functional methods (details are given in the Experimental Section).[9] A comparison with the computed structures of **2a**, **4a**, and **5a** will determine the influence of silicon on the structural features of the discussed molecules.

The fully optimized molecular structure[10] of **2** and a comparison of selected geometrical parameters with those data obtained by the single-crystal X-ray analysis are given in Table 1 (detailed geometrical parameters of compounds **4**, **4a**, **5**, and **5a** are given in the Supporting Information).

Table 1. Selected Geometrical Parameters of Compounds 2 and 2a at the B3LYP/6-31G(d) Level of Theory[a]

	2 (X-ray)[b] (C_i)	**2** (C_i)	**2a** (C_i)
C1−C2	1.3943(9)	1.398	1.396
C2−C3	1.4154(9)	1.420	1.400
C3−C4	1.3932(9)	1.398	1.396
C3−C7	1.5242(10)	1.532	1.520
C2-E8	1.8657(8)	1.882	1.535
C7-E8	1.8996(8)	1.927	1.591
E8-C9	1.8586(9)	1.891	1.533
E8-C10	1.8571(9)	1.891	1.533
∠C6C1C2	116.90(6)	117.0	112.5
∠C1C2C3	121.16(6)	121.4	123.8
∠C2C3C4	121.95(6)	121.6	123.7
∠C3C2E8	90.37(5)	90.7	93.6
∠C2E8C7	77.38(4)	76.8	85.9
∠E8C7C3	85.91(5)	85.8	87.0
∠C7C3C2	106.34(6)	106.6	93.5
∠C2E8C9	114.94(5)	117.1	114.8
∠C7E8C10	116.40(5)	116.3	114.0
∠C9E8C10	110.23(5)	110.0	111.2
∠C7E8C9	116.05(5)	116.3	114.0

[a] Distances are given in Å and angles in deg. The X-ray structure determination of compound **2** was carried out at 100 K. [b] Mean deviation given in parentheses.

The benzene subunit of the calculated structure **2** shows small but significant bond length alternations (Table 1). In comparison to their neighboring bonds the annelated bonds C2−C3 and C5−C6, respectively, are slightly elongated (0.022 Å). However, these small bond length alternations in the aromatic moiety do not affect the cyclic conjugation within the benzene ring. This is shown by a comparison of the NICS[11] value of the D_{6h}-symmetric benzene (−11.5) and the calculated NICS values of **14** (−10.2), **4a** (−11.4), **15** (−10.2), and **4** (−10.2), which are only negligibly less negative (Figure 4). This is in agreement with results by Schleyer and co-workers, who reported that even the NICS for "Kekule benzene" (with D_{3h} symmetry and carbon−carbon bond lengths fixed at 1.350 and 1.449 Å) is only 0.8 less negative than the NICS value for D_{6h} benzene at the GIAO-SCF/6-31+G(d)//MP2/6-31G(d) level of theory.[11] This confirms the relative insensitivity of diatropicity caused by geometric variations in aromatic systems.[12]

A comparison of the structural parameters of the benzene subunit of the tricyclic compound **2** and the silyl-substituted arene **4** reveals that the small bond length alternations in the benzene moiety are mainly due to substituent effects but are not related to any strain caused by the [*a*,*d*] annelation of the four-membered rings. Thus, the C2−C3 bond length in **2** (1.420 Å) with two annelated four-membered rings is nearly as long as in **4** (1.412 Å), in which only the substituent effects are operating. The same arguments hold for the C1−C2 bond length (1.398 Å in **2** and 1.404 Å in **4**). These substituent effects can also be found for the hydrocarbons **2a** and **4a** (C1−C2 = 1.396 and 1.398 Å, respectively, and C2−C3 = 1.400 and 1.408 Å).

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(8) Dunitz, J. D. *X-ray Analysis and the Structure of Organic Molecules*; Verlag Helvetica Chimica Acta, Zürich, 1995.

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(10) To be in accordance with the X-ray structure of compound **2**, all related calculations are based on a structure of C_i symmetry.

(11) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes Eikema, N. J. R. v. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

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These comparisons show clearly that the benzene moiety does not localize its bonds as a consequence of the annelation. The small bond length alternations can be rationalized by substituent effects.

The expected strain effects resulting from the two [*a*,*d*] annelated silicon-containing four-membered rings on the geometry of the benzene subunit in **2** becomes evident focusing on the bond angles. The exocyclic angles at the C2 (∠C3C2C8) and C3 (∠C2C3C7) atoms in **4** (122.5; 121.5°) decrease strongly on proceeding to **2** (90.7°, 106.6°), obviously caused by the strain of the annelated rings.[13] The average value in **2** (((∠C3C2C8) + (∠C2C3C7))/2) amounts to 98.7°, while in **2a** this angle is 93.6°. As a geometrical consequence, the endocyclic angle at C1 (**4**, 122.9°; **2**, 117.0°) decreases. Accordingly, the bond angle at C1 may be used as a qualitative indicator of ring strain.[13] Due to this hypothesis, there is less strain in silane **2** (∠C6C1C2 = 117.0°) as compared to the corresponding hydrocarbon **2a** (∠C6C1C2 = 112.0°).

One theoretical method used to get some information about the particular nature of bonding is based on the interpretation of the molecular graph of a molecule.[14] In most compounds the bond path (i.e. the path of maximum electron density) linking two nuclei is a straight line: e.g., in acyclic hydrocarbons. In those the bond path length R_b is identical with the geometrical bond length, R_g ($R_b = R_g$). However, for strained compounds, e.g., cyclopropane, the bond path between the carbon atoms is strongly bent ($R_b > R_g$).[14] The qualitative conclusion is that the more the strain is concentrated in a specific bond, the more strongly bent it is.

An equivalent approach to quantify the concept of strain results from the determination of the difference $\Delta\alpha$ between the bond path angle α_b and the geometric bond angle α_g.

As can be seen in Figure 3, the corresponding bonds in the four-membered rings of compound **2** are strained, similarly to those in **5**. While the silicon−carbon bonds are shown to be the most bent ones in both molecules, with ΔR reaching from 0.009 to 0.014 Å, the carbon−carbon bonds are not bent at all. This demonstrates that the origin of strain in **2** is comparable to that of silacyclobutene **5**. $\Delta\alpha$ for corresponding angles in **2** and **5** has comparable values, e.g., ∠C2Si8C7 = +12.9° in **2** is nearly as large as in **5**, ∠C2Si8C7 = +13.2°. This confirms the statements which resulted from the ΔR approach.

For a quantification of the strain energies, homodesmic reactions[15] for the model compounds **10**, **15**, and **18** were performed (Figure 4). This energy is 21.3 kcal mol^{-1} for silacyclobutene **10**, as calculated by the homodesmic reaction (b). Assuming that the silacyclobutene subunit is mainly responsible for the strain, compound **18** should exhibit a comparable strain energy, and for **15** it is expected to be approximately twice as much as calculated for **10**. The values of 22.4 kcal mol^{-1} for **18** and 44.2 kcal mol^{-1} for **15**, obtained from the homodesmic reactions (d) and (f), are in excellent agreement with this prediction.

The hydrocarbons **2a** and **5a** show a somewhat different picture. In comparison to the silicon-containing compounds **2** and **5**, in which only the silicon−carbon bonds are bent, all carbon−carbon bonds in both four-membered units of cyclobutene **5a** and of **2a** are nearly equally bent. However, due to the different bending force constants of carbon−carbon and silicon−carbon bonds, a direct connection between bond bending and strain is not given and the comparison only based on Δr or Δa values is therefore not allowed. Since it is a well-known fact that silicon−carbon bonds require less energy to be bent than carbon−carbon bonds,[16] it is likely that the hydrocarbons **2a** and **5a** do have greater ring strain. Indeed, replacement of a carbon atom in cyclobutene **6** by a silicon in **10** decreases the total strain by 8.3 kcal mol^{-1}. As in the case of the silacycles **10**, **15**, and **18**, the strain energies in **6**, **14**, and **16** are additive (Figure 4). These calculations are in good agreement with results published by Maksic and co-workers,[17] who reported qualitatively similar strain energies for a 1,2-disilacyclobutabenzene.

The calculation of the X−X difference electron density[8] is considered to be an experimental equivalent for the topological analysis of the wave function. When this electron density mapping is performed, distinct electron peaks are found directly at or close to the midpoint of bonds. Maxima associated with distinct bonds in strained three- and four-membered rings are clearly displaced outward from the internuclear axes.

A qualitative comparison of the experimentally determined X−X difference electron density and the molecular graph of the calculated structure of **2** (Figure 3) is in convincing agreement, confirming that the silicon−carbon bonds[18] are the most bent ones, whereas the bond paths in the benzene moiety linking two nuclei are characterized by straight lines.

Photoelectron Spectrum of 2. The butterfly compound **2** exhibits 74 valence electrons, which, according to the rule of thumb ($\sum(1s_H + np_E)/2 = IE^v_n(\text{He I})$),[19] should give rise to $n = 23$ ionizations within the He I measurement region. The photoelectron spectrum (Figure 5) shows three isolated bands at low energy and a tremendous ionization hill between 12 and 16 eV, resulting from at least 14 overlapping ionizations, as estimated from the approximate intensity ratio of 1:1:(2):6(5):14. Due to the unpredictable and widely differing electronic relaxation of individual radical cation states of medium-sized organic compounds,[20] only a tentative rough, but plausible assignment by a Koopmans analo-

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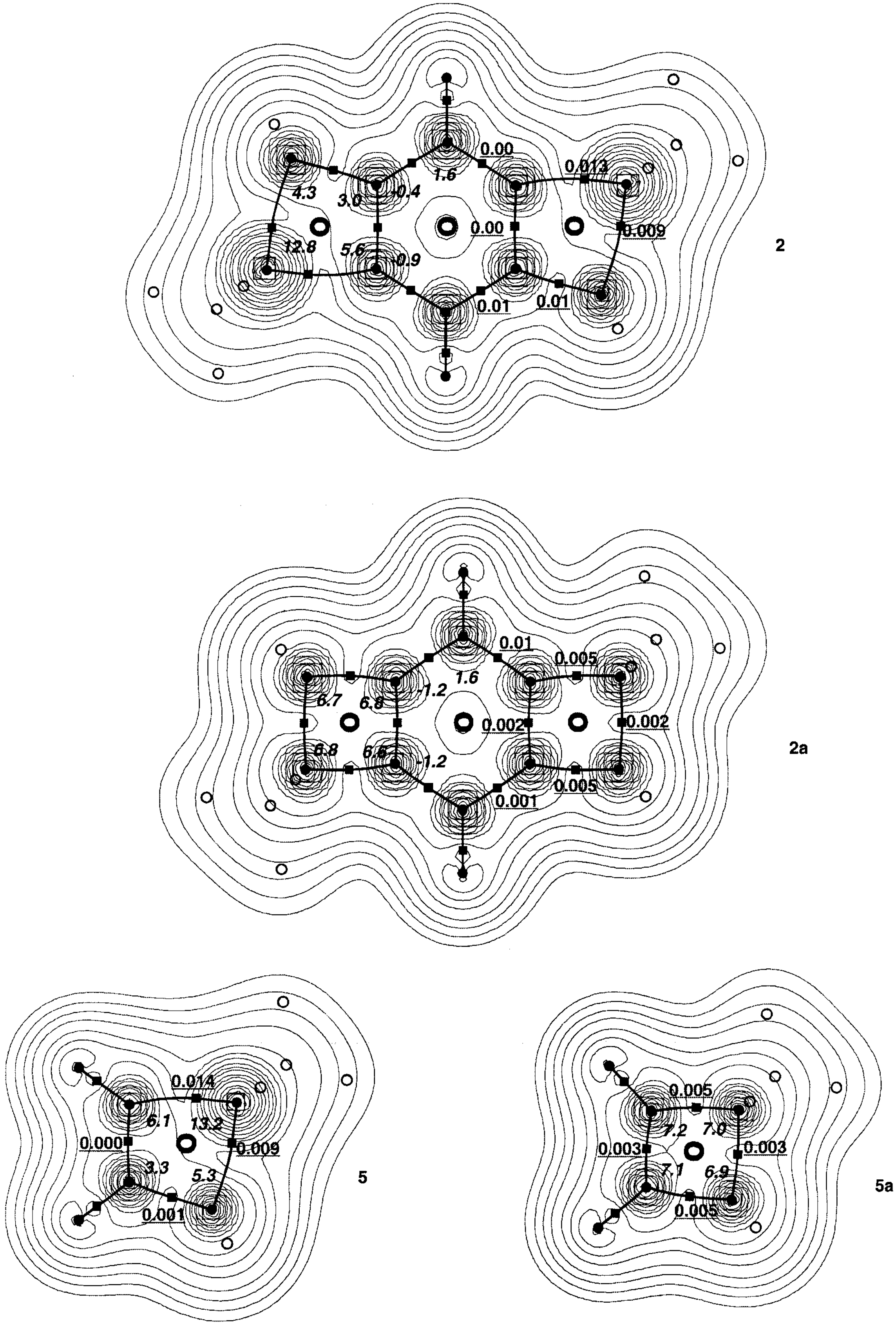

Figure 3. Molecular graphs and electron densities of structures **2**, **2a**, **5**, and **5a**, obtained from a HF/6-311G(d)//B3LYP/6-31G(d) wave function. The underlined values give $\Delta R = R_b - R_g$ in Å. The other values show the difference $\Delta\alpha$ between the bond path angle α_b and the geometrical bond angle α_g[14] in deg.

gous correlation can be suggested, on the basis of a single-point ab initio calculation. Accordingly (cf. Figure 5), the ground state of the radical cation of **2** $\tilde{X}(^2A_g)$ at 8.15 eV and the first exited state $\tilde{A}(^2A_g)$ at 8.7 eV should

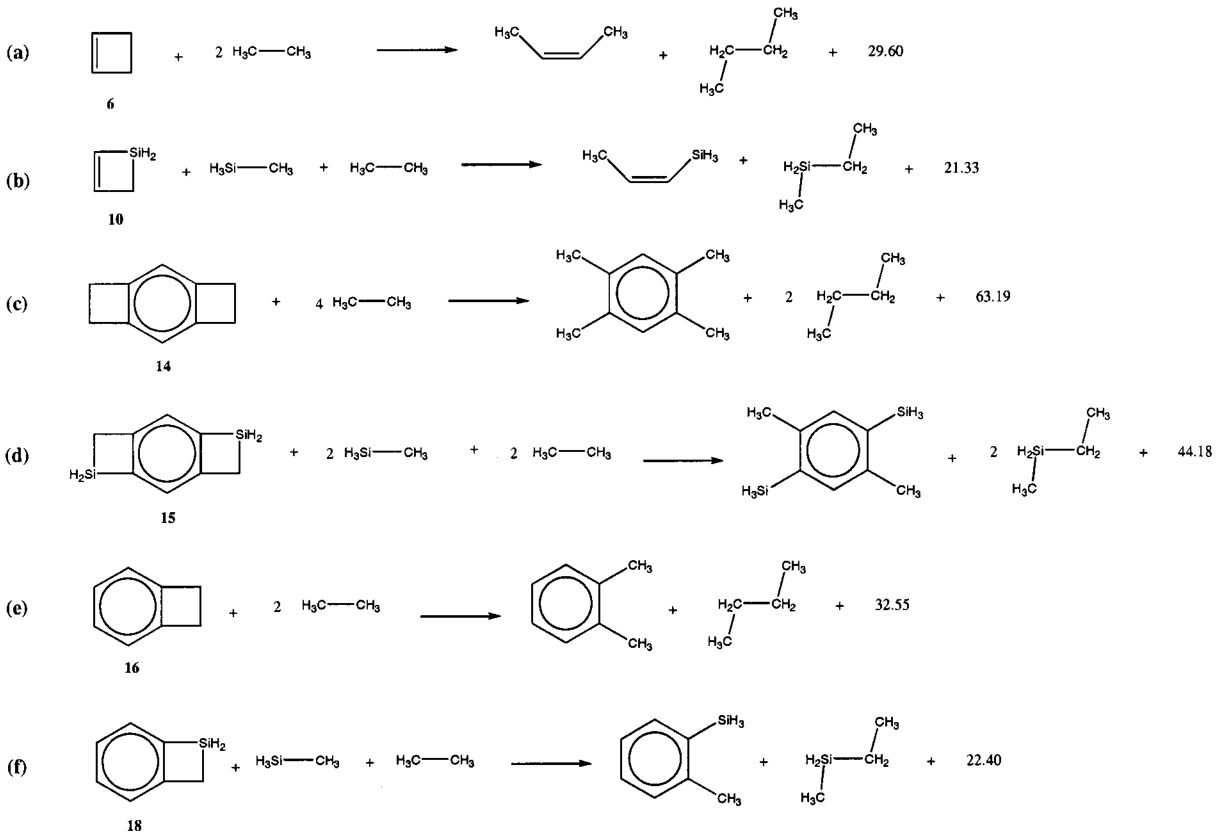

Figure 4. Total strain energies of selected compounds calculated by the homodesmic reactions (a)–(f) on the MP4(SDTQ)/6-311G(d)//B3LYP/6-31G(d) level, including B3LYP/6-31G(d) ZPE. All energies are given in kcal mol^{-1}.

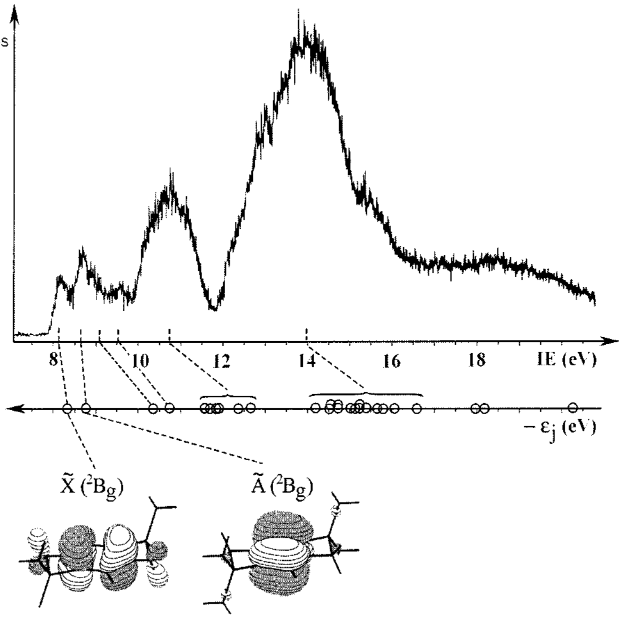

Figure 5. He I photoelectron spectrum of 1,2,4,5-tetrahydro-1,1,4,4-tetramethyl-1,4-disiladicyclobuta[*a*,*d*]benzene (**2**). The assignment of the ionization patterns is based on a HF/6-311+G(2df,p)//B3LYP/6-31G(d) wave function.

arise from π-electron ionization at the benzene molecule center. The doubly degenerate benzene π ionizations e_{1g} (9.247 eV)[21] are shifted by 0.9 and 0.55 eV, respectively. The calculated values of 8.36 and 8.84 eV are in good agreement with the vertical ionization energies. The second PE band with a maximum at 8.7 eV seems to contain more than one ionization. The maximum on its shoulder at approximately 9.2 eV and the next maximum at 9.6 eV could present the next two ionizations and can be assigned to the predominant contributions of the σ bonds $\tilde{B}(^2A_g)$ and $\tilde{C}(^2B_u)$. The following two overlapping PE band systems, the higher cation states, cannot be assigned exactly.

Conclusion

In this paper the synthesis, isolation, and structural characterization of the butterfly compound **2** is described. As it is the first silacyclobutene diannelated [*a*,*d*]benzene reported in the literature, it is an attractive target for the determination of its structural features. The structural directive influence of four-membered annelated rings on the bond lengths of the benzene ring moiety has already been investigated by several groups.[13,22] In general, the bond length alterna-

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Table 2. Crystal Data and Details of the Structure Determination of 1 at 120 K[6] and of 2 at 100 K

	1	**2**
temp (K)	120	100
empirical formula	$C_{16}H_{26}Si_2$	$C_{12}H_{18}Si_2$
fw	274.55	218.44
cryst syst	$P1$	mI
space group	$P\bar{1}$ (No. 2)	$I2/a$ (No. 15)
a (Å)	6.358(1)	10.735(2)
b (Å)	7.067(1)	9.614(2)
c (Å)	9.270(3)	12.340(2)
α (deg)	89.800(3)	
β (deg)	96.500(3)	93.97(3)
γ (deg)	97.240(3)	
V (Å^3)	410.5(2)	1270.5(4)
Z	1	4
ρ_{calc} (g/cm^3)	1.110	1.142
F_{000}	300	472
μ(Mo Kα) (mm^{-1})	0.2	0.2
cryst size	0.50 × 1.05 × 1.05	0.30 × 0.70 × 1.00
radiation (Å)	Mo Kα, 0.710 73	Mo Kα, 0.710 73
scan range (deg); type	$2.2 < \theta < 35.0$; $\omega/2\theta$	$5.2 < \theta < 37.0$; $\theta/2\theta$
limits	$-9 < h < 10$ $-11 < k < 11$ $0 < l < 14$ $1.40 + 0.35 \tan\theta$	$-17 < h < 17$ $-16 < k < 16$ $-19 < l < 19$ $1.40 + 0.35 \tan\theta$
N_{tot}, N_{unique}, R_{int}	3580, 3580, 0.000	6267, 3005, 0.111
N_{obs} ($I > 2.0\sigma(I)$)	3270	2756
N_{par}	135	100
R, wR2, GOF	0.0304, 0.0929, 1.16 $w = 1/[\sigma^2(F_o^2) + (0.0433P)^2 + 0.0993P]$ $P = (F_o^2 + 2F_c^2)/3$	0.0335, 0.0991, 1.05 $w = 1/[\sigma^2(F_o^2) + (0.0521P)^2 + 0.3618P$ $P = (F_o^2 + 2F_c^2)/3$
param shift on last cycle in units of esd's (max)	0.000	0.00
$\Delta\rho_e$ (min/max)	−0.30/0.49	−0.36/0.53

tions within the benzene moiety are explained by strain effects due to the annelated four-membered rings on the benzene subunit. The calculations reported in this paper reveal that the differences in the benzene bond lengths of **2**, as well as in the hydrocarbon **2a**, result primarily from substituent effects and are not caused by the ring strain. Of course, the benzene ring is affected by the ring annelation, not shown by bond length alternations but indicated by changes of the endocyclic bond angles at C1 and C4, which are a qualitative sign of the amount of strain the benzene ring has to pick up from the two four-membered rings attached. Forming strongly bent silicon−carbon bonds, the silicon atoms decrease the amount of strain in the model compounds, in the silacyclobutene **10** by 8.3 kcal/mol and in **15** by 19.01 kcal mol^{-1}, as compared to the corresponding hydrocarbon compounds. As can be seen from the calculations, the total strain energy is additive, depending on the number of annelated rings.

Experimental Section

2,5-Bis(1-methyl-1-silacyclobut-1-yl)-*p*-xylene (1). A 2.0 L round-bottom flask was charged with magnesium turnings (19.0 g, 0.78 mol) and 200 mL of ether. 2,5-Dibromo-*p*-xylene (51.5 g, 0.195 mol, purchased from Aldrich and used without purification) in 300 mL of dry diethyl ether was added dropwise with stirring and heating. 1,3-Dibromopropane was used to activate the Grignard reaction. After completion, the reaction mixture was heated for 6 h.

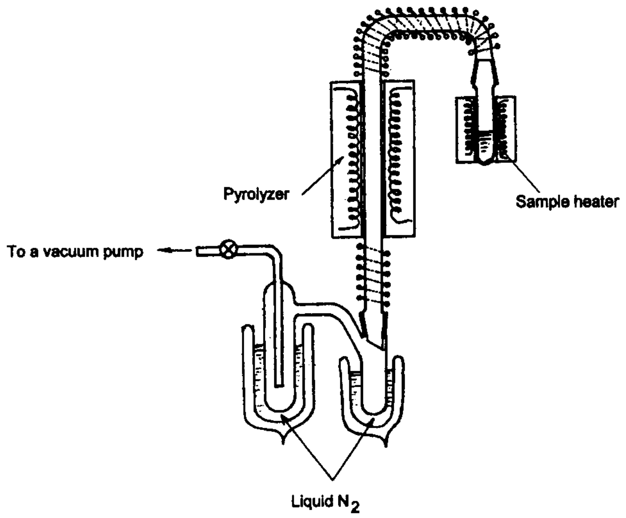

Figure 6. Pyrolysis unit.

1-Chloro-1-methyl-1-silacyclobutane[23] (47.1 g, 0.39 mol) was added dropwise with stirring to the greenish brown Grignard solution, and the reaction mixture was refluxed for 5 h. The residue was filtered, and the ether solution was treated with water. After separation of the layer the ether solution was dried over $CaCl_2$ and the solvent was removed by distillation. All volatile products were distilled by trap-to-trap distillation in vacuo. The remaining nonvolatile viscous liquid was crystallized on cooling to room temperature, yielding 39 g of the raw material. A pure sample of **1** (19.18 g, 0.07 mol, 35.9%) was obtained after recrystallization from hot ethanol, and a suitable single crystal was chosen for the X-ray analysis (Table 2). DSC: mp 66.8 °C.

Mass spectroscopic data (*m*/*z*) for **1** show $M^{\bullet+} = 274$ (15), fragment peaks corresponding to loss of a methyl radical $[M - CH_3]^+ = 259$ (4), and, as expected, by splitting off one and two ethylene fragments: $[M - C_2H_4]^{\bullet+} = 246$ (33) and $[M - 2\ C_2H_4]^{\bullet+} = 218$ (100). Also, the peak $[M - 2\ C_2H_4 - CH_3]^+ = 203$ (97) was next to the most abundant. In the IR spectrum of **1** characteristic absorptions for the silacyclobutane moiety were detected (437, 898, 922, and 1121 cm^{-1});[24] the deformation vibrations of the methyl groups attached to silicon are assigned to the bands at 817 and 1246 cm^{-1}, and for the benzene nucleus a band at 1335 cm^{-1} is characteristic. A strong absorption band at 862 cm^{-1} is due to a tetrasubstituted benzene ring[25] moiety. ^{1}H NMR (C_6D_6): δ 0.44 s (6H; C9, C13), 1.22 m (4H; C10, C14), 1.37 m (4H; C15, C17), 2.20 m (4H; C16, C18), 2.29 s (6H; C7, C11), 7.39 s (2H; C1, C4). ^{13}C NMR (C_6D_6): δ −0.30 (2C; C9, C13), 14.93 (4C; C10, C14, C15, C17), 18.68 (2C; C16, C18), 21.82 (2C; C7, C11), 135.00 (2C; C1, C4), 139.36 (4C; C2, C5, C3, C6). ^{13}C NMR ($CDCl_3$): δ −0.44 (2C; C9, C13), 14.56 (4C; C10, C14, C15, C17), 18.17 (2C; C16, C18), 21.67 (2C; C7, C11), 134.56 (2C; C1, C4), 139.14 (4C; C2, C5, C3, C6). ^{29}Si NMR (C_6D_6): δ 12.58. Anal. Calcd for $C_{16}H_{26}Si_2$: C, 70.07; H, 9.49; Si, 20.44. Found: C, 69.80; H, 9.30; Si, 20.60.

1,2,4,5-Tetrahydro-1,1,4,4-tetramethyl-1,4-disiladicyclobuta[*a*,*d*]benzene (2). For the synthesis of **2** the low-pressure pyrolysis (LPP) technique was used. The design is shown in Figure 6.

The flow hollow vertical cylindrical quartz reactor (i.d. 15 mm, length 150 mm, volume 26.5 cm^3) was combined with a vacuum line. An ampule with crystals of **1** (1.5 g, 5.47 mmol)

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was connected to the system, and vapor of the starting compound was passed through the reactor over 24 $^3/_4$ h (residence time 0.4 s) from the top to the bottom of the reactor, which was heated to 670−690 °C at 5 × 10^{-2} Torr. To avoid sublimation of **1**, the vacuum line, the ampule, the reactor, and the line between the pyrolyzer and the trap were heated. The pyrolysis products were collected in a trap cooled with liquid nitrogen. After completion of the pyrolysis, the trap was thawed and the gaseous products formed were collected in a 2 L vessel. A GC analysis (Squalane, 0.22 × 50) indicated ethylene to be the only gaseous reaction product. From the first trap a canary yellow solid was isolated (0.99 g). GC/MS analysis (SE−30) of its benzene solution indicated traces of **1** and a small amount (8%) of 3,4-benzosilacyclobutene **3**. The main reaction product (85%) was the butterfly compound **2**, which was purified by recrystallization from pentane (0.28 g, 1.28 mmol, 23.4%). **2**: DSC mp 71.3 °C.

Only two prominent fragments could be detected in the mass spectrum, i.e., the molecular ion at *m/z* 218 (68), $M^{\bullet+}$, and a fragment ion due to the loss of methyl at *m/z* 203 (100), $[M - CH_3]^+$. The IR spectrum of **2** proves the existence of the silacyclobutene moiety, showing bands at 463, 690, 800, 1043, 1372, and 3048 cm^{-1}.[24] The absorption bands at 690 and 800 cm^{-1} are assigned to ν_{CH}.[26] Deformation vibrations of the methyl groups at silicon are registered at 817 and 1246 cm^{-1}, and the absorption at 637 cm^{-1} is due to the skeleton SiC_2 stretching mode of the benzene nucleus (1335 cm^{-1}). A strong absorption band at 847 cm^{-1} was assigned to the tetrasubstituted benzene ring moiety.[25] ^1H NMR (C_6D_6): δ 0.32 s (12H; 3C9, 3C10, 3C13, 3C14), 2.19 s (4H; C7, C11), 7.30 s (2H; C1, C4). ^{13}C NMR (C_6D_6): δ −0.56 (4C; C9, C10, C13, C14), 20.15 (2C; C7, C11), 129.20 (2C; C1, C4); 148.04 (2C; C3, C6), 148.85 (2C; C2, C5). ^{29}Si NMR (C_6D_6): 8.16 (2Si; Si8, Si12).

When the ^1H NMR spectra of **1** is compared with the ^1H NMR spectrum of **2**, the latter becomes more simple. The multiplets resulting from coupling of the silacyclobutane methylene protons in **1** disappear, and the spectrum of **2** exhibits three singlets, assigned to the protons of the methyl groups at silicon, the methylene protons of the benzosilacyclobutene rings, and the two para protons of the central benzene nucleus. Correspondingly, the ^{13}C NMR spectrum of **2** shows only one signal for the methylene group of the benzosilacyclobutene ring instead of the two signals for the silacyclobutane methylene carbon atoms and the resonances for the methyl groups in the para position of the benzene unit. The ^{29}Si NMR resonance shifted by 4.42 ppm (12.58 (**1**) and 8.16 (**2**) ppm) to lower field.

As the only gaseous pyrolysis product of **1**, ethylene was isolated. From GC/MS investigations on the mixture of solid and liquid products formed, it became obvious that the starting material **1** was consumed nearly quantitatively. Some minor reaction products could be detected by GC but were not isolated from the reaction mixture. On the basis of the GC/MS analysis one of them was assigned to compound **3** (Scheme 2).

A suitable single crystal of **2**, obtained by recrystallization from cold *n*-pentane, was chosen for the X-ray analysis. The data set for the structure determination is listed in Table 2. Anal. Calcd for $C_{12}H_{18}Si_2$: C, 66.06; H, 8.25; Si, 25.69. Found: C, 66.20; H, 8.40; Si, 25.55.

GC/MS measurements were performed on a Carlo Erba/Kratos MFC 500 instrument. The capillary column SE-30 was used. The rate of programmed temperature increase over the range 50−250 °C was 8 °C/min, and the ionization energy was 70 eV. The direct inlet was used to run the mass spectrum of crystalline **2**.

Infrared spectra were recorded on a Philips Analytical PU9800 FTIR spectrometer in the range 350−3100 cm^{-1}. The samples were prepared as KBr pellets.

Nuclear magnetic resonance experiments were carried out on a Varian VXR-400 spectrometer at 400.1, 100.6, and 79.5 MHz, respectively. The ^1H, ^{13}C, and ^{29}Si spectra were referenced to tetramethylsilane (δ 0) as an external standard. The ^{29}Si NMR spectra were obtained without proton decoupling. A standard 5 mm $^{13}C/^1H$ probe head was used. All the measurements were carried out in C_6D_6 or $CDCl_3$ as solvent.

Crystal structure determinations were performed with single crystals obtained from ethanol (**1**) or pentane (**2**). Intensity data for the compounds were collected on a Siemens P3/PC diffractometer and on a Stoe IPDS at room temperature and on a Siemens P4/PC at 120 and 100 K, respectively. The data were corrected for Lorentz and polarization effects, but not for absorption. Atom form factors for neutral atoms were used. The structures were solved by direct methods and refined by full-matrix least-squares techniques to minimize $\sum w(F_o - F_c)$,[27] where $w^{-1} = \sigma^2(F) + KF^2$. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were localized by difference Fourier synthesis and refined isotropically. Crystal data and details of the structure determinations for compounds **1** and **2** are given in Table 2. All calculations were performed using SHELXTL PLUS (PC Version 4.0[28] or 5.0[29]) software and SHELX97_2[30,31] on IBM PC/AT computers.

Computational Details. We employed density functional theory (DFT) applying Becke's three-parameter hybrid functional using the LYP correlation functional (B3LYP)[32] and the 6-31G(d) basis set to fully optimize all structures of interest. Subsequent frequency calculations were performed to ensure that the optimized structures represent a local minimum on the potential energy surface.

Inclusion of zero-point energy differences at the B3LYP/6-31G(d) level of theory and single-point calculations at the MP4-(SDTQ) level of theory using the triply split 6-311G(d) basis set were used to get refined energies. This procedure results in more reliable reaction energies for the homodesmic reactions (a)−(f).

As a quantitative aromaticity criterion, nucleus-independent chemical shieldings (NICS)[11] were computed at ring centers at the GIAO-SCF/6-31G(d)//B3LYP/6-31G(d) level of theory. The topological analysis was performed using a HF/6-311G-(d) wave function.

The programs GAUSSIAN94[33a] and GAUSSIAN98[33b] were employed for the optimization, frequency, NICS, and single-

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point calculations, whereas MORPHY[34] was used for the topological analysis.

The photoelectron spectrum was recorded at room temperature by using a Leybold Heraeus UPG 200 high-performance spectrometer with an average resolution of 20 meV calibrated by the $^2P_{3/2}$ ionization of Ar at 15.76 eV. For the measurement a direct-inlet system was used. The tentative assignment by a Koopmans analogous correlation, $\mathrm{IE}_n^{\mathrm{v}} \approx -\epsilon_{\mathrm{J}}^{\mathrm{SCF}}$, is based on a HF/6-311+G(2df,p)//B3LYP/6-31G(d) single-point calculation, and MOLDEN[35] was used to plot the MOs.

Differential scanning calorimetry measurements were made using a DSC Mettler TA−4000 Instrument at a heating rate of 10 °C/min under a nitrogen atmosphere.

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Supporting Information Available: Listings of the crystallographic data, total energies, zero-point energies, and *xyz* coordinates from the optimized geometries. This material is available free of charge via the Internet at http://pubs.acs.org. Further details of the crystal structure analyses of the compounds described in this work have been deposited (without structure factor listings) with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC 119335, CCDC 119336, CCDC 119337, and CCDC 119338. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (phone, +441223/336-033; fax, +44-1223/336-033; e-mail, deposit@ccdc.cam.ac.uk).

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