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Tin(IV) and organotin(IV) complexes containing mono or bidentate N-donor ligands
II. [1] 4-Phenylimidazole derivatives. Crystal and molecular structure of [bis(4-phenylimidazole) trimethyltin(IV)] chloride

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Abstract

A series of 2 : 1 adducts of the type $[(L')_2R_nSnX_{4-n}] \cdot zH_2O$ (L′ = 4-phenylimidazole, R = Me, Et, ^{n}Bu, Ph or Cy, X = I, Br or Cl, n = 0, 1, 2 or 3, z = 0 or 1) has been characterized in the solid state and in solution by analyses, spectral (IR, far-IR, ^{1}H and ^{13}C) data and conductivity measurements. The derivatives $[(L')_2(Me)_3Sn]Cl$ (**1**) and $[(L')_2(Me)_2SnCl_2]$ (**3**) react with $NaClO_4$ in THF giving the ionic complexes $[(L')_2(Me)_3Sn]ClO_4$ and $(L')_3[(Me)_2Sn(ClO_4)_2] \cdot (H_2O)_4$ respectively. Whereas the triorganotin(IV) derivatives are completely dissociated in acetone solution, the diorganotin(IV) derivatives dissociate only partly and the tri- and tetrahalidetin(IV) complexes probably retain the hexacoordinate configuration. The crystal structure of $[(L')_2(Me)_3Sn]Cl$ (**1**) has been determined by X-ray analysis. The tin atom is coordinated to three methyl groups and two 4-phenylimidazole donors in a substantially regular trigonal bipyramidal geometry. The ionic chloride group and the two N–H moieties are involved in a hydrogen bond network.

Keywords: Sn; X-ray structure; Trimethyltin chloride; Imidazole adducts; H-bonding

1. Introduction

Since the first report on the antitumor activity of diorganotin compounds appeared in 1980 [1], there has been increased interest in the synthesis of tin-based antitumor drugs [2,3]. It seems that the coordinated organic ligand facilitates the transport of the complex across cell membranes, while the antitumor activity is exerted by the dissociated diorganotin(IV) moieties. The action mechanism of these derivatives requires a complete understanding of their structure. The correlation between X-ray crystallographic data and antitumor activity may facilitate the design and synthesis of even more active complexes [4–7]. The study of complexes with monodentate nitrogen donor ligands, such as imi-

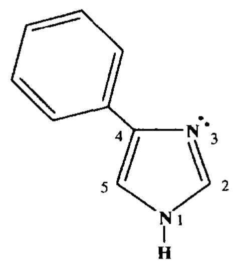

Fig. 1. 4-phenylimidazole.

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dazole which, as a part of histidine, plays an important role in many biological processes, could be very useful in increasing the understanding of interactions of these derivatives with DNA, where N-atoms of nucleic acid bases could be involved [8,9].

As an extension of our research on tin(IV) and organotin(IV) complexes of imidazoles [10], we now describe the synthesis and spectroscopic characterization of new adducts between R_nSnX_{4-n} (R = Me, Et, ^{n}Bu, Ph or Cy, n = 0, 1, 2 or 3, X = Cl, Br, I or ClO_4) acceptors and the 4-phenylimidazole donor (**L′**) (Fig. 1). We also report the X-ray crystal structure of one of these complexes, which is the first structurally characterized ionic triorganotin(IV) derivative containing two N-donor monodentate ligands.

2. Results and discussion

The reaction between 4-phenylimidazole (**L′**) (Fig. 1) and several R_nSnX_{4-n} acceptors (R = Me, X = Cl, n = 0, 1, 2 or 3; R = Me, Et or ^{n}Bu, X = Br, n = 2; R = Et, n = 2, X = Cl; R = ^{n}Bu, X = Cl, n = 1 or 2;

Table 1
Physical, analytical and conductivity data for derivatives **1–20**

Compound and formula [a]	No.	Yield (%)	M.p. (°C)	Elemental analysis (%); Found (Calc.)			Conductivities [b]		
				C	H	N	Solvent	Conc.	Λ
$[(L')_2(CH_3)_3Sn]Cl$	**1**	51	198–202	51.6	5.4	11.1	Acetone	2.8	3.6
$C_{21}H_{25}ClN_4Sn$				(51.7)	(5.2)	(11.5)			
$[(L')_2(C_6H_5)_3Sn]Cl$	**2**	40	131–135	63.6	4.9	8.0	Acetone	2.3	1.3
$C_{36}H_{31}ClN_4Sn$				(64.2)	(4.6)	(8.3)			
$[(L')_2(CH_3)_2SnCl_2]$	**3**	99	212–214	47.2	4.6	11.1	Acetone	5.3	4.1
$C_{20}H_{22}Cl_2N_4Sn$				(47.2)	(4.4)	(11.0)			
$[(L')_2(CH_3)_2SnBr_2]$	**4**	97	207–210	40.4	3.8	9.0	Acetone	2.2	17.3
$C_{20}H_{22}Br_2N_4Sn$				(40.2)	(3.7)	(9.4)			
$[(L')_2(CH_3)_2SnI_2]$	**5**	25	166–170	35.0	3.3	8.3	Acetone	2.5	84.0
$C_{20}H_{22}I_2N_4Sn$				(34.8)	(3.2)	(8.1)			
$[(L')_2(C_2H_5)_2SnCl_2]$	**6**	99	197–201	49.5	5.1	10.0	Acetone	2.5	6.0
$C_{22}H_{26}Cl_2N_4Sn$				(49.3)	(4.9)	(10.4)			
$[(L')_2(C_2H_5)SnBr_2]$	**7**	92	185–190	42.2	4.5	9.0	Acetone	2.6	12.7
$C_{22}H_{26}Br_2N_4Sn$				(42.3)	(4.2)	(9.0)			
$[(L')_2(C_2H_5)_2SnI_2]$	**8**	56	135–138	36.9	4.1	8.0	Acetone	1.6	63.1
$C_{22}H_{26}I_2N_4Sn$				(36.7)	(3.6)	(7.8)			
$[(L')_2(C_4H_9)_2SnCl_2]$	**9**	92	147–148	52.8	6.1	9.1	Acetone	2.2	6.4
$C_{26}H_{34}Cl_2N_4Sn$				(52.7)	(5.7)	(9.5)			
$[(L')_2(C_4H_9)_2SnBr_2]$	**10**	99	150–151	46.0	5.2	8.4	Acetone	2.0	11.0
$C_{26}H_{34}Br_2N_4Sn$				(45.8)	(5.0)	(8.2)			
$[(L')_2(C_6H_5)_2SnCl_2]$	**11**	99	172–174	55.7	4.1	8.4	Acetone	1.9	33.7
$C_{30}H_{26}Cl_2N_4Sn$				(57.0)	(4.1)	(8.9)			
$[(L')_2(C_6H_5)_2SnBr_2]$	**12**	34	170–176	50.0	3.9	8.1	Acetone	1.8	38.9
$C_{30}H_{26}Br_2N_4Sn$				(50.0)	(3.6)	(7.8)			
$[(L')_2(cyclo\text{-}C_6H_{11})_2SnBr_2]$	**13**	93	157–159	49.6	5.7	7.0	Acetone	1.7	3.5
$C_{30}H_{38}Br_2N_4Sn$				(49.1)	(5.2)	(7.6)			
$[(L')_2(cyclo\text{-}C_6H_{11})_2SnI_2]$	**14**	33	111–115	44.4	5.1	6.7	Acetone	1.4	35.7
$C_{30}H_{38}I_2N_4Sn$				(43.6)	(4.6)	(6.8)			
$[(L')_2CH_3SnCl_3]$	**15**	53	220 dec.	44.1	4.3	10.8	Acetone	2.8	45.0
$C_{19}H_{19}Cl_3N_4Sn$				(43.2)	(3.6)	(10.6)			
$[(L')_3(C_4H_9SnCl_3)_2]$	**16**	50	117–121	42.4	4.6	8.8	Acetone	2.9	166.5
$C_{35}H_{42}Cl_6N_6Sn_2$				(42.2)	(4.2)	(8.4)			
$[(L')_3(C_6H_5SnCl_3)_2] \cdot H_2O$	**17**	61	290 dec.	44.2	3.5	8.1	Acetone	1.5	109.3
$C_{39}H_{36}Cl_6N_6OSn$				(44.4)	(3.4)	(8.0)			
$[(L')_2SnCl_4] \cdot H_2O$	**18**	90	52 dec.	38.3	3.7	9.9	Acetone	2.3	41.3
$C_{18}H_{18}Cl_4N_4OSn$				(38.1)	(3.2)	(9.9)			
$[(L')_2(CH_3)_3Sn]ClO_4$	**19**	83	183–187	47.4	5.3	10.8	Acetone	3.2	130.6
$C_{21}H_{25}ClN_4O_4Sn$				(45.7)	(4.6)	(10.2)			
$(L')_3[(CH_3)_2Sn(ClO_4)_2]_2 \cdot (H_2O)_4$	**20**	26	204–206	31.6	3.7	6.5	Acetone	1.5	375.5
$C_{31}H_{44}Cl_4N_6O_{20}Sn_2$				(31.0)	(3.7)	(7.0)			

[a] L′ is 4-phenylimidazole.
[b] In Ω^{-1} cm^2 mol^{-1} at room temperature; conc. is molar concentration ($\times 10^3$).

R = Ph, n = 1, 2 or 3, X = Cl; R = Cy, X = Br, n = 2) was carried out in diethyl ether or benzene or dichloromethane solutions from which the colorless complexes **1–4**, **6**, **7**, **9–11**, **13**, and **15–18** (Table 1) were isolated as insoluble or sparingly soluble precipitates, in accordance with Eq. (1).

$$x(L') + R_nSnX_{4-n} \cdot zH_2O \xrightarrow{S} [(L')_x(R_nSnX_{4-n})] \cdot zH_2O \quad (1)$$

The reactions are rapid at room temperature, except those involving triorganotin(IV) derivatives which require a longer reaction time. This is in accordance with the low acidity of these organotin species [11].

The $[(L')_2R_2SnCl_2]$ type compounds **3**, **6**, and **13** are converted into the analogous di-iodide complexes **5**, **8**, and **14** respectively (Table 1), and the compound $[(L')_2Ph_2SnCl_2]$ (**11**) into the bromide $[(L')_2Ph_2SnBr_2]$ (**12**) on treatment with excess sodium halide in tetrahydrofuran suspension (Eq. (2)).

$$[(L')_2R_2SnCl_2] + 2NaX \xrightarrow{THF} [(L')_2R_2SnX_2] + 2NaCl \quad (2)$$

This conversion did not occur when $[(L')_2{}^nBu_2SnCl_2]$ was employed as starting material, whereas an incomplete substitution was observed when the reaction between sodium iodide and $[(L')_2Ph_2SnCl_2]$ was carried out under the same conditions.

The perchlorato complexes **19** and **20** were obtained when an ethanol solution of sodium perchlorate was added to a THF or ethanol solution of compounds **1** and **3** respectively.

All the complexes are generally air- and thermally-stable, soluble in acetone, moderately soluble in chlorinated solvents and insoluble in diethyl ether, ethanol, methanol, and water. Upon prolonged standing in acetone solution they are found to decompose somewhat, producing the starting materials or insoluble products for which the IR spectra and analytical data suggest an oxide nature.

The electrical conductivities were measured for all the compounds listed in acetone solution, in which a typical 1 : 1 electrolyte such as tetra-n-butylammonium bromide has a specific conductivity of 137 Ω^{-1} cm^2 mol^{-1}. Some of the compounds are non-electrolites (**1–4**, **6**, **7**, **9**, **10**, and **13**), other electrolytes (**16**, **17**, **19**, and **20**) and the remaining complexes are partly ionized.

2.1. IR data

In Table 2 we report the most relevant infrared data for the ligand and its tin(IV) and organotin(IV) complexes **1–20** in the range 4000–100 cm^{-1}. The spectra were recorded both in Nujol mull and in chloroform solution. By comparison with the data reported for other tin(IV) and organotin(IV) adducts containing N-donor ligands [12], we suggest for **1–20** the following assignments.

2.1.1. Ligand absorptions

In the 3200–3000 cm^{-1} region, the ligand exhibits weak bands typical of C–H stretching due to a pseudoaromatic ring, and in the region 1650–1500 cm^{-1}, some more intense absorptions due to ring breathing mode [13]. These bands do not shift markedly upon coordination to tin, suggesting a weak influence of the complexation on the bands within the donor. In the 2800–2600 cm^{-1} region, the ligand exhibits a broad band typical of N–H stretching. In the tin(IV) and organotin(IV) adducts this band shifts in the 3600–2800 cm^{-1} region, suggesting an important influence of the coordination to tin. The position and the broadening of the N–H stretching band are consistent with the presence of a hydrogen bond between the N–H moiety and the halide groups [14].

2.1.2. Sn–C stretching frequencies

Compound **1** shows a medium band at 546 cm^{-1} due to the Sn–C stretching vibrations. The appearance of only a single band due to ν_{asym} is taken to imply a C_{3v} symmetry of the C_3–Sn skeleton and a *trans*-pyramidal configuration of the two ligands [15]. In the triphenyltin(IV) derivative **2**, the ν_{asym} and ν_{sym} Sn–C are observed as medium bands at 282 and 274 cm^{-1}, respectively; these absorptions are consistent with an essentially trigonal pyramidal arrangement of phenyl groups with a marked deviation from planarity. Only a single Sn–C band appeared in the spectra of dimethyl- (**3**, **4**), diethyl- (**6–8**), di-n-butyl- (**9**, **10**), and dicyclohexyltin(IV) complexes (**13**, **14**), in accordance with a *trans*-octahedral configuration of the two alkyl groups [16]. Instead, two strong absorptions at 289 and 279 cm^{-1} were observed in the spectra of the diphenyltin(IV) complex **12**. These bands are similar to those previously assigned [17] to ν_{asym} and ν_{sym} Sn–C in markedly distorted *trans*-R_2 octahedral diphenyltin(IV) complexes containing N-donor ligands.

2.1.3. Sn–Cl stretching frequencies

In the triorganotin(IV) derivatives **1** and **2**, the tin(IV) chloride stretching frequencies are absent. On the basis of previous reports [18] on triorganotin(IV) complexes, we have hypothesized an ionic formulation of the type $[(L')_2R_3Sn]^+[Cl]^-$. The X-ray crystal structure determination of compound **1** (see Section 2.3) confirms our hypothesis. In the di- and mono-organotin complexes, the ν(Sn–Cl) are observed in the region 230–200 cm^{-1} and 260–245 cm^{-1}, respectively. These absorptions are downfield with respect to those observed for the 1-benzylimidazole tin(IV) adducts [10]: this is likely to be due to the presence of hydrogen bonds between the N–H moieties of imidazole and halide groups [14].

Table 2
Selected IR data (4000–100 cm^{-1}) [a]

Compound	(C–H)azolo	ν(N–H)	1650–1500	< 600	ν(Sn–C)	ν(Sn-X)	δ(C–Sn–C) + δ(Cl–Sn–Cl)
L′	3117w, 3083w, 3060sh	2800–2600br	1606w, 1576w, 1544w, 1516w, 1508w	521m, 435m, 428m, 352w, 345w, 308m, 280w, 179w, 159m			
1	3154w, 3060w	3194s br	1611w, 1587w, 1572w	500m, 446m, 438m, 361m, 192m, 164m	546m		
2	3126w, 3051w, 3031w	3200–2600br	1608w, 1586w, 1500sh	552w, 543w, 509m, 465w, 449w, 219m, 210m	282m, 274m		
3	3127w, 3113w	3214s br	1609m, 1589m, 1573m	493m, 440m, 367m	575m	229s 215sh	178m, 152s, 145s, 136s
4	3125w, 3110w, 3056w	3210br	1611m, 1587m, 1574w	508m, 432m, 361m, 439sh, 300w, 217w, 200m	567m		165m, 150m, 129br
5	3170w	3200br	1610w, 1585w, 1558w, 1500sh	505m, 428w, 358w, 297w, 278w, 213sh	563m, 505m		176m, 161m
6	3126w, 3076w, 3018w	3170br	1611m, 1590m, 1574m	498w, 445m, 364m, 296m	534m	217s	194m, 162w, 155w, 134s
7	3156w, 3120w, 3016w	3195br	1610w, 1589m, 1572w	496m, 445m, 364w, 293m, 278sh, 247w	523m	206m	188m, 150sh, 126br
8	3149w	3300–3000br	1610w, 1587w, 1558w	487m, 441m, 397sh, 360m, 301w, 280br, 229w, 208w	528m		178w, 163w
9	3126w	3200–2700br	1612w, 1590w, 1572w, 1558w	495m, 444m, 396m, 362m, 271m, 261m	631m	225sh, 218s br	185s, 154s, 128s
10	3124w	3200br	1610w, 1588w, 1569w	493m, 444m, 395w, 361m, 270w, 210m	627m	210s br, 205sh	179m, 156w, 140br, 133br
11	3145w	3300br	1609w, 1587w, 1574w	508m, 463s, 439m, 364m, 310m, 249w	287s	229s	206s, 201s, 177m, 159m, 148m
12	3132w	3300br	1609w, 1588w, 1507w, 1558w	507m, 494m, 458s, 439m, 420w, 398w, 364w, 352w, 326w, 302w	289s, 279s	230m	199m, 195m
13	3115w, 3060w, 3011w	3130br	1612w, 1590w, 1572w	509m, 443m, 398w, 360m, 329m, 256m	423m	218m	200m, 193m
14	3106w, 3020w	3136br	1609w, 1587w, 1568w	506w, 440w, 398m, 352m, 326m, 280m, 247m, 225m, 200m, 176m	419m		
15	3132w, 3060w	3350br, 3180br	1609w, 1587w, 1568w	506m, 437m, 355m, 303w, 225w	492m, 530w	264m	180br, 160s, 149s
16	3135w	3528br, 3200br	1617w, 1594w, 1576w	496m, 452w, 432m, 351m, 311m, 290w	615s br	245s br	
17	3156w, 3138w	3200br	1623w, 1597w, 1576w	509m, 454m, 352w 224m	282s	260s br	200m, 171m
18 [b]	3130w, 3110w	3380br, 3200br	1623w, 1596w, 1576w	418w, 398w, 351w, 280m, 254m, 247m, 226m, 203m, 177m		325m, 315w, 303m	
19 [c]	3139w, 3110w	3265br	1612m, 1590m, 1575m, 1500sh	504m, 441m, 363m	551s		
20 [b,d]	3147w	3230br	1622m, 1598m, 1579m	517w, 498w, 476w, 434w, 353m, 282m, 240m, 181w, 167w	567m		

[a] Nujol mull and/or $CHCl_3$ solution.
[b] $\nu(H_2O)$: 3300 cm^{-1} br.
[c] $\nu(ClO_4)$: 1100s br, 625s br.
[d] $\nu(ClO_4)$: 1100s br, 622s.

Table 3
^{1}H NMR data [a] for the ligand and its tin(IV) and organotin(IV) derivatives **1–20**

Compound	$H_2 + H_5$	N–H	H aromat.	R–Sn	$J(^{119}Sn–^1H)$	$J(^{117}Sn–^1H)$	
L′	7.71d	7.55d	9–10br	7.19t, 7.35t, 7.84d			
1	7.78d	7.55d		7.21t, 7.36t, 7.82d	0.65s	67.4	64.5
2	7.71d	7.59d		7.22t, 7.35–7.50m, 7.75d	7.30–7.40m, 7.40–7.50m, 7.85–7.90m		
3	7.95br	7.64br	5.29br	7.25t, 7.39t, 7.82d	1.20s	91.5	87.1
4	8.12br	7.72d	6.40br	7.28t, 7.41t, 7.82d	1.48s	93.5	89.6
5	8.25d	7.78d	10.2br	7.30t, 7.42t, 7.83d	1.88s	90.8	86.7
6	7.95d	7.65d	5.52br	7.25t, 7.39t, 7.82d	1.32t, 1.77q	75.0 (^2J), 154.5 (^3J)	71.8 (^2J), 147.5 (^3J)
7	8.32br	7.86br	9.51br	7.31t, 7.44t, 7.80d	1.22t, 1.94q	87.7 (^2J), 173.6 (^3J)	83.9 (^2J), 165.9 (^3J)
8	8.22br	7.41br	9.5br	7.23–7.33m, 7.30–7.42m, 7.64d	1.25t, 1.98q	56.1 (^2J), 147.3 (^3J)	50.1 (^2J), 140.7 (^3J)
9	7.94br	7.64br	5.56br	7.24t, 7.38t, 7.82d	0.89t, 1.27–1.50m, 1.65–1.90m	n.o.	n.o.
10	8.34br	7.86br	8.97br	7.30t, 7.43t, 7.81d	0.81t, 1.30ps, 1.55–1.75m, 1.90–2.01m	n.o.	n.o.
11	8.17d	7.69d	6.52br	7.26t, 7.30t, 7.77d	7.30t, 7.26–7.36m, 7.96–8.01m		
12	8.30br	7.80br	6.0br	7.0–8.0m	7.0–8.0m		
13	7.92br	7.64br	7.06br	7.23t, 7.38t, 7.83d	1.20–1.50m br, 1.50–1.95m br, 1.96–2.11m br, 2.35–2.60m	n.o.	n.o.
14	7.86br	7.60d	4.9br	7.21t, 7.36t, 7.83d	1.20–1.55m br, 1.50–1.80m br, 1.90–2.10m br, 2.36–2.51m	n.o.	n.o.
15	8.47br	7.83br	4.54br	7.30t br, 7.38t br, 7.78d br	1.28s	131.9	125.6
16	9.0br	8.1br	6.5–8.5br	7.3–7.6m, 8.85d	0.9t, 1.3–1.6m, 1.8–2.1m	n.o.	n.o.
16 [b]	9.05br	7.52br		7.30–7.50m br, 7.65br	0.99t, 1.51ps, 1.93m, 2.39t	n.o.	n.o.
17	9.1br	8.3br	12.3br	7.2–8.8m br	7.2–8.8m br		
18 [c]	9.01d	7.92d	5.0br	7.4–7.6m, 7.75d			
19	8.26br	7.70br		7.38t, 7.46t, 7.79d	0.87s	69.2	66.9
20	9.0br	8.0br	6.5br	7.3–7.6m, 7.85d	0.75s br, 0.82s br, 0.95s br	n.o.	n.o.

[a] Acetone solution; δ in ppm, J in Hz; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, ps = pseudosixtet, br = broad.
[b] $CdCl_3$ solution.
[c] CD_3OD solution.

2.1.4. Sn–N stretching frequencies

We are not able to assign the ν(Sn–N) vibrations because they are likely to be hidden under some absorptions characteristic of the azole ring system [13].

2.1.5. Skeletal bending modes

In our complexes, no skeletal bending mode assignments are straightforward: δ(C–Sn–C), δ(X–Sn–X), $\rho(Sn–C_3)$, $\rho(SnX_3)$ and ν(Sn–Br) fall in the region 120–180 cm^{-1} [19] and are far too close to resolve.

2.1.6. Other data

The perchlorato complexes **19** and **20** were found to be ionic; in fact a single broad absorption at ca. 1100 cm^{-1} and a sharp band at 620 cm^{-1} were observed [20].

Table 4
^{13}C NMR data [a] for the ligand and its tin(IV) and organotin(IV) derivatives

Compound	Aromatics	Imidazole	R–Sn	$J(^{119}Sn–C)$	$J(^{117}Sn–C)$
L′	125.8, 127.3, 129.6, 135.9	136.9			
1	125.3, 127.1, 129.2, 134.6	115.8, 136.5, 139.3	1.09	469.1 (^1J)	446.4 (^1J)
2	125.5, 127.7, 129.4, 132.9	118.4, 137.4	129.2, 129.8, 137.1, 143.7	13.0 (^2J), 69.7 (^3J), 47.3 (^4J)	12.9 (^2J), 69.5 (^3J), 47.1 (^4J)
3	125.4, 127.5, 129.3, 133.6	116.7, 136.7	14.2		
6	125.5, 127.5, 129.3, 135.6	117.1, 137.0	10.0, 19.4	683.6 (^1J), 48.8 (^2J)	
7	125.6, 128.1, 129.6, 131.9	119.7, 136.0, 137.7	11.0, 33.5	744.6 (^1J), 52.3 (^2J)	
9	125.5, 127.7, 129.4, 132.3	117.8, 137.2	13.8, 26.6, 28.1, 33.7	669.2 (^1J), 118.6 (^3J)	638.2 (^1J), 111.6 (^3J)
10	125.7, 128.2, 129.6, 131.9	119.2, 136.1, 137.6	13.8, 26.4, 40.1	746.4 (^1J), 41.9 (^2J), 136.0 (^3J)	
11	125.6, 128.4, 129.6, 131.4	119.5, 135.6, 137.7	128.3, 129.3, 136.2	92.3 (^3J), 68.0 (^4J)	
15	125.8, 128.6, 129.7	121.7, 138.0	28.0	1196.3 (^1J)	1145.7 (^1J)

[a] Acetone solution.

2.2. NMR data

The ^{1}H NMR spectra of the donor L′ and of its tin(IV) and organotin(IV) complexes **1–20** in acetone solution are reported in Table 3, with the exception of **18** which was recorded in methanol due to poor solubility in the former solvent. The ^{13}C NMR spectra (Table 4) were carried out only on the sufficiently soluble derivatives.

The spectra of the triorganotin(IV) complexes **1** and **2** indicate a complete dissociation into the starting reagents. In fact, the Δ (difference in chemical shift for the same type of proton in the free base and in its tin(IV) complex) value is in the range 0.01–0.07 ppm. The tin–proton and tin–carbon coupling constants observed are of the same order of magnitude as those reported for the starting triorganotin acceptors [21].

In the diorganotin(IV) complexes **3–14**, upon complexation the signals of the ligand L′ are generally displaced downfield. This is likely to be due to a σ-charge donation from the N-donor to the metal center and is evidence of the existence of the complex in solution. The deshielding observed is attenuated at positions remote from the metal (aromatic protons and carbons). For **3–14** the tin–proton and tin–carbon coupling constants are different from those observed for the starting organotin(IV) derivatives [22]; they are of the same order of magnitude as those observed in 1-benzylimidazole organotin derivatives [10] and smaller than those reported in the literature for undissociated *trans*-octahedral diorganotin(IV) complexes [23]. This indicates that in acetone the dissociation of **3–14** is only partial and, as previously described for the organotin(IV) derivatives of 1-benzylimidazole [10], much of the complex is still present.

It is worth noting that the Δ value for the tri- and tetrahalidetin(IV) derivatives **15–18** is larger than that for the diorganotin complexes. This is likely to be due to an increase in stability of the adducts and to a stronger bonding interaction between L′ and the acceptors with decreasing degree of alkylation of the metal center. This fact is in accordance with the well-known Lewis acid strength of tin(IV) and organotin(IV) acceptors [11].

In most of the ^{1}H spectra of our tin(IV) compounds, a broad signal appears in the range 5–12 ppm, strongly dependent on the concentration, and assignable to the N–H proton. This further supports the concept that the donor L′ coordinates to tin(IV) in the neutral form through the pyridinic nitrogen.

2.3. Diffraction study of $[(L')_2(CH_3)_3Sn]Cl]$ (1)

A drawing of the [bis(4-phenylimidazole)trimethyltin(IV)]chloride structure, from the diffraction study, is

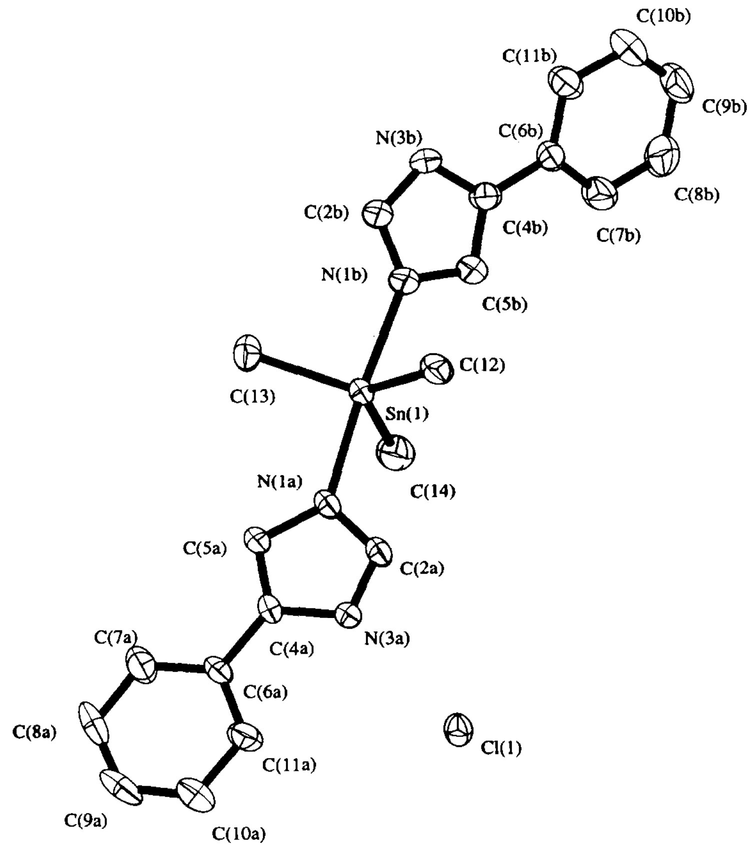

Fig. 2. The molecular structure of [bis(4-phenylimidazole)trimethyltin(IV)]chloride with atom numbering, as used in the crystallographic work.

Table 5
Interatomic distances (Å) with e.s.d.s in parentheses for {bis(4-phenylimidazole)}trimethyl-tin(IV) chloride

Sn(1)–N(1a)	2.351(5)	Sn(1)–N(1b)	2.351(6)
N(1a)–C(2a)	1.311(9)	N(1b)–C(2b)	1.318(9)
N(1a)–C(5a)	1.404(8)	N(1b)–C(5b)	1.39(1)
C(2a)–N(3a)	1.334(8)	C(2b)–N(3b)	1.345(9)
N(3a)–C(4a)	1.391(8)	N(3b)–C(4b)	1.370(9)
C(4a)–C(5a)	1.35(1)	C(4b)–C(5b)	1.35(1)
C(4a)–C(6a)	1.468(9)	C(4b)–C(6b)	1.46(1)
C(6a)–C(7a)	1.41(1)	C(6b)–C(7b)	1.39(1)
C(6a)–C(11a)	1.39(1)	C(6b)–C(11b)	1.39(1)
C(7a)–C(8a)	1.39(1)	C(7b)–C(8b)	1.39(1)
C(8a)–C(9a)	1.35(1)	C(8b)–C(9b)	1.38(1)
C(9a)–C(10a)	1.36(1)	C(9b)–C(10b)	1.35(1)
C(10a)–C(11a)	1.39(1)	C(10b)–C(11b)	1.39(1)
Sn(1)–C(12)	2.131(8)	Sn(1)–C(13)	2.130(7)
Sn(1)–C(14)	2.125(9)		

presented in Fig. 2 together with the numbering scheme. The bond distances and angles are listed in Tables 5 and 6, respectively. Analysis of the structure shows the tin atom pentacoordinate in a substantially regular trigonal bipyramidal configuration. The three methyls occupy the equatorial positions, and the two 4-phenylimidazole ligands the two axial sites. The chloride group is displaced from the Sn and involved in an H-bond network. It is worth noting that the two donor molecules coordinate the tin atom by means of their N(1) atoms. This is likely to be due to steric hindrance of the phenyl group in the 4-position, which requires a metal/proton exchange between the two nitrogen sites. In this structural study the occurrence of the trigonal bipyramidal geometry agrees well with the observation that in the solid state triorganotin(IV) halides seem to saturate their coordination with a coordination number equal to five [24]. However, in this case, the unusual 2 : 1 stochiometry, found for imidazole- [25] and 4-phenylimidazole-triorganotin(IV) halide derivatives, is a rather unexpected result; in fact, for example, even if 4-phenylimidazole and 1-benzylimidazole have the same value of pK_a (6.10 [26]), the latter, which presents a smaller steric hindrance than the former, gives, with trimethyltin(IV) chloride, a 1 : 1 adduct.

No crystal structure of triorganotin(IV) compounds coordinated to two imidazole-type donors is reported in the literature, so we have compared the structure of $[(L')_2(CH_3)_3Sn]Cl]$ with those of triorganotin derivatives bonded to two N-donor ligands with a trigonal bipyramidal coordination [27–30]. The Sn–N distances in $[(L')_2(CH_3)_3Sn]Cl]$ were found to be very close to the mean value (2.36 Å calculated from six Sn–N bonds) even if, because of the different chemical nature of the

Table 6
Bond angles (deg) with e.s.d.s in parentheses for {bis(4-phenylimidazole)}trimethyl-tin(IV) chloride

Sn(1)–N(1a)–C(2a)	121.3(4)	Sn(1)–N(1b)–C(2b)	125.8(5)
Sn(1)–N(1a)–C(5a)	133.1(4)	Sn(1)–N(1b)–C(5b)	126.7(5)
C(2a)–N(1a)–C(5a)	105.3(5)	C(2b)–N(1b)–C(5b)	105.8(6)
N(1a)–C(2a)–N(3a)	112.1(6)	N(1b)–C(2b)–N(3b)	110.7(6)
C(2a)–N(3a)–C(4a)	107.4(5)	C(2b)–N(3b)–C(4b)	108.0(6)
N(3a)–C(4a)–C(5a)	105.8(6)	N(3b)–C(4b)–C(5b)	105.9(7)
N(3a)–C(4a)–C(6a)	121.6(6)	N(3b)–C(4b)–C(6b)	123.0(6)
C(5a)–C(4a)–C(6a)	132.5(6)	C(5b)–C(4b)–C(6b)	130.8(7)
N(1a)–C(5a)–C(4a)	109.3(6)	N(1b)–C(5b)–C(4b)	109.5(7)
C(4a)–C(6a)–C(7a)	119.4(6)	C(4b)–C(6b)–C(7b)	119.5(7)
C(4a)–C(6a)–C(11a)	122.0(6)	C(4b)–C(6b)–C(11b)	122.0(7)
C(7a)–C(6a)–C(11a)	118.6(6)	C(7b)–C(6b)–C(11b)	118.5(7)
C(6a)–C(7a)–C(8a)	119.7(8)	C(6b)–C(7b)–C(8b)	120.1(9)
C(7a)–C(8a)–C(9a)	119.5(8)	C(7b)–C(8b)–C(9b)	120.3(9)
C(8a)–C(9a)–C(10a)	122.4(7)	C(8b)–C(9b)–C(10b)	119.5(8)
C(9a)–C(10a)–C(11a)	119.2(9)	C(9b)–C(10b)–C(11b)	121.2(9)
C(6a)–C(11a)–C(10a)	120.5(8)	C(6b)–C(11b)–C(10b)	120.3(8)
N(1a)–Sn(1)–C(12)	89.8(3)	N(1b)–Sn(1)–C(12)	87.2(3)
N(1a)–Sn(1)–C(13)	92.3(3)	N(1b)–Sn(1)–C(13)	91.6(3)
N(1a)–Sn(1)–C(14)	88.2(3)	N(1b)–Sn(1)–C(14)	91.1(3)
C(12)–Sn(1)–C(13)	120.8(4)	C(12)–Sn(1)–C(14)	122.3(4)
C(13)–Sn(1)–C(14)	116.9(4)	N(1a)–Sn(1)–N(1b)	176.0(2)

ligands, values ranging from 2.472 Å [27] to 2.29 Å [28] are reported.

We have also compared the Sn–N bond distance found in **1** with those reported in the literature for other tin(IV) imidazole adducts [31–36], without taking into account their coordination numbers and chemical nature. Also in these cases the mean value (2.347 Å) is very close to the one we found, the Sn–N bond lengths ranging from 2.29 to 2.41 Å. The spread of the Sn–N bond lengths in the imidazole–Sn interaction seems to be due to steric effects. It was noted [33], in fact, that the longer bond distances for the $[(ImH)_2R_2SnCl_2]$ (where ImH is a generic imidazole ligand) have been found when the imidazole is substituted in position 2 [33] (our numbering scheme), whereas substitution in positions 3 or 4 seems to produce a lesser effect [31] compared with unsubstituted imidazole adducts [32]. The Sn–N distance is longer than those reported for non-sterically hindered bis(imidazole)-diorganotin complexes. This fact indicates that an increase in the degree of tin acceptor alkylation produces a weaker bonding interaction and so a decrease in stability of the adducts.

The Sn–C distances in **1** are in good agreement with those reported in the literature for trimethyltin(IV) compounds [29].

The geometry of the two imidazole rings is not significantly different, with the exception of the internal angle on C(2) and the bond length between N(3) and C(4). The differences are, however, less than three times their e.s.d.s.

The torsion angles of the two imidazole rings with the bonded phenyl rings are 6.1° for ring A and 18.0° for ring B. The molecular parameters of the azole ring in **1** agree with those reported in the literature; the conjugation effect of phenyl on the ring geometry seems to be negligible, at least at this level of precision, even if the distance C(4)–C(6) is shorter than the value (1.488 Å) reported from CSD analysis [37] on a sample of 87 C(sp^2)–C(arylic) bond lengths.

The most interesting feature of this structure is the position of the Cl atom. In the solid state, the Cl is displaced from the Sn too far (4.564 Å) for any kind of bonding interaction. The Cl and the two N–H are involved in a hydrogen bond network, which connects each molecule of the adduct with another one related by the ($\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$) symmetry operation. They thus define a chain extending along the y direction (Fig. 3) which stabilizes the entire crystal packing. The N ··· Cl distances, which are 3.098(6) and 3.147(6) Å for N(3a) and N(3b) respectively, are below the sum of the Van Der Waals radii (3.3 Å) indicated by Hamilton and Ibers [38]. The angle values found for N(3a) ··· H(3a) ··· Cl(1) and N(3b) ··· H(3b) ··· Cl(1) are 164 and 170°, which are in good agreement with the geometrical requirement for the H-bonds. The angle N(3a) ··· Cl(1) ··· N(3b) is 82°.

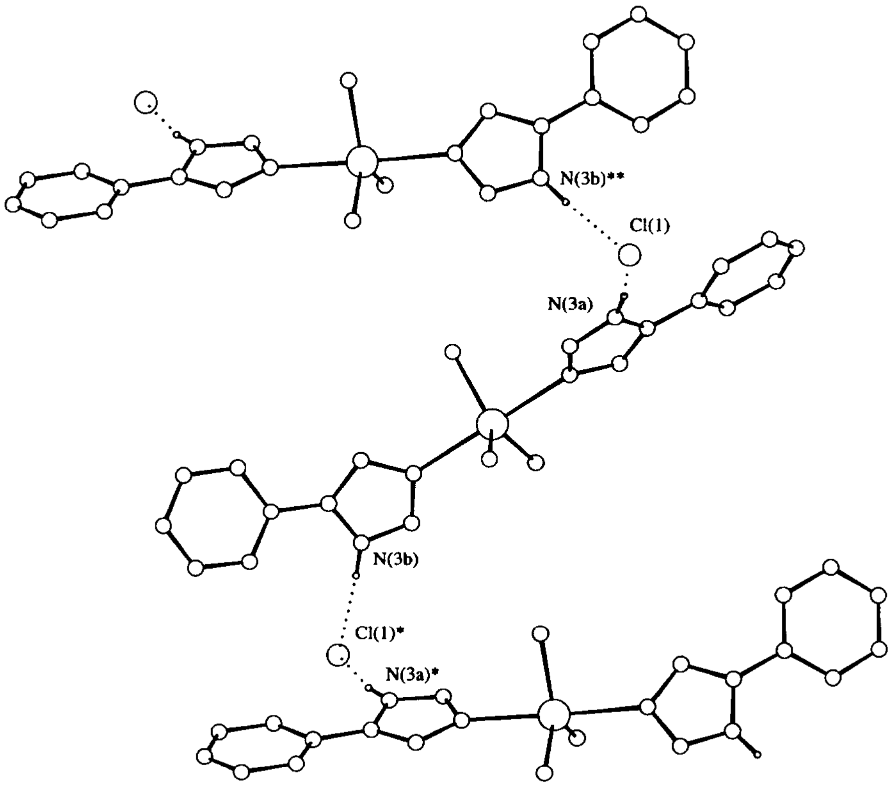

Fig. 3. Projection of the unit cell.

3. Experimental details

3.1. General comments

The tin(IV) and organotin(IV) halides were purchased from Alfa (Karlsruhe) and Aldrich (Milwaukee) and used as received. The ligand 4-phenylimidazole (**L′**) was obtained from Aldrich and was crystallized from diethyl ether/petroleum ether (1 : 2).

The samples for microanalysis were dried in vacuo to constant weight (20°C, ca. 0.1 Torr). Elemental analyses (C, H, N) were performed in-house with a Carlo-Erba model 1106 instrument. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin-Elmer System 2000 FT-IR instrument. ^1H and ^{13}C NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ^1H, 75 MHZ for ^{13}C). Melting points were taken on an IA 8100 electrothermal instrument. The electrical conductance of the solutions was measured with a Crison CDTM 522 conductimeter at room temperature.

3.2. Synthesis of the complexes

3.2.1. [Bis(4-phenylimidazole)trimethyltin(IV)]chloro (1)

To a stirred diethyl ether solution (100 cm^3) of $(CH_3)_3SnCl$ (548 mg, 2.8 mmol) at room temperature, a diethyl ether solution (25 cm^3) of 4-phenylimidazole (**L′**) (800 mg, 5.5 mmol) was added. A colorless precipitate was formed immediately, which was filtered off after 10 h, washed with diethyl ether and shown to be compound **1**. Adducts **3**, **4**, **6**, **7**, **9**, **11**, **13**, **15**, and **18** were obtained similarly.

3.2.2. [Bis(4-phenylimidazole)triphenyltin(IV)]chloro (2)

To a stirred diethyl ether solution (10 cm^3) of $(C_6H_5)_3SnCl$ (560 mg, 1.45 mmol), a diethyl ether/benzene (1:2) solution (100 cm^3) of 4-phenylimidazole (**L′**) (488 mg, 3.4 mmol) was added under N_2 stream. The mixture was heated at 40°C and stirred for 1 day. It was then allowed to cool and evaporated under reduced pressure. The colorless residue was crystallized twice from diethyl ether to yield the analytical sample **2**. Compound **16** was obtained similarly.

Table 7
Crystal data: data collection and refinement of the structure for {bis(4-phenylimidazole)}trimethyl-tin(IV) chloride

Formula	$C_{21}H_{25}N_4ClSn$
Formula weight	487.598
Space group	$C2/c$
a (Å)	19.474(1)
b (Å)	14.461(1)
c (Å)	15.989(1)
β (deg)	98.53(1)
V_c (Å^3)	4508.3(6)
Z	8
D_c (g cm^{-3})	1.437
μ(Mo K α) (cm^{-1})	104.35
F(000)	1968
Radiation (monochromated)	Cu K α (λ = 1.5406 Å)
Temperature of data collection (K)	293
Scan mode	$\omega/2\theta$
Scan width (deg)	$\Delta\omega = A + B * \tan(\theta)$, A = 1.365°, B = 0.32°
Scan speed max. (deg min^{-1})	32
Background/scan ratio	0.5
Data collection range (deg)	$5 \leq 2\theta \leq 124$
Standards (measured every 97 reflections)	0 − 2 3, − 1 − 3 2, 3 1 2
No. of unique reflections measured	3703
No. of data with $I \geq 3\sigma(I)$	2578
Refinement	Full-matrix least-squares on F
No. of parameters refined	244
R [a]	0.051
R_w [b]	0.058
S [c] (Goodness of fit)	1.21

[a] $R = (\Sigma \| F_o | k | F_c \|)/\Sigma | F_o |$.
[b] $R_w = [\Sigma w(| F_o | - k | F_c |)^2/\Sigma w | F_o |^2]^{1/2}$.
[c] $S = [\Sigma w(| F_o | - k | F_c |)^2/(N_{obs} - N_{par})]^{1/2}$.

3.2.3. [Bis(4-phenylimidazole)dimethyldi-iodotin(IV))] (5)

A dry THF solution of compound **3** (508 mg, 1.0 mmol) was introduced into a 250 cm^3 round-bottomed flask fitted with a condenser. Sodium iodide (600 mg, 4.0 mmol) was then added. The mixture was heated at reflux, under N_2 stream, with stirring for 1 day. It was then allowed to cool and was filtered off. The solvent was removed with a rotary evaporator and the residue was extracted with CH_2Cl_2(3×15 cm^3); the organic layer was dried on Na_2SO_4. It was then filtered and concentrated under reduced pressure. Et_2O (30 cm^3) was then added; the solution was left in a freezer for 1 day. A yellow precipitate was formed which was filtered off, washed with Et_2O and crystallized twice from CH_2Cl_2/Et_2O (1 : 2) to yield the analytical sample **5**. Compounds **8**, **12**, **14**, and **19** were obtained similarly.

3.2.4. [Bis(4-phenylimidazole)dibuthyldibromotin(IV)] (10)

Bu_2SnBr_2 (166 mg, 0.4 mmol) was added at room temperature to a stirred dichloromethane solution (100 cm^3) of the ligand **L′** (290 mg, 2.0 mmol). After 12 h, the solvent was removed with a rotary evaporator and the residue was crystallized twice from diethyl ether to yield the analytical sample **10**.

3.2.5. [Tris(4-phenylimidazole)(phenyltrichlorotin(IV)) · H_2O] (17)

$PhSnCl_3$ (500 mg, 1.8 mmol) was added at room temperature to a stirred saturated diethyl ether solution (110 cm^3) of the ligand **L′** (145 mg, 1.0 mmol). A colorless precipitate was formed immediately. After 5 min, the suspension was centrifuged, and the residue washed with diethyl ether to yield the analytical sample **17**.

3.2.6. [Tris(4-phenylimidazole)bis(dimethyltin(IV)diperchlorate)] (20)

An ethanol solution (100 cm^3) of compound **3** (330 mg, 0.6 mmol) was introduced into a 250 cm^3 round-bottomed flask fitted with a condenser. Sodium perchlorate (365 mg, 2.6 mmol) was then added. The mixture was heated at reflux, under N_2 stream, with stirring for 1 day. It was then allowed to cool and was filtered off. The solvent was removed with a rotary evaporator and the residue was extracted with CH_2Cl_2 (3×15 cm^3); the organic layer was dried on Na_2SO_4. It was then

Table 8
Atomic coordinates and isotropic equivalent thermal parameters (with e.s.d.s in parentheses) for {bis(4-phenylimidazole)}trimethyl-tin(IV) chloride

Atom	*x*	*y*	*z*	U_{eq} [a] (Å^2)
Sn(1)	0.18991(2)	0.06099(3)	0.27661(3)	0.0463(2)
Cl(1)	0.16914(8)	0.2693(1)	−0.1238(1)	0.0471(5)
N(1a)	0.1273(3)	0.1013(4)	0.1446(4)	0.051(2)
C(2a)	0.1559(3)	0.1493(5)	0.0898(4)	0.054(2)
N(3a)	0.1103(3)	0.1724(4)	0.0225(3)	0.050(2)
C(4a)	0.0463(3)	0.1359(5)	0.0340(4)	0.044(2)
C(5a)	0.0573(3)	0.0919(5)	0.1089(5)	0.051(2)
C(6a)	−0.0165(3)	0.1517(4)	−0.0274(4)	0.045(2)
C(7a)	−0.0812(4)	0.1233(7)	−0.0078(6)	0.071(4)
C(8a)	−0.1412(4)	0.1398(7)	−0.0649(7)	0.081(4)
C(9a)	−0.1366(5)	0.1844(7)	−0.1380(6)	0.077(4)
C(10a)	−0.0751(4)	0.2143(6)	−0.1584(6)	0.071(3)
C(11a)	−0.0144(4)	0.1974(6)	−0.1033(5)	0.058(3)
N(1b)	0.2595(3)	0.0246(5)	0.4053(4)	0.057(2)
C(2b)	0.2638(4)	−0.0561(5)	0.4421(4)	0.051(2)
N(3b)	0.3197(3)	−0.0604(4)	0.5025(3)	0.049(2)
C(4b)	0.3526(4)	0.0225(5)	0.5057(4)	0.049(2)
C(5b)	0.3153(4)	0.0746(5)	0.4456(5)	0.059(3)
C(6b)	0.4182(4)	0.0405(5)	0.5605(4)	0.049(3)
C(7b)	0.4412(5)	0.1302(6)	0.5735(6)	0.077(3)
C(8b)	0.5041(5)	0.1482(8)	0.6245(7)	0.092(4)
C(9b)	0.5452(5)	0.0772(8)	0.6602(6)	0.084(4)
C(10b)	0.5228(4)	−0.0099(8)	0.6477(6)	0.076(3)
C(11b)	0.4599(4)	−0.0296(6)	0.5983(6)	0.068(3)
C(12)	0.2715(4)	0.0090(6)	0.2149(5)	0.067(3)
C(13)	0.1089(4)	−0.0261(6)	0.3050(5)	0.061(3)
C(14)	0.1852(5)	0.2001(6)	0.3132(7)	0.079(4)

[a] U_{eq} is defined as the mean of the principal axes of the thermal ellipsoid.

filtered and concentrated under reduced pressure. Et_2O (30 cm^3) was then added. A colorless precipitate was formed which was filtered off, washed with diethyl ether, and shown to be compound **20**.

3.3. X-ray structure determination of [Bis(4-phenylimidazole)trimethyltin(IV)]chloro (1)

A summary of the experimental conditions is reported in Table 7. Atomic coordinates and isotropic equivalent thermal parameters are given in Table 8. Crystals of compound **1** were grown from a dichloromethane/diethyl ether solution by slow evaporation. A colorless crystal of approximate dimension $0.38 \times 0.5 \times 0.31$ mm^3 was mounted on a Rigaku AFC5 automatic four-circle rotating diffractometer (45 kV, 100 mA). The crystal system was found to be monoclinic, and accurate cell parameters were obtained by least-squares refinement of 40 reflections with $40° \leq 2\theta \leq 80°$; the space group was found to be $C2/c$.

A total of 3910 reflections were collected with $0 \leq h \leq 22$, $0 \leq k \leq 17$ and $-18 \leq l \leq 18$; no decay was observed during the data collection. The ψ-scan of three different reflections (−2 4 3, 0 2 3, 0 2 2) gave a minimum and maximum transmission factor equal to 0.3 and 1.0; the data were then corrected for the absorption by using a semi-empirical method [39].

The structure was solved by direct methods using the SIR92 program [40], all the non-hydrogen atoms in the asymmetric unit were found at this level.

A first isotropic refinement of all non-hydrogen atoms was performed using the CRYSTALS package [41], giving $R = 0.123$, and a successive anisotropic refinement of the same atoms lowered the value to $R = 0.060$. At this stage we were able to locate the hydrogens on the imidazoles by means of a Fourier difference map; all the other hydrogens were imposed by the model with $d = 1.06$ Å. The structure was then refined, with the hydrogens refined as riding (U_{iso} fixed at 20% greater than the bonded atoms), giving $R = 0.055$. A final refinement was performed after optimization of the weighting scheme [42–44] using $w^{-1} = P(F_c/F_c^{Max}) \times \{1 - (|F_0 - F_c|/[6 \times |F_0 - F_c|_{est}])^2\}^2$, where $P(F_c/F_c^{Max})$ is a third order optimized truncated Cheybishev polynomial with coefficients $a_1 = 7.56$, $a_2 = -2.18$, $a_3 = 5.84$, and $|F_0 - F_c|_{est}$ is estimated by using the polynomial to fit $|F_0 - F_c|$ against F_c.

The R factor was equal to 0.051 at the end of the last refinement cycle, with a maximum r.m.s. shift equal to 0.01. A difference Fourier gave minimum and maximum peaks equal to −1.41 and 0.31 e Å^3 near the Sn atom. All refinements were carried out taking into account the anomalous scattering contributions but without refining the extinction parameter.

The scattering factors and anomalous contributions were taken from the *International Tables for Crystallography* [45]. All calculations were carried out on a personal computer; the program PARST [46] was used for some geometrical calculations.

4. Supplementary material available

Tables of anisotropic thermal parameters for non-hydrogen atoms, tables of the least-squares planes, tables of hydrogen atom parameters, as well as tables of structure factors have been deposited at the Cambridge Crystallographic Data Centre.

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