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Synthesis, solution and solid-state NMR spectra of methyl 4,6-*O*-benzylidene-2,3-bis-*O*-(organostannylmethyl)-α-D-glucopyranosides Crystal structure of methyl 4,6-*O*-benzylidene-2,3-bis-*O*-[(dimethylphenylstannyl)methyl]-α-D-glucopyranoside

Simon J. Garden [a], William T.A. Harrison [b], R. Alan Howie [b,*], Helena Rufino [b], James L. Wardell [a,1]

[a] *Instituto de Quimica, Universidade Federal do Rio de Janeiro, C.P. 68563, 21945-970 Rio de Janeiro-RJ, Brazil*
[b] *Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, AB24 3UE, UK*

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Abstract

Methyl 4,6-*O*-benzylidene-2,3-bis-*O*-($Ph_nMe_{3-n}SnCH_2$)-α-D-glucopyranosides, (**3**: $n=3$; **4**: $n=2$; **5**: $n=1$), prepared from methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**6**) and $Ph_nMe_{3-n}SnCH_2I$, contain four co-ordinate tin centres in both solution and solid state. Whereas a single molecular arrangement is indicated in solution for **3**–**5**, evidence for several arrangements in the solid state was obtained for each compound from the ^{119}Sn- and ^{13}C-NMR spectra. An X-ray structure determination of **5** indicated the presence of three slightly differing molecular arrangements, and the absence of any intermolecular contacts. Assignments of the individual Sn signals in the solution NMR spectra of **3** and **5** to their attached CH_2 groups have been accomplished. The stannacyclic compound, methyl 4,6-*O*-benzylidene-2,3-bis-*O*-(2,2-diphenyl-2-stannapropylidene)-α-D-glucopyranoside (**7**) was similarly prepared from **6**, using $Ph_2Sn(CH_2I)_2$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbohydrate; Organotin; Crystal structures; Solid-state NMR

1. Introduction

Tetraorganotin compounds generally are molecular species with near tetrahedral tin centres, as shown by the various structures listed in the Cambridge Structural Database [1], accessed at the EPSRC's Chemical Database Service at Daresbury [2]. The coordination number of tin, however, can increase to 5 or even 6, if internal donor groups are suitably sited to complex with the tin centres [3–5]. Any intermolecular interactions of tetraorganotin compounds will involve centres other than tin, for example as in associations arising from hydrogen bonding and exemplified by 5-deoxy-1,2-*O*-isopropylidene-5-*C*-triphenylstannyl-α-L-xylofuranose [6]. In solution, tetraorganotin compounds, as shown by NMR spectroscopy, exist in single (or time-averaged) conformations at ambient temperatures [7].

Solid-state NMR spectroscopy and X-ray crystallography make a very powerful and practical combination for the investigation of intermolecular associations and molecular arrangements of related compounds in the solid state: particularly good use of the combined techniques was made in the studies on associated 1,3,2-dioxastannolenes, including **1** and **2** [8–11].

Bis(triorganostannylmethyl) derivatives (**3**–**5**) of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside, **6**, have been synthesized. In keeping with expectations, each of

* Corresponding author. Tel.: +44-1224-272907; fax: +44-1224-272921.
E-mail address: r.a.howie@abdn.ac.uk (R.A. Howie).
[1] On leave from the University of Aberdeen.

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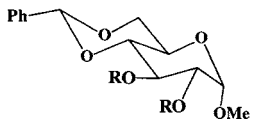
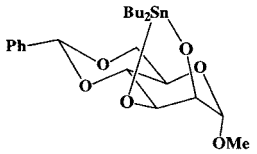
3–5 has solution ^{1}H-, ^{13}C- and ^{119}Sn-NMR spectra consistent with the presence of a single (or time-averaged) arrangement. In contrast in the solid state, as shown by their ^{13}C and ^{119}Sn-NMR spectra for **3–5**, and by X-ray crystallography for **5**, the compounds exist in several molecular arrangements, but with each arrangement having two 4-coordinate tin centres. We now report our findings.



1: -R, R- = -Bu_2Sn-
3: R=Ph_3SnCH_2
4: R= $MePh_2SnCH_2$
5: R = $Me_2PhSnCH_2$
6: R = H:
7: -R, R- = -$CH_2Sn(Ph_2)CH_2$-
11: R=IPh_2SnCH_2
12: R=IMePhSnCH$_2$



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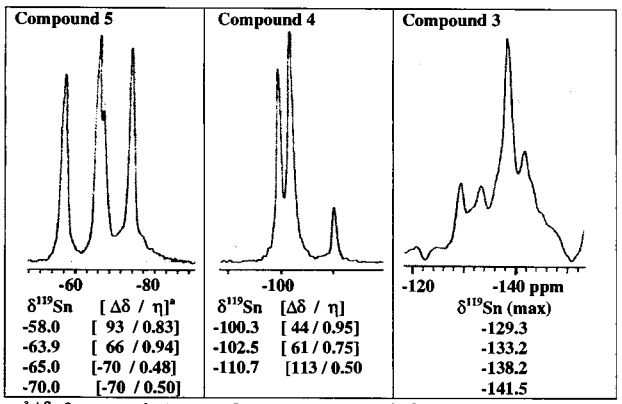
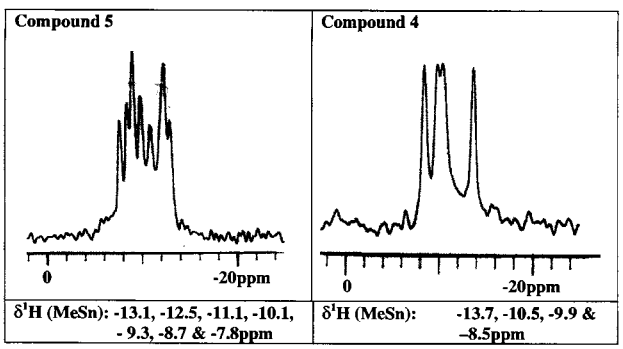
(a) Solid state ^{119}Sn NMR spectra of 3-5 at 111.9 MHz



δ^{119}Sn	[$\Delta\delta$ / η]^a	δ^{119}Sn	[$\Delta\delta$ / η]	δ^{119}Sn (max)
-58.0	[93 / 0.83]	-100.3	[44 / 0.95]	-129.3
-63.9	[66 / 0.94]	-102.5	[61 / 0.75]	-133.2
-65.0	[-70 / 0.48]	-110.7	[113 / 0.50	-138.2
-70.0	[-70 / 0.50]			-141.5

$^a\Delta\delta$ & η are anisotropy and asymmetry, respectively.

(b) Me-Sn regions in the solid state ^{13}C NMR spectra of 4 and 5 at 75.4 MHz.



δ^1H (MeSn): -13.1, -12.5, -11.1, -10.1, - 9.3, -8.7 & -7.8ppm	δ^1H (MeSn): -13.7, -10.5, -9.9 & –8.5ppm

Fig. 1. Selected solid-state NMR spectral details. (a) Solid-state ^{119}Sn-NMR spectra of **3–5** at 111.9 MHz. ($^a\Delta\delta$ and η are anisotropy and asymmetry, respectively. (b) Me–Sn regions in the solid-state ^{13}C-NMR spectra of **4** and **5** at 75.4 MHz.

2. Results and discussion

2.1. Synthesis of 3–5

Compounds **3–5** were obtained from methyl 4,6-*O*-benzylidene-α-D-glucopyranoside, (**6**), on reaction with $Ph_nMe_{3-n}SnCH_2I$ ($n = 1–3$) (1:2 mol. ratio) in DMF in the presence of NaH, by the adaption of a procedure used previously to prepare mono-(triorganostannylmethylated) carbohydrates [12,13].

2.2. Solution NMR spectra of 3–5

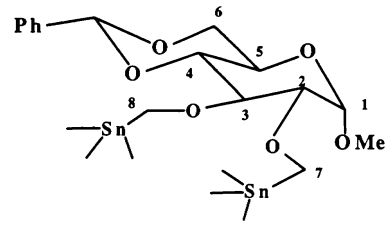
Assignments of the $CDCl_3$ solution ^{1}H- and ^{13}C-NMR spectra of **3–5** at 250 and 63.3 MHz, respectively, were obtained with the help of ^{1}H–^{1}H and ^{1}H–^{13}C correlation spectra: details are listed in Table 1. As shown by the J_{H-H} values, dialkylations of methyl 4,6-benzylidene-α-D-glucopyranoside by the iodomethylstannanes have negligible effects on the $^{4}C_1$ chair conformations of the pyranose rings in solution. Of interest, the $MePh_2Sn$ and Me_2PhSn moieties in **4** and **5** contain diastereomeric phenyl and methyl groups, respectively, as consequences of the nearby chiral moieties. The two tin centres in each of the ditin derivatives, **3–5**, exist in solution in slightly different environments as shown by the two δ^{119}Sn values. One dimensional ^{13}C measurements, at 127 MHz, with single frequency tin-119 and proton decoupling, was used to assign the tin peaks in **3** and **5** to their attached methylene groups. This was achieved on irradiating at the frequency of one tin site and observing the collapse of the ^{119}Sn satellites at the methylene carbon atom. In both **3** and **5**, the tin atom, having the higher field absorption, is linked to the higher field methylene carbon atom. It was assumed that a similar situation would also prevail for **4**.

The δ^{119}Sn values and $^{1}J_{Sn-C}$ coupling constants indicate 4-coordinate, tetrahedral tin geometries for all tin centres in **3–5**, the values are similar to those determined in other $Ph_nMe_{3-n}SnCH_2OR$ compounds, e.g. δ^{119}Sn values for $Ph_nMe_{3-n}SnCH_2OR$: ROH = methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside are -143.0, -100.1 and -59.8 for $n = 3$, 2 and 1, respectively [12], compared to values of -143.2 and -144.7 for **3**, -101.6 and -101.9 for **4** and -61.3 and -63.1 ppm for **5**.

2.3. Solid-state NMR spectra of 3–5

Solid-state ^{13}C- and ^{119}Sn-NMR spectra were obtained for **3–5**; the ^{119}Sn-NMR spectra and selected regions of the ^{13}C-NMR spectra are shown in Fig. 1. In each of the three compounds, the ^{13}C and ^{119}Sn spectra were more complex than expected for a single molecular arrangement: however, the δ^{119}Sn values in all cases

Table 1
Solution ($CDCl_3$) NMR spectral details



(a) ^{1}H-NMR spectra: values of δ (ppm) and J (Hz)

Compound	δH_1 [J_{H1-H2}]	δH_2 [J_{H2-H3}]	δH_3 [J_{H3-H4}]	δH_4 [J_{H4-H5}]	δH_5 [J_{H5-H6}]	δH_6 [$J_{H6-H6'}$]	$\delta H_{6'}$ [$J_{H5-H6'}$]	δH_7 [$J_{H7-H7'}$] {J_{Sn-H}}	$\delta H_{7'}$ {J_{Sn-H}}	δH_8 [$J_{H8-H8'}$] {J_{Sn-H}}	$\delta H_{8'}$ {J_{Sn-H}}	δOMe	δC*H*Ph	δPh	δMe {J_{Sn-H}}
6 [a]	4.72 [3.7]	3.57 [9.2]	3.90 [9.2]	3.45 [ca. 9]	3.78 [ca. 9.5]	3.71 [8.6]	4.27 [3.0]					3.41	5.51	7.36–7.52	
3	4.58 [3.8]	3.31 [9.2]	3.84 [9.3]	3.52 [9.3]	3.84 [9.9]	3.71 [10.1]	4.29 [4.4]	4.44 [10.3] {25.7}	4.53 {27.7}	4.62 [9.5] {24.4}	4.75 {28.0}	3.35	5.47	7.21–7.68	
4	4.72 [3.7]	3.30 [9.2]	3.77 [9.2]	3.51 [9.5]	3.84 [9.6]	3.72 [9.7]	4.30 [4.4]	4.28 [10.3] {nd [c]}	4.32 {nd}	4.44 [9.8] {15.9}	4.53 {24.9}	3.40	5.51	7.21–7.67	0.49 {56, 54}, 0.57 {56, 54}
5	4.81 [3.7]	3.26 [9.1]	3.65 [9.2]	3.49 [ca. 9.5]	3.82 [9.5]	3.72 [10.0]	4.29 [4.4]	4.07 [10.4] {nd}	4.16 {nd}	4.25 [10.1] {nd}	4.31 {nd}	3.42	5.53	7.21–7.57	0.30 {55, 53}, 0.31 {56, 54}, 0.40 {56, 54}, 0.40 {56, 54}
7	4.89 [3.9]	3.48 [8.8]	3.94 [9.0]	3.60 [9.5]	3.96 [9.9]	3.80 [10.0]	4.37 [4.7]	4.29 12.5] {8.1}	4.97 {nd}	4.41 [12.5] {5.6}	4.95 {5.2}	3.52	5.62	7.40–7.80	
11	4.76 [3.7]	3.43 [9.2]	3.87 [9.2]	3.53 [9.2]	3.79 [9.6]	3.71 [9.7]	4.28 [4.0]	4.62 [10.0] {9.1}	4.70 {nd}	4.72 [9.4] {nd}	4.85 {20.0}	3.36	5.45	7.32–7.78	
12	3.4–5.5 (m)														0.6–1.4 (br)

(b) 13C NMR: values of δ (ppm) and J (Hz)

	δC1	δC2	δC3	δC4	δC5	δC6	δC7 [J_{Sn-C}]	δC8 [J_{Sn-C}]	δOMe	CHPh	CHPh	Ph–Sn [b] [J_{Sn-C}]	Me–Sn [J_{Sn-C}]
6	99.8	72.7	71.3	80.9	62.3	68.8			55.4	101.8	126.3, 128.2, 129.1, 137.0		
3	96.7	83.9	83.6	82.3	62.1	69.1	64.8 [475.455]	65.5 [490, 468]	55.2	101.4	126.1, 128.0; 128.9, 136.9	128.3 & 128.4; 128.8 & 128.9; 137.1 [36]; 138.1 [500, 480] & 138.3 [502, 482]	
4	98.1	84.0 [43]	83.0 [56]	82.2	62.2	69.1	64.1 [460, 440]	65.6 [474, 453]	55.3	101.4	126.1, 128.2; 128.9, 137.4	128.09 & 128.11 [47], 128.27 & 128.30 [45]; 128.5, 128.7 [10]; 136.7 [35]; 139.36 & 139.38 [481, 459], 139.68 & 139.71 [483, 455]	−11.21, −11.15 [357, 341]
5	98.5	84.1 [41]	82.3 [51]	82.2	62.3	69.1	63.8 [442, 422]	65.8 [436, 418]	55.3	101.4	126.1, 128.1; 128.9, 137.4	127.9 & 128.2 [45]; 128.4 [10]; 136.167 136.19 [33]; 140.9 & 141.2 [460, 442]	−10.8, −10.7, −10.66, −10.63 [340, 325]
7	99.1	85.6	83.1	80.1	61.9	68.9	66.1 [435, 416]	65.3 [430, 411]	55.1	101.7	126.3, 128.1; 128.9, 137.2	128.5 [47]; 129.0 [11]; 136.78 & 136.80 [34]; 138.0 [419, 403] & 138.2 [421, 405]	
11	98.4	83.1 [47]	82.8 [64]	81.8	62.2	68.9	68.1 [506, 482]	68.6 [522, 500]	55.3	101.5	126.3, 128.1; 128.9, 137.2	128.7 [57] & 128.9 [60]; 129.9 [13] & 130.1 [13]; 132.26 & 136.28 [47]; 136.5 & 137.0 [nd]	
12	97.8	82.9 [43]	81.8 [46]	81.4	62.2	68.8	67.3 [495, 474]	69.4 [506, 484]	55.3	101.6	126.1–139.0	−3.08, −2.93, −2.75	

[a] δ(OH) = 3.09.
[b] The δC values are listed in the sequence C-*meta*, C-*para*, C-*ortho*, C-*ipso*.
[c] nd, not determined.

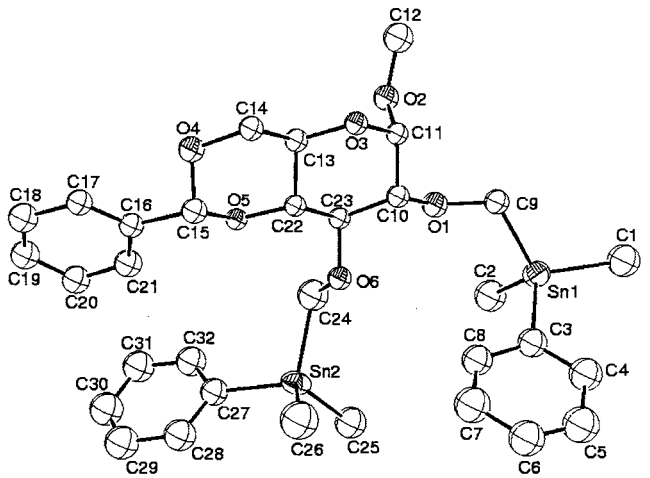


Fig. 2. Atom numbering system and atom arrangement for molecule 1 of compound **5**.

were in the regions expected for four coordinate species and were close to the values obtained in solution. The most complex situation was realised for **3**: an envelope of peaks between -125 and -150ppm was observed in the Sn-NMR spectrum, with four clear spikes or maxima apparent: deconvolution of the envelope indicates even more Sn resonances. The ^{13}C-NMR spectrum of **3** was particularly complex and was not resolved: the spectra of **4** and **5** were easier to assign, see Section 3. However, there are still complications in resolving together the ^{13}C and ^{119}Sn spectra of each compound. For example for **4**, there are four Me–Sn signals in the solid-state ^{13}C-NMR spectrum, but only three δ^{119}Sn values in the ^{119}Sn spectrum. For **5**, there are seven δ^{1}H Me–Sn and four tin chemical shift values, Fig. 1.

To resolve the problem over the complexity of the solid-state NMR spectra and to establish whether a single crystalline phase or polymorphic forms were present in the solid state, attempts were made to obtain suitable crystals for X-ray determinations. Unfortunately, the only success was had with **5**. However, as reported below, the X-ray determination did confirm a complex solid-state situation with the finding of three independent molecules within the same crystalline phase.

2.4. Crystal structure of **5**

The crystals of **5**, used in the crystallographic study, were grown by slow evaporation of a MeOH solution. The initial data set was collected at 300 K: due to the apparent disorder at the two tin sites in one of the independent molecules, as described in the Section 3, a further data set was subsequently collected using a different crystal at 120 K. The same space group, $P2_12_12_1$, with $z = 12$ and three independent molecules in the asymmetric unit, was found to be appropriate for both data sets. The refinement with the lower temperature data set removed problems with disorder at only one of these tin sites. As expected, there was a reduction of approximately 1% in the length of the cell edges in the 120 K refinement. It should be emphasised that the sugar moieties were well behaved at both temperatures and that the disorder was restricted to the tin environments in just one of the three independent molecules.

The three independent molecules are designated, molecules 1, 2 and 3. The atom arrangement in molecule 1, containing Sn1 and Sn2, is shown in Fig. 2: the molecular arrangements of molecule 2, containing Sn3 and Sn4, and molecule 3, containing Sn5 and Sn6, are basically similar. The numbering of atoms for each of the three molecules follows similar sequences:

molecule 1: Sn1, Sn2, C1–C32, O1–O6 and H atoms
molecule 2: Sn3, Sn4, C33–C64, O7–O12 and H atoms
molecule 3: Sn5, Sn6, C65–C96, O13–O18 and H atoms

Table 2 lists the Sn–C bond length and C-Sn-C bond angle ranges at each of the tin centres in the three molecules as determined at the two temperatures. As shown by the bond angles at Sn1 to Sn5, these tin atoms have slightly distorted tetrahedral geometries: there are only minor differences between the arrangements of the organic groups about the tin atoms. The bond angles determined at Sn6, the centre exhibiting the more persistent disorder, are somewhat more removed from ideal tetrahedral values, in covering a wider range. However, they provide no clear evidence for other than tetrahedral geometry. The pyranose rings in all three molecules are close to the $^{4}C_1$ chair conformations, as shown by the Cremer and Pople puckering parameter, θ, values being near 0°, see Table 2 [14,15]: the value of the other parameter, ϕ, indicates the direction of any distortion away from the ideal chair $^{4}C_1$ conformation [15]. There are essentially only minor differences between the pyranose ring conformations of the three molecules at a given temperature; furthermore, only slight conformational changes arise on changing the temperature. The same applies to the benzylidene rings, which have inverted chair conformations as indicated by the θ values being all close to 180°, Table 2. Differences, however, are realised in the exocyclic torsional angles, Sn–C(H_2)–O–C(pyranose ring) in molecule 3 compared to those in the other two molecules, Table 2: such differences will lead to differences in the tin chemical shift values.

The three independent molecules in the crystals of **5** examined have a total of six tin sites and 12 Me–Sn sites. As the δ^{119}Sn and δ^{13}C solid-state NMR spectra of **5** contain four Sn peaks and seven Me–Sn peaks, Fig. 1, some of these sites clearly must be equivalent.

There still remains the possibility of additional complexity from polymorphism: however attempts to obtain other crystalline forms of **5** were unsuccessful.

The single-crystal structure determinations indicate that **5**, a molecule with a significant hydrocarbon region, as well as a distinct polar area, has some freedom in packing in the solid state. Compounds **3** and **4**, with even larger hydrophobic areas, were never obtained as crystalline solids, but rather as amorphous powders. It is tempting to argue that **5** is near the limit of obtaining a sufficiently well ordered solid state, and that **3** and **4**, with greater degrees of freedom in packing, are beyond this limit.

2.5. Other synthesis

Methyl 4,6-*O*-benzylidene-2,3-bis-*O*-(2,2-diphenyl-2-stannapropylidene)-α-D-gluco-pyranoside (**7**) was obtained from **6** and $Ph_2Sn(CH_2I)_2$. The δ^{119}Sn value for **7** is at a significantly lower field value and the $^1J_{119,117Sn-13C}$ values are considerably smaller than those reported for non-stannacyclic $Ph_2Sn(CH_2OR)_2$ compounds (ROH = 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**8**) [16]; ROH = methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside (**9**) [12]; and ROH = 1,2:5,6-di-*O*-isopropylidene-α-D-glucopyranose (**10**) [17], see Table 3. These data indicate that a ring effect is at play in **7**.

The reaction of $Sn(CH_2I)_4$ and **6** was also attempted: this reaction provided a mixture of products, including a considerable amount of insoluble polymeric material. Chromatography led to the isolation of a major soluble fraction, which exhibited two major ^{119}Sn signals of approximately equivalent intensity [−68.8 and −70.1 ppm] but also three very minor ^{119}Sn signals of approximately equivalent intensity [−113.1, −116.5 and

Table 2
Selected geometric parameters for compound **5** at 120 and 300 K

	Molecule 1	Molecule 2	Molecule 3
Sn–C bond length range (Å)	(a) 120 K: 2.114(14)–2.146(15) at Sn1; 2.092(15)–2.174(12) at Sn2	(a) 120 K: 2.114(11)–2.160(12) at Sn3; 2.138(13)–2.152(12) at Sn4	(a) 120 K: 2.085(9)–2.145(15) at Sn5; 2.055(13)–2.221(9) at Sn6 [a]
	(b) 300 K: 2.081(16)–2.121(19) at Sn1; 2.08(2)–2.159(15) at Sn2	(b) 300 K: 2.102(17)–2.159(12) at Sn3; 2.120(14)–2.193(14) at Sn4	(b) 300 K: 2.094(12)–2.154(7) at Sn5 [a]; 2.098(12)–2.226(15) at Sn6 [a]
C–Sn–C bond angle range (°)	(a) 120 K: 105.5(5)–113.9(5) at Sn1; 104.9(5)–112.8(5) at Sn2	(a) 120 K: 105.9(5)–112.5(5) at Sn3; 106.0(5)–112.9(5) at Sn4	(a) 120 K: 107.0(8)–115.8(11) at Sn5; 99.8(6)–117.0(6) at Sn6 [a]
	(b) 300 K: 106.7(5)–112.6(6) at Sn1; 106.4(7)–111.8(6) at Sn2	(b) 300 K: 106.4(5)–112.8(6) at Sn3; 106.9(5)–112.6(7) at Sn4	(b) 300 K: 105.9(5)–116.9(6) at Sn5 [a]; 102.7(9)–126.1(9) at Sn6 [a]
Sn–C(H_2)–O–C torsion angles (°)	(a) 120 K: Sn1–C9–O1–C10 128.0(7); Sn2–C24–O6–C23 −159.7(7)	(a) 120 K: Sn3–C41–O7–C41 126.2(8); Sn4–C56–O12–C55 −162.0(7)	(a) 120 K: Sn5–C73–O13–C74 −165.6(8); Sn6 [a]–C88–O18–C87 174.1(8)
	(b) 300 K: Sn1–C9–O1–C10 126.1(8); Sn2–C24–O6–C23 −161.0(7)	(b) 300 K: Sn3–C41–O7–C41 126.3(8); Sn4–C56–O12–C55 −161.0(7)	(b) 300 K: Sn5 [a]–C73–O13–C74 −165.6(8); Sn6 [a]–C88–O18–C87 173.8(9)

Pucker parameters	Q (Å)	θ (°)	ϕ (°)	Q (Å)	θ (°)	ϕ (°)	Q (Å)	θ (°)	ϕ (°)
Pyranose									
120 K	0.582(11)	1.2(11)	228(68)	0.567(12)	1.9(12)	235(41)	0.594(12)	7.6(13)	309(9)
300 K	0.570(11)	4.2(11)	254(17)	0.560(12)	4.3(13)	257(14)	0.594(13)	3.6(13)	283(19)
Benzylidene									
120 K	0.593(12)	173.6(11)	297(10)	0.571(12)	177.9(12)	278(42)	0.609(12)	174.1(11)	300(10)
300 K	0.606(11)	176.1(10)	310(15)	0.568(12)	175.8(12)	339(19)	0.593(12)	174.7(12)	304(12)

[a] Disordered Sn site.

Table 3
Selected NMR parameters for $Ph_2Sn(CH_2OR)_2$ compounds in $CDCl_3$ solution

Compound	δ^{119}Sn (ppm)	[J(^{119,117}Sn–$^{13}C_i$)] (Hz)	[J(^{119,117}Sn–$^{13}C_\alpha$)] (Hz)	Ref.
7	−111.5	421, 405	435, 416	This study
8	−151.7	466, 446	452, 432	[14]
9	−147.0	468, 447	449, 429	[12]
10	−144.4	490, 468	456, 436	[15]

−118.6 ppm]. The two major peaks are assumed to arise from stereoisomers of monomer **6**: the minor peaks have not been assigned.

Rapid iodo-dephenylation of **3** and **4** took place with a 1:2 mole ratio of **3**–**4**:I_2 at room temperature to give the corresponding bis(iododiorganostannyl) derivatives, **11** and **12**, respectively. No selective cleavage of Ph–Sn bonds was met using a 1:1 mole ratio of reagents. The solution NMR data, especially the δ^{119}Sn and $^1J_{Sn-C}$ values of **11** and **12**, are similar to those determined for mono(iododiorganostannylmethyl) derivatives of methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside [12] and 1,2;3,4-di-*O*-isopropylidene-β-α-galactopyranose [16], which were established as being 4-coordinate species: in addition, no evidence was gained for any interaction between the two weakly Lewis acid centres in **11** and **12**. Attempts to get suitable crystals for a X-ray determination of **11** failed, due to its decomposition on further recrystallizations, as shown by the formation of yellow coloured solutions and the deposition of colourless amorphous powders. Compound **12** has two tin sites each with four different substituents. However, being triorganotin halide species, bearing internal donor groups, they will undergo fairly rapid racemisation in solution. Hence, stereoisomers in solution are unlikely to be detected by NMR spectroscopy. The reaction between **5** and I_2 (1:2 mole ratio) in chloroform, as shown by the ^{1}H- and ^{119}Sn-NMR spectra taken as quickly as possible after consumption of the iodine, resulted in the formation of a major product, **13**, (>95%), having a single δ^{119}Sn value of −160.6 ppm. The presence of iodobenzene (100%, based on I_2 used) in the reaction mixture indicated that complete Ph–Sn bond cleavage had occurred. However, it appeared that the bis(iododimethylstannyl) derivative, **14**, of compound **5**, was not present in the reaction solution: the expected δ^{119}Sn value of this compound would be approximately −10 ppm {cf. δ^{119}Sn for 4-coordinate iodo[6-*O*-(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranosyl]dimethylstannane is −8.9 ppm in $CHCl_3$ solution [16]}. The δ^{119}Sn value, −160.6 ppm, suggests that **13** could be an IMe_2SnO species. From earlier studies [17,18], we found that $Me_3SnCH_2OR^*$ (R*OH = carbohydrate) have limited stability on standing in air and undergo oxidative-hydrolysis and rearrangement to $[Me_3SnO_2CH]$: if a similar reaction sequence operates here, then $[IMe_2SnOC(O)H]$ would be formed.

3. Experimental

Solution NMR were generally obtained on Bruker 250 MHz and Varian 400 MHz instruments: the 500 MHz ^{1}H spectrum of **3** was obtained at the University of Edinburgh and the tin decoupling experiments on **3** and **5** were performed at the University of Marburg on a Bruker AMX-500 instrument at 300 K. For the latter, a triple resonance probe head was used, with the ^{1}H coil in inverse geometry: for the single frequency tin decoupling experiments, the coil was doubly tuned to ^{13}C at 125.7 MHz and a second multinuclear tuneable coil adjusted to ^{119}Sn at 186.4 MHz. Solid-state NMR spectra were recorded by the EPSRC service, based at the University of Durham, on a Varian VXR spectrometer with Doty Scientific MAS probes, with frequencies for ^{13}C and ^{119}Sn = 75.4 and 111.9 MHz. IR spectra were obtained on Philips Analytical PU 9800 FTIR and Nicolet 205 FTIR instruments.

Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside [19], $Ph_nMe_{3-n}SnCH_2I$ and $Ph_2Sn(CH_2I)_2$ [12,13] were obtained by published procedures. DMF was dried over CaH_2 and was distilled prior to use.

3.1. Reactions of the disodium salt of 6 with $Ph_nMe_{3-n}SnCH_2I$ (n = 1–3) or $Ph_2Sn(CH_2I)_2$. General procedure

To a dry DMF solution (20 ml) of **6** (5.00–10.0 mmol) and excess sodium hydride (0.5–1.0 g) under a nitrogen atmosphere was added $Ph_nMe_{4-n-m}Sn(CH_2I)_m$ (*m*:2 mole ratio of **6**: $Ph_nMe_{4-n-m}Sn(CH_2I)_m$). The reaction mixture was stirred at room temperature (r.t.) and was monitored by TLC [irrigant; petrol (60–80°C): ethyl acetate in ratios from 9:1 (v/v) to 2:3 (v/v)]. On complete reaction, methanol (10 ml) was slowly added, followed by water (50 ml) and ether (50 ml). The aqueous phase was separated and extracted with ether (3 × 30 ml). The combined ethereal solutions were washed with water (3 × 50 ml), dried over calcium chloride and rotary evaporated. Subsequent methods of purifications of the residues are detailed individually.

3.2. Methyl 4,6-O-benzylidene-2,3-bis-O-[(triphenylstannyl)methyl]-α-D-glucopyranoside (3)

The product was recrystallized successively from ethanol, and ethyl acetate–diethyl ether, yield 52%; m.p. 152–155°C.

Anal. Found: C, 61.82; H, 5.08. Calc. for $C_{52}H_{50}O_6Sn_2$: C, 61.94; H, 5.00%.

IR ($\nu \pm 4$ cm^{-1}): 3065, 3048, 3015, 2990, 2986, 2977, 2903, 2865, 1482, 1429, 1373, 1152, 1125, 1084, 1076, 1049, 1022, 1013, 997, 959, 727, 698, 448.

^{1}H-NMR and ^{13}C-NMR spectral details in $CDCl_3$ solution are listed in Table 1.

^{119}Sn-NMR ($CDCl_3$, 93.3 MHz): δ −143.2 (at C-8), −144.7 (at C-7).

^{119}Sn-NMR (solid state; 111.9 MHz; pulse sequence SXSEQ; cross polarisation with flip-back contact time 5.0 ms; relaxation delay 5.0 s; spin rate 40 300; AF time constant 0.005 s).

δ: see Fig. 1.

3.3. Methyl 4,6-O-benzylidene-2,3-bis-O-[(methyldiphenylstannyl)methyl-α-D-glucopyranoside (4)

The residue was purified using a chromatotron with petrol (60–80°C): ethyl acetate (10:1 (v/v)) as eluent. The collected product was recrystallized from ethanol, yield 54%; m.p. 80–82°C.

Anal. Found: C, 57.25; H, 5.28. Calc. for $C_{42}H_{46}O_6Sn_2$: C, 57.05; H, 5.24%.

IR ($\nu \pm 4$ cm^{-1}): 3063, 3044, 3004, 2988, 2901, 2865, 1482, 1453, 1429, 1385, 1373, 1127, 1098, 1086, 1076, 1049, 997, 959, 752, 727, 698, 523, 448.

^{1}H-NMR and ^{13}C-NMR spectral details in $CDCl_3$ solution are listed in Table 1.

^{13}C-NMR (solid state; 75.4 MHz; pulse sequence SXSEQ; relaxation delay 10.0 s; cross polarisation contact time 1.0 ms; spin rate 3220 Hz; AF time constant 0.02 s).

δ: −13.7, −10.5, −9.9 and −8.5 [Me–Sn], 54.1 [OMe], 63.6, 64.9, 66.3, 67.8 7 70.3(br) [C-5, C-6, C-7 and C-8], 81.3, 82.1(br), 88.6 and 90.7 [C-2, C-3 and C-4], 98.3, 99.9, 100.8 and 102.1 [PhCH and C-1], 125.9, 128.1(br), 137.7(br), 140.3, 141.8 and 143.4 [aryl-C].

^{119}Sn-NMR ($CDCl_3$; 93.3 MHz): δ −101.9 (at C-7), −101.6 (at C-8).

^{119}Sn-NMR (solid state; 111.9 MHz; pulse sequence SXSEQ; cross polarisation with flip-back): (relaxation delay 10.0 s; contact time 4.672 ms; spin rate 3500 Hz and relaxation delay 5.0 s; contact time 3.0 ms; spin rate 2620 Hz; AF time constant 0.015 s).

δ −110.5, −102.3, −100.1.

3.4. Methyl 4,6-O-benzylidene-2,3-bis-O-[(dimethylphenylstannyl)methyl-α-D-glucopyranoside (5)

The residue was purified using a chromatotron, with petrol (60–80°C)–ethyl acetate (6:1 (v/v)) as the eluent. The title compound was initially obtained as an oil in 64% overall yield. The oil crystallised on standing and was recrystallized from MeOH, m.p. 82°C.

^{119}Sn-NMR ($CDCl_3$; 93.3 MHz): δ −160.6 (br).

Anal. Found: C, 50.51; H, 5.63. Calc. for $C_{32}H_{42}O_6Sn_2$: C, 50.57; H, 5.57%.

IR ($\nu \pm 4$ cm^{-1}): 3063, 3050, 2986, 2915, 2874, 2832, 1466, 1451, 1428, 1368, 1080, 1055, 1030, 1020, 997, 748, 729, 700, 656, 532, 515, 448.

^{1}H-NMR and ^{13}C-NMR spectral details in $CDCl_3$ solution are listed in Table 1.

^{13}C-NMR (solid state; 75.4 MHz: pulse sequence SXSEQ; relaxation delay 5.0 s; cross polarisation contact time 1.0 ms; spin rate 4420 Hz).

δ −13.1, −12.5, −11.1, −10.1, −9.3, −8.7 and −7.8 [Me–Sn], 55.3 and 56.1 [OMe], 63.5, 64.1, 65.9, 66.9, 67.9 and 69.3 [C-5, C-6, C-7 and C-8], 81.1, 81.6, 82.7, 83.6, 84.3 and 87.3 [C-2, C-3 and C-4], 98.5, 99.0 and 99.6 [PhCH and C-1], 126.0, 128.8(br), 136.2, 136.9, 138.2, 139.2, 139.7, 141.0, 142.7, 143.4, 144.9 and 145.8 [aryl-C].

^{119}Sn-NMR ($CDCl_3$; 93.3 MHz): δ −61.3 (at C-8), −63.1 (at C-7).

^{119}Sn-NMR (solid state; 111.9 MHz; pulse sequence SXSEQ; cross polarisation with flip-back contact time 1.0 ms; relaxation delay 5.0 s; spin rates 2870 and 4400 Hz; AF time constant 0.015 s).

δ −58.0, −63.9, −65.0, −70.0.

3.5. Methyl 4,6-O-benzylidene-2,3-bis-O-(2,2-diphenyl-2-stannapropylidene)-α-D-glucopyranoside (7)

Purification of the residue was achieved using a chromatotron with petrol (60–80°C)–ethyl acetate (4:1 (v/v)) as eluent, yield 77%. The title compound was obtained as a low-melting foam.

Anal. Found: C, 58.2; H, 5.3. Calc. for $C_{28}H_{30}O_6Sn$: C, 57.9; H, 5.2%.

^{1}H-NMR and ^{13}C-NMR spectral details in $CDCl_3$ solution are listed in Table 1.

^{119}Sn-NMR ($CDCl_3$; 93.3 MHz): δ −111.5.

3.6. Reaction of 3 with iodine: formation of methyl 4,6-O-benzylidene-2,3-bis-O-[(iododiphenylstannyl)-methyl]-α-D-glucopyranoside (11)

To a stirred chloroform solution (3 ml) of **3** (1.01 g, 1.00 mmol) was added a $CHCl_3$ solution (12 ml) of iodine (0.508 g, 2.00 mmol). After decolourisation all volatiles were removed under low pressure and the residue of methyl 4,6-*O*-benzylidene-2,3-bis-*O*-[(iododiphenylstannyl)methyl]-α-D-glucopyranoside (**11**) was recrystallized from petroleum ether (60–80°C), yield 50%, m.p. 121–125°C. A further recrystallisation from petroleum ether (60–80°C) had a deleterious effect with the formation of a yellow coloured solution and a colourless amorphous solid, insoluble in $CHCl_3$.

IR ($\nu \pm 4$ cm^{-1}): 3065, 3044, 2992, 2919, 2869, 2843, 1482, 1466, 1431, 1370, 1191, 1175, 1125, 1084, 1051, 1028, 997, 727, 696, 448.

^{1}H-NMR and ^{13}C-NMR spectral details in $CDCl_3$ solution are listed in Table 1.

^{119}Sn-NMR ($CDCl_3$; 93.3 MHz): δ −127.3, −128.1.

Table 4
Crystal data and structure refinement for **5** at 120 and 300 K

	120(2) K	300(2) K
Empirical formula	$C_{32}H_{42}O_6Sn_2$	$C_{32}H_{42}O_6Sn_2$
Formula weight	760.04	760.04
Wavelength	0.71073	0.71073
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Orthorhombic, $P2_12_12_1$
Unit cell dimensions		
a (Å)	9.0948(2)	9.2047(4)
b (Å)	25.5410(7)	25.7231(10)
c (Å)	42.6480(11)	43.3462(18)
Volume (Å^3)	9906.7(4)	10 263.2(7)
Z, D_{calc} (Mg m^{-3})	12, 1.529	12, 1.476
Absorption coefficient (mm^{-1})	1.552	1.498
F(000)	4584	4584
Crystal colour, size (mm)	Colourless, $0.20\times0.10\times0.10$	Colourless, $0.50\times0.40\times0.30$
θ Range for data collection (°)	1.59–27.48	1.23–23.77
Index ranges	$-11\le h\le11$, $-22\le k\le32$, $-53\le l\le52$	$-10\le h\le10$, $-26\le k\le29$, $-49\le l\le48$
Reflections collected/unique	30 688/15 367 [$R_{int}=0.0606$]	55 721/15 627 [$R_{int}=0.0725$]
Completeness to $2\theta=27.48$	82.2%	99.7%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.846 and 0.770	0.862 and 0.609
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	15 367/10/499	15 627/20/484
Goodness-of-fit on F^2	0.969	1.025
Final R indices [$I>2\sigma(I)$]	$R_1=0.0672$, $wR_2=0.1433$	$R_1=0.0692$, $wR_2=0.1707$
R indices (all data)	$R_1=0.1521$, $wR_2=0.1718$	$R_1=0.1133$, $wR_2=0.1920$
Absolute structure parameter	0.05(3)	0.01(4)
Largest difference peak and hole (e Å^{-3})	0.865 and −1.297	1.030 and −0.933

3.7. Reaction of **4** with iodine: formation of methyl 2,3-bis-O-[(iodomethylphenylstannyl)methyl[-4,6-O-benzylidene-α-D-glucopyranoside (**12**)

To a solution of **4** (90 mg) in $CDCl_3$ (1 ml) at 0°C was added iodine (51 mg). Decolourisation readily occurred: the ^{1}H- and ^{13}C-NMR spectral details are listed in Table 1.

^{119}Sn-NMR ($CDCl_3$; 93.3 MHz): δ −68.4 (sharp), −71.7 (br).

3.8. Reaction of **5** with iodine

To a solution of **5** (100 mg) in $CDCl_3$ solution (1 ml) at 0°C was added iodine (1:2 mol. ratio). Decolourisation readily occurred. The ^{1}H-NMR spectrum indicated the presence of iodobenzene from the δ^1H values at 7.11(m), 7.36(m) and 7.72(m) ppm: other significant ^{1}H-NMR data in the poorly resolved spectrum were δ^1H 1.58(s, Me–Sn), 3.47(s, OMe), 3.7–4.8(m), 10.03(s, O_2CH?).

^{119}Sn-NMR ($CDCl_3$; 93.3 MHz): δ −160.6.

3.9. Crystallography

Intensity data at ambient temperature (300 K) were obtained with a Bruker SMART 1000 CCD diffractometer. SMART software was used for data collection and SAINT software for cell refinement and data reduction [20]. Absorption correction was made using SADABS by the multi-scan technique [21]. SHELXS-97 was used to solve the structure by the heavy atom technique [22]. The initial solution was expanded and refined with SHELXL-97 [23]. Three distinct molecules, with a total of 120 non-H atoms, were indicated. In the final stages of refinement, only Sn atoms were treated anisotropically. Isotropic refinement was used for all other non-H atoms. H atoms were placed in calculated positions and refined with a riding model. The environments of Sn5 and Sn6 were a source of particular difficulty because the C of the phenyl, methyl and methylene groups attached to Sn proved to be rather ill-defined. As a consequence, U_{iso} of these carbon atoms were forced to take the value of U_{equ} of the relevant Sn atom and soft constraints on the Sn–C distances [DFIX 2.15(2) Å] and C–Sn–C angles [DANG 3.45(4) Å] were also applied.

A further data set was obtained at 120 K by the EPSRC X-ray service at Southampton on an Enraf Nonius KappaCCD diffractometer. Data collection, data reduction and cell refinement were achieved with the DENZO [24] and COLLECT [25] software. The absorption correction was by SORTAV [26]. The parameters obtained from the 300 K refinement were used, with an appropriate adjustment of the unit cell parameters, as the starting model. The low temperature refinement revealed, in addition to the expected (approximately 1%) reduction in the length of the cell edges, a reduction of the displacement parameters by roughly a factor of two, again as expected. More significantly, however, the constraints of the type described above were now only necessary for Sn6, i.e. Sn5 and its environment could now be refined in the same (unconstrained) manner as Sn1 to Sn4.

The pucker parameters were calculated using PLATON [27].

Details of the crystal data and structure refinement for **5** at 120 and 300 K are listed in Table 4.

4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 146522 and 146523 for **5** at 120 and 300 K, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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