

## THE SYNTHESIS AND X-RAY STRUCTURE OF TRIS(PYRAZOLYL)BORATE(TRIMETHYL)TIN; A SIX-COORDINATE TRIALKYL TIN COMPLEX

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### Summary

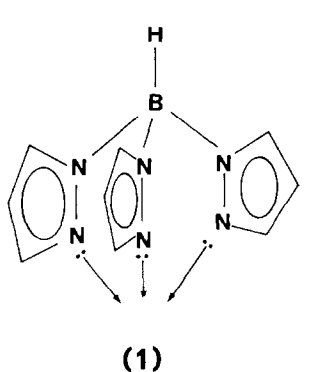
Reaction between  $\text{Me}_3\text{SnCl}$  and  $\text{K}[\text{HB}(\text{pz})_3]$  ( $\text{pz} = 1\text{-pyrazolyl}$ ,  $\text{C}_3\text{H}_3\text{N}_2$ ) affords  $[\text{HB}(\text{pz})_3]\text{SnMe}_3$  which was shown by a full X-ray structure determination (Trigonal, space group  $P\bar{3}$ ,  $a = b = 11.722(3)$ ,  $c = 8.211(2)$  Å,  $\gamma = 120^\circ$ ,  $Z = 2$ ) to contain six-coordinate tin bonded to three methyl groups and to three pyrazolyl groups.

### Introduction

The chemistry of tin involving coordination numbers greater than four has been extensively studied [1,2]. However, there have been no reports of structurally characterised complexes containing six-coordinate trialkyltin moieties, since the electron-donating organic groups lower the acidity of the tin centre to the point where only one extra ligand is bound as in, for example, the five-coordinate  $\text{Me}_3\text{SnCl}_2^-$  [3] or  $\text{Me}_3\text{Sn}(\text{pyridine})\text{Cl}$  [4]. The only evidence for higher coordination species containing triorganotin units comes from infrared studies on the 1 : 1 adducts of  $\text{Me}_3\text{SnCl}$  with 2,2'-bipyridyl and  $\text{Me}_3\text{SnNCS}$  with 1,10-phenanthroline which were interpreted in terms of 6-coordinate tin [5].

The Trofimenko ligand  $[\text{HB}(\text{pz})_3]^-$  (**1**) is a uni-negative, tridentate ligand ideally constrained to occupy three adjacent sites of an octahedral coordination sphere and has been used extensively to provide a number of unusual complexes of transition metals [6]. Of particular interest to the present study is the use of  $[\text{HB}(\text{pz})_3]^-$  to force higher than normal coordination; an example is five-coordinate  $\text{Pt}^{\text{II}}$  in  $[\text{HB}(\text{pz})_3\text{Pt}(\text{Me})(\text{CF}_3\text{CCCF}_3)]^-$  and related species [7]. This approach is not invariably successful - a recent report of  $[\text{HB}(\text{pz})_3\text{AuMe}_2]$  shows square-planar gold with one pyrazolyl group uncoordinated [8].

Surprisingly, the use of poly(pyrazolyl)borate ligands in Main Group chemistry is virtually unexplored. In this paper we describe the use of  $[\text{HB}(\text{pz})_3]^-$  to form an example of the elusive six-coordinate triorganotin complexes.



## Experimental

Reactions were conducted under dry nitrogen in standard Schlenk equipment. Solvents were dried and deoxygenated before use.  $\text{Me}_3\text{SnCl}$  was purchased from Strem Chemicals, and  $\text{K}[\text{BH}(\text{pz})_3]$  was a gift from Professor M.I. Bruce.

### Preparation of $\text{HB}(\text{pz})_3\text{SnMe}_3$

$\text{K}[\text{HB}(\text{pz})_3]$  (0.50 g, 2 mmol) was suspended in  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ) and a solution of  $\text{Me}_3\text{SnCl}$  (0.40 g, 2 mmol) in  $\text{CH}_2\text{Cl}_2$  (5  $\text{cm}^3$ ) was added by syringe. A visible change occurred as the  $\text{K}[\text{HB}(\text{pz})_3]$  dissolved and  $\text{KCl}$  precipitated. After filtration,  $\text{CH}_2\text{Cl}_2$  and any unreacted  $\text{Me}_3\text{SnCl}$  were pumped away and the residue recrystallised from  $\text{CH}_2\text{Cl}_2$ /hexane at  $-30^\circ\text{C}$  to give colourless crystals of  $\text{HB}(\text{pz})_3\text{SnMe}_3$  (0.45 g, 60%), m.p.  $108\text{--}110^\circ\text{C}$ . (Found: C, 37.88; H, 5.17; N, 21.71.  $\text{C}_{12}\text{H}_{19}\text{BN}_6\text{Sn}$  calcd.: C, 38.25; H, 5.08; N, 22.30%). Mass spectrum, cluster of peaks at 363 ( $P\text{--Me}$ )<sup>+</sup>.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $-60$  to  $+30^\circ\text{C}$ )  $\delta$  0.34 (s, 9H,  $\text{CH}_3$ ); 6.16 (m, 3H, H(4)); 7.59 (m, 6H, H(3,5)).

### Crystal structure of $\text{HB}(\text{pz})_3\text{SnMe}_3$

Suitable crystals were obtained by recrystallisation from  $\text{CH}_2\text{Cl}_2$ /hexane at  $-30^\circ\text{C}$ . Preliminary precession photography indicated three-fold Laue symmetry. A crystal of dimensions (0.62  $\times$  0.38  $\times$  0.25 mm) was sealed in a glass capillary and mounted on a Nicolet P3 diffractometer. Cell dimensions were obtained using 25 high angle reflections with  $\text{Mo-K}_\alpha$  X-rays.

*Crystal data:*  $\text{C}_{12}\text{H}_{19}\text{BN}_6\text{Sn}$ ,  $M = 376.83$ . Trigonal, space group  $P\bar{3}$  (No. 147),  $a = b = 11.722(3)$ ,  $c = 8.211(2)$  Å,  $\gamma = 120^\circ$ ,  $U = 977.088$  Å<sup>3</sup>.  $D_c = 1.28$  g  $\text{cm}^{-3}$  for  $Z = 2$ .  $F(000) = 376$ .  $\mu(\text{Mo-K}_\alpha) = 13$   $\text{cm}^{-1}$ ,  $\lambda(\text{Mo-K}_\alpha) = 0.7107$  Å.

A total of 4747 reflexions in the range  $0 < 2\theta < 55^\circ$  was collected for the  $0 < h < 16$ ,  $-16 < k < 16$ ,  $-11 < l < 11$  hemisphere. After correction for Lorentz, polarisation and absorption effects, symmetry related reflections were averaged ( $R = 0.015$ ) to give a unique set of 1516 reflections. Of these 1386 had  $I \geq 3\sigma(I)$  and were used in all calculations.

A Patterson map gave the position of the Sn atom, lying on a three-fold axis. A subsequent difference map revealed all other non-hydrogen atoms. After refinement of these with anisotropic temperature factors, all the hydrogen atoms associated with the  $\text{HB}(\text{pz})_3$  ligand were clearly revealed. These, and the methyl hydrogen atoms,

were included in their calculated positions with common isotropic temperature factors for each type of hydrogen, and the full matrix, least-squares refinement converged at  $R = 0.023$ ,  $R_w = 0.024$  where  $w = 1.00 [\sigma^2(F) + 0.0005F^2]^{-1}$ . A final difference map showed no significant residual electron density. All calculations were performed using the SHELX76 system [9].

Final positional parameters, bond lengths and bond angles are listed in Table 1. Figure 1 gives the atom labelling scheme. Tables of hydrogen atom coordinates and structure factors are available from the author.

TABLE 1  
FINAL POSITIONAL PARAMETERS FOR  $\{\text{HB}(\text{pz})_3\}\text{SnMe}_3$  (Å)

Atom	$x/a$	$y/b$	$z/c$
Sn(1)	0.3333(0)	0.6667(0)	0.3430(1)
B(1)	0.3333(0)	0.6667(0)	-0.0929(5)
N(1)	0.4771(2)	0.6683(2)	0.1357(2)
N(2)	0.4580(2)	0.6703(2)	-0.0273(2)
C(1)	0.5927(2)	0.6714(2)	0.1534(3)
C(2)	0.6480(2)	0.6757(2)	0.0015(3)
C(3)	0.5601(2)	0.6747(2)	-0.1084(3)
C(4)	0.5048(3)	0.8340(3)	0.4477(3)

Bond lengths for  $\{\text{HB}(\text{pz})_3\}\text{SnMe}_3$

N(1)---Sn(1)	2.388(2)
C(4)---Sn(1)	2.165(2)
N(2)---B(1)	1.539(2)
N(1)---N(2)	1.359(2)
N(1)---C(1)	1.345(2)
C(1)---C(2)	1.395(4)
N(2)---C(3)	1.348(2)
C(2)---C(3)	1.365(3)

Bond angles for  $\{\text{HB}(\text{pz})_3\}\text{SnMe}_3$  (deg)

C(4)---Sn(1)---N(1)	86.8(1)
C(4)---Sn(1)---C(4')	105.2(1)
N(1)---Sn(1)---N(1')	74.8(1)
N(1)---Sn(1)---C(4')	157.9(1)
N(1)---Sn(1)---C(4'')	88.8(1)
N(2)---B(1)---N(2')	108.4(1)
N(2)---B(1)---H(1)	110.5(2)
N(2)---N(1)---Sn(1)	125.5(1)
C(1)---N(1)---Sn(1)	128.3(2)
C(1)---N(1)---N(2)	106.1(2)
N(1)---N(2)---B(1)	120.4(2)
C(3)---N(2)---B(1)	129.9(2)
C(3)---N(2)---N(1)	109.7(2)
C(2)---C(1)---N(1)	110.4(2)
C(3)---C(2)---C(1)	104.8(2)
C(2)---C(3)---N(2)	109.0(2)

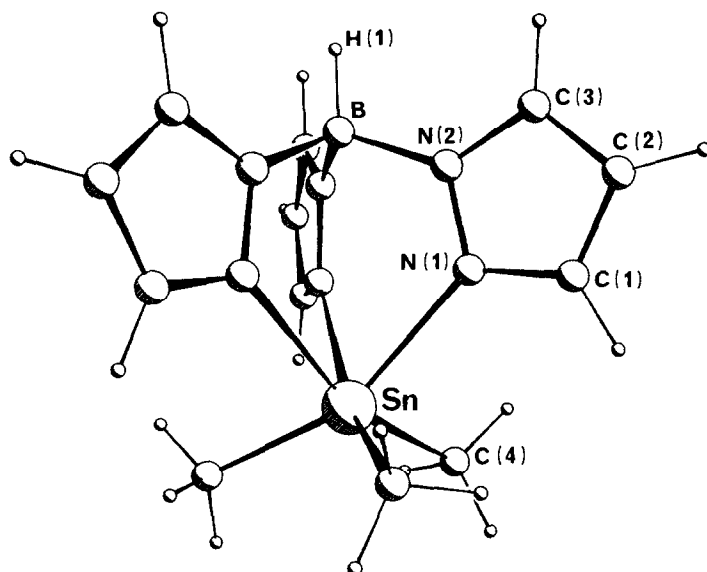
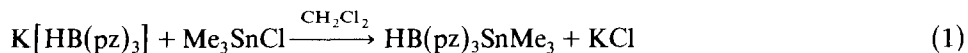


Fig. 1. A perspective view of  $\text{HB}(\text{pz})_3\text{SnMe}_3$ , showing atom numbering.

## Results and discussion

The reaction of  $\text{K}[\text{HB}(\text{pz})_3]$  with  $\text{Me}_3\text{SnCl}$  proceeds smoothly according to eq. 1. The product is easily isolated as colourless, slightly air-sensitive crystals which are very soluble in polar organic solvents, but not in petroleum spirit. Solutions of the complex are not particularly stable; in  $\text{CH}_2\text{Cl}_2$  decomposition is complete after about 5 h at room temperature.



The infrared and mass spectra of  $\text{HB}(\text{pz})_3\text{SnMe}_3$  were fully consistent with the assumed formulation and the  $^1\text{H}$  NMR spectra showed that all three pyrazolyl rings were equivalent between  $-60$  and  $+30^\circ\text{C}$ , suggesting that all three were coordinated to the tin atom, or that rapid exchange of the rings of a partially coordinated ligand was occurring. To establish unequivocally the geometry, a structure determination was carried out.

Crystals of  $\text{HB}(\text{pz})_3\text{SnMe}_3$  consist of individual molecules which lie on a  $C_3$  crystallographic axis which runs through the Sn and B atoms; the overall geometry approximates  $C_{3v}$ . The coordination about the tin atom is distorted octahedral with three *fac* Sn–C(methyl) bonds and three Sn–N bonds to the tris(pyrazolyl)borate ligand. The three methyl groups are splayed out to give C(4)–Sn–C(4') angles of  $105.2^\circ$ , with a concomitant closing of the N(1)–Sn–N(1') angles to  $74.8^\circ$ . This presumably arises from steric interactions between the adjacent methyl groups. We note that in  $\text{HB}(\text{pz})_3\text{Mo}(\text{CO})_3$ , which crystallises in the same space group and is superficially similar (although not isomorphous), the coordination is much closer to a regular octahedron [10].

The Sn–C(4) distance of  $2.165(2)$  Å is within the normal range for such bonds which appears to be  $2.10$ – $2.19$  Å [1,2]. Similarly, the Sn–N(1) bond at  $2.388(1)$  Å is

similar to that in the five-coordinate  $\text{Me}_3\text{SnN}_3$  [11] and is in the range observed for the six-coordinate  $[(\text{terpy})\text{SnMe}_2\text{Cl}]^+$ , 2.29–2.41 Å [12]. Hence there is no indication that the unusual six-coordination found herein for the trimethyltin group results in weaker bonds than those in more familiar complexes.

The invariance of the  $^1\text{H}$  NMR spectrum of  $\text{HB}(\text{pz})_3\text{SnMe}_3$  over the range  $-60$  to  $+30^\circ\text{C}$  suggests that a six-coordinate structure with equivalent pyrazolyl rings is maintained in solution, although a lower-coordination system with rapid exchange of rings cannot be ruled out.

Finally, preliminary experiments indicate that  $[\text{HB}(\text{pz})_3]^-$  forms complexes with  $\text{Me}_n\text{SnCl}_{4-n}$  ( $n = 0-3$ ) and that germanium analogues are also available; detailed results will be given in a future paper.

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