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Spacer-bridged ladder compounds—syntheses, structures and synthetic applications☆

Michael Mehring [a], Markus Schürmann [a], Ingo Paulus [a], Dagmar Horn [a], Klaus Jurkschat [a,*], Akihiro Orita [b], Junzo Otera [b], Dainis Dakternieks [c], Andrew Duthie [c]

[a] *Lehrstuhl für Anorganische Chemie II der Universität Dortmund, D-44221 Dortmund, Germany*
[b] *Department of Applied Chemistry, Okayama University of Science, Ridai-cho, Okayama 700-0005, Japan*
[c] *School of Biological and Chemical Science, Deakin University, Geelong, Victoria 3217, Australia*

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Abstract

The reaction of α,ω-bis(organodichlorostannyl)alkanes $[R(Cl_2)SnCH_2]_2Z$ with their corresponding organotin oxides $[R(O)SnCH_2]_2Z$ or $(t\text{-}Bu_2SnO)_3$ provides the new spacer-bridged tetraorganodistannoxanes $\{[R(Cl)SnCH_2]_2Z]O\}_n$ (**22**, $Z = CH_2$, $R = Me_3SiCH_2$; **23**, $Z = CH_2$, $R = Me_3CCH_2$; **24**, $Z = CH_2CH_2$, $R = Me_3SiCH_2$; **25**, $Z = CH_2CH_2$, $R = Me_3CCH_2$; **26**, $Z = CH_2CH_2$, $R = Me_2CHCH_2$; **27**, $Z = Me_2Si$, $R = Me_3SiCH_2$). The acetate substituted derivative **28** $\{[R(AcO)SnCH_2]_2CH_2]O\}_n$ ($R = Me_3SiCH_2$) is obtained by reaction of **22** with silver acetate or by treatment of the organotin oxide $[R(O)SnCH_2]_2CH_2$ ($R = Me_3SiCH_2$) with acetic acid. The crystal structures of **23**, **24**, and **28** are described and reveal that these compounds adopt double ladder structures. Depending on the identity of Z and R in chloroform solution the compounds are either dimers ($n = 2$, **25**–**28**) or tetramers ($n = 4$, **22**–**24**). Also reported are preliminary studies on the catalytic activity in acylation reactions of compounds **22**, **24**–**26**, and **28**. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Tin; Distannoxanes; Crystal structure; NMR; Catalysis

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1. Introduction

Dimeric tetraorganodistannoxanes of the type $[R_2XSnOSnXR_2]_2$ ($X = Cl$, OH, R′COO, NCS; R, R′ = alkyl, aryl) have been found to be efficient catalysts in a variety of organic reactions [1–14]. Their potential in organic synthesis has been demonstrated especially for transesterifications under virtually neutral conditions [2–6] and for the highly selective acylation of alcohols [7,8]. The catalytic activity of distannoxanes in this type of reaction was reported to be the result of their dimeric structure [1,4–6] in solution. X-ray crystallography of a great number of distannoxanes has confirmed that the so-called ladder geometry originally proposed by Okawara et al. [15,16] is retained in the solid state [17]. The characteristic structural feature of this ladder type arrangement (**A**) is the planar four membered Sn_2O_2 ring. However, cryoscopic measurements [18] and solution ^{119}Sn-NMR studies [19] for $[R_2(AcO)SnOSn(OAc)R_2]_2$ (R = Bu, Et, Me) indicate partial dissociation into the monomeric species at low concentrations (< 0.02 mol l^{-1}). Furthermore, ^{119}Sn-NMR studies in solution of an equimolar mixture of the tetraorganodistannoxanes $[Bu_2(X)SnOSn(X)Bu_2]_2$ and $[Bu_2(Y)SnOSn(Y)Bu_2]_2$ provided evidence for the formation of the mixed tetraorganodistannoxane $[Bu_2(X)SnOSn(Y)Bu_2]_2$ ($X = O_2CMe_2$, Cl, OPh, OMe; Y = Cl, OPh, OMe) [20].

Recently, we reported on the synthesis of spacer-bridged di- and tri-tin compounds such as $[R(Cl_2)Sn]_2$-

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☆ Dedicated to the memory of the late Professor Rokuro Okawara.

* Corresponding author. Tel. +49-231-755-3800; fax: +49-231-755-3797; e-mail: kjur@platon.chemie.uni-dortmund.de.

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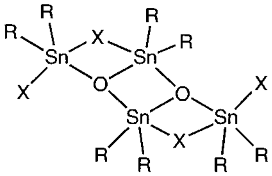
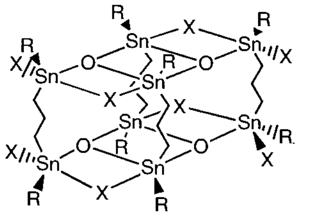
$(CH_2)_n$ ($R = Me_3SiCH_2$, $(Me_3Si)_2CH$, Ph; $n = 1$–4) [21] and $[(RCl_2Sn)(CH_2)_3]_2SnCl_2$ ($R = Me_3SiCH_2$) [22]. The reaction of $(Me_3SiCH_2(Cl_2)SnCH_2)_2CH_2$ with $(t\text{-}Bu_2SnO)_3$ [23] provided the first organostannoxane $\{[Me_3SiCH_2(Cl)Sn(CH_2)_3Sn(Cl)CH_2SiMe_3]O\}_4$ with a **B**-type double ladder structure [24]. A triple ladder structure was formed by the reaction of $\{[Me_3SiCH_2(Cl_2)Sn](CH_2)_3]_2SnCl_2$ with $(t\text{-}Bu_2SnO)_3$ [22]. In contrast the reaction of sterically crowded $[(Me_3Si)_2CH(Cl_2)SnCH_2]_2CH_2$ with KF/H_2O gave $\{(Me_3Si)_2CH(F)Sn(CH_2)_3Sn(F)CH(SiMe_3)_2]O\}_2$ with a dimeric **C**-type ladder structure of [25] whereas the reaction of $[(Me_3Si)_2CH(Cl_2)SnCH_2]_2CH_2$ with $(t\text{-}Bu_2SnO)_3$ provided the monomeric diorganostannoxane $\{(Me_3Si)_2CH(Cl)Sn(CH_2)_3Sn(Cl)CH(SiMe_3)_2]O\}$ (**D**-type) [25]. Apparently, the nature of both R and X control the degree of association in spacer-bridged organodistannoxanes of the general formula $\{[R(X)Sn(CH_2)_3Sn(X)R]O\}_n$.



(A)



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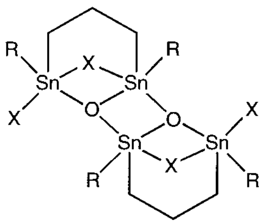

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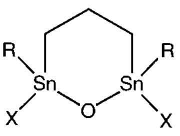


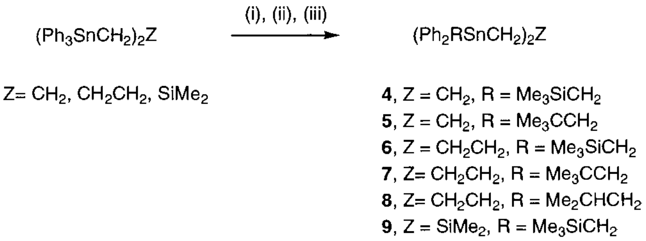
(D)

In continuation of our investigations on the influence of R, X, and the alkylidene spacer on the structure of organostannoxanes we now report on the syntheses of various compounds with **B**- and **C**-type ladder structures. Furthermore, we also report on the catalytic activity of some representative organostannoxanes in acylation reactions of alcohols.

2. Results and discussion

2.1. Synthetic aspects

The reaction of $(Ph_3SnCH_2)_2Z$ ($Z = CH_2$ [21a], CH_2CH_2 [26], $SiMe_2$ [22]) with iodine and subsequently with KF/H_2O gave the organotin fluorides $(Ph_2FSnCH_2)_2Z$ (**1**, $Z = CH_2$ [27]; **2**, $Z = CH_2CH_2$; **3**, $Z = SiMe_2$ [22]) which are almost insoluble in common organic solvents. They were used in subsequent reactions without further purification. Compounds **1**–**3** were converted into the tetraorganotin derivatives $(Ph_2RSnCH_2)_2Z$ (**4**, $Z = CH_2$, $R = Me_3SiCH_2$ [24]; **5**, $Z = CH_2$, $R = Me_3CCH_2$; **6**, $Z = CH_2CH_2$, $R = Me_3SiCH_2$; **7**, $Z = CH_2CH_2$, $R = Me_3CCH_2$; **8**, $Z = CH_2CH_2$, $R = Me_2CHCH_2$; **9**, $Z = SiMe_2$, $R = Me_3SiCH_2$) by reaction with the appropriate Grignard reagents RMgCl ($R = Me_3SiCH_2$, Me_3CCH_2, Me_2CHCH_2) (Scheme 1). Compounds **4**–**9** were obtained as oils and were used in subsequent reactions without further purification. The ^{119}Sn-NMR data of the intermediate products **4**–**9** are given in Table 1.



Scheme 1. Reaction sequence for the preparation of compounds **4**–**9**. (i) $2I_2$, -2 PhI, (ii) excess KF/H_2O, 2KI, (iii) 2RMgCl, -2MgClF ($R = Me_3SiCH_2$, Me_3CCH_2, Me_2CHCH_2).

Reaction of the tetraorganotin derivatives **4**–**9** with HCl or mercuric chloride afforded the tetrachloro derivatives $[R(Cl_2)SnCH_2]_2Z$ (**10**, $Z = CH_2$, $R = Me_3SiCH_2$ [24]; **11**, $Z = CH_2$, $R = Me_3CCH_2$; **12**, $Z = CH_2CH_2$, $R = Me_3SiCH_2$; **13**, $Z = CH_2CH_2$, $R = Me_3CCH_2$; **14**, $Z = CH_2CH_2$, $R = Me_2CHCH_2$; **15**, $Z = SiMe_2$, $R = Me_3SiCH_2$) (Eq. (1)). The tetrachloro derivatives **10**–**15** were isolated as crystalline solids. The ^{119}Sn-NMR data of compounds **10**–**15** are given in Table 1.

$$(Ph_2RSnCH_2)_2\ Z \xrightarrow[\text{or } 4HgCl_2/-4PhHgCl\ (10,\ 12,\ 15)]{4HCl/-4PhH} [R(Cl_2)SnCH_2]_2Z \qquad (1)$$

Table 1
^{119}Sn-NMR data of $(Ph_2RSnCH_2)_2Z$ (**4**–**9**) and $[R(Cl_2)SnCH_2]_2Z$ (**10**–**15**). Chemical shifts are given in ppm

	$(Ph_2RSnCH_2)_2Z$ $\delta(^{119}Sn)$		$[R(Cl)SnCH_2]_2Z$ $\delta(^{119}Sn)$	
$Z = CH_2$; $R = Me_3SiCH_2$ [24]	(**4**)	−62.4	(**10**)	132.8
$Z = CH_2$; $R = Me_3CCH_2$	(**5**)	−87.6	(**11**)	107.9
$Z = CH_2CH_2$; $R = Me_3SiCH_2$	(**6**)	−59.9	(**12**)	135.9
$Z = CH_2CH_2$; $R = Me_3CCH_2$	(**7**)	−83.3	(**13**)	113.4
$Z = CH_2CH_2$; $R = Me_2CHCH_2$	(**8**)	−76.9	(**14**)	120.2
$Z = SiMe_2$; $R = Me_3SiCH_2$	(**9**)	−89.7	(**15**)	134.7

where **10**, $Z = CH_2$, $R = Me_3SiCH_2$; **11**, $Z = CH_2$, $R = Me_3CCH_2$; **12**, $Z = CH_2CH_2$, $R = Me_3SiCH_2$; **13**, $Z = CH_2CH_2$, $R = Me_3CCH_2$; **14**, $Z = CH_2CH_2$, $R = Me_2CHCH_2$; **15**, $Z = SiMe_2$, $R = Me_3SiCH_2$.

Polymeric organotin oxides are usually obtained by complete hydrolysis of diorganotin dichlorides whereas partial hydrolysis of the latter gives dimeric tertaorganodistannoxanes [28]. In case of spacer-bridged di-tin compounds the reaction conditions of partial hydrolysis are difficult to control and normally lead to complex reaction mixtures. However, $(t\text{-}Bu_2SnO)_3$ can be used as source of anhydrous O^{2-} to convert the tetrachloro di-tin precursors **10**–**15** into their corresponding organotin-oxo-chloro-species (**B**–**D**) [22,24,25].

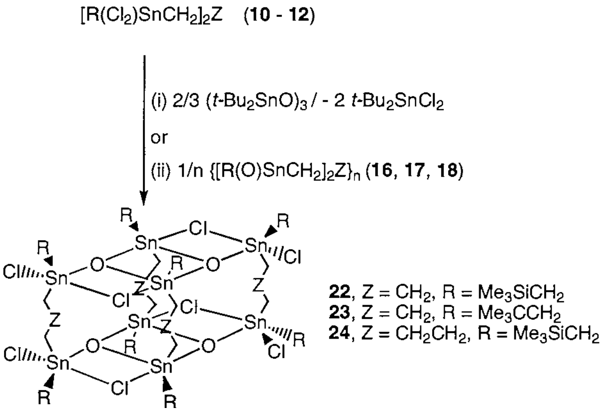
An alternative and even better method to obtain these compounds is the reaction of the tetrachloro di-tin derivatives with their corresponding organotin oxides [25]. The polymeric organotin oxides **16**–**21** were prepared by heating at reflux a mixture of the corresponding tetrachloro di-tin compounds **10**–**15** and sodium hydroxide in toluene/water (Eq. (2)). The almost insoluble organotin oxides **16**–**21** were isolated as colourless solids with melting points above 300°. The ^{119}Sn-MAS-NMR spectra of the organotin oxides **16**, **17**, and **21** show broad signals ($W_{1/2}$ ca. 3000 Hz) at -153 (**16**), -165 (**17**), and -157 ppm (**21**), which are indicative for polymeric structures with hypercoordinate tin atoms.

$$n\{R(Cl_2)SnCH_2]_2Z \xrightarrow{NaOH/water/toluene} \{[R(O)SnCH_2]_2Z\}_n \qquad (2)$$

where **16**, $Z = CH_2$, $R = Me_3SiCH_2$; **17**, $Z = CH_2$, $R = Me_3CCH_2$; **18**, $Z = CH_2CH_2$, $R = Me_3SiCH_2$; **19**, $Z = CH_2CH_2$, $R = Me_3CCH_2$; **20**, $Z = CH_2CH_2$, $R = Me_2CHCH_2$; **21**, $Z = SiMe_2$, $R = Me_3SiCH_2$.

Reaction of $[R(Cl_2)SnCH_2]_2Z$ (**10**, $Z = CH_2$, $R = Me_3SiCH_2$; **11**, $Z = CH_2$, $R = Me_3CCH_2$; **12**, $Z = CH_2CH_2$, $R = Me_3SiCH_2$) with $(t\text{-}Bu_2SnO)_3$ as well as the reaction of **10**–**12** with their corresponding organotin oxides **16**–**18** provided almost quantitatively the tin-oxo-chloro clusters **22**–**24** (Scheme 2). The use of polymeric $[Me_2SnO]_n$ instead of $(t\text{-}Bu_2SnO)_3$ as source of O^{2-} resulted in an incomplete conversion of the tetrachloro di-tin compounds into compounds of type **B**. Obviously, this is the result of a side reaction of Me_2SnCl_2 formed during the reaction with unreacted $[Me_2SnO]_n$ to give the tetraorganodistannoxane $[(Me_2ClSn)_2O]_2$ [29].

The ^{119}Sn-NMR spectra (Table 2) of **22**–**24** show two signals of equal integral ratio at $-96.1/-132.9$ ppm (**22**), $-106.0/-155.1$ ppm (**23**), and $-68.1/-143.0$ ppm (**24**), respectively. Furthermore, in the ^{119}Sn-NMR spectrum of the tetramethylene-bridged compound **24** there appeared two additional signals of minor but equal intensity (ca. 2%) at -68.9 and -141.2 ppm which are assigned to the **C**-type ladder compound (Scheme 3). For the tetramethylene-bridged organostannoxane **24** an equilibrium probably exists in solution between **B**- and **C**-type geometries with the **B**-type species dominating. The double ladder structures of compounds **22**–**24** in solution were confirmed by molecular weight determinations (Table 3).



Scheme 2. Synthesis of the double ladder compounds (**B**–type) **22**–**24**.

However, the negative ion ES mass spectrum of a solution of **24** in acetonitrile show cluster patterns at $m/z = 1126$, $m/z = 2217$, and $m/z = 2236$ which are indicative for the presence of $[$**24** (**B**-type) $+ 2\ OH]^{2-}$, $[$**24** (**B**-type) $- Cl + 2OH]^{-}$, and $[$**26** (**B**-type) $+ OH]^{-}$. Furthermore at $m/z = 590$ a cluster pattern being consistent with the anion **E** (Chart 2). The formation of **E** can be explained by dissociation of the **C**-type structure of **24** and complexation of a chloride.

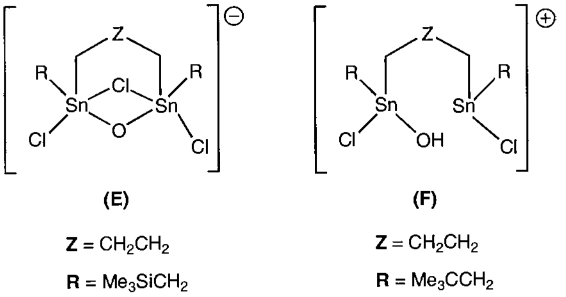
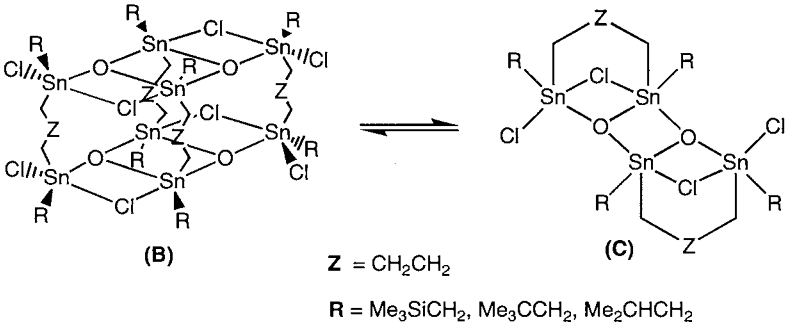


Table 2
^{119}Sn-NMR data of the ladder type compounds **22**–**28**[a]

	Sn_{exo}	Sn_{endo}
22	−96.1 [67]	−132.9 [69]
23	−106.0	−155.1
24	−68.1 [70] (48%); −68.9 (2%)	−141.2 (2%); −143.0 [70] (48%)
25	−84.7 [61] (25%); −86.1 [61] (25%)	−152.5 [61] (25%); −153.0 [61] (25%)
26	−77.6 [71] (10%); −78.8 [71] (40%)	−147.2 [71] (10%); −149.8 [71] (40%)
27	−60.6	−116.6 [82]
28[b]	−169.0 [191] (45%); −194.9 [112] (5%)	−202.0 [192] (45%); −224.4 [112] (5%)

[a] . The chemical shifts are given in ppm and the coupling constants ($^2J(^{119}Sn\text{–}O\text{–}^{117/119}Sn)$) in Hz.

[b] Concentration: 100 mg ml^{-1}.



Scheme 3. Proposed equilibrium between **B**-type and **C**-type ladder structures of **24**–**26** in solution.

In the solid state the double ladder structures of **22** [22], **23**, and **24** were confirmed by X-ray crystallography (see below). The ^{119}Sn-CP-MAS-NMR spectrum of compound **23** displays two resonances at -104 and -158 ppm which are very close to the resonances found in solution ($-106.0/-155.1$ ppm). This indicates the structure of the stannoxane to be basically the same in solution and in the solid state.

Replacement of $R = Me_3SiCH_2$ in the tetrachloro di-tin compound **12** by $R = Me_3CCH_2$ (**13**) or Me_2CHCH_2 (**14**) has a strong influence on the structure of the compounds formed by partial oxygen/chlorine exchange. The reaction of $[R(Cl_2)SnCH_2]_2Z$ (**13**, $Z = CH_2CH_2$, $R = Me_3CCH_2$; **14**, $Z = CH_2CH_2$, $R = Me_2CHCH_2$) with $(t\text{-}Bu_2SnO)_3$ as well as the reaction of **13** and **14** with their corresponding tin oxides **19** and **20** provided the tetraorgandistannoxanes **25** and **26** (Scheme 4). In solution, **25** and **26** exist in an equilibrium between **B**- and **C**-type ladder geometries as was described for **24** (Scheme 3). The ^{119}Sn-NMR spectrum of **25** and **26** each displays two sets of two signals at $-84.7/-152.5$ ppm and $-86.1/-153.0$ ppm for **25** with an integral ratio of 1:1:1:1 and at $-77.6/-147.2$ ppm and $-78.8/-149.8$ ppm for **26** with the integral ratio of 1:1:4:4. The resonances at low field are assigned to the exocyclic tins and those at high field to the endocyclic tins of both **B**- and **C**-type ladder structures.

The molecular weights in solution of **25** and **26** lie in between the expected values for a **B**- and **C**-type structure (Table 3) and support the proposed equilibrium according to Scheme 3. In addition the electrospray mass spectrum of a solution of **25** in acetonitrile indicates the presence of both **B**- and **C**-type structures. The negative ion mass spectrum shows a cluster pattern at $m/z = 2088$ which is consistent with the existence of [**25** (**B**-type) + 2OH − Cl]$^-$. The positive ion mass spectrum shows cluster patterns at $m/z = 2054$ for [**25** (**B**-type) − Cl]$^+$, $m/z = 2037$ for [**25** (**B**-type) − 2Cl + OH]$^+$, $m/z = 2017$ for [**25** (**B**-type) − 3Cl + 2OH]$^+$, and at $m/z = 523$ which is assigned to the presence of the cation **F** (Chart 2). The latter is formed by a dissociation/protonation process of the **C**-type structure of **25**.

To get further information on the influence of the spacer on the structure of spacer-bridged tin-oxo-chloro species we prepared $[Me_3SiCH_2(Cl_2)SnCH_2]_2SiMe_2$ (**15**) which has the more bulky $-CH_2SiMe_2CH_2-$spacer. Reaction of **15** with its corresponding tin oxide as well as its reaction with $(t\text{-}Bu_2SnO)_3$ gave the tetraorganodistannoxane **27** (Scheme 5). The molecular weight determination of **27** (Table 3) is consistent with the formation of a **C**-type structure in solution. Two signals of equal intensity at -60.6 and -116.6 ppm are observed in the ^{119}Sn-NMR spectrum of **27** in solution (Table 2). The ^{119}Sn-CP-MAS-NMR spectrum shows two broad resonances at -71 and -136 ppm which indicate the solution and solid state structures of **27** to be very similar.

The exchange of the chlorine atoms in compound **22** by acetate groups leads to the formation of the organotin-oxo-acetate cluster **28** (Scheme 6) with a **B**-type structure in the solid state which was confirmed by X-ray crystallography. In solution, compound **28** exhibits the same **B**-type/**C**-type equilibrium that was postulated for the tetramethylene-bridged ladder compounds **24**–**26**. The acetate substituted ladder compound **28** was prepared by the reaction of the **B**-type ladder compound **22** with silver acetate or by the reaction of the organotin oxide **16** with acetic acid. The molecular weight determination of **28** in $CHCl_3$ is in agreement with a **C**-type ladder structure dominating in solution at low concentration (Table 3). The ^{119}Sn-NMR spectrum of **28** in CH_2Cl_2 at low concentration (100 mg ml^{-1}) displays two major signals at -169.0 and -202.0 ppm and two signals of minor but equal intensity at -194.9 and -224.4 ppm. At a higher concentration (200 mg ml^{-1}) the intensity of the latter signals increases. When the concentration is lowered again, the intensity of these signals decrease. This concentration dependent ^{119}Sn-NMR spectrum can be explained by the existence of an equilibrium between **B**- and **C**-type structures with the **B**-type structure dominating at higher concentration. The ^{119}Sn-CP-MAS-NMR spectrum of **28** shows two equally intense signals at -179 and -194 ppm.

Table 3
Molecular weight determinations (g mol^{-1}) of ladder type compounds **22**–**28**

Compound	**B**-type (calc.)	**C**-type (calc.)	Found	Solvent	Concentration (mg ml^{-1})
22	2163	1082	1948	$CHCl_3$	7
23	2034	1017	2247	$CHCl_3$	20
24	2219	1105	2173	CH_2Cl_2	11
25	2090	1045	1207	CH_2Cl_2	16
26	1978	989	1213	$CHCl_3$	21
27	2334	1167	1048	$CHCl_3$	20
28	2352	1176	972	$CHCl_3$	20

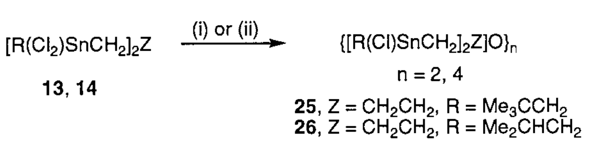
The infrared spectrum in KBr of **28** shows two $\nu(COO)_{as}$ and $\nu(COO)_{sym}$ absorptions. The $\nu(COO)_{as}$ at 1627 cm^{-1} is attributed to a monodentate acetate group and the $\nu(COO)_{as}$ at 1564 cm^{-1} to a bidentate acetate group [18,30]. In the free acid the asymmetric absorbtion $\nu(COO)_{as}$ is at 1718 cm^{-1} and in sodium acetate $\nu(COO)_{as}$ is observed at 1583 cm^{-1} [31]. For the monodentate acetate group the $\nu(COO)_{sym}$ appears at 1324 cm^{-1} whereas the $\nu(COO)_{sym}$ of the chelating carboxylate group appears at 1376 cm^{-1}. Thus, the $\Delta\nu$ values ($\Delta\nu = \nu(COO)_{as} - \nu(COO)_{sym}$) amount to 303 cm^{-1} for the monodentate and 188 cm^{-1} for the unsymmetrically chelating acetate group of **28**. These results are in line with the molecular structure discussed below. The infrared spectrum of **28** in solution (5% in $CHCl_3$) shows the same general trend that was found in the solid state. Two absorptions appear for $\nu(COO)_{as}$ at 1596 and 1555 cm^{-1} and two absorptions for $\nu(COO)_{sym}$ at 1423 and 1383 cm^{-1}, which are assigned to one bidentate and one monodentate acetate group. The $\Delta\nu$ value for the bidentate ligand amounts to 213 cm^{-1}, which indicates a weaker bonding of the acetate group to the tin atom in solution.

2.2. Molecular structures of **23**, **24**, and **28**

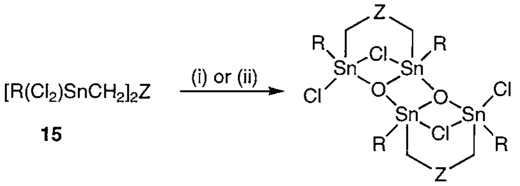
The molecular structures of compound **23**, **24**, and **28** are shown in Figs. 1–3 and selected bond distances and bond angles are given in Tables 4–6. The structures of **23**, **24**, and **28** contain a center of inversion and consist of typical double-ladder **B**-type arrangements [22,24] in which the monolayers are linked by four trimethylene (**23**, **28**) and four tetramethylene bridges (**24**). The $Sn_4Cl_4O_2$ layers in **23** and **24** are almost planar with the greatest deviation from the plane found in **23** for Cl(1) (0.159(1) Å) and in **24** for O(1) (0.080(6) Å). In the acetate derivative **28** a large distortion of the $Sn_4X_4O_2$ (X = OAc) layer was observed and the largest deviation is found for O(56) (0.806(4) Å).

The tin atoms in **23** and **24** each have a distorted trigonal bipyramidal geometry. For the exocyclic tin atoms, two carbons and one oxygen occupy the equatorial positions and two chlorines occupy the axial positions, while for the endocyclic tins the equatorial positions are occupied by two carbons and one oxygen and the axial positions by one oxygen and one chlorine. The bond lengths and bond angles in **23** and **24** show no peculiarities and are similar to those reported for **22** [24]. In **23** and **24** the shortest Sn–O bond lengths are found for the exocyclic tins (**23** Sn(1)–O(1) 2.020(3) Å; **24** Sn(4)–O(2) 2.010(6) Å) and the longest Sn–O bonds exist in the Sn_2O_2 core (**23** Sn(2)–O(2) 2.187(3) Å; **24** Sn(3)–O(2) 2.111(6) Å). It is worth noting that the difference in the Sn–O bond lengths is greater in **23** than **24**, which corresponds to the shorter Sn–Cl bond lengths of the bridging chlorine atoms found in **23** (Sn(2)–Cl(2) 2.577(2) Å, Sn(3)–Cl(4) 2.625(2) Å) compared to **24** (Sn(2)–Cl(4) 2.784(3) Å, Sn(3)–Cl(1) 2.829(3) Å).

In **28** the configuration around the tin atoms is best described as distorted trigonal bipyramid with each tin atom having two carbons and one oxygen in the equatorial positions and two oxygens in the axial positions. In contrast to **23**, **24**, $[(Me_2SnO_2CC_6H_4\text{-}p\text{-}CH_3)_2O]_2$ [17c], $[(n\text{-}Bu_2SnO_2CC_6H_4\text{-}o\text{-}CH_3)_2O]_2$ [17d], and $[(n\text{-}Bu_2SnO_2CC_6H_4\text{-}o\text{-}OH)_2O]_2$ [17d] the shortest Sn–O

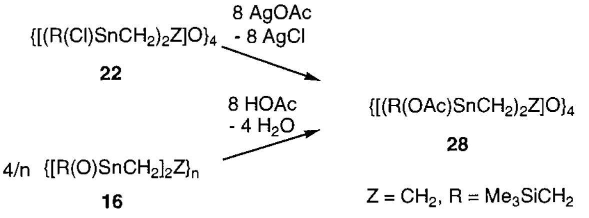


Scheme 4. Synthesis of ladder compounds starting from $[R(Cl_2)SnCH_2]_2Z$ (**13**, $Z = CH_2CH_2$, $R = Me_3CCH_2$; **14**, $Z = CH_2CH_2$, $R = MeCH_2CH_2$) by reaction with (i) $(t\text{-}Bu_2SnO)_3$ or (ii) the corresponding tin oxides $\{[R(O)SnCH_2]_2Z\}_n$ (**19**, **20**).



27, Z = $SiMe_2$, R = Me_3SiCH_2

Scheme 5. Synthesis of the **C**–type ladder compound **27**. (i) $(t\text{-}Bu_2SnO)_3$ or (ii) $\{[R(O)SnCH_2]_2Z\}_n$ (**21**) ($Z = SiMe_2$; $R = Me_3SiCH_2$).



Scheme 6. Preparation of the acetate ladder **28**.

bond lengths for **28** were found in the Sn_2O_2 core (Sn(2)–O(2) 2.036(5) Å; Sn(3)–O(1) 2.028(5) Å) as was previously described for $[(n\text{-}Bu_2SnO_2CCH_2\text{-}C_6F_6)_2O]_2$ [17e]. In **28** as well as in the above mentioned dicarboxylatotetraorganodistannoxanes two carboxylate groups of each layer are bonded in a bidentate fashion and two carboxylate groups show a monodentate coordination mode. The Sn–O bond distances for the chelating acetate lie in between the value for Sn(3)–O(52) (2.231(6) Å) and Sn(4)–O(56) (2.282(7) Å). The Sn–O bond lenghts for the monodentate acetate groups amount to 2.207(6) Å for Sn(1)–O(53) and 2.213(6) Å for Sn(4)–O(57). The bond angles of the bridging carboxylate ligands (O(51)–C(51)–O(52) 127.0(10)°; O(55)–C(55)–O(56) 127.3(10)°) correspond to a bidentate character, whereas the bond angles of the non-bridging carboxylate ligands (O(53)–C(53)–O(54) 119.4(11)°; O(58)–C(57)–O(57) 123.9(11)°) are indicative of a monodentate coordination mode. Furthermore, there are weak intramolecular Sn···O interactions between Sn(1) and O(54) (2.634(7) Å), Sn(2) and O(53) (3.124(7) Å), Sn(3) and O(57) (3.077(7) Å), and Sn(4) and O(58) (2.622(7) Å), which result in distortions from the ideal trigonal bipyramidal geometries at the tin atoms. The structural arrangement within the ladder layer of **28** represents that of the most common type of dicarboxylatotetraorganodistannoxanes [17b].

2.3. *Distannoxane-catalyzed acylation of alcohols*

Acylation of alcohols [32] as well as transesterifications [1,33] are the most important synthetic routes for the convenient synthesis of ester functionalized organic reagents. Due to their synthetic importance a large variety of catalysts has been studied in the last decade. For the acylation of alcohols with acetic anhydride either basic systems such as 4-(dialkylaminopyridine)-catalysts [34], Bu_3P [35], $MgBr_2$–R_3N [36] and an aminophosphine superbase [37] or *Lewis* acidic catalysts such as $Sc(OTf)_3$ [38] and $TiCl(OTf)_3$ [39] were used. The reversibility of the transesterification limits their application, but this problem can be overcome by the use of enol esters, which are transformed into aldehydes or ketones upon the interchange reaction. Normally, this process requires protic reaction conditions [40]. Recently, the use of $Cp^{*}_{2}Sm(THF)_2$ and SmI_2 as catalysts in the transesterification under inert conditions has been reported [41].

Previously, we reported that 1,3-dichlorotetrabutyidistannoxane [16], which adopts a ladder structure, serves as an efficient catalyst in the acylation of alcohols as well as in transesterification (enol-ester route) under virtually neutral conditions [8]. We therefore investigated the properties of selected spacer-bridged stannoxanes as catalysts in acylation reactions of alcohols with acetic anhydride (Scheme 7) and in acylation reactions with alkenyl acetates (Scheme 8).

In the acylation reaction of $PhCH_2CH_2OH$ and $n\text{-}C_8H_{17}OH$ with Ac_2O the compounds **22** and **24**–**26** have been tested (Table 8). Although all compounds show moderate catalytic activities it is worth noting that the conversion rate of $PhCH_2CH_2OH$ catalyzed by **22** is very low (entry 1), whereas **24**–**26** show no significant differences in activity. For the conversion of $n\text{-}C_8H_{17}OH$, high yields were obtained by the use of **25** (entry 7), but only moderate yields were obtained with **22**, **24**, and **26**.

Transesterifications with alkenyl acetates were carried out with the compounds **22**, **24**–**26**, and **28** as catalysts (Scheme 8, Table 9). In the presence of **25**, 2-phenylethanol as well as *n*-octanol were converted in high yields (entries 3, 7 and 11) and the same holds for **24** (entry 2) and **26** (entries 4 and 12). The trimethylene-bridged acetate double ladder **28** shows slightly lower conversion rates (entries 5, 9 and13) than the tetramethylene-bridged compounds **24**–**26**. In contrast to these results only low yields of conversion have been observed for the trimethylene-bridged double-ladder **22** (entries 1, 6 and 10).

These preliminary experiments suggest that the tetramethylene-bridged compounds **24**–**26** are more efficient catalysts in acylation reactions than the trimethylene-bridged compound **22**. Furthermore, the catalytic activity of the trimethylene-bridged and acetate containing compound **28** is only slightly lower than the activity of the tetramethylene-bridged derivatives **24**–**26**. These differences in catalytic activity seem to correlate with their structures in solution. We have shown the double-ladder structure of **22** to be kinetically inert in solution, whereas **24**–**26** and **28** are kinetically labile and show an equilibrium between **B**- and **C**-type structures in solution. Although all of the compounds tested here are less efficient catalysts when compared to the simple 1,3-dichlorotetrabutyldistannoxane, they can serve as models to study the relationship of structure and catalytic activity. Furthermore, preliminary investigations show compound **25** to discriminate effectively between primary and secondary alcohols in acetylation reactions.

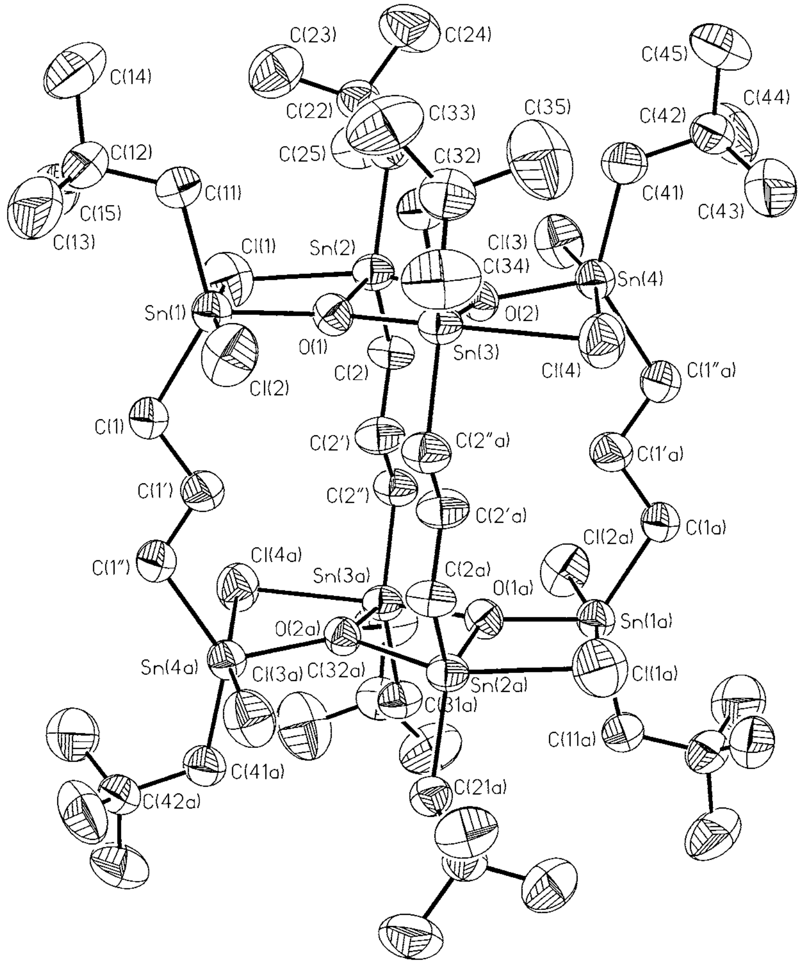


Fig. 1. General view (SHELXTL-PLUS) of a molecule showing 30% probability displacement ellipsoids and the atom numbering (symmetry transformations used to generate equivalent atoms: $a = -x, -y, -z$) for **23**.

3. Experimental

All solvents were dried and purified by standard procedures. Bruker DPX-300 and DRX400 spectrometers were used to obtain ^{1}H-, ^{13}C-, ^{29}Si- and ^{119}Sn-NMR spectra. Chemical shifts δ are given in ppm and were referenced against Me_4Si or Me_4Sn. ^{119}Sn-CP-MAS spectra were obtained from a Bruker MSL 400 spectrometer using cross-polarization and high power proton decoupling. Cy_4Sn was used as a secondary reference (δ -97.35 ppm). The IR spectra were recorded on a Bruker IFS 28 spectrometer. Molecular weight determinations were performed on a Knaur osmometer.

The electrospray mass spectra obtained with a Platform II single quadrupole mass spectrometer (Micromass, Altrincham, UK) using an acetonitrile mobile phase. Acetonitrile solutions of the compounds were injected directly into the spectrometer via a Rheodyne injector equipped with a 50 μl loop. A Harvard 22 syringe pump delivered the solutions to the vaporization nozzle of the electrospray ion source at a flow rate of 10 μl min^{-1}. Nitrogen was used as both a drying gas and for nebolization with flow rates of approx 200 ml min^{-1}, and 20 ml min^{-1}, respectively. Pressure in the mass analyzer region was usually about 4×10^{-5} mbar. Typically ten signal averaged spectra were collected.

The organotin fluorides $(Ph_2FSnCH_2)_2Z$ (**1**, $Z = CH_2$; **2**, $Z = CH_2CH_2$; **3**, $Z = SiMe_2$) were prepared according to literature procedures [27] and were used in further reactions without purification. Published procedures were used to prepare $[Ph_3SnCH_2]_2(CH_2)_2$ [26], $[Ph_2(Me_3SiCH_2)SnCH_2]_2CH_2$ (**4**), $[(Me_3SiCH_2)(Cl_2)SnCH_2]_2CH_2$ (**10**), $\{[Me_3SiCH_2(Cl)Sn(CH_2)_3Sn(Cl)CH_2SiMe_3]O\}_4$ (**22**) [24] and di(*tert*-butyl)tin oxide [23].

The typical experimental procedures for the acylation reactions follow below.

3.1. Acylation with acetic anhydride

An acetonitrile solution (1 ml) of alcohol (5 mmol), Ac_2O (10 mmol) and an organotin cluster (0.05 mmol) was stirred at 30°C for 20–50 h. The reaction mixture was washed with a $NaHCO_3$ solution and extracted

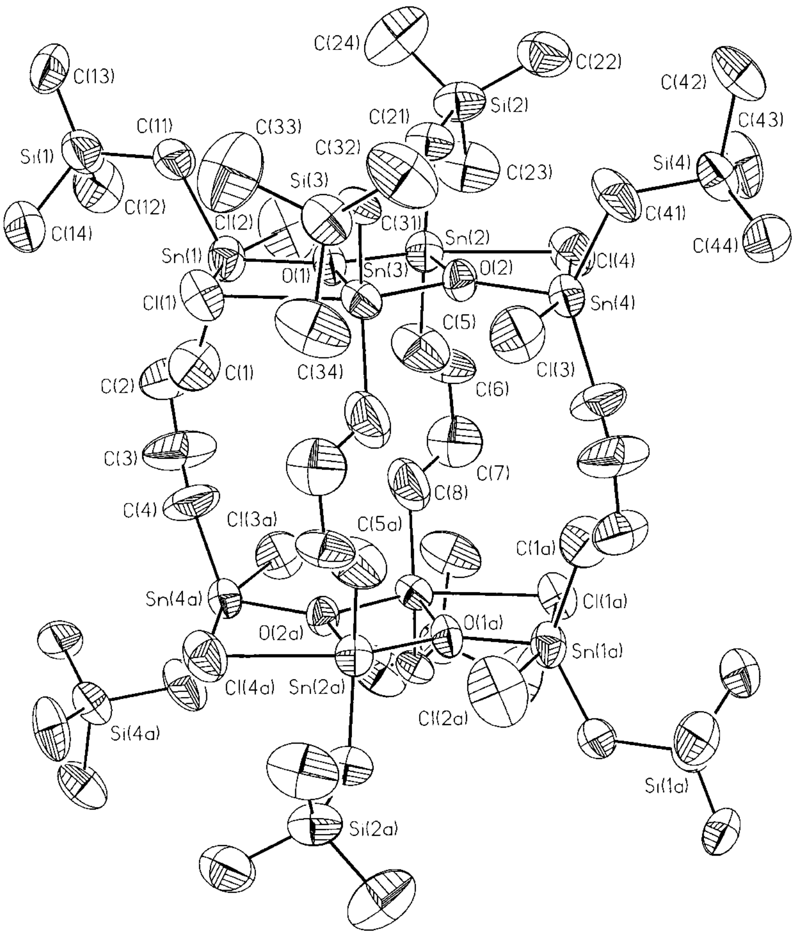


Fig. 2. General view (SHELXTL-PLUS) of a molecule showing 25% probability displacement ellipsoids and the atom numbering (symmetry transformations used to generate equivalent atoms: $a = -x, \ -y+1, \ -z+1$) for **24**.

with EtOAc. The solvent was removed in vacuum and the residue subjected for GLC analysis with $C_{18}H_{38}$ as internal standard. The crude mixture was purified by column chromatography on silica gel.

3.2. Acylation with alkenyl esters

To an alkenyl ester solution (3 ml) was added alcohol (5 mmol) and an organotin cluster (0.05 mmol). The solution was stirred for 24–48 h. The alkenyl ester was evaporated and the residue was subjected for GLC analysis with $C_{18}H_{38}$ as internal standard. The crude mixture was purified by column chromatography on silica gel.

3.3. Crystallography

Intensity data for the colorless crystals were collected on a Nonius KappaCCD diffractometer with graphite-monochromated Mo–K_α radiation (0.71069 Å) at 291 K. The data collections covered the sphere of reciprocal space with 360 frames via ω-rotation ($D/\omega = 1°$) at two times 5 s (**23**) and 10 s (**24**, **28**) per frame. The crystal-to-detector distance was 2.6 cm (**23**) and 2.7 cm (**24**, **28**). Crystal decay was monitored by repeating the initial frames at the end of data collection. Analyzing the duplicate reflections showed no indication of any decay. The structures were solved by direct methods SHELXS86 [42] and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods SHELXL93 [43].

The H atoms were placed in geometrically calculated positions using a riding model and refined with a common isotropic temperature factor (C_{aryl}–H 0.93 Å, $C_{prim.}$–H 0.96, $C_{sec.}$–H 0.97, U_{iso} 0.104(8) (**23**), 0.202(8) (**24**), and 0.106(8) (**28**) Å^2).

Disordered $SiMe_3$ groups were found in **24** with an occupancy of 0.65 (C(42), C(43)), 0.35 (C(42′), C(43′)), and 0.5 (C(12), C(13), C(14), C(44); C(12′), C(13′), C(14′), C(44′)) and in **28** with an occupancy of 0.7 (Si(1), C(12), C(13), C(14); Si(4), C(42), C(43), C(44)) and 0.3 (Si(1′), C(12′), C(13′), C(14′); Si(4′), C(42′), C(43′), C(44′)). Solvent molecules benzene **24** and toluene **28** (with an occupancy of 0.5) and the C atoms of the disordered $SiMe_3$ groups in **28** were refined isotropically.

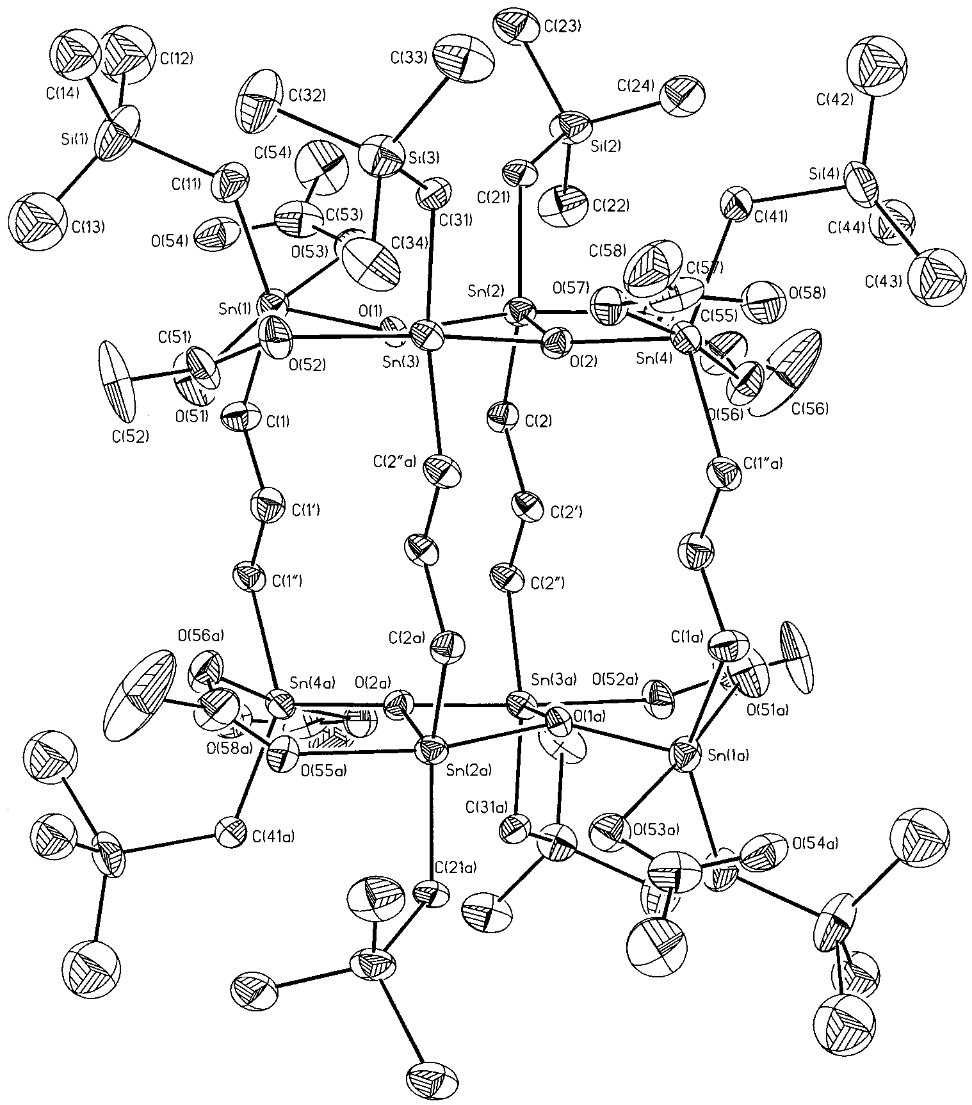


Fig. 3. General view (SHELXTL-PLUS) of a molecule showing 30% probability displacement ellipsoids and the atom numbering (symmetry transformations used to generate equivalent atoms: $a = -x, -y, -z+1$) for **28**.

Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from reference [44]. Figures were created by SHELXTL-Plus [45]. Crystallographic data are given in Table 7 and selected bond distances and bond angles are listed in Table 4 (**23**), Table 5 (**24**) and Table 6 (**28**).

3.4. Synthesis of $[(Me_3CCH_2)(Cl_2)SnCH_2]_2CH_2$ (**11**)

To a solution of Me_3CCH_2MgBr prepared from Me_3CCH_2Br (7.98 g, 53 mmol) and magnesium turnings (1.41 g, 58 mmol) in 70 ml THF, 1,3-bis(diphenylfluorostannyl)propane (**1**) (9.95 g, 16 mmol) was added in small portions. The reaction mixture was stirred for 16 h at room temperature and than heated at reflux for 1 h. The solvent was removed in vacuo to give a yellow oil which was dissolved in 70 ml diethyl ether and washed with 250 ml aqueous 2 M HCl. The aqueous solution was extracted two times with 50 ml diethyl ether and the etheral extract dried over Na_2SO_4. After filtration the solvent was removed in vacuo, yielding 10.61 g of 1,3-bis[diphenyl(2,2-dimethylpropyl)stannyl] propane (**5**) (^{119}Sn-NMR ($CDCl_3$/Cr(acac)$_3$, 111.92 MHz): $\delta = -87.6$ ppm) as a yellow oil. The oily residue was dissolved in 100 ml methylene chloride and a stream of HCl gas passed through the solution for 2 h. The solid material was filtered, the solvent removed in vacuo and the residue recrystallized from hexane to give 4.54 g (56%) **11** as colourless crystals of m.p. 72–73°C.

^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ 1.12 (s, 18H, $C(CH_3)_3$); δ 1.87 (t, 4H, CH_2Sn); δ 2.08 (s, 4H, CH_2Sn); δ 2.37 (complex pattern, 2H, CH_2). ^{13}C-NMR ($CDCl_3$, 100.63 MHz): δ 20.8 (CH_2); δ 30.0, 32.1 (CH_2Sn); δ 33.1 (Me_3C); δ 46.8 ($Me_3\mathit{C}$). ^{119}Sn-NMR ($CDCl_3$, 111.92 MHz): δ 107.9. Anal. Calc. for

Table 4
Selected bond distances (Å) and angles (°) for **23**

Sn(1)–O(1)	2.020(3)	Sn(2)–O(2)	2.187(3)	Sn(3)–O(2)	2.046(3)
Sn(2)–O(1)	2.056(3)	Sn(3)–O(1)	2.157(3)	Sn(4)–O(2)	2.029(3)
Sn(1)–Cl(1)	2.735(2)	Sn(2)–Cl(1)	2.577(2)	Sn(4)–Cl(3)	2.437(2)
Sn(1)–Cl(2)	2.452(2)	Sn(3)–Cl(4)	2.625(2)	Sn(4)–Cl(4)	2.809(2)
Sn(1)–C(1)	2.129(5)	Sn(2)–C(21)	2.122(5)	Sn(4)–C(1″a)	2.134(5)
Sn(1)–C(11)	2.124(5)	Sn(3)–C(2″a)	2.119(5)	Sn(4)–C(41)	2.127(5)
Sn(2)–C(2)	2.114(5)	Sn(3)–C(31)	2.125(5)		
O(1)–Sn(1)–C(11)	107.1 (2)	O(1)–Sn(2)–Cl(1)	79.78(10)	C(41)–Sn(4)–C(1″a)	135.0(2)
O(1)–Sn(1)–C(1)	114.9(2)	C(2)–Sn(2)–Cl(1)	88.7(2)	O(2)–Sn(4)–Cl(3)	91.77(9)
C(11)–Sn(1)–C(1)	135.1(2)	C(21)–Sn(2)–Cl(1)	100.71(14)	C(41)–Sn(4)–Cl(3)	97.7(2)
O(1)–Sn(1)–Cl(2)	91.31(9)	O(2)–Sn(2)–Cl(1)	152.39(8)	C(1″a)–Sn(4)–Cl(3)	98.0(2)
C(11)–Sn(1)–Cl(2)	98.3(2)	O(2)–Sn(3)–C(2″a)	117.7(2)	O(2)–Sn(4)–Cl(4)	75.07(9)
C(1)–Sn(1)–Cl(2)	96.0(2)	O(2)–Sn(3)–C(31)	108.5(2)	C(41)–Sn(4)–Cl(4)	88.8(2)
O(1)–Sn(1)–Cl(1)	76.52(9)	C(2″a)–Sn(3)–C(31)	133.7(2)	C(1″a)–Sn(4)–Cl(4)	85.5(2)
C(11)–Sn(1)–Cl(1)	89.1(2)	O(2)–Sn(3)–O(1)	74.44(11)	Cl(3)–Sn(4)–Cl(4)	166.59(5)
C(1)–Sn(1)–Cl(1)	85.9(2)	C(2″a)–Sn(3)–O(1)	97.9(2)	Sn(2)–Cl(1)–Sn(1)	82.74(6)
Cl(2)–Sn(1)–Cl(1)	167.24(6)	C(31)–Sn(1)–O(1)	94.9(2)	Sn(3)–Cl(4)–Sn(4)	81.88(4)
O(1)–Sn(2)–C(2)	117.7(2)	O(2)–Sn(3)–Cl(4)	79.24(9)	Sn(1)–O(1)–Sn(2)	119.1(2)
O(1)–Sn(2)–C(21)	110.2(2)	C(2″a)–Sn(3)–Cl(4)	88.7(2)	Sn(1)–O(1)–Sn(3)	133.1 (2)
C(2)–Sn(2)–C(21)	132.1(2)	C(31)–Sn(3)–Cl(4)	99.3(2)	Sn(2)–O(1)–Sn(3)	105.58(13)
O(1)–Sn(2)–O(2)	73.60(11)	O(1)–Sn(3)–Cl(4)	152.95(9)	Sn(4)–O(2)–Sn(3)	122.0(2)
C(2)–Sn(2)–O(2)	97.1(2)	O(2)–Sn(4)–C(41)	106.6(2)	Sn(4)–O(2)–Sn(2)	130.69(14)
C(21)–Sn(2)–O(2)	95.3(2)	O(2)–Sn(4)–C(1″a)	114.8(2)	Sn(3)–O(2)–Sn(2)	104.85(12)

$C_{13}H_{28}Cl_4Sn_2$: C, 27.70; H, 4.97. Found: C, 27.60; H, 5.00%.

*3.5. Synthesis of [(Me$_3$SiCH$_2$)(Cl$_2$)SnCH$_2$]$_2$(CH$_2$)$_2$ (**12**)*

To a solution of $[Ph_3SnCH_2]_2(CH_2)_2$ (90.0 g, 0.12 mol) in 200 ml methylene chloride was added iodine (60.4 g, 0.24 mol) at 0°C in small portions. The reaction mixture was stirred for 16 h at room temperature before evaporating the solvent in vacuo and removing the iodobenzene by distillation at 60°C (1×10^{-3} Torr). The residue was dissolved in 200 ml acetone and added dropwise to a magnetically stirred solution of KF (42.0 g, 0.72 mol) in 90 ml water. The suspension was stirred for 4 h at room temperature and the precipitate filtered and washed with 150 ml water and 150 ml diethyl ether to give quantitatively $[Ph_2FSnCH_2]_2(CH_2)_2$ (**2**) as a colourless solid (75 g, m.p. > 300°C), which was used in subsequent reactions without further purification. To a solution of Me_3SiCH_2MgCl, prepared from Me_3SiCH_2Cl (16.1 g, 0.13 mol) and Mg (3.51 g, 0.14 mol) in 250 ml THF, was added **2** (35.0 g, 55 mmol) in small portions. The reaction mixture was heated at reflux for 2 h and hydrolyzed with 150 ml of saturated ammonia chloride solution. The organic phase was separated and the aqueous solution extracted three times with 150 ml diethyl ether. The combined organic phases were dried over sodium sulfate which was then removed by filtration and the solvent evaporated in vacuo to give 36.60 g (86%) $[Ph_2(Me_3SiCH_2)SnCH_2]_2(CH_2)_2$ (**6**) as yellow oil (^{119}Sn-NMR (CH_2Cl_2/D_2O-cap., 111.92 MHz): $\delta = -59.9$ ppm). To a solution of **6** (36.60 g, 47 mmol) in 250 ml acetone was added a solution of $HgCl_2$ (51.18 g, 188 mmol) in 200 ml acetone at 0°C, followed by stirring for 15 h at room temperature. The precipitate of PhHgCl was removed by filtration and the solvent removed in vacuo. Diethyl ether (100 ml) was added to the residue and the suspension was stirred at room temperature for 10 min. After filtration the solvent was removed in vacuo. This procedure was repeated three times giving a colourless solid which was recrystallized from diethyl ether/hexane (1:1) to give 24.86 g (87% from **6**) of **12** as colourless crystals of m.p. 64–65°C.

^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ 0.17 (s, 18H, $SiMe_3$); δ 0.86 (s, 4H, $SiCH_2$, $^2J(^1H-^{117/119}Sn) = 87/91$ Hz); δ 1.73 (t, 4H, $SnCH_2$, $^2J(^1H-^{117/119}Sn) = 52$ Hz); δ 1.91 (quint, CH_2). ^{13}C-NMR ($CDCl_3$, 100.63 MHz): δ 1.1 ($SiMe_3$, $^3J(^{13}C-^{117/119}Sn) = 29$ Hz; $^1J(^{13}C-^{29}Si) = 53$ Hz; δ 14.8 ($SiCH_2$, $^1J(^{13}C-^{117/119}Sn) = 378/395$ Hz); 20.8 (CH_2); δ 28.5 (CH_2, $^2J(^{13}C-^{117/119}Sn) = 40$ Hz; $^3J(^{13}C-^{117/119}Sn) = 112/117$ Hz); δ 29.8 ($SnCH_2$, $^1J(^{13}C-^{117/119}Sn) = 556/583$ Hz). ^{119}Sn-NMR ($CDCl_3$, 149.21 MHz): δ 135.9. ^{29}Si-NMR (acetone-d_6, 79.49 MHz): δ 2.2. Anal. Calc. for $C_{12}H_{30}Cl_4Si_2Sn_2$: C, 27.70; H, 4.97. Found: C, 27.60; H, 5.00%.

*3.6. Synthesis of [(Me$_3$CCH$_2$)Ph$_2$SnCH$_2$]$_2$(CH$_2$)$_2$ (**7**)*

To a solution of Me_3CCH_2MgBr prepared from Me_3CCH_2Br (16.0 g, 0.106 mol) and Mg (2.83 g, 0.116 mol) in 250 ml THF was added 1,4-bis(diphenylfluorostannyl)butane (**2**) (35.0 g, 55 mmol) in small portions. The reaction mixture was heated at reflux for 1

Table 5
Selected bond distances (Å) and angles (°) for **24**

Sn(1)–O(1)	2.018(6)	Sn(2)–O(2)	2.078(6)	Sn(3)–O(2)	2.111(6)
Sn(2)–O(1)	2.105(5)	Sn(3)–O(1)	2.063(7)	Sn(4)–O(2)	2.010(6)
Sn(1)–Cl(1)	2.677(3)	Sn(2)–Cl(4)	2.784(3)	Sn(4)–Cl(3)	2.514(4)
Sn(1)–Cl(2)	2.497(4)	Sn(3)–Cl(1)	2.829(3)	Sn(4)–Cl(4)	2.722(4)
Sn(1)–C(1)	2.142(13)	Sn(2)–C(21)	2.068(10)	Sn(4)–C(4″a)	2.10(2)
Sn(1)–C(11)	2.082(11)	Sn(3)–C(8″a)	2.15(2)	Sn4)–C(41)	2.094(10)
Sn(2)–C(5)	2.069(13)	Sn(3)–C(31)	2.085(9)		
O(1)–Sn(1)–C(11)	115.2(3)	O(1)–Sn(2)–Cl(4)	149.6(2)	C(41)–Sn(4)–C(4″a)	139.2(7)
O(1)–Sn(1)–C(1)	108.2(4)	C(5)–Sn(2)–Cl(4)	90.0(4)	O(2)–Sn(4)–Cl(3)	84.3(2)
C(11)–Sn(1)–C(1)	135.5(5)	C(21)–Sn(2)–Cl(4)	87.1 (3)	C(41)–Sn(4)–Cl(3)	93.9(4)
O(1)–Sn(1)–Cl(2)	83.6(2)	O(2)–Sn(2)–Cl(4)	75.3(2)	C(4″a)–Sn(4)–Cl(3)	97.0(7)
C(11)–Sn(1)–Cl(2)	96.3(4)	O(2)–Sn(3)–C(8″a)	94.2(4)	O(2)–Sn(4)–Cl(4)	77.8(2)
C(1)–Sn(1)–Cl(2)	98.0(4)	O(2)–Sn(3)–C(31)	101.8(3)	C(41)–Sn(4)–Cl(4)	92.4(4)
O(1)–Sn(1)–Cl(1)	78.3(2)	C(8″a)–Sn(3)–C(31)	146.4(5)	C(4″a)–Sn(4)–Cl(4)	89.1(6)
C(11)–Sn(1)–Cl(1)	91.4(3)	O(2)–Sn(3)–O(1)	74.5(2)	Cl(3)–Sn(4)–Cl(4)	162.06(12)
C(1)–Sn(1)–Cl(1)	87.0(4)	C(8″a)–Sn(3)–O(1)	104.5(5)	Sn(1)–Cl(1)–Sn(3)	82.19(8)
Cl(2)–Sn(1)–Cl(1)	161.88(13)	C(31)–Sn(1)–O(1)	108.1 (3)	Sn(2)–Cl(4)–Sn(4)	82.19(8)
O(1)–Sn(2)–C(5)	97.8(4)	O(2)–Sn(3)–Cl(1)	148.5(2)	Sn(1)–O(1)–Sn(2)	128.4(3)
O(1)–Sn(2)–C(21)	101.0(3)	C(8″a)–Sn(3)–Cl(4)	94.7(4)	Sn(1)–O(1)–Sn(3)	125.1 (3)
C(5)–Sn(2)–C(21)	147.3(5)	C(31)–Sn(3)–Cl(1)	86.9(3)	Sn(2)–O(1)–Sn(3)	105.9(3)
O(1)–Sn(2)–O(2)	74.3(2)	O(1)–Sn(3)–Cl(1)	74.0(2)	Sn(4)–O(2)–Sn(3)	130.0(3)
C(5)–Sn(2)–O(2)	102.4(5)	O(2)–Sn(4)–C(41)	110.5(4)	Sn(4)–O(2)–Sn(2)	124.6(3)
C(21)–Sn(2)–O(2)	108.3(3)	O(2)–Sn(4)–C(4″a)	109.6(6)	Sn(3)–O(2)–Sn(2)	105.1(2)

day and hydrolyzed with 150 ml of saturated ammonia chloride solution. The organic phase was separated and the aqueous solution extracted three times with 150 ml diethyl ether. The combined organic phases were dried over sodium sulfate, which was then removed by filtration and the solvent evaporated in vacuo to give **7** (23.0 g, 83%) as a colourless solid of m.p. 65–66°C.

^{1}H-NMR (CDCl$_3$, 400.13 MHz): δ 0.96 (s, 18H, CMe$_3$); δ 1.24 (t, 4H, SnCH$_2$); δ 1.41 (s, 4H, CCH$_2$, $^2J(^1H-^{117/119}Sn) = 56$ Hz); δ 1.61 (quint, 4H, CH$_2$); 7.26–7.51 (complex pattern, 20H, H$_{aryl}$). ^{13}C-NMR (CDCl$_3$, 100.63 MHz): δ 11.7 (SnCH$_2$, $^1J(^{13}C-^{117/119}Sn) = 349/361$ Hz); δ 30.3 (C); δ 31.5 (CH$_2$, $^2J(^{13}C-^{117/119}Sn) = 20$ Hz, $^3J(^{13}C-^{117/119}Sn) = 66$ Hz); δ 31.7 (CCH$_2$); δ 33.4 (CMe$_3$ $^3J(^{13}C-^{117/119}Sn) = 35$ Hz); δ 128.2 (C$_m$, $^3J(^{13}C-^{117/119}Sn) = 45$ Hz); δ 128.22 (C$_p$);136.8 (C$_o$, $^2J(^{13}C-^{117/119}Sn) = 33$ Hz); δ 140.1 (C$_i$, $^1J(^{13}C-^{117/119}Sn) = 414/432$ Hz). ^{119}Sn-NMR (CH$_2$Cl$_2$/D$_2$O-Cap., 111.92 MHz): δ −83.3. Anal. Calc. for $C_{38}H_{50}Sn_2$: C, 61.33; H, 6.77. Found: C, 61.37; H, 6.36%.

3.7. Synthesis of [(Me$_3$CCH$_2$)(Cl$_2$)SnCH$_2$]$_2$(CH$_2$)$_2$ (13)

To a solution of **7** (21.78 g, 29 mmol) in 250 ml acetone was added a solution of HgCl$_2$ (31.78 g, 117 mmol) in 150 ml acetone at 0°C. The mixture was stirred for 15 h at room temperature before removing the precipitate of PhHgCl by filtration and evaporating the solvent in vacuo. Diethyl ether (100 ml) was added to the residue and the suspension stirred at room temperature for 10 min, followed by filtration and removal of the solvent in vacuo. This procedure was repeated until no precipitate was formed. The crude product was crystallized from diethyl ether/hexane (1:1) to give 13.66 g (81%) of **13** as colourless crystals of m.p. 76–78°C.

^{1}H-NMR (CDCl$_3$, 400.13 MHz): δ 1.11 (s, 18H, CMe$_3$); δ 1.77 (t, 4H, SnCH$_2$, $^2J(^1H-^{117/119}Sn) = 44$ Hz); δ 1.94 (quint, 4H, CH$_2$); δ 2.07 (s, 4H, CCH$_2$, $^2J(^1H-^{117/119}Sn) = 69$ Hz). ^{13}C-NMR (acetone-d$_6$, 100.63 MHz): δ 27.9 (CH$_2$, $^2J(^{13}C-^{117/119}Sn) = 35/42$ Hz, $^3J(^{13}C-^{117/119}Sn) = 76$ Hz); δ 29.8 (SnCH$_2$, $^1J(^{13}C-^{117/119}Sn) = 465/486$ Hz); δ 31.9 (C, $^2J(^{13}C-^{117/119}Sn) = 24$ Hz); δ 32.4 (CMe$_3$, $^3J(^{13}C-^{117/119}Sn) = 62$ Hz); δ 47.1 (CCH$_2$, $^1J(^{13}C-^{117/119}Sn) = 456/477$ Hz). ^{119}Sn-NMR (CH$_2$Cl$_2$/D$_2$O-Cap., 111.92 MHz): δ 113.4. Anal. Calc. for $C_{14}H_{30}Cl_4Sn_2$: C, 29.11; H, 5.23. Found: C, 28.95; H, 5.45%.

3.8. Synthesis of [(Me$_2$CHCH$_2$)(Cl$_2$)SnCH$_2$]$_2$(CH$_2$)$_2$ (14)

To a solution of Me$_2$CHCH$_2$MgBr prepared from Me$_2$CHCH$_2$Br (12.85 g, 94 mmol) and Mg (2.51 g, 103 mmol) in 250 ml THF was added, 1,4-bis(diphenylfluorostannyl)butane (**2**) (25.00 g, 39 mmol) in small portions. The reaction mixture was heated at reflux for 1 day and hydrolyzed with 150 ml of saturated ammonia chloride solution. The organic phase was separated and the aqueous solution extracted three times with 150 ml diethyl ether. The combined etheral phase was dried over sodium sulfate, filtered and the solvent evaporated in vacuo to give 26.88 g (96%) of [Ph$_2$(Me$_2$CHCH$_2$)-

Table 6
Selected bond distances (Å) and angles (°) for **28**

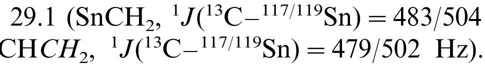
Sn(1)–O(1)	2.061(5)	Sn(2)–O(2)	2.036(5)	Sn(3)–O(52)	2.231(6)
Sn(1)–O(51)	2.263(7)	Sn(2)–O(55)	2.232(6)	Sn(4)–O(2)	2.054(5)
Sn(1)–O(53)	2.207(6)	Sn(3)–O(1)	2.028(5)	Sn(4)–O(56)	2.282(7)
Sn(2)–O(1)	2.167(5)	Sn(3)–O(2)	2.161(5)	Sn(4)–O(57)	2.213(6)
Sn(1)–C(1)	2.107(8)	Sn(2)–C(21)	2.103(7)	Sn(4)–C(1″a)	2.112(8)
Sn(1)–C(11)	2.110(8)	Sn(3)–C(2″a)	2.132(8)	Sn(4)–C(41)	2.106(8)
Sn(2)–C(2)	2.122(7)	Sn(3)–C(31)	2.112(7)	Sn(1)···O(54)	2.634(7)
Sn(2)···O(53)	3.124(7)	Sn(3)···O(57)	3.077(7)	Sn(4)···O(58)	2.622(7)
O(1)–Sn(1)–C(1)	107.3(3)	C(21)–Sn(2)–O(55)	89.1(3)	C(41)–Sn(4)–O(57)	98.0(3)
O(1)–Sn(1)–C(11)	104.3(3)	C(2)–Sn(2)–O(55)	86.2(3)	C(1″a)–Sn(4)–O(57)	93.1(3)
C(1)–Sn(1)–C(11)	147.6(4)	O(1)–Sn(2)–O(55)	165.4(2)	O(2)–Sn(4)–O(56)	90.7(2)
O(1)–Sn(1)–O(53)	84.8(2)	O(1)–Sn(3)–C(31)	106.1(3)	C(41)–Sn(4)–O(56)	88.8(3)
C(1)–Sn(1)–O(53)	95.3(3)	O(1)–Sn(3)–C(2″a)	117.2(3)	C(1″a)–Sn(4)–O(56)	83.5(3)
C(11)–Sn(1)–O(53)	94.7(3)	C(31)–Sn(3)–C(2″a)	136.6(3)	O(57)–Sn(4)–O(56)	172.1(2)
O(1)–Sn(1)–O(51)	91.0(2)	O(1)–Sn(3)–O(2)	76.0(2)	Sn(3)–O(1)–Sn(1)	129.1(2)
C(1)–Sn(1)–O(51)	83.4(3)	C(31)–Sn(3)–O(2)	98.9(3)	Sn(3)–O(1)–Sn(2)	103.0(2)
C(11)–Sn(1)–O(51)	88.9(3)	C(″2a)–Sn(3)–O(2)	93.9(3)	Sn(1)–O(1)–Sn(2)	124.3(2)
O(53)–Sn(1)–O(51)	175.0(3)	O(1)–Sn(3)–O(52)	91.0(2)	Sn(2)–O(2)–Sn(4)	129.2(3)
O(2)–Sn(2)–C(21)	107.3(3)	C(31)–Sn(3)–O(52)	88.4(3)	Sn(2)–O(2)–Sn(3)	103.0(2)
O(2)–Sn(2)–C(2)	116.3(2)	C(2″a)–Sn(3)–O(52)	88.5(3)	Sn(4)–O(2)–Sn(3)	124.5(2)
C(21)–Sn(2)–C(2)	136.1(3)	O(2)–Sn(3)–O(52)	166.4(2)	O(51)–C(51)–O(52)	127.0(10)
O(2)–Sn(2)–O(1)	75.7(2)	O(2)–Sn(4)–C(42)	106.0(3)	O(55)–C(55)–O(56)	127.3(10)
C(21)–Sn(2)–O(1)	100.0(3)	O(2)–Sn(4)–C(1″a)	109.0(3)	O(53)–C(53)–O(54)	119.4(11)
C(2)–Sn(2)–O(1)	94.7(3)	C(41)–Sn(4)–C(1″a)	144.2(3)	O(58)–C(57)–O(57)	123.9(11)
O(2)–Sn(2)–O(55)	90.9(2)	O(2)–Sn(4)–O(57)	83.8(2)		

$SnCH_2]_2(CH_2)_2$ (**8**) as a yellow oil (^{119}Sn-NMR (CH_2Cl_2/D_2O-Cap., 111.92 MHz): $\delta = -76.9$ ppm). Through a solution of **8** (26.88 g, 38 mmol) in 400 ml CH_2Cl_2 was passed a stream of HCl gas for 4 h at room temperature. The solvent was evaporated in vacuo and the residue crystallized from diethyl ether/hexane (1:1) to give 19.84 g (96%) of **14** as a colourless solid of m.p. 105–106°C.

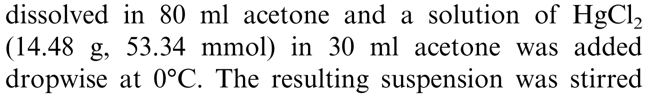
^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ 1.06 (d, 12H, $CHMe_2$); δ 1.77 (t, 4H, $SnCH_2$); δ 1.90 (d, 4H, $CHCH_2$, $^{2}J(^{1}H-^{117/119}Sn) = 58/61$ Hz); δ 1.92 (quint, 4H, CH_2); 2.29 (sept, 2H, CH).^{13}C-NMR (acetone-d_6, 100.63 MHz): δ 25.8 ($CHMe_2$, $^{3}J(^{13}C-^{117/119}Sn) = 77$ Hz); δ 26.1 (CH, $^{2}J(^{13}C-^{117/119}Sn = 33$ Hz); δ 28.5 (CH_2, $^{2}J(^{13}C-^{117/119}Sn) = 38$ Hz, $^{3}J(^{13}C-^{117/119}Sn) = 101/105$ Hz); δ 29.1 ($SnCH_2$, $^{1}J(^{13}C-^{117/119}Sn) = 483/504$ Hz); δ 40.2 ($CHCH_2$, $^{1}J(^{13}C-^{117/119}Sn) = 479/502$ Hz). ^{119}Sn-NMR (CH_2Cl_2/D_2O-Cap., 111.92 MHz): δ 120.2. Anal. Calc. for $C_{12}H_{26}Cl_4Sn_2$: C, 26.23; H, 4.77. Found: C, 26.51; H, 4.21%.

*3.9. Synthesis of $[(Me_3SiCH_2)(Cl_2)SnCH_2]_2SiMe_2$ (**15**)*

To a solution of Me_3SiCH_2MgCl prepared from chloromethyltrimethylsilane (6.50 g, 53 mmol) and magnesium turnings (1.30 g, 54 mmol) in 40 ml THF was added 1,3-bis(diphenylfluorostannylmethyl)dimethylsilane (**3**) (11.00 g, 16 mmol) in small portions. The reaction mixture was stirred for 18 h at room temperature and heated at reflux for 1 h. The solvent was removed in vacuo, the resulting oily residue dissolved in 70 ml diethyl ether and hydrolyzed with 60 ml aqueous 2 M HCl. After washing the aqueous solution three times with 20 ml of diethyl ether the combined organic extracts were dried over Na_2SO_4. After filtration the solvent was removed in vacuo to give 10.1 g of bis[diphenyl(trimethylsilylmethyl)stannylmethyl]dimethylsilane (**9**) as a yellow oil (^{119}Sn-NMR ($CDCl_3$/Cr(acac)$_3$, 111.92 MHz): $\delta = -89.7$). The oily residue was dissolved in 80 ml acetone and a solution of $HgCl_2$ (14.48 g, 53.34 mmol) in 30 ml acetone was added dropwise at 0°C. The resulting suspension was stirred overnight before removing the PhHgCl by filtration. After removing the solvent in vacuo the solid residue was suspended in 70 ml diethyl ether, the solid material filtered off and the solvent removed in vacuo. The residue was recrystallized from 80 ml hexane to give 4.41 g (43%) of **15** as a colourless solid of m.p. 109–111°C.



Scheme 7. Stannoxane catalyzed acylation with Ac_2O.



Scheme 8. Stannoxane catalyzed acylation with alkenyl acetates.

Table 7
Crystallographic data for **23**, **24**, and **28**

	23	**24**	**28**
Formula	$C_{52}H_{112}Cl_8O_4Sn_8$	$C_{48}H_{120}Cl_8O_4Si_8Sn_8 \cdot C_6H_6$	$C_{60}H_{136}O_{20}Si_8Sn_8 \cdot C_7H_8$
Formula weight	2034.54	2297.39	2444.06
Crystal system	Monoclinic	Triclinic	Monoclinic
Crystal size (mm)	0.15 × 0.10 × 0.10	0.20 × 0.10 × 0.08	0.25 × 0.20 × 0.20
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a (Å)	15.743(1)	13.015(1)	16.026(1)
b (Å)	11.335(1)	13.888(1)	22.323(1)
c (Å)	22.889(1)	16.186(1)	16.744(1)
α (°)	90	82.693(1)	90
β (°)	106.920(1)	70.904(1)	116.984(1)
γ (°)	90	61.167(1)	90
V (Å^3)	3907.7(5)	2420.3(3)	5338.0(5)
Z	2	1	2
$\rho_{calc.}$ (mg m^{-3})	1.729	1.576	1.521
μ (mm^{-1})	12.820	2.380	1.981
F(000)	1984	1130	2436
θ range (°)	4.55–25.67	2.81–19.61	2.55–23.00
Index ranges	$-19 \le h \le 19$ $-13 \le k \le 13$ $-27 \le l \le 26$	$-12 \le h \le 12$ $-10 \le k \le 13$ $-14 \le l < 15$	$-17 \le h \le 17$ $-24 \le k \le 24$ $-18 \le l \le 16$
No. of reflections collected	48 629	12 166	26 738
Completeness to θ_{max}	99.6	96.5	91.5
No. of independent reflections (R_{int})	7335/0.054	4104/0.027	6825/0.051
No. of reflections observed with ($I > 2\sigma(I)$)	4041	2097	3861
Absorption correction	None	None	None
No. of refined parameters	338	433	474
Goodness-of-fit on F^2	0.859	0.864	0.917
R_1 (F) ($I > 2\sigma(I)$)	0.0330	0.0380	0.0447
wR_2 (F^2) (all data)	0.0672	0.0954	0.0933
$(\Delta/\sigma)_{max}$	0.001	< 0.001	< 0.001
Largest difference peak/hole (e Å^{-3})	0.740/−0.877	0.452/−0.379	1.196/−0.694

^{1}H-NMR ($CDCl_3$, 200.13 MHz): δ 0.18 (s,18H, $SiMe_3$); δ 0.36 (s, 6H, $SiMe_2$); δ 0.88 (s, 4H, $SnCH_2$, $^2J(^{119}Sn-^1H) = 97$ Hz); δ 0.97 (s, 4H, $SnCH_2$, $^2J(^{119}Sn-^1H) = 81$ Hz). ^{13}C-NMR ($CDCl_3$, 100.63 MHz): δ 1.1 ($SiMe_3$); δ 2.2 (CH_2Si); δ 13.3 (CH_2Sn); δ 13.7 (CH_2Sn). ^{119}Sn-NMR ($CDCl_3$/Cr(acac)$_3$, 111.92 MHz): δ 134.7. Anal. Calc. for $C_{12}H_{32}Cl_4Si_3Sn_2$: C, 22.56; H, 4.85. Found: C, 22.10; H, 4.90%.

Table 8
Acylation with Ac_2O[a]

Entry	ROH	Compound	Reaction time (h)	Yield (%)
1	$PhCH_2CH_2OH$	**22**	48	48[b]
2		**24**	20	79[b]
3		**25**	20	82[b]
4		**26**	48	76[b]
5	n-$C_8H_{17}OH$	**22**	50	73[c]
6		**24**	30	75[c]
7		**25**	30	93[c]
8		**26**	50	70[c]

[a] Reaction conditions: ROH (5 mmol); compound (0.05 mmol); Ac_2O (10 mmol); CH_3CN (1 ml).

[b] Isolated yield after column chromatography.

[c] GLC yield.

*3.10. Synthesis of [(Me$_3$SiCH$_2$)(O)SnCH$_2$]$_2$CH$_2$ (**16**)*

To a solution of **10** (3.56 g, 5.88 mmol) in 80 ml toluene, was added dropwise at room temperature a solution of NaOH (7.17 g, 0.18 mol) in 50 ml water. The reaction mixture was heated at reflux for 55 h. The aqueous phase was separated and the precipitate isolated by filtration to give **16** (2.50 g, 88%) as a colourless solid with a m.p. > 300°C.

^{119}Sn-CP-MAS-NMR: δ −153 ppm. Anal. Calc. for $C_{11}H_{28}O_2Si_2Sn_2$: C, 27.18; H, 5.81. Found: C, 27.10; H, 6.30%.

*3.11. Synthesis of [(Me$_3$CCH$_2$)(O)SnCH$_2$]$_2$CH$_2$ (**17**)*

To a solution of NaOH (4.24 g, 0.11 mmol) in 75 ml water was added dropwise at room temperature a solution of **11** (2.00 g, 3.55 mmol) in 75 ml methanol. The reaction mixture was stirred for 65 h. The precipitate was isolated by filtration to give **17** (0.93 g, 58%) as a colourless solid with a m.p. > 300°C.

Table 9
Acylation with alkenyl acetates[a]

Entry	ROH	R′	Compound	Reaction time (h)	Yield (%)
1	$PhCH_2CH_2OH$	H	**22**	48	57(20)[b]
2			**24**	24	94(72)[b]
3			**25**	24	95(72)[b]
4			**26**	48	92(66)[b]
5			**28**	48	88
6		CH_3	**22**	48	15
7			**25**	48	85
8			**26**	48	75
9			**28**	48	88
10	n-$C_8H_{17}OH$		**22**	48	67
11			**25**	24	98
12			**26**	48	97
13			**28**	48	76

[a] Reaction conditions: ROH (5 mmol); compound (0.05 mmol); alkenyl ester (3 ml).

[b] GLC yield; isolated yield after column chromatography in parenteses.

^{119}Sn-CP-MAS-NMR: −165 ppm. Anal. Calc. for $Cl_3H_{28}O_2Sn_2$: C, 34.41; H, 6.22. Found: C, 35.00; H, 6.55%.

*3.12. Synthesis of [(Me$_3$SiCH$_2$)(O)SnCH$_2$]$_2$(CH$_2$)$_2$ (**18**)*

To a solution of NaOH (5.90 g, 148 mmol) in 50 ml water was added, dropwise at 0°C, a solution of **12** (3.00 g, 5 mmol) in 30 ml methanol. The reaction mixture was stirred for 4 days. The precipitate was isolated by filtration and washed with 100 ml water and 150 ml methanol to give **18** (1.65 g, 67%) as colourless a solid with a m.p. > 350°C.

Anal. Calc. for $C_{12}H_{30}O_2Si_2Sn_2$: C, 28.83; H, 6.05. Found: C, 28.60; H, 6.10%.

*3.13. Synthesis of [(Me$_3$CCH$_2$)(O)SnCH$_2$]$_2$(CH$_2$)$_2$ (**19**)*

In a similar manner to **18**, compound **19** was prepared from NaOH (6.23 g, 156 mmol) and **13** (3.00 g, 5 mmol) and was obtained as a colourless solid (2.06 g, 85%) of m.p. > 350°C. Anal. Calc. for $C_{14}H_{30}O_2Sn_2$: C, 35.95; H, 6.46. Found: C, 35.30; H, 6.70%.

*3.14. Synthesis of [(Me$_2$CHCH$_2$)(O)SnCH$_2$]$_2$(CH$_2$)$_2$ (**20**)*

In a similar manner to **18**, compound **20** was prepared from NaOH (8.73 g, 218 mmol) and **14** (3.00 g, 5 mmol) and was obtained as a colourless solid (2.24 g, 93%) of m.p. > 350°C.

Anal. Calc. for $C_{12}H_{26}O_2Sn_2$: C, 32.78; H, 5.96. Found: C, 32.40; H, 5.90%.

*3.15. Synthesis of [(Me$_3$SiCH$_2$)(O)SnCH$_2$]$_2$SiMe$_2$ (**21**)*

To a solution of **15** (1.18 g,1.84 mmol) in 35 ml toluene was added dropwise a solution of NaOH (2.21 g, 55.20 mol) in 20 ml water. The reaction mixture was heated at reflux for 3 days. The precipitate which formed was isolated by filtration to give **21** (0.85 g, 87%) as a colourless solid of m.p. > 300°C.

^{119}Sn-CP-MAS-NMR: −157 ppm. Anal. Calc. for $C_{12}H_{32}O_2Si_3Sn_2$: C, 27.19; H, 6.09. Found: C, 27.40; H, 6.20%.

*3.16. Synthesis of {[(Me$_3$CCH$_2$(Cl)SnCH$_2$)$_2$CH$_2$]O}$_4$ (**23**)*

3.16.1. Method A

To a solution of **11** (800 mg, 1.40 mmol) in 10 ml methylene chloride was added (t-Bu_2SnO)$_3$ (353 mg, 0.50 mmol) at room temperature. The resulting solution was heated at reflux for 10 min and left for 2 h at room temperature. The precipitate was filtered and dried in vacuo to give 616 mg (86%) of **23** as a colourless solid of m.p. 295–297°C.

3.16.2. Method B

To a solution of **11** (274 mg, 0.49 mmol) in 10 ml methylene chloride was added **17** (222 mg, 0.49 mmol) at room temperature. The resulting suspension was stirred at room temperature until the solution became clear. Recrystallization from methylene chloride at −20°C yielded 277 mg (57%) of **23** as a colourless solid of m.p. 300–302°C.

^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ 1.09 (s, 36H, $(CH_3)_3C$); δ 1.21 (s, 36H, $(CH_3)_3C$); δ 1.73 (complex pattern, 8H, CH_2); δ 1.86 (s, 8H, CH_2Sn); δ 2.02 (s, 8H, CH_2Sn); δ 2.43 (complex pattern, 8H, CH_2Sn); δ 2.55 (complex pattern, 8H, CH_2Sn). ^{13}C-NMR ($CDCl_3$, 100.63 MHz): δ 20.9 (CH_2); δ 21.5 (CH_2); δ 31.8 (Me_3*C*); δ 32.3 (Me_3*C*); δ 33.4 (Me_3C); δ 33.7 (Me_3C); δ 38.1 (CH_2Sn); δ 39.9 (CH_2Sn); δ 48.2 (CH_2Sn); δ 52.5 (CH_2Sn). ^{119}Sn-NMR ($CDCl_3$, $Cr(acac)_3$, 111.92 MHz): δ −106.0; δ −155.1. Molecular weight determination ($CHCl_3$): 2247 g mol^{-1}. Anal. Calc. for $C_{64}H_{112}Cl_8O_4Sn_8$: C, 30.70; H, 5.55. Found: C, 31.20; H, 5.95%.

3.17. Synthesis of {[(Me_3SiCH_2(Cl)$SnCH_2$)$_2$(CH_2)$_2$]O}$_4$ (**24**)

To a solution of **12** (1.52 g, 2.50 mmol) in 50 ml toluene was added **18** (1.25 g, 2.50 mmol) at room temperature. The reaction mixture was heated at reflux for 12 h. After filtration the solvent was evaporated in vacuo and the residue crystallized from toluene to give **24** (2.42 g, 87%) as colourless crystals of m.p. 203–204°C.

^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ 0.13 (s, 36H, Me_3Si); δ 0.17 (s, 36H, Me_3Si); δ 0.88 (s, 8H, CH_2Si); δ 0.92 (s, 8H, CH_2Si); δ 1.67–2.06 (complex pattern, 32H, CH_2Sn/CH_2). ^{13}C-NMR ($CDCl_3$, 100.63 MHz): δ 1.28 (CH_3Si, $^3J(^{13}C-^{117/119}Sn) = 52/60$ Hz); δ 1.84 (CH_3Si, $^3J(^{13}C-^{117/119}Sn) = 52/60$ Hz); δ 18.10 ($SiCH_2$); δ 19.41 ($SiCH_2$); δ 28.31 (CH_2); δ 29.14 (CH_2); δ 30.94 ($SnCH_2$); δ 32.65 ($SnCH_2$). ^{119}Sn-NMR (toluene, D_2O-Cap., 111.92 MHz): δ −68.1 ($^2J(^{119}Sn-^{117/119}Sn) = 70$ Hz, 48%); δ −68.9 (2%); δ −141.2 (2%); δ −143.0 ($^2J(^{119}Sn-^{117/119}Sn) = 70$ Hz, 48%). Molecular weight determination ($CHCl_3$): 2173 g mol^{-1}. Anal. Calc. for $C_{48}H_{120}Cl_8O_4Si_8Sn_8$: C, 25.98; H, 5.45. Found: C, 25.80; H, 5.60%.

3.18. Synthesis of {[(Me_3CCH_2(Cl)$SnCH_2$)$_2$(CH_2)$_2$]O}$_2$ (**25**)

3.18.1. Method A

In a similar manner to **23** (method A), compound **25** was prepared from **13** (1.85 g, 3.2 mmol) and **19** (1.50 g, 3.2 mmol) and obtained as a colourless solid (2.86 g, 85%) of m.p. 183–184°C.

^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ 1.08 (s, 9H, Me_3C); δ 1.09 (s, 9H, Me_3C); δ 1.18 (s, 9H, Me_3C); δ 1.20 (s, 9H, Me_3C); δ 1.62–2.24 (complex pattern, 16H, CH_2Sn/CH_2); δ 2.04 (CH_2Sn); δ 2.05 (CH_2Sn); δ 2.12 (CH_2Sn); δ 2.13 (CH_2Sn). ^{13}C-NMR ($CDCl_3$, 100.63 MHz): δ = 24.84, 27.01, 27.53, 29.07, 30.05, 32.05 34.54 (CH_2/$SnCH_2$); 31.98, 32.00, 32.03 (C); 33.04, 33.14, 33.28 (C*Me*$_3$); 49.91; 50.10, 52.56, 52.65 (C*CH*$_2$) [46]. ^{119}Sn-NMR (toluene, D_2O-Cap., 111.92 MHz): δ −84.7 ($^2J(^{119}Sn-^{117/119}Sn) = 61$ Hz, 25%); δ −86.1 ($^2J(^{119}Sn-^{117/119}Sn) = 61$ Hz, 25%); δ −152.5 ($^2J(^{119}Sn-^{117/119}Sn) = 61$ Hz, 25%); δ −153.0 ($^2J(Sn-^{117/119}Sn) = 61$ Hz, 25%). Molecular weight determination (CH_2Cl_2): 1207 g mol^{-1}. Anal. Calc. for $C_{28}H_{60}Cl_4O_2Sn_4$: C, 32.17; H, 5.78. Found: C, 31.70; H, 5.50%.

3.18.2. Method B (in situ generation)

Compound **13** (200 mg, 0.346 mol) and (*t*-Bu_2SnO)$_3$ (86 mg, 0.115 mmol) were dissolved in 3 ml $CHCl_3$ and heated to 50°C for 2 min. A ^{119}Sn-NMR spectrum of this solution was recorded. ^{119}Sn-NMR ($CHCl_3$, D_2O-Cap., 111.92 MHz): δ 53.9 (*t*-Bu_2SnCl_2); δ −83.9 (22%); δ −86.2 (28%); δ −147.6 (28%); δ −148.2 (22%).

3.19. Synthesis of {[(Me_2CHCH_2(Cl)$SnCH_2$)$_2$ (CH_2)$_2$]O}$_2$ (**26**)

3.19.1. Method A

In a similar manner to **23** (method A), compound **26** was prepared from **14** (0.62 g, 1.14 mmol) and **20** (0.50 g, 1.14 mmol) and obtained as a colourless solid (1.08 g, 96%) with a m.p. 215–216°C.

^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ 1.02–1.06 (complex pattern, 24H, *Me*$_2$CHCH$_2$); 1.73–1.97 (complex pattern, 24H, $SnCH_2/CH_2$); 2.25–2.40 (complex pattern, 4H, *Me*$_2$*CH*CH$_2$). ^{13}C-NMR ($CDCl_3$, 100.63 MHz): δ = 24.50, 24.86, 24.99 (Me_2*CH*CH_2); 24.70, 24.81, 25.06, 25.13 (*Me*$_2$CHCH$_2$); 26.57, 27.09, 27.70, 28.04, 30.00, 31.36, 32.78, 41.95, 42.55, 43.13, 43.43 (CH_2Sn) [46]. ^{119}Sn-NMR (toluene, D_2O-Cap., 111.92 MHz): δ −77.6 ($^2J(^{119}Sn-^{117/119}Sn) = 71$ Hz, 10%); δ −78.8 ($^2J(^{119}Sn-^{117/119}Sn) = 71$ Hz, 40%); δ −147.2 ($^2J(^{119}Sn-^{117/119}Sn) = 71$ Hz, 40%); δ −149.8 ($^2J(^{119}Sn-^{117/119}Sn) = 71$ Hz, 10%). Molecular weight determination ($CHCl_3$): 1213 g mol^{-1}. Anal. Calc. for $C_{24}H_{52}Cl_4O_2Sn_4$: C, 29.14; H, 5.30. Found: C, 28.90; H, 5.10%.

3.19.2. Method B

Compound **14** (200 mg, 0.364 mmol) and (*t*-Bu_2SnO)$_3$ (91 mg, 0.121 mmol) were dissolved in 3 ml $CHCl_3$ and heated at 50°C for 2 min. A ^{119}Sn-NMR spectrum of this solution was recorded. ^{119}Sn-NMR ($CHCl_3$, D_2O-Cap., 111.92 MHz): δ 53.6 (*t*-Bu_2SnCl_2); δ −78.1 ($^2J(^{119}Sn-^{117/119}Sn)$ not observed, 10%); δ −78.4 ($^2J(^{119}Sn-^{117/119}Sn) = 72$ Hz, 40%); δ −144.1 ($^2J(^{119}Sn-^{117/119}Sn) = 72$ Hz, 40%); δ −145.4 ($^2J(^{119}Sn-^{117/119}Sn)$ not observed, 10%).

3.20. Synthesis of {[(Me_3SiCH_2(Cl)$SnCH_2$)$_2$$SiMe_2$]O}$_2$ (**27**)

3.20.1. Method A

To a solution of **15** (362 mg, 0.57 mmol) in 35 ml methylene chloride was added **21** (300 mg, 0.57 mmol). The reaction mixture was heated at reflux for 20 h and after filtration the solvent was evaporated to give 540 mg (82%) **27** as a colourless solid of m.p. 123–126°C.

^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ 0.12 (s, 18H, Me_3Si); δ 0.20 (s, 18H, Me_3Si); δ 0.26 (s, 6H, Me_2Si); δ 0.34 (s, 6H, Me_2Si); δ 0.67-1.23 (complex pattern, 16H, CH_2Sn). ^{13}C-NMR ($CDCl_3$, 100.63 MHz): δ 1.2 (Me_3Si, $^1J(^{13}C-^{29}Si) = 29$ Hz); 1.8 (Me_3Si, $^1J(^{13}C-^{29}Si) = 30$ Hz); δ 3.7 (Me_2Si); δ 5.8 (Me_2Si, $^1J(^{13}C-^{29}Si) = 50$ Hz); δ 14.9 (CH_2Sn); δ 17.7 (CH_2Sn); 19.8 (CH_2Sn); 21.2 (CH_2Sn). ^{119}Sn-NMR ($CDCl_3$, 111.92 MHz): δ -60.6; δ -116.6 ($^2J(^{119}Sn-^{117/119}Sn) = 82$ Hz). ^{29}Si-NMR ($CDCl_3$, 59.63): 1.2 ($SiMe_2$); 1.9 ($^2J(^{29}Si-^{119}Sn) = 39$ Hz, Me_3Si); δ 4.7 ($^2J(^{29}Si-^{119}Sn) = 59$ Hz, Me_3Si). ^{119}Sn-CP-MAS-NMR: δ -71; δ -136 ppm. Molecular weight determination ($CHCl_3$): 1048 g mol^{-1}. Anal. Calc. for $C_{24}H_{64}O_2Cl_2Si_6Sn_4$: C, 24.64; H, 5.52. Found: C, 25.00; H, 5.90%.

3.20.2. Method B

Compound **15** (100 mg, 0.17 mmol) and (t-$Bu_2SnO)_3$ (84 mg, 0.34 mmol) were dissolved in 3 ml $CHCl_3$ and heated at 50°C for 2 min. A ^{119}Sn-NMR spectrum of this solution was recorded. ^{119}Sn-NMR ($CHCl_3$, D_2O-Cap., 111.92 MHz): δ -64.8 $^2J(^{119}Sn-^{117/119}Sn) = 80$ Hz; δ -121.3 $^2J(^{119}Sn-^{117/119}Sn)$ 78 Hz).

3.21. Synthesis of $\{[(Me_3SiCH_2(OAc)SnCH_2)_2CH_2]O\}_4$ (**28**)

3.21.1. Method A

Silver acetate (1.11 g, 6.66 mmol) was added at room temperature to a solution of **22** (1.80 g, 0.832 mmol) in 250 ml toluene and the reaction mixture stirred for 8 days in the dark. The solid material was removed by filtration and the solution concentrated to 10 ml. Crystallization at 0°C yielded 740 mg (38%) of **28** as colourless crystals of m.p. 163–167°C.

^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ 0.09 (s, 36H, $SiMe_3$); δ 0.12 (s, 36H, SiMe3); δ 0.26 (AA′-pattern, 4H, $SiCH_2$); δ 0.50 (AA′-pattern, 4H, $SiCH_2$); δ 0.64 (AA′-pattern, 4H, $SiCH_2$); δ 0.85 (AA′-pattern, 4H, $SiCH_2$); δ 1.35-1.65 (complex pattern, 16H, $SnCH_2$); δ 1.91 (s, 12H, $C(O)CH_3$); δ 1.96 (s, 12H, $C(O)CH_3$); δ 2.25–2.45 (complex pattern, 8H, CH_2). ^{13}C-NMR ($CDCl_3$, 100.63 MHz): δ 0.1, 0.2 ($SiMe_3$); δ 10.8, 11.3 (CH_2Si); δ 21.4, 22.1 ($C(O)\mathit{CH}_3$); δ 20.8, 23.1, 28.1, 28.8 (CH_2/CH_2Sn); δ 176.7, 180.0 ($\mathit{C}(O)CH_3$). ^{119}Sn-NMR (100 mg ml^{-1} $CDCl_3$, 149.21 MHz): δ -168.9; δ -194.9; δ -201.5; δ -224.0 (integral ratio 10:1:10:1). ^{119}Sn-NMR (500 mg ml^{-1}, $CDCl_3$, 149.21 MHz): δ -169.0; δ -195.0; δ -202.0; δ -224.4 (integral ratio 5:1:5:1). Molecular weight determination ($CHCl_3$, 20 mg ml^{-1}): 972 g mol^{-1}. IR (KBr): ν(COO) as 1627, 1564 cm^{-1}; $\nu(COO)_{sym}$ 1376, 1324 cm^{-1}. IR ($CHCl_3$): ν(COO) as 1596, 1555 cm^{-1}; $\nu(COO)_{sym}$ 1422, 1383 cm^{-1}. Anal. Calc. for $C_{60}H_{136}O_{20}Si_8Sn_8$: C, 30.64; H, 5.82. Found: C, 30.85; H, 6.15%.

3.21.2. Method B (in situ generation of **28**)

Compound **16** (300 mg, 0.62 mmol) and acetic acid (74 mg, 1.23 mmol) were dissolved in 40 ml toluene. The reaction mixture was heated at reflux in a Dean Stark apparatus for 6 h. The solvent was removed in vacuo and the residue dissolved in 2.5 ml $CHCl_3$/$CDCl_3$. The clear solution was examined by ^{119}Sn-NMR spectroscopy. ^{119}Sn-NMR ($CHCl_3$/$CDCl_3$, 111.92 MHz): δ -169.6; δ -196.1; δ -204.3; δ -225.5 (integral ratio 5:1:5:1).

4. Supplementary material available

Tables of anisotropic thermal parameters and hydrogen atom coordinates, complete bond lengths, angles and torsions angles for compounds **23**, **24**, and **28** are available from KJ.

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References

[1] J. Otera, T. Yano, R. Okawara, Organometallics 5 (1986) 1167.

[2] (a) J. Otera, Chem. Rev. 93 (1993) 1449. (b) J. Otera, S. Ioka, H. Nozaki, J. Org. Chem. 54 (1989) 4013.

[3] J. Otera, T. Yano, A. Kawabata, H. Nozaki, Tetrahedron Lett. 27 (1986) 2383.

[4] J. Otera, N. Dan-Oh, H. Nozaki, J. Chem. Soc., Chem. Commun. (1991) 1742.

[5] J. Otera, N. Dan-Oh, H. Nozaki, J. Org. Chem. 56 (1991) 5307.

[6] J. Otera, in: J. M. Coxan (Ed), Advances in Detailed Reaction Mechanisms, vol. 3, JAI Press, London, 1994, p. 167.

[7] J. Otera, N. Dan-Oh, H. Nozaki, Tetrahedron 48 (1992) 1449.

[8] A. Orita, A. Mitsutome, J. Otera, J. Org. Chem. 63 (1998) 2420.

[9] J. Otera, T. Yano, Y. Himeno, H. Nozaki, Tetrahedron Lett. 27 (1986) 4501.

[10] J. Otera, H. Nozaki, Tetrahedron Lett. 27 (1986) 5743.

[11] J. Otera, K. Kawada, T. Yano, Chem. Lett. (1996) 225.

[12] R.P. Houghton, A.W. Mulvaney, J. Organomet. Chem. 517 (1996) 107.

[13] R.P. Houghton, A.W. Mulvaney, J. Organomet. Chem. 518 (1996) 21.

[14] E.N. Suciu, B. Kuhimann, G.A. Knudsen, R.C. Michaelson, J. Organomet. Chem. 556 (1998) 41.

[15] R. Okawara, Proc. Chem. Soc. (1961) 383.

[16] R. Okawara, M. Wada, J. Organomet. Chem. 1 (1963) 81.

[17] (a) T.P. Lockhart, W.F. Manders, E.M. Holt, J. Am. Chem. Soc. 108 (1986) 6611. (b) E.R.T. Tiekink, Appl. Organomet. Chem. 5 (1991) 1. (c) F. Ribot, C. Sanchez, A. Meddour, M. Gielen, E.R.T. Tiekink, M. Biesemans, R. Willem, J. Organomet. Chem. 552 (1998) 177. (d) S.P. Narula, S. Kaur, R. Shankar, S.K. Bharadwaj, R.K. Chadha, J. Organomet. Chem. 506 (1996) 181. (e) E.R.T. Tiekink, M. Gielen, A. Bouhdid, M. Biesemans, R. Willem, J. Organomet. Chem. 494 (1995) 247. (f)

H. Puff, E. Friedrichs, F. Visel, Z. Anorg. Allg. Chem. 477 (1981) 50. (g) H. Puff, I. Bung, E. Friedrichs, A. Jansen, J. Organomet. Chem. 254 (1983) 23. (h) R. Hamalainen, U. Turpeinen, J. Organomet. Chem. 333 (1987) 323. (i) E.R.T. Tiekink, Acta Cryst. (Sect. C) 47 (1991) 661. (j) R. Graziani, U. Casellato, G. Plazzagno, Acta Cryst. (Sect. C) 39 (1983) 1188. (k) D. Dakternieks, R.W. Gable, B.F. Hoskins, Inorg. Chim. Acta 85 (1984) L43. (l) J.A. Blair, R.A. Howie, J.L. Wardell, P.J. Cox, Polyhedron 16 (1997) 881 and references therein.

[18] Y. Meada, R. Okawara, J. Organomet. Chem. 10 (1967) 247.

[19] T. Yano, K. Nakashima, J. Otera, R. Okawara, Organometallics 4 (1985) 1501.

[20] (a) D. C. Gross, Inorg. Chem. 28 (1989) 2355. (b) O. Primel, M.-F. Llauro, R. Pétiaud, A. Michel, J. Organomet. Chem. 558 (1998) 19.

[21] D. Dakternieks, K. Jurkschat, D. Schollmeyer, H. Wu, J. Organomet. Chem. 492 (1995) 145.

[22] M. Mehring, M. Schürmann, H. Reuter, D. Dakternieks, K. Jurkschat, Angew. Chem. 36 (1997) 1112.

[23] H. Puff, W. Schuh, R. Sievers, W. Wald, R. Zimmer, J. Organomet. Chem. 260 (1984) 271.

[24] D. Dakternieks, K. Jurkschat, D. Schollmeyer, H. Wu, Organometallics 13 (1994) 4121.

[25] B. Zobel, M. Schürmann, K. Jurkschat, D. Dakternieks, A. Duthie, Organometallics (in press).

[26] Y. Azuma, M. Newcomb, Organometallics 3 (1984) 9.

[27] $(Ph_2FSnCH_2)_2Z$ ($Z = CH_2$, CH_2CH_2, $SiMe_2$) were prepared in a similar manner to $Ph_2FSn(CH_2)_2SnFPh_2$, D. Daktemieks, K. Jurkschat, H. Zhu, E.R.T. Tiekink, Organometallics 14 (1995) 2512.

[28] J.F. Vollano, R.O. Day, R.R. Holmes, Organometallics 3 (1984) 745.

[29] P.G. Harrison, M.J. Begley, K. C. Molloy, J. Organomet. Chem. 186 (1980) 213.

[30] (a) S.-G. Teoh, S.-H. Ang, E.-S. Looi, C.-A. Keok, S.-B. Teo, H.-K. Fun, J. Organomet. Chem. 527 (1997) 15. (b) J. Tao, W. Xiao, J. Organomet. Chem. 526 (1996) 21.(c) C. Vatsa, V.K. Jain, T. Kesavadas, E.R.T. Tiekink, J. Organomet. Chem. 408 (1991) 157.

[31] D. Dolphin, A. Wick, in: D. Dolphin (Ed.), Tabulation of Infrared Spectral Data, Wiley, New York, 1977.

[32] (a) G. Höfle, W. Steglich, Synthesis (1972) 619. (b) A. Hassner, L.R. Krebski, V. Alexanian, Tetrahedron 34 (1978) 2069. (c) T. Shimizu, R. Ohmori, T. Nakata, Synlett (1995) 650.

[33] M.G. Stanton, C.B. Allen, R.M. Kissling, A. L. Lincoln, M.R. Gagné, J. Am. Chem. Soc. 120 (1998) 5981 and references therein.

[34] G. Höfle, W. Steglich, H. Vorbrüggen, Angew. Chem., Int. Ed. Engl. 17 (1978) 569.

[35] (a) E. Vedjes, S.T. Diver, J. Am. Chem. Soc. 115 (1993) 3358. (b) E. Vedjes, N.S. Bennett, L.M. Conn, S.T. Diver, M. Gingras, S. Lin, P.A. Oliver, M.J. Peterson, J. Org. Chem. 58 (1993) 7268.

[36] E. Vedjes, O. Daugulis, J. Org. Chem. 61 (1996) 5702.

[37] B.A. D'Sa, J.G. Verkade, J. Org. Chem. 61 (1996) 2963.

[38] K. Ishihara, M. Kubota, H. Kurihara, H. Yamamoto, J. Am. Chem. Soc. 117 (1995) 4413.

[39] J. Izumi, I. Shlina, T. Mukalyama, Chem. Lett (1995) 141.

[40] (a) E. Rothmann, S. Hecht, P.E. Pfeffer, L.S. Silbert, J. Org. Chem. 37 (1972) 3551. (b) Y. Kita, H. Maeda, F. Takahashi, S. Fukui, J. Chem. Soc., Chem. Commun. (1993) 410. (c) Y. Kita, H. Maeda, K. Omori, T. Okuno, Y. Tamura, J. Chem. Soc., Perkin Trans 1 (1993) 2999.

[41] Y. Ishii, M. Takeno, Y. Kawasaki, A. Muromachi, Y. Nishlyama, S. Sakaguchi, J. Org. Chem. 61 (1996) 3088.

[42] G.M Sheldrick, Acta Cryst. A46 (1990) 467.

[43] G.M. Sheldrick, University of Göttingen, 1993.

[44] International Tables for Crystallography, vol. C, Kluwer Academic Publishers, Dordrecht, 1992.

[45] G.M. Sheldrick, SHELXTL-Plus. Release 4.1, Siemens Analytical X-Ray Instruments Inc., Madison, WI, USA, 1991.

[46] Some carbon resonances were not detected due to overlapping signals.