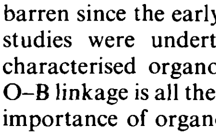
Sterically Hindered Organotin Compounds. Part 3.[1] The Reaction Between Di-*tert*-butyltin Oxide and Organoboronic Acids†

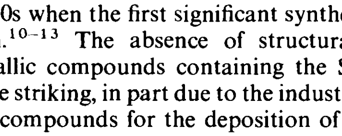
Paul Brown, Mary F. Mahon and Kieran C. Molloy*
School of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK

The reaction between $(\mathrm{Bu^t_2SnO})_3$ and $\mathrm{BR(OH)_2}$ [R = Ph or 2,4,6-$\mathrm{Me_3C_6H_2}$ (mes)] has been investigated and found to yield two classes of product. The first is a boron-rich species, *cyclo*-$\mathrm{Bu^t_2SnO(RBO)_2}$, which exists alongside its acyclic hydrolysis product $\mathrm{SnBu^t_2[OB(OH)R]_2}$. The second product, which is tin-rich, $\mathrm{SnBu^t_2(OH)_2[(Bu^t_2SnO)_2OBR]_2}$, can be formulated as *cyclo*-$\mathrm{RBO(Bu^t_2SnO)_2}$ chelated across one Sn–O–Sn unit by a molecule of $\mathrm{SnBu^t_2(OH)_2}$. The crystal and molecular structures of $\mathrm{SnBu^t_2[OB(OH)Ph]_2}$ and $\mathrm{SnBu^t_2(OH)_2[(Bu^t_2SnO)_2OBC_6H_2Me_3\text{-}2,4,6]_2{\cdot}2MeCN}$ have been determined.

We have been interested for some time in the synthesis of organotin heterocycles,[2] both rings[3,4] and cages,[5] as these could serve as precursors to porous lattices of zeolite-type structure containing a Lewis acidic, redox-active centre (Sn).[6] Heterocycles based on Sn–O–B linkages are interesting targets in this respect, as boron can itself act as a Lewis-acid centre, and furthermore there is a rich and diverse chemistry associated with B–O compounds, in which triangular $\mathrm{BO_3}$ and tetrahedral $\mathrm{BO_4^-}$ units generate a plethora of ring and cage compounds.[7] Moreover, there are structural parallels between the organometallic oxides of the two elements, provided the strongly Lewis-acidic tin centre is sterically protected to generate oligomers rather than polymers containing the metal in an expanded co-ordination sphere. For example, $\mathrm{SnBu^t_2O}$ is a cyclic trimer **1**[8] while organoboronic acids **2** can also be condensed to similar rings **3**.[9] It was of interest to us to examine the possibility of synthesising rings such as those above containing both tin and boron in the same compound, and the results of such efforts are reported herein.



1

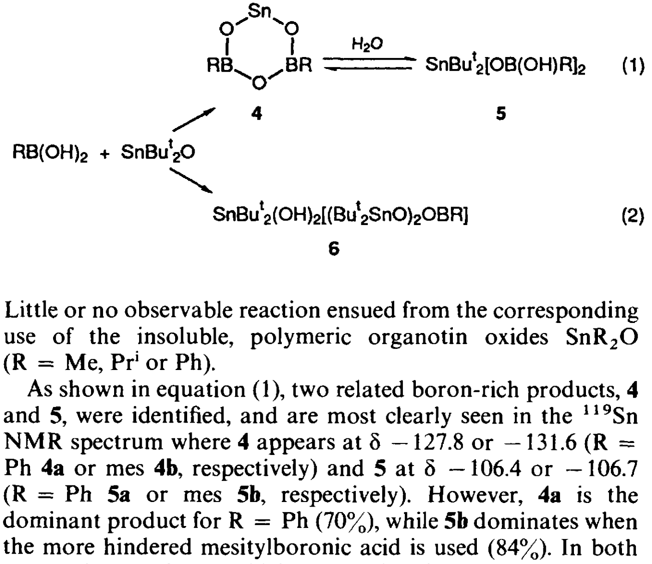


2 **3**

Surprisingly, the chemistry of stannaboroxanes has remained barren since the early 1970s when the first significant synthetic studies were undertaken.[10–13] The absence of structurally characterised organometallic compounds containing the Sn–O–B linkage is all the more striking, in part due to the industrial importance of organotin compounds for the deposition of tin oxide on glass (where such compounds might act as models for any interactions with borosilicate surfaces),[14] and further due to recent interest in organometallic Si–O–B compounds.[15–18] Structures of inorganic tin borates, *e.g.* $\mathrm{MSn(BO_3)_2}$ (M = Mg or Sr), are, however, known.[19]

Results and Discussion

Reaction of equimolar quantities of $\mathrm{SnBu^t_2O}$ and an arylboronic acid $\mathrm{RB(OH)_2}$ [R = Ph or 2,4,6-$\mathrm{Me_3C_6H_2}$ (mes)] in benzene, with removal of water *via* a Dean and Stark trap, yielded two classes of product which have been separated by repeated crystallisations. These two types of product, which differ in their Sn:B ratio, are shown in equations (1) and (2).



Little or no observable reaction ensued from the corresponding use of the insoluble, polymeric organotin oxides $\mathrm{SnR_2O}$ (R = Me, $\mathrm{Pr^i}$ or Ph).

As shown in equation (1), two related boron-rich products, **4** and **5**, were identified, and are most clearly seen in the ^{119}Sn NMR spectrum where **4** appears at δ −127.8 or −131.6 (R = Ph **4a** or mes **4b**, respectively) and **5** at δ −106.4 or −106.7 (R = Ph **5a** or mes **5b**, respectively). However, **4a** is the dominant product for R = Ph (70%), while **5b** dominates when the more hindered mesitylboronic acid is used (84%). In both cases, the products which crystallise from these solution mixtures are of type **5**. In both pairs of compound the ratio of boron to tin was established as 2:1 from integration of the aryl and alkyl proton resonances in the ^{1}H NMR spectrum. The isolated solid compounds **5a** and **5b** exhibit broad ν(OH) bands at 3250 and 3300 cm^{-1} in their IR spectra, respectively, which can be correlated with the presence of δ(BOH) at 6.05 and 6.22 in the ^{1}H NMR spectra of the mixtures. The integration for the BOH signal of **5b** (2 H) can be entirely accounted for by correlation with the integrated intensities for the dibutyltin (18 H), $\mathrm{CH_3}$ (18 H) and aryl signals (4 H), suggesting that **4b** retains its B–O–B linkages. The ^{1}H NMR spectrum of the **4a**, **5a** mixture can be interpreted similarly, though in this case the signals due to the hydrolysis product **5a** are in the minority (30%). We therefore assign the structure of **4** to the six-membered $\mathrm{B_2SnO_3}$ heterocycle, which can be viewed as the incorporation of one tin atom into the $\mathrm{B_3O_3}$ trimer **3** at the

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

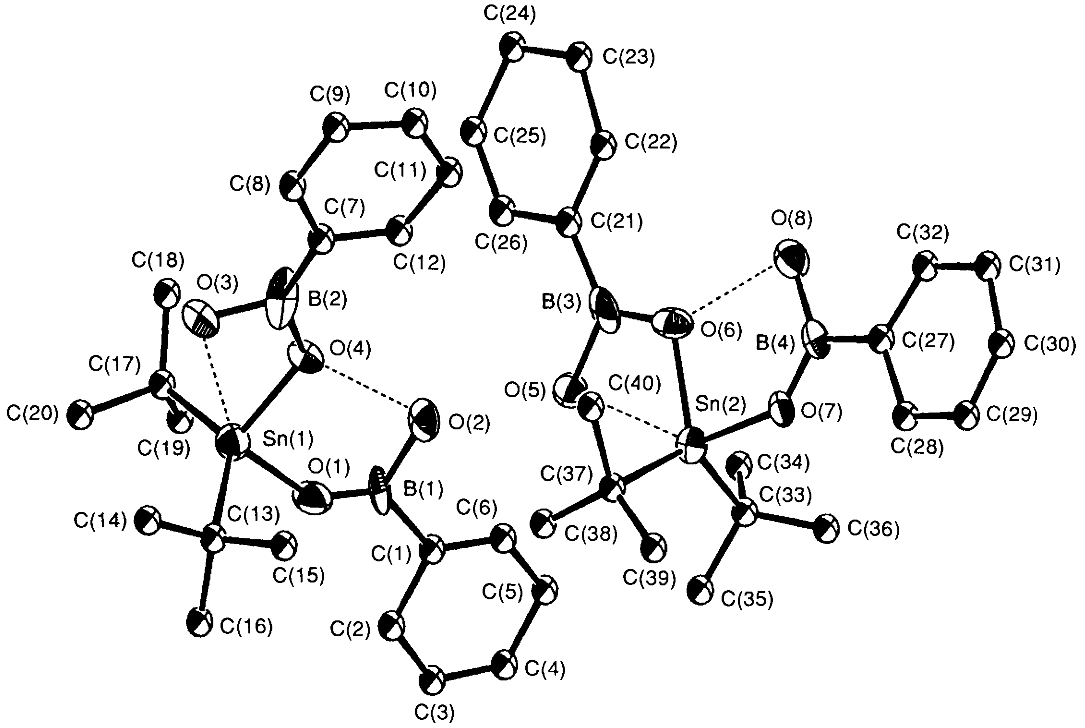


Fig. 1 The asymmetric unit (two independent molecules) of compound **5a** showing the atomic labelling. Thermal ellipsoids are at the 30% probability level

expense of boron. Furthermore, **5** can be rationalised as the acyclic hydrolysis product of **4**, in which one B–O–B linkage has been cleaved and two B(OH) moieties generated, a formulation which we have confirmed crystallographically for **5a**.

The structure of compound **5a**, determined crystallographically, is shown in Fig. 1. The asymmetric unit consists of two independent molecules, both essentially identical and of *cis*-$\mathrm{R_2SnO_3}$ stereochemistry. The Mössbauer quadrupole splitting (q.s.) values of 2.81 mm s^{-1} for **5a** and 2.66 mm s^{-1} for **5b** are consistent with this structure.[20] In each molecule the tin is chelated in an anisobidentate manner by one RB(O)OH unit [Sn(1)–O(4) 1.97(2), Sn(1)–O(3) 2.78(2), Sn(2)–O(6) 1.97(2), Sn(2)–O(5) 2.75(2) Å], while the other bonds to tin in a monodentate fashion [Sn(1)–O(1) 1.99(2), Sn(2)–O(7) 1.99(2) Å] with the oxygen of the second hydroxyl group outside the co-ordination sphere of the metal [Sn(1) $\cdots$ O(2) 3.46, Sn(2) $\cdots$ O(8) 3.47 Å]. The covalent Sn–O bonds are similar in length to those found in the precursor oxide, $(\mathrm{Bu^t{}_2SnO})_3$, and its related congener $[(\mathrm{MeCH_2CMe_2})_2\mathrm{SnO}]_3$, which lie in the range 1.95–1.98 Å.[8] The co-ordination sphere about tin is markedly distorted from an ideal *cis*-$\mathrm{R_2SnO_3}$ trigonal bipyramid, presumably due mainly to the small bite angle of the $\mathrm{RBO_2}$ ligand [O(3)–Sn(1)–O(4) 54.6(6), O(5)–Sn(2)–O(6) 55.9(6)°]. Chelation by the $\mathrm{RBO_2}$ ligand also reduces the O–B–O angle [O(3)–B(2)–O(4) 103(3)°] compared to the corresponding unidentate ligand [O(1)–B(1)–O(2) 120(3)°], though the difference is less marked in the second molecule of the asymmetric unit [112(2), 118(2)°, respectively]. The axial O–Sn–O angles are significantly reduced from 180° [O(1)–Sn(1)–O(3) 146.3(6), O(5)–Sn(2)–O(7) 145.7(6)°], while the C–Sn–C angle is widened from 120° [C(13)–Sn(1)–C(17) 135(1), C(33)–Sn(2)–C(37) 133(1)°], in keeping with both the steric demands of the ligands and the accepted ideas of isovalent rehybridations.[21] The sum of the equatorial angles about the metal [352, 353° for Sn(1) and Sn(2), respectively] is, however, more consistent with the proposed trigonal-bipyramidal geometry (360°) than a tetrahedral one (328.5°). The atoms of the two $\mathrm{BO_2}$ units exhibit large thermal displacements precluding unambiguous analysis of the bonding in this part of the molecule. The B–O bond lengths in the bidentate boronate units [B(2)–O(3) 1.48(4), B(2)–O(4) 1.43(4), B(3)–O(5) 1.41(4), B(3)–O(6) 1.38(4) Å] are all similar and are within the range cited for trigonal $\mathrm{BO_3}$ species (1.28–1.43 Å).[22] Direct comparison can be made with the equivalent bonds in the parent phenylboronic acid (1.36, 1.38 Å).[23] In the unidentate ligands two distinct B–O bonds are suggested, one similar to those already described [B(1)–O(2) 1.47(4), B(4)–O(8) 1.39(3) Å] while the other [B(1)–O(1) 1.20(3), B(4)–O(7) 1.28(3) Å] is shorter and is more like the B=O found for $\mathrm{B_2O_3}$ in the gas phase [1.20(3)].[24] Interestingly, the oxygen atoms involved in these short B–O bonds [O(1), O(7)] are the only oxygen atoms not involved in hydrogen bonding (see below). In addition, the Sn–O bonds involving the same oxygen atoms, which are axial and hence expected to be relatively long, are the same length as the equatorial Sn–O linkages. Collectively, these data suggest that one of the oxygen lone pairs on each of O(1) and O(7) is delocalised into the vacant p orbital on boron (introducing some B=O character), and to a lesser extent into a vacant d orbital on tin. The involvement of lone pairs on the remaining oxygen atoms in a hydrogen-bonding network precludes this type of interaction.

The lattice structure of compound **5a** is dominated by an extensive network of hydrogen bonds. Hydrogen bonds occur between BOH $\cdots$ OB units in both an intramolecular [O(2) $\cdots$ O(4) 2.74, O(8) $\cdots$ O(6) 2.70 Å] (Fig. 1) and intermolecular manner [O(2) $\cdots$ O(5) 2.70, O(3′) $\cdots$ O(8) 2.67 Å]. The intermolecular network links molecules into a polymeric chain (Fig. 2), the latter adopting a helical conformation of four molecules per complete turn (Fig. 3). No hydrogen bonding between helical chains is observed.

The second class of compound derived from the reaction of $\mathrm{SnBu^t{}_2O}$ with an arylboronic acid [equation (2), R = Ph **6a** or mes **6b**] is a more complex formulation. Spectra for **6a** and **6b** follow parallel patterns, so only the data for **6b**, for which a crystallographic analysis is available, are discussed in detail. The ^{119}Sn NMR spectrum contains two distinct tin resonances in 2:1 ratio, with upfield chemical shifts typical of co-ordination numbers higher than four (δ −260.3, −278.5).[20] The same

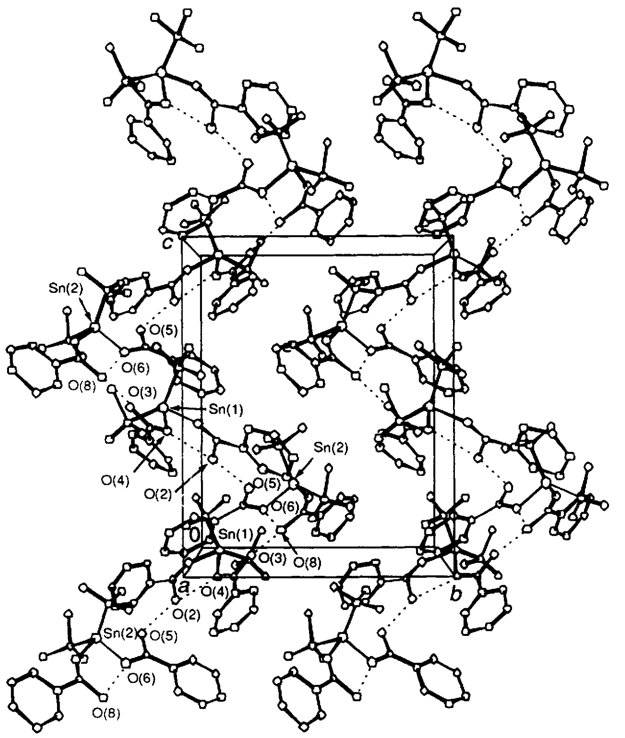


Fig. 2 The unit cell of compound **5a** viewed along *a*, showing the hydrogen-bonded polymeric lattice

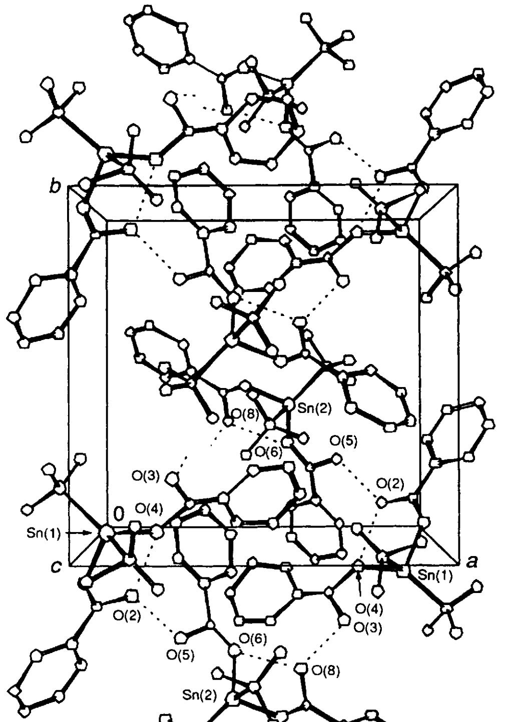


Fig. 3 The unit cell of compound **5a** viewed along *c*, showing the four-fold helical nature of the polymer propagation

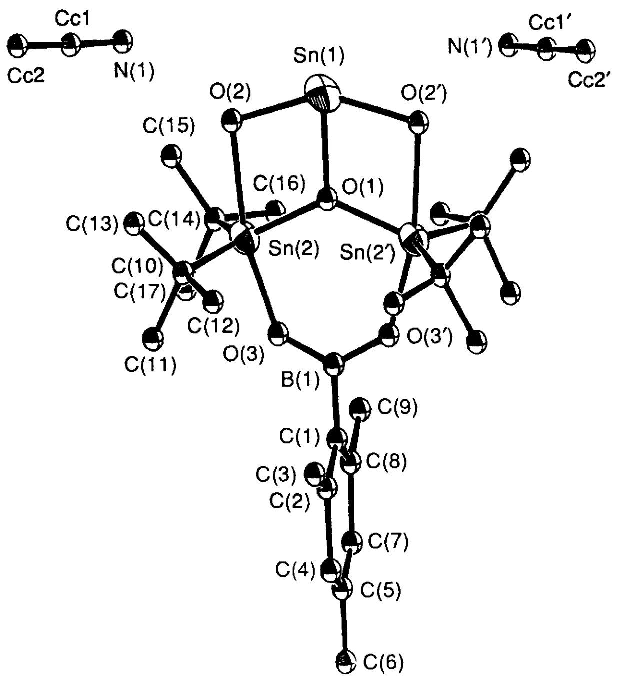
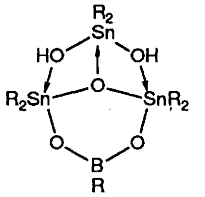


Fig. 4 The asymmetric unit of compound **6b**, showing the atomic labelling. The Bu^t groups attached to Sn(1) (not shown) are severely disordered, and could not be located with any consistency in the electron-density maps. Thermal ellipsoids are at the 30% probability level

pattern is reflected in both the ^{1}H and ^{13}C NMR spectra, which indicate two types of Bu^t groups in the ratio 2:1. The distinctions between the two Bu$^t{}_2$Sn environments are clearly minor, and the similarity of the Mössbauer q.s. data (2.31 mm s^{-1}) to those for **5** suggests a similar *cis*-R_2SnO_3 co-ordination sphere. Integration of the alkyl and aryl protons establishes the Sn:B ratio as 3:1, while the IR spectrum of the compound recrystallised from a non-co-ordinating solvent (*e.g.* light petroleum, $CHCl_3$) reveals a sharp ν(OH) at 3670 cm^{-1}. On the other hand, recrystallisation from MeCN or acetone causes the ν(OH) to broaden and lower in wavenumber (3480 cm^{-1}), typical of a hydrogen-bonded OH group. In particular, recrystallisation from MeCN yields crystals of an adduct, formulated as (Bu$^t{}_2$SnO)$_3$OB(mes)·H_2O·2MeCN on the basis of the foregoing spectral data, along with microanalytical figures. Ostensibly, this formulation is suggestive of incorporation of one B–O unit into the six-membered Sn_3O_3 ring of the parent oxide, solvated with both H_2O and MeCN. However, the crystallographic analysis of the compound reveals a more complex formulation.

The structure of compound **6b** is shown in Fig. 4. The low initial crystal quality followed by decay of the crystal within the X-ray beam during data collection (*ca.* 33% loss in the intensity of the monitor reflection by the end of data collection) have led to large errors in the resulting geometric data, compounded by disorder of the two Bu^t groups on Sn(1). These appear as a smear of electron density in the Fourier maps, and attempts to correlate and refine carbon atom positions with peaks appearing within this smear failed to yield chemically consistent positions. Invariably, the thermal parameters for such atom positions were excessively large, the atom positions moved irrationally, and new electron-dense positions emerged in the Fourier difference maps. Despite these difficulties, the gross structure shown in Fig. 4 confirms the empirical formulation, and can be viewed as being derived from the incorporation of one RBO unit into the precursor Sn_3O_3 heterocycle, yielding an eight-membered Sn_3BO_4 ring as previously suggested. In addition, this ring contains a central oxygen atom, generating two four-membered Sn_2O_2 rings and one six-membered Sn_2BO_3 ring within the larger heterocycle. Notably, the six-membered Sn_2BO_3 ring is the chemical inverse of that in **4**. All nine ring atoms are essentially coplanar [maximum deviation from mean plane: B(1) −0.10 Å], with a pseudo-mirror plane containing these atoms (also bisecting the two pairs of Bu^t groups and dividing in two the mesityl ligand) only broken by the two MeCN molecules which both lie above the ring plane. The molecule does possess a crystallographically imposed mirror plane, orthogonal to the above pseudo-mirror, containing Sn(1), O(1), B(1) and all the atoms of the mesityl ligand.

Given the hydrolytic relationship between compounds **4** and **5** discussed earlier, the correct interpretation of the structure of **6b** rests on the assignment of hydrogen atoms to one or more of the oxygen atoms, *i.e.* are the elements of H_2O present as a water molecule or has it converted an M–O–M unit into two M–OH groups (M = Sn or B) as in **5**? Given the low quality of the crystallographic data for this compound, location of the relevant hydrogen atoms in the Fourier maps proved impossible. However, the positions of the two MeCN solvent molecules [N(1) ··· O(2) 2.87 Å], which the IR data suggest induce hydrogen bonding from the hydroxyl groups, leads us to position one hydrogen atom on each of O(2) and O(2′). A schematic of our preferred formulation for both compounds **6a** and **6b** based on the structure of the latter is therefore as shown.



The Sn–O bond length data lend some support to the above interpretation. All the Sn–O bonds save Sn(2)–O(2) [and its symmetry-related Sn(2′)–O(2′)] are in the range 2.04(2)–2.18(2) Å, slightly longer than, but still comparable with, those already noted in compound **5a**. On the other hand, Sn(2)–O(2), the nominally co-ordinate interaction between tin and the hydrogen-bonded hydroxyl group, is notably longer at 2.33(3) Å. This bond, in which oxygen both co-ordinates tin and is involved in hydrogen bonding, is longer than examples of non-hydrogen-bonded hydroxyl groups involved in either terminal Sn–OH [e.g. $(R_2Sn)_2(OH)_2(\mu\text{-}O)$, R = $(Me_3Si)_2CH$, 2.032(7);[25] $Sn(trop)_3(OH)$ (Htrop = 2-hydroxycyclohepta-2,4,6-trien-1-one), 1.974(6) Å[26]], or bridging Sn–OH [*e.g.* $SnPh_3(OH)$ 2.197(5) Å[27]]. The compound $\{[(OH)Bu^t$-$^{(}\langle^{e}{}_{3}SiCH_2)Sn]_2O\}_2$ also shows distinct terminal [2.016(8) Å] and bridging [2.299(7) Å] Sn–OH bonds.[28]

The co-ordination spheres about all three tin atoms are, not unexpectedly, severely distorted, and this is most clearly seen in deviations of the axial O–Sn–O moiety away from the ideal angle of 180°. It would appear that the tin of the $Bu^t{}_2Sn(OH)_2$ unit [O(2)–Sn(1)–O(2′) 149.8(8)°] is more affected than the tin of the nominal six-membered Sn_2BO_3 [O(2)–Sn(2)–O(3) 166(1)°]. The angles within the four-membered $Sn_2(\mu\text{-}OH)(\mu\text{-}O)$ rings are surprisingly similar to those in rings of analogous content, also incorporating five-co-ordinate tin. For example, the internal angles at Sn(1), Sn(2), O(1) and O(2) in compound **6b** [75.0(7), 72.3(9), 112.4(7) and 100(1)°, respectively] compare well with the analogous angles in $\{[(OH)(Cl)Pr^i Sn]_2O\}_2$ [74.7(6), 72.4(5), 113.8(8) and 98.9(6)°][29] and $\{[(OH)Bu^t(Me_3SiCH_2)Sn]_2O\}_2$ [70.1(3), 73.4(3), 115.4(4) and 99.9(3)°, respectively].[28] The across-ring Sn(1) ··· Sn(2) separation (3.460 Å) is, however, much longer than in $(R_2Sn)_2(\mu\text{-}O)_2$, R = $(Me_3Si)_2CH$ (2.94 Å), which is orange and may involve weak Sn ··· Sn interactions.[25] Within the six-membered Sn_2BO_3 sub-ring, the internal angles at O(1) and O(3) [135(1), 134(3)°] are identical with those in the parent $(Bu^t{}_2SnO)_3$ [133(1)°],[8] but the internal angles at tin [O(1)–Sn(2)–O(3) 93(1)°] are significantly different due to the increase in the co-ordination number at the metal from four to five. The internal angle at trigonal boron [129(6)°] is also wider than normally found, though the large error in this parameter negates confident analysis. In general, though, the ring angles in related planar six-and eight-membered heterocycles containing four-co-ordinate silicon and three-co-ordinate boron, *e.g.* $Ph_5Si_2BO_3$,[16,17] $Ph_6Si_2B_2O_4$,[17] $Bu^t{}_4Ph_2Si_2B_2O_4$[18] and $Bu^t{}_4Me_2FSi_3O_4$, are all very close to the ideal tetrahedral or trigonal values for silicon and boron, respectively. However, unlike **6b**, significant angular distortions at two-co-ordinate oxygen are common, with internal angles at oxygen varying between 118 and 168°.[17,18]

The presence of $Bu^t{}_2Sn(OH)_2$ as a sub-unit of the structure of compound **6b** is the first structural evidence for the existence of a discrete organotin dihydroxide. While such species have been claimed in the past,[30,31] no crystallographic studies have been reported, largely due to the instability of such species with respect to the corresponding dehydration product, SnR_2O. The recently reported monomeric $[R_2Sn(OH)]_2O$ [R = $(Me_3Si)_2CH$],[25] or dimers of the same formulation, $\{[Bu^t(Me_3SiCH_2)Sn(OH)]_2O\}_2$,[28] can be viewed as intermediate between these two extremes.

Experimental

Spectra were recorded on the following instruments: JEOL GX270 (^1H, ^{13}C NMR), GX400 (^{11}B, ^{119}Sn NMR); Perkin Elmer 599B (IR). Details of our Mössbauer spectrometer and related procedures are given elsewhere.[32] The NMR spectra were recorded as saturated $CDCl_3$ solutions at room temperature; ^{11}B and ^{119}Sn chemical shifts are relative to $BF_3 \cdot OEt_2$ and $SnMe_4$, respectively.

The compounds $SnBu^t{}_2Cl_2$ and $SnBu^t{}_2O$ were prepared by literature methods.[8,33]

Synthesis of Mesitylboronic Acid.—Mesitylmagnesium bromide, from magnesium (3.7 g, 152 mmol) and mesityl bromide (30 g, 151 mmol) in diethyl ether (100 cm^3), and trimethyl borate (15.6 g, 150 mmol) were simultaneously added to stirred ether (200 cm^3) at −78 °C. After *ca.* 75% of the reagents had been added, more solvent (100 cm^3) was added to enable efficient stirring to continue. The mixture was allowed to warm to room temperature and stirring continued for 17 h. Water was then added to the slurry to hydrolyse the remaining methoxy groups, the mixture extracted with ether, and dried over anhydrous magnesium sulfate. After solvent evaporation *in vacuo*, the solid residue was recrystallised from chloroform–light petroleum (b.p. 40–60 °C) (1 : 1) to yield mesitylboronic acid as a colourless crystalline solid (8.1 g, 33%; m.p. 177 °C) [Found (Calc. for $C_9H_{13}BO_2$): C, 65.20 (65.90); H, 8.00 (8.00)%]. NMR: ^1H, δ 2.25 (s, 3 H, $p\text{-}CH_3C_6H_2$), 2.32 (s, 6 H, $o\text{-}CH_3C_6H_2$), 5.09 (s, 2 H, BOH) and 6.80 (s, 2 H, C_6H_2); ^{13}C, δ 21.1 ($p\text{-}CH_3C_6H_2$), 22.0 ($o\text{-}CH_3C_6H_2$), 127.2, 138.6, 139.6 and 143.5 (*m*-, *o*-, *p*-C of C_6H_2); ^{11}B, δ 29.6 (br).

Reaction of Di-tert-*butyltin Oxide and an Arylboronic acid.*—Di-*tert*-butyltin oxide (1.0 g, 4 mmol) and phenylboronic acid (0.49 g, 4 mmol) were heated to reflux in benzene (30 cm^3) and the water generated in the reaction separated in a Dean and Stark apparatus. After continued reflux for 17 h the solution was cooled and the solvent evaporated *in vacuo* to yield a white solid. Repeated recrystallisation from acetone yielded two fractions, one containing a mixture of compounds **4a** and **5a**, from which **5a** crystallised on standing, the other **6a**.

2,2-*Di*-tert-*butyl*-4,6-*diphenyl*-1,3,5-*trioxa*-2-*stannadiborinane* **4a**. NMR: ^1H, δ 1.47 [s, 18 H, C_4H_9; ^3J(Sn–H) = 99, 103 Hz], 7.44 (m, 6 H, *m*-,*p*-H of Ph) and 8.11 (m, 4 H, *o*-H of Ph); ^{13}C, δ 29.4 (C_4H_9), 127.5, 130.5, 135.1 (*m*, *o*-, *p*-C of Ph); ^{11}B, δ 26.3 (br); ^{119}Sn, δ −127.8.

Di-tert-*butylbis*[*hydroxy*(*phenyl*)*boryloxy*]*stannane* **5a**. Found (Calc. for $C_{20}H_{30}B_2O_4Sn$): C, 50.70 (50.60); H, 6.50 (6.35)%. NMR: ^1H, δ 1.46s, 18 H, C_4H_9; ^3J(Sn–H) = 101, 105 Hz], 6.05 (s, 2 H, BOH), 7.44 (m, 6 H, *m*-,*p*-H of Ph) and 7.87 (m, 4 H, *o*-H of Ph); ^{13}C, δ 29.5 (C_4H_9), 127.7, 130.5, 134.2 (*m*-, *p*-, *o*-C of Ph); ^{11}B, δ 26.3 (br); ^{119}Sn, δ −106.4. ^{119}Sn Mössbauer: i.s. = 1.46, q.s. = 2.81 mm s^{-1}. IR: ν(OH) 3250 cm^{-1},

μ-*Dioxophenylborato*-1 : 2κ^{2}O : O′-*di*-μ-*hydroxo*-1 : 3κ^{2}O; 2 : 3κ^{2}O-μ$_3$-*oxo*-*tris*[*bis*(tert-*butyl*)*tin*] **6a**. Found (Calc. for

$C_{30}H_{61}BO_5Sn_3{\cdot}2CH_3CN$): C, 42.80 (42.95); H, 7.20 (7.10); N, 2.75 (2.95)%. NMR: ^1H, δ 1.38 [s, 36 H, C_4H_9, ^3J(Sn–H) = 100, 106], 1.39 [s, 18 H, C_4H_9, ^3J(Sn–H) = 100, 104 Hz], 7.28 (m, 3 H, *m*-, *p*-H of Ph) and 7.94 (m, 2 H, *o*-H of Ph); ^{13}C, δ 30.7 (C_4H_9), 30.8 (C_4H_9), 126.8, 128.1, 135.4 (*m*-, *p*-, *o*-C of Ph); ^{11}B, δ 25.0 (br); ^{119}Sn, δ −261.8 and −277.8. ^{119}Sn Mössbauer, i.s. = 1.20, q.s. = 2.36 mm s^{-1}. IR: ν(OH) 3680 (recrystallisation from light petroleum, $CHCl_3$): 3510br cm^{-1} (recrystallisation from MeCN or acetone).

Table 1 Crystallographic data for compounds **5a** and **6b**[a]

	5a	**6b**
Empirical formula	$C_{20}H_{30}B_2O_4Sn$	$C_{37}H_{73}BN_2O_5Sn_3$
M_r	474.8	993.0
a/Å	12.402(3)	16.482(4)
b/Å	12.404(3)	16.482(4)
c/Å	15.787(9)	18.395(6)
$\alpha = \beta$/°	90.0	90.0
γ/°	90.0(1)	90.0
U/Å^3	2428.5	4997.2
Crystal system	Monoclinic	Tetragonal
Space group	$P2_1$ (unique c)	$P4_2nm$
Z	2[b]	4[c]
D_c/g cm^{-3}	1.30	1.35
Crystal size/mm	0.3 × 0.3 × 0.25	0.3 × 0.2 × 0.2
μ/cm^{-1}	9.75	13.99
F(000)	968	2064
Absorption factors	1.01, 0.96	1.10, 0.97
h,k,l limits	0–13, 13–13, −16 to 16	0–17, 0–17, 0–19
Data collected	5392	3400
Unique data, $I > 3\sigma(I)$	3016	1257
No. variables	144[d]	100
Maximum shift/e.s.d.	0.016	−0.006
Maximum, minimum residuals/e Å^{-3}	0.39, −0.53	0.27, −0.21
R[e]	0.0718	0.0794

[a] Details in common: data collected on a Hilger and Watts Y290 four-circle diffractometer at room temperature using Mo-Kα radiation (λ = 0.710 69 Å); empirical absorption correction; 2θ range 4–44°. [b] Two molecules per asymmetric unit. [c] Half a molecule per asymmetric unit (see Fig. 4). [d] Refined in two blocks, each comprising the variables for one molecule of the asymmetric unit. [e] Unit weights.

Using the same methodology and mesitylboronic acid as reagent, a solution mixture of compounds **4b** and **5b** was obtained from which **5b** crystallised on standing, along with **6b**. 2,2-Di-*tert*-butyl-4,6-dimesityl-1,3,5-trioxa-2- stannadiborinane **4b** was only present as 16% of the mixture with **5b** making reliable assignments of the ^1H and ^{13}C NMR data tenuous. NMR: ^{11}B, δ 28.0 (br); ^{119}Sn, δ −131.6.

Di-tert-*butylbis[hydroxy(mesityl)boryloxy]stannane* **5b**. Found (Calc. for $C_{26}H_{42}B_2O_4Sn$): C, 56.00 (55.85); H, 7.75 (7.55)%. NMR: ^1H, δ 1.49 [s, 18 H, C_4H_9, ^3J(Sn–H) = 100, 104 Hz], 2.30 (s, 6 H, *p*-$CH_3C_6H_2$), 2.39 (s, 12 H, *o*-$CH_3C_6H_2$), 6.22 (s, 2 H, BOH) and 6.82 (m, 4 H, *m*-$CH_3C_6H_2$); ^{13}C, δ 21.1 (*p*-$CH_3C_6H_2$), 22.4 (*o*-$CH_3C_6H_2$), 29.4 (C_4H_9), 127.0, 137.1, 139.3 (*m*-, *p*-, *o*-C of $CH_3C_6H_2$); ^{11}B, δ 28.0 (br); ^{119}Sn, δ −106.7. ^{119}Sn Mössbauer: i.s. = 1.37, q.s. = 2.66 mm s^{-1}. IR: ν(OH) 3300 cm^{-1}.

Di-μ-hydroxo-1:3κ^{2}O; 2:3κ^{2}O-*μ-mesityldioxoborato*-1:2κ^{2}O:O′-μ_3-*oxo-tris*(tert-*butyl*)*tin*] **6b**. Found (Calc. for $C_{33}H_{67}BO_5Sn_3{\cdot}2CH_3CN$): C, 44.80 (44.75); H, 7.55 (7.40); N, 3.05 (2.80)%. NMR: ^1H, δ 1.33 [s, 36 H, C_4H_9, ^3J(Sn–H) = 101, 104], 1.39 [s, 18 H, C_4H_9, ^3J(Sn–H) = 100, 104 Hz], 1.95 (s, 6 H, CH_3CN), 2.23 (s, 3 H, *p*-$CH_3C_6H_2$), 2.49 (s, 6 H, *o*-$CH_3C_6H_2$) and 6.73 (s, 2 H, $CH_3C_6H_2$); ^{13}C, δ 21.1 (*p*-$CH_3C_6H_2$), 23.5 (*o*-$CH_3C_6H_2$), 30.7 (C_4H_9), 39.2 (C_4H_9), 126.5, 134.4, 139.7 (*m*-, *p*-, *o*-C of $CH_3C_6H_2$); ^{11}B, δ 26.5 (br); ^{119}Sn, δ −260.3 and −278.5. ^{119}Sn Mössbauer: i.s. = 1.16, q.s. = 2.31 mm s^{-1}; IR: ν(OH) 3670 (recrystallisation from light petroleum, $CHCl_3$); 3480br cm^{-1} (recrystallisation from MeCN).

Crystal Structures of Compounds **5a** *and* **6b**.—Details of the crystal and experimental data relating to both compounds are given in Table 1. For both structures, scattering factors used were for neutral atoms,[34] while the program suites used were SHELX 86,[35] SHELX 76[36] and DIFABS.[37]

Due to initial uncertainty in the crystal system, data for compound **5a** were collected in the ranges h 0–13, k −13 to 13 and l −16 to 16. Photographic data indicated that the space

Table 2 Fractional atomic coordinates for compound **5a**

Atom	x	y	z
Sn(1)	0.0966(2)	0.081 5(1)	1.000 00
B(1)	0.0545(3)	−0.120 8(3)	0.900 0(2)
B(2)	0.3047(3)	0.154 3(3)	0.927 8(3)
O(1)	0.036 6(2)	−0.054 7(1)	0.954 0(1)
O(2)	0.146 0(2)	−0.106 1(1)	0.842 3(1)
O(3)	0.268 0(1)	0.225 9(1)	0.997 2(1)
O(4)	0.218 7(1)	0.078 3(1)	0.919 8(1)
Sn(2)	0.418 4(2)	−0.403 3(1)	0.750 3(2)
B(3)	0.348 4(4)	−0.203 7(3)	0.684 2(2)
B(4)	0.624 6(3)	−0.441 6(2)	0.644 9(2)
O(5)	0.275 4(1)	−0.234 1(1)	0.748 0(1)
O(6)	0.423 4(1)	−0.283 8(1)	0.668 6(1)
O(7)	0.552 7(1)	−0.463 7(1)	0.700 9(1)
O(8)	0.607 3(2)	−0.352 3(1)	0.593 3(1)
C(1)	−0.012 2(24)	−0.228 3(20)	0.877 5(18)
C(2)	−0.093 7(25)	−0.250 4(23)	0.939 2(19)
C(3)	−0.153 5(30)	−0.342 2(26)	0.923 3(23)
C(4)	−0.132 2(27)	−0.408 2(27)	0.859 6(21)
C(5)	−0.054 1(28)	−0.387 5(26)	0.798 8(22)
C(6)	0.010 6(26)	−0.297 5(22)	0.818 8(18)
C(7)	0.401 5(23)	0.164 8(18)	0.887 8(15)
C(8)	0.497 7(26)	0.242 1(23)	0.901 8(19)
C(9)	0.573 8(27)	0.246 7(23)	0.858 3(18)
C(10)	0.606 0(33)	0.168 0(25)	0.802 5(21)
C(11)	0.530 1(33)	0.083 9(32)	0.734 6(27)
C(12)	0.432 5(29)	0.089 8(25)	0.828 7(19)
C(13)	0.158 1(32)	0.027 2(28)	1.120 7(23)
C(14)	0.187 1(32)	0.117 2(29)	1.173 2(25)
C(15)	0.234 3(30)	−0.050 7(29)	1.099 5(24)
C(16)	0.064 1(30)	−0.027 2(29)	1.163 7(26)
C(17)	−0.026 3(27)	0.196 9(24)	0.960 3(18)
C(18)	0.016 4(31)	0.269 5(28)	0.902 5(24)
C(19)	−0.119 3(28)	0.144 2(27)	0.933 8(22)
C(20)	−0.038 3(31)	0.260 2(29)	1.052 7(21)
C(21)	0.335 2(22)	−0.096 7(18)	0.592 8(16)
C(22)	0.409 8(24)	−0.070 4(20)	0.579 0(16)
C(23)	0.409 0(30)	0.027 2(25)	0.526 4(23)
C(24)	0.330 1(27)	0.103 1(28)	0.542 8(20)
C(25)	0.257 6(22)	0.073 1(19)	0.613 3(16)
C(26)	0.258 2(23)	−0.019 8(19)	0.653 4(17)
C(27)	0.725 8(23)	−0.507 4(19)	0.631 3(16)
C(28)	0.748 7(25)	−0.594 2(20)	0.684 0(19)
C(29)	0.846 1(27)	−0.654 2(25)	0.671 5(21)
C(30)	0.908 5(27)	−0.632 1(22)	0.609 1(19)
C(31)	0.885 7(30)	−0.556 5(26)	0.550 0(23)
C(32)	0.800 1(27)	−0.492 0(26)	0.567 3(20)
C(33)	0.298 0(28)	−0.523 0(24)	0.711 4(19)
C(34)	0.228 2(27)	−0.483 5(25)	0.648 6(21)
C(35)	0.237 8(38)	−0.542 3(36)	0.791 5(27)
C(36)	0.358 2(26)	−0.622 0(23)	0.679 7(20)
C(37)	0.473 4(32)	−0.345 9(28)	0.874 1(23)
C(38)	0.379 9(27)	−0.305 8(27)	0.925 3(23)
C(39)	0.530 0(29)	−0.437 5(27)	0.914 7(24)
C(40)	0.544 1(27)	−0.253 8(24)	0.854 7(21)

Table 3 Selected bond lengths (Å) and angles (°) for compound **5a**

Sn(1)–O(1)	1.99(2)	Sn(1)–O(4)	1.97(2)
Sn(1) ··· O(2)	3.46	Sn(1)–O(3)	2.78(2)
Sn(1)–C(13)	2.16(4)	Sn(1)–C(17)	2.18(3)
B(1)–O(1)	1.20(3)	B(1)–O(2)	1.47(4)
B(1)–C(1)	1.61(4)	B(2)–O(3)	1.48(4)
B(2)–O(4)	1.43(4)	B(2)–C(7)	1.36(5)
Sn(2)–O(6)	1.97(2)	Sn(2)–O(7)	1.99(2)
Sn(2)–O(5)	2.75(2)	Sn(2) ··· O(8)	3.47
Sn(2)–C(33)	2.19(3)	Sn(2)–C(37)	2.19(4)
B(3)–O(5)	1.41(4)	B(3)–O(6)	1.38(4)
B(3)–C(21)	1.52(4)	B(4)–O(7)	1.28(3)
B(4)–O(8)	1.39(3)	B(4)–C(27)	1.51(4)
C(4)–Sn(1)–O(1)	92.0(7)	C(13)–Sn(1)–O(1)	101(1)
C(13)–Sn(1)–O(4)	107(1)	C(17)–Sn(1)–O(1)	101(1)
O(3)–Sn(1)–O(4)	54.6(6)	O(1)–Sn(1)–O(3)	146.3(6)
C(17)–Sn(1)–O(4)	111.4(9)	C(17)–Sn(1)–C(13)	135(1)
O(2)–B(1)–O(1)	120(3)	C(1)–B(1)–O(1)	129(3)
C(1)–B(1)–O(2)	111(2)	C(4)–B(2)–O(3)	103(3)
C(7)–B(2)–O(3)	124(3)	C(7)–B(2)–O(4)	133(3)
B(1)–O(1)–Sn(1)	140(2)	B(2)–O(4)–Sn(1)	120(2)
O(7)–Sn(2)–O(6)	90.0(7)	C(33)–Sn(2)–O(6)	110.3(9)
O(5)–Sn(2)–O(7)	145.7(6)	C(5)–Sn(2)–O(6)	55.9(6)
C(33)–Sn(2)–O(7)	102(1)	C(37)–Sn(2)–O(6)	109(1)
C(37)–Sn(2)–O(7)	102(1)	C(37)–Sn(2)–C(33)	133(1)
O(6)–B(3)–O(5)	112(2)	C(21)–B(3)–O(5)	120(3)
C(21)–B(3)–O(6)	128(3)	O(8)–B(4)–O(7)	118(2)
C(27)–B(4)–O(7)	124(2)	C(27)–B(4)–O(8)	118(2)
B(3)–O(6)–Sn(2)	114(2)	B(4)–O(7)–Sn(2)	140(2)

Table 4 Fractional atomic coordinates for compound **6b**

Atom	x	y	z
Sn(1)	0.2199(2)	0.2199(2)	1.0000
Sn(2)	0.2982(1)	0.1344(1)	0.8432(2)
O(1)	0.2184(11)	0.2184(11)	0.8859(14)
O(2)	0.3121(14)	0.1318(13)	0.9693(14)
O(3)	0.2673(15)	0.1610(14)	0.738 6(13)
B(1)	0.2108(36)	0.2108(36)	0.7068(41)
C(1)	0.2092(23)	0.2092(23)	0.6260(28)
C(2)	0.1539(18)	0.1539(18)	0.5944(21)
C(3)	0.1050(22)	0.1050(22)	0.6272(27)
C(4)	0.1539(22)	0.1539(22)	0.5041(32)
C(5)	0.1993(24)	0.1993(24)	0.4678(29)
C(6)	0.1980(28)	0.1980(28)	0.3882(35)
C(7)	0.2501(21)	0.2501(21)	0.4982(32)
C(8)	0.2617(19)	0.2617(19)	0.5816(23)
C(9)	0.3122(17)	0.3122(17)	0.6197(22)
C(10)	0.2602(20)	0.0103(20)	0.8351(25)
C(11)	0.2929(28)	−0.0220(27)	0.7621(23)
C(12)	0.2964(41)	−0.0397(39)	0.8920(37)
C(13)	0.1781(27)	0.0036(26)	0.8199(23)
C(14)	0.4270(23)	0.1701(23)	0.8321(30)
C(15)	0.4784(27)	0.1387(27)	0.8978(25)
C(16)	0.4252(24)	0.2652(25)	0.8229(23)
C(17)	0.4498(29)	0.1338(30)	0.7580(28)
Cc1	0.0782(25)	0.3699(27)	1.5795(22)
Cc2	0.931(26)	0.4445(27)	1.5694(22)
N(1)	0.1088(27)	0.5166(29)	1.5623(24)

Table 5 Selected bond lengths (Å) and angles (°) for compound **6b**

Sn(1)–O(1)	2.10(3)	Sn(1)–O(2)	2.17(2)
Sn(2)–O(1)	2.06(1)	Sn(2)–O(2)	2.33(3)
Sn(2)–O(3)	2.04(2)	Sn(2)–C(10)	2.14(3)
Sn(2)–C(14)	2.21(4)	O(3)–B(1)	1.37(4)
B(1)–C(1)	1.48(8)	Cc1–Cc2	1.27(5)
Cc2–N(1)	1.23(6)		
O(2)–Sn(1)–O(1)	75.0(7)	O(2)–Sn(2)–O(1)	72.3(9)
O(3)–Sn(2)–O(1)	93(1)	O(3)–Sn(2)–O(2)	166(1)
C(10)–Sn(2)–Sn(1)	110(1)	C(10)–Sn(2)–O(1)	119(1)
C(10)–Sn(2)–O(2)	95(1)	C(10)–Sn(2)–O(3)	94(1)
C(14)–Sn(2)–O(1)	118(1)	C(14)–Sn(2)–C(10)	122(1)
C(14)–Sn(2)–O(2)	90(1)	C(14)–Sn(2)–O(3)	95(2)
Sn(2)–O(1)–Sn(2)	135(1)	Sn(2)–O(1)–Sn(1)	112.4(7)
Sn(2)–O(2)–Sn(1)	100(1)	B(1)–O(3)–Sn(2)	134(3)
O(3)–B(1)–O(3)	129(6)	C(1)–B(1)–O(3)	115(3)
N(1)–Cc2–Cc1	178(5)		

group has only one mirror plane (orthogonal to the mounted axis), and that the Weissenberg axes were equal in length. Least-squares refinement of the unit-cell parameters (based on 12 reflections with θ in the range 12–16°) upheld that two axes (*a* and *b*) were the same length within the bounds of experimental error and that the γ angle was 90.0°. After processing the corrected data the only systematic absence was in the 0,0,*l* subgroup of reflections. The reflection condition was itself ambiguous and of the two possibilities for an observed reflection, $l = 2n$ and $l = 4n$, only the latter reflections were intense. In addition, the volume indicated that there ought to be four molecules of $C_{20}H_{30}B_2O_4Sn$ per unit cell. The space group possibilities were therefore $P4_122$, $P4_222$, $P4_1$, $P4_2$, $P4_3$, $P4_2/m$ of the tetragonal system and $P2_1$ from the monoclinic class, and a Patterson synthesis was run on them all; $P4_122$ and $P4_222$ were unlikely as they both require eight molecules per unit cell and they both failed to yield any heavy-atom positions and had unfavourable *R*(int) values of 0.28 23; $P4_1$, P4$_2$ and $P4_3$ also failed to produce any heavy-atom positions but had more reasonable *R*(int) values of 0.1010. Although $P4_2/m$ managed to yield two tin positions (at 0.5, 0.5, 0.25 and 0.8215, 0.0171, 0.000 with site occupancy factors of 0.25 and 0.50, respectively) and the map also contained another high peak with an intensity approximately 80% of that given for the tin positions, and was inconsistent with the available chemical evidence. The complete structure was solved, and subsequently refined, in space group $P2_1$ [*R*(int) = 0.0851] with two molecules, identical structurally within the bounds of experimental error, per asymmetric unit. Hydrogen atoms were included at calculated positions [*d*(C–H) 1.08 Å] with fixed isotropic thermal parameters (0.05 Å^2). It would appear that, as shown in the packing diagram (Fig. 3), the four-fold helical hydrogen bonding found within this structure is responsible for the tetragonal pseudo-symmetry observed. In the final stages of refinement the atoms of both Sn(O$_2$B)$_2$ units were treated anisotropically. Atomic coordinates and selected geometric data are given in Tables 2 and 3, respectively. The asymmetric unit, incorporating the atomic numbering scheme used in both the Tables and text, is shown in Fig. 1.

The unit cell for compound **6b** was determined from 12 reflections in the θ range 11–17°. Other experimental details are given in Table 1. The data collected showed systematic absences *h*00, *h* odd, 0*k*0, *k* odd, 00*l*, *l* odd, 0*kl*, $k + l$ odd and *h*0*l*, $h + l$ odd, though the latter appears to be more apparent than real as no space group requires more than the first four absences listed without the need for additional conditions which were not found. The apparent *h*0*l* condition is probably a consequence of the high degree of pseudo-symmetry in the molecule. Of the available tetragonal space groups, $P\bar{4}/m$, $P\bar{4}n2$ and $P4_2nmn$ yielded heavy-atom positions from the Patterson syntheses in numbers and positions inconsistent with the chemical formula. The structure could be solved in both $P4_2$ and $P4_2nm$, with generally the same limitations in both cases [the Bu^t groups on Sn(1) could not be located in either space group], so the final data presented relate to the higher-symmetry option ($P4_2nm$), which requires all the systematic absences (save *h*0*l*, $h + l$ odd). The Bu^t groups on Sn(1) appeared as a smear of electron density from which chemically consistent atom positions could not be refined. However, the spectral data for this compound and the requirements of the unit-cell volume leave no doubt surrounding the existence of these two groups. In the light of these difficulties, the final stages of refinement only involved anisotropic treatment of the heavy-atom positions. Atomic coordinates and selected geometric data are given in Tables 4 and 5, respectively. The asymmetric unit, incorporating the atomic numbering scheme used in both the Tables and text, is shown in Fig. 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

References

1 Part 2, P. Brown, M. F. Mahon and K. C. Molloy, *J. Organomet. Chem.*, 1992, **435**, 265.
2 K. C. Molloy, *Adv. Organomet. Chem.*, 1991, **33**, 171.
3 P. Brown, M. F. Mahon and K. C. Molloy, *J. Chem. Soc., Chem. Commun.*, 1989, 1621.
4 M. F. Mahon, K. C. Molloy and P. C. Waterfield, *J. Organomet. Chem.*, 1989, **361**, C5.
5 P. Brown, K. C. Molloy and M. F. Mahon, in *Chemistry and Technology of Silicon and Tin*, eds. V. G. Kumar Das, S. W. Ng and M. Gielen, Oxford Science Publications, Oxford, 1992, p. 559.
6 P. Brown, M. F. Mahon and K. C. Molloy, *J. Chem. Soc., Dalton Trans.*, 1990, 2643.
7 C. L. Christ and J. R. Clark, *Phys. Chem. Minerals*, 1977, **2**, 59.
8 H. Puff, W. Schuh, R. Sievers, W. Wald and R. Zimmer, *J. Organomet. Chem.*, 1985, **260**, 271.
9 C. P. Brock, P. Minton and K. Niedenzu, *Acta Crystallogr., Sect. C*, 1987, **43**, 1775.
10 S. K. Mehrotra, G. Srivastava and R. C. Mehrotra, *J. Organomet. Chem.*, 1973, **47**, 39.
11 S. K. Mehrotra, G. Srivastava and R. C. Mehrotra, *J. Organomet. Chem.*, 1974, **65**, 361.
12 S. K. Mehrotra, G. Srivastava and R. C. Mehrotra, *J. Organomet. Chem.*, 1974, **65**, 367.
13 S. K. Mehrotra, G. Srivastava and R. C. Mehrotra, *J. Organomet. Chem.*, 1974, **73**, 277.
14 C. J. Evans, in *Chemistry of Tin*, ed. P. G. Harrison, Blackie, Glasgow, 1989, p. 430.
15 O. Graalmann, U. Klingebiel, W. Clegg, M. Haase and G. M. Sheldrick, *Z. Anorg. Allg. Chem.*, 1984, **519**, 87.
16 D. A. Foucher, A. J. Lough and I. Manners, *J. Organomet. Chem.*, 1991, **414**, C1.
17 B. J. Brisdon, M. F. Mahon, K. C. Molloy and P. J. Schofield, *J. Organomet. Chem.*, 1992, **436**, 11.
18 A. Mazzah, A. Haoudi-Mazzah, M. Noltemeyer and H. W. Roesky, *Z. Anorg. Allg. Chem.*, 1991, **604**, 93.
19 J. Vicat and S. Aleonard, *Bull. Soc. Fr. Mineral. Cristallogr.*, 1966, **89**, 271.
20 A. G. Davies and P. J. Smith, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, p. 523.
21 H. A. Bent, *Chem. Rev.*, 1961, **61**, 275.
22 J. B. Farmer, *Adv. Inorg. Chem. Radiochem.*, 1982, **25**, 187.
23 S. J. Rettig and J. Trotter, *Can. J. Chem.*, 1977, **55**, 3071.
24 P. A. Akishin and V. P. Spiridonov, *Dokl. Akad. Nauk SSSR*, 1960, **131**, 557.
25 M. A. Edelman, P. B. Hitchcock and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1990, 1116.
26 J. J. Park, D. M. Collins and J. L. Hoard, *J. Am. Chem. Soc.*, 1970, **92**, 3636.
27 C. Glidewell and D. C. Liles, *Acta Crystallogr., Sect. B*, 1978, **34**, 129.
28 H. Puff, E. Friedrichs and F. Visel, *Z. Anorg. Allg. Chem.*, 1981, **477**, 50.
29 H. Puff, I. Bung, E. Friedrichs and A. Jansen, *J. Organomet. Chem.*, 1983, **254**, 23.
30 C. K. Chu and J. D. Murray, *J. Chem. Soc. A*, 1971, 360.
31 R. C. Poller, *J. Chem. Soc.*, 1963, 706.
32 K. C. Molloy, T. G. Purcell, K. Quill and I. W. Nowell, *J. Organomet. Chem.*, 1984, **267**, 237.
33 S. A. Kandil and A. L. Allred, *J. Chem. Soc. A*, 1970, 2987.
34 *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
35 G. M. Sheldrick, SHELX 76, A program for crystal structure determinations, University of Cambridge, 1976.
36 G. M. Sheldrick, SHELX 86, A program for the solution of crystal structures, University of Göttingen, 1986.
37 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

Received 6th July 1992; *Paper* 2/03527H