Pergamon

0277-5387(95)00384-3

Polyhedron Vol. 15, No. 8, pp. 1263–1276, 1996

0277-5387/96 $15.00+0.00

TIN(IV) AND ORGANOTIN(IV) COMPLEXES CONTAINING MONO OR BIDENTATE *N*-DONOR LIGANDS—I. 1-BENZYLIMIDAZOLE DERIVATIVES

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(*Received* 16 *May* 1995; *accepted* 16 *August* 1995)

Abstract—The interaction between 1-benzylimidazole, L, and several tin(IV) and organotin(IV) acceptors in diethyl ether or THF, gave 1:1 $[(L)R_3SnCl]$ (R = Me or Ph), 2:1 $[(L)_2R_nSnX_{4-n}]$ (R = Me, $n = 2$, X = Cl or Br; R = Et, Bu or Ph, $n = 2$, X = Cl, Br or I; R = cy, $n = 2$, X = Br or I; R = Me, Ph or Bu, $n = 0$ or 1, X = Cl; R = Me, $n = 0$ or 1, X = I; $n = 0$, X = Br), $[(L)_2Ph_2SnBrCl]$ and 4:1 $[(L)_4(CH_3)_2Sn]I_2$, adducts which are air- and thermally stable solids. The compounds have been characterized in the solid state and in solution by analyses, spectral (IR and ^1H, ^{13}C and ^{119}Sn NMR) data and conductivity measurements. The molecular weight determinations and the NMR data indicate that the triorganotin complexes generally dissociate in chloroform and in acetone solution, whereas only a slight dissociation of the di-, tri- and tetrahalidetin(IV) adducts in $CHCl_3$ is found: these $[(L)_2R_nSnX_{4-n}]$ complexes most likely retain the six-coordinate configuration. They are not fluxional when $n = 0$ or 1. The ^{119}Sn NMR chemical shift is a function of the number and type of substituents directly linked to the tin atom. In the diorganotin derivatives, the coupling constants $^2J_{^{119}Sn-^1H}$ and $^1J_{^{119}Sn-^{13}C}$ were used to establish the stereochemistry of the tin atom by applying the Lockhart and Holecek equations, which allow the magnitude of the C—Sn—C bond angles to be derived.

Tin(IV) and organotin(IV) compounds, a deceptively simple area of inorganic and metal–organic chemistry, have been receiving increasing attention in recent years, not only because of their intrinsic interest, but also owing to the importance of tin-based anti-tumour drugs; indeed, several books[1] and review articles both on the tin(IV) complexes, and their industrial[2] and pharmacological[3] applications have recently appeared. On the other hand, the chemistry of R_nSnX_{4-n} derivatives of azoles is well known,[4] but to date a systematic study on tin(IV) and organotin(IV) complexes of 1-alkyl- and 1-aryl-imidazoles, which occupy a very important position amongst heterocyclic rings for their relevance to the chemistry of natural products,[5] has not been carried out.

Here we report the synthesis and spectroscopic characterization of several new adducts between R_nSnX_{4-n} (R = Me, Et, Bu, Ph or cy, $n = 0$, 1, 2 or 3, X = Cl, Br or I) acceptors and the 1-benzylimidazole donor. The compounds obtained are

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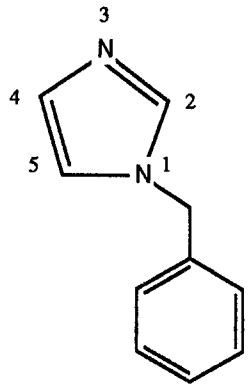


Fig. 1. 1-Benzylimidazole (L).

compared with some related derivatives of other azoles.

EXPERIMENTAL

The tin(IV) and organotin(IV) halides were purchased from Alfa (Karlsruhe) and Aldrich (Milwaukee) and used as received. The ligand 1-benzylimidazole was obtained from Aldrich and was used without further purification.

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. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ^{1}H, 75 MHz for ^{13}C and 111.9 MHz for ^{119}Sn). 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. The molecular weight determinations were performed by the Pascher Mikroanalytisches Laboratorium, Remagen, Germany.

Synthesis of the complexes

[*Bis*(1 - *benzylimidazole*)*dimethyldichlorotin*(IV)]. To a stirred diethyl ether solution (25 cm^3) of $(CH_3)_2SnCl_2$ (440 mg, 2.0 mmol) at room temperature, a diethyl ether solution (25 cm^3) of 1-benzylimidazole, L, (633 mg, 4.0 mmol) was added. A colourless precipitate was formed immediately, and was filtered off, washed with diethyl ether and shown to be compound **3**. Adducts **1**, **2**, **4**, **6**, **7**, **9**, **10**, **12**, **16**, **18–20** and **22** were obtained similarly.

[*Bis*(1 - *benzylimidazole*)*diethyldiiodotin*(IV)]. Compound **6** (1.0 mmol) and sodium iodide (5.0 mmol) were introduced into a 250-cm^3 round-bottomed flask fitted with a condenser. The apparatus was flame-dried, and after cooling, dry THF (150 cm^3) was added. The mixture was heated at reflux, under a N_2 stream, with stirring for 3–5 days. It was then allowed to cool and filtered off. The solvent was removed with a rotary evaporator and the residue was extracted with CH_2Cl_2 (3×15 cm^3); after evaporating the extract to dryness, the solid residue was crystallized twice from CH_2Cl_2–Et_2O (1 : 2) to yield the analytical sample **8**. Compounds **5**, **11**, **13**, **14**, **15**, **17**, **21** and **24** were obtained similarly.

[*Bis*(1 - *benzylimidazole*)*tetrabromotin*(IV) · 1/2 *dichloromethane*]. To a stirred diethyl ether solution of the ligand L (633 mg, 4.0 mmol) a 1 M dichloromethane solution of $SnBr_4$ (2.0 cm^3, 2.0 mmol) was added. A colourless precipitate was formed, which was filtered off after 1 day and washed with Et_2O, and shown to be compound **23**.

RESULTS AND DISCUSSION

The reaction between 1-benzylimidazole L (Fig. 1) and various R_nSnX_{4-n} (R = Me, X = Cl or Br, $n = 0$, 1, 2 or 3; R = Et or Bu, $n = 2$, X = Cl or Br; R = Ph, $n = 2$ or 3, X = Cl; R = cy, X = Br, $n = 2$) was carried out in diethyl ether solution from which the colourless complexes **1–4**, **6**, **7**, **9**, **10**, **12**, **16**, **18–20**, **22** and **23** (Table 1) were isolated as

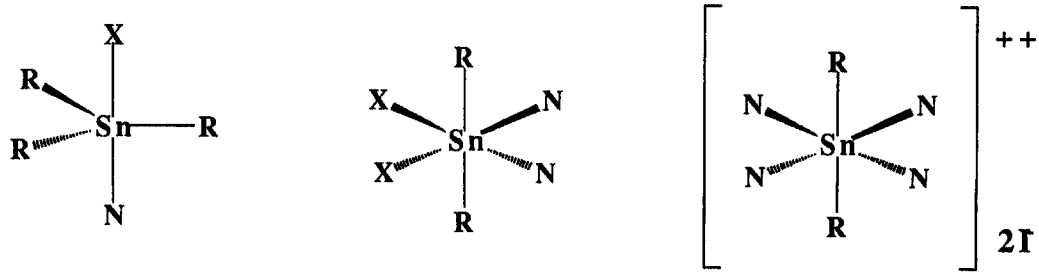


Fig. 2. 1 : 1, 2 : 1 and 4 : 1 adducts obtained from interaction between 1-benzylimidazole and R_nSnX_{4-n}.

an insoluble, or sparingly soluble, precipitate in accordance with eq. (1).

$$x(L) + R_nSnX_{4-n} \cdot zH_2O \xrightarrow{Et_2O} [(L)_x(R_nSnX_{4-n})] \cdot zH_2O \quad (1)$$

2 : 1 Adducts (Fig. 2) were always obtained with di-, tri- and tetrahalidetin(IV) compounds when the reaction was carried out in a strong excess of the *N*-donor ligand, whereas 1 : 1 complexes were found when triphenyl- or trimethyltin(IV) chloride was employed as acceptor, in agreement with the lower acidity of these organotin(IV) species.

Compounds **6**, **9**, **12** and **16** were converted into the yellow diiodide complexes **8**, **11**, **15** and **17**, respectively, and, analogously, compound **12** into the dibromide **14**, on treatment with a strong excess of sodium halide (*ca* 1 : 5 molar ratio) in tetrahydrofuran suspension [eq. (2)].[6]

$$[L_2R_2SnCl_2] + 2NaX \xrightarrow{THF} [L_2R_2SnX_2] + 2NaCl \quad (2)$$

This conversion proceeded with good yields when sodium iodide was employed as halide source, whereas an incomplete substitution was observed when the reaction between sodium bromide and the derivative **12**, in a 2 : 1 molar ratio, was refluxed for 2 days, the derivative **13** [$L_2Ph_2SnBrCl$] being formed in this case.

The reaction between $[L_2(CH_3)_2SnCl_2]$ and NaI, carried out in 1 : 2 stoichiometry, resulted in the unexpected formation of $[L_4(CH_3)_2Sn]I_2$ (**5**). The weight of material isolated (98% yield of **5**) suggested an almost quantitative disproportionation:

$$2L_2(CH_3)_2SnCl_2 + 4NaI \longrightarrow [L_4(CH_3)_2Sn]I_2 + (CH_3)_2SnI_2 + 4NaCl \quad (3)$$

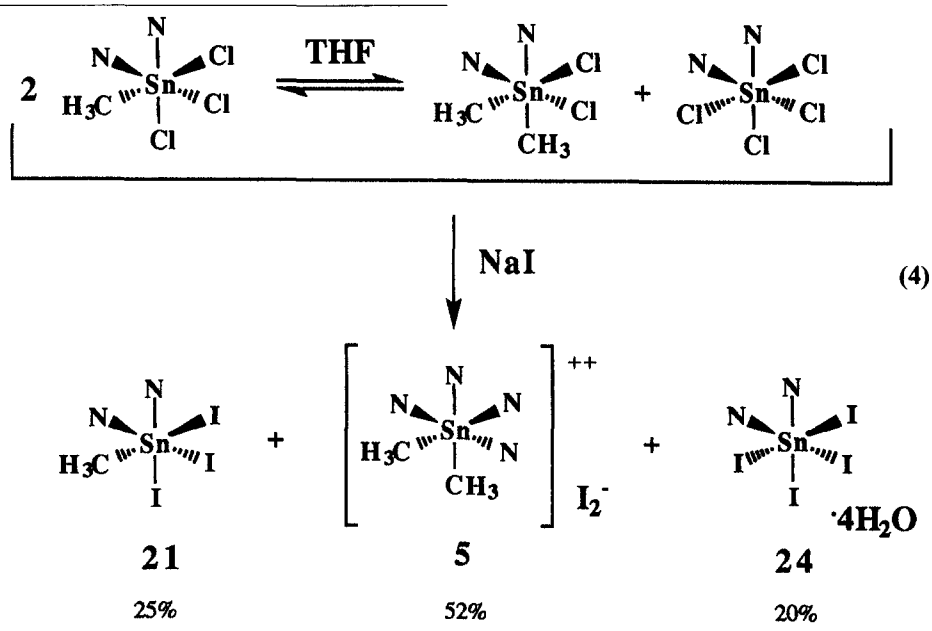
The formation of this kind of complex gives further support to the possibility of the existence of the $Sn(CH_3)_2^{2+}$ cation, not only in solution,[7] but also in the solid state as previously described by Martinez *et al.*[8]

When $[L_2(CH_3)SnCl_3]$ reacted with NaI in THF, the three different complexes **5**, **21** and **24**, in approximately 2 : 1 : 1 molar ratio, were obtained from the filtered suspension. This was most likely due to instability in solution of the starting complex, which tended to disproportionate as indicated in eq. (4).

All the compounds were identified through analytical (Table 1), IR (Table 2) and, for the sufficiently soluble compounds, NMR (Tables 3–5) data. With the exception of the diphenyltin complexes sparingly soluble in most of the common organic solvents, all the mono-, di- and triorganotin(IV) derivatives were generally soluble in chloroform, acetone, acetonitrile and dimethylsulphoxide, and insoluble in water and alcohol.

The stability, both in solution and in the solid state, of the compounds decreased with increasing degree of alkylation, whereas an opposite trend was observed for the solubility.

The electrical conductivities were measured in acetone solution for all the compounds listed in



(4)

Table 1. Physical, analytical and conductivity data of derivatives **1–24**

Compound and formula[a]	Compound no.	Yield %	M.p. (°C)	Elemental analysis (%)[b] C	H	N	Conductivities[c] Solvent	Conc.	Λ
(L)$(CH_3)_3SnCl$	**1**	60	56–59	44.0	5.5	8.2	Acetone	1.1	4.9
$C_{13}H_{19}ClN_2Sn$				(43.7)	(5.4)	(7.8)			
(L)$(C_6H_5)_3SnCl$	**2**	39	116–118	61.4	4.8	4.8	Acetone	1.1	25.8
$C_{28}H_{25}ClN_2Sn$				(61.9)	(4.6)	(5.1)	CH_2Cl_2	1.1	1.8
$(L)_2(CH_3)_2SnCl_2$	**3**	98	144–146	49.2	5.1	10.5	Acetone	0.9	29.0
$C_{22}H_{26}Cl_2N_4Sn$				(49.3)	(4.9)	(10.5)	CH_2Cl_2	1.1	1.0
							DMSO	0.9	37.4
$(L)_2(CH_3)_2SnBr_2$	**4**	83	142–143	42.3	4.4	9.0	Acetone	1.0	34.5
$C_{22}H_{26}Br_2N_4Sn$				(42.3)	(4.2)	(9.0)			
$[(L)_4(CH_3)_2Sn]I_2$	**5**	98	181–183	48.5	4.6	10.6	Acetone	0.8	140.5
$C_{42}H_{46}I_2N_8Sn$				(48.7)	(4.5)	(10.8)	CH_2Cl_2	0.7	4.5
$(L)_2(C_2H_5)_2SnCl_2$	**6**	88	123–125	50.9	5.6	9.7	Acetone	1.2	18.0
$C_{24}H_{30}Cl_2N_4Sn$				(51.1)	(5.4)	(9.9)			
$(L)_2(C_2H_5)_2SnBr_2$	**7**	96	140 (dec.)	44.0	4.8	8.2	Acetone	1.0	29.9
$C_{24}H_{30}Br_2N_4Sn$				(44.1)	(4.6)	(8.6)	CH_2Cl_2	0.8	0.5
$(L)_2(C_2H_5)_2SnI_2$	**8**	96	154–156	38.8	4.2	7.4	Acetone	1.1	87.2
$C_{24}H_{30}Br_2N_4Sn$				(38.6)	(4.1)	(7.5)	CH_2Cl_2	0.6	4.0
$(L)_2(n\text{-}C_4H_9)_2SnCl_2$	**9**	95	120–121	54.2	6.5	8.8	Acetone	1.0	20.1
$C_{28}H_{38}Cl_2N_4Sn$				(54.2)	(6.2)	(9.0)			
$(L)_2(n\text{-}C_4H_9)_2SnBr_2$	**10**	88	133–135	47.4	5.7	7.7	Acetone	0.9	38.0
$C_{28}H_{38}Br_2N_4Sn$				(47.4)	(5.4)	(7.9)			
$(L)_2(n\text{-}C_4H_9)_2SnI_2$	**11**	94	133–134	42.2	4.9	6.9	Acetone	0.9	93.6
$C_{28}H_{38}I_2N_4Sn$				(41.9)	(4.8)	(7.0)	DMSO	0.8	38.8
$(L)_2(C_6H_5)_2SnCl_2 \cdot H_2O$	**12**	91	192–194	56.5	4.9	8.3	Acetone	0.7	51.3
$C_{32}H_{32}Cl_2N_4OSn$				(56.7)	(4.8)	(8.3)			

$(L)_2(C_6H_5)_2SnBrCl$	**13**	93	189–190	54.0	4.4	7.9	Acetone	0.6	43.8
$C_{32}H_{30}BrClN_4Sn$				(54.5)	(4.3)	(8.0)			
$(L)_2(C_6H_5)_2SnBr_2$	**14**	90	193–196	48.9	4.1	7.2	Acetone	0.5	50.9
$C_{32}H_{30}Br_2N_4Sn$				(49.0)	(4.4)	(7.1)			
$(L)_2(C_6H_5)_2SnI_2$	**15**	92	182–184	45.8	3.8	6.8	Acetone	0.5	164.0
$C_{32}H_{30}I_2N_4Sn$				(45.6)	(3.6)	(6.6)			
$(L)_2(cyclo\text{-}C_6H_{11})_2SnBr_2$	**16**	89	134–136	50.4	5.9	7.0	Acetone	0.8	29.6
$C_{32}H_{42}Br_2N_4Sn$				(50.5)	(5.6)	(7.4)	DMSO	0.9	39.0
$(L)_2(cyclo\text{-}C_6H_{11})_2SnI_2$	**17**	90	139–142	45.1	5.2	6.4	Acetone	0.5	91.5
$C_{32}H_{42}I_2N_4Sn$				(44.9)	(4.9)	(6.6)			
$(L)_2(CH_3)SnCl_3$	**18**	54	170 (dec.)	45.6	4.0	9.9	Acetone	1.1	26.7
$C_{21}H_{23}Cl_3N_4Sn$				(45.3)	(4.2)	(10.1)			
$(L)_2(n\text{-}C_4H_9)SnCl_3$	**19**	99	134–137	48.2	5.2	9.0	Acetone	1.0	20.4
$C_{24}H_{29}Cl_3N_4Sn$				(48.2)	(4.9)	(9.4)	CH_2Cl_2	1.0	1.8
$(L)_2(C_6H_5)SnCl_3$	**20**	78	164–167	50.4	4.1	9.0	Acetone	1.0	22.1
$C_{26}H_{25}Cl_3N_4Sn$				(50.0)	(4.3)	(8.7)			
$(L)_2(CH_3)SnI_3$	**21**	25	130 (dec.)	30.6	3.0	6.9	Acetone	0.3	96.0
$C_{21}H_{23}I_3N_4Sn$				(30.4)	(2.8)	(6.7)			
$(L)_2SnCl_4 \cdot 1/3[C_4H_{10}O]$	**22**	82	281–284	42.4	3.9	9.2	Acetone	0.7	36.3
$C_{21.3}H_{23.3}Cl_4N_4O_{0.3}Sn$				(42.6)	(3.9)	(9.3)	CH_2Cl_2	0.7	3.0
$(L)_2SnBr_4 \cdot 1/2[CH_2Cl_2]$	**23**	98	241–243	30.8	2.8	6.8	Acetone	0.6	82.5
$C_{20.5}H_{21}Br_4ClN_4Sn$				(30.9)	(2.7)	(7.0)			
$(L)_2SnI_4 \cdot 4[H_2O]$	**24**	20	109–111	23.8	2.8	5.1	Acetone	0.4	210.0
$C_{20}H_{28}I_4N_4O_4Sn$				(23.7)	(2.8)	(5.5)			

[a] L = 1-benzylimidazole.

[b] Calculated values in parentheses.

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

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

Compound	>3000 cm^{-1}	1600–1500 cm^{-1}	<600 cm^{-1}	ν(Sn—C)	ν(Sn—X)	δ(C—Sn—C)+δ(Cl—Sn—Cl)
L	3137w, 3102w, 3085w 3065w, 3026m	1602m, 1584m, 1500sh	573m, 465m, 349m 316m, 246w, 203m			
1	3115m, 3100m, 3066w 3031w	1606m, 1520s, 1497m	573m, 467m, 372m 321m, 277w, 205m	543s, 516w	226s br	170s, 158m
2	3125w, 3100w	1605w, 1575w, 1527s 1511m, 1496m	571w, 458m, 446m 344w, 321w	277s, 229m	243m	206m, 199m, 142m
3	3159w, 3139m, 3088w	1610w, 1529m, 1512m 1497m	573w, 456m, 353w 325w, 279sh, 210m	566s	244s br	173s, 149m, 140m
4	3152w, 3122w	1592m, 1526m, 1514m 1495m	578m, 476m, 460m 348m, 323m, 279s	565s	214s	160s, 138s, 100m
5	3149w, 3125w, 3082m	1575w, 1531m, 1518m	570m, 474w, 469w 373w, 283w, 221w	557s		171s, 151m
6	3147w, 3122w, 3104w	1595m, 1518m, 1501m	572m, 468m, 382m 313m, 291m, 280m	539s	225s	174m, 159m, 147m
7	3140w, 3127w, 3087w	1603w, 1575w, 1530m 1513m, 1494m	574w, 480br, 461m 350m, 293m, 280m	536s	203s	159s, 141s, 122s
8	3119w, 3080w	1600w, 1575w, 1528m 1511m, 1495m	575m, 461m, 348w 290m, 216w	529m	153m	186w, 135w, 114w
9	3152w, 3134w, 3114w 3080w	1605w, 1586w, 1576w 1539w, 1514m, 1497m	574m, 458m, 392m 338m, 273m, 209m	616m	241s	181s, 146s br
10	3147w, 3128w, 3110w	1604w, 1523m, 1511m 1496m	574m, 459m, 390m 348m, 338m, 271m	616m	210s	186m, 155s, 142s br
11	3146w, 3120m, 3087w 3031w	1606w, 1587w, 1526m 1508m, 1495m	574w, 460m, 393w 353w, 334w, 268w	616m	151m	211m, 181m
12[b]	3152w, 3132m, 3069m	1595w, 1574w, 1530m 1510m, 1495m	460m, 399w, 373w 307w	287m, 232m	253m br	219m, 200m, 180m 166m

13	3156w, 3132w, 3088w 3067w, 3049w, 3031w	1592w, 1572w, 1531m 1511m, 1496m	574w, 460m, 338w	289m, 237m	218w, 200m	174m, 152m
14	3148w, 3108w, 3128w 3060w	1587w, 1574w, 1558w 1528m, 1510m	573w, 460m, 348w	288m, 239m	214m, 203br	170m, 152m
15	3152w, 3127m, 3107w 3088w, 3065w	1606w, 1588w, 1573m 1527m, 1510m, 1496m	573w, 459m, 338w	286m, 234m	151m	215m, 199m, 168m, 141m
16	3150w, 3123w, 3065w	1609w, 1588w, 1530m 1510m, 1497m	573w, 486w, 474w 459m, 352w, 328m	427m	254br	220m, 206m, 169m, 151m
17	3148w, 3109m, 3063w 3025w	1608w, 1527m, 1513m 1497m	568w, 482w, 455w 342w, 322w 250w br	425m		210s, 154m
18	3159w, 3128m, 3109w 3088w, 3065w	1608w, 1573w, 1528m 1510m, 1496m	475w, 456w, 364w 347w, 248w, 228w	530m	279s br	203w, 175s, 150s
19	3159w, 3130m, 3100w 3060sh	1596w, 1532m, 1519m 1495m	577w, 473m, 453m 399m, 380m, 356m 333m	615m, 601m	273s br	227m, 199m, 182m, 153m
20	3151w, 3124m, 3060sh	1601w, 1587w, 1576w 1535w, 1522m, 1495m	576m, 466m, 459m 365m, 346m, 337m	286s, 229m	270s, 262m	254m, 201m, 174m, 154m
21	3124m, 3084m	1602w, 1586w, 1569m 1535w, 1522m, 1495m	569w, 558m, 467m 373w, 360w, 280m	530w	171s br	
22	3149w, 3133m, 3080sh	1616br, 1541m, 1519m 1497m	569w, 454w, 369w 284w, 235w		322s, 305s	192m, 183m, 178m 158m, 159m
23	3127w, 3118w, 3080w	1602m, 1586m, 1570m 1537m, 1515m, 1495m	584w, 570w, 456m 364m, 336m, 269m		234s, 210s 221s	115m, 103m
24[b]	3127w, 3100w	1569m, 1537m	458w, 346w, 280w		151m	

[a] Nujol mull and/or $CHCl_3$ solution.
[b] $\nu(H_2O)$: 3300 cm^{-1} br.

Table 3. ^{1}H NMR data for the ligand and its tin(IV) derivatives **1–24**[a]

Compound	Solvent	δ values for azole substituents in position				$J(^{119}Sn–^1H)$	$J(^{117}Sn–^1H)$
		1	2	4+5	R—Sn		
L	$CDCl_3$	5.00s, 6.95–7.40m	7.47br	6.84pt, 7.12br			
	Acetone	5.39s, 7.38–7.56m	7.82s	7.10pt, 7.25pt			
1	$CDCl_3$	5.32s, 7.29–7.45m	7.96s	7.04br, 7.23br	0.64s	69	64
	Acetone	5.33s, 7.26–7.44m	7.99s	7.06br, 7.25br	0.64s	70	67
2	Acetone	5.40s, 7.30–7.35m 7.45–7.64m, 7.9–8.1m	7.72s	6.77br, 7.30br	7.30–7.35m 7.45–7.64m; 7.9–8.1m		
3	$CDCl_3$	5.17s, 7.15–7.42m	8.15s	6.92br, 7.46br	1.29s	100	97
	Acetone	5.41s, 7.26–7.50m	8.24s	7.24pt, 7.46pt	1.08s	108	103
4	$CDCl_3$	5.20s, 7.20–7.50m	8.40s	6.90br, 7.62br	1.53s	109	105
	Acetone	5.41s, 7.40m	8.44s	7.32pt, 7.52pt	1.39s	114	103
5	$CDCl_3$	5.18s, 7.20–7.45br	8.05s	6.92br, 7.35br	1.88s	101	97
	Acetone	5.39s, 7.33–7.40br	8.23s	7.23pt, 7.31pt	1.79s	108	104
6	Acetone	5.44s, 7.29–7.47br	8.32s	7.28br, 7.47br	1.05t, 1.58q	$99(^2J)$, $173(^3J)$	$94(^2J)$, $166(^3J)$
6(0.05 M)	$CDCl_3$	5.15s, 7.12–7.43m	8.30s	6.90br, 7.58br	1.15t, 1.78q	$97(^2J)$, $179(^3J)$	$93(^2J)$, $171(^3J)$
6(0.1 M)	$CDCl_3$	5.15s, 7.12–7.43m	8.30s	6.90br, 7.58br	1.12t, 1.78q	$99(^2J)$, $182(^3J)$	$95(^2J)$, $174(^3J)$
6(0.2 M)	$CDCl_3$	5.15s, 7.12–7.43m	8.30s	6.90br, 7.58br	1.09t, 1.75q	$102(^2J)$, $184(^3J)$	$98(^2J)$, $176(^3J)$
7	Acetone	5.45s, 7.30–7.50m	8.42s	7.31pt, 7.54pt	1.06t, 1.82q	$120(^2J)$, $184(^3J)$	$108(^2J)$, $174(^3J)$
7	$CDCl_3$	5.18s, 7.15–7.45m	8.43s	6.90s, 7.65s	1.10t, 1.96q	$112(^2J)$, $189(^3J)$	$108(^2J)$, $179(^3J)$
7+L (1:5)	$CDCl_3$	5.08s, 7.00–7.40m	7.62s	6.82s	1.03, 1.93q	$119(^2J)$, $191(^3J)$	$114(^2J)$, $183(^3J)$
8	Acetone	5.46s, 7.40m	8.49s	7.37pt, 7.49pt	1.12t, 1.13t, 2.08q, 2.10q	$90(^2J)$, $176(^3J)$	$86(^2J)$, $169(^3J)$
9	Acetone	5.43s, 7.30–7.42m	8.27s	7.28pt, 7.39pt	0.76t, 1.21ps, 1.40–1.70m		
9	$CDCl_3$	5.18s, 7.10–7.45m	8.23s	6.92s, 7.53s br	0.80t, 1.25ps, 1.52m, 1.80m		
9+L (1:4)	$CDCl_3$	5.10s, 7.10–7.45m	7.70s	6.90pt, 7.1–7.45	0.72t, 1.18ps, 1.40m, 1.70m		

10	Acetone	5.46s, 7.32–7.40m	8.48s	7.31pt, 7.61pt	0.72t, 1.14ps, 1.40m, 1.83m		
11	Acetone	5.46s, 7.35–7.39m	8.52s	7.36pt, 7.52pt	0.78t, 1.26ps, 1.46m, 2.10m		
12[b]	Acetone	5.41s, 7.20–7.60m	8.31s	7.20–7.60m	7.20–7.60m, 8.08–8.18m		
13	Acetone	5.42s, 7.18–7.50m	8.23s	7.18–7.50m	7.20–7.50m, 7.75–7.85m		
		5.62	7.89br				
14	Acetone	5.42s, 7.20–7.50m	8.24s	7.20–7.50m	7.20–7.50m, 7.70–7.80m		
15	Acetone	5.49s, 7.0–7.30br	8.55br	7.47pt, 7.39br	7.70br, 7.37–7.45br		
		5.63s, 7.37–7.45br					
	$CDCl_3$	5.18s, 7.20–7.50m	7.90br	6.90br, 7.2–7.5m	7.2–7.5m, 7.65–7.75m		
16	Acetone	5.40s, 7.22–7.50s	8.20s	7.27pt	1.00–1.40m, 1.60–2.40m		
17	Acetone	5.38s, 7.25–7.50m	8.10s	7.22br	1.10–2.05m, 2.10–2.40m		
18	Acetone	5.42s, 7.10–7.60m	8.60s	7.10–7.60m	1.17s	131	126
19	Acetone	5.43s, 7.35–7.43m	8.60s	7.23br, 7.50br	0.81t, 1.28s, 1.65m		
20	Acetone	5.42s, 7.11–7.35m	8.54s	7.27br	7.11–7.35m, 7.80m		
		5.44s	8.70s	7.29br			
21	Acetone	5.52s, 7.35–7.40m	8.70s	7.45pt, 7.48pt	1.83	93	88
22	Acetone	5.42s, 5.46s, 5.49s	8.70s	7.44pt, 7.47pt			
		5.58s, 7.36–7.40br	8.80pt	7.72pt, 8.34br			
23	Acetone	5.49s, 5.51s, 5.60s	8.82br	8.73pt, 7.83pt			
		5.67s, 7.30–7.60m	9.30br	8.93pt, 7.70br, 7.74br			
24[c]	Acetone	5.68s, 7.40–7.60m	0.18s	7.65pt, 7.75pt			

[a] δ in ppm, J in Hz; s = singlet, m = multiplet, br = broad, ps = pseudo-sextet; pt = pseudo-triplet; the imidazole signals are often pseudo-triplet because the *ortho* J_{H-H} is of the same order of magnitude as *meta* J_{H-H}.

[b] 3.05br (H_2O).

[c] 3.70br (H_2O).

Table 4. ^{13}C NMR data for the ligand and its tin(IV) and organotin(IV) derivatives (in $(CD_3)_2CO$)

Compound	CH_2	C(2)	C(4)	Aromatics + C(5)	R—Sn	$^1J(^{119}Sn—C)$	$^1J(^{117}Sn—C)$
L	51.2	138.7	120.5	128.7, 129.0, 130.0, 130.4, 139.1			
1	51.3	138.2	120.9	128.3, 128.4, 128.8, 129.6, 137.8	2.3, 2.4	525	500
2[a]	51.2	139.1	120.9	128.1, 128.7, 128.9, 129.5, 137.6	129.0, 129.9, 135.7, 137.0		
3	51.5	138.5	120.7	128.0, 128.5, 129.6, 128.9, 137.5	20.3	959	
4	51.7	139.0	120.8	128.1, 128.6, 129.0, 129.7, 137.3	28.0	1027	981
5	51.9	138.6	121.2	128.5, 129.0, 129.3, 130.1, 138.2	not observed		
5($CDCl_3$)	51.3	138.0	119.4	127.5, 128.5, 129.0, 135.0	32.3	1000	950
6[b]	51.5	138.9	120.7	128.4, 128.9, 129.6, 137.5	10.5, 33.0	966	924
7[c]	51.6	139.3	120.7	128.4, 128.7, 128.9, 129.6, 137.4	11.0, 37.6	940	910
8	51.6	139.2	120.8	128.5, 128.9, 129.6, 137.3	11.9, 38.7	1051	
9[d]	51.5	138.9	120.7	128.4, 128.5, 128.8, 129.6, 137.6	13.8, 26.7, 28.5, 38.7	882	840
10[e]	51.6	139.3	120.8	128.4, 128.7, 128.9, 129.6, 137.5	13.8, 26.3, 29.0, 44.7	914	872
11[f]	51.6	139.1	120.9	128.3, 128.5, 128.9, 129.6, 137.4	13.8, 25.9, 29.6, 45.1		
12	51.7	138.3	121.0	127.4, 128.2, 128.5, 128.9, 129.2	[i]		
				129.6, 136.6, 137.2			
16[g]	51.4	139.2	120.7	128.2, 128.8, 129.1, 129.6, 137.8	27.2, 29.5, 31.7, 55.0	725	698
18							
19[h]	52.1	139.6	120.3	127.5, 128.6, 129.1, 129.7, 136.7	14.0, 26.1, 28.9, 46.8	1205	1150
20	52.1	139.7	119.8	127.2, 128.0, 128.6, 129.2, 129.7	[i]		
			121.0	134.0, 136.8			
21	52.2	138.1	121.6	125.9, 128.8, 129.2, 129.7, 136.6	26.6br		
22	52.4br	139.4	120.8	126.7, 126.8, 128.6, 128.8, 129.0			
			120.9	129.3, 129.8, 136.4, 138.8			
23	52.2	136.0	118.6	125.8, 126.1, 126.4, 126.5, 128.8			
	52.5	136.4	120.2	129.0, 129.3, 129.4, 129.8, 129.9			
	53.4	137.8	120.5				
		138.8	121.2				
			122.8				

[a] $^2J(^{119}Sn—^{13}C)$: 57 Hz; $^3J(^{119}Sn—^{13}C)$: 70 Hz; $^4J(^{119}Sn—^{13}C)$: 14 Hz.
[b] $^2J(^{119}Sn—^{13}C)$: 54 Hz.
[c] $^2J(^{119}Sn—^{13}C)$: 54 Hz.
[d] $^3J(^{119}Sn—^{13}C)$: 150 Hz; $^3J(^{117}Sn—^{13}C)$: 143 Hz.
[e] $^3J(^{119}Sn—^{13}C)$: 166 Hz; $^3J(^{117}Sn—^{13}C)$: 159 Hz.
[f] $^3J(^{119}Sn—^{13}C)$: 154 Hz; $^3J(^{117}Sn—^{13}C)$: 148 Hz.
[g] $^2J(^{119}Sn—^{13}C)$: 14 Hz; $^3J(^{119}Sn—^{13}C)$: 129 Hz; $^3J(^{117}Sn—^{13}C)$: 122 Hz; $^4J(^{119}Sn—^{13}C)$: 33 Hz.
[h] $^3J(^{119}Sn—^{13}C)$: 230 Hz; $^3J(^{117}Sn—^{13}C)$: 218 Hz; $^2J(^{119}Sn—^{13}C)$: 15 Hz.
[i] The Ph—Sn signals are hidden under ligand absorptions

Table 5. ^{119}Sn NMR data (in $CDCl_3$)

Compound	δ(ppm) from $(CH_3)_4Sn^{IV}$
1	−14.51
2	−125.9
3	−273.6
4	−309.2
5	−335.4
6	−267.8
7	−254.5
8	−602.6
9	−264.1
11	−559.6
15	−732.5
18	−464.8
19	−463.8
20	−510.6, −531.9

which a typical 1 : 1 electrolyte such as tetra-n-butylammonium bromide has a specific conductivity of 137 ohm^{-1} cm^2 mol^{-1}. Some of them are non-electrolytes (**1**, **6**, **9**, **19** and **20**), others are electrolytes (**5**, **15** and **24**) and the remaining complexes are at least partly ionized. For the non-electrolytes an incomplete dissociation into the starting reagents is likely on the basis of the low values of molecular weight found in both chloroform and acetone solution; for example, in the former solvent the ratio *r* between the vaporimetric molecular weight (concentrations *ca* 1.0% w/w) and the formula weight for compounds **3**, **4**, **6**, **7**, **9** and **10** lies in the range 0.65–0.85, in reasonable agreement with eq. (5).

$$[L_2R_2SnX_2] \rightleftharpoons [LR_2SnX_2] + L \rightleftharpoons R_2SnX_2 + 2L \quad (5)$$

For the other tin(IV) and organotin(IV) complexes, the following different kinds of ionic dissociation are possible:

$$[L_2R_2SnX_2] + n\,\text{solvent} \rightleftharpoons [L_2R_2SnX(\text{solvent})_n]^+ + [X^-] \quad (6)$$

$$2[L_2R_2SnX_2] \rightleftharpoons [L_2R_2Sn]^{2+} + [R_2SnX_4]^{2-} \quad (7)$$

The latter type of dissociation is ruled out by the observation that the molecular weight found vaporimetrically in acetone is always smaller than the formula weight (*r* for compounds **8**, **11** and **23** lies in the range 0.55–0.80).

The value of molar conductivity in acetone and CH_2Cl_2 for **5** suggests a different behaviour of this complex in solution. In acetone, **5** behaves as a 1 : 1 electrolyte whereas the conductivity in CH_2Cl_2 is typical of a non-electrolyte. This is likely to be due to interchange that can take place between the ligands of the coordination sphere and the I^- ions.[9]

IR data

In Table 2, we report the most relevant IR data for the ligand and its tin(IV) and organotin(IV) complexes, **1**–**24**, in the range 4000–100 cm^{-1}. The spectra were recorded both in Nujol mulls and in chloroform solution.

By comparison with the data reported for other tin(IV) and organotin(IV) adducts containing *N*-donor ligands,[10] we suggest the following assignments for these complexes.

(*a*) *Ligand absorptions.* In the 3150–3000 cm^{-1} region, the ligands exhibit weak bands typical of C—H stretching due to a pseudoaromatic ring, and in the region 1600–1500 cm^{-1} some more intense absorption due to a ring breathing mode. These bands do not shift markedly upon coordination to tin, suggesting a weak influence of the complexation on the bands within the donor.

(*b*) Sn—C *Stretching frequencies.* Compound **1** shows a strong band at 543 cm^{-1} and an absorption of very low intensity at *ca* 516 cm^{-1} due to antisymmetric and symmetric Sn—C stretching vibrations, respectively. On this basis a local C_{3v} symmetry of the C_3—Sn skeleton with slight deviation from planarity is suggested.[11] The spectrum of the triphenyltin(IV) derivative **2** is also consistent with an essentially pyramidal arrangement of phenyl groups, the ν_{asym} and ν_{sym} Sn—C being observed at *ca* 277 and 229 cm^{-1}, respectively.[11]

The appearance of only a single band in the spectra of dimethyl- (**3**–**5**) diethyl- (**6**–**8**), di-n-butyltin (**9**–**11**) and dicyclohexyltin(IV) complexes (**16** and **17**) at *ca* 570, 540, 610 and 430 cm^{-1}, respectively, is taken to imply a *trans*-octahedral configuration of the two alkyl groups.[11,12]

On changing the halide groups linked to tin(IV) little shift of the ν(Sn—C) is observed. This absorption seems to be sensitive to the degree of alkylation: the ν(Sn—C) in the methyltin(IV) trichloride derivatives lies *ca* 35 cm^{-1} lower than that observed in the dimethyltin(IV) compounds.

In the diphenyltin(IV) dihalide complexes the ν_{asym} and ν_{sym} are observed as strong bands at *ca* 280 and 230 cm^{-1},[13] respectively. For a *trans*-R_2Sn structure, on the basis of symmetry arguments, the intensity of ν_{sym}(Sn—C) should be expected to be very low, and for this reason in our compounds, also on the basis of previous reports in literature[13] and of the presence of a single Sn—Cl stretching

band, we hypothesized a marked distortion from a regular *trans*-R_2 octahedral configuration.

(c) Sn—X *stretching frequencies*. The tin–chloride stretching frequencies in the mono- (**1**, **2**), di- (**3**, **6**, **9**, **12**) and tri-halidetin(IV) compounds (**18**–**20**) fall as strong broad bands at *ca* 230, 250 and 270 cm^{-1}. These bands are lowered by 90–120 cm^{-1} with respect to those observed in the spectra of the starting tin(IV) reagents[14] and are generally far too broad to obtain the hoped for ν_{asym} from ν_{sym}(Sn—Cl) stretches.

In the tetrachlorotin(IV) complex (**22**), we observed three strong bands and one of medium intensity at *ca* 322, 310, 305, and 295 cm^{-1} respectively. This trend is also reported for other [$SnCl_4$(ligand)$_2$] complexes for which a *cis* structure is suggested.[10]

The tin–bromide and iodide stretches, where detected, are shifted with respect to tin–chloride by *ca* 40–50 and 90–100 cm^{-1}, respectively, in accordance with trends previously observed.[10,15]

(d) *Skeletal bending modes*. In our complexes the assignments of all the skeletal bending modes is not straightforward: the δ(C—Sn—C), δ(Cl—Sn—Cl), ρ(Sn—C_3) and ρ($SnCl_3$) fall in the region 120–180 cm^{-1},[14] and are too close to resolve.

(e) Sn—N *stretching modes*. We noted some weak bands at *ca* 320–370 cm^{-1} which were absent in the spectrum of the free donor. They appeared, however, in most of the tin(IV) and organotin(IV) complexes. Previously, in analogous cases these absorptions were assigned to ν(Sn—N);[16] however, we think this assumption is not necessarily valid because these bands can be due to changes in the conformation of the donor upon coordination.

NMR data

The proton NMR data of compounds **1**–**24** are reported in Table 3. The choice of solvent was dictated by solubility, the order of preference being $CDCl_3$ and $(CD_3)_2CO$. The spectra reveal that the organic ligand does not undergo any alteration when the complexes are formed.

In $CDCl_3$, upon complexation, the signals of the donor are displaced to lower field: the shift, generally not negligible, is additional evidence of the existence of the complexes in solution and reflects changes in the electron density and in π-electron circulation about the heterocyclic ring. In fact, a σ-charge donation from the *N*-donor, L, to the metal centre removes electron density from the ligand and produces a deshielding which will attenuate at positions remote from the metal (H-5, N-CH_2 and aromatic protons).

The considerably larger coordination shifts of the adducts of 1-benzylimidazole with respect to those observed for the derivatives of pyrazole and bis(pyrazol-1-yl)alkanes[17] appear to support a stronger bonding interaction between this *N*-donor ligand and tin(IV) compounds. However, the spectra of our compounds also agree with a partial dissociation, into the starting reagents, of the type suggested above [eq. (5)] on the basis of molecular weight measurements: for example, the diorganotin(IV) adduct **6** shows strong dependence on the concentration of the solution, $^2J_{^{119}Sn-^1H}$ and $^3J_{^{119}Sn-^1H}$ being 97 and 179 Hz, 99 and 182 Hz, 102 and 184 Hz at concentrations of *ca* 0.05, 0.1 and 0.2 M, respectively. The coupling constants observed for compounds **3**, **4**, **5**, **6** and **9** are of the same order as those reported in the literature for six-coordinate diorganodihalobis(*N*-donor ligand) tin(IV) derivatives,[18] and are larger than those observed for the trimethyltin(IV) 1:1 adduct **1**, for which a bipyramidal trigonal configuration is likely.[11d] By applying the Lockhart equation,[18] which can to be used to establish the stereochemistry of the tin atom in dimethyl derivatives, we obtain C—Sn—C angles of *ca* 162.4, 179.8 and 164.3° for compounds **3**, **4** and **5**, respectively, which are indicative of a distorted *trans*-octahedral or skewed bipyramidal trapezoidal configuration.

In acetone solution the compounds exhibit a different spectral behaviour: the coordination shifts of the signals of 1-benzylimidazole are smaller with respect to those observed in $CDCl_3$. We also noted that this shift, negligible for the triorganotin(IV) adducts, of *ca* 0.1–0.2 ppm for the diorganotin, is larger for the tri- and tetrahalide compounds, in accordance with the decrease in stability of the adducts and a weaker bonding interaction between the donor and the acceptors, with increasing degree of alkylation of the metal centre.

In compounds **13**, **15**, **20**, **22**, and **23**, the existence of isomers is revealed by the presence of two or more CH_2 groups both in the ^1H and ^{13}C NMR spectra. It thus seems that isomers are present when the acceptor ability of tin is enhanced by electronegative or bulky substituents. The complexity of absorptions found in the spectra of **22** and **23** is also accounted for in terms of the presence of an equilibrium of the type shown in Fig. 3.

In the ^{13}C NMR spectra of the complexes (Table 4), which are generally consistent with the conclusions drawn from ^1H NMR results, the signals of L are shifted only very slightly from their position in the spectrum of the free donor ligand. However, the magnitude of $J_{^{119}Sn-^{13}C}$ and $J_{^{117}Sn-^{13}C}$ and the values of the chemical shift of the carbons bonded to tin(IV) are different from those reported for the starting organotin(IV) derivatives and are very

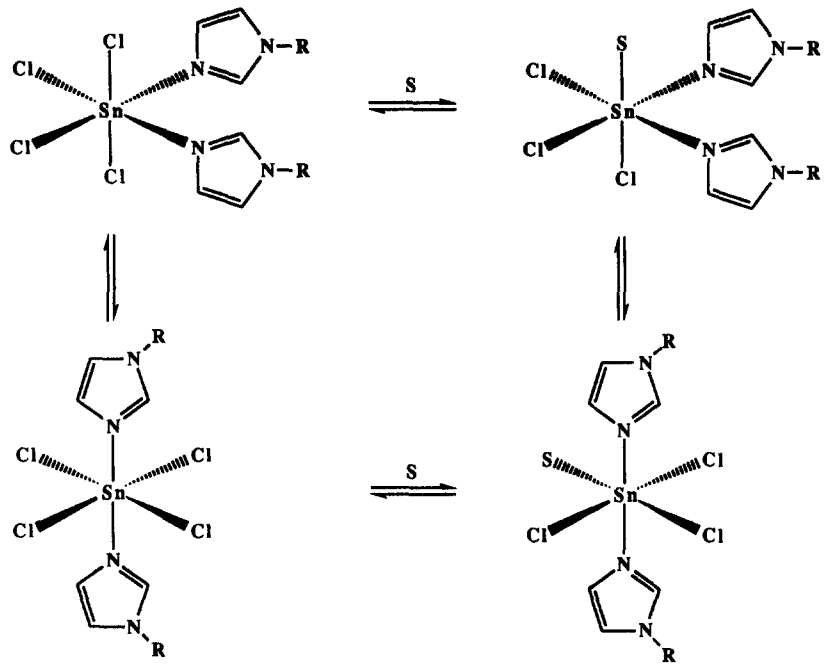


Fig. 3. Equilibrium suggested for the tetrachloridetin(IV) adduct in acetone solution.

similar to those indicated for hexacoordinate tin(IV) complexes.[19] This observation proves that the dissociation established through molecular weight determinations is only partial and that much of the complex is still present: in fact, when L is added to a $CDCl_3$ solution of compound **7** until a 1 : 5 molar ratio is achieved, in the ^1H and ^{13}C spectra the coupling constants from 112 and 189 Hz (^2J and $^3J_{^{119}Sn-^1H}$, respectively) and 940 Hz ($^1J_{^{119}Sn-^{13}C}$) rise to 119, 191 and 960 Hz, respectively.

For compounds **3**, **4**, **8** and **9**, the (C—Sn—C) angle, calculated on the basis of the Lockhart (dimethyltin(IV) derivatives)[19] and Holecek (di-n-butyltin(IV) derivatives) equations[20] by the magnitude of ($^1J_{^{119}Sn-^{13}C}$) is 160.4°, 166.8°, 163.0° and 166.0°, respectively.

The ^{119}Sn NMR spectra (Table 5), recorded only for some complexes owing to solubility problems, support our hypotheses: the triorganotin(IV) derivatives **1** and **2** exhibit a single absorption at *ca* −14.5 and −125.9 ppm, respectively, typical of a four- and five-coordinate central tin atom, respectively. These signals are shifted upfield with respect to those reported for the starting acceptor (Me_3SnCl: +164.2 ppm,[21] Ph_3SnCl: −44.7 ppm[22]). The ^{119}Sn chemical shift of the dialkyltin(IV) complexes, ranging from 264.1 to 732.5 ppm is typical of octahedral, pseudo-octahedral or skew-bipyramidal trapezoidal arrangements.[23] It has been noted[23] that the magnitude of the chemical shift ($\delta_{^{119}Sn}$) of complexes having the same coordination number depends primarily on the type of substituents on the metal atom, on their electronegativity and on the geometric distortion, which modifies the interbond angles at tin. In our compounds, the effect of ligand electronegativity is well illustrated by the change in chemical shift along the series $R_2SnX_2(L)_2$, as X changes from Cl to Br or I (compound **3**: −273.5 ppm; **4**: −309.1 ppm; **8**: −602.6 ppm) or R changes from Bu^n (compound **12**: −559.60 ppm; **18**: −463.7 ppm) to Ph (**15**: −735.5 ppm; **19**: −510.55 and −531.60 ppm).

CONCLUSION

The reactivity of 1-benzylimidazole towards tin(IV) and organotin(IV) acceptors depends on the electronic and steric features of the groups bonded to tin: the ligand/metal ratio can range from 1 : 1 in $[(L)R_3SnCl]$ (R = Me or Ph) to 4 : 1 in $[L_4(CH_3)_2Sn]I_2$ which is the first cationic $Sn(CH_3)_2^{2+}$ derivative containing four monodentate *N*-donor ligands.

The NMR data and molecular weight measurements indicate that the bonding interaction between L and R_nSnX_{4-n} generally increases with decreasing *n* and that the donor is coordinated to tin through the pyridine nitrogen.

1-Benzylimidazole (L) is a better ligand compared with monodentate pyrazoles or bidentate bis(pyrazol-1-yl)alkanes: this can also be deduced from the formation of adducts with triorganotin(IV) acceptors and from the fairly good stability of the

2:1 and 4:1 adducts both in solid state and in solution.

Combined analytical and spectral data (IR, far-IR, ^{1}H, ^{13}C and ^{119}Sn NMR) suggest a bipyramidal trigonal configuration for 1:1 adducts, whereas a distorted octahedral or pseudo-octahedral structure is likely for all the other derivatives.

Acknowledgements—Financial support from the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST) and the Consiglio Nazionale delle Ricerche (C.N.R.-Rome) is gratefully acknowledged.

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