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Pyrazaboles of the Type $RR'B(\mu\text{-pz})_2BRR'$ and Related Studies[1]

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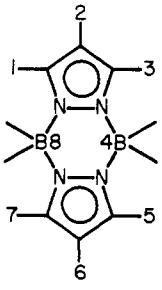
Boron-bonded hydrogen or organylthio groups of pyrazaboles, $R_2B(\mu\text{-pz}^*)_2BR_2$ (Hpz* = pyrazole or C-substituted derivatives thereof), can be replaced by reaction with either $(C_2H_5)_2O{\cdot}BF_3$ or $CH_3OH{\cdot}BF_3$ to give the corresponding $F_2B(\mu\text{-pz}^*)_2BF_2$ species. Attempts to replace boron-bonded hydrocarbon groups require much more forcing conditions and usually result in a complete breakdown of the molecule. However, under mild conditions the B-C bond is not attacked and $(C_6H_5)FB(\mu\text{-pz})_2B(C_6H_5)F$ is readily obtained from the reaction of $(C_6H_5)(C_2H_5S)B(\mu\text{-pz})_2B(C_6H_5)(SC_2H_5)$ with BF_3. 4,8-Dihalopyrazaboles, $RXB(\mu\text{-pz})_2BRX$, are also obtained from the reaction of dihaloboranes, RBX_2, with *N*-(trimethylsilyl)pyrazole, $(CH_3)_3Si(pz)$; the halogen of the pyrazabole can be displaced readily by reaction with a Grignard reagent or an alcohol. The compound $[(C_2H_5)_2N](pz)B(\mu\text{-pz})_2B[N(C_2H_5)_2](pz)$ was also prepared by the cited procedure. The diethylamino group of the latter species is easily displaced by reaction with pyrazole. Several additional pyrazaboles of the type $RR'B(\mu\text{-pz})_2BRR'$ have been prepared. $(C_6H_5)(pz)B(\mu\text{-pz})_2B(C_6H_5)(pz)$, which is accessible by various preparative routes, was separated into isomers that exhibit distinctly different ^1H NMR spectra. The mass spectral fragmentations of such (cis and trans) isomers are significantly different with respect to their loss of the first fragments from the parent ions.

Introduction

The unusual chemical stability of the pyrazaboles of the general structure **1** permits various organic substitution reactions at the carbon sites of the species. However, relatively little is known



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about chemical transformations at the boron atoms of such species, although *B*-hydropyrazaboles have been found to react with proton acidic compounds under relatively stringent conditions.[2] More recently, the halogenation of *B*-hydropyrazaboles has been studied in detail and subsequent reactions of *B*-halopyrazaboles gave access to several new types of B-substituted derivatives.[3] The present study reports the preparation and characterization of additional B-substituted pyrazaboles.

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 $CDCl_3$ on a Varian XL-200 or GEMINI-200 instrument. Chemical shift data are given in ppm with positive values indicating downfield 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. Abbreviations are as follows: s = singlet; d = doublet; t = triplet; q = quartet; p = quintuplet; m = unresolved multiplet. An asterisk denotes a broad signal. Coupling constants *J* are given in Hz. Relevant details for 2D NMR experiments (performed on a Varian VXR-400 instrument) have been given elsewhere.[4] Mass spectral data (70 eV unless otherwise noted) were obtained on a VG ZAB-2F spectrometer; data are listed to *m/z* 30 for 5% or more relative abundances (in parentheses) only.

Preparation of $F_2B(\mu\text{-pz}^*)_2BF_2$ from $H_2B(\mu\text{-pz}^*)_2BH_2$ (General Procedure). A stirred mixture of 2-3 g of $H_2B(\mu\text{-pz}^*)_2BH_2$ (Hpz* = C-substituted pyrazole) and 40-50 mL of freshly distilled $(C_2H_5)_2O{\cdot}BF_3$ was refluxed for 6-8 h. Volatiles were distilled off under reduced pressure at 50-60 °C, and the solid residue was then recrystallized to give product yields on the order of 70-95%.

Alternatively, $CH_3OH{\cdot}BF_3$ ($\delta(^{11}B)$ -0.4 (s, $h_{1/2}$ = 50 Hz), in CD_3OD) may be used as the reaction medium and fluorinating agent. In this case, the reaction generally proceeds even somewhat faster.

$F_2B(\mu\text{-pz}^*)_2BF_2$ (Hpz* = 3-methylpyrazole) was obtained from $H_2B(\mu\text{-pz}^*)_2BH_2$[5] in 78% yield as an isomer mixture of the 1,5- and 1,7-dimethyl species; mp 145-164 °C (recrystallized from cyclohexane), 150-164 °C (recrystallized from methanol). No effort was made to separate the isomers. Anal. Calcd for $C_8H_{10}B_2F_4N_4$ (M_r = 259.81): C, 36.98; H, 3.88; B, 8.32; F, 29.25; N, 21.57. Found: C, 36.86; H, 3.76; B, 8.29; F, 28.99; N, 21.45.

NMR data: $\delta(^1H)$ 7.88* (1 H, unresolved), 6.31* (1 H, unresolved), 2.58 + 2.57 (3 H, two s); $\delta(^{11}B)$ (high resolution) 0.3 (3 B, t, J = 26), -0.1 (4 B, t, J = 24), -0.5 (3 B, t, J = 23).

$F_2B(\mu\text{-pz}^*)_2BF_2$ (Hpz* = 3,5-dimethylpyrazole) was prepared from $H_2B(\mu\text{-pz}^*)_2BH_2$.[6] The product was recrystallized from toluene to give colorless crystals (69% yield), which melted near 280 °C with massive sublimation. Anal. Calcd for $C_{10}H_{14}B_2F_4N_4$ (M_r = 287.86): C, 41.72; H, 4.90; B, 7.51; F, 26.50; N, 19.46. Found: C, 41.26; H, 4.83; B, 7.48; F, 26.42; N, 19.19.

NMR data: $\delta(^1H)$ 6.09 (1 H, s), 2.50 (6 H, s); $\delta(^{11}B)$ 1.25 (t, J = 26). Mass spectrum: *m/z* 288 (20), 287 (15), 269 (12), 268 (9), 220 (23), 219 (8), 205 (18), 193 (45), 192 (19), 146 (5), 145 (73), 144 (100), 143 (40), 129 (5), 127 (5), 125 (5), 102 (9), 90 (19), 89 (6), 84 (12), 57 (8), 54 (7), 49 (7), 41 (8), 39 (10).

$F_2B(\mu\text{-pz}^*)_2BF_2$ (Hpz* = 4-chloropyrazole) was prepared from $H_2B(\mu\text{-pz}^*)_2BH_2$.[6] The product was recrystallized from *n*-hexane to give colorless crystals, mp 185-186 °C (89% yield). Anal. Calcd for $C_6H_4B_2Cl_2F_4N_4$ (M_r = 300.65): C, 23.97; H, 1.34; B, 7.19; Cl, 23.58; F, 25.28; N, 18.64. Found: C, 24.12; H, 1.36; B, 7.09; Cl, 23.61; F, 25.34; N, 18.15.

NMR data: $\delta(^1H)$ 7.97 (s); $\delta(^{11}B)$ -0.6 (s, $h_{1/2}$ = 60 Hz). Mass spectrum: *m/z* 302 (23), 301 (14), 300 (37), 299 (17), 283 (10), 282 (6), 281 (16), 280 (7), 234 (7), 232 (11), 201 (8), 200 (5), 199 (26), 198 (12), 152 (58), 151 (22), 150 (100), 149 (46), 131 (9), 123 (13), 104 (6), 76 (22), 75 (17), 49 (18), 48 (11), 40 (7).

$F_2B(\mu\text{-pz})_2BF_2$ was prepared by stirring a mixture of 2-3 g of $(C_2H_5S)_2B(\mu\text{-pz})_2B(SC_2H_5)_2$[7] or $(-CH_2S)_2B(\mu\text{-pz})_2B(SCH_2-)_2$,[7] respectively, and 40-50 mL of $(C_2H_5)_2O{\cdot}BF_3$ for 10-15 h at room temperature. After removal of all volatile material at 50 °C under vacuum, the residue was purified by recrystallization from methanol and sublimation (80-85% yield). Using $CH_3OH{\cdot}BF_3$, it was sufficient to warm the reaction mixture to 40-50 °C for 3-4 h. The compound has previously been characterized in detail.[3]

$(C_6H_5)FB(\mu\text{-pz})_2B(C_6H_5)F$ was prepared in a manner analogous to that of the preceding compound, originating from $(C_6H_5)(C_2H_5S)B(\mu\text{-pz})_2B(C_6H_5)(SC_2H_5)$.[7] The crude material was recrystallized from

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toluene to give a pure product melting at 186–188 °C (with massive sublimation). (Additional material was precipitated from the toluene solution with petroleum ether (bp 30–60 °C) to give a product contaminated with about 15% of $F_2B(\mu\text{-pz})_2BF_2$. This latter mixture was purified by recrystallization from methanol to give additional pure product). Anal. Calcd for $C_{18}H_{16}B_2F_2N_4$ (M_r = 347.97): C, 62.13; H, 4.63; B, 6.21; F, 10.92; N, 16.10. Found: C, 61.64; H, 4.92; B, 6.02; F, 10.99; N, 16.02.

NMR data: $\delta(^1H)$ 7.74 (2 H, d, J = 2.4), 7.5 (2 H, m), 7.4 (3 H, m), 6.46 (1 H, t, J = 2.5); $\delta(^{11}B)$ 3.5 (s, $h_{1/2}$ = 190 Hz). Mass spectrum (17 eV): m/z 272 (13), 271 (100), 270 (45), 269 (6), 203 (16), 202 (8), 155 (16), 128 (16), 127 (5), 107 (9). A small parent ion cluster was observed in the m/z 348 region.

$(C_6H_5)ClB(\mu\text{-pz})_2B(C_6H_5)Cl$. A solution of 21.84 g (156 mmol) of *N*-(trimethylsilyl)pyrazole, $(CH_3)_3Si(pz)$ (Petrarch Systems, Inc.), in 25 mL of hexane was added dropwise with stirring to a solution of 24.73 g (156 mmol) of dichlorophenylborane, $Cl_2BC_6H_5$,[8] in 200 mL of hexane. After the mixture stood overnight, the solid material was collected, washed with hexane, and dried to give 29 g (essentially quantitative yield) of crude product. The latter was recrystallized twice from cyclohexane (with substantial losses) to give a colorless material, mp 164–176 °C, as a mixture of the cis and trans isomers (as based on the wide melting range). Anal. Calcd for $C_{18}H_{16}B_2Cl_2N_4$ (M_r = 380.88): C, 56.76; H, 4.23; B, 5.68; Cl, 18.62; N, 14.17. Found: C, 56.56; H, 4.24; B, 5.64; Cl, 17.80; N, 14.38.

NMR data: $\delta(^1H)$ 7.64 (2 H, d, J = 2.5), 7.56 (2 H, m), 7.36 (3 H, m), 6.47 (1 H, t, J = 2.5); $\delta(^{11}B)$ 2.6 (s, $h_{1/2}$ = 200 Hz).

$(CH_3O)(C_6H_5)B(\mu\text{-pz})_2B(OCH_3)(C_6H_5)$. Crude $(C_6H_5)ClB(\mu\text{-pz})_2B(C_6H_5)Cl$ (5.5 g) was dissolved in 25 mL of anhydrous triethylamine, and 20 mL of anhydrous methanol was added with cooling (ice bath). A vigorous reaction occurred, and the mixture was stirred at ambient temperature for 24 h. A small amount of precipitate was filtered off (and identified as the triply bridged pyrazabole $RB(\mu\text{-pz})_2(\mu\text{-OBRO})BR$ with R = C_6H_5[9]), and volatiles were removed from the clear filtrate under vacuum. The solid residue was washed with three aliquots of 10 mL of water and dried over P_4O_{10}. The colorless product was dissolved in a minimum of boiling pentane/*n*-hexane (6:1 by volume). When the solution was cooled to room temperature, one isomer (A) of $(CH_3O)(C_6H_5)B(\mu\text{-pz})_2B(OCH_3)(C_6H_5)$ precipitated as colorless crystals, mp 136–138 °C, in ca. 60% yield. (An isomer mixture, mp 106–110 °C, was obtained on concentration of the filtrate; it was not further separated.)

NMR data for A: $\delta(^1H)$ 7.88 (2 H, d, J = 2.4), 7.12 (5 H, m, unresolved), 6.57 (1 H, t, J = 2.1), 3.09 (3 H, s); $\delta(^{11}B)$ 3.5 (s, $h_{1/2}$ = 130 Hz).

$(C_6H_5)(CH_3)B(\mu\text{-pz})_2B(C_6H_5)(CH_3)$ was obtained from crude $(C_6H_5)ClB(\mu\text{-pz})_2B(C_6H_5)Cl$ and CH_3MgBr as an isomer mixture. After the normal workup,[3] the crude product was dissolved in petroleum ether and one essentially pure isomer (A), mp 105–108 °C, precipitated as the first fraction on concentration of the solution (54% yield). Further concentration yielded additional product as an isomer mixture, mp 40–60 °C.

The compound was also prepared by reaction of $(C_6H_5)FB(\mu\text{-pz})_2B(C_6H_5)F$ (see above) with CH_3MgI or by reaction of $(CH_3)BrB(\mu\text{-pz})_2B(CH_3)Br$[10] with C_6H_5MgBr. The two isomers A and B were obtained in approximately 2:1 molar ratio (as based on the ^1H NMR data).

NMR data for A: $\delta(^1H)$ 7.65 (2 H, d, J = 2.3), 6.8 (3 H, m) + 6.6 (2 H, m), 6.41 (1 H, t, J = 2.4), 0.50 (3 H, s); $\delta(^{11}B)$ 0.6 (s, $h_{1/2}$ = 200 Hz but with very broad base line). For the second isomer (B), the ^1H NMR signals of the pz groups are observed at 7.49 (d, 4 = 2.3) and 6.31 (t, J = 2.4) ppm and the signal for the CH_3 groups appears at 0.22 (s) ppm (as deduced from the spectrum of the mixture).

$(C_6H_5)(pz)B(\mu\text{-pz})_2B(C_6H_5)(pz)$. A mixture of 1.7 g (5.5 mmol) of *B*-triphenylborazine, $(-BC_6H_5NH-)_3$,[11] and 4.1 g (60 mmol) of pyrazole was heated in an oil bath at 190–195 °C for 9 h. Excess pyrazole was sublimed off, and the residue was washed with ether to give 2.5 g (68%) of crude product, mp 193–207 °C. The material was treated with hot cyclohexane to leave 1.7 g of insoluble residue. This residue was recrystallized from benzene and then dimethylformamide to give a pure product (isomer A), mp 240–241 °C, identical with an authentic sample of the previously described[12] material, for which the crystal structure has been determined (as the trans isomer).[13] On cooling of the cyclohexane solution and concentration, 0.5 g of additional product with mp 206–220 °C was obtained. Recrystallization from ether/methylene chloride gave a small amount of sharp-melting isomer B, mp 236 °C, as the initial precipitate.

Alternatively, the compound was obtained from the reaction of either $(-BC_6H_5NCH_3-)_3$[11] or $C_6H_5B[N(CH_3)_2]_2$[14] with an excess of pyrazole following the above procedure. In both cases mixtures of isomers A (major product) and B were obtained.

Isomer A (trans species) NMR data: $\delta(^1H)$ 7.56 (2 H, d, J = 2.6), 7.54 (1 H, unresolved), 7.20–7.08 (3 H, m), 6.82 (2 H, d, J = 8.0, of d, J = 1.7), 6.73 (1 H, *d*, J = 2.4, of d, J = 0.6), 6.55 (1 H, t, J = 2.5), 5.89 (1 H, two closely overlapping d, J = 2.4); $\delta(^{11}B)$ 2.3 ($h_{1/2}$ = 200 Hz); $\delta(^{13}C)$ 142.2 (d, J = 182, of unresolved t), 138.4 (d, J = 192, of t, J = 7), 134.5 (d, J = 184, of two d, J = 9), 132.5 (d, J = 164, of t, J = 7), 129.0 (d, J = 166, of t, J = 7), 127.6 (d, J = 158, of d, J = 7), 107.0 (d, J = 184, of t, J = 8), 104.7 (d, J = 174, of t, J = 10). Lit.[12] NMR: $\delta(^1H)$ 7.56 (3 H, d, J = 2.5), 7.3–6.7 (6 H, m), 6.53 (1 H, t, J = 2.6), 5.88 (1 H, unsym t = two overlapping d).

Isomer B NMR data: $\delta(^1H)$ 7.64 (1 H, d, J = 1.6, of d, J = 0.6), 7.51 (2 H, d, J = 2.4), 7.10–6.97 (3 H, m), 6.88 (1 H, d, J = 2.3, of d, J = 0.5), 6.75 (2 H, d, J = 8.0, of d, J = 1.5), 6.55 (1 H, t, 4 = 2.4), 6.05 (1 H, two closely overlapping d, J = 2.4); $\delta(^{11}B)$ 2.3 ($h_{1/2}$ = 200 Hz); $\delta(^{13}C)$ 142.3 (d, J = 182, of t, J = 7), 138.1 (d, J = 192, of t, J = 7), 134.8 (d, J = 194, of two d, J = 9), 132.5 (d, J = 155, of t, J = 7), 127.9 (d, J = 159, of t, J = 7.5), 127.5 (d, J = 158, of d, J = 7), 107.1 (d, J = 183, of t, J = 8), 104.9 (d, J = 175, of t, J = 10).

***cis*-(pz)$(C_2H_5)B(\mu\text{-pz})_2B(pz)(C_2H_5)$.**[11] NMR data: $\delta(^{13}C)$ 141.4 (d, J = 182, of t, J = 7), 136.5 (d, J = 191, of t, J = 7), 132.2 (d, J = 183, of two d, J = 9), 107.8 (d, J = 183, of t, J = 8), 105.3 (d, J = 175, of two d, J = 9), 14.8* (unresolved), 8.3 (q, J = 125, of t, J = 4.5). Detailed ^1H and ^{11}B NMR as well as X-ray diffraction data have been presented previously.[11]

***trans*-(pz)$(C_2H_5)B(\mu\text{-pz})_2B(pz)(C_2H_5)$.**[11] NMR data: $\delta(^{13}C)$ 141.8 (d, J = 182, of t, J = 7), 136.7 (d, J = 191, of t, J = 7), 132.1 (d, J = 182, of two d, J = 9), 107.3 (d, J = 183, of t, J = 8), 105.1 (d, J = 174, of two d, J = 9), 13.2* (unresolved), 8.5 (q, J = 124, of unresolved t). Detailed ^1H and ^{11}B NMR as well as X-ray diffraction data have been presented previously.[11]

$(C_2H_5)_2B(\mu\text{-pz})_2B(C_2H_5)_2$.[6] NMR data: $\delta(^1H)$ 7.60 (2 H, d, 4 = 2.4), 6.46 (1 H, t, J = 2.4), 0.68 (4 H, q, J = 8), 0.48 (6 H, t, J = 7); $\delta(^{11}B)$ 2.4 (s, $h_{1/2}$ = 130 Hz); $\delta(^{13}C)$ (proton decoupled) 133.4, 105.8, 17.0, 8.5. Lit.[6] NMR: $\delta(^1H)$ 7.59 (2 H, d), 6.40 (1 H, t), 0.5 (10 H, m); $\delta(^{11}B)$ 2.2 (s).

$[(C_2H_5)_2N]ClB(\mu\text{-pz})_2B[N(C_2H_5)_2]Cl$. A solution of 6.5 g (41 mmol) of (diethylamino)dichloroborane, $(C_2H_5)_2NBCl_2$,[15] in 20 mL of cyclohexane was added slowly to a cooled (ice bath) and stirred solution of 5.8 g (41 mmol) of $(CH_3)_3Si(pz)$ in 100 mL of cyclohexane. The mixture was stirred at ambient temperature for 24 h. Volatiles were stripped off under reduced pressure to leave about 6.5 g (87% yield) of reddish crystalline material. The latter was washed with pentane and recrystallized from cyclohexane/hexane (1:2 by volume) to give a slightly pink and extremely moisture-sensitive material, mp 74–76 °C. Anal. Calcd for $C_{14}H_{26}B_2Cl_2N_6$ (M_r = 370.93): C, 45.33; H, 7.07; **B**, 5.83; Cl, 19.12; N, 22.66. Found: C, 44.09; H, 7.16; B, 5.81; Cl, 19.14; N, 21.27.

NMR data: $\eta(^1H)$ 8.07 (4 H, J = 2.4), 8.01 (2 H, d, J = 2.4), 6.52 (2 H, t, J = 2.4), 6.51 (1 H, t, J = 2.4), 2.83 (4 H, q, J = 7), 2.79 (8 H, q, J = 7), 1.03 (6 H, t, J = 7), 0.97 (12 H, t, J = 7); $\eta(^{11}B)$ 2.9 (s, $h_{1/2}$ = 150 Hz).

$[(C_2H_5)_2N](pz)B(\mu\text{-pz})_2B[N(C_2H_5)_2](pz)$. A solution of 2.9 g (19 mmol) of $(C_2H_5)_2NBCl_2$ in 20 mL of hexane was added dropwise with stirring to a cooled (ice bath) solution of 5.4 g (38 mmol) of $(CH_3)_3Si(pz)$ in 10 mL of hexane. The mixture was stirred at ambient temperature for 1 h, and a colorless precipitate (A, ca. 0.5 g; see below) was filtered off, washed with pentane, and dried under vacuum. Solvent was removed from the clear filtrate under vacuum and $[(C_2H_5)_2N](pz)B(\mu\text{-pz})_2B[N(C_2H_5)_2](pz)$ remained as a gelatinous material (ca. 3.6 g). It is readily soluble in organic solvents, is highly moisture-sensitive, melts at 61–62 °C, and decomposes near 90 °C. It was not further purified.

NMR data: $\delta(^1H)$ 8.25 (2 H, d, J = 2.5), 7.27 (1 H, d, J = 1.6), 6.64 (1 H, t, J = 2.4), 6.10 (1 H, d, J = 2.7), 5.61 (1 H, t, J = 2.7), 2.54 (4 H, g, J = 7), 0.97 (6 H, t, J = 7); $\delta(^{11}B)$ 2.9 (ca. 8 B, s, $h_{1/2}$ ca. 200 Hz) and a small (ca. 1 B) peak at 0.6. A number of minor peaks in the ^1H NMR spectrum indicate the presence of an isomer, as is supported by the ^{11}B NMR data. On standing of the sample solution, there is a slow and steady change in the ^1H NMR spectrum whereby the intensity of the smaller peaks increases with concurrent decrease of the major signals,

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indicating that an isomerization is occurring. The highest peak in the mass spectrum of the material was observed in the m/z region 434 (very low abundance). Major peaks were observed in the regions m/z 217 (58), 188 (100), 147 (49), 120 (43), 79 (52), and 58 (43).

$[\{(C_2H_5)_2HN\}_2B(pz)_2]Cl$. The (extremely hygroscopic) product A mentioned in the preceding procedure was identified (without further purification) by NMR data as the salt $[\{(C_2H_5)_2HN\}_2B(pz)_2]Cl$ (see also text): $\delta(^1H)$ 10.2* (1 H, s), 7.75 (1 H, d, J = 1.7), 7.15 (1 H, d, J = 2.2), 6.32 (1 H, unsym t, J = 2.0), 3.05 (4 H, q, J = 7), 1.46 (6 H, t, J = $\delta(^{11}B)$ 0.2 (s, $h_{1/2}$ = 40 Hz). At −40 °C the quartet at 3.05 ppm loses its fine structure and becomes a broad unresolved signal whereas the signal at 10.2 ppm sharpens and migrates to 9.4 ppm. The mass spectrum of the material shows only three major peaks at m/z 73, 68, and 58.

$(pz)_2B(\mu\text{-}pz)_2B(pz)_2$ was obtained from the reaction (6 h at 110–120 °C) of $[(C_2H_5)_2N](pz)B(\mu\text{-}pz)_2B[N(C_2H_5)_2](pz)$ with slightly more than 2 molar equiv of pyrazole. The compound was purified by subliming excess pyrazole under vacuum and subsequently recrystallizing the residue from toluene (54% yield). It has previously been described[11] and was characterized extensively by NMR data.[4]

$[CH_3S(CH_2)_3]HB(\mu\text{-}pz)_2B[(CH_2)_3SCH_3]H$. A mixture of 6.5 g (0.1 mol) of Hpz, 10.2 g (0.1 mol) of $CH_3S(CH_2)_3BH_2$ (as a 1 M solution in toluene; Aldrich Chemical Co.), and 200 mL of toluene was refluxed for 5 h. After removal of solvent under reduced pressure, the pasty residue was washed with water, dried over P_4O_{10}, and distilled under vacuum (3 Torr) to give approximately 9 g of a pasty material, bp ~190 °C (2–3 Torr). Anal. Calcd for $C_{14}H_{26}B_2N_4S_2$ (M_r = 336.12): C, 50.03; H, 7.79; B, 6.43; N, 16.67; S, 19.08. Found: C, 50.06; H, 8.04; B, 6.74; N, 16.54; S, 18.74.

NMR data: $\delta(^1H)$ 7.63 (2 H, d, J = 2.0), 6.29 (1 H, t, J = 2.3), 3.7* (1 H, s), 2.52 (2 H, t, J = 7.1), 2.05 (s) + 2.03 (s) (3 H total), 1.55 (2 H, m), 0.93 (2 H, m); $\delta(^{11}B)$ −2.9 (s, $h_{1/2}$ = 600 Hz); $\delta(^{13}C$, proton decoupled) 134.5, 105.4, 37.7, 26.6, 26.5, 15.5. A strong B–H stretching mode near 2380 cm^{-1} was observed in the IR spectrum of the compound. Mass spectrum (14 eV): m/z 247 (22), 246 (10), 201 (12), 200 (5), 167 (8), 159 (100), 158 (44), 157 (16), 156 (8).

$[CH_3S(CH_2)_3]HB(\mu\text{-}pz^*)_2B[(CH_2)_3SCH_3]H$ (Hpz* = 3,5-Dimethylpyrazole). A mixture of 9.6 g (0.1 mol) of Hpz*, 10.2 g (0.1 mol) of $CH_3S(CH_2)_3BH_2$, and 200 mL of toluene was reacted and worked up in a fashion similar to that described for the preceding compound to give a pasty material, bp 210 °C (3 Torr). Anal. Calcd for $C_{18}H_{34}B_2N_4S_2$ (M_r = 392.24): C, 55.12; H, 8.74; B, 5.51; N, 14.28; S, 16.35. Found: C, 54.28; H, 9.41; B, 5.98; N, 14.24; S, 16.07.

NMR data: $\delta(^1H)$ 6.00 (1 H, s), 5.85 (s) + 5.83 (s) (1 H), 3.9* (2 H), 2.42 (4 H, t, J = 7.1 Hz), 2.35 (s) + 2.30 (s) + 2.24 (s) (12 H), 1.99 (3 H, s), 1.97 (3 H, s), 1.50 (4 H, m), 0.74 (4 H, m); $\delta(^{11}B)$ −5.7* (s, $h_{1/2}$ = 400 Hz); $\delta(^{13}C$, proton decoupled 145.4, 144.1, 107.7, 106.2, 105.9, 37.8, 27.4, 24.0, 15.0, 12.5. A strong B–H stretching mode was observed in the IR spectrum of the compound near 2395 cm^{-1}.

$[CH_3S(CH_2)_3](pz^*)B(\mu\text{-}pz^*)_2B[(CH_2)_3SCH_3](pz^*)$ (Hpz* = 3,5-Dimethylpyrazole). A mixture of 19.2 g (0.2 mol) of Hpz*, 10.2 g (0.1 mol) of $CH_3S(CH_2)_3BH_2$, and 300 mL of toluene was refluxed for 24 h. The solvent was removed under reduced pressure, and the remaining material was heated to gentle reflux for 4 h (bath temperature ca. 230 °C). After the mixture was cooled to room temperature, the product was treated with hexane and the hexane solution was filtered and concentrated. The resultant crystalline precipitate was sublimed under vacuum to give ca. 4 g of a pure material, mp 172–176 °C. Anal. Calcd for $C_{28}H_{26}B_2N_8S_2$ (M_r = 580.46): C, 57.94; H, 7.99; B, 3.72; N, 19.30; S, 11.05. Found: C, 58.01; H, 8.17; B, 3.67; N, 18.98, S, 11.31.

NMR data: $\delta(^1H)$ 5.93 (1 H, s), 5.89 (1 H, s), 5.87 (1 H, s), 5.80 (1 H, s), 2.52 (2 H, t, J = 7.6), 2.34 (2 H, ill-resolved t), 2.27 (6 H, s), 2.07 (6 H, s), 2.00 (3 H, s), 1.67 (6 H, s), 1.59 (6 H, s), 1.50 (3 H, s), 13* (6 H, m), 0.94* (2 H, m); $\delta(^{11}B)$ 1.9 (s, $h_{1/2}$ = 425 Hz). A very small parent ion cluster was observed in the mass spectrum of the compound in the region m/z 580.

Results and Discussion

B-Fluorination of Pyrazaboles. Tetra-*B*-fluoropyrazabole, $F_2B(\mu\text{-}pz)_2BF_2$ (Hpz = pyrazole), has recently been obtained by the reaction of $H_2B(\mu\text{-}pz)_2BH_2$ with $(C_2H_5)_2O{\cdot}BF_3$.[3] This same reaction has now been employed for the preparation of C-substituted tetra-*B*-fluoropyrazaboles, $F_2B(\mu\text{-}pz^*)_2BF_2$ (Hpz* = C-substituted pyrazole). The reaction is relatively slow and usually requires about 6–8 h of heating to reflux with excess $(C_2H_5)_2O{\cdot}BF_3$ as solvent, but the products are generally obtained in good yield. The species with Hpz* = 3-methylpyrazole, 3,5-dimethylpyrazole, and 4-chloropyrazole were obtained by this procedure. No halogen exchange was observed in the case of Hpz* = 4-chloropyrazole.

Another convenient agent for the fluorination of *B*-hydropyrazaboles is the complex $CH_3OH{\cdot}BF_3$. In general, here the fluorination begins immediately on mixing of the reagents at room temperature in a mildly exothermic reaction. The reaction is essentially completed (with gentle heating of the reaction mixture) within 3–4 h.

The NMR spectra of the various tetra-*B*-fluoropyrazaboles are readily interpreted, including those of $F_2B(\mu\text{-}pz^*)_2BF_2$ where Hpz* = 3-methylpyrazole. In this latter compound, the methyl groups of the originating isomer mixture of the tetra-*B*-hydro derivative are attached to the pyrazabole skeleton in either the 1,5- or 1,7-positions (see numbering in **1**).[5] On the basis of the signal intensities of the fluorination product, the ^{11}B NMR signal at −0.1 ppm is assigned to the 1,5-dimethyl derivative and the two signals at 0.3 and −0.5 ppm are assigned to the 1,7-dimethyl derivative. The ^{11}B NMR signal for $F_2B(\mu\text{-}pz)_2BF_2$ (−0.2 ppm, J = 23 Hz[3]) is at higher field than for the compound derived from Hpz* = 3,5-dimethylpyrazole (1.25 ppm, J = 26 Hz). Hence, the signal observed at 0.3 ppm (J = 26 Hz) in the spectrum of $F_2B(\mu\text{-}pz^*)_2BF_2$ where Hpz* = 3-methylpyrazole can likely be assigned to that of B(8) in the 1,7-dimethyl-4,4,8,8-tetrafluoropyrazabole. It is noteworthy that the slightly different environments of the three boron atoms in the isomer mixture (caused by the positioning of the $(C)CH_3$ groups) are not only evidenced by different chemical shifts but are also reflected by the B–F coupling constant data.

The B-fluorination of pyrazaboles using either $(C_2H_5)_2O{\cdot}BF_3$ or $CH_3OH{\cdot}BF_3$ is not limited to the conversion of BH_2 groups of pyrazaboles into BF_2 moieties but works even faster (i.e., within a few hours at room temperature) for the replacement of boron-bonded organylthio groups. For example, $F_2B(\mu\text{-}pz)_2BF_2$ was readily obtained by treatment of either $(C_2H_5S)_2B(\mu\text{-}pz)_2B(SC_2H_5)_2$ or $(-CH_2S)_2B(\mu\text{-}pz)_2B(SCH_2-)_2$ with $(C_2H_5)_2O{\cdot}BF_3$ at room temperature. In addition, $(C_2H_5S)(C_6H_5)B(\mu\text{-}pz)_2B(SC_2H_5)(C_6H_5)$ was readily converted to $(C_6H_5)FB(\mu\text{-}pz)_2B(C_6H_5)F$. The relatively sharp melting point of the latter compound suggests that it was obtained as a pure isomer, presumably the trans species. This is likely to result from the fact that the performed pyrazabole structure in the starting alkylthio derivative appears to be only one isomer.[8]

The formation of some $F_2B(\mu\text{-}pz)_2BF_2$ was observed as a byproduct in the preparation of $(C_6H_5)FB(\mu\text{-}pz)_2B(C_6H_5)F$ as described above, although boron-bonded hydrocarbon groups of pyrazaboles are not readily replaced by fluorine in the reaction of a tetra-*B*-organylpyrazabole with $(C_2H_5)_2O{\cdot}BF_3$. (Rather, in this latter case much more stringent reaction conditions are generally required and complete breakdown of the pyrazabole skeleton was found to be the predominant occurrence. Hence, the reaction was not further studied.) The fact that even under mild conditions both $(C_6H_5)FB(\mu\text{-}pz)_2B(C_6H_5)F$ (the major product) and $F_2B(\mu\text{-}pz)_2BF_2$ are obtained in the reaction of $(C_6H_5)(C_2H_5S)B(\mu\text{-}pz)_2B(C_6H_5)(SC_2H_5)$ with $(C_2H_5)_2O{\cdot}BF_3$ suggests two competing mechanisms for the process. The predominating one is likely to be a (relatively fast) electrophilic halogenation at the boron sites similar to the previously described bromination with BBr_3.[13] Thus, the fluorination of boron by displacement of a *B*-alkylthio group seems to proceed mainly without opening of the central B_2N_4 pyrazabole ring. This is, however, in contrast to the reaction of $H_2B(\mu\text{-}pz)_2BH_2$ with $(C_2H_5)_2O{\cdot}BF_3$, where $F_2B(\mu\text{-}pz)_2BH_2$ could be isolated as an intermediate. The formation of the latter species was interpreted by an intermediate opening of the central B_2N_4 ring during the (relatively slow) reaction.[3] It seems reasonable to assume that some ring opening occurs during the reaction under consideration here, whereby a B(SR)R′ group is replaced by BF_2, causing the formation of $F_2B(\mu\text{-}pz)_2BF_2$ as a byproduct.

The assumption of two competing mechanisms for the fluorination of pyrazaboles is supported by the results of an experiment where partial fluorination of $H_2B(\mu\text{-}pz^*)_2BH_2$ (Hpz* = 3,5-dimethylpyrazole) with $(C_2H_5)_2O{\cdot}BF_3$ was studied by reaction at room temperature for 2 h. The NMR data of the resultant product mixture showed that it contained ca. 30–40% unreacted starting

material as well as ca. 15% of $F_2B(\mu\text{-}pz^*)_2BF_2$. In addition, four partially fluorinated species could be observed in the ^1H NMR spectrum of the mixture ($\delta(^1H)$ 6.06, 6.01, 5.97, 5.94, 2.50, 2.48, 2.43, 2.33 (all s, with each set of two related signals in about 3:2:3:1 area ratio). In the ^{11}B NMR spectrum of the mixture, signals for the partially fluorinated species were observed as a triplet for an additional BF_2 group ($\delta(^{11}B)$ 0.6) and several overlapping signals in the −2 to −4 ppm range. No effort was made to separate the various species, but the data clearly suggest the formation of pyrazaboles of the composition $B_2(pz^*)_2F_3H$, $B_2(pz^*)_2F_2H_2$ (probably two isomers), and $B_2(pz^*)_2FH_3$, thus lending credence to a competition between two different reaction mechanisms.

Pyrazaboles of the Type $RR'B(\mu\text{-}pz)_2BRR'$. Disubstitution at the boron sites of $H_2B(\mu\text{-}pz)_2BH_2$ normally leads to 4,8-disubstituted products rather than 4,4-disubstituted products.[2] The only known exception is the interaction of pyrazabole with $(C_2H_5)_2O\cdot BF_3$, where $F_2B(\mu\text{-}pz)_2BH_2$ was obtained as an intermediate product.[3]

Pyrazaboles of the type $RR'B(\mu\text{-}pz)_2BRR'$ are accessible by several preparative methods, most of which result in the formation of isomer mixtures (with either cis or trans orientation of the terminal boron substituents). The previously mentioned[3] formation of 4,8-dihalopyrazaboles by reaction of a trigonal haloborane with *N*-(trimethylsilyl)pyrazole, $(CH_3)_3Si(pz)$, has been used advantageously for the preparation of additional compounds of the same type, including (originating from $(C_2H_5)_2NBCl_2$) the species $[(C_2H_5)_2N]ClB(\mu\text{-}pz)_2B[N(C_2H_5)_2]Cl$ and, with use of 2 molar equiv of $(CH_3)_3Si(pz)$, $[(C_2H_5)_2N](pz)B(\mu\text{-}pz)_2B[N(C_2H_5)_2](pz)$. Hence, this reaction seems to be general and provides for very convenient access to 4,8-dihalopyrazaboles of the type $RXB(\mu\text{-}pz)_2BRX$. However, the product is always a mixture of cis and trans isomers that is difficult to separate.

The compound $[(C_2H_5)_2N]ClB(\mu\text{-}pz)_2B[N(C_2H_5)_2]Cl$ is very difficult to handle and was never obtained in a completely pure state. It is moisture-sensitive and reacts violently with water or alcohols. NMR data, however, clearly substantiate the structure and illustrate that the species is formed in an approximately 2:1 molar ratio of isomers (cis and trans with respect to the Cl arrangements). Similarly, the species $[(C_2H_5)_2N](pz)B(\mu\text{-}pz)_2B[N(C_2H_5)_2](pz)$ was obtained as a moisture-sensitive material, and the observation of two distinct sets of ^1H NMR signals for pz groups showed it to be an isomer mixture. The diethylamino groups of the latter compound are readily displaced by reaction with excess pyrazole to give $(pz)_2B(\mu\text{-}pz)_2B(pz)_2$. An analogous reaction with 3,5-dimethylpyrazole (=Hpz*) at ca. 180 °C yielded only a mixture of all possible species of the composition $B_2(pz)_{6-n}(pz^*)_n$ (with n = 0–6). The mass spectral fragmentation of this latter product mixture is very similar to that found for the reaction product of $H_2B(\mu\text{-}pz)_2BH_2$ with Hpz*.[16] Thus, extensive redistribution seems to occur during the high-temperature reaction.

It is likely that at room temperature the N-bonded protons in the salt $[\{(C_2H_5)_2HN\}_2B(pz)_2]Cl$ are labile and are not localized at the diethylamino groups. However, the collapse of the clean quartet of the CH_2 moiety of the latter in the low-temperature ^1H NMR spectrum suggests additional coupling and, thereby, localization of the proton at the diethylamino nitrogen at low temperatures. This situation is similar to that observed for analogous species obtained for the interaction of (dimethylamino)boranes with pyrazole.[17]

The pyrazabole $(C_6H_5)(CH_3)B(\mu\text{-}pz)_2B(C_6H_5)(CH_3)$ was found to be accessible from various $RXB(\mu\text{-}pz)_2BRX$ species (R = C_6H_5, X = Cl, F; R = CH_3, X = Br) via Grignard reactions. An isomer mixture was obtained in each case, and one of the isomers could be obtained fairly readily in a pure state. Reaction of $(C_6H_5)ClB(\mu\text{-}pz)_2B(C_6H_5)$ with CH_3OH in the presence of $(C_2H_5)_3N$ gave another representative of the still rare *B*-alkoxypyrazaboles, $(C_6H_5)(CH_3O)B(\mu\text{-}pz)_2B(C_6H_5)(OCH_3)$. (This is only the third such compound known. Previously, the species $(C_2H_5)(RO)B(\mu\text{-}pz)_2B(C_2H_5)(OR)$ with R = CH_3, C_2H_5 have been isolated and characterized.[18]) Again, the compound was obtained as an isomer mixture and one of the isomers could be isolated in a pure state.

Table I. ^1H and ^{13}C NMR Signals (in ppm; Assignments Determined by HETCOR Experiments) of the H(C) Units of Bridging and Terminal pz Groups of the Isomers of $R(pz)B(\mu\text{-}pz)_2BR(pz)$

	^1H (^{13}C) NMR signals	
	bridging pz	terminal pz
R = C_2H_5		
cis isomer (mp 152–153 °C)	7.64 (136.5)/ 6.52 (107.8)	7.61 (141.4)/ 7.17 (132.2)/ 6.14 (105.3)
trans isomer (mp 210–212 °C)	7.67 (136.7)/ 6.55 (107.3)	7.64 (141.8)/ 7.27 (132.1)/ 6.24 (105.1)
R = C_6H_5		
cis isomer (mp 236 °C)	7.51 (138.1)/ 6.55 (107.1)	7.64 (142.3)/ 6.88 (134.8)/ 6.05 (104.9)
trans isomer (mp 240–241 °C)	7.56 (138.4)/ 6.55 (107.1)	7.54 (142.2)/ 6.73 (134.5)/ 5.89 (104.7)

Additional species of the type $RR'B(\mu\text{-}pz)_2BRR'$ were obtained by reaction of $CH_3S(CH_2)_3BH_2$ with 1 molar equiv of pyrazole to yield $[CH_3S(CH_2)_3]H$ $b(\mu\text{-}pz)_2BH[(CH_2)_3SCH_3]$; $[CH_3S(CH_2)_3]HB(\mu\text{-}pz^*)_2BH[(CH_2)_3SCH_3]$ (Hpz* = 3,5-dimethylpyrazole) was obtained in an analogous fashion. The latter compound was converted to $[CH_3S(CH_2)_3](pz^*)B(\mu\text{-}pz^*)_2B(pz^*)[(CH_2)_3SCH_3]$ by reaction with Hpz*.

The compound $(C_6H_5)(pz)B(\mu\text{-}pz)_2B(C_6H_5)(pz)$ was first obtained by Trofimenko in about 15% yield from the reaction of $Cl_2BC_6H_5$ with Kpz as colorless crystals, mp 239–240 °C.[12] A crystal structure study of this species showed a central B_2N_4 ring in the (relatively rare for pyrazaboles) chair conformation with a trans arrangement of the terminal boron substituents. The terminal pz groups were found to be in pseudoaxial positions, and the best *R* value was obtained by assuming their random orientation.[13] Considerably better yields of the cited compound (on the order of 80–85%) were obtained from $(-BRNR'-)_3$ or $RB(\mu\text{-}pz)(\mu\text{-}NHR')BR$ (R = C_6H_5, R' = H, CH_3) in refluxing Hpz.[11] However, in these last two cases the original product had a wide melting range and the ^1H NMR spectrum suggested the presence of two isomers. In the present work, a second isomer of the cited compound with mp 236 °C could, indeed, be isolated from the mixture and was characterized by its NMR data.

The formation of the second isomer may well be due to the fact that the cited pyrazabole is obtained via a high-temperature reaction and, when the product originates from a borazine, presumably via the intermediate $(pz)RB(\mu\text{-}pz)(\mu\text{-}NHR')BR(pz)$. Replacement of the bridging amino group almost certainly involves a ring-opened intermediate. The latter is attacked by pyrazole, and the process may proceed via a pyrazabole of the type $(R'HN)RB(\mu\text{-}pz)_2BR(pz)$. (Such species are known and were found to exist in cis and trans arrangements of the terminal boron substituents,[17] and the related species $[(C_2H_5)_2N]XB(\mu\text{-}pz)_2B[N(C_2H_5)_2]X$ (X = Cl, pz) have been obtained in the present study; see above.) The high-temperature reaction of $C_6H_5B[N(CH_3)_2]_2$ with Hpz is likely to involve a $C_6H_5B(pz)_2$ monomer as intermediate that can dimerize in random fashion and, thus, will always produce an isomer mixture.

The separation of the isomers of $(C_6H_5)(pz)B(\mu\text{-}pz)_2B(pz)(C_6H_5)$ is only the second case where both isomers of a pyrazabole of the type $RR'B(\mu\text{-}pz)_2BBR'$ could be cleanly separated and characterized. Previously, the species with R = C_2H_5 and R' = pz were also found to be distinctly different. By COSY and HETCOR NMR experiments it was possible to assign the $\delta(^1H)$ ($\delta(^{13}C)$) signals for the bridging and terminal pz groups of the

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Table II. MIKES Data of P^+ for the Isomers of $Ru(pz)B(\mu\text{-}pz)_2BR(pz)$ with R = C_2H_5 (P^+ = m/z 348) and R = C_6H_5 (P^+ = M/z 444)

energy, eV	daughter ions, m/z	rel abund: cis isomer	rel abund: trans isomer	fragment loss
		R = C_2H_5		
7330	319	70.0	6.7	$C_2H_5^+$
6460	281	100.0	100.0	pz^+
5770	251	12.0	6.9	$C_2H_5^+ + pz^+$
		R = C_6H_5		
6793	377	100.0	100.0	pz^+
6613	367	4.7	0.6	$C_6H_5^+$
5568	309	2.4	7.5	$2\ pz^+$
5405	300	1.5	0.2	$pz^+ + C_6H_5^+$
4180	232	0.5	0.1	$2\ pz^+ + C_6H_5^+$
4018	223	1.2	0.5	$pz^+ + 2\ C_6H_5^+$

isomers of the two cited species. The resultant data are given in Table I.

On the basis of all of the preceding results, the newly identified second isomer of $(C_6H_5)(pz)B(\mu\text{-}pz)_2B(C_6H_5)(pz)$ is assigned as the cis isomer and should contain the pz groups again in pseudoaxial positions. However, this has not yet been confirmed by X-ray data.

Noteworthy is the fact that the mass spectral fragmentations of the two isomers differ with respect to the loss of the first and second fragments from the parent ion. This feature has been studied for the two species $(pz)RB(\mu\text{-}pz)_2BR(pz)$ with R = C_2H_5, C_6H_5. The normal 70-eV mass spectra of the two compounds differ most in the relative abundance of the parent ion. The species with R = C_2H_5 produced only a very weak parent ion, whereas a strong parent ion was observed for the species with R = C_6H_5. The resultant mass spectral analysis of both isomers of each species gave virtually identical spectra. However, differences between the two isomers of a given compound became apparent when mass-selected ions were analyzed by high-energy (8-kV) mass-analyzed ion kinetic spectroscopy (MIKES). Here, the precursor ions are selected by mass prior to their unimolecular fragmentation in the second field-free region (after the magnetic sector and before the electric sector). The resulting daughter ion(s) transmitted to the detector are determined by varying the electric sector voltage. The observed MIKES data of the daughter ions of the parent ion P (R = C_2H_5, P^+ = m/z 348) are listed in Table II. The ions of the two isomers produced distinctly different daughter ion spectra. The peaks m/z 319 ($P^+ - C_2H_5$) and m/z 251 ($P^+ - (pz + C_2H_5)$) show the greatest observable difference versus the reference (base) peak at m/z 281 for the two isomers: both are significantly more abundant (relative to m/z 281) in the MIKES spectrum of the cis isomer as compared to the abundance in the spectrum of the trans isomer. MIKES analyeses of m/z 319 and 281 peaks of both isomers produced essentially identical spectra. Also listed in Table II are MIKES data for the parent ion of the two isomeric species with R = C_6H_5 (P^+ = m/z 444). These ions also produce different and slightly more complex (as compared to the species with R = C_2H_5) daughter ion spectra. The MIKES spectra of the ions m/z 377, 367, 309, and 300, respectively, were again identical for each isomer.

These observations suggest that, although each isomer of each species loses the pz substituent easiest, the cis isomer of the ethyl compound tends to lose the first C_2H_5 group more easily than the trans species. In the case of the phenyl compound, the cis isomer again loses the first hydrocarbon substituent more easily than the trans species; in addition, the cis isomer appears to lose the second pz substituent more easily the second phenyl group, and the trans compound loses the second phenyl group more easily than the second pz group.

Conclusions

The present data show that the replacement of boron-bonded hydrogen and organylthio groups is readily effected by using BF_3 adducts with $(C_2H_5)_2O$ and CH_3OH, respectively, as the halogenating agent. The conversion is generally not impaired by hydrocarbon substituents at either carbon or boron sites of the pyrazabole skeleton. Boron-bonded hydrocarbon groups are not readily displaced by fluorine in an analogous process. Rather, in most cases complete breakdown of the species was observed on reaction of tetra-*B*-organylpyrazaboles with BF_3.

Pyrazaboles of the type $RR'B(\mu\text{-}pz)_2BRR'$ are accessible by various procedures. They can exist as cis and trans isomer mixtures. The two isomers of such species exhibit distinctly different ^1H NMR spectra and can also be distinguished by mass spectral data.

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Registry No. $1,5\text{-}F_2B(\mu\text{-}pz^*)_2BF_2$ (Hpz* = 3-methylpyrazole), 115419-87-9; $F_2B(\mu\text{-}pz^*)_2BF_2$ (Hpz* = 3,5-dimethylpyrazole), 115419-88-0; $F_2B(\mu\text{-}pz^*)_2BF_2$ (Hpz* = 4-chloropyrazole), 115419-89-1; $F_2B(\mu\text{-}pz)_2BF_2$, 109088-13-3; *trans*-$(C_6H_5)FB(\mu\text{-}pz)_2B(C_6H_5)F$, 115419-90-4; *cis*-$(C_6H_5)ClB(\mu\text{-}pz)_2B(C_6H_5)Cl$, 115509-06-3; $(CH_3O)(C_6H_5)B(\mu\text{-}pz)B(OCH_3)(C_6H_5)$, 115419-91-5; *trans*-$(C_6H_5)(CH_3)B(\mu\text{-}pz)B(C_6H_5)(CH_3)$, 115419-92-6; *cis*-$(C_6H_5)(CH_3)B(\mu\text{-}pz)B(C_6H_5)(CH_3)$, 115509-10-9; *trans*-$(C_6H_5)(pz)B(\mu\text{-}pz)_2B(C_6H_5)(pz)$, 77255-14-2; *cis*-$(C_6H_5)(pz)B(\mu\text{-}pz)_2B(C_6H_5)(pz)$, 115509-07-4; *cis*-$(pz)(C_2H_5)B(\mu\text{-}pz)_2B(pz)(C_2H_5)$, 105336-01-4; *trans*-$(pz)(C_2H_5)B(\mu\text{-}pz)_2B(pz)(C_2H_5)$, 105452-41-3; $(C_2H_5)_2B(\mu\text{-}pz)_2B(C_2H_5)_2$, 14695-69-3; $[(C_2H_5)_2N]ClB(\mu\text{-}pz)B[N(C_2H_5)_2]Cl$, 115419-93-7; $[(C_2H_5)_2N](pz)B(\mu\text{-}pz)B[N(C_2H_5)_2](pz)$, 115419-94-8; $[\{(C_2H_5)_2NH\}_2B(pz)_2Cl$, 115419-95-9; $(pz)_2B(\mu\text{-}pz)_2B(pz)_2$, 16243-58-6; $[CH_3S(CH_2)_3]HB(\mu\text{-}pz)_2B[(CH_2)_3SCH_3]H$, 115419-96-0; $[CH_3S(CH_2)_3]HB(\mu\text{-}pz^*)_2B[(CH_2)_3SCH_3]H$ (Hpz* = 3,5-dimethylpyrazole), 115419-97-1; $[CH_3S(CH_2)_3](pz^*)B(\mu\text{-}pz^*)_2B[(CH_2)_3SCH_3](pz^*)$ (Hpz* = 3,5-dimethylpyrazole), 115419-98-2; $1,7\text{-}F_2B(\mu\text{-}pz^*)_2BF_2$ (Hpz* = 3-methylpyrazole), 115461-82-0; $H_2B(\mu\text{-}pz^*)_2BH_2$ (Hpz* = 3-methylpyrazole), 95911-40-3; $H_2B(\mu\text{-}pz^*)_2BH_2$ (Hpz* = 3,5-dimethylpyrazole), 16998-92-8; $H_2B(\mu\text{-}pz^*)_2BH_2$ (Hpz* = 4-chloropyrazole), 18601-55-3; $(C_2H_5S)_2B(\mu\text{-}pz)_2B(SC_2H_5)_2$, 77189-77-6; $(C_6H_5)(C_2H_5S)B(\mu\text{-}pz)_2B(C_6H_5)(SC_2H_5)$, 115509-08-5; $(CH_3)_3Si(pz)$, 18156-75-7; $Cl_2BC_6H_5$, 873-51-8; *trans*-$(C_6H_5)ClB(\mu\text{-}pz)_2B(C_6H_5)Cl$, 115509-09-6; $(C_6H_5)B(\mu\text{-}pz)_2(\mu\text{-}OB(C_6H_5)BO)B(C_6H_5)$, 99593-93-8; CH_3MgBr, 75-16-1; $(CH_3)BrB(\mu\text{-}pz)_2B(CH_3)Br$, 112840-88-7; C_6H_5MgBr, 100-58-3; $(-BC_6H_5NH-)_3$, 976-29-4; $(-BC_6H_5NCH_3-)_3$, 909-21-7; $C_6H_5B[N(CH_3)_2]_2$, 1201-45-2; $(C_2H_5)_2NBCl_2$, 868-30-4; $CH_3S(CH_2)_3BH_2$, 33329-32-7; pyrazole, 288-13-1; 3,5-dimethylpyrazole, 67-51-6.