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Syntheses and crystal structures of two bulky aminohalogenostannanes, $[(Me_3Si)_2CH]_2Sn(Cl)N(H)(C_6H_2\text{-}2,4,6\text{-t-}Bu_3)$ and $[(Me_3Si)_2CH]_2Sn(F)N(H)(C_6H_2\text{-}2,4,6\text{-t-}Bu_3)$

Annie Raharinirina, Roland Boese * and Günter Schmid
Universität-GH Essen, Universitätsstr. 4–7, 4300 Essen (F.R.G.)

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Abstract

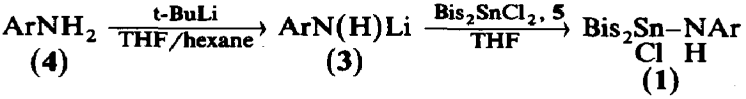
The sterically hindered aminohalogenostannanes $Bis_2Sn(X)N(H)Ar$ (**1**: X = Cl; **2**: X = F) (Bis = "bisyl" = $(Me_3Si)_2CH$) have been prepared in good yield by the reactions of the lithium salt of the amine $ArNH_2$, (Ar = 2,4,6-tri-t-butylphenyl) with the dibisyldichlorostannane Bis_2SnCl_2 and the dibisyldifluorostannane Bis_2SnF_2, respectively. Their NMR spectra (^1H, ^{19}F, ^{119}Sn) are described. The structures of these new compounds have been determined by X-ray crystallography.

Introduction

Substituent effects have considerable influence on the outcome of reactions of the dihalogenostannanes R_2SnX_2 with the lithium salts LiNHR, both on the course of reaction and the stability of products [1,2]. From di-t-butyl-dichlorostannane and lithium-t-butylamide the stable di-t-butylstannylbis(t-butylamine) is formed [3]. The combined steric effects of a bisyl group $(Me_3Si)_2CH$ on tin and a "supermesityl" (2,4,6-tri-t-butylphenyl) group on nitrogen markedly stabilize the aminohalogenostannanes $Bis_2Sn(C)N(H)Ar$, **1**, and $Bis_2Sn(F)N(H)Ar$, **2**.

Results and discussion

Trans-metallation between the lithioamine **3** (prepared by treating t-butyllithium (1.7 *M* in hexane) and (2,4,6-tri-t-butylphenyl)amine, **4**, in THF) and the bis[bis(trimethylsilyl)methyl]dichlorotin **5** [4] gives **1** (eq. 1):



$$\underset{(4)}{ArNH_2} \xrightarrow[\text{THF/hexane}]{\text{t-BuLi}} \underset{(3)}{ArN(H)Li} \xrightarrow[\text{THF}]{Bis_2SnCl_2,\ 5} \underset{(1)}{Bis_2\underset{Cl}{Sn}-\underset{H}{N}Ar} \qquad (1)$$

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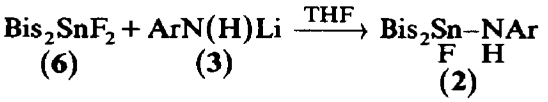
Table 1

Spectroscopic data for $Bis_2Sn(X)N(H)Ar$ (**1**: X = Cl; **2**: X = F)

Compound in C_6D_6	^1H	^{19}F	^{119}Sn
$Bis_2Sn(Cl)N(H)Ar$	18H(Me_3Si) δ 0.252(s) 18H(Me_3Si) δ 0.325(s) 9H(*p*-^tBu) δ 1.363(s) 18H(*o*-^tBu) δ 1.562(s) 1H(NH) δ 4.416(brs) 2H(ArH) δ 7.307(s)		δ 44.95(s)
$Bis_2Sn(F)N(H)Ar$	18H(Me_3Si) δ 0.203(s) 18H(Me_3Si) δ 0.291(s) 9H(*p*-^tBu) δ 1.379(s) 18H(*o*-^tBu) δ 1.581(s) 1H(NH) δ 4.223(brs) 2H(ArH) δ 7.348(s)	δ −161.6(s) $^1J(^{19}F^{117/119}Sn)$ 2692/2820Hz	δ 10.9(d) $^1J(^{119}Sn^{19}F)$ 2820Hz

Chemical shifts are reported in ppm from external Me_4Si for ^1H, external $C_6H_5CF_3$ for ^{19}F and external Me_4Sn for ^{119}Sn. Downfield shifts are positive in all cases.

Compound **2** was synthesized analogously from the lithioamine **3** and bis[bis(trimethylsilyl)methyl]difluorotin **6** [5] in THF (eq. 2):



$$\underset{(6)}{Bis_2SnF_2} + \underset{(3)}{ArN(H)Li} \xrightarrow{THF} \underset{(2)}{Bis_2\underset{F}{Sn}-\underset{H}{N}Ar} \qquad (2)$$

Colourless crystals of **1** and **2** were obtained by keeping a saturated solution in diethyl ether at −80 °C for several days until some small crystals were observed, then warming the solution to −40 °C. Both **1** and **2** were somewhat unstable in solution and slowly decomposed to give a gel. They immediately decomposed on admission of small amounts of air. Thus isolation and purification of both products had to be performed with great care.

The ^{119}Sn, ^{19}F, ^1H NMR data in C_6H_6 for the isolated crystals are reported in Table 1. Unfortunately only decomposition products were detected in the 70 eV electron-impact mass spectrum, and to provide unambiguous confirmation of the identities of the products it was necessary to carry out on X-ray crystallographic study. The ^{19}F NMR spectrum of **2** shows the presence of satellites due to coupling of ^{117}Sn and ^{119}Sn. The value of $^1J(^{119}Sn-^{19}F) = 2820$ Hz observed in the fluorine and the tin spectrum is close to that (2715 Hz) reported for $Bis_2Sn(F)P(H)Ar$ [5] but somewhat larger than those for compounds $(Me_2PhCCH_2)_3SnF$ [6], $(Me_2PhSi)_3CSnMe_2F$, $(Me_3Si)_3CSnPh_2F$ and $(Me_3Si)_3CSnMe_2F$ [7] (2298, 2374, 2463 and 2376 Hz., respectively). The ^1H-NMR spectra of **1** and **2** show two equivalent peaks in the $SiMe_3$ proton region, and these are attributed to the prochirality of the tin atom [8,9].

The structures revealed by the X-ray study are shown in Figs. 1 and 2. It will be seen that the geometry of the four-coordinate tin atom is markedly distorted from tetrahedral: the Bis–Sn–Bis angles are 127.6(1)° and 129.4(1)° respectively, in **1** and **2**, the C(1)–Sn–Cl angle is 99.6(1)° in **1**, and the C(1)–Sn–F angle is 97.7(1)° in **2**. Repulsions between the bulky substituents, the bis(trimethylsilyl)methyl on tin and the 2,4,6-tri-t-butylphenyl on nitrogen, and the chlorine in **1** or the fluorine in **2**,

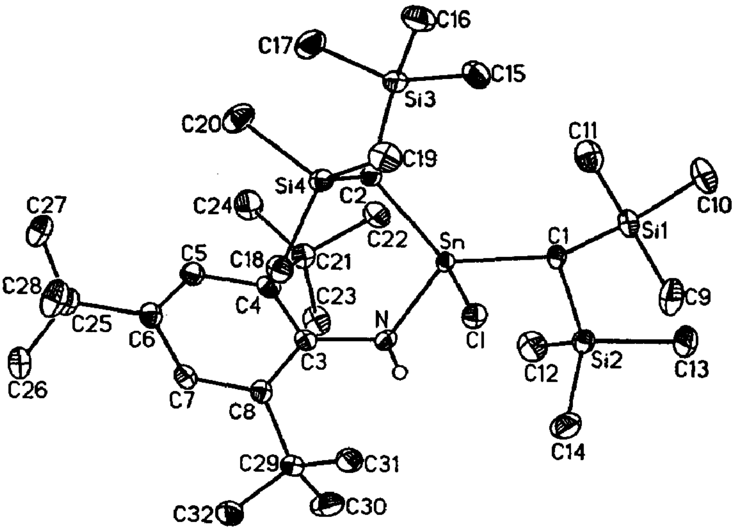


Fig. 1. Thermal ellipsoid plot of $Bis_2Sn(Cl)N(H)Ar$ (**1**) with ellipsoids drawn at 50% probability level.

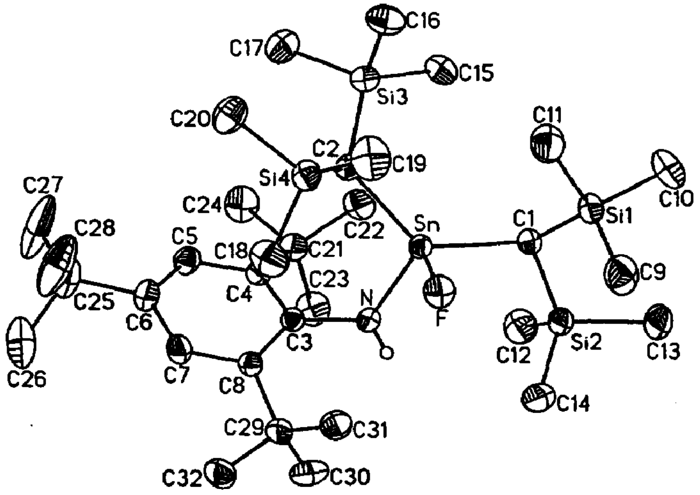


Fig. 2. Thermal ellipsoid plot of $Bis_2Sn(F)N(H)Ar$ (**2**) with ellipsoids drawn at 30% probability level.

are undoubtedly responsible for these distortions. The Sn–N and Sn–Cl bond lengths (208.3(2) pm and 239.3(1) pm, respectively) in **1** are in accord with those of single bonds as indicated by the sum of the covalent radii, 210 pm and 239 pm, respectively. The observed Sn–F distance (195.4(2) pm) in **2** is somewhat less than the sum of the relevant covalent radii, i.e. 204 pm, but is in good agreement with the Sn–F bond length (196.5(2) pm) in a four-coordinated tin compound reported by Al-Juaid et al. [7].

Structure determinations

The structures of **1** and **2** are very similar. Details of data collection procedure are given in Table 2. The unit cell dimensions and the intensity data were obtained

Table 2

Details of data collection procedure for compounds 1 and 2

	1	2
Formula	$C_{32}H_{68}ClNSi_4Sn$	$C_{32}H_{68}FNSi_4Sn$
Crystal size	0.35 × 0.31 × 0.27	0.35 × 0.42 × 0.56
Space group	$P\bar{1}$	$P\bar{1}$
No in International Tables for X-Ray Crystallography	2	2
Z	2	2
a(Å)	10.134(1)	9.995(1)
b(Å)	12.204(1)	12.442(1)
c(Å)	17.761(2)	18.277(2)
α(°)	90.33(1)	84.79(1)
β(°)	97.17(1)	96.64(1)
γ(°)	111.64(1)	112.78(1)
V(Å^3)	2022.7(4)	2079.1(9)
T(K)	125	RT
d calcd (g/cm^3)	1.204	1.152
Radiation	Mo-K_α	Mo-K_α
2θ Range (°)	$3 \leqslant 2\theta \leqslant 47$	$3 \leqslant 2\theta \leqslant 45$
Scan mode	Wyckoff	Wyckoff
Scan range in ω (°)	0.75	0.80
μ(mm^{-1})	0.84	0.76
Total no. of unique reflections	6024	5453
Observed reflections ($F_o \geqslant 4\sigma(F)$)	5871	5223
$R = \Sigma \lVert F_o\rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.023	0.026
$R_w[w^{-1} = \sigma^2(F_o) + g(F_o^2)]$	0.028	0.031
g	0.00023	0.00061
Number of parameters	422	457
Residual electron density (e/Å^3)	0.426 (1.10 Å from C(14))	0.665 (1.75 Å from C(27))

with a Nicolet R 3m/V four-circle diffractometer. All calculations were performed on a MicroVax II computer with SHELXTL-PLUS software [10]. The data were corrected for Lorentz and polarization effects. Empirical absorption corrections

Table 3

Selected bond lengths (pm) and angles (°) for 1 and 2

1		2	
Sn–N	208.3(2)	Sn–N	208.0(2)
Sn–Cl	239.3(1)	Sn–F	195.4(2)
Sn–C(1)	216.5(2)	Sn–C(1)	214.7(3)
Sn–C(2)	214.4(2)	Sn–C(2)	214.2(3)
N–C(3)	142.9(3)	N–C(3)	142.6(4)
N–Sn–Cl	105.5(1)	N–Sn–F	102.7(1)
N–Sn–C(1)	107.5(1)	N–Sn–C(1)	108.8(1)
N–Sn–C(2)	108.3(1)	N–Sn–C(2)	109.4(1)
C(1)–Sn–C(2)	127.6(1)	C(1)–Sn–C(2)	129.4(1)
C(3)–N–Sn	120.8(1)	C(3)–N–Sn	119.3(2)

based on ψ scans over the range $3 \leqslant 2\theta \leqslant 40$ and $3 \leqslant 2\theta \leqslant 32$ were applied to the data of **1** and **2**, respectively. Extinction corrections were applied to the data of **1** [$F_c^* = F_c(1 - 0.0001 \times 0.000571 \times F_c^2/\sin\theta)$] as well as to those of **2** [$F_c^* = F_c(1 - 0.0001 \times 0.001849 \times F_c^2/\sin\theta)$].

The position of the Sn atom was found by Patterson synthesis. All other heavy atoms were located from successive cycles of difference Fourier synthesis and the structure was refined by full matrix least squares with anisotropic temperature factors. A difference Fourier map revealed the positions of the hydrogen atoms, which were refined with isotropic temperature factors. All methyl hydrogen atoms

Table 4

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement factors (pm^2) for **1**

Atom	x	y	z	U_{eq} [a]
Sn	7734(1)	7812(1)	7215(1)	131(1)
Cl	9413(1)	7203(1)	7997(1)	201(2)
Si(1)	7155(1)	5128(1)	6415(1)	210(2)
Si(2)	8735(1)	7409(1)	5514(1)	196(2)
Si(3)	4189(1)	6925(1)	7613(1)	202(2)
Si(4)	6757(1)	7891(1)	8980(1)	187(2)
N	8883(2)	9545(1)	6970(1)	167(6)
C(1)	7408(2)	6703(2)	6200(1)	168(7)
C(2)	6162(2)	7828(2)	7914(1)	151(7)
C(3)	8854(2)	10517(2)	7411(1)	146(7)
C(4)	7596(2)	10792(2)	7299(1)	168(7)
C(5)	7407(2)	11515(2)	7852(1)	184(7)
C(6)	8457(2)	12081(2)	8461(1)	189(7)
C(7)	9785(2)	11987(2)	8448(1)	178(7)
C(8)	10032(2)	11244(2)	7934(1)	165(7)
C(9)	8892(3)	4892(2)	6577(1)	321(9)
C(10)	5960(3)	4134(2)	5591(1)	315(9)
C(11)	6210(3)	4638(2)	7265(1)	287(8)
C(12)	8326(3)	8626(2)	5029(1)	285(8)
C(13)	8629(3)	6336(2)	4729(1)	309(9)
C(14)	10628(2)	7985(2)	6004(1)	314(9)
C(15)	3715(2)	6292(2)	6604(1)	266(8)
C(16)	3456(3)	5644(2)	8207(1)	348(9)
C(17)	3204(2)	7926(2)	7716(1)	303(9)
C(18)	8565(2)	9056(2)	9265(1)	247(8)
C(19)	6763(3)	6442(2)	9332(1)	294(9)
C(20)	5517(3)	8394(2)	9470(1)	312(9)
C(21)	6608(2)	10545(1)	6517(1)	189(7)
C(22)	5870	9259	6211	204(7)
C(23)	7570(2)	11250(2)	5938(1)	249(8)
C(24)	5394(2)	11018(2)	6532(1)	280(8)
C(25)	8269(2)	12865(2)	9074(1)	226(8)
C(26)	9234(3)	14159(2)	8993(1)	307(9)
C(27)	6710(2)	12794(2)	9018(1)	284(9)
C(28)	8670(3)	12481(2)	9865(1)	351(10)
C(29)	11594(2)	11325(2)	7912(1)	191(7)
C(30)	11993(2)	11643(2)	7110(1)	303(9)
C(31)	11858(2)	10201(2)	8147(1)	256(8)
C(32)	12669(2)	12325(2)	8462(1)	265(8)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 5

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement factors ($pm^2/10^{-1}$) for **2**

Atom	x	y	z	U_{eq}[a]
Sn	7498(1)	7416(1)	7127(1)	38(1)
Si(1)	7122(1)	4936(1)	6382(1)	54(1)
Si(2)	8719(1)	7357(1)	5489(1)	53(1)
Si(3)	3891(1)	6314(1)	7627(1)	59(1)
Si(4)	6565(1)	6946(1)	8883(1)	58(1)
N	8612(3)	9192(2)	6902(1)	41(1)
F	8986(2)	6956(2)	7698(1)	60(1)
C(1)	7306(3)	6502(2)	6154(1)	43(1)
C(2)	5908(3)	7172(3)	7883(2)	45(1)
C(3)	8493(3)	10011(2)	7363(1)	38(1)
C(4)	7212(3)	10266(2)	7265(1)	40(1)
C(5)	6925(3)	10803(3)	7821(2)	49(1)
C(6)	7907(3)	11208(3)	8440(2)	52(1)
C(7)	9252(3)	11154(3)	8433(2)	48(1)
C(8)	9613(3)	10596(2)	7907(1)	41(1)
C(9)	8911(5)	4803(4)	6611(3)	93(2)
C(10)	6110(5)	4034(3)	5584(2)	87(2)
C(11)	6039(6)	4284(4)	7189(2)	92(2)
C(12)	8244(5)	8571(3)	5005(2)	78(2)
C(13)	8760(5)	6428(3)	4743(2)	87(2)
C(14)	10604(4)	7962(3)	5979(2)	76(2)
C(15)	3448(4)	5929(3)	6633(2)	77(2)
C(16)	3138(5)	4892(3)	8173(3)	95(2)
C(17)	2891(4)	7238(4)	7820(2)	86(2)
C(18)	8355(4)	8106(4)	9147(2)	84(2)
C(19)	6764(6)	5512(4)	9095(2)	96(2)
C(20)	5264(5)	7113(5)	9490(2)	98(2)
C(21)	6295(3)	10164(3)	6505(2)	48(1)
C(22)	5546(3)	8945(3)	6221(2)	59(1)
C(23)	7341(4)	10960(3)	5949(2)	67(1)
C(24)	5072(4)	10635(3)	6526(2)	72(2)
C(25)	7524(4)	11741(4)	9080(2)	73(2)
C(26)	8721(7)	13014(6)	9177(4)	147(4)
C(27)	6130(6)	11870(7)	8938(3)	149(4)
C(28)	7703(8)	11090(7)	9784(2)	144(4)
C(29)	11229(3)	10749(2)	7890(2)	49(1)
C(30)	11748(4)	11354(3)	7150(2)	75(2)
C(31)	11511(3)	9610(3)	8014(2)	62(1)
C(32)	12217(3)	11534(3)	8497(2)	75(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

were included as rigid groups (C–H bond lengths at 0.96 Å, H–C–H angle at 109.5 °). Final atomic parameters are given in Tables 3, 4 and 5: the structures of **1** and **2** with the numbering scheme are shown in Figs. 1 and 2, respectively. Tables of thermal parameters, and complete lists of bond lengths and angles, and lists of observed and calculated structure factors are available from the authors.

Experimental section

Syntheses were performed under dry nitrogen by standard Schlenk and high-vacuum line techniques. Solvents were dried by distillation over sodium/

potassium/benzophenone immediately prior to use. ^1H, ^{19}F and ^{119}Sn NMR were recorded on a Varian XL 200 spectrometer.

$(Bis)_2SnCl_2$. This was prepared as described by Lappert et al. [4].

Preparation of $Bis_2Sn(Cl)N(H)Ar$. A solution of 2.5 mmol tBuLi in 1.43 ml pentane was added dropwise to a solution of 0.577 g (2.2 mmol) $ArNH_2$ in 15 ml of THF. The mixture was stirred for one hour at room temperature then slowly added to a solution of 1.02 g (2 mmol) Bis_2SnCl_2 in 20 ml THF at −55 °C then allowed to warm to room temperature and stirred for a further three hours. Volatiles were removed in vacuum and replaced by pentane, and the solution was filtered to remove LiCl. The filtrate was evaporated to dryness and the residue (0.88 g, 59.86%) was recrystallized from diethyl ether to give colourless crystals of **1**.

Preparation of $Bis_2Sn(F)N(H)Ar$. A yellow solution of ArN(H)Li (prepared from 1.38 g (5.3 mmol) $ArNH_2$ and 3.12 ml (5.3 mmol) of a solution of tBuLi (1.7 N) in pentane and 30 ml of THF) was added to a solution of 2.19 g of Bis_2SnF_2 (4.6 mmol) in 20 ml of THF at −55 °C. The mixture was allowed to warm to room temperature and then stirred for two hours, after which the ^{119}Sn NMR spectrum of the solution showed that complete conversion to **2** had occured (in THF/C_6D_6, ^{119}Sn 9.9 ppm, $^1J(^{119}Sn-^{19}F)$ 2811.7 Hz). The solvents were removed under reduced pressure and replaced by pentane, the solution was filtered through Celite. The NMR spectrum (C_6D_6) of the product recovered after one week showed the presence of **2** and an unidentified byproduct (δ ^{119}Sn 0.8 ppm, $^1J(^{119}Sn-^{19}F)$ 2851 Hz; δ ^{19}F −149.36 ppm). Recrystallisation from diethyl ether allowed isolation of pure **2**.

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