*Journal of Organometallic Chemistry*, 273 (1984) 303–312
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# SYNTHESIS AND SPECTROSCOPIC INVESTIGATIONS OF BIS(ORGANOSTANNYL)METHANES

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(Received April 10th, 1984)

## Summary

The synthesis of bis(organostannyl)methanes $(Ph_2XSn)_2CH_2$ (X = Cl, Br, I, OH, $OCH_3$, SPh, $OCOCH_3$, $OCOMe_3$), $(PhBr_2Sn)_2CH_2$, $[(AcO)_3Sn]_2CH_2$ and $(Ph_2SnCH_2SnPh_2X)_2$ (X = O,S) has been described and the products investigated by means of $^1H$, $^{13}C$ and $^{119}Sn$ NMR spectroscopy and mass spectrometry.

## Introduction

In recent papers we and others have shown that bis(halostannyl)methanes are suitable precursors for tin-containing heterocycles and exhibit a particular behaviour towards HMPA and DMSO [1–6]. In this work we describe the synthesis and spectroscopic properties of a series of bis(organostannyl)methanes.

## Syntheses

The reaction of bis(triphenylstannyl)methane, **1**, [7] with methanolic HCl or with bromine or iodine in methanol/benzene gives the corresponding bis(halophenylstannyl)methane in good yield (eqs. 1–3):

$$\underset{(\mathbf{1})}{(Ph_3Sn)_2CH_2} + 2\ HCl \xrightarrow{CH_3OH/C_6H_6} \underset{(\mathbf{2})}{(ClPh_2Sn)_2CH_2} + 2\ PhCl \tag{1}$$

$$(Ph_3Sn)_2CH_2 + 2\ X_2 \xrightarrow{CH_3OH/C_6H_6} \underset{\begin{array}{c}(\mathbf{3}, X = Br;\\ \mathbf{4}, X = I)\end{array}}{(XPh_2Sn)_2CH_2} + 2\ PhX \tag{2}$$

*(Continued on p. 306)*

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TABLE 1

$^1$H NMR DATA FOR COMPOUNDS **1–7** AND **9–13** ($CDCl_3$, $T$ 302 K)

| Compound | Chemical shifts (ppm) | | | Coupling constants (Hz) | | | |
|---|---|---|---|---|---|---|---|
| | $CH_2$ | o-Ph | m,p-Ph | $^2J(^{113}Sn–C–^1H)$ | $^3J(^{119}Sn–C–C–^1H)$ | $^3J(^1H–C–C–^1H)$ | $^4J(^1H–C–C–C–^1H)$ |
| **1** | 0.96 | 7.19–7.33 | | 63.7 | | | |
| **2** | 1.54 | 7.55 | 7.37 | 64.6 | 63 | | |
| **3** | 1.68 | 7.51 | 7.35 | 64.5 | 60 | 7.2 | 2.0 |
| **4** | 1.87 | 7.46 | 7.33 | 64.2 | 60 | 7.2 | 1.8 |
| **5** | 2.33 | 7.60 | 7.50 | 68.2 | 90 | 6.9 | 3.0 |
| **6** [a] | 1.09 | | | 60.0 | | | |
| **7** [b] | 1.76 | | | 126.1 | | | |
| **9** [c] | 1.81 | 7.58 | 7.30 | 79.7 | 60 | 7.4 | 1.8 |
| **10** [d] | 0.90 | 7.56 | 7.17 | | 64 | | |
| **11** | 1.19 | | | 65.2 | | | |
| **12** | | | | | | | |
| **13** [e] | 1.31 | 7.65 | 7.35 | 57.0 | 57 | | |

[a] $Sn–CH_3$ 0.82 ppm. $^2J(^{119}Sn–C–^1H)$ 60 Hz [b] $\delta$ ($CH_3$) 1.76 ppm. [c] $\delta$ ($CH_3$) 2.16 ppm. [d] $\delta$ ($CH_3$) 0.95 ppm. [e] In pyridine-$d_5$

TABLE 2. $^{13}C$ NMR DATA FOR THE COMPOUNDS **1**–**7** AND **9**–**13** ($CDCl_3$, $T$ 302 K)

| Compound | Chemical shifts (ppm) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $CH_2$ | Phenyl carbon atoms | | | | $C$=O | C(O)$CH_3$ | OCH$_3$ |
| | | $i$ | $o$ | $m$ | $p$ | | | |
| **1** | −16.23 | 139.35 | 136.89 | 128.36 | 128.78 | | | |
| **2** | 0.01 | 138.29 | 135.71 | 129.03 | 130.39 | | | |
| **3** | −0.38 | 137.82 | 135.75 | 128.95 | 130.27 | | | |
| **4** | −1.68 | 136.91 | 135.89 | 128.84 | 130.10 | | | |
| **5** | 16.26 | 137.58 | 134.42 | 129.49 | 131.73 | | | |
| **6** | 2.76 | | | | | | | |
| **7**[a] | 23.91 | | | | | 183.28 | 19.00 | |
| **9** | 2.26 | 143.10 | 135.89 | 128.29 | 129.03 | 180.86 | 23.22 | |
| **10** | 10.43 | 143.50 | 136.10 | 128.08 | 128.82 | | | |
| **11** | −8.62 | 138.31 | 135.95 | 128.34 | 129.27 | | | |
| **12** | 0.97 | 142.61 | 136.40 | 127.94 | 128.30 | | | 50.64 |
| **13**[c] | −5.04 | 141.81 | 136.58 | 128.95 | 129.71 | | | |

[a] All signals are broadened. [b] $\delta$ ($CH_3$) 27.52, $\delta$ ($C^1$) 37.99. [c] In pyridine-$d_5$.

TABLE 3. $^{119}Sn-^{13}C$ COUPLING CONSTANTS OF COMPOUNDS **1**–**6**, **9**, **11** AND **13** (Hz)

| Compound | $^1J(^{119}Sn-^{13}CH_2)$ | $^1J(^{119}Sn-C_i)$ | $^3J(^{119}Sn-C-Sn-^{13}C_i)$ | $^2J(^{119}Sn-^{13}C_o)$ | $^3J(^{119}Sn-^{13}C_m)$ | $^4J(^{119}Sn-^{13}C_p)$ |
|---|---|---|---|---|---|---|
| **1** | 293.9 | 514.2 | 9.2 | 38.0 | 50.2 | |
| **2** | 309.2 | 624.5 | 6.5 | 51.8 | 65.6 | 14.0 |
| **3** | 294.1 | 602.2 | 7.6 | 51.4 | 65.9 | 14.0 |
| **4** | 272.6 | 571.1 | 7.8 | 49.9 | 63.9 | 13.3 |
| **5** | 359.7 | 779.5 | 5.6 | 67.1 | 91.2 | 18.7 |
| **6**[a] | 273.4 | | | | | |
| **9** | 497.5 | 807.3 | 6.6 | 48.1 | 70.2 | 14.9 |
| **11** | 274.0 | 542.0 | | 43.0 | 47.4 | |
| **13** | 298.0 | 551.0 | | 46.2 | 58.3 | |

[a] $^1J(^{119}Sn-^{13}CH_3)$ 382.3. $^3J(^{119}Sn-C-Sn-^{13}CH_3)$ 44.0 Hz.

$$(\mathrm{Ph_3Sn})_2\mathrm{CH_2} + 4\ \mathrm{Br_2} \xrightarrow{\mathrm{CH_3OH/C_6H_6}} \underset{(\mathbf{5})}{(\mathrm{Br_2PhSn})_2\mathrm{CH_2}} + 4\ \mathrm{PhBr} \qquad (3)$$

In contrast to earlier observations [8] bis(bromodimethylstannyl)methane, **6**, can also be obtained by the reaction of bis(trimethylstannyl)methane with bromine (eq. 4):

$$(\mathrm{Me_3Sn})_2\mathrm{CH_2} + \mathrm{Br_2} \xrightarrow{\mathrm{CH_3OH/C_6H_6}} \underset{(\mathbf{6})}{(\mathrm{Me_2BrSn})_2\mathrm{CH_2}} + 2\ \mathrm{MeBr} \qquad (4)$$

The compound **1** reacts with acetic acid, with cleavage of all of the phenyl–tin bonds, to give bis(triacetatostannyl)methane, **7** (eq. 5):

$$(\mathrm{Ph_3Sn})_2\mathrm{CH_2} \xrightarrow[\text{reflux}]{\mathrm{CH_3COOH}} \underset{(\mathbf{7})}{[(\mathrm{AcO})_3\mathrm{Sn}]_2\mathrm{CH_2}} + 6\ \mathrm{C_6H_6} \qquad (5)$$

The halides **2** and **3** are easily converted into bis(hydroxydiphenylstannyl)methane, **8**, by alkaline hydrolysis (eq. 6):

$$\underset{\mathrm{X = Cl,\ Br}}{(\mathrm{Ph_2XSn})_2\mathrm{CH_2}} \xrightarrow[-\mathrm{NaX}]{\mathrm{NaOH/H_2O/CH_3OH}} \underset{(\mathbf{8})}{(\mathrm{Ph_2OHSn})_2\mathrm{CH_2}} \qquad (6)$$

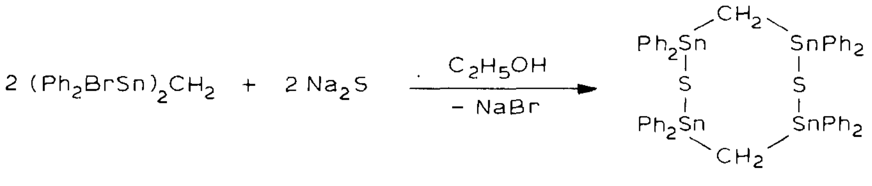
The reaction of the dihydroxy compound **8** with a carboxylic acid or mercaptan gives the corresponding carboxylate or thiolate, **9–11**, in high yield (eq. 7):

$$(\mathrm{Ph_2OHSn})_2\mathrm{CH_2} + 2\ \mathrm{HX} \xrightarrow[-\mathrm{H_2O}]{\mathrm{C_6H_6}} \underset{\substack{(\mathbf{9},\ \mathrm{X = OCOCH_3};\\ \mathbf{10},\ \mathrm{X = OCOC(CH_3)_3};\\ \mathbf{11},\ \mathrm{X = SPh})}}{(\mathrm{Ph_2XSn})_2\mathrm{CH_2}} \qquad (7)$$

The dialkoxide **12** can be prepared by the reaction of the halides **2** and **3** with sodium methanolate (eq. 8):

$$\underset{\mathrm{X = Cl,\ Br}}{(\mathrm{Ph_2XSn})_2\mathrm{CH_2}} + 2\ \mathrm{NaOCH_3} \xrightarrow[-\mathrm{NaCl}]{\mathrm{CH_3OH}} \underset{(\mathbf{12})}{(\mathrm{Ph_2CH_3OSn})_2\mathrm{CH_2}} \qquad (8)$$

With sodium sulphide, a tetrastannadithiacyclooctane is obtained from the bromide **3** (eq. 9):



(13)

(9)

The compounds **1–3**, **5**, **6** and **8–10** are monomeric and occur as crystalline solids which are soluble in organic solvents, whereas **4** and **11** are oils and **7** and **13** are amorphous solids.

## NMR spectroscopic investigations

Details of the $^1$H NMR spectra are listed in Table 1. The methylene protons show a low field shift which increases in the sequence **1**, **6**, **11**, **13**, **2**, **3**, **4**, **9**, **10**, **12**, **5**,

TABLE 4

$^{119}Sn$ NMR DATA FOR COMPOUNDS **1–7** AND **9–13** ($CDCl_3$, $T$ 302 K)

| | | |
|---|---|---|
| **1** | −79.25 | 244 |
| **2** | 20.43 | 218 |
| **3** | −0.03 | 221 |
| **4** | −67.62 | 231 |
| **5** | −33.42 | 231 |
| **6** | 137.28 | 250 |
| **7** [a] | −540.0 | |
| **9** [b] | −188.25 | |
| **10** | −206.10 | 326 |
| **11** | −3.26 | 183 |
| **12** [a] | −156.50 | |
| **13** [c] | 16.20 | 201 |

[a] Very broad. [b] Broad. [c] In pyridine-$d_5$, $^2J(^{119}Sn{-}S{-}^{117}Sn)$ 367 Hz.

TABLE 5

MASS SPECTRA OF COMPOUNDS **2–13**

| Compound | $m/e$, relative intensity (%) (fragmention) |
|---|---|
| **2** | 597, 100 ($Ph_4ClSn_2Ch_2$); 555, 87 ($Ph_3Cl_2Sn_2CH_2$); 443, 1 ($Ph_2ClSn_2CH_2$); 351, 10 ($Ph_3Sn$); 309, 15 ($Ph_2ClSn$); 289, 1 ($ClSn_2CH_2$); 288, 6 ($Ph_2SnCH_2$); 274, 1 ($Ph_2Sn$); 273, 10 ($PhSnC_6H_4$); 232, 1 (PhClSn); 211, 7 ($PhSnCH_2$); 197, 42 (PhSn); 156, 6 (SnHCl); 155, 22 (ClSn) 145, 2 ($C_2HSn$); 121, 0.5 (HSn); 120, 9 (Sn) |
| **3** | 643, 100 ($Ph_3Br_2Sn_2CH_2$); 489, 1 ($PhBr_2Sn_2CH_2$); 487, 2 ($Ph_2BrSn_2Ch_2$); 353, 13 ($Ph_2BrSn$); 351, 12 ($Ph_3Sn$); 288, 5 ($Ph_2SnCH_2$); 211, 7 ($PhSnCH_2$); 199, 20 (BrSn); 197, 56 (PhSn); 145, 2 ($C_2HSn$); 145, 2 ($C_2HSn$); 120, 15 (Sn) |
| **4** | 739, 12 ($Ph_3I_2Sn_2CH_2$); 689, 100 ($Ph_4ISn_2CH_2$); 535, 3 ($Ph_2ISn_2CH_2$); 401, 6 ($Ph_2ISn$); 351, 15 ($Ph_3Sn$); 247, 6 (ISn); 211, 5 ($PhSnCH_2$); 197, 33 (PhSn); 145, 1 ($C_2HSn$); 120, 10 (Sn) |
| **5** | 724, trace ($Br_4Ph_2Sn_2Ch_2$); 647, 9 ($Br_4PhSn_2CH_2$); 645, 100 ($Br_3Ph_2Sn_2Ch_2$); 477, 3 ($Br_3Sn_2$); 369, 6 ($Br_2PhSnCH_2$; 355, 4 ($Br_2PhSn$), 353, 9 ($BrPh_2Sn$); 290, 11 ($BrPhSnCH_2$); 276, trace (PhBrSn); 199, 46 (BrSn); 197, 34 (PhSn); 145, 2 ($C_2HSn$); 134, 2 ($SnCH_2$); 120, 9 (Sn) |
| **6** | 457, 100 ($Me_3Br_2Sn_2CH_2$); 427, 11 ($MeBr_2Sn_2CH_2$); 412, 3 ($Br_2Sn_2CH_2$); 393, 23 ($Me_4BrSn_2CH_2$); 363, 7 ($Me_2BrSn_2CH_2$); 333, 7 ($BrSn_2CH_2$), 319, 4 ($BrSn_2$); 243, 5 ($Me_2BrSnCH_2$); 229, 6 ($Me_2BrSn$); 214, 1 (MeBrSn); 213, 2 ($BrSnCH_2$); 199, 15 (BrSn); 165, 6 ($Me_3Sn$); 164, 9 ($Me_2SnCH_2$); 151, 11 ($Me_2SnH$); 150, 1 ($Me_2Sn$); 135, 19 (MeSn); 121, 3 (SnH); 120, 2 (Sn) |
| **7** | 297, 4 ($(CH_3CO_2)_3Sn$); 253, 39 ($CH_3Sn(CH_3CO_2)_2$); 238, 4 ($(CH_3CO_2)_2Sn$); 223, 3 ($(CH_3)_2(CH_3CO_2)SnCH_2$); ($(CH_3)_2Sn(CH_3CO_2)$); 194, 3 ($CH_3(CH_3CO_2)Sn$); 179, 100 ($CH_3CO_2Sn$); 137, 40 ($CH_3SnH_2$); 135, 9 ($CH_3Sn$); 120, 12 (Sn) |
| **8** | 639, 58 ($Ph_3Sn_2CH_2$); 351, 100 ($Ph_3Sn$); 274, 17 ($Ph_2Sn$); 197, 51 (PhSn); 120, 29 (Sn) |
| **9** | 621, 67 ($Ph_4(OCOCH_3)Sn_2CH_2$); 603, 100 ($Ph_3(OCOCH_3)_2Sn_2CH_2$); 563, 11 ($Ph_4HSn_2CH_2$); 467, 8 ($Ph_2(OCOCH_3)Sn_2CH_2$); 449, 9 ($Ph(OCOCH_3)_2Sn_2CH_2$); 351, 25 ($Ph_3Sn$); 333, 64 ($Ph_2(OCOCH_3)Sn$); 315, 29 ($Ph(OCOCH_3)_2Sn$); 289, 10 ($Ph_2MeSn$); 271, 14($PhMe(OCOCH_3)Sn$); 211, 9 ($PhSnCH_2$); 197, 63 (PhSn); 179, 42 ($SnCO_2CH_3$); 120, 25 (Sn) |
| **10** | 687, 7 ($Ph_3(t\text{-}BuCO_2)_2Sn_2CH_2$); 663, 61 ($Ph_4(t\text{-}BuCO_2)Sn_2CH_2$); 399, 3 ($Ph(t\text{-}BuCO_2)_2Sn$); 375, 93 ($Ph_2(t\text{-}BuCO_2)Sn$); 351, 100 ($Ph_3Sn$); 274, 9 ($Ph_2Sn$), 273, 5 ($PhSnC_6H_4$); 221, 11 ($t\text{-}BuCO_2Sn$); 197, 62 (PhSn); 120, 28 (Sn) |
| **11** | 703, 8 ($Ph_3(PhS)_2Sn_2CH_2$); 671, 100 ($Ph_4(PhS)Sn_2CH_2$); 639, 46 ($Ph_5Sn_2CH_2$); 594, 1 ($Ph_3(PhS)Sn_2CH_2$); 593 ($Ph_3(PhS)Sn_2OH$); 562, 1 ($Ph_4Sn_2Ch_2$); 561, 5 ($Ph_4Sn_2CH$); 415, 1 ($Ph(PhS)_2Sn$); 351, 50 ($Ph_3Sn$); 229, 19 (PhSSn); 211, 3 ($PhSnCH_2$); 197, 62 (PhSn); 120, 19 (Sn) |
| **12** | 639, 87 ($Ph_5Sn_2CH_2$); 593, 11 ($Ph_4(CH_3O)Sn_2CH_2$); 562, 6 ($Ph_4Sn_2CH_2$); 351, 100 ($Ph_3Sn$); 305, 2 ($Ph_2(CH_3O)Sn$); 275, 11 ($Ph_2SnH$); 274, 17 ($Ph_2Sn$); 197, 91 (PhSn); 120, 50 (Sn) |
| **13** | 803, 26 ($Ph_3Sn_4S_2(CH_2)_2$); 657, 3 ($Ph_5Sn_2S$); 655, 2 ($Ph_3S_2Sn_3$); 639, 15 ($Ph_5Sn_2CH_2$); 594, 10 ($Ph_4SSn_2CH_2$); 517, 25 ($Ph_3Sn_2SCH_2$); 503, 3 ($Ph_3Sn_2S$); 485, 6 ($Ph_3Sn_2CH_2$); 383, 0.5 ($Ph_3SnS$); 351, 68 ($Ph_3Sn$); 274, 1 ($Ph_2Sn$); 273, 4 ($PhSnC_6H_4$); 229, 7 (PhSnS); 211, 3 ($PhSnCH_2$); 197, 100 (PhSn); 120, 28 (Sn) |

reflecting an increased deshielding of these protons. A similar tendency has been observed in a series of mercuriomethanes [9]. The values for the *ortho*-phenyl protons, which are well separated from those for the *meta* and *para* ones, vary in the opposite direction. The $^{2}J(^{119}\mathrm{Sn}-\mathrm{C}-{}^{1}\mathrm{H})$ coupling constants for the compounds **1**–**4** and **11** differ only slightly, whereas larger values are observed for compounds **5**, **7**, **9** and **10**. Compound **5** also shows a large $^{3}J(^{119}\mathrm{Sn}-{}^{1}\mathrm{H})$ coupling.

Details of the $^{13}$C NMR spectra are given in Tables 2 and 3. The methylene carbon atoms show a low field shift which increases in the sequence **1**, **11**, **13**, **4**, **3**, **2**, **12**, **9**, **6**, **10**, **5**, **7**. The values for the *ipso*-carbon atoms move to lower field in the sequence **4**, **3**, **2**, **11**, **5**, **1**, **13**, **12**, **9**, **10**, whereas the *ortho*, *meta* and *para* carbon atoms show only very small differences in chemical shift. Both series of $^{1}J(^{119}\mathrm{Sn}-{}^{13}\mathrm{C})$ coupling constants show considerable variation, being largest for compounds **9** and **10**. Because of solubility problems the couplings for compound **12** have not been observed. Compound **5** exhibits the largest $^{2}J(^{119}\mathrm{Sn}-{}^{13}\mathrm{C}_{o})$, $^{3}J(^{119}\mathrm{Sn}-{}^{13}\mathrm{C}_{m})$ and $^{4}J(^{119}\mathrm{Sn}-{}^{13}\mathrm{C}_{p})$ coupling constants.

Sharp signals have been observed in the $^{119}$Sn NMR spectra for all the compounds, except for **7**, **9** and **12** (which show a broad signal). Band positions and $^{2}J(^{119}\mathrm{Sn}-{}^{117}\mathrm{Sn})$ coupling constants are given in Table 4.

TABLE 6

PHYSICAL CONSTANTS, YIELDS AND ANALYTICAL DATA OF COMPOUNDS **1–13**

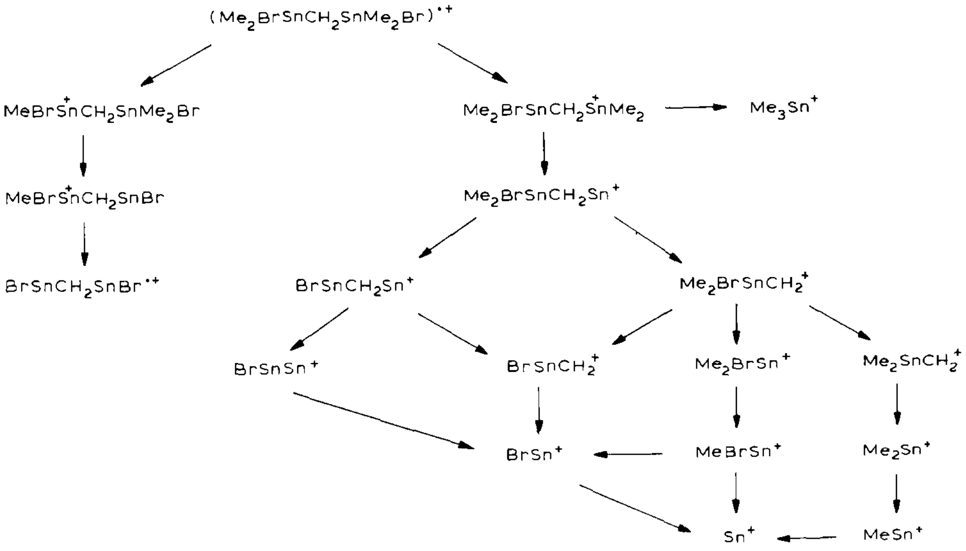
| Compound | M.p (°C) | Yield (%) | Formula | Analysis (Found (calcd.) (%)) | | |
|---|---|---|---|---|---|---|
| | | | | C | H | Halogen |
| **1** | 100–102 | 70 | $C_{37}H_{32}Sn_2$ | 62.11 | 4.41 | |
| | | | | (62.24) | (4.49) | |
| **2** | 142–144 | 73 | $C_{25}H_{22}Cl_2Sn_2$ | 47.43 | 3.43 | 11.14 |
| | | | | (47.60) | (3.49) | (11.25) |
| **3** | 104–106 | 70 | $C_{25}H_{22}Br_2Sn_2$ | 41.49 | 2.97 | 22.16 |
| | | | | (41.71) | (3.06) | (22.22) |
| **4** | oil | 75 | $C_{25}H_{22}J_2Sn_2$ | 36.32 | 2.55 | 30.85 |
| | | | | (36.89) | (2.70) | (31.21) |
| **5** | 72 | 70 | $C_{13}H_{12}Br_4Sn_2$ | 21.43 | 1.57 | 44.20 |
| | | | | (21.52) | (1.65) | (44.08) |
| **6** | 70– 73 | 40 | $C_5H_{14}Br_2Sn_2$ | 12.62 | 2.93 | 34.22 |
| | | | | (12.73) | (2.97) | (33.91) |
| **7** | – | 90 | $C_{13}H_{20}/O_{12}Sn_2$ | 25.50 | 3.17 | |
| | | | | (25.78) | (3.30) | |
| **8** | 183–185 | 95 | $C_{25}H_{24}O_2Sn_2$ | 50.31 | 3.98 | |
| | | | | (50.56) | (4.04) | |
| **9** | 197–199 | 90 | $C_{29}H_{28}O_4Sn_2$ | 50.88 | 4.22 | |
| | | | | (51.37) | (4.13) | |
| **10** | 173 | 90 | $C_{35}H_{40}O_4Sn_2$ | 54.87 | 5.09 | |
| | | | | (55.16) | (5.25) | |
| **11** | oil | 95 | $C_{37}H_{32}S_2Sn_2$ | 56.83 | 4.03 | |
| | | | | (57.11) | (4.12) | |
| **12** | 155–160 | 60 | $C_{27}H_{28}O_2Sn_2$ | 52.35 | 4.57 | |
| | | | | (52.14) | (4.50) | |
| **13** | 180–182 | 40 | $C_{50}H_{44}Sn_2Sn_4$ | 50.23 | 3.65 | |
| | | | | (50.73) | (3.72) | |

## Mass spectra

Details of the 70 eV monoisotopic mass spectra of compounds **2** to **13** are given in Table 5.

They show the expected [7] fragment-ions. For example, a possible fragmentation scheme is given for compound **6** in Scheme 1.

SCHEME 1



## Discussion

The spectra of compounds **1–6** and **11** are unexceptional and are comparable with those of $Ph_3SnX$ (X = Me, Ph, Cl, Br, I, SR), $Ph_2SnBr_2$ [10–12] and $Me_3SnBr$ [12,13]. Obviously, in solution the tin atoms are tetracoordinated without any intermolecular Sn–X interaction. For compound **4** this conclusion is supported by a comparison of the observed values with those for the $^{13}C$ and $^{119}Sn$ NMR spectra of

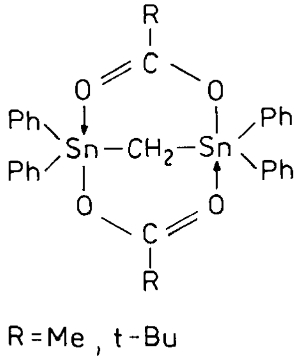


Fig. 1.

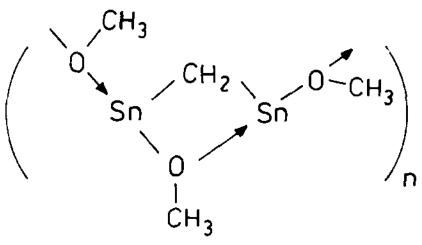


Fig. 2.

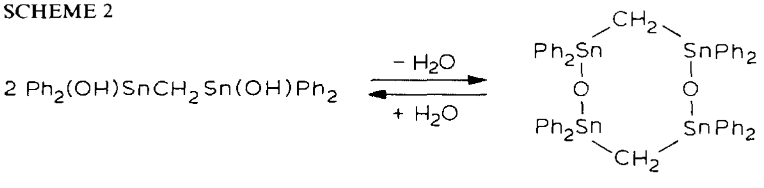
$Ph_2MeSnI$ ($\delta$ ($^{119}Sn$) $-68.22$, $C_i$ 137.1, $C_o$ 135.57, $C_m$ 128.72, $C_p$ 129.87 ppm; $^1J(^{119}Sn-^{13}C_i)$ 548, $^2J(^{119}Sn-^{13}C_o)$ 48.0; $^3J(^{119}Sn-^{13}C)$ 61.0 Hz).

In compounds **9**, **10** and **12** the tin atoms have a coordination number greater than four. As has already been pointed out for the HMPA complexes of compounds **2**–**4** [4], pentacoordination causes a low field shift for the *ipso* carbon atoms and increases the $^1J(^{119}Sn-^{13}C_i)$ coupling constants. Also, the $^{119}Sn$ NMR chemical shift is in agreement with this coordination number. For compounds **9** and **10** a structure with bridging carboxylate groups (Fig. 1) can be assumed. This assumption is also supported by the low IR frequencies for the carbonyl groups (**9**, $\nu$(CO) 1560 $cm^{-1}$; **10**, $\nu$(CO) 1550 $cm^{-1}$, in KBr). A similar structure has been suggested for $Ph_4Sn_2(OCOCH_3)_2$ [14] and $Me_4Sn_2(OCOR)_2$ [15].

In compound **12** the tin atoms achieve the coordination number of five by the intra- and inter-molecular oxygen bridging which is typical of tin alkoxides [16] (Fig. 2). The low solubility of the alkoxide **12** and its broad $^{119}Sn$ NMR signal agree with this assumption.

Compound **8** gives unusual spectra. The $^{119}Sn$ NMR spectrum of an analytical pure sample in $CDCl_3$ shows two signals (integration ratio 3 : 2), a sharp one at $-12.54$ ppm, having two satellites of 524 and 422 Hz, and a broad one at $-200.3$ ppm. The $^{13}C$ NMR spectrum of the same sample contains two signals for the methylene carbon, a broad one at 8.70 ppm ($^1J(^{119}Sn-^{13}C)$ 577 Hz) and a sharp one at $-4.26$ ppm ($^1J(^{119}Sn-^{13}C)$ 421.0 Hz). Also the *ipso* carbon atoms give two signals, at 145.38 ppm (broad) ($^1J(^{119}Sn-^{13}C_i)$ 771 Hz) and 142.85 ppm (sharp) ($^1J(^{119}Sn-^{13}C_i)$ 610 Hz). The $^1H$ NMR spectrum displays a sharp signal at 0.99 ppm ($^2J(^{119}Sn-C-^1H)$ 58 Hz) and further broad resonances at 0.78, 1.38 and 1.44 ppm. The phenyl protons appear as unresolved, broad signals between 7.22 and 7.64 ppm. The IR spectrum of this solution contains two sharp $\nu$(OH) peaks, at 3595 and 3645 $cm^{-1}$. The spectrum in KBr shows a broad $\nu$(OH) peak at 3600 $cm^{-1}$.

SCHEME 2



(8) (8a)

These results can be interpreted in terms of an equilibrium between the diol **8** and the corresponding eight-membered ring stannoxane **8a** (Scheme 2). The sharp signals in all of the spectra can be assigned to **8a** and the broad ones to **8**. For **8** an auto-associated structure similar to that characteristic of compound **12** can be proposed. Hydroxy-bridged polymeric structures of triorganotin hydroxides have been discussed in the literature [17].

## Experimental

The solvents were dried by standard methods and were freshly distilled before use. The $^1H$ and $^{13}C$ NMR spectra were recorded with a Bruker WP 270 spectrometer and the $^{119}Sn$ NMR measurements with a Bruker WP 200 instrument. The mass spectra were recorded on a AEI MS 902S instrument. Physical constants, yields and analytical data of compounds **1**–**13** are given in Table 6. Bis(triphenylstannyl)methane, **1**, has been described elsewhere [1].

*Bis(chlorodiphenylstannyl)methane, 2.* To a solution of 12.5 g (0.02 mol) **1** in 100 ml benzene and 30 ml methanol, 0.05 mol HCl (as a methanolic solution) was added. The mixture was stirred at room temperature for 4 days, the solvent was evaporated and the residue recrystallized from ether/hexane.

*Bis(bromodiphenylstannyl)methane, 3.* To 25 g (0.035 mol) **1**, dissolved in 200 ml benzene and 50 ml methanol, 9 g (0.056 mol) bromine in 50 ml methanol was added dropwise. The solvent was evaporated and the resulting oil recrystallized from hexane.

*Bis(iododiphenylstannyl)methane, 4.* To 5 g (0.007 mol) **1**, dissolved in 100 ml benzene and 30 ml methanol, a solution of 3.6 g (0.014 mol) iodine in 50 ml methanol was added dropwise. The mixture was stirred for two days, the solvent was evaporated and the resulting residue dissolved in ether. This solution was treated with hexane and cooled to −20 °C, when **4** separated as an oil. It was shown to be pure by $^1$H NMR spectroscopy.

*Bis(dibromophenylstannyl)methane, 5.* To 8 g (0.0112 mol) **1**, dissolved in 100 ml benzene and 30 ml methanol, a solution of 7.16 g (0.0448 mol) bromine in 40 ml methanol was added dropwise. After evaporation of the solvent the residue was recrystallized from hexane.

*Bis(bromodimethylstannyl)methane, 6.* To a solution of 10 g (0.0293 mol) bis(trimethylstannyl)methane [17] in 50 ml benzene and 50 ml methanol, a solution of 9.36 g bromine, dissolved in 30 ml methanol, was added dropwise under stirring at 0 °C. The solvents and volatile products were removed in vacuo (15 mmHg, bath temperature 80 °C). The residue was recrystallized from hexane.

*Bis(triacetatostannyl)methane, 7.* Compound **1** (6 g, 0.0084 mol) was suspended in 100 ml acetic acid and refluxed under magnetical stirring for 30 h. The solvent was then evaporated and the residue dried in vacuo.

*Bis(hydroxydiphenylstannyl)methane, 8.* The bromide **3**, (10 g, 0.0139 mol) dissolved in 30 ml methanol, was added under magnetical stirring to 1.22 g NaOH dissolved in 30 ml water. The mixture was stirred for 3 h and then the precipitate was filtered off, washed with water and small amounts of methanol, and dried.

*Bis(acetatodiphenylstannyl)methane, 9* and *bis(pivalatodiphenylstannyl)methane, 10.* Equimolar quantities of the diol **8** and acetic acid or pivalic acid, were dissolved in benzene and refluxed for 30 min. The solvent was then evaporated and the residue recrystallized from benzene/ether.

*Bis(thiophenoxydiphenylstannyl)methane, 11.* Compound **10** (5 g, 0.008 mol) was suspended in 50 ml benzene and treated with 1.77 g (0.016 mol) thiophenol. The mixture was refluxed for 15 min and the solvent was then evaporated. The diol was obtained **8** as an oil.

*Bis(methoxydiphenylstannyl)methane, 12.* Sodium (0.7 g, 0.03 mol) was dissolved in 100 ml methanol. To this solution, 10 g (0.0139 mol) **3**, dissolved in 40 ml methanol, were added dropwise under magnetical stirring. The mixture was refluxed for 2 h, the solvent was evaporated and the residue was extracted with boiling benzene. The solution was cooled and compound **10** was filtered off and dried.

*2,2,4,4,6,6,8,8-Octaphenyl-2,4,6,8-tetrastanna-3,7-dithiacyclooctane, 13.* The bromide **3** (5 g, 0.0069 mol) and 1.16 g (0.0069 mol) $Na_2S \cdot 5H_2O$ were refluxed for

2 h with vigorous stirring in 500 ml ethanol. The solvent was then removed in vacuo and the residue recrystallized from pyridine/benzene.

## Acknowledgements

We are indebted to Dr. I. Vanden Eynde for writing the program ISOMAS used to calculate the monoisotopic mass spectra, to Mr. M. Desmet for recording the mass spectra and to Mr. F. Resseler for recording the $^1$H and $^{13}$C NMR spectra.

The financial support obtained from the "Ministerie van Nationale Opvoeding en Nederlandse Cultuur (Bestuur voor Internationale en Culturele Betrekkingen) for the postdoctoral stay of K.J. is gratefully acknowledged. We also thank the "Nationaal Fonds voor Wetenschappelijke Onderzoek" (N.F.W.O.) for a grant.

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