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Complex salts derived from the reactions of Me_2SnCl_2 with some aromatic Schiff bases. Crystal structure of bis[*N*-(2-methoxy-1-naphthalidene)-3-methoxyanilinium]-hexachlorotetramethyldistannate(IV)dihydrate: $[CH_3OC_{10}H_6CH:NHC_6H_4OCH_3]_2[(CH_3)_4Sn_2Cl_6][H_2O]_2$

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Abstract

Several dimethyltin(IV) salts $[LH^+]_2[Me_4Sn_2Cl_6]^{2-}$, where L represents the Schiff bases *N*-(2-methoxy-1-naphthalidene)-2-methoxyaniline, *N*-(4-methoxy-1-naphthalidene)-2-methoxyaniline and *N*-(2-methoxy-1-naphthalidene)-3-methoxyaniline, respectively, and LH^+ are the corresponding protonated Schiff bases, have been synthesized. An X-ray structural study has been carried out on $[L'H]_2[Me_4Sn_2Cl_6]^{2-}$ [L′ = *N*-(2-methoxynaphthalidene)-3-methoxyaniline], $[CH_3OC_{10}H_6CH:NHC_6H_4OCH_3]_2[(CH_3)_4Sn_2Cl_6][H_2O]_2$.

Introduction

The reactions of aromatic Schiff base [1], tetraselenafulvalene [2–4], and tetrathiafulvalene [2–4] derivatives with tin(IV) and organotin(IV) compounds have been shown to give complex salts containing stannate(IV) and organostannate(IV) moieties, respectively. Our recent study [5] of the interactions of *N*-(4-hydroxybenzalidene)-2-methoxyaniline and *N*-(4-hydroxybenzalidene)-4-methoxyaniline with tin(IV), mono- and diorganotin(IV) chlorides in a 1:1 mixture of dichloromethane and methanol led to the isolation of complex salts in which the *N*-(4-hydroxybenzalidene)-2-methoxyanilinium and *N*-(4-hydroxybenzalidene)-4-methoxyanilinium cations are accompanied by various stannate(IV) and organostannate(IV)

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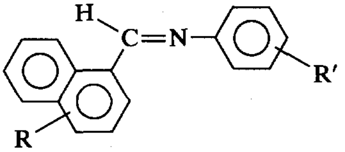
counter ions. The stability of the cations has been ascribed to the inductive effect of the substituent in the aniline fragment [5].

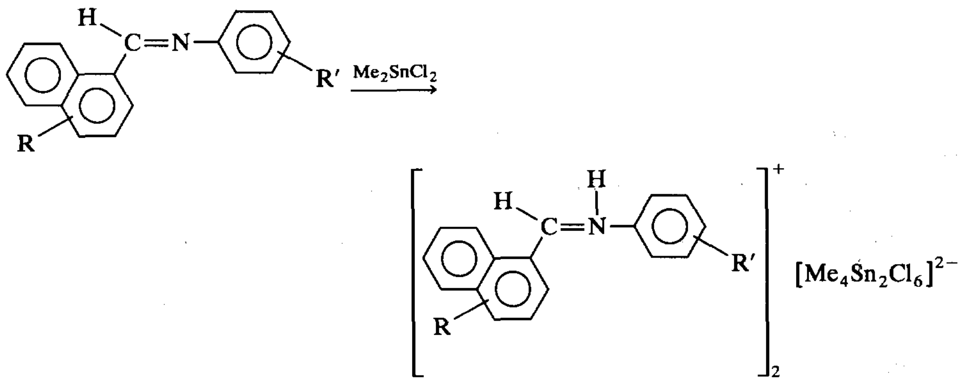
In the present study, the Schiff base ligands *N*-(2-methoxy-1-naphthalidene)-2-methoxyaniline (**1**) and *N*-(4-methoxy-1-naphthalidene)-3-methoxyaniline (**2**) were first obtained by the reactions of 2-methoxy-1-naphthaldehyde with 2-methoxy- and 3-methoxyaniline, respectively, whilst *N*-(4-methoxy-1-naphthalidene)-2-methoxyaniline (**3**) was obtained from the reaction of 4-methoxy-1-naphthaldehyde with 2-methoxyaniline.



		R	R'
(1)	$2\text{-}OCH_3C_{10}H_6CH:NC_6H_4(2\text{-}OCH_3)$	$2\text{-}OCH_3$	$2\text{-}OCH_3$
(2)	$2\text{-}OCH_3C_{10}H_6CH:NC_6H_4(3\text{-}OCH_3)$	$2\text{-}OCH_3$	$3\text{-}OCH_3$
(3)	$4\text{-}OCH_3C_{10}H_6CH:NC_6H_4(2\text{-}OCH_3)$	$4\text{-}OCH_3$	$2\text{-}OCH_3$

These ligands were subsequently reacted with Me_2SnCl_2.

The reactions of Me_2SnCl_2 with **1**, **2** and **3** resulted in the formation of the complex salts **4**, **5** and **6**, respectively. These reactions are summarized in the following equation:



(**4**) $R = 2\text{-}OCH_3$, $R' = 2\text{-}OCH_3$
(**5**) $R = 2\text{-}OCH_3$, $R' = 3\text{-}OCH_3$
(**6**) $R = 4\text{-}OCH_3$, $R' = 2\text{-}OCH_3$

An X-ray crystal structural study was carried out on bis[*N*-(2-methoxy-1-naphthalideneaniline)-3-methoxyanilinium] hexachlorotetramethyldistannate(IV) dihydrate.

Experimental

2- and 4-Methoxy-1-naphthaldehyde and 2- and 3-methoxyaniline were purchased from Fluka Chemie AG. Dimethyltin(IV) chloride was obtained from the Aldrich Chemical Company.

Microanalyses were carried out at Universiti Sains Malaysia. The IR spectra were recorded on a Beckman IR 20A spectrophotometer in the frequency range 4000–250 cm^{-1} with the samples in KBr discs. ^1H NMR spectra were recorded on a Bruker AC-P 300 MHz NMR spectrometer. DMSO-d^6 was used as the solvent with TMS as internal standard.

Preparation of N-*(2-methoxy-1-naphthalidene)-2-methoxyaniline (1)*

A solution of 2-methoxy-1-naphthaldehyde (18.6 g, 0.1 mol) in 95% ethanol was treated with 2-methoxyaniline (11.3 ml, 0.1 mol) in the same solvent. The mixture was stirred, and a yellow solid compound separated upon cooling to 0°C; m.p. 73–75°C. Anal. Found: C, 78.02; H, 5.77; N, 4.76. $C_{19}H_{17}NO_2$ calc.: C, 78.32; H, 5.89; N, 4.81%. IR: ν(CH=N) 1620 cm^{-1}. ^1H NMR: δ(CH=N) 9.49 ppm.

Preparation of N-*(2-methoxy-1-naphthalidene)-3-methoxyaniline (2)*

This compound was made similarly but from 3-methoxyaniline (11.3 ml, 0.1 mol) and 2-methoxy-1-naphthaldehyde (18.6 g, 0.1 mol). The yellow solid obtained had m.p. 78–80°C. Anal. Found: C, 78.57; H, 5.71; N, 4.71. $C_{19}H_{17}NO_2$ calc.: C, 78.32; H, 5.89; N, 4.81%. IR: ν(CH=N) 1620 cm^{-1}. ^1H NMR: δ(CH=N) 9.46 ppm.

Preparation of N-*(4-methoxy-1-naphthalidene)-2-methoxyaniline (3)*

This ligand was prepared by adding 2-methoxyaniline (11.3 ml, 0.1 mol) to 4-methoxy-1-naphthaldehyde (18.6 g, 0.1 mol). The mixture was kept at 0°C for a day during which a brownish yellow precipitate separated; m.p. 142–144°C. Anal. Found: C, 78.11; H, 5.80; N, 4.78. $C_{19}H_{17}NO_2$ calc.: C, 78.32; H, 5.89; N, 4.81%. IR: ν(CH=N) 1630 cm^{-1}.

*Preparation of bis[*N-*(2-methoxy-1-naphthalidene)-2-methoxyanilinium] hexachlorotetramethyldistannate(IV) (4)*

The synthesis was carried out by adding a solution of Me_2SnCl_2 (0.66 g, 3 mmol) in dichloromethane to a solution of **1** (1.75 g, 6 mmol) in the same solvent. Stirring of the solution and slow evaporation at room temperature gave a brownish yellow solid; m.p. 157–159°C. Anal. Found: C, 46.20; H, 4.57; N, 2.52; Sn, 21.82. $C_{21}H_{24}NO_2Cl_3Sn$ calc.: C, 46.08; H, 4.43; N, 2.56; Sn, 21.68%. IR: ν(N–H) 3430 cm^{-1}; ν(CH=N) 1625 cm^{-1}. ^1H NMR: δ(C=NH) 10.77 ppm; δ(CH=N) 9.12 ppm.

*Preparation of bis[*N-*(2-methoxy-1-naphthalidene)-3-methoxyanilinium] hexachlorotetramethyldistannate(IV) (5)*

A solution of Me_2SnCl_2 (0.66 g, 3 mmol) in dichloromethane was treated with compound **2** (1.75 g, 6 mmol). The mixture was stirred and then kept at 0°C for 1 day, during which a reddish solid appeared; m.p. 136–138°C. Anal. Found: C, 46.34; H, 4.21; N, 2.63; Sn, 21.04. $C_{21}H_{24}NO_2Cl_3Sn$ calc.: C, 46.08; H, 4.43; N, 2.56; Sn, 21.68%. IR: ν(N–H) 3245 cm^{-1}; ν(CH=N) 1625 cm^{-1}. ^1H NMR: δ(C=NH) 10.78 ppm; δ(CH=N) 9.15 ppm.

*Preparation of bis[*N-*(4-methoxy-1-naphthalidene)-2-methoxyanilinium] hexachlorotetramethyldistannate(IV) (6)*

A procedure similar to that described for **4** was used, ligand **3** (1.75 g, 6 mmol) being treated with Me_2SnCl_2 (0.66 g, 3 mmol) to give a brownish solid as the

Table 1

Crystal data and details of structure refinement for $[(CH_3OC_{10}H_6CH:NHC_6H_4OCH_3)^+]_2$-$[(CH_3)_4Sn_2Cl_6]^{2-}[H_2O]_2$

Formula	$C_{42}H_{52}N_2O_6Cl_6Sn_2$	D_c (g cm^{-3})	1.518
Formula weight	1131.32	$F(000)$	568
Crystal system	Triclinic	μ (mm^{-1})	1.263
Space group	$P\bar{1}$	Data collected	4698
a (Å)	9.998(2)	Unique data	4447
b (Å)	10.147(1)	Data with $I > 2.5\sigma(I)$	3648
c (Å)	13.414(3)	R	0.0946
α (°)	111.71(2)	R_w	0.0983
β (°)	98.64(2)	w	$k/[\sigma^2(F_o)+gF_o^2]$
γ (°)	94.19(1)	k	6.9019
V (Å^3)	1237.65(7)	g	0.001122
Z	1	$(\Delta\rho)_{max}$	1.38 (near Sn atom)

Table 2

Atomic coordinates ($\times 10^4$) and B_{eq} (Å^2) values for non-hydrogen atoms, with e.s.d.s in parentheses ($B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3$)

	x	y	z	B_{eq}
Sn(1)	1224(1)	−1741(1)	−217(1)	4.51
Cl(1)	2314(4)	−2864(5)	987(3)	8.00
Cl(2)	−277(3)	−368(3)	−1490(2)	5.62
Cl(3)	1895(3)	−3330(3)	−1962(2)	5.83
C(2)	−671(12)	−2943(11)	−528(9)	5.32
C(21)	2859(14)	−145(17)	126(14)	7.91
C(19)	1161(17)	3138(15)	7848(10)	7.85
O(1)	789(8)	2882(8)	6720(6)	5.53
C(1)	−661(10)	1791(9)	5008(7)	4.10
C(2)	−303(10)	1934(10)	6096(8)	4.54
C(3)	−1062(15)	1123(13)	6517(11)	6.53
C(4)	−2185(15)	216(11)	5877(10)	6.46
C(5)	−2609(12)	11(11)	4773(10)	5.67
C(6)	−3766(16)	−963(15)	4132(12)	7.97
C(7)	−4204(16)	−1132(15)	3076(13)	8.23
C(8)	−3481(14)	−364(13)	2619(11)	6.73
C(9)	−2322(12)	586(11)	3211(8)	5.29
C(10)	−1851(11)	794(10)	4308(8)	4.85
C(11)	83(9)	2610(8)	4551(7)	3.95
N(1)	1124(8)	3614(8)	5108(7)	4.35
C(12)	1873(9)	4500(8)	4712(6)	3.58
C(13)	3013(10)	5405(9)	5430(8)	4.67
C(14)	3767(9)	6287(10)	5112(8)	4.69
C(15)	3371(11)	6286(11)	4076(9)	5.43
C(16)	2263(11)	5381(11)	3369(9)	5.27
C(17)	1492(10)	4471(10)	3675(8)	4.53
O(2)	4870(9)	7244(9)	5750(7)	6.85
C(18)	5288(14)	7316(15)	6829(11)	7.26
OW(1)	4694(10)	4453(19)	729(13)	7.75

product; m.p. 206°C (decom). Anal. Found: C, 46.19; H, 4.51; N, 2.50; Sn, 20.90%. $C_{21}H_{24}NO_2Cl_3Sn$ calc.: C, 46.08; H, 4.43; N, 2.56; Sn, 21.68%. IR: ν(N–H) 3200 cm^{-1}; ν(CH=N) 1635 cm^{-1}.

Crystallography

Single crystals of bis[*N*-(2-methoxy-1-naphthalidene)-3-methoxyanilinium] hexachlorotetramethyldistannate(IV) (**5**) which has co-crystallized with two water molecules were grown from the mixed solvent system of CH_2Cl_2 and n-hexane at

Table 3

Bond distances (Å) and angles (deg) with e.s.d.s in parentheses for non-hydrogen atoms

Cl(1)–Sn(1)	2.471(3)	Cl(2)–Sn(1)–Cl(1)	174.0(1)
Cl(2)–Sn(1)	2.899(3)	Cl(3)–Sn(1)–Cl(1)	97.6(1)
Cl(3)–Sn(1)	2.524(2)	Cl(3)–Sn(1)–Cl(2)	87.4(1)
C(20)–Sn(1)	2.073(11)	C(20)–Sn(1)–Cl(1)	93.7(3)
C(21)–Sn(1)	2.084(13)	C(20)–Sn(1)–Cl(2)	82.5(3)
O(1)–C(19)	1.421(13)	C(20)–Sn(1)–Cl(3)	94.6(3)
C(2)–O(1)	1.339(12)	C(21)–Sn(1)–Cl(1)	96.2(5)
C(2)–C(1)	1.400(13)	C(21)–Sn(1)–Cl(2)	86.8(5)
C(10)–C(1)	1.451(13)	C(21)–Sn(1)–Cl(3)	92.9(4)
C(11)–C(1)	1.429(11)	C(21)–Sn(1)–C(20)	166.6(6)
C(3)–C(2)	1.397(14)	C(2)–O(1)–C(19)	120.3(9)
C(4)–C(3)	1.349(18)	C(10)–C(1)–C(2)	119.4(8)
C(5)–C(4)	1.409(17)	C(11)–C(1)–C(2)	122.8(8)
C(6)–C(5)	1.399(17)	C(11)–C(1)–C(10)	117.8(8)
C(10)–C(5)	1.420(12)	C(1)–C(2)–O(1)	117.5(8)
C(7)–C(6)	1.360(19)	C(3)–C(2)–O(1)	121.3(1)
C(8)–C(7)	1.382(17)	C(3)–C(2)–C(1)	121.2(1)
C(9)–C(8)	1.377(15)	C(4)–C(3)–C(2)	119.7(12)
C(10)–C(9)	1.407(15)	C(5)–C(4)–C(3)	122.4(9)
N(1)–C(11)	1.315(11)	C(6)–C(5)–C(4)	120.5(1)
C(12)–N(1)	1.423(1)	C(10)–C(5)–C(4)	119.6(1)
C(13)–C(12)	1.391(12)	C(10)–C(5)–C(6)	119.8(11)
C(17)–C(12)	1.374(12)	C(7)–C(6)–C(5)	120.8(1)
C(14)–C(13)	1.353(13)	C(8)–C(7)–C(6)	119.8(12)
C(15)–C(14)	1.387(15)	C(9)–C(8)–C(7)	121.5(13)
O(2)–C(14)	1.355(11)	C(10)–C(9)–C(8)	120.0(1)
C(16)–C(15)	1.365(14)	C(5)–C(10)–C(1)	117.6(1)
C(17)–C(16)	1.374(13)	C(9)–C(10)–C(1)	124.3(8)
C(18)–O(2)	1.418(15)	C(9)–C(10)–C(5)	118.1(9)
		N(1)–C(11)–C(1)	124.3(9)
		C(12)–N(1)–C(11)	127.0(8)
		C(13)–C(12)–N(1)	116.5(8)
		C(17)–C(12)–N(1)	122.0(7)
		C(17)–C(12)–C(13)	121.4(8)
		C(14)–C(13)–C(12)	119.8(9)
		C(15)–C(14)–C(13)	119.1(9)
		O(2)–C(14)–C(13)	125.1(1)
		O(2)–C(14)–C(15)	115.8(9)
		C(16)–C(15)–C(14)	120.9(9)
		C(17)–C(16)–C(15)	120.8(1)
		C(16)–C(17)–C(12)	118.0(8)
		C(18)–O(2)–C(14)	117.9(9)

room temperature. The crystal selected for X-ray analysis was coated with epoxy glue to prevent loss of crystallinity after exposure to air for a long period. Intensity data for a crystal of dimensions $0.5 \times 0.3 \times 0.2$ mm^3 were measured at room temperature on a Syntex $P2_1$ diffractometer fitted with graphite monochromated Mo-K_α radiation, $\lambda = 0.71069$ Å. The θ–2θ scan was employed to measure a total of 4698 reflections such that $\theta_{max} \leq 26°$. Corrections were applied for Lorentz and polarization effects but not for absorption. There were 4447 unique data of which 3648 satisfied the $I \geq 2.5\sigma(I)$ criterion of observability and were used in the subsequent analysis. The structure was solved by using SHELXS-86 [6] and refined by a full matrix least squares procedure based on F using SHELX-76 [7]. All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in their idealized positions (C–H = 0.96 Å). A weighting scheme of the form $w = k/[\sigma^2(F) + gF^2]$ was used and the refinement continued to final $R = 0.094$, $R_w = 0.098$ for $k = 6.902$ and $g = 0.00112$. The analysis of variance showed no special features and the maximum residual electron density peak in the final difference map was 0.72 e Å^{-3}. The scattering factors for all the atoms were used as incorporated in SHELX-76. Crystal data and refinement parameters are summarized in Table 1. Fractional atomic coordinates are listed in Table 2 and bond lengths and angles in Table 3. Additional data, including hydrogen atom coordinates, anisotropic temperature factors and a listing of observed and calculated structure factors are available on request from the authors.

Results and discussions

The molecular structure of complex **5**, bis[*N*-(2-methoxy-1-naphthalidene)-3-methoxyanilinium] hexachlorotetramethyldistannate(IV) (Fig. 1) showed it to be a complex salt in which the doubly charged anion consists of two $Me_2SnCl_3^-$ anions held together by two chlorine atom bridges between two six-coordinated tin atoms.

The angle subtended by the carbon atoms at either of the tin atoms (166.6°) is larger than those reported for $[Pt(S_2N_2H)(PEt_3)_2]^+$ $[Me_2SnCl_3]^-$ (159.5(5)°) [8] and for $[C_9H_8N]^+$ $[Me_2SnCl_3]^-$ (152.2(5)°) [9], and as a result the length of the bond between the tin atom and the adjacent chlorine atom Cl2^i (2.835(3) Å; symmetry operation: $-x, -y, -z$) becomes very much shorter than those in those two salts (3.205(3) and 3.486(7) Å, respectively). The dianion may thus be regarded as a strongly associated dimer.

Along with the dinegative anion are two singly positive Schiff base ligands, **2**.

The emergence of a new band assignable to the N–H stretching vibration at 3245 cm^{-1} in the IR spectrum of the complex salt, **5**, supports the presence of the positively charged Schiff bases, similar to that found for the protonated ligand pair in the pseudo-complex of 1-(salicylideneimino)-2-methoxybenzene and triphenyltin isothiocyanate [1]. In addition, the stretching vibration of C=N is shifted to a higher frequency upon complex salt formation, and this can be attributed to the protonation of the imine N atom of the Schiff base, **2**.

A new peak present at $\delta = 10.78$ ppm in the ^{1}H NMR spectrum of the salt, **5**, but absent from the spectrum of the ligand, **2**, again suggests that a proton is attached to the imine N atom of the ligand. A peak attributable to the azomethine proton at $\delta = 9.46$ ppm is shifted upfield, as was previously observed [5], confirming protonation of the imine N atom.

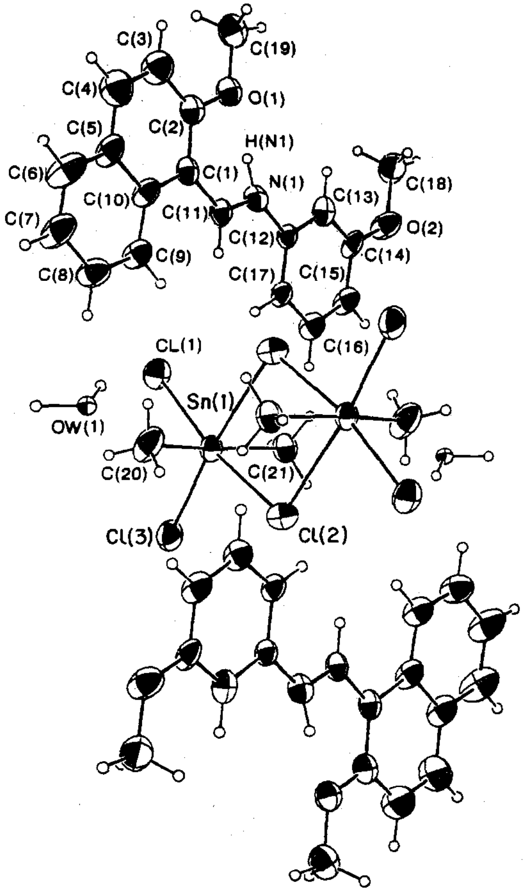


Fig. 1. Molecular structure and atom numbering scheme employed for $[CH_3OC_{10}H_6$-$CH:NHC_6H_4OCH_3]_2[(CH_3)_4Sn_2Cl_6][H_2O]_2$.

Although water molecules are present in the lattice they are not involved in any direct bonding with either of the tin atoms.

The microanalytical data obtained are in agreement with the formulation $[2\text{-}OCH_3C_{10}H_6CH:HNC_6H_4(3\text{-}OCH_3)^+]_2[Me_4Sn_2Cl_6]^{2-}$ rather than $[2\text{-}OCH_3$-$C_{10}H_6CH:HNC_6H_4(3\text{-}OCH_3)^+]_2[Me_4Sn_2Cl_6]^{2-}[H_2O]_2$ because of the ready loss of the lattice water molecules on exposure to the atmosphere. The thermogram of the freshly prepared complex salt, **5**, which shows expulsion of water molecules at 130°C, confirms the presence of water molecules in the crystal lattice. Similarly, the initial IR spectrum of the complex shows the presence of a new peak at 3400 cm^{-1} which is characteristic of the OH from the water molecule. However, this peak gradually disappears after 0.5 h, indicating that the water molecules are readily lost from the crystal lattice.

The microanalytical results for **4** and **6** are in agreement with the formulations $[2\text{-}OCH_3C_{10}H_6CH:HNC_6H_4(2\text{-}OCH_3)^+][Me_2SnCl_3]^-$ and $[4\text{-}OCH_3C_{10}H_8$-$CH:HNC_6H_4(2\text{-}OCH_3)^+][Me_2SnCl_3]^-$, respectively. Close similarities between the IR and ^1H NMR spectra of these complexes and those of **5** indicate that the structures of the complexes are similar to that of **5**, suggesting that they involve similar pairs of anionic $[Me_2SnCl_3]^-$ moieties. Although diorganotrihalogenostannate(IV) anions have been studied by a variety of physical techniques, such as infrared [10] and Mössbauer spectroscopy [11,12], single crystal structure studies have shown that the salt contains the loosely associated dimer of two $[Me_2SnCl_3]^-$ units [9,12,13], *i.e.* $[Me_4SnCl_6]^{2-}$.

Preliminary attempts to obtain complex salts by treating Ph_2SnCl_2 with **1**, **2** and **3** were unsuccessful, probably because the phenyl groups sterically inhibit the association of two anionic units to give the chloride-bridged dimer.

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