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Convenient Synthesis, Separation, and X-ray Crystal Structure Determinations of 1(e),3(e),5(e)-Trimethylcycloborazane and 1(e),3(e),5(a)-Trimethylcycloborazane

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1,3,5-Trimethylcycloborazane $[CH_3N(H)BH_2]_3$ is obtained as a mixture of eee and eea isomers in good yield from the reaction of $BH_3\cdot THF$ and methylamine. The isomers are separated by fractional crystallization from benzene and characterized by mass, infrared, and ^1H, ^{13}C, and ^{11}B NMR spectroscopies. The eee isomer crystallizes in the monoclinic space group $P2_1/c$, with $a = 8.514$ (2) Å, $b = 13.577$ (4) Å, $c = 8.927$ (2) Å, $\beta = 112.09$ (2)°, $Z = 4$, $V = 956.1$ (4) Å^3, and $\rho = 0.89$ g cm^{-3}. Least-squares refinement gave $R_F = 8.3\%$ and $R_{wF} = 6.1\%$. The compound displays a six-membered ring structure with alternating boron and nitrogen atoms in a chair conformation. The methyl groups on the nitrogen atoms are all in equatorial positions. The average B–N bond distance is 1.565 Å. The eea isomer crystallizes in the monoclinic space group Cc, with $a = 9.481$ (3) Å, $b = 12.477$ (4) Å, $c = 8.329$ (2) Å, $\beta = 114.05$ (2)°, $Z = 4$, $V = 900.0$ (5) Å^3, and $\rho = 0.95$ g cm^{-3}. Least-squares refinement gave $R_F = 4.8\%$ and $R_{wF} = 4.5\%$. This isomer also has a six-membered ring structure with alternating boron and nitrogen atoms in a chair conformation. Two methyl groups are found in equatorial positions, and one methyl group is found in an axial position. The average B–N distance is 1.578 Å.

Introduction

There is currently a great deal of interest in the utilization of simple boron–nitrogen compounds as precursors to polymers and solid-state materials. On the basis of tantalizing observations in the literature,[1,2] the relatively stable cycloborazanes (parent molecule $B_3H_6N_3H_6$) appear to be one family of compounds with potential as solid-state-material precursors. With increased interest in cycloborazanes has come renewed attention to the development of routine syntheses for these molecules. In this regard, improved syntheses and characterization of 1,3,5-trimethylcycloborazane, $[CH_3N(H)BH_2]_3$ (**1**), are of interest to us.

Bissot and Parry[3] reported the first synthesis and characterization of **1** from the gentle thermolysis of the amine borane adduct $CH_3NH_2\cdot BH_3$ at 100° (eq 1). Subsequently, Gaines and

$$B_2H_6 + 2CH_3NH_2 \rightarrow CH_3NH_2\cdot BH_3 \xrightarrow{100\ °C} [CH_3N(H)BH_2]_3 \quad (1)$$

Schaeffer[4] observed that **1** could be prepared in two isomeric forms from 1,3,5-trimethylborazene according to eq 2. More simply,

$$2B_3H_3N_3(CH_3)_3 + 6HCl \xrightarrow{Et_2O} 2[B_3H_3N_3(CH_3)_3\cdot 3HCl] \xrightarrow[\text{monoglyme}]{6NaBH} 2[CH_3N(H)BH_2]_3 + 3B_2H_6 + 6NaCl \quad (2)$$

they observed that **1** is formed directly from the reaction of methylamine hydrochloride and sodium borohydride as described in eq 3. Brown and co-workers[5] also observed (eq 4) that thermal

$$3NaBH_4 + 3CH_3NH_3Cl \xrightarrow[\text{reflux}]{\text{monoglyme}} [CH_3N(H)BH_2]_3 + 3NaCl + 3H_2 \quad (3)$$

$$6RNH_2\cdot BH_3 \xrightarrow{\text{heat}} 3H_2 + [RN(H)BH_2]_3 \quad (4)$$

decomposition of the appropriate amine boranes, produced $[RN(H)BH_2]_3$ with R = CH_3, C_2H_5, *n*-C_3H_7, *i*-C_3H_7, *n*-C_4H_9, and *t*-C_4H_9. Obviously there are several suitable laboratory routes to *N*-alkyl-substituted cycloborazanes. Reactions 1 and 2, in particular, provide good overall yields of the mixed isomers of **1**, 88% and 70%, respectively. However, the first reaction suffers from the disadvantage of utilizing B_2H_6 as a starting material while the second reaction produces B_2H_6 as a byproduct. The pyrophoric character of this gaseous reagent tends to reduce the attractiveness of these reactions in process conditions. Reaction 3 is particularly convenient from a reactant standpoint and it circumvents the appearance of diborane; however, the yield of **1** is usually reduced (~50%) and is more susceptible to variations in experimental conditions.[6] We report here a simplified, convenient synthesis of **1** from commercially available and easily handled reagents. In addition, a complete set of characterization data and the single-crystal X-ray diffraction structure determinations for the two isomers are described.

Experimental Section

General Information. All experimental manipulations were performed under rigorously anhydrous conditions in a high-vacuum system or in Schlenk equipment. Monoglyme was successively distilled from NaH, $LiAlH_4$, and sodium benzophenone ketyl. Commercial borane–tetrahydrofuran solutions (Aldrich) were used after checking their purity by ^{11}B NMR. Methylamine was dried over KOH.

The ^1H, ^{13}C, and ^{11}B NMR spectra were recorded on Varian FT-80A or Nicolet 360-MHz spectrometers and referenced with $(CH_3)_4Si$ (^1H, ^{13}C) and $BF_3\cdot Et_2O$, (^{11}B). Infrared spectra were obtained on a Nicolet 6000 FTIR spectrometer from KBr pellets. Mass spectra were obtained on a Finnegan GC/MS system using a solids inlet probe.

Preparation of $[CH_3N(H)BH_2]_3$ (1). Borane–tetrahydrofuran complex (100 mL, 1 M solution; 100 mmol) was syringed into a dry, nitrogen-filled 250-mL Schlenk vessel containing a stir bar. The flask was frozen and degassed and dry methylamine (3.1 g, 100 mmol) condensed onto the solution at −78 °C. The flask was backfilled with nitrogen, and the mixture was slowly warmed to room temperature and then stirred at 25 °C for 1 h. The volatiles were removed in vacuo leaving a white, solid sample of $CH_3NH_2\cdot BH_3$ (yield 4.33 g, 98%; ^{11}B NMR, δ −18.4]. The resulting solid was dissolved in 15 mL of dry monoglyme, and the flask was outfitted with a condenser and nitrogen bubbler. The solution was refluxed under nitrogen until gas evolution ceased (~18 h), and the volatiles were removed in vacuo. The residue was washed with water, dried in air, and then sublimed (0.001 Torr, 70 °C). The sublimate was a white crystalline solid (yield 2.83 g, 69%), which contained a mixture of isomers I and II. The isomers were separated by dissolving the mixture in a minimum of hot benzene. Slow cooling of this solution deposited crystals of isomer I. When no evidence for isomer I was found in the solution by infrared analysis the crystals of isomer I were collected by filtration and washed with a minimum of cold benzene. The filtrate was slowly evaporated and crystalline isomer II was obtained [yields: isomer I 50%, isomer II 19% based upon $BH_3\cdot THF$]. Analytical data melting points, sublimation temperatures, and solubility data for the isomers are in agreement with literature data.[4] Infrared spectra (cm^{-1}) (KBr pellet): isomer I 3224 (s, ν_{NH}), 2995 (m, ν_{CH}) 2950 (w), 2351 (s, ν_{BH}), 2312 (w), 1460 (w), 1415 (w), 1367 (m), 1270 (m), 1193 (s), 1174 (s), 1151 (w), 1024 (w), 964 (w), 914 (w); isomer II 3276 (m, ν_{NH}), 3241 (m, ν_{NH}), 2996 (m, ν_{CH}), 2950 (w), 2890 (w), 2361 (s, ν_{BH}), 2342 (m, ν_{BH}), 1458 (m), 1417 (w), 1385 (m), 1365 (m), 1266 (w), 1233 (w), 1202 (s), 1177 (s), 1133 (w), 1065 (w), 1047 (w), 1021 (w), 984 (w), 962 (w), 925 (w), 908 (w). Mass spectra (70 eV) (unstripped): isomer I, *m/e* 129 [M$^+$]

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Table I. Experimental Data for the X-ray Diffraction Study of 1(e),3(e),5(e)-Trimethylcyclοborazane (Isomer I) and 1(e),3(e),5(e)-Trimethylcycloborazane (Isomer II): $B_3N_3C_3H_{18}$

	isomer I	isomer II
(A) Crystal Parameters at 20 (2) °C		
cryst dimens	0.09 × 0.12 × 0.35	0.09 × 0.51 × 0.64
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	*Cc*
a, Å	8.514 (2)	9.481 (3)
b, Å	13.577 (4)	12.477 (4)
c, Å	8.927 (2)	8.329 (2)
β, deg	112.09 (2)	114.05 (2)
Z	4	4
V, Å^3	956.1 (4)	900.0 (5)
M_r	128.68	128.68
ρ_{calcd}, (g cm^{-3})	0.89	0.95
μ, cm^{-1}	0.49	0.60
F(000)	288	288
(B) Data Collection		
reflcns measd	$\pm h,k,l$	$h,k,\pm l$
2θ range, deg	1–50	1–57
scan type:	θ–2θ	θ–2θ
scan speed, deg min^{-1}	3–30	3–30
scan range, deg	1.40 + $2\theta(K\alpha_1)$ to $2\theta(K\alpha_1)$ − 1.25	$2\theta(K\alpha_1)$ + 1.3 to $2\theta(K\alpha_1)$ − 1.3
total no. of reflcns collcd	4896	2610
no. of unique reflcns collcd	2199	2294
no. of obsd reflcns used in refinement	702 [$I > 4\sigma(I)$]	1320 [$I > 5\sigma(I)$]
no. of params	82	82
R_F	0.083	0.047
R_{wF}	0.061	0.045
GOF	2.09	1.44

diffractometer: Syntex P3/F
radiation: Mo Kα (λ = 0.71069 Å)
monochromator: highly oriented graphite cryst
bkgd measurement: stationary cryst and counter; at the beginning and end of each scan, each for one-half of the total scan time
std reflcns: 3 measured every 141 reflcns; no significant changes in intensities obsd [$\bar{2}11$, $0\bar{6}0$, $\bar{1}\bar{1}4$][$\bar{3}10$, 040, 043]

(0.5), 128 (17), 127 (12), 126 (4), 125 (1), 115 (1), 114 (30), 113 (17), 112 (3), 111 (0.5), 110 (1), 109 (0.5), 85 (10), 84 (5), 83 (18), 82 (8), 81 (3), 80 (1), 72 (2), 71 (23), 70 (5), 69 (3), 68 (2), 67 (3), 66 (2), 57 (2), 56 (5), 55 (3), 54 (8), 53 (4), 52 (5), 51 (3), 44 (1), 43 (8), 42 (100), 41 (33), 40 (22); isomer II, *m/e* 129 [M$^+$] (0.5), 128 (22), 127 (16), 126 (5), 125 (1), 124 (0.5), 123 (0.2), 115 (1), 114 (40), 113 (20), 112 (5), 111 (0.5), 110 (1), 109 (0.5), 85 (15), 84 (8), 83 (22), 82 (13), 81 (4), 80 (1), 72 (2), 71 (28), 70 (8), 69 (5), 68 (2), 67 (3), 66 (2), 57 (2), 56 (5), 55 (3), 54 (7), 53 (4), 52 (5), 51 (3), 44 (2), 43 (6), 42 (100), 41 (33), 40 (22). NMR spectra [$(CD_3)_2CO$] (25 °C): ^{11}B, isomer I and II $\delta - 5.4$ (J_{BH} = 107 Hz); ^{1}H, isomer I δ 2.98 (NH), 2.11 (BH) (J_{BH} = 105 Hz), 2.09 (CH) (J_{HH} = 5.2 Hz), 1.55 (BH) (J_{BH} = 105 Hz); ^{1}H isomer II δ 3.43 (NH), 3.23 (NH), 3.00 (NH), 2.37 (CH) (J_{HH} = 6.7), 2.10 (CH) (J_{HH} = 4.9); ^{13}C, isomer I δ 34.47; ^{13}C, isomer II δ 38.33, 35.52.

Crystallographic Measurements and Structure Solution. The crystals were obtained as long needles, and a suitable crystal of each isomer was glued to a glass fiber. Each crystal was centered on a Syntex P3/F automated diffractometer and determinations of crystal class, orientation matrix, and unit cell dimensions were performed in a standard manner.[7] Data were collected in the θ–2θ scan mode by using Mo Kα radiation, a scintillation counter and a pulse-height analyzer. The data collection parameters are summarized in Table I. Examinations of the collected reflections indicated the respective space groups. The space group for isomer II suggested to be *Cc* from statistics was confirmed by satisfactory refinement in this space group. An empirical absorption correction based on azimuthal scans was applied for both crystals. For isomer I, the correction improved the agreement of the azimuthal scan data from 2.86% to 2.77% and the estimated maximum and minimum transmission factors were 0.879 and 0.835. For isomer II, the correction improved the agreement of the azimuthal scan data from 6.30% to 4.85% and the estimated maximum and minimum transmission factors were 0.941 and 0.721. The data were corrected for Lorentz and polarization effects, redundant data averaged, space group extinct reflections removed, and remaining data converted to unscaled $|F_o|$ values. The atomic scattering factors for the neutral atoms were taken from the analytical expressions given in ref 8.

Table II. Fractional Coordinates and Their Esd's for 1(e),3(e),5(e)-Trimethylcycloborazane (Isomer I) and 1(e),3(e),5(e)-Trimethylcycloborazane (Isomer II)

atom	*x/a*	*y/b*	*z/c*
	Isomer I		
N(1)	0.4305 (4)	0.6960 (3)	0.0910 (4)
B(2)	0.2676 (6)	0.6365 (4)	−0.0096 (6)
C(7)	0.5836 (5)	0.6442 (4)	0.0920 (6)
N(3)	0.1078 (4)	0.6953 (3)	−0.0144 (4)
B(4)	0.0993 (7)	0.8071 (5)	0.0642 (7)
C(8)	−0.0484 (5)	0.6437 (4)	0.1161 (7)
N(5)	0.2687 (5)	0.8581 (3)	0.0403 (4)
B(6)	0.4355 (6)	0.8063 (5)	0.0443 (7)
C(9)	0.2673 (6)	0.9619 (3)	−0.0062 (6)
	Isomer II		
N(1)	0.5000	0.1982 (2)	0.7500
B(2)	0.5942 (4)	0.2932 (2)	0.8675 (4)
C(7)	0.4832 (4)	0.1098 (3)	0.8592 (4)
N(3)	0.6059 (3)	0.3856 (2)	0.7436 (3)
B(4)	0.6753 (4)	0.3481 (3)	0.6068 (5)
C(8)	0.4625 (5)	0.4492 (3)	0.6605 (5)
N(5)	0.5792 (3)	0.2489 (2)	0.5012 (3)
B(6)	0.5653 (4)	0.1535 (3)	0.6181 (5)
C(9)	0.6451 (5)	0.2095 (3)	0.3781 (5)

All calculations were performed with the R3/SHELXTL structure determination package.[9] Least-squares refinements in this package use a block-cascade algorithm with full-matrix blocks of 103 parameters.[10] Both structures were solved by direct methods, and the best *E*-map gave trial positions for all non-hydrogen atoms. For isomer I, isotropic least-squares refinement initially on 914 reflections with $F > 3\sigma(F)$ and 37 variables gave R_F = 0.24. Anisotropic refinement on the heavy atoms with the hydrogen atoms included in fixed idealized positions 0.96 Å from their parent atom converged at R_F = 0.086 on 702 reflections with $F > 4\sigma(F)$ and 82 variables. Anisotropic refinement in the same manner but with B–H bond distances fixed at 1.10 Å and N–H bond distances fixed at 0.85 Å (obtained from the more accurate structure determination of isomer II) led to R_F = 0.083 and R_{wF} = 0.061 with GOF = 2.09. The final difference map showed four peaks, which were judged to be insignificant. For isomer II isotropic least-squares refinement on 1320 reflections with $F > 5\sigma(F)$ and 37 variables gave R_F = 0.134, and anisotropic refinement on the non-hydrogen atoms converged with R_F = 0.114. A difference map showed hydrogen atom positions for all hydrogen atoms. The hydrogen atoms were included in idealized positions 0.96 Å from their parent atoms and given fixed *U*'s equal to 1.2 times the last U_{equiv} of their parent atom. The resulting agreement factors were R_F = 0.055 and R_{wF} = 0.051 and GOF = 1.44. The final cycles of block least-squares refinement also allowed the hydrogen atoms to vary in positions with the results R_F = 0.048, R_{wF} = 0.045, and GOF = 1.37 for 134 parameters and 1320 reflections. The model was inverted with the same result. The final difference map showed no peak higher than 0.32 e Å^{-3}. The final fractional coordinates are listed in Table II.

Results and Discussion

In this study 1,3,5-trimethylcycloborazane was prepared in good yield from the combination of a commercial solution of borane–tetrahydrofuran complex and methylamine in equimolar amounts followed by reflux of a monoglyme solution of the amine–borane

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(10) A general description of the least-squares algebra is found in: Ahmed, F. R.; Hall, S. R.; Huber, C. P., Eds. *Crystallographic Computing*; Munksgaard: Copenhagen, 1970; p 187. The least-squares refinements minimize $\sum w(|F_o| - |F_c|)^2$ where $w = 1/[\sigma(F_c)^2]$ for isomer I and $w = 1/[\sigma(F_o)^2 + g(F)^2]$ g = 0.00041 for isomer II: $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_{wF} = [\sum (|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, and GOF = $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, where n = number of parameters and m = number of reflections.

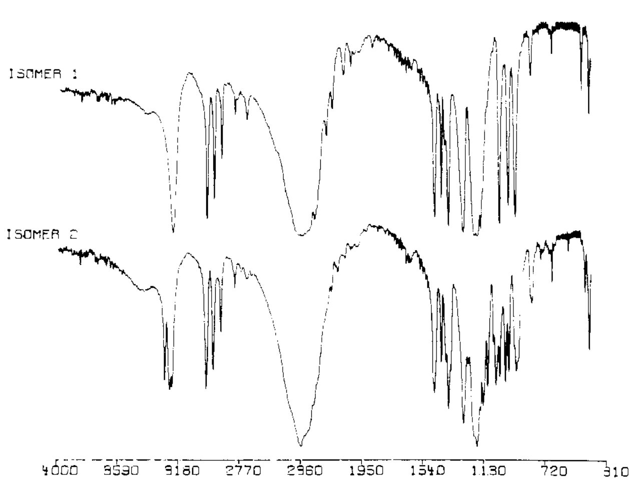

Figure 1. Infrared spectra for isomer I (top) and isomer II (bottom) recorded from KBr pellets.

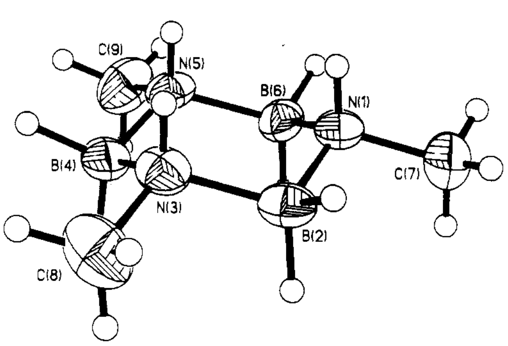

Figure 2. Molecular geometry and atom labeling scheme for 1(e),3(e),5(e)-trimethylcycloborazane (isomer I) (25% probability ellipsoids). Selected bond distances (Å) and bond angles (deg): B(2)-N(1) = 1.565 (6), B(2)-N(3) = 1.564 (7), B(4)-N(3) = 1.575 (8), B(4)-N(5) = 1.556 (6), B(6)-N(1) = 1.558 (8), B(6)-N(5) = 1.573 (7), N(1)-C(7) = 1.478 (6), N(3)-C(8) = 1.476 (5), N(5)-C(9) = 1.467 (6); B(2)-N(1)-B(6) = 116.7 (3), B(2)-N(3)-B(4) = 116.5 (4), B(4)-N(5)-B(6) = 116.7 (3), N(1)-B(2)-N(3) = 109.1 (4), N(3)-B(4)-N(5) = 108.9 (4), N(1)-B(6)-N(5) = 108.7 (4), B(2)-N(1)-C(7) = 110.3 (4), B(6)-N(1)-C(7) = 110.3 (4), B(2)-N(3)-C(8) = 110.4 (4), B(4)-N(3)-C(8) = 110.4 (4), B(4)-N(5)-C(9) = 110.5 (4), B(6)-N(5)-C(9) = 110.3 (4).

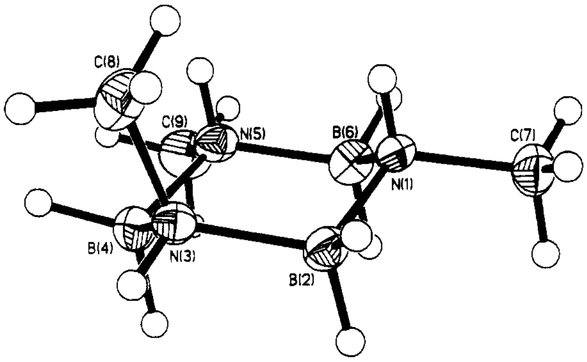

Figure 3. Molecular geometry and atom labeling scheme for 1(e),3(e)-5(a)-trimethylcycloborazane (isomer II) (25% probability ellipsoids). Selected bond distances (Å) and bond angles (deg): B(2)-N(1) = 1.565 (3), B(2)-N(3) = 1.582 (4), B(4)-N(3) = 1.600 (6), B(4)-N(5) = 1.576 (4), B(6)-N(1) = 1.567 (5), B(6)-N(5) = 1.577 (5), N(1)-C(7) = 1.479 (4), N(3)-C(8) = 1.480 (4), N(5)-C(9) = 1.485 (6); B(2)-N(1)-B(6) = 114.9 (2), B(2)-N(3)-B(4) = 114.3 (2), B(4)-N(5)-B(6) = 115.0 (2), N(1)-B(2)-N(3) = 108.5 (2), N(3)-B(4)-N(5) = 108.4 (3) N(1)-B(6)-N(5) = 108.7 (2), B(2)-N(1)-C(7) = 110.9 (2), B(6)-N(1)-C(7) = 109.8 (2), B(2)-N(3)-C(8) = 113.6 (3), B(4)-N(3)-C(8) = 112.9 (3), B(4)-N(5)-C(9) = 109.6 (3), B(6)-N(5)-C(9) = 109.9 (3).

complex. The course of the reaction is summarized by the eq 5 and 6. The formation of the intermediate amine–borane (98%

$$H_3B{\cdot}THF + CH_3NH_2 \xrightarrow[(2)\ 25\ °C]{(1)\ -78\ °C} CH_3N(H)_2{\cdot}BH_3 \quad (5)$$

$$CH_3N(H)_2{\cdot}BH_3 \xrightarrow{\text{monoglyme}} [CH_3N(H)BH_2]_3 + H_2 \quad (6)$$

yield) was proven by comparison of the ^{11}B NMR spectrum (^{11}B, δ −18.4 (J_{BH} = 94 Hz, quartet)) with data in the literature.[11] The cycloborazane was purified initially by gentle sublimation (70 °C) from which a mixture of the two isomers was obtained in 69% yield. The two isomers 1(e),3(e),5(e)-trimethylcycloborazane (isomer I) and 1(e),3(e),5(a)-trimethylcycloborazane (isomer II) were separated by fractional crystallization from benzene.

Mass, infrared, and ^{1}H and ^{11}B NMR spectroscopic data have been reported, in part, in previous studies;[4,5] however, a more complete set of data on the separated isomers is provided in this study. Brown and Hezeltine reported that both isomers display a weak parent ion in their mass spectra, and a most intense peak at *m/e* 114 (M − 15)$^+$. In the present study both isomers were found to give similar spectra with a weak parent ion, *m/e* 129, but the most intense peak appeared at *m/e* 42 (BNCH$_5$)$^+$. These results suggest that the mass spectra of **1** are very sensitive to spectrometer inlet and ion-source conditions, and care must apparently be exercised in comparing spectra of **1** obtained from different instruments. The infrared spectra (Figure 1) for the isomers are in general agreement with the spectra reported previously, and more complete listings are presented here. The ^{11}B{^{1}H} NMR spectra for both isomers are identical, showing a single resonance at δ −5.4. Restoration of the proton coupling results in broad triplets with $J_{BH} \sim 107$ Hz. The ^{13}C{^{1}H} NMR spectrum for isomer I shows a single resonance at δ 34.47, which is consistent with a single environment for the three amino methyl groups. The ^{13}C{^{1}H} NMR spectrum for isomer II shows two peaks at δ 38.33 and 35.52 in approximately a 1:2 ratio. This observation is consistent with two inequivalent methyl group environments (axial and equatorial) with the axial methyl resonance appearing at lower field. The proton NMR spectra have been recorded at high field and found to agree for the most part with the assignments provided earlier.[4] The high-field spectra for both isomers show the N–H resonances clearly separated from the severely overlapping B–H and C–H resonances. In isomer I there is a single broad N–H resonance centered at δ 2.98 while in isomer II three resonances at δ 3.43, 3.23, and 3.00 in an approximately 1:2:0.5 ratio are observed. In the former case one N–H resonance is expected since there is only one proton environment (axial), and the broadening results from ^{14}N quadruple interactions. In the latter case a broad two-resonance pattern (intensity ratio 1:2) is expected for the axial and equatorial N–H protons. It is assumed that the resonances at δ 3.43 and 3.23 can be assigned to these protons while the resonance at δ 3.00 is an impurity. In isomer I the inequivalent B–H protons give rise to two sets of 1:1:1:1 quartets centered at δ 2.11 (J_{BH} = 105 Hz) and 1.55 (J_{BH} = 105 Hz). Although B–H resonances are observed in isomer II, accurate chemical shifts for the complicated pattern have not been determined. The methyl protons in isomer I give rise to a single doublet at δ 2.09 (J_{CH} = 5.2 Hz) consistent with one methyl environment while isomer II displays two doublets at δ 2.37 (J_{HH} = 6.7 Hz) and 2.10 (J_{HH} = 4.9 Hz) in a 1:2 area ratio. The areas indicate that the downfield doublet can be assigned to the unique axial methyl group.

Single-crystal X-ray diffraction analyses provide unambiguous confirmation of the chair-form cyclohexane-like structures for the two isomers proposed originally by Gaines and Schaeffer.[4] A view of the eee isomer (I) is shown in Figure 2, and a view of the eea isomer (II) is shown in Figure 3. In the eee isomer the average B–N bond length is 1.565 Å, which can be compared with the average B–N bond lengths in [H$_2$NBH$_2$]$_3$[12] (1.576 Å), [H$_2$NBCl$_2$]$_3$[13] (1.575 Å), and [MeNBH$_2$]$_3$[14] (1.59 Å). The average

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terminal N–CH_3 distance is 1.474 Å, which compares well with the average of equatorial and axial N–CH_3 distances in $[Me_2NBH_2]_3$, 1.49 Å. The average N–B–N angle in isomer I, 108.9°, is consistent with the anticipated tetrahedral environment for the boron atoms, and the angle is similar to the average N–B–N angles in $[H_2NBH_2]_3$ (107.2°) and $[H_2NBCl_2]_3$ (109°). The average N–B–N angle in $[Me_2NBH_2]_3$, 114°, on the other hand, is considerably more open. The average B–N–B angle, 116.5°, is more open than the N–B–N angle, and it resembles the average angles in $[H_2NBH_2]_3$ (115.9°), $[H_2NBCl_2]_3$ (120.1°), and $[Me_2NBH_2]_3$ (113°). The B–N–C angles are essentially constant in the eee isomer at 110.4°, and this angle is related to the B–N–C angle in $[Me_2NBH_2]_3$. Least-squares-planes calculations provide dihedral angles between the basal four-atom planes and the three-atom planes (three symmetry-related sets), and the B–N–B planes, 47.6°, are slightly more tilted than the N–B–N planes, 44.3°, from the B_2N_2 planes.

The structure of the eea isomer, of course, closely resembles that of the eee isomer with the axial methyl group positioned on N(3). As expected this slightly distorts the parameters involving N(3). The average B–N bond distance is 1.578 Å with the average B–N bond distance involving N(3) being 1.591 Å and the average derived from bonds to N(1) and N(2) being 1.571 Å. On the other hand, the N–CH_3 distances are nearly constant, $(N–C)_{av}$ = 1.481 Å. The average N–B–N angle, 108.5°, compares favorably with that found in isomer I while the average B–N–B angle, 114.7°, is closed down compared to the angle in isomer I. Interestingly, the B–N–C angles for N(3) are significantly more open, $(B–N(3)–C)_{av}$ = 113.4°, than the average of the remaining B–N–C angles, 110.1°. In addition, the dihedral angle between the B(2)N(3)B(4) plane and the N(1)B(2)B(4)N(5) basal plane, 50.1°, is greater than the dihedral angle between the N(1)B(6)N(5) plane and the basal plane, 47.7°.

Although no serious attempt has been made in this study to elucidate the mechanism for the formation of 1,3,5-trimethylcycloborazane from $H_3B·THF$ and $MeNH_2$, it is worth pointing out that two sets of experiments were performed which possibly impact on the mechanism proposed by Beachley[15] involving ionic four-coordinate boron species. Heating $CH_3NH_2·BH_3$ in monoglyme and following the reaction by ^{11}B NMR spectroscopy did not result in the observation of tricoordinate or tetracoordinate ionic boron species (δ –25 to –30 and –10 to +8) in the ^{11}B NMR spectrum. Instead, the resonance for the amine borane (δ –18.0) slowly decreased and the resonance for **1** (δ –5.4) grew in without appearance of intermediate species. Similarly, the reaction of $MeNH_2·HCl + LiBH_4$ in a 1:1 ratio in monoglyme was followed by ^{11}B NMR. After 4 h at 25 °C the ^{11}B NMR spectrum showed only peaks for $LiBH_4$ (δ –40.5) and $MeNH_2·BH_3$ in a 1:4 ratio. Refluxing the mixture for 2 h showed **1**, $LiBH_4$, and $MeNH_2BH_3$ in a 4:19:1 ratio, and after 18 h only **1** and $MeNH_2·BH_3$ were observed in an 18:1 ratio. Clearly, ionic species may only be present in these systems if their lifetimes are short. More detailed experiments would be required to provide further information regarding the interesting condensation process acting in the formation of **1**.

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Registry No. **1** (isomer I), 60619-50-3; **1** (isomer II), 60619-49-0; $CH_3NH_2·BH_3$, 1722-33-4; $H_3B·THF$, 14044-65-6; CH_3NH_2, 74-89-5.

Supplementary Material Available: Listings of anisotropic thermal factors and hydrogen atom parameters (4 pages); listings of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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Electron Transfer. 78. Reduction of Carboxylato-Bound Chromium(V) with Bisulfite. A "Clock Reaction" Involving Chromium(IV)[1]

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The chelated chromium(V) complex bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I) reacts with HSO_3^- in aqueous solutions buffered by the ligand acid, 2-ethyl-2-hydroxybutyric acid. The stoichiometry, in the presence of excess HSO_3^-, lies close to 1:1, but the reaction passes through an intermediate, the properties of which correspond to those of a Cr(IV) complex. The latter functions as a catalyst for the primary conversion. The slow buildup of this intermediate, followed by its sudden consumption (after Cr^V is depleted), results in a "clocklike" character for this reaction if monitored at or near 600 nm. The proposed mechanism for this reaction (eq 2–5 in the text) involves 1e oxidations of HSO_3^- to the radical anion $SO_3^{\bullet-}$ by both Cr(V) and Cr(IV) and competition for $SO_3^{\bullet-}$ between Cr(IV) and Cr(V). Differential equations based on the proposed mechanism, in conjunction with suitably selected values for the component rate constants and for molar absorbances for the chromium species, reproduce the observed kinetic profiles. The reaction of HSO_3^- with Cr(V) is much slower than that with the more strongly reducing Cr(IV); the rate ratio is consistent with an outer-sphere mechanism for both HSO_3^- reactions. In contrast, the radical anion $SO_3^{\bullet-}$ reacts with Cr(V) 20–35 times more rapidly than with Cr(IV). This inversion of relative rates, which is the basis for the autocatalyis, suggests the operation of an inner-sphere path for the Cr(V)–radical reaction.

Carboxylato chelates of chromium(V), the facile preparations of which were described in 1979,[3] react with an array of inorganic reductants, and these reactions exhibit considerable mechanistic diversity. Early studies[4] presupposed that "even-electron" reductants would reduce Cr(V) smoothly to Cr(III), whereas 1e reductants would react through the intermediate state, Cr(IV), which, depending upon its reactivity, might or might not be detectable. It is now clear that this is an oversimplification. Reduction by hydroxylamine[5] yields, instead of a Cr(III) species,

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