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Conversion of *nido*-$[(CH_3)_3Si]_2C_2B_4H_6$ to *nido*-$[(CH_3)_3Si]C_2B_4H_7$ and Molecular Structure of 2-(Trimethylsilyl)-2,3-dicarba-*nido*-hexaborane(8), Studied by Gas-Phase Electron Diffraction

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The reaction of liquid *nido*-$[(CH_3)_3Si]_2C_2B_4H_6$ (I) with solid $NaHF_2$ in a Pyrex-glass reactor at 413 K produced *nido*-$[(CH_3)_3Si]C_2B_4H_7$ (II) and $(CH_3)_3SiF$ in quantitative yields without etching the glass walls of the reactor. A similar reaction with HCl in a stainless-steel reactor also produced II and $(CH_3)_3SiCl$ in good yields. The abstraction of the second C–$Si(CH_3)_3$ group was not achieved even in the presence of excess $NaHF_2$ or HCl. Compound II was easily isolated in multigram quantities in high purity by vacuum fractionation. The molecular structure of II in the gas phase was investigated by electron diffaction. Bond lengths (r_a) in the basal plane of the carborane cage were C–C = 146.0 (11), C–B = 154.4 (8), and B–B = 175.8 (16) pm, while distances to the apical boron atom were C–B = 183.2 (17) pm and B–B = 176.1 (12) and 168.7 (19) pm. The trimethylsilyl group was positioned so that the silicon atom was very nearly in the plane of the cage base, with one Si–C(methyl) bond eclipsing the cage C–C bond. All Si–C distances were close to 188 pm, the CCSi angle was 121.9 (11)°, and the C(cage)SiC(methyl) angles were 114.0 (4)°.

Introduction

Recently we have reported[1] several reactions that lead to the formation of tris((trimethylsilyl)-1-alkenyl)borane and also to several air-stable derivatives of *C*-trimethylsilyl-substituted $C_2B_4H_8$. These reactions conveniently avoid the use of Lewis bases such as $(C_2H_5)_3N$. Although the trivinylborane derivatives could be produced in almost quantitative yields, the *nido*-carboranes were obtained in much lower yields with the exception of *nido*-$[(CH_3)_3Si]_2C_2B_4H_6$ (**I**). Since I is produced in multigram quantities (12–13 g per batch; over 73% yield), it has been the major subject for most of our recent investigations.[2-6] For example, the *nido*-carborane I has led to high-yield formation of a *C*-trimethylsilyl-substituted *closo*-osmacarborane,[2] a *closo*-ruthenacarborane,[3] a *closo*-stannacarborane,[4] *nido*-$C_4B_8H_{12}$ derivatives,[5] a *closo*-hafnacarborane,[6] and a *closo*-rhodacarborane.[6]

It is believed that the reactivity of mono-*C*-trimethylsilyl-substituted dicarba-*nido*-hexaborane(8) is sufficiently different from that of the disubstituted derivative[7] to warrant further investigation. Studies of 2-$[(CH_3)_3Si]$-2,3-$C_2B_4H_7$ (II), and of its metalla derivatives, have been hampered by the lack of efficient, inexpensive, high-yield routes to this carborane.[1,8] We report here two new methods by which I is converted quantitatively to II in multigram quantities, safely, cleanly, and with minimal separation problems. Furthermore, these syntheses are of interest in that they demonstrate the significance of the trimethylsilyl moiety in synthetic carborane transformations. These syntheses also avoid the use of expensive starting materials[9] such as $(CH_3)_3SiC{\equiv}CH$, needed in preparations that have been reported previously.[1,8]

The structures of most of the parent carboranes have been determined by X-ray or electron diffraction or by microwave spectroscopy.[10] However, with the exception of *nido*-2,3,4,5-$C_4B_2H_6$,[11] all of the reported electron diffraction data were for *closo*-carboranes. In 1964, Lipscomb et al.[12] determined the structures of *nido*-$C_2B_4H_8$ and *nido*-$(CH_3)_2C_2B_4H_6$ by X-ray diffraction on crystals grown at low temperatures. However, no structural studies of *nido*-carboranes having a bulky trimethylsilyl group on a cage carbon atom have been reported to date. We report here the molecular structure of 2-(trimethylsilyl)-2,3-dicarba-*nido*-hexaborane(8), as found in an electron-diffraction study of the gas phase.

Experimental Section

Materials. 2,3-Bis(trimethylsilyl)-2,3-dicarba-*nido*-hexaborane(8) was prepared by using the method described elsewhere.[1] White cylindric tablets of sodium bifluoride, $NaHF_2$ ($^1/_8$ in. length × $^1/_8$ in. diameter), were obtained from Harshaw Chemical Co., Catalyst Division, Beachwood, OH, and were dried in vacuo before use. Gaseous hydrogen chloride (Matheson, LaPorte, TX) was purified by passing through 153 K traps in vacuo: its purity was checked by IR spectroscopy.

Instrumentation. Proton, boron-11, carbon-13, and silicon-29 pulse Fourier-transform NMR spectra, at 200.13, 64.2, 50.3, and 39.76 MHz respectively, were recorded on an IBM-200 SY NMR spectrometer. Mass spectra were obtained on a Hewlett-Packard GC/MS 5988A instrument. Infrared spectra were recorded on a Perkin-Elmer Model 283 infrared spectrometer. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN.

Synthetic Procedures. All small-scale experiments were carried out in Pyrex-glass round-bottom flasks of 250-mL capacity, containing a magnetic stirring bar and fitted with high-vacuum Teflon valves. All large-scale experiments were carried out in stainless-steel single-ended cylinders of 500-mL capacity (obtained from Tech Controls, Inc., Dallas, TX) fitted with forged-body shutoff valves of $^1/_4$ in. male npt and $^1/_4$ in. Swagelok fittings (obtained from Texas Valve and Fitting Co., Dallas, TX).

All known compounds among the products were identified by comparing their infrared and ^1H NMR spectra with those of authentic samples.

Reaction of *nido*-2,3-$[(CH_3)_3Si]_2$-2,3-$C_2B_4H_6$ (I) with $NaHF_2$. A. In a Pyrex-Glass Reactor. A greaseless Pyrex-glass reactor of 250-mL capacity was charged with 2.10 g (33.9 mmol) of $NaHF_2$ tablets and was evacuated. Freshly distilled, pure carborane I (3.33 g, 15.14 mmol) was condensed into the reactor at 77 K, after which the mixture was warmed to room temperature and stirred for 24 h. The reactor was then cooled to 250 K and the volatiles were distilled out. Most of the reactant

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(9) The cost of $(CH_3)_3SiC{\equiv}CSi(CH_3)_3$ and $(CH_3)_3SiC{\equiv}CH$ for 100 g of each sample are $66.00 and $196.00, respectively. The yields of I and II are 73% and 14%, respectively.

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Table I. Weighting Functions and Other Experimental Electron-Diffraction Data

camera height, mm	Δs, nm^{-1}	$s_{\min}$, nm^{-1}	sw_1, nm^{-1}	sw_2, nm^{-1}	$s_{\max}$, nm^{-1}	correln param	scale factor	wave-length, pm
285.37	2	20	40	124	144	0.275	0.703 (10)	5.701
128.35	4	60	80	300	352	0.465	0.644 (16)	5.699

mixture remained in the reactor. Fractionation of the volatile compounds gave $(CH_3)_3SiF$ (0.048g, 0.52 mmol) and 2-[$(CH_3)_3Si$]-3-[H]-2,3-$C_2B_4H_6$ (II) (0.074 g, 0.50 mmol) collected in traps held at 77 and 228 K, respectively. The *lower half* of the Pyrex-glass reactor, containing most of the reactant mixture, was then immersed in an oil bath maintained at a temperature of 413 K with constant stirring. The heating and stirring were continued for 48 h. After the mixture was cooled to 77 K, accumulated noncondensable gas, presumably H_2 ($\sim$1.0 mmol), was pumped out. All the volatile products were transferred to the main vacuum-line traps and fractionated through traps at 273, 250, 228, and 77 K. The unreacted carborane I (0.83 g, 3.77 mmol) was recovered in both the 273 and the 250 K traps. The carborane II (1.62 g, 10.95 mmol; 96% yield based on I consumed), in very high purity, was collected at 228 K. The most volatile product, $(CH_3)_3SiF$ (1.05 g, 11.41 mmol), was condensed into a trap held at 77 K. HF and SiF_4 were not identified among the products. The unreacted $NaHF_2$ and the nonvolatile product NaF (not measured) remained in the reactor. No etching due to HF on the inside wall of the Pyrex-glass reactor and main vacuum-line manifold was observed. The carborane II (vp 5.0 torr; bp 425–426 K) has been characterized as described elsewhere;[1] its molecular structure is described in a subsequent section of this paper.

B. In a Stainless-Steel Reactor. For large scale syntheses, I (10.68g, 48.55 mmol) and $NaHF_2$ (6.61g, 106.61 mmol) were allowed to react at 413 K for 72 h in a high-vacuum stainless-steel reactor of 500-mL capacity. As described elsewhere,[1,13] only the *lower half* of the reactor was immersed in an oil bath maintained at a temperature of 413 K. The volatile products consisted of pure carborane II (5.23 g, 35.34 mmol; 90% yield based on I consumed), unreacted carborane I (2.03 g, 9.23 mmol), and $(CH_3)_3SiF$ (3.67g, 39.89 mmol). A small quantity of noncondensable gas, presumably H_2 (3.10 mmol), was pumped out.

Reaction of *nido*-2,3-[$(CH_3)_3Si$]$_2$-2,3-$C_2B_4H_6$ (I) with HCl in a Stainless-Steel Reactor. Carborane I (5.32 g, 24.18 mmol) and anhydrous HCl (25.95 mmol) were condensed at 77 K into a 500-mL high-vacuum, stainless-steel reactor. In a procedure identical with that employed in the reaction described above, the mixture was allowed to react at 413 K for 48 h. The volatile products consisted of pure carborane II (1.28 g, 8.65 mmol; 62% yield based on I consumed), unreacted carborane I (2.25 g, 10.23 mmol), and $(CH_3)_3SiCl$ (1.65 g, 15.21 mmol) collected at 228, 250 and 77 K, respectively. Unreacted HCl was not identified among the products. A syrupy material of extremely low volatility (not measured), collected at 273 K, was not identified.

At room temperature, in a Pyrex-glass reactor, the reaction of I with HCl produced only a trace of II and $(CH_3)_3SiCl$, and almost all of the reactants were recovered unchanged.

Electron Diffraction. Electron-diffraction scattering intensities were recorded on Kodak Electron Image plates by using the Edinburgh diffraction apparatus,[14] with nozzle-to-plate distances of 128 and 285 mm (five and three plates, respectively) and an accelerating voltage of ca. 44 kV. The sample and nozzle were at room temperature (291 K) during experiments. Data were obtained in digital form by using a Joyce-Loebl MDM6 densitometer[15] at the SERC Daresbury Laboratory, and all analysis of data was performed in Edinburgh with standard data reduction[15] and least-squares refinement[16] programs, using scattering factors of Schäfer et al.[17] Weighting points used in setting up the off-diagonal weight matrix are given in Table I, with other pertinent data. The electron wavelengths were obtained by analysis of scattering data for gaseous benzene, recorded on the same occasion as the sample data.

Structural Model. In principle, *nido*-2-(trimethylsilyl)-2,3-dicarbahexaborane has no symmetry and is therefore a particularly difficult subject for study by electron diffraction. We have had to make several assumptions about the structure, to reduce the problems to manageable proportions. The carborane group has been assumed to have a plane of symmetry, with all atoms except the apical boron and hydrogen and the bridging hydrogens coplanar. The assumption of a plane of symmetry is, of course, a major one. However, we have often observed that the structural influence of a silyl group is much the same as that of a single hydrogen atom, and we therefore expect any distortion away from C_s symmetry for the carborane group to be small. In the model all the terminal B–H bonds were of equal length, as were all B–H bridge bonds and all C–H bonds, including those in the $SiMe_3$ group. The terminal B–H and C–H bonds were all assumed to be directed away from a point defined as the mean position of the five carbon and boron atoms in the planar ring (i.e. the point represented by the average of the appropriate Cartesian coordinates). The geometry of this ring was then defined by the C–C, C–B, and B–B distances and the CCB angle, and the position of the apical boron atom was defined by two coordinates. (In the coordinate system used, the origin was taken to be the midpoint of the C–C bond, which was parallel to y. The ring lay in the xy plane.) The hydrogen atom positions were defined by the B–H (bridge and terminal) and C–H distances and the angle between the B–H–B bridge planes and the ring. This angle was taken to be positive for displacements of the bridge atoms away from the apex of the cage.

The C–$Si(CH_3)_3$ group was assumed to have C_3 local symmetry, with each Si–CH_3 group also having C_{3v} local symmetry. Its structure was then defined by six parameters, chosen to be the mean Si–C distance, the difference between the Si–C(cage) and Si–C(methyl) distances, the C–H distance, the valence angles C(cage)SiC(methyl) and SiCH, and a twist angle for the methyl groups, taken to be zero for the staggered conformation.

Finally, the relative positions of the $SiMe_3$ group and the carborane cage were defined by three angles: CCSi, the displacement of the whole $SiMe_3$ group out of the ring plane (i.e. twisting about the C–C bond, positive for displacement away from the apical boron atom), and the twist about the Si–C(cage) bond. This last parameter was defined to be zero when one Si–C(methyl) bond eclipsed the C–C bond. Thus the whole structure depended on 18 parameters, as listed in Table II: all of them were refined at some stage of the study.

Refinement of the Structure. The refinement of the structure of this compound was surprisingly straightforward, considering the complexity of the problem. All of the parameters relating to the positions of the heavy atoms could be refined simultaneously, together with some of the parameters describing hydrogen atom positions and several vibrational amplitudes or groups of amplitudes. Eventually, some of these parameters had to be fixed, because of lack of computing space, but there was no evidence that any of the parameters treated in this way were strongly correlated, and so the uncertainties quoted in Table II (which are estimated standard deviations obtained in the least-squares refinements, increased to allow for systematic errors) are believed to be realistic. The only major problem encountered was with the amplitudes of vibration for the bonded C–C, C–B, and B–B distances. When they were allowed to refine (as a group, with fixed relative values) they became somewhat unreasonably large (ca. 6.5 pm), and the C–C distance increased, while the C–B distance decreased. They were therefore kept at fixed values thereafter.

The final parameters are listed in Table II, and the least-squares correlation matrix is given in Table III. The observed and difference intensity data are shown in Figure 1, the radial distribution curves in Figure 2, and perspective views of the molecule in Figure 3. Atom coordinates are listed in Table IV. These are given so that interatomic distances and angles not listed in the paper may be calculated easily.

Results and Discussion

The significance of the exo-polyhedral *C*-trimethylsilyl moiety in the chemistry of *closo*-metallacarboranes and their *nido*-carborane precursors has only recently begun to be investigated.[1-4,6] We have previously shown that *nido*-[$(CH_3)_3Si$]$_2C_2B_4H_6$ (I) undergoes thermolytic ligand fusion without involving either a metal–complex intermediate or a metal catalyst to produce *nido*-[$(CH_3)_3Si$]$_2C_4B_8H_{10}$ by elimination of trimethylsilane in almost quantitative yields.[5] The object of our present investigation is to establish the versatility of *C*-trimethylsilyl-substituted $C_2B_4H_8$ derivatives as effective precursors for the syntheses of a variety of C-substituted carboranes, particularly *C*-metal-substituted carborane derivatives, without affecting the B–H (terminal) and B–H–B (bridge) hydrogens of the *nido*-C_2B_4-cage.

Reactions of *nido*-[$(CH_3)_3Si$]$_2C_2B_4H_6$ (I) with $NaHF_2$ and HCl. Although the reaction of I with $NaHF_2$ or HCl at room temperature quantitatively produced II and $(CH_3)_3SiX$ (X = F or

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Table II. Structure (r_a) of Gaseous *nido*-$[(CH_3)_3Si]C_2B_4H_7$

(a) Geometrical Parameters (pm or deg)

*p*1	*r*(C–C)	146.0 (11)	*p*10	*r*(B–H(bridge))^a	130.1 (26)
*p*2	*r*(C–B)	154.4 (8)	*p*11	*r*(B–H(terminal))^a	118.4 (26)
*p*3	*r*(B–B)	175.8 (16)	*p*12	∠(BCC)	114.0 (8)
*p*4	*x*(B apex)^a	18.9 (15)	*p*13	∠(CCSi)	121.9 (11)
*p*5	*z*(B apex)^a	111.2 (24)	*p*14	dihedral BCCSi	177 (5)^b
*p*6	*r*(Si–C(mean))	188.0 (4)	*p*15	∠(C(cage)SiC(Me))	114.0 (4)
*p*7	*r*(Si–C(cage-Me))^a	–0.1^b	*p*16	∠(SiCH)	109.4 (12)
*p*8	*r*(C–H)^a	109.4 (7)	*p*17	∠(Me_3Si twist)^a	–5 (9)^b
*p*9	∠(BHB/cage base)^a	26 (15)	*p*18	∠(CH_3 twist)^a	0 (10)^b

(b) Interatomic Distances (pm)^c

		dist	amplitude of vibration^d			dist	amplitude of vibration^d
*d*1	C–C	146.0 (11)	4.5	*d*20	C···C	430.9 (15)	15.7 (33)^b
*d*2	C–B	154.4 (8)	4.5	*d*21	C···B	461.3 (15)	
*d*3	B–B	175.8 (16)	4.5	*d*22	C···B	460.3 (17)	
*d*4	C–B(apex)	183.2 (17)	4.5	*d*23	C···B	493.5 (19)	
*d*5	B–B(apex)	176.1 (12)	4.5	*d*24	C···B	425.6 (17)	
*d*6	B–B(apex)	168.7 (19)	4.5	*d*25	Si···B	430.3 (13)	13.5 (21)
*d*7	C···B	251.9 (10)	6.0	*d*26	Si···B	446.7 (17)	
*d*8	C···B	263.1 (15)	6.0	*d*27	Si···B	353.9 (16)	
*d*9	B···B	271.4 (25)	6.0	*d*28	C···B	499.4 (27)	17.6 (36)^b
*d*10	Si–C(cage)	187.9 (5)	5.2 (5)	*d*29	C···B	545.1 (17)	
*d*11	Si–C(Me)	188.0 (5)	5.2 (5)	*d*30	C···B	553.5 (18)	
*d*12	C···C	297.6 (9)	8.4 (10)	*d*31	C···B	571.9 (20)	
*d*13	C···C	315.2 (10)		*d*32	C···B	536.3 (21)	
*d*14	Si···C	292.6 (15)		*d*33	C···B	540.2 (22)	
*d*15	Si···B	302.7 (15)		*d*34	C–H	109.4 (7)	7.0
*d*16	C···C	345.0 (23)	12.9 (36)^b	*d*35	B–H(terminal)	118.4 (26)	8.0 (13)^b
*d*17	C···B	384.5 (22)		*d*36	B–H(bridge)	130.1 (26)	8.0
*d*18	C···B	382.0 (23)		*d*37	Si···H(Me)	246.9 (12)	10.4 (18)
*d*19	C···C	423.9 (16)					

^{a} For definition of parameters, see text. Errors quoted in parentheses are estimated standard deviations obtained in the least-squares refinements, increased to allow for systematic errors. ^{b} Not included in final refinement, but refined earlier to the quoted value. ^{c} Other C···H, B···H, Si···H and H···H distances were included in the refinements but are not listed here. ^{d} Amplitudes for which no error is quoted were not refined.

Table III. Least-Squares Correlation Matrix (×100)^a

*p*5	*p*10	*p*11	*p*12	*p*16	*μ*10	
–92			80			*p*3
			–83			*p*5
–56			58		–54	*p*6
	71	–80		–52		*p*8
				–63		*p*9
		–78		–59		*p*10
				–52		*μ*37

^{a} Only elements with absolute values >50 are listed.

Table IV. Atom Coordinates

	x	*y*	*z*
C(1)	0.0000	0.7301	0.0000
C(2)	0.0000	–0.7301	0.0000
B(3)	1.4108	1.3573	0.0000
B(4)	1.4108	–1.3573	0.0000
B(5)	2.5278	0.0000	0.0000
B(6)	1.2589	0.0000	–1.1112
H	2.6327	1.2246	0.4294
H	2.6327	–1.2246	0.4294
H	1.6991	2.5054	0.0000
H	1.6991	–2.5054	0.0000
H	3.7116	0.0000	0.0000
H	1.2589	0.0000	–2.2949
H	–0.9039	1.3469	0.0000
Si	–1.5921	–1.7241	0.0809
C	–3.1511	–0.6749	0.0210
C	–1.7716	–2.7525	1.6446
C	–1.7949	–2.9568	–1.3241
H	–4.0287	–1.3265	0.0728
H	–3.1701	–0.1071	–0.9143
H	–3.1560	0.0157	0.8699
H	–2.7199	–3.2975	1.6130
H	–1.7568	–2.0916	2.5167
H	–0.9417	–3.4630	1.7083
H	–2.7421	–3.4913	–1.2033
H	–0.9654	–3.6702	–1.3029
H	–1.7945	–2.4216	–2.2786

Cl) as sole products, the absolute quantities of both products obtained were very small and the reactions are extremely slow. At higher tempertures, the reaction with $NaHF_2$ in a stainless-steel reactor produced II in multigram quantities safely with minimal problems of separation. However, when HCl was used, the yield of II was much lower. In both cases, II was isolated in high purity.

To date, the normal method of preparation of $C_2B_4H_8$ derivatives is that described by Hosmane and Grimes.[18] This method involves the use of Lewis bases, such as $(C_2H_5)_3N$, and is limited to a maximum of 1–2 g of carboranes per synthesis. Furthermore, a large-scale preparation of $R_2C_2B_4H_6$ (R = CH_3, C_2H_5, or C_3H_7) resulted in an explosion.[19] A better method for the preparation of these types of subicosahedral carboranes would be to produce *nido*-$[(CH_3)_3Si]_2C_2B_4H_6$ (I) by using the method described in ref 1 and then converting I into II, by substituting the C(cage)–$Si(CH_3)_3$ group via the new method described in this paper. The absence of etching due to HF on the inside wall of the Pyrex-glass reactor indicates that the desorption of HF in situ from sodium bifluoride at 413 K is a slow process and that the released HF attacks the C(cage)–Si bond immediately. However, the exact mechanism of the substitution reaction is not known.

It has already been established that the *C*-$Si(CH_3)_3$-substituted carboranes are relatively unstable thermally,[5,20] and the C(cage)–Si bond can be cleaved by both acids and bases.[20] Furthermore, the acid-catalyzed cleavage of phenylsilanes to form benzene is well-known.[21] It is therefore probable that the reaction in our

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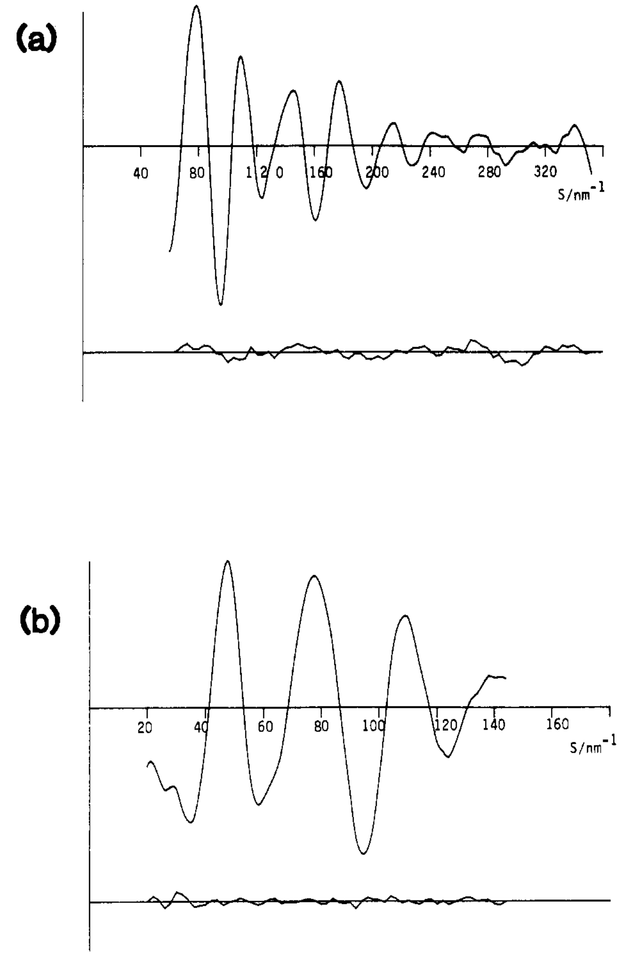


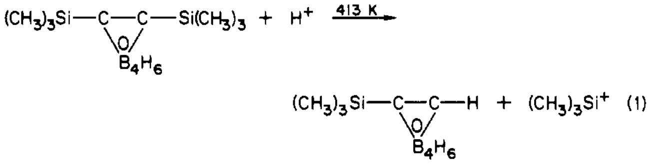
Figure 1. Observed and final weighted difference molecular scattering intensities at nozzle-to-plate distances of (a) 128 and (b) 285 mm.

Table V. Structures of *nido*-$B_4C_2H_8$ Derivatives

	parent carborane[a]	Me-substituted on both carbon atoms[a]	$SiMe_3$-substituted on one carbon atom[b]
C(1)-C(2)/pm	141.8 (6)	143.2 (5)	146.0 (11)
C(1)-B(3)/pm	150.9 (6) 148.9 (6)	152.0 (5)	154.4 (8)
B(3)-B(5)/pm	178.3 (6) 179.8 (6)	177.8 (5)	175.8 (16)
C(1)-B(6)/pm	174.8 (6) 175.1 (6)	176.2 (5)	183.2 (17)
B(3)-B(6)/pm	177.9 (6) 176.5 (6)	176.8 (5)	176.1 (12)
B(5)-B(6)/pm	171.4 (6)	170.5 (5)	168.7 (19)
C(1)C(2)B(4)/deg	116	117	114.0 (8)
C(1)C(2)x/deg[c]		121	121.9 (11)

[a] Reference 12. [b] This work. [c] x = substituent.

study proceeds by the cleavage of the C(cage)-Si bond by acid as shown in eq 1 and 2.



$$(CH_3)_3Si-\underset{B_4H_6}{\underset{\backslash O/}{C-C}}-Si(CH_3)_3 + H^+ \xrightarrow{413\ K} (CH_3)_3Si-\underset{B_4H_6}{\underset{\backslash O/}{C-C}}-H + (CH_3)_3Si^+ \quad (1)$$

$$(CH_3)_3Si^+ + X^- \rightarrow (CH_3)_3SiX \quad (2)$$

The cleavage of only one C(cage)-Si bond even in the presence of excess acid is very intriguing. The removal of only one C(cage)-$Si(CH_3)_3$ group was also found in the oxidative ligand fusion reactions of carborane I.[5] No satisfactory explanation for the low reactivity of the second C(cage)-$Si(CH_3)_3$ group is apparent at this time.

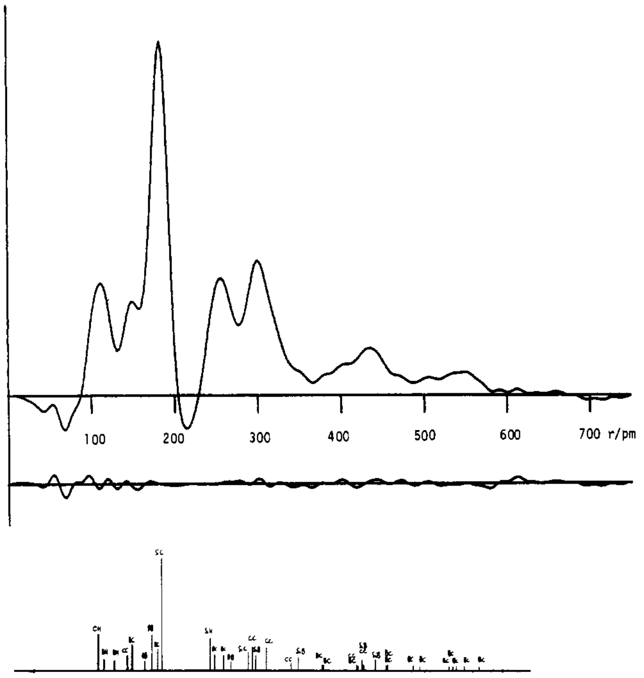


Figure 2. Observed and final difference radial distribution curves, $P(r)/r$, showing the positions and relative magnitudes of the major contributing peaks.

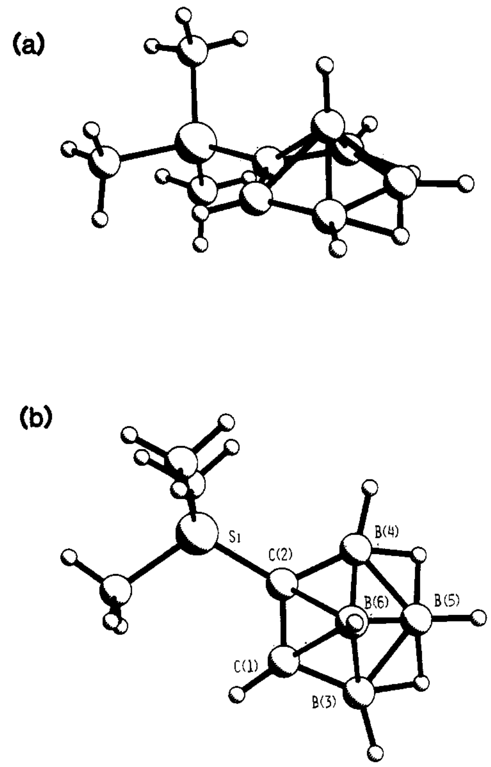


Figure 3. Perspective views of a molecule of *nido*-$[(CH_3)_3Si]C_2B_4H_7$. The numbering of the atoms of the skeleton relates to the atomic coordinates given in Table IV.

With such a complicated molecule it was necessary to make many assumptions about the structure, but the refinement proceeded smoothly, and we are confident that the results are reliable. The apparent distribution of distances within the C_2B_4 cage must depend to some extent on the values chosen for the vibrational amplitudes. However, these distances are in good agreement with those determined by X-ray crystallography for the parent carborane and the derivative having methyl substituents on both carbon atoms[12] (Table V). The main difference seems to be that in the $(CH_3)_3Si$ derivative all bonds to the carbon atoms are slightly lengthened, with a concomitant shortening of B–B bonds and a consequential reduction of the CCB angles in the ring plane.

The trimethylsilyl group has C(cage)SiC(Me) angles much greater than C(Me)SiC(Me) (114 and 105°, respectively), but otherwise there is no sign of steric strain in the molecule. The two types of Si–C bond have essentially the same length. The preferred conformation has one Si–C(Me) bond eclipsing the ring C–C bond. A conformation in which an Si–C(Me) bond eclipsed a ring C–B bond also gave an *R* factor minimum, but it was significantly worse than the favored conformation. In this form the BCCSi dihedral angle went down to 164°, so that the trimethylsilyl group lay well below the plane of the ring atoms. Of course, it may be that there is fairly free rotation about the Si–C bond, but we have not considered models in which more than one conformer is present at one time.

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Structure Determination and Investigation of the High-Spin ↔ Low-Spin Transition of $[Fe(2\text{-pic})_3]Br_2\cdot EtOH$[†]

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A single-crystal X-ray diffraction analysis was carried out on the spin-crossover compound $[Fe(2\text{-pic})_3]Br_2\cdot EtOH$ (2-pic = 2-(aminomethyl)pyridine) in the temperature region between room temperature and 110 K. $[Fe(2\text{-pic})_3]Br_2\cdot EtOH$ crystallizes monoclinically ($Z = 4$) in the space group $P2_1/n$ (No. 14) with lattice constants $a = 11.164$ (12) Å, $b = 22.281$ (16) Å, $c = 11.713$ (12) Å, $\beta = 118.02$ (5)°, and $V = 2572$ (5) Å^3 at 215 K. The structure in the high-spin state at 215 K was refined to a reliability index of $R = 0.050$ ($R_w = 0.076$). The dependence of the lattice dimensions on temperature is expressed in terms of the tensor of thermal expansion α and a deformation tensor ϵ due to the high-spin ↔ low-spin transition. The high-spin fraction $\gamma(T)$ was determined by susceptibility and Mössbauer measurements. $\gamma(T)$ shows a hysteresis of 2 K width. The X-ray structure was also investigated at 124 K, below the hysteresis region, and is isomorphous to the high-spin structure at 215 K. This compound is the first example that shows hysteresis in $\gamma(T)$ without a structural phase transition.

Introduction

The temperature-dependent low-spin (LS) ↔ high-spin (HS) transition has been the subject of increasing interest in recent years. The number of systems exhibiting this phenomenon is continuously growing, and several theoretical models have been published.[1–3] The models have in common that the interaction between the LS and HS complexes, which is cooperative in nature, is considered as an elastic interaction as a result of the change of the size of the complexes on going from LS to HS and of the shape of the complexes. Qualitatively, all types of observed transition curves can be reproduced theoretically, ranging from very gradual transition curves to those exhibiting hysteresis typical for first-order thermodynamic transitions. On the grounds of these theoretical models, changes of the crystal structure are driven by the spin change of the complex molecules, whereas earlier papers argued in the opposite direction; for example, order–disorder phenomena[4] or, especially, the structural changes accompanying transitions with hysteresis were considered as the primary phenomenon. This view seemed to be supported by the entropy changes involved. The spin change from $S = 0$ to $S = 2$ in the case of an octahedrally coordinated Fe^{2+} ion results in an entropy change of $\Delta S = -Nk_B \ln 5 = 14$ J mol^{-1}, which is to be compared with values of about 50 J mol^{-1} K^{-1} obtained[5] from calorimetric measurements in $[Fe(phen)_2(NCS)_2]$. The main part of ΔS obviously stems from changes of vibrational frequencies and not from the spin change.

In the theoretical model,[3] which has been successfully applied to the gradual spin transition in the mixed-crystal system $[Fe_xM_{1-x}(2\text{-pic})_3]Cl_2\cdot EtOH$ (2-pic = 2-picolylamine = 2-(aminomethyl)pyridine; M = Zn,[3] M = Co[6]), the whole cationic complex molecule is considered rather than the isolated central metal ion. In that case, the change of the intramolecular vibrational frequencies, which has been observed by far-IR spectroscopy[7,8] for such systems, turns out to be the main contribution to the total entropy change. In view of this model it is justified to consider the change of the spin state and along with it the changes in size and shape of the cationic complex to be the driving force of the cooperative spin transition.

In order to support this conception experimentally, we looked for a HS/LS system that undergoes a first-order phase transition with a hysteresis but that is not accompanied by a structural phase transition of the lattice. In the course of our systematic investigation of the system $[Fe_xM_{1-x}(2\text{-pic})_3]Cl_2\cdot EtOH$, we found that the interaction constant $\Gamma(x = 1)$ in the equation of the free energy f per isolated complex molecule[3]

$$f = f_0(\gamma) + \Delta(x)\,\gamma - \Gamma(x)\,\gamma^2 \qquad (1)$$

(f_0 is the free energy of isolated complexes, $\Delta(x)$ is an energy shift proportional to the concentration x, γ is the HS fraction) is just below the value that gives rise to a hysteresis in the curve of the HS fraction $\gamma(T)$. Γ is interpreted in the frame of elasticity theory. It depends on the volume V_c and the volume change ΔV_{HL} of the crystal per formula on going from the LS to the HS state, the bulk modulus K, and the Eshelby constant γ_0:[3]

$$\Gamma(x) = \frac{1}{2}xK\frac{\Gamma_0 - 1}{\Gamma_0}\,\frac{(\Delta V_{HL})^2}{V_c} \qquad (2)$$

[†] Dedicated to Professor Gerhard Gattow on the occasion of his 60th birthday.

[‡] In partial fulfillment of the Ph.D. Thesis.

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