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Organoelement derivatives of steroids: Synthesis and structural features of organo-silicon, -tin and -lead derivatives of cholesterol and desoxycholic acid

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Some organo-Main-Group-IV-element compounds of steroids of the type $R_3M(COL)$, $R_2Sn(COL)_2$ and $(R_3M)_2(HDCA)$ (where R = Me or Ph; M = Si, Sn and Pb; HCOL = cholest-5-en-3β-ol; H_3DCA = 3α,12α-dihydroxy-5β-cholan-24-oic acid), have been synthesized. The structures of these compounds have been investigated by vibrational, mass, NMR (^1H, ^{13}C, ^{29}Si, ^{119}Sn and ^{207}Pb) and ^{119}Sn Mössbauer spectroscopy. For $Me_3Sn(COL)$ both in solution and in the solid state an associated structure with distorted trigonal bipyramidal geometry around tin and three-coordinated oxygen atoms is postulated. Discrete tetrahedral geometries are assigned to $Ph_3M(COL)$ complexes and to $R_2Sn(COL)_2$ complexes in solution. The latter compounds probably have an associated distorted trigonal bipyramidal structure in the solid state. The complexes $(Ph_3M)_2(HDCA)$ also have tetrahedral geometries around the central atoms M in solution, but for $(Ph_3Sn)_2(HDCA)$ a polymeric structure with both tin atoms penta-coordinated in the solid state is proposed.

Keywords: Organotin, organosilicon, organolead, steroids, structures, anti-tumor agents

INTRODUCTION

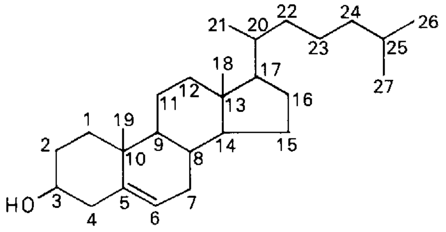
It has long been recognized that tin is present in mammalian tissue and it is considered to be a vital trace nutrient in the rat.[1] Injected organotin compounds have been shown to possess an affinity to tumors in rats whereas other elements of the same periodic group do not.[2] As such, organotin compounds have generated considerable interest, and are being studied as antitumor agents.[3–7] In fact, it was suggested that tin materials ingested by mammalians are changed in the thymus to anti-oncogenic tin steroids which then circulate either as a hormonal factor or are carried by T cells throughout the body.[8] Some organotin steroids have recently been patented[9] as antineoplastic agents and it has been hypothesized that, in tumor suppresion, the steroid head of such a compound enables the penetration of the phospholipid/protein membrane and subsequently an attack of the mitotic peripheral tumor cells. With our continued interest in the study of the interactions of organoelement moieties with biomolecules with a view to understanding the biochemical action of these compounds,[10,11] and considering the lack of basic knowledge of organotin and other organoelement compounds of steroids, we decided to study such compounds more deeply.

We report here the synthesis and structural characterization of organo-silicon, -tin and -lead compounds of cholesterol (cholest-5-en-3β-ol; HCOL) and desoxycholic acid (3α,12α-dihydroxy-5β-cholan-24-oic acid; H_3DCA).

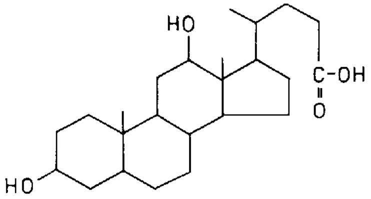
EXPERIMENTAL

All solvents and chemicals were dried and purified by standard methods before use. Organotin hydroxides or alkoxides were freshly prepared according to the literature.[12] Cholesterol (Aldrich) and desoxycholic acid (Fluka) were used as such. Organoelement compounds were prepared by one of the following three methods.

(a) Triphenyltin chloride (2.5×10^{-3} mol) was refluxed with HCOL (2.5×10^{-3} mol) in 50 cm^3 THF in the presence of Et_3N (3×10^{-3} mol) for



Cholest-5-en-3β-ol; cholesterol; HCOL



3α,12α-Dihydroxy-5β-cholan-24-oic acid; desoxycholic acid; H_3DCA

two days. Precipitated $[Et_3N]HCl$ was filtered and the solvent was taken off. The resulting product was dissolved in 10 cm^3 $CHCl_3$, 2 cm^3 pentane was added and the flask was left in a freezer overnight. The contents were filtered, the solvent was evaporated and the solid product was dried at 35°C/0.01 mm for 2 h.

(b) Dimethyltin dimethoxide (2.5×10^{-3} mol) in 50 cm^3 methanol was refluxed with HCOL (5×10^{-3} mol) for six days. The solvent was evaporated and the product was treated as above.

(c) Triphenyltin hydroxide (5.0×10^{-3} mol) was refluxed with H_3DCA (2.5×10^{-3} mol) in 50 cm^3 THF in the presence of 2,2-dimethoxypropane. Refluxing was stopped after 15 days and the flask was left in a freezer overnight. The contents were filtered. The solid product was washed with ether and dried.

Elemental analyses were performed on a Carlo Erba Strumentazione Elemental Analyzer 1106. Melting points were measured in glass capillaries and are uncorrected. Molecular weights were determined osmometrically in methanol or chloroform at 45°C. Raman spectra of powders or solutions were recorded in capillary tubes. IR spectra were recorded as nujol mulls, KBr wafers or in chloroform solution on a Perkin–Elmer 580B grating spectrophotometer.

All NMR spectra were recorded on a Bruker AM-300 spectrometer or as mentioned. 300 MHz ^1H NMR spectra were recorded as 5% w/v solutions in $CDCl_3$ with Me_4Si as external standard at 297 K. ^{13}C NMR spectra (standard Me_4Si) were recorded at 75.4 MHz (digital resolution 1.2 Hz) with FIDs collecting in 32 K datapoints using 21.000 Hz spectral width. Steroid spectra have been taken from literature and C-atoms have been numbered accordingly.[13] Assignments for compounds are based on proton noise decoupled and DEPT spectral measurements. ^{29}Si NMR spectra (DEPT, standard Me_4Si) were recorded at 59.62 MHz (digital resolution 1.79 Hz) using 29.500 Hz spectral width. ^{119}Sn NMR spectra (standard Me_4Sn) were measured at 111.9 MHz (digital resolution 6.7 Hz). ^1H gated decoupled FIDs were collected into 16 K or 8 K datapoints with 55.000 Hz spectral width and approximately 0.11 s acquisition time. ^{207}Pb NMR spectra (standard Me_4Pb) were recorded at 62.79 MHz. Mass spectra were recorded on a Finigan MAT 8230 system at 70 eV. Chemical ionization spectra were obtained using isobutane.

^{119}Sn Mössbauer spectra were measured at 10 K with constant acceleration and triangular waveform, using a Laben 8001 multichannel analyzer, a CTI-Cryogenics Mössbauer closed refrigerator system SC Cryodine Cryocooler[21] and a Lake Shore Cryotronics digital temperature controller DRC-80C. Data reductions were effected by computer programs fitting experimental lines to Lorentzian lineshapes.

RESULTS AND DISCUSSION

The new organoelement compounds listed in Table 1 were obtained by reaction of the appropriate organoelement chlorides [method (a); see the Experimental section], methoxides [method (b)] or Ph_3SnOH [method (c)] with HCOL or H_3DCA in moderate-to-good yields. The analytical data and physical characteristics are tabulated also in Table 1. The white solid products are hydrolyzable in nature and fairly soluble in common organic solvents.

The mass spectral data for some of the compounds are given in Table 2. From the absence of ions of greater mass than the parent molecular

Table 1 Analytical data for organoelement derivatives of steroids

Compound	Preparative method	Yield (%)	M.p. (°C)	Mol. wt found (calcd.)	Analyses (%) C found (calcd.)	H found (calcd.)
$Me_3Sn(COL)$, $C_{30}H_{54}OS_n$, **1**	(a)	80	119	276[a] 282[b] (548.7)	65.0 (65.61)	9.9 (9.84)
$Ph_3Sn(COL)$, $C_{45}H_{60}OSn$, **2**	(a)	55	180	355[a] 363[b] (734.7)	73.0 (73.50)	8.3 (8.16)
$Ph_3Si(COL)$, $C_{45}H_{60}OSi$, **3**	(a)	30	95	378[a] (644.0)	84.0 (83.85)	9.4 (9.31)
$Ph_3Pb(COL)$, $C_{45}H_{60}OPb$, **4**	(a)	43	136	431[a] (823.0)	65.4 (65.61)	7.6 (7.29)
$(Ph_3Sn)_2(HDCA)$, $C_{60}H_{68}O_4Sn_2$, **5**	(c)	68	67	555[a] 507[b] (1089.4)	65.2 (66.09)	5.9 (6.24)
$(Ph_3Si)_2(HDCA)$, $C_{60}H_{68}O_4Si_2$, **6**	(a)	79	72	302[a] 445[b] (908.0)	78.9 (79.29)	8.0 (7.48)
$Me_2Sn(COL)_2$, $C_{56}H_{96}O_2Sn$, **7**	(b)	56	c	337[b] (918.7)	72.7 (73.14)	10.8 (10.44)
$Ph_2Sn(COL)_2$, $C_{66}H_{100}O_2Sn$, **8**	(b)	29	123	421[a] (1042.7)	74.8 (75.95)	9.3 (9.59)

[a] Molecular weight determined in $CHCl_3$, [b] Molecular weight determined in MeOH, [c] Does not melt up to 220°C.

Table 2 Mass spectral data[a] for some of the organoelement derivatives of steroids

$Ph_3Sn(COL)$, **2**			$Ph_3Si(COL)$, **3**			$(Ph_3Si)_2(HDCA)$, **6**			$Ph_3Sn(H_2DCA)$, **9**[b]		
m/z	Fragment	(%)	*m/z*	Fragment	(%)	*m/z*	Fragment	(%)	*m/z*	Fragment	(%)
735	$C_{45}H_{59}OSn$	1.82	644	$C_{45}H_{60}OSi$	9.14	910	$C_{60}H_{70}O_4Si_2$	0.09	741	$C_{42}H_{53}O_4Sn$	2.85
679	$C_{41}H_{51}OSn$	3.99	566	$C_{39}H_{54}OSi$	34.29	655	$C_{44}H_{39}O_2Si_2$	3	665	$C_{36}H_{49}O_4Sn$	6.44
658	$C_{39}H_{54}OSn$	1.41	368	$C_{25}H_{24}OSi$	29.13	535	$C_{36}H_{31}OSi_2$	6	647	$C_{36}H_{47}O_3Sn$	5.71
406	$C_{21}H_{18}OSn$	26.56	315	$C_{21}H_{19}OSi$	41.52	457	$C_{30}H_{25}OSi_2$	8.5	629	$C_{36}H_{45}O_2Sn$	3.89
350	$C_{18}H_{14}Sn$	100	259	$C_{18}H_{15}Si$	57.55	397	$C_{26}H_{25}O_2Si$	38	351	$C_{18}H_{15}Sn$	100
197	C_6H_5Sn	6.75	199	$C_{12}H_{11}OSi$	100	276	$C_{18}H_{16}OSi$	50			
120	Sn	3.43	181	$C_{12}H_9Si$	3.86	199	$C_{12}H_{11}OSi$	100			
			28	Si	5.67	715	$C_{47}H_{47}O_3Si_2$	0.8			

[a] Only Si- or Sn-bearing fragments are given. Mass numbers are based on ^{1}H, ^{12}C, ^{16}O, ^{28}Si and ^{120}Sn. [b] See text.

ions (**2**, **3**, **6**, **9**) or of ions containing more than one tin or silicon atom (**2**, **3**, **9**), it may be inferred that these compounds are not polymeric. However, the possibility of linking by coordination is not excluded. Mass spectral fragmentation patterns are conventional as reported for organosilicon and tin complexes with oxygen-containing ligands.[14]

Vibrational, NMR (^{29}Si, ^{119}Sn, ^{207}Pb) and ^{119}Sn Mössbauer data for the compounds are given in Table 3. IR spectra of the cholesterol compounds **1**–**4**, **7** and **8** show the disappearance

Table 3 Vibrational, NMR and ^{119}Sn Mössbauer spectral data for organoelement derivatives of steroids

	Vibrational spectral data		X NMR spectral data[b]	^{119}Sn Mössbauer spectral data[c]						Structure (see Fig. 1)
	$\nu_{as}(X\text{–}C)$[a]	$\nu_{sym}(X\text{–}C)$[a]		IS	$\lvert\Delta E_{exp.}\rvert$	Γ_1	Γ_2	$\Delta E_{calcd.}$[d]	η	
Me$_3$Sn(COL), **1**	555R	518R	149.28[e]	1.314	3.373	0.935	0.968	−2.179	0.05	I
			121.20[f]					−2.870	0.00	II
			51.40[g]					−3.331	0.75	III
								+1.994	0.89	IV
Ph$_3$Sn(COL), **2**	272R	215R	−86.23[e] (8)	1.121	1.606	0.910	0.920	−1.960	0.05	I
			−92. 57[e] (1)					−2.420	0.00	II
			−84.23[f] (8)					−3.141	0.86	III
			−89.90[f] (0.7)					−1.175	0.87	IV
Ph$_3$Si(COL), **3**	512	—	−12.87 (8.0)							
			−15.18 (12.0)							
			−18.62 (11.0)							
			−21.90 (6.0)							
Ph$_3$Pb(COL), **4**	—	208	−187.57[h]							
(Ph$_3$Sn)$_2$(HDCA), **5**	272	—	−109.76	1.248	3.022	1.107	1.116	−2.830	0.00	II
	1590, 1528[i]	1482, 1432[k]	−118.12					−3.519	0.82	III
								−2.231	0.65	IV
(Ph$_3$Si)$_2$(HDCA), **6**	510	—	−14.47 (8.5)							
	1710, 1590[i]	1450, 1432[k]	−15.39 (12)							
			−18.64 (5.5)							
			−21.84 (4.8)							
Me$_2$Sn(COL)$_2$, **7**	555R	525R	128.75 (12)	1.036	2.658	1.022	1.126	−2.502	0.94	V
			148.44 (1)					−2.632	0.33	VI
Ph$_2$Sn(COL)$_2$, **8**	270	—	−45.02	0.892	1.889	1.011	1.013	−2.251	0.94	V
								+2.240	0.285	VI

[a] X = Si, Sn or Pb, [b] Spectra of compounds with nuclei X = ^{29}Si, ^{119}Sn and ^{207}Pb were recorded for 0.2 mol dm^{-3} solutions except **1**, which was 0.5 mol dm^{-3}. Intensity of signal given in parentheses, [c] Isomer shifts δ and nuclear quadruple resonance ΔE determined at 10 K ($\delta \pm 0.002$ mm s^{-1}, $\Delta E \pm 0.002$ mm s^{-1}). Absorber thicknesses were *ca* 0.5 mg ^{119}Sn cm^{-2}. Isomer shift δ with respect to room-temp. CaSnO$_3$. Γ_1 and Γ_2: full width at half-height of the Lorentzian fits of the resonant peaks, [d] The partial quadrupole splittings, p.q.s. (mm s^{-1}) employed in the calculations are: $([\mathrm{Alk}]-[\mathrm{Hal}])^{tet} = -1.37$,[23] $([\mathrm{Ph}]-[\mathrm{Hal}])^{tet} = -1.26$,[23] $([\mathrm{CO}]-[\mathrm{Hal}])^{tet} = -0.27$,[25] $\mathrm{Alk}^{tba} = -0.94$;[24] $\{\mathrm{Alk}\}^{tbe} = -1.13$;[24] $\{\mathrm{Ph}\}^{tba} = -0.89$;[24] $\{\mathrm{Ph}\}^{tbe} = -0.98$;[24] $\{\mathrm{O}\}^{tba}{}_{bridg} = -0.13$;[25] $\{\mathrm{O}\}^{tbe}{}_{bridg} = +0.02$;[25] $\{\mathrm{COO}\}^{tba}{}_{bridg} = +0.075$;[24,25] $\{\mathrm{COO}\}^{tbe}{}_{bridg} = +0.29$.[24,25] Asymmetry parameter $\eta = (V_{xx} - V_{zz})$, [e] Measured at 323 K, [f] Measured at 273 K, [g] Measured at 223 K, [h] Solution in THF with DMSO-d$_6$ as external lock, [i] ν_{as}CO$_2$, [k] ν_sCO$_2$.

of the strong band at 3600–3200 cm^{-1} due to νOH of HCOL, indicating its deprotonation. Solid-state IR and Raman spectra of **1** show two bands due to ν_{as}(Sn—C) and ν_s(Sn—C), which suggest a highly distorted trigonal bipyramidal or tetrahedral geometry. Keeping in view the tendency of Me_3SnX compounds to form linear chains in the solid state by self association,[15] it would be reasonable to exclude a tetrahedral arrangement around tin and to propose a trigonal bipyramidal structure for **1**. It is expected that the bulkiness of the COL group will cause great distortion in the trigonal bipyramidal geometry.

The Mössbauer data for **1** (Table 3) are in accordance with this proposal. The Isomer Shift (IS) value is characteristic of an organotin(IV) derivative,[16] and this is true for the values of the other compounds as well, including the usual variations on going from Me to Ph derivatives and from triorgano- to diorgano-tin(IV) compounds.[16] The ΔE_{exp} value of 3.373 mm s^{-1} would favour a trigonal bipyramidal structure, when compared with other Me_3Sn compounds.[17] The rationalization of the ΔE_{exp} values, by applying the point charge model formalism[18] to the idealized structures I–VI (Fig. 1) and using p.q.s. values from literature[16,18,19] (see Table 3), allows a probable configuration for **1** to be proposed. Taking into account the maximum accepted difference[20] $|\Delta E_{exp.} - \Delta E_{calcd.}| = 0.4$ mm s^{-1}, the obtained $E_{calcd.}$ value would rule out a tetrahedral structure for **1**, as well as polymeric trigonal bipyramidal configurations with regularly arranged equatorial or facial methyl groups (Fig. 1, structures I, II and IV). However, it would suggest a polymeric trigonal bipyramidal structure with a T-shaped (Fig. 1, structure III) or a heavily distorted equatorial arrangement of the methyl groups, (distorted version of structure II in Fig. 1).

The ^{119}Sn NMR chemical shift for **1** in $CDCl_3$ solution is indicative of four-coordinate tin, which means the polymeric structure breaks down in solution. Correspondingly, the intensity of the IR band due to ν_s(Sn—C) is higher in solutions of **1** in $CDCl_3$ than in solid **1**. The degree of dissociation of **1**, as measured by its ^{119}Sn chemical shift, will be expected to increase/decrease with increase/decrease in temperature.[21] The value of $\delta = 51.4$ ppm ($\delta_{297K} - \delta_{223K} = +70.8$ ppm) on lowering the temperature to 223 K suggests that, at 223 K, either **1** is not dissociated at all and retains the distorted trigonal bipyramidal geometry or the degree of dissociation is very low. However, the low-field increase in the chemical shift by 28 ppm on increasing the temperature to 323 K suggests the complete dissociation of the molecule to give a monomeric tetrahedral species. The ^{119}Sn chemical shift value of $\delta = 121.2$ ppm at 297 K can then be interpreted as **1** existing in solution in a temperature-dependent equilibrium such as

$$\text{Linear chain polymer} \rightleftarrows \text{Monomer}$$

Similar observations have been made for triorganotin alkoxides and self-associated species have been proposed in the solid and solution state.[22] In this respect it is noteworthy that the coupling constant $^1J(^{119}Sn^{13}C)$ value of 411.98 Hz (Table 4) obtained for **1** lies between the values of five-coordinated $Me_3SnCl \cdot Py$ (476 Hz) and four-coordinated Me_3SnCl (386 Hz) and is very similar to that of Me_3SnOEt (416 Hz),[23] for which a similar equilibrium has been proposed.

^{1}H NMR chemical shift values for the Ph_3M(COL) complexes **2**, **3** and **4** in $CDCl_3$ have been given in Table 5. The ratio of protons of the Ph_3M moiety and of the ligand support formation of the R_3M(COL) type of compound. ^2J and $^3J(^{119}Sn^{13}C)$ values of 43.24 and 58.50 Hz, respectively, for **2** suggest that a four-coordinate species is present in solution. This conclusion obtains further support from the ^{29}Si, ^{119}Sn and ^{207}Pb chemical shift values (Table 3) which are markedly different from those reported for five-coordinate compounds and are in agreement with values for four-coordinate species.[24–26] Tetracoordination is also plausible since, with monodentate ligands, Ph_3M compounds generally tend to acquire tetrahedral geometries in solution.

In the ^{119}Sn NMR spectrum of **2**, in addition to the main signal at $\delta = -84.23$ ppm, a signal of low intensity is observed at $\delta = -89.90$ ppm. However, no assignment is made at the present stage of investigations. Compound **2** when treated with D_2O (20% v/v in $CDCl_3$), gives Ph_3SnOH (checked by ^{119}Sn NMR; $\delta = -83.62$ ppm). There seems to be no substantial change in the ^{119}Sn chemical shift of **2** on increasing the temperature to 323 K, ruling out the possibility of self-association in solution.

Solutions of the complexes **1** and **2** in $CDCl_3$ were placed at 323 K for 24 h in closed NMR tubes, and ^{119}Sn NMR spectra showed no change in the nature of species present in so-

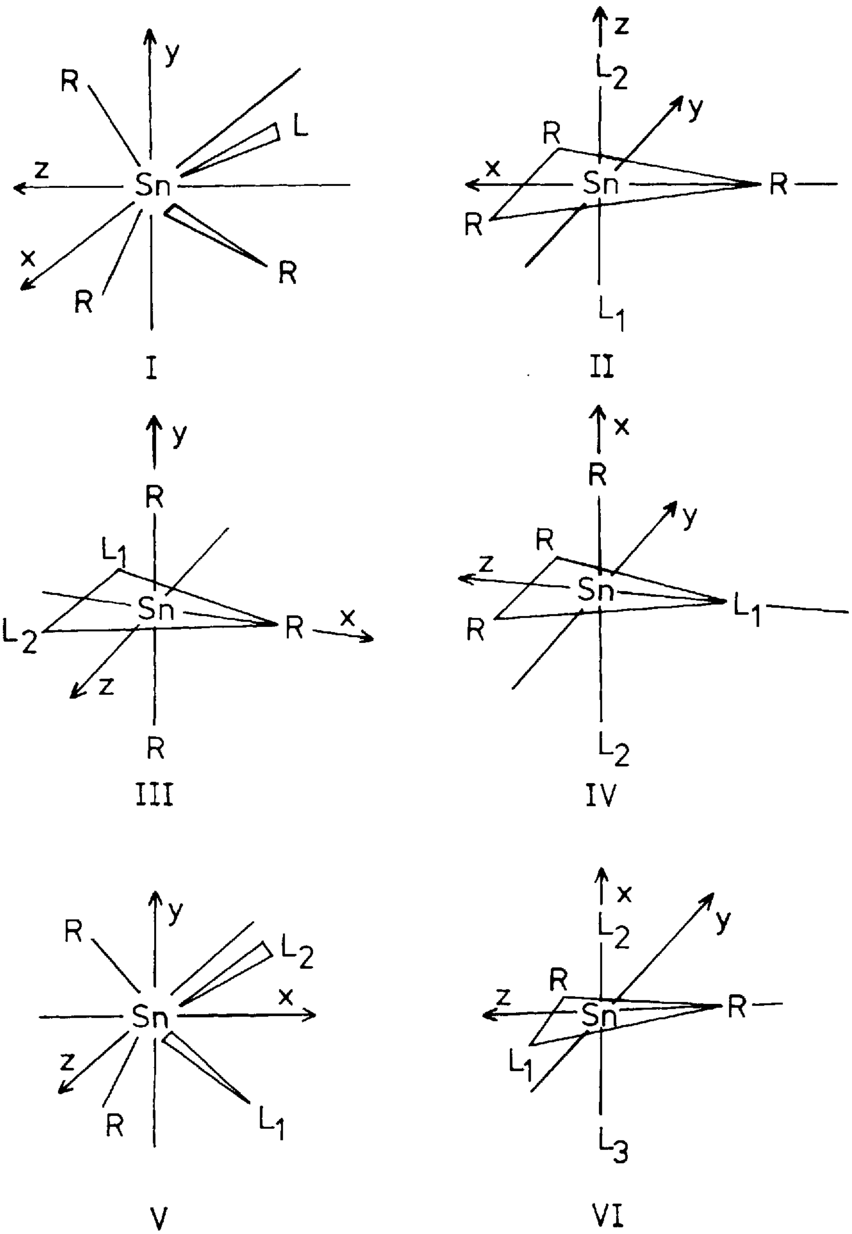


Figure 1 Idealized tetrahedral and trigonal bipyramidal structures of tin(IV) environments assumed in the point charge estimates of ΔE. The directions of the E.F.G. tensor V_{xx}, V_{yy}, V_{zz} as obtained from the computer output are also indicated.

lution. In the ^1H NMR spectra of all compounds downfield shifts are observed for 18- and 21-CH_3 protons while 19-CH_3 protons are not substantially affected. Ph_3M groups cause the splitting of 21-CH_3 and 26/27-CH_3 protons. The ^1H NMR spectrum of **3** shows two sets of signals for all protons which may indicate that two isomeric forms are present in solution.

From the $\Delta E_{exp.}$ value of 1.606 mm s^{-1} a tetrahedral configuration around tin (Fig. 1, structure I) can be safely proposed for **2** in the solid state, even if a polymeric trigonal bipyramidal structure cannot be fully excluded a priori.

The IR spectrum of solid **5** gives a mean $\Delta\nu(\nu_{as}CO_2 - \nu_sCO_2)$ value of 102 cm^{-1} (ν_{as} and ν_s are split; Table 3), suggesting chelating and/or

Table 4 ^{13}C NMR spectral data[a] for organoelement derivatives of steroids

	Compound							
C-atom	**1**	**2**	**3**	**4**	**6**	**7**	**8**	**9**
1	37.18	37.26	37.23–37.20	37.24	36.37	37.22	37.23	36.37
2	31.59	31.64	31.62	31.62	31.67	31.52	31.59	31.20
3	71.63	71.67	71.77–73.45	71.73	73.13	71.42	71.69	71.74
4	42.18	42.30	42.37	42.29	35.91	42.25	42.28	35.97
5	140.71	140.76	141.04–140.67	140.70	41.96	140.74	140.67	42.03
6	121.41	121.58	121.67–121.30	121.63	28.32	121.50	121.60	28.50
7	31.79	31.89	31.87	31.89	27.41	31.85	31.87	27.46
8	31.79	31.89	31.87	31.89	35.35	31.85	31.87	35.19
9	50.00	50.12	50.10–50.02	50.10	35.10	50.08	50.08	35.14
10	36.39	36.49	36.48	36.47	—	36.46	36.45	34.06
11	20.97	21.07	21.02–21.07	21.07	30.52	21.03	21.06	30.43
12	28.13	28.23	28.23	28.22	73.60	28.18	28.22	73.07
13	42.25	42.30	42.30–42.26	42.29	46.39	42.25	42.23	46.43
14	56.63	56.74	56.73	56.74	48.07	56.71	56.72	48.17
15	24.19	24.29	24.29	24.28	26.00	24.23	24.27	25.57
16	39.66	39.77	39.75	39.76	27.05	39.74	39.74	27.09
17	56.02	56.13	56.11–56.08	56.13	47.39	56.10	56.11	47.36
18	11.76	11.86	11.84	11.85	12.67	11.80	11.84	12.60
19	19.30	19.39	19.40	19.39	23.05	19.33	19.39	23.12
20	35.68	35.78	35.78	35.77	35.91	35.74	35.76	—
21	18.61	18.71	18.71	18.71	17.34	18.66	18.70	17.28
22	36.07	36.07	36.17	36.17	33.41	36.13	36.17	33.58
23	23.73	23.82	23.81	23.82	33.50	—	23.82	31.65
24	39.40	39.50	39.50	39.50	180.03	39.46	39.49	181.19
25	27.89	28.00	28.01	28.00	—	27.94	27.98	—
26[b]	22.73	22.81	22.83	22.81	—	22.76	22.81	—
27[b]	22.47	22.55	22.57	22.56	—	22.48	22.55	—
i	−0.23	—	135.37	—	135.31	−3.92	137.24	137.82
o	—	139.39	134.90–135.11	136.34	134.91	—	136.04	136.39
m	—	128.81	127.70–127.85	129.41	127.65	—	129.06	128.94
p	—	129.35	129.79–130.03	130.30	129.70	—	130.38	130.20

[a] Chemical shift values (ppm), [b] Assignments may interchange.

Additional data. $^{n}J(^{119}Sn^{13}C)$ (Hz): **1**: $^{1}J=411.98$. **2**: $^{2}J=43.24$; $^{3}J=58.50$; $^{4}J=12.72$. **8**: $^{2}J=48.32$; $^{3}J=63.58$; $^{4}J=12.72$. **9**: $^{2}J=45.78$; $^{3}J=63.58$.

bridging bonding.[27,28] In the Mössbauer spectrum of **5** only one doublet ($\Delta E_{exp.}=3.022\,mm\,s^{-1}$) is observed. This suggests that identical coordination spheres around the two tin atoms would follow, though the high Γ values might indicate that these two bands result from two doublets with difference in splitting. Pentacoordination can be inferred from $\Delta E_{exp.}$ and on comparing it with $\Delta E_{calcd.}$ (Fig. 1, structure II) a polymeric trigonal bipyramidal configuration with equatorial phenyl groups and axial O-atoms (bridging carboxylate groups and/or tricoordinated O-atoms) is assumed.

In the IR spectrum of solid **6** the bands at 1710 and 1450 cm^{-1} can be assigned provisionally to $\nu_{as}CO_2$ and $\nu_{s}CO_2$, respectively. From these data ($\Delta\nu=260\,cm^{-1}$) monodentate ester-like bonding of the carboxylate group to silicon, and, consequently, tetracoordination at silicon can be inferred.

In another reaction Ph_3SnCl was refluxed with H_3DCA in a molar ratio of 2:1 for 48 h resulting in a product differing from **5**, which had been obtained from Ph_3SnOH and H_3DCA also in a molar ratio of 2:1 [see the Experimental section, method (c)]. The ^{119}Sn NMR spectra of the solution of the product showed two signals at $\delta=-49.91$ and -116.57 ppm which can be assigned to Ph_3SnCl and $Ph_3Sn(H_2DCA)$ (**9**). The fragmentation patterns in the mass spectrum

Table 5 ^{1}H NMR spectral data for organoelement derivatives of steroids[a]

Compound	18-CH_3	19-CH_3	21-CH_3	26/27-CH_3	3-H	6-H	R_nM[b]
$Me_3Sn(COL)$, **1**	0.60	0.93	0.79 d $J=6.5$	0.84 d $J=6.3$	3.44 m	5.28	0.55
$Ph_3Sn(COL)$, **2**	0.60	0.92	0.79[c] $J=5.2$	0.84 d $J=6.5$	3.44 m	5.27 d $J=5.1$	7.38
$Ph_3Si(COL)$, **3**	0.57	0.91	0.77[c] $J=1$	0.81 d $J=6.5$	3.53 m	5.17 d $J=5.1$	7.33
	0.60	0.92	0.79	0.83	3.75 m	5.31 d	7.56
$Ph_3Pb(COL)$, **4**	0.65	0.98	0.84[c] $J=5.3$	0.89 d $J=6.5$	3.50 m	5.33 d $J=5.1$	7.45
$(Ph_3Si)_2(HDCA)$, **6**	0.63	0.81	0.94 d $J=5.7$	—	3.82	3.95[d] m	7.45
$Me_2Sn(COL)_2$, **7**	0.65	0.98	0.84 d $J=6.3$	0.89 d $J=6.4$	3.50 m	5.33	0.38
$Ph_2Sn(COL)_2$, **8**	0.65	0.98	0.84[c] $J=5.6$	0.89 d $J=6.4$	3.50 m	5.32 d $J=4.2$	7.57

[a] Chemical shift values (ppm); coupling constants $^2J(^1H^1H)$ (Hz); solvent $CDCl_3$. [b] $R=Me$, Ph; $M=Si$, Sn, Pb; center of multiplet for Ph. [c] A set of two doublets. [d] Proton shift for 12-H. Abbreviations: d = doublet; m = multiplet.

taken at different temperatures support the formation of this compound. ^{13}C NMR of **9** shows a considerable shift for the carbonyl-carbon atom indicating its involvement in bonding with the Ph_3Sn moiety, although coupling constants $^nJ(^{119}Sn^{13}C)$ and ^{119}Sn chemical shift values suggest a four-coordinate tin in solution.

^{119}Sn NMR spectra of **5** give two signals at $\delta=-109.76$ and $\delta=-118.12$ ppm. By analogy to **9**, the signal at $\delta=-118.12$ ppm can be safely assigned to the Ph_3Sn moiety attached to the carbonyl oxygen at C-24 and the signal at $\delta=-109.76$ ppm to the Ph_3Sn moiety at C-3. As these values do not fall into the range reported for five-coordinated triphenyltin compounds, it can be suggested that only four-coordinated species are present in solution. However, for **6** only four-coordinated species are postulated in solution and in the solid state, although a very weak interaction between carbonyl-oxygen and silicon atoms cannot be completely excluded in the solid state.

R_2Sn compounds with two monodentate ligands are expected to have tetrahedral geometries around the tin atom. Presence of both ν_{as} and ν_s(Sn—C) frequencies in the Raman spectrum of **7** and $^nJ(^{119}Sn^{13}C)$ values in the ^{13}C NMR spectrum of **8** would be consistent with tin being four-coordinate in solutions of these compounds. This is also supported by the ^{119}Sn NMR chemical shifts. In the ^{119}Sn NMR spectrum of **7** an additional signal of very low intensity at $\delta=+148.44$ ppm is observed which may be assigned to **1**, which is presumably produced by the disproportionation of **7**.

The $\Delta E_{exp.}$ values for solid **7** and **8**, 2.658 and 1.889 mm s^{-1}, respectively, could indicate a tetrahedral configuration around tin, but do not exclude a polymeric trigonal bipyramidal structure. Also point charge formalism is not able to distinguish between the tetrahedral structure V and the polymeric structure VI of Fig. 1. Considering the generally observed structural features of diorganotin compounds with oxygen-bonded ligands,[29] it would be reasonable to assume the existence of more or less strongly associated structures and the intermolecular association leading necessarily to trigonal bipyramidal structural patterns.

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