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Reactions of Some Boron Heterocycles with Pyrazole

by

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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 $RR'B(\mu\text{-}pz)_2BRR'$ = **1** (**1a**: R = R′ = F from $[(CH_3)_2NBF_2]_2$ (**C**); **1b**: R = CH_3, R′ = pz from either $(pz)(CH_3)B(\mu\text{-}pz)(\mu\text{-}NHCH_3)B(pz)(CH_3)$ (**3a**) or $CH_3B(\mu\text{-}pz)(\mu\text{-}NHCH_3)(\mu\text{-}NCH_3CSNCH_3)BCH_3$ (**Ic**); **1c**: R = C_2H_5, R′ = pz from $C_2H_5B[\mu\text{-}N(CH_3)_2](\mu\text{-}NCH_3CONCH_3)(\mu\text{-}NCH_3CONHCH_3)BC_2H_5$ (**J**)) and the type $RB(\mu\text{-}pz)_2(\mu\text{-}X)BR$ = **2** (**2a**: R = CH_3, X = $NS(CH_3)_2N$ from $HN(\mu\text{-}BCH_3N)_2S(CH_3)_2$ (**H**)) have been obtained. In addition, the following pyrazabole relatives of type **3** = $(pz)RB(\mu\text{-}pz)(\mu\text{-}X)BR(pz)$ (**3a**: R = CH_3, X = $NHCH_3$ from $CH_3N(\mu\text{-}BCH_3NCH_3)_2Si(CH_3)_2$ (**F**); **3b**: R = CH_3, X = NH_2 from $S[\mu\text{-}BCH_3NSi(CH_3)_2]_2S$ (**E**); **3c**: R = C_2H_5, X = $N(CH_3)_2$ from $C_2H_5B[\mu\text{-}N(CH_3)_2](\mu\text{-}NCH_3CONCH_3)(\mu\text{-}NCH_3CONHCH_3)BC_2H_5$ (**J**)) and the novel type **4** (general formula **5**) = $RB(\mu\text{-}pz)(\mu\text{-}X)(\mu\text{-}Y)BR$ (**4a**: R = C_2H_5, X = $NHCH_3$, Y = NCH_3CONCH_3 from $CH_3N(\mu\text{-}BC_2H_5NCH_3)_2CO$ (**Ia**); **4b**: R = C_2H_5, X = $N(CH_3)_2$, Y = NCH_3CONCH_3 from **J** (see above); **4c**: R = CH_3, X = $NHCH_3$, Y = NCH_3CSNCH_3 from $CH_3N(\mu\text{-}BCH_3NCH_3)_2CS$ (**Ic**); **4d**: R = CH_3, X = NHC_2H_5, Y = $NC_2H_5CSNC_2H_5$ from $C_2H_5N(\mu\text{-}BCH_3NC_2H_5)_2CS$ (**Id**); **4e**: R = C_6H_5, X = $NHCH_3$, Y = NCH_3CSNCH_3 from $CH_3N(\mu\text{-}BC_2H_5NCH_3)_2CS$ (**Ie**)) have been isolated and characterized. The amine-borane complex $(CH_3)H_2N\cdot B(CH_3)(pz)_2$ (*6*) was obtained from the reaction of either $CH_3B(\mu\text{-}NCH_3)(\mu\text{-}NCH_3NCH_3)BCH_3$ (**G**) or $CH_3N(\mu\text{-}BCH_3NCH_3)_2Si(CH_3)_2$ (**F**) with Hpz.

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Reactions of Some Boron Heterocycles with Pyrazole[1]

C. Habben,[†] L. Komorowski,[‡§] W. Maringgele,[†] A. Meller,[†*] and K. Niedenzu[‡*]

Received........................

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 $RR'B(\mu-pz)_2BRR'$ = **1** (**1a**: R = R' = F from $[(CH_3)_2NBF_2]_2$ (**C**); **1b**: R = CH_3, R' = pz from either $(pz)(CH_3)B(\mu-pz)(\mu-NHCH_3)B(pz)(CH_3)$ (**3a**) or $CH_3B(\mu-pz)(\mu-NHCH_3)(\mu-NCH_3CSNCH_3)BCH_3$ (**Ic**); **1c**: R = C_2H_5, R' = pz from $C_2H_5B[\mu-N(CH_3)_2](\mu-NCH_3CONCH_3)(\mu-NCH_3CONHCH_3)BC_2H_5$ (**J**)) and the type $RB(\mu-pz)_2(\mu-X)BR$ = **2** (**2a**: R = CH_3, X = $NS(CH_3)_2N$ from $HN(\mu-BCH_3N)_2S(CH_3)_2$ (**H**)) have been obtained. In addition, the following pyrazabole relatives of type **3** = $(pz)RB(\mu-pz)(\mu-X)BR(pz)$ (**3a**: R = CH_3, X = $NHCH_3$ from $CH_3N(\mu-BCH_3NCH_3)_2Si(CH_3)_2$ (**F**); **3b**: R = CH_3, X = NH_2 from $S[\mu-BCH_3NSi(CH_3)_2]_2S$ (**E**); **3c**: R = C_2H_5, X = $N(CH_3)_2$ from $C_2H_5B[\mu-N(CH_3)_2](\mu-NCH_3CONCH_3)(\mu-NCH_3CONHCH_3)BC_2H_5$ (**J**)) and the novel type **4** (general formula **5**) = $RB(\mu-pz)(\mu-X)(\mu-Y)BR$ (**4a**: R = C_2H_5, X = $NHCH_3$, Y = NCH_3CONCH_3 from $CH_3N(\mu-$

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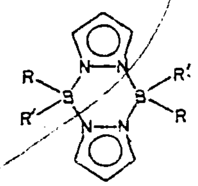
$BC_2H_5NCH_3)_2CO$ (Ia); 4b: R = C_2H_5, X = $N(CH_3)_2$, Y = NCH_3CONCH_3 from J (see above); 4c: R = CH_3, X = $NHCH_3$, Y = NCH_3CSNCH_3 from $CH_3N(\mu-BCH_3NCH_3)_2CS$ (Ic); 4d: R = CH_3, X = NHC_2H_5, Y = $NC_2H_5CSNC_2H_5$ from $C_2H_5N(\mu-BCH_3NC_2H_5)_2CS$ (Id); 4e: R = C_6H_5, X = $NHCH_3$, Y = NCH_3CSNCH_3 from $CH_3N(\mu-BC_2H_5NCH_3)_2CS$ (Ie)) have been isolated and characterized. The amine–borane complex $(CH_3)H_2N{\cdot}B(CH_3)(pz)_2$ (6) was obtained from the reaction of either $CH_3B(\mu-NCH_3)(\mu-NCH_3NCH_3)BCH_3$ (G) or $CH_3N(\mu-BCH_3NCH_3)_2Si(CH_3)_2$ (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 two decades. They contain the skeleton >B(μ-pz)$_2$B< and almost 100 different B- and/or C-substituted derivatives have been described.[2] Triply bridged pyrazaboles of type 2 with X = –OBRO– 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, $(-RBNR'-)_3$, with



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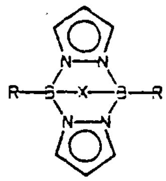

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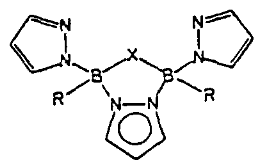
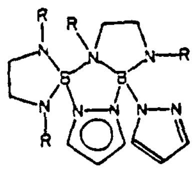


3

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]



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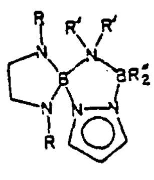


B

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 (^{1}H, ^{13}C) instrument. Chemical shift data are given in ppm with positive values indicating downfield from the reference (internal $(CH_3)_4Si$ for ^{1}H 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 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.

$F_2B(\mu\text{-}pz)_2BF_2$ (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, $F_2B(\mu\text{-}pz)_2BF_2$ (1a), mp 164 °C ($\delta(^{19}F)$ −150.1 (q, J = 21 Hz) 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 $CH_3B(\mu\text{-}NCH_3)(\mu\text{-}NCH_3NCH_3)BCH_3$ (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 on warming of the mixture 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: $\delta(^{1}H)$ 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 ca. 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 with hexane and dried to give 0.5 g of a material mp 170–230 °C. It was identified (^{1}H 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 d 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 of mp 134–136 °C, identical (NMR data) to 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 $CH_3N[Si(pz)(CH_3)_2]_2$. 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 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 $(CH_3)(pz)B(\mu-pz)(\mu-NHCH_3)B(CH_3)(pz)$ (3a). The material was recrystallized from hexane to give a product of 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 the 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, 7.57; 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 of Hpz was sublimed off under vacuum (80–90 °C bath temperature) to leave 0.95 g (85% yield) of an isomer mixture 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) with mp 158–195 °C were 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 ca. 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). For 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 isomers 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, t, 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) was formed and 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 a 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 to 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 to 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 latter 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, 38.5, 26.8, 0.5*. The EI mass spectrum exhibited the highest peak in the region 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 of 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.

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. On slow warming (after ca. 10 min and when a temperature near 50 °C was reached) a colorless precipitate began to form. When refluxing initiated on further heating of the mixture, a clear solution was again obtained and was heated to reflux for 18 h. On cooling to room temperature, 1.6 g of precipitate was formed and collected. Benzene was evaporated from the filtrate to leave an oily residue. This latter 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 and 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(μ–pz)(μ–$NHCH_3$)(μ–NCH_3CSNCH_3)BC_6H_5 (4e). To a solution of 2.0 g (6.5 mmol) of CH_3N(μ–$BC_6H_5NCH_3)_2CS$ (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 gel–like precipitate began to form. The mixture was stirred at room temperature for 22 h and reduced to 1/3 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

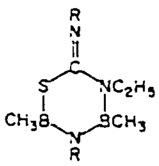
Dimeric (dimethylamino)difluoroborane (C), a four–membered B_2N_2 heterocycle containing four–coordinate boron,[21] interacted smoothly with pyrazole (= Hpz) in boiling benzene to yield *B*–tetrafluoropyrazabole (1a) according to eq (1). The reaction may proceed via monomeric $(CH_3)_2NBF_2$ and then can be viewed as a simple

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

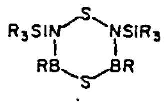
transamination, which is followed by immediate dimerization of the initially formed (1–pyrazolyl)difluoroborane to yield **1a**.

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]

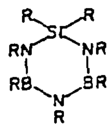
No reaction was observed when the eight-membered B_4N_4 heterocycle $[-ClBN(t-C_4H_9)-]_4$ containing three-coordinate boron[22] was treated with Hpz in either boiling ether or toluene. This lack of reaction may be explained by a steric protection of the annular nitrogen by the t-butyl group. Very similarly, the heterocycle **D** (R =



D



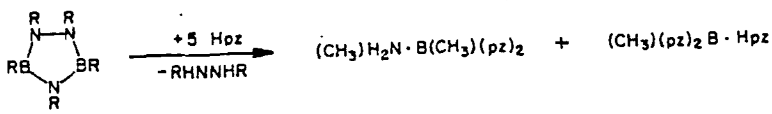
E
(R = CH_3)



F
(R = CH_3)

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.

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



(2)

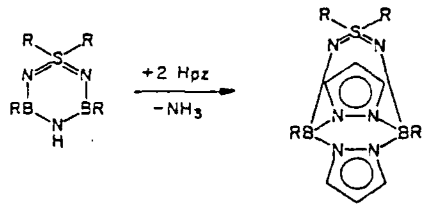
G
(R = CH_3)

6

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.

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 $CH_3B(\mu-NC_6H_5)(\mu-SS)BCH_3$ 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-diborane ring the nitrogen is clearly the most basic site; and in the case of the 1,3,4-triaza-2,5-diborane 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



(3)

H **2a**

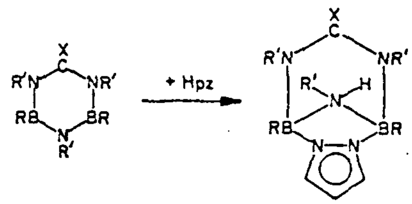
$R = CH_3$

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 $(CH_3)(pz)B(\mu-pz)(\mu-NH_2)B(CH_3)(pz)$ (**3b**: $R = CH_3$, $X = NH_2$). The 1-sila-2,4,6-triaza-3,5-diborane 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.)

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.

The 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



(4)

I 4

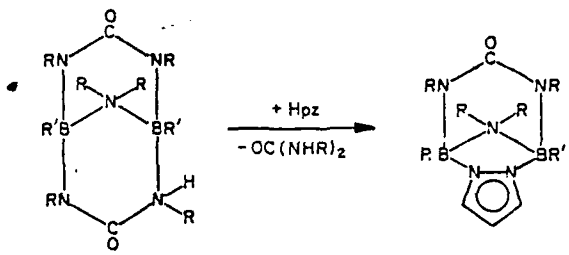
a: R = C_2H_5, R´ = CH_3, X = 0

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

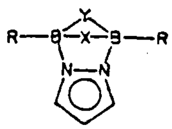
shown in eq (4). Compounds of type **4** are also accessible by the reaction of the recently described[20] triply bridged species J with Hpz under displacement of one *N*, *N*'–dimethylurea moiety as shown in eq (5).



(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



5

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.

The latter ring system of the 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 the 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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