of the triangle towards the molybdenum. This would be a sterically unfavorable position, and thus this complex would not be expected to coordinate strongly even to small cations such as Li^+ in a 1:1 complex.

A second interesting feature in the molecular structure of **4** is the conformation of the metallacrown ether ring. The plane containing the three ether oxygens is nearly perpendicular to the plane containing P1, P2, Mo, C1 and C2 (dihedral angle 95.1 (1)°). The chelate ring is distorted from the symmetric conformation observed in solution, as shown by the very different torsion angles for the two halves of the ring. This distortion appears to be primarily due to the different rotations of the diphenylphosphino groups about the molybdenum-phosphorus bonds.

The X-ray structure of **4** also confirms the coordination geometry about molybdenum inferred from the spectroscopic data. The coordination geometry at molybdenum is a slightly distorted octahedron composed of four carbonyls and two phosphine donor groups in a cis geometry. The P1-Mo-P2 angle (93.78 (2)°) is significantly distorted from the ideal 90° angle as is generally observed in *cis*-$Mo(CO)_4(phosphine)_2$ complexes.

Summary. Ligands of the type $Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$ (n = 3-5) can be synthesized in high yields from the reaction of $LiPPh_2$ with the appropriate bis(mesylate), $MsO(CH_2CH_2O)_{n+1}Ms$. The ligands react with *cis*-$Mo(CO)_4(nbd)$ in dilute solution to form mononuclear *cis*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2\}$ (n = 3-5) complexes in good yields. These complexes are quite different from the *cis*-$Mo(CO)_4\{Ph_2PO(CH_2CH_2O)_nPPh_2\}$ (n = 1-4) complexes reported by Powell and co-workers. The alkali-metal cation selectivities of the two types of complexes differ significantly for complexes with equal numbers of ether oxygens but are similar for complexes with similar numbers of atoms in the metallacrown ether rings. This suggests that the alkali-metal cation selectivities exhibited by metallacrown ether complexes are primarily due to the ring size and not to the number of oxygens in the ring. The reactions of organolithium compounds with the two types of complexes are also quite different. Organolithium compounds react with the *cis*-$Mo(CO)_4\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2\}$ complexes to yield *cis*-$Mo(CO)_4(Ph_2PCH{=}CH_2)_2$ via an unusual C—O bond cleavage, but react with the *cis*-$Mo(CO)_4\{Ph_2PO(CH_2CH_2O)_nPPh_2\}$ complexes to yield acyl complexes.

The results from this and earlier studies indicate that metallacrown ethers formed from bis(P donor)-polyether ligands with sufficient numbers of oxygens and sufficiently large cavities are capable of solubilizing salts of alkali-metal cations in organic solvents, and thus these complexes may be useful as phase-transfer catalysts. The ease with which the metallacrown ethers form hard/soft bimetallic complexes suggested that related complexes may also be useful for the activation of small, bifunctional molecules. The type of bis(P donor)-polyether ligand used in these complexes will have significant effects upon the reactivities of the complexes and thus upon their usefulness in these various processes.

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Supplementary Material Available: Tables of the ^{13}C data for the titration of **6** with $NaBPh_4$ (Table 1), the thermal parameters for **4** (Table 2), the calculated H positions for **4** (Table 3), other bond distances and angles in **4** (Table 4), and the least-squares planes for **4** (Table 5) (5 pages); a table of observed and calculated structure factors for **4** (29 pages). Ordering information is given on any current masthead page.

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Poly(pyrazolyl)borate Complexes of Tin(II). Crystal and Molecular Structures of $[H_2B(pz)_2]SnCl$ and $[B(pz)_4]_2Sn$ (pz = Pyrazolyl Ring)

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The complexes $[H_nB(pz)_{4-n}]_mSnCl_{2-m}$ (n = 0-2; m = 1, 2; pz = pyrazolyl ring) have been prepared by the reaction of $SnCl_2$ and the ligand salts in the appropriate stoichiometries. The complexes are air stable in the solid phase with solution stability increasing with the number of poly(pyrazolyl)borate ligands and the number of pyrazolyl rings present in the ligand. The structure of $[H_2B(pz)_2]SnCl$ (**1**) has been determined by X-ray crystallography: monoclinic, $P2_1/n$, a = 4.894 (5) Å, b = 27.079 (23) Å, c = 7.744 (6) Å, β = 100.32 (7) °, V = 1009.8 (16) Å^3, Z = 4, $R(F)$ = 5.67%. The basic geometry about the three-coordinate tin is trigonal pyramidal. The donor atom angles through the tin atom average 86°, and the lone pair on tin presumably occupies the fourth vertex. There are also weak tin-chlorine bridging interactions forming centrosymmetric dimeric units. In both the solution and solid phases, $[H_2B(pz)_2]_2Sn$ (**2**) has a trigonal-bipyramidal geometry with each ligand spanning an axial and equatorial site. The tin lone pair presumably occupies the remaining equatorial vertex. The molecule shows two types of dynamic processes in solution. The axial and equatorial positions equilibrate with a barrier of 10.2 kcal/mol at -58 °C. Also, the barrier to the boat-boat flip of the SnN_4B rings formed by each ligand is determined to be 10.3 kcal/mol at -52 °C. $[HB(pz)_3]SnCl$ (**3**) and $[B(pz)_4]SnCl$ (**5**) are believed to have a similar trigonal-bipyramidal geometry, and both are fluxional in solution. An X-ray crystallographic study of $[B(pz)_4]_2Sn$ (**6**) shows it to be four-coordinate with a highly distorted trigonal-bipyramidal structure: monoclinic, $P2_1/n$, a = 10.754 (3) Å, b = 17.109 (4) Å, c = 15.566 (3) Å, β = 91.236 (20)°, V = 2863.6 (12) Å^3, Z = 4, $R(F)$ = 3.63%. Each ligand is bidentate with one of the noncoordinated pyrazolyl rings located fairly close to the tin. Correlations from the ^{119}Sn NMR chemical shifts of these complexes indicate that **6** is also four-coordinate in solution. The ^1H NMR spectra show that **6** is dynamic in solution. All of the pyrazolyl rings are equivalent at ambient temperatures with a 3/1 pattern observed at -80 °C. The low-temperature spectrum can be explained by a low-energy process that equilibrates the three pyrazolyl rings in each ligand close to tin, but the fourth ring remains unique. At higher temperatures, the fourth ring also equilibrates by a boat-boat flip of the six-membered ring (10.5 kcal/mol barrier). The ^{119}Sn data indicate that $[HB(pz)_3]_2Sn$ (**4**) may be five-coordinate in solution.

Introduction

We have recently initiated an investigation into the synthesis and characterization of poly(pyrazolyl)borate complexes of main-group metals. In our initial publications, we have described the preparation and characterization of an extensive series of stable group-13 complexes of gallium[1a,b] and indium[1c] of the general formula $[H_2B(pz)_2]_mMCl_n(CH_3)_p$ ($m + n + p = 3$; pz = pyrazolyl

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ring; M = Ga, In). The solid-state structures of three members of the series and the acetate complex $[H_2B(pz)_2]_2Ga(O_2CCH_3)$ have been determined crystallographically.[1] These complexes, including the organometallics, are generally air stable in solution, demonstrating that the dihydrobis(pyrazolyl)borate ligand imparts considerable stability to main-group metal complexes. In addition to our work, others have published the syntheses and structures of $\{[HB(3,5\text{-}Me_2pz)_3]_2Ga\}GaCl_4$, $[HB(3,5\text{-}Me_2pz)_3]InCl_2(NCCH_3)$,[2] $[H_2B(pz)_2]_3In$,[3] and $[(CH_3)_2B(pz)_2]Ga(CH_3)_2$.[4] Also, very recently the preparations of poly(pyrazolyl)borate complexes of aluminum have been reported.[5]

This success in preparing stable complexes of group-13 metals encouraged us to explore the chemistry of group-14 metals in the +2 oxidation state. Extensive chemistry, including several poly(pyrazolyl)borate complexes ($[H_2B(pz)_2]SnMe_xCl_{3-x}$ and $[HB(pz)_3]SnMe_xCl_{3-x}$ (x = 0–3)),[6] has been published concerning these metals in the +4 oxidation state, but relatively little has been published on the coordination chemistry in the +2 oxidation state.[7] With poly(pyrazolyl)borate ligands, Cowley et al. have reported the structures of $[HB(3,5\text{-}Me_2pz)_3]_2Sn$ and $[HB(3,5\text{-}Me_2pz)_3]SnCl$.[8] $[HB(3,5\text{-}Me_2pz)_3]_2Sn$ is five-coordinate, containing one noncoordinated pyrazolyl ring. In both structures, the lone pair on tin(II) is stereochemically active. Trofimenko has also briefly mentioned the synthesis of $[HB(pz)_3]_2Pb$ and $[B(pz)_4]_2Pb$, chemistry which we have extensively elaborated.[10] Reported here is the synthesis and characterization of $[H_nB(pz)_{4-n}]_mSnCl_{2-m}$ (n = 0–2; m = 1, 2) complexes. The solid-state structures of $[H_2B(pz)_2]SnCl$ and $[B(pz)_4]_2Sn$ have been determined crystallographically. Tin-119 chemical shift data are also reported.

Experimental Section

General Procedure. All operations were carried out under a nitrogen atmosphere either by standard Schlenk techniques or in a Vacuum Atmospheres HE-493 drybox. All solvents were dried, degassed, and distilled prior to use. Infrared spectra were recorded on a Nicolet DX V4.56 spectrometer. The ^{1}H, ^{119}Sn, and ^{11}B solution NMR spectra were recorded on a Bruker AM-300 or AM-500 spectrometer using a 5-nm broad-band probe. Proton, tin, and boron chemical shifts are reported in ppm vs Me_4Si, Me_4Sn, and $BF_3{\cdot}OEt_2$, respectively. In the ^{1}H NMR spectra of the $H_2B(pz)_2$ and $HB(pz)_3$ complexes, the BH_2 or BH resonances are broad (cover ca. 1.3 ppm) with the center located as indicated for each compound. The tin spectra were run with a spectral width of 1000 ppm, and the chemical shifts were checked for aliasing by varying the center of the window. Each tin spectrum was acquired in 15–80 min. Mass spectra were run on a Finnigan 4521 GC–mass spectrometer or a VG 70SQ spectrometer. Clusters assigned to specific ions show appropriate isotopic patterns as calculated for the atoms present. Elemental analyses were performed by Robertson Laboratory, Inc. $K[H_2B(pz)_2]$, $K[HB(pz)_3]$, and $Na[B(pz)_4]$ were prepared by the published methods.[9] Anhydrous $SnCl_2$ was purchased from Aldrich Chemical Co. Molecular weights were determined by freezing point depression measurements in an apparatus as described in earlier publications.[1b,c]

Table I. Crystallographic Data for the Structural Analysis of $[H_2B(pz)_2]SnCl$ (**1**) and $[B(pz)_4]_2Sn$ (**6**)

	1	6
formula	$C_6H_8BN_4ClSn$	$C_{24}H_{24}B_2N_{16}Sn$
fw	301	678
space group	$P2_1/n$	$P2_1/n$
a, Å	4.894 (5)	10.754 (3)
b, Å	27.079 (23)	17.109 (4)
c, Å	7.744 (6)	15.566 (3)
β, deg	100.32 (7)	91.236 (20)
V, Å^3	1009.8 (16) Å^3	2863.6 (12) Å^3
Z	4	4
T, °C	24	24
λ, Å	0.71073	0.71073
ρ_{calc}, g cm^{-3}	1.980	1.569
μ, cm^{-1}	27.65	9.39
transm coeff	1.13	1.27
$R(F)$	5.67	3.63
$R_w(F)$	6.13	3.93

Chloro(dihydrobis(1-pyrazolyl)borato)tin(II), $[H_2B(pz)_2]SnCl$ (1). $SnCl_2$ (0.30 g, 1.6 mmol) and $K[H_2B(pz)_2]$ (0.29 g, 1.6 mmol) were placed in a round-bottomed flask. CH_2Cl_2 (30 mL) was added via syringe. The mixture was stirred overnight at room temperature and filtered. The solvent was evaporated under vacuum to yield a white solid (0.38 g, 1.3 mmol, 81%); mp 140–143 °C. ^{1}H NMR ($CDCl_3$; δ): 7.78, 7.62 (2, 2; broad, d; J = 2.1 Hz, 3-H, 5-H (pz)); 6.31 (2, broad, 4-H (pz)); 3.9 (broad, BH_2). IR (CH_2Cl_2, cm^{-1}): 2463, 2448 (BH_2). ^{119}Sn NMR ($CDCl_3$; δ): −307 ($w_{1/2}$ = 3500 Hz); (−58 °C) −389 ($w_{1/2}$ = 300 Hz). The mass spectrum shows clusters for M^+ and $M^+ - HCl$ at m/e 301 and 265. Cryoscopic molecular weight, benzene solution, formula weight 301 (observed molality, observed molecular weight): 0.0884, 360; 0.116, 364. Anal. Calcd for $C_6H_8N_4BClSn$: C, 23.91; H, 2.68. Found: C, 23.90; H, 2.63.

Bis[dihydrobis(1-pyrazolyl)borato]tin(II), $[H_2B(pz)_2]_2Sn$ (2). This complex was prepared as described for **1** by using $SnCl_2$ (0.25 g 1.3 mmol) and $K[H_2B(pz)_2]$ (0.49 g, 2.6 mmol) to yield a white solid (0.44 g, 1.1 mmol, 81%); mp 131–135 °C. ^{1}H NMR ($CDCl_3$; δ): 7.62, 7.26 (4, 4; d, d; J = 1.8, 1.6 Hz; 3-H, 5-H (pz)); 6.17 (4; t; J = 2.1 Hz; 4-H (pz)); 4.0 (broad, BH_2). ^{11}B NMR ($CDCl_3$; δ): −8.59 (t; J_{BH} = 102.2 Hz, line narrowed). ^{119}Sn NMR ($CDCl_3$; δ): −652 ($w_{1/2}$ = 400 Hz). IR (Nujol mull, cm^{-1}): 2458, 2435 (BH_2). The mass spectrum shows a complex multiplet for $M^+ - nH$ (n = 0–3) and a cluster for $M^+ - H_2B(pz)_2$ centered at m/e 411 and 266. Accurate mass spectrum for M^+ (m/e): calcd for $C_{12}H_{16}N_8B_2{}^{118}Sn$, 412.0700; found, 412.0666.

Chloro(hydrotris(1-pyrazolyl)borato)tin(II), $[HB(pz)_3]SnCl$ (3). This complex was prepared as described for **1** by using $SnCl_2$ (1.05 g, 5.5 mmol) and $K[HB(pz)_3]$ (1.40 g, 5.5 mmol) to yield a white solid (1.39 g, 3.8 mmol, 69%); mp 192–197 °C. ^{1}H NMR ($CDCl_3$; δ): 7.93, 7.73 (3, 3; d, d; J = 2.1, 2.2 Hz; 3-H, 5-H (pz)); 6.29 (3; t; J = 2.2 Hz; 4-H (pz)); 4.8 (broad, BH). ^{119}Sn NMR ($CDCl_3$; δ): −569 ($w_{1/2}$ = 450 Hz). IR (CH_2Cl_2, cm^{-1}): 2306 (BH). The mass spectrum shows clusters for M^+, $M^+ - HCl$, and $M^+ - pz$ at m/e 367, 331, and 300. Anal. Calcd for $C_9H_{10}N_6BClSn$: C, 29.41; H, 2.74. Found: C, 29.04; H, 2.99.

Bis[hydrotris(1-pyrazolyl)borato]tin(II), $[HB(pz)_3]_2Sn$ (4). This complex was prepared as described for **1** by using $SnCl_2$ (1.00 g, 5.27 mmol) and $K[HB(pz)_3]$ (2.66 g, 10.6 mmol) to yield a white solid (2.45 g, 4.50 mmol, 85%); mp 159–162 °C. ^{1}H NMR ($CDCl_3$; δ): 7.67, 7.35, (6, 6; d, d; J = 1.8, 1.6 Hz; 3-H, 5-H (pz)); 6.15 (6; t; J = 2.0 Hz; 4-H (pz)); 4.8 (broad, BH). ^{119}Sn NMR ($CDCl_3$; δ): −877 ($w_{1/2}$ = 2000 Hz); (−58 °C) −871 ($w_{1/2}$ = 600 Hz). IR (Nujol mull, cm^{-1}): 2442 (BH). The mass spectrum shows clusters for $M^+ - H$ and $M^+ - HB(pz)_3$ at m/e 544 and 333. Anal. Calcd for $C_{18}H_{20}N_{12}B_2Sn$: C, 39.64; H, 3.70. Found: C, 39.73; H, 3.54.

Chloro(tetrakis(1-pyrazolyl)borato)tin(II), $[B(pz)_4]SnCl$ (5). This complex was prepared as described for **1** by using $SnCl_2$ (0.50 g, 2.6 mmol) and $K[B(pz)_4]$ (0.84 g, 2.6 mmol) to yield a white solid (0.94 g, 2.2 mmol, 85%); mp 111–114 °C. ^{1}H NMR ($CDCl_3$; δ): 7.88, 7.56 (4, 4; d, d; J = 1.7, 2.3 Hz; 3-H, 5-H (pz)); 6.36 (4; t; J = 2.2 Hz; 4-H (pz)). ^{119}Sn NMR ($CDCl_3$; δ): −528 ($w_{1/2}$ = 3700 Hz); (−58 °C) −597 ($w_{1/2}$ = 3000 Hz). The mass spectrum shows clusters for M^+, $M^+ - Cl$, and $M^+ - pz$ at m/e 434, 399, and 367. Anal. Calcd for $C_{12}H_{12}N_8BClSn$: C, 33.23; H, 2.79. Found: C, 33.04; H, 2.37.

Bis[tetrakis(1-pyrazolyl)borato]tin(II), $[B(pz)_4]_2Sn$ (6). $SnCl_2$ (0.20 g, 1.0 mmol) and $Na[B(pz)_4]$ (0.66 g, 2.2 mmol) were placed in a round-bottomed flask. CH_2Cl_2 (10 mL) was added via syringe. The mixture was stirred at room temperature overnight and filtered. The solvent was evaporated under vacuum to yield a white solid (0.60 g, 0.89

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Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for **1**

	x	*y*	*z*	U^a
Sn	973.7 (12)	5861.4 (2)	9891.1 (8)	42.6 (2)
Cl	−1501 (5)	5302 (1)	11635 (3)	52 (1)
N(1)	−1661 (16)	6466 (3)	10888 (11)	45 (2)
N(2)	−2766 (17)	6829 (2)	9733 (10)	45 (2)
N(3)	−2637 (16)	5872 (2)	7653 (10)	42 (2)
N(4)	−3748 (14)	6314 (2)	7061 (9)	40 (2)
B	−2446 (26)	6792 (4)	7785 (15)	51 (4)
C(1)	−2402 (22)	6554 (3)	12410 (13)	52 (3)
C(2)	−4059 (23)	6967 (3)	12301 (13)	56 (3)
C(3)	−4259 (22)	7128 (3)	10578 (15)	57 (3)
C(4)	−4235 (18)	5518 (3)	6794 (11)	45 (3)
C(5)	−6473 (23)	5729 (4)	5660 (14)	58 (3)
C(6)	−6029 (21)	6230 (4)	5859 (13)	55 (3)

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

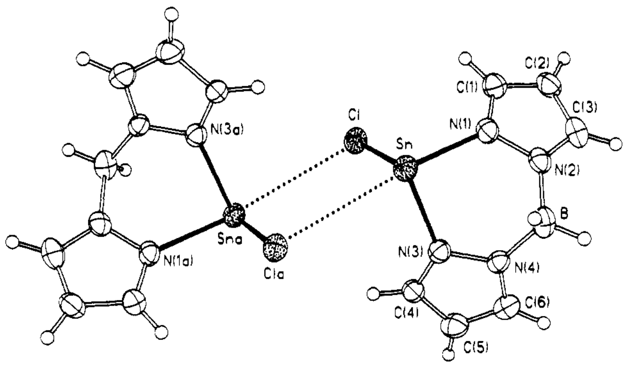


Figure 1. Molecular structure and labeling scheme for **1** drawn with 40% thermal ellipsoids.

mmol, 89%); mp 244–247 °C. ^{1}H NMR (CDCl$_3$; δ): 7.61, 7.25 (8, 8; d, d; J = 1.3, 2.2 Hz; 3-H, 5-H (pz)), 6.29 (8; t; J = 2.1 Hz, 4-H (pz)); (−80 °C (C_7D_8)) 7.98, 7.22, 6.96, 6.94, (2, 6, 2, 6; d, d, d, d; J = 1.8, 2.1, 1.8, 2.1 Hz, line narrowed; 3-H, 5-H (pz)), 6.15, 5.37 (2, 6; t, t; J = 1.8, 2.1 Hz, line narrowed; 4-H (pz)). ^{119}Sn NMR (CDCl$_3$; δ): −743 ($w_{1/2}$ = 150 Hz). The mass spectrum shows clusters for M$^+$ and M$^+$ − B(pz)$_4$ at *m/e* 678 and 399. Anal. Calcd for $C_{24}H_{24}N_{16}B_2Sn$: C, 42.53; H, 3.57. Found: C, 42.79; H, 3.58.

Crystallographic Analysis of 1 and 6. Crystal, data collection, and refinement parameters for **1** and **6** are collected in Table I. Colorless crystals, grown from toluene–hexane at 0 °C, were mounted on glass fibers with epoxy cement. The unit cell parameters were obtained from the least-squares fit of 25 reflections (20° ≤ 2θ ≤ 25°). Three standard reflections monitored every 197 reflections showed insignificant variations. A correction for a linear decay of 20% in reflection intensity for **1** was applied to the data. Empirical corrections for absorptions were applied (216 ψ-scan reflections, pseudoellipsoid model). The tin atom was located from Patterson syntheses. All hydrogen atoms were included as idealized isotropic contributions (d(CH) = 0.960 Å; U = 1.2U of attached atom). All non-hydrogen atoms were refined with anisotropic thermal parameters. All computer programs and the sources of the scattering factors are contained in the SHELXTL program library (5.1) (G. Sheldrick, Nicolet Corp., Madison, WI). Tables II and III contain the atomic coordinates and isotropic thermal parameters for **1** and **6**, respectively, and Tables IV and V contain selected bond distances and angles.

Results and Discussion

[H$_2$B(pz)$_2$]SnCl. The reaction of SnCl$_2$ with 1 equiv of K[H$_2$B(pz)$_2$] yields [H$_2$B(pz)$_2$]SnCl (**1**, eq 1). Complex **1** is a

$$SnCl_2 + K[H_2B(pz)_2] \rightarrow \underset{\mathbf{1}}{[H_2B(pz)_2]SnCl} + KCl \qquad (1)$$

high-melting solid that is soluble in aromatic solvents and halocarbon solvents but not in saturated hydrocarbon solvents. It is reasonably air stable as a solid, decomposing only slightly over several months, but rapidly decomposes in solution in air. Molecular weight studies for **1** in benzene solution yield an average value of 362, a value 20% higher than expected for a monomer (301), indicating possible oligomerization in solution.

Table III. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for **6**

	x	*y*	*z*	U^a
Sn	2502.9 (3)	1622.3 (2)	1683.9 (2)	36.1 (1)
N(1)	3118 (3)	384 (2)	1392 (2)	38 (1)
N(2)	2441 (3)	−250 (2)	1607 (2)	38 (1)
N(3)	579 (4)	878 (2)	1016 (3)	45 (1)
N(4)	237 (3)	236 (2)	1475 (2)	40 (1)
N(5)	1407 (3)	333 (2)	2880 (2)	40 (1)
C(7)	528 (5)	686 (3)	3349 (3)	60 (2)
N(7)	726 (4)	−972 (2)	2333 (3)	44 (1)
N(8)	250 (5)	−1489 (2)	1737 (3)	63 (2)
N(9)	3134 (3)	1847 (2)	338 (2)	36 (1)
N(10)	4076 (3)	2334 (2)	122 (2)	35 (1)
N(11)	4651 (4)	1731 (2)	1909 (2)	42 (1)
N(12)	5445 (3)	2184 (2)	1463 (2)	40 (1)
N(13)	4172 (4)	3391 (2)	1243 (2)	41 (1)
C(19)	4530 (6)	3924 (4)	1828 (4)	91 (3)
N(15)	6023 (4)	3121 (2)	321 (3)	46 (1)
N(16)	6891 (4)	2641 (3)	−43 (3)	66 (2)
B(1)	1183 (5)	−177 (3)	2067 (3)	38 (2)
B(2)	4937 (5)	2767 (3)	782 (3)	38 (2)
C(1)	4116 (4)	120 (3)	995 (3)	44 (2)
C(2)	4106 (5)	−679 (3)	956 (3)	52 (2)
C(3)	3027 (5)	−902 (3)	1349 (3)	45 (2)
C(4)	−438 (5)	1105 (3)	585 (3)	55 (2)
C(5)	−1425 (5)	611 (3)	743 (4)	61 (2)
C(6)	−964 (4)	82 (3)	1316 (3)	55 (2)
C(9)	1078 (6)	956 (3)	4084 (4)	70 (2)
C(8)	2308 (6)	761 (3)	4021 (3)	60 (2)
N(6)	2534 (4)	373 (2)	3299 (3)	53 (1)
C(10)	62 (5)	−2140 (3)	2179 (5)	68 (2)
C(11)	403 (5)	−2058 (3)	3032 (5)	73 (2)
C(12)	827 (5)	−1311 (3)	3108 (4)	60 (2)
C(13)	2531 (5)	1664 (3)	−393 (3)	48 (2)
C(14)	3076 (5)	2016 (3)	−1080 (3)	51 (2)
C(15)	4049 (4)	2434 (3)	−736 (3)	44 (2)
C(16)	5326 (5)	1363 (3)	2513 (3)	51 (2)
C(17)	6541 (5)	1577 (4)	2466 (4)	70 (2)
C(18)	6584 (5)	2089 (3)	1804 (4)	62 (2)
C(20)	3547 (5)	4323 (3)	2090 (4)	63 (2)
C(21)	2594 (6)	4003 (4)	1662 (4)	88 (3)
N(14)	2951 (4)	3432 (3)	1146 (4)	87 (2)
C(22)	7687 (5)	3121 (4)	−402 (4)	69 (2)
C(23)	7386 (6)	3876 (4)	−277 (4)	77 (2)
C(24)	6314 (5)	3867 (3)	171 (4)	63 (2)

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

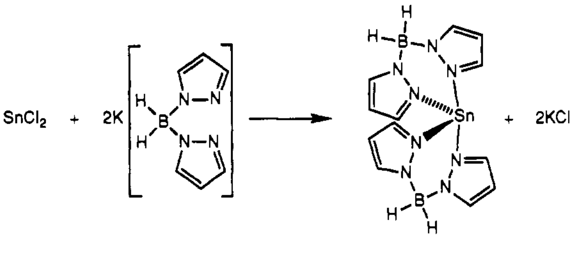
Table IV. Selected Bond Distances and Angles for **1**

(a) Bond Distances (Å)			
Sn–Cl	2.485 (3)	N(1)–N(2)	1.371 (10)
Sn–Cl(a)	3.390 (3)	N(3)–N(4)	1.359 (9)
Sn–N(1)	2.302 (8)	N(4)–B	1.506 (12)
Sn–N(3)	2.243 (7)	N(2)–B	1.548 (15)
(b) Bond Angles (deg)			
N(1)–Sn–N(3)	80.7 (3)	Sn–Cl–Sn(a)	107.6 (2)
Cl–Sn–N(1)	84.0 (2)	Sn–N(1)–N(2)	118.0 (6)
Cl–Sn–N(3)	92.0 (2)	Sn–N(3)–N(4)	119.0 (5)
Cl–Sn–Cl(a)	72.4 (2)	N(3)–N(4)–B	120.9 (7)
Cl(a)–Sn–N(1)	149.4 (2)	N(2)–B–N(4)	107.9 (8)
Cl(a)–Sn–N(3)	80.9 (3)		

In order to determine the degree of association in the solid state, a crystallographic analysis of **1** was carried out. Figure 1 shows an ORTEP drawing of the centrosymmetric dimeric unit observed in the solid phase. The two [H$_2$B(pz)$_2$]SnCl units are associated by extremely long bridging halide interactions of 3.390 (3) Å (Table IV). Given the normal Sn–Cl bonding distance of 2.485 (3) Å, the bridging interactions are very weak.

Excluding the weak bridging interaction, the geometry about tin is pyramidal, a geometry frequently observed in tin(II) structures.[7] The intraligand N(1)–Sn–N(3) bond angle is 80.7 (3)°, and the N–Sn–Cl angles are 84.0 (2) and 92.0 (2)°. The larger N–Sn–Cl angle is the one bisected by the weak bridging interaction, but the difference in the two angles is small. These bond angles are typical for pyramidal tin(II) complexes.[7] The tin(II) lone pair presumably occupies the remaining vertex of the pyramid. Finally, the six-membered BN_4Sn ring is in the shallow boat configuration generally observed for this ligand with a B···Sn distance of 3.292 (8) Å.[1]

$[H_2B(pz)_2]_2Sn$. A similar reaction of $SnCl_2$ with 2 equiv of $K[H_2B(pz)_2]$ yields $[H_2B(pz)_2]_2Sn$ (**2**, eq 2). Complex **2** is also a relatively high melting solid that is soluble in aromatic solvents and halocarbon solvents but not in saturated hydrocarbon solvents. Analogous to **1**, compound **2** is reasonably stable as a solid in air, but unlike **1**, it only slowly decomposes in solution.



(2)

2

An X-ray data set was collected on a marginal quality crystal of **2**. Although it did not prove possible to obtain a fully refined structure, the basic coordination geometry about Sn(II) was determined to be a distorted trigonal bipyramid (as pictured in eq 2) with the lone pair on tin presumably occupying an equatorial site. Each ligand occupies an axial and equatorial position, and the SnN_4B six-membered chelate rings are in the typical boat configuration.[1]

A similar structure in solution is supported by the variable-temperature ^1H NMR data of **2**. Three resonances are observed at ambient temperature, one for each of the three nonequivalent hydrogen atoms on the pyrazolyl rings. One of these resonances is already broad in the 500-MHz spectrum, and all three resonances broaden at lower temperatures. At −89 °C, each resonance type appears as two equal-intensity resonances. These changes with temperature for the resonance at δ 7.3 are shown in the left column of Figure 2. The low-temperature spectrum is as expected for the axial and equatorial pyrazolyl rings observed in the solid state. The barrier to equilibration of the pyrazolyl rings is 10.2 kcal/mol, measured at the coalescence temperature of −58 °C for the resonance shown in Figure 2.

An interesting feature of these NMR spectra is the BH_2 region, shown in the right column of Figure 2. At ambient temperature, the resonance is broad due to quadrupolar coupling and relaxation effects from the boron atom, but at low temperatures the boron becomes self-decoupled from the hydrogen atoms leading to sharper resonances.[12] At low temperatures, the BH_2 hydrogen atoms are nonequivalent, as expected for an axial and equatorial orientation in the boat configuration observed for the six-membered BN_4Sn ring of bidentate poly(pyrazolyl)borate ligands. Coalescence of the two resonances is observed at −52 °C (300 MHz). The insert shows the resonances for the BH_2 group at 500 MHz and −54 °C. At the higher field, coalescence will be at a higher temperature due to the greater separation of the resonances, but the effects of the self-decoupling are not dependent on field.[12] As observed, at 500 MHz the two resonances are still well-defined, demonstrating that the coalescence at 300 MHz is indeed due to a dynamic process and not the onset of line broadening from quadrupolar coupling. The process responsible for equilibration of the hydrogen atoms is a rapid boat–boat flip and associated ligand rearrangements of the six-membered ring. The barrier to this flip at −52 °C is calculated to be 10.3 kcal/mol. Barriers of this magnitude have been measured for a variety of η^2-$R_2B(pz)_2$ ligands,[13] but to our knowledge, this is the *first time the barrier has been determined for the parent, R = H, system.*

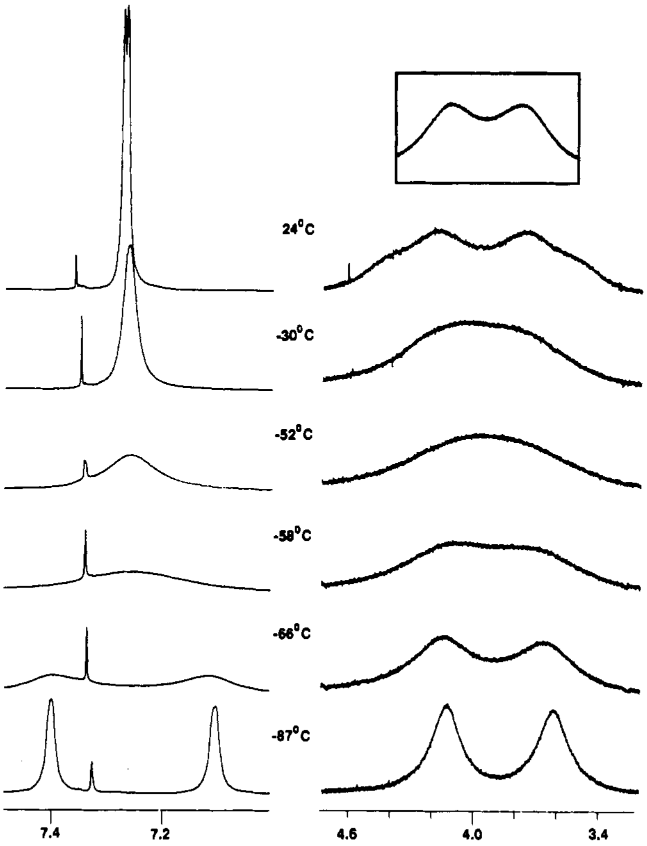
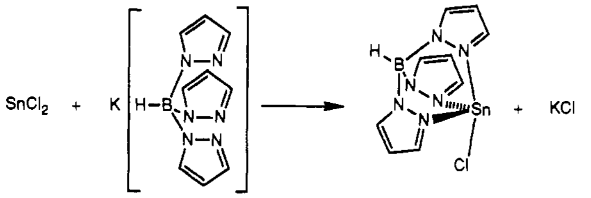


Figure 2. Variable-temperature ^1H spectra for **2** at 300 MHz. The left column pictures the central resonance of the three types of pyrazolyl ring hydrogen atoms at the indicated temperatures. The small resonance at δ 7.35 is due to a solvent impurity. The right column pictures the BH_2 resonances at an increased intensity. The insert is the BH_2 resonance at −54 °C measured at 500 MHz.

$[HB(pz)_3]SnCl$, $[HB(pz)_3]_2Sn$, and $[B(pz)_4]SnCl$. The reaction of $SnCl_2$ with 1 equiv of $K[HB(pz)_3]$ yields $[HB(pz)_3]SnCl$ (**3**, eq 3).



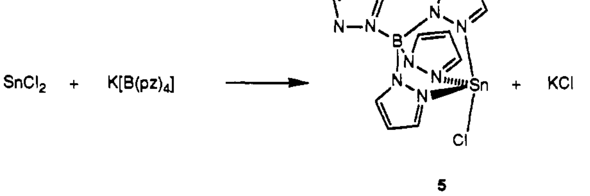
(3)

3

The reaction of $SnCl_2$ with 2 equiv of $K[HB(pz)_3]$ yields $[HB(pz)_3]_2Sn$ (**4**, eq 4).

$$SnCl_2 + 2K[HB(pz)_3] \rightarrow \underset{\mathbf{4}}{[HB(pz)_3]_2Sn} + 2KCl \quad (4)$$

Finally, the reaction of 1 equiv of $K[B(pz)_4]$ with $SnCl_2$ yields $[B(pz)_4]SnCl$ (**5**, eq 5).



(5)

5

All three complexes are high-melting solids that are soluble in aromatic solvents and halocarbon solvents but not in saturated hydrocarbon solvents. They are reasonably air stable as solids, decomposing only slightly over several months. In solution, **3** decomposes rapidly, **4** decomposes slowly, and **5** decomposes only very slowly in air.

The structures of complexes **3** and **5** are expected to be the typical trigonal bipyramid pictured in the equations with the lone

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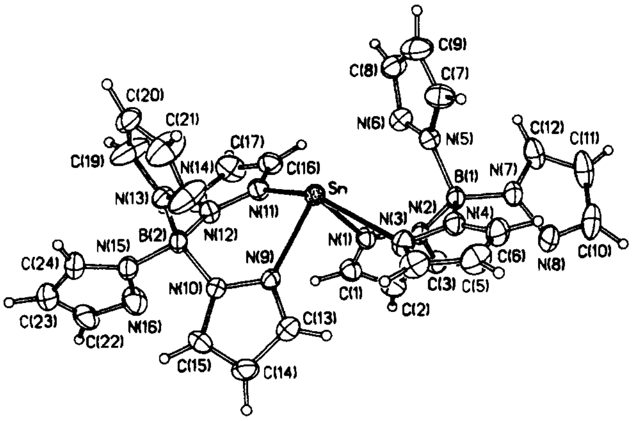

Figure 3. Molecular structure and labeling scheme for **6** drawn with 40% thermal ellipsoids.

pair in an equatorial site as described above for **2** and as determined crystallographically for $[HB(3,5\text{-}Me_2pz)_3]SnCl$.[8] Both complexes are fluxional at room temperature showing equivalent pyrazolyl rings. The barrier(s) to the processes which equilibrate the rings is(are) low because even for **5** only initial line broadening is observed at −89 °C.

The ^1H NMR spectrum of **4** shows all the rings as equivalent and does not change at low temperatures. Repeated attempts to obtain crystallographic quality crystals of **4** have proven unsuccessful.

$[B(pz)_4]_2Sn$. The compound $[B(pz)_4]_2Sn$ (**6**) was synthesized by the reaction of 2 equiv of $Na[B(pz)_4]$ with $SnCl_2$ (eq 6).

$$SnCl_2 + 2Na[B(pz)_4] \rightarrow \underset{\mathbf{6}}{[B(pz)_4]_2Sn} + 2NaCl \qquad (6)$$

Complex **6** is a very high melting solid, soluble in aromatic solvents and halocarbon solvents but not in saturated hydrocarbon solvents. It is air stable both as a solid and in solution.

Solid-State Structure of 6. Figure 3 shows an ORTEP drawing of **6**, and Table V shows selected bond distances and angles. The molecule is monomeric with no short intermolecular contacts. Surprisingly, each ligand is coordinated to the tin atom in only a bidentate fashion. The geometry about the tin atom is best described as a highly distorted trigonal bipyramid with the lone pair on tin occupying an equatorial site, somewhat analogous to the structure observed for **2**. Each ligand occupies an axial and equatorial site with the N–Sn–N bond angles formed by the chelate rings of 79.2 (1) and 79.0 (1)°. The equatorial N(1)–Sn–N(9) bond angle is 83.0 (1)°. The equatorial Sn–N(1) distance of 2.268 (3) Å and Sn–N(9) distance of 2.248 (3) Å are nearly equal. The axial N(3)–Sn–N(11) bond angle is 150.1 (1)°. The Sn–N(3) distance of 2.625 (4) Å and Sn–N(11) distance of 2.336 (4) Å are very different. The average of these axial bond distances is 2.480 (4) Å, considerably longer than the equatorial bond distances. Compression of the equatorial bond angle and shorter equatorial bond distances are general features of four-coordinate, pseudo trigonal bipyramidal tin(II) structures,[11] but the asymmetry in the two axial bond distances is very unusual and does not appear to arise from any close intramolecular contacts.

The six-membered BN_4Sn rings are arranged in shallow boat configurations with Sn···B distances of 3.581 (7) and 3.447 (7) Å. One of the noncoordinated pyrazolyl rings on each ligand is close to the tin atom with Sn···N(6) and Sn···N(14) distances of 3.299 (4) and 3.247 (4) Å. There is clearly not a bonding interaction because the planes of these pyrazolyl rings, the planes in which the lone pairs on the nitrogen atoms are located, are oriented oblique from the Sn–N vectors. Rotation of these rings so as to move the N(6) and/or N(14) atoms toward the tin atom would bring them into bonding range. We anticipated that one or possibly both ligands would be tridentate, especially considering that $[HB(3,5\text{-}Me_2pz)_3]_2Sn$[8] is five-coordinate with one tridentate and one bidentate ligand. There are no obvious contacts that would prevent coordination of either of these potential donor atoms, and numerous examples of the $B(pz)_4$ ligand acting as a tridentate ligand exist.[14] Two molecules in which the $B(pz)_4$ ligand coordinates in a bidentate manner where tridentate coordination may have been anticipated are $[\eta^2\text{-}B(pz)_4]Rh(\eta^4\text{-}1,5\text{-cyclooctadiene})$ and $[\eta^2\text{-}B(pz)_4]Rh(\eta^4\text{-norbornadiene})$.[15] As with **6**, there are no obvious steric reasons that prevent tridentate coordination in these two rhodium complexes. However, tridentate coordination is observed in the very similar molecule $[\eta^3\text{-}B(pz)_4]Rh(\eta^4\text{-}1,4\text{-duroquinone})$. Both tridentate and bidentate coordination of poly(pyrazolyl)borate ligands also have been observed in very similar platinum complexes.[16]

Table V. Selected Bond Distances and Angles for **6**

(a) Bond Distances (Å)			
Sn–N(1)	2.268 (3)	N(11)–N(12)	1.355 (5)
Sn–N(3)	2.625 (4)	N(9)–N(10)	1.360 (5)
Sn–N(9)	2.248 (3)	N(2)–B(1)	1.549 (6)
Sn–N(11)	2.336 (4)	N(4)–B(1)	1.531 (6)
N(1)–N(2)	1.354 (5)	N(10)–B(2)	1.556 (6)
N(3)–N(4)	1.365 (5)	N(12)–B(2)	1.548 (6)

(b) Bond Angles (deg)			
N(1)–Sn–N(3)	72.5 (1)	N(8)–N(7)–B(1)	120.9 (4)
N(1)–Sn–N(9)	83.0 (1)	N(9)–Sn–N(11)	79.0 (1)
N(1)–Sn–N(11)	79.2 (1)	N(9)–N(10)–B(2)	124.4 (3)
N(1)–N(2)–B(1)	122.0 (3)	N(10)–B(2)–N(12)	109.9 (3)
N(2)–B(1)–N(4)	109.6 (4)	N(10)–B(2)–N(13)	108.9 (4)
N(2)–B(1)–N(5)	107.5 (4)	N(10)–B(2)–N(15)	109.5 (4)
N(2)–B(1)–N(7)	110.3 (4)	N(11)–N(12)–B(2)	120.1 (3)
N(3)–Sn–N(9)	88.0 (1)	N(12)–B(2)–N(13)	108.2 (4)
N(3)–Sn–N(11)	150.1 (1)	N(12)–B(2)–N(15)	108.6 (4)
N(3)–N(4)–B(1)	120.2 (4)	N(13)–B(2)–N(15)	111.8 (4)
N(4)–B(1)–N(5)	108.7 (4)	Sn–N(1)–N(2)	122.6 (3)
N(4)–B(1)–N(7)	111.4 (4)	Sn–N(3)–N(4)	113.7 (3)
N(5)–N(6)–B(1)	122.5 (4)	Sn–N(9)–N(10)	125.3 (2)
N(5)–B(1)–N(7)	109.2 (4)	Sn–N(11)–N(12)	127.0 (3)

Variable-Temperature NMR Data of 6. The ambient-temperature ^1H NMR spectrum (Figure SI (supplementary material)) of **6** shows three resonances, one for each of the three types of hydrogen atoms in the pyrazolyl rings. At −80 °C, each resonance type has split into two resonances with *3/1 integrated intensities*. Appropriate line broadening is observed at intermediate temperatures with a barrier to the fluxional process of 10.5 kcal/mol, as calculated from the coalescence at −43 °C of the upfield resonance. This 3/1 pattern is surprising given the solid-state structure.

An interpretation of these data can be made on the basis of the solid-state structure. In this structure, all eight pyrazolyl rings are nonequivalent. Nevertheless, the 3/1 integrated intensity of the two resonances observed for each type of ring hydrogen atom at −80 °C can be explained if a low-energy process equilibrates the three rings in each ligand that are "close" to the tin. Such a process would involve the coordination of the pyrazolyl ring nitrogen donor atom that is ca. 3.3 Å away from the tin with dissociation of one of the coordinated rings (A → B), presumably through a five-coordinate intermediate. A five-coordinate intermediate is clearly reasonable given the solid-state structure of

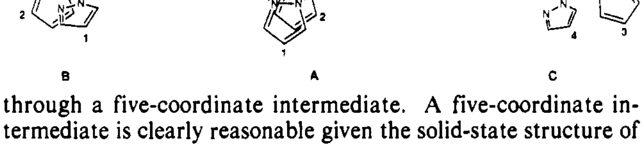

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Table VI. Tin-119 NMR Data in $CDCl_3$

compd	chem shift, δ	compd	chem shift, δ
$[H_2B(pz)_2]SnCl$ (**1**)	−307	$[H_2B(pz)_2]_2Sn$ (**2**)	−652
$[B(pz)_4]SnCl$ (**5**)	−528	$[B(pz)_4]_2Sn$ (**6**)	−743
$[HB(3,5\text{-}Me_2pz)_3]SnCl$	−567	$[HB(pz)_3]_2Sn$ (**4**)	−877
$[HB(pz)_3]SnCl$ (**3**)	−569	$[HB(3,5\text{-}Me_2pz)_3]_2Sn$	−934

$[HB(3,5\text{-}Me_2pz)_3]_2Sn$. Repetition of this process for the three close rings of each ligand (rings 1, 2, and 3) would equilibrate these six rings but leave the remaining two rings (rings 4) unique. If this mechanism is correct, it is unusual to have such a *low barrier for a bond making–bond breaking process* such that no line broadening is observed at −80 °C.

One ring on each ligand remains unique if the six-membered BN_4Sn rings do not undergo a rapid boat–boat flip. Such a ring flip (A → C) coupled with the A → B process equilibrates all of the pyrazolyl rings. This process would explain the equilibration of all eight rings observed in the ambient-temperature ^1H NMR spectrum. The measured barrier to the ring-flip fluxional process observed for complex **6** of 10.5 kcal/mol is similar to the value observed for the ring flip in **2** and is the same as that measured for the equilibration of the noncoordinated pyrazolyl rings in $[\eta^2\text{-}B(pz)_4]MoCp(CO)_2$, a barrier also attributed to the boat–boat flip of the six-membered ring.[13b]

It is also possible that the solution structure is different from that observed in the solid state. Other examples of poly(pyrazolyl)borate complexes in which the coordination number is proposed to be higher in solution than in the solid state are known.[15,16] For example, $[B(pz)_4]Rh(\eta^4\text{-}1,5\text{-cyclooctadiene})$ is four-coordinate in the solid state with a bidentate tetrakis(pyrazolyl)borate ligand but demonstrates variable-temperature ^1H NMR spectra very similar to that of **6**. It was proposed that in solution the ligand is tridentate, forming a five-coordinate complex analogous to the structure actually observed in the solid state for $[B(pz)_4]Rh(\eta^4\text{-}1,4\text{-duroquinone})$.[15] The NMR data for **6** can be explained by a five-coordinate solution geometry via a process similar to that shown above, through either a four-coordinate intermediate (formed from dissociation of a pyrazolyl ring from the tridentate ligand) or through a six-coordinate intermediate (formed by association of a pyrazolyl ring from the bidentate ligand). A six-coordinate solution structure that has parallel faces of the N_3 donor atoms of each ligand or one of lower symmetry that was fluxional so as to equilibrate the coordinated pyrazolyl rings is also possible. In all cases, the boat–boat flip of a bidentate ligand is a reasonable explanation for the equilibration of all four pyrazolyl rings observed at higher temperatures.

The interpretations of the ^1H NMR data from either a four-, five-, or six-coordinate ground-state geometry are all very similar. At −80 °C, the three close or coordinated rings from each ligand equilibrate fast on the NMR time scale, and at higher temperatures, the unique ring equilibrates with the other three by a boat–boat flip of the six-membered ring.

Tin-119 NMR Spectroscopy. In an attempt to determine the coordination number of the tin atom in **4** and **6** in solution, we have measured the ^{119}Sn chemical shifts of all the complexes reported here (Table VI). In general, the resonances have a half-height width of ca. 400 Hz, but those for **1**, **4**, and **5** are much broader. For both **1** and **4**, the half-height widths narrow considerably at −58 °C, but that for **5** remains broad. Also reported are the chemical shifts of $[HB(3,5\text{-}Me_2pz)_3]_2Sn$ and $[HB(3,5\text{-}Me_2pz)_3]SnCl$.[17] Structural correlations using ^{119}Sn NMR spectroscopy have been useful in tin(IV) chemistry,[18] but only limited information, mainly of metallocene complexes, has been reported for tin(II).[19]

With the measurement of the chemical shifts for only eight complexes, only tentative conclusions can be made from these data. The chemical shifts of the four-coordinate chlorotin complexes **3**, **5**, and $[HB(3,5\text{-}Me_2pz)_3]SnCl$ are all fairly similar. Three-coordinate **1** is over 200 ppm downfield from these values, clearly distinguishing it from the four-coordinate chlorotin complexes. Four-coordinate **2**, containing no chloride ligand, resonates ca. 100 ppm upfield from the four-coordinate chlorotin complexes.

The remaining three complexes can potentially be four-, five-, or six-coordinate in solution. $[HB(3,5\text{-}Me_2pz)_3]_2Sn$, shown to be five-coordinate in the solid phase, has the most shielded resonance. **6**, shown to be four-coordinate in the solid phase, has the most deshielded resonance of the three, located 91 ppm to higher field than four-coordinate **2**. **4** resonates between **6** and $[HB(3,5\text{-}Me_2pz)_3]_2Sn$ but much closer to the latter (57 vs 134 ppm). It is reasonable to interpret these data as indicating that **2** and **6** are four-coordinate in solution as observed in the solid phase and **4** and $[HB(3,5\text{-}Me_2pz)_3]_2Sn$ are five-coordinate in solution, but more data on tin(II) complexes are needed to verify these conclusions.

Conclusion

The complete series of complexes $[H_nB(pz)_{4-n}]_mSnCl_{2-m}$, where n = 0, 1, and 2 and m = 1 and 2, have been prepared and characterized. $[H_2B(pz)_2]SnCl$ (**1**) is basically-three coordinate in the solid phase with very weak Sn–Cl bridging interactions. $[H_2B(pz)_2]_2Sn$ (**2**) has the expected trigonal-bipyramidal geometry with the tin(II) lone pair presumably occupying an equatorial vertex. The six-membered SnN_4B rings formed by each ligand are fluxional at room temperature undergoing a boat–boat flip. The barrier to this process has been measured to be 10.3 kcal/mol. $[HB(pz)_3]SnCl$ (**3**) and $[B(pz)_4]SnCl$ (**5**) have a structure similar to that of **2** and are fluxional in solution, with ^1H NMR showing the pyrazolyl rings as equivalent even at low temperatures. The structure of $[HB(pz)_3]_2Sn$ has not been determined, but ^{119}Sn NMR data indicate that it is probably five-coordinate in solution. $[B(pz)_4]_2Sn$ (**6**) is four-coordinate in the solid phase with a highly distorted pseudo trigonal bipyramidal structure. ^{119}Sn NMR spectroscopy indicates **6** probably retains this coordination number in solution. **6** is also fluxional in solution, with ^1H NMR showing equivalent rings at ambient temperature and a 3/1 pattern at −80 °C. These low-temperature NMR data can be explained by a process that for each ligand equilibrates three of the rings that are close to the tin atom, but the fourth ring remains unique because the boat–boat flip of the six-membered ring is slow on the NMR time scale. At room temperature, this flip is fast, equilibrating all of the pyrazolyl rings.

Acknowledgment is made to the National Science Foundation and the University of South Carolina for support through the EPSCoR program (Grant RII-8922165). The NSF (Grants CHE-8411172 and CHE-8904942) and NIH (Grant RR-02425) have supplied funds to support NMR equipment, and the NIH (Grant RR-02849) has supplied funds to support mass spectroscopy equipment.

Supplementary Material Available: Tables SI–SIX, listing crystallographic data, complete bond distances and angles, anisotropic thermal parameters, and positional parameters of H atoms, and Figure SI, showing NMR spectra of **6** (9 pages); Tables SX and SXI, listing structure factor amplitudes (32 pages). Ordering information is given on any current masthead page.

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(17) The ^{119}Sn chemical shift data for $[HB(3,5\text{-}Me_2pz)_3]_2Sn$ and $[HB(3,5\text{-}Me_2pz)_3]SnCl$ are reported in ref 8 in CD_2Cl_2. Our measured value in $CDCl_3$ for $[HB(3,5\text{-}Me_2pz)_3]_2Sn$ is very close to the reported value (δ −935) in ref 8 but very different from the reported value (δ −1460) for $[HB(3,5\text{-}Me_2pz)_3]SnCl$. Given the data for the analogous compounds **3** and **5** in Table VI, the value reported in ref 8 is certainly incorrect. A foldover resonance at this value would be observed if the low-field edge of the acquisition window was set at ca. −1000 ppm. The values in Table VI were confirmed by acquiring spectra at various window settings.

(18) Davies, A. G.; Smith, P. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Able, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 2, p 399.

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