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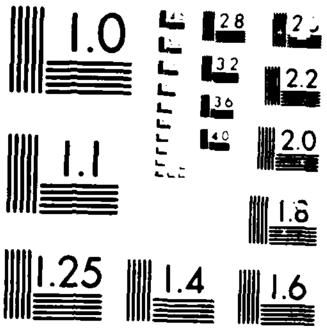
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A series of 4,4,8,8-tetrahalopyrazaboles of the type $X_2B(\mu\text{-}pz^*)_2BX_2$ (Hpz* = C-substituted pyrazole; X = Cl, Br) has been prepared by reaction of the corresponding B-tetrahydro derivatives with elemental halogen. The reaction of $(C_2H_5)_2O \cdot BF_3$ with pyrazabole, $H_2B(\mu\text{-}pz)_2BH_2$, has been used for the preparation of both $F_2B(\mu\text{-}pz)_2BF_2$ and $F_2B(\mu\text{-}pz)_2BH_2$ (Hpz = pyrazole). The later was chlorinated to yield the unsymmetrical B-tetrahalopyrazabole $Cl_2B(\mu\text{-}pz)_2BF_2$. 4,8-Dihalopyrazaboles, $XRB(\mu\text{-}pz)_2BXR$, have been obtained (as isomer mixtures) by the reaction of RBX_2 with $(CH_3)_3Si(pz)$. In addition, the 4,4-dihalopyrazaboles $X_2B(\mu\text{-}pz)_2B(C_6H_5)_2$ with X = F or Cl have been prepared. Representative reactions of the cited types of B-halogenated pyrazaboles, e.g., with organometallics, carboxylic acid anhydrides, and alcohols are described. New types of B-substituted pyrazaboles include the first example of a pyrazabole where each boron atom is bonded to two different terminal hydrocarbon substituents. The structures of three species have been determined. $F_2B(\mu\text{-}pz)_2BF_2$ crystallizes in the monoclinic system in space group $P2_1/c$ with $\underline{a}$ = 7.636(1) Å, $\underline{b}$ = 19.729(5) Å, $\underline{c}$ = 7.213(3) Å, β

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19. ABSTRACT (ctd.)

= 117.64(28)°, and Z = 4. cis-$(C_2H_5)ClB(\mu\text{-}pz)_2BCl(C_2H_5)$ crystallizes in the orthorhombic system in space group Pbcn with a = 12.344(8) Å, b = 7.794(6) Å, c = 15.091(10) Å, and Z = 4. $Cl_2B(\mu\text{-}pz)_2B(C_6H_5)_2$ crystallizes in the orthorhombic system in space groups Pbca with a = 7.940(3) Å, b = 15.270(4) Å, c = 31.064(9) Å, and Z = 8.

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STUDIES ON B-HALOGENATED PYRAZABOLES[1]

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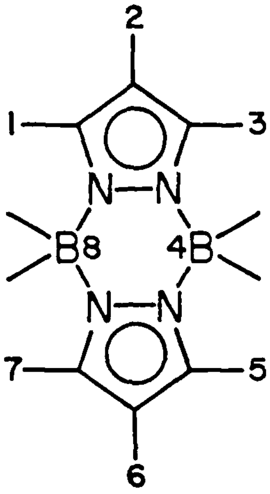
Abstract

A series of 4,4,8,8-tetrahalopyrazaboles of the type $X_2B(\mu\text{-pz*})_2BX_2$ (Hpz* = C-substituted pyrazole, X = Cl, Br) has been prepared by reaction of the corresponding B-tetrahydro derivatives with elemental halogen. The reaction of $(C_2H_5)_2O \cdot BF_3$ with pyrazabole, $H_2B(\mu\text{-pz})_2BH_2$, has been used for the preparation of both $F_2B(\mu\text{-pz})_2BF_2$ and $F_2B(\mu\text{-pz})_2BH_2$ (Hpz = pyrazole). The later was chlorinated to yield the unsymmetrical B-tetrahalopyrazabole $Cl_2B(\mu\text{-pz})_2BF_2$. 4,8-Dihalopyrazaboles, $XRB(\mu\text{-pz})_2BXR$, have been obtained (as isomer mixtures) by the reaction of RBX_2 with $(CH_3)_3Si(pz)$. In addition, the 4,4-dihalopyrazaboles $X_2B(\mu\text{-pz})_2B(C_6H_5)_2$ with X = F or Cl have been prepared. Representative reactions of the cited types of B-halogenated pyrazaboles, e.g., with organometallics, carboxylic acid anhydrides, and alcohols are described. New types of B-substituted pyrazaboles include the first example of a pyrazabole where each boron atom is bonded to two different terminal hydrocarbon substituents. The structures of three species have been determined. $F_2B(\mu\text{-pz})_2BF_2$ crystallizes in the monoclinic system in space group $P2_1/c$ with a = 7.636(1) Å, b = 19.729(5) Å, c = 7.213(3) Å, β = 117.64(28)°, and Z = 4. *cis*-$(C_2H_5)ClB(\mu\text{-pz})_2BCl(C_2H_5)$ crystallizes in the orthorhombic system in space group Pbcn with a = 12.344(8) Å, b = 7.794(6) Å, c = 15.091(10) Å, and Z = 4. $Cl_2B(\mu\text{-pz})_2B(C_6H_5)_2$ crystallizes in the orthorhombic system in space group Pbca with a = 7.940(3) Å, b = 15.270(4) Å, c = 31.064(9) Å, and Z = 8.

Introduction

Although many pyrazaboles containing the skeleton 1 are known, their chemical behavior has hardly been explored.[2] This includes the B-halogenated pyrazaboles, where the only reported reaction is that of $Br_2B(\mu\text{-}pz^*)_2BBr_2$ with Kpz (Hpz = pyrazole; Hpz* = dimethylpyrazole) to yield $(pz)_2B(\mu\text{-}pz^*)_2B(pz)_2$.[3] Structural data are known only for $Cl_2B(\mu\text{-}pz)_2BCl_2$[4] and $Br_2B(\mu\text{-}pz)_2BBr_2$[5] which contain a planar central B_2N_4 ring, and for $HBrB(\mu\text{-}pz^*)_2BHBr$ (Hpz* = 4-chloropyrazole) containing a central B_2N_4 ring in boat conformation and the Br atoms in *cis* arrangement.[4] The present study reports on the preparation, characterization, and chemical transformations of a series of B-halogenated pyrazaboles.



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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 on solutions in $CDCl_3$ (unless otherwise noted) on a Varian XL-200 instrument. Chemical shift data are given in ppm with positive values indicating downfield shifts from the reference (internal Me_4Si for ^1H and ^{13}C NMR, external $Et_2O{\cdot}BF_3$ for ^{11}B NMR); s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, m = unresolved multiplet, and an asterisk denotes a broad signal. Coupling constants *J* are given in Hz. Mass spectral data (70 eV unless otherwise noted) were obtained on a VG ZAB-2F spectrometer at the University of

Kentucky Mass Spectrometry Center; data are listed to *m/z* 30 for 5% or more relative abundances (in parentheses) only.

Crystal data were obtained on a Syntex P3 automated diffractometer using graphite-monochromated Mo Kα radiation and standard operating techniques at 25 °C. Unit cell parameters were obtained from the least-squares refinement of the diffracting positions of high-angle reflections. Intensity data were collected in the $\omega/2\theta$-scan technique [$F_2B(\mu\text{-pz})_2BF_2$] and peak profile fitting method [$(C_2H_5)ClB(\mu\text{-pz})_2B(C_2H_5)Cl$ and $Cl_2B(\mu\text{-pz})_2B(C_6H_5)_2$], respectively. All data were corrected for intensity changes noted for the check reflections (2 after every 48 data), and for Lorentz and polarization effects. An empirical absorption correction was also applied for $(C_2H_5)ClB(\mu\text{-pz})_2B(C_2H_5)Cl$ (ψ-scan, XEMP program, transmission factors 0.848-0.867). Scattering factors for neutral atoms were taken as implemented in the *SHELXTL* structure solution package (versions 3.0 and 4.1, respectively). The structures were solved by direct methods, the E-maps revealing the positions of all non-hydrogen atoms. After refining all parameters isotropically and anisotropically, all hydrogen atoms were found in the difference Fourier synthesis. These were included in the final blocked cascade refinement of $F_2B(\mu\text{-pz})_2BF_2$ with fixed isotropic $U_i = 0.06$ and of $Cl_2B(\mu\text{-pz})_2B(C_6H_5)_2$ with fixed isotropic $U_i = 0.07$, while U_i of the hydrogen atoms in $(C_2H_5)ClB(\mu\text{-pz})_2B(C_2H_5)Cl$ were also freely refined in the final steps. Definitions for the discrepancy factors are: $R = \Sigma|\Delta F|/\Sigma|F_0|$ and $R_w = \Sigma\sqrt{w}|\Delta F|/\Sigma\sqrt{w}|F_0|$ with $w = (\sigma^2(F) + g(F)^2)^{-1}$. A summary of crystallographic data and data collection procedures is given in Table I.

Table I

General Procedure for the Preparation of 4,4,8,8-Tetrahydropyrazaboles. All 4,4,8,8-tetrahydropyrazaboles were prepared on a 20-50 mmol scale in a general procedure[6] by refluxing an equimolar mixture of trimethylamine-borane and the appropriate pyrazole in toluene for 8 h. If needed, the resulting solution was filtered while hot and the solvent was subsequently removed under reduced pressure. The residue was purified by either recrystallization or sublimation.

General Procedure for the Halogenation of B-Hydropyrazaboles. The B-hydropyrazabole (10-25 mmol) was dissolved in a minimal amount of CCl_4 (or $CHCl_3$ or CH_2Cl_2; CH_2Br_2 for bromination) and the elemental halogen (chlorine as gas, bromine as stock solution in CH_2Br_2) was added with stirring until the halogen color persisted.[7] Frequently the halogenated species precipitated in essentially pure form. A second and generally smaller crop could then be obtained by removal of all volatiles under reduced pressure at room temperature.

$F_2B(\mu\text{-pz})_2BF_2$. Ten mL of $(C_2H_5)_2O{\cdot}BF_3$ were slowly added to 0.86 g (5.39 mmol) of $H_2B(\mu\text{-pz})_2BH_2$.[6] The mixture was stirred at room temperature for 12 h and excess $(C_2H_5)_2O{\cdot}BF_3$ was distilled off at 66 $^{\circ}$C/55 torr to leave a colorless residue which was dried under vacuum. A quantity, 0.22 g, of $F_2B(\mu\text{-pz})_2BH_2$ was sublimed off and the sublimation residue was recrystallized from methanol to give 0.68 g (55%) of the desired compound, mp 148-153 $^{\circ}$C.; after subsequent sublimation the mp was 166-168 $^{\circ}$C. (Note: The previously described reaction of $(CH_3)_3N{\cdot}BF_3$ with Hpz gives only a low yield of product, mp 170-172 $^{\circ}$C.[7] The reaction of $C_2H_5NH_2{\cdot}BF_3$ with Hpz, which was investigated in the present study, gave a 15% yield after 40 h reflux in toluene).

NMR data: δ (^{1}H) 8.04 (2 H, unresolved d), 6.58 (1 H, t, J = 2.2); δ (^{11}B) -0.2 (t, J = 23); δ (^{13}C) (proton decoupled) 136.5, 107.1; δ (^{19}F) -29.5(q). Mass spectrum *m/z* 233 (6), 232 (71), 231 (34), 214 (5), 213 (56), 212 (26), 165 (100), 164 (54), 163 (12), 116 (89), 115 (24), 97 (23), 96 (6), 89 (12), 76 (17), 75 (5), 69 (7), 49 (26), 48 (7), 41 (15), 40 (7), 39 (6).

$F_2B(\mu\text{-pz})_2BH_2$. Mp (after sublimation and recrystallization from hexane) 99-102 $^{\circ}$C; lit.[8] mp 87-88 $^{\circ}$C. NMR data: δ (^{1}H) 7.94 (1 H, d, J = 2.2), 7.70 (1 H, unresolved d), 6.44 (1 H, t, J = 2.2; resolution-enhanced: 2 overlapping d), 3.6* (1 H); δ (^{11}B) 3.3 (1 B, t, J = 22), -5.3 (1 B, t, J = 122). NMR data (solution in CCl_4): δ (^{1}H) 7.86 (1 H, d, J = 1.9), 7.64 (1 H, unresolved), 6.38 (1 H, t, J = 2.2); δ (^{11}B) (proton decoupled) 0.1 (1 B), -6.2 (1 B). NMR data:[8] δ (^{1}H) 7.91 (1 H, d, J = 2.1), 7.65 (1 H, unresolved d), 6.39 (1 H, t, J = 2); 4-1* (1 H); δ (^{11}B) -0.6 (t, J = 21), -8.2 (t, J = 110). Mass spectrum *m/z* 195 (14), 194 (6), 177 (8), 160 (9), 159 (100), 158 (70), 157 (53), 156 (22), 155 (7), 132 (6), 131 (7), 130 (10), 129 (6), 104 (6), 91 (6), 79 (24), 78.5 (5), 78 (8), 77 (9), 76 (8), 68 (7), 52 (17), 51 (9), 38 (5).

$Cl_2B(\mu\text{-pz})_2BF_2$ was prepared by the chlorination of $F_2B(\mu\text{-pz})_2BH_2$ in CCl_4 as outlined in the general procedure (see above). After solvent evaporation the remaining product was recrystallized from toluene to give a 90 % yield of pure compound, mp 170-173 $^{\circ}$C. Anal. Calcd for $C_6H_6B_2Cl_2F_2N_4$ (mol wt 264.67): C, 27.23; H, 2.29; B, 8.17; Cl, 26.79; F, 14.36; N, 21.17. Found: C, 27.19; H, 2.30; B, 8.09; Cl, 26.69; F, 14.31; N, 21.18.

NMR data: δ (^{1}H) 8.30 (1 H, unresolved d) 8.11 (1 H, unresolved d), 6.67 (1 H, unresolved t); δ (^{11}B) 2.1 (1 B, s, $h_{1/2}$ = 20 Hz), -0.2 (1 B, t, J = 22). Mass spectrum m/z 245 (5), 231 (8), 230 (18), 229 (100), 228 (38), 227 (5), 193 (5), 113 (11), 86 (9).

$F_2B(\mu\text{-pz})_2B(C_6H_5)_2$ was prepared by adding a solution of 16.9 g (0.05 mol) of $K[(C_6H_5)_2B(pz)_2]$[3] in 50 mL of tetrahydrofuran to a solution of 13 mL (ca. 0.1 mol) of freshly distilled $(C_2H_5)_2O{\cdot}BF_3$ in 50 mL of ether. A slightly exothermic reaction occurred and the mixture was stirred for 1 h. All volatile material was removed under vacuum at room temperature and the solid residue was washed thoroughly with water. The remaining material (16 g = ca. 90% yield) was recrystallized from cyclohexane to give colorless crystals of the desired compound, mp 210-211 °C. Anal. Calcd for $C_{18}H_{16}B_2F_2N_4$ (mol wt 347.97): C, 62.13; H, 4.63; B, 6.21; F, 10.96; N, 16.10. Found: C, 62.21; H, 4.82; B, 5.95; F, 11.09; N, 15.91.

NMR data: δ (^{1}H) 8.05 (1 H, d, J = 2.2), 7.49 (1 H, d, J = 1.6), 7.29-7.22 (3 H, m), 6.98-6.93 (2 H, m), 6.50 (1 H, t, J = 2.4); δ (^{11}B) 1.8*, -0.1 (t, J = 21). Mass spectrum m/z 272 (14), 271 (100), 270 (48), 269 (6), 203 (22), 202 (11), 155 (17), 128 (19), 127 (6), 101 (10), 77 (51), 56 (11). A weak molecular ion cluster was observed: m/z 348 (4.3), 347 (2.8).

$Cl_2B(\mu\text{-pz})_2BCl_2$.[7] NMR data: δ (^{1}H) 8.39* (2 H, unresolved), 6.79 (1 H, unresolved t); δ (^{11}B) 2.1 (s, $h_{1/2}$ = 5 Hz). Mass spectrum m/z 265 (12), 264 (9), 263 (39), 262 (22), 261 (42), 260 (20), 225 (6), 191 (7), 113 (19), 106 (5), 86 (20), 85 (8), 83 (5), 81 (8), 62 (26), 61 (6), 59 (6), 45 (100), 44 (27), 39 (5), 36 (8).

$(C_2H_5)ClB(\mu\text{-pz})_2B(C_2H_5)Cl$.[9] Mass spectrum m/z 259 (10), 258 (11), 257 (71), 256 (49), 255 (100), 254 (46), 253 (5), 249 (10), 248 (5), 229 (12), 228 (6), 227 (15), 226 (7), 191 (17), 190 (8), 113 (9), 106 (6), 105 (7), 96 (13), 88 (5), 86 (19), 85 (7), 81 (22), 79 (26), 78 (10), 75 (8), 73 (5), 72 (6), 68 (11), 52 (34), 51 (13), 49 (9), 47 (19), 42 (6), 41 (14), 40 (8), 39 (11), 38 (10), 37 (10), 36 (22).

An alternate procedure (as opposed to the reaction of $SOCl_2$ with $RB(\mu\text{-pz})_2(\mu\text{-OBRO})BR$ ($R = C_2H_5$)) for the preparation of $RClB(\mu\text{-pz})_2BRCl$ was performed as follows: A solution of $(CH_3)_3Si(pz)$ in hexane was added dropwise with stirring to a solution of $RBCl_2$ in hexane. The resultant mixture was refluxed for 1 h and hexane and $(CH_3)_3SiCl$ were distilled off. The remaining crude solid product (essentially quantitative yield) was recrystallized from toluene to give various fractions, the first of which was reasonably pure *trans*-$RClB(\mu\text{-pz})_2BRCl$, mp (after subliming off traces of $RB(\mu\text{-pz})_2(\mu\text{-OBRO})BR$ under vacuum) 240-243 °C. After repeated recrystallization and sublimation of this fraction a material of mp 267-270 °C was obtained exhibiting δ (^1H) 8.16 (2 H, d, J = 2.3), 6.60 (1 H, t, J = 2.1), 1.8-1.2 (5 H, m); δ(^{11}B) -0.4 (s, $h_{1/2}$ = 200 Hz). The mp of subsequent fractions was lower and of substantially wider range and the last fraction consisted primarily of the previously described[9] *cis* compound. No completely pure isomers could be obtained from the recrystallization, which gave an overall yield of 70-75%.

$(C_6H_5)_2(\mu\text{-pz})_2BH_2$.[3] Mass spectrum *m/z* 312 (8), 311 (38), 310 (24), 309 (10), 243 (20), 242 (13), 235 (25), 234 (84), 233 (100), 232 (6), 231 (9), 206 (5), 167 (6), 163 (11), 157 (17), 156 (9), 155 (6), 128 (5), 117 (5), 113 (8), 78 (17), 77 (29), 52 (12), 51 (21), 50 (6), 39 (3).

$Cl_2B(\mu\text{-pz})_2B(C_6H_5)_2$ was prepared by chlorination of $(C_6H_5)_2B(\mu\text{-pz})_2BH_2$ in the general procedure given above (87% yield); mp (after recrystallization from toluene) 246-248 °C. Anal. Calcd for $C_{18}H_{16}B_2Cl_2N_4$ (mol wt 380.88): C, 56.76; H, 4.23; B, 5.68; Cl, 18.62; N, 14.71. Found: C, 57.10; H, 4.43; B, 5.65; Cl, 18.59; N, 14.71.

NMR data: δ (^1H) 8.34 (1 H, unresolved d), 7.55 (1 H, d, J = 2.4), 7.2 (3 H, m), 6.9 (2 H, m), 6.59 (1 H, t, J = 2.4) (pz group signals assigned by selective decoupling: 8.34/7.55/6.59); δ (^{11}B) 2.1 (s, $h_{1/2}$ = 15 Hz) and an extremely broad peak in the same area the chemical shift of which (ca. 1.8 ppm) could not be exactly determined. In CD_3CN: δ (^{11}B) 3.0 (s, $h_{1/2}$ = 20 Hz) with a broad baseline with a maximum centered at about 1.8 ppm.

Mass spectrum *m/z* 346 (9), 308 (10), 307 (14), 306 (59), 305 (40), 304 (100), 303 (47), 302 (6), 278 (5), 270 (6), 269 (6), 239 (5), 238 (6), 237 (25), 236 (15), 235 (40), 234 (19), 233 (11), 32 (5), 207 (5), 201 (5), 193 (7), 192 (5), 191 (23), 190 (10), 165 (5), 163 (9), 155 (5), 137 (8), 135 (8), 134 (21), 128 (23), 127 (10), 123 (7), 113 (7), 111 (16), 101 (15), 100 (5), 87 (7), 86 (7), 77 (8), 68 (7), 61 (5), 51 (7), 41 (5).

$(C_6H_5)ClB(\mu\text{-pz})_2B(C_6H_5)Cl$ was obtained from $C_6H_5BCl_2$ and $(CH_3)_3Si(pz)$ in a fashion analogous to the procedure described above for the preparation of the corresponding ethyl compound. Part of the crude product was recrystallized from toluene to give a material of mp 166-170 °C.

NMR data: δ (^1H) 7.64 (2 H, d, J = 2.5), 7.59-7.54 (2 H, m), 7.38-7.33 (3 H, m), 6.47 (1 H, t, J = 2.5); δ (^{11}B) 2.9 (s, $h_{1/2}$ = 215 Hz). Mass spectrum (14 eV) *m/z* 347 (16), 346 (16), 345 (47), 344 (23), 307 (11), 306 (16), 305 (63), 304 (29), 303 (100), 302 (47), 301 (8), 235 (7), 228 (8), 227 (6), 226 (14), 225 (7), 197 (7). A very weak parent ion cluster was observed near *m/z* 380.

A product recrystallized from cyclohexane had a mp 180-186 °C but the ^{1}H NMR and mass spectral data were identical with those of the above material. A product recrystallized from chlorobenzene had a mp 144-150 °C. The pz signals on the ^{1}H NMR spectrum of this latter material were observed at δ 7.62 and 6.46, and δ (^{11}B) showed a minor shift to 2.5 ppm ($h_{1/2}$ = 170 Hz). Other than that, spectroscopic data were identical to those of the above material. No sharp melting materials could be obtained from either recrystallization.

$Cl_2B(\mu\text{-pz*})_2BCl_2$ (Hpz* = 3-methylpyrazole) was prepared from $H_2B(\mu\text{-pz*})_2BH_2$[10] in 70% yield; mp (after recrystallization from toluene) 228-270 °C. Fractional crystallization of the compound from toluene gave an initial fraction of mp 232-235 °C; the ^{1}H NMR spectrum of this product was identical to that of the initial material but the ^{11}B NMR signal was observed at 2.9 ppm. NMR data: δ (^{1}H) 8.30* (1 H, unresolved), 6.53 (1 H, d, J = 1.9), 2.80 (3 H, s); δ (^{11}B) 2.0 (s, $h_{1/2}$ = 15 Hz). Mass spectrum m/z 292 (24), 291 (93), 290 (54), 289 (100), 288 (47), 287(6), 254 (7), 253 (18), 252 (8), 218 (8), 212 (7), 129 (6), 128 (13), 127 (30), 126 (5), 108 (8), 106 (11), 105 (6), 102 (6), 99 (6), 88 (9), 87 (5), 86 (28), 85 (11), 83 (9), 81 (14), 72 (6), 71 (5), 59 (5), 54 (5), 47 (6), 39 (5), 36 (8).

$Cl_2B(\mu\text{-pz*})_2BCl_2$ (Hpz* = 4-isopropylpyrazole).[7] NMR data: δ (^{1}H) 8.13 (2 H, s), 2.97 (1 H, p, J = 7), 2.92 (6 H, d, J = 7); δ (^{11}B) 1.7 (s, $h_{1/2}$ = 15 Hz). Mass spectrum m/z 350 (6), 349 (30), 348 (27), 347 (94), 346 (57), 345 (100), 344 (47), 343 (7), 269 (6), 268 (7), 267 (7), 177 (11), 175 (17), 174 (6), 155 (5), 139 (5), 112 (6), 108 (5), 92 (9), 87 (7), 81 (8), 53 (13), 43 (11), 41 (12), 39 (7).

$H_2B(\mu\text{-pz*})_2BH_2$ (Hpz* = 3-*t*-butylpyrazole) was prepared by the general method as outlined above; mp (after recrystallization from methanol) 148 °C. NMR data: δ (^{1}H) 7.50 (1 H, d, J = 2.3), 6.11 (1 H, d, J = 2.3) 3.7* (2 H), 1.42 (9 H, s); δ (^{11}B) -9.1 (unresolved t; proton decoupled: $h_{1/2}$ = 160 Hz).

$Cl_2B(\mu\text{-pz*})_2BCl_2$ (Hpz* = 3-*t*-butylpyrazole). Yield by chlorination of the B-tetrahydro compound: 79%; mp (after recrystallization from hexane) 170-173 °C. NMR data: δ (^{1}H) 8.54* (1 H, unresolved d), 6.65 (1 H, d, J = 2.5), 1.67 (9 H, s); δ (^{11}B) 3.0 (s, $h_{1/2}$ = 11 Hz). Mass spectrum m/z 378 (6), 377(29), 376 (30), 375 (93), 374 (56), 373 (100), 372 (52), 371 (8), 359 (12), 358 (8), 357 (12), 356 (5), 337 (5), 299 (5), 287 (5), 283 (10), 282 (6), 265 (5), 251 (6), 249 (6), 191 (18), 190 (7), 189 (27), 188 (8), 179 (5), 177 (8), 161 (5), 158 (5), 154 (10), 153 (21), 152 (5), 151 (5), 145 (7), 135 (8), 126 (5), 124 (7), 117 (10), 115 (11), 113 (7), 110 (5), 109 (45), 108 (6), 106 (5), 86 (14), 85 (7), 83 (5), 81 (8), 80 (6), 77 (5), 65 (5), 57 (82), 55 (7), 53 (9), 51 (6), 42 (9), 41 (94), 39 (30), 38 (11), 36 (27), 35 (6), 31 (6).

$H_2B(\mu\text{-pz*})_2BH_2$ (Hpz* = 3-phenylpyrazole) was obtained by the general procedure in 79% yield; mp (after recrystallization from ethanol) 174-177 °C. NMR data: δ (^{1}H) 7.6 (3 H, m including d (J = 2.4) at 7.56), 7.5 (3 H, m), 6.40 (1 H, d, J = 2.9), 4.7* (2 H); δ (^{11}B) -9.3 (unresolved t; proton decoupled: $h_{1/2}$ = 250 Hz).

$Cl_2B(\mu\text{-pz*})_2BCl_2$ (Hpz* = 3-phenylpyrazole) was obtained in 88% yield, mp (after recrystallization from toluene) 246-249 °C. NMR data: δ (^{1}H) 8.42 (1 H, unresolved), 7.84-7.78 (2 H, m), 7.56-7.48 (3 H, m), 6.65 (1 H, d, J = 2.5); δ (^{11}B) 2.4 (s, $h_{1/2}$ = 5 Hz). Mass spectrum *m/z* 419 (9), 418 (33), 417 (33), 416 (95), 415 (59), 414 (100), 413 (47), 412 (6), 380 (8), 379 (5), 378 (6), 344 (7), 225 (6), 189 (14), 171 (8), 153 (7), 148 (5), 145 (9), 144 (100), 143 (9), 117 (23), 116 (8), 115 (20), 104 (5), 95 (5), 91 (6), 90 (23), 89 (25), 88 (5), 83 (5), 81 (7), 78 (8), 77 (42), 76 (7), 75 (6), 74 (5), 72 (5), 71 (6), 69 (5), 65 (8), 63 (20), 62 (11), 61 (6), 57 (7), 55 (7), 51 (30), 50 (18), 49 (5), 45 (110, 44 (20), 43 (13), 41 (7), 40 (7), 39 (18), 38 (38), 37 (12), 36 (75), 32 (5).

$Cl_2B(\mu\text{-pz*})_2BCl_2$ (Hpz* = 4-perfluoroisopropylpyrazole) was obtained from $H_2B(\mu\text{-pz*})_2BH_2$[6] in 86% yield, mp (after recrystallization from toluene or cyclohexane) 165-168 °C. Anal. Calcd for $C_{12}H_4B_2Cl_4F_{14}N_4$ (mol wt 633.60): C, 22.75; H, 0.64; B, 3.41; Cl, 22.38; F, 41.98; N, 8.84. Found: C, 23.13; H, 0.98; B, 3.23; Cl, 21.89; F, 41.90; N, 8.77.

NMR data: δ (^{1}H) 8.55 (s); δ (^{11}B) 2.3 (s, $h_{1/2}$ = 15 Hz). Mass spectrum *m/z* 602 (30), 601 (26), 597 (100), 580 (5), 528 (15), 299 (9), 297 (13), 282 (6), 281 (15), 92 (5), 83 (5), 81 (8), 75 (14), 69 (8), 65 (9).

$H_2B(\mu\text{-pz*})_2BH_2$ (Hpz* = 4-chloropyrazole).[6] NMR data: δ (^{1}H) 7.59 (1 H, s), 3.5* (1 H, s); δ (^{11}B) -8.4 (unresolved t; proton decoupled: $h_{1/2}$ = 120 Hz).

$Cl_2B(\mu\text{-pz*})_2BCl_2$ (Hpz* = 4-chloropyrazole) was prepared from $H_2B(\mu\text{-pz*})_2BH_2$ in 93% yield; mp (after recrystallization from toluene) 238-240 °C. NMR data: δ (^{1}H) 8.30 (s); δ (^{11}B) 1.8 (s, $h_{1/2}$ = 30 Hz). Mass spectrum *m/z* 335 (20), 334 (14), 333 (63), 332 (4), 331 (100), 330 (55), 329 (70), 328 (33), 297 (5), 294 (5), 293 (5), 261 (5), 259 (7), 184 (9), 182 (10), 149 (13), 148 (11), 147 (23), 146 (6), 134 (5), 122 (5), 120 (6), 110 (5), 106 (5), 85 (8), 83 (15), 81 (270, 80 (7), 40 (10).

$Cl_2B(\mu$-pz*$)_2BCl_2$ (Hpz* = 3,5-dimethylpyrazole).[7] NMR data: δ (^{1}H) 6.23 (s) + 6.00 [illegible] (2 H, ratio 3:1), 2.72 (s) + 2.45 (s) (6 H, ratio 3:1); δ (^{11}B) 1.7 (s, $h_{1/2}$ = 20 Hz); δ (^{13}C) 151.8 (s), 145.3 (s), 114.2 (d, *J* = [illegible]), 106.7 (d, *J* = 182), 15.6 (q, *J* = 131), 11.5 (q, *J* = 131), with the major pz signals at 145.3 and 106.7 ppm. Mass spectrum *m/z* 332 (5), 321 (31), 320 (26), 319 (96), 318 (58), 317 (100), 316 (48), 315 (6), 285 (6), 283 (11), 282 (6), 281 (8), 247 (7), 246 (5), 100 (6), 81 (6), 73 (9), 54 (5), 47 (130, 42 (6), 39 (14), 36 (11). A very weak molecular ion cluster could be detected: *m/z* 356 (0.49), 354 (0.79), 353 (0.49), 352 (0.65).

$H_2B(\mu$-pz*$)_2BH_2$ (Hpz* = 3,4,5-trimethylpyrazole).[6] NMR data: δ (^{1}H) 3.4* (2 H), 2.34 (6 H, s), 1.91 (3 H, s); δ (^{11}B) -12.6 (unresolved t; proton decoupled: $h_{1/2}$ = 130 Hz).

$Cl_2B(\mu$-pz*$)_2BCl_2$ (Hpz* = 3,4,5-trimethylpyrazole) was obtained in 72% yield and was purified by recrystallization from toluene. The material decomposes near 357 °C. NMR data: δ (^{1}H) 2.71 (s) + 2.41 (s) (2 H, ratio 4:1), 2.03 (s) + 1.97 (s) (1 H, ratio 4:1); δ (^{11}B) 1.7 (s, $h_{1/2}$ = 25 Hz). Mass spectrum *m/z* 351 (7), 350 (28), 349 (27), 348 (94), 347 (58), 346 (100), 345 (46), 344 (7), 312 (15), 276 (5). A very weak molecular ion cluster could be detected: *m/z* 384 (0.41), 383 (0.31), 382 (0.91), 381 (0.51), 380 (0.74), 379 (0.27).

$Cl_2B(\mu$-pz*$)_2BCl_2$ (Hpz* = 3,5-dimethyl-4-butylpyrazole).[7] NMR data: δ (^{1}H) 2.72 (6 H, s), 2.45 (2 H, t, *J* = 7.5), 1.43 (4 H, m), 0.96 (3 H, t, *J* = 7); δ (^{11}B) 1.7 (s, $h_{1/2}$ = 20 Hz). Mass spectrum *m/z* 434 (10), 433 (10), 432 (29), 431 (19), 430 (31), 429 (16), 221 (6), 134 (10), 126 (8), 109 (6), 78 (27), 77 (6), 44 (100), 43 (7), 41 (5), 39 (6), 38 (6), 36 (15), 32 (16).

$Cl_2B(\mu$-pz*$)_2BCl_2$ (Hpz* = 3,4,5-tribromopyrazole) was prepared from $H_2B(\mu$-pz*$)_2BH_2$[6] (slurry in $CHCl_3$) in 79% yield. The precipitate was washed with petrol ether and was recrystallized from chlorobenzene to give colorless crystals decomposing near 294-298 °C. Anal. Calcd for $C_6B_2Br_6Cl_4N_4$ (mol wt 770.95): C, 9.35; B, 2.80; Br, 62.19; Cl, 18.39; N, 7.27. Found: C, 9.27; B, 2.90; Br, 61.19; Cl, 17.89; N, 7.08.

Mass spectrum *m/z* 741 (5), 739 (24), 738 (6), 737 (49), 736 (13), 735 (50), 734 (8), 733 (17), 707 (47), 706 (25), 705 (71), 704 (61), 703 (95), 702 (67), 701 (100), 699 (81), 698 (60), 697 (57), 696 (17), 673 (5), 671 (60), 670 (51), 669 (81), 668 (67), 667 (90), 666 (71), 665 (86), 664 (67), 663 (67), 662 (49), 661 (24), 623 (6), 620 (17), 619 (5), 618 (8), 589 (21), 588 (6), 587 (48), 586 (18), 585 (45), 584 (10), 583 (10), 543 (6), 541 (6), 539 (5), 386 (5), 352 (14), 351 (13), 350 (17), 349 (6), 335 (5), 334 (15), 333 (210, 332 (9), 317 (16), 316 (7), 315 (16), 314 (5), 306 [illegible] 284 (23), 283 (8), 282 (5), 275 (5), 274 (5), 273 (17), 272 (56), 271 (56), 270 (63), 269 (34), 268 (34), 244 (5), [illegible] (14), 211 (5), 200 (5), 198 (18), 196 (6), 192 (15), 191 (5), 190 (6), 129 (6), 127 (56), 126 (5), 125 (48), 112 (22), 111 (5), 93 (6), 91 (6), 83 (12), 82 (58), 81 (50), 80 (59), 79 (17), 77 (13), 76 (6), 72 (28), 49 (8), 47 (59), 46 [illegible], 36 (45), 32 (25), 31 (21).

Br$_2$B(μ-pz*)$_2$BBr$_2$ (Hpz* = 3-phenylpyrazole) was obtained from the tetrahydro compound in 44% yield, mp (after recrystallization from toluene) 248-252 °C. NMR data: δ (^{1}H) 8.66 (1 H, unresolved), 7.90-7.85 (2 H, m), 7.55-7.52 (3 H, m), 6.79 (1 H, d, J = 2.5); δ (^{11}B) -6.5 (s, $h_{1/2}$ = 20 Hz). Mass spectrum *m/z* 551 (6), 550 (32), 549 (12), 548 (76), 547 (62), 546 (100), 545 (52), 544 (38), 543 (15), 468 (15), 467 (12), 466 (28), 465 (16), 464 (16), 463 (7), 390 (7), 389 (32), 388 (24), 387 (43), 386 (210, 385 (11), 308 (7), 307 (33), 306 (19), 305 (6), 282 (5), 280 (5), 279 (11), 278 (23), 277 (12), 235 (16), 234 (23), 233 (26), 232 (8), 208 (5), 206 (6), 203 (6), 194 (7), 193 (45), 192 (21), 181 (6), 179 (5), 177 (5), 155 (6), 154 (5), 153 (80), 152 (39), 151 (5), 150 (5), 144 (34), 140 (5), 139 (13), 126 (6), 81 (5), 80 (11), 77 (16), 51 (9), 31 (6).

Br$_2$B(μ-pz*)$_2$BBr$_2$ (Hpz* = 3,5-dimethylpyrazole).[3] The compound was recrystallized from toluene, mp 335 °C dec. NMR data: δ (^{1}H) 6.36 (s) + 6.11 (s) (1 H, ratio 4:1), 2.88 (s) + 2.54 (s) (6 H, ratio 4:1); δ (^{11}B) -7.5 (s, $h_{1/2}$ = 25 Hz). Mass spectrum *m/z* 455 (30), 454 (26), 453 (94), 452 (57), 451 (100), 450 (47), 449 (38), 448 (16), 371 (5), 316 (5), 293 (27), 292 (35), 291 (42), 290 (37), 289 (18), 211 (8), 196 (5), 194 (5), 187 (15), 186 (17), 185 (14), 170 (5), 169 (5), 143 (6), 141 (5), 130 (5), 118 (6), 117 (9), 116 (6), 91 (6), 82 (7), 80 (8), 44 (15), 39 (10).

Br$_2$B(μ-pz*)$_2$BBr$_2$ (Hpz* = 4-chloropyrazole) was prepared in 44% yield from H$_2$B(μ-pz*)$_2$BH$_2$,[6] mp (after recrystallization from toluene) 150-154 °C. NMR data: δ (^{1}H) 8.45 (s); δ (^{11}B) -7.5 (s, $h_{1/2}$ = 20 Hz). Mass spectrum *m/z* 469 (180), 468 (14), 467 (63), 466 (36), 465 (100), 464 (54), 463 (81), 462 (37), 461 (25), 460 (10), 385 (6), 383 (7), 307 (220), 306 (15), 305 (53), 304 (27), 303 (35), 302 (16), 276 (5), 224 (6), 198 (6), 197 (6), 196 (5), 194 (5), 193 (19), 192 (19), 191 (16), 189 (5), 178 (5), 176 (5), 171 (8), 166 (9), 165 (7), 164 (7), 163 (5), 154 (5), 153 (5), 152 (15), 151 (9), 150 (6), 141 (5), 140 (7), 139 (11), 138 (5), 131 (5), 130 (5), 129 (5), 127 (13), 125 (10), 118 (5), 116 (7), 102 (7), 87 (7), 86 (5), 85 (18), 84 (9), 82 (9), 81 (5), 79 (5), 71 (5), 40 (15), 38 (5), 36 (6), 32 (5), 31 (5).

$(CF_3COO)ClB(\mu\text{-pz})_2B(OCOCF_3)Cl$. Ten mL of $(CF_3CO)_2O$ were added with stirring to a mixture of 1.30 g (4.36 mmol) of $Cl_2B(\mu\text{-pz})_2BCl_2$ and 10 mL of benzene. The mixture was refluxed for 20 h. After cooling to room temperature volatile material was removed under vacuum to leave 1.73 g (87%) of crude product, mp 94-98 °C. After recrystallization from cyclohexane the compound melted at 111-112 °C. Anal. Calcd for $C_{10}H_6B_2Cl_2F_6N_4O_4$ (mol wt 452.70): C, 26.53; H, 1.34; B, 4.78; Cl, 15.66; F, 25.18; N, 12.38; O, 14.14. Found: C, 26.18; H, 1.69; B, 5.09; Cl, 14.98; F, 25.91; N, 12.40.

NMR data: δ (^{1}H) 8.36* (2 H, unresolved d), 6.76* (1 H, unresolved t); δ (^{11}B) 1.1 (s, $h_{1/2}$ = 10 Hz). Mass spectrum *m/z* 419 (24), 418 (21), 417 (76), 416 (36), 415 (36), 414 (5), 341 (23), 340 (13), 339 (36), 338 (17), 323 (10), 247 (25), 246 (15), 245 (39), 244 (20), 231 (15), 230 (11), 229 (47), 228 (22), 175 (9), 159 (20), 158 (10), 133 (6), 131 (17), 130 (5), 114 (10), 113 (13), 112 (41), 96 (19), 95 (5), 86 (28), 84 (12), 69 (16), 68 (100), 67 (6).

$(CF_3COO)_2B(\mu\text{-pz*})_2B(OCOCF_3)_2$ (Hpz* = 3,5-dimethylpyrazole). Seven mL of $(CF_3CO)_2O$ were added to a mixture of 1.13 g (3.16 mmol) of $Cl_2B(\mu\text{-pz*})_2BCl_2$ and 6 mL of benzene and the mixture was refluxed with stirring for 6 h. Volatile materials were removed under vacuum at room temperature to leave 2.07 g (98%) of colorless crude product. It was recrystallized from cyclohexane to give a material of mp 239-240 °C. Anal. Calcd for $C_{18}H_{14}B_2F_{12}N_4O_8$ (mol wt 663.93): C, 32.56; H, 2.13; B, 3.26; F, 34.34; N, 8.44; O, 19.28. Found: C, 32.04; H, 2.17; B, 3.53; F, 34.36; N, 8.41.

NMR data: δ (^{1}H) 6.27 (1 H, s), 2.47 (6 H, s); δ (^{11}B) -0.8 (s, $h_{1/2}$ = 20 Hz).

$(C_6H_5)_2B(\mu\text{-pz})_2B(OCOCF_3)_2$. To a stirred solution of 0.94 g (2.5 mmol) of $(C_6H_5)_2B(\mu\text{-pz})_2BCl_2$ in 10 mL of benzene was added 2 mL (15.5 mmol) of $(CF_3CO)_2O$ and the mixture was heated to reflux for 3.5 h. After cooling to room temperature volatile material was removed under vacuum to give 1.2 g of colorless solid residue. The latter was washed with hot petroleum ether (bp 30-60 °C) and then sublimed under vacuum to give 350 mg of colorless crystals, mp 106-108 °C.. Additional product may be recovered from the petroleum ether to provide for an overall yield of 70-80%. Anal. Calcd for $C_{22}H_{16}B_2F_6N_4O_4$ (mol wt 536.00): C, 49.30; H, 3.01; B, 4.02; F, 21.27; N, 10.45; 0, 11.94. Found: C, 49.12; H, 3.07; B, 4.09; F, 21.30; N, 10.67.

NMR data: δ (^{1}H) (1 H, d, *J* = 1.3), 7.60 (1 H, unresolved), 7.26-7.24 (3 H, unresolved), 6.92-6.90 (2 H, unresolved), 6.60 (1 H, unresolved t); δ (^{11}B) 2* (1 B), -0.3 (1 B, s, $h_{1/2}$ = 20 Hz).

$(CH_3O)_2B(\mu\text{-pz})_2B(C_6H_5)_2$. To a slurry of 1.02 g (2.7 mmol) of $Cl_2B(\mu\text{-pz})_2B(C_6H_5)_2$ in 10 mL of benzene was added 5 mL of CH_3OH, 5 mL of $(C_2H_5)_3N$, and 0.2 g (5 mmol) of metallic potassium. The mixture was refluxed with stirring for 3 h. After cooling to room temperature volatile material was removed under reduced pressure. The solid residue was washed with water, dried and sublimed under vacuum to give 0.7 g (71%) of colorless crystals, mp 118-123 ^{o}C dec. Anal. Calcd for $C_{20}H_{22}B_2N_4O_2$ (mol wt 372.04): C, 64.58; H, 5.96; B, 5.81; N, 15.06; O, 8.60. Found: C, 64.47; H, 5.99; B, 5.76; N, 14.92.

NMR data: δ (^1H) 7.95 (1 H, d, J = 1.9), 7.46 (1 H, d, J = 1.7), 7.26-7.19 (3 H, m), 6.98-6.92 (2 H, m,), 6.47 (1 H, t, J = 2.4), 2.88 (3 H, s); δ (^{11}B) 3.3 (s, $h_{1/2}$ = 90 Hz) with a broad baseline indicating an additional signal at ca. 2 ppm.

$(C_2H_5)(CH_3)B(\mu\text{-pz})_2B(C_2H_5)(CH_3)$. Twelve mL of a 1.2 *M* solution of methyllithium in diethyl ether were slowly added to 1.01 g (3.5 mmol) of *cis*-$(C_2H_5)ClB(\mu\text{-pz})_2BCl(C_2H_5)$ slurried in 10 mL of ether. The mixture was heated to reflux for 2 h. After cooling to room temperature, volatile material was removed under reduced pressure. The oily residue was washed twice with 10 mL of water each and was dried under vacuum to give 350 mg of a waxy colorless product. The latter was dried over P_4O_{10} and was sublimed under vacuum to give 200 mg of crystalline material, mp 39-40 ^{o}C.

NMR data: δ (^1H) 7.62 (d, J = 2.4) + 7.61 (d, J = 2.4) (2 H), 6.42 (t, J = 2.4) + 6.39 (t, J = 2.4) (1 H), 0.62-0.60 (m) + 0.39 (t, J = 7) (5 H), 0.24 (3 H, s); δ (^{11}B) 1.2 (s, $h_{1/2}$ = 120 Hz). Mass spectrum *m/z* 231 (7), 230 (50), 229 (23), 217 (12), 216 (100), 215 (47), 214 (6), 171 (21), 170 (10).

A sublimed material obtained (65% yield) from CH_3MgBr and a mixture of *cis*- and *trans*-$(C_2H_5)ClB(\mu\text{-pz})_2B(C_2H_5)Cl$ (see above) had a mp 47-49 ^{o}C. The ^1H NMR spectrum was identical to that of the product of the preceding reaction but with different isomer ratio. In both cases the pz signals δ (^1H) 7.59/6.37 were those of the most abundant isomer, but their area ratio as compared to those of the second isomer was approximately 4:1 in the former reaction product and about 4:3 in the latter.

$(CH_3)_2B(\mu\text{-pz})_2B(C_6H_5)_2$. Five mL of a 3 *M* solution of CH_3MgBr in diethyl ether was added to a warm solution of 1.19 g (3.4 mmol) of $Cl_2B(\mu\text{-pz})_2B(C_6H_5)_2$ in 10 mL of benzene and the mixture was refluxed for 20 h. After cooling to room temperature the excess of Grignard reagent was destroyed by addition of 1 mL of C_2H_5Br, and the mixture was then treated with 30 mL of aqueous 0.01 *M* HCl. The organic phase was separated, dried over anhydrous $MgSO_4$, and volatile material was removed under vacuum. The remaining 1.15 g of solid residue was recrystallized from cyclohexane to yield 1.03 g (88%) of the desired compound, mp 139-141 ^oC.

NMR data: δ (^1H) (calibrated to internal dioxane) 7.73 (1 H, d, $J = 2.4$, of d, $J = 0.85$), 7.38 (1 H, d, $J = 2.4$, of d, $J = 0.85$), 7.23-7.19 (3 H, m), 6.98-6.94 (2 H, m), 6.39 (1 H, t, $J = 2.4$), -0.08 (3 H, s); δ (^{11}B) 1.1* (s, $h_{1/2} = 210$ Hz) with a very broad baseline suggesting an additional signal near 2 ppm.

An analogous reaction utilizing $F_2B(\mu\text{-pz})_2B(C_6H_5)_2$ gave a yield of only about 10% after 2 d of reflux.

$(CH_3)_2B(\mu\text{-pz})_2B(CH_3)_2$ was prepared in 71% yield in analogous fashion as the preceding compound using $Cl_2B(\mu\text{-pz})_2BCl_2$ (slurried in benzene) and CH_3MgBr. After sublimation the compound melted at 59-60 ^oC.

NMR data: δ (^1H) (calibrated to internal $CHCl_3$) 7.65 (2 H, d, $J = 2.3$), 6.40 (1 H, t, $J = 2.3$), 0.26 (3 H, s); δ (^{11}B) 1.2 (s, $h_{1/2} = 200$ Hz). Mass spectrum *m/z* 202 (12), 201 (61), 200 (28), 199 (8), 185 (11), 184 (7), 171 (15), 170 (8), 133 (21), 132 (13), 93 (55), 92 (13), 68 (22), 66 (41), 65 (13), 45 (10), 43 (27), 41 (100), 40 (34), 39 (37).

The same compound was obtained in 72% yield from $Cl_2B(\mu\text{-pz})_2BCl_2$ and $LiCH_3$ (6 h reflux in diethyl ether).

$(CH_3)_2B(\mu\text{-pz*})_2B(CH_3)_2$ (Hpz* = 3,5-dimethylpyrazole). To a slurry of 1.45 g (4.1 mmol) of $Cl_2B(\mu\text{-pz*})_2BCl_2$ in 10 mL of benzene was added 10 mL of a 3 *M* solution of CH_3MgBr in diethyl ether. The mixture was refluxed with stirring for 3 h and the excess of Grignard reagent was destroyed by addition of 1.5 mL of C_2H_5Br. After cooling to room temperature, the mixture was treated with 20 mL of dilute aqueous acid. The organic phase was separated, dried over anhydrous $MgSO_4$, and solvents were evaporated to leave 1.04 g (93%) of crude product, mp 142-148 ^oC. It was sublimed under vacuum to give a pure product, mp 158-160 ^oC, in 72% yield.

NMR data: δ (^1H) (calibrated to internal $CHCl_3$) 5.99 (1 H, s), 2.43 (6 H, d, $^2J = 0.64$), 0.18 (6 H, s); δ (^{11}B) 0.5 (s, $h_{1/2} = 150$ Hz).

$(C_6H_5)_2B(\mu\text{-pz*})_2B(C_6H_5)_2$ (Hpz* = 3,5-dimethylpyrazole) was prepared in analogous fashion from $Cl_2B(\mu\text{-pz*})_2BCl_2$ and C_6H_5MgBr solution. After work-up and recrystallization from toluene a 73% yield of colorless product, mp 250-252 ^oC, was obtained.

NMR data: δ (^{1}H) 7.05 (6 H, m), 6.94 (4 H, m), 5.93 (1 H, s), 1.60 (6 H, s); δ (^{11}B) 1.4 (s, $h_{1/2}$ = 300 Hz); δ (^{13}C) (proton decoupled) 148*, 147.8, 133.4, 127.1, 126.0, 111.3, 15.4.

Results and Discussion

4,4,8,8-Tetrahalopyrazaboles. B-Tetrahalogenated pyrazaboles of the type $X_2B(\mu\text{-pz*})_2BX_2$ have previously been described for Hpz* = pyrazole and X = F,[7] Cl,[7] Br;[4,7] Hpz* = 4-isopropylpyrazole, X = Cl;[7] Hpz* = 3,5-dimethylpyrazole, X = Cl[7] or Br;[3] and Hpz* = 3,5-dimethyl-4-butylpyrazole, X = Cl.[7] These compounds were readily obtained by reaction of the corresponding B-tetrahydropyrazaboles with elemental halogen. The B-tetrahydro derivatives were easily formed on interaction of trimethylamine-borane with pyrazole or C-substituted derivatives thereof.[6] These basic procedures were also utilized in the present work.

The B-tetrahydropyrazabole derived from 3-methylpyrazole has previously been reported to consist of a mixture of the 1,5- and 1,7-dimethyl isomers. This was illustrated by ^{1}H and ^{11}B NMR data and the wide melting range of the material. Although the B-tetrabromo derivative of this latter pyrazabole gave no NMR evidence for the existence of isomers, the wide melting range of the product suggested an accidental overlap of the NMR signals of the isomers.[10] The same holds true for the B-tetrachloro derivative obtained in the present study, but repeated recrystallization of the material gave a relatively sharp melting product (mp 232-235 °C) as the initial fraction, the ^{11}B NMR signal of which showed a small but clearly noticeable shift in its position from 2.0 to 2.9 ppm, suggesting an isomer enrichment.

In the present work it was observed that 3-substituted pyrazoles containing bulky substituents (*t*-butyl, phenyl) react with trimethylamine-borane to yield only one structural isomer, presumably the sterically favored 1,5-disubstituted B-tetrahydropyrazabole. This conclusion is based on the sharp melting points as well as the NMR data of the materials. Subsequent halogenation of these pyrazaboles occurred without apparent isomerization to give the sharp melting 1,5-disubstituted 4,4,8,8-tetrahalopyrazaboles.

Previously,[7] the chlorination of $H_2B(\mu\text{-pz*})_2BH_2$ with Hpz* = 4-perfluoroisopropylpyrazole has been reported to give the 4,8-dichloro derivative. This result could not be repeated; rather, chlorination gave the tetrahalo compound in good yield. On the other hand, the chlorination of $H_2B(\mu\text{-pz*})_2BH_2$ with Hpz* =

3,5-bis(trifluoromethyl)pyrazole was extremely sluggish, gave evidence for the formation of BHCl-containing species (see below), and even by extensive treatment the chlorination could not be driven to completeness.

4,4,8,8-Tetrafluoropyrazabole was previously prepared by the reaction of $(CH_3)_3N{\cdot}BF_3$ with Hpz at elevated temperatures.[7] In the present work, replacing $(CH_3)_3N{\cdot}BF_3$ by $C_2H_5NH_2{\cdot}BF_3$ gave an approximately 15% yield of the desired product after 24 h reflux in toluene; a 55% yield was obtained from the reaction of $H_2B(\mu\text{-pz})_2BH_2$ with a large excess of $(C_2H_5)_2O{\cdot}BF_3$ (12 h at room temperature). A substantial amount of $F_2B(\mu\text{-pz})_2BH_2$ was obtained as by-product in this latter process (see below).

An interesting B-tetrahalopyrazabole is the unsymmetrical species $Cl_2B(\mu\text{-pz})_2BF_2$. This latter compound was obtained by chlorination of $F_2B(\mu\text{-pz})_2BH_2$. It may be of interest for subsequent chemical transformations, since the BCl_2 group of a pyrazabole seems to be considerably more reactive than a BF_2 group (see below).

Surprisingly, ^1H and/or ^{13}C NMR spectral data of $X_2B(\mu\text{-pz*})_2BX_2$ (Hpz* = 3,5-dimethylpyrazole or 3,4,5-trimethylpyrazole, X = Br or Cl) gave evidence for the existence of conformational isomers. This feature was not apparent from either the melting point or ^{11}B NMR data. It appears that in those cases, at least in solution, both boat and chair conformation of the central B_2N_4 ring coexist.

A distinct feature of the ^{11}B NMR spectral data of the 4,4,8,8-tetrahalopyrazaboles is the sharpness of the resonance signals with $h_{1/2}$ ranging from 5-25 Hz. Moreover, the frequency range of the ^{11}B signals is rather limited and does not seem to reflect any C-substitution effect, e.g., the range of the signals of the various tetrachloro derivatives is less than 2 ppm.

Mass spectra of pyrazaboles have been studied previously[12,13] but did not include B-halogenated species. The earlier investigations resulted in several major findings. The ready loss of boron substituents was common to all pyrazaboles and competed with symmetrical cleavage of the molecule. Both processes were followed by further breakdown under electron impact. Furthermore, if the pyrazole rings were not C-substituted, rearrangement processes were identified that led to species containing B_2N_3 and B_2N_2 heterocyclic systems. However, carbon-bonded halogen, in particular, was found to prevent such rearrangement processes.

The mass spectrum of $F_2B(\mu\text{-pz})_2BF_2$ showed a strong peak for the molecular ion as well as symmetrical cleavage of the species. In contrast, the mass spectra of the B-tetrachloropyrazaboles generally lacked a molecular ion; rather, the parent peak of the spectrum was that of the molecular ion *M* minus Cl (although sometimes in low abundance). The only exceptions were $Cl_2B(\mu\text{-pz*})_2BCl_2$ with Hpz* = 3,5-dimethylpyrazole or 3,4,5-trimethylpyrazole where a very weak molecular ion could be observed (and where NMR data suggested the presence of conformational isomers).

The central B_2N_4 ring of pyrazaboles can exist in either planar (D_{2h}), chair (C_i), or boat (C_{2v}) conformation.[14] The energy differences between these conformations are, however, small[15] (although the boat conformation should be the preferred one). As noted above, the present NMR data on $X_2B(\mu\text{-pz*})_2BX_2$ (Hpz* = 3,5-dimethylpyrazole, X = Br or Cl) indicated the existence of conformational isomers which could not be separated. Hence, it appears that individual structures depend on the substitutents and packing effects. This is clearly shown by the structures of the B-tetrahalopyrazaboles. Both $Cl_2B(\mu\text{-pz})_2BCl_2$[4] and $Br_2B(\mu\text{-pz})_2BBr_2$[5] have been found to contain a planar B_2N_4 ring. This is in contrast to the structure of 4,4,8,8-tetrafluoropyrazabole which was determined in the present study. The structure of $F_2B(\mu\text{-pz})_2BF_2$ is shown in Figure 1, atomic coordinates are listed in Table II, and bond distances and angles are given in Table III.

Figure 1

Table II

Table III

As can be seen, the $F_2B(\mu\text{-pz})_2BF_2$ molecule contains the central B_2N_4 ring in boat conformation. The four N atoms of the B_2N_4 ring lay in a plane; the normal to this plane forms angles of 31.8° and 29.2°, respectively, with the normals to the planes B1-N1-N4 and B2-N2-N3. The planes of the pyrazole rings are bent out of the N_4 plane by 22.5° and 22.8°, respectively, in a butterfly arrangement. The B-F bond distances can be considered equal on the basis of the 3σ criterion, although the experimental data indicate slightly longer bonds to the F atoms in axial positions. The distances compare well with those found in other four-coordinate boron-fluorine compounds.[16-18] The $F_2B(\mu\text{-pz})_2BF_2$ molecule contains four equivalent B-N bonds with an average length of 1.560 Å. This value is larger than that found in $Cl_2B(\mu\text{-pz})_2BCl_2$[4] (1.538 Å) and $Br_2B(\mu\text{-pz})_2BBr_2$[5] (1.521 Å), suggesting an increase of the Lewis acidity of the BX_2 groups within the cited series.

4,8-Dihalopyrazaboles. The number of dihalopyrazaboles of the type XRB(μ-pz*)$_2$BXR is relatively limited, although the direct halogenation of B-tetrahydropyrazaboles can be stopped at this intermediate stage by using stoichiometric quantities[4,5] or variations[3] of reagents. However, as noted above, the chlorination of H_2B(μ-pz*)$_2BH_2$ with Hpz* = 4-perfluoroisopropylpyrazole could not be held at the reported[7] intermediate stage HClB(μ-pz*)$_2$BHCl and only the B-tetrachloro derivative was obtained in the present study. On the other hand, the chlorination of H_2B(μ-pz*)$_2BH_2$ with Hpz* = bis(trifluoromethyl)pyrazole proceeded with extreme difficulty and no clean material was obtained (even after extensive chlorination in refluxing CCl_4). The reaction progress was monitored by ^{11}B NMR spectroscopy. The unresolved triplet of the starting B-tetrahydro compound rapidly disappeared on chlorination and two new signals appeared simultaneously: A sharp singlet at δ (^{11}B) 3.8 ($h_{1/2}$ = 25 Hz) gave evidence for conversion of a BH_2 to a BCl_2 group, and a doublet at δ (^{11}B) -3.7 (J = 105 Hz) suggested the formation of a BHCl moiety. After prolonged chlorination the latter signal lost in intensity but never disappeared completely. Surprisingly, with a decrease in the -3.7 ppm signal intensity an additional sharp singlet appeared at 3.2 ppm. This observation suggests that Cl_2B(μ-pz*)$_2BCl_2$ may exist in conformational isomers. No effort was made to isolate and characterize a HClB(μ-pz*)$_2$BHCl or Cl_2B(μ-pz*)$_2$BHCl species.

The only reasonably well characterized 4,8-dihalopyrazaboles, RXB(μ-pz*)$_2$BRX, which have been reported in the literature are those with Hpz* = 4-chloropyrazole, R = H and X = Br;[4] and Hpz* = 3,5-dimethylpyrazole, R = H and X = Br.[3] In addition, the species with Hpz* = pyrazole, R = C_2H_5 and X = Cl was recently obtained from the reaction of RB(μ-pz)$_2$(μ-OBRO)BR with $SOCl_2$.[9]

In the present study it was observed that 4,8-dihalopyrazaboles can be obtained from the reaction of an organyldihaloborane, RBX_2, with an equimolar amount of N-trimethylsilylpyrazole. The reaction proceeded readily according to eq (1) to give an essentially quantitative yield of the desired 4,8-dihalopyrazabole. However, in

$$2\,RBX_2 + 2\,(CH_3)_3Si(pz) \longrightarrow RXB(\mu\text{-}pz)_2BRX + 2\,(CH_3)_3SiCl \qquad (1)$$

contrast to the cited reaction of RB(μ-pz)$_2$(μ-OBRO)BR with $SOCl_2$, which leads to the pure *cis* isomer (see below), reaction according to eq (1) gave a mixture of *cis* and *trans* isomers which could not be separated completely. It was, however, possible to assign the ^1H NMR spectra of the individual species with R = C_2H_5 and X

= Cl, and it was also established that the *trans* isomer has a considerably higher melting point than the *cis* species. This latter observation is in consonance with the findings on the two isomers of $(C_2H_5)(pz)B(\mu\text{-}pz)_2B(C_2H_5)(pz)$, both of which have been characterized by X-ray crystallographic analysis.[19] In any case, separation is not necessary if the 4,8-dihalopyrazabole is used in subsequent reactions, e.g., with organometallics.

The structure of the pyrazabole $HBrB(\mu\text{-}pz^*)_2BHBr$ (Hpz* = 4-chloropyrazole) has previously been shown to involve a central B_2N_4 ring in boat conformation with the two Br atoms in *cis* arrangement in axial positions.[4] In the present study, the structure of $(C_2H_5)ClB(\mu\text{-}pz)_2B(C_2H_5)Cl$ (obtained from the chlorination of $C_2B_5B(\mu\text{-}pz)_2(\mu\text{-}OBC_2H_5O)BC_2H_5$ with $SOCl_2$[9]) has been determined. The molecular structure of the species is depicted in Figure 2, atomic coordinates are listed in Table IV, and bond distances and angles are given in Table V.

Figure 2

Table IV

Table V

The $(C_2H_5)ClB(\mu\text{-}pz)_2BCl(C_2H_5)$ molecule contains the central B_2N_4 ring in chair conformation with the two Cl atoms in *cis* arrangement and in axial positions, and a crystallographically imposed two-fold axis. The two B-N bonds at each boron atom are nonequivalent, the bond distances differ only slightly but nevertheless significantly. All other bond lengths are in the expected ranges. The four N atoms of the pyrazabole ring lie almost in a plane with deviations of 0.7 pm from the best plane comprising these four atoms. The pyrazole rings are planar. A θ_1 angle of 40.6° was found for the two BN_2 planes in the molecule, and the roof angle θ_2 for the two pyrazole rings was found to be 24.4°. Hence, the geometry of this particular pyrazabole closely resembles that of $H_2B(\mu\text{-}pz^*)_2BH_2$ with Hpz* = 3,5-dimethylpyrazole.[14] It should be noted that the best plane incorporating Cl1-B1-C4-C5 stands almost perpendicular (88.6°) to the B1-N1-N2$^+$ or the N1-N2-N1$^+$-N2$^+$ planes. Consequently, Cl···Cl contacts are much less important in the packing of the molecule in the lattice than is the case for $Cl_2B(\mu\text{-}pz)_2BCl_2$.

4,4-Dihalopyrazaboles. 4,4-Dihalopyrazaboles of the type $R_2B(\mu\text{-}pz^*)_2BX_2$ are known for Hpz* = pyrazole, R = H and X = F,[8] R = C_2H_5 and X = Cl,[8] and R = C_6H_5 and X = Br,[3] and Hpz* = 3,5-dimethylpyrazole, R =

C_2H_5 and X = Br.[3] They are usually prepared by forming an unsymmetrical 4,4-dihydropyrazabole, $R_2B(\mu\text{-}pz^*)_2BH_2$ (from $K[H_2B(pz)_2]$ by reaction with R_2BX where X is a readily leaving group[3,8]), which is subsequently halogenated. Alternatively, $K[R_2B(pz)_2]$ may be reacted with $(C_2H_5)_2O{\cdot}BF_3$ to give $R_2B(\mu\text{-}pz)_2BF_2$.[8] In the present work, this latter method was used to obtain $F_2B(\mu\text{-}pz)_2B(C_6H_5)_2$ whereas the former procedure was used for the synthesis of $Cl_2B(\mu\text{-}pz)_2B(C_6H_5)_2$.

The crystal and molecular structure of $Cl_2B(\mu\text{-}pz)_2B(C_6H_5)_2$ was also determined in the present study. The molecular structure of the species is depicted in Figure 3, atomic coordinates for the non-hydrogen atoms are listed in Table VI, and selected bond distances and angles are given in Table VII.

Figure 3

Table VI

Table VII

The central B_2N_4 ring of the molecule exists in boat conformation. Both B-Cl bonds are of equal length (within standard deviations) despite the fact that one Cl atom is in axial and the other one in equatorial position; the same holds true for the two B-C bonds. However, the N-B(Cl_2) bonds are significantly shorter than the N-B(C_2) bonds. This feature signals the difference in acceptor behavior of the BCl_2 group versus the $B(C_6H_5)_2$ unit which results from the differing inductive effects of Cl and C_6H_5, respectively. The observed B-N bond distances compare favorably with those of related molecules, e.g., $Cl_2B(\mu\text{-}pz)_2BCl_2$.[4]

The larger steric requirement of C_6H_5 versus Cl results in larger deviations from tetrahedral angles at B2. In addition, this causes the N4-B2-N2 plane to be tilted against the N1-N2-N3-N4 plane by an angle θ_1 of 30.7°, while θ_1 at B1 is only 21.3°. The roof angle θ_2 formed by the planes of the two pz units is 26.8°, i.e., the butterfly arrangement of the two bridging pz groups is fairly flat as compared to that in other boat-shaped pyrazaboles.[14] This is obviously a consequence of the small θ_1 at B1.

In contrast to $Cl_2B(\mu\text{-}pz)_2BCl_2$, which contains a planar B_2N_4 ring and where the molecules are arranged in chain-type formation via close intermolecular Cl···Cl contacts, the molecules of $Cl_2B(\mu\text{-}pz)_2B(C_6H_5)_2$ are found in pairs. The Cl···Cl distance (3.899 Å) is slightly larger than that expected for van der Waals interaction but is nevertheless short enough to suggest a pairing effect. However, the crystal packing cannot be optimized due to the steric demands exerted by the phenyl groups.

As noted above, in the present study $F_2B(\mu\text{-pz})_2BF_2$ was obtained from the reaction of $H_2B(\mu\text{-pz})_2BH_2$ with $(C_2H_5)_2O{\cdot}BF_3$. This procedure always gave substantial quantities of $F_2B(\mu\text{-pz})_2BH_2$ as a by-product. This observation suggests that, in contrast to the chlorination and bromination of B-tetrahydropyrazaboles, which have been shown to proceed via 4,8-dihalogenated species,[4,7] the cited fluorination occurs via a 4,4-dihalogenated species. Indeed, when the (slow!) reaction of $H_2B(\mu\text{-pz})_2BH_2$ with either BF_3 or $(C_2H_5)_2O{\cdot}BF_3$ was followed by ^{11}B NMR spectroscopy, no signs for the formation of an intermediate BHF grouping were observed. The formation of $F_2B(\mu\text{-pz})_2BF_2$ can essentially be excluded by performing the reaction in ether and using a 1:1.2 molar ratio of $H_2B(\mu\text{-pz})_2BH_2$ and $(C_2H_5)_2{\cdot}BF_3$. However, it was extremely difficult to separate (by fractional sublimation under vacuum) unreacted pyrazabole from the 4,4-difluoro compound and the outlined procedure appears to be more suitable for preparative purposes. It is likely that the fluorination of pyrazabole in the cited reaction proceeds via a dissociative step whereby the B_2N_4 ring is opened at one B-N linkage to give $H_2B(\mu\text{-pz})BH_2(pz)$ as the reactive species. The latter interacts with the $(C_2H_5)_2O{\cdot}BF_3$ at the terminal pz site and addition of BF_3 occurs with displacement of diethyl ether to form a $H_2B(\mu\text{-pz})BH_2(\mu\text{-pz})BF_3$ intermediate. The B_2N_4 ring is then regenerated with the release of "H_2BF" to yield the observed 4,4-difluoropyrazabole. Such a mechanism would be in accord with the slow rate as compared to the reaction with BCl_3 or BBr_3 as Lewis acid. The equilibrium concentration of the non-cyclic form of pyrazabole would certainly be very low and, consequently, the substitution process is slow.

The mass spectrum of $F_2B(\mu\text{-pz})_2BH_2$ shows the expected symmetrical cleavage of the molecule under electron impact. However, the loss of fluorine from the parent is dominant and there are indications for rearrangement processes of the parent to yield B_2N_3 (*m/z* 130) and B_2N_2 (*m/z* 104) ring systems. This latter aspect is further substantiated by a metastable transition $158^+ \longrightarrow 131^+ + 27$. A weak molecular ion was observed in the mass spectrum of $F_2B(\mu\text{-pz})_2B(C_6H_5)_2$ and the base peak corresponded to a loss of a phenyl group from the molecular species.

Additional B-Halogenated Pyrazaboles. In addition to the three types of B-halogenated pyrazaboles as discusssed above, a few other species are known. Four B-monobromo pyrazaboles of the type BrRB(μ-pz*)$_2$BBR$_2$ (Hpz* = pyrazole, R = H,[4,5] C_2H_5,[4] SCH_3;[4] Hpz* = 4-bromopyrazole, R = H[4]) have been described and Br$_2$B(μ-pz)$_2$BHBr has been identified in mixture.[4,5]

The results of the chlorination of H$_2$B(μ-pz*)$_2$BH$_2$ with Hpz* = 3,5-bis(trifluoromethyl)pyrazole as outlined above sugges that Cl$_2$B(μ-pz*)$_2$BHCl exists although no effort was made to isolate and characterize the species. Furthermore, in the present work it was observed that the halogenation of $(C_6H_5)_2$B(μ-pz)$_2$BH$_2$ with elemental bromine proceeded stepwise and the intermediate $(C_6H_5)_2$B(μ-pz)$_2$BHBr was readily identified by its characteristic NMR data, i.e., δ (^{1}H) 8.50 (1 H, d, *J* = 2.1), 8.08 (1 H, d, *J* = 2.6), 6.52 (1 H, t, *J* = 2.4); δ (^{11}B) (for the BHBr group) -5.9 (d, *J* = 114 Hz). However, the species could not be separated from accompanying $(C_6H_5)_2$B(μ-pz)$_2$BBr$_2$. Reaction of $(C_6H_5)_2$B(μ-pz)$_2$BH$_2$ with one third molar equivalent of BBr$_3$ also gave a product mixture, mp 178-182 °C (dec), consisting largely of the desired $(C_6H_5)_2$B(μ-pz)$_2$BHBr but no pure material could be isolated.

Chemical Behavior of B-Halogenated Pyrazaboles. Chemical transformations at the boron site of B-halogenated pyrazaboles have been studied only sparingly. Until most recently, only the conversion of Br$_2$B(μ-pz*)$_2$BBr$_2$ (Hpz* = 3,5-dimethylpyrazole) with Kpz to yield (pz)$_2$B(μ-pz*)$_2$B(pz)$_2$ had been reported.[3] A few reactions of (C_2H_5)ClB(μ-pz)$_2$B(C_2H_5)Cl have since been studied[9] and most seem to be, in principle, applicable to other B-halogenated pyrazaboles. On the other hand, there is clear evidence that the reactivity of B-halogenated pyrazaboles is strongly influenced by substituent effects. For example, the reaction of (C_2H_5)ClB(μ-pz)$_2$B(C_2H_5)Cl with $(CX_3CO)_2O$ with X = H or F proceeded smoothly to give the desired $(C_2H_5)(CX_3COO)$B(μ-pz)$_2$B$(C_2H_5)(OCOCX_3)$.[9] Similarly, the reaction of $(CF_3CO)_2O$ with $(C_6H_5)_2$B(μ-pz)$_2$BCl$_2$ gave $(C_6H_5)_2$B(μ-pz)$_2$B$(OCOCF_3)_2$. In contrast, reaction of Cl$_2$B(μ-pz)$_2$BCl$_2$ with $(CF_3CO)_2O$ stopped at the stage (CF_3COO)ClB(μ-pz)$_2$B$(OCOCF_3)$Cl (and no reaction with $(CH_3CO)_2O$ was observed) but, under essentially identical conditions, Cl$_2$B(μ-pz*)$_2$BCl$_2$ with Hpz* = 3,5-dimethylpyrazole gave the desired $(CF_3COO)_2$B(μ-pz*)$_2$B$(OCOCF_3)_2$.

The pyrazabole $(C_2H_5)ClB(\mu\text{-pz})_2B(C_2H_5)Cl$ has previously been converted to the 4,8-dialkoxy derivative by reaction with alkali metal alkoxide (low yield) or with alcohol in the presence of a tertiary amine as hydrogen chloride acceptor (high yield).[9] In contrast, reaction of $Cl_2B(\mu\text{-pz})_2BCl_2$ with alcohol in the presence of a tertiary amine led to complete breakdown of the pyrazabole system; 96% of the pz content of the pyrazabole were recovered as Hpz. On the other hand, no reaction was observed when $(C_6H_5)_2B(\mu\text{-pz})_2BCl_2$ was treated with alcohol in the presence of a tertiary amine, some conversion to $(C_6H_5)_2B(\mu\text{-pz})_2B(OCH_3)_2$ occurred with potassium methoxide in methanol, but an essentially quantitative yield of the dimethoxypyrazabole was obtained using a combination of the two methods.

B-Halogenated pyrazaboles have also been found to react readily with organometallics. For example, on treatment of $Cl_2B(\mu\text{-pz*})_2BCl_2$ with either lithium alkyl or Grignard reagents the expected B-tetraorganyl pyrazaboles were obtained, and reaction of *cis*-$(C_2H_5)ClB(\mu\text{-pz})_2BCl(C_2H_5)$ with $LiCH_3$ gave the species $(C_2H_5)(CH_3)B(\mu\text{-pz})_2B(C_2H_5)(CH_3)$. However, during this latter process some isomerization occurred to give a mixture of *cis* and *trans* species, as was clearly evident from the ^1H NMR spectroscopic data. The cited compound is the first known pyrazabole where two different hydrocarbon substituents are bonded to the same boron atom. Reaction of $(C_6H_5)_2B(\mu\text{-pz})_2BCl_2$ with either lithium alkyl or Grignard reagents gave access to pyrazaboles where the two boron atoms have different hydrocarbon substituents. (Only one such compound had previously been described but was obtained by a quite different procedure.[3]) It is of interest to note that the reaction of $(C_6H_5)_2B(\mu\text{-pz})_2BF_2$ with CH_3MgBr was found to proceed much more sluggish than that of the 4,4-dichloropyrazabole, and the same held true for the use of $X_2B(\mu\text{-pz})_2BX_2$ with X = F versus Cl in order to prepare $(CH_3)_2B(\mu\text{-pz})_2B(CH_3)_2$.

These representative reactions illustrate the versatility of B-halogenated pyrazaboles for the preparation of novel types of B-substituted pyrazaboles.

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Supplementary Material Available: Anisotropic thermal parameter and structure factor tables for 4,4,8,8-tetrafluoropyrazabole (9 pages), 4,8-dichloro-4,8-diethylpyrazabole (6 pages) and 4,4-dichloro-8,8-diphenylpyrazabole (17 pages including complete listing of bond distances and angles and hydrogen atom coordinates). Ordering information is given on any current masthead page.

FOOTNOTES AND REFERENCES

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(1) Boron-Nitrogen Compounds. 113 (K.N.). Part 112: Reference 9.

(2) Niedenzu, K.; Trofimenko, S. *Topics Current Chem.* **1986**, *131*, 1-37.

(3) Layton, W. J.; Niedenzu, K.; Niedenzu, P. M.; Trofimenko, S. *Inorg. Chem.* **1985**, *24*, 1454-1457.

(4) Niedenzu, K.; Nöth, H. *Chem. Ber.* **1983**, *116*, 1132-1153.

(5) Hanecker, E.; Hodgkins, T. G.; Niedenzu, K.; Nöth, H. *Inorg. Chem.* **1985**, *24*, 459-462.

(6) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3165-3170.

(7) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 4948-4952.

(8) Trofimenko, S. *Inorg. Chem.* **1969**, *8*, 1714-1716.

(9) Hsu, L.-Y.; Mariategui, F. J.; Niedenzu, K.; Shore, S. G. *Inorg. Chem.* **1987**, in press.

(10) Niedenzu, K.; Niedenzu, P. M.; Warner, K. *Inorg. Chem.* **1985**, *24*, 1604-1606.

(11) Niedenzu, K.; Niedenzu, P. M. *Inorg. Chem.* **1984**, *23*, 3713-3716.

(12) May, C. E.; Niedenzu, K.; Trofimenko, S. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1976**, *31B*, 1662-1666.

(13) May, C. E.; Niedenzu, K.; Trofimenko, S. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 220-223.

(14) Brock, C. P.; Niedenzu, K.; Hanecker, E.; Nöth, H. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 1458-1463.

(15) Companion, A. L.; Liu, F.; Niedenzu, K. *Inorg. Chem.* **1985**, *24*, 1738-1740.

(16) Geller, S.; Hoard, J. L. *Acta Crystallogr.* **1950**, *3*, 121-129.

(17) Hoard, J. C.; Geller, S.; Owens, T. B. *Acta Crystallogr.* **1951**, *4*, 405-407.

(18) Hess, H. *Acta Crystallogr., Sect. B* **1969**, *B25*, 2338-2341.

(19) Bielawski, J.; Das, M. K.; Hanecker, E.; Niedenzu, K.; Nöth, H. *Inorg. Chem.* 1986, in press.

Table I. Summary of Crystallographic Data and Data Collection Procedures[a]

compound	$F_2B(\mu\text{-pz})_2BF_2$	$(C_2H_5)ClB(\mu\text{-pz})_2BCl(C_2H_5)$	$Cl_2B(\mu\text{-pz})_2B(C_6H_5)_2$
formula	$C_6H_5B_2F_4N_4$	$C_{10}H_{16}B_2Cl_2N_4$	$C_{18}H_{16}B_2Cl_2N_4$
fw	231.8	284.8	380.9
cryst size, mm	0.3 x 0.2 x 0.25	0.2 x 0.2 x 0.3	0.5 x 0.5 x 0.4
space group	$P2_1/c$	Pbcn	Pbca
a, Å	7.626(1)	12.344(8)	7.940(3)
b, Å	19.729(5)	7.794(6)	15.270(4)
c, Å	7.213(3)	15.091(10)	31.064(9)
α, deg	90	90	90
β, deg	117.64(28)	90	90
γ, deg	90	90	90
Z	4	4	8
V, Å^3	962.6(6)	1451.9	3767.2
d_{calcd}, g/cm^3	1.600	1.303	1.372
μ, cm^{-1}	1.47	4.33	3.52
$F(000)$	463.87	591.87	1567.7
2θ, deg	2-48	2-50	2-50
scan speed, deg/min	1-29.3	2-29.3	2.9-29.3
scan width, deg	0.8	0.8	1.4
total no. of reflcns	1698	5767	3742
no. of unique reflcns ($I \geq 3\sigma(I)$)	1263	817[b]	2271
no. of variables used	163	114	283
res electron density (e/Å^3)	0.197	0.371	0.304
R	0.0503	0.047	0.0586
R_w	0.0554	0.032	0.0529
g	0.00035	0	0.0003

[a] In this and subsequent tables esd's are given in parentheses. [b] Intensity averaged reflections.

Table II. Atomic Coordinates (x 10^4) and Equivalent Isotropic Temperature Factors ($Å^2$ x 10^3) for Non-Hydrogen Atoms (isotropic fixed U for hydrogen atoms) for $F_2B(\mu\text{-pz})_2BF_2$

atom	x	y	z	U[a]
N1	7798(3)	4257(1)	1188(3)	45(1)
N2	6090(3)	3971(1)	945(3)	45(1)
N3	7057(3)	2876(1)	9(3)	43(1)
N4	8788(3)	3154(1)	289(3)	47(1)
C4	7306(4)	2205(2)	168(5)	53(1)
C6	10059(4)	2644(2)	610(4)	56(1)
C5	9169(4)	2043(2)	529(5)	57(1)
C3	5409(4)	4351(2)	2022(4)	54(1)
C1	8161(4)	4805(2)	2403(4)	55(1)
C2	6673(5)	4878(2)	2959(5)	61(1)
B1	9042(5)	3938(2)	204(6)	57(2)
B2	5229(4)	3329(2)	-426(5)	50(1)
F1	10975(3)	4106(1)	1422(4)	104(1)
F2	8343(4)	4154(1)	-1816(3)	97(1)
F3	4052(3)	2994(1)	204(4)	86(1)
F4	4262(3)	3493(1)	-2505(3)	87(1)
H1	9242(42)	5095(15)	2719(43)	60
H2	6623(37)	5234(15)	3899(42)	60
H3	4239(37)	4267(14)	2057(43)	60
H4	6534(37)	2001(13)	9(41)	60
H5	9747(42)	1636(15)	728(44)	60
H6	11178(39)	2713(13)	722(44)	60

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table III. Bond Distances (Å) and Selected Bond Angles (deg) of $F_2B(\mu\text{-pz})_2BF_2$

atoms	distance	atoms	distance
B1-F1	1.363(4)	B2-F3	1.352(5)
B1-F2	1.367(5)	B2-F4	1.368(4)
B1-N1	1.558(5)	B2-N2	1.554(4)
B1-N4	1.565(4)	B2-N3	1.561(4)
N1-N2	1.355(3)	N3-N4	1.356(3)
N1-C1	1.338(4)	N3-C4	1.335(4)
C1-C2	1.377(6)	C4-C5	1.360(5)
C2-C3	1.366(4)	C5-C6	1.354(4)
C3-N2	1.345(4)	C6-N4	1.341(4)
C1-H1	0.941(31)	C4-H4	0.678(28)
C2-H2	0.989(32)	C5-H5	0.895(30)
C3-H3	0.920(32)	C6-H6	0.831(32)

(continued)

Table III. (continued)

atoms	angles	atoms	angles
F1-B1-F2	112.5(4)	F3-B2-F4	112.3(2)
N1-B1-F1	108.4(3)	N2-B2-F3	109.6(3)
N1-B1-F2	110.0(3)	N2-B2-F4	111.0(2)
N2-N1-B1	121.8(2)	N4-N3-B2	121.2(2)
N3-N4-B1	121.6(20	N1-N2-B2	121.3(3)
N1-B1-N4	105.6(3)	N2-B2-N3	105.3(2)
N4-B1-F1	109.4(2)	N3-B2-F3	109.0(3)
N4-B1-F2	110.8(3)	N3-B2-F4	109.5(3)
C1-N1-B1	129.8(3)	C3-N2-B2	131.2(3)
C6-N4-B1	130.9(3)	C4-N3-B2	131.5(2)
N1-N2-C3	107.5(2)	N4-N3-C4	107.3(2)
N2-N1-C1	108.4(3)	N3-N4-C6	107.5(2)
N1-C1-C2	109.1(3)	N3-C4-C5	110.1(3)
C1-C2-C3	105.4(3)	C4-C5-C6	105.2(3)
C2-C3-N2	109.6(3)	C5-C6-N4	109.9(3)

Table IV. Atomic Coordinates (x 10^4) and Equivalent Isotropic Temperature Factors (Å^2 x 10^3) for Non-Hydrogen Atoms (isotropic thermal parameters for hydrogen atoms) for $(C_2H_5)ClB(\mu\text{-}pz)_2BCl(C_2H_5)$

	x	y	z	U^a
Cl1	4344(1)	-1380(1)	1375(1)	57(1)
B1	4431(3)	1027(5)	1582(2)	43(1)
N1	3850(2)	1431(3)	2473(1)	42(1)
N2	4358(2)	1448(3)	3281(1)	40(1)
C1	2804(2)	1778(4)	2615(2)	54(1)
C2	2612(3)	2012(5)	2497(2)	57(1)
C3	3604(3)	1793(5)	3897(2)	51(1)
C4	3913(3)	2077(6)	787(2)	55(1)
C5	3946(4)	4005(6)	863(3)	81(2)
H1	2314(22)	1883(37)	2157(16)	55(10)
H2	1905(23)	2258(36)	3765(17)	62(10)
H3	3793(20)	1875(36)	4523(18)	57(9)
H4a	4243(18)	1691(33)	241(17)	44(8)
H4b	3187(22)	1695(36)	719(17)	54(10)
H5a	4736(29)	4461(49)	916(23)	111(16)
H5c	3628(27)	4619(50)	400(22)	113(15)

^{a}Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table V. Bond Distances (Å) and Angles (deg) of $(C_2H_5)ClB(\mu\text{-pz})_2BCl(C_2H_5)$

atoms	distance	atoms	distance
Cl1-B1	1.904(4)	B1-N1	1.557(4)
B1-C4	1.587(5)	B1-N2a	1.544(4)
N1-N2	1.371(3)	N1-C1	1.336(3)
N2-C3	1.343(4)	N2-B1a	1.544(4)
C1-C2	1.364(5)	C4-C5	1.508(6)
C2-C3	1.377(5)	C4-H4a	0.967(25)
C1-H1	0.922(26)	C4-H4b	0.949(27)
C2-H2	0.981(29)	C5-H5a	0.972(35)
C3-H3	0.975(27)	C5-H5b	1.041(36)
		C5-H5c	0.934(35)

(continued)

Table V. (continued)

atoms	angles	atoms	angles
Cl1-B1-N1	108.3(2)	Cl1-B1-C4	111.2(2)
N1-B1-C4	111.3(3)	Cl1-B1-N2a	106.6(2)
N1-B1-N2a	106.7(2)	C4-B1-N2a	112.5(3)
B1-N1-N2	124.0(2)	B1-N2-C1	128.6(2)
N2-N1-C1	107.3(2)	N1-N2-C3	107.5(2)
N1-N2-B1a	124.0(2)	C3-N2-B1a	128.3(2)
N1-C1-C2	110.5(3)	N1-C1-H1	122.2(16)
C2-C1-H1	127.2(16)	C1-C2-C3	104.9(3)
C1-C2-H2	125.7(16)	C3-C2-H2	129.4(16)
N2-C3-C2	109.7(3)	N2-C3-H3	121.2(15)
C2-C3-H3	129.1(15)	B1-C4-C5	116.5(3)
B1-C4-H4a	108.2(15)	C5-C4-H4a	111.3(15)
B1-C4-H4b	107.5(16)	C5-C4-H4b	110.3(17)
H4a-C4-H4b	102.0(210	C4-C5-H5a	110.9(23)
C4-C5-H5b	111.8(22)	H5a-C5-H5b	109.5(29)
C4-C5-H5c	116.2(24)	H5a-C5-H5c	101.7(30)
H5b-C5-H5c	106.1(30)		

Table VI. Atomic Coordinates (x 10^4) and Equivalent Isotropic Temperature Factors (Å^2 x 10^3) for Non-Hydrogen Atoms for $Cl_2B(\mu\text{-}pz)_2B(C_6H_5)_2$

atom	x	y	z	U^a
Cl1	2966(2)	607(1)	4814(1)	78(1)
Cl2	1068(1)	1500(1)	5527(1)	59(1)
B1	2899(5)	787(3)	5405(1)	44(1)
N1	2707(4)	-94(2)	5629(1)	41(1)
N2	3472(4)	-271(2)	6015(1)	40(1)
C1	1823(5)	-810(3)	5516(2)	62(2)
C2	2010(5)	-1438(3)	5821(1)	65(2)
C3	3055(5)	-1083(3)	6125(1)	55(1)
N3	4552(4)	1213(2)	5547(1)	41(1)
N4	5293(3)	1027(2)	5933(1)	38(1)
C4	5512(5)	1821(3)	5346(1)	57(1)
C5	6854(5)	2025(3)	5597(1)	61(2)
C6	6696(4)	1518(2)	5961(1)	51(1)
B2	4410(5)	444(3)	6290(1)	36(1)
C10	3084(4)	1034(2)	6554(1)	38(1)
C11	1417(5)	778(3)	6630(1)	50(1)
C12	316(5)	1280(3)	6875(1)	64(2)
C13	836(6)	2064(3)	7045(1)	68(2)
C14	2468(6)	2335(3)	6980(1)	64(2)
C15	3566(5)	1830(2)	6741(1)	50(1)
C20	5812(4)	-40(2)	6578(1)	38(1)
C21	7015(5)	585(3)	6392(1)	56(1)

(continued)

Table VI. (continued)

atom	x	y	z	U^a
C22	8177(5)	-1054(3)	6629(1)	62(2)
C23	8168(4)	-986(3)	7075(1)	61(2)
C24	7022(5)	-453(3)	7266(1)	60(2)
C25	5852(5)	14(3)	7026(1)	49(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table VII. Selected Bond Distances (Å) and Bond Angles (deg) of $Cl_2B(\mu\text{-}pz)_2B(C_6H_5)_2$

atoms	distance	atoms	distance
B1-Cl1	1.857(4)	B2-N4	1.586(5)
B1-Cl2	1.855(4)	N1-N2	1.369(4)
B1-N1	1.523(5)	N3-N4	1.365(4)
B1-N3	1.530(5)	B2-C10	1.609(5)
B2-N2	1.575(5)	B2-C20	1.608(5)

atoms	angle	atoms	angle
Cl1-B1-Cl2	108.2(2)	C10-B2-C20	115.3(3)
N1-B1-N3	109.2(3)	N2-B2-N4	102.6(2)
Cl1-B1-N1	108.9(3)	C10-B2-N2	110.8(3)
Cl1-B1-N3	109.0(2)	C10-B2-N4	109.3(3)
Cl2-B1-N1	110.2(2)	C20-B2-N2	108.1(3)
Cl2-B1-N3	111.3(3)	C20-B2-N4	109.9(3)

CAPTIONS FOR FIGURES

Figure 1. ORTEP plot of 4,4,8,8-tetrafluoropyrazabole.

Figure 2. ORTEP plot of *cis*-4,8-dichloro-4,8-diethylpyrazabole.

Figure 3. ORTEP plot of 4,4-dichloro-8,8-diphenylpyrazabole.

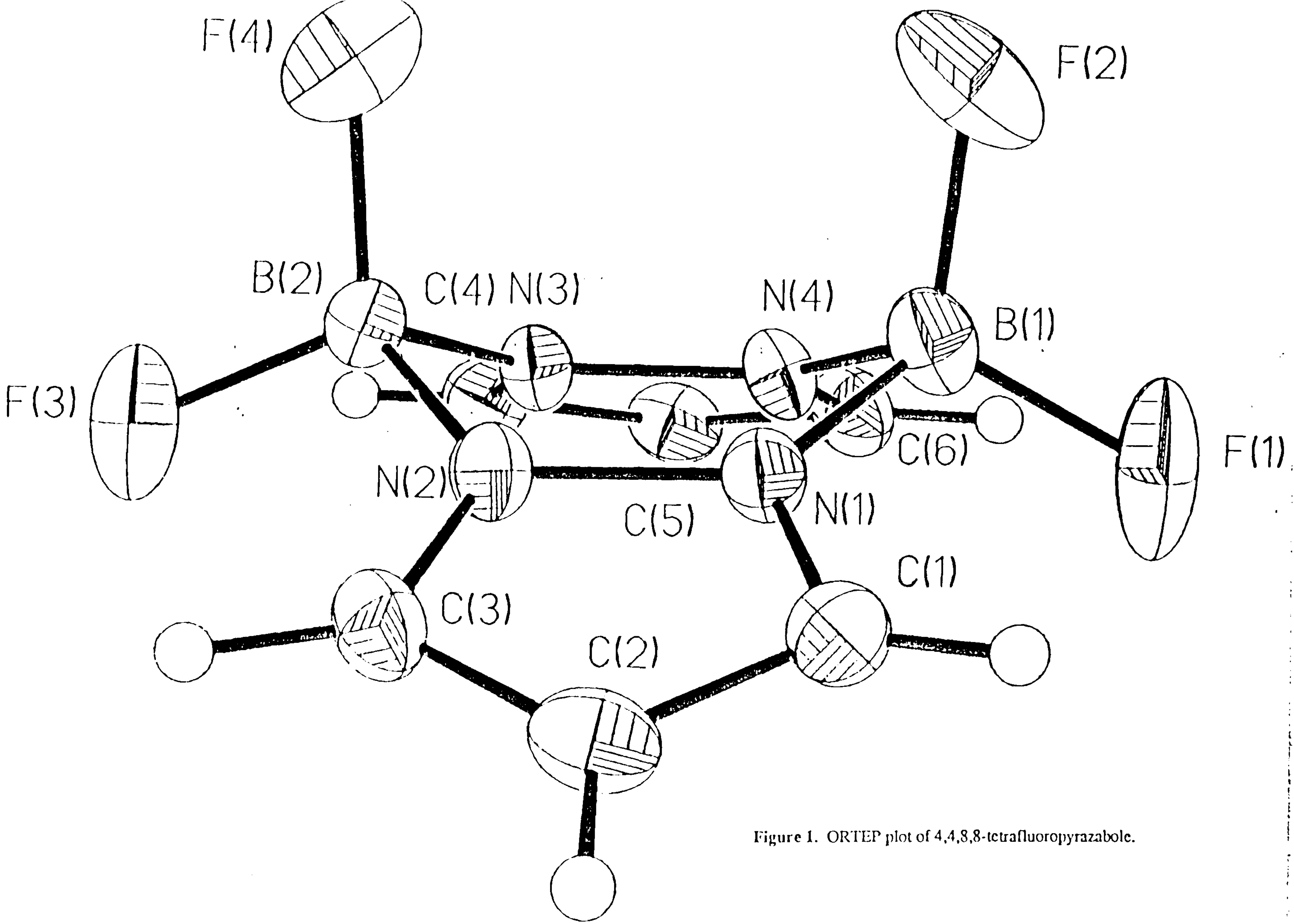


Figure 1. ORTEP plot of 4,4,8,8-tetrafluoropyrazabole.

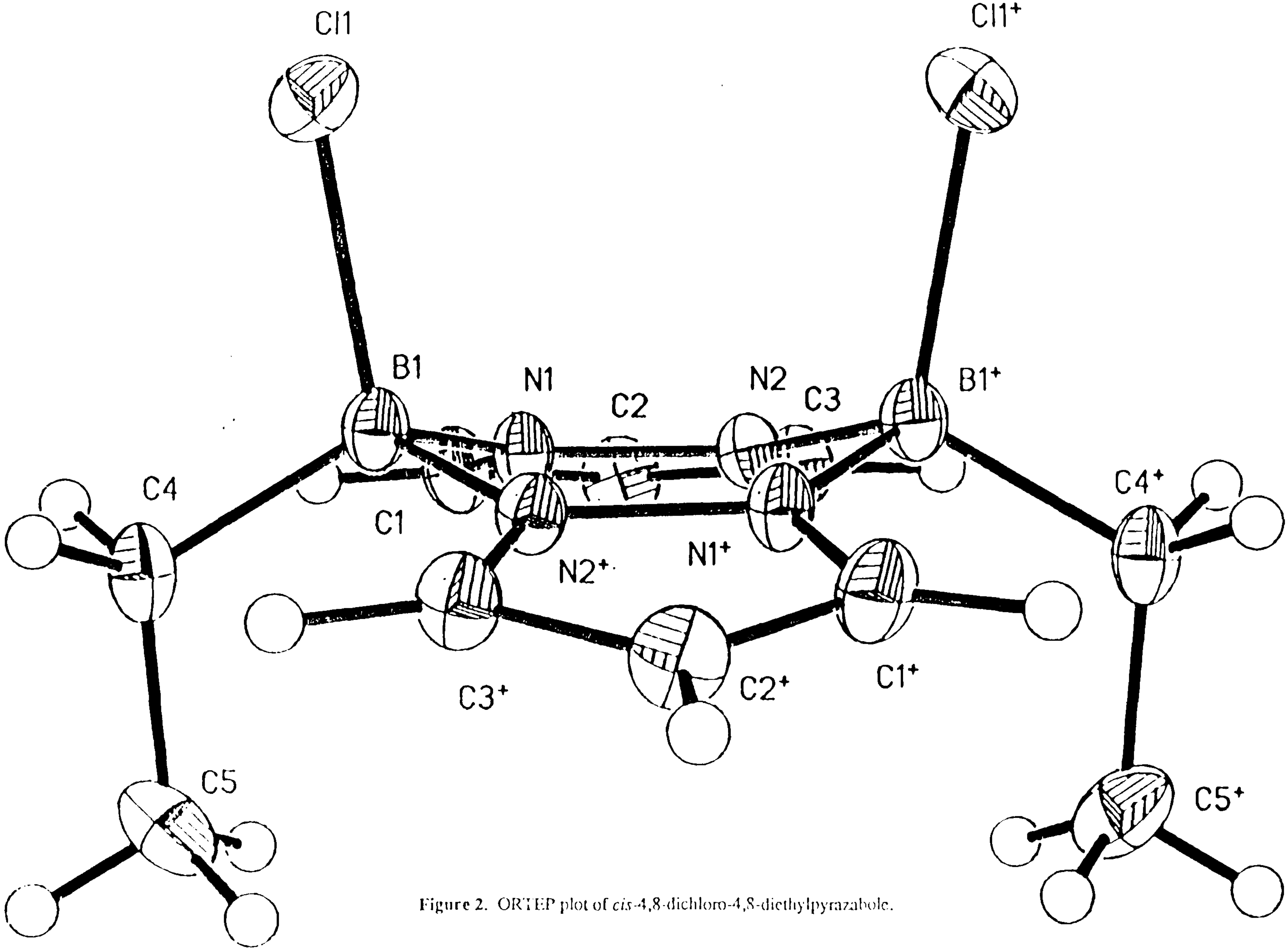
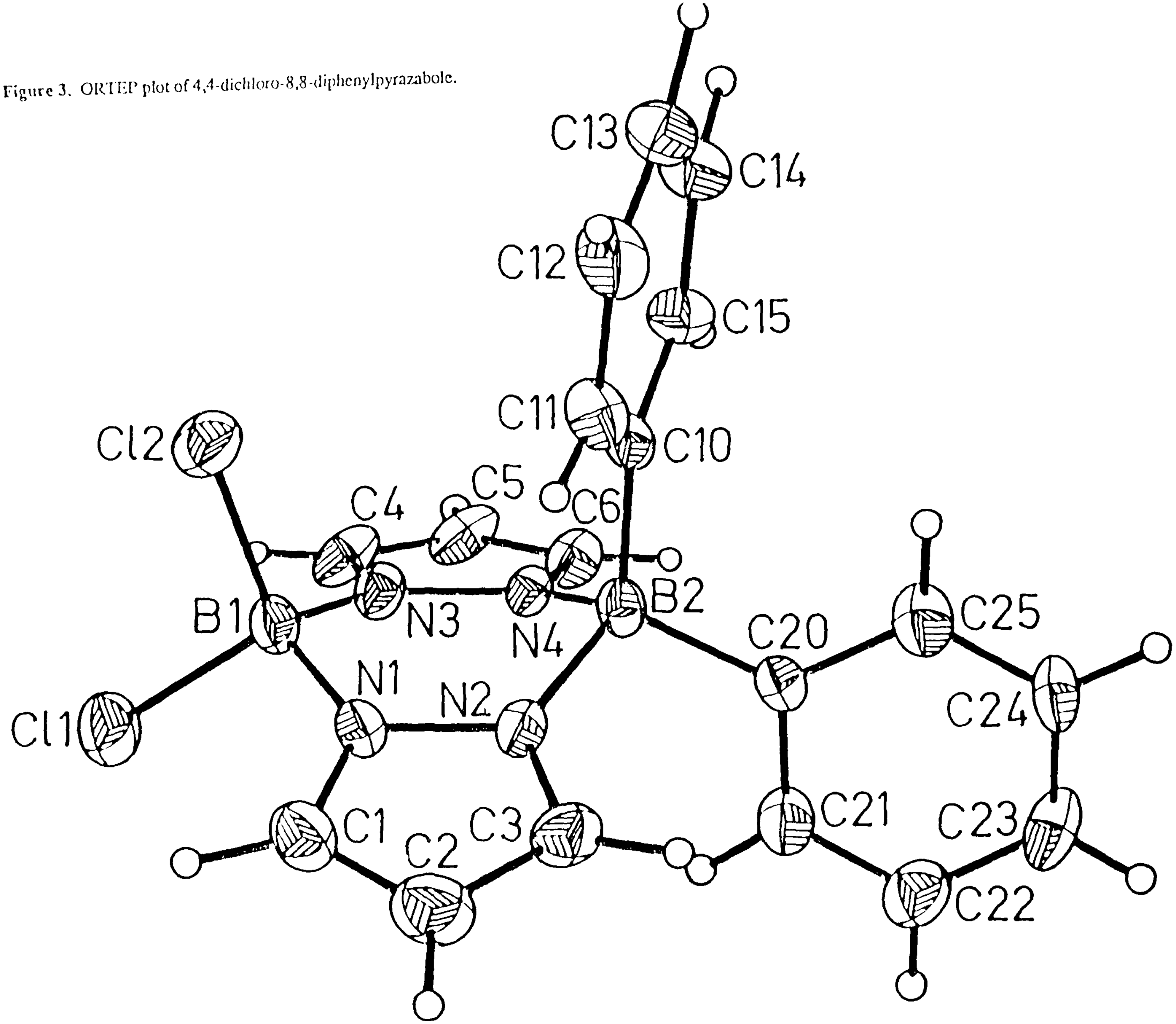


Figure 2. ORTEP plot of *cis*-4,8-dichloro-4,8-diethylpyrazabole.

Figure 3. ORTEP plot of 4,4-dichloro-8,8-diphenylpyrazabole.



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