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Pyrazole Complexes of Three-Coordinated Boranes[1]

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Both BF_3 and $B(C_2H_5)_3$ form 1:1 molar complexes with pyrazole (=Hpz) and C-substituted derivatives thereof (=Hpz*). Provided the pyrazole is a relatively strong base, the BF_3 complexes slowly decompose on prolonged standing at room temperature with the elimination of HF to form the corresponding dimeric 1-pyrazolylboranes = pyrazaboles, e.g., $F_2B(\mu\text{-pz})_2BF_2$. Deprotonation of $Hpz{\cdot}B(C_2H_5)_3$ with NaH yields the ion $[(C_2H_5)_3B(pz)]^-$, and the salt $K[(C_2H_5)_2B(pz)_2]$ is obtained on heating of an equimolar mixture of $Hpz{\cdot}B(C_2H_5)_3$ and Kpz in Hpz. Species of the type $K[R_2B(pz)_2]$ are also obtained by the reaction of (dimethylamino)diorganylboranes, $(CH_3)_2NBR_2$, with Kpz and Hpz; they were converted to the representative Pd complexes $Pd[(\mu\text{-pz})_2B(C_2H_5)_2]_2$ and $R_2B(\mu\text{-pz})_2Pd(\pi\text{-}CH_2CHCH_2)$ (R = C_2H_5, n-C_3H_7, C_6H_5), respectively. Interaction of $(CH_3)_2NBR_2$ with 1 molar equiv of Hpz gives 1:1 complexes of the type $(CH_3)_2HN{\cdot}BR_2(pz)$, which can react with an additional molar equivalent of Hpz at elevated temperatures to form $Hpz{\cdot}BR_2(pz) = R_2B(pz)_2H$, or form mixtures of the desired compound with the pyrazabole relative $R_2B(\mu\text{-pz})[\mu\text{-}N(CH_3)_2]BR_2$. Steric factors may prevent the intermediate formation of the 1:1 complexes to lead directly to $Hpz{\cdot}BR_2(pz)$. The complexes $Hpz{\cdot}BR_2(pz)$ can be thermolyzed to yield the pyrazaboles $R_2B(\mu\text{-pz})_2BR_2$. However, whereas the reaction of $[(CH_3)_2NBF_2]_2$ with Hpz ultimately yields the pyrazabole $F_2B(\mu\text{-pz})_2BF_2$, the reaction of the cited aminoborane with Hpz and Kpz causes redistribution of fluorine and $K[F_3B(pz)]$ is obtained as the only product containing B-F bonds. The complex $(pz)_2B(C_2H_5)(H_2NCH_3)$ is formed on reaction of the borazine $(C_2H_5BNCH_3)_3$ with a large excess of Hpz, and $H(pz)_3B(NHCH_3)$ is obtained in analogous fashion originating from the borazine $[(CH_3)_2NBNCH_3]_3$. The reaction of $[(CH_3)_2NNH]_3B$ with excess of Hpz yields the complex $(CH_3)_2NNH_2{\cdot}B(pz)_3$.

Introduction

Ever since their first discovery, N-bonded boron derivatives of pyrazoles have received considerable attention. Although several types of such compounds are known, the application of the poly(1-pyrazolyl)borate ions, $[R_nB(pz^*)_{4-n}]^-$ (R = noncoordinating substituent, Hpz* = pyrazole or C-substituted derivatives thereof, n = 0, 1, 2), as polydentate ligands in coordination chemistry has resulted in a concentration of efforts in this area.[2] Thus, principal aspects of the interaction of pyrazoles with boranes have hardly been explored. For example, although various poly(1-pyrazolyl)borates have been described, only two such compounds are known where at least one of the boron substituents R is not a pz group but does contain a coordinating site and, thus, can act as hybrid ligand.[3,4] On the other hand, such hybrid species should be available by simple complexation of pyrazole with a trigonal boron compound that contains a substituent with a donor site. The resultant species may also be formulated (or can react) as species containing an acidic hydrogen, e.g., H(pz)BRR'R''. Only a few such acids have been described,[4-9] and it has been established that $[(pz)_3BN(CH_3)_2]^-$ does indeed act as a multidentate hybrid ligand.[4] Interestingly, only one example of a mono(1-pyrazolyl)borate ion, i.e., $[(pz^*)BH_3]^-$ with Hpz* = 3,5-dimethylpyrazole, is known so far.[7]

The present work is concerned with a fundamental study of the interaction between pyrazole and trigonal boranes under various conditions, in order to explore the formation and general chemistry of such adducts.

Experimental Section

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

NMR spectra were recorded for solutions in $CDCl_3$ (unless otherwise noted) on a Varian VXR-400 (high resolution spectra), XL-200 (^{11}B), or GEMINI-200 (^1H, ^{13}C) instrument. Chemical shift data are given in parts per million 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); s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, h = septet, m = unresolved multiplet, and an asterisk denotes a broad signal. Coupling constants J are given in hertz. Unless otherwise noted, ^{13}C NMR spectra were recorded in the proton decoupled mode. Electron impact (EI) mass spectral data (70 eV unless otherwise noted) were obtained in a VG ZAB-2F spectrometer under standard operating conditions. Data are listed to m/z 30 for 5% or greater relative abundances (in parentheses) only. Field desorption (FD) mass spectra were recorded on a Finnigan MAT 250 instrument.

Triethylborane was obtained from Callery Chemical Co., Callery, PA. All other nonreferenced reagents were obtained from Aldrich Chemical Co., Milwaukee, WI, and used as received; only pyrazole (Hpz) was distilled over a small amount of metallic sodium and stored under anhydrous conditions. Experiments were generally performed under argon cover.

Hpz*·BF_3 (General Experiment). Gaseous BF_3 was slowly introduced into a solution of the pyrazole in methylene choride (unless otherwise noted) until the exit gas indicated BF_3. The gas introduction was then continued for another 1-2 h. The solvent and excess of BF_3 were evaporated to leave the desired Hpz*·BF_3, which was not further purified.

Hpz·BF_3 (Hpz = pyrazole) was prepared in chloroform and obtained as a viscous liquid. NMR data (solution in $(CD_3)_2CO$): $\delta(^1H)$ 12.6* (1 H), 8.26 (1 H, d, J = 2.6), 8.10 (1 H, d, J = 2.4), 6.76 (1 H, unsym t = two overlapping d, J = 2.1); $\delta(^{11}B)$ 0.3 (s, $h_{1/2}$ = 25 Hz).

Hpz*·BF_3 (Hpz* = 3-methylpyrazole) was prepared in the absence of solvent as a crystalline mixture of the two possible isomers A and B (depending to which N atom of the Hpz* the boron is coordinated) in about 1:2 molar ratio, mp 68-80 °C. NMR data: isomer A, $\delta(^1H)$ 11.5* (1 H), 7.78 (1 H, d, J = 2.2), 6.31 (1 H unresolved), 2.4* (3 H, s); isomer B, $\delta(^1H)$ 11.3* (1 H), 7.71 (d, J = 2.2), 6.31 (1 H, unresolved), 2.4* (3 H, s); $\delta(^{11}B)$ (for both isomers) 0.25 (s, $h_{1/2}$ = 40 Hz).

Hpz*·BF_3 (Hpz* = 3,5-dimethylpyrazole) was obtained as a waxy solid, mp 60-65 °C. NMR data: $\delta(^1H)$ 10.5* (1 H), 6.21 (1 H, s), 2.40 + 2.39 (6 H, two closely spaced s); $\delta(^{11}B)$ 0.2 (s, $h_{1/2}$ = 60 Hz).

Hpz*·BF_3 (HPz* = 3,5-bis(trifluoromethyl)pyrazole) was obtained as a crystalline material, mp 108-113 °C. NMR data: $\delta(^1H)$ 8.1* (1 H), 7.20 (1 H, s); $\delta(^{11}B)$ -0.6 (s, $h_{1/2}$ = 40 Hz).

Hpz*·BF_3 (Hpz* = 3,4,5-tribromopyrazole) was obtained as a crystalline product, mp 123-126 °C dec. NMR data: $\delta(^1H)$ 11.6*; $\delta(^{11}B)$ -0.7 (s, $h_{1/2}$ = 50 Hz).

Hpz*·$B(C_2H_5)_3$ (General Experiment). Equimolar amounts of Hpz* and $B(C_2H_5)_3$ were combined in toluene and the mixture was stirred for 1 h at room temperature. Toluene was evaporated under vacuum and the remaining liquid was studied by NMR spectroscopy without further purification.

Hpz·$B(C_2H_5)_3$. NMR data: $\delta(^1H)$ 10.1* (1 H), 7.62 (2 H, d, J = 2.6), 6.41 (1 H, t, J = 2.5), 0.69 (9 H, t, J = 7), 0.40 (6 H, q, J = 7); $\delta(^{11}B)$ -0.3 (s, $h_{1/2}$ = 125 Hz).

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Hpz*·B(C_2H_5)$_3$ (Hpz* = 3-Methylpyrazole). NMR data: δ(^{1}H) 10* (1 H), 7.50 (1 H, d, J = 1.7), 6.12 (1 H, d, J = 1.7), 2.36 (3 H, s), 0.63 (9 H, t, J = 7), 0.40 (6 H, q, J = 7); δ(^{11}B) −1.1 (s, $h_{1/2}$ = 150 Hz).

Hpz*·B(C_2H_5)$_3$ (Hpz* = 3,5-Dimethylpyrazole). NMR data: δ(^{1}H) 9.8* (1 H), 5.89 (1 H, s), 2.30 (6 H, s), 0.64 (9 H, t, J = 7), 0.47 (6 H, q, J = 7); δ(^{11}B) 0.9 (s, $h_{1/2}$ = 150 Hz).

Na[(C_2H_5)$_3$B(pz)]. A solution of 2.4 g (15 mmol) of Hpz·B(C_2H_5)$_3$ (see above) in 30 mL of toluene was slowly added to a stirred slurry of 0.35 g (15 mmol) of NaH in 10 mL of toluene. Vigorous gas evolution occurred in a slightly exothermic reaction and a clear solution was obtained. The mixture was stirred for 15 min and toluene was evaporated under reduced pressure. The residual oil was heated under vacuum for 3 h in an oil bath of 50 °C. The remaining solid material was washed with several 25-mL portions of petroleum ether to leave 2 g (73%) of extremely hygroscopic product, mp 58–63 °C dec.

NMR data: δ(^{1}H) 7.74 (2 H, d), 6.33 (1 H, unsym t), 0.66 (9 H, t), 0.32 (6 H, q); δ(^{11}B) −3.8 (s, $h_{1/2}$ = 350 Hz). Solution in C_6H_6: δ(^{1}H) 7.80* (1 H, unresolved), 7.35* (1 H, unresolved), 6.17 (1 H, unsym t = two overlapping d), 1.06 (9 H, t, J = 7), 0.49 (6 H, q, J = 7); δ(^{11}B) −4.1 (s, $h_{1/2}$ = 320 Hz); δ(^{13}C) 139.8, 136.7, 104.8, 17*, 10.6.

K[F_3B(pz)]. A stirred mixture of 4.2 g (23 mmol) of (dimethylamino)difluoroborane dimer, [$(CH_3)_2NBF_2]_2$,[10] 4.8 g (45 mmol) of Kpz (mp 280 °C; prepared by dissolving Hpz in toluene and adding metallic potassium, collecting the precipitated Kpz, and drying it under vacuum), and 11.0 g (162 mmol) of Hpz was heated at 150 °C for 1 h. After that time no more dimethylamine was given off and the mixture was cooled to room temperature. It was washed extensively with chloroform to leave 1.9 g of colorless solid, which began to sinter at 290 °C and was completely melted near 350 °C. Anal. Calcd for $C_3H_3BF_3KN_2$ (M_r = 173.97): C, 20.71; H, 1.74; B, 6.21; F, 32.76; K, 22.47; N, 16.10. Found: C, 20.29; H, 1.69; B, 6.22; F, 32.39; K, 22.58; N, 15.99.

NMR data (solution in D_2O): δ(^{1}H) 7.76* (2 H), 6.48* (1 H); δ(^{11}B) 0.15 (q, J = 15 Hz).

K[(C_2H_5)$_2$B(pz)$_2$]. To a solution of 6.5 g (39 mmol) of Hpz·B(C_2H_5)$_3$ in 30 mL of toluene was added 4.13 g (39 mmol) of Kpz (see above) and 5.3 g (78 mmol) of Hpz. The mixture was heated with stirring and solvent was distilled off under atmospheric pressure. Subsequently the temperature was raised to 160–170 °C (oil bath) and elimination of ethane started. The mixture was kept at that temperature for 10 h and excess of Hpz was distilled off under reduced pressure. The residue was washed with chloroform to leave 6.8 g (72%) of the desired compound, mp 141–143 °C (after recrystallization from benzene). The compound is slightly soluble in chloroform or ether.

NMR data: δ(^{1}H) 7.58 (1 H, d, J = 1.9), 7.35 (1 H, unresolved d), 6.17 (1 H, unsym t = two overlapping d), 0.57 (3 H, t, J = ca. 6), 0.47 (2 H, ill resolved q, J = ca. 6); δ(^{11}B) 0.8 (s, $h_{1/2}$ = 500 Hz); δ(^{13}C) 139.1, 133.5, 103.7, 14.6*, 9.2. Solution in $(CD_3)_2CO$: δ(^{1}H) 7.46 (1 H, d of d, ^1J = 2.1, ^2J = 0.6), 7.29 (1 H, d, J = 1.6), 5.95 (1 H, unsym t = 2 overlapping d, J = ca. 1.8), 0.90 (2 H, q, J = 7.7), 0.60 (3 H, t, J = 7.6); δ(^{11}B) 0.85 (s, $h_{1/2}$ = 115 Hz); δ(^{13}C) 138.0, 131.6, 102.4, 14.5*, 10.2.

(CH_3)$_2$HN·B(C_2H_5)$_2$(pz). To a solution of 2.9 g (42.5 mmol) of Hpz in 80 mL of ether was added 4.8 g (42.5 mmol) of (dimethylamino)diethylborane, $(CH_3)_2NB(C_2H_5)_2$.[11] Some precipitate was formed in a slightly exothermic reaction and the mixture was stirred at ambient temperature for 15 min. It was filtered and solvent was evaporated from the clear filtrate to leave 5.5 g (71.5%) of the desired product, which melted near 108 °C. The compound slowly decomposes on standing.

NMR data: δ(^{1}H) 7.59 (1 H, d, J = 1.6), 7.52 (1 H, d, J = 2), 6.18 (1 H, unsym t = two overlapping d, J = ca. 2), 5.3* (1 H, s), 2.33 (6 H, d, J = 6), 0.9–0.4 (10 H, m); δ(^{11}B) 2.4 (s, $h_{1/2}$ = 100 Hz); δ(^{13}C) 139.5, 132.2, 103.3, 37.3, (ca. 10* ?) 9.3.

K[R_2B(pz)$_2$] (General Procedure). To a stirred solution of 35 mmol of $(CH_3)_2NBR_2$ in 100 mL of toluene was added 35 mmol of Kpz (see above) and the mixture was briefly heated to reflux. After the mixture cooled to room temperature, 35 mmol of Hpz was added in small portions. The mixture was then heated to reflux for 2 h and allowed to stand overnight. The precipitate (90–95% yield) was collected, washed with toluene, and dried under vacuum at 50–60 °C to remove traces of unreacted Hpz.

K[(C_2H_5)$_2$B(pz)$_2$] was obtained from $(CH_3)_2NB(C_2H_5)_2$[11] and was identical (NMR data) with the material described above. The salt was also obtained on treatment of (CH_3)$_2$HN·B(C_2H_5)$_2$(pz) (see above) with Kpz in refluxing benzene.

K[(*n*-C_3H_7)$_2$B(pz)$_2$], mp 175–176 °C (after recrystallization from cyclohexane), was obtained from (dimethylamino)di-*n*-propylborane, $(CH_3)_2NB(n\text{-}C_3H_7)_2$.[12] NMR data: δ(^{1}H) 7.63 (1 H, d, J = 1.8), 7.39 (1 H, d, J = 1.5), 6.20 (1 H, unsym t = two overlapping d), 0.82 (5 H, unresolved m), 0.62 (2 H, unresolved m); δ(^{11}B) 0.8 (s, $h_{1/2}$ = 750 Hz); δ(^{13}C) 139.4, 133.7, 104.1, 27.6*, 19.1, 18.5.

K[(C_6H_5)$_2$B(pz)$_2$], mp 295–297 °C dec (after recrystallization from toluene/acetonitrile), was prepared from (dimethylamino)diphenylborane, $(CH_3)_2NB(C_6H_5)_2$.[13] NMR data (solution in $(CD_3)_2(CO)$: δ(^{1}H) 7.41 (1 H, d, J = 1.6), 7.29 (1 H, d, J = 2.1), 7.2–7.0 (5 H, m), 6.00 (1 H, unsym t = two overlapping d); δ(^{11}B) 1.8 (s, $h_{1/2}$ = 115 Hz); δ(^{13}C) 154.5*, 139.2, 135.3, 135.1, 127.0, 125.6, 102.6. The compound has previously been prepared by the reaction of Kpz with $H_3N·B(C_6H_5)_3$ in molten Hpz.[14]

Pd[(μ-pz)$_2$B(C_2H_5)$_2$]$_2$. To a stirred slurry of 0.50 g (2.8 mmol) of finely ground $PdCl_2$ in 40 mL of acetonitrile was added 1.4 g (5.8 mmol) of K[(C_2H_5)$_2$B(pz)$_2$] (see above). The orange solution decolorized immediately and a colorless precipitate (KCl) appeared. After about 30 min all of the $PdCl_2$ had dissolved and the mixture was filtered. The residue was treated with three 50-mL portions of acetonitrile and the solvent was evaporated from the combined liquids to leave 1.2 g (83%) of crude material. It was recrystallized first from heptane and then twice from benzene to give a pale green product, mp 235–236 °C. Anal. Calcd for $C_{20}H_{32}B_2N_8Pd$ (M_r = 512.55): C, 46.87; H, 6.29; B, 4.22; N, 21.86; Pd, 20.76. Found: C, 46.66; H, 6.21; B, 4.32; N, 21.94; Pd, 20.88.

NMR data: δ(^{1}H) 7.56 (2 H, d, J = 2.3), 7.11 (2 H, d, J = 2.2), 6.18 (2 H, unsym t = two overlapping d), 2.04* (2 H, unresolved), 1.12* (5 H, unresolved), 0.7* (3 H, unresolved); δ(^{11}B) 1.4 (s, $h_{1/2}$ = 380 Hz); δ(^{13}C) 140.8, 134.0, 104.9, 16.4*, 10.2*, 9.5, 9.4. The 14-eV EI mass spectrum exhibits only an ion cluster at m/z 482.

(C_2H_5)$_2$B(μ-pz)$_2$Pd(π-CH_2CHCH_2). A mixture of 0.80 g (3.3 mmol) of K[(C_2H_5)$_2$B(pz)$_2$] (see above), 0.60 g (3.3 mmol of monomer) of $[ClPd(\pi\text{-}CH_2CHCH_2)]_2$, and 30 mL of methylene chloride was stirred for 12 h at room temperature and a milky precipitate developed. The mixture was filtered and the clear solution was evaporated to give 1.0 g (88%) of pale green material, mp 101–102 °C (after recrystallization from hexane). Anal. Calcd for $C_{13}H_{21}BN_4Pd$ (M_r = 350.47): C, 44.55; H, 6.02; B, 3.08; N, 15.99; Pd, 30.36. Found: C, 44.55; H, 6.12; B, 3.17; N, 16.12; Pd, 30.13.

NMR data: δ(^{1}H) 7.64 (2 H, d, J = 1.8), 7.44 (2 H, d, J = 1.7), 6.17 (2 H, two overlapping d, J = 2.1), 5.65 (1 H, high resolution: t of t, ^1J = 12.3, ^2J = 7.0), 3.88 (2 H, d, J = 6.9), 3.07 (2 H, d, J = 12.3), 1.09 (2 H, q, J = 7.6), 0.92 (2 H, q, J = 7.6), 0.82 (3 H, t, J = 7.6), 0.62 (3 H, t, J = 7.6) (the signals 1.09/0.82 and 0.92/0.62 are coupled to show two magnetically different but equally abundant C_2H_5 groups); δ(^{11}B) 0.9 (s, $h_{1/2}$ = 135 Hz); δ(^{13}C) 142.6, 133.2, 115.3, 103.9, 57.4, 14.8*, 13.2*, 9.4, 9.3. The EI mass spectrum exhibited a strong ion cluster at m/z 320.

(*n*-C_3H_7)$_2$B(μ-pz)$_2$Pd(π-CH_2CHCH_2) was prepared in analogous fashion as the preceding compound by reaction of $[ClPd(\pi\text{-}CH_2CHCH_2)]_2$ with K[(*n*-C_3H_7)$_2$B(pz)$_2$] (see above) in methylene chloride. The compound was obtained in essentially quantitative yield as a pale green material, mp 138–139 °C (after recrystallization from hexane). Anal. Calcd for $C_{15}H_{25}BN_4Pd$ (M_r = 378.60): C, 47.59; H, 6.65; B, 2.86; N, 14.80; Pd, 28.10. Found: C, 47.84; H, 6.85; B, 2.77; N, 14.74; Pd, 28.18.

NMR data: δ(^{1}H) 7.61 (2 H, d, J = 2.4), 7.45 (2 H, d, J = 1.9), 6.17 (2 H, two overlapping d), 5.66 (1 H, high resolution: t, J = 12.1, of t, J = 6.5), 3.89 (2 H, d, J = 6.9), 3.07 (2 H, d, J = 12.3), 1.18–0.83 (14 H, m); δ(^{11}B) 0.2 (s, $h_{1/2}$ = 185 Hz); δ(^{13}C) 142.3, 132.9, 115.0, 103.8, 57.2, 27.3*, 26.1*, 19.14, 19.09, 18.6, 18.5. The EI mass spectrum exhibited a strong ion cluster at m/z 334.

(C_6H_5)$_2$B(μ-pz)$_2$Pd(π-CH_2CHCH_2) was prepared in analogous fashion as the two preceding compounds by the reaction of K[(C_6H_5)$_2$B(pz)$_2$] (see above) with $[ClPd(\pi\text{-}CH_2CHCH_2)]_2$. The crude product was recrystallized from heptane/benzene (10:1 by volume) and was obtained as a colorless material, mp 185–186 °C. Anal. Calcd for $C_{21}H_{21}BN_4Pd$ (M_r = 446.63): C, 56.47; H, 4.74; B, 2.43; N, 12.54; Pd, 23.82. Found: C, 56.63; H, 4.74; B, 2.33; N, 12.71; Pd, 23.93.

NMR data: δ(^{1}H) 7.49 (4 H, d, J = 2.2), 7.24–7.15 (6 H, m), 7.00–6.95 (2 H, m), 6.83–6.78 (2 H, m), 6.19 (2 H, t, J = 2.2), 5.11 (1 H, high resolution: t, J = 12.1, of t, J = 6.9), 3.56 (2 H, d, J = 6.9), 2.28 (2 H, d, J = 12.3) (the signals 7.49/6.19 are coupled and, thus, identify the pz groups); δ(^{11}B) 1.7 (s, $h_{1/2}$ = 170 Hz); δ(^{13}C) 143.2, 136.8, 134.4, 134.0, 127.0, 126.8, 126.3, 126.1, 114.4, 103.9, 57.6. The EI mass

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spectrum exhibited a strong ion cluster at m/z 368.

Hpz·B($C_{12}H_8$)(pz). To a solution of 2.0 g (8.5 mmol) of 9-(diethylamino)-9-borafluorene, $(C_{12}H_8)BN(C_2H_5)_2$ (purified by sublimation under vacuum),[15] in 120 mL of ether was added 5.1 g (75 mmol) of pyrazole. The mixture was stirred at room temperature for 2 days and 1.2 g of colorless precipitate was collected. Concentration of the filtrate under vacuum gave a second crop of crystalline material. The solids were combined and washed with 10–20 mL of ether, and the remaining excess of pyrazole was sublimed off the product under high vacuum at a temperature not to exceed 50–60 °C to leave 2.7 g (86%) of crude material. It was recrystallized from acetonitrile (warmed not higher than 60 °C) to give colorless crystals which melted at 208–209 °C, resolidified near 215 °C, and then began melting again near 305 °C. Anal. Calcd for $C_{18}H_{15}BN_4$ (M_r = 298.16): C, 72.51; H, 5.07; B, 3.63; N, 18.79. Found: C, 70.39; H, 4.94; B, 3.55; N, 18.54.

NMR data: δ(^{1}H) 11.6* (1 H, s), 7.80 (d, J = 2.2) + 7.68 to 7.64 (m) + 7.56 to 7.53 (m) + 7.38 (d, J = 2.1) + 7.33 to 7.15 (m) (12 H total), 6.22 (2 H, unsym t = 2 overlapping d) (the signals at 7.79, 7.38, and 6.22 are coupled and assigned to the pz groups); δ(^{11}B) 6.3* (ca. 1 B, s) + 0.7* (ca. 3 B, s) (the ^{11}B NMR spectrum in CD_3OD, however, exhibited only one signal at δ 6.4 ($h_{1/2}$ = 150 Hz), see also text); δ(^{13}C) 149.4; 149.2, 135.6, 134.4, 133.5, 130.5, 130.3, 128.7, 128.2, 127.1, 126.9, 119.5, 119.2, 109.9, 105.2, 105.1. The EI mass spectrum (170 °C inlet temperature) is essentially identical with that of $(C_{12}H_8)B(\mu\text{-pz})_2B(C_{12}H_8)$ (see below) but for the additional appearance of peaks at m/z 68 (base peak) and 67, and that the peak group in the region m/z 230 is of much higher abundance than that in the m/z 460 region.

($C_{12}H_8$)B(μ-pz)$_2$B($C_{12}H_8$). A quantity, 1.5 g (5.2 mmol), of crude Hpz·B($C_{12}H_8$)(pz) (see above) was heated to 150 °C for 4 h under vacuum in a sublimation apparatus and Hpz sublimed off. The residue was recrystallized from toluene to give 0.9 g (75%) of the desired pyrazabole, mp 326–328 °C. Anal. Calcd for $C_{30}H_{22}B_2N_4$ (M_r = 460.17): C, 78.31; H, 4.82; B, 4.70; N, 12.17. Found: C, 77.61; H, 4.86; B, 3.67; N, 12.21.

NMR data: δ(^{1}H) 7.73 (2 H, d, J = 7.7, of unresolved d), 7.39 to 7.35 (m) + 7.33 (d, J = 1.5) + 7.25 + 7.14 (m) (8 H total), 6.20 (1 H, t, J = 2.4) (the signals 7.33 and 6.20 are coupled and are assigned to the pz groups); δ(^{11}B) 1.3 (s, $h_{1/2}$ = 280 Hz); δ(^{13}C) 151.2*, 148.8, 136.4, 129.3, 128.7, 127.3, 119.6, 107.6. EI mass spectrum (13 eV): m/z 461 (29), 460 (100), 459 (70), 458 (11), 230 (21).

Hpz·B($C_{13}H_9$)$_2$(pz). A mixture of 1.5 g (3.4 mmol) of (diisopropylamino)di-9-fluorenylborane, $(i\text{-}C_3H_7)_2NB(C_{13}H_9)_2$ (crude material washed with ether and then recrystallized from toluene to give a product of mp 310–312 °C dec),[16] 0.7 g of Hpz, and 50 mL of toluene was heated to reflux with stirring for 4 h. Most of the toluene was evaporated and the resultant precipitate was collected and dried to give 1.10 g (68%) of crude product, mp 254–255 °C (after recrystallization from toluene). Anal. Calcd for $C_{32}H_{25}BN_4$ (M_r = 476.39): C, 80.68; H, 5.29; B, 2.27; N, 11.76. Found: C, 77.92; H, 5.22; B, 2.24; N, 11.40.

NMR data: δ(^{1}H) 7.67 to 7.10 (18 H, complex m with distinct d at 7.24, J = 1.9), 6.50 (2 H, d, J = 2.3), 6.29* (1 H), 5.97 (2 H, unsym t, J ca. = 2.2), 4.46 (2 H, s); δ(^{11}B) 3.2 (s, $h_{1/2}$ = 230 Hz). The EI mass spectrum (180 °C) was essentially identical with that of the following compound $(C_{13}H_9)_2B(\mu\text{-pz})_2B(C_{13}H_9)_2$, except for the additional appearance of a strong peak at m/z 68.

($C_{13}H_9$)$_2$B(μ-pz)$_2$B($C_{13}H_9$)$_2$. A mixture of 2.0 g (4.5 mmol) of $(i\text{-}C_3H_7)_2NB(C_{13}H_9)_2$ (crude product purified as outlined in the preceding experiment), 0.4 g (5.8 mmol) of Hpz, and 30 mL of toluene was refluxed with stirring for 18 h. The insoluble material was collected (1.3 g, 70% yield) and recrystallized from toluene to give 0.7 g of product, mp 251–252 °C. Anal. Calcd for $C_{58}H_{42}B_2N_4$ (M_r = 816.62): C, 85.31; H, 5.18; B, 2.65; N, 6.86. Found: C, 84.99; H, 5.09; B, 2.43; N, 6.82.

NMR data: δ(^{1}H) 7.78 to 7.26 (10 H, complex m with a distinct signal at 7.52), 6.32 (1 H, t, J = 2), 3.92 (1 H, s); δ(^{11}B) 2.2 (s, $h_{1/2}$ = 200 Hz). Both the EI and the FD mass spectra exhibited a peak cluster in the m/z region 408 as the peak of highest mass, suggesting the ready fragmentation into the monomeric di-9-fluorenyl-1-pyrazolylborane, $(C_{13}H_9)_2B(pz)$; major ion clusters were observed in the EI mass spectrum of the compound at m/z 166/165, 85, 68/67, 41/40.

(CH_3)H$_2$N·B(C_2H_5)(pz)$_2$. A mixture of 2.0 g (9.7 mmol) of *B,B',B''*-triethyl-*N,N',N''*-trimethylborazine, $(C_2H_5BNCH_3)_3$,[17] 4.0 g (59 mmol) of Hpz, and 50 mL of hexane was stirred at room temperature for 18 h. Half of the solvent was evaporated and the precipitate was collected and dried to give 4.5 g (64%) of crude product. It was recrystallized twice from hexane to give a pure material, mp 126–128 °C dec. Anal. Calcd for $C_9H_{16}BN_5$ (M_r = 205.07): C, 52.71; H, 7.86; B, 5.27; N, 34.15. Found: C, 50.41; H, 7.70; B, 4.80; N, 31.90.

NMR data: δ(^{1}H) 7.57 (2 H, unresolved d), 7.36 (2 H, unresolved d), 6.3* (2 H), 6.21 (2 H, unresolved unsym t = two overlapping d), 2.05 (3 H, t, J = 5.8), 0.96 (2 H, q, J = 7.4), 0.67 (3 H, t, J = 7.5); δ(^{11}B) 1.4 (s, $h_{1/2}$ = 180 Hz); δ(^{13}C) 140.1, 132.6, 104.7, 28.2, 10.4*, 7.9.

(CH_3)$_2$HN·B(C_2H_5)(pz)$_2$.[17] Additional NMR data: δ(^{13}C) 141.2, 134.6, 104.9, 38.2, 10*, 9.0.

(CH_3)H$_2$N·B(pz)$_3$. A mixture of 2.3 g (9.1 mmol) of *B,B',B''*-tris(dimethylamino)-*N,N',N''*-trimethylborazine, $[(CH_3)_2NBNCH_3]_3$,[18] 4.0 g (59 mmol) of Hpz, and 100 mL of ether was stirred at room temperature for 17 h. The colorless precipitate (3.7 g) was collected, washed with ether, and recrystallized from toluene to give a pure product, mp 185–186 °C dec. Anal. Calcd for $C_{10}H_{14}BN_7$ (M_r = 243.08): C, 49.41; H, 5.80; B, 4.45; N, 40.34. Found: C, 49.14; H, 5.73; B, 3.59; N, 39.84.

NMR data: δ(^{1}H) 7.61 (3 H, unresolved d), 7.5* (1 H; the signal shifts to 7.9 at −39 °C), 7.05 (3 H, d, J = 2.2 Hz), 6.3* (1 H), 6.23 (3 H, unresolved unsym t), 2.41* (3 H); δ(^{11}B) 0.03 (s, $h_{1/2}$ = 30 Hz); δ(^{13}C) 141.6, 134.1, 105.4, 27.4.

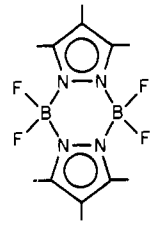
(CH_3)$_2$NNH$_2$·B(pz)$_3$. A mixture of 1.65 g (8.8 mmol) of tris(*N,N*-dimethylhydrazino)borane, $[(CH_3)_2NNH]_3B$,[19] and 3.04 g (44 mmol) of Hpz was dissolved in 30 mL of ether. After the solution was allowed to stand at room temperature for a few days, a crystalline precipitate developed. It was collected, washed with ether, and dried to give 1.8 g (75%) of the colorless product, mp 107–109 °C dec.

NMR data: δ(^{1}H) 7.89* (2 H, s), 7.69 (3 H, unresolved), 7.20 (3 H, d, J = 2.3), 6.28 (3 H, unsym t = two overlapping d, J = ca. 1.2), 2.53 (6 H, s); δ(^{11}B) 0.5 (s, $h_{1/2}$ = 20 Hz); δ(^{13}C) 140.2, 135.6, 105.4, 48.9. Solution in CD_2Cl_2: δ(^{1}H) 7.65 (3 H, d, J = 1.1), 7.29* (2 H, s), 7.18 (3 H, d, J = 2), 6.25 (3 H, unsym t = two overlapping d, J = ca. 1.7); δ(^{11}B) 0.7 (s, $h_{1/2}$ = 15 Hz); δ(^{13}C) 140.9, 135.8, 105.2, 47.5.

Very small additional signals in the NMR spectra indicated a minor impurity. Thermal decomposition of the material under vacuum (30 min at 100 °C) proceeded with ready elimination of *N,N*-dimethylhydrazine and a mixture of what appeared to be (NMR and mass spectral data) $(pz)_2B(\mu\text{-pz})_2B(pz)_2$ and $(pz)_2B(\mu\text{-pz})[\mu\text{-}(CH_3)_2NNH]B(pz)_2$, which could not be separated.

Results and Discussion

Pyrazole as well as C-substituted derivatives thereof (Hpz*) were reacted with BF_3 to form 1:1 molar adducts of the type Hpz*·BF_3. These adducts slowly decomposed with the elimination of HF to yield dimeric 1-pyrazolylboranes, pyrazaboles (**1**),



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$F_2B(\mu\text{-pz*})_2BF_2$, provided Hpz* is a relatively strong base. Thus, after a few days of standing of the BF_3 complexes with Hpz* = pyrazole, 3-methylpyrazole, or 3,5-dimethylpyrazole, the presence of the respective pyrazabole could be detected in the ^{1}H NMR spectrum of the material. On the other hand, no such HF elimination was observed in the case of Hpz* = 3,5-bis(trifluoromethyl)pyrazole.

Also, several adducts of triethylborane with pyrazoles, Hpz*·B(C_2H_5)$_3$, were prepared by direct combination of the reagents in toluene. These latter adducts were stable at room temperature but their thermal decomposition gave the corresponding (known[20]) pyrazaboles $(C_2H_5)_2B(\mu\text{-pz*})_2B(C_2H_5)_2$ with the elimination of ethane.

With the sole exception of Hpz*·BH_3 (Hpz* = 3,5-dimethylpyrazole),[7] the preceding species are the only characterized boron complexes containing only one pyrazole moiety bonded to the boron. (Note: The complex $(CH_3)_3N\cdot BH_2$(pz*) (Hpz* = 3,5-bis(trifluoromethyl)pyrazole) is also known but does not

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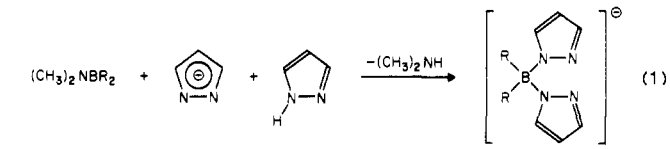
contain a N-bonded proton.[20]) These complexes of the type $Hpz^*{\cdot}BR_3$ contain an acidic proton. This is demonstrated by the reaction $Hpz{\cdot}B(C_2H_5)_3$ with NaH to give the salt $Na[(C_2H_5)_3B(pz)]$. Similarly, the reaction of NaH with $Hpz^*{\cdot}BH_3$ (Hpz^* = 3,5-dimethylpyrazole) has previously been described to give the salt $Na[H_3B(pz^*)]$.[7]

1-Pyrazolylborates of the type $[R_2B(pz)_2]^-$ (**2**) have been prepared by the reaction of trialkylboranes, BR_3, with $[pz]^-$ ion and subsequent heating with excess of Hpz.[21] Alternatively, a solution of $Hpz{\cdot}BR_3$ can be mixed with 1 equiv of Kpz and, after solvent evaporation, thermolyzed using excess Hpz as solvent. The same compounds of the type $K[R_2B(pz)_2]$ are also readily obtained by the reaction of a (dimethylamino)borane, $(CH_3)_2NBR_2$, with Kpz and Hpz, eq 1. Since a wide variety of monoaminoboranes are known,[22] this latter process seems to be quite versatile and useful for the preparation of bis(1-pyrazolyl)borate ions with various substituents, R, at the boron.



(1)

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In contrast to $Na[(C_2H_5)_2B(pz)_2]$, which was found difficult to crystallize,[21] the corresponding potassium salt was readily purified by recrystallization. The salts $K[R_2B(pz)_2]$ ($R = C_2H_5$, n-C_3H_7, C_6H_5) were converted to $Pd[(\mu\text{-}pz)_2BR_2]_2$ ($R = C_2H_5$) and $R_2B(\mu\text{-}pz)_2pd(\pi\text{-}CH_2CHCH_2)$ ($R = C_2H_5$, n-C_3H_7, C_6H_5), respectively. The puckered conformation of the PdN_4B ring in these complexes has been well documented.[2] It is clearly evident in the present case by the observation of different NMR signals for the two boron-bonded R groups.

The reaction of $(CH_3)_2NBR_2$ ($R = C_2H_5$) with 1 molar equiv of Hpz at room temperature gave the complex $(CH_3)_2HN{\cdot}BR_2(pz)$. However, reaction of the latter with additional Hpz did not proceed cleanly to give the complex $Hpz{\cdot}BR_2(pz)$. Rather, a product mixture was obtained that, as based on NMR data, contained the desired species but also the pyrazabole relative $R_2B(\mu\text{-}pz)[\mu\text{-}N(CH_3)_2]BR_2$, which could not be separated and isolated in pure form. Also, the reaction of $(CH_3)_2HN{\cdot}BR_2(pz)$ with $(CH_3)_2NBR_2$ did not proceed cleanly to form the cited pyrazabole relative. In contrast, reaction of $(CH_3)_2HN{\cdot}B(C_2H_5)_2(pz)$ with Kpz in refluxing benzene proceeded cleanly to give the salt $K[(C_2H_5)_2B(pz)_2]$ in excellent yield.

It is of interest to note that in the case of $R_2B = (C_8H_{14})B$ (where $(C_8H_{14})BH$ = 9-borabicyclo[3.3.1]nonane), the complex $(CH_3)_2HN{\cdot}B(C_8H_{14})(pz)$ has previously been isolated and was then transformed into $Hpz{\cdot}B(C_8H_{14})(pz)$.[23] Furthermore, in the present work 9-(diethylamino)-9-borafluorene, $(C_2H_5)_2NB(C_{12}H_8)$, was found to react with Hpz even at room temperature by simultaneous displacement of diethylamine and complexation to form the adduct $Hpz{\cdot}B(C_{12}H_8)(pz)$. The ^1H NMR data of the species indicated that the two pz groups are equivalent, since only one signal set was observed for these; on that basis the adduct can be formulated $(C_{12}H_8)B(pz)_2H$. However, whereas in CD_3OD solution only one ^{11}B NMR signal was observed, two signals (both indicating four-coordinate boron) were observed for a solution in $CDCl_3$ at room temperature. At 45 °C, these signals were observed as a singlet at 0.9 ppm ($h_{1/2}$ = ca. 300 Hz) and a very broad singlet at 6.5* ppm of about equal area; but at −38 °C only a single line, $\delta(^{11}B)$ 0.5 ($h_{1/2}$ = 700 Hz), was observed. These data suggest that in chloroform solution an equilibrium of different species but involving only four-coordinate boron may be prevailing at room temperature, but which shifts to one side at −38 °C. The compound lost Hpz on thermal treatment with the formation of the pyrazabole $(C_{12}H_8)B(\mu\text{-}pz)_2B(C_{12}H_8)$. This thermal decomposition occurs even below the melting point at temperatures near 210 °C.

On the other hand, (diisopropylamino)di-9-fluorenylborane, $(i\text{-}C_3H_7)_2NB(C_{13}H_9)_2$, did not interact with Hpz either at room temperature or in boiling ether or benzene. However, in boiling toluene a transamination occurred with the release of diisopropylamine. When the reaction was performed with 2 molar equiv of Hpz, the species $Hpz{\cdot}B(C_{13}H_9)_2(pz)$ was obtained as a crystalline material. On refluxing of an equimolar mixture of the two reagents in toluene, the product appeared to be the pyrazabole $(C_{13}H_9)_2B(\mu\text{-}pz)_2B(C_{13}H_9)_2$. As is based on the NMR spectroscopic data, the latter product seems to exist in solution as the cited dimer (i.e., the pyrazabole with four-coordinate boron). However, both the EI and the FD mass spectrum of the material showed only peaks for the monomeric di-9-fluorenyl-1-pyrazolylborane. This would suggest that at elevated temperatures the pyrazabole structure readily breaks down into the monomeric units, which are then observed in the mass spectrum of the material. A similar observation has been reported for the pyrazabole $[(CH_3)_2N](pz)B(\mu\text{-}pz)_2B(pz)[N(CH_3)_2]$.[6] However, whereas in the latter species the terminal dimethylamino groups may weaken the central B_2N_4 ring by adding electron density to the boron, in the former case steric factors may render the central B_2N_4 ring thermally less stable and promote the formation of the monomeric 1-pyrazolylborane.

The preceding observations suggest that the steric factors play a role to determine the product resulting from the interaction of monoaminoboranes with Hpz. The significance of additional factors is illustrated by the following. The reaction of $[(CH_3)_2NBF_2]_2$ with Hpz ultimately leads to the formation of the pyrazabole $F_2B(\mu\text{-}pz)_2BF_2$.[9] Depending on the conditions, the reaction progresses via the complex $(CH_3)_2HN{\cdot}BF_2(pz)$ and the pyrazabole relative $F_2B(\mu\text{-}pz)[\mu\text{-}N(CH_3)_2]BF_2$, which could not be separated. However, regardless of the reaction conditions the BF_2 moiety was retained in all cases. Surprisingly, in an attempt to prepare $K[F_2B(pz)_2]$ from the reaction of $[(CH_3)_2NBF_2]_2$ with Kpz/Hpz, extensive fluorine redistribution occurred under the influence of the $[pz]^-$ ion and the salt $K[F_3B(pz)]$ was obtained as the only species containing B–F bonds. No $F_2B(\mu\text{-}pz)_2BF_2$ was formed under these circumstances. On the other hand, the reaction of $(C_2H_5)_2O{\cdot}BF_3$ with $[pz^*]^-$ (Hpz^* = 3,5-dimethylpyrazole) has been reported to yield $[F_2B(pz^*)_2]^-$, which was isolated as the Co^{2+} and Ni^{2+} chelates.[21]

As based on ^{11}B NMR studies, the salt $K[F_3B(pz)]$ was also obtained when BF_3 gas was bubbled through a slurry of Kpz in benzene at room temperature, until the exit gas indicated BF_3. However, in this case substantial amounts of $K[B(pz)_4]$ and $K[BF_4]$ were also formed. On the other hand, when Kpz was introduced in small portions into a saturated solution of BF_3 in benzene (and maintaining BF_3 excess), a mixture of $K[F_3B(pz)]{\cdot}xBF_3$ and $K[BF_4]$ was obtained as the major product. Finally, on refluxing of equimolar quantities of Kpz and $(C_2H_5)_2O{\cdot}BF_3$ in benzene, $K[F_3B(pz)]$ was formed as the main product.

The reaction of tris(dimethylamino)borane, $[(CH_3)_2N]_3B$, with Hpz at room temperature has previously been described to yield the species $(CH_3)_2HN{\cdot}B(pz)_3$; and bis(dimethylamino)phenylborane, $[(CH_3)_2N]_2BC_6H_5$, reacted to give the complex $(CH_3)_2HN{\cdot}B(pz)_2(C_6H_5)$.[6] Furthermore, the complex $(CH_3)_2HN{\cdot}B(pz)_2(C_2H_5)$ has been prepared from $[(CH_3)_2N]_2BC_2H_5$ and Hpz. Also, reaction of an excess of borazines, $(RBNR')_3$, with Hpz led to the formation of pyrazabole relatives of the type $R(pz)B(\mu\text{-}pz)(\mu\text{-}NHR')BR(pz)$. The latter were found to react with additional Hpz at elevated temperatures to yield pyrazaboles of the type $R(pz)B(\mu\text{-}pz)_2BR(pz)$.[17]

It has now been observed that when the borazine $(C_2H_5BNCH_3)_3$ is reacted with an excess of Hpz at room temperature, the reaction can be directed to yield the adduct $(CH_3)H_2N{\cdot}B(pz)_2(C_2H_5)$. (Under analogous conditions the reaction of $(C_6H_5BNCH_3)_3$ with Hpz gave a mixture of $(C_6H_5)(pz)B(\mu\text{-}pz)(\mu$-

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$NHCH_3)B(pz)(C_6H_5)$ and $(C_6H_5)(pz)B(\mu\text{-}pz)_2B(pz)(C_6H_5)$.) Similarly, reaction of the borazine $[(CH_3)_2NBNCH_3]_3$ with a large excess of Hpz at room temperature gave $(CH_3)H_2N{\cdot}B(pz)_3$. This latter result shows that the terminal dimethylamino groups are readily displaced but the annular methylamine moiety of the original borazine is retained in the final product.

It is of interest to compare the ^1H NMR spectra of the two adducts $(CH_3)H_2N{\cdot}B(C_2H_5)(pz)_2$ and $(CH_3)H_2N{\cdot}B(pz)_3$. The former exhibited a signal for the N-bonded protons at 6.3 (2 H) ppm, whereas the latter exhibited two signals at 5.3 (1 H) and 7.55 (1 H) ppm, respectively. For the compound $(CH_3)_2HN{\cdot}B(pz)_3$, the (N)H signal was previously observed at 7.8 ppm and it was noted that in solution and at room temperature the (N)H is not localized and the N atoms of both the $(CH_3)_2N$ and the pz groups participate in the bonding; only at low temperatures the proton was found to be localized at the $(CH_3)N$ site.[6] Since at room temperature the CH_3 signal of $(CH_3)H_2N{\cdot}B(C_2H_5)(pz)_2$ is observed as a triplet, there is no doubt that the N-bonded H atoms with $\delta(^1H)$ 6.3 are located at the $N(CH_3)$ site. (Note that the (N)H signal of $(CH_3)H_2N{\cdot}B(CH_3)(pz)_2$ is also observed at 6.3 ppm.[9]) It is, therefore, reasonable to assume that for $(CH_3)H_2N{\cdot}B(pz)_3$ one (N)H is located at the $N(CH_3)$ site and gives rise to the signal at 6.3 ppm, whereas the other (N)H is fluxional and is evidenced at 7.5 ppm, migrating to 7.9 ppm at −39 °C. It is certainly surprising that the $B(pz)_3$ unit affects the (N)H protons of the coordinated CH_3NH_2 so differently as compared to the $B(pz)_2R$ (R = CH_3, C_2H_5) unit.

Finally, the reaction of $[(CH_3)_2NNH]_3B$ with excess of Hpz proceeded analogous to that of $[(CH_3)_2N]_3B$[6] to yield the complex $(CH_3)_2NNH_2{\cdot}B(pz)_3$. However, the latter is thermally much less stable than $(CH_3)_2HN{\cdot}B(pz)_3$ and it decomposed on attempts for purification. When heated to its melting point, it decomposed with the formation of what appeared to be (NMR and mass spectroscopic data) a mixture of $(pz)_2B(\mu\text{-}pz)_2B(pz)_2$ and $(pz)_2B(\mu\text{-}pz)[\mu\text{-}(CH_3)_2NNH]B(pz)_2$, which could not be separated.

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Resonance Raman Signatures of Oxomolybdenum Thiolate and Dithiolene Models of Molybdenum Proteins

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Resonance Raman (RR) data are reported for molybdenum compounds having ligands related to those which may be present at the active site of Mo redox enzymes: $Mo^{VI}O_2$(dttd) (**1**) (dttd = 2,3:8,9-dibenzo-1,4,7,10-tetrathiadecane), $Mo^{IV}(S_2C_2(CO_2Me)_2)_3^{2-}$ (**2**), and $Mo^{IV}O(S_2C_2(CO_2Me)_2)_2^{2-}$ (**3**). For **1** RR bands are observed at 922/865 and 375/356 cm^{-1} and are assigned to symmetric/asymmetric Mo=O and Mo—S(thiolate) stretchings, respectively. Excitation profiles (EP's) show the 922-cm^{-1} Mo=O band to reach maximum enhancement in resonance with a strong 410-nm electronic absorption of **1**, which is assigned to an O—Mo charge-transfer (CT) transition. In contrast, the 356-cm^{-1} Mo—S band EP has a dispersive shape with a maximum at 520 nm and a dip at 480 nm. This behavior is indicative of interference between scattering contributions from the strong 410-nm transition and a weaker transition at ~480 nm, attributed to thiolate–Mo CT. For **2**, the 647.1-nm-excited RR spectrum in resonance with a broad ~650-nm electronic absorption, shows a strong band at 365 cm^{-1} and a weaker one at 702 cm^{-1}, assigned to Mo—S and C—S stretching modes, respectively. Weak enhancement is also observed for bands at 1475, 1488, and 1525 cm^{-1}, one or more of which may arise from C=C stretching of the dithiolene ring. Replacement of a dithiolene ligand by an oxo ligand (giving **3**) produces marked RR changes. The Mo—S and C=C stretches, now at 393 and 1535 cm^{-1}, are seen with violet excitation, 406.7 nm, while yellow excitation (568.2 nm) reveals the Mo=O stretch, at 910 cm^{-1}, albeit weakly. The altered RR pattern implies a substantial electronic rearrangement, which is also reflected in the shifted ground-state vibrational frequencies.

Introduction

Molybdenum enzymes are distinguished by having extractable Mo-containing cofactors, which can reconstitute activity in Mo-deficient protein preparations.[1] The cofactors are of two kinds, the Fe–Mo cofactor of nitrogenase,[2,3] which contains Fe–Mo–S clusters, and the Mo–pterin cofactor of the Mo oxidase/reductase enzymes.[4-6] Although extractable, both cofactors are labile once extracted and have resisted definitive structural characterization, despite intense effort.

In the case of the Mo–pterin cofactor, for which model chemistry has been extensively investigated,[7] Rajagopalan[8,9] and coworkers have made the intriguing structural proposal shown in Figure 1, in which a *cis*-dioxo (or *cis*-oxo–sulfido) Mo(VI) unit (in the reduced Mo(IV)-containing form, an oxo or sulfido ligand is replaced by OH or SH^-) is bound via a dithiolene chelate to the pterin side-chain. The remaining Mo coordination sites presumably offer points of attachment for protein side-chain ligands, which are likely to be cysteine thiolate groups, as judged from EXAFS[10,11] and EPR[12] evidence, although nitrogen or oxygen ligands may sometimes be involved.[11] While based on compelling evidence from the chemical nature of cofactor degradation

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