Thermal Conversion of *closo*-1,2-$(SiMe_3)_2$-1,2-$C_2B_4H_4$ to *closo*-1,6-$(SiMe_3)_2$-1,6-$C_2B_4H_4$: Structure Determination by Ab Initio Calculations, Gas-Phase Electron Diffraction, and Low-Temperature X-Ray Diffraction

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Dedicated to Professor Walter Siebert on the occasion of his 60th birthday

Abstract: *closo*-1,2-$(SiMe_3)_2$-1,2-$C_2B_4H_4$ undergoes thermal conversion to 1,6-$(SiMe_3)_2$-1,6-$C_2B_4H_4$. The reaction pathway was monitored by ^{11}B NMR spectroscopy. The structures of the 1,2- and 1,6-isomers were optimized at the HF/6-31 G* ab initio level. Gas-phase electron diffraction studies for both isomers are reported, as well as low-temperature X-ray crystal structure determinations. Comparison of calculated structural data with the data obtained experimentally shows good agreement between theory and experiment.

Keywords
ab initio calculations · carboranes · electron diffraction · rearrangements · structure elucidation

Introduction

The thermal rearrangements of the icosahedral carboranes, from 1,2- to 1,7-$C_2B_{10}H_{12}$ at 450–550 °C[1] and the subsequent conversion of 1,7- to 1,12-$C_2B_{10}H_{12}$ at even higher temperatures,[2] have been known for more than 30 years. Although a general process for such rearrangements was proposed by Lipscomb shortly after their discovery,[3] the exact mechanism remained the subject of debate.[4–6] The same problem arises in the case of the octahedral *closo*-$C_2B_4H_6$ carboranes. Both have been known for some time, and thermal conversion of the 1,2-isomer to the more stable 1,6-isomer has been studied.[7] Theoretical investigations of the intermediate or transition-state structures that might be involved in the thermal rearrangement have also been carried out. In the most recent and extensive study, McKee[8] concluded that isomerization might proceed through a "local bond rotation" to a benzvalene-type transition state. However, as the author pointed out, none of the computational investigations identifies the specific reaction pathway; they can only show that some are more likely than others. A major problem associated with mechanistic studies of carborane isomerizations is the difficulty in determining the fate of a specific boron atom arising from or going to a set of nearly equivalent atoms. One way of tracing the movement of a particular boron atom in an isomerization reaction is to label it by replacing its hydrogen atom with another substituent group. Such experiments would require the ability to obtain accurate structural information on compounds of low symmetry that may be reasonably volatile or crystallize only at very low temperatures. This type of structural information can be obtained by low-temperature X-ray diffraction or gas-phase electron diffraction (GED) techniques. Many of the GED studies are aided by parallel theoretical calculations, such as those described in the GED structural determinations of several boranes and heteroboranes.[10a–c] The *C*-trimethylsilyl-substituted carboranes are excellent candidates for such substituent studies; they are more stable than their H- or alkyl-substituted analogues, and their structures can be more easily determined.[9] Since a high-yield synthesis of *closo*-1,2-$(SiMe_3)_2$-1,2-$C_2B_4H_4$ has recently been reported,[11] the thermal isomerization of this compound was chosen for an initial study. The results of this investigation

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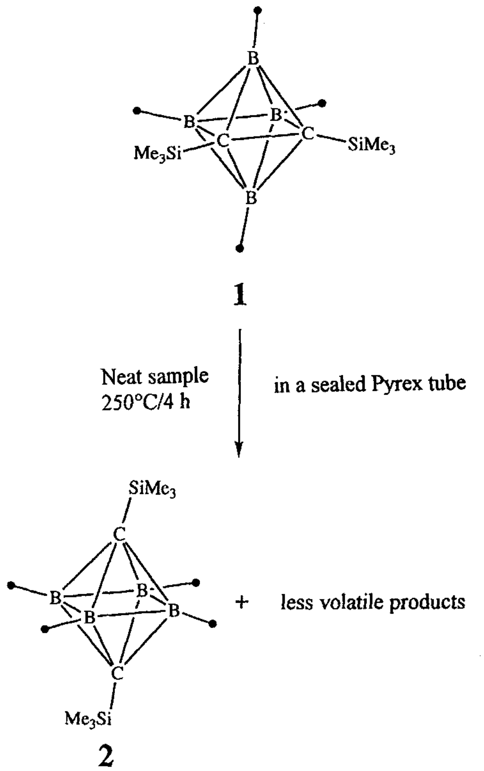
serve as a basis for assessing the effects of cage substituents on the isomerization reactions of the octahedral *closo*-carboranes. In addition, once these effects are understood, the use of highly substituted carboranes should also prove useful in determining the mechanism for the reductive cage opening reactions found for these compounds.[12] We report herein the results of our study on the thermolysis of *closo*-1,2-$(SiMe_3)_2$-1,2-$C_2B_4H_4$, along with the structures of the starting carborane and some of the reaction products, determined by IR and NMR spectroscopy, low-temperature X-ray diffraction, and GED measurements, supported by ab initio molecular orbital calculations.

Results and Discussion

Depending on temperature and reaction time, the thermolysis of *closo*-1,2-$(SiMe_3)_2$-1,2-$C_2B_4H_4$ (**1**) was found to give mixtures of products with varying compositions (Scheme 1). Figure 1 shows the ^{11}B NMR spectra of the reaction mixtures at different times and temperatures. No reaction is detectable below 250 °C. However, at or above this temperature the spectra show the disappearance of the doublets at $\delta = 8.4$ and -11.6, which are due to the 1,2-isomer, and concomitant growth of a doublet at $\delta = -13.9$, which is characteristic of the 1,6-isomer. After 6 h, resonances due to the 1,2-isomer are essentially absent from the spectrum of the thermolysis mixture. These results differ from those found by Onak and co-workers in their study of the thermolysis of the parent molecule, *closo*-1,2-$C_2B_4H_6$, for which no significant change in the ^{11}B NMR spectra was noted unless heating to 250 °C was continued for at least 20 h.[7a] The thermolysis of the parent compound produced rather pure 1,6-isomer (90% *closo*-1,6-$C_2B_4H_6$ and 10% unreacted *closo*-1,2-$C_2B_4H_6$), while in the present study only 35% yield of the 1,6-isomer could be obtained even under the most favorable conditions; the polymeric by-product could not be fully characterized. Figures 2 and 3 show the molecular structures, and Tables 1 and 2 list selected bond lengths and angles derived from theoretical calculations and experimental data (GED, X-ray diffraction) for **1** and **2**.



Scheme 1. Thermolysis of *closo*-1,2-$(SiMe_3)_2$-1,2-$C_2B_4H_4$ (**1**).

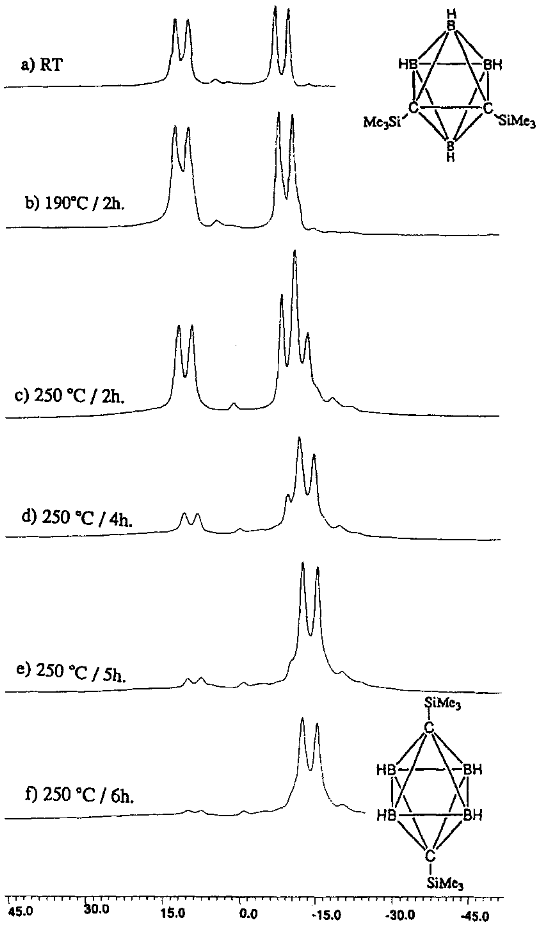


Figure 1. ^{11}B NMR spectra showing the temperature- and time-dependent conversion of *closo*-1,2-$(SiMe_3)_2$-1,2-$C_2B_4H_4$ (**1**) to *closo*-1,6-$(SiMe_3)_2$-1,6-$C_2B_4H_4$ (**2**).

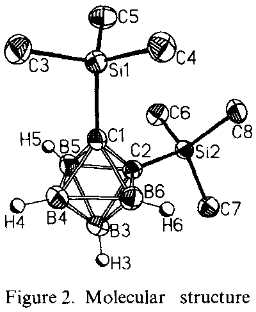


Figure 2. Molecular structure and atom numbering for **1**. Ellipsoids are drawn at the 70% probability level, and hydrogen atoms are of arbitrary size.

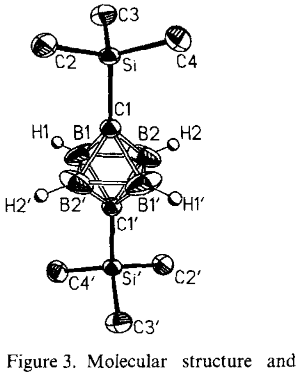


Figure 3. Molecular structure and atom numbering for **2**. Ellipsoids are drawn at the 70% probability level, and hydrogen atoms are of arbitrary size.

Table 1. Geometric parameters of **1** from GED, X-ray crystallography, and ab initio calculations (HF/6-31 G*).

	GED [a]		X-ray [b]	HF/6-31 G*
C1–C2	1.59(4)	p_1	1.582(2)	1.577
$(B-C)_{mean}$	1.587(7)	p_2	1.635(2)	1.625
Δ(BC) = (B4–C1) – (B5–C1)	0.040 [20] [c]		0.026	0.039
B4–C1	1.613(12)		1.653(2)	1.651
B5–C1	1.573(10)		1.627(2)	1.612
$(B-B)_{mean}$	1.698(6)	p_3	1.723(2)	1.726
Δ(BB) = (B3–B5) – (B3–B4)	0.050 [20] [c]		0.033	0.050
B3–B4	1.658(16)		1.697(2)	1.686
B3–B5	1.708(8)		1.730(2)	1.736
C1–Si	1.867(2) [d]		1.873(1)	1.890
$Si-C_m$	1.867(2)	p_4	1.862(1)	1.888
C–H	1.097(5)	p_5	0.98 [e]	1.087
B–H	1.20 [e]		1.08(2)	1.180
C1-C2-Si	133.1(6)	p_6	134.4(1)	135.2
C_m-Si-C_m	112.5(8)	p_7	110.8(1)	109.7
H-C-H	107.2(3)	p_8	109.5 [e]	107.5
ϕ(C1-C2-Si-C_m)	41.3(19)	p_9	44.5(2)	44.0

[a] Distances r_a [Å] and angles $\measuredangle_\alpha$ [°]; uncertainties are 3σ values; for atom numbering see Figure 2; C_m are methyl carbon atoms. [b] Mean values; error limits are σ values. [c] Ab initio value with estimated uncertainty in square brackets. [d] Set equal to Si–C_m. [e] Not refined.

Table 2. Geometric parameters of **2** from GED, X-ray crystallography, and ab initio calculations (HF/6-31 G*).

	GED [a]		X-ray [b]	HF/6-31 G*
B–B	1.699(8)	p_1	1.674(2)	1.696
B–C	1.636(3)	p_2	1.624(1)	1.632
$(Si-C)_{mean}$	1.867(2)	p_3	1.867(1)	1.889
Δ(SiC) = (C1–Si) – (Si–C_m)	–0.005(14)	p_4	0.005(2)	–0.005
C1–Si	1.863(11)		1.871(1)	1.888
$Si-C_m$	1.868(4)		1.866(1)	1.893
C–H	1.102(5)	p_5	0.98 [c]	1.087
B–H	1.212(26)	p_6	1.08(2)	1.169
C_m-Si-C_m	110.9(10)	p_7	110.7(1)	110.1
C1-Si-C_m	108.0(10)		108.0(1)	108.8
H-C-H	107.7(7)	p_8	109.5 [c]	107.6

[a] Distances r_a [Å] and angles $\measuredangle_\alpha$ [°]; uncertainties are 3σ values; for atom numbering see Figure 2; C_m are methyl carbon atoms. [b] Mean values; uncertainties are σ values. [c] Not refined.

For **1** the bond lengths of the carborane skeleton obtained by X-ray diffraction agree perfectly with the calculations, whereas the GED values are considerably shorter. On the other hand, the X-ray and GED values for the Si–C moiety are in excellent agreement, and the calculated bond lengths are slightly longer. The $SiMe_3$ groups in **1** cause substantial lengthening of the C–C bond [1.59(4) Å from GED and 1.582(2) Å from X-ray diffraction] compared to that in the unsubstituted *closo*-1,2-carborane [1.535(2) Å[17a]]. This lengthening is similar to that found when comparing the experimental C–C bond lengths in *nido*-2,3-$C_2B_4H_8$ (1.418 Å) and *nido*-[2-(CH_3)-3-($SiMe_3$)-2,3-$C_2B_4H_6$] (1.460 Å),[17b,c] and could well be the result of the increased steric interactions between the cage carbon substituents.

In the case of **2** both experimental methods and the calculations give very similar bond lengths for the carborane cage. As with **1** the calculated Si–C distances are slightly longer than the experimental values.

Experimental Section

Materials: All solvents were purified by standard procedures.[13] The carborane *closo*-1,2-$(SiMe_3)_2$-1,2-$C_2B_4H_4$ was prepared by the method described in the literature.[11]

Spectroscopic and Analytical Procedures: ^{1}H, ^{11}B, and ^{13}C NMR spectra were recorded at 200, 64.2, and 50.3 MHz, respectively, on an IBM-WP 200SY multinuclear NMR spectrometer. IR spectra were recorded on a Nicolet Magna FT-IR 550 spectrophotometer. Mass spectra were obtained from the Washington University Resource for Mass Spectrometry, Washington University, St. Louis, MO; elemental analyses were obtained from E & R Microanalytical Laboratory, Corona, NY.

Synthetic Procedures: Manipulations of all nonvolatile compounds were performed under strictly inert conditions in a Vacuum Atmospheres drybox or evacuable glove bags filled with dry nitrogen. Volatile compounds were synthesized, isolated, and purified by using standard high-vacuum techniques. All known compounds were identified by comparing their m.p./b.p., IR and/or NMR spectra with those of authentic samples.

Thermolysis of *closo*-1,2-$(SiMe_3)_2$-1,2-$C_2B_4H_4$ (1): A vacuum-sealed pyrex tube (8 mm diameter) containing **1** (2.20 g, 10.1 mmol) was heated in stages from room temperature to ca. 300 °C. The extent of the thermolysis reaction at each stage was monitored in situ by means of the ^{11}B NMR spectrum of the reaction mixture.

Figure 1 shows the ^{11}B NMR spectra at several times during a typical reaction. From such measurements the optimum conditions for the disappearance of the ^{11}B NMR doublets at $\delta = 8.4$ and -11.6, characteristic of **1**, and the formation of a new doublet at $\delta = -13.9$, assigned to *closo*-1,6-$(SiMe_3)_2$-1,6-$C_2B_4H_4$ (**2**), were found to be a thermolysis temperature of 250–255 °C for 5–6 h. When the ^{11}B NMR spectra showed the reaction to be complete, the tube was cooled to –196 °C, opened in a glove bag, and the contents transferred to a 15 mL flask equipped with a teflon stopcock. The flask was then attached to a vacuum-line, and the reaction mixture was slowly heated to 70–80 °C and fractionated through a series of traps maintained at 0, –45, –78, and –196 °C. The colorless liquid that collected in the –45 °C trap was identified as *closo*-1,6-$(SiMe_3)_2$-1,6-$C_2B_4H_4$ (**2**) (0.77 g, 3.5 mmol, 35% yield). B.p. 110–120 °C/10^{-3} mmHg. ^{1}H NMR (C_6D_6, relative to external Me_4Si): $\delta = 0.98-3.67$ (q, 4H, $^1J_{BH} = 188.6$ Hz), 0.39 (s, 18H, $SiMe_3$); ^{11}B NMR (C_6D_6, relative to external $F_3B \cdot OEt_2$): $\delta = -13.9$ (d, 4B, $^1J_{BH} = 187.5$ Hz); ^{13}C NMR (C_6D_6, relative to external Me_4Si): $\delta = 109.02$ [s, br, C(cage)], –0.41 (q, $SiMe_3$, $^1J_{CH} = 121.10$ Hz); IR (C_6H_6, KBr): $\tilde{\nu}$ = 2955 (sh), 2884 (sh), 2790 (w), 2625 (vs, νBH), 2484 (w), 2108 (w), 2003 (w), 1878 (m), 1655 (w), 1561 (m), 1508 (m), 1443 (m), 1408 (s), 1323 (s), 1249 (vs), 1226 (vs), 1173 (vs), 1049 (vs), 1014 (w), 955 (w), 873 (vs), 844 (vs), 808 (vs), 761 (s), 697 (m), 626 (m) cm^{-1}; GC–MS: m/z (%) = 218 (6) [M^+], 203 (100) [M^+ – Me]. $C_8H_{22}B_4Si_2$ (218.1): calcd C 44.14, H 10.19; found C 44.22, H 9.75. The polymeric residue, collected in the 0 °C trap, could not be characterized satisfactorily.

Calculations: Ab initio molecular orbital calculations were carried out on either an IBM RS6000 or a SGI Indigo(2) with the SPARTAN[14] or GAUSSIAN-92[15] series of programs. The geometries of the molecules were optimized at the 6-31 G* level of calculation under the assumption of C_1 symmetry. The calculations show **2** to be more stable than **1** by 22.8 kJ mol^{-1}. This value is not too different from the 27.5 kJ mol^{-1} calculated at the same level of theory by McKee for the parent *closo*-$C_2B_4H_6$ carboranes. The difference in these relative stabilities is small. This is counter to what would be expected on steric grounds and is not consistent with the observation of an elongation of the C–C bond in going from the parent carborane to **2** (vide supra). Therefore, the difference may well be due to the level of theory used in the calculations.

Electron Diffraction Analyses: The GED intensities were recorded with a Gasdiffractograph KD-G2[18] at nozzle-to-plate distances of 25 and 50 cm and with an accelerating voltage of ca. 60 kV. The electron wavelength was calibrated with ZnO powder diffraction in each experiment. The sample reservoirs were heated to 45 °C (**1**) and 38 °C (**2**), and the inlet system and nozzle to 55 and 45 °C, respectively. A nozzle with 0.8 mm diameter was used. The camera pressure during the experiments was ca. 2×10^{-5} Torr. The photographic plates were analyzed by standard methods[19] and averaged molecular intensities in the s ranges of 2–18 and 8–35 Å^{-1} were used in the analyses [$s = (4\pi/\lambda)\sin\theta/2$; λ = electron wavelength, θ = scattering angle]. The radial distribution functions (RDFs) were calculated by Fourier transform of the molecular scattering intensities with an artificial damping function $\exp(-\gamma s^2)$ ($\gamma = 0.0019$ Å^2). Analyses of the RDFs (Figures 4 and 5) resulted in preliminary geometric parameters for these molecules.

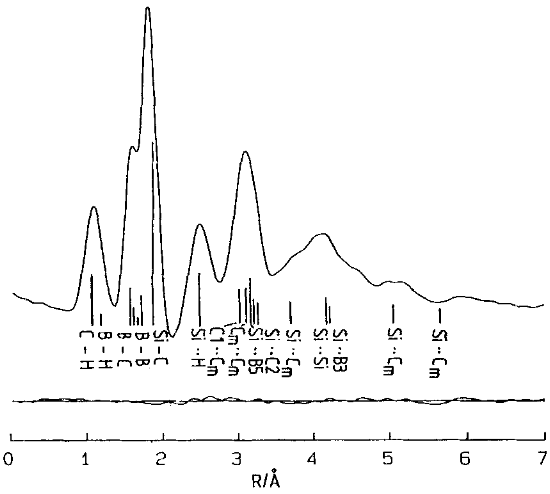


Figure 4. Experimental radial distribution function and difference curve for **1**. The positions of important interatomic distances are indicated by vertical bars.

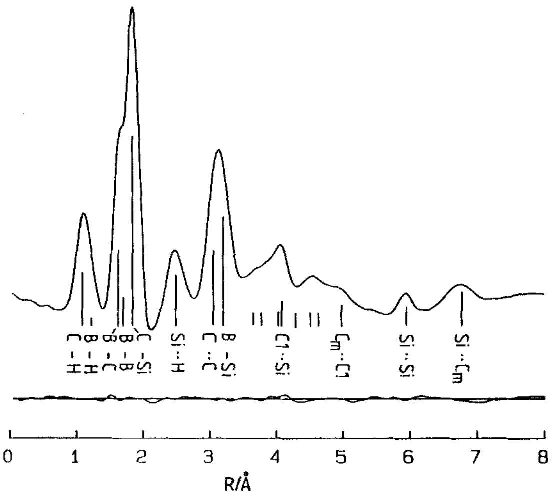


Figure 5. Experimental radial distribution function and difference curve for **2**. The positions of important interatomic distances are indicated by vertical bars.

In the subsequent least-squares refinements, the molecular intensities were modified with a diagonal weight matrix, and known scattering amplitudes and phases were used.[20] Local C_{3v} symmetry was assumed for the trimethylsilyl and methyl groups in both compounds. Vibrational amplitudes were collected in groups according to type (dependent or independent of torsional vibrations) and distance.

For the skeleton of **1**, C_{2v} symmetry was assumed. The orientation of the $SiMe_3$ groups is described by the dihedral angle ϕ(C2-C1-Si-C_m) (C_m is a methyl carbon atom), and torsion of both $SiMe_3$ groups in the same direction (C_2 overall symmetry) led to better agreement with the experimental RDF than torsion in opposite directions (C_s overall symmetry). Mean values for the two types of B–C and of B–B distances were refined in the least-squares analyses, and the differences in bond lengths Δ(BC) = (B4–C1) – (B5–C1) and Δ(BB) = (B3–B5) – (B3–B4) were constrained to the ab initio values. An uncertainty of ±0.02 Å was estimated for these differences and was taken into account in the error limits of the individual bond lengths. The two types of Si–C bonds, C1–Si and Si–C_m, are predicted by the ab initio calculations to differ by only 0.002 Å, and therefore these distances were set to be equal in the least-squares analyses. With these assumptions, nine geometric parameters and seven vibrational amplitudes[21] were simultaneously refined. The following correlation coefficients had values larger than |0.6|: $p_1/p_2 = 0.94$, $p_1/p_6 = 0.72$, $p_2/p_6 = 0.68$. Numbering of geometric parameters p_i and the final results are included in Table 1.

Local D_{4h} symmetry was assumed for the carborane skeleton of **2**. The GED intensities and the RDF are not sensitive towards the orientation of the $SiMe_3$ groups relative to the skeleton. Least-squares analyses with different fixed orientations or with freely rotating $SiMe_3$ groups resulted in nearly identical agreement factors. Since rotation about the C1–Si bond (C1 is the skeletal carbon atom) is governed by a 12-fold potential, very low barriers and free internal rotation at room temperature are expected. The final refinement was performed for a model with C_{2h} overall symmetry (Figure 3). The two types of Si–C bonds in this molecule (i.e., C1–Si and Si–C_m) were described by a mean value $(Si-C)_{mean}$ together with the bond length difference Δ(SiC) = (C1–Si) – (Si–C_m). On the basis of these assumptions, eight geometric parameters p_i and twelve vibrational amplitudes[21] were refined simultaneously. The following correlation coefficients had values larger than |0.6|: $p_1/p_4 = 0.73$, $p_2/p_4 = -0.68$. Numbering of geometric parameters p_i and the final values are included in Table 2.

X-Ray Structural Analyses of 1 and 2: Samples for X-ray structure investigations were prepared by condensing small amounts of the compounds into carefully cleaned X-ray capillaries ($d = 0.2$ mm) under high vacuum ($p \leq 10^{-5}$ Torr). While cooled the capillaries were sealed by means of a resistance-heated platinum wire. Single crystals of both compounds were grown from the melt at temperatures close to the melting point (5 °C for **1**, 20.5 °C for **2**) in situ on a four-circle diffractometer (Syntex/Siemens $P2_1$, $Mo_{K\alpha}$ radiation). A limited data set was first collected for **1** at –34 °C. The structure could be solved and refined in space group $P2_1/c$. To improve the structural model by reduction of thermal vibration the crystal was slowly cooled to –175 °C. At this temperature an extended data set ($2\theta \leq 56°$; h, k, $\pm l$) was collected and used for the final refinement. Pertinent data are given in Table 3.[22] All hydrogen atoms were easily localized in difference Fourier maps. The positions of hydrogen atoms bonded to boron atoms were refined with inclusion of isotropic displacement parameters, and the methyl groups were included in the final cycles of refinement as rigid units. Compound **2** crystallized in the triclinic space group $P\bar{1}$ with one molecule in the unit cell arranged about a center of symmetry. The structure was completely solved with a data set collected at –33 °C. After refinement including anisotropic displacement parameters, the ellipsoids of the boron atoms showed unusually large elongations within the plane of the four-membered ring. To explore in more detail the background of this unusual feature the crystal was cooled to –179 °C at 2 °C h⁻¹. A second data set was collected at this temperature out to $2\theta = 70°$ (Table 3[22]). As indicated by the refined anisotropic displacement parameters, thermal vibration was considerably reduced in the expected way. Although elongation of the boron ellipsoids was still distinct, localization of hydrogen atoms presented no problem at this stage of refinement. To investigate the distribution of electron density within the plane of the boron atoms, difference Fourier maps were derived from a model that included only Si and C atoms with isotropic displacement parameters. As depicted in Figure 6, at

Table 3. Crystallographic data for **1** and **2**.

	1	**2**
formula	$C_8H_{22}B_4Si_2$	$C_8H_{22}B_4Si_2$
M_r	217.68	217.68
space group (no.)	$P2_1/c$ (14)	$P\bar{1}$ (2)
a/pm	974.6(1)	634.9(1)
b/pm	1250.0(1)	635.1(1)
c/pm	1195.1(1)	1089.9(2)
α/°	90	74.54(2)
β/°	91.55(1)	87.00(2)
γ/°	90	61.22(1)
$V/10^6$ pm^3	1455.4(2)	369.74(12)
Z	4	1
T/°C	–175±2	–179±2
ρ_{calcd}/g cm^{-3}	0.993	0.978
$\lambda(Mo_{K\alpha})$/pm	71.073	71.073
$\mu(Mo_{K\alpha})$/mm^{-1}	0.207	0.203
$F(000)$	472	118
no. of measured reflections	3717	4371
no. of unique reflections	3518	3273
no. of refined parameters	149	75
R_{int}	0.0159	0.0237
$R1$(all data)	0.0344	0.0434
$wR2$(all data)	0.0791	0.1113
GOF	1.063	1.113

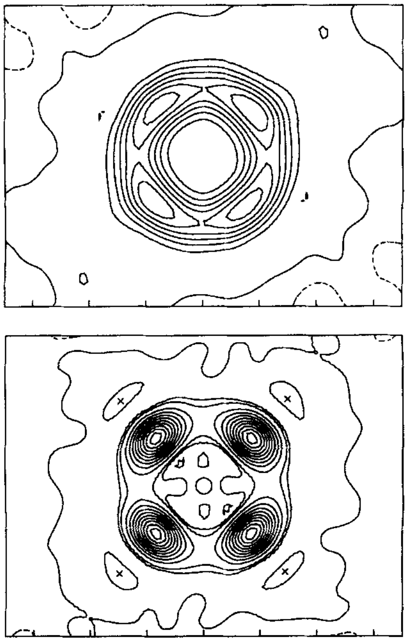


Figure 6. Difference Fourier maps for **2** in the plane through the boron atoms (top: −34 °C; bottom: −179 °C; crosses indicate the positions of hydrogen atoms).

−33 °C there are only four very shallow maxima, which are much more distinct at −179 °C. This indicates dynamic behavior of the planar B_4 unit in terms of extensive oscillation or hindered rotation about the C1–C1′ axis of the molecule. It is remarkable that low barriers were derived in the gas phase (see above), which are still observable at rather low temperatures. The dynamics also manifest themselves in a distinct increase by 1.62% of the molecular volume for the 1,6 isomer as compared to the 1,2 isomer.

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[22] Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-406136 (**1**), -406135 (**2**, −33 °C), and -406134 (**2**, −179 °C).