Equations A9 and A10 can be readily cast into the matrix formula [a] × [b] = [c], where [a] is the 2 × 2 matrix containing the coefficients of the fluxes, [b] is the 1 × 2 matrix containing the fluxes, and [c] is the 1 × 2 matrix containing the concentration terms. The solution for matrix [b] could then be found by Gaussian elimination. The advantage of this method becomes apparent when one considers the multicomponent thianthrene diiron system.

The reaction mechanism proposed for the thianthrene diiron complexes comprises eq 10–16 and can be cast in general as

$$\begin{gathered} A + e^- \rightleftharpoons B \\ B \rightarrow C + X \\ A + X \rightleftharpoons B + Y \\ B + e^- \rightleftharpoons D \\ D \rightarrow E + X \\ C + e^- \rightleftharpoons E \\ E \rightarrow Z + X \end{gathered}$$

By analogous derivation, we can write expressions similar to those above in eq A7 and A8 for the electroactive species:

$$f_A = k_{fAB}[C_A(1) - f_A\Delta x/2D_A] - k_{bAB}[C_B(1) - f_B\Delta x/2D_B] \quad (A11)$$

$$f_B = k_{bAB}[C_B(1) - f_B\Delta x/2D_B] - k_{fAB}[C_A(1) - f_A\Delta x/2D_A] + k_{fBD}[C_B(1) - f_B\Delta x/2D_B] - k_{bBD}[C_D(1) - f_D\Delta x/2D_D] \quad (A12)$$

$$f_C = k_{fCE}[C_C(1) - f_C\Delta x/2D_C] - k_{bCE}[C_E(1) - f_E\Delta x/2D_E] \quad (A13)$$

$$f_D = k_{bBD}[C_D(1) - f_D\Delta x/2D_D] - k_{fBD}[C_B(1) - f_B\Delta x/2D_B] \quad (A14)$$

$$f_E = k_{bCE}[C_E(1) - f_E\Delta x/2D_E] - k_{fCE}[C_C(1) - f_C\Delta x/2D_C] \quad (A15)$$

Once again, we rearrange these expressions, separating concentration terms and flux terms:

$$[1 + k_{fAB}\Delta x/2D_A]f_a + [-k_{bAB}\Delta x/2D_B]f_B = k_{fAB}C_A(1) - k_{bAB}C_B(1) \quad (A16)$$

$$[1 + k_{bAB}\Delta x/2D_B + k_{fBF}\Delta x/2D_B]f_B + [-k_{fAB}\Delta x/2D_A]f_A + [-k_{bBD}\Delta x/2D_D]f_D = k_{bAB}C_B(1) - k_{fAB}C_A(1) + k_{fBD}C_B(1) - k_{bBD}C_D(1) \quad (A17)$$

$$[1 + k_{fCE}\Delta x/2D_C]f_C + [-k_{bCE}\Delta x/2D_E]f_E = k_{fCE}C_C(1) - k_{bCE}C_E(1) \quad (A18)$$

$$[1 + k_{bBD}\Delta x/2D_D]f_D + [-k_{fBD}\Delta x/2D_B]f_B = k_{bBD}C_D(1) - k_{fBD}C_B(1) \quad (A19)$$

$$[1 + k_{bCE}\Delta x/2D_E]f_E + [-k_{fCE}\Delta x/2D_C]f_C = k_{bCE}C_E(1) - k_{fCE}C_C(1) \quad (A20)$$

Finally, a matrix can be set up directly from eq A16–A20 that enables one to solve for f_A, f_B, f_C, f_D, and f_E:

$$\underset{[a]}{\begin{bmatrix} 1+\frac{k_{fAB}\Delta x}{2D_A} & -\frac{k_{bAB}\Delta x}{2D_B} & 0 & 0 & 0 \\ -\frac{k_{fAB}\Delta x}{2D_A} & 1+\frac{k_{bAB}\Delta x}{2D_B}+\frac{k_{fBD}\Delta x}{2D_B} & 0 & -\frac{k_{bBD}\Delta x}{2D_D} & 0 \\ 0 & 0 & 1+\frac{k_{fCE}\Delta x}{2D_C} & 0 & -\frac{k_{bCE}\Delta x}{2D_E} \\ 0 & -\frac{k_{fBD}\Delta x}{2D_B} & 0 & 1+\frac{k_{bBD}\Delta x}{2D_D} & 0 \\ 0 & 0 & -\frac{k_{fCE}\Delta x}{2D_C} & 0 & 1+\frac{k_{bCE}\Delta x}{2D_E} \end{bmatrix}} \times \underset{[b]}{\begin{bmatrix} f_A \\ f_B \\ f_C \\ f_D \\ f_E \end{bmatrix}} = \underset{[c]}{\begin{bmatrix} k_{fAB}C_A(1) - k_{bAB}C_B(1) \\ \begin{matrix} k_{bAB}C_B(1) - k_{fAB}C_A(1) \\ k_{fBD}C_B(1) - k_{bBD}C_D(1) \end{matrix} \\ k_{fCE}C_C(1) - k_{bCE}C_E(1) \\ k_{bBD}C_D(1) - k_{fBD}C_B(1) \\ k_{bCE}C_E(1) - k_{fCE}C_C(1) \end{bmatrix}}$$

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Reactions of Boron Heterocycles with Pyrazole[1]

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The interaction of pyrazole (=Hpz) with heterocycles containing two annular boron atoms generally seems to proceed by initial attack of the pyrazole NH moiety at the most basic site of the heterocycle. Subsequent reactions depend on the particular reaction conditions. For example, several pyrazaboles of the type $\mathrm{RR'B(\mu\text{-}pz)_2BRR'}$ (**1**) (**1a**, R = R′ = F from $\mathrm{[(CH_3)_2NBF_2]_2}$ (C); **1b**, R = $\mathrm{CH_3}$, R′ = pz from either $\mathrm{(pz)(CH_3)B(\mu\text{-}pz)(\mu\text{-}NHCH_3)B(pz)(CH_3)}$ (**3a**) or $\mathrm{CH_3B(\mu\text{-}pz)(\mu\text{-}NHCH_3)(\mu\text{-}NCH_3CSNCH_3)BCH_3}$ (Ic); **1c**, R = $\mathrm{C_2H_5}$, R′ = pz from $\mathrm{C_2H_5B[\mu\text{-}N(CH_3)_2](\mu\text{-}NCH_3CONCH_3)(\mu\text{-}NCH_3CONHCH_3)BC_2H_5}$ (J)) and the type $\mathrm{RB(\mu\text{-}pz)_2(\mu\text{-}X)BR}$ (**2**) (**2a**, R = $\mathrm{CH_3}$, X = $\mathrm{NS(CH_3)_2N}$ from $\mathrm{HN(\mu\text{-}BCH_3N)_2S(CH_3)_2}$ (H)) have been obtained. In addition, the following pyrazabole relatives of type **3** = $\mathrm{(pz)RB(\mu\text{-}pz)(\mu\text{-}X)BR(pz)}$ (**3a**, R = $\mathrm{CH_3}$, X = $\mathrm{NHCH_3}$ from $\mathrm{CH_3N(\mu\text{-}BCH_3NCH_3)_2Si(CH_3)_2}$ (F); **3b**, R = $\mathrm{CH_3}$, X = $\mathrm{NH_2}$ from $\mathrm{S[\mu\text{-}BCH_3NSi(CH_3)_2]_2S}$ (E); **3c**, R = $\mathrm{C_2H_5}$, X = $\mathrm{N(CH_3)_2}$ from $\mathrm{C_2H_5B[\mu\text{-}N(CH_3)_2](\mu\text{-}NCH_3CONCH_3)(\mu\text{-}NCH_3CONHCH_3)BC_2H_5}$ (J)) and the novel type **4** (general formula **5**) = $\mathrm{RB(\mu\text{-}pz)(\mu\text{-}X)(\mu\text{-}Y)BR}$ (**4a**, R = $\mathrm{C_2H_5}$, X = $\mathrm{NHCH_3}$, Y = $\mathrm{NCH_3CONCH_3}$ from $\mathrm{CH_3N(\mu\text{-}BC_2H_5NCH_3)_2CO}$ (Ia); **4b**, R = $\mathrm{C_2H_5}$, X = $\mathrm{N(CH_3)_2}$, Y = $\mathrm{NCH_3CONCH_3}$ from J (see above); **4c**, R = $\mathrm{CH_3}$, X = $\mathrm{NHCH_3}$, Y = $\mathrm{NCH_3CSNCH_3}$ from $\mathrm{CH_3N(\mu\text{-}BCH_3NCH_3)_2CS}$ (Ic); **4d**, R = $\mathrm{CH_3}$, X = $\mathrm{NHC_2H_5}$, Y = $\mathrm{NC_2H_5CSNC_2H_5}$ from $\mathrm{C_2H_5N(\mu\text{-}BCH_3NC_2H_5)_2CS}$ (Id); **4e**, R = $\mathrm{C_6H_5}$, X = $\mathrm{NHCH_3}$, Y = $\mathrm{NCH_3CSNCH_3}$ from $\mathrm{CH_3N(\mu\text{-}BC_2H_5NCH_3)_2CS}$ (Ie)) have been isolated and characterized. The amine–borane complex $\mathrm{(CH_3)H_2N\cdot B(CH_3)(pz)_2}$ (**6**) was obtained from the reaction of either $\mathrm{CH_3B(\mu\text{-}NCH_3)(\mu\text{-}NCH_3NCH_3)BCH_3}$ (G) or $\mathrm{CH_3N(\mu\text{-}BCH_3NCH_3)_2Si(CH_3)_2}$ (F) with Hpz.

Introduction

There exist three principal types of neutral heterocyclic pyrazole (=Hpz) derivatives containing two four-coordinate annular boron atoms. The pyrazaboles of type **1** have been known for more than 2 decades. The contain the skeleton $\mathrm{>B(\mu\text{-}pz)_2B<}$, and almost 100 different B- and/or C-substituted derivatives have been described.[2] Triply bridged pyrazaboles of type **2** with X = –OBRO–

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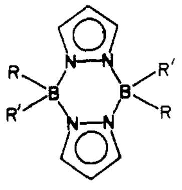
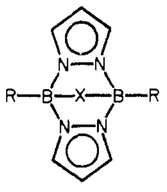
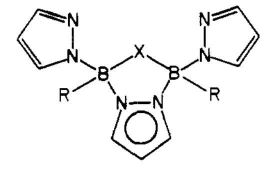


1



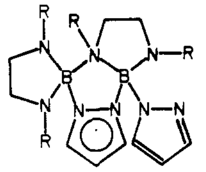
2

were accidentally discovered in recent studies of the interaction of boroxins, $(-RBO-)_3$, with pyrazole,[3,4] and only one additional representative of this type **2** (with X = SS) has since been reported.[5] In addition, several dibora monocations of the structural type **2** where X = pz have been described.[3,6-8] Compounds of type **3** were obtained from the reaction of borazines, $(-RBNR'-)_3$,

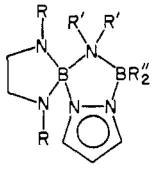


3

with pyrazole, and only three such species (X = NHR') have been reported.[9] Only most recently, four additional species containing the central B_2N_2X ring of **3** have been obtained from the reaction of bis(diorganoboryl) chalcogenides, $(R_2B)_2X$ ($R = C_2H_5$, X = O; R_2 = 1,5-C_8H_{14}, X = O or S or Se), with pyrazole. Other variations of **3** are the low-temperature dimerization products of 1-pyrazolylboranes containing trigonal boron (A) as well as addition products of the latter with monoaminoboranes (B); however, such compounds are stable only at low temperatures.[11,12]



A



B

All of the known compounds of types **2** and **3** were obtained from the interaction of pyrazole with boron heterocycles or bis(diorganoboryl) chalcogenides. Hence, a broad investigation of the reactions of heterocyclic species containing two annular boron atoms with pyrazole, the topic of the present study, appeared to be an interesting venture.

Experimental Section

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

NMR spectra were recorded for solutions in $CDCl_3$ (unless otherwise noted) on a Varian XL-200 or VXR-400 (^{11}B) or GEMINI-200 (^1H, ^{13}C) instrument. Chemical shift data are given in ppm with positive values indicating peaks downfield from the reference (internal $(CH_3)_4Si$ for ^1H and ^{13}C NMR, external $(C_2H_5)_2O \cdot BF_3$ from ^{11}B NMR). Abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, and m = unresolved multiplet; an asterisk denotes a broad signal. Coupling constants J are given in hertz. All ^{13}C NMR spectra were recorded in the proton-decoupled mode. EI mass spectral data were obtained on a VG ZAB-2F spectrometer, and FI mass spectra were obtained on Varian MAT-CH5 instrument.

All reactions were performed under dry nitrogen cover. Pyrazole (=Hpz) was distilled over a small amount of sodium and stored under anhydrous conditions.

$F_2B(\mu$-pz$)_2BF_2$ (1a) from $[(CH_3)_2NBF_2]_2$ (C) and Hpz. A mixture of 9.3 g (50 mmol) of (dimethylamino)difluoroborane dimer (C),[13] 6.8 g (100 mmol) of Hpz, and 70 mL of toluene was refluxed with stirring for 8 h. Toluene was evaporated, and the residue was recrystallized from methanol to give 8.2 g (71%) of *B*-tetrafluoropyrazabole, $F_2B(\mu$-pz$)_2BF_2$ (**1a**), mp 164 °C ($\delta(^{19}F)$ −150.1 (q, J = 21) versus $CFCl_3$ as standard), which has previously been characterized in detail.[14]

$(CH_3)H_2N \cdot B(CH_3)(pz)_2$ (6) from the Reaction of $CH_3B(\mu$-$NCH_3)(\mu$-$NCH_3NCH_3)BCH_3$ (G) with Hpz. A solution of 2.78 g (20 mmol) of G[15] in 15 mL of ether was added dropwise with stirring to a solution of 2.72 g (40 mmol) of Hpz in 25 mL of ether. A clear solution resulted, but when the mixture was warmed to 30 °C, a colorless precipitate began to form. The mixture was heated to gentle reflux for 3 h. The precipitate was collected, washed extensively with ether, and dried under vacuum to give 1.1 g of **6**, mp 134–136 °C (after recrystallization from acetonitrile). Anal. Calcd for $C_8H_{14}BN_5$ (M_r = 191.04): C, 50.30; H, 7.39; B, 5.66; N, 36.66. Found: C, 49.91; H, 7.30; N, 36.66.

NMR data: $\delta(^1H)$ 7.54 (2 H, d, J = 1.5), 7.27 (2 H, d, J = 2.2), 6.33* (2 H, s), 6.18 (2 H, unsym t = two overlapping d, $J \simeq 2$), 2.15 (3 H, t, J = 6), 0.42 (3 H, s); $\delta(^{11}B)$ 0.6 (s, $h_{1/2}$ = 150 Hz); $\delta(^{13}C)$ 140.4, 132.5, 104.8, 26.6, 3.0*. Only two peak groups near m/z 123 and 68 were observed in the FI mass spectrum of the compound.

Ether was evaporated from the filtrate, and the remaining material was slurried in hexane. The insoluble material was collected, washed and hexane, and dried to give 0.5 g of material, mp 170–230 °C. It was identified (^1H NMR spectrum, mass spectrum) as a trace of the above adduct in mixture with a trace of $CH_3B(\mu$-pz$)_2(\mu$-$OBCH_3O)BCH_3$[5] as well as isomers of $(CH_3)($pz$)B(\mu$-Pz$)(\mu$-$NHCH_3)B(CH_3)($pz$)$ (**3a**; see below) and $(CH_3)($pz$)B(\mu$-pz$)_2B(CH_3)($pz$)$ (**1b**; see below). If the same mixture of reagents as noted above was refluxed for 10 h in toluene solution, a mixture of the two latter species was obtained as the product, accounting for more than 90% of the employed Hpz.

In the presence of excess Hpz the reaction proceeded as illustrated in eq 2 (see below). However, no effort was made to separate the two amine–borane type species.

$(CH_3)H_2N \cdot B(CH_3)(pz)_2$ (6) from the Reaction of $CH_3N(\mu$-$BCH_3NCH_3)_2Si(CH_3)_2$ (F) with Hpz. To a solution of 2.0 g (12 mmol) of F[16] in 60 mL of hexane was added with stirring 2.5 g (37 mmol) of Hpz. The mixture was stirred at room temperature for 4 days, and the precipitate was collected (the filtrate was not further studied), washed with hexane, and dried under vacuum to yield 2.6 g (74%) of material, mp 132–135 °C. The product was recrystallized from acetonitrile to give colorless crystals, mp 134–136 °C, identical (NMR data) with the material described above.

Reaction of $CH_3N(\mu$-$BCH_3NCH_3)_2Si(CH_3)_2$ (F) with Hpz at Elevated Temperature—Formation of $(CH_3)($pz$)B(\mu$-pz$)(\mu$-$NHCH_3)B(CH_3)($pz$)$ (3a) and $CH_3N[Si($pz$)(CH_3)_2]$. To a solution of 3.0 g (18 mmol) of F[16] in 50 mL of hexane was added with stirring 3.7 g (54 mmol) of Hpz. The

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latter dissolved slowly, and a new colorless precipitate was formed. The mixture was refluxed for 5 h to give a clear solution. After refluxing for an additional 6 h, the mixture was cooled to room temperature and 2.0 g of colorless precipitate (mp 105–106 °C) was obtained. A second crop of 0.8 g (mp 103–106 °C) was obtained on concentration of the solution to give a total yield of 53% of $(CH_3)(pz)B(\mu\text{-}NHCH_3)B(CH_3)(pz)$ (**3a**). The material was recrystallized from hexane to give the product, mp 105–106 °C. Anal. Calcd for $C_{12}H_{19}B_2N_7$ (M_r = 282.90): C, 50.95; H, 6.77; B, 7.64; N, 34.04. Found: C, 49.94; H, 6.79; N, 34.11.

NMR data: $\delta(^1H)$ 7.88 (2 H, d, $J = 2.3$), 7.82 (2 H, d, $J = 1.6$), 7.35 (2 H, d, $J = 2.3$), 6.7* (1 H, t, $J = 2.3$), 6.41 (2 H, unsym t = two overlapping d), 2.35 (3 H, d, $J = 6.0$), 0.57 (6 H, s) (additional signals of less than 10% of the total intensity in these same general regions indicated the presence of an isomer; maximum differences were observed for the signal δ 2.35 where a counterpart was observed at δ 2.02, and for the signal δ 0.58 where a counterpart at δ 0.80 was observed); $\delta(^{11}B)$ 2.3 (s, $h_{1/2}$ = 125 Hz). A parent ion cluster was observed in EI mass spectrum of the compound at *m/z* 283; additional peaks of high intensity were observed at *m/z* 229, 199, 187, 172, and 147.

$CH_3N[Si(pz)(CH_3)_2]_2$. After complete removal of solvent from the filtrate from the preceding process, a colorless liquid remained. The latter was distilled under vacuum over a small column to give 3.2 g of product, bp 105–108 °C (1 Torr), as the major fraction, which was identified as $CH_3N[Si(pz)(CH_3)_2]_2$. Anal. Calcd for $C_{11}H_{21}N_5Si_2$ (M_r = 279.46): C, 47.28; H, 7.75; N, 25.05; Si, 20.10. Found: C, 46.99; H, 7.85; N, 25.38; Si, 20.09.

NMR data: $\delta(^1H)$ 7.77 (2 H, unresolved d), 7.63 (2 H, d, $J = 2.0$), 6.31 (2 H, t, $J = 2.0$), 2.54 (3 H, s), 0.49 (12 H, s); $\delta(^{13}C)$, 143.5, 134.5, 106.4, 30.5, −1.2.

$(CH_3)(pz)B(\mu\text{-}pz)_2B(CH_3)(pz)$ (1b) from $(CH_3)(pz)B(\mu\text{-}pz)(\mu\text{-}NHCH_3)B(CH_3)(pz)$ (3a) and Hpz. A mixture of 1.0 g (3.5 mmol) of **3a** (see above) and 2.0 g (29 mmol) of Hpz was heated for 1 h in an oil bath of 150 °C. Excess Hpz was sublimed off under vacuum (80–90 °C bath temperature) to leave 0.95 g (85% yield) of an isomer mixture of *cis*- and *trans*-$(CH_3)(pz)B(\mu\text{-}pz)_2B(pz)(CH_3)$ (**1b**), mp 157–185 °C. Treatment of the crude product with cyclohexane leaves 0.2 g of one isomer (A), mp 196–198 °C; 0.5 g of material (A and the second isomer B), mp 158–195 °C, was recovered from the cyclohexane.

NMR data for isomer A: $\delta(^1H)$ 7.62 (3 H, d, $J = 2.4$), 7.30 (1 H, d, $J = 2.3$), 6.52 (1 H, t, $J = 2.5$), 6.24 (1 H, unsym t = two overlapping d, $J \simeq 2$), 0.42 (3 H, s); $\delta(^{11}B)$ 1.1 (s, $h_{1/2}$ = 140 Hz); $\delta(^{13}C)$ 141.9, 136.4, 132.2, 107.3, 105.0 (the B-bonded C was not observed). The ^1H NMR signals δ 7.62/7.30/6.24 and 7.62/6.52 belong to the two different types of pyrazolyl groups. EI mass spectrum: *m/z* 305 (24), 304 (13), 254 (15), 253 (100), 252 (53), 251 (10), 185 (9), 184 (6), 66 (9). NMR data for the mixture of A and B: additional (to those given for A) ^1H NMR signals were observed at δ 7.65, 6.99, 6.55, 6.09, and 0.78 to account for the presence of about 30% of a second isomer.

$CH_3B(\mu\text{-}pz)_2[\mu\text{-}NS(CH_3)_2N]BCH_3$ (2a). A solution of 1.05 g (15.4 mmol) of Hpz in 30 mL of ether was added to a hot solution of 1.20 g (6.9 mmol) of $HN(\mu\text{-}BCH_3N)_2S(CH_3)_2$ (H)[17] in 100 mL of benzene. The stirred mixture was heated to reflux for 18 h. The resultant pale yellow solution was evaporated under vacuum. The solid residue was dissolved in ether from which two crops of product (1.6 g total = 84% yield) were obtained on concentration. They were combined and recrystallized from benzene/cyclohexane (1:3 by volume) to give a colorless crystalline product, mp 218–220 °C. Anal. Calcd for $C_{10}H_{18}B_2N_6S$ (M_r = 275.97): C, 43.52; H, 6.57; B, 7.83; N, 30.45; S, 11.62. Found: C, 43.12; H, 6.90; B, 7.69; N, 30.31; S, 11.73.

NMR data: $\delta(^1H)$ 7.67 (2 H, d, $J = 2.4$), 6.27 (1 H, t, $J = 2.4$), 2.54 (3 H, s), 0.57 (3 H, s); $\delta(^{11}B)$ 0.45 (s, $h_{1/2}$ = 180 Hz); $\delta(^{13}C)$ 135.5, 105.1, 51.3, 5.1*. The EI mass spectrum of the material exhibited a very weak parent ion; major ion clusters were observed in the regions *m/z* 261 (base peak), 228, 209, 193, 165, 148, and 134.

$(CH_3)(pz)B(\mu\text{-}pz)(\mu\text{-}NH_2)B(pz)(CH_3)$ (3b) from $S[\mu\text{-}BCH_3NSi(CH_3)_3]_2S$ (E) and Hpz. A mixture of 1.9 g (27.9 mmol) of Hpz, 2.0 g (6.9 mmol) of E,[18] and 50 mL of benzene was refluxed with stirring for 16 h. Volatile material was removed under vacuum to leave a slightly yellow solid. The crude material was treated with three 50-mL portions of cyclohexane to leave 0.8 g of product, mp 140–143 °C (after recrystallization from cyclohexane), which was identified as a mixture of $(CH_3)(pz)B(\mu\text{-}pz)(\mu\text{-}NH_2)B(pz)(CH_3)$ (**3b**), with one isomer predominating. On concentration of all cyclohexane solutions, an additional crop of 0.5 g of material, mp 121–150 °C, was obtained. Anal. Calcd for $C_{11}H_{17}B_2N_7$ (M_r = 269.92): C, 48.49; H, 6.35; B, 9.78; N, 36.70. Found: C, 48.77; H, 6.46; N, 36.31.

NMR data: $\delta(^1H)$ (assignments made by selective decoupling) for isomer A (major product) 7.61 (2 H, d, $J = 1.5$)/7.58 (2 H, d, $J = 2.3$)/6.28 (2 H, unsym t = two overlapping d) for the terminal pz groups, and 7.42 (2 H, d, $J = 2.1$)/6.46 (1 H, $J = 2.1$) for the bridging pz group; isomer B 7.75 (2 H, d, $J = 2.2$)/7.68 (2 H, d, $J = 2.3$)/6.30 (2 H, unsym t = two overlapping d) for the terminal pz groups, 7.28 (2 H, d, $J = 2.4$)/6.39 (1 H, t, $J = 2.2$) for the bridging pz group; for both isomers δ 4.8* (s) for the bridging NH_2 group, 0.54 (s) for the CH_3 groups; $\delta(^{11}B)$ 1.7 ($h_{1/2}$ = 125 Hz). The EI mass spectrum exhibited major peaks at *m/z* 187, 134, and 68.

$C_2H_5B(\mu\text{-}pz)[\mu\text{-}N(CH_3)_2](\mu\text{-}NCH_3CONCH_3)BC_2H_5$ (4b). A slurry of 0.58 g (8.5 mmol) of Hpz in 50 mL of toluene was added to a hot solution of 1.4 g (4.7 mmol) of $C_2H_5B[\mu\text{-}N(CH_3)_2](\mu\text{-}NCH_3COCH_3)(\mu\text{-}NCH_3CONHCH_3)BC_2H_5$ (J; R = CH_3, R′ = C_2H_5)[19] in 100 mL of toluene. The mixture was refluxed with stirring overnight. Toluene was evaporated under reduced pressure, and the remaining viscous liquid was covered with 50 mL of ether. A colorless precipitate (0.3 g) formed and was collected. Ether was evaporated from the filtrate and again a viscous liquid remained. The latter was again treated with ether to give an additional 0.4 g of colorless precipitate (54% overall yield). The solids were combined and recrystallized from ether to give 0.4 g of material, mp 170–175 °C. Traces of the *N,N′*-dimethylurea were sublimed off under vacuum (90 °C bath temperature), and the remainder of the product was then further purified by sublimation (150 °C bath temperature) to give pure product **4b**, mp 175–177 °C. Anal. Calcd for $C_{12}H_{25}B_2N_5O$ (M_r = 276.96): C, 52.04; H, 9.10; B, 7.81; N, 25.27; O, 5.78. Found: C, 51.82; H, 9.04; N, 26.20.

NMR data: $\delta(^1H)$ 7.38 (2 H, d, $J = 2.2$), 6.31 (1 H, t, $J = 2.2$), 2.84 (6 H, s), 2.60 (3 H, s), 2.11 (3 H, s), 1.15–0.7 (10 H, m); $\delta(^{11}B)$ −0.4 (s, $h_{1/2}$ = 135 Hz); $\delta(^{13}C)$ 163.1, 130.0, 107.4, 40.7, 40.3, 30.6, 8.5, 3.5*. EI mass spectrum: *m/z* 192 (100), 190 (63), 189 (5), 176 (32), 175 (19), 81 (6). The highest ion cluster was observed at *m/z* 277 in very low abundance.

Alternate Reaction—Formation of $(C_2H_5)(pz)B(\mu\text{-}pz)_2B(C_2H_5)(pz)$ (1c). Reaction of a large excess of Hpz (12.6 g, 185 mmol) with J (R = CH_3, R′ = C_2H_5)[19] (1.5 g, 4.4 mmol) at 150 °C for 20 h gave the previously[9] described pyrazabole $(C_2H_5)(pz)B(\mu\text{-}pz)_2B(C_2H_5)(pz)$ (**1c**) in ca. 60% yield.

$C_2H_5B(\mu\text{-}pz)(\mu\text{-}NHCH_3)(\mu\text{-}NCH_3CONCH_3)BC_2H_5$ (4a). A mixture of 1.3 g (6.7 mmol) of $CH_3N(\mu\text{-}BC_2H_5NCH_3)_2CO$ (Ia),[20] 1.0 g (14.7 mmol) of Hpz, and 50 mL of benzene was refluxed with stirring for 6 h. Benzene was evaporated under vacuum; the remaining material was washed with ether and dried to give 0.95 g (54%) of crude product. This was recrystallized twice from benzene to give colorless crystals, mp 148–149 °C. Anal. Calcd for $C_{11}H_{23}B_2N_5O$ (M_r = 262.96): C, 50.24; H, 8.82; B, 8.22; N, 26.63; O, 6.08. Found: C, 49.69; H, 8.95; N, 26.20.

NMR data: $\delta(^1H)$ 7.45 (2 H, d, $J = 2.2$), 6.39 (1 H, t, $J = 2.2$), 2.74 (6 H, s), 2.45* (1 H, s), 2.28 (3 H, d, $J = 5.5$), 0.95–0.75 (10 H, m); $\delta(^{11}B)$ −2.1 (s, $h_{1/2}$ = 140 Hz); $\delta(^{13}C)$ 160.4, 129.9, 107.9, 29.6, 26.6, 7.9, 7.0*. The EI mass spectrum exhibited the highest peak at *m/z* 195, indicating a ready loss of Hpz from the species.

$CH_3B(\mu\text{-}pz)(\mu\text{-}NHCH_3)(\mu\text{-}NCH_3CSNCH_3)BCH_3$ (4c). A mixture of 1.5 g (8.2 mmol) of $CH_3N(\mu\text{-}BCH_3NCH_3)_2CS$ (Ic),[20] 1.2 g (17.6 mmol) of Hpz, and 25 mL of benzene was refluxed with stirring for 24 h. Benzene was evaporated, and the remaining solid was washed with ether and dried to give 1.3 g (63%) of crude product. This was recrystallized from acetonitrile to give colorless crystals, mp 188–189 °C. Anal. Calcd for $C_9H_{19}B_2N_5S$ (M_r = 250.96): C, 43.07; H, 7.63; B, 8.61; N, 27.91; S, 12.77. Found: C, 43.01; H, 7.78; B, 8.39; N, 27.95; S, 12.95.

NMR data: $\delta(^1H)$ 7.46 (2 H, d, $J = 2.3$), 6.39 (1 H, t, $J = 2.3$), 3.20 (6 H, s), 2.79* (1 H, s), 2.26 (3 H, d, $J = 6$), 0.30 (6 H, s); $\delta(^{11}B)$ 1.2 ($h_{1/2}$ = 120 Hz); $\delta(^{13}C)$ 186.9, 130.2, 108.1, 385, 26.8, 0.5*. The EI mass spectrum exhibited the highest peak in the region at *m/z* 183, indicating a ready loss of Hpz from the species.

The same material (**4c**) was obtained when a mixture of the two reagents was heated for 4 h to 120 °C in the absence of solvent. However, at higher temperatures the following reaction occurred.

Alternate Reaction—Formation of $(CH_3)(pz)B(\mu\text{-}pz)_2B(CH_3)(pz)$ (1b). A mixture of 1.9 g (10.4 mmol of $CH_3N(\mu\text{-}BCH_3NCH_3)_2CS$ (Ic)[20] and 4.8 g (70.6 mmol) of Hpz was heated to 170 °C for 2 h. Excess Hpz was sublimed off under vacuum, and the remaining material was washed with ether. On treatment with hot benzene, most of the residue dissolved. Benzene was evaporated from the filtered clear solution to leave a slightly yellow crystalline material. This was washed with acetonitrile to give 0.6 g of colorless product, mp 193–194 °C. Anal. Calcd for $C_{14}H_{18}B_2N_8$ (M_r = 319.91): C, 52.56; H, 5.67; B, 6.76; N, 35.00. Found: C, 52.49; H, 5.71; B, 6.31; N, 34.72.

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The NMR data of the material were identical with those obtained for the isomer A of the compound obtained from the reaction of (CH_3)-$(pz)B(\mu\text{-}pz)(\mu\text{-}NHCH_3)B(CH_3)(pz)$ (**3a**) with Hpz (see above).

$CH_3B(\mu\text{-}pz)(\mu\text{-}NHC_2H_5)(\mu\text{-}NC_2H_5CSNC_2H_5)BCH_3$ (4d). To a solution of 2.0 g (8.9 mmol) of $C_2H_5N(\mu\text{-}BCH_3NC_2H_5)_2CS$ (Id)[20] in 30 mL of benzene was added with stirring 1.2 g (17.8 mmol) of Hpz to give a clear solution. When the solution was slowly warmed (after ca. 10 min and when a temperature near 50 °C was reached), a colorless precipitate began to form. When refluxing was initiated on further heating of the mixture, a clear solution was again obtained, and this was heated to reflux for 18 h. When the solution was cooled room temperature, 1.6 g of precipitate was formed and collected. Benzene was evaporated from the filtrate to leave an oily residue. This was treated with 50 mL of ether to give an additional 0.6 g of product as insoluble material for an overall yield of 84%. The two precipitates were combined, a small amount of Hpz was sublimed off, and the desired product, mp 174–176 °C, remained. Anal. Calcd for $C_{12}H_{25}B_2N_5S$ (M_r = 293.01): C, 49.19; H, 8.60; B, 7.38; N, 23.89; S, 10.94. Found: C, 49.34; H, 8.60; N, 23.80; S, 11.07.

NMR data: $\delta(^1H)$ 7.46 (2 H, d, J = 2.3), 6.39 (1 H, t, J = 2.3), 4.01 (2 H, two closely overlapping q), 3.84 (2 H, two closely overlapping q), 2.77 (2 H, two closely overlapping q), 1.9* (1 H, s), 1.27 (3 H, t, J = 7.4), 1.15 (6 H, t, J = 7.0), 0.40 (6 H, s); $\delta(^{11}B)$ 1.2 (s, $h_{1/2}$ = 130 Hz); $\delta(^{13}C)$ 186.3, 128.9, 108.1, 45.0, 36.9, 36.8, 15.0, 14.9, 0.2*.

$C_6H_5B(\mu\text{-}pz)(\mu\text{-}NHCH_3)(\mu\text{-}NCH_3CSNCH_3)BC_6H_5$ (4e). To a solution of 2.0 g (6.5 mmol) of $CH_3N(\mu\text{-}BC_6H_5NCH_3)_2CS$ (Ie)[20] in 150 mL of benzene was added with stirring 0.9 g (13.2 mmol) of Hpz. A clear solution was obtained, but after a few min a gellike precipitate began to form. The mixture was stirred at room temperature for 22 h and reduced to one-third volume under reduced pressure. Insoluble material was collected, washed with benzene, and dried to give 1.6 g (66%) of product, mp 178–180 °C (after recrystallization from acetonitrile). Anal. Calcd for $C_{19}H_{23}B_2N_5S$ (M_r = 375.07): C, 60.84; H, 6.18; B, 5.76; N, 18.66; S, 8.55. Found: C, 59.64; H, 6.16; N, 19.23; S, 8.29.

NMR data: $\delta(^1H)$ 7.98 (2 H, d, J = 1.4), 7.5 + 7.4 (10 H, unresolved m), 6.74 (1 H, t, J = 2.3), 3.8* (1 H, s), 3.16 (6 H, s), 1.50 (3 H, d, J = 6.3); $\delta(^{11}B)$ 3.2 (s, $h_{1/2}$ = 250 Hz); $\delta(^{13}C)$ 190.5, (139.5?), 133.2, 132.6, 128.4, 128.1, 110.7, 41.5; 31.8.

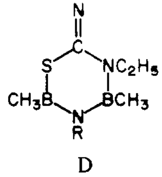
Results

Dimeric (dimethylamino)difluoroborane (C), a four-membered B_2N_2 heterocycle containing four-coordinate boron,[21] interacted smoothly with pyrazole (=Hpz) in boiling benzene to yield *B*-tetrafluoropyrazabole (**1a**) according to eq 1. The reaction may proceed via monomeric $(CH_3)_2N$-BF_2 and then can be viewed as a simple transamination, which is followed by immediate dimerization of the initially formed (1-pyrazolyl)difluorobrane to yield **1a**.

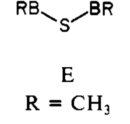
$$\underset{\textbf{C}}{[(CH_3)_2NBF_2]_2} + 2Hpz \rightarrow \underset{\textbf{1a}}{F_2B(\mu\text{-}pz)_2BF_2} + 2(CH_3)_2NH \qquad (1)$$

Pyrazaboles of type **1** were also the ultimate products of the interaction of excess of Hpz with the heterocycles F and G (see below) as well as the species of type **3** at high temperatures. The latter reaction type has been observed previously.[9]

No reaction was observed when the eight-membered B_4N_4 heterocycle $[-ClBN(t\text{-}C_4H_9)-]_4$, containing three-coordinate boron,[22] was treated with Hpz in either boiling ether or toluene. This lack of reaction may be explained by a steric protection of the annular nitrogen by the *tert*-butyl group. Very similarly, the heterocycle D (R = C_6H_3-2,6-$(CH_3)_2$)[23] was unaffected by Hpz, even when a mixture of the two reagents was molten and kept at 170–190 °C for 3 h.

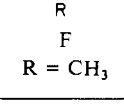


D



E

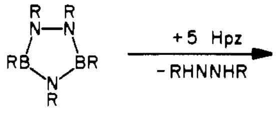
R = CH_3



F

R = CH_3

The five-membered B_2N_3 heterocycle E interacted with Hpz in boiling ether to give the adduct $(CH_3)H_2N\cdot B(CH_3)(pz)_2$ (**6**) as well as $(CH_3)(pz)_2B\cdot Hpz$ and *N,N'*-dimethylhydrazine as shown in eq 2. The ^1H NMR data of the complex **6** indicate that in solution the N-bonded protons are not localized and the two boron-bonded pz groups are equivalent.



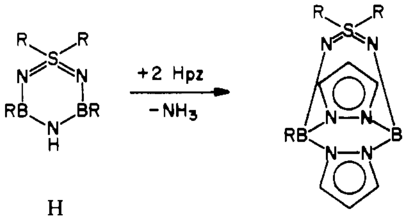
G

R = CH_3

$$\underset{\textbf{6}}{(CH_3)H_2N\cdot B(CH_3)(pz)_2} + (CH_3)(pz)_2B\cdot Hpz \qquad (2)$$

When the same reaction was carried out in boiling toluene, the initial complex underwent condensations and the species $(CH_3)(pz)B(\mu\text{-}pz)(\mu\text{-}NHCH_3)B(CH_3)(pz)$ (**3a**, R = CH_3, X = $NHCH_3$) and the pyrazabole $(CH_3)(pz)B(\mu\text{-}pz)_2B(CH_3)(pz)$ (**1b**, R = CH_3, R′ = pz; see below) were the major products of the cited reaction.

At first glance these reactions may seem to be in contrast with that of $CH_3B(\mu\text{-}NC_6H_5)(\mu\text{-}SS)BCH_3$ with Hpz which led to a species of type **2** (R = CH_3, X = SS).[5] However, the results of the present study suggest that whenever Hpz interacts with a heterocycle containing trigonal boron, the Hpz attacks the most basic site of the ring system as the initial step of the reaction. Subsequent processes then depend on the particular reaction conditions and lead to the observed products. In the cited case of the 1-aza-3,4-dithia-2,5-diborolidine ring the nitrogen is clearly the most basic site, and in the case of the 1,3,4-triaza-2,5-diborolidine ring of G the pyrazole NH seems to attack initially at the hydrazine nitrogens. This view concerning the mode of attack finds support in the reactions of Hpz with various other heterocycles containing two annular boron atoms. In the case of F, the NH moiety was readily displaced to give the triply bridged pyrazabole **2a** as is shown in eq 3. This result suggests that the NH group of the originating heterocycle is the most basic site and interaction with Hpz initiates at this site. On the other hand, when E was reacted with Hpz, the reaction yielded $(CH_3)(pz)B(\mu\text{-}pz)(\mu\text{-}NH_2)B(CH_3)(pz)$ (**3b**, R = CH_3, X = NH_2). The 1-sila-2,4,6-triaza-3,5-diboracyclohexane heterocycle F was attacked by Hpz via initial cleavage of the B–N(Si) bonds and also gave the complex $(CH_3)H_2N\cdot B(CH_3)(pz)_2$ (**6**). (The (1-pyrazolyl)silane $CH_3N[Si(CH_3)_2(pz)]_2$ was obtained as a byproduct in this reaction.)



(3)

H

R = CH_3

2a

The two complexes $(CH_3)(pz)_2B\cdot L$, where L = CH_3NH_2 (**6**) or Hpz, respectively, may be viewed as poly(1-pyrazolyl)boric acids with the anion $[(CH_3)(pz)_2B(L - H)]^-$. As such, **6** is an interesting variation of the well-known poly(1-pyrazolyl)borates of the type $[R_nB(pz)_{4-n}]$ with n = 0–2, which play an important role as chelating ligands in coordination chemistry.[24] It is possible that **6** may function as a hybrid poly(1-pyrazolyl)borate ligand, only two examples of which have been described in the literature.[25,26] This feature is presently being studied.

Complex **6** was again converted at elevated temperatures (refluxing hexane) and in the presence of additional pyrazole to yield $(CH_3)(pz)$-$B(\mu\text{-}pz)(\mu\text{-}NHCH_3B(CH_3)(pz)$ (i.e., **3**, with R = CH_3 X = $NHCH_3$) and, ultimately, a mixture of the two isomers of $(CH_3)(pz)B(\mu\text{-}pz)_2B$-$(CH_3)(pz)$ (i.e., **1**, with R = CH_3, R′ = pz).

A novel type of triply bridged diboron species (**4**), which can be considered as a relative of the pyrazaboles, was obtained from reactions of 1,3,5-triaza-2,6-diboracyclohexan-4-ones or corresponding 4-thiones (I) with Hpz as shown in eq 4. Compounds of type **4** are also accessible

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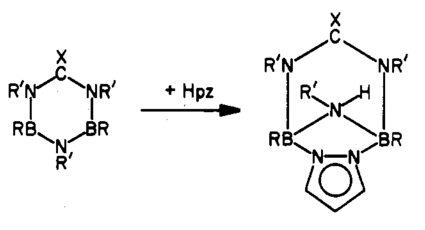
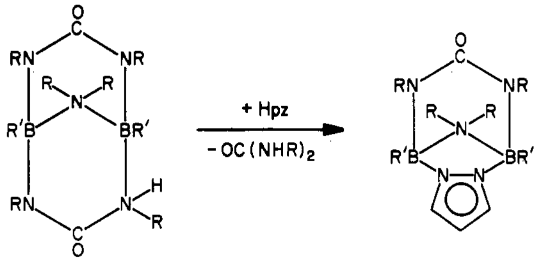


(4)

I 4

a: $R = C_2H_5$; $R' = CH_3$; $X = O$
c: $R = R' = CH_3$; $X = S$
d: $R = CH_3$; $R' = C_2H_5$; $X = S$
e: $R = C_6H_5$; $R' = CH_3$; $X = S$

by the reaction of the recently described[20] triply bridged diboron species J with Hpz under displacement of one *N,N'*-dimethylurea moiety as shown in eq 5.



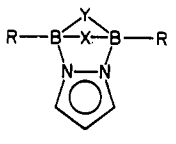
(5)

J **4b**: $R = CH_3$; $R' = C_2H_5$

The compounds of type **4** are the first representatives of a novel type of relatives of the pyrazaboles that may be illustrated in general form by **5**. Species of type **5** are related to triply bridged pyrazaboles of type **2**, in which one bridging pz group has then been replaced by another bridging moiety, just as in species of type **3** one of the bridging pz groups of **1** has been replaced by another bridging group.

Discussion

The present data suggest that when pyrazole (=Hpz) interacts with heterocycles containing two annular boron atoms, the NH moiety of Hpz seeks out the most basic site of the ring. Whenever possible, the pyrazolyl nitrogens will attach to the boron atoms, but the nature of the ultimate product is a function of the specific reaction conditions, primarily the ratio of the reactants and the temperature. These can lead to a complete breakdown of the original heterocycle to yield amine-borane type adducts of (1-pyrazolyl)boranes as examplified by **6**. Alternatively, fragments of the original ring systems are retained, leading to pyrazaboles of type **2** or the pyrazabole relatives of types **3** or **4**, respectively.



5

The ring system of general formula **5** is a novel type which is specifically related to the triply bridged pyrazaboles of type **2**. Hence, it is not surprising that under forcing conditions and in the presence of sufficient Hpz, **5** converts to pyrazaboles of type **1** (with R = pz). In general, the latter seem to be the thermodynamically favored products in reactions of boron derivatives with Hpz. Consequently, species of type **3** can also be converted to those of type **1**.

Although at this time compounds of type **3** are limited to those where X is an amino or a chalcogenyl group and those of type **5** to species where X is an amino group and Y a bridging urea moiety, it is reasonable to assume that compounds containing bridging groups X and Y other than those cited will also become available.

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A Study of the ^{13}C Chemical Shift Anisotropy in Metal Acetylides

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The anisotropy of the ^{13}C chemical shielding in five metal acetylides, Li_2C_2, Na_2C_2, CaC_2, SrC_2, and BaC_2, is measured with ^{13}C nuclear magnetic resonance (NMR) spectroscopy. The chemical shift anisotropies of the acetylides range from 180 to 235 ppm, compared to 160 ppm for $HC\equiv CH$. The shielding perpendicular to the $C\equiv C$ bond in the acetylides is invariant with cation and is $\sim$315 ppm, relative to TMS. However, the shielding parallel to the $C\equiv C$ bond varies by over 110 ppm and correlates with the distances to cations in the plane bisecting the $C\equiv C$ bond. For compounds with bonding along the $C\equiv C$ axis (the alkaline-earth-metal acetylides and acetylene) the isotropic shift is proportional to the acetylide-nearest-neighbor distance and the ionization potential of the nearest neighbor. The spectral broadening in the ^{13}C NMR spectra of the alkaline-earth-metal acetylides decreases and the isotropic shift moves to higher frequency as the size of the cation increases. Both trends are attributed to the paramagnetic component of the shielding, relative to a gauge origin at the carbon nucleus.

Introduction

The anisotropy of the chemical shielding at a nucleus is of fundamental and practical interest. It offers, for example, the intrinsic merit of characterizing chemical bonding; chemical shift anisotropy, and especially the identification of the diamagnetic and paramagnetic contributions for a given gauge origin, can be used to corroborate calculations of electronic wave functions. It also has potential for chemical analysis of solid samples; the chemical shift anisotropy differentiates between similar species of a carbon functionality when the isotropic shift may show no trend. Discussions of the trends in ^{13}C chemical shift anisotropies are offered in a recent review[1] and a compilation.[2] Although ab initio calculations of chemical shift anisotropies are improving, chemical analysis of solids is almost exclusively by comparison to the spectra of reference compounds. However, there is a lack of reference data; for acetylenic carbons the chemical shift anisotropy has been reported for only four compounds.[2] The principal components of the ^{13}C shielding tensor for five inorganic acetylides are reported here. Furthermore, trends within the compounds

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(1) Veeman, W. S. *Prog. NMR Spectrosc.* **1984**, *16*, 193.
(2) Duncan, T. M. *J. Phys. Chem. Ref. Data* **1987**, *16*, 125.