

## BIS- AND TRIS-(PYRAZOLYL)BORATE COMPLEXES OF METHYLTIN CHLORIDES AND THE X-RAY STRUCTURE OF FIVE-COORDINATE [BIS(PYRAZOLYL)BORATE]CHLORODIMETHYLTIN(IV)

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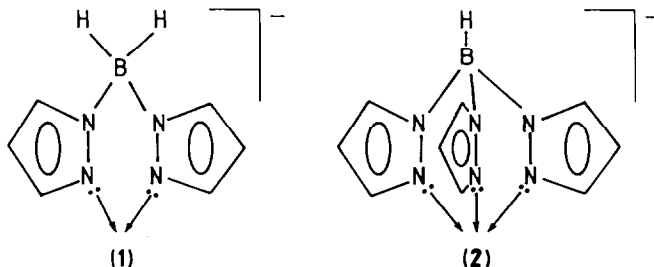
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### Summary

The two series of complexes, five-coordinate  $\text{Me}_n\text{Cl}_{3-n}\text{Sn}[(\text{pz})_2\text{BH}_2]$  and six-coordinate  $\text{Me}_n\text{Cl}_{3-n}\text{Sn}[(\text{pz})_3\text{BH}]$  ( $\text{pz}$  = 1-pyrazolyl,  $n = 0-3$ ) have been prepared from the appropriate methyltin chlorides and  $\text{K}[(\text{pz})_2\text{BH}_2]$  or  $\text{K}[(\text{pz})_3\text{BH}]$  in dichloromethane. The complexes have been fully characterised by infrared and mass spectroscopy and by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR where solubility permitted. The X-ray crystal structure of  $\text{Me}_2\text{ClSn}[(\text{pz})_2\text{BH}_2]$  shows a distorted trigonal-bipyramidal tin atom with a pyrazolyl-nitrogen and a chlorine atom in the axial sites.

### Introduction

Since their introduction by Trofimenko the bis- and tris-(pyrazolyl)borate ligands  $[(\text{pz})_2\text{BH}_2]^-$  (1) and  $[(\text{pz})_3\text{BH}]^-$  (2) have been widely used to prepare complexes of



the transition metals in high and low oxidation states, and a variety of interesting chemistry has resulted [1]. In contrast there appears to have been virtually no development of Main Group chemistry involving the pyrazolyl-borate ligands. Our earlier report of the preparation of  $\text{Me}_3\text{Sn}[(\text{pz})_3\text{BH}]$  and the confirmation by an X-ray crystal structure analysis that it incorporated a six-coordinate tri-alkyl-tin

group is the only previous work that we are aware of on Group IV elements with these ligands [2]. Tin was chosen as the metal for our initial studies because the wide diversity of coordination geometries found for tin complexes [3] suggested the versatile bonding properties of the pyrazolyl-borate ligands **1** and **2** could be fully exploited.

This paper describes the preparation and characterisation of the two series of complexes  $\text{Me}_n\text{Cl}_{3-n}\text{Sn}[(\text{pz})_2\text{BH}_2]$  and  $\text{Me}_n\text{Cl}_{3-n}\text{Sn}[(\text{pz})_3\text{BH}]$  ( $n = 0-3$ ), and the structure of  $\text{Me}_2\text{ClSn}[(\text{pz})_2\text{BH}_2]$ .

## Experimental

All reactions were conducted under a dry nitrogen atmosphere using standard Schlenk techniques. Infrared spectra were recorded on a Shimadzu IR-27G spectrometer as KBr discs and NMR spectra with a JEOL FX90Q machine, in  $\text{CDCl}_3$  when solubility permitted; chemical shifts are reported relative to TMS for  $^1\text{H}$  and  $^{13}\text{C}$  and to  $\text{Me}_4\text{Sn}$  for  $^{119}\text{Sn}$ . Mass spectra were run on a Varian CH5 spectrometer. Microanalyses were conducted by the Microanalytical Service, University of Otago. The methyltin halides were prepared by literature routes [4], as were the ligands  $\text{K}[(\text{pz})_2\text{BH}_2]$  and  $\text{K}[(\text{pz})_3\text{BH}]$  [5]. The synthesis of  $\text{Me}_3\text{Sn}[(\text{pz})_3\text{BH}]$  has been reported previously [2].

*Preparation of  $\text{Cl}_3\text{Sn}[(\text{pz})_3\text{BH}]$  (3).* Solid  $\text{K}[(\text{pz})_3\text{BH}]$  (1.0 g, 4.0 mmol) was added to  $\text{SnCl}_4$  (1.0 g, 4.4 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 ml). After vigorous stirring for 90 min the solvent was evaporated and the residue transferred to a Soxhlet apparatus and extracted for 3 d with  $\text{CH}_2\text{Cl}_2$ . The extract was concentrated and cooled to give white crystals of  $\text{Cl}_3\text{Sn}[(\text{pz})_3\text{BH}]$ , 1.33 g, 77%, m.p.  $> 300^\circ\text{C}$ . Found: C, 24.53; H, 2.45; N, 18.99.  $\text{C}_9\text{H}_{10}\text{BCl}_3\text{N}_6\text{Sn}$  calcd.: C, 24.68; H, 2.28; N, 19.18%;  $m/z$  437,  $P^+$ .  $\nu(\text{B-H})$  2510  $\text{cm}^{-1}$ .

*Preparation of  $\text{MeCl}_2\text{Sn}[(\text{pz})_3\text{BH}]$  (4).*  $\text{MeSnCl}_3$  (1.33 g, 5.5 mmol) and  $\text{K}[(\text{pz})_3\text{BH}]$  (1.39 g, 5.5 mmol) were combined in  $\text{CH}_2\text{Cl}_2$  (20 ml). After 30 min the mixture was filtered and evaporated. The residue was extracted with  $\text{CH}_2\text{Cl}_2$  ( $4 \times 10$  ml) and the combined extracts concentrated to ca. 10 ml. Hexane (10 ml) was carefully added and the mixture cooled to give white crystals of  $\text{MeCl}_2\text{Sn}[(\text{pz})_3\text{BH}]$ , 0.89 g, 68%, m.p.  $> 300^\circ\text{C}$ . Found: C, 30.80; H, 3.99; N, 17.1.  $\text{C}_{10}\text{H}_{13}\text{BCl}_2\text{N}_6\text{Sn}$  calcd.: C, 30.74; H, 3.76; N, 18.5%.  $\nu(\text{B-H})$  2450  $\text{cm}^{-1}$ .

*Preparation of  $\text{Me}_2\text{ClSn}[(\text{pz})_3\text{BH}]$  (5).*  $\text{Me}_2\text{SnCl}_2$  (1.72 g, 7.8 mmol) and  $\text{K}[(\text{pz})_3\text{BH}]$  (1.96 g, 7.8 mmol) were stirred together in  $\text{CH}_2\text{Cl}_2$  (20 ml) for 30 min. After filtration and concentration, hexane was added and the mixture cooled to  $-10^\circ\text{C}$  to give colourless rods of  $\text{Me}_2\text{ClSn}[(\text{pz})_3\text{BH}]$ , 3.1 g, 67%, m.p.  $166-170^\circ\text{C}$ . Found: C, 34.95; H, 4.39; N, 19.28.  $\text{C}_{11}\text{H}_{16}\text{BClN}_6\text{Sn}$  calcd.: C, 35.88; H, 4.97; N, 18.91%.  $\nu(\text{B-H})$  2520  $\text{cm}^{-1}$ .

*Preparation of  $\text{I}_3\text{Sn}[(\text{pz})_3\text{BH}]$  (6).*  $\text{SnI}_4$  (1.24 g, 1.98 mmol) was added to a stirred suspension of  $\text{K}[(\text{pz})_3\text{BH}]$  (0.5 g, 1.98 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 ml). After 10 min the yellow suspension was filtered, washed with water to remove KI, and dried under vacuum to give yellow  $\text{I}_3\text{Sn}[(\text{pz})_3\text{BH}]$ , 1.01 g, 70%, m.p.  $> 300^\circ\text{C}$ . Found: C 14.45; H, 1.37; N, 11.18.  $\text{C}_9\text{H}_{10}\text{BI}_3\text{N}_6\text{Sn}$  calcd.: C, 15.51; H, 1.40; N, 11.97%.  $\nu(\text{B-H})$  2530  $\text{cm}^{-1}$ .

*Preparation of  $\text{Cl}_3\text{Sn}[(\text{pz})_2\text{BH}_2]$  (7).* To  $\text{SnCl}_4$  (0.95 g, 3.65 mmol) was added  $\text{CH}_2\text{Cl}_2$  (20 ml) and  $\text{K}[(\text{pz})_2\text{BH}_2]$  (0.68 g, 3.65 mmol). After vigorous stirring for 2

h the solvent was evaporated and the residue transferred to a Soxhlet apparatus and extracted with  $\text{CH}_2\text{Cl}_2$ . White feather-like crystals of  $\text{Cl}_3\text{Sn}[(\text{pz})_2\text{BH}_2]$  were thus obtained, 1.17 g, 83%, m.p. 120–123°C. Found: C, 20.58; H, 3.03; N, 14.72.  $\text{C}_6\text{H}_8\text{BCl}_3\text{N}_4\text{Sn}$  calcd.: C, 19.38; H, 2.15; N, 15.06%.  $\nu(\text{B-H})$  2427, 2490  $\text{cm}^{-1}$ .

*Preparation of  $\text{MeCl}_2\text{Sn}[(\text{pz})_2\text{BH}_2]$  (8).*  $\text{MeSnCl}_3$  (1.38 g, 5.78 mmol) and  $\text{K}[(\text{pz})_2\text{BH}_2]$  (1.07 g, 5.8 mmol) were reacted in  $\text{CH}_2\text{Cl}_2$  for 15 min. The mixture was filtered, concentrated and cooled to give white crystals of  $\text{MeCl}_2\text{Sn}[(\text{pz})_2\text{BH}_2]$ , 0.45 g, 63%, m.p. 86–92°C. Found: C, 21.55; H, 3.15; N, 15.11.  $\text{C}_7\text{H}_{11}\text{BCl}_2\text{N}_4\text{Sn}$  calcd.: C, 23.92; H, 3.13; N, 15.93%.  $\nu(\text{B-H})$  2400, 2450  $\text{cm}^{-1}$ .

*Preparation of  $\text{Me}_2\text{ClSn}[(\text{pz})_2\text{BH}_2]$  (9).*  $\text{Me}_2\text{SnCl}_2$  (0.76 g, 3.4 mmol) was reacted with  $\text{K}[(\text{pz})_2\text{BH}_2]$  (0.65 g, 3.4 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 ml) for 12 min. The solution was filtered, concentrated to ca. 5 ml and an equal volume of hexane added. Colourless crystals of  $\text{Me}_2\text{ClSn}[(\text{pz})_2\text{BH}_2]$  were obtained, 0.60 g, 52%, m.p. 83–87°C. Found: C, 28.31; H, 4.26; N, 16.52.  $\text{C}_8\text{H}_{14}\text{BClN}_4\text{Sn}$  calcd.: C, 29.02; H, 4.32; N, 16.92%.  $\nu(\text{B-H})$  2250, 2390, 2410  $\text{cm}^{-1}$ .

*Preparation of  $\text{Me}_3\text{Sn}[(\text{pz})_2\text{BH}_2]$  (10).*  $\text{Me}_3\text{SnCl}$  (1.42 g, 7.2 mmol) and  $\text{K}[(\text{pz})_2\text{BH}_2]$  (7.2 mmol) were stirred in  $\text{CH}_2\text{Cl}_2$  (20 ml) for 15 min. The mixture was filtered and evaporated to give a viscous oil which could not be crystallised but was characterised spectroscopically as  $\text{Me}_3\text{Sn}[(\text{pz})_2\text{BH}_2]$ .  $\nu(\text{B-H})$  2290, 2354, 2440  $\text{cm}^{-1}$ .

#### *X-Ray crystal structure of $\text{Me}_2\text{ClSn}[(\text{pz})_2\text{BH}_2]$*

An irregular fragment was chipped from a large block-shaped crystal obtained from  $\text{CH}_2\text{Cl}_2$ /hexane. Preliminary precession photography indicated orthorhombic symmetry. Lattice parameters were determined using 25 high-angle reflections accurately centred on a Nicolet P3 diffractometer with monochromated  $\text{Mo-K}_\alpha$  X-radiation ( $\lambda$  0.7107 Å).

*Crystal data.*  $\text{C}_8\text{H}_{14}\text{N}_4\text{B}_2\text{ClSn}$ ,  $M = 331.82$ , Orthorhombic, space group  $Pbca$ ,  $a$  26.880(6),  $b$  6.875(2),  $c$  13.761(3) Å,  $U$  2541.3 Å<sup>3</sup>.  $D_c$  1.73 g  $\text{cm}^{-3}$  for  $Z = 8$ .

TABLE 1

FINAL POSITIONAL PARAMETERS FOR  $\text{Me}_2\text{ClSn}[(\text{pz})_2\text{BH}_2]$

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Sn	0.08316(1)	0.80465(6)	0.48341(3)
Cl	0.0140(1)	0.8862(3)	0.3703(1)
C(1)	0.0382(2)	0.6493(10)	0.5825(5)
C(2)	0.1142(3)	1.0856(10)	0.4834(5)
N(11)	0.1952(2)	0.6255(8)	0.5143(3)
N(12)	0.1526(2)	0.6729(7)	0.5619(3)
C(13)	0.1582(2)	0.6159(10)	0.6539(4)
C(14)	0.2046(3)	0.5361(10)	0.6666(5)
C(15)	0.2269(3)	0.5425(10)	0.5766(5)
N(21)	0.1568(2)	0.5664(7)	0.3531(3)
N(22)	0.1079(2)	0.6157(7)	0.3674(3)
C(23)	0.0805(2)	0.5060(9)	0.3082(4)
C(24)	0.1103(3)	0.3851(10)	0.2546(4)
C(25)	0.1585(3)	0.4296(10)	0.2852(4)
B	0.2002(3)	0.6743(13)	0.4059(5)

TABLE 2

SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR  $\text{Me}_2\text{ClSn}[(\text{pz})_2\text{BH}_2]$ 

Sn-Cl	2.488(2)	C(23)-N(22)	1.333(7)
Sn-C(1)	2.112(6)	C(15)-N(11)	1.337(7)
Sn-C(2)	2.103(7)	C(25)-N(21)	1.327(8)
Sn-N(12)	2.339(5)	C(13)-C(14)	1.373(8)
Sn-N(22)	2.164(5)	C(23)-C(24)	1.371(9)
N(11)-N(12)	1.358(6)	C(14)-C(15)	1.376(9)
N(21)-N(22)	1.370(6)	C(24)-C(25)	1.395(9)
C(13)-N(12)	1.334(7)	N(11)-B	1.534(8)
N(21)-B	1.562(8)		
C(1)-Sn-Cl	95.2(2)	N(12)-Sn-N(22)	82.1(2)
C(2)-Sn-C(1)	133.7(3)	C(2)-Sn-Cl	95.1(2)
N(12)-Sn-Cl	166.5(1)	N(11)-B-N(21)	106.4(5)
N(22)-Sn-Cl	84.5(1)	Sn-N(12)-N(11)	122.9(3)
N(12)-Sn-C(1)	87.9(2)	Sn-N(22)-N(21)	123.3(4)
N(12)-Sn-C(2)	92.3(2)	B-N(11)-N(12)	119.4(5)
N(22)-Sn-C(1)	110.4(2)	B-N(21)-N(22)	112.2(5)
N(22)-Sn-C(2)	115.4(2)		

$F(000) = 1296$ ,  $\mu(\text{Mo-K}\alpha) 20 \text{ cm}^{-1}$ ,  $T 23^\circ\text{C}$ . A total of 1673 unique reflections in the range  $3^\circ < 2\theta < 45^\circ$  were collected. After correction for Lorentz, polarisation and absorption effects 1289 had  $I > 2\sigma(I)$  and were used in all calculations.

The structure was solved routinely by direct methods. In the final cycles of full-matrix least-squares refinement non-hydrogen atoms were assigned anisotropic temperature factors while hydrogen atoms were included in calculated positions

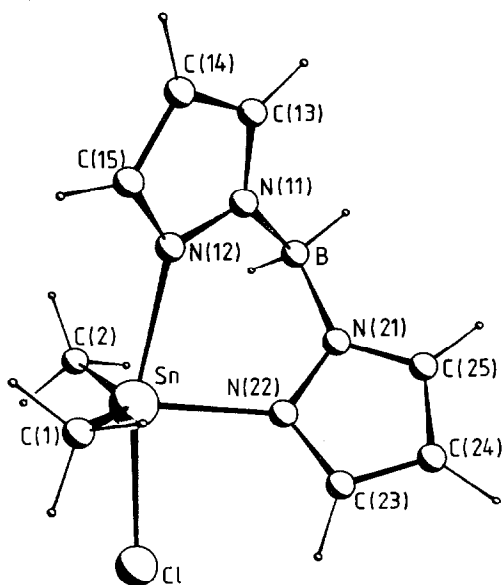
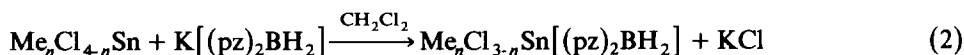
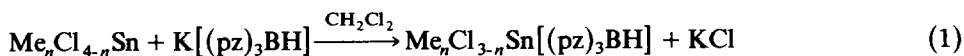


Fig. 1. A view of the structure of  $\text{Me}_2\text{ClSn}[(\text{pz})_2\text{BH}_2]$  emphasising the distorted trigonal-bipyramidal geometry of the tin atom, and showing the atom labelling scheme.

with common isotropic temperature factors for each type. Final  $R = R_w = 0.029$  where  $w = [\sigma^2(F) + 0.002F^2]^{-1}$ . Calculations were performed using the SHELX76 set of programs [6]. Final positional parameters are given in Table 1, selected bond parameters in Table 2, and the structure and atom labelling scheme shown in Fig. 1.

## Results and discussion

The 1 : 1 reactions of the methyltin chlorides with  $K[(pz)_3BH]$  or  $K[(pz)_2BH_2]$  in  $CH_2Cl_2$  are quite rapid and clean, giving the appropriate complexes in good yields (eqs. 1,2).



The trichloro derivatives **3** and **7** were only sparingly soluble in organic solvents and were best purified by Soxhlet extraction, while the methylated derivatives were all sufficiently soluble in  $CH_2Cl_2$  to be recrystallised to give the pure complexes. The tri-iodo complex  $I_3Sn[(pz)_3BH]$  was sufficiently stable to hydrolysis to be separated from the co-product KI by washing with water.

The complexes **3–10** are all indefinitely stable in the solid state under an inert atmosphere, but the tri- and di-methyl derivatives showed some deterioration when exposed to air for several hours, while the mono-methyl and trichloro complexes were much less affected. The  $Me_3Sn[(pz)_3BH]$  complex was unstable in  $CHCl_3$

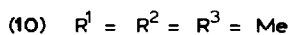
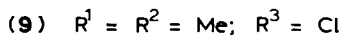
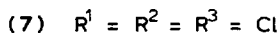
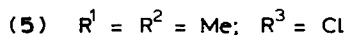
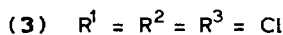
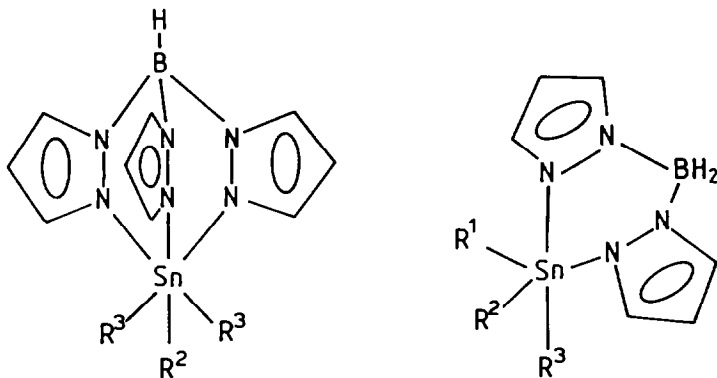


TABLE 3

NMR DATA FOR  $\text{Me}_{3-n}\text{Cl}_n\text{Sn}[(\text{pz})_3\text{BH}]$  AND  $\text{Me}_{3-n}\text{Cl}_n\text{Sn}[(\text{pz})_2\text{BH}_2]$  <sup>a</sup>

Complex	<sup>1</sup> H NMR			<sup>13</sup> C NMR				<sup>119</sup> Sn NMR
	CH <sub>3</sub>	4-H	3,5-H	CH <sub>3</sub>	C <sup>4</sup>	C <sup>3</sup>	C <sup>5</sup>	
Me <sub>3</sub> Sn[(pz) <sub>3</sub> BH]	0.34	6.16	7.59	-11.0	105.2	134.7	138.9	-194.6
Me <sub>2</sub> ClSn[(pz) <sub>3</sub> BH]	0.83	6.24	7.60, 7.81	15.1	104.9	134.6	139.1	-333.6
MeCl <sub>2</sub> Sn[(pz) <sub>3</sub> BH]	1.37	6.34	7.73, 7.93					
Me <sub>3</sub> Sn[(pz) <sub>2</sub> BH <sub>2</sub> ]	0.54	6.23	7.26, 7.61					-105.0
Me <sub>2</sub> ClSn[(pz) <sub>2</sub> BH <sub>2</sub> ]	1.30	6.36	7.69, 7.97	10.12	105.0	137.6	139.1	-181.7
Me <sub>3</sub> SnCl	0.66							+164
Me <sub>2</sub> SnCl <sub>2</sub>	1.24							+141
MeSnCl <sub>3</sub>	1.68							+20

<sup>a</sup> In CDCl<sub>3</sub>. δ in ppm; chemical shifts are from Me<sub>4</sub>Si (<sup>1</sup>H, <sup>13</sup>C) and Me<sub>4</sub>Sn (<sup>119</sup>Sn).

solution, even under nitrogen, with free pyrazole being produced over a few hours, as indicated by NMR spectroscopy and confirmed by gas chromatography of the resulting solution; a rather unusual cleavage of a B-N bond of the pyrazolyl-borate ligand is apparently occurring. The fate of the tin was not determined.

The infra-red spectra of the complexes show the expected peaks. The tris(pyrazolyl)borate complexes show a sharp  $\nu(\text{B-H})$  absorption at ca. 2500 cm<sup>-1</sup> while the bis(pyrazolyl)borate analogues show a complex band at ca. 2400 cm<sup>-1</sup> for the BH<sub>2</sub> group [7]. There appears to be no systematic shift in these frequencies along either series of complexes.

The NMR data for the compounds sufficiently soluble for study are given in Table 3. For the <sup>1</sup>H NMR the assignment of the 3,5 H signals was not attempted since it is not straightforward [7,8]. The <sup>1</sup>H and <sup>13</sup>C NMR parameters are unremarkable, showing the expected shifts with changes in the Me/Cl substitution on the tin atom. In the six-coordinate species MeCl<sub>2</sub>Sn[(pz)<sub>3</sub>BH] and Me<sub>2</sub>ClSn[(pz)<sub>3</sub>BH] the pyrazolyl rings are not all equivalent in the static structures but there was no sign of splitting of the signals in the <sup>1</sup>H or <sup>13</sup>C NMR spectra, suggesting rapid equilibration in solution. Similarly the five-coordinate complexes Me<sub>3-n</sub>Cl<sub>n</sub>Sn[(pz)<sub>2</sub>BH<sub>2</sub>] showed no splitting of the pyrazolyl signals despite the inequivalence of the two rings arising from the axial-equatorial occupancy by the ligand (see below); again fluxionality is not unexpected.

More useful information comes from the <sup>119</sup>Sn spectra. For the R<sub>3</sub>Sn[(pz)<sub>3</sub>BH] (R<sub>3</sub> = Me<sub>3</sub>, Me<sub>2</sub>Cl) complexes the <sup>119</sup>Sn chemical shifts are in the range found for six-coordinate tin [9] which strongly indicates that the structure found for Me<sub>3</sub>Sn[(pz)<sub>3</sub>BH] in the solid state [2] is maintained in solution. Since the Me<sub>3</sub>Sn group is the weakest Lewis acid in the Me<sub>3-n</sub>SnCl<sub>n</sub> series it can be safely assumed that all of the Me<sub>3-n</sub>SnCl<sub>n</sub>[(pz)<sub>3</sub>BH] species have structures involving coordination of all three pyrazolyl rings to give six-coordinate tin centres. For the R<sub>3</sub>Sn[(pz)<sub>2</sub>BH<sub>2</sub>] (R<sub>3</sub> = Me<sub>3</sub>, Me<sub>2</sub>Cl) complexes the <sup>119</sup>Sn shifts are to higher field than those of the corresponding [(pz)<sub>3</sub>BH]<sup>-</sup> ligand which support five-coordinate geometries in solution, as is found for Me<sub>2</sub>ClSn[(pz)<sub>2</sub>BH<sub>2</sub>] in the solid state (see below). Again it seems probable that the complete series Me<sub>3-n</sub>Cl<sub>n</sub>Sn[(pz)<sub>2</sub>BH<sub>2</sub>] involves five-coordinate tin. In view of its insolubility and high melting point there is a possibility that Cl<sub>3</sub>Sn[(pz)<sub>2</sub>BH<sub>2</sub>] expands its coordination by chloride bridging in the solid but this

appears unlikely since the puckered nature of the  $[(pz)_2BH_2]^-$  ligand tends to discourage oligomerisation [1].

All the complexes studied herein gave clean mass spectra. However, parent peaks were only observed for  $Cl_3Sn[(pz)_3BH]$  and  $MeCl_2Sn[(pz)_3BH]$ . There is ready loss of Me and/or Cl groups (Me before Cl) to give strong  $SnL^+$  peaks ( $L = (pz)_3BH$  or  $(pz)_2BH_2$ ).

#### Structure of $Me_2ClSn[(pz)_2BH_2]$

The crystal structure of **9** consists of individual molecules, with a smallest  $Sn \cdots Cl$  intermolecular distance of 3.92 Å, which is too long to be considered as bonding. Thus the tin atom is genuinely five-coordinate, which is relatively unusual for di-organo-tin complexes where hexa-coordination via bridging is commonly observed in the solid state for ostensibly five-coordinate species [3]. The overall geometry is trigonal-bipyramidal with the bidentate ligand occupying one axial and one equatorial site, the chlorine in an axial site and the two methyl groups equatorial (Fig. 1). This *fac* distribution is that expected in that the more electronegative atoms are found in the axial positions, with the six-membered ring chelate axial-equatorial [10].

The trigonal bipyramid is considerably distorted with a  $N(12)-Sn-N(22)$  angle of  $82.1^\circ$  (presumably relating to the optimum "bite" of the ligand) and a  $Cl-Sn-N(12)$  angle of  $166.5^\circ$ . The two bulky methyl groups are splayed out to give a  $C(1)-Sn-C(2)$  angle of  $133.7^\circ$ . Although steric factors will encourage this distortion, an electronic rationale is also reasonable, whereby the bond to the highly-electronegative equatorial nitrogen atom involves an excess *p*-orbital contribution from the tin atom, with a corresponding greater *s*-orbital participation in the tin orbitals involved in the  $Sn-C$  bonds (c.f. Bent's Rule [11]). This hybridisation scheme would lead to a  $C-Sn-C$  angle greater than  $120^\circ$  and corresponding  $N-Sn-C$  angles less than  $120^\circ$ . An interesting comparison is with  $Me_2ClSn[S_2CNMe_2]$  which has a superficially similar structure but where the methyl groups compete with an equatorial sulphur atom (which has a lower electronegativity than nitrogen) and so the  $C-Sn-C$  angle is less widened at  $128.2^\circ$  [12].

The observed values of bond lengths in **9** are well within normal ranges; the  $Sn-N$  bonds (2.338 (axial) and 2.163 (equatorial) Å) are towards the shorter end of the range for such bonds (2.06–2.75 Å [3]) which suggests the ligand is quite strongly coordinated.

The six-membered  $\overline{B-N-N-Sn-N-N}$  ring is boat-shaped (Fig. 2) with a dihedral angle between the pyrazolyl rings of  $119^\circ$ . This is common for bis(pyrazolyl)borate ligands where the puckering opens the "bite" of the chelating atoms without disturbing the tetrahedral bonding at the boron atom [1]. This puckering has the effect of directing one of the hydrogen atoms on the boron towards the central tin atom, but the distance observed (3.3 Å) is too far to suggest a 2-electron-3-centre  $B-H-Sn$  bond similar to the  $B-H-Mo$  interaction found in  $(\eta^3-C_7H_7)(CO)_2Mo[(3,5-Me_2pz)_2BH_2]$  [13] or the  $B-H-Ta$  bond in  $Me_3ClTa-[(Me_2pz)_2BH_2]$  [14]. Nevertheless the crowding about the tin atom is increased by this arrangement which may explain the reluctance of **9** to form bridged oligomers.

From the structure observed for **9** it can be predicted that the other  $Me_{3-n}Cl_nSn[(pz)_2BH_2]$  complexes are also trigonal-bipyramidal with the chelate axial-equatorial. For the  $Cl_3Sn$  and  $Me_3Sn$  complexes this defines the geometry,

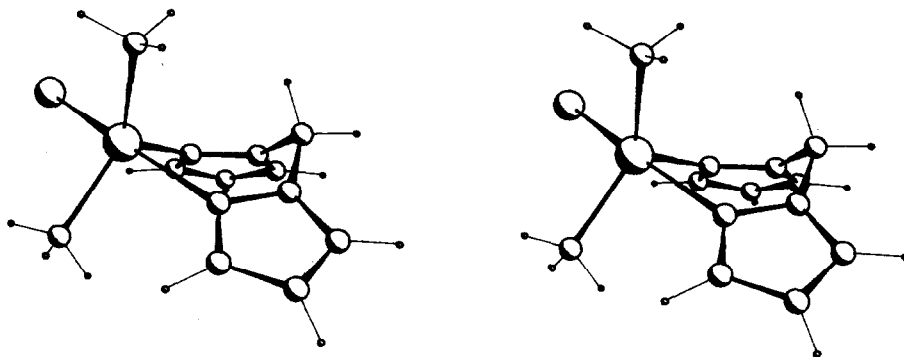


Fig. 2. A stereoview of  $\text{Me}_2\text{ClSn}[(\text{pz})_2\text{BH}_2]$  showing the puckered conformation of the chelate ligand.

while for the remaining member of the series,  $\text{MeCl}_2\text{Sn}[(\text{pz})_2\text{BH}_2]$ , two isomers are still possible; however, the one with the methyl and one chloro equatorial and the other chloro axial is most probable.

An analogy is often drawn between  $[(\text{pz})_2\text{BH}_2]^-$  and ketoenolate ligands such as  $\text{acac}^-$ , which are also uni-negative bidentate ligands. However, differences in coordination behaviour are often observed since the puckered nature of the former makes it sterically more demanding than the latter [1]. There are notable differences in their tin chemistry. Thus  $\text{Cl}_3\text{Sn}[(\text{pz})_2\text{BH}_2]$  is quite stable whereas  $\text{Cl}_3\text{Sn}(\text{acac})$  cannot be isolated since it undergoes rapid disproportionation to the six-coordinate  $\text{Cl}_2\text{Sn}(\text{acac})_2$  and  $\text{SnCl}_4$ ; other five-coordinate tin complexes undergo similar disproportionation e.g.  $\text{Me}_3\text{SnL}$  where  $\text{L} = \text{benzoylacetato}$  [16] or 8-hydroxyquinolino [17].

The pyrazolyl-borate ligand  $[(\text{pz})_2\text{BH}_2]^-$  is a stronger chelate than  $\text{Me}_2\text{NCS}_2^-$  towards tin, because although the two complexes  $\text{Me}_2\text{ClSn}[(\text{pz})_2\text{BH}_2]$  and  $\text{Me}_2\text{ClSn}(\text{S}_2\text{CNMe}_2)$  are both five-coordinate and analogous, the fully methylated  $\text{Me}_3\text{Sn}(\text{S}_2\text{CNMe}_2)$  is only four-coordinate [18] while for  $\text{Me}_3\text{Sn}[(\text{pz})_2\text{BH}_2]$  both pyrazolyl rings are coordinated, despite the lower acidity of the tin centre.

The reactivities of the complexes reported herein have not yet been examined in much detail. Initial studies show that  $\text{Cl}_3\text{Sn}[(\text{pz})_3\text{BH}]$  does not react with  $\text{MeMgI}$ , even in refluxing tetrahydrofuran, while with  $\text{Co}(\text{CO})_4^-$  a complicated series of reactions involving loss of  $[(\text{pz})_3\text{BH}]^-$  from the tin atom is observed [19].

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### References

- 1 S. Trofimenko, *Acc. Chem. Res.*, 4 (1971) 17; *Chem. Rev.*, 72 (1972) 497; *Adv. Chem. Ser.*, 150 (1976) 289; A. Shaver, *J. Organomet. Chem. Library*, 3 (1977) 157.
- 2 B.K. Nicholson, *J. Organomet. Chem.*, 265 (1984) 153.
- 3 B.Y.K. Ho and J.J. Zuckerman, *J. Organomet. Chem.*, 49 (1973) 1; J.A. Zubieta and J.J. Zuckerman, *Prog. Inorg. Chem.*, 24 (1978) 251; A. Tzschach, H. Weichmann and K. Jurkschat, *J. Organomet.*



- Chem. Library, 12 (1981) 293; P.J. Smith, J. Organomet. Chem. Library, 12 (1981) 97; J.L. Lefferts, K.C. Molloy, M.B. Hossain, D. Van der Helm and J.J. Zuckerman, J. Organomet. Chem., 240 (1982) 349.
- 4 K.A. Kocheshkov, Chem. Ber., 66 (1933) 1661; W.P. Neumann and G. Burkhardt, Justus Liebigs Ann. Chem., 663 (1963) 11; M.E. Pavlovskaya and K.A. Kochenshkov, Compt. Rend. Acad. Sci. URSS 49 (1945) 263 (Chem. Abs. 40 (1946) 5696).
  - 5 S. Trofimenko, Inorg. Synth., 12 (1970) 99.
  - 6 G.M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, University of Cambridge, (1976).
  - 7 S. Trofimenko, J. Amer. Chem. Soc., 89 (1967) 3170.
  - 8 A.J. Canty, N.J. Minchin, J.M. Patrick and A.H. White, Aust. J. Chem., 36 (1983) 1107.
  - 9 V.S. Petrosyan, Prog. Nucl. Magn. Res. Spect., 11 (1977) 115; P.J. Smith and A.P. Tupciauskas, Ann. Rep. on NMR Spect., 8 (1978) 291; NMR and the Periodic Table, R.K. Harris and B.E. Mann (Eds.), Academic Press, London, (1978); H.C. Clark, V.K. Jain, R.C. Mehrotra, B.P. Singh, G. Srivastava and T. Birchall, J. Organomet. Chem., 279 (1985) 385.
  - 10 R.R. Holmes, Prog. Inorg. Chem., 32 (1984) 119.
  - 11 H.A. Bent, Chem. Rev., 61 (1961) 275.
  - 12 K. Furue, T. Kimura, N. Yasuoka, N. Kasai and M. Kakudo, Bull. Chem. Soc. Japan, 43 (1970) 1661.
  - 13 F.A. Cotton, M. Jeremic and A. Shaver, Inorg. Chim. Acta, 6 (1972) 543.
  - 14 D.L. Reger, C.A. Swift and L. Lebioda, J. Amer. Chem. Soc., 105 (1983) 5343.
  - 15 P.W. Thompson and J.F. Lefelhocz, J. Organomet. Chem., 47 (1973) 103.
  - 16 S.K. Brahma, W.H. Nelson and W.F. Howard, J. Organomet. Chem., 273 (1984) 47.
  - 17 K. Kawakami and R. Okawara, J. Organomet. Chem., 6 (1966) 249.
  - 18 G.M. Sheldrick and W.S. Sheldrick, J. Chem. Soc., A (1970) 490; G.M. Sheldrick, W.S. Sheldrick, R.F. Dalton and K. Jones, J. Chem. Soc., A (1970) 493.
  - 19 O.J. Curnow and B.K. Nicholson, to be published.