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Articles

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Diorganyltin(IV) Bis[poly(1-pyrazolyl)borates] and Related Species

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Compounds of the type L_2SnR_2 (L = poly(1-pyrazolyl)borate, R = hydrocarbon substituent) have been obtained from the reaction of R_2SnCl_2 with ML (M = Na, K). Complexes with L = $[B(pz)_4]^-$ (Hpz = pyrazole; R = CH_3, C_2H_5, n-C_4H_9) do not hydrolyze readily but are of relatively low thermal stability; complexes with L = $[R_2B(pz)_2]^-$ (R = H, C_2H_5, C_6H_5) are, in general, not only thermally unstable but also extremely sensitive to moisture. Hydrolysis of the latter species leads to dimeric (boryloxy)diorganyltin(IV) pyrazolides, $[R_2B(\mu\text{-}O)(\mu\text{-}pz)SnR'_2]_2$ (**1**), in addition to, ultimately, pyrazaboles, $R_2B(\mu\text{-}pz)_2BR_2$. The same compounds containing the $B(\mu\text{-}O)(\mu\text{-}pz)Sn$ ring system can also be obtained by the reaction of R_2BOH with $R'_2Sn(pz)_2$, and the complexes with R = C_2H_5 and R' = CH_3, R = R' = C_2H_5, R = C_2H_5 and R' = n-C_4H_9, R = C_2H_5 and R' = C_6H_5, and R = C_6H_5 and R' = CH_3 have been prepared. The compound $[(C_2H_5)_2B(\mu\text{-}O)(\mu\text{-}pz)Sn(CH_3)_2]_2$ crystallizes in the triclinic system in space group $P\bar{1}$ (No. 2) with a = 7.764 (1) Å, b = 8.317 (1) Å, c = 10.578 (3) Å, α = 107.12 (2)°, β = 97.04 (2)°, γ = 101.23 (1)°, and Z = 2. The anhydrous acid $HB(pz)_4$ has been characterized by NMR data.

Introduction

Current studies on the interaction of main-group-element halides with alkali-metal poly(1-pyrazolyl)borates, $M[R_nB(pz)_{4-n}]$ (Hpz = pyrazole; R = H or hydrocarbon substituent; n = 0, 1, 2), include relevant reactions of diorganyltin(IV) halides. It has previously been reported that the organyltin halides $RSnX_3$ and R_2SnX_2 interact with even an excess of $K[HB(pz)_3]$ by displacement of only one halogen by the poly(1-pyrazolyl)borate ligand.[1] Likewise, other reports on tin(IV) complexes with various poly(1-pyrazolyl)borate ligands also describe only 1:1 reaction products.[2] On the other hand, the two complexes $[HB(pz)_3]_2SnR_2$ (R = CH_3, n-C_4H_9) have been mentioned elsewhere.[3] Although the two latter species were not characterized in detail, they reportedly were prepared by essentially the same procedure that was used in the other work. The present studies were specifically directed to an investigation of complexes of the type L_2SnR_2 (L = poly(1-pyrazolyl)borate).

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 (^{11}B, ^{119}Sn, variable temperature) or GEMINI-200 (^{1}H, ^{13}C) instrument. Chemical shift data are given in ppm with positive values indicating a downfield shift from the reference (internal $(CH_3)_4Si$ for ^{1}H and ^{13}C NMR, external $(C_2H_5)_2O\cdot BF_3$ for ^{11}B NMR, and external $(CH_3)_4Sn$ for ^{119}Sn NMR); s = singlet, d = doublet, t = triplet, q = quartet, 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 at the University of Kentucky Mass Spectrometry Center, and field desorption (FD) spectra on a Finnigan MAT 250 instrument, courtesy of Professor A. Meller, University of Göttingen, Göttingen, Germany.

All nonreferenced reagents were obtained from Aldrich Chemical Co., Milwaukee, WI, and used as received. Preparation and handling of materials were generally done in anhydrous atmosphere under argon cover.

Caution! All poly(1-pyrazolyl)borates used in the present work are hygroscopic. Formation of pyrazole in any of the reactions indicates the use of insufficiently dried reagents!

$HB(pz)_4$ (Hpz = pyrazole) was prepared by acidification of a clear aqueous solution of $K[B(pz)_4]$ (ca. 1 g/100 mL of water) with glacial acetic acid.[4] The colorless precipitate was collected, washed extensively with water, and air-dried to give 1.2 g of colorless solid, mp 90–92 °C. The ^{1}H NMR spectrum of this material exhibited a signal for (N)H at δ 6.4* (the exact position of this signal depends on the concentration) and a small water signal near 2 ppm. After being heated under vacuum to 50 °C for 2 h, the product had a melting point of 116–120 °C, and the (N)H signal had shifted to about 14 ppm. Finally, the product was heated for 3 h to 70 °C under vacuum to give the anhydrous material, mp 128–134 °C dec (lit.:[4] mp 70–71 °C). Anal. Calcd for $C_{12}H_{13}N_8B$ (M_r = 279.90): C, 51.45; H, 4.68; B, 3.86; N, 40.01. Found: C, 51.74; H, 4.67; B, 4.06; N, 39.84.

NMR data: δ(^{1}H) 15.3 (1 H, s), 7.72 (4 H, d, J = 1.9), 7.15 (4 H, d, J = 2.2), 6.32 (4 H, unsym t = two overlapping d, J = 2.0); δ(^{11}B) 0.2 (s, $h_{1/2}$ = 30 Hz); δ(^{13}C) 139.8, 135.6, 106.0.

The material readily absorbs water on exposure to the atmosphere. This is evidenced by a decrease in the melting point and a shift of the (N)H NMR signal to higher field, which is accompanied by an increase in signal intensity.

$[B(pz)_4]_2Sn(CH_3)_2$. A mixture of 0.50 g (2.3 mmol) of $(CH_3)_2SnCl_2$, 1.45 g (4.6 mmol) of $K[B(pz)_4]$, and 50 mL of dichloromethane was stirred at room temperature for 1 h. The mixture was filtered, and solvent was evaporated from the clear filtrate to leave 1.58 g (98%) of crude product. It was washed with hot toluene (to remove traces of the byproduct $[B(pz)_4]SnCl(CH_3)_2$) and dried under vacuum at <100 °C to give a solid, mp 278–280 °C dec. The compound could not be further purified by recrystallization, due to its decomposition in suitable hot solvents. Anal. Calcd for $C_{26}H_{30}B_2N_{16}Sn$ (M_r = 706.54): C, 44.16; H, 4.28; B, 3.06; N, 31.70; Sn, 16.80. Found: C, 44.32; H, 4.30; B, 3.29; N, 31.36; Sn, 16.96.

NMR data: δ(^{1}H) 7.77 (4 H, d, J = 1.6), 7.06* (4 H, s), 6.33 (4 H, unsym t = two overlapping d, J = ca. 2.0), 0.15* (3 H, s, ^2J(Sn–H) = 88); δ(^{11}B) 0.5 (s, $h_{1/2}$ = 25 Hz); δ(^{13}C) 142.6, 136.7, 107.0, 12.7; δ(^{119}Sn) −343 (s, $h_{1/2}$ = 95 Hz). The EI mass spectrum exhibited a very weak parent ion cluster at m/z 706 in the correct calculated isotopic distribution. Major additional peak groups were observed at m/z 481, 451, 397, 217, and 187.

The same material was obtained (as the only identified product containing both boron and tin) from the reaction of equimolar amounts of $(CH_3)_3SnCl$ and $K[B(pz)_4]$ in dichloromethane (2 h of stirring at room temperature).

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$[B(pz)_4]_2Sn(C_2H_5)_2$ was obtained in a fashion analogous to that for the preceding compound by the reaction of 0.60 g (2.4 mmol) of $(C_2H_5)_2SnCl_2$ with 1.90 g (5.97 mmol) of $K[B(pz)_4]$ (60 mL of dichloromethane; 2 h of stirring at room temperature). After filtration and solvent evaporation, 1.80 g (100%) of crude material was obtained, which was recrystallized from benzene to give a product, mp 235–237 °C dec. Anal. Calcd for $C_{28}H_{34}B_2N_{16}Sn$ (M_r = 734.56): C, 45.74; H, 4.67; B, 2.94; N, 30.49; Sn, 16.16. Found: C, 45.56; H, 4.65; B, 2.65; N, 29.96; Sn, 16.07.

NMR data: $\delta(^{1}H)$ 7.84 (4 H, d, J = 1.6), 7.10* (4 H, s), 6.34 (4 H, unsym t = two overlapping d, J = 2.1), 0.66 (2 H, q, J = 7.6), 0.24 (3 H, t, J = 7.5); $\delta(^{11}B)$ 0.5 (s, $h_{1/2}$ = 25 Hz); $\delta(^{13}C)$ 142.4, 136.0*, 106.1, 25.4, 9.4; $\delta(^{119}Sn)$ −335 (s, $h_{1/2}$ = 65 Hz). The FD mass spectrum exhibited a peak group at m/z 707 in the correct isotopic pattern calculated for $[M - 29]^+$.

$[B(pz)_4]_2Sn(n\text{-}C_4H_9)_2$ was prepared in a fashion analogous to that for the preceding compounds from 1.01 g (3.29 mmol) of $(n\text{-}C_4H_9)_2SnCl_2$ and 2.34 g (7.35 mmol) of $K[B(pz)_4]$ (60 mL of dichloromethane; 90 min of stirring at room temperature) to give 2.30 g (89%) of crude material. It was recrystallized from benzene to give a colorless solid product, sintering near 160 °C and melting at 182–186 °C dec. Anal. Calcd for $C_{32}H_{42}B_2N_{16}Sn$ (M_r = 790.63): C, 48.57; H, 5.35; B, 2.73; N, 28.33; Sn, 15.02. Found: C, 48.33; H, 5.32; B, 2.57; N, 27.81; Sn, 15.14.

NMR data: $\delta(^{1}H)$ 7.84 (4 H, d, J = 1.5), 7.1* (4 H, s), 6.34 (4 H, unsym t = two overlapping d, J = ca. 2.1), 0.85–0.35 (9 H, unresolved m); $\delta(^{11}B)$ 0.5 (s, $h_{1/2}$ = 30 Hz); $\delta(^{13}C)$ 142.4, 135.9*, 106.2, 32.0, 26.8, 24.9, 13.0; $\delta(^{119}Sn)$ −345 (s, $h_{1/2}$ = 70 Hz). The FD mass spectrum exhibited a peak group at m/z 733 in the correct isotopic pattern calculated for $[M - C_4H_9]^+$.

$[H_2B(pz)_2]_2Sn(CH_3)_2$ was prepared from 0.63 g (2.9 mmol) of $(CH_3)_2SnCl_2$ and 1.07 g (5.73 mmol) of $K[H_2B(pz)_2]^4$ (20 mL of dichloromethane; 5 h of stirring at room temperature) as a crude solid product, mp 98–100 °C dec, in 79% yield.

NMR data: $\delta(^{1}H)$ 7.66 (2 H, d, J = 2.1), 7.56* (2 H, s), 6.26 (2 H, unsym t, J = 2.2), ca. 3.5* (1 H), 1.15 (3 H, s, ^2J(Sn–H) = 88); $\delta(^{11}B)$ −8.3 (s, $h_{1/2}$ = 325 Hz); $\delta(^{13}C)$ 138.9, 137.2, 105.1; $\delta(^{119}Sn)$ −157 (s, $h_{1/2}$ = 30 Hz).

$[H_2B(pz)_2]_2Sn(C_2H_5)_2$ was prepared as outlined above from 0.63 g (2.54 mmol) of $(C_2H_5)_2SnCl_2$ and 0.95 g (5.09 mmol) of $K[H_2B(pz)_2]$ (30 mL of dichloromethane; 5 h of stirring at room temperature). After filtration and solvent evaporation, the crude product (0.95 g, 70%) was redissolved in a minimal amount of dichloromethane and the clear solution was cooled to −78 °C. The resultant precipitate was collected and dried; mp 90–92 °C.

NMR data: $\delta(^{1}H)$ 7.70 (2 H, d, J = 2.1), 7.68 (2 H, d, J = 2.1), 6.30 (2 H, unsym t, J = 2.1), ca. 3.7* (1 H, very broad), 1.74 (2 H, q, J = 7.9, ^2J(Sn–H) = 108), 0.32 (3 H, t, J = 7.8, ^2J(Sn–H) = 180); $\delta(^{11}B)$ −7.9 (s, $h_{1/2}$ = 340 Hz; the signal narrows on proton decoupling); $\delta(^{13}C)$ 139.1, 137.1, 104.9, 30.9, 8.2; $\delta(^{119}Sn)$ −331 (s, $h_{1/2}$ = 55 Hz).

$[(C_2H_5)_2B(pz)_2]_2Sn(CH_3)_2$ was prepared in a manner analogous to that for the preceding compounds by employing 0.32 g (1.45 mmol) of $(CH_3)_2SnCl_2$ with 0.70 g (2.9 mmol) of $K[(C_2H_5)_2B(pz)_2]^5$ (10 mL of dichloromethane, 15 min stirring at room temperature); 0.6 g (75%) of crude solid product were obtained, which could not be purified. The material sintered at 78–80 °C and melted at 130–134 °C dec. (*Caution*! The compound is extremely sensitive to hydrolysis!) Anal. Calcd for $C_{22}H_{38}B_2N_8Sn$ (M_r = 554.59): C, 47.60; H, 6.91; B, 3.90; N, 20.20; Sn, 21.39. Found: C, 44.28; H, 5.92; B, 4.56; N, 22.73; Sn, 21.65.

NMR data: $\delta(^{1}H)$ 7.71 (2 H, d, J = 2.1), 7.39* (2 H, s), 6.27 (s H, ill-resolved t), 0.95 (s) + 0.9–0.4 (m) (13 H); $\delta(^{11}B)$ 2.2 (s, $h_{1/2}$ = 270 Hz); $\delta(^{13}C)$ 138.0*, 135.5*, 104.7, 15.3*, 8.8 (see text); $\delta(^{119}Sn)$ −367 (s, $h_{1/2}$ = 360 Hz).

$[(C_2H_5)_2B(pz)_2]_2Sn(C_2H_5)_2$ was prepared as outlined above from 0.64 g (2.58 mmol) of $(C_2H_5)_2SnCl_2$ and 1.25 g (5.16 mmol) of $K[(C_2H_5)_2B(pz)_2]$ (40 mL of dichloromethane; 30 min of stirring at room temperature). The oily product was obtained in essentially quantitative yield; it could not be purified.

NMR data: $\delta(^{1}H)$ 7.74 (2 H, d, J = 2.0), 7.61* (2 H, s), 6.30 (s H, two overlapping d, J = 2.1), 1.65* (2 H, s), 0.86 (4 H, q, J = 7.7), 0.70 (6 H, t, J = ca. 6.5), 0.50* (3 H, m); $\delta(^{11}B)$ 1.9 (s, $h_{1/2}$ = 330 Hz), $\delta(^{13}C)$ 139.5*, 135.3*, 104.5, 14.9*, 8.8 (see text); $\delta(^{119}Sn)$ −354 (s, $h_{1/2}$ = 200 Hz). At −75 °C (in CD_2Cl_2), two additional signals, δ 27.0 and 8.3, were observed in the ^{13}C NMR spectrum.

$[(C_2H_5)_2B(pz)_2]_2Sn(n\text{-}C_4H_9)_2$ was obtained in 86% yield as an impure oily material from 0.88 g (2.9 mmol) of $(n\text{-}C_4H_9)_2SnCl_2$ and 1.41 g (5.82 mmol) of $K[(C_2H_5)_2B(pz)_2]$ (20 mL of dichloromethane; 2 h of stirring at room temperature).

NMR data: $\delta(^{1}H)$ 7.76* (2 H, s), 7.57* (2 H, s), 6.32* (2 H, t, J = 2), 1.8–0.4 (19 H, m); $\delta(^{11}B)$ 2.2 (s, $h_{1/2}$ = 220 Hz).

$[(C_6H_5)_2B(pz)_2]_2Sn(CH_3)_2$ was prepared in analogous manner as outlined above by the reaction of 1.70 g (7.74 mmol) of $(CH_3)_2SnCl_2$ with 4.98 g (15.5 mmol) of $Na[(C_6H_5)_2B(pz)_2]^6$ in 20 mL of dichloromethane (2 h of stirring at room temperature), to give an essentially quantitative yield of pasty material, which could not be purified.

NMR data: $\delta(^{1}H)$ 7.40* (2 H, s), 7.25* (s) + 7.15* (s) + 6.8* (s) (12 H total), 6.20 (2 H, ill-resolved t), −0.15 (3 H, s); $\delta(^{11}B)$ 1.8 (s, $h_{1/2}$ = 380 Hz); $\delta(^{119}Sn)$ −351 (s, $h_{1/2}$ = 70 Hz).

$[(C_2H_5)_2B(\mu\text{-}O)(\mu\text{-}pz)Sn(CH_3)_2]_2$. A few drops of water (at least 0.06 g (3.3 mmol)) were added to a solution of 1.84 g (3.3 mmol) of $[(C_2H_5)_2B(pz)_2]_2Sn(CH_3)_2$ in 10 mL of cyclohexane. The mixture was stirred for 10 min at room temperature and a crystalline precipitate formed, which dissolved on heating of the mixture to 60 °C. After the mixture was cooled to room temperature, 0.82 g (82%) of precipitate was collected and dried under vacuum; mp 176–178 °C dec. (Note: The pyrazabole $(C_2H_5)_2B(\mu\text{-}pz)_2B(C_2H_5)_2$ can be recovered from the cyclohexane solution.) Anal. Calcd for $C_{18}H_{38}B_2N_4O_2Sn_2$ (M_r = 601.28): C, 35.92; H, 6.37; B, 3.59; N, 9.31; O, 5.32; Sn, 39.48. Found: C, 35.78; H, 6.07; B, 3.67; N, 9.41; Sn, 39.44.

NMR data: $\delta(^{1}H)$ 7.38 (1 H, d, J = 2.0), 7.34 (1, H, d, J = 2.0), 6.37 (1 H, unsym t, J = 2.0), 0.79 (6 H, s, ^2J(Sn–H) = 74), 0.6–0.3 (10 H, m); $\delta(^{11}B)$ 5.2 (s, $h_{1/2}$ = 220 Hz); $\delta(^{13}C)$ 132.2, 131.1, 107.1, 19.0*, 8.8, 4.0; $\delta(^{119}Sn)$ −148 (s, $h_{1/2}$ = 60 Hz). The EI mass spectrum exhibited major peak groups at m/z 572, 437, 381, 273, 217, and 185. The FD mass spectrum showed only one peak group at m/z 572, for which the calculated and observed isotopic abundances substantiate the ion $[M - 29]^+$.

Alternate Procedure. To a solution of 0.70 g (3.2 mmol) of $(CH_3)_2SnCl_2$ in 20 mL of dichloromethane was added 0.68 g (6.4 mmol) if K(pz). The mixture was stirred for 2 h and filtered, and 0.27 g (3.2 mmol) of $(C_2H_5)_2BOH^7$ was added to the clear filtrate. The mixture was stirred for 90 min at room temperature, and solvent was evaporated. The remaining crude solid was recrystallized from cyclohexane to give 0.6 g (62%) of $[(C_2H_5)_2B(\mu\text{-}O)(\mu\text{-}pz)Sn(CH_3)_2]_2$, identical (NMR spectra) with the preceding material. Additional but impure product can be obtained by concentration of the mother liquor.

Crystal data on $[(C_2H_5)_2B(\mu\text{-}O)(\mu\text{-}pz)Sn(CH_3)_2]_2$, empirical formula $C_9H_{19}BN_2OSn$ with a formula weight of 300.8, were obtained on a Siemens R3m/V automated diffractometer by using graphite-monochromated Mo Kα radiation, λ = 0.710 69 Å, and standard operating techniques. Unit cell parameters were obtained from the least-squares refinement of the diffracting positions of 25 reflections ($20° < 2\theta < 27°$). The colorless compound crystallizes in the triclinic system in space group $P\bar{1}$ (No. 2) with a = 7.764 (1) Å, b = 8.317 (1) Å, c = 10.578 (3) Å, α = 107.12 (2)°, β = 97.04 (2)°, γ = 101.23 (1)°, V = 628.4 (2) Å^3, Z = 2, and d_{calcd} = 1.590 Mg/m^3; μ = 2.013 mm^{-1}, U = 0.066, and $F(000)$ = 300. Intensity data (crystal size 0.31 × 0.22 × 0.40 mm) were collected at 293 K by using ω scans and a scan width of 1.10°. After intensity correction (two control measurements after every 48 measurements; variation <±2%) and adjustment of symmetry-equivalent reflections (R_{merge} = 0.0093), there were a total of 2217 independent reflections, 1639 of which had $I > 3\sigma(I)$, which were converted to structure factors after applying Lp and an empirical absorption correction were applied (maximum and minimum transmission 0.6432 and 0.5782). The structure was solved (SHELXTL PLUS Micro VAX II solution package) by direct methods, and the best E map revealed the positions of all nonhydrogen atoms. After convergence was achieved in further refinement with anisotropic temperature factors, all hydrogen positions were revealed from a difference Fourier map. Refinement of their positions was included with use of fixed isotropic temperature factors (U = 0.05 Å^2) in the final refinement (full-matrix least-squares method). The final refinement converged at R = 0.019, R_w = 0.025 for 184 refined parameters (largest Δ/σ = 0.0201; highest residual electron density = 0.43 and 0.42 e/Å^3 close to Sn, all others less than 0.3 e/Å^3). 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 $w^{-1} = \sigma^2(F_o) - g(F_o)^2$. Atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms are listed in Table I.

$[(C_2H_5)_2B(\mu\text{-}O)(\mu\text{-}pz)Sn(C_2H_5)_2]_2$. To a solution of 1.50 g (2.58 mmol) of freshly prepared $[(C_2H_5)_2B(pz)_2]_2Sn(C_2H_5)_2$ in 20 mL of cyclohexane was added ca. 0.09 g (5 mmol) of water and the mixture was stirred overnight. The clear solution was separated from traces of unreacted water, and solvent was evaporated to leave a gummy material. It was heated in a sublimator for 5 h (70 °C bath temperature, 2 Torr) and the residue was dissolved in a minimum amount of hexane. The solution was cooled to −70 °C, and 0.5 g (60%) of crystalline material,

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Table I. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$) for Non-Hydrogen Atoms for $[(C_2H_5)_2B(\mu\text{-}O)(\mu\text{-}pz)Sn(CH_3)_2]_2$[a]

atom	*x*	*y*	*z*	U^b
Sn	4321 (1)	1064 (1)	9041 (1)	33 (1)
O	4553 (3)	−1329 (3)	8952 (2)	37 (1)
B	4058 (6)	−2911 (5)	7677 (4)	40 (1)
N(1)	3019 (5)	−549 (4)	6898 (3)	46 (1)
N(2)	3038 (4)	−2237 (4)	6596 (3)	43 (1)
C(3)	2222 (6)	−3047 (6)	5308 (4)	58 (2)
C(4)	1654 (6)	−1884 (7)	4776 (4)	63 (2)
C(5)	2163 (7)	−346 (7)	5800 (4)	59 (2)
C(6)	1770 (6)	1624 (7)	9415 (5)	54 (2)
C(7)	6264 (7)	2649 (6)	8487 (5)	57 (2)
C(8)	5794 (5)	−3417 (5)	7116 (4)	47 (1)
C(9)	7077 (7)	−2012 (8)	6811 (6)	69 (2)
C(10)	2692 (6)	−4498 (5)	7859 (5)	49 (1)
C(11)	925 (6)	−4176 (7)	8200 (6)	64 (2)

[a] In this and all subsequent tables, esd's are given in parentheses. [b] Equivalent isotropic *U* for non-hydrogen atoms defined as one-third of the trace of the orthogonalized U_{ij} tensor.

mp 84–86 °C dec, was obtained. Anal. Calcd for $C_{22}H_{46}B_2N_4O_2Sn_2$ (M_r = 657.34): C, 40.16; H, 7.05; B, 3.29; N, 8.52; O, 4.87; Sn, 36.11. Found: C, 40.37; H, 6.86; B, 3.26; N, 8.28; Sn, 35.76.

NMR data: $\delta(^1H)$ 7.44 (1 H, d, J = 2.0), 7.40 (1 H, d, J = 2.0), 6.36 (1 H, t, J = 2.0), 1.47 (4 H, q, J = 7, $^2J(Sn\text{–}H)$ = 60), 1.19 (6 H, t, J = 8, $^2J(Sn\text{–}H)$ = 128), 0.66–0.52 (6 H, m), 0.50–0.28 (4 H, m); $\delta(^{11}B)$ 5.2 (s, $h_{1/2}$ = 290 Hz); $\delta(^{13}C)$ 134.3, 131.4, 106.5, 18.1*, 15.7, 9.6, 9.2; $\delta(^{119}Sn)$ −173 (s, $h_{1/2}$ = 40 Hz). The EI mass spectrum exhibited the highest (but weak) peak group at *m/z* 299. The FD mass spectrum exhibited only one peak group at *m/z* 629 in the correct isotopic ratio calculated for $[M - C_2H_5]^+$.

$[(C_2H_5)_2B(\mu\text{-}O)(\mu\text{-}pz)Sn(n\text{-}C_4H_9)_2]_2$ was prepared in an analogous manner to the preceding compound by addition of (at least) 0.06 g (3.3 mmol) of water to a solution of 2.10 g (3.3 mmol) of freshly prepared $[(C_2H_5)_2B(pz)_2]_2Sn(n\text{-}C_4H_9)_2$ in 30 mL of cyclohexane and stirring the mixture overnight. After treatment in a sublimator (100 °C bath temperature at 2 Torr for 5 h), an oily product remained (which still contained traces of Hpz and $(C_2H_5)_2B(\mu\text{-}pz)_2B(C_2H_5)_2$). The material could not be purified by distillation without decomposition, which yielded additional $(C_2H_5)_2B(\mu\text{-}pz)_2B(C_2H_5)_2$ and $[(n\text{-}C_4H_9)_2BO]_n$.

NMR data: $\delta(^1H)$ 7.43* (1 H, ill-resolved d), 7.36* (1 H, ill-resolved d), 6.35* (1 H, ill-resolved t), 1.6–1.0 (12 H, m), 0.87 (6 H, t, J = 7.0), 0.6–0.2 (10 H, m); $\delta(^{11}B)$ 5.1 (s, $h_{1/2}$ = 530 Hz); $\delta(^{13}C)$ 134.0, 131.4, 106.5, 27.3, 26.7, 23.8, 18.0*, 13.2, 9.2; $\delta(^{119}Sn)$ −175 (s, $h_{1/2}$ = 25 Hz). The EI mass spectrum showed a strong peak group at *m/z* 243, which corresponds to the molecular ion of $(C_2H_5)_2B(\mu\text{-}pz)_2B(C_2H_5)_2 - 29$, indicating the thermal decomposition of the original compound under the operating conditions of the mass spectrometer (150 °C inlet temperature).

Alternate Procedure. A mixture of 2.12 g (20 mmol) of K(pz), 3.05 g (10 mmol) of $(n\text{-}C_4H_9)_2SnCl_2$, and 35 mL of dichloromethane was stirred for 2 h at room temperature. The mixture was filtered, and 1 mL (ca. 10 mmol) of $(C_2H_5)_2BOH$ was added with stirring to the clear filtrate. The mixture was stirred at ambient temperature for 2 h, and solvent was evaporated. Some impurities were sublimed off the remaining crude product (100 °C bath temperature, 2 Torr) to leave 3.15 g (82%) of oily residue, identical (^1H NMR data) with the material described above.

$[(C_2H_5)_2B(\mu\text{-}O)(\mu\text{-}pz)Sn(C_6H_5)_2]_2$ was obtained from a mixture of 2.01 g (2.96 mmol) of freshly prepared (from 0.83 g (2.42 mmol) of $(C_6H_5)_2SnCl_2$ and 1.17 g (4.83 mmol) of $K[(C_2H_5)_2B(pz)_2]$ in 20 mL of dichloromethane; 1 h of stirring) crude $[(C_2H_5)_2B(pz)_2]_2Sn(C_6H_5)_2$ ($\delta(^{11}B)$ 2.6 (s, $h_{1/2}$ = 510 Hz); $\delta(^{119}Sn)$ −488 (s, $h_{1/2}$ = 15 Hz)) and 20 mL of cyclohexane by addition of ca. 0.10 g (5.55 mmol) of water. The mixture was stirred overnight; the precipitate was collected and dried under vacuum to give 0.82 g (65%) of product, mp 154–156 °C dec (after recrystallization from cyclohexane). Anal. Calcd for $C_{38}H_{46}B_2O_2N_4Sn_2$ (M_r = 849.34): C, 53,69; H, 5.46; B, 2.54; N, 6.59; O, 3.77; Sn, 27.95. Found: C, 54.10; H, 5.35; B, 2.24; N, 6.61; Sn, 27.96.

NMR data: $\delta(^1H)$ 7.70 (4 H, m), 7.38 (7 H, m), 6.98 (1 H, d, J = 2.1), 6.20 (1 H, unsym t, J = 2.1), 0.40–0.25 (10 H, m); $\delta(^{11}B)$ 6.1 (s, $h_{1/2}$ = 625 Hz); $\delta(^{13}C)$ 136.0, 134.1, 131.8, 130.0, 128.7, 107.2, 18*, 9.3; $\delta(^{119}Sn)$ −323 (s, $h_{1/2}$ = 20 Hz). The peak group of highest mass observed in the EI mass spectrum was at *m/z* 354. The FD mass spectrum exhibited only one peak group at *m/z* 821 in the correct isotopic ratio calculated for the ion $[M - C_2H_5]^+$.

$[(C_6H_5)_2B(\mu\text{-}O)(\mu\text{-}pz)Sn(CH_3)_2]_2$ was obtained from 0.80 g (1.07 mmol) of crude freshly prepared $[(C_6H_5)_2B(pz)_2]_2Sn(CH_3)_2$ dissolved in 30 mL of cyclohexane and ca. 0.05 g (2.8 mmol) of water. The mixture was stirred overnight at room temperature; the precipitate was collected and dried under vacuum to give an essentially quantitative yield of material, mp (after recrystallization from toluene) 200–202 °C dec. Anal. Calcd for $C_{34}H_{38}B_2N_4O_2Sn_2$ (M_r = 793.28): C, 51.43; H, 4.83; B, 2.72; N, 7.06; O, 4.03; Sn, 29.93. Found: C, 51.80; H, 4.85; B, 2.57; N, 7.22; Sn, 29.67.

NMR data: $\delta(^1H)$ 7.49 (2 H, d, J = 1.7), 7.45 (4 H, d, J = 1.6), 7.36–7.22 (6 H, m), 6.26 (1 H, unsym t, J = 2), 0.32 (6 H, s, $^2J(Sn\text{–}H)$ = 78); $\delta(^{11}B)$ 3 (s, $h_{1/2}$ = 600 Hz); $\delta(^{13}C)$ 133.5, 133.3, 132.8, 127.5, 126.5, 107.6, 3.8; $\delta(^{119}Sn)$ −148 (s, $h_{1/2}$ = 20 Hz). The cluster of highest mass in the EI mass spectrum was observed in the region *m/z* 289. The FD mass spectrum exhibited only one peak group at *m/z* 717 in the correct isotopic ratio calculated for the ion $[M - C_6H_5]^+$.

Alternate Procedure. A mixture of 0.55 g (2.5 mmol) of $(CH_3)_2SnCl_2$ and 0.53 g (5 mmol) of K(pz)[5] was slurried in 20 mL of dichloromethane and stirred for 2 h. The mixture was filtered, and a solution of 0.46 g (2.5 mmol) of $(C_6H_5)_2BOH$ in 5 mL of dichloromethane was added to the clear filtrate. After the mixture was allowed to stand overnight the solvent was evaporated, and the solid residue was dissolved in hot cyclohexane. On slow cooling, the first precipitate was the desired compound, identical (NMR data) with the material described above.

$(C_6H_5)_2B(\mu\text{-}OH)(\mu\text{-}pz)B(C_6H_5)_2$. A solution of 0.09 g (1.3 mmol) of Hpz in a minimal amount of dichloromethane was added to a stirred solution of 0.47 g (1.4 mmol) of $[(C_6H_5)_2B]_2O$ in 5 mL of dichloromethane. The mixture was stirred at ambient temperature for 15 min, and solvent was evaporated. The solid residue was recrystallized from cyclohexane to give an essentially quantitative yield of product, mp 148–150 °C dec.

NMR data: $\delta(^1H)$ 7.73 (2 H, d, J = 2.4), 7.25 (20 H, m), 6.66 (1 H, t, J = 2.4), 5.15* (1 H, s); $\delta(^{11}B)$ 7.6 (s, $h_{1/2}$ = 430 Hz).

$(C_6H_5)_2B(\mu\text{-}OH\cdot Hpz)(\mu\text{-}pz)B(C_6H_5)_2$. A solution of 0.04 g (0.59 mmol) of Hpz in a minimal amount of dichloromethane was added to a solution of 0.23 g (0.56 mmol) of $(C_6H_5)_2B(\mu\text{-}OH)(\mu\text{-}pz)B(C_6H_5)_2$ in 2 mL of dichloromethane. The mixture was stirred at ambient temperature for 5 min, and solvent was evaporated. The solid residue was recrystallized from cyclohexane to give an essentially quantitative yield of product, mp 160–162 °C dec.

NMR data: $\delta(^1H)$ 9.6* (2 H, s), 7.70 (s, H, d, J = 2.3), 7.22 (8 H, m), 7.33 (12 H, m), 7.08 (2 H, d, J = 2.2), 6.60 (1 H, t, J = 2.3), 6.09 (1 H, t, J = 2.2); $\delta(^{11}B)$ 6.6 (s, $h_{1/2}$ = 400 Hz). The compound slowly decomposes on standing in solution.

Results and Discussion

General Remarks. All complexes of the type L_2SnR_2 (L = poly(1-pyrazolyl)borate, R = hydrocarbon substituent) were prepared by stirring a 1:2 molar mixture of R_2SnCl_2 and (carefully dried) KL (or NaL) in dichloromethane at room temperature under inert atmosphere.

One initial observation made in those reactions where $K[B(pz)_4]$ (Hpz = pyrazole) was employed as reagent was the frequent formation of the acid $HB(pz)_4$. Moreover, the generation of some free pyrazole was consistently observed in many of the initial reactions of the various poly(1-pyrazolyl)borates, and it has been noted that $[HB(pz)_3]Sn(CH_3)_3$ decomposed with the formation of pyrazole when allowed to stand in chloroform solution.[2b]

It has now been established that all of the alkali-metal poly(1-pyrazolyl)borates employed in the present study are more or less hygroscopic and that some water can adhere strongly to the species. Hence, unless rigorously dried reagents are used, the potential presence of water must be taken into consideration. It should be emphasized that the adhering water is generally difficult to detect. Although it may not necessarily interfere with the preparation of a given material, the latter may interact with any water that is introduced into the system with the poly(1-pyrazolyl)borate reagent. This reaction may be slow, but it can impair results quite dramatically. In principle, any formation of pyrazole is clear evidence that at least traces of water have been present. These results demonstrate a highly unusual hydrolytic B–N cleavage of poly(1-pyrazolyl)borates.

The Acid $HB(pz)_4$. The observations outlined above have prompted a tangential study of the acid $HB(pz)_4$. The preparation of this acid from $K[B(pz)_4]$ and acetic acid has previously been described and a melting point of 70–71 °C was reported for a (laboriously purified) material, but no further characterization was attempted.[4] The anhydrous species, mp 128–134 °C, has now been prepared by the reported procedure although in a simplified fashion. It was initially obtained as a partially hydrated material, mp 90–92 °C; the anhydrous acid could be obtained only on prolonged drying of the compound under vacuum at elevated temperatures.

The ^1H NMR spectra of the anhydrous and hydrated species differ distinctly with respect to the appearance of the (N)H signal. The latter is observed for the anhydrous compound as a sharp singlet at δ 15.3 with the correct intensity as compared to the intensity of the (C)H signals. The intensity of the (N)H signal increases and broadens (accompanied by an upfield shift) with increasing stages of hydration. The signal migration comes to rest in the 6–8 ppm region (depending on the concentration), and at this stage, a water peak emerges near 2 ppm.

The exact nature of the acid has not been established.[4] It contains the $[B(pz)_4]^-$ ion, since it is readily reconverted to a metal salt by neutralization. However, a formulation such as $Hpz{\cdot}B(pz)_3$ would imply two different types of pz moieties, for which there is no (NMR) evidence. Rather, the anhydrous acid appears more likely to have a highly fluxional chelating proton: even at −90 °C, there are essentially no changes in the appearance of the three (C)H NMR signals and no additional signals could be detected. In accordance with the literature,[8] $HB(pz)_4$ decomposed at high temperatures with the formation of the pyrazabole $(pz)_2B(\mu\text{-}pz)_2B(pz)_2$ and Hpz.

Complexes of the Type $[B(pz)_4]_2SnR_2$. The reaction of $(CH_3)_2SnCl_2$ with 2 molar equiv of $K[B(pz)_4]$ yields $[B(pz)_4]_2Sn(CH_3)_2$, as is clearly evidenced by the NMR spectroscopic data. Surprisingly, the reaction could be realized only when working in dilute (ca. 0.05 M) solution; in more concentrated (e.g., ca. 0.2 M) solution, the reaction came to rest at the stage of $[B(pz)_4]SnCl(CH_3)_2$! This concentration effect may explain the failure to obtain products of the type L_2SnR_2 in a previous study.[1]

It is worth noting that the reaction of $(CH_3)_3SnCl$ with $K[B(pz)_4]$ also yielded $[B(pz)_4]_2Sn(CH_3)_2$ as the only identified boron- and tin-containing product. This observation indicates that redistribution of methyl groups occurred during the course of the reaction and seems to be in consonance with the reported[2b] instability of $[HB(pz)_3]Sn(CH_3)_3$. Reaction of CH_3SnCl_3 with 3 molar equiv of $K[B(pz)_4]$ gave a mixture of products, and no defined material containing both tin and boron could be isolated.

The complex $[B(pz)_4]_2Sn(CH_3)_2$ is thermally sensitive and could not be purified by recrystallization. However, it can be stored under inert atmosphere at room temperature for several months without showing any changes of decomposition. Also, no changes were observed in the ^1H NMR spectrum of a material that was kept in the atmosphere for several hours. However, when a solution in dichloromethane was stirred with excess of water for a few hours at room temperature, the compound decomposed with the formation of pyrazole and boric acid.

Interestingly, the room-temperature ^1H NMR spectrum of $[B(pz)_4]_2Sn(CH_3)_2$ exhibits signals for only one type of pz groups, suggesting a highly fluxional species. It is noteworthy that one of the three (C)H signals of the pz groups is broad but the other two are clearly resolved. When the temperature was lowered to −45 °C, a second set of signals emerged, and at −90 °C, a multitude of signals indicated the arrest of at least four different structural arrangements. The latter spectrum could not be assigned due to the overlap of the signals.

The complexes $[B(pz)_4]_2SnR_2$ ($R = C_2H_5$, $n\text{-}C_4H_9$) were obtained in a fashion analogous to that outlined above for the species with $R = CH_3$. The properties of the various complexes parallel each other. All compounds feature room-temperature ^1H NMR spectra that show only the three signals for one type of pz group, where one of the signals (and also one ^{13}C NMR signal) is broad but the other two are clearly resolved. The ^{119}Sn chemical shifts are all observed in an extremely small range with δ −340 ± 5. The compounds decompose at elevated temperatures, e.g., their melting points, and the pyrazabole $(pz)_2B(\mu\text{-}pz)_2B(pz)_2$ could be identified as one decomposition product; the fate of the tin was not explored.

It is noteworthy that, even in great dilution and with prolonged reaction times, the compound $[B(pz)_4]_2Sn(C_6H_5)_2$ could not be obtained. Rather, the reaction stopped at the stage of the (recently described[2c]) complex $[B(pz)_4]SnCl(C_6H_5)_2$.

Complexes of the Type $[R_2B(pz)_2]_2SnR'_2$. Under strictly anhydrous conditions, reaction of $(CH_3)_2SnCl_2$ with 2 molar equiv of $K[(C_2H_5)_2B(pz)_2]$ yields the expected $[(C_2H_5)_2B(pz)_2]_2Sn(CH_3)_2$. The formation of the compound is clearly substantiated by the NMR data. However, the material is thermally quite sensitive and could not be purified by recrystallization, and the results of the elemental analysis are not satisfactory. Moreover, the compound is extremely sensitive to moisture and could only be obtained if carefully dried solvents and reagents were employed. It is of interest to note that the formation of pyrazole as a hydrolysis product could be clearly documented by ^1H NMR data; thus, the process involves a highly unusual B–N cleavage of a poly(1-pyrazolyl)borate ligand.

In addition to the preceding compound, the complexes $[(C_2H_5)_2B(pz)_2]_2SnR_2$ with $R = C_2H_5$ or $n\text{-}C_4H_9$ as well as $[(C_6H_5)_2B(pz)_2]_2Sn(CH_3)_2$ and $[H_2B(pz)_2]_2Sn(CH_3)_2$ were obtained in reasonable purity and could be characterized by their NMR data. The compound $[(C_2H_5)_2B(pz)_2]_2Sn(C_6H_5)_2$ was prepared only as an intermediate and was not fully characterized.

All of the compounds of the type $[R_2B(pz)_2]_2SnR'_2$ are thermally quite sensitive and could not be purified by recrystallization. Also, they decompose slowly on storage of the neat materials, much more rapidly in solution, with the formation of the corresponding pyrazabole $R_2B(\mu\text{-}pz)_2BR_2$ (as identified by ^1H NMR spectroscopy). Furthermore, they are all *extremely* sensitive to hydrolysis (see below).

At least one of the ^1H NMR signals of the pz groups of the species was generally broad. Otherwise, the ^1H NMR spectra offered no special features. However, for some of the compounds, i.e., $[H_2B(pz)_2]_2Sn(CH_3)_2$ and $[(C_2H_5)_2B(pz)_2]_2SnR_2$ (with $R = CH_3$, C_2H_5), the ^{13}C NMR signals of the Sn-bonded alkyl groups could not be detected in the room-temperature spectra despite the fact that the corresponding proton signals were clearly observed. However, when the temperature was lowered, the missing ^{13}C NMR signals slowly emerged, initially as broad signals but sharpening with increasingly lower temperature. For example, in the ^{13}C NMR spectrum of $[(C_2H_5)_2B(pz)_2]_2Sn(C_2H_5)_2$, only the signals for the pz groups and the B-bonded C_2H_5 groups were observed at room temperature. Two additional but very broad signals emerged at 0 °C. These sharpened and increased in intensity when the temperature was lowered even further: at −45 °C they were clearly apparent, and at −75 °C they were observed as sharp and intense signals with δ 27.0 and 8.3, respectively. Similarly, the missing ^{13}C NMR signal of the methyl groups in $[H_2B(pz)_2]_2Sn(CH_3)_2$ emerged at δ 21.9 on lowering of the temperature.

Hydrolysis of $[R_2B(pz)_2]_2SnR'_2$—Formation of $[R_2B(\mu\text{-}O)(\mu\text{-}pz)SnR'_2]_2$. The major tin-containing product of the hydrolysis of $[(C_2H_5)_2B(pz)_2]_2Sn(CH_3)_2$ was stable at room temperature but it decomposed as its melting point. The ^1H NMR spectrum of the species suggested a composition $(C_2H_5)_2B(\mu\text{-}O)(\mu\text{-}pz)Sn(CH_3)_2$; however, mass spectral data indicated that the material was a dimer, and the overall hydrolysis can be described by eq 1.

$$\begin{aligned}&[(C_2H_5)_2B(pz)_2]_2Sn(CH_3)_2 + H_2O \rightarrow\\ &\qquad \tfrac{1}{2}(C_2H_5)_2B(\mu\text{-}pz)_2B(C_2H_2)_2 +\\ &\qquad \tfrac{1}{2}\underset{\mathbf{1}}{[(C_2H_5)_2B(\mu\text{-}O)(\mu\text{-}pz)Sn(CH_3)_2]_2} + 2Hpz \quad (1)\end{aligned}$$

The dimeric nature of the compound is readily established by the FD mass spectrum. The latter exhibits only one peak group corresponding to the ion $[M\ \text{minus}\ C_2H_5]^+$ in the calculated isotopic ratio, suggesting a structure for **1** ($R = C_2H_5$, $R' = CH_3$) as shown.

Analogous results were obtained for the hydrolysis products of other $[R_2B(pz)_2]_2SnR'_2$ complexes. The FD mass spectra clearly established the dimeric nature of the species. Under the

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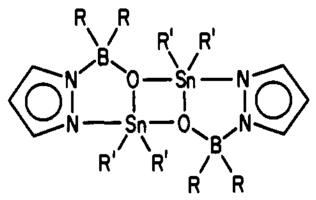
[8] Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 4948–4952.



1

normal conditions for the recording of EI mass spectra (200 °C inlet temperature), however, generally only spectra for thermal decomposition products of 1 are observed. Indeed, the compounds are thermally stable only up to a point. For example, $[(C_2H_5)_2B(\mu\text{-}O)(\mu\text{-}pz)Sn(CH_3)_2]_2$ decomposes at its melting point with the formation of the pyrazabole $(C_2H_5)_2B(\mu\text{-}pz)_2B(C_2H_5)_2$. Also, on attempts to purify the oily $[(C_2H_5)_2B(\mu\text{-}O)(\mu\text{-}pz)Sn(n\text{-}C_4H_9)_2]_2$ by distillation under vacuum, the compound decomposed with the formation of $(C_2H_5)_2B(\mu\text{-}pz)_2B(C_2H_5)_2$ and $[(n\text{-}C_4H_9)_2SnO]_n$.

The observed NMR data of all of the $[R_2B(\mu\text{-}O)(\mu\text{-}pz)SnR'_2]_2$ species are clearly in consonance with 1. The ^{119}Sn chemical shifts are affected by the substituent R′ at the tin, migrating from δ −148 for $R' = CH_3$ to −173 for $R' = C_2H_5$ and −175 for $R' = n\text{-}C_4H_9$ to −323 for $R' = C_6H_5$.

Equation 1 is a simplification of the true processes involved in the hydrolysis of $[R_2B(pz)_2]_2SnR'_2$ species. Although the generation of pyrazole is readily verified, the pyrazabole is apparently formed via various intermediates. Independent experiments (see below) suggest that the $[R_2B(\mu\text{-}O)(\mu\text{-}pz)SnR'_2]_2$ species are formed directly in an initial step which can be described by eq 2. Subsequently, the complex $R_2BOH{\cdot}Hpz$ is altered. Initially,

$$[R_2B(pz)_2]_2SnR'_2 + 2H_2O \rightarrow \tfrac{1}{2}[R_2B(\mu\text{-}O)(\mu\text{-}pz)SnR'_2]_2 + R_2BOH{\cdot}Hpz + 2Hpz \quad (2)$$

it may lose water and rearrange to form a pyrazole adduct of a pyrazabole analogue according to eq 3. (Note: Species of the type $R_2B(\mu\text{-}OH)(\mu\text{-}pz)BR_2$ have recently been obtained by the reaction of 1,3,2-diboroxanes, $(R_2B)_2O$, with Hpz.[9]) The latter ultimately can lose more water to yield a pyrazabole as is shown in eq 4. Which of the cited intermediates can be isolated and/or

$$2R_2BOH{\cdot}Hpz \rightarrow R_2B(\mu\text{-}OH{\cdot}Hpz)(\mu\text{-}pz)BR_2 + H_2O \quad (3)$$

$$R_2B(\mu\text{-}OH{\cdot}Hpz)(\mu\text{-}pz)BR_2 \rightarrow R_2B(\mu\text{-}pz)_2BR_2 + H_2O \quad (4)$$

identified seems to depend on the amount of water in the system, the reaction time, and the employed temperature. However, the relevant pyrazaboles are always obtained on heating of the byproduct mixture to melting.

In order to substantiate the nature of the proposed hydrolysis intermediates, the acid R_2BOH ($R = C_6H_5$) was reacted with Hpz. The resultant product was not uniform but consisted primarily of the acid–base adduct $R_2BOH{\cdot}Hpz$ in mixture with $R_2B(\mu\text{-}OH{\cdot}Hpz)(\mu\text{-}pz)BR_2$. Characteristic ^1H NMR signals for $R_2BOH{\cdot}Hpz$ could be assigned at δ 12.0* (2 H, s), 7.76 (1 H, d, $J = 2.2$), 7.44 (1 H, d, $J = 2.2$), 7.21 (m) + 6.93 (m) (10 H total), and 6.36 (1 H, unsym t, $J = 2.2$), and the ^{11}B NMR signal was observed at δ 1.9. The nature of the byproduct mixture was established by independent synthesis of $R_2B(\mu\text{-}OH)(\mu\text{-}pz)BR_2$ ($R = C_6H_5$) from $(R_2B)_2O$ and Hpz to give $R_2B(\mu\text{-}OH)(\mu\text{-}pz)BR_2$, which was subsequently treated with 1 equiv of Hpz to form $R_2B(\mu\text{-}OH{\cdot}Hpz)(\mu\text{-}pz)BR_2$. Both of these latter compounds could be obtained in pure form and were characterized by their NMR data. Furthermore, when a solution of the original mixture obtained from R_2BOH and Hpz was allowed to stand, the ^1H and ^{11}B NMR signals of $R_2BOH{\cdot}Hpz$ slowly diminished with a corresponding increase in the signals for $R_2B(\mu\text{-}OH{\cdot}Hpz)(\mu\text{-}pz)BR_2$. Heating of either species to melting resulted in the formation of the pyrazabole $R_2B(\mu\text{-}pz)_2BR_2$ with the generation of water.

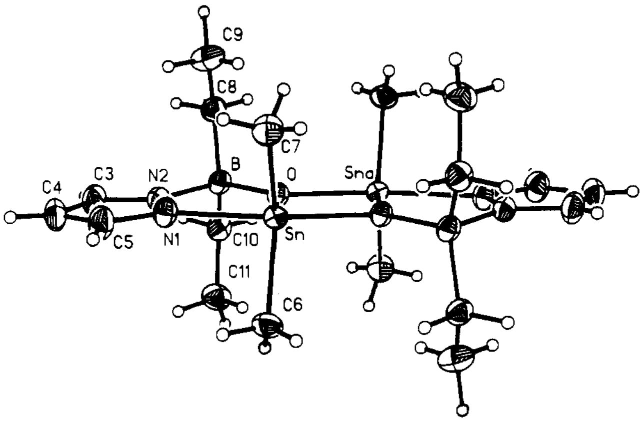


Figure 1. ORTEP plot of $[(C_2H_5)_2B(\mu\text{-}O)(\mu\text{-}pz)Sn(CH_3)_2]_2$ (1: $R = C_2H_5$, $R' = CH_3$).

Table II. Selected Bond Distances (Å) for $[(C_2H_5)_2B(\mu\text{-}O)(\mu\text{-}pz)Sn(CH_3)_2]_2$

Sn–O	2.030 (3)	O–B	1.526 (4)
Sn–C(6)	2.109 (5)	N(1)–N(2)	1.348 (5)
Sn–C(7)	2.108 (5)	N(2)–C(3)	1.340 (5)
Sn–O(A)	2.145 (2)	N(1)–C(5)	1.338 (6)
O–Sn(A)	2.145 (2)	C(3)–C(4)	1.369 (8)
Sn–N(1)	2.240 (3)	C(4)–C(5)	1.359 (6)
B–N(2)	1.605 (6)	C(8)–C(9)	1.520 (8)
B–C(8)	1.617 (6)	C(10)–C(11)	1.514 (7)
B–C(10)	1.600 (6)		

Table III. Selected Bond Angles (deg) for $[(C_2H_5)_2B(\mu\text{-}O)(\mu\text{-}pz)Sn(CH_3)_2]_2$

O–Sn–N(1)	76.8 (1)	O–Sn–C(6)	117.8 (2)
N(1)–Sn–C(6)	91.9 (2)	O–Sn–C(7)	116.3 (2)
N(2)–Sn–C(7)	93.1 (2)	C(6)–Sn–C(7)	125.4 (2)
O–Sn–O(A)	74.7 (1)	N(1)–Sn–O(A)	151.4 (1)
C(6)–Sn–O(A)	99.3 (2)	C(7)–Sn–O(A)	101.5 (2)
Sn–O–B	124.9 (2)	Sn–O–Sn(A)	105.3 (1)
B–O–Sn(A)	129.8 (2)	O–B–N(2)	102.8 (3)
O–B–C(8)	112.6 (3)	N(2)–B–C(8)	106.8 (3)
O–B–C(10)	111.6 (3)	N(2)–B–C(10)	108.5 (3)
C(8)–B–C(10)	113.8 (3)	Sn–N(1)–N(2)	114.3 (2)
Sn–N(1)–C(5)	137.9 (3)	N(2)–N(1)–C(5)	107.6 (3)
B–N(2)–N(1)	120.6 (3)	N(2)–C(3)–C(4)	109.6 (4)
N(1)–N(2)–C(3)	107.8 (4)	N(1)–C(5)–C(4)	110.1 (5)
C(3)–C(4)–C(5)	104.9 (4)	B–C(10)–C(11)	116.4 (4)

Compounds of the type $[R_2B(\mu\text{-}O)(\mu\text{-}pz)SnR'_2]_2$ were also found to be accessible by the reaction of R_2BOH with $R'_2Sn(pz)_2$ in a one-pot process as is illustrated by eqs 5 and 6.

$$R'_2SnCl_2 + 2Kpz \rightarrow R'_2Sn(pz)_2 + 2KCl \quad (5)$$

$$R'_2Sn(pz)_2 + R_2BOH \rightarrow \tfrac{1}{2}[R_2B(\mu\text{-}O)(\mu\text{-}pz)SnR'_2]_2 + Hpz \quad (6)$$

A complication of this latter procedure is the fact that the acid R_2BOH may interact with Hpz as is indicated in eq 2 and was confirmed by an independent experiment (see above). Nevertheless, the yields of 1 prepared according to eqs 5 and 6 are quite reasonable, even if only a 1:1 molar ratio of the reagents cited in eq 6 is employed. This is understandable, since the Hpz has first to be generated according to eq 6 before it can react with any remaining R_2BOH.

In any case, both procedures that lead to species of type 1, i.e., the hydrolysis of $[R_2B(pz)_2]_2SnR'_2$ or the direct preparation according to eqs 5 and 6, give ready access to the $[R_2B(\mu\text{-}O)(\mu\text{-}pz)SnR'_2]_2$ (1) species.

Structure of $[(C_2H_5)_2B(\mu\text{-}O)(\mu\text{-}pz)Sn(CH_3)_2]_2$. The crystal and molecular structure of $[(C_2H_5)_2B(\mu\text{-}O)(\mu\text{-}pz)Sn(CH_3)_2]_2$ was determined by single-crystal X-ray diffraction. The structure consists of two $(C_2H_5)_2B(\mu\text{-}O)(\mu\text{-}pz)Sn(CH_3)_2$ units that are linked by additional coordination of the tin of one monomeric unit to the oxygen of the second one to give a fused pentacyclic system

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[9] Yalpani, M.; Köster, R.; Boese, R. *Chem. Ber.* **1989**, *122*, 19–24.

containing five-coordinate tin and a central Sn_2O_2 ring as is observed for **1**. It has a crystallographic center of inversion in the center of the Sn_2O_2 ring. An ORTEP plot of the compound is shown in Figure 1; selected bond distances and angles are given in Tables II and III, respectively.

Surprisingly, the five individual heterocycles of the (dimeric) molecule are essentially coplanar. Of course, planarity would be expected for the pyrazolyl rings. On the other hand, several members of the pentacyclic system should be considered as either sp^3 hybridized (boron and oxygen atoms) or sp^{3}d hybridized (tin atoms), and still the polycyclic system is almost coplanar. The boron atoms deviate most from the mean plane (9.3 pm); the bond angles are close to tetrahedral (109.5 ± 3.0°). The B–C distances are similar to those found in pyrazaboles,[10] but the B–O bond of 1.54 Å is rather long and even on the long side when compared to those of borates containing tetrahedral boron atoms.[11]

The oxygen atoms may be viewed as sp^3 hybridized, as is indicated by the sum of their three bond angles (328.8 versus 328.5° for the ideal case). However, the individual bond angles exhibit quite significant deviations from a tetrahedral bond angle, especially the rather acute angle of only 74.7 (1)° for Sn–O–Sn(a), while the other two, with values of 124.9 and 129.8°, respectively, would seem to be in better agreement with sp^2 hybridization.

The sharp Sn–O–Sn(a) angle forces the tin atoms fairly close together. Thus, the Sn–Sn distance within the four-membered Sn_2O_2 ring is only 3.32 Å, corresponding to a mere 18% increase over the Sn–Sn distance in metallic tin (2.80 Å). Hence, there may be bonding interaction between the two tin atoms. However, the tin is clearly five-coordinate. Inspection of the bond angles indicates a distorted trigonal-bypyramidal coordination sphere, since the sum of the bond angles between the equatorial atoms C(6), C(7), and O(1) is 359.5°, while the bond angle to the axial atoms deviates by 28.6° from the ideal value of 180°. The tin atoms contribute one axial and one equatorial bond to the formation of the central dioxadistannetane ring. As is to be expected for this kind of geometry, a short (equatorial) and a long (axial) Sn–O bond were found, although both values are on the short side of known Sn–O bond distances.[12]

The Sn-bonded nitrogen of the pyrazolyl group is in axial position; hence, the Sn–N distance is long as compared to other known Sn–N bonds.[13] Also, the B–N bond is quite long as compared to that of pyrazaboles containing the skeletal $B(\mu\text{-pz})_2B$ arrangement.[10]

In principle, the molecule belongs to a class of tin compounds of the general formula $(CH_3)_2Sn(OR)X$, where X is an electron-withdrawing group. This results in an increase of the Lewis acidity at the tin center and leads to acid–base interaction with the lone pairs of electrons at the oxygen atom, thus leading to an increase in the coordination of tin.[14]

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Supplementary Material Available: Tables of atomic coordinates and isotropic displacement coefficients for hydrogen atoms and anisotropic displacement coefficients (2 pages); a table of observed and calculated structure factors for $[(C_2H_5)_2B(\mu\text{-O})(\mu\text{-pz})Sn(CH_3)_2]_2$ (8 pages). Ordering information is given on any current masthead page.

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[10] Brock, C. P.; Niedenzu, K.; Hanecker, E.; Nöth, H. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 1458–1463 and references cited therein.

[11] Wells, R. G. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, England, 1984.

[12] Veith, M. *J. Organomet. Chem. Libr.* **1981**, *12*, 319.

[13] Sn–N bond distances to five-coordinate tin are on the order of 2.2–2.4 Å; see, for example: Allmann, R.; Olejnik, S.; Wakowska, A. *Z. Kristallogr.* **1981**, *154*, 244–245. Matsubayashi, G.; Tanaka, T.; Nishigaki, S.; Nakatsu, K. *J. Chem. Soc., Dalton Trans.* **1979**, 501–505.

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Ene Reactions of 1,2-Dehydro-*o*-carborane[1]

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1,2-Dehydro-*o*-carborane undergoes the ene reaction with a variety of hydrocarbon substrates. This reaction appears to be a concerted 2 + 4 process.

Introduction

o-Carborane, $C_2B_{10}H_{12}$ (**1**), is a three-dimensional analogue of benzene. Carborane **1** accommodates 26 electrons in a system of 13 filled bonding molecular orbitals and thus resembles its simpler two-dimensional aromatic cousin benzene.[2] This similarity in molecular orbital description results in vast thermodynamic stability for **1**,[2] as well as reactivity reminiscent of benzene (aromatic substitution).[3] The aromaticity of the icosahedral carboranes has been remarked many times.[2,4]

1

In this and all subsequent figures the dots represent carbon. All other vertices are boron, and there is an unshown hydrogen at each vertex.

We have recently generated 1,2-dehydro-*o*-carborane (**2**), the carborane version of benzyne,[5] and described its reactions with a variety of dienes.[4] Some of these revealed **2** to be especially

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[1] Support for this work by the National Science Foundation through Grant CHE-8800448 and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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[5] Comment seems in order on the nature of the "extra" bond in **2**. Many seem caught up in the question of whether this is a "double" or "triple" bond. The answer is a resounding "neither!". As in dehydrobenzene, a pair of singly occupied orbitals extends radially from the framework. Questions of "doubleness" or "tripleness" are not productive and in this case are essentially meaningless, as the carborane framework is constructed from three-center, two-electron bonding. The question addressed in ref 4, as well as in this work, is the extent of overlap in the "extra" bond. Future questions (computational work in progress) concern the C–C bond length in **2**.

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