228 *Inorg. Chem.* **1992**, *31*, 228–233

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Preparation and Characterization of Polyborazines

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Received August 6, 1991

The reaction of the borazine $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ with *B*-monohaloborazines gives reasonable yields of diborazinyls $(C_2H_5)_3B_3N_3H_2[R_2B_3N_3R_3']$ (**1**); in addition, small amounts of polyborazinyls (**2, 3**) are formed and species containing up to four borazine rings in an individual molecule could be identified. The triborazinyl $[(C_2H_5)_3B_3N_3H_2]_2[C_2H_5]B_3N_3H_3$ (**4**) was prepared in analogous fashion. Poly(borazin-2-yl)amines containing borazine rings linked by nitrogen (**5, 6**) have been obtained by the interaction of *B*-monohaloborazines with either $HN[Si(CH_3)_3]_2$, $N[Si(CH_3)_3]_3$, or *N*-lithioaminoborazines, but the reaction of NH_3 with *B*-haloborazines containing annular NH groups preferentially leads to inseparable oligomer mixtures. The reaction of (methylthio)borane species such as $B(SCH_3)_3$, $(CH_3SBNCH_3)_3$, or $(CH_3S)(C_2H_5)_2B_3N_3H_3$ with aminoborazine derivatives generally also gives product mixtures in a series of sequential processes, although the 2,4-bis(borazin-2-ylamino)borazine $(CH_3)_3N_3B_3[C_2H_5][HN(C_2H_5)_2B_3N_3(CH_3)_3]_2$ (**8**) was obtained from the reaction of $(CH_3S)_2(C_2H_5)B_3N_3(CH_3)_3$ with 2 molar equiv of $(H_2N)(C_2H_5)_2B_3N_3(CH_3)_3$. The 2,4,6-tris(borazin-2-ylamino)borazine $[(CH_3)_3N_3B_3(CH_3)_2NH]_3B_3N_3(CH_3)_3$ (**10b**) was prepared by the reaction of $(ClBNCH_3)_3$ with 3 molar equiv of $(LiHN)(CH_3)_2B_3N_3(CH_3)_3$.

Introduction

The knowledge of well-characterized polyborazines containing the six-membered B_3N_3 heterocycle as a structural unit is extremely limited. Three principal types of polyborazines have been described, i.e., species where borazine rings are (a) connected directly in biphenyl-type fashion by an interannular B–N or B–B bond, (b) fused in naphthalene-type fashion, or (c) linked via additional units such as CH_2, NH, or O. However, most of the relevant studies were performed prior to 1970, and the reported compounds have been scarcely characterized.[1]

An increasing interest in materials based on boron–nitrogen frameworks has promoted several studies on polyborazines of more recent vintage, but well-characterized species are still exceedingly rare.[2] The syntheses of the polyborazines depend largely on an easy access to unsymmetrically substituted borazines that contain reactive sites as starting materials. Such species have recently become available in good yield and purity by the reaction of symmetrically substituted 2,4,6-triorganylborazines with boron trihalides, which proceeds by successive displacement of the organic boron substituents by halogen. This work was initially performed with $(C_2H_5BNCH_3)_3$,[3] but the method later was also found useful for the preparation of unsymmetrically B-substituted borazines containing annular NH groups.[4] The present report describes a study on the preparation and characterization of selected types of polyborazines utilizing such unsymmetrically substituted borazines.

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, ^{13}C) instrument. Chemical shift data are given in ppm with positive values indicating a downfield shift from the reference (internal $(CH_3)_4Si$ for ^1H and ^{13}C NMR, external $(C_2H_5)_2O{\cdot}BF_3$ for ^{11}B NMR); s = singlet, d = doublet, t = triplet, q = quartet, *m* = unresolved multiplet, and sh = shoulder, 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. 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 usually listed to *m/z* 30 for 5% or greater relative abundances (in parentheses) only.

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.

$(C_2H_5)_3B_3N_3H_2[(C_2H_5)_2B_3N_3H_3]$ (1a). A mixture of 3.0 g (14 mmol) of $Br(C_2H_5)_2B_3N_3H_3$[4] and 3.3 g (14 mmol) of $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$[4] was heated for 3 h in a bath of 150 °C to give a clear liquid. $(CH_3)_3SiBr$ was removed under reduced pressure and the residue, 4.15 g, was distilled under vacuum to give a forerun of $(C_2H_5BNH)_3$[5] (ca. 1 g), and **1a** (ca. 1.25 g) distilled at 100 °C (1 Torr). Anal. Calcd for $C_{10}H_{30}B_6N_6$ (M_r = 299.04): C, 40.17; H, 10.11; B, 21.69; N, 28.10. Found: C, 40.01; H, 10.20; B, 21.51; N, 28.24.

NMR data: $\delta(^1H)$ 4.94* (2 H, s), 4.73* (1 H, s), 4.48* (2 H, s), 1.0–0.75 (25 H, m); $\delta(^{11}B)$ 36.2 (5 B, s, $h_{1/2}$ = 520 Hz), 31.3 (1 B, s, $h_{1/2}$ = 520 Hz); $\delta(^{13}C)$ 10.1*, 9.3*, 9.21, 8.64, 8.60. Mass spectrum (14 eV): *m/z* 301 (10), 300 (74), 299 (100), 298 (65), 297 (19), 296 (5), 271 (23), 270 (29), 269 (21), 268 (6).

Approximately 1.9 g of viscous distillation residue remained. Mass spectroscopic data suggested the presence of the polyborazinyls $(C_2H_5)_3B_3N_3H[(C_2H_5)_2B_3N_3H_3]_2$ (**2a**; calcd for $[M - C_2H_5]^+$ *m/z* 407 (8), 406 (54), 405 (100), 404 (93), 403 (52), 402 (19), 401 (5); obsd *m/z* 407 (7), 406 (51), 405 (100), 404 (96), 403 (59), 402 (25), 401 (5)) and $(C_2H_5)_3B_3N_3[(C_2H_5)_2B_3N_3H_3]_3$ (**3a**; calcd for $[M - C_2H_5]^+$ *m/z* 542 (7), 541 (37), 540 (82), 539 (100), 538 (78), 537 (42), 536 (16), 535 (5); obsd *m/z* 541 (38), 540 (80), 539 (100), 538 (78), 537 (45), 536 (18), 535 (5)).

Reaction of 1a with BCl_3. A mixture of 1.16 g (3.93 mmol) of **1a** and 40 mL of a 1 M solution of BCl_3 in heptane was heated to reflux for 10 h. Volatiles were evaporated, and the residue was studied by NMR and mass spectroscopy. The ^1H NMR spectrum showed the presence of some residual C_2H_5 (which could not be removed even on prolonged reaction times) besides broad (N)H signals at δ 5.3 and 5.1 (in approximately 2:1 ratio), and the 10-eV mass spectrum suggested the product to be a mixture of $(C_2H_5)Cl_4B_6N_6H_5$ (calcd for M^+ *m/z* 330 (7), 329 (10), 328 (34), 327 (45), 326 (85), 325 (95), 324 (100), 323 (84), 322 (44), 321 (14); obsd *m/z* 327 (67), 326 (79), 325 (91), 324 (100), 323 (94), 322 (55), 321 (24), 320 (9)) and $Cl_5B_6N_6H_5$ (calcd for M^+ *m/z* 336 (14), 335 (19), 334 (50), 333 (61), 332 (96), 331 (100), 330 (94), 329 (73), 328 (37), 327 (11); obsd *m/z* 337 (7), 336 (14), 335 (23), 334 (51), 333 (58), 332 (98), 331 (100), 330 (93), 329 (74), 328 (49), 327 (26)), which could not be separated. The ^{11}B NMR spectrum exhibited a very broad and unsymmetrical signal with maxima at 30.8, 30.1, and 29.6 ppm and a shoulder at 28.8 ppm.

$(C_2H_5)_3B_3N_3H_2[(C_2H_5)_2B_3N_3(CH_3)_3]$ (1b) was prepared in a fashion analogous to that for **1a** by the reaction of 2.70 g (11.4 mmol) of $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$[4] with 2.94 g (11.4 mmol) of $Br(C_2H_5)_2B_3N_3(CH_3)_3$[4] (48 h of heating at 190 °C bath temperature; generated $(CH_3)_3SiBr$ was distilled off during the reaction). The compound **1b**, bp 146–149 °C (1 Torr), was obtained in 62% yield (2.4 g). Anal. Calcd for $C_{13}H_{36}B_6N_6$ (M_r = 341.34): C, 45.74; H, 10.63; B, 19.00; N, 24.62. Found: C, 45.89; H, 10.28; B, 18.60; N, 24.38.

NMR data: $\delta(^1H)$ 4.96* (2 H, s), 2.97 (3 H, s), 2.68 (6 H, s), 1.1–0.8 (21 H, m), 0.58 (4 H, q, *J* = 8; coupled with a clearly recognizable t at 0.89); $\delta(^{11}B)$ 36.2* (unsymmetric s with a pronounced shoulder at 32.1); $\delta(^{13}C)$ 33.0, 32.4, 9.2*, 8.6, 8.4, 7.7, 7.0*. Mass spectrum (14 eV): *m/z*

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

[2] Paine, R. T.; Narula, C. K. *Chem. Rev.* **1990**, *90*, 73–91 and references cited therein.

[3] Bai, J.; Niedenzu, K. *Inorg. Chem.* **1991**, *30*, 2955–2956.

[4] Bai, J.; Niedenzu, K.; Serwatowska, J.; Serwatowski, J. *Inorg. Chem.* **1991**, *30*, 4631.

[5] Bielawski, J.; Das, M. K.; Hanecker, E.; Niedenzu, K.; Nöth, H. *Inorg. Chem.* **1986**, *25*, 4623–4628.

343 (7), 342 (50), 341 (96), 340 (41), 339 (16), 314 (6), 313 (76), 312 (100), 311 (69), 310 (19), 309 (6).

An additional small amount of distillate, bp 160–195 °C (1 Torr), was obtained. It appeared to contain the diborazinyl $(C_2H_5)_3B_3N_3[H][Si(CH_3)_3][(C_2H_5)_2B_3N_3(CH_3)_3]$, as is suggested by the observation of a molecular ion cluster in the 14-eV mass spectrum (calcd for $C_{16}H_{44}B_6N_6Si$ *m/z* 415 (20), 414 (83), 413 (100), 412 (57), 411 (17); obsd *m/z* 415 (19), 414 (69), 413 (100), 412 (41), 411 (10)).

$(C_2H_5)_3B_3N_3H_2[(CH_3)_2B_3N_3(CH_3)_3]$ (1d) was prepared in a fashion analogous to that for the preceding compound by the reaction of 6.13 g (26.7 mmol) of $Br(CH_3)_2B_3N_3(CH_3)_3$ (see below) with 6.33 g (26.7 mmol) of $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$[4] (60 h of heating at 180–190 °C bath temperature). $(C_2H_5BNH)_3$ (1.1 g) was distilled from the crude reaction mixture, and ca. 0.7 g of $Br(CH_3)_2B_3N_3(CH_3)_3$ was then sublimed off. The remaining material was distilled under vacuum to give 4.55 g (54%) of **1d**, bp 125–128 °C (1 Torr). Anal. Calcd for $C_{11}H_{32}B_6N_6$ (M_r = 313.28): C, 42.17; H, 10.30; B, 20.70; N, 26.83. Found: C, 42.46; H, 10.53; B, 20.46; N, 26.33.

NMR data: $\delta(^1H)$ 4.97* (2 H, s), 2.90 (3 H, s), 2.66 (6 H, s), 1.01 (3 H, t, *J* = 6), 0.93 (2 H, q, *J* = 6), 0.90 (6 H, t, *J* = 7), 0.60 (4 H, q, *J* = 7), 0.49 (6 H, s); $\delta(^{11}B)$ 36.2* (unsymmetric s with a distinct shoulder at 31.9); $\delta(^{13}C)$ 34.4, 33.1, 9.3*, 8.6, 8.4, –0.4*. Mass spectrum (7 eV): *m/z* 315 (4), 314 (10), 313 (10), 312 (8), 286 (10), 285 (79), 284 (100), 283 (62), 282 (21).

About 1 g of distillation residue remained. Mass spectroscopic data suggested that it contained both the polyborazinyl $(C_2H_5)_3B_3N_3H[(CH_3)_2B_3N_3(CH_3)_3]_2$ (**2c**; calcd for $[M - C_2H_5]^+$ *m/z* 435 (9), 434 (55), 433 (100), 432 (92), 431 (51), 430 (18), 429 (5); obsd *m/z* 434 (59), 433 (100), 432 (91), 431 (59), 430 (23)) and the diborazinyl $(C_2H_5)_3B_3N_3[H][Si(CH_3)_3][(CH_3)_2B_3N_3(CH_3)_3]$ (calcd for $[M - C_2H_5]^+$ *m/z* 358 (17), 357 (80), 356 (100), 355 (58), 354 (19); obsd *m/z* 358 (20), 357 (66), 356 (100), 355 (59), 354 (56), 353 (40)).

$Br(CH_3)_2B_3N_3(CH_3)_3$. A mixture of 49.4 g (197 mmol) of BBr_3 and 50 mL of dichloromethane was added slowly to a stirred solution of 32.5 g (197 mmol) of $(CH_3BNCH_3)_3$[1] in 50 mL of dichloromethane. An exothermic reaction occurred, and the mixture was stirred at ambient temperature for 3 h. After standing overnight, the colorless precipitate was collected and the clear filtrate was concentrated to give additional precipitate of the compound for a total of 43.1 g (95%), mp 129–132 °C (lit.[5] mp 116–118 °C). Anal. Calcd for $C_5H_{15}B_3BrN_3$ (M_r = 229.54): C, 26.16; H, 6.59; B, 14.13; Br, 34.81; N, 18.32. Found: C, 26.22; H, 6.60; B, 14.12; Br, 34.80; N, 18.18.

NMR data: $\delta(^1H)$ 3.04 (2 H, s), 2.88 (1 H, s), 0.52 (2 H, s); $\delta(^{11}B)$ 37.0 (2 B, s, $h_{1/2}$ = 210 Hz), 31.2 (1 B, s, $h_{1/2}$ = 130 Hz); $\delta(^{13}C)$ 37.0, 34.5, 0.3*. Mass spectrum (11 eV): *m/z* 231 (6), 230 (75), 229 (69), 228 (100), 227 (67), 226 (12).

$(C_2H_5)_3B_3N_3H_2[(C_6H_5)_2B_3N_3H_3]$ (1c) in Mixture with 2b and 3b. A mixture of 1.32 g (5.62 mmol) of $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$[4] and 1.50 g (5.62 mmol) of $Cl(C_6H_5)_2B_3N_3H_3$[4] was heated for 1 h in an oil bath of 190–200 °C. Volatile material was removed under reduced pressure, and the remaining oil was distilled under vacuum in a short-path distillation equipment. A forerun of pure $(C_2H_5BNH)_3$ and two major fractions was distilled off, and a substantial amount of residue remained. As is suggested by mass spectroscopic data, the three latter materials contained variable amounts of **1c** (calcd for $C_{18}H_{30}B_6N_6$ *m/z* 397 (16), 396 (80), 395 (100), 394 (58), 393 (19); obsd *m/z* 398 (15), 397 (26), 395 (100), 394 (56), 393 (24), 392 (9)) as well as the polyborazinyls $(C_2H_5)_3B_3N_3H[(C_6H_5)_2B_3N_3H_3]_2$ (**2b**; calcd for $C_{30}H_{42}B_9N_9$ *m/z* 628 (17), 627 (64), 626 (100), 625 (86), 624 (46), 623 (16); obsd *m/z* 631 (17), 630 (32), 629 (49), 628 (59), 627 (83), 626 (100), 625 (94), 624 (51), 623 (31), 622 (17)) and $(C_2H_5)_3B_3N_3[(C_6H_5)_2B_3N_3H_3]_3$ (**3b**; calcd for $[M - 2(C_6H_5)]^+$ *m/z* 705 (12), 704 (45), 703 (88), 702 (100), 701 (75), 700 (39); obsd *m/z* 709 (12), 708 (15), 707 (27), 706 (38), 705 (44), 704 (68), 703 (94), 702 (100), 701 (79), 700 (53)), which could not be separated.

$[(C_2H_5)_3B_3N_3H_2]_2[C_2H_5]B_3N_3H_3$ (4). A mixture of 1.83 g (6.88 mmol) of $Br_2(C_2H_5)B_3N_3H_3$[4] and 3.25 g (13.8 mmol) of $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$[4] was heated in an oil bath of 135 °C for 3 h. $(CH_3)_3SiBr$ was distilled off, and 3.1 g of liquid material remained. Distillation under vacuum gave about equal amounts (ca. 1 g each) of $(C_2H_5BNH)_3$ and **4**, bp 190–195 °C (1 Torr), and a solid residue remained. Anal. Calcd for $C_{14}H_{42}B_9N_9$ (M_r = 433.54): C, 38.75; H, 9.76; B, 22.42; N, 29.07. Found: C, 38.89; H, 9.80; B, 22.51; N, 28.59.

NMR data: $\delta(^1H)$ 4.9* (4 H, s), 4.5* (2 H, s), 4.2* (1 H, s), 1.05–0.75 (35 H, m); $\delta(^{11}B)$ 35.9 (broad unsymmetric s, $h_{1/2}$ = ca. 600 Hz, with shoulders on both sides at ca. 39 and 32 ppm, respectively); $\delta(^{13}C)$ 10.2*, 9.4*, 9.31, 8.74, 8.71, 8.62. The 13-eV mass spectrum exhibited a parent ion cluster at *m/z* 436 (12), 435 (53), 434 (100), 433 (94), 432 (58), 431 (23) (calcd for $C_{14}H_{42}B_9N_9$ *m/z* 436 (9), 435 (55), 434 (100), 433 (92), 432 (51), 431 (19)).

The distillation residue, melting from 100 to 110 °C, was insoluble in common organic solvents. The 13-eV mass spectrum of this material exhibited ion clusters as high as *m/z* 942, with major additional clusters at *m/z* 888, 808, 675, and 434.

Reaction of $(C_2H_5BNH)_3$ with LiC_4H_9 and $Br(C_2H_5)_2B_3N_3(CH_3)_3$. A solution of 2.91 g (17.7 mmol) of $(C_2H_5BNH)_3$[5] in 20 mL of hexane was cooled to −78 °C, and 8.8 mL of a 2 M solution of LiC_4H_9 (17.6 mmol) in cyclohexane was added with stirring. The mixture was allowed to warm to room temperature and cooled again to −78 °C, and 4.56 g (17.7 mmol) of $Br(C_2H_5)_2B_3N_3(CH_3)_3$[3] was added. The mixture was slowly warmed to room temperature and stirred overnight. LiBr was filtered off, and volatiles were evaporated under reduced pressure. The liquid residue was distilled under vacuum to give 1.47 g of a fraction A, bp 52–55 °C (1 Torr); 1.86 g of fraction B, bp 56–161 °C (1 Torr); and 0.58 g of fraction C, bp 162–165 °C (1 Torr). As is based on mass spectral and NMR data, the first fraction (A) consisted mainly of $(C_2H_5BNH)_3$ and some $(C_4H_9)(C_2H_5)_2B_3N_3H_3$, the second fraction (B) was a mixture of the borazines $(C_4H_9)(C_2H_5)_2B_3N_3H_3$ and $(C_4H_9)(C_2H_5)_2B_3N_3(CH_3)_3$ and the diborazinyl (of type **1**) $(C_4H_9)(C_2H_5)_2B_3N_3H_2[(C_2H_5)_2B_3N_3(CH_3)_3]$, and the last fraction (C) consisted of the latter diborazinyl and $(C_2H_5)_3B_3N_3H_2[(C_2H_5)_2B_3N_3(CH_3)_3]$ (**1b**). No individual pure compound could be isolated.

Fraction A. The ^1H NMR spectrum exhibited a broad singlet at δ 4.70 and unresolved multiplets at δ 1.4–1.2 (small) and 1.0–0.75; $\delta(^{11}B)$ 35.9 (s, $h_{1/2}$ = 210 Hz). Mass spectral data (10 eV): calcd for $(C_2H_5BNH)_3$ *m/z* 166 (8), 165 (100), 164 (71), 163 (17), obsd *m/z* 166 (10), 165 (100), 164 (68), 163 (20); calcd for $(C_4H_9)(C_2H_5)_2B_3N_3H_3$ *m/z* 194 (10), 193 (100), 192 (71), 191 (17), obsd *m/z* 194 (13), 193 (100), 192 (72), 191 (23).

Fraction B. The ^1H NMR spectrum exhibited a broad singlet at δ 4.71, sharp singlets at δ 2.95, 2.94, 2.93, 2.91, 2.86, 2.82, 2.77, and 2.74, and unresolved multiplets at δ 1.4–1.1 and 1.0–0.8; $\delta(^{11}B)$ 35.9 (s, $h_{1/2}$ = 350 Hz) and 2.98 (s, ca. 10% of the total intensity). Mass spectral data (10-eV) (in addition to the parent ion pattern for $(C_4H_9)(C_2H_5)_2B_3N_3H_3$ as given above): calcd for $(C_4H_9)(C_2H_5)_2B_3N_3(CH_3)_3$ *m/z* 236 (13), 235 (100), 234 (75), 233 (18), obsd *m/z* 236 (15), 235 (100), 234 (81), 233 (31); calcd for $(C_4H_9)(C_2H_5)_2B_3N_3H_2[(C_2H_5)_2B_3N_3(CH_3)_3]$ *m/z* 371 (13), 370 (78), 369 (100), 368 (59), 367 (19), obsd *m/z* 371 (13), 370 (66), 369 (100), 368 (42), 367 (14).

Fraction C. The ^1H NMR spectrum exhibited a broad singlet at δ 4.1, sharp singlets at δ 2.95, 2.94, 2.85, 2.82, 2.77, and 2.74, and unresolved multiplets at δ 1.4–1.2 and 1.1–0.7; $\delta(^{11}B)$ 37.1* (2 B), 29.5 (1 B). Mass spectral data (14-eV) (in addition to the parent ion pattern for $(C_4H_9)(C_2H_5)_2B_3N_3H_2[(C_2H_5)_2B_3N_3(CH_3)_3]$ as given above): calcd for the diborazinyl $(C_2H_5)_3B_3N_3H_2[(C_2H_5)_2B_3N_3(CH_3)_3]$ (of type **1**) *m/z* 343 (12), 342 (77), 341 (100), 340 (59), 339 (19), obsd *m/z* 344 (14), 343 (35), 342 (75), 341 (100), 340 (71), 339 (57), 338 (31), 337 (14).

$HN[(C_2H_5)_2B_3N_3(CH_3)_3]_2$ (5a). A solution of 4.98 g (30.9 mmol) of $HN[Si(CH_3)_3]_2$ in 20 mL of ether was added to a solution of 15.9 g (61.7 mmol) of $Br(C_2H_5)_2B_3N_3(CH_3)_3$[3] in 20 mL of ether. The mixture was stirred overnight at ambient temperature, volatile material was removed under reduced pressure, and the liquid residue was distilled under vacuum to give 8.2 g (72%) of **5a**, bp 195–198 °C (1 Torr), mp 34–36 °C. Anal. Calcd for $C_{14}H_{39}B_6N_7$ (M_r = 370.38): C, 45.40; H, 10.61; B, 17.51; N, 26.47. Found: C, 45.94; H, 10.26; B, 17.29; N, 26.19.

NMR data: $\delta(^1H)$ 2.93 (6 H, s), 2.77 (12 H, s), 2.43* (1 H, s), 1.1–0.91 (20 H, m); $\delta(^{11}B)$ 36.7 (2 B, s, $h_{1/2}$ = 480 Hz), 28.4 (1 B, s, $h_{1/2}$ = 440 Hz); $\delta(^{13}C)$ 33.0, 32.4, 7.9, 7.0*. Mass spectrum (12 eV): *m/z* 372 (16), 371 (77), 370 (100), 369 (56), 368 (22), 367 (8), 342 (10), 341 (19), 340 (39), 339 (45), 338 (13), 337 (13), 193 (10), 192 (5), 138 (8).

$HN[(C_2H_5)_2B_3N_3H_3][(CH_3)_2B_3N_3(CH_3)_3]$ (5b). A solution of 65 g (3.9 mmol) of $(H_2N)(CH_3)_2B_3N_3(CH_3)_3$[4] in 15 mL of ether was cooled to −78 °C, and 2.8 mL of a 1.4 M solution of $LiCH_3$ (3.9 mmol) in ether was added with stirring. The mixture was slowly warmed to room temperature and stirred overnight. The mixture was cooled down again, a solution of 0.84 g (3.9 mmol) of $Br(C_2H_5)_2B_3N_3H_3$[4] in 10 mL of ether was added, and the mixture was warmed to room temperature and again stirred overnight. Ether was evaporated, and 30 mL of hexane was added to the residue. After brief stirring, the mixture was filtered and solvent was evaporated from the clear filtrate to leave a colorless solid residue. Some volatiles were sublimed off at 60–80 °C bath temperature (1 Torr), and the remainder was sublimed at 150 °C (1 Torr) to give 0.83 g (71%) of **5b**, mp 50–54 °C. Anal. Calcd for $C_9H_{29}B_6N_7$ (M_r = 300.25): C, 36.00; H, 9.74; B, 21.60; N, 32.66. Found: C, 35.85; H, 9.79; B, 21.54; N, 32.45.

NMR data: $\delta(^1H)$ 4.47* (1 H, s), 4.09* (2 H, s), 2.89 (3 H, s), 2.85 (6 H, s), 2.67* (1 H, s), 0.95 (6 H, t, *J* = 7), 0.79 (4 H, q, *J* = 7), 0.50 (6 H, s); $\delta(^{11}B)$ 36.7 (4 B, s, $h_{1/2}$ = 440 Hz), 28.2 (1 B, s), 26.0 (1 B, s); $\delta(^{13}C)$ 34.3, 33.9, 9.3*, 8.5, –0.3*. Mass spectrum (10 eV): *m/z* 302

(12), 301 (72), 300 (100), 299 (52), 298 (18), 297 (5), 286 (6), 285 (8), 284 (16), 283 (22), 282 (11), 281 (5).

$N[(C_2H_5)_2B_3N_3H_3]_3$ (6a). A mixture of 3.1 g (14 mmol) of $Br(C_2H_5)_2B_3N_3H_3$,[4] 1.1 g (4.8 mmol) of $N[Si(CH_3)_3]_3$, and 20 mL of ether was stirred for 12 h at room temperature. The milky solution was centrifuged, and volatiles were evaporated off the clear liquid to leave 2.0 g (98%) of **6a**, mp 130–135 °C. It was purified by dissolving the product in a minimum amount of hexane and cooling the solution to −78 °C. The precipitate was collected and dried and was identical (NMR and mass spectroscopic data) to the previously described[4] material.

Reaction of $(H_2N)(CH_3)_2B_3N_3(CH_3)_3$ with $(CH_3S)(C_2H_5)_2B_3N_3H_3$. A stirred mixture of 0.56 g (3.4 mmol) of $(H_2N)(CH_3)_2B_3N_3(CH_3)_3$[4] and 1.24 g (6.79 mmol) of $(CH_3S)(C_2H_5)_2B_3N_3H_3$[4] was heated for 20 h in an oil bath of 75–80 °C. The mixture solidified on cooling to room temperature and was dissolved in boiling hexane. On cooling of the clear solution, ca. 0.5 g of $HN[(CH_3)_2B_3N_3(CH_3)_3]_2$[4] precipitated, and ca. 0.8 g of solid residue remained after evaporation of the solvent from the clear filtrate. As is based on 10-eV mass spectroscopic data, the residue consisted of a mixture of $N[(C_2H_5)_2B_3N_3H_3]_3$ (**6a**) and $N[(C_2H_5)_2B_3N_3H_3]_2[(CH_3)_2B_3N_3(CH_3)_3]$ (**6b**; calcd for $C_{13}H_{41}B_9N_{10}$ *m/z* 437 (8), 436 (54), 435 (100), 434 (92), 433 (51), 432 (18); obsd *m/z* 437 (12), 436 (53), 435 (100), 434 (89), 433 (48), 432 (18)), but no pure compound could be isolated.

$[NH\{(C_2H_5)B_3N_3(CH_3)_3\}]_n$ (7). To a solution of 5.94 g (19.2 mmol) of $Br_2(C_2H_5)B_3N_3(CH_3)_3$[3] in 20 mL of ether was added 3.09 g (19.2 mmol) of $HN[Si(CH_3)_3]_2$. The mixture was stirred at ambient temperature for 16 h, and volatile material was removed under reduced pressure to leave 3.12 g of a solid residue, mp 103–135 °C. The ^1H NMR spectrum of this material exhibited signals at δ 2.86 (6 H, s), 2.58 (3 H, s), 2.26* (1 H, s), 1.02–0.95 (5 H, m); $\delta(^{11}B)$ 29.2 with a shoulder at 36.7 in approximately 2:1 ratio. The 14-eV mass spectrum exhibited ion clusters at *m/z* 490 and 327, suggesting the presence of species with $n = 3$ and 2.

The crude product was sublimed to give 0.7 g of sublimate, mp 160–168 °C, which exhibited a ^1H NMR spectrum identical to that of the crude product as described above, in addition to a very minor component with $\delta(^1H)$ 2.76, 2.63, and 2.34*. The 12-eV mass spectrum of this material exhibited an ion cluster at *m/z* 654 to indicate a species **7** with $n = 4$. The sublimation residue, mp 158–180 °C, exhibited a more complex ^1H NMR spectrum with δ 2.86 (6 H, s), 2.75–2.58 (21 H, m), 2.47* (s) + 2.38* (s) (total 3 H), 1.0–0.9 (15 H, m). The 9-eV mass spectrum of this latter material was dominated by an ion cluster at *m/z* 654 and minor clusters at *m/z* 194 and 179. The elemental analyses of all fractions corresponded closely to an empirical composition $C_6H_{15}B_3N_4$ = **7**.

$[\{(CH_3)_3N_3B_3(C_2H_5)_2\}NH]_2[C_2H_5]B_3N_3(CH_3)_3$ (8, $n = 1$, R = CH_3 R′ = C_2H_5). A mixture of 2.22 g (9.14 mmol) of $(CH_3S)_2(C_2H_5)B_3N_3(CH_3)_3$[3] and 3.54 g (18.3 mmol) of $(H_2N)(C_2H_5)_2B_3N_3(CH_3)_3$[3] was stirred at 90 °C for 4 h. The mixture was distilled under vacuum to give 4.1 g (84%) of **8**, bp 318 °C (0.1 Torr). Anal. Calcd for $C_{19}H_{54}B_9N_{11}$ (M_r = 534.02): C, 42.73; H, 10.19; B, 18.22; N, 28.85. Found: C, 45.01; H, 10.21; B, 17.63; N, 26.43.

NMR data: $\delta(^1H)$ 2.92 (9 H, unsym s), 2.76 (18 H, unsym s), 2.42* (2 H, s), 1.1–0.9 (25 H, m); $\delta(^{11}B)$ 36.6 (5 B, s, $h_{1/2}$ = 590 Hz), 28.5 (s) + 26.4 (s) (4 B total); $\delta(^{13}C)$ 33.0, 32.4, 7.9, 6.8*. Mass spectrum (10 eV): *m/z* 537 (16), 536 (64), 535 (100), 534 (95), 533 (51), 532 (18), 531 (6), 522 (7), 521 (7), 520 (8), 519 (7), 518 (6), 507 (8), 506 (23), 505 (60), 504 (92), 503 (73), 502 (45), 501 (15), 500 (6), 476 (8), 475 (13), 474 (6), 473 (13), 472 (7), 342 (24), 341 (25), 340 (13), 339 (7), 304 (15), 303 (19), 302 (10).

Reaction of $(H_2N)(C_2H_5)_2B_3N_3(CH_3)_3$ with $B(SCH_3)_3$. Formation of 5a. A stirred mixture of 3.68 g (19.0 mmol) of $(H_2N)(C_2H_5)_2B_3N_3(CH_3)_3$[3] and 0.96 g (6.3 mmol) of $B(SCH_3)_3$[6] was heated in an oil bath of 70–80 °C for 20 h. The 15-eV mass spectrum of the crude product (*m/z* 535 (6), 534 (17), 533 (16), 532 (8), 505 (6), 504 (10), 503 (10), 502 (7), 399 (5), 398 (7), 397 (7), 396 (5), 372 (14), 371 (64), 370 (93), 369 (54), 368 (22), 367 (6), 357 (6), 356 (7), 355 (8), 354 (5), 343 (7), 341 (68), 340 (100), 339 (98), 338 (52), 337 (7), 327 (7), 326 (8), 325 (23), 324 (27), 323 (16), 322 (5)) suggested the formation of the desired $B[(NH)(C_2H_5)_2B_3N_3(CH_3)_3]_3$ of type **9**, but the ^1H NMR spectrum was complex and indicated the material to be a mixture. It was distilled under vacuum to give 0.3 g of a forerun (bp 90–110 °C (1 Torr), $\delta(^{11}B)$ 36.6 (8 B, s, $h_{1/2}$ = 280), 28.6 (ca. 1 B, s), 26.3 (ca. 1 B, s)) and 1.52 g of a material of bp 195–198 °C (1 Torr), which was identified (NMR and mass spectroscopic data) to be $HN[(C_2H_5)_2B_3N_3(CH_3)_3]_2$ (**5a**) as described above. A small amount of solid intractible distillation residue remained.

$(CH_3S)(CH_3)_2B_3N_3(CH_3)_3$ from $B(SCH_3)_3$ and 5e. A mixture of 3.1 g (10 mmol) of $HN[(CH_3)_2B_3N_3(CH_3)_3]_2$ (**5e**) and 1.8 g (12 mmol) of $B(SCH_3)_3$[6] was heated for 20 h in an oil bath of 190–200 °C. The viscous product was distilled, and after a forerun of $B(SCH_3)_3$, 3.4 g (86%) of $(CH_3S)(CH_3)_2B_3N_3(CH_3)_3$[4] distilled off at 98–102 °C (1 Torr); some solid residue remained.

$(CH_3SBNCH_3)_3$. A stirred mixture of 6.80 g (30.1 mmol) of $(ClBNCH_3)_3$,[1] 27 g (90 mmol) of $Pb(SCH_3)_2$, and 75 mL of hexane was heated to reflux for 32 h. The mixture was filtered, the residue was washed with hexane, and solvent was evaporated from the combined solutions under reduced pressure. The residue was distilled under vacuum to give 6.36 g (81%) of material, bp 158–162 °C (1 Torr). Anal. Calcd for $C_6H_{18}B_3N_3S_3$ (M_r = 260.86): C, 27.63; H, 6.96; B, 12.43; N, 16.11; S, 36.87. Found: C, 27.19; H, 6.86; B, 12.19; N, 15.92; S, 36.63.

NMR data: $\delta(^1H)$ 3.08 (1 H, s), 2.18 (1 H, s); $\delta(^{11}B)$ 36.9 (s, $h_{1/2}$ = 210 Hz); $\delta(^{13}C)$ 36.5, 11.6. Mass spectrum (11 eV): *m/z* 263 (16), 262 (21), 261 (100), 260 (62), 259 (17), 247 (8), 246 (20), 245 (15), 244 (5), 214 (39), 213 (21), 212 (6).

Reaction of $(CH_3SBNCH_3)_3$ with $(H_2N)(C_2H_5)_2B_3N_3(CH_3)_3$. A mixture of 1.66 g (8.57 mmol) of $(H_2N)(C_2H_5)_2B_3N_3(CH_3)_3$[3] and 0.75 g (2.8 mmol) of $(CH_3SBNCH_3)_3$ was heated for 16 h to 70–80 °C. Some volatile material was distilled off the viscous product under reduced pressure, and the residue solidified on cooling to room temperature. (It could not be sublimed at temperatures as high as 400 °C.) Most of it dissolved in 5 mL of ether (and most other common organic solvents), and the solute was recovered from the ether and studied by spectroscopy.

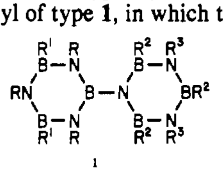
The ^1H NMR spectrum exhibited an approximate ratio of methyl protons in the region of δ 2.92–2.73 (dominated by singlets at δ 2.92 (3 H) and 2.76 (6 H)) to ethyl protons at δ 1.0–0.95 as calculated for $[(CH_3)_3N_3B_3(C_2H_5)_2NH]_3B_3N_3(CH_3)_3$ (**10a**) and also featured a broad singlet at δ 2.60 for (N)H protons. The ^{11}B NMR spectrum showed a strong but slightly unsymmetrical singlet at δ 36.7 and a broad unsymmetrical signal of about equal intensity with maxima at δ 28.5 (highest intensity) and 26.3 and a shoulder at δ 24.0. The 13-eV mass spectrum featured an ion cluster at *m/z* 697 corresponding to the parent ion of **10**, but it was dominated by peak groups at *m/z* 370 and 193.

$[(CH_3)_3N_3B_3(CH_3)_2NH]_3B_3N_3(CH_3)_3$ (10b). A solution of 3.04 g (18.4 mmol) of $(H_2N)(CH_3)_2B_3N_3(CH_3)_3$[4] in 20 mL of ether was cooled to −78 °C, and a solution of $LiCH_3$ (18.4 mmol, 13.1 mL of a 1.4 M solution) in ether was slowly added. The mixture was warmed to ambient temperature, stirred overnight, and cooled again. A solution of 1.39 g (6.15 mmol) of $(ClBNCH_3)_3$[1] in 10 mL of ether was added, and the stirred mixture was slowly warmed to room temperature and stirred overnight. The mixture was filtered and ether was evaporated off. The colorless solid residue was dissolved in a minimum of dichloromethane and then slowly concentrated to precipitate a total of 2.7 g (73%) of **10b**, mp 75–80 °C. Anal. Calcd for $C_{18}H_{57}B_{12}N_{15}$ (M_r = 613.49): C, 35.24; H, 9.36; B, 21.15; N, 34.25. Found: C, 35.41; H, 9.33; B, 21.10; N, 34.37.

NMR data: $\delta(^1H)$ 2.83 (3 H, s), 2.77 (6 H, s), 2.60 (3 H, s), 2.36* (1 H, s), 0.45 (6 H, s); $\delta(^{11}B)$ 36.4 (ca. 1 B, s), 28.4 (ca. 1 B, s); $\delta(^{13}C)$ 34.3, 33.1, 32.0, −0.4*. The 10-eV mass spectrum exhibited a parent ion cluster at *m/z* 616 (10), 615 (42), 614 (84), 613 (100), 612 (74), 611 (47), 610 (21); calcd for $C_{18}H_{57}B_{12}N_{15}$ *m/z* 616 (7), 615 (38), 614 (83), 613 (100), 612 (77), 611 (41), 610 (16).

Results and Discussion

Borazine Analogues of Polyphenyls. Only three polyborazine analogues of biphenyl of type **1**, in which the two borazine rings are linked by an interannular B–N bond, have been reported in the literature, i.e., the parent compound, the decamethyl derivative, and the *B*-pentabutyl derivative. Furthermore, two species containing a B–B linkage have been obtained by the reaction of 2-monochloroborazines with metallic potassium. However, neither of the cited compounds has been well characterized.[1]



1

1a: R = R^3 = H, R^1 = R^2 = C_2H_5

1b: R = CH_3, R^1 = R^2 = C_2H_5, R^3 = H

1c: R = R^3 = H, R^1 = C_6H_5, R^2 = C_2H_5

1d: R = R^1 = CH_3, R^2 = C_2H_5, R^3 = H

In the present work, diborazinyls of type **1** have been obtained by condensation of two unsymmetrically substituted borazines; e.g., the reaction of $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ and $Br(C_2H_5)_2$-

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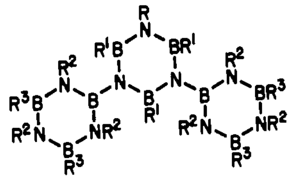
(6) Cragg, R. H.; Husband, J. P. H.; Weston, A. F. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3685–3689.

$B_3N_3H_3$ proceeded with the elimination of $(CH_3)_3SiBr$ to yield **1a**. However, the crude reaction product not only contained a substantial amount of $(C_2H_5BNH)_3$ but a considerable amount of viscous residue remained after distillative workup. The residue contained the polyborazinyls $(C_2H_5)_3B_3N_3H[(C_2H_5)_2B_3N_3H_3]_2$ (**2a**) and $(C_2H_5)_3B_3N_3[(C_2H_5)_2B_3N_3H_3]_3$ (**3a**), as identified by mass spectroscopy.

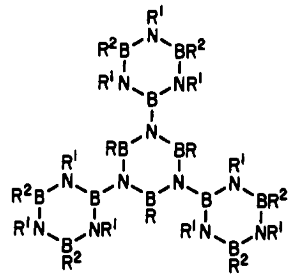


2

2a: $R = R^2 = H, R^1 = R^3 = C_2H_5$

2b: $R = R^2 = H, R^1 = C_2H_5, R^3 = C_6H_5$

2c: $R = H, R^1 = C_2H_5, R^2 = R^3 = CH_3$



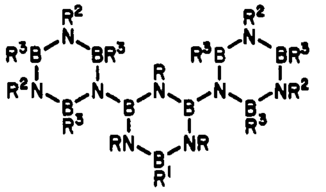
3

3a: $R = R^2 = C_2H_5, R^1 = H$

3b: $R = C_2H_5, R^1 = H, R^2 = C_6H_5$

In an analogous reaction of $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ with $Br(C_2H_5)_2B_3N33(CH_3)_3$, **1b** was the major product, but again some $(C_2H_5BNH)_3$ and also a small amount (but insufficient for detailed characterization) of the diborazinyl $(C_2H_5)_3B_3N_3[H]$-$[Si(CH_3)_3][(C_2H_5)_2B_3N_3(CH_3)_3]$ (identified by mass spectroscopic data) were obtained. Furthermore, the reaction of $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ with $Br(CH_3)_2B_3N_3(CH_3)_3$ yielded the diborazinyl **1d**, but the polyborazinyls **2c** and $(C_2H_5)_3B_3N_3[H][Si(CH_3)_3][(CH_3)_2B_3N_3(CH_3)_3]$ could be identified by mass spectroscopy as byproducts. Similar to the preceding, the reaction of $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ with $Cl(C_6H_5)_2B_3N_3H_3$ led to the formation of the desired diborazinyl **1c**, but, as based on mass spectroscopic data, $(C_2H_5BNH)_3$, $(C_2H_5)_3B_3N_3H[(C_6H_5)_2B_3N_3H_3]_2$ (**2b**), and $(C_2H_5)_3B_3N_3[(C_6H_4)_2B_3N_3H_3]_3$ (**3b**) were also formed. However, **1c** could not be isolated in pure state.

Reaction of 2 molar equiv of $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ with 1 equiv of $Br_2(C_2H_5)B_3N_3H_3$ gave the triborazinyl **4**. Again, $(C_2H_5BNH)_3$ was a substantial byproduct, and some unreacted $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ was also found in the crude reaction mixture.



4

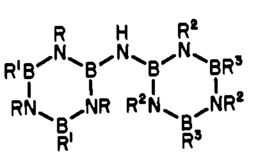
$R = R^2 = H, R^1 = R^3 = C_2H_5$

The cited formation of polyborazinyls as byproducts in the described condensation reactions may suggest that an initially formed diborazinyl of type **1** can rearrange with the formation of $(C_2H_5BNH)_3$ and the observed additional polyborazinyls. Alternatively, the polyborazinyls could be formed during the principal condensation reaction. This latter assumption would imply that the original condensations proceed via substantial cleavage of borazine rings. In view of the observed thermal stabilities of the diborazinyls of type **1**, this latter interpretation appears to have more credence, especially since a simple proton transfer within a given diborazinyl can be excluded in view of the formation of a considerable amount of $(C_2H_5BNH)_3$ during the preparation of **1d**. Furthermore, it is noteworthy that a condensation by hydrogen halide elimination also takes place, as is indicated by the formation of N-trimethylsilylated diborazinyls, although this seems to occur to a much lesser extent. (Indeed, no reaction occurred between $(C_2H_5BNH)_3$ and a *B*-monohaloborazine under the same experimental conditions as employed for the cited condensations. This last observation suggests a substantial effect of the N-bonded $Si(CH_3)_3$ group on the reactivity of the $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ reagent, which is under further investigation.)

An alternate approach for the synthesis of **1b** was also studied, whereby $(C_2H_5BNH)_3$ was first reacted with 1 molar equiv of LiC_4H_9 (assuming that the *N*-monolithio intermediate was formed but which was not isolated), and the mixture was subsequently treated with 1 molar equiv of $Br(C_2H_5)_2B_3N_3(CH_3)_3$. Distillative workup of the reaction product gave an initial fraction which consisted of the borazines $(C_2H_5BNH)_3$ and $(C_4H_9)(C_2H_5)_2B_3N_3H_3$, a second fraction consisting of the borazines $(C_4H_9)(C_2H_5)_2B_3N_3H_3$ and $(C_4H_9)(C_2H_5)_2B_3N_3(CH_3)_3$ as well as the diborazinyl (of type **1**) $(C_4H_9)(C_2H_5)_2B_3N_3H_2[(C_2H_5)_2B_3N_3(CH_3)_3]$, and a third fraction consisting of the latter diborazinyl and the desired **1b**. This reaction was not further pursued, since the process did not appear to be selective but yielded mixtures of similar species, rendering the isolation of individual compounds difficult.

The interaction of a boron trihalide with species of type **1** was studied for the reaction of **1a** with BCl_3. The expected alkyl/halogen exchange did not proceed as cleanly as in the case of the simple borazines of the type $(RBNR')_3$.[3] Rather, four of the five C_2H_5 groups of **1a** were readily exchanged for Cl, but the displacement of the last alkyl group required much more forcing conditions and considerably longer reaction times; indeed, no pure B-perhalogenated species could be obtained. However, it should be emphasized that even under these circumstances, there were no indications that breakage of the B–N link between the two borazine rings had occurred. This may be taken as additional evidence that, once formed, polyborazinyls are chemically quite stable. This conclusion further tends to support the assumption that borazine rings open during the initial condensation reactions of the unsymmetrically substituted borazines and that the polyborazinyls are formed at this stage rather than during workup of the reaction mixtures.

Poly(borazin-2-yl)amines. Very few bis(borazin-2-yl)amines of type **5**, in which two borazine rings are linked at boron sites with a NH group, have been reported;[1] only two such species, i.e., $HN[(CH_3)_2B_3N_3(CH_3)_3]_2$ (**5e**)[4,7] and $CH_3N[(CH_3)_2B_3N_3(CH_3)_3]_2$,[7] have been characterized in detail. These were obtained by the reaction of $Cl(CH_3)_2B_3N_3(CH_3)_3$ with $HN[Si(CH_3)_3]_2$ or $CH_3N[Si(CH_3)_3]_2$, respectively,[7] or (in the case of **5a**) also by



5

5a: $R = R^2 = CH_3, R^1 = R^3 = C_2H_5$

5b: $R = H, R^1 = C_2H_5, R^2 = R^3 = CH_3$

5c: $R = R^2 = H, R^1 = R^3 = C_2H_5$

5d: $R = R^2 = H, R^1 = R^3 = C_6H_5$

5e: $R = R^1 = R^2 = R^3 = CH_3$

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(7) Narula, C. K.; Lindquist, D. A.; Fan, M.-M.; Borek, T. T.; Duesler, E. N.; Datye, A. K.; Schaeffer, R.; Paine, R. T. *Chem. Mater.* **1990**, *2*, 377–384.

the thermal condensation of $(H_2N)(CH_3)_2B_3N_3(CH_3)_3$.[4]

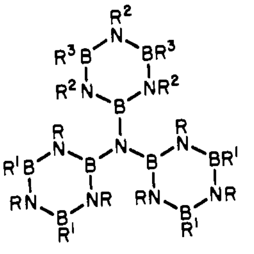
The cleavage of the Si–N bonds of $HN[Si(CH_3)_3]_2$ on reaction with a *B*-monohaloborazine was utilized for the preparation of $HN[(C_2H_5)_2B_3N_3(CH_3)_3]_2$ (**5a**) from $Br(C_2H_5)_2B_3N_3(CH_3)_3$ as an example of an additional symmetrical bis(borazin-2-yl)amine of type **5**. (Even in the presence of a large excess of $HN[Si(CH_3)_3]_2$, **5a** was the major product and only a very small amount of the aminoborazine $[(CH_3)_3SiHN][C_2H_5]_2B_3N_3(CH_3)_3$ was formed.) Unsymmetrical species of type **5** can be prepared by the reaction according to eq 1.

$$(LiHN)(C_2H_5)_2B_3N_3(CH_3)_3 + Br(C_2H_5)_2B_3N_3H_3 \rightarrow LiBr + \underset{\mathbf{5b}}{HN[(C_2H_5)_2B_3N_3(CH_3)_3][(C_2H_5)_2B_3N_3H_3]} \quad (1)$$

The interaction of bis(borazin-2-yl)amines of type **5** with a boron trihalide not only results in the expected alkyl/halogen exchange[3,4] but the B–NH–B bridge is also attacked. For example, when $HN[(C_2H_5)_2B_3N_3(CH_3)_3]_2$ (**5a**) was reacted with 1 molar equiv of BBr_3, equimolar quantities of both $Br(C_2H_5)_2B_3N_3(CH_3)_3$ and $Br_2(C_2H_5)B_3N_3(CH_3)_3$ were obtained, besides a much lesser amount of $(C_2H_5BNH)_3$; no $C_2H_5BBr_2$ was observed among the reaction products. This result can be interpreted by an initial C_2H_5/Br exchange to yield $HN[(C_2H_5)_2B_3N_3(CH_3)_3][Br(C_2H_5)B_3N_3(CH_3)_3]$ as an intermediate. The byproduct $C_2H_5BBr_2$ can then interact with the bridging NH moiety of the cited bis(borazin-2-yl)amine to form the two borazines $Br_2(C_2H_5)B_3N_3(CH_3)_3$ and $[(C_2H_5)BrB–NH][C_2H_5]_2B_3N_3(CH_3)_3$, of which the latter subsequently decomposes with the formation of $Br(C_2H_5)_2B_3N_3(CH_3)_3$ and $^1/_3$ $(C_2H_5BNH)_3$. Thus, the overall process can be described by eq 2.

$$\underset{\mathbf{5a}}{HN[(C_2H_5)_2B_3N_3(CH_3)_3]} + BBr_3 \rightarrow Br(C_2H_5)_2B_3N_3(CH_3)_3 + Br_2(C_2H_5)B_3N_3(CH_3)_3 + \tfrac{1}{3}(C_2H_5BNH)_3 \quad (2)$$

As noted previously,[4] the reaction of $Br(C_2H_5)_2B_3N_3H_3$ with NH_3 did not yield the desired $(H_2N)(C_2H_5)_2B_3N_3H_3$; rather, this borazine was obtained only in mixture with condensation products. Similarly, the reaction of $Br_2(C_2H_5)B_3N_3H_3$ with NH_3 gave only an inseparable product mixture. Furthermore, when $Cl(C_6H_5)_2B_3N_3H_3$ was reacted with anhydrous NH_3 in order to form the corresponding monoaminoborazine, only a mixture of products was obtained. As is based on mass spectral data, the mixture contained $(H_2N)(C_6H_5)_2B_3N_3H_3$, the bis(borazin-2-yl)amine **5d**, and the tris(borazin-2-yl)amine **6c**, but it could not be separated. Thermal treatment of the crude reaction mixture at 150 °C did not yield a uniform material.



6

6a: $R = R^2 = H, R^1 = R^3 = C_2H_5$

6b: $R = H, R^1 = C_2H_5, R^2 = R^3 = CH_3$

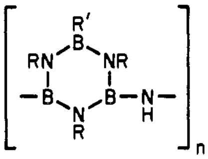
6c: $R = R^2 = H, R^1 = R^3 = C_6H_5$

The first tris(borazin-2-yl)amine of type **6**, i.e., **6a**, was recently obtained as a secondary product of the interaction of $Br(C_2H_5)_2B_3N_3H_3$ with anhydrous ammonia.[4] It was thought to be formed from the interaction of the initial $(H_2N)(C_2H_5)_2B_3N_3H_3$ and its first autocondensation product, i.e., $HN[(C_2H_5)_2B_3N_3H_3]_2$. The separation of the two compounds was exceedingly difficult. However, **6a** has now been obtained in essentially quantitative yield from the reaction of $N[Si(CH_3)_3]_3$ with 3 molar equiv of $Br(C_2H_5)_2B_3N_3H_3$.

The thermal behavior of **6a** is quite interesting. When it was attempted to distill and/or sublime the compound, the material deteriorated and increasing amounts of the previously prepared[4] bis(borazin-4-yl)amine (**5c**) as well as $(C_2H_5BNH)_3$ were formed. This observation suggests that borazine rings of **6a** are cleaved at higher temperatures and that a rearrangement occurs whereby originally annular NH groups are converted into bridging units. In addition, the process is accompanied by the formation of a small amount of an insoluble material.

The interaction of either $Cl(C_6H_5)_2B_3N_3H_3$ or $Br(C_6H_5)_2B_3N_3H_3$ with either $HN[Si(CH_3)_3]_2$ or $N[Si(CH_3)_3]_3$ did not proceed cleanly. When the reaction with $HN[Si(CH_3)_3]_2$ was performed at room temperature, a slightly exothermic process occurred, which gave a mixture of products that contained (mass spectroscopic data) $(C_6H_5BNH)_3$, some of the desired $HN[(C_6H_5)_2B_3N_3H_3]_2$ (**5d**), and unreacted starting material. Even in the presence of excess of $HN[Si(CH_3)_3]_2$ and refluxing of the reaction mixture in toluene for several hours, the cited reaction could not be developed as a procedure for the preparation of **5d**. The same holds true for the reaction of $Cl(C_6H_5)_2B_3N_3H_3$ with $N[Si(CH_3)_3]_3$: The desired $N[(C_6H_5)_2B_3N_3H_3]_3$ (**6c**) could not be obtained, but only a mixture of unseparable products was formed, which contained (as based on mass spectroscopic data) **5d** but not **6c**.

When $Br_2(C_2H_5)B_3N_3(CH_3)_3$ was reacted with 1 molar equiv of $HN[Si(CH_3)_3]_2$ (16 h of stirring at room temperature), an oligomeric mixture of species of type **7** was obtained. Mass spectral data on the relatively low melting (103–135 °C) product suggested the dominance of species **7** with $n = 2$ and 3. When the material was heated under vacuum, a fraction melting at 160–168 °C sublimed off, and the mass spectral data indicated the predominance of species **7** with $n = 4$. The sublimation residue now had a melting range of 158–180 °C, suggesting that additional oligomerization occurred during the thermal treatment. However, no well-defined single species could be isolated, although elemental analysis data of the material corresponded reasonably well with those calculated for **7**.



7

$R = CH_3, R' = C_2H_5$

As is based on mass spectroscopic data, the thermolysis of $(H_2N)_2(C_2H_5)B_3N_3(CH_3)_3$[3] (6 h at 220 °C under atmospheric pressure) gave a mixture of products containing species of type **7** with *n* up to 6. However, ion peaks indicating the presence of the bis(borazin-2-yl)amine (of type **5**) $HN[(H_2N)(C_2H_5)B_3N_3(CH_3)_3]_2$ and $[(CH_3)_3N_3B_3(C_2H_5)(NH_2)(NH)]_2(C_2H_5)B_3N_3(CH_3)_3$ (of type **8**; see below) dominated the mass spectrum; unreacted starting material was also observed. No single defined species could be isolated.

The reaction of $Br_2(C_2H_5)B_3N_3H_3$ with anhydrous ammonia also failed to give a uniform product. Rather, a mixture was obtained and, after thermal treatment at 210 °C, a species of type **7** with $n = 4$ seemed to be a major product (mass spectroscopic data).

Reactions of (Methylthio)borane Species with Aminoborazine Derivatives. The preparation of such polyborazines where individual borazine rings are linked via nitrogen was also studied by the reaction of (methylthio)borane species with various aminoborazine derivatives.

In an attempt to synthesize the unsymmetrical tris(borazin-2-yl)amine $N[(C_2H_5)_2B_3N_3H_3]_2[(CH_3)_2B_3N_3(CH_3)_3]$ (**6b**), the borazines $(H_2N)(CH_3)_2B_3N_3(CH_3)_3$ and $(CH_3S)(C_2H_5)_2B_3N_3H_3$ were reacted in 1:2 molar ratio for 20 h at 75–80 °C. A multitude of products was obtained, and the following proposed processes would account for the identified (by NMR and mass spectral data) products (**5c**, **5e**, **6a**, **6b**) in the mixture:

$$2(CH_3S)(C_2H_5)_2B_3N_3H_3 + (H_2N)(CH_3)_2B_3N_3(CH_3)_3 \rightarrow 2CH_3SH + \underset{\mathbf{6b}}{N[(C_2H_5)_2B_3N_3H_3]_2[(CH_3)_2B_3N_3(CH_3)_3]} \tag{3a}$$

$$2(H_2N)(CH_3)_2B_3N_3(CH_3)_3 \rightarrow NH_3 + \underset{\mathbf{5e}}{HN[(CH_3)_2B_3N_3(CH_3)_3]_2} \tag{3b}$$

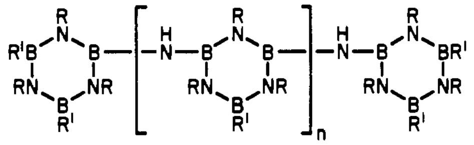
$$NH_3 + (CH_3S)(C_2H_5)_2B_3N_3H_3 \rightarrow CH_3SH + (H_2N)(C_2H_5)_2B_3N_3H_3 \tag{3c}$$

$$2(H_2N)(C_2H_5)_2B_3N_3H_3 \rightarrow NH_3 + \underset{\mathbf{5c}}{HN[(C_2H_5)_2B_3N_3H_3]_2} \tag{3d}$$

$$3(H_2N)(C_2H_5)_2B_3N_3H_3 \rightarrow 2NH_3 + \underset{\mathbf{6a}}{N[(C_2H_5)_2B_3N_3H_3]_3} \tag{3e}$$

However, with the exception of $HN[(CH_3)_2B_3N_3(CH_3)_3]_2$ (**5e**), no pure product could be isolated from the reaction mixture.

On the other hand, the reaction of $(CH_3S)_2(C_2H_5)B_3N_3(CH_3)_3$ with 2 molar equiv of $(H_2N)(C_2H_5)_2B_3N_3(CH_3)_3$ proceeded cleanly with the formation of the 2,4-bis(borazin-2-ylamino)borazine **8** (with $n = 1$, $R = CH_3$, $R' = C_2H_5$) in good yield.



8

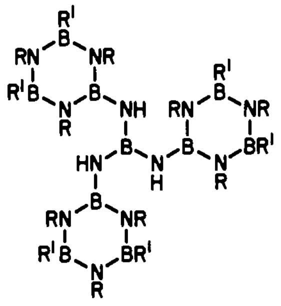
$n = 1, R = CH_3, R' = C_2H_5$

In another approach to synthesize tris(borazin-2-yl)amines, the reaction of $HN[(CH_3)_2B_3N_3(CH_3)_3]_2$ (**5e**) with $(CH_3S)(C_2H_5)_2B_3N_3H_3$ was attempted in refluxing hexane. No reaction whatever occurred over a period of 16 h. The reaction of $HN[(C_2H_5)_2B_3N_3H_3][(CH_3)_2B_3N_3(CH_3)_3]$ (**5b**) with $(CH_3S)(C_2H_5)_2B_3N_3H_3$ (1:1 molar ratio, 20 h of heating at 120 °C) gave a mixture of products, in which $N[(C_2H_5)_2B_3N_3H_3]_3$ (**6a**), $N[(C_2H_5)_2B_3N_3H_3]_2[(CH_3)_2B_3N_3(CH_3)_3]$ (**6b**), and $HN[(CH_3)_2B_3N_3(CH_3)_3]_2$ (**5e**) could be identified by NMR and mass spectroscopic data, but no pure compound could be isolated.

The bis(borazin-2-yl)amine $HN[(CH_3)_2B_3N_3(CH_3)_3]_2$ (**5e**) was the only isolated product from the reaction of $(H_2N)(CH_3)_2B_3N_3(CH_3)_3$ with $B(SCH_3)_3$ in 3:1 molar ratio (4 h at 75–80 °C). Surprisingly, the interaction of **5e** with additional $B(SCH_3)_3$ proceeded with the formation of the borazine $(CH_3S)(CH_3)_2B_3N_3(CH_3)_3$.

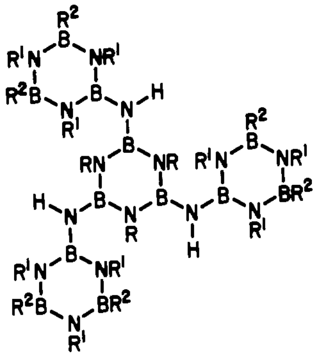
Mass spectroscopic data of the crude product from an analogous reaction between $B(SCH_3)_3$ and $(H_2N)(C_2H_5)_2B_3N_3(CH_3)_3$ suggested the formation of the tris(borazin-2-ylamino)borane $B[NH(C_2H_5)_2B_3N_3(CH_3)_3]_3$ (**9**). However, the ^1H NMR spectrum clearly showed it to be a mixture. When a purification was attempted by distillation, only $HN[(C_2H_5)_2B_3N_3(CH_3)_3]_2$ (**5a**) could be isolated and identified.

The product of the reaction of $(CH_3SBNCH_3)_3$ with 3 molar equiv of $(H_2N)(C_2H_5)_2B_3N_3(CH_3)_3$ gave some evidence for the formation of the 2,4,6-tris(borazin-2-ylamino)borazine **10a**.



9

$R = CH_3, R' = C_2H_5$



10

10a: $R = R^2 = CH_3, R^1 = C_2H_5$

10b: $R = R^1 = R^2 = CH_3$

However, no pure material could be isolated, since side reactions similar to those described above for the interaction between $(CH_3S)(C_2H_5)_2B_3N_3H_3$ and $(H_2N)(CH_3)_2B_3N_3(CH_3)_3$ (as given in eqs 3) occurred to yield an inseparable product mixture. On the other hand, **10b** could be obtained from the reaction of $(ClBNCH_3)_3$ with 3 molar equiv of $(LiHN)(CH_3)_2B_3N_3(CH_3)_3$.

Concluding Remarks. The current study suggests that condensation reactions of $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ with *B*-haloborazines by elimination of trimethylhalosilane proceed with substantial opening of borazine rings. Nevertheless, the process can be utilized for the preparation of borazine analogues of polyphenyls in reasonable yield. Once formed, the polyborazinyls seem to be chemically and thermally significantly more stable than those polyborazines, where individual borazine rings are bridged by nitrogen moieties. Of the latter, polyborazines of the bis(borazin-2-yl)amine type or oligomeric species (of presumably cyclic structure) appear to be the preferential products of condensation reactions. The condensation of (methylthio)borane species with aminoborazines can be used only in limited instances for the preparation of polyborazines, since various side reactions can occur to give mixtures of quite similar products, which are difficult to separate.

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