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# Reactions of Alkali-Metal Poly(1-pyrazolyl)borates with Main-Group-Element Halides

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*Received June 25, 1991*

The pyrazabole analogues $R_2B(\mu\text{-pz})_2M(C_2H_5)_2$ (Hpz = pyrazole; M = Al, R = $C_2H_5$; M = Ga, R = $C_2H_5$, $C_6H_5$, pz) have been prepared by the reaction of $K[R_2B(pz)_2]$ with $(C_2H_5)_2MCl$. $K[B(pz)_4]$ reacts with 1 molar equiv of $MCl_4$ (M = Si, Ge, Sn) to form the complexes $B[(pz)_4]MCl_3$. Organosilicon as well as organogermanium poly(1-pyrazolyl)borates are unstable, but NMR data for autogeneously decomposing (at room temperature) $[B(pz)_4]_2GeR_2$ (R = $CH_3$, $C_2H_5$) could be obtained. Reaction of $K[(C_2H_5)_2B(pz)_2]$ with $R_2MCl_2$ (M = Si, R = $CH_3$; M = Ge, R = $C_2H_5$) proceeded by cleavage of a B–N bond of the ligand and $pz^-$ ion transfer from B to M to give $(C_2H_5)_2B(\mu\text{-pz})_2B(C_2H_5)_2$ and $R_2M(pz)_2$. The complexes $LSnCl_3$, $LSnCl_2(CH_3)$, $LSnCl(CH_3)_2$, and $LSnCl(C_6H_5)_2$ (L = $[B(pz)_4]$) as well as $L'SnCl(CH_3)_2$ (L' = $[(C_6H_5)_2B(pz)_2]$ or $[(C_2H_5)_2B(pz)_2]$) have been prepared. $[(C_6H_5)_2B(pz)_2]SnCl(CH_3)_2$ crystallizes in the triclinic system in space group $P\bar{1}$ with $a = 10.185$ (4) Å, $b = 10.613$ (5) Å, $c = 21.184$ (9) Å, $\alpha = 77.54$ (3)°, $\beta = 76.66$ (3)°, $\gamma = 75.59$ (3)°, and $Z = 4$ at 293 K. $[B(pz)_4]SnCl(CH_3)_2$ also crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.881$ (1) Å, $b = 9.502$ (1) Å, $c = 12.198$ (2) Å, $\alpha = 71.66$ (1)°, $\beta = 74.98$ (1)°, $\gamma = 80.45$ (1)°, and $Z = 2$ at 293 K. Phosphorus as well as sulfur chlorides interact with poly(1-pyrazolyl)borates by cleavage of one B–N bond of the ligand; pyrazaboles were obtained as the only boron-containing product. The same holds true for the reaction of $(CH_3)_2AsBr$ with $K[(C_2H_5)_2B(pz)_2]$, but the complex $[B(pz)_4]As(CH_3)_2$ was obtained on reaction with $K[B(pz)_4]$.

## Introduction

The poly(1-pyrazolyl)borate ions, $[R_nB(pz)_{4-n}]^-$ (Hpz = pyrazole; $n$ = 0–2; R = noncoordinating substituent), have been known for a long time and have been widely used as chelating agents in the study of transition-metal complexes.[1] However, the knowledge of poly(1-pyrazolyl)borates of main-group elements is rather limited. As a matter of fact, interest in the poly(1-pyrazolyl)borate chemistry of main-group elements other than alkali- or alkaline-earth-metal species has evolved only most recently. The preparation and characterization of some Al,[2] Ga,[2a,3] In,[2a,4] Tl(I),[5] Sn(II),[6] Sn(IV),[7] and Pb(II)[8] derivatives have been reported.

The current study describes some reactions of alkali-metal poly(1-pyrazolyl)borates with various main-group-element halides. Particular interest was placed on the synthesis of analogues of the pyrazaboles, i.e., species containing a $B(\mu\text{-pz})_2M$ arrangement (where M is a main-group-element atom). The pyrazaboles (=dimeric 1-pyrazolylboranes) of the general type $R_2B(\mu\text{-pz})_2BR_2$ feature two pyrazolyl groups which are bridging two four-coordinate boron atoms to form a $B(N_2)_2B$ six-membered-ring system; they constitute an interesting class of compounds of considerable chemical stability.[1] If they are viewed as poly(1-pyrazolyl)borates of boron, i.e., as species which are formally composed of $R_2B^+$ and $[(pz)_2BR_2]^-$ moieties, unsymmetrically substituted pyrazaboles are readily accessible by the reaction of alkali-metal poly(1-pyrazolyl)borates with three-coordinate boranes that contain a readily leaving group.[9] This same preparative approach has been utilized in the present work, which is ultimately directed to study the effects of the replacement of one of the boron atoms of a pyrazabole structure by another main-group-element atom.

## Experimental Section

Elemental analyses were performed by 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 ($^{11}B$, $^{27}Al$, $^{29}Si$, $^{119}Sn$; variable-temperature, high-resolution) or GEMINI-200 ($^1H$, $^{13}C$) instrument. Chemical shift data are given in ppm with positive values indicating downfield from the reference (internal $(CH_3)_4Si$ for $^1H$, $^{13}C$, and $^{29}Si$ NMR, external $(C_2H_5)_2O\cdot BF_3$ for $^{11}B$ NMR, external $[Al(H_2O)_6]^{3+}$ for $^{27}Al$ NMR, external $(CH_3)_4Sn$ for $^{119}Sn$ NMR); s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, m = unresolved multiplet, and an asterisk denotes a broad signal. Coupling constants $J$ are given in hertz. $^{13}C$ NMR spectra were generally recorded in the proton-decoupled mode. Electron impact (EI) mass spectral data (70 eV unless otherwise noted) were obtained on a VG ZAB-2F spectrometer under standard operating conditions. Field desorption (FD) mass spectra were recorded on a Finnigan MAT 250 instrument, and field ionization (FI) spectra were obtained on a Varian MAT-CH5 spectrometer.

Nonreferenced reagents were obtained from Aldrich Chemical Co., Milwaukee, WI, and used as received. All reactions were performed under anhydrous conditions and argon cover.

**Crystal data** were obtained on a Siemens R3m/V automated diffractometer by using graphite-monochromated Mo Kα radiation, $\lambda = 0.71069$ Å, and standard operating techniques. Unit cell parameters were obtained from the least-squares refinement of the diffracting positions of 25 reflections (20° < $2\theta$ < 27°) for $[(C_6H_5)_2B(pz)_2]SnCl(CH_3)_2$ and of 22 reflections (20° < $2\theta$ < 32°) for $[B(pz)_4]SnCl(CH_3)_2$. Intensity data were collected in the ω-scan mode in the range 3.0° < $2\theta$ <

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

| | $[B(pz)_4]$-$SnCl(CH_3)_2$ | $[(C_6H_5)_2B(pz)_2]$-$SnCl(CH_3)_2$ |
|---|---|---|
| formula | $C_{14}H_{18}BClN_8Sn$ | $C_{20}H_{22}BClN_4Sn$ |
| fw | 463.13 | 483.17 |
| cryst size, mm | 0.20 × 0.28 × 0.60 | 0.35 × 0.4 × 0.5 |
| space group | $P\bar{1}$ (No. 2) | $P\bar{1}$ (No. 2) |
| $a$, Å | 8.881 (1) | 10.185 (4) |
| $b$, Å | 9.502 (1) | 10.613 (5) |
| $c$, Å | 12.198 (2) | 21.184 (9) |
| $\alpha$, deg | 71.66 (1) | 77.54 (3) |
| $\beta$, deg | 74.98 (1) | 76.66 (3) |
| $\gamma$, deg | 80.45 (1) | 75.59 (3) |
| $Z$ | 2 | 4 |
| $V$, Å$^3$ | 939.7 (2) | 2127.3 (14) |
| $d_{calcd}$, g/cm$^3$ | 1.637 | 1.509 |
| $\mu$, mm$^{-1}$ | 1.521 | 1.342 |
| $F(000)$ | 460 | 968 |
| $2\theta$, deg | $3 \leq 2\theta \leq 52$ | $3 \leq 2\theta \leq 48$ |
| scan speed, deg/min | 2.00–29.30 | 2.69–29.30 |
| scan width, deg | 0.80 | 0.40 |
| tot. no. of reflcns | 4917 | 7152 |
| no. of unique reflcns ($I - 3\sigma(I)$) | 3883 | 5622 |
| no. of variables used | 280 | 487 |
| res electron density, e/Å$^3$ | 0.29–0.65 | 1.65 |
| $R$ | 0.0258 | 0.0463 |
| $R_w$ | 0.049 | 0.0540 |
| $g$ | 0.0023 | 0 |

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

48.0° (52°). All data were corrected for intensity changes noted for the check reflections (2 control measurements after every 48 measurements; maximum variation ±1.5%) and for Lorentz and polarization effects. The structures were solved (SHELXTL PLUS program, MicroVAX II computer) by direct methods for $[(C_6H_5)_2B(pz)_2]SnCl(CH_3)_2$ and for $[B(pz)_4]SnCl(CH_3)_2$ by the sharpened Patterson method, followed by least-squares refinement. After convergence was achieved in further refinement with anisotropic temperature factors, all hydrogen positions were revealed from a difference Fourier map. They were included in the final refinement using the riding model with fixed C–H distances (0.96 Å) and fixed isotropic temperature factors ($U$ = 0.08 Å$^2$) (full-matrix least-squares method) for $[(C_6H_5)_2B(pz)_2]SnCl(CH_3)_2$, while the hydrogen positions were freely refined for $[B(pz)_4]SnCl(CH_3)_2$ with fixed $U_i$ = 0.05 Å$^2$. Definitions are $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \sum(w_{1/2}||F_o| - |F_c||/\sum(w_{1/2}|F|)$, where $w^{-1} = \sigma^2(F_o) - g(F_o)^2$. A summary of crystallographic data and data collection procedures is given in Table I.

**$(C_2H_5)_2B(\mu\text{-pz})_2Al(C_2H_5)_2$.** A solution of $(C_2H_5)_2AlCl$ in hexane (25%, 1.24 g = 10.3 mmol of $(C_2H_5)_2AlCl$) was added dropwise to a stirred slurry of 2.50 g (10.3 mmol) of $K[(C_2H_5)_2B(pz)_2]$[10] in 50 mL of dichloromethane at 0 °C. The mixture was warmed to ambient temperature, stirred for 10 min, and filtered. Solvent was evaporated off the clear filtrate under reduced pressure to leave 2.9 g (98%) of crude oily product, which was purified by distillation. The compound, bp 100–101 °C (1 Torr), is extremely sensitive to oxygen and moisture. Anal. Calcd for $C_{14}H_{26}AlBN_4$ ($M_r$ = 288.18): C, 58.35; H, 9.09; Al, 9.36; B, 3.75; N, 19.45. Found: C, 51.70; H, 8.92; Al, 9.32; B, 3.42; N, 18.83.

NMR data: $\delta(^1H)$ 7.78 (1 H, d, $J$ = 2.3), 7.74 (1 H, d, $J$ = 2.3), 6.41 (1 H, unsym t = two overlapping d, $J$ = 2.3), 0.94 (3 H, t, $J$ = 8.1), 0.8–0.5 (5 H, m), 0.07 (2 H, q, $J$ = 8.1); $\delta(^{11}B)$ 2.3 (s, $h_{1/2}$ = 180 Hz); $\delta(^{13}C)$ 139.0, 136.5, 105.6, 17.5*, 8.6, 8.4, 0.0*; $\delta(^{27}Al)$ 154.0 ($h_{1/2}$ = ca. 3800 Hz). The EI mass spectrum exhibited an ion group at $m/z$ 259 for $[M - 29]^+$ as the most prominent (and that of highest mass) of the spectrum.

**$(C_2H_5)_2B(\mu\text{-pz})_2Ga(C_2H_5)_2$.** To a stirred solution of 2.76 g (16.9 mmol) of $(C_2H_5)_2GaCl$[11] (NMR data: $\delta(^1H)$ 1.19 (3 H, t), 0.89 (2 H, q); $\delta(^{13}C)$ 11.3, 8.8) in 30 mL of dichloromethane was added 4.09 g (16.9 mmol) of $K[(C_2H_5)_2B(pz)_2]$. An exothermic reaction occurred, and the mixture was stirred at ambient temperature for 30 min and filtered. Solvent was evaporated off the clear filtrate to leave 5.3 g (95%) of an oily liquid, which was purified by distillation, bp 104–106 °C (1 Torr). Anal. Calcd for $C_{14}H_{26}BGaN_4$ ($M_r$ = 330.92): C, 50.81; H, 7.92; B, 3.27; Ga, 21.07; N, 16.93. Found: C, 50.40; H, 7.56; B, 3.49; Ga, 20.64; N, 17.13.

NMR data: $\delta(^1H)$ 7.77 (1 H, d, $J$ = 2.3), 7.58 (1 H, d, $J$ = 2.3), 6.36 (1 H, unsym t, $J$ = 2.3), 0.98 (3 H, t, $J$ = 8.3), 0.8–0.6 (5 H, m), 0.55 (2 H, q, $J$ = 8.3); $\delta(^{11}B)$ 2.0 (s, $h_{1/2}$ = 180 Hz); $\delta(^{13}C)$ 138.5, 135.6, 104.9, 14.0*, 9.3, 8.7, 4.1. FI mass spectrum: $m/z$ 304 (4), 303 (42), 302 (6), 301 (100), 300 (7).

**$(C_6H_5)_2B(\mu\text{-pz})_2Ga(C_2H_5)_2$**, mp 104–108 °C dec, was prepared in a fashion analogous to that for the preceding compound using 1.00 g (6.12 mmol) of $(C_2H_5)_2GaCl$ and 2.07 g (6.12 mmol) of $K[(C_6H_5)_2B(pz)_2]$[9c] in 30 mL of dichloromethane (30 min of stirring at room temperature). After filtration and solvent evaporation, the solid compound, mp 104–108 °C dec, remained in 92% yield (2.39 g). Anal. Calcd for $C_{22}H_{26}BGaN_4$ ($M_r$ = 427.01): C, 61.88; H, 6.14; B, 2.53; Ga, 16.33; N, 13.12. Found: C, 61.71; H, 6.36; B, 2.40; Ga, 16.48; N, 13.02.

NMR data: $\delta(^1H)$ 7.68 (1 H, d, $J$ = 2.2), 7.49 (1 H, d, $J$ = 2.3), 7.25 (3 H, m), 6.80 (2 H, m), 6.37 (1 H, two overlapping d, $J$ = 2.2), 0.82 (3 H, t, $J$ = 8.3), 0.55 (2 H, q, $J$ = 8.2); $\delta(^{11}B)$ −2.5 (s, $h_{1/2}$ = 50 Hz); $\delta(^{13}C)$ 139.5, 139.0, 133.6, 127.5, 126.9, 104.8, 9.2, 2.7. FI mass spectrum: $m/z$ 400 (9), 399 (72), 398 (39), 397 (100), 396 (19).

**$(pz)_2B(\mu\text{-pz})_2Ga(C_2H_5)_2$** was prepared in a manner analogous to that of the two preceding compounds by the reaction of 4.80 g (15.0 mmol) of $K[B(pz)_4]$[8] with 2.46 g (15.0 mmol) of $(C_2H_5)_2GaCl$ (35 mL of dichloromethane, 1 h of stirring at room temperature). After solvent evaporation, 4.6 g (75%) of material was obtained. It was recrystallized from hexane to give the pure compound, mp 122–123 °C. Anal. Calcd for $C_{16}H_{22}BGaN_8$ ($M_r$ = 406.94): C, 47.22; H, 5.45; B, 2.66; Ga, 17.13; N, 27.54. Found: C, 47.22; H, 5.19; B, 2.41; Ga, 16.83; N, 27.25.

NMR data: $\delta(^1H)$ 7.75 (2 H, d, $J$ = 1.6), 7.37* (1 H, s), 6.70* (1 H, s), 6.50* (1 H, s), 6.27* (1 H, s), 0.90 (3 H, t, $J$ = 8.2), 0.15 (2 H, q, $J$ = 8.2); $\delta(^{11}B)$ 0.2 (s, $h_{1/2}$ = 30 Hz); $\delta(^{13}C)$ 142.9, 140.7, 138.6, 134.1, 106.6, 106.0, 9.1, 2.4. FI mass spectrum: $m/z$ 380 (12), 379 (67), 378 (30), 377 (100), 376 (37).

**$[B(pz)_4]SiCl_3$.** A mixture of 1.25 g (3.93 mmol) of $K[B(pz)_4]$, 30 mL of dichloromethane, and 0.67 g (3.93 mmol) of $SiCl_4$ (as 1 M solution in dichloromethane) was stirred for 90 min at room temperature. The mixture was filtered, and solvent was evaporated off the clear filtrate. The solid residue was washed with hot toluene and dried under vacuum to give a colorless product, mp 288–290 °C dec. Some toluene was adhering and could only be removed by heating to 90–100 °C under vaccum for several hours. Anal. Calcd for $C_{12}H_{12}BCl_3N_8Si$ ($M_r$ = 413.54): C, 34.85; H, 2.93; B, 2.61; Cl, 25.72; N, 27.10; Si, 6.79. Found: C, 34.94; H, 2.77; B, 3.14; Cl, 25.18; N, 26.95; Si, 6.29.

NMR data: $\delta(^1H)$ 8.71 (3 H, d, $J$ = 1.7), 8.00 (2 H, d, $J$ = 1.7), 7.84 (3 H, d, $J$ = 1.8), 6.72 (1 H, two overlapping d, $J$ = 1.8), 6.39 (3 H, two overlapping d, $J$ = 1.8); $\delta(^{11}B)$ −2.5 (s, $h_{1/2}$ = 50 Hz); $\delta(^{13}C)$ 144.1, 143.3, 134.5, 108.7, 105.8; $\delta(^{29}Si)$ −196.6 (s). The FD mass spectrum exhibited an ion cluster for $[M - Cl]^+$ in the calculated isotopic distribution.

**$[B(pz)_4]GeCl_3$** was prepared in a fashion analogous to that for the preceding compound using 3.31 g (15.4 mmol) of $GeCl_4$, 4.90 g (15.4 mmol) of $K[B(pz)_4]$, and 40 mL of dichloromethane (1 h of stirring at room temperature). The product (5.2 g) melted at 250–254 °C dec; some adhering solvent could be removed by heating to 180 °C under vacuum, but the material contained minor additional impurities (as evidenced by $^1H$ NMR data) which could not be removed. Anal. Calcd for $C_{12}H_{12}BCl_3GeN_8$ ($M_r$ = 458.04): C, 31.47; H, 2.64; B, 2.36; Cl, 23.22; Ge, 15.85; N, 24.46. Found: C, 31.82; H, 2.88; B, 2.40; Cl, 24.52; Ge, 13.45; N, 23.47.

NMR data: $\delta(^1H)$ 8.54 (3 H, d, $J$ = 2.0), 7.99 (2 H, d, $J$ = 2.0), 7.82 (3 H, d, $J$ = 2.0), 6.72 (1 H, two overlapping d, $J$ = ca. 2), 6.40 (3 H, overlapping d, $J$ = ca. 2); $\delta(^{11}B)$ −2.1 (s, $h_{1/2}$ = 20 Hz); $\delta(^{13}C)$ 142.7, 140.9, 134.1, 107.9, 105.2. The FD mass spectrum exhibited an ion cluster for $[M - Cl]^-$ in the calculated isotopic distribution. EI mass spectrum (14 eV): $m/z$ 427 (11), 426 (10), 425 (60), 424 (43), 423 (100), 422 (26), 421 (60), 420 (23), 419 (37), 418 (8), 355 (7), 353 (22), 352 (5), 351 (11), 350 (6), 349 (7), 232 (7), 213 (8), 212 (69), 211 (31), 185 (7), 92 (51), 91 (26), 84 (10), 68 (9), 49 (15).

**$[B(pz)_4]SnCl_3$** was prepared in a manner analogous to that for the two preceding compounds from a mixture of 5.2 mL of a 1 M solution of $SnCl_4$ in dichloromethane, 1.65 g (5.2 mmol) of $K[B(pz)_4]$, and 30 mL of dichloromethane (2 h of stirring at room temperature). The crude product (2.4 g, 92%) was recrystallized from toluene to give a material melting at 290–300 °C dec, which was dried for 3 h at 180 °C to remove adhering toluene. Anal. Calcd for $C_{12}H_{12}BCl_3N_8Sn$ ($M_r$ = 504.14): C, 28.59; H, 2.40; B, 2.14; Cl, 21.10; N, 22.23; Sn, 23.54. Found: C, 28.40; H, 2.28; B, 2.20; Cl, 21.29; N, 21.92; Sn, 23.64.

NMR data: $\delta(^1H)$ 8.27 (3 H, d, $J$ = 2.3), 8.00 (1 H, d, $J$ = 1.5), 7.98 (1 H, d, $J$ = 2.5), 7.85 (3 H, d, $J$ = 2.6), 6.71 (1 H, unresolved unsym t), 6.42 (3 H, unsym t = two overlapping d, $J$ = ca. 2.4) (the spectrum

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was essentially unchanged over the temperature range from +80 to −70 °C); $\delta(^{11}\mathrm{B})$ −1.5 (s, $h_{1/2}$ = 20 Hz); $\delta(^{13}\mathrm{C})$ 143.3, 142.1, 136.6, 135.6, 108.5, 106.5; $\delta(^{119}\mathrm{Sn})$ −670 (s, $h_{1/2}$ = 20 Hz). The EI mass spectrum exhibited a very weak parent ion cluster at $m/z$ 504. Lit.[7e] mp: 300 °C dec. Lit.[7e] NMR data (solution in CD$_2$Cl$_2$): $\delta(^{1}\mathrm{H})$ 8.24 (3 H), 8.01 (2 H), 7.88 (3 H), 6.72 (1 H), 6.44 (3 H); $\delta(^{13}\mathrm{C})$ 143.4, 142.1, 137.1, 136.0, 108.7, 106.7; $\delta(^{119}\mathrm{Sn})$ −618.

**[B(pz)$_4$]SnCl$_2$(CH$_3$)** was prepared from 0.90 g (3.75 mmol) of CH$_3$SnCl$_3$ and 1.19 g (3.75 mmol) of K[B(pz)$_4$] (30 mL of dichloromethane, 2 h stirring) to give 1.7 g (94%) of product mp 266–270 °C (after recrystallization from toluene). Anal. Calcd for C$_{13}$H$_{15}$BCl$_2$N$_8$Sn ($M_r$ = 483.73): C, 32.28; H, 3.13; B, 2.23; Cl, 14.66; N, 23.16; Sn, 24.54. Found: C, 33.11; H, 3.12; B, 2.29; Cl, 14.61; N, 23.16; Sn, 25.27.

NMR data: $\delta(^{1}\mathrm{H})$ 8.35* (1 H, s), 7.99 (d, $J$ = 1.6) +7.96 (d, $J$ = 2.4) (6 H), 7.30* (1 H, s), 6.68 (1 H, t, $J$ = 1.9), 6.36* (3 H, s), 1.40 (3 H, s, $^{2}J$(Sn–H) = 116); for solution in C$_6$D$_5$CD$_3$ $\delta(^{1}\mathrm{H})$ 8.30* (1 H), 7.78* (1 H), 7.56* (5 H), 6.80* (1 H), 6.24* (1 H), 5.55* (3 H), 1.28 (3 H, s); at 80 °C, $\delta(^{1}\mathrm{H})$ 7.80* (4 H), 7.35 (4 H), 6.28* (1 H), 5.69* (3 H), 1.28 (3 H, s); for solution in CD$_2$Cl$_2$, $\delta(^{1}\mathrm{H})$ 8.30* (1 H), 8.00* (6 H), 7.35* (1 H), 6.70* (1 H), 6.40* (3 H), 1.37 (3 H, s, $^{2}J$(Sn–H) = 116); $\delta(^{11}\mathrm{B})$ −1.3 (s, $h_{1/2}$ = 15 Hz); $\delta(^{13}\mathrm{C})$ 143.6, 141.5, 136.7, 136.4, 108.8, 106.7, 20.8; $\delta(^{119}\mathrm{Sn})$ −474 (s, $h_{1/2}$ = 40 Hz); at −40 °C, $\delta(^{1}\mathrm{H})$ 8.25 (1 H, d, $J$ = 2.3), 8.03 (2 H, d, $J$ = 2.3), 7.97 (4 H, unresolved), 7.13 (1 H, d, $J$ = 2.6), 6.66 (1 H, two overlapping d, $J$ = 2.4), 6.39 (2 H, two overlapping d, $J$ = 2.2), 6.31 (1 H, unsym t = two overlapping d, $J$ = ca. 2.5), 1.35 (3 H, s); spin-decoupling experiments showed that individual pz groups are observed at $\delta(^{1}\mathrm{H})$ 8.25 (1 H)/7.13 (1 H)/6.66 (1 H), 8.03 (2 H)/7.97 (2 H)/6.39 (2 H), and 7.97 (2 H)/6.66 (1 H), respectively. Lit.[7e] mp: 248–250 °C. Lit.[7e] NMR data (solution in CD$_2$Cl$_2$): $\delta(^{1}\mathrm{H})$ 8.30*, 8.05*, 8.00, 7.98, 7.35*, 6.69, 6.38, 1.36; $\delta(^{13}\mathrm{C})$ 143.1, 141.0, 136.5, 136.2, 108.3, 106.4, 20.5; $\delta(^{119}\mathrm{Sn})$ −474.

**[B(pz)$_4$]SnCl(CH$_3$)$_2$** was prepared from 0.40 g (1.82 mmol) of (CH$_3$)$_2$SnCl$_2$ and 0.58 g (1.82 mmol) of K[B(pz)$_4$] (20 mL of dichloromethane, 30 min stirring) to give 0.85 g (100%) of crude material. The compound, mp 162–164 °C dec, was purified by recrystallization from toluene. Anal. Calcd for C$_{14}$H$_{18}$BClN$_8$Sn ($M_r$ = 463.31): C, 36.29; H, 3.92; B, 2.33; Cl, 7.65; N, 24.19; Sn, 25.62. Found: C, 36.02; H, 3.85; B, 2.67; Cl, 7.37; N, 23.15; Sn, 25.12.

NMR data: $\delta(^{1}\mathrm{H})$ 7.99 (2 H, d, $J$ = 1.5), 7.33 (2 H, d, $J$ = 2.1), 6.41 (2 H, two sets of overlapping d, $J$ = ca. 2), 0.82 (3 H, s, $^{2}J$(Sn–H) = 76); $\delta(^{11}\mathrm{B})$ −1.0 (s, $h_{1/2}$ = 35 Hz); $\delta(^{13}\mathrm{C})$ 142.0, 136.3, 106.4, 11.3; $\delta(^{119}\mathrm{Sn})$ −222 (s, $h_{1/2}$ = 40 Hz). Lit.[7e] mp: 133–135 °C. Lit.[7e] NMR data: $\delta(^{1}\mathrm{H})$ 7.97, 7.61, 7.29, 6.39, 6.36, 0.88; $\delta(^{13}\mathrm{C})$ 141.8, 136.1, 133.8, 106.4, 105.2, 13.0; $\delta(^{119}\mathrm{Sn})$ −323.

**[B(pz)$_4$]SnCl(C$_6$H$_5$)$_2$**, sintering near 200 °C and melting at 210–220 °C dec, was obtained in 94% yield from 1.05 g (3.05 mmol) of Cl$_2$Sn(C$_6$H$_5$)$_2$ and 0.97 g (3.05 mmol) of K[B(pz)$_4$] (30 mL of dichloromethane, 3 h of stirring). Anal. Calcd for C$_{24}$H$_{22}$BClN$_8$Sn ($M_r$ = 587.45): C, 49.07; H, 3.78; B, 1.84; Cl, 6.04; N, 19.07; Sn, 20.20. Found: C, 49.49; H, 3.91; B, 1.69; Cl, 6.02; N, 18.93; Sn, 20.44.

NMR data: $\delta(^{1}\mathrm{H})$ 7.85* (2 H, s), 7.73* (2 H, s), 7.51 (2 H, m), 7.25 (3 H, m), 6.29* (2 H, s); $\delta(^{11}\mathrm{B})$ −1.2 (s, $h_{1/2}$ = 20 Hz); $\delta(^{119}\mathrm{Sn})$ −444 (s, $h_{1/2}$ = 40 Hz). Lit.[7e] mp: 221–223 °C. Lit.[7e] NMR data: $\delta(^{1}\mathrm{H})$ (pz groups) 8.48, 8.15, 7.98, 7.86, 7.72, 7.68, 7.57, 6.72, 6.38, 6.33; $\delta(^{119}\mathrm{Sn})$ −445.

**[(C$_2$H$_5$)$_2$B(pz)$_2$]SnCl(CH$_3$)$_2$** was obtained from 0.53 g (2.4 mmol) of (CH$_3$)$_2$SnCl$_2$ and 0.58 g (2.4 mmol) of K[(C$_2$H$_5$)$_2$B(pz)$_2$] (20 mL of dichloromethane, 30 min of stirring). The oily material (0.89 g, 96%) was characterized by NMR spectroscopy without further purification.

NMR data: $\delta(^{1}\mathrm{H})$ 8.09* (1 H, s), 7.77 (1 H, d, $J$ = 2.1), 6.38 (1 H, t, $J$ = 2.3), 1.16 (3 H, s, $^{2}J$(Sn–H) = 77), 0.9–0.6 (5 H, m); $\delta(^{11}\mathrm{B})$ 1.4 (s, $h_{1/2}$ = 220 Hz); $\delta(^{13}\mathrm{C})$ 138.8, 135.4, 104.0, 13*, 9.5, 7.4; $\delta(^{119}\mathrm{Sn})$ −82 (s, $h_{1/2}$ = 45 Hz).

**[(C$_6$H$_5$)$_2$B(pz)$_2$]SnCl(CH$_3$)$_2$** was prepared from 1.23 g (5.60 mmol) of (CH$_3$)$_2$SnCl$_2$ and 1.89 g (5.60 mmol) of K[(C$_6$H$_5$)$_2$B(pz)$_2$] (40 mL of dichloromethane, 2 h of stirring) to give 1.4 g (52%) of product sintering at 184 °C, mp 190–194 °C. Anal. Calcd for C$_{20}$H$_{22}$BClN$_4$Sn ($M_r$ = 483.38): C, 49.70; H, 4.59; B, 2.24; Cl, 7.33; N, 11.59; Sn, 24.55. Found: C, 49.79; H, 4.74; B, 1.96; Cl, 7.50; N, 11.80; Sn, 24.62.

NMR data: $\delta(^{1}\mathrm{H})$ 8.19* (1 H, s), 7.55 (1 H, d, $J$ = 2.4), 7.23 (3 H, m), 6.85 (2 H, m), 6.40 (1 H, unsym t, $J$ = ca. 2.3), 0.62 (3 H, s, $^{2}J$(Sn–H) = 77); $\delta(^{11}\mathrm{B})$ 1.5 (s, $h_{1/2}$ = 350 Hz); $\delta(^{119}\mathrm{Sn})$ −177 (s, $h_{1/2}$ = 35 Hz).

**[B(pz)$_4$]As(CH$_3$)$_2$** was prepared from 3.8 g (12 mmol) of K[B(pz)$_4$] and 1.7 g (9 mmol) of (CH$_3$)$_2$AsBr (30 mL of dichloromethane, 2 h of stirring) to give 3.4 g of product (after filtration and solvent evaporation). The crude material was purified by dissolution in a minimal amount (ca. 5 mL) of dichloromethane, cooling the solution to −78 °C, and collecting the precipitate: mp 104 °C dec. Anal. Calcd for C$_{14}$H$_{18}$AsBN$_8$ ($M_r$ = 384.09): C, 43.78; H, 4.73; As, 19.51; B, 2.81; N, 29.17. Found: C, 43.15; H, 4.72; As, 19.09; B, 3.05; N, 29.95.

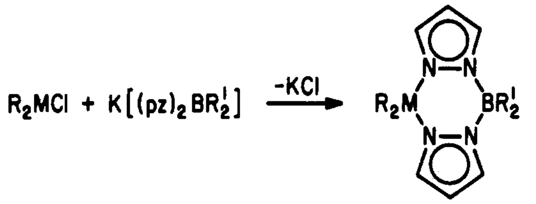
NMR data: $\delta(^{1}\mathrm{H})$ 7.76* (2 H, s), 7.27* (2 H, s), 6.34* (2 H, s), 1.56 (3 H, s); $\delta(^{11}\mathrm{B})$ 0.8 (s, $h_{1/2}$ = 50 Hz); $\delta(^{13}\mathrm{C})$ 141.1*, 135.2*, 106.1*, 19.1.

## Results and Discussion

**General Remarks.** The goal of the current work was centered on the synthesis and characterization of selected pyrazabole analogues, i.e., compounds in which one of the two boron atoms of a pyrazabole, R$_2$B($\mu$-pz)$_2$BR$_2$ (Hpz = pyrazole), is replaced by a main-group-element atom M to give a B($\mu$-pz)$_2$M structural arrangement containing a B(N$_2$)$_2$M ring system.

All preparations were performed by a standard procedure originating from alkali-metal poly(1-pyrazolyl)borates, which were reacted with various main-group-element halides. The reactions were performed in dichloromethane medium at room temperature and generally proceeded without major complications. However, care was taken to work in a dry atmosphere and to employ anhydrous reagents. It has recently been shown that alkali-metal poly(1-pyrazolyl)borates are hygroscopic, and some adhering moisture is difficult to detect and to remove from the materials.[7h]

**Aluminum and Gallium Poly(1-pyrazolyl)borate Derivatives.** Of the known aluminum poly(1-pyrazolyl)borate derivatives,[2] only two have a structure truly analogous to that of pyrazaboles, i.e., (pz*)HB($\mu$-pz*)$_2$Al(CH$_3$)$_2$ and H$_2$B($\mu$-pz*)$_2$Al(CH$_3$)$_2$ (Hpz* = 3-*tert*-butylpyrazole). The existence of a pyrazabole-analogue structure in the former is due to the bulky *tert*-butyl substituent, since Al can accommodate a higher coordination than 4, e.g., in HB($\mu$-pz′)$_3$Al(CH$_3$)$_2$ (Hpz′ = 3,5-dimethylpyrazole).[2c] These pyrazabole analogues have been reported only recently, at a time when the "aluminapyrazabole" (C$_2$H$_5$)$_2$B($\mu$-pz)$_2$Al(C$_2$H$_5$)$_2$ (**1**) had already been prepared by the reaction of K[(C$_2$H$_5$)$_2$B(pz)$_2$] with (C$_2$H$_5$)$_2$AlCl (eq 1). In consonance with the earlier data on species of type **1**, the latter aluminapyrazabole was found to be extremely reactive, possibly due to the lack of coordinative saturation at Al. It may also be an indication of a fairly weak Al–N bond and thereby suggest an equilibrium R$_2$B($\mu$-pz)$_2$AlR$_2$ ⇄ R$_2$B(pz)($\mu$-pz)AlR$_2$. This assumption finds support by the broadness and location of the $^{27}$Al NMR signal.



(1)

**1**: M = Al, R = R′ = C$_2$H$_5$

**2**: M = Ga, R = C$_2$H$_5$

a: R′ = C$_2$H$_5$

b: R′ = C$_6$H$_5$

c: R′ = pz

While the current work was in progress, the "gallapyrazaboles" H$_2$B($\mu$-pz)$_2$GaRR′ of type **2** (R = R′ = CH$_3$;[3c,3d] R = CH$_3$, R′ = Cl;[3c] R = CH$_3$, R′ = OCOCH$_3$[3c]), (CH$_3$)$_2$B($\mu$-pz)$_2$Ga(CH$_3$)$_2$,[3d] and the accidentally obtained (CH$_3$)$_2$B($\mu$-pz)$_2$GaCH$_3$(OH)[3d] have been described. In the present work, the species R$_2$B($\mu$-pz)$_2$Ga(C$_2$H$_5$)$_2$ with R = C$_2$H$_5$ (**2a**), C$_6$H$_5$ (**2b**), and pz (**2c**) have been prepared. The structures of these compounds were readily deduced from the NMR data. Interestingly, the mass spectra of the three new gallapyrazaboles (**2**) exhibited no parent ion, but in all cases a strong peak for the [M − C$_2$H$_5$]$^+$ ion was observed. This observation suggests the ready loss of one ethyl group from Ga (rather than the loss of a B substituent), which seems to be in consonance with the observed[3c] reactivity of such gallapyrazaboles. However, in contrast to the aluminapyrazaboles containing the B($\mu$-pz)$_2$Al moiety, the gallapyrazaboles are stable in air.

The species (pz)$_2$B($\mu$-pz)$_2$Ga(C$_2$H$_5$)$_2$ (**2c**) was of particular interest, since the two terminal B-bonded pz groups could possibly function as coordinating sites in a fashion similar to those of the related *B*-(1-pyrazolyl)pyrazaboles.[12,13] However, **2c** reacted with anhydrous $NiCl_2$ to form the complexes $ClNi[B(pz)_4]$ (stirring of the reagents in toluene medium for 12 h at room temperature) and $Ni[B(pz)_4]_2$[1] (in refluxing toluene), respectively, as the only boron-containing species. Analogous observations were made when **2c** was reacted with $CoCl_2$ or $ZnCl_2$. These observations suggest that the $B(\mu\text{-pz})_2Ga$ moiety is considerably less stable than the $B(\mu\text{-pz})_2B$ system and that the former is not suitable for the construction of chain-type molecules similar to those obtained from corresponding pyrazaboles.

**Studies on Silicon and Germanium Compounds.** The reaction of $K[B(pz)_4]$ with either $SiCl_4$ or $GeCl_4$ in 1:1 molar ratio readily yielded the species $[B(pz)_4]MCl_3$ (M = Si, Ge; in the case of M = Ge only as a slightly impure material). When the reaction was carried out in 4:1 molar ratio, again only $[B(pz)_4]MCl_3$ was obtained and excess of $K[B(pz)_4]$ could be recovered. The $^1H$ NMR spectra of the $[B(pz)_4]MCl_3$ complexes showed the presence of two types of pz groups in a 1:3 ratio. This observation suggests that M is six-coordinate, which is supported by the observation of $\delta(^{29}Si)$ −196.6 in the species where M = Si. Hence, the compounds can be formulated as $(pz)B(\mu\text{-pz})_3MCl_3$.

Reaction of $K[(C_2H_5)_2B(pz)_2]$ with $SiCl_4$ did not proceed cleanly, and the $^1H$ NMR spectrum of the crude product exhibited a multitude of signals in the pz region and at least five different types of ethyl groups were observed. However, the pyrazabole $(C_2H_5)_2B(\mu\text{-pz})_2B(C_2H_5)_2$[14] could be identified in the crude reaction product, and it was ultimately (on gentle heating of the material) obtained as the only boron-containing product. This observation documents that the poly(1-pyrazolyl)borate reagent transfers a $pz^-$ ion to Si via a rather unusual B–N bond cleavage of the ligand.

In the case of organosilicon chlorides such as $CH_3SiCl_3$, $(CH_3)_2SiCl_2$, or $(CH_3)_3SiCl$, no single defined species were formed on interaction with $K[B(pz)_4]$. Rather, as is based on $^1H$ NMR data, a mixture of products resulted which could not be separated. The $^1H$ NMR spectrum of the mixture suggested that redistribution of the organic substituents had occurred under the reaction conditions, since a multitude of $CH_3$ signals was observed.

Reaction of 2 molar equiv of $K[(C_2H_5)_2B(pz)_2]$ with $(CH_3)_2SiCl_2$ gave again the pyrazabole $(C_2H_5)_2B(\mu\text{-pz})_2B(C_2H_5)_2$ (as the only boron-containing product) and $(CH_3)_2Si(pz)_2$ (eq 2).

$$(CH_3)_2SiCl_2 + 2K[(pz)_2BR_2] \rightarrow 2KCl + (CH_3)_2Si(pz)_2 + R_2B(\mu\text{-pz})_2BR_2 \quad (2)$$

When equimolar quantities of the reagents were employed, the cited pyrazabole also was the only B-containing product. The Si-containing product of this latter reaction was a mixture consisting of $(CH_3)_2Si(pz)_2$ [perhaps contaminated with a very minor amount of $(CH_3)_2SiCl(pz)$] and unreacted $(CH_3)_2SiCl_2$. This was verified by the independent synthesis of $(CH_3)_2Si(pz)_2$ by the reaction of $(CH_3)_2SiCl_2$ with 2 molar equiv of Kpz [NMR data: $\delta(^1H)$ 7.85 (2 H, d, *J* = 1.5), 7.59 (2 H, d, *J* = 2.4), 6.39 (2 H, unsym t = two overlapping d, *J* = 1.5), 0.98 (6 H, s); $\delta(^{13}C)$ 144.8, 135.2, 107.4, 2.8. The parent ion of the species was observed in the EI mass spectrum.] On the other hand, $(CH_3)_2SiCl(pz)$ could not be prepared by this same procedure. Even when an excess of $(CH_3)_2SiCl_2$ was employed, no pure $(CH_3)_2SiCl(pz)$ could be isolated and the major product was again $(CH_3)_2Si(pz)_2$. These observations tend to suggest a ready ligand exchange according to $2(CH_3)_2SiCl(pz) \rightarrow (CH_3)_2SiCl_2 + (CH_3)_2Si(pz)_2$.

Reaction of $GeCl_4$ with $K[(C_2H_5)_2B(pz)_2]$ followed the same pattern as that observed for $SiCl_4$, but in this case the formation of the cited pyrazabole as the sole B-containing material was forced by heating of the crude material to 100 °C under vacuum.

Similar to the case of the corresponding Sn(IV) species,[7e,h] crude $[B(pz)_4]_2Ge(CH_3)_2$, mp 74–78 °C dec, could be prepared from $K[B(pz)_4]$ and $(CH_3)_2GeCl_2$, and the following NMR data were assigned for this compound: $\delta(^1H)$ 7.73 (4 H, d), 7.18 (4 H, d), 6.32 (4 H, unsym t), 0.63 (3 H, s); $\delta(^{11}B)$ −0.4 (s, $h_{1/2}$ = 45 Hz). However, on standing of the compound in solution, major changes occurred readily in the $CH_3$ region, where an originally very small signal at $\delta(^1H)$ 0.41 increased in intensity accompanied by a decrease of the signal at δ 0.63. Furthermore, the $^1H$ NMR spectrum of the original material could not be reproduced after standing of the dry material under inert atmosphere for a few hours.

Reaction of $(C_2H_5)_2GeCl_2$ with 2 molar equiv of $K[B(pz)_4]$ led to the initial formation of $[B(pz)_4]_2Ge(C_2H_5)_2$. The following NMR data were assigned to the cited compound as contained in the crude material, mp 90–100 °C dec: $\delta(^1H)$ 7.72 (4 H, d, *J* = 1.9), 7.17 (4 H, d, *J* = 2.4), 6.32 (4 H, two overlapping d, *J* = ca. 2), 1.15 (5 H, m); $\delta(^{11}B)$ 0.2 (s, $h_{1/2}$ = 25 Hz); $\delta(^{13}C)$ 140.2, 136.0, 106.2, 12.3, 7.2. The material decomposed on standing in solution as well as in the solid state, and the formation of various (but unidentified) ethylgermanium species could be observed by NMR spectroscopy.

The reaction of $(C_2H_5)_2GeCl_2$ with $K[(C_2H_5)_2B(pz)_2]$ proceeded analogously to that of $(CH_3)_2SiCl_2$. Interaction of equimolar amounts of the two reagents led to the formation of the pyrazabole $(C_2H_5)_2B(\mu\text{-pz})_2B(C_2H_5)_2$ and, as is based on $^1H$ NMR data, at least two different ethylgermanium species. The most abundant of the latter was $(C_2H_5)_2Ge(pz)_2$ (which was identified independently; see below). In addition, unreacted $(C_2H_5)_2GeCl_2$ was recovered and traces of another species, perhaps $(C_2H_5)_2GeCl(pz)$, were observed in the $^1H$ NMR spectrum [indicated by $\delta(^1H)$ for a $(Ge)C_2H_5$ group at δ 1.09 (t) for the $CH_3$ moiety, the $CH_2$ quartet being camouflaged by the triplet of $(C_2H_5)_2Ge(pz)_2$]. As expected, reaction of $K[(C_2H_5)_2B(pz)_2]$ with $(C_2H_5)_2GeCl_2$ in a 2:1 molar ratio gave only the pyrazabole $(C_2H_5)_2B(\mu\text{-pz})_2B(C_2H_5)_2$ besides $(C_2H_5)_2Ge(pz)_2$. The (hydrolytically sensitive) compound $(C_2H_5)_2Ge(pz)_2$ was prepared independently by the reaction of $(C_2H_5)_2GeCl_2$ with 2 molar equiv of Kpz. [NMR data: $\delta(^1H)$ 7.83 (2 H, d, *J* = 1.5), 7.52 (2 H, d, *J* = 2.3), 6.40 (2 H, unsym t = two overlapping d), 1.85 (4 H, q, *J* = 7.7), 1.25 (6 H, t, *J* = 7.9); $\delta(^{13}C)$ 143.3, 135.0, 106.5, 8.2, 7.0. The EI mass spectrum did not exhibit a parent ion, but $[M - 29]^+$ was observed.] The preceding observations again document the ready loss of $pz^-$ from the poly(1-pyrazolyl)borate reagent via a B–N bond cleavage and a transfer of the $pz^-$ ion from B to Ge.

**Tin(IV) Compounds.** Several tin(IV) poly(1-pyrazolyl)borates containing the ligand L = $[HB(pz)_3]$ have previously been reported, i.e., $LSnCl_3$,[7b,d] $LSnX_2R$ (X = Cl; R = $CH_3$,[7b,d] $C_4H_9$, $C_6H_5$;[7d] X = Cl, NCS, R = $CH_2CH_2COOCH_3$[7f]), $LSnClR_2$ (R = $CH_3$,[7b,d] $C_2H_5$, $C_4H_9$, $C_6H_5$[7d]), $LSnBrR_2$ (R = $CH_3$, $C_4H_9$[7d]), and $LSnR_3$ (R = $CH_3$,[7a] $C_4H_9$, $C_6H_5$[7c]). In addition, four compounds with L′ = $[H_2B(pz)_2]$, i.e., $L'SnCl_3$, $L'SnCl_2(CH_3)$, $L'SnCl(CH_3)_2$, and $L'Sn(CH_3)_3$, have been described.[7b] X-ray crystal structure studies are available on $[HB(pz)_3]Sn(CH_3)_3$[7a] and $[HB(pz)_3]SnX_2(CH_2CH_2COOCH_3)$ (X = Cl, NCS),[7f] and the species were found to contain six-coordinate tin; $[H_2B(pz)_2]SnCl(CH_3)_2$ contains five-coordinate tin.[7b] Furthermore, several tin(IV) tetrakis(1-pyrazolyl)borates of the type $[B(pz)_4]R_nSnX_{3-n}$ (R = $CH_3$, $C_2H_5$, $C_4H_9$, $C_6H_5$; X = Cl, Br; *n* = 0–2)[7e] and the species $[HB(pz^*)_3]SnR_nX_{3-n}$ (Hpz* = 3,5-dimethylpyrazole; R = $CH_3$, $C_2H_5$, $C_4H_9$, $C_6H_5$; X = Cl, Br; *n* = 0–2)[7g] have recently been described, and $[HB(pz)_3]_2Sn(CH_3)_2$ as well as $[HB(pz)_3]_2Sn(C_4H_9)_2$ has been reported elsewhere.[7c] Some additional species of the latter type $L_2SnR_2$ (L = poly(1-pyrazolyl)borate) have also become available; however, these were found to be thermally sensitive and, in particular, hydrolyzed with extreme ease to yield a novel type of polycyclic system.[7h]

In the present work, the reaction of $SnCl_4$ with 1 molar equiv of $K[B(pz)_4]$ gave ready access to $[B(pz)_4]SnCl_3$ in analogy to previous results.[7e] The reaction of $SnCl_4$ with either 2 or 4 molar equiv of $K[B(pz)_4]$ also led to the formation of $[B(pz)_4]SnCl_3$ as the only identified tin-containing product. Once isolated, $[B(pz)_4]SnCl_3$ did not react with additional $K[B(pz)_4]$ under the

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[14] Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3165–3170.

**Table II.** $^{119}$Sn Chemical Shift Data for Selected Sn(IV) Poly(1-pyrazolyl)borates (Hpz = Pyrazole; Solvent $CDCl_3$)

| compd | $\delta(^{119}Sn)$ | $h_{1/2}$, Hz | presumed tin coordn |
|---|---|---|---|
| $[B(pz)_4]SnCl_3$ | $-670^a$ | 20 | 6 |
| $[HB(pz)_3]SnCl_3$[7d] | $-620^b$ | ? | 6 |
| $[B(pz)_4]SnCl_2(CH_3)$ | −474 | 40 | 6 |
| $[HB(pz)_3]SnCl_2(CH_3)$[7d] | $-478^b$ | ? | 6 |
| $[B(pz)_4]SnCl(C_6H_5)_2$ | −444 | 40 | 6 |
| $[HB(pz)_3]Sn(C_6H_5)_3$ | −373 | 20 | 6 |
| $[HB(pz)_3]SnCl(CH_3)_2$[7b] | −334 | ? | 6 |
| $[B(pz)_4]SnCl(CH_3)_2$ | $-222^c$ | 40 | 6 |
| $[HB(pz)_3]Sn(CH_3)_3$[7b] | −195 | ? | 6 |
| $[H_2B(pz)_2]SnCl(CH_3)_2$[7b] | −182 | ? | 5 |
| $[(C_2H_5)_2B(pz)_2]SnCl(CH_3)_2$ | −182 | 45 | 5 |
| $[(C_6H_5)_2B(pz)_2]SnCl(CH_3)_2$ | −177 | 35 | 5 |
| $[H_2B(pz)_2]Sn(CH_3)_3$[7b] | −105 | ? | 5 |
| $[H_2B(pz)_2]SnCl_2(CH_3)$ | −103 | 150 | 5 |

[a] Lit.:[7e] −618. [b] Solvent: acetone? [c] Lit.:[7e] −323 (printing error?).

usual conditions; rather, the starting materials could be recovered unchanged.

In consonance with the recently reported data,[7e] even at room temperature the $^1$H NMR spectrum of $[B(pz)_4]SnCl_3$ clearly exhibited signals for two types of pyrazolyl groups in different environments in a 3:1 ratio. The spectrum did not change over the temperature range from +80 to −70 °C. These data suggest that the compound is static and that the tin is in a six-coordinate environment (three N and three Cl atoms), and the compound may be written as $(pz)B(\mu\text{-}pz)_3SnCl_3$. The $^{119}$Sn chemical shift of the compound with $\delta$ −670 compares well with that reported for $[HB(pz)_3]SnCl_3$ ($\delta$ −620), which also contains six-coordinate tin.[7d]

The reaction of $CH_3SnCl_3$ with 1 molar equiv of $K[B(pz)_4]$ gave the expected $[B(pz)_4]SnCl_2(CH_3)$, in consonance with recent work[7e] and also similar to the reported preparation of $[HB(pz)_3]SnCl_2(CH_3)$[7d] and $[H_2B(pz)_2]SnCl_2(CH_3)$,[7b] respectively. As expected, the $^{119}$Sn NMR signals of $[HB(pz)_3]SnCl_2(CH_3)$ ($\delta$ −478)[7d] and $[B(pz)_4]SnCl_2(CH_3)$ ($\delta$ −474) compare well, since the tin center should be in an octahedral environment in both cases (three N atoms of the pz groups, two Cl atoms, and the $CH_3$ group). As compared to that for $[B(pz)_4]SnCl_3$, the $^{119}$Sn chemical shift datum for $[B(pz)_4]SnCl_2(CH_3)$ reflects the decreased Lewis acidity of the organotin moiety.

The $^1$H NMR spectrum of $[B(pz)_4]SnCl_2(CH_3)$ is noteworthy. The room-temperature spectrum exhibited the expected two types of pz groups in a 1:3 ratio, which can still be observed at 80 °C. At −40 °C, however, the spectrum showed the presence of pz groups in three different environments in a 1:2:1 ratio. Analogous observations have been reported for both $[HB(pz)_3]SnCl_2(CH_3)$ and $[HB(pz)_3]SnCl(CH_3)_2$, clearly substantiating the octahedral environment about tin.[7d]

The reaction of $(CH_3)_2SnCl_2$ with $K[B(pz)_4]$ in a 1:1 molar ratio gave the expected $[B(pz)_4]SnCl(CH_3)_2$, as has been documented previously.[7e] The $^{119}$Sn NMR data for $[HB(pz)_3]SnCl(CH_3)_2$ ($\delta$ −334,[7b] −329[7d]) compare well with $\delta(^{119}Sn)$ −222 for $[B(pz)_4]SnCl(CH_3)_2$ ($\delta$ −323 is given in the literature[7e] and may be a printing error). Apparently, the monochlorotin compounds with presumed 6-fold coordination of tin have a wider $^{119}$Sn chemical shift range than the dichloro compounds, as is also substantiated by $\delta(^{119}Sn)$ −444 observed for $[B(pz)_4]SnCl(C_6H_5)_2$. On the other hand, the $\delta(^{119}Sn)$ values for $[H_2B(pz)_2]SnCl(CH_3)_2$ ($\delta$ −182[7b]) and $[(C_6H_5)_2B(pz)_2]SnCl(CH_3)_2$ ($\delta$ −177), both of which presumably contain five-coordinate tin, are in excellent agreement.

The $^{119}$Sn chemical shifts of some Sn(IV) poly(1-pyrazolyl)borates are compiled in Table II. Overall, the chemical shifts are roughly additive, as has been noted earlier.[7d,e] Of the listed compounds, only those containing Sn(IV) in a five-coordinate environment are true pyrazabole analogues.

**Crystal and Molecular Structures of $[(C_6H_5)_2B(pz)_2]SnCl(CH_3)_2$ and $[B(pz)_4]SnCl(CH_3)_2$.** Crystal data on $[(C_6H_5)_2B(pz)_2]SnCl(CH_3)_2$ were obtained for a crystal that precipitated on slow evaporation of a chloroform solution of the compound. Atomic coordinates and equivalent isotropic displacement factors for the non-hydrogen atoms are given in Table III.

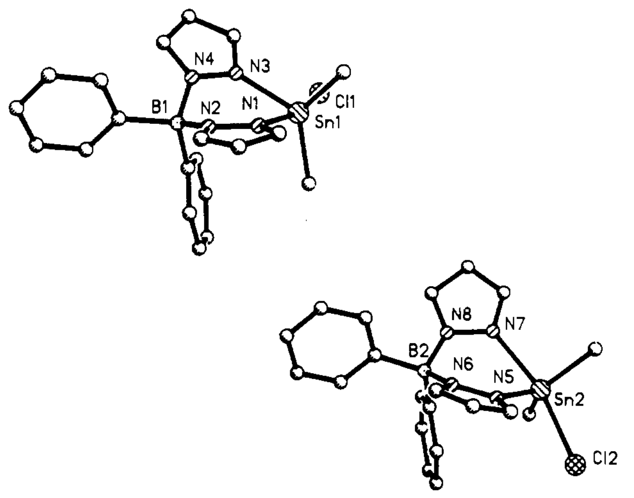

**Figure 1.** View along the B–Sn axis of the two geometrical isomers of $[(C_6H_5)_2B(pz)_2]SnCl(CH_3)_2$.

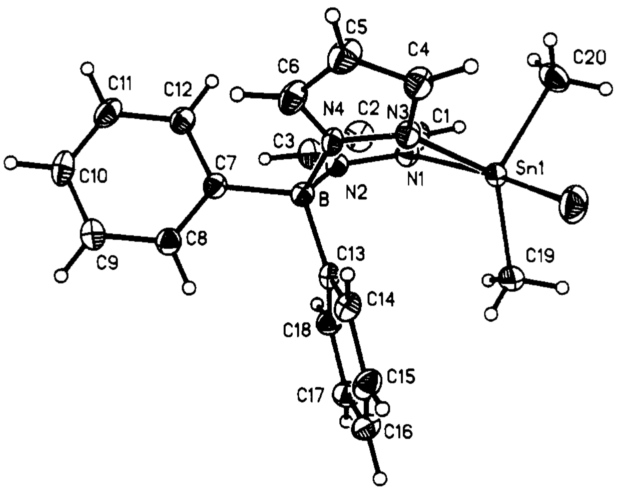

**Figure 2.** ORTEP plot and numbering scheme of isomer A of $[(C_6H_5)_2B(pz)_2]SnCl(CH_3)_2$.

The unit cell of $[(C_6H_5)_2B(pz)_2]SnCl(CH_3)_2$ contains two independent molecules in the asymmetric unit. The tin atoms are pentacoordinate with the Cl and one N atom located in axial positions and one N and two C atoms in the equatorial positions of a distorted trigonal-bipyramidal environment. The distortion is documented not only by Cl–Sn–N bond angles of 163.7 (1) and 165.0 (1)°, respectively, but also by two wide bond angles and one small bond angle within the trigonal plane. The molecules have no symmetry, and hence, the tin atom is a center of asymmetry. Therefore, one finds two enantiomers each in the unit cell, due to the fact that the $B(N_2)_2Sn$ six-membered ring adopts a boat conformation with different orientations of the phenyl rings in the two independent molecules. Figure 1 depicts a view of the two species along the Sn–B axis, illustrating that they are two geometrical isomers. The intraplanar angles of the two molecules are nevertheless quite similar for the $Sn(N_2)_2B$ ring (N(4)/N(2) = 27.0 and 24.9°, N(4)/N(2) = 44.7 and 46.2°, respectively) but differ significantly for the two pz rings (126.3 and 131.5°) and phenyl rings (88.7 and 100.5°). This readily explains that only one type of molecule is observed by NMR spectroscopy in solution, since inversion of the boat conformation is certain to require a minimal energy of activation.

The individual structures of the two conformations of $[(C_6H_5)_2B(pz)_2]SnCl(CH_3)_2$ are shown in Figures 2 and 3, selected bond distances are given in Table IV, and selected bond angles are given in Table V.

**Table III.** Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Coefficients (Å$^2$ × 10$^3$) for the Non-Hydrogen Atoms of $[(C_6H_5)_2B(pz)_2]SnCl(CH_3)_2$

| atom | *x* | *y* | *z* | *U*[a] |
|---|---|---|---|---|
| Sn(1) | 3263 (1) | 979 (1) | 6765 (1) | 40 (1) |
| Cl(1) | 5158 (2) | 1070 (2) | 7320 (1) | 70 (1) |
| N(1) | 1834 (6) | 1295 (5) | 6022 (3) | 44 (2) |
| N(2) | 1800 (6) | 2263 (5) | 5475 (2) | 39 (2) |
| N(3) | 4639 (5) | 1539 (5) | 5867 (2) | 43 (2) |
| N(4) | 4287 (6) | 2359 (5) | 5314 (2) | 40 (2) |
| B(1) | 2787 (8) | 3258 (8) | 5294 (3) | 37 (3) |
| C(1) | 817 (8) | 701 (8) | 6072 (3) | 55 (3) |
| C(2) | 118 (8) | 1230 (8) | 5577 (4) | 63 (4) |
| C(3) | 733 (7) | 2211 (8) | 5211 (4) | 53 (3) |
| C(4) | 5982 (7) | 967 (8) | 5727 (3) | 54 (3) |
| C(5) | 6508 (8) | 1409 (8) | 5078 (4) | 64 (4) |
| C(6) | 5428 (7) | 2300 (8) | 4842 (3) | 53 (3) |
| C(7) | 2771 (7) | 4053 (6) | 4551 (3) | 40 (3) |
| C(8) | 2694 (7) | 5397 (7) | 4405 (3) | 46 (3) |
| C(9) | 2798 (8) | 6092 (7) | 3771 (3) | 55 (3) |
| C(10) | 2992 (8) | 5430 (9) | 3252 (3) | 61 (4) |
| C(11) | 3063 (8) | 4111 (8) | 3374 (3) | 57 (3) |
| C(12) | 2949 (7) | 3415 (7) | 4012 (3) | 49 (3) |
| C(13) | 2413 (7) | 4202 (6) | 5840 (3) | 37 (2) |
| C(14) | 3421 (7) | 4562 (7) | 6068 (3) | 47 (3) |
| C(15) | 3079 (8) | 5450 (7) | 6505 (3) | 54 (3) |
| C(16) | 1711 (9) | 6013 (7) | 6716 (3) | 56 (3) |
| C(17) | 709 (8) | 5688 (7) | 6494 (3) | 54 (3) |
| C(18) | 1034 (7) | 4795 (7) | 6062 (3) | 45 (3) |
| C(19) | 1792 (8) | 2211 (7) | 7364 (3) | 55 (3) |
| C(20) | 3707 (8) | −1099 (6) | 6859 (4) | 61 (3) |
| Sn(2) | 7957 (1) | −835 (1) | 8390 (1) | 39 (1) |
| Cl(2) | 10406 (2) | −875 (2) | 7818 (1) | 76 (1) |
| N(5) | 6001 (6) | −1159 (5) | 9122 (2) | 39 (2) |
| N(6) | 5914 (5) | −2144 (5) | 9662 (2) | 36 (2) |
| N(7) | 8823 (6) | −1574 (5) | 9276 (2) | 40 (2) |
| N(8) | 8340 (5) | −2417 (5) | 9814 (2) | 37 (2) |
| B(2) | 7235 (8) | −3211 (7) | 9810 (3) | 34 (3) |
| C(31) | 4725 (7) | −491 (7) | 9094 (3) | 49 (3) |
| C(32) | 3803 (7) | −1009 (8) | 9594 (4) | 60 (3) |
| C(33) | 4571 (7) | −2056 (7) | 9936 (3) | 49 (3) |
| C(34) | 9872 (7) | −1175 (7) | 9409 (4) | 51 (3) |
| C(35) | 10073 (8) | −1761 (7) | 10033 (4) | 56 (3) |
| C(36) | 9095 (7) | −2520 (7) | 10267 (3) | 46 (3) |
| C(37) | 6892 (6) | −4077 (6) | 10539 (3) | 35 (2) |
| C(38) | 6360 (7) | −3470 (7) | 11099 (3) | 45 (3) |
| C(39) | 6131 (8) | −4211 (7) | 11724 (3) | 53 (3) |
| C(40) | 6400 (8) | −5554 (8) | 11809 (3) | 57 (3) |
| C(41) | 6929 (8) | −6181 (7) | 11265 (3) | 55 (3) |
| C(42) | 7154 (7) | −5441 (6) | 10645 (3) | 42 (3) |
| C(43) | 7797 (6) | −4086 (6) | 9228 (3) | 34 (2) |
| C(44) | 6880 (7) | −4600 (6) | 9005 (3) | 43 (3) |
| C(45) | 7330 (8) | −5371 (7) | 8518 (3) | 52 (3) |
| C(46) | 8699 (8) | −5643 (7) | 8231 (3) | 51 (3) |
| C(47) | 9630 (8) | −5156 (6) | 8436 (3) | 47 (3) |
| C(48) | 9178 (7) | −4388 (6) | 8933 (3) | 39 (3) |
| C(49) | 7453 (8) | 1222 (5) | 8350 (3) | 57 (3) |
| C(50) | 7645 (9) | −1935 (7) | 7738 (3) | 59 (3) |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

**Table IV.** Selected Bond Distances (Å) for $[(C_6H_5)_2B(pz)_2]SnCl(CH_3)_2$

| | | | |
|---|---|---|---|
| Cl(1)–Sn(1) | 2.511 (3) | Cl(2)–Sn(2) | 2.503 (2) |
| Sn(1)–C(19) | 2.104 (7) | Sn(2)–C(49) | 2.102 (6) |
| Sn(1)–C(20) | 2.112 (7) | Sn(2)–C(50) | 2.112 (9) |
| Sn(1)–N(1) | 2.300 (6) | Sn(2)–N(5) | 2.276 (5) |
| Sn(1)–N(3) | 2.153 (1) | Sn(2)–N(7) | 2.166 (5) |
| N(1)–N(2) | 1.374 (7) | N(5)–N(6) | 1.376 (6) |
| N(2)–B(1) | 1.564 (10) | N(6)–B(2) | 1.573 (8) |
| B(1)–N(4) | 1.591 (9) | B(2)–N(8) | 1.567 (11) |
| B(1)–C(7) | 1.620 (9) | B(2)–C(37) | 1.628 (8) |
| B(1)–C(13) | 1.610 (11) | B(2)–C(43) | 1.616 (10) |
| N(4)–N(3) | 1.363 (7) | N(7)–N(8) | 1.365 (7) |

It is not surprising to find two different Sn–N bond lengths for these species, with the axial one being longer by about 0.015 Å than the equatorial distance. The data also show the presence of two different B–N as well as B–C distances, the axial B–C bond being slightly longer than the equatorial one.

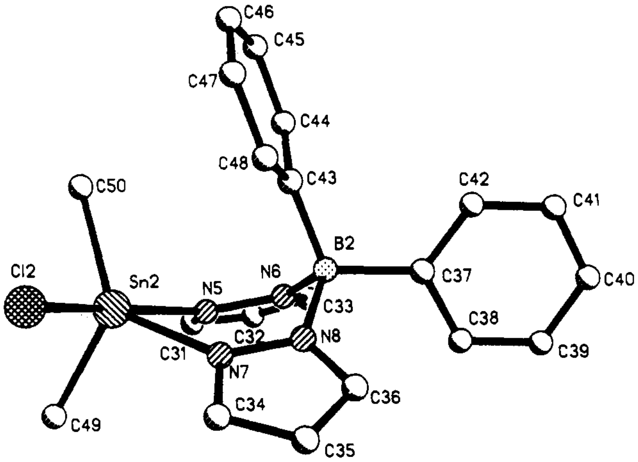

**Figure 3.** Structure and numbering scheme of isomer B of $[(C_6H_5)_2B(pz)_2]SnCl(CH_3)_2$ (hydrogen atoms omitted).

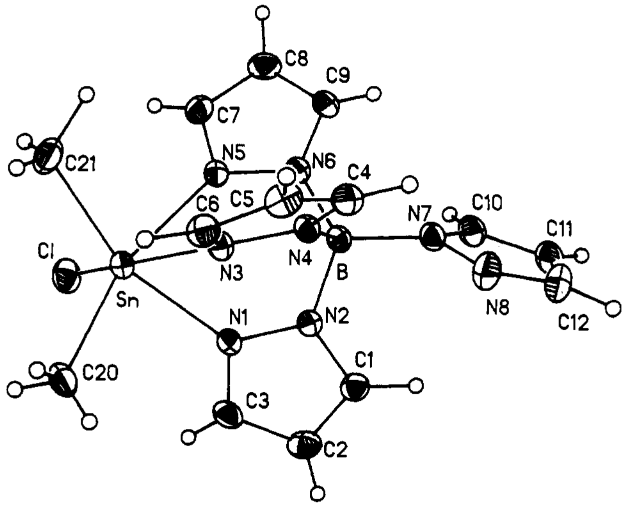

**Figure 4.** Structure and numbering scheme of $[B(pz)_4]SnCl(CH_3)_2$.

**Table V.** Selected Bond Angles (deg) for $[(C_6H_5)_2B(pz)_2]SnCl(CH_3)_2$

| | | | |
|---|---|---|---|
| Cl(1)–Sn(1)–C(19) | 91.8 (2) | Cl(2)–Sn(2)–C(50) | 91.9 (2) |
| Cl(1)–Sn(1)–C(20) | 95.4 (3) | Cl(2)–Sn(2)–C(49) | 94.2 (2) |
| Cl(1)–Sn(1)–N(1) | 163.7 (1) | Cl(2)–Sn(2)–N(5) | 165.0 (1) |
| Cl(1)–Sn(1)–N(3) | 84.8 (2) | Cl(2)–Sn(2)–N(7) | 84.9 (1) |
| C(20)–Sn(1)–C(19) | 129.4 (3) | C(49)–Sn(2)–C(50) | 128.3 (3) |
| C(20)–Sn(1)–N(1) | 94.1 (3) | C(49)–Sn(2)–N(5) | 93.7 (2) |
| C(20)–Sn(1)–N(3) | 102.2 (2) | C(49)–Sn(2)–N(7) | 103.9 (3) |
| C(19)–Sn(1)–N(1) | 92.5 (3) | C(50)–Sn(2)–N(5) | 93.2 (2) |
| C(19)–Sn(1)–N(3) | 128.3 (2) | C(50)–Sn(2)–N(7) | 127.8 (2) |
| N(1)–Sn(1)–N(3) | 80.2 (2) | N(5)–Sn(2)–N(7) | 80.8 (2) |
| Sn(1)–N(1)–N(2) | 125.0 (5) | Sn(2)–N(5)–N(6) | 126.1 (4) |
| Sn(1)–N(3)–N(4) | 127.0 (4) | Sn(2)–N(8)–N(7) | 126.8 (4) |
| N(1)–N(2)–B(1) | 121.6 (6) | N(5)–N(6)–B(2) | 120.5 (5) |
| N(2)–B(1)–N(4) | 104.9 (5) | N(6)–B(2)–N(8) | 105.7 (5) |
| C(7)–B(1)–C(13) | 113.7 (5) | C(43)–B(2)–C(37) | 113.8 (5) |
| N(2)–B(1)–C(7) | 110.6 (6) | N(8)–B(2)–C(43) | 109.8 (6) |
| N(2)–B(1)–C(13) | 110.1 (5) | N(8)–B(2)–C(37) | 108.4 (6) |
| N(4)–B(1)–C(7) | 107.9 (5) | N(6)–B(2)–C(43) | 109.8 (6) |
| N(4)–B(1)–C(13) | 109.3 (6) | N(6)–B(2)–C(37) | 109.6 (5) |
| B(1)–N(4)–N(3) | 122.9 (4) | B(2)–N(8)–N(7) | 122.5 (5) |

A crystal of $[B(pz)_4]SnCl(CH_3)_2$ was obtained from toluene solution. Atomic coordinates and equivalent isotropic displacement factors for the non-hydrogen atoms are listed in Table VI. The structure of the molecule is depicted in Figure 4. Selected bond distances and bond angles are given in Tables VII and VIII, respectively.

**Table VI.** Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for the Non-Hydrogen Atoms of $[B(pz)_4]SnCl(CH_3)_2$

| atom | *x* | *y* | *z* | $U^a$ |
|---|---|---|---|---|
| Sn | 28294 (2) | 20900 (2) | 34512 (1) | 38 (1) |
| Cl | 4838 (1) | 1286 (1) | 1897 (1) | 57 (1) |
| B | −0484 (4) | 4223 (3) | 2573 (2) | 35 (1) |
| N(1) | 2486 (3) | 4303 (2) | 2086 (2) | 39 (1) |
| N(2) | 1043 (3) | 5002 (2) | 1967 (2) | 37 (1) |
| N(3) | 0550 (3) | 3122 (2) | 4409 (2) | 38 (1) |
| N(4) | −0692 (3) | 3827 (2) | 3929 (2) | 34 (1) |
| N(5) | 1019 (3) | 1792 (2) | 2437 (2) | 39 (1) |
| N(6) | −0288 (3) | 2739 (2) | 2249 (2) | 39 (1) |
| N(7) | −1812 (3) | 5274 (2) | 2126 (2) | 38 (1) |
| N(8) | −2544 (4) | 6354 (3) | 2660 (3) | 56 (1) |
| C(1) | 1219 (4) | 6407 (3) | 1249 (2) | 44 (1) |
| C(2) | 2783 (4) | 6611 (4) | 0896 (3) | 52 (1) |
| C(3) | 3522 (4) | 5274 (4) | 1434 (3) | 48 (1) |
| C(4) | −1922 (4) | 3987 (3) | 4802 (2) | 42 (1) |
| C(5) | −1474 (4) | 3416 (3) | 5866 (2) | 46 (1) |
| C(6) | 0079 (4) | 2890 (3) | 5577 (2) | 44 (1) |
| C(7) | 0847 (4) | 0581 (3) | 2173 (3) | 48 (1) |
| C(8) | −0527 (4) | 0715 (4) | 1827 (3) | 54 (1) |
| C(9) | −1226 (4) | 2083 (4) | 1901 (3) | 43 (1) |
| C(10) | −2076 (4) | 5641 (4) | 1011 (3) | 49 (1) |
| C(11) | −3010 (4) | 6933 (4) | 0827 (3) | 59 (1) |
| C(12) | −3251 (5) | 7336 (4) | 1864 (4) | 64 (1) |
| C(20) | 4337 (5) | 3043 (5) | 4082 (4) | 57 (1) |
| C(21) | 2408 (5) | −0065 (4) | 4653 (4) | 60 (2) |

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

**Table VII.** Selected Bond Distances (Å) for $[B(pz)_4]SnCl(CH_3)_2$

| | | | |
|---|---|---|---|
| Sn–Cl | 2.463 (1) | Sn–N(1) | 2.266 (2) |
| Sn–N(3) | 2.294 (2) | Sn–N(5) | 2.366 (3) |
| Sn–C(20) | 2.140 (5) | Sn–C(21) | 2.135 (3) |
| B–N(2) | 1.562 (4) | B–N(4) | 1.544 (4) |
| B–N(6) | 1.552 (4) | B–N(7) | 1.512 (4) |
| N(1)–N(2) | 1.363 (3) | N(1)–C(3) | 1.331 (4) |
| N(2)–C(1) | 1.355 (3) | N(3)–N(4) | 1.360 (3) |
| N(3)–C(6) | 1.333 (4) | N(4)–C(4) | 1.340 (3) |
| N(5)–N(6) | 1.368 (3) | N(5)–C(7) | 1.329 (4) |
| N(6)–C(9) | 1.337 (5) | N(7)–N(8) | 1.372 (4) |
| N(7)–C(10) | 1.365 (4) | N(8)–C(12) | 1.326 (4) |
| C(1)–C(2) | 1.371 (5) | C(2)–C(3) | 1.377 (4) |
| C(4)–C(5) | 1.374 (4) | C(5)–C(6) | 1.381 (4) |
| C(7)–C(8) | 1.365 (6) | C(8)–C(9) | 1.364 (5) |
| C(10)–C(11) | 1.354 (5) | C(11)–C(12) | 1.389 (6) |

**Table VIII.** Selected Bond Angles (deg) for $[B(pz)_4]SnCl(CH_3)_2$

| | | | |
|---|---|---|---|
| Cl–Sn–N(1) | 88.0 (1) | Cl–Sn–N(3) | 161.6 (1) |
| N(1)–Sn–N(3) | 78.7 (1) | Cl–Sn–N(5) | 85.1 (1) |
| N(1)–Sn–N(5) | 73.4 (1) | N(3)–Sn–N(5) | 78.9 (1) |
| Cl–Sn–C(20) | 97.5 (1) | N(1)–Sn–C(20) | 89.6 (1) |
| N(3)–Sn–C(20) | 95.1 (1) | N(5)–Sn–C(20) | 162.8 (1) |
| Cl–Sn–C(21) | 97.8 (1) | N(1)–Sn–C(21) | 160.8 (2) |
| N(3)–Sn–(C21) | 107.6 (2) | N(5)–Sn–C(21) | 88.8 (2) |
| C(20)–Sn–C(21) | 107.6 (2) | N(2)–B–N(4) | 108.7 (3) |
| N(2)–B–N(6) | 108.1 (2) | N(4)–B–N(6) | 107.4 (2) |
| N(2)–B–N(7) | 107.5 (2) | N(4)–B–N(7) | 113.0 (2) |
| N(6)–B–N(7) | 112.0 (3) | Sn–N(1)–N(2) | 122.7 (1) |
| Sn–N(1)–C(3) | 129.4 (2) | N(2)–N(1)–C(3) | 106.8 (2) |
| B–N(2)–N(1) | 122.7 (2) | B–N(2)–C(1) | 128.7 (2) |
| N(1)–N(2)–C(1) | 108.6 (2) | Sn–N(3)–N(4) | 126.1 (2) |
| Sn–N(3)–C(6) | 125.7 (2) | N(4)–N(3)–C(6) | 107.0 (2) |
| B–N(4)–N(3) | 118.3 (2) | B–N(4)–C(4) | 132.7 (2) |
| N(3)–N(4)–C(4) | 109.0 (2) | Sn–N(5)–N(6) | 124.8 (2) |
| Sn–N(5)–C(7) | 128.2 (2) | N(6)–N(5)–C(7) | 105.6 (3) |
| B–N(6)–N(5) | 117.7 (2) | B–N(6)–C(9) | 132.9 (3) |
| N(5)–N(6)–C(9) | 109.2 (2) | B–N(7)–N(8) | 120.4 (3) |
| B–N(7)–C(10) | 126.3 (2) | N(8)–N(7)–C(10) | 109.7 (2) |
| N(7)–N(8)–C(12) | 104.6 (3) | N(2)–C(1)–C(2) | 108.8 (3) |
| C(1)–C(2)–C(3) | 104.9 (3) | N(1)–C(3)–C(2) | 110.9 (3) |
| N(4)–C(4)–C(5) | 108.9 (3) | C(4)–C(5)–C(6) | 104.9 (2) |
| N(3)–C(6)–C(5) | 110.2 (3) | N(5)–C(7)–C(8) | 111.5 (3) |
| C(7)–C(8)–C(9) | 104.9 (4) | N(6)–C(9)–C(8) | 108.8 (3) |
| N(7)–C(10)–C(11) | 108.6 (3) | C(10)–C(11)–C(12) | 104.4 (3) |
| N(8)–C(12)–C(11) | 112.6 (3) | | |

The crystal structure data clearly demonstrate the 6-fold coordination about the tin, which was assumed on the basis of the $^{119}Sn$ NMR data. There is no correlation between the Sn–N bond lengths in $(pz)B(\mu\text{-}pz)_3SnCl(CH_3)_2$ and the trans substituent. The longest and shortest Sn–N bonds are trans to a $CH_3$ group. While three of the four B–N bonds can be considered as equal in length, the B–N bond to the endocyclic pz group is significantly shorter (by 0.04 Å), indicating that the formal negative charge at the boron atom is not uniformly distributed over all four pz groups.

It is a well-known fact that the bond lengths increase as the coordination increases. Comparison of the structural parameters of the two species under consideration here is in accord with this general rule. The average Sn–N bond distance in $[B(pz)_4]SnCl(CH_3)_2$ = $(pz)B(\mu\text{-}pz)_3SnCl(CH_3)_2$ is 2.307 Å. This is slightly longer than the axial Sn–N bond length found for $(C_6H_5)_2B(\mu\text{-}pz)_2SnCl(CH_3)_2$ ($\Delta$ = 0.19 Å). However, the Sn–Cl bond in the hexacoordinated tin compound is shorter than the axial Sn–Cl bond in the pentacoordinated species. Indeed, the latter is almost as long as the axial Sn–Cl bond found in $[(CH_3)_2Cl\text{-}Sn\text{-}O\text{-}SnCl(CH_3)_2]_2$, which also features five-coordinate tin.[15]

**Concluding Remarks.** The poly(1-pyrazolyl)borates have generally been considered to be resistant to hydrolysis. However, recent studies[6b,7g] have shown that, at least in the presence of certain metal species, a hydrolytic B–N bond cleavage of these ligands can indeed occur, even under mild reaction conditions. A feature which emerged during the course of the present study is the transfer of a $pz^-$ ion from a poly(1-pyrazolyl)borate to another central atom, which proceeds by a B–N bond cleavage. This process occurred readily on reaction of organosilicon and organogermanium species with poly(1-pyrazolyl)borates and led to the formation of pyrazaboles as the sole boron-containing products. Also, the pyrazabole $(pz)_2B(\mu\text{-}pz)_2B(pz)_2$ was the only boron-containing product isolated from the reaction of $(C_6H_4\text{-}1,2\text{-}O_2)PCl$ with $K[B(pz)_4]$, and only $(C_2H_5)_2B(\mu\text{-}pz)_2B(C_2H_5)_2$ was obtained from the reaction of $K[(C_2H_5)_2B(pz)_2]$ with $(C_6H_4\text{-}1,2\text{-}O_2)PCl$, $CH_3OP(O)Cl_2$, $(CH_3)_2AsBr$, or $SO_2Cl_2$. On the other hand, the reaction of $(CH_3)_2AsBr$ with $K[B(pz)_4]$ proceeded with the formation of $[B(pz)_4]As(CH_3)_2$. The latter species is fluxional, as is indicated by the three broad $^1H$ NMR signals for the pz groups of the species. These signals begin to separate at −60 °C, and new signals appear at the low-field side of each signal. However, even at −90 °C the signals are not sharp and no valid conclusions about the ratio of the two different types of pz groups can be drawn. In any case, the observations suggest that the barriers are exceedingly low.

No general trends are yet clearly apparent, but the current results seem to suggest that the $pz^-$ ion transfer may be related to the electronegativity of the atom or group to which the $pz^-$ is being transferred. It is worth noting that B–N bond cleavage of a poly(1-pyrazolyl)borate moiety and $pz^-$ ion transfer have also been observed in reactions of such ligands with some transition-metal species, although, in these cases, the fate of the boron was not explored.[16] In addition, the current results suggest that the $B(pz)_4$ moiety may be more stable than those where less than four pz groups are bonded to the boron atom. This is also indicated by the decomposition of the gallapyrazabole $(pz)_2B(\mu\text{-}pz)_2Ga(C_2H_5)_2$ on reaction with transition-metal halides (as noted above), where the $B(pz)_4$ moiety remained intact and bonded as such to the transition metal, and by the formation of the species $[B(pz)_4]MCl_3$ (M = Si, Ge) as well as $[B(pz)_4]As(CH_3)_2$, whereas, as noted above, the reaction of $K[(C_2H_5)_2B(pz)_2]$ with $GeCl_4$ or

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$SiCl_4$ and other main-group-element halides proceeded with a breakdown of the $(C_2H_5)_2B(pz)_2$ moiety.

As shown in this study, although the poly(1-pyrazolyl)borate ligands have been known for a long time and have been used effectively in coordination chemistry, their chemical character is not yet fully understood. A noteworthy step to explore this situation is a recent X-ray crystal structure determination of $M[B(pz)_4]\cdot H_2O$ (M = Na, K) as well as detailed NMR studies on $[H_nB(pz)_{4-n}]^-$ ($n$ = 0–2) species. As a result, it has been stated that poly(1-pyrazolyl)borates constitute moderate electron-releasing substituents which are comparable to alkyl groups, but where the electron-releasing ability decreases with increasing number of pz groups bonded to the boron.[17]

**Acknowledgment.** This work was supported by the Office of Naval Research (K.N.) and Fonds der Chemischen Industrie (A.M.). Travel funds from the North Atlantic Treaty Organization (A.M. and K.N.) are also gratefully acknowledged.

**Supplementary Material Available:** Complete listings of bond distances and angles, H atom coordinates, and anisotropic thermal parameters for $[(C_6H_5)_2B(pz)_2]SnCl(CH_3)_2$ and $[B(pz)_4]SnCl(CH_3)_2$ (8 pages); structure factor tables for $[(C_6H_5)_2B(pz)_2]SnCl(CH_3)_2$ and $[B(pz)_4]SnCl(CH_3)_2$ (37 pages). Ordering information is given on any current masthead page.

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# Synthesis and Reactivity of the Pentaamminecobalt(III) Linkage Isomers of Succinimide

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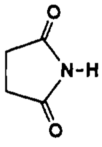
*Received April 11, 1991*

The linkage isomers of (succinimido)pentaamminecobalt(III) have been selectively synthesized and characterized by $^1H$ and $^{13}C$ NMR, IR, and UV–visible spectroscopies. The deprotonated imide ligand bonds to the metal through oxygen or nitrogen. The oxygen-bonded isomer is the less stable form. In water ($k^s_{ON} = 1.7 \times 10^{-4}$ s$^{-1}$, 25 °C) and $Me_2SO$ ($k^s_{ON} = 5.1 \times 10^{-5}$ s$^{-1}$) it spontaneously isomerizes to the nitrogen-bonded form; in aqueous acid ($pK_a = 2.7$, $I = 0.1$ M, $LiClO_4$) and acidified $Me_2SO$ it protonates and rapidly solvolyzes; the protonated species in water has reactivity comparable ($k_H = 2.3 \times 10^{-2}$ s$^{-1}$, $I = 0.1$ M, $LiClO_4$, 25 °C) to the most reactive isolable $[(NH_3)_5CoX]^{n+}$ species known. In aqueous base three competing reactions have been detected, namely solvolysis (40%, 25 °C), base-catalyzed O- to N-bonded linkage isomerization (30%), and nucleophilic attack on the coordinated carbonyl group by hydroxide ion leading to the formation of the carboxylate-bonded isomer of (succinamato)pentaamminecobalt(III) (30%) ($k_{OH}$(obsd) = $9.0 \times 10^{-2}$ M$^{-1}$ s$^{-1}$, $I = 0.1$ M, KF, 25 °C). The individual rates and rate laws for all these reactions have been determined. In acid and base the nitrogen-bonded imido complex is less reactive than the O-bonded form. It is base hydrolyzed relatively slowly, and a term second order with respect to hydroxide ion is dominant in the rate law ($k_N = 6.1 \times 10^{-3}$ M$^{-2}$ s$^{-1}$, $I = 1.0$ M, $NaClO_4$, 25 °C); $^{18}O$ studies establish the reversible addition of $OH^-$ in the first step. The product is the nitrogen-bonded succinamato complex, which has been characterized through crystallization in its basic and acidic forms ($pK_a$ = 1.8 (amide) and 3.55 (carboxylic acid), $I = 1.0$ M, NaCl, 25 °C). The succinimido-*N* complex is protonated in water and $Me_2SO$ only in very strong acid. The protonated species has been crystallized and characterized; it is a strong acid ($pK_a < 1$), and in acidic solution it solvolyzes very slowly ($t_{1/2}$ = days, 25 °C). A N- to O-bonded isomerization reaction has not been detected. The structure and reactivity of these imide complexes are compared with those of the related amide and urea complexes.

## Introduction

This paper describes the syntheses, solution structures, and reactions of oxygen- and nitrogen-bonded (succinimido)pentaamminecobalt(III).[1] There have been complexes of succinimide (**1**) reported since the time of Werner; the ligand has been coordinated to a range of metal ions mostly via nitrogen[2,3] but also via oxygen.[4,5] However, the pentaammine complexes described here are the first examples of an imide bonded to Co(III) and the first pair of imide linkage isomers to be reported. Succinimide forms a planar ring.[6] The imide proton is acidic ($pK_a$ 9.5 in aqueous solution[7]), and the resulting anion **2** has a highly delocalized electronic structure with the potential to coordinate to a metal ion via the endocyclic nitrogen or either of the equivalent exocyclic oxygens. A similar ligand is 1-oxo-3-iminoisoindoline (**3**), whose complexes with cobalt(III) via the exocyclic (**4**) and endocyclic (**5**) nitrogens have been synthesized,[8] but no isomerization or ligand hydrolysis reactions were reported.



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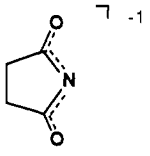

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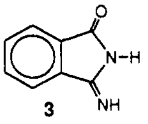

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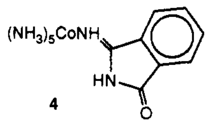

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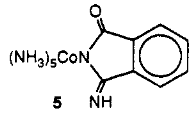

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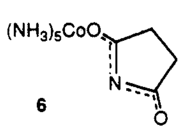
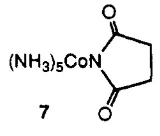
Our studies of the reactions of amide-containing ligands bonded to cobalt(III) have produced, inter alia, the following linkage isomers:



**6**



**7**

The reactions of these complexes have been studied in detail for several reasons. First, the oxygen-bonded isomer **6** is novel in that the ligand is coordinated solely via the amide oxygen while the

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