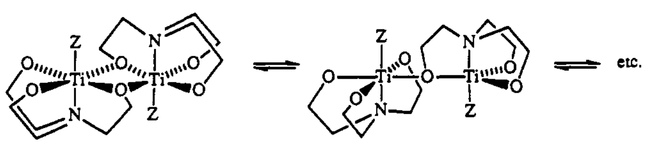
Inorg. Chem. **1991**, *30*, 4631–4635

Scheme II



in 7 (229.0 (5) pm) is within experimental error of that in 4 (226.4 (3) pm)).

NMR Spectra. Titanatranes **1**–**8** can be divided into three categories on the basis of their NMR spectra in $CDCl_3$ as a function of temperature. In the first category are **1**, **3**, **4**, and **5**, whose ^1H and ^{13}C NMR spectra are largely temperature-independent. Because of the bulky nature of the apical substituents, these compounds display spectra consistent with monomeric behavior. In the case of **1**, some broadening of the ^1H NMR signals can be observed at −60 °C, owing to the relatively decreased bulk of the *i*-Pr group, which allows this compound to form a dimer in the solid state.

Titanatranes **2**, **6**, and **7** constitute a class for which the ^1H and ^{13}C NMR spectra are broadened at room temperature, presumably owing to an exchange process which is slow on the NMR time scale. Because dilution of solutions of these dimers does not affect the breadth of the ^1H NMR peaks of these compounds, the exchange process can be envisioned as being dominated by an intramolecular "gearing" fluxional motion around their Z–Ti–N axes (depicted in Scheme II) rather than by a dissociation into monomers. This gearing motion requires the breakage of only one bridge bond at a time with the subsequent formation of a new one as opposite rotations about the Z–Ti–N axes occur. At 60 °C the ^1H NMR resonances become sharp for **2**, **6**, and **7**, and a single time-averaged spectrum is observed wherein the three CH_2CH_2O groups are equivalent. At −60 °C the ^1H NMR spectra are still broad for **2** and **6**, whereas for **7** the exchange process is essentially frozen out and two types of CH_2CH_2O groups can be distinguished in a 2:1 ratio. The coalescence temperature for this process in $CDCl_3$ is +10 °C. Presumably because of the bidentate nature of the acetato group in **7**, the gearing fluxionality for this dimer is less facile than for **2** and **6**. These dimers are robust to adduct formation by strong donors. Thus, addition of pyridine, DMSO, acetone, and acetonitrile failed to reveal NMR evidence for interaction with these compounds.

In the case of **8**, the ^1H and ^{13}C NMR spectra at room temperature display sharp resonances for two types of CH_2CH_2O groups in a 2:1 ratio consistent with the presence of a stable dimer. Upon heating, the ^{13}C NMR resonances broaden until at 60 °C only one type of CH_2CH_2O group is observed. The relative robustness of dimeric **8** compared with dimers **2**, **6**, and **7** may be ascribed to an electron donation effect of the Me_2N group which enhances oxygen bridging as in **1**. A final conclusion on this point depends on the growth of crystals of **8** suitable for X-ray diffraction experiments.

Acknowledgment. We are grateful to the National Science Foundation for financial support in the form of a grant to J.G.V. and to Dr. A. Naiini for experimental assistance.

Registry No. **1**, 87654-61-3; **2**, 136736-74-8; **3**, 136736-75-9; **4**, 6026-51-3; **5**, 136736-76-0; **6**, 15364-28-0; **7**, 136736-78-2; **8**, 136736-79-3; $CpTi(OCH_3)_3$, 12145-64-1.

Supplementary Material Available: Tables of bond distances, bond angles, least-squares planes, positional and thermal parameters for calculated hydrogen atoms, and general displacement parameter expressions (12 pages); tables of structure factors (15 pages). Ordering information is given on any current masthead page.

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Preparation of Unsymmetrically B-Substituted Borazines and Characterization of Tris(4,6-diethylborazin-2-yl)amine

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Symmetrically substituted *B,B′,B″*-triorganylborazines, $(RBNR')_3$, react with an equimolar quantity of boron trihalide, BX_3 (X = Cl, Br), to form *B*-monohaloborazines, $XR_2B_2N_3R_3$, as well as RBX_2, and with 2 molar equiv of BX_3 to form the *B,B′*-dihaloborazines, $X_2RB_3N_3R'_3$. The compounds are obtained in good yield and purity, and are easily converted to other unsymmetrically B-substituted borazines. The borazines $X(CH_3)_2B_3N_3(CH_3)_3$ (X = SCH_3, NH_2, C_4H_9, $N[Si(CH_3)_2]$), $X(C_2H_5)_2B_3N_3H_3$ (X = Br, SCH_3), $Cl(C_2H_5)_2B_3N_3(CH_3)_3$, $X_2(C_2H_5)_2B_3N_3H_3$ (X = Br, SCH_3), $Cl(C_6H_5)_2B_3N_3H_3$, and $Cl_2(C_2H_5)B_3N_3(CH_3)_3$ have been prepared and characterized. The compound $(H_2N)(C_2H_5)_2B_3N_3H_3$ could not be obtained in the pure state; instead, it slowly condenses (even at room temperature) with the formation of the bis(borazin-2-yl)amine $HN[(C_2H_5)_2B_3N_3H_3]_2$ and the tris(borazin-2-yl)amine $N[(C_2H_5)_2B_3N_3H_3]_3$. The borazine $(H_2N)(CH_3)_2B_3N_3(CH_3)_3$ condenses at temperatures from 250 to 270 °C to give $HN[(CH_3)_2B_3N_3(CH_3)_3]_2$. Reaction of this bis(borazin-2-yl)amine with LiC_4H_9 yields $(C_4H_9)(CH_3)_2B_3N_3(CH_3)_3$ and $(NHLi)(CH_3)_2B_3N_3(CH_3)_3$; the latter then reacts with $Cl(CH_3)_2B_3N_3(CH_3)_3$ to regenerate $HN[(CH_3)_2B_3N_3(CH_3)_3]_2$. The unsymmetrically N-substituted borazine $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ has been isolated and characterized.

Introduction

Borazine is the foremost example of an inorganic compound that can be closely compared to an organic species, i.e., benzene. Hence, studies on this six-membered B_3N_3 heterocyclic system have been popular and literally hundreds of borazine derivatives are known. However, most of them are symmetrically substituted species of the type $(RBNR')_3$. Relatively few unsymmetrically substituted derivatives have been described and their chemistry has been investigated only sparingly.[1]

Within the context of preparative studies on discrete polycyclic boron–nitrogen systems as potential precursors for macromolecular materials, the synthesis of the tris(borazin-2-yl)amine framework seemed to be an interesting point of origin. Detailed studies on such species require convenient access to unsymmetrically B-substituted borazines of the types $XR_2B_3N_3R'_3$ and $X_2RB_3N_3R'_3$ (and where X is a reactive site) in high purity. The present report describes the preparation and characterization of various such unsymmetrically B-substituted borazines as well as attempts to synthesize the tris(borazin-2-yl)amine skeleton.

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined on a Mel-Temp block.

NMR spectra were recorded for solutions in $CDCl_3$ (unless otherwise noted) on a Varian VXR-400 or XL-200 (^{11}B) or GEMINI-200 (^1H,

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[1] *Gmelin Handbuch der Anorganischen Chemie*; Springer-Verlag: West Berlin, 1978; Vol. 51, Supplement Boron Compounds 17.

^{13}C) instrument. Chemical shift data are given in ppm with positive values indicating shifts downfield from the reference (internal $\mathrm{(CH_3)_4Si}$ for ^{1}H and ^{13}C NMR; external $\mathrm{(C_2H_5)_2O{\cdot}BF_3}$ for ^{11}B NMR); s = singlet, d = doublet, t = triplet, q = quartet, m = unresolved multiplet, and an asterisk denotes a broad signal. Coupling constants J are given in hertz. All ^{13}C NMR spectra were recorded in the proton-decoupled mode. Field desorption (FD) mass spectra were recorded on a Finnigan MAT 250 instrument, and field ionization (FI) mass spectra were obtained on a Varian MAT-CH5 instrument, courtesy of Professor A. Meller, University of Göttingen, Göttingen, Germany. Electron impact (EI) mass spectral data (70 eV unless otherwise noted) were obtained on a VG ZAB-2F spectrometer under standard operating conditions. Data are listed to m/z 30 for 5% or greater relative abundances (in parentheses) only. Infrared spectra (frequencies in cm^{-1}) were recorded on a BOMEM Model DA3 spectrometer under standard operating conditions.

Nonreferenced reagents were obtained from Aldrich Chemical Co., Milwaukee, WI, and used as received. All preparations were performed in an anhydrous atmosphere under argon cover, solvents were dried by standard procedures.

$\mathrm{Cl(CH_3)_2B_3N_3(CH_3)_3}$.[2] NMR data: $\delta(^{1}\mathrm{H})$ 3.00 (2 H, s), 2.90 (1 H, s), 0.52 (2 H, s); $\delta(^{11}\mathrm{B})$ 37.2 (2 B, s, $h_{1/2}$ = 175 Hz), 30.7 (1 B, s, $h_{1/2}$ = 125 Hz); $\delta(^{13}\mathrm{C})$ 34.6, 34.5, –0.6*. Solution NMR data in $\mathrm{CCl_4}$:[3] $\delta(^{1}\mathrm{H})$ 2.99 (2 H, s), 2.89 (1 H, s), 0.51 (2 H, s). EI mass spectrum: m/z 187 (14), 186 (33), 185 (62), 184 (100), 183 (28), 182 (15), 172 (18), 171 (16), 170 (62), 169 (44), 168 (14), 167 (7), 166 (12), 165 (8), 152 (8), 129 (22), 128 (11), 115 (10), 102 (11), 101 (5), 95 (9), 88 (6), 86 (16), 85 (10), 79 (6), 68 (7), 66 (16), 65 (11), 54 (18), 53 (6), 52 (15), 51 (12), 44 (15), 43 (24), 42 (8), 41 (16), 40 (9), 39 (6), 38 (7), 32 (19).

$\mathrm{(CH_3S)(CH_3)_2B_3N_3(CH_3)_3}$ (2d). A stirred mixture of 15.2 g (49 mmol) of $\mathrm{Pb(SCH_3)_2}$, 11.6 g (62 mmol) of (crude) $\mathrm{Cl(CH_3)_2B_3N_3(CH_3)_3}$, and 150 mL of hexane was heated to reflux for 12 h. The mixture was filtered, and the solvent was evaporated from the clear filtrate under reduced pressure to leave an oily residue. Some volatile impurities were sublimed off at 40 °C (3 Torr) and the remaining product was distilled under vacuum to give 7.0 g (57%) of the compound, bp 98–102 °C (1 Torr). Anal. Calcd for $\mathrm{C_6H_{18}B_3N_3S}$ (M_r = 196.73): C, 36.63; H, 9.22; B, 16.49; N, 21.36; S, 16.30. Found: C, 36.81; H, 9.28; B, 16.31; N, 21.33; S, 16.28.

NMR data: $\delta(^{1}\mathrm{H})$ 2.98 (2 H, s), 2.84 (1 H, s), 2.14 (1 H, s), 0.46 (2 H, s); $\delta(^{11}\mathrm{B})$ 35.6 (s, $h_{1/2}$ = 250 Hz); $\delta(^{13}\mathrm{C})$ 35.5, 34.2, 11.5, –0.8*. EI mass spectrum (13 eV): m/z 199 (7), 198 (15), 197 (100), 196 (96), 195 (18), 185 (11), 184 (9), 183 (9), 182 (18), 181 (15), 180 (9), 167 (7), 166 (6), 150 (44), 149 (18), 148 (7), 48 (44).

$\mathrm{(H_2N)(CH_3)_2B_3N_3(CH_3)_3}$ (2e). Dry ether (15 mL) was mixed with ca. 10 mL of anhydrous liquid $\mathrm{NH_3}$ at –50 °C. A solution of 2.93 g (14.9 mmol) of $\mathrm{(CH_3S)(CH_3)_2B_3N_3(CH_3)_2}$ in 10 mL of ether was added, and the stirred reaction mixture was slowly warmed to room temperature. It was heated to reflux (30 min), and solvent was evaporated to leave a colorless residue. The latter was purified by sublimation under vacuum to give 2.1 g (84%) of product, mp 84–85 °C (lit.[2] mp 87 °C).

NMR data: $\delta(^{1}\mathrm{H})$ 2.80 (3 H, s), 2.72 (6 H, s), 2.30* (2 H), 0.42 (6 H, s); $\delta(^{11}\mathrm{B})$ 36.1 (2 B, s, $h_{1/2}$ = 180 Hz), 25.9 (1 B, s, $h_{1/2}$ = 140 Hz); $\delta(^{13}\mathrm{C})$ 34.3, 31.6, –0.4*. EI mass spectrum (8 eV): m/z 167 (16), 166 (100), 165 (76), 165 (25), 163 (5).

$\mathrm{HN[(CH_3)_2B_3N_3(CH_3)_3]_2}$ (1a). Method A. $\mathrm{(H_2N)(CH_3)_2B_3N_3(CH_3)_3}$ (7.0 g, 42 mmol) was slowly heated with stirring. Evolution of $\mathrm{NH_3}$ began at a temperature near 150 °C, and the material was ultimately heated to 280 °C for 4 h. It was cooled to room temperature and then recrystallized from hexane to give 4.5 g (68%) of pure, hydrolytically very sensitive product: mp 139–142 °C; bp 358–360 °C, 240 °C (2 Torr). Anal. Calcd for $\mathrm{C_{10}H_{31}B_6N_7}$ (M_r = 314.27): C, 38.22; H, 9.94; B, 20.64; N, 31.20. Found: C, 38.17; H, 9.71; B, 20.89; N, 31.34.

NMR data: $\delta(^{1}\mathrm{H})$ 2.86 (6 H, s), 2.75 (12 H, s), 2.40 (1 H, s), 0.47 (12 H, s); $\delta(^{11}\mathrm{B})$ 37.0 (2 B, s, $h_{1/2}$ = 340 Hz), 28.3 (1 B, s, $h_{1/2}$ = 270 Hz); $\delta(^{13}\mathrm{C})$ 34.7, 33.4, –0.2*. FD mass spectrum: m/z 317 (8), 316 (84), 315 (100), 314 (62), 313 (14); FI mas spectrum: m/z 316 (12), 315 (78), 314 (100), 313 (61). Major fragments in the EI mass spectrum appeared at m/z 284 and 269. The IR spectrum exhibited a strong N–H stretching band at 3409 cm^{-1}. Lit.[4] mp: 142–145 °C (material obtained by method B, below). NMR data: $\delta(^{1}\mathrm{H})$ 2.87, 2.78, 0.5; $\delta(^{11}\mathrm{B})$ 37.2, 30.0.

Method B. A solution of 1.8 g (11 mmol) of $\mathrm{[(CH_3)_3Si]_2NH}$ in 15 mL of ether was added to a solution of 4.0 g (22 mmol) of $\mathrm{Cl(CH_3)_2B_3N_3(CH_3)_3}$ in 40 mL of ether. The mixture was stirred at ambient temperature for 12 h, and volatiles were removed under reduced pressure to leave a colorless solid material. The latter was recrystallized from hexane to give 2.8 g (82%) of **1a**, mp 140–142 °C, identical (NMR data) to the material obtained by the preceding procedure.

$\mathrm{O[(CH_3)_2B_3N_3(CH_3)_3]_2}$.[5] NMR data: $\delta(^{1}\mathrm{H})$ 2.87 (1 H, s), 2.72 (2 H, s), 0.47 (2 H, s); $\delta(^{11}\mathrm{B})$ 37.3 (2 B, s, $h_{1/2}$ = 340 Hz), 23.6 (1 B, s, $h_{1/2}$ = 260 Hz); $\delta(^{13}\mathrm{C})$ 34.3, 31.2, –0.7*. Solution NMR data in $\mathrm{C_6D_6}$:[4] $\delta(^{1}\mathrm{H})$ 2.79, 2.77, 0.49; $\delta(^{11}\mathrm{B})$ 37, 24; $\delta(^{13}\mathrm{C})$ 34.45, 31.55, –0.25. EI mass spectrum (13 eV): m/z 316 (30), 315 (45), 314 (31), 313 (13), 301 (19), 300 (26), 299 (16), 284 (5), 140 (5), 139 (5), 126 (14), 125 (9), 113 (7), 112 (8), 111 (100), 110 (80), 109 (19), 31 (25), 30 (32).

Reaction of $\mathrm{HN[(CH_3)_2B_3N_3(CH_3)_3]_2}$ (1a) with $\mathrm{LiC_4H_9}$ and $\mathrm{Cl(CH_3)_2B_3N_3(CH_3)_3}$. A mixture of 1.01 g (3.5 mmol) of $\mathrm{HN[(CH_3)_2B_3N_3(CH_3)_3]_2}$ (**1a**) and 10 mL of ether was cooled to –78 °C, and 2.2 mL of a 1.6 M solution of n-$\mathrm{C_4H_9Li}$ in hexane was added slowly with stirring. The mixture was stirred at –50 °C for 4 h to give a clear solution. A solution of 0.65 g (3.5 mmol) of $\mathrm{Cl(CH_3)_2B_3N_3(CH_3)_3}$ in 10 mL of ether was added, and the mixture was stirred for 4 h at –50 °C and then for 10 h at ambient temperature. LiCl was filtered off and solvent was evaporated from the clear filtrate to leave a mixture of $\mathrm{HN[(CH_3)_2B_3N_3(CH_3)_3]_2}$ (**1a**) and $\mathrm{(C_4H_9)(CH_3)_2B_3N_3(CH_3)_3}$ (**2f**).

The latter compound (**2f**) was purified by distillation to give 0.59 g (82%) of product, bp 75–78 °C (1 Torr). NMR data: $\delta(^{1}\mathrm{H})$ 2.89 (6 H, s), 2.86 (3 H, s), 1.27–1.41 (4 H, m), 1.05 (2 H, m), 0.91 (3 H, t, J = 7), 0.47 (6 H, s); $\delta(^{11}\mathrm{B})$ 36.2 (s, $h_{1/2}$ = 230 Hz); $\delta(^{13}\mathrm{C})$ 34.3, 34.0, 26.6, 26.2, 15.3*, 13.7, –0.5*. EI mass spectrum (13 eV): m/z 208 (10), 207 (68), 206 (58), 205 (15), 192 (5), 178 (5), 166 (16), 165 (91), 164 (100), 163 (30), 162 (5), 150 (41), 149 (26), 148 (7).

$\mathrm{[\{(CH_3)_3Si\}_2N](CH_3)_2B_3N_3(CH_3)_3}$ (2g). A mixture of 1.81 g (9.89 mmol) of $\mathrm{NaN[Si(CH_3)_3]_2}$ and 15 mL of ether was cooled to –40 °C and a solution of 1.82 g (9.80 mmol) of $\mathrm{Cl(CH_3)_2B_3N_3(CH_3)_3}$ in 15 mL of ether was added dropwise with stirring. The mixture was stirred at –78 °C for 2 h and for 12 h at ambient temperature. The precipitate (NaCl) was filtered off, and solvent was removed under reduced pressure from the clear filtrate. The liquid residue was distilled under vacuum to give 1.3 g (43%) of product, bp 113 °C (1 Torr).

NMR data: $\delta(^{1}\mathrm{H})$ 2.85 (2 H, s), 2.84 (1 H, s), 0.44 (2 H, s), 0.07 (6 H, s); $\delta(^{11}\mathrm{B})$ 37.8 (2 B, s, $h_{1/2}$ = 310 Hz), 30.6 (1 B, s, $h_{1/2}$ = 300 Hz); $\delta(^{13}\mathrm{C})$ 34.5, 34.3, 2.5, –0.2*. EI mass spectrum (13 eV): m/z 311 (6), 310 (19), 309 (14), 308 (5), 297 (10), 296 (21), 295 (100), 294 (62), 293 (17), 239 (7), 238 (5), 224 (5).

$\mathrm{Cl(C_2H_5)_2B_3N_3(CH_3)_3}$ (2h). A solution of 15.6 mmol of $\mathrm{BCl_3}$ in heptane (15.6 mL of a 1 M solution) was added to 3.22 g (15.6 mmol) of cold (ice bath) $\mathrm{(C_2H_5BNCH_3)_3}$. The stirred mixture was warmed to ambient temperature, and after 5 h volatile material was removed under reduced pressure. The residue was distilled under vacuum to give 2.9 g (89%) of product, bp 84–86 °C (1 Torr). Anal. Calcd for $\mathrm{C_7H_{19}B_3ClN_3}$ (M_r = 213.14): C, 39.45; H, 8.98; B, 15.22; l, 16.63; N, 19.72. Found: C, 29.40; H, 9.02; B, 15.09; Cl, 16.61; N, 19.76.

NMR data: $\delta(^{1}\mathrm{H})$ 3.01 (6 H, s), 2.96 (3 H, s), 1.1–0.9 (10 H, m); $\delta(^{11}\mathrm{B})$ 37.3 (2 B, s, $h_{1/2}$ = 250 Hz), 31.1 (1 B, s, $h_{1/2}$ = 170 Hz); $\delta(^{13}\mathrm{C})$ 33.9, 33.1, 7.5, 6.7*. EI spectrum (9 eV): m/z 215 (35), 214 (35), 213 (100), 212 (74), 211 (21).

$\mathrm{Cl(C_6H_5)_2B_3N_3H_3}$ (2a). To a stirred mixture of 3.30 g (10.7 mmol) of $\mathrm{(C_6H_5BNH)_3}$[1] and 60 mL of toluene kept at 10 °C, 10.7 mL of a 1 M solution of $\mathrm{BCl_3}$ in heptane was added dropwise. The mixture was slowly warmed to room temperature and then heated to 80 °C until a clear solution was obtained (ca. 1 h). Volatiles were removed under reduced pressure to leave 2.80 g (98%) of crude solid containing traces of unreacted $\mathrm{(C_6H_5BNH)_3}$. The material was purified by sublimation under vacuum at a bath temperature of 90 °C (not higher!) to give a pure compound, mp 62–65 °C. Anal. Calcd for $\mathrm{C_{12}H_{13}B_3ClN_3}$ (M_r = 267.00): C, 53.93; H, 4.91; B, 12.13; Cl, 13.30; N, 15.73. Found: C, 53.27; H, 4.97; B, 12.05; Cl, 13.10; N, 15.58.

NMR data: $\delta(^{1}\mathrm{H})$ 7.70 (4 H, m), 7.48 (6 H, m), 5.90* (1 H, s), 5.60* (2 H, s); $\delta(^{11}\mathrm{B})$ 33.5 (2 B, s, $h_{1/2}$ = ca. 375 Hz), 30.3 (1 B, s, $h_{1/2}$ = ca. 300 Hz); $\delta(^{13}\mathrm{C})$ 132.1, 130.7, 128.5. EI mass spectrum (11 eV): m/z 270 (8), 269 (38), 268 (35), 267 (100), 266 (68), 265 (18).

$\mathrm{(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]}$ (5) was obtained as a byproduct in the synthesis of $\mathrm{(C_2H_5BNH)_3}$ from $\mathrm{C_2H_5BCl_2}$ and $\mathrm{HN[Si(CH_3)_3]_2}$.[6] After $\mathrm{(C_2H_5BNH)_3}$ was distilled off from the crude reaction mixture, variable amounts of higher boiling material remain. From this, **5** was obtained as a colorless liquid, bp 52–54 °C (1 Torr). Anal. Calcd for $\mathrm{C_9H_{26}B_3N_3Si}$ (M_r = 236.71): C, 45.63; H, 11.07; B, 13.69; N, 17.74; Si, 11.87.

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Found: C, 45.55; H, 11.14; B, 13.71; N, 17.78; Si, 12.08.

NMR data: $\delta(^1H)$ 4.9* (2 H, s), 0.97 (12 H, unsymmetric s with broad unresolved base), 0.84 (3 H, t), 0.27 (9 H, s); $\delta(^{11}B)$ 38.5 (2 B, s), 35.7 (1 B, s); $\delta(^{13}C)$ 12.8*, 9.8, 8.9*, 8.3, 4.6. The 20-eV EI mass spectrum exhibited a small parent ion cluster at *m/z* 237 and a base peak for $[M - 15]^+$ at *m/z* 222.

$Br(C_2H_5)_2B_3N_3H_3$ (2b). A stirred solution of 3.80 g (23.3 mmol) of $(C_2H_5BNH)_3$[6] in 20 mL of dichloromethane was cooled to −10 °C, and 5.80 g (23.3 mmol) of BBr_3 was added dropwise. The resultant thick slurry was warmed to room temperature to form a clear solution. It was stirred for 30 min at ambient temperature, and volatiles were removed under reduced pressure. A colorless wet solid remained, which was purified by sublimation under vacuum to give 4.9 g (97%) of material, mp 34–36 °C. (A small amount of the byproduct $Br_2(C_2H_5)B_3N_3H_3$ could not be removed.) Anal. Calcd for $C_4H_{13}B_3BrN_3$ (M_r = 215.40): C, 22.28; H, 6.08; B, 15.04; Br, 37.09; N, 19.51. Found: C, 21.98; H, 5.94; B, 14.91; Br, 37.31; N, 19.27.

NMR data: $\delta(^1H)$ 5.10* (2 H, s), 4.95* (1 H, s), 1.05–0.80 (10 H, m); $\delta(^{11}B)$ 36.6 (2 B, s, $h_{1/2}$ = 200 Hz), 27.6 (1 B, s, $h_{1/2}$ = 150 Hz); $\delta(^{13}C)$ 9.0*, 8.2. EI mass spectrum (10 eV): *m/z* 217 (67), 216 (60), 215 (100), 214 (54), 213 (19). The 70-eV EI mass spectrum exhibited an ion cluster at *m/z* 186 as the strongest peak group of the spectrum, with the parent ion cluster appearing in about 80% relative intensity thereof.

$(CH_3S)(C_2H_5)_2B_3N_3H_3$ (2c). A stirred mixture of 1.32 g (6.13 mmol) of $Br(C_2H_5)_2B_3N_3H_3$, 3.0 g (10 mmol) of $Pb(SCH_3)_2$, and 10 mL of hexane was refluxed for 24 h and filtered, and solvent was evaporated off the clear filtrate under reduced pressure. The remaining crude liquid (0.75 g, 67%) was purified by distillation under vacuum, bp 44–45 °C (1 Torr). Anal. Calcd for $C_5H_{16}B_3N_3S$ (M_r = 182.59): C, 32.86; H, 8.83; B, 17.75; N, 23.00; S, 17.56. Found: C, 32.93; H, 8.91; B, 17.41; N, 22.74; S, 17.31.

NMR data: $\delta(^1H)$ 4.75* (s, 3 H), 2.10 (3 H, s), 0.97 (6 H, unsymmetric t), 0.87 (4 H, unsymmetric q); $\delta(^{11}B)$ 35.9 (2 B, s), 34.2 (1 B, s); $\delta(^{13}C)$ 9.0*, 8.3, 8.2. The EI mass spectrum exhibited a parent ion cluster at *m/z* 183 as the base peak of the spectrum.

Reaction of NH_3 with $Br(C_2H_5)_2B_3N_3H_3$—Formation of $HN[(C_2H_5)_2B_3N_3H_3]_2$ (1b) and $N[(C_2H_5)_2B_3N_3H_3]_3$ (4). Dry ether (15 mL) was mixed with ca. 30 mL of anhydrous liquid NH_3 at −78 °C. A solution of 3.65 g (17.0 mmol) of $Br(C_2H_5)_2B_3N_3H_3$ in 15 mL of ether was added, and the stirred reaction mixture was slowly warmed to room temperature. It was filtered, and volatiles were evaporated under reduced pressure to leave 2.5 g of crude product.

When the volatile material was removed rapidly and a ^{11}B NMR spectrum was recorded on the crude product, $(H_2N)(C_2H_5)_2B_3N_3H_3$ could be identified ($\delta(^{11}B)$ 36.2 (2 B, $h_{1/2}$ = 230 Hz), 25.5 (1 B, $h_{1/2}$ = 170 Hz)). However, even at room temperature the compound condensed with formation of the bis(borazin-2-yl)amine $HN[(C_2H_5)_2B_3N_3H_3]_2$ (**1b**) and also of the tris(borazin-2-yl)amine **4**.

A small amount (200 mg) of liquid, bp 115–120 °C (1 Torr), was distilled off the crude product and identified as **1b**. NMR data: $\delta(^1H)$ 4.5* (2 H, s), 4.2* (4 H, s), 2.7* (1 H, s), 1.05–0.92 (m) and 0.88–0.64 (m) (20 H total); $\delta(^{11}B)$ 36.4 (2 B, $h_{1/2}$ = 450 Hz), 26.3 (1 B, $h_{1/2}$ = 440 Hz). EI mass spectrum (12 eV): *m/z* 288 (14), 287 (79), 286 (100), 285 (55), 284 (28), 283 (7), 260 (10), 259 (31), 258 (33), 257 (21), 256 (10). Calculated for the parent ion: *m/z* 288 (8), 287 (74), 286 (100), 285 (60), 284 (19), 283 (3).

During the distillation, ca. 300 mg of a second material, **4**, mp 146–148 °C, deposited in the distillation head. Anal. Calcd for $C_{12}H_{39}B_9N_{10}$ (M_r = 420.51): C, 34.24; H, 9.35; B, 23.11; N, 33.30. Found: C, 34.14; H, 9.29; B, 23.19; N, 33.19. NMR data: $\delta(^1H)$ 4.6* (3 H, s), 0.95 (6 H, unsymmetric t), 0.83 (4 H, unsymmetric q); $\delta(^{11}B)$ 36.8 (2 B, $h_{1/2}$ = ca. 680 Hz), 28.5 (1 B, $h_{1/2}$ = ca. 730 Hz); $\delta(^{13}C)$ 9.3*, 8.5. EI mass spectrum (10 eV): *m/z* 423 (7), 422 (87), 421 (100), 420 (87), 419 (20), 418 (6), 287 (6), 286 (28), 285 (53), 284 (21), 283 (5). Calculated for the parent ion of **4**: *m/z* 423 (8), 422 (54), 421 (100), 420 (92), 419 (51), 418 (19), 417 (5).

On the basis of NMR and mass spectroscopic data, the residue consisted primarily of **4**. The material deteriorated during the distillation and increasing amounts of an intractible white solid (boron nitride?) formed.

$Br_2(C_2H_5)B_3N_3H_3$ (3b) was obtained by adding 76.2 g (0.304 mol) of BBr_3 to a stirred solution of 25.0 g (0.152 mol) of $(C_2H_5BNH)_3$ in 100 mL of dichloromethane at −10 °C over a period of 1 h. The mixture was warmed to room temperature and then refluxed for 1 h to give an almost clear solution. It was filtered, and volatiles were evaporated under reduced pressure to leave 40.2 g (99%) of crude product. This was sublimed under vacuum (40–50 °C bath temperature) to give a material of mp 27–29 °C. (The material contains traces of $(BrBNH)_3$, which are difficult to remove.) Anal. Calcd for $C_2H_8B_3Br_2N_3$ (M_r = 266.26): C, 9.01; H, 3.03; B, 12.17; Br, 60.02; N, 15.77. Found: C, 8.83; H, 2.92; B, 12.01; Br, 60.24; N, 15.45.

NMR data: $\delta(^1H)$ 5.3* (3 H, s), 1.05–0.8 (5 H, m); $\delta(^{11}B)$ 37.3 (1 B, s, $h_{1/2}$ = 190 Hz), 27.9 (2 B, s, $h_{1/2}$ = 140 Hz); $\delta(^{13}C)$ 7.9, 7.7*. The 15-eV EI mass spectrum exhibited a parent ion cluster at *m/z* 267 in the calculated isotopic distribution.

$(CH_3S)_2(C_2H_5)B_3N_3H_3$ (3c) was prepared in a manner analogous to that of **2c** (above) from 4.6 g (17 mmol) of $Br_2(C_2H_5)B_3N_3H_3$ and 11.0 g (36.5 mmol) of $Pb(SCH_3)_2$ (65 mL of hexane, 24 h reflux). After filtration, the clear solution was concentrated to a volume of about 10 mL and cooled, and 2.45 g (71%) of **3c** precipitated; mp 58–62 °C. Anal. Calcd for $C_4H_{14}B_3N_3S_2$ (M_r = 200.63): C, 23.92; H, 7.03; B, 16.15; N, 20.93; S, 31.97. Found: C, 23.41; H, 7.02; B, 16.08; N, 20.64; S, 31.88.

NMR data: $\delta(^1H)$ 4.7* (3 H, s), 2.10 (6 H, s), 1.1–0.8 (5 H, m); $\delta(^{11}B)$ 35.8 (1 B, s, $h_{1/2}$ = 290 Hz), 34.1 (2 B, s, $h_{1/2}$ = 175 Hz); $\delta(^{13}C)$ 9.1*, 8.24, 8.16. The EI mass spectrum exhibited a parent ion cluster at *m/z* 201.

$Cl_2(C_2H_5)B_3N_3(CH_3)_3$ (3d) was prepared from 41.2 mL of a 1 M solution of BCl_3 in heptane and 4.25 g (20.6 mmol) of $(C_2H_5BNCH_3)_3$ (stirring overnight at ambient temperature and then for 6 h at 60 °C). After removal of volatiles under reduced pressure, the residue was distilled under vacuum to give 4.35 g (96%) of **3d**, bp 78–80 °C (1 Torr). Anal. Calcd for $C_5H_{14}B_3N_3Cl_2$ (M_r = 219.53): C, 27.36; H, 6.43; B, 14.77; Cl, 32.30; N, 19.14. Found: C, 27.32; H, 6.48; B, 14.20; Cl, 31.19; N, 19.07.

NMR data: $\delta(^1H)$ 3.10 (3 H, s), 3.05 (6 H, s), 1.09 (2 H, q, *J* = 7), 0.98 (3 H, t, *J* = 7); $\delta(^{11}B)$ 37.9 (1 B, s, $h_{1/2}$ = 250 Hz), 31.4 (2 B, s, $h_{1/2}$ = 140 Hz); $\delta(^{13}C)$ 35.1, 34.2, 7.4, 7.1*. Mass spectrum (10 eV): *m/z* 223 (19), 222 (12), 221 (78), 220 (62), 219 (100), 218 (72), 217 (22), 216 (8).

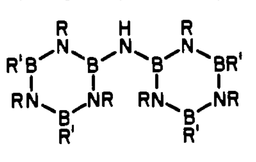
Results and Discussion

The chemistry of unsymmetrically substituted borazines has not yet been well explored, since access to such species in the pure state is fairly difficult.[1] The most readily available unsymmetrically B-substituted borazine of the type $XR_2B_3N_3R'_3$ is probably the monochloro compound $Cl(CH_3)_2B_3N_3(CH_3)_3$, which can be obtained from $(ClBNCH_3)_3$ by a Grignard reaction. However, the purification of the product is fairly laborious.[2] On the other hand, it has now been observed that the crude material as obtained from the cited Grignard reaction can be converted to $(CH_3S)(CH_3)_2B_3N_3(CH_3)_3$ (**2d**) by reaction with $Pb(SCH_3)_2$ according to eq 1, and the resultant (liquid) monomethylthio compound is then readily purified by distillation.

$$2Cl(CH_3)_2B_3N_3(CH_3)_3 + Pb(SCH_3)_2 \rightarrow 2(CH_3S)(CH_3)_2B_3N_3(CH_3)_3 + PbCl_2 \quad (1)$$

In many instances the (B)SCH_3 site is just about as reactive as a (B)Cl site. For example, 2-amino-1,3,4,5,6-pentamethylborazine has previously been prepared by the reaction of $Cl(CH_3)_2B_3N_3(CH_3)_3$ with NH_3.[2,7] In the present work, the reaction of $(CH_3S)(CH_3)_2B_3N_3(CH_3)_3$ with anhydrous NH_3 gave a good yield of $(H_2N)(CH_3)_2B_3N_3(CH_3)_3$ (**2e**), which has now been characterized by NMR data. Thermal condensation of **2e** was found to begin near 150–160 °C, but temperatures as high as 250–270 °C were required for efficient conversion of the compound to yield the bis(borazin-2-yl)amine $HN[(CH_3)_2B_3N_3(CH_3)_3]_2$ (**1a**) with the elimination of NH_3 (eq 2). The same bis(borazin-2-yl)amine has previously been mentioned as the product of such a thermal condensation but was not characterized.[8] More recently, it has been obtained by the interaction of $Cl(CH_3)_2B_3N_3(CH_3)_3$ with $HN[Si(CH_3)_3]_2$ and the structure of the species has been determined by single-crystal X-ray diffraction methods.[4]

$$2(H_2N)(CH_3)_2B_3N_3(CH_3)_3 \rightarrow NH_3 + \mathbf{1a} \quad (2)$$



a: R = R′ = CH_3
b: R = H, R′ = C_2H_5

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$HN[(CH_3)_2B_3N_3(CH_3)_3]_2$ (**1a**) is extremely sensitive to moisture and hydrolizes with the formation of the previously described.[4,5,9] $O[(CH_3)_2B_3N_3(CH_3)_3]_2$ as the initial product. On the other hand, it is thermally quite stable. For example, when the pure compound is heated to its boiling point under atmospheric pressure, no thermal condensation to yield $N[(CH_3)_2B_3N_3(CH_3)_3]_3$ was observed but increasing amounts of hexamethylborazine were slowly formed in a rearrangement process.

In another approach to generate the tris(borazin-2-yl)amine skeleton, $HN[(CH_3)_2B_3N_3(CH_3)_3]_2$ was reacted with 1 molar equiv each of *n*-C_4H_9Li and then $Cl(CH_3)_2B_3N_3(CH_3)_3$. It was intended to form, initially, the N-lithiated bis(borazinyl)amine, which was then expected to react with the chloroborazine to form tris(pentamethylborazin-2-yl)amine. However, the reaction proceeded unexpectedly. Apparently, initial cleavage of the bis(borazinyl)amine according to eq 3 occurs under the impact of LiC_4H_9, and the original bis(borazinyl)amine is subsequently regenerated according to eq 4. (It should be noted that the reaction according to eq 3 has a precedent, i.e., it parallels the interaction of the diborylamine $HN[B(CH_3)_2]_2$ with $LiCH_3$ to yield $(CH_3)_2BNHLi$ and $B(CH_3)_3$.[10])

$$HN[(CH_3)_2B_3N_3(CH_3)_3]_2 + n\text{-}C_4H_9Li \rightarrow (LiHN)(CH_3)_2B_3N_3(CH_3)_3 + n\text{-}C_4H_9(CH_3)_2B_3N_3(CH_3)_3 \quad (3)$$

$$(LiHN)(CH_3)_2B_3N_3(CH_3)_3 + Cl(CH_3)_2B_3N_3(CH_3)_3 \rightarrow LiCl + HN[(CH_3)_2B_3N_3(CH_3)_3]_2 \quad (4)$$

In additional attempts to synthesize $N[(CH_3)_2B_3N_3(CH_3)_3]_3$, the interaction of equimolar amounts of $(CH_3S)(CH_3)_2B_3N_3(CH_3)_3$ and $HN[(CH_3)_2B_3N_3(CH_3)_3]_2$ at temperatures as high as 200 °C was studied. However, the starting materials were recovered unchanged. Similarly, no reaction occurred when $Cl(CH_3)_2B_3N_3(CH_3)_3$ was treated with $[\{(CH_3)_3Si\}_2N](CH_3)_2B_3N_3(CH_3)_3$ in 2:1 molar ratio in refluxing hexane.

The preceding results seemed to suggest that the formation of the tris(borazinyl)amine is impaired by the presence of the N-bonded organic substituents. Thus, attention was directed to the preparation of unsymmetrically B-substituted borazines containing annular NH groups.

A very convenient approach for the synthesis of unsymmetrically B-substituted borazines has emerged recently, when the reaction of $(C_2H_5BNCH_3)_3$ with BBr_3 was studied. It was found that a Br/C_2H_5 exchange occurred readily and proceeded with the exclusive transfer of only one Br from BBr_3 to the borazine. Thus, interaction of a 1:1 molar ratio of the reagents gave $Br(C_2H_5)_2B_3N_3(CH_3)_3$ in excellent yield and high purity, and a 1:2 ratio provided for $Br_2(C_2H_5)B_3N_3(CH_3)_3$.[11] In an extension of this work, $(C_2H_5BNH)_3$ was reacted with BBr_3 to give $Br(C_2H_5)_2B_3N_3H_3$ (**2b**) and $Br_2(C_2H_5)B_3N_3H_3$ (**3b**), respectively, depending on the stoichiometry of the reagents, as is shown in eqs 5 and 6.

$$BBr_3 + (C_2H_5BNH)_3 \rightarrow C_2H_2BBr_2 + Br(C_2H_5)_2B_3N_3H_3 \quad (5)$$

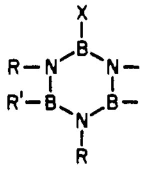
$$2BBr_3 + (C_2H_5BNH)_3 \rightarrow 2C_2H_5BBr_2 + Br_2(C_2H_5)B_3N_3H_3 \quad (6)$$

Moreover, the catalyst as previously employed[11] was found to be not required. Hence, this method provides for a very convenient and efficient access to unsymmetrically B-substituted borazines, since the $C_2H_5BBr_2$ can be recovered and reconverted to the originating borazine, $(C_2H_5BNH)_3$.

It should be noted that the reactions accordings to eqns 5 or 6 must be performed in the presence of solvent: A substantial amount of solid intermediate is formed, which impairs the stirring of a neat reagent mixture. This formation of intermediates seems to be an effect of the annular NH groups, but the presence of NH rather than NCH_3 groups does not affect the yield of final product, which was excellent in all cases. The effect of the annular NH groups is further seen in the properties of the products. Whereas $Br(C_2H_5)_2B_3N_3(CH_3)_3$ is thermally stable and can be purified by distillation, $Br(C_2H_5)_2B_3N_3H_3$ is thermally fairly sensitive and not only begins to decompose at its melting point, but slow decomposition is also observed on prolonged storage of the material at ambient temperature. Hence, it is suggested that only freshly purified (sublimed) material be employed in any subsequent reactions.

It has also been found that the halogen/alkyl group exchange as described in eqs 5 and 6 is not limited to the use of BBr_3 as halogen source, but reactions analogous to that of *B,B′,B″*-triorganylborazines with BBr_3 proceed equally well when BCl_3 is employed as reagent. Thus, the species $Cl(C_2H_5)_2B_3N_3(CH_3)_3$ and $Cl_2(C_2H_5)B_3N_3(CH_3)_3$ could be obtained readily and in good yield. However, under the same experimental conditions, the reaction of $(C_2H_5BNH)_3$ with BCl_3 did not proceed as cleanly as in the case of $(C_2H_5BNCH_3)_3$. For example, for the 1:1 molar reaction the major product clearly was the desired $Cl(C_2H_5)_2B_3N_3H_3$ [bp 53–55 °C (1 Torr); $\delta(^1H)$ 4.9* (3 H, s), 1.0–0.8 (10 H, m); $\delta(^{11}B)$ 36.6 (2 B, s, $h_{1/2}$ = 220 Hz), 29.9 (1 B, s, $h_{1/2}$ = 170 Hz)], but $Cl_2(C_2H_5)B_3N_3H_3$ [bp 38–42 °C (1 Torr), mp 28.5 °C; $\delta(^1H)$ 5.1* (3 H, s), 0.96 (3 H, t), 0.87 (2 H, q); $\delta(^{11}B)$ 37.2 (1 B, s, $h_{1/2}$ = 240 Hz), 29.9 (2 B, s, $h_{1/2}$ = 140 Hz)] as well as $(ClBNH)_3$ was also formed, and it was extremely difficult to separate the products. Similar results were obtained when the reaction was performed in 1:2 molar ratio. Hence, in this case this reaction is not as useful for preparative purposes as that employing BBr_3, and it again illustrates that differences exist between the reactivity of borazines containing annular NH groups as compared to those containing a N-bonded hydrocarbon substituent. On the other hand, $Cl(C_6H_5)_2B_3N_3H_3$ was readily obtained from the reaction of $(C_6H_5BNH)_3$ with BCl_3, suggesting that the boron substituents may also affect the process.

Several additional unsymmetrically B-substituted borazines of the types $XR_2B_3N_3R'_3$ (**2**) and $X_2RB_3N_3R'_3$ (**3**) were subsequently prepared originating from the halogenated species. The following unsymmetrically B-substituted (mono)borazines have been prepared and characterized during the course of the present study.



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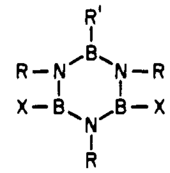

3

2
- **a**: X = Cl, R = H, R′ = C_6H_5
- **b**: X = Br, R = H, R′ = C_2H_5
- **c**: X = SCH_3, R = H, R′ = C_2H_5
- **d**: X = SCH_3, R = R′ = CH_3
- **e**: X = NH_2, R = R′ = CH_3
- **f**: R = C_4H_9, R = R′ = CH_3
- **g**: X = $N[Si(CH_3)_3]_2$, R = R′ = CH_3
- **h**: X = Cl, R = CH_3, R′ = C_2H_5

3
- **a**: X = Cl, R = H, R′ = C_2H_5
- **b**: X = Br, R = H, R′ = C_2H_5
- **c**: X = SCH_3, R = H, R′ = C_2H_5
- **d**: X = Cl, R = CH_3, R′ = C_2H_5

When $Br(C_2H_5)_2B_3N_3H_3$ was reacted with anhydrous NH_3, the desired $(H_2N)(C_2H_5)_2B_3N_3H_3$ could be identified in the crude reaction product only when the excess of NH_3 and the solvent were removed rapidly [$\delta(^{11}B)$ 36.2 (2 B, $h_{1/2}$ = 230 Hz), 25.5 (1 B, $h_{1/2}$ = 170 Hz)]. However, even at room temperature the compound condensed with formation of the bis(borazin-2-yl)amine $HN[(C_2H_5)_2B_3N_3H_3]_2$ [**1b**: $\delta(^{11}B)$ 36.4 (2 B, $h_{1/2}$ = 450 Hz), 26.3 (1 B, $h_{1/2}$ = 440 Hz)]. After a short period of time, the formation of a third species was observed [$\delta(^{11}B)$ 36.8 (2 B, $h_{1/2}$ = ca. 680 Hz), 28.5 (1 B, $h_{1/2}$ = ca. 730 Hz)], which was identified as the tris(borazin-2-yl)amine **4**. Ultimately, only a mixture of $HN[(C_2H_5)_2B_3N_3H_3]_2$ (**1b**) and **4** remained, from which small amounts of pure **1b** and **4** could be isolated and characterized.

The separation of **1b** and **4** proved quite difficult. The bis(borazin-2-yl)amine is thermally quite stable and has no ready tendency to undergo condensation to form **4** when heated under atmospheric pressure at 200 °C for several h. On the other hand, when **1b** was heated at 200 °C under vacuum for 1 h, most of

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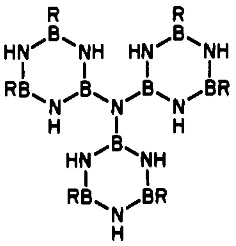


4
R = C_2H_5

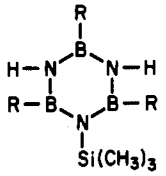
it converted to **4**, but adhering traces of **1b** were difficult to remove and the formation of an intractible material indicated additional decomposition processes.

Compound **4** is the first known tris(borazin-2-yl)amine and seems to offer great potential for the preparation of two-dimensional network structures of linked borazine rings. Ongoing studies are directed to explore this possibility.

It is of interest to note the distinct broadening of the ^{11}B NMR signals in the above series monoaminoborazine–bis(borazinyl)amine (**1b**)–tris(borazinyl)amine (**4**). It is definitely not due to an overlap of signals from mixtures of compounds of similar ^{11}B chemical shifts, but parallels the observations made in the series $(H_2N)(CH_3)_2B_3N_3(CH_3)_3$ (**2e**)–$HN[(CH_3)_2B_3N_3(CH_3)_3]_2$ (**1a**). It is possible that this indicates the overlap of signals, which would suggest that the borazine rings of individual poly(borazine) species are not coplanar. This has indeed been established by an X-ray structure determination of **1a**,[4] but variable-temperature NMR studies on **4** were inconclusive.

In summary, the current study clearly documents that unsymmetrically B-substituted borazines of types **2** and **3** are conveniently obtained originating from symmetrically substituted *B,B′,B″*-triorganylborazines. Thus, such compound are no longer laboratory curiosities but are readily available starting materials for molecular architecture, which opens the door for an extensive exploration of the chemistry of unsymmetrically B-substituted borazines. Most interesting seems to be the application of the species for the formation of poly(borazines), i.e., compounds in which individual borazine rings are linked to form polycyclic systems. The bis(borazin-2-yl)amines **1a** and **1b** and the tris(borazin-2-yl)amine $N[(C_2H_5)_2B_3N_3H_3]_3$ (**4**) are examples of such materials, and the synthesis of a variety of poly(borazine) structures is currently under investigation.

Finally, one other observation is worth mentioning. During the course of preparing the starting material $(C_2H_5BNH)_3$ by the reaction of $C_2H_5BCl_2$ with $HN[Si(CH_3)_3]_2$,[6] considerable variations in the yield were observed, even under apparently identical reaction conditions. Concurrently, the formation of variable amounts of a byproduct was noted, the amount of which increased when the yield of $(C_2H_5BNH)_3$ decreased. This (higher boiling) byproduct has now been identified as the unsymmetrically N-substituted borazine $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ (**5**). Attempts to modify the reaction conditions in order to make **5** the main product did not yet lead to any reasonable conclusions. However, yields of $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ (**5**) ranging from 10–40% were usually obtained, especially when the reaction was performed on a relatively large scale. Thus, it presents the possibility of studying N-unsymmetrically substituted borazines in more detail.



5
R = C_2H_5

Acknowledgment. This work was supported by the Office of Naval Research (K.N.).

Registry No. **1a**, 127232-88-6; **1b**, 136237-51-9; **2a**, 136237-52-0; **2b**, 136237-53-1; **2c**, 136237-54-2; **2d**, 136237-55-3; **2e**, 89417-01-6; **2f**, 136237-56-4; **2g**, 69562-24-9; **2h**, 98425-56-0; **3b**, 136237-57-5; **3c**, 136237-58-6; **3d**, 66535-66-8; **4**, 136237-59-7; **5**, 136237-60-0; $Cl(CH_3)_2B_3N_3(CH_3)_3$, 13058-05-4; $Pb(SCH_3)_2$, 35029-96-0; $O[(CH_3)_2B_3N_3(CH_3)_3]_2$, 15270-88-9; $NaN[Si(CH_3)_3]_2$, 1070-89-9; BCl_3, 10294-34-5; $(C_2H_5BNCH_3)_3$, 715-62-8; $(C_6H_5BNH)_3$, 976-28-3; $C_2H_5BCl_2$, 1739-53-3; $[(CH_3)_3Si]_2NH$, 999-97-3; BBr_3, 10294-33-4; $(C_2H_5BNH)_3$, 7443-22-3.

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Perfluorocarbon Phosphonic and Sulfonic Acids Containing Discretely Varying Terminal Functional Groups

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Received June 25, 1991

Several new per- and polyfluorocarbon phosphonic and sulfonic acids and their salts (or ethyl esters) $C_6F_5CH_2P(O)(OH)_2$, $(CF_3)_2CFP(O)(OH)_2$, $CF_3CH_2N(H)P(O)(OH)_2$, and $(CF_3)_3CCFHCF_2SO_3Na$ were prepared from the corresponding alkyl iodides or alkenes and tetraethyl pyrophosphite or sodium hydrogen sulfite, respectively. We have also prepared the previously reported acid $CF_3CFHCF_2SO_3H$ and completed the spectroscopic characterization of this material.

Introduction

Our continuing interest in the potential of per- and polyfluorocarbon sulfonic and phosphonic acids for use as catalytic additives or for replacement of phosphoric acid as the electrolyte of choice in fuel cells, as well as our interest in inert surfaces, has prompted us to synthesize perfluorocarbon phosphonic and/or sulfonic acids of discretely varying structure. It has been well established that the structure and composition of the terminal group of poly- and perfluorocarbon chains are largely responsible for their observed behavior on surfaces and in solution.[1,2] This is particularly important with respect to the behavior of these acids in fuel cells[3] and in coating applications. Within fuel cells, the degree and nature of the interactions of the electrolyte or additive with the Teflon surface of the electrodes have a dramatic impact on the operating efficiency of the fuel cell.

A large number of per- and polyfluorinated sulfonic and disulfonic acids,[4-7] phosphonic acids,[8-11] and mixed sulfonic/

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