Organotin(IV) compounds 2-(Me₂NCHR)C₆H₄(SnR′R″Br) with a fixed *s-cis* arrangement of the chiral carbon and tin centers. Crystal structure of 2-(Me₂NCHBuᵗ)C₆H₄SnMePhBr *

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Abstract

A series of novel pentacoordinate triorganotin bromides SnR′R″Br[C₆H₄CH(R)NMe₂-2] have been synthesized and characterized in which R is H, Me, Et, i-Pr or t-Bu. The crystal structure of one of these compounds (R = t-Bu, R′ = Me and R″ = Ph) has been determined. The tin center has a distorted trigonal-bipyramidal coordination geometry. The organic ligands occupy the equatorial sites, while the more electronegative Br and N ligands are in the axial positions. As a requirement of the space group symmetry the unit cell contains 8 enantiomeric pairs of diastereoisomers $(R)_C(S)_{Sn}$ and $(S)_C(R)_{Sn}$. The given configuration at the chiral benzylic carbon atom is combined with a configuration at the chiral tin atom in such a way that the sterically most favorable diastereoisomer is formed.

The influence of the steric requirements of the *ortho*-substituent Z = CHRNMe₂ in 2-ZC₆H₄ (SnRR′Br) on the configuration of the Sn center has been studied. These compounds contain a fixed *s-cis* Z–C–C–Sn orientation. ¹H and ¹¹⁹Sn NMR spectroscopic studies show that in solution at low temperatures (−25°C) all these compounds are pentacoordinate as a result of intramolecular coordination. At higher temperatures a fluxional process becomes operative involving Sn–N bond dissociation/association. However, even at +110°C the Sn center is configurationally stable on the NMR time scale. For the compounds in which the Sn atom is also a chiral center (R′ = Me and R″ = Ph) in solution there is an equilibrium between two diastereoisomers, the ratio being dependent on the bulk of the benzylic substituent R. For R = t-Bu the equilibrium lies completely to the side of the sterically most favorable one.

Introduction

It has been well established that the tin center in triorganotin halogenides undergoes rapid inversion of configuration [1]. However, the configurational stability of the tin atom in this type of compound can be increased considerably by using

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* Dedicated to Professor Peter Pauson on the occasion of his retirement from the Freeland Chair of Chemistry.

potentially bidentate organic ligands C–Y, in which Y is a heteroatom containing substituent, e.g., NR_2 [2–5], $P(=O)R_2$ [6], C(O)R [7] or =NR [8,9]. These compounds have a trigonal bipyramidal coordination geometry at the tin atom in which the electronegative ligands occupy the axial sites and the three carbon atoms equatorial sites, as schematically shown in A below.
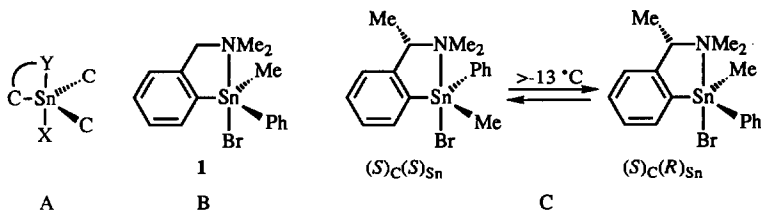
An example of a triorganotin halogenide of this type is $SnBrMePh(Me_2NCH_2-C_6H_4-2)$ [2] (1). In this compound the tin atom is a chiral center, and this is reflected in the diastereotopicity of the prochiral NMe_2 and CH_2 resonances observed in the ^1H NMR spectrum below 25°C. The coalescence of the NMe_2 resonances at 30°C is explained in terms of a Sn–N dissociation/association process, which becomes fast on the NMR time scale above this temperature. That the CH_2 resonances remain diastereotopic to at least 123°C (the highest temperature used) indicates that inversion of configuration at the chiral tin center is still slow on the NMR time scale. That inversion of configuration at the tin center in this type of compounds does, however, occur was shown by using the chiral labeling approach, i.e. by introducing a second configurationally stable chiral center in the molecule. When diastereoisomerically pure $(S)_C(S)_{Sn}$-$SnBrMePh(Me_2NCH(Me)C_6H_4-2)$ [3] is dissolved at −40°C this diastereoisomer remains unaltered, but at −13°C an epimerization process starts, and finally leads to a 40/60 mixture of the $(S)_C(S)_{Sn}$ and the $(S)_C(R)_{Sn}$ diastereoisomer (see C).

Recently we have shown that reaction of racemic $LiCH(SiMe_3)(Me_2NC_6H_4-2)$ with $SnMePhBr_2$ affords only one diastereoisomeric pair $((R)_C(R)_{Sn}/(S)_C(S)_{Sn})$ of $SnBrMePh[CH(SiMe_3)(Me_2NC_6H_4-2)]$, which has a configurationally stable chiral tin center [4].

From these studies it appeared that the configuration at the chiral tin center in these compounds is controlled by the configuration of the second chiral center present in the five membered chelate ring. To gain more insight in the factors which control these configurational preferences we have now extended our studies in this field to a series of triorganotin bromides containing the 2-[(dimethylamino)methyl] phenyl group with various substituents in the benzylic position.

Results and discussion

Synthesis of the aryllithium compounds 2a–5a

Previously we reported on the synthesis of diastereoisomerically pure $(S)_C(S)_{Sn}$-$SnBrMePh\{Me_2NCH(Me)C_6H_4-2\}$, starting from the enantiomerically pure organo-copper compound $Cu_4\{(S)_C\text{-}Me_2NCH(Me)C_6H_4-2\}_4$ and $SnBr_2MePh$ [3]. Attempts to prepare this compound starting from $Li\{(S)_C\text{-}Me_2NCH(Me)C_6H_4-2\}$ and $SnBr_2MePh$ failed, since it was not recognized at that time that the lithiation reaction of the parent arene $(S)_C\text{-}Me_2NCH(Me)C_6H_5$ with n-BuLi proceeds only to

the extent of 50%. The lithiation product consists of butyllithium–aryllithium mixed aggregates in which both butyl and aryl groups are bound to the lithium core [10], and reaction with $SnBr_2MePh$ gives mixtures of organotin products.

We recently showed that pure $Li\{Me_2NCH(R)C_6H_4-2\}$ (R = Me or R = Et) can be readily prepared via a lithiation reaction of the parent arene with t-BuLi (eq. 1) instead of n-BuLi [10].
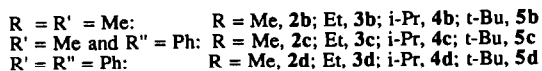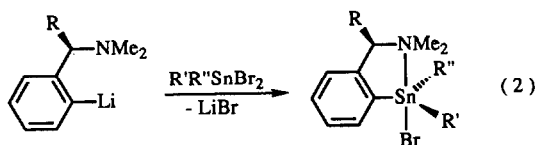
However, the corresponding aryllithium compounds with an α-i-propyl or t-butyl group appeared not to be accessible via this route and no reaction at all was observed. These lithium compounds had to be synthesized via a lithium/halogen exchange reaction of the corresponding 2-bromo compounds with n-BuLi (eq. 1). This route has the disadvantage that the formation of the aryllithium species is accompanied by the formation of one equivalent of butyl bromide which in most cases has to be removed prior to further reaction.

$$ (1) $$

2a R = Me, R' = t-Bu, X = H
3a R = Et, R' = t-Bu, X = H
4a R = i-Pr, R' = n-Bu, X = Br
5a R = t-Bu, R' = n-Bu, X = Br
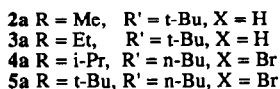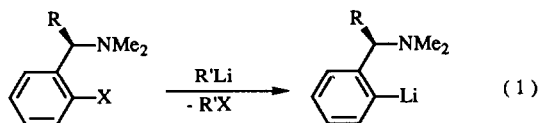
The aryllithium compounds 2a–5a are air-sensitive white solids, for which preparative details, solution behaviour, and stereochemical features will be described in a separate paper [11].

Synthesis of the triorganotin bromides 2b–2d, 3b–d, 4b–d and 5b–d

Treatment of $SnBr_2Me_2$, $SnBr_2MePh$ or $SnBr_2Ph_2$ with one of the aryllithium compounds 2a–5a in a 1/1 molar ratio gives in high yield the corresponding triorganotin bromides 2b–d, 3b–d, 4b–d and 5b–d (eq. 2).

$$ (2) $$

R = R' = Me: R = Me, 2b; Et, 3b; i-Pr, 4b; t-Bu, 5b
R' = Me and R" = Ph: R = Me, 2c; Et, 3c; i-Pr, 4c; t-Bu, 5c
R' = R" = Ph: R = Me, 2d; Et, 3d; i-Pr, 4d; t-Bu, 5d

These triorganotin bromides are white crystalline solids and were characterized by their elemental analyses, molecular weight data and ^1H and ^{119}Sn NMR spectra, see Tables 1 and 3. Since the triorganotin bromides 2b–d were prepared from the enantiomerically pure organolithium compound (S)-2a, they were obtained in enantiomerically pure form. However, the organolithium compounds, 3a, 4a and 5a, were obtained from racemic precursors and consequently the triorganotin bromides 3b–d, 4b–d and 5b–d are likewise racemic mixtures.

In the triorganotin bromides 2c, 3c, 4c and 5c two chiral centers are present, i. the benzylic carbon atom and ii. the tin atom. Previously it was shown for 2c that in solution there is an equilibrium between two different diastereoisomers [3]. Indeed

Table 1

Elemental analysis and physical data for the triorganotin bromides **2b–d**, **3b–d**, **4b–d** and **5b–d**

Compound	α-R	SnR′	SnR″	Yield [a] (%)	M.p. (°C)	Elemental anal. [b] C	H	N	M_r [c]
2b	Me	Me	Me	74	118	38.1 (38.2)	5.2 (5.3)	3.6 (3.7)	391 (377)
3b	Et	Me	Me	61	147	40.1 (39.9)	5.8 (5.7)	3.7 (3.6)	380 (391)
4b	i-Pr	Me	Me	88	76	40.9 (41.5)	5.8 (6.0)	3.3 (3.5)	418 (405)
5b	t-Bu	Me	Me	61	160	43.4 (43.0)	6.2 (6.2)	3.2 (3.3)	403 (419)
2c	Me	Me	Ph	68	47	46.5 (46.5)	4.9 (5.0)	3.2 (3.2)	441 (439)
3c	Et	Me	Ph	55	128	46.9 (47.7)	5.3 (5.3)	2.9 (3.1)	444 (453)
4c	i-Pr	Me	Ph	55	101	48.1 (48.9)	5.6 (5.6)	2.9 (3.0)	481 (467)
5c	t-Bu	Me	Ph	41	138	49.5 (49.9)	5.9 (5.9)	2.8 (2.9)	472 (481)
2d	Me	Ph	Ph	55	168	51.0 (52.7)	4.4 (4.8)	2.6 (2.8)	512 (501)
3d	Et	Ph	Ph	71	185	52.8 (53.7)	5.0 (5.1)	2.6 (2.7)	522 (515)
4d	i-Pr	Ph	Ph	67	160	54.1 (54.5)	5.3 (5.3)	2.6 (2.6)	518 (529)
5d	t-Bu	Ph	Ph	58	178	54.7 (55.3)	5.4 (5.5)	2.5 (2.6)	538 (543)

[a] After recrystallization from boiling methanol. [b] Found (calcd.) in %. [c] By osmometry in benzene: found (calcd.).

the ^{1}H and ^{119}Sn NMR spectra of **2c**, **3c** and **4c** show the presence of two different diastereoisomers, denoted as **c'** and **c''** (see eq. 3 and Table 3). For **5c**, however the ^{1}H and ^{119}Sn NMR spectra show the presence of only one diastereoisomer, denoted **5c'**. In order to establish the configuration of this diastereoisomer, an X-ray structure determination was carried out.

(3)

2c' R=Me	(R)$_C$(S)$_{Sn}$	60%	2c'' R=Me	(R)$_C$(R)$_{Sn}$ 40%
3c' R=Et	(R)$_C$(S)$_{Sn}$	60%	3c'' R=Et	(R)$_C$(R)$_{Sn}$ 40%
4c' R=i-Pr	(R)$_C$(S)$_{Sn}$	80%	4c'' R=i-Pr	(R)$_C$(R)$_{Sn}$ 20%
5c' R=t-Bu	(R)$_C$(S)$_{Sn}$	>98%	5c'' R=t-Bu	(R)$_C$(R)$_{Sn}$ < 2%

Molecular geometry and crystal structure of 5c'

The crystal structure of **5c'** involves the packing of 16 discrete mononuclear molecules in the unit cell. The asymmetric unit contains two independent molecules A and B which are chemically identical, but which differ slightly but not significantly in structure. As a requirement of the space group symmetry the unit cell contains 8 enantiomeric pairs of diastereoisomers $(R)_C(S)_{Sn}$ and $(S)_C(R)_{Sn}$. The molecular geometry of one diastereoisomer $(R)_C(S)_{Sn}$ is shown in Fig. 1a, and selected geometrical parameters are listed in Table 2. The tin center has a distorted trigonal-bipyramidal coordination geometry. The organic ligands occupy the equatorial sites, while the more electronegative Br and N ligands are in the axial
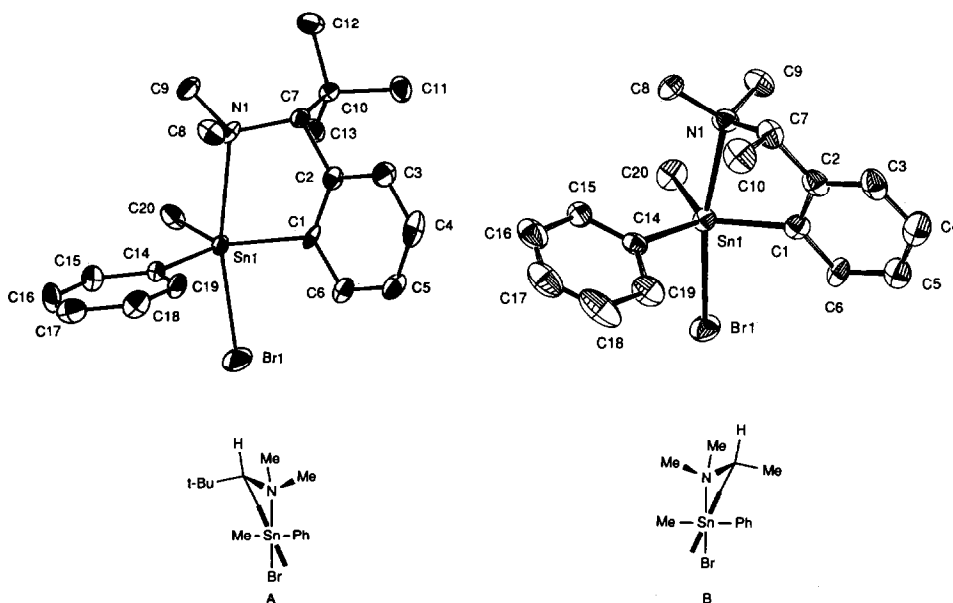

Fig. 1. ORTEP drawing of **5c** (A) with the numbering scheme used, compared with the structure of earlier reported [3] **2c''** (B). A schematic projection along the Sn–C$_{ipso}$ bond is given for both compounds, showing the relative positions of the α-substituents.

Table 2

Selected geometrical data for **5c′** compared with the values of **2c″**

	5c′ (molecule A)	**5c′** (molecule B)	**2c″**
Bond lengths (Å)			
Sn1–C1	2.143(5)	2.139(5)	2.158(9)
Sn1–C14	2.142(5)	2.122(6)	2.127(8)
Sn1–C20	2.137(6)	2.128(6)	2.160(10)
Sn1–N1	2.552(5)	2.482(5)	2.476(7)
Sn1–Br1	2.6725(9)	2.6702(7)	2.683(1)
Bond angles (°)			
C1–Sn1–C14	108.1(3)	115.8(3)	116.1(3)
C1–Sn1–C20	138.8(3)	132.5(3)	127.8(3)
C14–Sn1–C20	111.6(3)	110.9(4)	114.8(4)
N1–Sn1–C1	73.2(3)	74.1(2)	75.2(3)
N1–Sn1–C14	93.8(3)	91.5(3)	94.2(3)
N1–Sn1–C20	93.3(3)	96.9(6)	90.5(3)
Br1–Sn1–C1	96.0(2)	95.4(2)	94.5(2)
Br1–Sn1–C14	96.2(2)	92.2(2)	94.1(2)
Br1–Sn1–C20	90.4(2)	90.9(3)	92.6(3)
N1–Sn1–Br1	167.2(1)	169.4(1)	168.9(2)

positions. The overall structural features around the tin atom (bond distances and angles) are in the range as reported for related pentacoordinate triorganotin bromides [3,4,12].

The five-membered chelate ring, present in **5c′**, is puckered in such a way that it places the bulky t-butyl substituent perpendicular to the substituted aryl ring, which is sterically a favourable position. The resulting five-membered ring conformation is furthermore combined with a configuration at tin in which the less bulky Me group is at the side of the α-t-butyl substituent. The X-ray structure determination of the diastereoisomer of **2c** obtained by kinetic resolution shows that the structure of this diastereoisomer contains a five-membered chelate ring with a similar puckering placing the α-Me substituent likewise perpendicular (Fig. 1b). However, in this diastereoisomer, denoted **2c″** this ring conformation is combined with a configuration at tin which instead places the bulky phenyl substituent alongside this Me group. That this diastereoisomer, $(S)_C(S)_{Sn}$ or its enantiomer $(R)_C(R)_{Sn}$, is sterically the less favourable one is reflected in the fact that in solution the other, $(S)_C(R)_{Sn}$, diastereoisomer **2c′** or its enantiomer $(R)_C(S)_{Sn}$ is the more abundant one, and it is this configuration that we found for **5c′** both in the solid state and in solution.

Solution behaviour of the triorganotin bromides

^{1}H NMR spectra at various temperatures (see Table 3) indicate that in solution the triorganotin bromides **2b–d, 3b–d, 4b–d** and **5b–d** have structures comparable to that found for **2c″** and **5c** in the solid state; i.e. a trigonal bipyramidal coordination geometry around the tin atom with the C-ligands in the equatorial positions and the N and Br ligands in the remaining axial sites. Furthermore, the ^{1}H NMR spectra of **2c–4c** show two NMR patterns, which indicates that in solution these triorganotin bromides exist as two diastereoisomers the ratio of which depends

on the α-substituent. For **2c'** and **2c''** the respective resonance patterns could be assigned unambiguously, because when pure **2c''**, for which the configuration is known from an X-ray structure determination, is dissolved at $-40\,^{\circ}$C, the ^{1}H NMR spectrum shows only one resonance pattern (that for **2c''**). When the temperature of this solution is raised to about $-13\,^{\circ}$C an epimerisation process starts, finally giving a 60/40 equilibrium mixture of **2c'** and **2c''**. Since the ^{1}H NMR spectrum of a solution of **5c** shows the presence of only one diastereoisomer, it is obvious that this isomer is **5c'**, for which the configuration is also known from an X-ray structure determination. However, for **3c** and **4c** no structural data are available, but it is most likely that in solution the most abundant diastereoisomers are **3c'** and **4c'**, respectively. These are sterically the most favourable because they have the benzylic substituent and the unsubstituted phenyl group on opposite sides of the molecule.

The presence of the chiral centers is reflected in the observation of diastereotopicity in the ^{1}H NMR spectra of the prochiral groups present in these molecules. The diastereotopicity of the NMe$_2$ groups at low temperature indicates that Sn–N coordination is inert on the NMR time-scale. Coalescence of these NMe$_2$ resonances at higher temperatures (see Table 3) points to a proces involving Sn–N dissociation/association. Since the chiral benzylic carbon atom is configurationally stable the only way in which the NMe$_2$ methyl groups can become homotopic is via the sequence: (i) Sn–N dissociation; (ii) pyramidal inversion of the nitrogen atom; (iii) rotation around the C_{benzyl}–N bond; and finally (iv) Sn–N recoordination. A dynamic ^{1}H NMR study and line shape analysis of the diastereotopic diethylamino methylene protons in penta-coordinate SnBrMe$_2$[C$_6$H$_4$CH$_2$N(C$_2$H$_5$)$_2$] points to a similar Sn–N dissociation/association process [21,22]. The ^{1}H NMR spectra of the compounds **2b–5b** (R' = R'' = Me) and **2d–5d** (R' = R'' = Ph) show that the chemical shift difference between the diastereotopic NMe$_2$ resonances increases with increasing size of the benzylic substituent R (see Table 3). Probably this is a result of the formation of a more crowded molecule when the benzylic substituent

Table 3

Relevant ^{1}H [a] and ^{119}Sn [b] NMR data of the triorganotin bromides **2a–c, 3a–c, 4a–c** and **5a–c**

	NMe$_2$	α-H	SnMe	H(6)	^{119}Sn
2b	1.48; 1.38/1.52 [c] (313)	3.01 (q)	0.71 (62, 64) [d]/0.79 (64, 66) [d]	8.85	− 55.7
3b	1.61; 1.33/1.45 [c] (295)	2.53 (d of d)	0.54 (66, 68) [d]/0.64 (63, 66) [d]	8.85	− 53.7
4b	1.73; 1.39/1.63 [c] (268)	2.62 (d)	0.64 (66, 68) [d]/0.87 (65, 67) [d]	8.71	− 46.2
5b	1.75; 1.31/1.80 [c] (282)	2.63 (s)	0.61 (56, 58) [d]/1.09 (63, 66) [d]	9.07	− 35.5
2c'	1.36; 1.30/1.41 [c] (320)	3.08 (q)	0.91 (65, 67) [d]	9.04	−117.0
2c''	1.39; 1.18/1.68 [c] (312)	3.07 (q)	0.99 (66, 68) [d]	9.03	−117.7
3c'	1.49; 1.06/1.55 [c] (302)	2.50 (d of d)	1.04 (65, 68) [d]	8.87	−115.4
3c''	1.58; 1.37/1.43 [c] (272)	2.57 (d of d)	0.88 (59, 62) [d]	8.91	−112.6
4c'	1.60; 1.11/1.62 [c] (281)	2.63 (d)	1.15 (67, 69) [d]	8.89	−114.6
4c''	1.76; 1.40/1.61 [c] (257)	2.56 (d)	0.86 (68, 71) [d]	8.89	−112.4
5c'	1.65; 1.35/1.85 [c] (291)	2.58 (s)	1.31 (65, 67) [d]	9.15	−102.7
2d	1.65; 1.53/1.71 [c] (332)	3.42 (q)	–	8.72	−189.4
3d	1.61; 1.49/1.72 [c] (315)	2.65 (d of d)	–	8.67	−187.5
4d	1.68; 1.31/1.69 [c] (248)	2.55 (d)	–	9.04	−181.6
5d	1.75; 1.33/1.90 [c] (280)	2.62 (s)	–	9.15	−165.3

[a] All values are in δ relative to Me$_4$Si; toluene-d_8 solvent; at 50°C. [b] δ-values relative to Me$_4$Sn; toluene-d_8 solvent; at 25°C. [c] At $-25\,^{\circ}$C; T_c ($^{\circ}$C) in parentheses. [d] $^3J(^{117}$Sn, ^{1}H), $^3J(^{119}$Sn, ^{1}H).

becomes more bulky. However, for the compounds **2c–5c** (R' = Me, R'' = Ph) it seems that also the configuration ((S) or (R)) contribute to the chemical shift differences, but we does not yet understand completely how this works out.

In the triorganotin bromides **2b**, **3b**, **4b** and **5b** the SnMe$_2$ moiety is also a prochiral group which remains diastereotopic at least up to 125°C (the highest temperature studied). This indicates that the Sn atom is configurationally stable on the NMR time scale. This is further confirmed by the observation in the ^{1}H NMR spectra of two different resonance patterns and two different [119]Sn resonances of the two different diastereoisomers of the corresponding compounds, **2c–4c**, which contain the SnMePh moiety. When epimerisation of configuration at the chiral tin center in these compounds becomes fast on the NMR time scale this will lead to one averaged ^{1}H NMR resonance pattern as well as to one ^{119}Sn NMR resonance.

For the triorganotin bromides which have one (**2c–5c**) or two (**2b–5b**) methyl groups bonded to tin, the $^2J(^{117,119}\text{Sn}-^1\text{H})$ is about 65 Hz, a value normally observed for triorganotin halogenides with five coordination at tin [3–5,13,14].

Although the theoretical understanding of the factors contributing to [119]Sn chemical shifts is still in its infancy, the $\delta(^{119}\text{Sn})$ values available today may be used as an indication of the type and number of substituents present [15]. Hence, ^{119}Sn NMR spectra may be used to prove the purity of a given tin compound and to investigate the equilibrium of this compound with other species in solution and, of course, the dynamic properties in general [16]. An illustrative example is provided by tetra-s-butyltin. Owing to the presence of four identical chiral centers around the tin atom, three diastereoisomeric compounds should exist. Neither ^{1}H nor ^{13}C NMR are indicative, but in the ^{119}Sn NMR spectrum three signals are found with relative intensities close to the ratio predicted, assuming a random distribution [17,18].

The ^{119}Sn NMR data of the compounds we studied show two interesting trends. When we compare the compounds of type **b**, in which two methyl groups are bonded to tin, with compounds of type **c**, in which one of these methyl groups is substituted by a phenyl group, an upfield shift of about 65 ppm for the $\delta(^{119}\text{Sn})$ value is observed. When the second methyl group is also substituted by a phenyl group (compounds **c**) this again results in an upfield shift of about 65 ppm. Secondly, when the $\delta(^{119}\text{Sn})$ values of a series of compounds with the same substituents at tin, but which differ in the substituent at the benzylic carbon atom, e.g. **2a**, **3a**, **4a** and **5a** are compared, the $\delta(^{119}\text{Sn})$ value shifts slightly downfield with increasing size of this substituent. Although the shift differences are relatively small (2 to 16 ppm) they are consistent for all compounds we studied (see Table 3). Moreover, for the triorganotin bromides which exist in solution as two different diastereoisomers (compounds of type **c**), two well-resolved [119]Sn resonances are observed.

For the diastereoisomers SnBrMePh[C$_6$H$_4$CH(R)NMe$_2$-2] of type **c** the ratio of **c'** and **c''** appears to depend on the bulk of the benzylic substituent R (see eq. 2). Most likely the difference in thermodynamic stability between the two diastereoisomers is caused by a difference in steric repulsion between this substitution and the group present at tin. NMR spectra have shown that the diastereoisomers having the benzylic substituent and the less bulkier methyl group at tin at the same side of the molecule are the most abundant in solution, **2c'** 60%, **3c'** 60%, **4c'** 80% and **5c'** > 98%, and obviously thermodynamically the most stable ones. In **5c** the equilibrium between **5c'** and **5c''** lies nearly completely to the side of **5c'**. The same

conclusion was reached for $SnBrMePh[CH(SiMe_3)Me_2NC_6H_4-2]$, which in both the solid state and in solution is present completely as the $(S)_C(S)_{Sn}$ diastereoisomer and its enantiomer [4].

It is noteworthy that although **2c′** is the most abundant diastereoisomer in the equilibrium, it is **2c″** which crystallizes from a solution of **2c** [3]. This preferential crystallization represents an example of an asymmetric transformation of the second order [23] because ultimately the whole sample of **2c** could be crystallized from the solution as the $(S)_C(S)_{Sn}$ diastereoisomer. The marked stereoselectivity of this process is most probably a result of the formation of a more stable crystal structure in the case of the $(S)_C(S)_{Sn}$ diastereoisomer which has both the α-Me and the phenyl(-Sn) group on the same side of the molecule.

Experimental

Syntheses were carried out by standard Schlenk techniques under purified nitrogen. The solvents were dried and distilled from sodium prior to use. ^{1}H and ^{119}Sn NMR spectra were recorded on a Bruker AC 200 spectrometer.

Synthesis of 2-[1-(dimethylamino)ethyl]-(2a) and 2-[1-(dimethylamino)propyl]phenyllithium (3a)

To a solution of 2-[1-(dimethylamino)ethyl]- or 2-[1-(dimethylamino)propyl]benzene (20 mmol) in pentane (30 ml) was added a solution of t-BuLi (20 mmol) in pentane (15 ml). The mixture was stirred for 24 h, during which a white suspension was formed. The solid was filtered off, washed with cold pentane, and dried in vacuo, giving **2a** and **3a** as white crystalline solids in 80% yield.

Synthesis of 2-[1-(dimethylamino)-2-(methyl)propyl]- (4a) and 2-[1-(dimethylamino)-2,2-(dimethyl)propyl]phenyllithium (5a)

To a solution of 2-[1-(dimethylamino)-2-(methyl)propyl]- or 2-[1-(dimethylamino)-2,2-(dimethyl)propyl]bromobenzene, 20 mmol in pentane (20 ml) was added a solution of n-BuLi, (20 mmol) in hexane (15 ml). The mixture was stirred for 2 h., during which a white precipitate was formed. The solid was filtered off, washed with cold pentane and dried in vacuo, giving **4a** and **5a** as white crystalline solids in 60 and 80%, respectively.

Synthesis of the triorganotin bromides 2b–5b, 2c–5c and 2d–5d, general procedure

To a solution of the appropriate diorganotin dibromide (5 mmol) (Me_2SnBr_2, $MePhSnBr_2$ or Ph_2SnBr_2) in diethyl ether (20 ml) at $-20\degree$C a solution of the organolithium compound **2a**, **3a**, **4a** or **5a** was added during 30 min. The mixture was stirred for 30 min at room temperature, and the solvent then removed in vacuo. The residue was extracted with two 25 ml portions of warm (50°C) benzene. The combined benzene extracts were evaporated under reduced pressure to leave an oily residue. This was stirred with pentane to give a white solid, which was filtered off, washed with pentane, and dried in vacuo. The triorganotin bromides thus obtained were almost pure, but for analytical purposes they were recrystallized from methanol. The yields and physical properties of the triorganotin bromides are given in Table 1.

Crystal structure determination of 5c′

Transparent yellow crystals of **5c′**, $C_{20}H_{28}BrNSn$, obtained by vapour diffusion of pentane into a benzene solution of **5c′**, are orthorhombic, space group *Pbca* with sixteen molecules in a unit cell of dimensions *a* 16.8556(8), *b* 30.3778(12) and *c*

Table 4

Atomic fractional coordinates for **5c′**

Atom	x	y	z
Sn1	0.25653(3)	0.34522(1)	0.12581(3)
Br1	0.12347(7)	0.30168(4)	0.08872(9)
N1	0.3961(4)	0.3696(2)	0.1661(4)
C1	0.2993(5)	0.2983(2)	0.2138(4)
C2	0.3786(5)	0.3006(2)	0.2391(4)
C3	0.4012(5)	0.2782(3)	0.3094(6)
C4	0.3452(7)	0.2538(3)	0.3535(5)
C5	0.2690(6)	0.2505(3)	0.3274(6)
C6	0.2458(5)	0.2728(3)	0.2577(5)
C7	0.4392(5)	0.3279(2)	0.1922(5)
C8	0.3884(5)	0.3974(3)	0.2415(6)
C9	0.4350(6)	0.3973(3)	0.1045(6)
C10	0.4829(5)	0.3000(3)	0.1235(5)
C11	0.5126(6)	0.2569(3)	0.1627(7)
C12	0.5599(6)	0.3219(3)	0.0917(8)
C13	0.4308(5)	0.2881(3)	0.0492(6)
C14	0.2001(5)	0.3976(2)	0.1917(5)
C15	0.1893(6)	0.3953(3)	0.2757(5)
C16	0.1519(6)	0.4281(3)	0.3178(6)
C17	0.1204(6)	0.4648(3)	0.2765(7)
C18	0.1295(6)	0.4665(3)	0.1936(7)
C19	0.1683(6)	0.4335(3)	0.1498(6)
C20	0.2732(5)	0.3615(3)	−0.0011(5)
Sn1a	0.10788(3)	0.10835(1)	0.17189(3)
Br1a	−0.04303(5)	0.09687(4)	0.12671(6)
N1a	0.2535(4)	0.1084(2)	0.1947(4)
C1a	0.1564(4)	0.0651(2)	0.0809(5)
C2a	0.2387(4)	0.0637(2)	0.0722(4)
C3a	0.2720(5)	0.0304(2)	0.0262(6)
C4a	0.2252(7)	−0.0010(3)	−0.0141(6)
C5a	0.1441(6)	0.0007(3)	−0.0046(6)
C6a	0.1095(5)	0.0329(3)	0.0416(5)
C7a	0.2923(5)	0.0981(2)	0.1120(5)
C8a	0.2701(5)	0.0698(3)	0.2472(6)
C9a	0.2813(6)	0.1472(3)	0.2386(6)
C10a	0.3118(5)	0.1369(3)	0.0528(6)
C11a	0.3820(6)	0.1662(4)	0.0854(8)
C12a	0.3437(7)	0.1175(4)	−0.0277(7)
C13a	0.2419(6)	0.1658(3)	0.0312(7)
C14a	0.0873(5)	0.0801(3)	0.2894(5)
C15a	0.0824(5)	0.1069(3)	0.3587(6)
C16a	0.0689(5)	0.0883(4)	0.4360(6)
C17a	0.0593(6)	0.0445(4)	0.4457(6)
C18a	0.0646(7)	0.0175(4)	0.3791(7)
C19a	0.0774(7)	0.0348(4)	0.3023(6)
C20a	0.0919(6)	0.1778(3)	0.1755(7)

16.2357(7) Å. 7754 independent intensities $(5 < 2\theta < 129)$ were measured on a Nonius CAD4 diffractometer, at $25°C$, using graphite monochromated Cu-K_α radiation $(\lambda(\text{Cu-}K_\alpha) = 1.5418 \text{ Å})$; 2618 of these were below the 2.5 $\sigma(I)$ level and were treated as unobserved.

The Sn positions were located by means of the symbolic addition program set SIMPEL [19]. The positions of the C and N atoms were obtained by standard difference Fourier techniques. After isotropic block-diagonal least-squares refinement an empirical absorption correction (DIBAFS [20]) was applied (crystal dimensions $0.25 \times 0.5 \times 0.5$ mm; $\mu(\text{Cu-}K_\alpha)$ 122.6 cm^{-1}). Continued anisotropic refinement converged to $R = 0.046$. At this stage all H atoms were found in a ΔF synthesis and were introduced into the refinement. Continued refinement, anisotropic for Sn, Br, N, C and isotropic for H converged to $R = 0.042$ ($R_w = 0.068$). A weighting scheme $\omega = 1/(7.2 + F_o + 0.014 \ F_o^2)$ was applied and the anomalous dispersions of Sn and Br were taken into account. Coordinates of the non-hydrogen atoms are given in Table 4. A complete table of bond lengths and angles, and lists of thermal parameters and observed and calculated structure factors are available from the authors.

Acknowledgement

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