Organotin-Oxo Clusters

by
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B. Sc. Hons.

A thesis presented for the degree of Doctor of Philosophy

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November 2002
I certify that the thesis entitled "Organotin-Oxo Clusters" submitted for the degree of Doctor of Philosophy is the result of my own work and that where reference is made to the work of others, due acknowledgment is given. I also certify that any material in the thesis which has been accepted for a degree or diploma by any other university or institution is identified in the text.

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Signed…………………………………
Date…………………………………...
Acknowledgments

I would like to thank the following people for their assistance throughout the duration of my PhD candidature.

- Professor Dainis Dakternieks for the helpful supervision in relation to the research undertaken and the thesis writeup.

- Associate Professor Edward R. T. Tiekink for crystal structure determinations.

- Dr François Ribot for the collection of $^{119}$Sn MAS NMR spectra, and powder X-ray diffraction data.

- Professor Dr Klaus Jurkschat for many helpful discussions.

- Ms Gail Dyson for the collection of NMR spectra, and proof reading.

- Mr Andrew Duthie for crystal structure determinations, proof reading and help throughout the research.

- Dr Jens Beckmann, Dr Bernhard Zobel, Dr Silke Kühn, Mr Allan Lim, Ms Cassandra Mitchell, Mr Richard Foitzik, Ms Laura Thompson and Ms Naomi Smith for proof reading and help throughout the research.

- All the administration and technical staff for their day to day services.

- My family and Mrs Jean Carr for their encouragement and support.
This thesis reports on the development and expansion of reliable synthetic di- and multi-tin precursors for the assembly of oligomeric organotin-oxo compounds in which the shape, dimension and tin nuclearity can be controlled.

The reaction of polymeric diorganotin oxides, $(R_2SnO)_m$ ($R = Me, Et, n-Bu, n-Oct, c-Hex, i-Pr, Ph$), with saturated aqueous $NH_4X$ solutions ($X = F, Cl, Br, I, OAc$) in refluxing 1,4-dioxane afforded in high yields dimeric tetraorganodistannoxanes, $[R_2(X)SnOSn(X)R_2]_2$, and in a few cases diorganotin dihalides or diacetates, $R_2SnX_2$. This method appears to be particularly good for the synthesis of halogenated tetraorganodistannoxanes but a less suitable method for the preparation of dicarboxylato tetraorganodistannoxanes. Identification of $[R_2(OH)SnOSn(X)R_2]_2$ ($R = n-Bu; X = Cl, Br$) and $[R_2(OH)SnOSn(X)R_2][R_2(X)SnOSn(X)R_2]$ suggest a serial substitution mechanism starting from $[R_2(OH)SnOSn(OH)R_2]_2$.

A series of $\alpha,\omega$-bis(triphenylstannyl)alkanes, $[Ph_3Sn]_2(CH_2)_n$ ($n = 3-8, 10, 12$) and some of their derivatives were synthesised and characterised. These $\alpha,\omega$-bis(triphenylstannyl)alkanes, $[Ph_3Sn]_2(CH_2)_n$ were converted to the corresponding halides $[R(Cl)2Sn]_2(CH_2)_n$ ($R = CH_2SiMe_3$) and subsequently to the polymeric oxides $\{[R(O)Sn]_2(CH_2)_n\}_m$. Reaction of $\{[R(O)Sn]_2(CH_2)_n\}_m$ with $[R(Cl)2Sn]_2(CH_2)_n$ ($n = 3, n' = 4$ and $n = 4, n' = 3$) in toluene at $100^\circ C$ results in a mixture of symmetric and asymmetric double ladders, where different spacer chain lengths ($n$ and $n'$) provide the source of asymmetry. The coexistence at high temperature of separate $^{119}Sn$ NMR signals belonging to symmetric and asymmetric double ladders suggests an equilibrium that is slow on the $^{119}Sn$ NMR time scale and the position of which is temperature dependent. However, $^{119}Sn$ NMR spectroscopic experiments of $\{[R(O)Sn]_2(CH_2)_3\}_m$ with $[R(Cl)2Sn]_2(CH_2)_n$ for longer spacers ($n = 5, 6, 8, 10, 12$) reveal that molecular self-assembly of symmetric spacer-bridged di-tin precursors of equal chain length is preferred over asymmetric species.

An ether-bridged di-tin tetrachloride $[R(Cl)2Sn(CH_2)_3]_2O$ ($R = CH_2SiMe_3$) and its corresponding polymeric oxide $\{[R(O)Sn(CH_2)_3]_2O\}_m$ were synthesised and characterised. Reaction of $[R(Cl)2Sn(CH_2)_3]_2O$ with $\{[R(O)Sn(CH_2)_3]_2O\}_m$ results in a unique functionalised double ladder $\{[[RSn(Cl)](CH_2)_3O(CH_2)_3[RSn(Cl)]]O\}_4$.
whose structure in the solid state was determined by X-ray analysis. Identification of
tetrameric functionalised double ladder as well as dimeric and monomeric species
suggest the existence of an equilibrium in solution. The feasibility of the
functionalised double ladder to form host-guest complexes with a variety of metal
cations is investigated using electrospray mass spectrometry (ESMS). Evidence for
such complexes is found only for sodium cations.

The reaction between \([\text{R(O)Sn}_2\text{(CH}_2\text{n})_m\text{(n = 3, 4, 8, 10)}]\) and triflic acid is
described. The initial formed products \([\text{RSn(CH}_2\text{n})_\text{SnR}(\text{OTf})_4]\) are easily hydrolysed.
For \(n = 3\), self-assembly leads to a discrete double ladder type structure,
\(\{[[\text{RSn(OH)}]\text{(CH}_2\text{n})][\text{RSn(H}_2\text{O)}]\}\text{O}_4\text{4OTf}\), which is the first example of a cationic
double ladder. For \(n > 3\), hydrolysis gives polymeric products, as demonstrated by
the crystal structure of \(\{[(\text{H}_2\text{O})(\text{OH})\text{RSn}]_2\text{(CH}_2\text{n})_4\text{2OTf2H}_2\text{O}\}_m\).

Two spacer-bridged tetra-tin octachlorides \([\text{R(Cl)}_2\text{Sn(CH}_2\text{n})_\text{Sn(Cl)}_m\text{(CH}_2\text{n})]\)
\((\text{R} = \text{CH}_2\text{SiMe}_3; n = 1, 8)\) and their corresponding polymeric oxides
\(\{[[\text{RSn(OR)}]\text{(CH}_2\text{n})_\text{Sn(O)}]\}_2\text{(CH}_2\text{n})\}_m\) were successfully synthesised and characterised.
Attempts were made to synthesise quadruple ladders from these precursors.
Reactions of \([\text{R(Cl)}_2\text{Sn(CH}_2\text{n})_\text{Sn(Cl)}_m\text{Cl}_2\text{CH}_2\] with \(\{[[\text{R(O)Sn(CH}_2\text{n})_\text{Sn(O)}]\\text{CH}_2\text{]}_m\) or
\((\text{t}-\text{Bu}_2\text{SnO})_3\) result in, mostly insoluble, amorphous solids. Reactions of
\([\text{R(Cl)}_2\text{Sn(CH}_2\text{n})_\text{Sn(Cl)}_m\text{Cl}_2\text{(CH}_2\text{n})_8\] with \(\{[[\text{R(O)Sn(CH}_2\text{n})_\text{Sn(O)}]\\text{(CH}_2\text{n})_8\}_m\) or \((\text{t}-\text{Bu}_2\text{SnO})_3\) result in new tin-containing species which are presumably oligomeric.

The synthesis of a series of alkyl-bridged di-tin hexacarboxylates
\(\{[(\text{RCO}_2\text{)}_3\text{Sn}]_2\text{(CH}_2\text{n})\} (n = 3, 4; \text{R} = \text{Ph, c-C}_6\text{H}_{11,} \text{ CH}_3, \text{ ClCH}_2)\) is also reported. The
hydrolysis of these compounds is facile and complex. There appears to be no
correlation between spacer chain length and hydrolysis product. However, the
conjugate acid strength of the carboxylate does appear to be important. In general
only insoluble amorphous polymeric organotin-oxo compounds were obtained.
Publications

Shown below is a list of publications that have arisen from work in this thesis.


“The crystal structure of the propylene-bridged double ladder, {[Me₃SiCH₂Sn(Cl)]₂O}₂{CH₂CH₂CH₂}₄{[Me₃SiCH₂Sn(Cl)]₂O}₂ as its toluene solvate (1/1)” Dakternieks, D.; Kuan, F. S.; Duthie, A.; Tiekink, E. R. T. Main Group Metal Chemistry, 2000, 23, 731.
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Chapter 1

Introduction
1.1 Organotin-Oxo Compounds

The rich cluster chemistry of organotin-oxo compounds has come to the fore of main group chemistry research in recent years. Work in this field began as early as 1922.¹ Due to difficulties in structure elucidation it wasn’t until the 1950’s that, on the advent of numerous technological advances and the increasing awareness of possible commercial applications, a resurgence of research activities took place. One particularly important technique for study of organotin compounds has been $^{119}$Sn NMR. The $^{119}$Sn NMR chemical shifts has been shown to be dependent on several structural parameters, for example, the type of substituents present at tin, the interbond angles at tin and also the coordination environment around tin.² More recently solid state $^{119}$Sn MAS NMR has begun to become more common. Another useful technique is electrospray mass spectrometry (ESMS) that is capable of detecting usually pre-existence ions in solution.

It has been shown that organotin units can be linked in a number of ways affording a variety of structures. Most of these structures are based on distannoxane Sn$_2$O$_2$ framework.

Organotin halides provide a useful synthetic pathway to organotin-oxo compounds. Hydrolysis of organotin halides has been shown to proceed in a stepwise fashion, with the nature of the products increasing in complexity with increasing halide content of the precursor. Triorganotin halides $R_3SnX$ ($R =$ alkyl, aryl) (1) are hydrolysed to produce organotin hydroxides $R_3SnOH$ (2), which in most cases are readily dehydrated to the bis(triorganotin) oxides ($R_3Sn$)$_2$O (3) (Scheme 1).³

$$\begin{align*}
R_3SnX & \xrightarrow{OH^-} R_3SnOH - X^- \\
- X^- & \xrightarrow{-H_2O} R_3SnOH - H_2O \\
- H_2O & \xrightarrow{1/2 (R_3Sn)_2O} 1/2 (R_3Sn)_2O
\end{align*}$$

Scheme 1

Hydrolysis of diorganotin dihalides $R_2SnX_2$ ($R =$ alkyl, aryl) (4) also proceeds in a stepwise fashion, with the formation of dimeric tetraorganodistannoxanes containing halides or hydroxyl groups.
[R₂(X)SnOSn(X)R₂]₂ (5), [R₂(X)SnOSn(OH)R₂]₂ (6), [R₂(OH)SnOSn(OH)R₂]₂ (7) and finally polymeric diorganotin oxides (R₂SnO)ₙ (8) (Scheme 2).³,⁴

The diorganotin oxides (8) are usually amorphous polymeric solids which are insoluble in most common solvents. The polymeric nature of these compounds is thought to stem from intermolecular associations facilitated by Lewis acid-Lewis base interactions (Figure 1).³

The nature of the products resulting from the hydrolysis of organotin trihalides RSnX₃ (9) is more complex and the intermediates are poorly characterised compared to those from R₂SnX₂. However a similar sequence may be described (Scheme 3).³
Scheme 3

The ultimate hydrolysis products of $\text{RSnX}_3$ are the so-called organostannonic acids $\text{RSn(O)OH}$ (10). These compounds generally are insoluble amorphous powders and are also thought to be associated, although no structures have yet been reported.
1.2 Dimeric Tetraorganodistannoxanes / Single Ladders

Tetraorganodistannoxanes with dimeric ladder structures $[\text{R}_2(X)\text{SnOSn(Y)R'}_2]_2$ ($\text{R, R'} = \text{alkyl or aryl; X, Y = halides, OH, OR, OSiMe}_3$, $\text{OOOCR, OB(OR)}_2$, $\text{OReO}_3$, $\text{OSP(OR)}_2$, $\text{NO}_3$, $\text{N}_3$, $\text{NCS}$, $\text{NCO}$, $\text{SH}$, $\text{ROO}$, $\text{RSO}_3$, $\text{RS}$) (11), have been widely exploited over recent years. This interest arises primarily because of the enormous potential of such compounds in a range of commercial applications. They have been used as catalysts in a range of organic syntheses$^{5-16}$ and polymerisation reactions.$^{17-27}$ They are instrumental in cross-linking room temperature-vulcanised (RTV) silicone elastomers$^{28}$ and catalysing chemical modifications$^{7,10,29-31}$ of immiscible polymer blends, resulting in improved compatibility.$^{32-38}$ In addition, these important catalytic compounds have been shown to exhibit in vitro activity against leukaemia$^{39,40}$ and various cancer tumour cell lines,$^{41-50}$ as well as in the control of phyto-pathogenic fungi and bacteria.$^{51}$

![Dimeric tetraorganodistannoxanes](image)

R = alkyl, aryl; X, Y = halides, OH, OR, OSiMe$_3$, OOOCR, OB(OR)$_2$, OReO$_3$, OSP(OR)$_2$, NO$_3$, N$_3$, NCS, NCO, SH, ROO, RSO$_3$, RS

Dimeric tetraorganodistannoxanes (11) and their structure have been the subject of many investigations since their discovery in 1914.$^{52}$ In 1963, Okawara and Wada,$^{53}$ proposed that in solution the dimeric tetraorganodistannoxanes are represented by a dimeric ladder structure. Subsequent X-ray analyses have shown that the ladder structure is the predominant structure adopted in the solid state.$^{41-50,54-76}$
In the solid state, tetraorganodistannoxanes (11) are dimeric and contain \( \text{Sn}_4\text{O}_2\text{X}_2\text{Y}_2 \) structural motifs with ladder-like or staircase arrangements depending on their planarity. Tetraorganodistannoxanes reported to date generally have a dimeric ladder structure, however a staircase conformation has been reported for the trimethylsiloxyl derivative, \([\text{Me}_2(\text{OSiMe}_3)\text{SnOSn(OSiMe}_3)\text{Me}_2]_2\).\(^{77}\) The \( \text{Sn}_4\text{O}_2\text{X}_2\text{Y}_2 \) structural motif within ladder structures is essentially coplanar. Each tin possesses two organic groups. The ladder structure contains two distinct pentacoordinated tin environments. The endo-cyclic tin atoms are located within the four-membered ring containing the two oxygens and attached to these oxygens are the exo-cyclic tin atoms.

The activity and selectivity of ladders as catalysts are dependent on the nature of both the \( X \) and \( R \) substituents. It appears that the residual Lewis acidity of tin and its ability to form hypervalent species is important in mechanisms for such catalytic activity.

A series of physicochemical techniques such as vapour phase osmometry studies,\(^{52,77-81}\) cyroscopic measurements,\(^{53,77,82,83}\) IR\(^{83,84}\) and \(^{119}\)Sn NMR\(^{34,37,41-50,52,54-58,84-90}\) spectroscopy have demonstrated that the solid state dimeric structure is retained in solution although the systems are labile. The solution \(^{119}\)Sn NMR spectra generally contain two distinct \(^{119}\)Sn resonances, each of which shows a characteristic coupling pattern due to \(^{119}\)Sn\text{exo}^{117/119}\)Sn\text{endo}.

For dimeric tetraorganodistannoxanes in which \( X \) and \( Y \) are potentially chelating anions, \( e.g. \) as in \( X = Y = \text{carboxylate} \), the structures become modified as a consequence of the bidentate capabilities of these ligands.\(^{50,91}\) Recent reviews of the structures of organotin carboxylates have demonstrated that there are five types of
structure that can be adopted in the crystalline state by the dimeric dicarboxylato tetraorganodistannoxanes (12-16) (Figure 3).75,92

Figure 3. Different structure adopted by dicarboxylato tetraorganodistannoxanes.

These structures feature a planar Sn₂O₂ core with the exo-cyclic tin atoms being connected to the core via the oxygen atoms and contain carboxylate ligands which may be monodentate, bidentate or tridentate. Structure 12, shown in Figure 3, is by far the predominant structural form, with 16 out of 23 characterised dicarboxylato tetraorganodistannoxanes adopting this structural form.92 Structure 12
involves a centrosymmetric structure built up around a four-membered cyclic Sn₂O₂ core in which the two exo-cyclic tin atoms are pentacoordinated. In contrast, structure 14 shows all carboxylate ligands to be bidentate leading to hexacoordinated tin atoms. In structure 15 three intramolecular and one intermolecular bidentate acetate ligands are present giving two penta- and two hexacoordinate tin centres.

Dimeric tetraorganodistannoxanes with X, Y = halide, OH are accessible by the controlled hydrolysis of diorganotin dihalides R₂SnX₂ (R = alkyl, aryl) (4), through which many examples with X = Y = halides and X = OH, Y = halides have been synthesised over the years (Scheme 4). Derivatives with X = Y = halide generally can be obtained by two methods. The first involves the reaction of an equivalent amount of R₂SnX₂ with a polymeric diorganotin oxide (R₂SnO)ₙ (R = alkyl, aryl) (8). A shortcoming of this method is the requirement that the diorganotin oxide must be sufficiently soluble in organic solvents. The second method uses the reaction between R₂SnX₂ and the soluble trimeric molecular tin oxide, (t-Bu₂SnO)₃ (12). However these reactions fail to provide fluorinated tetraorganodistannoxanes due to the generally poor solubility of diorganotin difluorides. Consequently, only few examples of fluoride containing ladders have been reported so far.

![Scheme 4](image)

Dimeric tetraorganodistannoxanes are well-known compounds that have found enormous potential in a range of commercial applications. It would therefore be extremely useful to be able to easily synthesise a range of tetraorganodistannoxanes, which are not accessibly by existing methods.
1.3 Double Ladders

In 1994 Dakternieks, Jurkschat and coworkers\textsuperscript{98} reported the synthesis of the first example of a spacer-bridged double ladder, \{[[RSn(Cl)](CH\textsubscript{2})\textsubscript{3}[RSn(Cl)]]O\}_4 (R = CH\textsubscript{2}SiMe\textsubscript{3}) (17). Double ladder 17, which contains a centre of symmetry, consists of two Sn\textsubscript{4}O\textsubscript{2}Cl\textsubscript{4} layers which are connected through four trimethylene bridges.

\begin{center}
\includegraphics[width=\textwidth]{17.png}
\end{center}

17; R = CH\textsubscript{2}SiMe\textsubscript{3}

Double ladders are accessible by various synthetic routes starting from precursors containing two tin atoms linked by appropriate organic spacers. The reaction of a spacer-bridged di-tin tetrachloride R(Cl)\textsubscript{2}Sn–Z–Sn(Cl)\textsubscript{2}R (18) with di-\textit{tert}-butyltin oxide (t-Bu\textsubscript{2}SnO)\textsubscript{3} as the oxygen transfer reagent was found to produce double ladders \{[[RSn(Cl)](–Z–)[RSn(Cl)]]O\}_4 (R = alkyl, aryl; Z = organic spacer) (19). An alternative route for the preparation of these compounds is the reaction of a spacer-bridged di-tin tetrachloride R(Cl)\textsubscript{2}Sn–Z–Sn(Cl)\textsubscript{2}R (18) with the corresponding spacer-bridged polymeric di-tin oxide [R(O)Sn–Z–Sn(O)R]\textsubscript{m} (20) (Scheme 5).
Systematic studies into organic substituents (R), electronegative groups (X) and organic spacers (Z) have been investigated to determine their influence on the geometry of double ladders. Early work in this field has focused on the synthesis of spacer-bridged double ladders containing different R moieties attached to tin.\textsuperscript{99} Compounds prepared include $\{[RSn(Cl)](CH_2)_4[RSn(Cl)]\}O_4$ (R = CH$_2$SiMe$_3$ (21), R = CH$_2$CMe$_3$ (22), R = CH$_2$CHMe$_2$ (23)). The application of these compounds as catalysts in acylation reactions of alcohols was investigated.\textsuperscript{99} In the acylation reaction of PhCH$_2$CH$_2$OH and $n$-C$_8$H$_{17}$OH with Ac$_2$O, compounds 21-23 show moderate catalytic activities. Furthermore, preliminary investigations show compound 22 to discriminate effectively between primary and secondary alcohols in acetylation reactions.\textsuperscript{99}

Asymmetric double ladders, where the organic substituents (R) provides the asymmetry, were reported recently.\textsuperscript{100} The double ladders, $\{[R(\text{Cl})\text{Sn}(\text{CH}_2)_4\text{Sn(\text{Cl})}]\}[R'(\text{Cl})\text{Sn}(\text{CH}_2)_4\text{Sn(\text{Cl})}R']\text{O}_2\}_2$ (R = CH$_2$CMe$_3$, R’ = CH$_2$CHMe$_2$) (24), (R = CH$_2$CMe$_3$, R’ = CH$_2$SiMe$_3$) (25) both contain two different
organic moieties R and R' attached to tin. Compound 24 was prepared using the spacer-bridged di-tin tetrachloride \([(\text{Me}_3\text{CCH}_2)\text{Cl}_2\text{Sn}]_2\text{CH}_2]_4\) (26a) with the spacer-bridged polymeric di-tin oxide \([(\text{Me}_2\text{CHCH}_2)\text{O}\text{Sn}]_2\text{CH}_2]_4\) (27b), as well as the reaction of \([(\text{Me}_2\text{CHCH}_2)\text{Cl}_2\text{Sn}]_2\text{CH}_2]_4\) (27a) with the spacer-bridged polymeric di-tin oxide \([(\text{Me}_3\text{CCH}_2)\text{O}\text{Sn}]_2\text{CH}_2]_4\)_m (26b) (Scheme 6).

Analogously, the reaction of \([(\text{Me}_3\text{SiCH}_2)\text{Cl}_2\text{Sn}]_2\text{CH}_2]_4\) (28a) with \([(\text{Me}_2\text{CHCH}_2)\text{O}\text{Sn}]_2\text{CH}_2]_4\)_m (26b) and \([(\text{Me}_2\text{CHCH}_2)\text{Cl}_2\text{Sn}]_2\text{CH}_2]_4\) (26a) with \([(\text{Me}_3\text{SiCH}_2)\text{O}\text{Sn}]_2\text{CH}_2]_4\)_m (28b) gave compound 27. It is worthwhile to point out that the mixed double ladders 24 and 25 were also formed by mixing equimolar amounts of the symmetrically substituted double ladders \{[(\text{RSn(Cl)})\text{-Z-}\text{RSn(Cl)}]_4\} (R = \text{CH}_2\text{CMe}_3) (26) and (R = \text{CH}_2\text{CHMe}_2) (27), and (R = \text{CH}_2\text{CMe}_3) (26) and (R = \text{CH}_2\text{SiMe}_3) (28) (Scheme 6), indicating the lability of double ladders on the preparative time scale.

\[
\begin{align*}
2 & \text{R(Cl)}_2\text{Sn-Z-Sn(Cl)}_2\text{R} + 2/m\ [\text{R(O)Sn-Z-Sn(O)R}]_m \\
26a;\ R = \text{CH}_2\text{CMe}_3 & \quad 27b;\ R = \text{CH}_2\text{CHMe}_2 \\
27a;\ R = \text{CH}_2\text{CHMe}_2 & \quad 26b;\ R = \text{CH}_2\text{CMe}_3 \\
28a;\ R = \text{CH}_2\text{SiMe}_3 & \quad 26b;\ R = \text{CH}_2\text{CMe}_3 \\
26a;\ R = \text{CH}_2\text{CMe}_3 & \quad 28b;\ R = \text{CH}_2\text{SiMe}_3 \\
\end{align*}
\]

Scheme 6
Organotin compounds can behave as Lewis acids, accepting electron density from nearby Lewis bases. Double ladders have the potential to utilise this Lewis acidity by providing a cavity into which reactive Lewis bases (guest compounds) could enter. Upon entering, the guest compound can interact with the Lewis acidic tin atoms and other atoms present in the double ladder structure.

In the double ladders \[\{[[RSn(Cl)](CH_2)_n[RSn(Cl)]]}O\}_4\ (R = CH_2SiMe_3)\] the distance between the two Sn_4Cl_4O_2 layers was found to be 6.04 Å for \(n = 3\) and 7.07 Å for \(n = 4\) which appears too small to contemplate any genuine host-guest chemistry. With the goal to increase the Sn_4O_2Cl_4 interlayer separation, a series of double ladders having organic spacers with between 5 and 12 methylene groups \[\{[[RSn(Cl)](CH_2)_n[RSn(Cl)]]}O\}_4\ (R = CH_2SiMe_3; \ n = 5-8 \ (29-32), \ n = 10 \ (33), \ n = 12 \ (34)\), was subsequently synthesised.\[101\]

\[29-32, \ 33, \ 34; \ R = CH_2SiMe_3, \ (CH_2)_n = 5-8, \ 10, \ 12\]

In the solid state, these compounds exhibit a double ladder structure (tetramers, eight tin atoms), \[\{[[RSn(Cl)](CH_2)_n[RSn(Cl)]]}O\}_4\ (R = CH_2SiMe_3; \ n = 3 \ (17), \ n = 4 \ (21), \ n = 5-8 \ (29-32), \ n = 10 \ (33), \ n = 12 \ (34)\). In solution, equilibria between double ladders (tetramers, eight tin atoms) and single ladders (dimers, four tin atoms), \[\{[[RSn(Cl)](CH_2)_n[RSn(Cl)]]}O\}_2\ (R = CH_2SiMe_3; \ n = 5-8 \ (29a-32a), \ n = 10 \ (33a), \ n = 12 \ (34a)\) have been observed (Scheme 7).
Replacement of a methylene group with either a -SiMe$_2$- (35), -Me$_2$SiC≡CSiMe$_2$- (36) or -Me$_2$SiOSiMe$_2$- (37) in the trimethylene spacer and reactions of these precursors with ($t$-Bu$_2$SnO)$_3$ affords only the dimeric tetraorganodistannoxanes ladders (Scheme 8) with no evidence observed for the tetrameric double ladders.\textsuperscript{102}

This observation was believed to be due to the steric hindrance of the spacers 35-37, which prevented association to double ladder structures. However, cis-trans equilibria are possible for these compounds. The crystal structure of 36a (X = Cl) shows that both the acetylenic spacers are on the same side of the tetraorganodistannoxane core, i.e. 36a adopts the lower symmetry cis-configuration. Consequently, compound 36a shows asymmetry in both the ladder core and the configuration of the spacers.

The tetrachloro-substituted distannoxanes 36a (X = Cl) and 37a/37b (X = Cl) react almost quantitatively with NEt$_3$/H$_2$O/CH$_2$Cl$_2$ to give the dihydroxy-substituted distannoxane 36a (X = OH) and 37a/37b (X = OH) respectively (Scheme 8).
Recent efforts have been directed to the synthesis of new double ladders that have little or no symmetry as well as to increase the size of interlayer region. The reaction of a rigid and bulky silicon-containing spacer di-tin precursors \( p-[\text{R(Cl)}_2\text{SnCH}_2\text{SiMe}_2]\text{C}_6\text{H}_4 (\text{R} = \text{CH}_2\text{SiMe}_3) (38a) \) leads to the first example of a chiral double ladder \( p-\{[\text{RSn(Cl)}](\text{CH}_2\text{SiMe}_2\text{C}_6\text{H}_4\text{CH}_2\text{SiMe}_2)[\text{RSn(Cl)}])\text{O}\}_4 (\text{R} = \text{CH}_2\text{SiMe}_3) (38) \) (Scheme 9).\(^{103}\) An X-ray investigation of 38 revealed that the two layers within 38 are twisted with respect to one another, resulting in a helical motif and a total absence of molecular symmetry so that there are eight chiral tin atoms within the system.

Less sterically demanding di-tin precursors such as \( m-[\text{R(Cl)}_2\text{SnCH}_2]\text{C}_6\text{H}_4 (\text{R} = \text{CH}_2\text{SiMe}_3) (41a) \) have been investigated.\(^{103}\) X-ray structure analysis of the double ladder \( m-\{[\text{RSn(Cl)}](\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2)[\text{RSn(Cl)}])\text{O}\}_4 (\text{R} = \text{CH}_2\text{SiMe}_3) (41) \) reveals that the two layers within 41 are parallel, and the molecule contains only two kinds of tin atom. The use of other rigid di-tin precursors \( p-[\text{R(Cl)}_2\text{SnCH}_2\text{SiMe}_2]\text{C}_6\text{H}_4 (\text{R} = \text{CH}_2\text{SiMe}_3) (40a) \) and \( m-[\text{R(Cl)}_2\text{SnCH}_2]\text{C}_6\text{H}_4 (\text{R} = \text{CH}_2\text{SiMe}_3) (40a) \) and \( m-[\text{R(Cl)}_2\text{SnCH}_2]\text{C}_6\text{H}_4 (\text{R} = \text{CH}_2\text{SiMe}_3) (40a) \)
CH$_2$SiMe$_3$) (39a), analogues of 38a and 41a respectively, have also been investigated.$^{104}$

\[
\begin{align*}
2 \text{ R(Cl)}_2\text{Sn–Z–Sn(Cl)}_2\text{R} & \quad + \quad 2/m \quad [\text{R(O)Sn–Z–Sn(O)}\text{R}]_m \\
\text{a} & \\
\text{R} = \text{CH}_2\text{SiMe}_3
\end{align*}
\]

\[
\begin{array}{c}
\text{Scheme 9}
\end{array}
\]

1.4 Triple and Higher-Order Ladders

Dimeric tetraorganodistannoxanes / single ladders \([\text{R}_2(\text{X})\text{SnOSn(\text{X})R}_2]_2\) (X = Cl, OH) (11) can be formed from the hydrolysis of diorganotin dichlorides \(\text{R}_2\text{SnCl}_2\) (4). The controlled hydrolysis or oxygenolysis of a spacer-bridged di-tin tetrachloride \(\text{R(Cl)}_2\text{Sn–Z–Sn(Cl)}_2\text{R}\) (18), was found to produce the spacer-bridged double ladders \({\{[\text{RSn(Cl)}](–\text{Z})[\text{RSn(Cl)}]\}}\text{O}_4\) (R = alkyl, aryl; Z = organic spacers) (19). These results led to the question whether pillar shaped triple and quadruple ladders can be constructed from appropriate tri- and tetra-tin precursors.

In 1997, three years after the first spacer-bridged double ladder was reported, Dakternieks et al.$^{105}$ demonstrated that indeed a triple ladder \({\{[\text{RSn(Cl)}](–\text{Z})[\text{RSn(Cl)}](–\text{Z})[\text{RSn(Cl)}]\}}\text{O}_{3/2}\}4\) (R = CH$_2$SiMe$_3$; Z = (CH$_2$)$_3$) (43) was formed by the reaction of the spacer-bridged tri-tin hexachloride \(\text{R(Cl)}_2\text{Sn–Z–(Cl)}_2\text{Sn–Z–Sn(Cl)}_2\text{R}\) (R = CH$_2$SiMe$_3$; Z = (CH$_2$)$_3$) (42) with (t-
Bu$_2$SnO)$_3$ (Scheme 10). The triple ladder 43 consists of the three parallel Sn$_4$O$_2$Cl$_4$ layers connected through eight trimethylene bridges.

**Scheme 10**

The first attempted synthesis of a quadruple ladder, using the spacer-bridged tetra-tin octachloride R(Cl)$_2$Sn−Z−(Cl)$_2$Sn−Z′−Sn(Cl)$_2$−Z−Sn(Cl)$_2$R (R = CH$_2$SiMe$_3$; Z = (CH$_2$)$_3$, Z′ = CH$_2$SiMe$_2$CH$_2$) (44), was reported in 1997. It was found that the reaction of 44 with (t-Bu$_2$SnO)$_3$ afforded a ‘folded’ double ladder (45) instead of a quadruple ladder (Scheme 11). This observation was believed to be due to the additional gain of entropy by formation of the Si−CH$_2$Sn−O−Sn−CH$_2$ six-membered chelate intermediate, which prevented association to the anticipated quadruple ladder structure.
1.5 Higher Oligomeric Organotin-Oxo Clusters

Over recent years, there has been growing interest in the synthesis and characterisation of monoorganotin-oxo compounds of high tin nuclearity. This interest is driven, in part by their utility as catalysts for a range of organic synthesis\textsuperscript{106,107} and polymerisation reactions\textsuperscript{106} as well as in the field of new materials science.\textsuperscript{108-113} They also have some potential as precursors of intercalates in montmorillonite clays to produce new materials with catalytic applications.
Early work on monoorganotin-oxo clusters traces back as early as 1921 when Lambourne\textsuperscript{1,114} established compositions of monoorganotin-oxo compounds resulting from condensation reactions between alkylstannonic acids and carboxylic acids. Although there were further reports on related compounds,\textsuperscript{115-118} there had been no advances made in structure assignment until 1985 when Chandrasekhar \textit{et al}\textsuperscript{119} first reported the drum-shaped molecule, \([\text{PhSn(O)O}_2\text{C}_6\text{H}_{11}]_6\) (46).

\begin{center}
\includegraphics[width=\textwidth]{image.png}
\end{center}

Subsequently, a wide variety of compounds with diverse geometries, for example, drum (47),\textsuperscript{106} oxygen-capped (48),\textsuperscript{120,121} cube (49),\textsuperscript{120,122} crown (50),\textsuperscript{123} extended ladder (51),\textsuperscript{124} butterfly (52),\textsuperscript{120} double cube\textsuperscript{123} and cage clusters\textsuperscript{125} have been reported (Figure 4).
Drum $[\text{MeSn}(\text{O})(\text{OAc})]_6$ (47)

Oxygen-capped $[n-\text{BuSn(OH)O}_2\text{PPh}_2]_3\text{O}[\text{Ph}_2\text{PO}_2]$ (48)
Chapter 1

Cube \([n\text{-BuSn(O)O}_2\text{P(C}_6\text{H}_{11})_2]_4\) (49)

Crown \([\text{MeSn(O)O}_2\text{P(t-Bu)}_2(\text{MeSn(OH)(OMe)}_2\text{P(t-Bu)}_2)[H][O}_2\text{P(t-Bu)}_2]\cdot4\text{MeOH}\cdot2\text{H}_2\text{O}\) (50)
Figure 4. ORTEP plots of examples of monoorganotin-oxo clusters. Pendant atoms and some solvent molecules have been omitted for clarity.
Common to all the compounds above are hexacoordinated tin with octahedral (or distorted octahedral) geometry, and the four-membered dimeric distannoxane ring ($\text{SnO}_2$) as a subunit.\textsuperscript{126} The number of tin atoms in these clusters varies from two to six, excluding five. Another very important feature of these clusters is their interconversion from one form to another, and interconversion routes between different types of clusters have been proposed.\textsuperscript{106} These oligomers were generally prepared \textit{via} hydrolysis or condensation reactions of organostannonic acid with carboxylic or phosphorus-based acids,\textsuperscript{106} for example, the cube structure (49) from Figure 4 (Scheme 12).

\[
\begin{align*}
4 \text{n-BuSn(O)(OH)} & \quad 4 \left(\text{C}_6\text{H}_{11}\right)\text{P(O)(OH)} \\
\text{10} & \quad [-4 \text{H}_2\text{O}] \\
\quad \rightarrow & \quad [\text{n-BuSn(O)O}_2\text{P(C}_6\text{H}_{11})\text{O}]_4 \\
\quad \text{49} & \quad \text{Scheme 12}
\end{align*}
\]

Although such reactions have provided many examples of discrete organotin-oxo oligomers, the reaction conditions provide little control over the resulting product.

Organostannonic acids such as 10 are common starting materials for many monoorganotin-oxo clusters yet their definitive structure is still unknown. Having the empirical formula, $\text{RSn(O)OH}$, they are usually prepared by hydrolysis of monoorganotin trihalides, and are considered to be polymeric or oligomeric.\textsuperscript{120,127} There is some evidence that organostannonic acids may exist as cyclic trimers when freshly prepared.\textsuperscript{127} Very recently, Janssen and coworkers\textsuperscript{128} reported the synthesis and X-ray structure of the trimeric monoorganostannonic acid $[\text{TsiSnO(OH)}]_3$ ($\text{Tsi} = \text{C(SiMe}_3)_3$).

In Section 1.1 it was mentioned that monoorganotin trihalides also provide a potential pathway to oligomeric monoorganotin-oxo clusters. The ultimate hydrolysis products of $\text{RSnX}_3$ (9) are the organostannonic acids $\text{RSn(O)OH}$ (10). However, a few examples of soluble, discrete oligomers have found along the hydrolysis pathway. The first case was reported by Puff and Reuter in 1989 who obtained crystals of $([i\text{-PrSn}]_9\text{O}_8(\text{OH})_6\text{Cl}_5\text{-dmso}$ and $[(i\text{-PrSn})_{12}\text{O}_{14}(\text{OH})_6]\text{Cl}_2$ (53a) (Figure 5) from the hydrolysis reaction of $i\text{-PrSnCl}_3$.\textsuperscript{129} The latter has the near organostannonic acid composition $\text{RSn(O)OH}$. 

22
The structure of $53a$ comprises a football-shaped organotin-oxo core, containing twelve tin atoms, linked together by triply- and doubly-bridged hydroxyl groups. There are six five-coordinate tin atoms with square-pyramid geometry, situated across the centre of the molecules and three six-coordinate tin atom with distorted octahedral geometry at either end. The organic groups are bonded to tin atoms and point to the outside of the clusters. An overall charge of positive two on the organotin-oxo core is offset by two closely associate anions, \textit{i.e.} Cl$^-$.

Dakternieks and coworkers$^{130}$ later reported the efficient synthesis of the $n$-butyl analogue $[(n$-BuSn)$_{12}$O$_{14}$(OH)$_6$]Cl$_2$ ($53b$) which is more soluble in many organic solvents than the previously prepared clusters.

Subsequently oligomeric “Sn$_{12}$” monoorganotin-oxo clusters have also been formed upon the hydrolysis of $RSn(OR')_3$ ($54$) and $RSn(C\equiv CR')_3$ ($55$) (Scheme 13).$^{131,132}$

\[
\begin{align*}
RSnX_3 & \xrightarrow{H_2O} [(RSn)_{12}O_{14}(OH)_6](OH)_2 \\
54; & \quad X = OR' \\
55; & \quad X = C\equiv CR'
\end{align*}
\]

Scheme 13

More recently, Dakternieks \textit{et al.}$^{133}$ reported the structure of a hitherto unknown “Sn$_{12}$” cluster $[Sn(CH_2)3Sn]_6(ClCH_2CO_2)_{14}(OH)_2O_{10}$ ($56$) (Figure 5) from the controlled hydrolysis of trimethylene bridged di-tin hexachloroacetate $[(ClCH_2CO_2)_2Sn]_2(CH_2)_3$. $56$ has all twelve tin atoms nearly coplanar, in stark contrast to previously described “Sn$_{12}$” clusters $53$, which have a spherical football structure.

Molecular football $[(RSn)_{12}O_{14}(OH)_6]Cl_2$; R = \textit{i}-Pr ($53a$)
1.6 Research Plan

It can be seen that a considerable amount of research has been directed towards the preparation of discrete oligomeric organotin-oxo clusters. Surprisingly, much of the research to date has lacked synthetic strategies aimed at controlling the oligomer formation process. Many of the examples given above have resulted from serendipitous chemistry. If organotin oligomers are to be successfully employed as
discrete tin-containing clusters to prepare inorganic-organic hybrid materials, techniques which enable the controlled synthesis of these oligomers need to be developed.

The research plan is based on the synthesis of discrete and well-characterised precursors containing a number of tin atoms. In general the tin atoms are linked by organic bridges. The plan was subsequently to react these pre-assembled multi-tin precursors to produce new organotin-oxo oligomers. The plan also involved efforts to include donor functionality with the organic spacers bridging the tin atoms in the precursors. The influence of factors such as spacer length between tin in the precursors was also to be investigated.
Chapter 2

A Novel Route for the Preparation of

Dimeric Tetraorganodistannoxanes
2.1 Introduction

For the past four decades dimeric tetraorganodistannoxanes of the type
\[ [R_2(X)SnOSn(Y)R']_2 \] (R, R' = alkyl or aryl; X, Y = halide, OH, OR, OSiMe_3,
OOCR, OSP(OH)_2, NO_3, N_3, NCS, SH, OReO_3, NCO, OB(OR)_2, ROO, RSO_3, RS) (11)
have attracted considerable attention owing to both their unique structural
features and their applications in homogenous catalysis. More recently
dimeric tetraorganodistannoxanes bearing fluorinated organic substituents were used as catalysts in three liquid phase
systems involving fluorinated solvents. This allows easy separation of the tin
catalyst from the product.

\[ \begin{array}{c}
R = \text{alkyl, aryl;} \quad X, Y = \text{halides, OH, OR, OSiMe}_3, \\
\text{OOCR, OSP(OH)}_2, \text{NO}_3, \text{N}_3, \text{NCS, SH, OReO}_3, \text{NCO, OB(OR)}_2, \\
\text{ROO, RSO}_3, \text{RS} \\
\end{array} \]

R = alkyl, aryl; X, Y = halides, OH, OR, OSiMe_3, OCR, OB(OR)_2,
OReO_3, OSP(OH)_2, NO_3, N_3, NCS, NCO, SH, ROO, RSO_3, RS

In the past, dimeric tetraorganodistannoxanes with X, Y = halide, OH have
been prepared by the partial hydrolysis of diorganotin dihalides. However this
method is not always straightforward and requires specific conditions for each
product, which are unpredictable for new systems. A more general
approach for the synthesis of derivatives with X = Y = halide is from a reaction
between equimolar amounts of diorganotin oxide and diorganotin dihalide. A
shortcoming of this method is the requirement that the diorganotin oxide must be
sufficiently soluble in organic solvents. Furthermore, this method fails to provide
fluorinated tetraorganodistannoxanes due to the generally poor solubility of
diorganotin difluorides. Consequently, only few examples have been reported so
far.
Earlier work showed that reaction between diorganotin oxides and ammonium halides in methylcyclohexane at reflux resulted in formation of diorganotin dihalides. This suggested the further investigation of this reaction as a general pathway for tetraorganodistannoxanes.

This Chapter reports a new and facile way of generating dimeric tetraorganodistannoxanes with $X = Y = \text{halide}$ using $(R_2\text{SnO})_m$ ($R = \text{Me, Et, } n\text{-Bu, } n\text{-Oct, } c\text{-Hex, } i\text{-Pr, Ph}$) and a biphasic solvent mixture consisting of saturated aqueous $\text{NH}_4X$ solution ($X = \text{F, Cl, Br, I, OAc}$) and 1,4-dioxane. The new reaction scheme enables generation of a number of already reported as well as some hitherto unknown dimeric tetraorganodistannoxanes. This Chapter also reports the identification of $[R_2(\text{OH})\text{SnOSn(X)R}_2]_2$ ($R = n\text{-Bu; } X = \text{Cl, Br}$) and $[R_2(\text{OH})\text{SnOSn(X)R}_2][R_2(X)\text{SnOSn(X)R}_2]$, suggesting a serial substitution mechanism starting from $[R_2(\text{OH})\text{SnOSn(OH)R}_2]_2$. Compounds were characterised by solution and solid state $^{119}\text{Sn}$ NMR spectroscopy and in some representative cases by X-ray crystallography.

### 2.2 Synthetic Aspects

The reaction of the diorganotin oxides, $(R_2\text{SnO})_m$ ($R = \text{Me, Et, } n\text{-Bu, } n\text{-Oct, } c\text{-Hex, } i\text{-Pr, Ph}$), with aqueous $\text{NH}_4X$ ($X = \text{halide, OAc}$) was performed in refluxing dioxane (Scheme 14). The reactions were usually complete when all of the polymeric diorganotin oxide had dissolved (12-96 h). In most cases pure dimeric tetraorganodistannoxane, $[R_2(X)\text{SnOSn(X)R}_2]_2$ (hereafter denoted with $b$) were obtained after standard work-up procedure. In a few cases diorganotin dihalides or diacetates, $R_2\text{SnX}_2$ (hereafter denoted with $a$), were obtained in good to high yields. Reaction conditions and yields are summarised in Table 1.

\[
(R_2\text{SnO})_n + \text{sat. } \text{NH}_4X \xrightarrow{1,4\text{-dioxane}} \xrightarrow{\text{reflux, 12-96 h}} R_2\text{SnX}_2 + [R_2(X)\text{SnOSn(X)R}_2]_2
\]

$R = \text{Me, Et, } n\text{-Bu, } n\text{-Oct, } c\text{-Hex, } i\text{-Pr, Ph}$

$X = \text{halides, OAc}$

Scheme 14
Table 1. Reaction conditions and yields for the preparation of diorganotin dihalides or diacetates (a) and dimeric tetraorganodistannoxanes (b)

<table>
<thead>
<tr>
<th>Entry</th>
<th>NH₄X</th>
<th>(R₂SnO)m</th>
<th>Time [h]</th>
<th>Product(s)</th>
<th>Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>F</td>
<td>Me</td>
<td>48</td>
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<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>Et</td>
<td>24</td>
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<td></td>
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<td>3</td>
<td></td>
<td>n-Bu</td>
<td>48</td>
<td>59b</td>
<td>75</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>n-Oct</td>
<td>48</td>
<td>Complex mixture a</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>c-Hex</td>
<td>48</td>
<td>61b</td>
<td>86</td>
</tr>
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<td></td>
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<td></td>
<td>Ph</td>
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<td>64b</td>
<td>82</td>
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<td></td>
<td>Et</td>
<td>24</td>
<td>65b</td>
<td>60 b</td>
</tr>
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<td>48</td>
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<td></td>
<td>i-Pr</td>
<td>20</td>
<td>69a</td>
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<td>70a</td>
<td>95</td>
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<tr>
<td>15</td>
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<td>48</td>
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<td>72b</td>
<td>60 c</td>
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<td></td>
<td>n-Oct</td>
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<td>74b</td>
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<td>Ph</td>
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<td>92</td>
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</table>

*a* poor yield (see text and experimental); *b* an additional signal at $\delta$ 89.9; *c* an additional signal at $\delta$ 92.4; *d* isolated as water adduct.

### 2.2.1 Reaction of $(R_2SnO)_m$ with NH$_4$F

The reaction of $(R_2SnO)_m$ with NH$_4$F afforded dimeric tetraorganodistannoxanes $[R_2(F)SnOSn(F)R_2]_2$ ($R = n$-Bu ($59b$), *c*-Hex ($61b$)). However, for $R = Me$, Et, *n*-Oct, *i*-Pr and Ph only inseparable mixtures were obtained. Moreover, for $R = Me$, Et and Ph the low yield of these mixtures suggests that substantial amounts of organotin species were not extracted from the aqueous layers. This observation might be tentatively attributed to the formation of charged organotin species, such as $[R_2SnF_3]^{-}$, $[(R_2SnF_2)_2F]^{-}$ and $[R_2SnF_4]^{2-}$.152,153 For $R = n$-Oct and *i*-Pr the $^{119}$Sn NMR spectra of the crude mixtures revealed 12 and 17 signals, respectively, in the region between $\delta$ −15.0 and −190.0, which could not be assigned.

In CDCl$_3$ solution, $[n$-Bu$_2(F)SnOSn(F)n$-Bu$_2]_2$ ($59b$) and $[c$-Hex$_2(F)SnOSn(F)c$-Hex$_2]_2$ ($61b$) are unambiguously characterised by $^{119}$Sn NMR spectroscopy, which reveals for each compound two triplets centred at $\delta$ −142.2 [$^1J(^{119}$Sn-$^{19}$F) = 771 Hz] and −159.4 [$^1J(^{119}$Sn-$^{19}$F) = 1795 Hz] for $59b$ and at $\delta$ −237.6 [$^1J(^{119}$Sn-$^{19}$F) = 1950 Hz] and −212.0 [$^1J(^{119}$Sn-$^{19}$F) = 783 Hz] for $61b$. The observation of well-resolved triplets for $59b$ somewhat contradicts the results of Jain et al. who reported a broad signal at $\delta$ −156.0 for this compound.88
2.2.2 Reaction of $(R_2SnO)_m$ with NH$_4$Cl

The reaction of $(R_2SnO)_m$ with NH$_4$Cl provided dimeric tetraorganodistannoxanes $[R_2(Cl)SnOSn(Cl)R_2]_2$ ($R = Me$ (64b),$^{52}$ Et (65b),$^{52}$ $n$-Bu (66b),$^{52}$ $n$-Oct (67b), $c$-Hex (68b)) and diorganotin dichlorides $R_2SnCl_2$ ($R = i$-Pr (69a),$^{154}$ Ph (70a)$^{155}$) respectively. In view of the fact that $c$-Hex groups are bulkier than Ph groups, the formation of 68b and 70a suggests that not only the steric demand of the substituents, but also the group electronegativities of the substituents determines the favoured product of the reactions.

The course of reaction between $(n$-$Bu_2SnO)_m$ and NH$_4$Cl was monitored using $^{119}$Sn NMR spectroscopy. A representative sample was taken after 24 h (total reaction time 48 h), the $^{119}$Sn NMR spectrum (CDCl$_3$) of which revealed eight signals between $\delta$ $-80.2$ and $-190.0$. The connectivity of these signals was established by 1D and 2D INADEQUATE $^{119}$Sn NMR spectroscopy (Figure 6). Accordingly, the signals were assigned, by reference to previously reported spectra on pure compounds, to $[n$-$Bu_2(OH)SnOSn(Cl)n$-$Bu_2]_2$ (66d, $\delta(^{119}$Sn): $-138.8$, $-159.8$; total integral 12.0%),$^{86}$ $[n$-$Bu_2(OH)SnOSn(Cl)n$-$Bu_2][n$-$Bu_2(Cl)SnOSn(Cl)n$-$Bu_2]$ (66c, $\delta(^{119}$Sn): $-93.4$, $-125.6$, $-132.2$, $-175.2$; total integral 61.0%), and $[n$-$Bu_2(Cl)SnOSn(Cl)n$-$Bu_2]_2$ (66b, $\delta(^{119}$Sn): $-90.7$, $-139.1$; total integral 27.0%).$^{86}$ The coexistence of the latter three tetraorganodistannoxanes demonstrates that the redistribution reaction between these species is slow on the $^{119}$Sn NMR time scale.$^{87}$
Figure 6. $^{119}$Sn 2D INADEQUATE spectrum (CDCl$_3$) from the reaction of ($n$-Bu$_2$SnO)$_n$ with NH$_4$Cl after 24 h.
Scheme 15 summarises a plausible set of equilibria consistent with the observation described above. The reaction mechanism appears to involve the initial formation of tetrahydroxide species \([n\text{-}\text{Bu}_2(\text{OH})\text{SnOSn(\text{OH})n\text{-}\text{Bu}_2}]_2\ (66f)\) from which hydroxides are replaced in a stepwise fashion by chlorides. Although in the literature there are numerous examples of compounds of type \(b^{59-61,68,94,97}\) and \(d^{60,69,137,141}\), only three compounds of type \(f\) are known \((R = \text{Me}_3\text{SiCH}_2, 67\) Neophyl\(^{95}\) and a mixed \('\text{Bu}/\text{Me}_3\text{SiCH}_2\)^{156}\). The presence of \(66c\) found in this study appears to be the first evidence of compound of monohydroxide ladder \([n\text{-}\text{Bu}_2(\text{OH})\text{SnOSn(\text{X})n\text{-}\text{Bu}_2}]_2\) reported to date.

\[
\begin{align*}
\text{(R}_2\text{SnO)}_n & \quad + \quad \text{NH}_4\text{X} & \quad \text{R}_2\text{SnX}_2 \\
\text{f} & & 66; \text{R} = \text{n-Bu}, \text{X} = \text{Cl} \\
\text{e} & & 73; \text{R} = \text{n-Bu}, \text{X} = \text{Br} \\
\end{align*}
\]

**Scheme 15**
2.2.3 Reaction of \((R_2SnO)_m\) with NH₄Br

The reaction of \((R_2SnO)_m\) with NH₄Br produced tetraorganodistannoxanes \([R_2(Br)SnOSn(Br)R_2]_2\) (\(R = Et\) (72b),\(^{53}\) \(n\)-Bu (73b),\(^{53}\) \(n\)-Oct (74b), \(i\)-Pr (76b)) and diorganotin dibromides \(R_2SnBr_2\) (\(R = c\)-Hex (75a),\(^{157}\) Ph (77a)) respectively.

The reaction of \((Me_2SnO)_m\) with NH₄Br provided a mixture of unknown products, which could not be separated. The \(^{119}\)Sn NMR spectrum (CDCl₃) of this mixture revealed 12 signals between \(\delta -131.5\) and \(-153.5\), which could not be assigned.

The course of reaction between \((n\text{-}Bu}_2SnO)_m\) and NH₄Br was monitored using \(^{119}\)Sn NMR spectroscopy. A representative sample was taken after 24 h (total reaction time 48 h), the \(^{119}\)Sn NMR spectrum (CDCl₃) of which revealed eight signals between \(\delta -80.3\) and \(-181.6\). Accordingly, the signals were assigned, by reference to literature values, to \([n\text{-}Bu}_2(OH)SnOSn(Br)n\text{-}Bu_2]_2\) (73d, \(\delta^{(119)}\text{Sn}: -161.0, -174.5\); total integral 22.0\%), \([n\text{-}Bu}_2(OH)SnOSn(Br)n\text{-}Bu_2][n\text{-}Bu}_2(Br)SnOSn(Br)n\text{-}Bu_2]_2\) (73e, \(\delta^{(119)}\text{Sn}: -79.8, -120.9, -154.6, -181.4\); total integral 35.0\%), and \([n\text{-}Bu}_2(Br)SnOSn(Br)n\text{-}Bu_2]_2\) (73b, \(\delta^{(119)}\text{Sn}: -81.4, -129.9\); total integral 43.0\%). These results also suggest that the reaction mechanism appears to involve the initial formation of tetrahydroxide species \([n\text{-}Bu}_2(OH)SnOSn(OH)n\text{-}Bu_2]_2\) (73f) from which hydroxides are replaced in a stepwise fashion by halide (Scheme 15).

2.2.4 Reaction of \((R_2SnO)_m\) with NH₄I

The reaction of \((R_2SnO)_m\) with NH₄I afforded only dimeric tetraorganodistannoxanes for \(R = n\text{-}Bu\) (80b) and \(n\)-Oct (81b), whereas diorganotin diiodides were isolated for \(R = Me\) (78a), \(c\)-Hex (82a), \(i\)-Pr (83a) and Ph (84a). For \(R = Et\) a complex mixture was obtained, which could not be separated. The \(^{119}\)Sn NMR spectrum of this mixture revealed seven signals between \(\delta -30.5\) and \(-200.0\), which could not be assigned.
2.2.5 Synthesis of $[\text{c-Hex}_2(\text{Cl})\text{SnOSn(F)c-Hex}_2]_2$

Recently, redistribution reactions were described between two symmetric dimeric tetraorganodistannoxanes, $[\text{R}_2(\text{X})\text{SnOSn(X)R}_2]_2$ and $[\text{R}_2(\text{Y})\text{SnOSn(Y)R}_2]_2$. Hasha and coworkers\(^87,88,158,159\) demonstrated that binary mixtures of $[\text{R}_2(\text{X})\text{SnOSn(X)R}_2]_2/[\text{R}_2(\text{Y})\text{SnOSn(Y)R}_2]_2$ ($\text{R} = \text{n-Bu; X} = \text{Cl}, \text{Y} = \text{Br}$) and ($\text{R} = \text{n-Bu; X} = \text{Cl}, \text{Y} = \text{OAc}$) reach equilibrium rapidly, producing all five possible mixed tetraorganodistannoxane dimers. The mixed dimers differ in the relative number and positions of the $\text{X}$ and $\text{Y}$ ligands: one 3:1 ($\text{X}:\text{Y}$) dimer, one 1:3 and three 2:2 dimers. They showed that formation of the mixed tetraorganodistannoxane dimers takes place via bimolecular collisions producing a four-centered transition state, which in turn undergoes a concerted exchange of the halides.

Given the easy access to the fluoride \(61b\), it was decided to investigate the lability of the halides in the fluoride system $[\text{c-Hex}_2(\text{F})\text{SnOSn(F)c-Hex}_2]_2$ \((61b)\) and the chloride system $[\text{c-Hex}_2(\text{Cl})\text{SnOSn(Cl)c-Hex}_2]_2$ \((68b)\). Reaction between \(61b\) and \(68b\) in toluene at 100°C provided a white solid, which has elemental analysis consistent with the formula $[\text{c-Hex}_2(\text{Cl})\text{SnOSn(F)c-Hex}_2]_2$ \((93)\) in almost quantitative yield (Scheme 16).

\[
\begin{align*}
[\text{R}_2(\text{F})\text{SnOSn(F)R}_2]_2 \\
\text{61b} \\
+ \\
[\text{R}_2(\text{Cl})\text{SnOSn(Cl)R}_2]_2 \\
\text{68b} \quad \xrightarrow{\text{Toluene} \quad 100 \ ^\circ \text{C}} \quad [\text{R}_2(\text{Cl})\text{SnOSn(F)R}_2]_2 \\
\text{93} \\
\text{R} = \text{c-Hex}
\end{align*}
\]

Scheme 16

Compound \(93\) is colourless, high-melting solid, which is poorly soluble in most common organic solvents. However, it was possible to obtain a \(^{119}\text{Sn}\) NMR spectrum ($d_8$-toluene) at 100°C that displays a doublet and a doublet of doublets centred at $\delta$ $-175.3$ [$^1J(^{119}\text{Sn}-^{19}\text{F}) = 1240$ Hz; $^2J(^{119}\text{Sn-O-}^{117/119}\text{Sn}) = 220$ Hz] and $-226.1$ [$^1J(^{119}\text{Sn}-^{19}\text{F}) = 1540$ Hz; $^2J(^{119}\text{Sn-O-}^{117/119}\text{Sn}) = 221/217$ Hz; $^3J(^{119}\text{Sn-O-Sn-}^{19}\text{F}) = 32$ Hz] of equal intensity (total integral 80.0%). Additionally, the spectrum shows 15 low intensity signals between $\delta$ $-135$ and $-247$ (total integral 20.0%).
which were not assigned. However, the fact that these minor signals are reproducible
with the same integral ratio for solutions of samples which had been recrystallised
several times suggests the species belonging to these signals are in equilibrium with
$\text{93.}^{156}$ The $^{19}$F NMR spectrum ($d_8$-toluene, r.t.) of $\text{93}$ reveals one major signal at $\delta
-124.1$ [$^{1}J(\text{F}-^{117/119}\text{Sn}) = 1220 \text{ Hz}; ^{1}J(\text{F}-^{117/119}\text{Sn}) = 1489 \text{ Hz}$] and two minor
signals at $\delta$ $-123.2$ and $123.5$ respectively. An X-ray structure analysis (see below)
indeed confirmed the existence of a dimeric tetraorganodistannoxane containing F
and Cl atoms. The $^{119}$Sn MAS NMR spectrum of $\text{93}$ shows three signals at $\delta
-183.0$ [$^{1}J(\text{Sn}-^{19}\text{F}) = 1150 \text{ Hz}; -226.0$ [$^{1}J(\text{Sn}-^{19}\text{F}) = 1550 \text{ Hz}$] and $-234.0$ [$^{1}J(\text{Sn}-
^{19}\text{F}) = 1630 \text{ Hz}$] with a total manifold integration of 2:1:1. The number of signals is
consistent with the existence of a non-symmetric tetrameric unit or two independent
molecules, i.e a and b, in the crystallographic unit cell, each situated about a centre.

2.2.6 Reaction of (R$_2$SnO)$_m$ with NH$_4$OAc

The reaction of (R$_2$SnO)$_m$ with NH$_4$OAc afforded only one dimeric
tetraorganodistannoxane, namely, [Me$_2$(OAc)SnOSn(OAc)Me$_2$]$_2$ (85b), and on
almost all other occasions, diorganotin diacetates, R$_2$Sn(OAc)$_2$ (R = Et (86a), n-Oct
(88a), c-Hex (89a), i-Pr (90a) and Ph (91a)).

For (n-Bu$_2$SnO)$_m$, a mixture of [n-Bu$_2$(OAc)SnOSn(OAc)n-Bu$_2$]$_2$ (87b;
$\delta(^{119}\text{Sn})$: $-205.9$, $-220.6$; total integral 52.0%)$^{86}$ and n-Bu$_2$Sn(OAc)$_2$ (87a; $\delta(^{119}\text{Sn})$:
$-156.3$; total integral 48.0%) was obtained.

It is worth mentioning that c-Hex$_2$Sn(OAc)$_2$ (89a) was isolated as its water
adduct c-Hex$_2$Sn(OAc)$_2$·H$_2$O (89a·H$_2$O). X-ray analysis of 89a·H$_2$O was carried out
on a crystal obtained from a slow evaporation of a hexane solution (see below).

The recrystallisation of a chloroform / hexane solution (1:3) of i-Pr$_2$Sn(OAc)$_2$
(90a) afforded small amount of crystals. Subsequent X-ray analysis showed it to be
hexameric i-propyloxotin acetate [i-PrSn(O)(OAc)]$_6$ (92·4CHCl$_3$), which has been
characterised as its tetra chloroform solvate. The unexpected formation of 92·4CHCl$_3$
presumably results from the hydrolysis of the impurity i-PrSn(OAc)$_3$, which was
within the material being recrystallised. The molecular structure of 92·4CHCl$_3$ is
shown in Figure 7, and the selected geometric parameters are collected in Table 2.
The drum motif found for 92·4CHCl₃ has been found previously described for several other derivatives. The centrosymmetric structure may be described as being comprised of two (i-PrSnO)₃ rings that are linked in two ways. Firstly, each of the bridging-oxo atoms of each ring connects a Sn atom of the adjacent ring leading to the presence of six μ₃-oxo groups. The girth of the drum may be thought of as six Sn₂O₂ rectangles arranged so as to form a tube. Further links between the rings afforded by six bidentate bridging acetate bridges, each of which spans, diagonally, a Sn₂O₂ rectangle. The isopropyl groups are directed above and below the (i-PrSnO)₃ rings. Each tin atom exists in a distorted octahedral geometry defined by three O atoms derived from three μ³-O atoms, two carboxylate O atoms and a C atom of the organic substituent.

### Table 2. Selected interatomic (Å, deg.) parameters for [i-PrSn(O)(OAc)]₆·4CHCl₃ (92·4CHCl₃).

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Symmetry operation \(i: -x, y, -z\).
Figure 7. Molecular structure (50% probability ellipsoids) and crystallographic numbering scheme employed for \([i\text{-PrSn(O)(OAc)}]_6\cdot 4\text{CHCl}_3\) (92·4CHCl₃). a) perspective view and b) top view.

2.3 Molecular Structures and Solid State $^{119}$Sn MAS NMR
2.3.1 $[c\text{-Hex}_2(F)\text{SnOSn(F)F}c\text{-Hex}_2]_2$:

X-ray analysis of $[c\text{-Hex}_2(F)\text{SnOSn(F)F}c\text{-Hex}_2]_2$ (61b) was carried out on a crystal obtained from the slow evaporation of a chloroform/hexane solution. The molecular structure of 61b is shown in Figure 8 and selected bond lengths and angles are listed in Table 3. The intramolecular Sn(1)···F(2) separations are 3.472(4) Å. The key difference between the two structures is found in the association of two chloroform molecules to the tetrameric unit as illustrated in Figure 8. Hydrogen bonding interactions between the terminal F(2) atoms are noted so that H···F(2) is 1.91 Å, C(25)···F(2) is 2.868(10) Å and the angle subtended at H is 161°. While full details are not reported here, a preliminary structure of the chloride analogue, 68b, has been determined. Difficulties in the refinement owing to the lack of resolution of two cyclohexyl rings preclude a full report, but suffice to say that the structure resembles very closely the prototype 61b.

The $^{119}$Sn CP-MAS NMR spectrum of 61b shows only six signals rather than the anticipated eight signals i.e. two doublets of doublets (Figure 9). Very recently, the crystal structure of a closely related mixed butyl analogue was obtained, i.e. $[n\text{-Bu}_2(F)\text{SnOSn(F)F}n\text{-Bu}_2]_2$. In this structure the fluoride bridges are similar with Sn(1)-F(1) and Sn(2)-F(1) being 2.168(1) and 2.249(1) Å, respectively and the Sn(1)···F(2) separation is 3.500(1) Å. The $^{119}$Sn MAS NMR spectrum of the mixed butyl analogue shows eight signals. The $^{119}$Sn CP-MAS NMR spectrum of 61b shows six signals at $\delta$ −215.5, −232.4, −245.9, −259.2, −270.5 and −282.8, two of which appear to have higher intensity however could not be unambiguously assigned due to overlapping spinning sidebands.


**Figure 9.** $^{119}$Sn CP-MAS NMR spectrum of $[c\text{-Hex}_2(F)\text{SnOSn(F)c-Hex}_2]_2$ (61b) ($\nu_{\text{mas}} = 12$ KHz). Isotropic chemical shifts are indicated by arrows.

**Table 3.** Selected interatomic (Å, deg.) parameters for $[c\text{-Hex}_2(F)\text{SnOSn(F)c-Hex}_2]_2$ (61b).

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Symmetry operation \( i : 1/2-x, 1/2-y, 1-z \).
Figure 8. Molecular structure (50% probability ellipsoids) and crystallographic numbering scheme employed for \([\text{c-Hex}_2(\text{F})\text{SnOSn(F)\text{c-Hex}_2}]_2\) (61b).
2.3.2 \([c-\text{Hex}_2(\text{Cl})\text{SnOSn(F)}c-\text{Hex}_2]_2\)

Slow evaporation of a chloroform/hexane solution of \([c-\text{Hex}_2(\text{Cl})\text{SnOSn(F)}c-\text{Hex}_2]_2\) (93) gave crystals suitable for X-ray analysis. The molecular structure of 93 crystallises with two independent centrosymmetric molecules comprising the asymmetric unit. One of the molecules is shown in Figure 10 and the other is in essential agreement with this. Selected geometric parameters for both independent molecules are collected in Table 4. From Figure 10 it is apparent that the more electronegative fluorine atoms function as symmetric bridges between the endo- and exo-cyclic tin atoms. The chlorine atoms occupy terminal positions with Sn(1)--Cl(1) being 3.707(3) Å and Sn(3)--Cl(2) being 3.814(3) Å, distances again not indicative of significant bonding interactions. Very recently, the crystal structure of the phenyl analogue was reported, \(i.e\) \([\text{Ph}_2(\text{F})\text{SnOSn(Cl)}\text{Ph}_2]_2\). In this structure the fluoride bridges are similar with Sn(1)-F(1) and Sn(2)-F(1) being 2.175(4) and 2.222(5) Å, respectively and the Sn(1)--Cl(1) separation is 3.663(2) Å.

Table 4. Selected interatomic (Å, deg.) parameters for \([c-\text{Hex}_2(\text{F})\text{SnOSn(Cl)}c-\text{Hex}_2]_2\) (93).

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O(2)\textsuperscript{i}-Sn(3)-C(25) 99.8(2) 99.7(2)
O(2)\textsuperscript{i}-Sn(3)-C(31) 103.3(2) 102.7(18)
F(2)-Sn(3)-C(25) 93.5(2) 92.8(2)
F(2)-Sn(3)-C(31) 89.5(2) 88.74(19)
C(25)-Sn(3)-C(31) 130.5(3) 136.0(2)
O(2)-Sn(4)-F(2) 71.40(15) 72.35(14)
O(2)-Sn(4)-Cl(2) 87.12(12) 90.80(12)
O(2)-Sn(4)-C(37) 109.1(2) 111.1(2)
O(2)-Sn(4)-C(43) 115.7(2) 114.5(3)
F(2)-Sn(4)-Cl(2) 158.5(9) 163.0(10)
F(2)-Sn(4)-C(37) 84.84(19) 86.71(19)
F(2)-Sn(4)-C(43) 91.5(2) 87.7(4)
Cl(2)-Sn(4)-C(37) 103.9(17) 101.8(17)
Cl(2)-Sn(4)-C(43) 96.9(2) 97.7(3)
C(37)-Sn(4)-C(43) 131.2(2) 129.7(3)
Sn(3)-O(2)-Sn(4) 114.1(18) 113.2(17)
Sn(3)-O(2)-Sn(4)\textsuperscript{i} 140.7(2) 140.5(2)
Sn(3)-O(2)-Sn(3)\textsuperscript{i} 105.2(18) 106.2(18)
Sn(3)-F(2)-Sn(4) 101.5(14) 101.4(13)

symmetry operation i : $-x, 1-y, -z$. $-x, -y, -1-z$. 

45
Figure 10. Molecular structure (50% probability ellipsoids) and crystallographic numbering scheme employed for one of the two independent molecules of $[c$-Hex$_2$(F)SnOSn(Cl)c-Hex$_2]$$_2$ (93).
2.3.3 \([i-{\text{Pr}_2}\text{Br}]\text{SnOSn(Br)}{i-\text{Pr}_2}]_2\)

X-ray analysis of \([i-{\text{Pr}_2}\text{Br}]\text{SnOSn(Br)}{i-\text{Pr}_2}]_2\) (76b) was carried out on a crystal obtained from the slow evaporation of a chloroform/hexane solution. The molecular structure of 76b is shown in Figure 11 and selected bond lengths and angles are listed in Table 5. The molecular structure of 76b shows a centrosymmetric \((i-{\text{Pr}_2}\text{Sn})_2\text{O}_2\) core connected, via the oxygen atoms, to two \(i-{\text{Pr}_2}\text{Sn}\) entities. Almost symmetric bromide bridges between the endo- and exo-cyclic tin atoms are present. The Sn(2)-bound Br(2) atoms are terminal in that the intramolecular Sn(1)---Br(2) separations of 3.530(3) Å are not indicative of significant bonding interactions between these atoms. The coordination geometries for the tin atoms are both based on trigonal bipyramids. In the case of Sn(1), the O(1) and Br(1) atoms occupy the axial positions, and two bromides occupy the axial positions about the Sn(2) atom. The influence of the close Sn(1)---Br(2) interaction is such to expand the C(1)-Sn(1)-C(4) angle to 135.6(2)° compared with 126.5(3)° for C(7)-Sn(2)-C(10). The \(^{119}\text{Sn}\) MAS NMR spectrum of 76b showing two signals at \(\delta -72.0\) and \(-148.0\), is in agreement with the centrosymmetric space group found in the X-ray diffraction experiment.

**Table 5.** Selected interatomic (Å, deg.) parameters for \([i-{\text{Pr}_2}\text{Br}]\text{SnOSn(Br)}{i-\text{Pr}_2}]_2\) (76b).

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Symmetry operation i: −x, −y, −z.
Figure 11. Molecular structure (50% probability ellipsoids) and crystallographic numbering scheme employed for \([i-\text{Pr}_2(\text{Br})\text{SnOSn(Br)}i-\text{Pr}_2]_2\) (76b).
2.3.4 [Me₂(OAc)SnOSn(OAc)Me₂]₂

Slow evaporation of a chloroform/hexane solution of [Me₂(OAc)SnOSn(OAc)Me₂]₂ (85b) gave crystals suitable for X-ray analysis. The molecular structure of 85b is shown in Figure 12 and selected bond lengths and angles are listed in Table 6. The molecular structure of 85b represents a second polymorph of the compound with the monoclinic polymorph also crystallising in a non-centrosymmetric space group Pa (see Experimental). Of the structures with the general formula \([R₂Sn(O₂CR')]₂O\), i.e. with \(R = R' = Me\), is an atypical structure, being the sole example of one of five motifs known for compounds of this type. The structure is constructed about a central \((Me₂Sn)₂O₂\) core to which is linked, via the oxygen atoms, two \(Me₂Sn\) entities. Further links between the endocyclic \(Sn(1)\) and \(Sn(2)\) atoms, and exocyclic \(Sn(3)\) and \(Sn(4)\) atoms, with the exception of the \(Sn(1)\) and \(Sn(4)\) pair, are afforded by bidentate bridging acetate groups that form essentially symmetric \(Sn-O\) bonds. The coordination geometry about the \(Sn(4)\) atom is completed by a monodentate acetate ligand. Bridges between neighbouring tetrameric units are present so that the \(O(10)\) atom forms an interaction with a symmetry related \(Sn(3)\) atom. The \(Sn(3)-O(10)\) distance of 2.523(12) \(\text{Å}\) is not so much longer than the other \(Sn-O_{acetate}\) bond distances, which lie in the range 2.212(9) to 2.329(13) \(\text{Å}\), and hence, the structure is properly described as polymeric with the chain extending along the crystallographic \(z\)-axis. The \(Sn(1)\) and \(Sn(4)\) atom exist in distorted trigonal bipyramidal geometries with the \(O(1)\) and \(O(3)\), and \(O(1)\) and \(O(5)\) atoms defining the axial positions, respectively. A close intramolecular contact between the \(Sn(1)\) and \(O(9)\) atoms of 2.904(11) \(\text{Å}\) is not considered to represent a significant bonding interaction between these atoms but may be responsible for the expansion of the \(C(9)-Sn(1)-C(10)\) angle to 141.8(5)°. Similarly, a close contact between the \(Sn(4)\) and \(O(10)\) atoms of 2.881(11) \(\text{Å}\) is noted which is also probably responsible for the widening of the \(C(15)-Sn(4)-C(16)\) angle to 140.8(8)°. By contrast to the trigonal bipyramidal geometries found for \(Sn(1)\) and \(Sn(4)\), a skew-trapezoidal bipyramidal geometry, defined by a \(C₂O₄\) donor set, is the best description for the coordination geometry for the \(Sn(2)\) atom where the methyl groups lie over the weaker \(Sn(2)-O(5)\), \(O(7)\) bonds. A \(C₂O₄\) donor set is also found about the \(Sn(3)\) atom which tends towards a distorted octahedral geometry based on
a consideration of the angles, the disparity in the Sn-O bond distances notwithstanding. As mentioned above, 85b is one of two polymorphs for which full structure determinations are available.

Table 6. Selected interatomic (Å, deg.) parameters for [Me2(OAc)SnOSn(OAc)Me2]2 (85b).

<p>| | | | |</p>
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**Symmetry Operation i:** 1−x, 1−y, ½+z
Figure 12. Molecular structure (50% probability ellipsoids) and crystallographic numbering scheme employed for [Me$_2$(OAc)SnOSn(OAc)Me$_2$]$_2$ (85b).
Compound **85b** crystallised as a mixture of different polymorphs from a solution of CHCl$_3$ / hexane (1:2) within 3 days, as evidenced by the number of $^{119}$Sn MAS NMR signals (approximately 6). From this mixture, a crystal was selected for the X-ray structure analysis, which showed a new polymorph for **85b**. The molecular structures for the two polymorphs are in essential agreement with each other. The $^{119}$Sn MAS NMR spectrum of this mixture shows six signals at $\delta$ $-169.1$, $-175.9$, $-207.8$, $-287.7$, $-294.9$ and $-300.0$ with a total manifold integration of $1 : 4 : 5(4+1) : 4 : 1 : 5(4+1)$ (Figure 13). The number of signals is consistent with the existence of two polymorphs for **85b** in an approximate ratio of 4:1. The comparison of the $^{119}$Sn MAS NMR of previously reports$^{58}$ spectrum on pure compound suggests that the major component of this mixture comprise mostly of the first polymorph reported by Lockhart in 1986.$^{76}$ The six large sideband manifolds in the spectrum (Figure 13) were used to perform a tensor analysis according to the method of Herzfeld and Berger.$^{162,163}$ The isotropic chemical shift ($\delta_{\text{iso}}$), anisotropy ($\zeta$) and asymmetry ($\eta$), represented in the Haeberlen convention$^{164}$ are listed in Table 7. It is worth emphasising that the $^{119}$Sn NMR parameters of $\delta$ $-207.8$ and $-300.0$ are the average of two independent tin sites.
Figure 13. $^{119}\text{Sn}$ MAS NMR spectrum of $[\text{Me}_2(\text{OAc})\text{SnOSn(OAc)Me}_2]_2$ (85b) ($\nu_{\text{mas}} = 11.2$ KHz). Isotropic chemical shifts are indicated by arrows.

Table 7. Selected $^{119}\text{Sn}$ MAS NMR parameters for $[\text{Me}_2(\text{OAc})\text{SnOSn(OAc)Me}_2]_2$ (85b).

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<th>$\delta_{\text{iso}}$ (ppm)</th>
<th>$\zeta$ (ppm)</th>
<th>$\eta$</th>
<th>%</th>
<th>$\sigma_{11}$ (ppm)</th>
<th>$\sigma_{22}$ (ppm)</th>
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<td>0.55</td>
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<td>620</td>
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<td>21.5</td>
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<td>796</td>
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<td>560</td>
<td>0.80</td>
<td>25.5</td>
<td>$-296$</td>
<td>152</td>
<td>768</td>
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<td>$-287.7$</td>
<td>680</td>
<td>0.30</td>
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<td>50</td>
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<td>0.40</td>
<td>3.5</td>
<td>$-160$</td>
<td>100</td>
<td>945</td>
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<tr>
<td>$-300.0$</td>
<td>700</td>
<td>0.30</td>
<td>25.3</td>
<td>$-155$</td>
<td>55</td>
<td>1000</td>
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</table>
To further confirm the existence of a mixture of different polymorphs in the bulk material of 85b, a powder X-ray diffraction experiment was performed and the result was compared with the simulated X-ray powder diffraction data from single crystal experiment. The experiment powder X-ray diffraction profile for the bulk material of 85b indeed shows mostly the diffraction peaks of the first polymorph for 85b, indicating that the first polymorph correspond to the major component of the mixture (as observed by $^{119}$Sn MAS NMR) (Figure 14). In addition, the profile also shows two new peaks at 10.80 and 13.27° (as indicated by arrows), which is assigned to the new polymorph. The simulated powder X-ray diffraction profile from a single crystal of the new polymorph shows two distinct peaks at 10.87 and 13.34° (as indicated by arrows) which further confirm the assignment (Figure 15).

Figure 14. Experimental powder X-ray diffraction profile for the first polymorph of 85b (top) and bulk material of 85b (bottom).
2.3.5 \textit{c-Hex}_2\text{Sn(OAc)}_2\cdot\text{H}_2\text{O}

The molecular structure of \textit{c-Hex}_2\text{Sn(OAc)}_2\cdot\text{H}_2\text{O} (89a \cdot \text{H}_2\text{O}) is shown in Figure 16, and the selected geometric parameters are collected in Table 8. The coordination number of tin in 89a \cdot \text{H}_2\text{O} is seven, which is also reflected in the $^{119}\text{Sn}$ MAS NMR resonance being observed at $\delta$ $-401.8$. The tin atom is located on a crystallographic two-fold axis that also bisects the coordinated water molecule into the coordination sphere. The coordination geometry is distorted pentagonal bipyramidal with the five oxygen donor atoms defining the equatorial plane and the two tin-bound carbon atoms derived from the cyclohexyl groups occupying the axial positions (C-Sn-C $161.44(19)^\circ$). The mean deviation of the five oxygen atoms from their least-squares plane is 0.112 Å and the tin atom does not deviate from this plane (from symmetry). The acetate ligand forms disparate Sn-O bond distances of 2.227(2) Å and 2.485(3) Å with the longer distance being greater than that formed by the coordinated water molecule of 2.412(4) Å. A closely related structure featuring a \textit{trans-C}_2\text{SnO}_5 polyhedron has been reported for \textit{n-Bu}_2\text{Sn(O_2CH}_2\text{Ph})_2\cdot\text{H}_2\text{O} by Ng \textit{et al.}
The $^{119}$Sn NMR spectrum of the 89a in CDCl$_3$ shows a signal at $\delta \sim 215.3$, indicating five coordinated tin atoms and that the coordinated water found in the crystal structure has dissociated in solution.

**Table 8.** Selected interatomic (Å, deg.) parameters for $c$-Hex$_2$Sn(OAc)$_2$·H$_2$O (89a·H$_2$O).

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<td>2.151(4)</td>
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symmetry operation $i: -x, y, -z$. 
Figure 16. Molecular structure (50% probability ellipsoids) and crystallographic numbering scheme employed for $c\text{-Hex}_2\text{Sn(OAc)}_2\cdot\text{H}_2\text{O}$ (89a·H$_2$O).

2.4 Summary
The reaction of polymeric diorganotin oxides, \((R_2SnO)_m\) (\(R = \text{Me, Et, } n\text{-Bu, n-Oct, } c\text{-Hex, } i\text{-Pr, Ph}\)), with saturated aqueous \(\text{NH}_4X\) (\(X = \text{F, Cl, Br, I, OAc}\)) lead to the formation of dimeric tetraorganodistannoxanes, \([R_2(X)SnOSn(X)R_2]_2\), and in a few cases diorganotin dihalides or diacetates, \(R_2SnX_2\) is described. This method appears to be particularly good for the synthesis of halogenated tetraorganodistannoxanes but a less suitable method for the preparation of dicarboxylato tetraorganodistannoxanes. Identification of \([R_2(OH)SnOSn(X)R_2]_2\) (\(R = n\text{-Bu}; X = \text{Cl, Br}\)) and \([R_2(OH)SnOSn(X)R_2][R_2(X)SnOSn(X)R_2]\) suggests a serial substitution mechanism starting from \([R_2(OH)SnOSn(OH)R_2]_2\). X-ray structures are reported for \([c\text{-Hex}_2(F)SnOSn(F)c\text{-Hex}_2]_2\) (61b), \([c\text{-Hex}_2(Cl)SnOSn(F)c\text{-Hex}_2]_2\) (93), \([i\text{-Pr}_2(\text{Br})SnOSn(\text{Br})i\text{-Pr}_2]_2\) (76b) and \([\text{Me}_2(OAc)SnOSn(OAc)\text{Me}_2]_2(85b)\), respectively.
Chapter 3

Mixed and Self-Assembled Double Ladders

3.1 Introduction
Chapter 2 discussed a new and facile way of generating dimeric tetraorganodistannoxanes \([R_2(X)SnOSn(X)R_2]_2\) using polymeric diorganotin oxides and saturated aqueous ammonia halide. Of the large number of dimeric tetraorganodistannoxanes that have been previously synthesised, few of these are asymmetric and only four of these compounds have been characterised by X-ray crystallography. As mentioned in Chapter 1, Dakternieks et. al. synthesised the first spacer-bridged dimeric tetraorganodistannoxanes with an asymmetric double ladder structure. Asymmetric double ladders (24 and 25) contain two different organic groups R and R'. Both of these compounds appear to be thermodynamically more stable than the related symmetric species.\(^{100}\) Due to their potential as catalysts for asymmetric syntheses a study was undertaken to expand their chemistry.

![Diagram of asymmetric double ladders 24 and 25](image)

*24; R = CH\(_2\)CMe\(_3\), R' = CH\(_2\)CHMe\(_2\)  
*25; R = CH\(_2\)CMe\(_3\), R' = CH\(_2\)SiMe\(_3\)*

The preparation of asymmetric double ladders using \{[R(O)Sn\(_2\)](CH\(_2\))\(_n\}\(_m\) (R = CH\(_2\)SiMe\(_3\)) and [R(Cl)\(_2\)Sn\(_2\)](CH\(_2\))\(_n\)' was investigated. In particular, it was thought that the scrambling reaction between \{[R(O)Sn\(_2\)](CH\(_2\))\(_n\}\(_m\) and [R(Cl)\(_2\)Sn\(_2\)](CH\(_2\))\(_n\)' could lead to the formation of asymmetric double ladders where the different spacer chain lengths (n and n') provide the source of asymmetry. These reactions were also undertaken to gain some insight into the mechanism of double ladder formation. This Chapter describes the preparation and characterisation of a series of α,ω-bis(triphenylstannyl)alkanes, [Ph\(_3\)Sn\(_2\)](CH\(_2\))\(_n\) (n = 3-8 \(94c-h\)), n = 10 \(94i\), n = 12 \(94j\)) and some of their derivatives. Results of the mixed reaction between \{[R(O)Sn\(_2\)](CH\(_2\))\(_n\}\(_m\) and [R(Cl)\(_2\)Sn\(_2\)](CH\(_2\))\(_n\)' (R = CH\(_2\)SiMe\(_3\); n = 3, n' = 4-6, 8, 10, 12 and n = 4, n' = 3, 5-6, 8, 10, 12) are also reported in this Chapter.
3.2 Preparation of α,ω-Bis(triphenylstannyl)alkanes, [Ph₃Sn]₂(CH₂)ₙ

The synthesis of the series of alkyl-bridged di-tin precursors, namely α,ω-bis(triphenylstannyl)alkanes, [Ph₃Sn]₂(CH₂)ₙ (n = 3-8 (94c-h), n = 10 (94i), n = 12 (94j)) was achieved by the procedures shown in Scheme 17. Reaction of one molar equivalent of α,ω-dichloroalkane, Cl(CH₂)ₙCl (n = 3, 4), with two molar equivalents of Ph₃SnNa in liquid ammonia afforded α,ω-bis(triphenylstannyl)alkanes, [Ph₃Sn]₂(CH₂)ₙ (n = 3 (94c)¹³⁰, n = 4 (94d)) (Scheme 17).

\[
\begin{align*}
\text{Cl(CH₂)ₙCl} & \quad (n = 3, 4) \\
\text{Ph₃SnNa (2.0 eq)} & \quad \text{Liq. NH₃, } -78 \degree \text{C} \\
\text{Ph₃Sn(CH₂)ₙSnPh₃} & \quad \text{1. Mg, THF} \\
\text{Br(CH₂)ₙBr} & \quad (n = 5-8, 10, 12) \\
& \quad 2. \text{Ph₃SnCl (2.0 eq)}
\end{align*}
\]

**Scheme 17**

Reaction of one molar equivalent of the di-Grignard reagents, BrMg(CH₂)ₙMgBr (n = 5-8, 10, 12), with two molar equivalents of Ph₃SnCl in THF afforded α,ω-bis(triphenylstannyl)alkanes, [Ph₃Sn]₂(CH₂)ₙ (n = 5-8 (94e-h), n = 10 (94i), n = 12 (94j))¹⁶⁶ (Scheme 17).

The compounds 94c-h, 94i, and 94j are white crystalline solids all have satisfactory elemental analysis. ¹¹⁹Sn NMR spectra (CDCl₃) of the compounds gave chemical shifts within the region of δ –98.4 to –102.9 range usually associated with four coordinate tin. This series of compounds was also characterised by X-ray structure analysis (discussed in Section 3.5.1).

3.3 Derivatisation of α,ω-Bis(triphenylstannyl)alkanes, [Ph₃Sn]₂(CH₂)ₙ

---

63
The hexaphenylditin precursors, \([\text{Ph}_3\text{Sn}]_2(\text{CH}_2)_n\) (n = 3-6 (94c-f), 8 (94h), 10 (94i), 12 (94j)) form the basis for the synthesis of the series of di-tin compounds outlined in Schemes 18 to 21.

Dihalogenation of 94c-f, 94h, 94i and 94j by the slow addition of two molar equivalents of iodine gave \([\text{IPh}_2\text{Sn}]_2(\text{CH}_2)_n\) (n = 3-6 (95c-f), n = 8 (95h), n = 10 (95i), n = 12 (95j)) quantitatively as brown oils (Scheme 18).

\[
\begin{align*}
\text{Ph}_3\text{Sn}(\text{CH}_2)_n\text{SnPh}_3 & \xrightarrow{\text{I}_2 (2.0 \text{ eq})} \text{IPh}_2\text{Sn}(\text{CH}_2)_n\text{SnPh}_2\text{I} \\
94c; n = 3-6 & \quad 95c; n = 3-6 \\
h; n = 8 & \quad h; n = 8 \\
i; n = 10 & \quad i; n = 10 \\
j; n = 12 & \quad j; n = 12
\end{align*}
\]

**Scheme 18**

Reaction of two molar equivalents of the Grignard reagent, \(\text{Me}_3\text{SiCH}_2\text{MgCl}\), with one molar equivalent of 95c-f, 95h, 95i and 95j afforded \([\text{RPh}_2\text{Sn}]_2(\text{CH}_2)_n\) (R = \(\text{CH}_2\text{SiMe}_3\); n = 3-6 (96c-f), n = 8 (96h), n = 10 (96i), n = 12 (96j)) as brown oils with yields between 80% and 86% (Scheme 19).

\[
\begin{align*}
\text{IPh}_2\text{Sn}(\text{CH}_2)_n\text{SnPh}_2\text{I} & \xrightarrow{\text{RMgCl (2.0 eq)}} \text{RPh}_2\text{Sn}(\text{CH}_2)_n\text{SnPh}_2\text{R} \\
95c; n = 3-6 & \quad 96c; n = 3-6 \\
h; n = 8 & \quad h; n = 8 \\
i; n = 10 & \quad i; n = 10 \\
j; n = 12 & \quad j; n = 12 \\
\text{R} = \text{CH}_2\text{SiMe}_3
\end{align*}
\]

**Scheme 19**

The selective cleavage of two phenyl substituents from mixed alkyl tin species has previously been achieved by the addition of concentrated hydrochloric acids. Reaction of excess concentrated hydrochloric acid with 96c-f, 96h, 96i and 96j afforded \([\text{R(Cl)}_2\text{Sn}]_2(\text{CH}_2)_n\) \((\text{R} = \text{CH}_2\text{SiMe}_3; \quad \text{n} = 3-6 (97c-f), \quad \text{n} = 8 (97h), \quad \text{n} = 10 (97i), \quad \text{n} = 12 (97j))\) as white solids with yields between 80% and 85% (Scheme 20). The compounds 97c-h, 97i, and 97j all have satisfactory elemental analysis. \[^{119}\text{Sn}\]NMR spectra (CDCl₃) of the compounds gave chemical shifts within the region of δ 132.0 to 139.8. The chemical shifts are similar to that of the known compound,
[R(Cl)₂Sn]₂(CH₂)₃, δ 132.8.¹³⁰ Compound 97c was also characterised by X-ray structure analysis (discussed in Section 3.5.2).

\[
\text{RPh₂Sn(CH₂)ₙSnPh₂R} \xrightarrow{\text{KOH / H₂O}} \text{[R(O)Sn(CH₂)ₙSn(O)R]ₘ}
\]

3.4 Mixing and Self-Assembling of Double Ladders

3.4.1 NMR Studies of Reactions of \{[R(O)Sn]₂(CH₂)₃\}ₘ with [R(Cl)₂Sn]₂(CH₂)ₙ
Reaction of one molar equivalent of \(\{[R(O)Sn]_2(CH_2)_3\}_m\) \((R = CH_2SiMe_3 (98c))\) with one molar equivalent of \([R(Cl)_2Sn]_2(CH_2)_4\) \((97d)\) (Scheme 22) gave a complex reaction mixture as evidenced by \(^{119}\text{Sn}\) NMR spectroscopy. The \(^{119}\text{Sn}\) NMR spectrum (toluene) of the mixture at 25 °C displayed 13 signals in the region usually associated with tetraorganodistannoxanes \((\delta -66.0 \text{ to } -141.0)\). Two of the tin containing species were assigned to the tetramethylene-bridged double ladder, \(\{[[RSn(Cl)](CH_2)_4[RSn(Cl)]]O\}_4\) \((21)\) \([\delta(^{119}\text{Sn}): -66.0 \text{ (33.0%) / } -140.9 \text{ (32.0%)}]\)\(^99\) and the trimethylene-bridged double ladder, \(\{[[RSn(Cl)](CH_2)_3[RSn(Cl)]]O\}_4\) \((17)\) \([\delta(^{119}\text{Sn}): -95.5 \text{ (2.0%) / } -137.1 \text{ (2.0%)}]\)\(^130\). The relatively low intensity of the latter was attributed to poor solubility at 25 °C. Additionally, the spectrum shows 9 minor signals at \(\delta -76.1 \text{ (2.5%), } -76.3 \text{ (3.5%), } -77.9 \text{ (5.0%), } -92.7 \text{ (3.0%), } -93.0 \text{ (2.0%), } -129.4 \text{ (3.0%), } -134.8 \text{ (3.5%), } -135.2 \text{ (3.5%) and } -136.6 \text{ (3.5%)},\) for which no assignment is made.

\[
[R(O)Sn(CH_2)_n or n'Sn(O)R]_m + R(Cl)_2Sn(CH_2)_n' or n'(Cl)_2R
\]

\(98c; n = 3\)
\(d; n' = 4\)
\(97d; n' = 4\)
\(c; n = 3\)

Toluene, 100 °C

\(\{[[R(Cl)Sn](CH_2)_n or n'[R(Cl)Sn]]O\}_4\)

\(17; n, n, n, n\)
\(21; n', n', n', n'\)
\(99; n, n', n, n'\)

Scheme 22

There was a significant change in spectral appearance of the \(^{119}\text{Sn}\) NMR spectrum measured in toluene at 100 °C. The \(^{119}\text{Sn}\) NMR spectrum of the mixture displays seven signals at \(\delta -71.4, -80.0, -95.4, -98.3, -137.6, -141.8 \text{ and } -142.3\) with an integral ratio of 1:1:1:1:1:1:2, respectively. The number of signals suggests the existence in solution of a statistical mixture of symmetric and asymmetric double ladders. The two pairs of signals of equal integral ratio at \(\delta -71.4 \text{ (12.0%) / } -141.8 \text{ (10.0%) and } -98.3 \text{ (12.0%) / } -137.6 \text{ (14.0%)}\) are tentatively assigned to \(21\) and \(17\), respectively, which are confirmed by a 2D INADEQUATE \(^{119}\text{Sn}\) NMR experiment (Figure 17). The remaining three signals at \(\delta -80.0 \text{ (15.0%), } -95.4 \text{ (11.0%) and } -98.3 \text{ (12.0%)},\)
−142.3 (27.0%) are assigned to the two of the seven possible isomers of the asymmetric double ladders (99a/99b) (Scheme 23). The missing signal is likely to be superimposed with the signal at δ −142.3. In principle, these signals could also be assigned to the asymmetric double ladder (99c), for which four signal of equal integral ratio are expected. However, the 2D INADEQUATE $^{119}$Sn NMR experiment of the mixture shows only two different correlations for these signals (Figure 17). The signal at δ −80.8 correlates to the signal at −142.3 and signal at −95.4 correlates to the second signal superimposed at −142.3 and thus we assign the four signals to the asymmetric double ladders 99a and 99b rather than to 99c. Other combinations of asymmetric double ladders are also possible i.e. 99d-99g (Scheme 23). However, for each of these combinations of asymmetric double ladders only three signals of 1:1:2 integral ratios are expected. Furthermore, a rather complex correlation would also be expected for these signals.

It is worth mentioning that $^{119}$Sn NMR data indicate that pure trimethylene-17 and tetramethylene-bridged double ladders 21 do not undergo dissociation reactions in solution. Therefore, these signals could not be due to the mono-layer ladder species (dimers, four tin atoms) being in equilibrium with the double ladders 17 and 21 (tetramers, eight tin atoms).
Figure 17. $^{119}$Sn 2D INADEQUATE spectrum (Toluene, 100 °C) from the reaction of $\{[R(O)Sn]_2(CH_2)_3\}_m$ (R = CH$_3$SiMe$_3$) (98c) with [R(Cl)$_2$Sn]$_2$(CH$_2$)$_4$ (97d).
Scheme 23. Proposed symmetric-asymmetric double ladders equilibrium in solution. Some R groups have been omitted for clarity.

Upon cooling to 25 °C, the original spectrum of the mixture is observed. In contrast to the asymmetric double ladders 24 and 25 (where the organic substituent (R) provides the asymmetry) reported, the asymmetric double ladders 99a and 99b (where the spacer chain length (n) provides the asymmetry) reported here appear to be thermodynamically less stable than the related symmetric species, since more symmetric double ladders were detected upon cooling to 25 °C.

Similar observations hold for the alternate reaction of \([R(O)Sn]_2(CH_2)_4\) (98d) with \([R(Cl)Sn]_2(CH_2)_3\) (97c) (Scheme 22). It is interesting to note that similar observations were also obtained by mixing equimolar amounts of the pure trimethylene- 17 and tetramethylene-bridged double ladders 21.

The \(^{119}\text{Sn}\) NMR data for these mixtures can be explained in terms of a temperature dependent equilibrium between the symmetric and asymmetric double ladders (Scheme 23). At high temperature an equilibrium exists in solution between
symmetric double ladders 17, 21 and the asymmetric double ladders 99a, 99b as indicated by the integral ratio of 1:1:1:1. Lowering the temperature decreases the solubility of 17 and causes the equilibrium to shift towards formation of 17 and 21. This assignment is further support by the isolation and characterisation of 17 as its toluene solvate (17-C7H8) (see Section 3.5.3). Attempts to isolate a single isomer of the asymmetric double ladder were unsuccessful.

Replacement of spacer chain length, n = 4 in the tetrachloride di-tin precursor [R(Cl)2Sn]2(CH2)n with n = 5, 6, 8, 10 or 12 has a strong influence on the structure of the double ladders formed by partial oxygen/chlorine exchange. The reaction between \{[R(O)Sn]2(CH2)3\}m (98c) with [R(Cl)2Sn]2(CH2)5 (97e) (Scheme 24) gave a less complex reaction mixture as evidenced by 119Sn NMR (toluene, 25 °C) spectroscopy. The two major pairs of signals of equal integral ratio were assigned to the pentamethylene-bridged double ladder, \{[[RSn(Cl)](CH2)5[RSn(Cl)]]}O4 (100) \[\delta(119Sn): -86.5 \ (34.0\%) / -134.7 \ (35.0\%)]\textsuperscript{101} and the trimethylene-bridged double ladder, \{[[RSn(Cl)](CH2)3[RSn(Cl)]]}O4 (17) \[\delta(119Sn): -96.5 \ (11.0\%) / -137.2 \ (13.0\%)]\textsuperscript{98} respectively. In addition to the major signals, three minor signals were observed at \(\delta \ -84.1 \ (4.0\%), \ -90.3 \ (4.0\%) \) and \(-137.5 \ (5.0\%), \) for which no assignment is made. At 80 °C the 119Sn NMR spectrum of the same sample principally shows the same picture, except for the increase in the intensity for the pair of signals assigned to 17. This observation is consistent with the increase in solubility of 17 at high temperature.

\[
[R(O)Sn(CH2)3Sn(O)R]_m + R(Cl)2Sn(CH2)nSn(Cl)2R \\
98c \quad 97e, f, h-j; n = 5, 6, 8, 10, 12 \\
\text{Toluene, 100 °C} \\
\{[[RSn(Cl)](CH2)3[RSn(Cl)]]}O4 + \{[[R(Cl)Sn](CH2)n[RSn(Cl)]}O4 \\
17 \quad 100-104; n = 5, 6, 8, 10, 12
\]

\textbf{Scheme 24}

Similar observations hold for the reaction of \{[R(O)Sn]2(CH2)3\}m (98c) with [R(Cl)2Sn]2(CH2)n \(n = 6 \ (97f), n = 8 \ (97h), n = 10 \ (97i), n = 12 \ (97j))\). The 119Sn
NMR spectra for the reaction mixture in toluene at both 25 °C and 100 °C showed two pairs of signals of equal integral ratio which were assigned to the trimethylene-bridged double ladder 17 and the respective symmetric double ladders (101-104). In view of the fact that \{[R(O)Sn]_2(CH_2)_3\}_m (98c) and [R(Cl)_2Sn]_2(CH_2)_n (n = 5 (97e), n = 6 (97f), n = 8 (97h), n = 10 (97i), n = 12 (97j)) are the only two starting di-tin precursors of the reaction, the formation, almost exclusively, of symmetric double ladders suggests an initial oxygen/chlorine exchange between the two starting di-tin precursors resulted in a mixture of di-tin precursors containing different spacer chain length. Also, it appears that in a mixture of di-tin precursors, association occurs preferentially between the same di-tin precursors of equal chain length, thus performing self-self recognition and that the symmetric double ladders are likely to be the dominant products.

3.4.2 NMR Studies of Reactions of \{[R(O)Sn]_2(CH_2)_4\}_m with [R(Cl)_2Sn]_2(CH_2)_n

Reaction of one molar equivalent of \{[R(O)Sn]_2(CH_2)_4\}_m (98d) with one molar equivalent of [R(Cl)_2Sn]_2(CH_2)_5 (97e) (Scheme 25) gave a complex reaction mixture as evidenced by \(^{119}\text{Sn}\) NMR spectroscopy. The \(^{119}\text{Sn}\) NMR spectrum (toluene) of the mixture at 25 °C displayed 11 signals in the region usually associated with tetraorganodistannoxanes adopting ladder-type structures (δ −67.0 to −153.0). Two of the minor tin containing species were assigned to the tetramethylene-bridged double ladder, \{[[RSn(Cl)](CH_2)_4[RSn(Cl)]]O\}_4 (21) [δ(^{119}\text{Sn}): −66.8 (2.0%) / −138.7 (3.0%)\] and the pentamethylene-bridged double ladder, \{[[RSn(Cl)](CH_2)_5[RSn(Cl)]]O\}_4 (100) [δ(^{119}\text{Sn}): 89.1 (9.0%) / −135.0 (8.0%)\], respectively. The assignments of the remaining organotin species formed were not conclusive. In addition to the 11 signals, two signals of major intensity were observed in the penta- and hexacoordinate region at δ −270.0 (31.0%) and −450.8 (16.0%), respectively. There was no significant change in spectral appearance of the \(^{119}\text{Sn}\) NMR spectrum measured in toluene in 100 °C.
\[
[R(O)Sn(CH_2)_4Sn(O)R]_m + R(Cl)_2Sn(CH_2)_nSn(Cl)_2R
\]

| 98d | 97e, f, h-j; n = 5, 6, 8, 10, 12 |

Toluene, 100 °C

\[
\{[RSn(Cl)](CH_2)_4[RSn(Cl)]\}O_4 \quad \{[R(Cl)Sn](CH_2)_n[RSn(Cl)]\}O_4^+ \\
21 \quad 100-104; n = 5, 6, 8, 10, 12
\]

Scheme 25

Similar observations hold for the reaction of \{[R(O)Sn]_2(CH_2)_4\}_m (98d) with \[R(Cl)Sn]_2(CH_2)_n (n = 6 (97f), n = 8 (97h), n = 10 (97i), n = 12 (97j)) (Scheme 25). The \(^{119}\)Sn NMR spectra for the reaction mixture in toluene at both 25 °C and 100 °C showed signals belonging to tetramethylene-bridged double ladder (21), the respective symmetric double ladders (101-104), as well as the two signals for penta- and hexacoordinated tin containing species.

### 3.5 Molecular Structures

#### 3.5.1 \[\text{Ph}_3\text{Sn}]_2(CH_2)_n

The recrystallisation from an ethanol solution of 94a-94c and chloroform/hexane (30:70) solution of 94e-94h afforded crystals suitable for X-ray structure analysis. The X-ray structure analysis was carried out by Associate Professor Edward R. T. Tiekink at the University of Adelaide on crystals supplied by the author. The crystal structure of 94d has been previously reported\(^{168}\) and therefore no attempt was made to grow a suitable crystal for X-ray structure analysis.

The molecular structures of the two independent molecules comprising the asymmetric unit of 94a are shown in Figure 18 and selected geometric parameters are collected in Table 9. The unit cells of 94b and 94c also each comprise of two independent molecules with a featuring the asymmetric dinuclear structure and b featuring the centrosymmetric dinuclear structure. The two independent molecules of 94b and 94c are illustrated in Figure 19 and 20, respectively and selected geometric parameters are collected in Table 10 and 11. The molecular structures of 94e-94h are
shown in Figures 21-24, respectively and selected geometric parameters are collected in Tables 12-15.

In this series of structures \textbf{94a-94h} \([\text{Ph}_3\text{Sn}]_2(\text{CH}_2)_n\), two \text{Ph}_3\text{Sn} entities are separated by a polymethylene group with a zig-zag confirmation. The exception was found in the structure of \([\text{Ph}_3\text{Sn}]_2(\text{CH}_2)_6\) where an unusual curved conformation is observed. The reason for this disparity is not obvious. The two tin atoms in the series are bonded to four carbon atoms. The Sn-Ph distances lie in the range of 2.11(32) Å to 2.16(42) Å and the Sn-CH\(_2\) distances lie in the range of 2.12(16) Å to 2.19(55) Å.

\begin{table}[h]
\centering
\caption{Selected interatomic (Å, deg.) parameters for \([\text{Ph}_3\text{Sn}]_2\text{CH}_2\) (\textbf{94a}).}
\begin{tabular}{llll}
\hline
 & Molecule \textit{a} & & Molecule \textit{b} \\
\hline
\text{Sn}(1)-\text{C}(21) & 2.133(7) & \text{Sn}(3)-\text{C}(91) & 2.140(1) \\
\text{Sn}(1)-\text{C}(31) & 2.141(40) & \text{Sn}(3)-\text{C}(81) & 2.140(13) \\
\text{Sn}(1)-\text{C}(11) & 2.154(31) & \text{Sn}(3)-\text{C}(71) & 2.144(35) \\
\text{Sn}(1)-\text{C}(1) & 2.152(6) & \text{Sn}(3)-\text{C}(2) & 2.154(7) \\
\text{Sn}(2)-\text{C}(61) & 2.145(9) & \text{Sn}(4)-\text{C}(2) & 2.119(16) \\
\text{Sn}(2)-\text{C}(1) & 2.140(33) & \text{Sn}(4)-\text{C}(111) & 2.134(17) \\
\text{Sn}(2)-\text{C}(51) & 2.132(17) & \text{Sn}(4)-\text{C}(121) & 2.137(30) \\
\text{Sn}(2)-\text{C}(41) & 2.144(20) & \text{Sn}(4)-\text{C}(101) & 2.142(33) \\
\hline
\text{C}(21)-\text{Sn}(1)-\text{C}(31) & 111.34(21) & \text{C}(91)-\text{Sn}(3)-\text{C}(81) & 107.57(20) \\
\text{C}(21)-\text{Sn}(1)-\text{C}(11) & 103.82(21) & \text{C}(91)-\text{Sn}(3)-\text{C}(71) & 112.70(22) \\
\text{C}(31)-\text{Sn}(1)-\text{C}(11) & 107.59(22) & \text{C}(81)-\text{Sn}(3)-\text{C}(71) & 107.60(23) \\
\text{C}(21)-\text{Sn}(1)-\text{C}(1) & 110.70(23) & \text{C}(91)-\text{Sn}(3)-\text{C}(2) & 104.05(21) \\
\text{C}(31)-\text{Sn}(1)-\text{C}(1) & 113.72(19) & \text{C}(81)-\text{Sn}(3)-\text{C}(2) & 115.57(20) \\
\text{C}(11)-\text{Sn}(1)-\text{C}(1) & 109.12(20) & \text{C}(71)-\text{Sn}(3)-\text{C}(2) & 109.44(19) \\
\text{C}(61)-\text{Sn}(2)-\text{C}(1) & 111.22(21) & \text{C}(2)-\text{Sn}(4)-\text{C}(111) & 109.11(22) \\
\text{C}(61)-\text{Sn}(2)-\text{C}(51) & 108.65(20) & \text{C}(2)-\text{Sn}(4)-\text{C}(121) & 109.49(20) \\
\text{C}(1)-\text{Sn}(2)-\text{C}(51) & 110.96(22) & \text{C}(111)-\text{Sn}(4)-\text{C}(121) & 108.73(21) \\
\text{C}(61)-\text{Sn}(2)-\text{C}(41) & 106.72(19) & \text{C}(2)-\text{Sn}(4)-\text{C}(101) & 115.46(22) \\
\text{C}(1)-\text{Sn}(2)-\text{C}(41) & 107.38(19) & \text{C}(111)-\text{Sn}(4)-\text{C}(101) & 108.15(21) \\
\text{Sn}(2)-\text{C}(1)-\text{Sn}(1) & 121.49(25) & \text{Sn}(4)-\text{C}(2)-\text{Sn}(3) & 121.54(24) \\
\hline
\end{tabular}
\end{table}

\textit{a}
Figure 18. Molecular structures (25% probability ellipsoids) and crystallographic numbering scheme employed for the two independent molecules of \([\text{Ph}_3\text{Sn}]_2\text{CH}_2\) (94a).

Table 10. Selected interatomic (Å, deg.) parameters for \([\text{Ph}_3\text{Sn}]_2(\text{CH}_2)_2\) (94b).
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<td>Sn(1)-C(21)</td>
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symmetry operation $i: -x, 1-y, 1-z.$
Figure 19. Molecular structures (25% probability ellipsoids) and crystallographic numbering scheme employed for the two independent molecules of \([\text{Ph}_3\text{Sn}]\text{(CH}_2\text{)}_2\) (94b).

Table 11. Selected interatomic (Å, deg.) parameters for \([\text{Ph}_3\text{Sn}]_2\text{(CH}_2\text{)}_3\) (94c).
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Figure 20. Molecular structures (25% probability ellipsoids) and crystallographic numbering scheme employed for the two independent molecules of $[\text{Ph}_3\text{Sn}]_2(\text{CH}_2)_3$ (94c).

Table 12. Selected interatomic (Å, deg.) parameters for $[\text{Ph}_3\text{Sn}]_2(\text{CH}_2)_5$ (94e).
Sn(1)-C(11) 2.140(4)  Sn(2)-C(61) 2.133(34)
Sn(1)-C(1) 2.140(34)  Sn(2)-C(41) 2.132(4)
Sn(1)-C(31) 2.146(20)  Sn(2)-C(51) 2.141(15)
Sn(1)-C(21) 2.146(4)  Sn(2)-C(5)  2.145(4)

C(11)-Sn(1)-C(1) 109.00(14)  C(61)-Sn(2)-C(41) 110.95(14)
C(11)-Sn(1)-C(31) 107.56(14)  C(61)-Sn(2)-C(51) 109.81(15)
C(1)-Sn(1)-C(31) 110.94(15)  C(41)-Sn(2)-C(51) 109.06(14)
C(11)-Sn(1)-C(21) 111.67(15)  C(61)-Sn(2)-C(5)  111.85(15)
C(1)-Sn(1)-C(21) 108.33(15)  C(41)-Sn(2)-C(5)  105.32(15)
C(31)-Sn(1)-C(21) 109.36(15)  C(51)-Sn(2)-C(5)  109.74(15)

**Figure 21.** Molecular structure (25% probability ellipsoids) and crystallographic numbering scheme employed for [Ph₃Sn]₂(CH₂)₅ (94e).

**Table 13.** Selected interatomic (Å, deg.) parameters for [Ph₃Sn]₂(CH₂)₆ (94f).
Sn-C(21) 2.139(14) Sn-C(1) 2.150(7)
Sn-C(11) 2.137(17) Sn-C(31) 2.152(8)

C(21)-Sn-C(11) 108.16(11) C(21)-Sn-C(31) 108.27(14)
C(21)-Sn-C(1) 106.91(13) C(11)-Sn-C(31) 108.68(12)
C(11)-Sn-C(1) 113.41(12) C(1)-Sn-C(31) 111.24(12)

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Figure 22. Molecular structure (25% probability ellipsoids) and crystallographic numbering scheme employed for [Ph₃Sn]₂(CH₂)₆ (94f).

Table 14. Selected interatomic (Å, deg.) parameters for [Ph₃Sn]₂(CH₂)₇ (94g).
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Figure 23. Molecular structure (25% probability ellipsoids) and crystallographic numbering scheme employed for $\text{[Ph}_3\text{Sn}]_2(\text{CH}_2)_7$ (94g).

Table 15. Selected interatomic (Å, deg.) parameters for $\text{[Ph}_3\text{Sn}]_2(\text{CH}_2)_8$ (94h).
Chapter 3

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Symmetry operation i: $l-x$, $-l-y$, $l-z$.

**Figure 24.** Molecular structure (25% probability ellipsoids) and crystallographic numbering scheme employed for $[\text{Ph}_3\text{Sn}]_2(\text{CH}_2)_8$ (94h).

### 3.5.2 $[\text{Me}_3\text{SiCH}_2]\text{(Cl)}_2\text{Sn}_2(\text{CH}_2)_3$
Slow evaporation of a chloroform/hexane solution (30:70) of \([(\text{Me}_3\text{SiCH}_2)(\text{Cl})_2\text{Sn}]_2(\text{CH}_2)_3\) (97c) gave crystals suitable for X-ray analysis. The molecular structure of 97c is shown in Figure 25 and Table 16 lists important geometric parameters. The X-ray analysis reveals that a C2Cl2 donor set is found for both independent tin centres in the crystal structure. The greatest deviation from the ideal geometry is found in the C-Sn-C angle of 128.0(5)° for Sn(1) and 129.1(6)° for Sn(2). In the lattice, molecules associate via weak Sn⋯Cl interactions that result in the formation of (Sn⋯Cl)2 rectangles. In this way, Sn(1) is 3.319(5) Å from Cl(3) and Sn(2) is 3.510(5) Å from Cl(2).

Table 16. Selected interatomic (Å, deg.) parameters for \([(\text{Me}_3\text{SiCH}_2)(\text{Cl})_2\text{Sn}]_2(\text{CH}_2)_3\) (97c).

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Figure 25. Molecular structure (50% probability ellipsoids) and crystallographic numbering scheme employed for \([\text{Me}_3\text{SiCH}_2\text{Cl})_2\text{Sn}]_2\text{(CH}_2)_3\) (97c).

3.5.3 \([(\text{Me}_3\text{SiCH}_2)\text{Sn(Cl)}]_2\text{(CH}_2)_3\)O\(_4\)-C\(_7\text{H}_8\)

The molecular structure of \([(\text{Me}_3\text{SiCH}_2)\text{Sn(Cl)}]_2\text{(CH}_2)_3\)O\(_4\)-C\(_7\text{H}_8\) (17\(\cdot\)C\(_7\text{H}_8\)) is shown in Figure 26, and the selected geometric parameters are collected in Table 17. The structure resembles closely the unsolvated form.\(^{98}\) The molecule is centrosymmetric and there is one solvent molecule of toluene per cluster. The cluster comprises two \([(\text{Me}_3\text{SiCH}_2)\text{Sn(Cl)}]_2\)O\(_2\) units linked by four trimethylene spacers such that the average distance between the two Sn\(_4\)O\(_2\) planes is 7.2 Å. Significant buckling is noted in the central Sn\(_2\)O\(_2\) core, however, as seen in the Sn(1)/O(1)/Sn(2)/O(2) torsion angle of \(-11.34(9)^\circ\). The tin atoms exist in trigonal bipyramidal geometries with apical Cl and O atoms for Sn(1 and 2), and Cl atoms for Sn(3 and 4).

Table 17. Selected interatomic (Å, deg.) parameters for \([(\text{Me}_3\text{SiCH}_2)\text{Sn(Cl)}]_2\text{(CH}_2)_3[\text{(Me}_3\text{SiCH}_2)\text{Sn(Cl)}]_2\)O\(_4\)-C\(_7\text{H}_8\) (17\(\cdot\)C\(_7\text{H}_8\)).

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<td>Sn(2)-O(2)</td>
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<td>Cl(2)-Sn(2)-O(1)</td>
<td>150.5(7)</td>
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Figure 26. Molecular structure (50% probability ellipsoids) and crystallographic numbering scheme employed for \{\{(Me_3SiCH_2)Sn(Cl)(CH_2)\}_2\}(Me_3SiCH_2)Sn(Cl)\} O_4\cdot C_7H_8 (17\cdot C_7H_8).

3.6 Summary

The preparation and characterisation of a series of $\alpha,\omega$-bis(triphenylstannyl)alkanes, [Ph$_3$Sn]$_2$(CH$_2$)$_n$ (n = 1-8 (94a-h), 10 (94i), 12 (94j)) are described. Some of these compounds are used as starting materials for the assembly of higher organotin-oxo oligomers (Chapter 6). The derivatisation of a series of $\alpha,\omega$-bis(triphenylstannyl)alkanes, [Ph$_3$Sn]$_2$(CH$_2$)$_n$ (n = 3-6 (95c-f-98c-f), 8 (95h-98h), 10 (95i-98i), 12 (95j-98j)) are also described. A $^{119}$Sn NMR spectroscopic investigation of the reaction between \{[R(O)Sn]$_2$(CH$_2$)$_n$\}$_m$ and [R(Cl)$_2$Sn](CH$_2$)$_{n'}$ (n = 3, n' = 4
and $n = 4, n' = 3$) shows the presence of a mixture of symmetric and asymmetric double ladders, where different spacer chain lengths ($n$ and $n'$) provide the source of asymmetry. The coexistence at high temperature of different sets of $^{119}$Sn NMR signals belonging to symmetric and asymmetric double ladders suggests an equilibrium (i) that is slow on the $^{119}$Sn NMR time scale, and (ii) the position of which is temperature dependent. However, a $^{119}$Sn NMR spectroscopic experiment of $\{[\text{R(O)Sn}]_2(\text{CH}_2)_3\}_m$ with $[\text{R(Cl)Sn}]_2(\text{CH}_2)_{n'}$ ($n' = 5, 6, 8, 10, 12$) reveals the molecular self-assembly of symmetric spacer-bridged di-tin precursors of equal chain length is preferred over asymmetric species.
Chapter 4

Functionalised and Cationic Double Ladders
4.1 Introduction

Up until now double ladder compounds have only been made with alkylidene-\textsuperscript{98,99,101,105} or silicon-containing spacers\textsuperscript{102,103}. Double ladders containing functional groups within the spacer are not yet known. Consequently, attention was directed to the synthesis of a new class of double ladder that contains an oxygen atom within the spacer linkage. Conceptually, the double ladder \textsuperscript{112} contains two layers of multiple Lewis acid tin sites, which are linked by four ether-bridged spacers.

It is hypothesised that this oxygen-functionalised double ladder, may bind selectively to metal cations, in a manner analogous to that observed for organic macrocycles such as crown ethers and cryptands. This Chapter describes the synthesis and characterisation of a unique functionalised double ladder, \{[RSn(Cl)](CH\textsubscript{2})\textsubscript{3}O(CH\textsubscript{2})\textsubscript{3}[RSn(Cl)]\}O\textsubscript{4} (R = CH\textsubscript{2}SiMe\textsubscript{3} (\textsuperscript{112})). Investigations into the complexation ability of this double ladder with various metal cations by electrospray mass spectrometry (ESMS) are also described.

In a recent series of papers Dakternieks et. al. reported alkylidene-bridged double and triple ladder compounds\textsuperscript{98,99,102,105} which shows lower catalytic activity in acylation reactions when compared with simple \([n-\text{Bu}_2(\text{Cl})\text{SnOSn(\text{Cl})n-\text{Bu}_2}]_2\textsuperscript{66b}\).\textsuperscript{99} This decreased activity was attributed to the higher kinetic stability of the former compounds.

Recent studies have shown that the introduction of cationic character to organotin-oxo compounds gives rise to greatly increased catalytic activity and
selectivity compared to neutral organotin-oxo compounds.\textsuperscript{107,169} For example, cationic organotin-oxo compounds, \([R_2Sn(OH)(H_2O)]_2^{2+}\) (\(R = t\)-Bu, \(n\)-Bu; Counterion : TfO\(^-\)) and \([(n-BuSn)_{12}O_{14}(OH)_6]^{2+}\) (Counterion : OH\(^-\), Cl\(^-\)) (\textsuperscript{53b}), catalyse alcohol acetylation at faster rates than neutral organotin-oxo compounds.\textsuperscript{107} \textsuperscript{53b} has also shown high chemoselectivity by selectively acetylating a primary alcohol in the presence of a secondary alcohol.\textsuperscript{107}

The synthesis of cationic ladder compounds \([R_2(OH)SnOSn(OTf)R_2]_2\) (\(R = Et, n\)-Bu, \(n\)-Oct) was reported recently using \(R_2SnO\) and 0.5 molar equivalents of triflic acid, TfOH.\textsuperscript{170}

The above results suggested that the synthesis of cationic double ladders as an interesting target which may provide useful catalytic properties. In particular, the synthesis and characterisation of \(\{[RSn(OH)](CH_2)_n[RSn(H_2O)]\}_4\cdot4OTf\) (\(R = CH_2SiMe_3; n = 3\) (\textsuperscript{113c}), \(n = 4\) (\textsuperscript{113d}), \(n = 8\) (\textsuperscript{113h}), \(n = 10\) (\textsuperscript{113i})) are described in this Chapter.

### 4.2 Oxygen-Functionalised Double Ladder

#### 4.2.1 Preparation of Ether-Bridged Di-Tin Precursors

The initial proposition was to utilise the commercially available, 2-chloroethyl ether as starting point for the synthesis of the ether-bridged di-tin precursor. Reaction of one molar equivalent of 2-chloroethyl ether, \([Cl(CH_2)_2]_2O\), with 2.5 molar equivalents of Ph\(_3\)SnNa in liquid ammonia results in formation of a mixture of \([Ph_3Sn(CH_2)_2]_2O\) (\textsuperscript{105}) and Ph\(_3\)Sn(CH\(_2\))\(_2\)O(CH\(_2\))\(_2\)Cl (\textsuperscript{106}) in the ratio of 1:5 as evidenced by \(^{119}\)Sn NMR spectroscopy (CDCl\(_3\)) (\(\delta -102.0, -101.5\)) (Scheme 26). The assignment of \textsuperscript{105} and \textsuperscript{106} was confirmed by \(^1\)H and \(^{13}\)C NMR spectroscopies. For example, the \(^{13}\)C NMR spectrum (CDCl\(_3\)) of the reaction mixture after 24 h showed 6 peaks in the aliphatic region, corresponding to the 2 and 4 different methylene groups of the di- and mono-substituted products, respectively. Reaction of up to 3.5 molar equivalents of Ph\(_3\)SnNa with \([Cl(CH_2)_2]_2O\) has little effect on the ratio of the two products.
Attempts to prepare [Ph$_3$Sn(CH$_2$)$_2$]$_2$O (105) from the di-Grignard reagent, [ClMg(CH$_2$)$_2$]$_2$O, with 2.5 molar equivalents of Ph$_3$SnCl in THF gave no reaction (Scheme 27), as evident by $^{119}$Sn NMR spectroscopy which indicated the presence of only Ph$_3$SnCl.

In light of the above results, an alternative approach for connecting Ph$_3$Sn moieties to the ether-bridged spacer was investigated, this time beginning with (CH$_2$=CHCH$_2$)$_2$O a hydrostannylation reaction. Reaction of one molar equivalent of (CH$_2$=CHCH$_2$)$_2$O with 2.5 molar equivalents of Ph$_3$SnH in the presence of catalytic amounts of Pd(OH)$_2$/C afforded [Ph$_3$Sn(CH$_2$)$_3$]$_2$O (107) (Scheme 28). The $^{119}$Sn NMR spectrum (CDCl$_3$) of the reaction mixture indicates the presence of by-products such as Ph$_3$SnOH, Ph$_4$Sn, (Ph$_3$Sn)$_2$ as well as several tin containing species which could not be identified. Purification by Kugelrohr distillation and column chromatography afforded analytically pure 107 in 70% yield; $^{119}$Sn NMR (CDCl$_3$): $\delta$ -98.4.
Dihalogenation of 107 by the slow addition of two molar equivalents of iodine gave [IPh₂Sn(CH₂)₃]₂O (108) as a white solid in 95% yield after workup (Scheme 29); $^{119}$Sn NMR (CDCl₃): $\delta$ –85.8.

Reaction of 2.2 molar equivalents of the Grignard reagent, Me₃SiCH₂MgCl, with 108 in THF gave [(Me₃SiCH₂)Ph₂Sn(CH₂)₃]₂O (109) (Scheme 30). Purification by column chromatography afforded 109 as a colourless oil in 80% yield; $^{119}$Sn NMR (CDCl₃): $\delta$ –56.5.
The reaction of $109$ with excess concentrated hydrochloric acid afforded $[(\text{Me}_3\text{SiCH}_2)(\text{Cl})_2\text{Sn(CH}_2_3)_3]_2\text{O}$ (110) as a brown oil in 70% yield after workup (Scheme 31); $^{119}\text{Sn}$ NMR (CDCl$_3$): $\delta$ 79.1

\[ \begin{align*}
\text{RPh}_2\text{Sn} & \quad \text{O} \quad \text{SnPh}_2\text{R} \\
\text{R} = \text{CH}_2\text{SiMe}_3
\end{align*} \]

\[ \text{R(Cl)}_2\text{Sn} \quad \text{O} \quad \text{Sn(Cl)}_2\text{R} \]

Scheme 31

The subsequent hydrolysis of 110 with excess aqueous potassium hydroxide resulted in $\{[(\text{Me}_3\text{SiCH}_2)(\text{O})\text{Sn(CH}_2_3)_3]_2\text{O}\}_m$ (111) as an insoluble white solid in 86% yield (Scheme 32).

\[ \begin{align*}
\text{R(Cl)}_2\text{Sn} & \quad \text{O} \quad \text{Sn(Cl)}_2\text{R} \\
\text{R} = \text{CH}_2\text{SiMe}_3
\end{align*} \]

\[ \text{KOH / H}_2\text{O} \quad \text{Toluene, 100 }^\circ\text{C} \]

Scheme 32
4.2.2 Synthesis of the Oxygen-Functionalised Double Ladder

The reaction between 110 and 111 in toluene produced the target compound, \{[RSn(Cl)](CH_2)_3O(CH_2)_3[RSn(Cl)]\}_4 \ (R = CH_2SiMe_3 \ (112)) in 92% yield (Scheme 33).

$$\begin{align*}
R(Cl)_2Sn & \quad O \quad Sn(Cl)_2R \\
\text{110} & \\
+ & \\
\left[ R(O)Sn \quad O \quad Sn(O)R \right]_n \\
\text{111} & \\
R = CH_2SiMe_3 & \quad \text{Toluene, 100 °C} \\
\text{112} \\
\text{Scheme 33}
\end{align*}$$

Compound 112 is a colourless, high melting solid, which is soluble in most common organic solvents. Slow evaporation of a chloroform/hexane solution (30:70) of 112 gave crystals suitable for X-ray analysis. The molecular structure of 112 is shown in Figure 27 and Table 18 lists important geometric parameters. The structure may be described as being a construction of two \{[(Me_3SiCH_2)Sn(Cl)]_2O\}_2 units linked by four -(CH_2)_3O(CH_2)_3- spacers and with the remaining tin-bound groups being CH_2SiMe_3. To a first approximation the Sn_4Cl_4O_2 face of the molecule is planar with the range of deviations from their least squares plane being −0.0125 Å for Cl(1) to −0.2641 Å for O(2). The average separation between the two layers of 10.2 Å of 112 is marginally shorter than the comparable distance found for the - (CH_2)_7- analogue of 10.9 Å.\textsuperscript{171} The tin atoms exits in distorted trigonal bipyramidal geometries with trigonal C_2O and axial O, Cl donor sets for Sn(1) and Sn(2), and trigonal C_2O and axial Cl, Cl donor sets for Sn(3) and Sn(4). The interior of the cavity is defined by a crown of four oxygen atoms, where the average O···O distance is 4.36 Å and the average distance from the center of the cavity to the O atoms is...
3.11 Å. On the basis of a van der Waals radius\textsuperscript{172} of 1.40 Å for oxygen, the interior of the cavity could thus host a species with a radius of approximately 1.71 Å. The structure, including its centrosymmetricity, resembles that observed previously for related systems.\textsuperscript{98-100,105}

<p>| Table 18. | Selected interatomic (Å, deg.) parameters for ${(\text{Me}_3\text{SiCH}_2)\text{Sn(Cl)}(\text{CH}_2)_3\text{O(\text{CH}_2}_3{((\text{Me}_3\text{SiCH}_2)\text{Sn(Cl)}}_4}$ (112). |
| Sn(1)-O(1) | 2.048(5) | Sn(3)-O(1) | 2.019(5)  |
| Sn(1)-C(13) | 2.098(13) | Sn(3)-C(7) | 2.114(13) |
| Sn(1)-C(1) | 2.108(8) | Sn(3)-C(21) | 2.112(12) |
| Sn(1)-O(2) | 2.143(8) | Sn(3)-Cl(3) | 2.455(6)  |
| Sn(1)-Cl(1) | 2.700(6) | Sn(3)-Cl(1) | 2.761(4)  |
| Sn(2)-O(2) | 2.048(5) | Sn(4)-O(2) | 2.007(5)  |
| Sn(2)-C(17) | 2.104(10) | Sn(4)-C(10) | 2.123(10) |
| Sn(2)-C(4) | 2.115(14) | Sn(4)-C(25) | 2.125(11) |
| Sn(2)-O(1) | 2.127(9) | Sn(4)-Cl(4) | 2.455(4)  |
| Sn(2)-Cl(2) | 2.724(6) | Sn(4)-Cl(2) | 2.745(2)  |
| O(1)-Sn(1)-C(13) | 105.93(23) | C(7)-Sn(3)-Cl(3) | 97.99(32) |
| O(1)-Sn(1)-C(1) | 115.13(27) | C(21)-Sn(3)-Cl(3) | 97.03(24) |
| C(13)-Sn(1)-C(1) | 138.15(30) | O(1)-Sn(3)-Cl(1) | 76.17(14) |
| O(1)-Sn(1)-O(2) | 74.18(17) | C(7)-Sn(3)-Cl(1) | 89.03(30) |
| C(13)-Sn(1)-O(2) | 99.38(21) | C(21)-Sn(3)-Cl(1) | 89.24(24) |
| C(13)-Sn(1)-Cl(1) | 77.22(15) | C(7)-Sn(3)-Cl(1) | 163.13(9) |
| C(13)-Sn(1)-Cl(1) | 90.1(2) | O(2)-Sn(4)-C(10) | 114.72(28) |
| C(1)-Sn(1)-Cl(1) | 91.24(23) | O(2)-Sn(4)-C(25) | 112.33(25) |
| O(2)-Sn(1)-Cl(1) | 151.35(13) | O(2)-Sn(4)-Cl(4) | 87.93(14) |
| O(2)-Sn(2)-C(17) | 107.48(26) | C(10)-Sn(4)-Cl(4) | 97.06(24) |
| O(2)-Sn(2)-C(4) | 113.49(23) | C(25)-Sn(4)-Cl(4) | 96.95(23) |
| C(17)-Sn(2)-C(4) | 137.89(27) | O(2)-Sn(4)-Cl(2) | 76.73(14) |
| O(2)-Sn(2)-O(1) | 74.53(17) | C(10)-Sn(4)-Cl(2) | 89.38(24) |
| C(17)-Sn(2)-O(1) | 98.92(24) | C(25)-Sn(4)-Cl(2) | 89.12(23) |
| C(4)-Sn(2)-O(1) | 100.82(22) | Cl(4)-Sn(4)-Cl(2) | 164.66(7) |</p>
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<td>Sn(1)-O(1)-Sn(2)</td>
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<td>O(1)-Sn(3)-C(21)</td>
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<td>127.97(22)</td>
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<tr>
<td>O(1)-Sn(3)-Cl(3)</td>
<td>86.99(14)</td>
<td>Sn(2)-O(2)-Sn(1)</td>
<td>104.76(19)</td>
</tr>
</tbody>
</table>

Symmetry operation i: –x, –y, –z.
Figure 27. Molecular structure (25% probability ellipsoids) and crystallographic numbering scheme employed for \( \{ [[\text{RSn(Cl)}](\text{CH}_2)_3\text{O}(\text{CH}_2)_3[\text{RSn(Cl)}])\text{O}]_4 \) (R = \( \text{CH}_2\text{SiMe}_3 \) (112)).

The \(^{119}\text{Sn}\) NMR spectrum (CDCl\(_3\)) of an analytically pure sample of 112 shows 19 signals at \( \delta \) –80.0 (1.4%), –84.0 (4.5%), –93.4 (14.0%), –96.0 (5.0%),
−100.1 (1.0%), −103.6 (8.0%), −123.9 (8.1%), −127.6 (5.8%), −132.0 (2.0%), −133.0 (2.0%), −133.8 (5.0%), −136.0 (17.0%), −137.8 (1.4%), −148.7 (2.8%), −150.2 (11.0%), −153.5 (0.5%), −154.5 (0.5%), −155.5 (0.5%) and −175.5 (0.5%). Attempts were made to establish the connectivity of these signals using variable temperature 2D INADEQUATE $^{119}$Sn NMR spectroscopy (Figure 28). Signals at δ −103.6 and −123.9 appear correlated and are tentatively assigned to the tetramer of 112. There also appears to be a correlation between −84.0 and −133.8. The other broader signals could not be correlated. At −35°C, the $^{119}$Sn NMR signals at δ −93.4, −136.0 and −150.2 become broad. At −55°C, the signals at δ −150.2 sharpen considerably while the signals at δ −93.4 and −136.0 remain broad. Reproducible signals, with the same integral ratio, were obtained for solutions of samples that had been recrystallised several times and suggests several species are in equilibrium with compound 112.
Figure 28. $^{119}$Sn 2D INADEQUATE spectrum (CDCl$_3$, 25 °C) of \{$\{(\text{Me}_3\text{SiCH}_2)\text{Sn(Cl)}\}\text{(CH}_2\text{)}_3\text{O(CH}_2\text{)}_3\{(\text{Me}_3\text{SiCH}_2)\text{Sn(Cl)}\}\}_4$ (112).

4.3 Studies into Complexation Behaviour of the Oxygen-Functionalised Double Ladder
4.3.1 ESMS of Oxygen-Functionalised Double Ladder

The positive mode spectrum of 112 in acetonitrile solution at a cone voltage of 20V contains peaks at m/z = 1125.0 (34%) for $[1/2\text{M} - 3\text{Cl} + 2\text{OH}]^+$ and m/z = 1143.0 (50%) which is assigned to the presence of $[1/2\text{M} - 2\text{Cl} + \text{OH}]^+$. The experimental isotope patterns agree with the calculated (Figure 29).

The negative mode spectrum of 112 shows dominant peaks at m/z = 634.9 (20%) and m/z = 688.9 (100%) which are indicative for the presence of $[1/4\text{M} + \text{Cl}]^-$ and $[1/4\text{M} - \text{O} + 3\text{Cl}]^-$.

![Figure 29. The calculated (top) and experimental (bottom) isotopic pattern of $[1/2\text{M} - 3\text{Cl} + 2\text{OH}]^+$ (m/z = 1125.0) and $[1/2\text{M} - 2\text{Cl} + \text{OH}]^+$ (m/z = 1143.0).](image)

Both negative and positive mode spectra of solutions of 112 indicate the presence of both monomer and dimer of 112 as the dominant species. This observation suggests the existence in solution of an equilibrium between tetrameric double ladder 112 and dimeric as well as monomeric species (Scheme 34). This assignment is further supported by the additional signals observed in the $^{119}\text{Sn}$ NMR spectrum (CDCl$_3$) of an analytically pure sample of 112. In contrast to the
functionalised double ladder 112 reported here, the polymethylene analogue, \{[[RSn(Cl)](CH_2)_n[RSn(Cl)]]O\}_4 undergo less dissociation in solution (Table 19).\textsuperscript{101} Notably, the position of the equilibrium is dependent on the spacer length. One reason for the observation of significant amount of monomer is the possibility that the tin atom in the monomer can become pentacoordinate.

\[ \text{Scheme 34. Proposed equilibrium occurring in solution.} \]

<table>
<thead>
<tr>
<th>{[<a href="CH_2">RSn(Cl)</a>_n[RSn(Cl)]]O}_4</th>
<th>Tetramer</th>
<th>Dimer</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 6 (30)</td>
<td>90 %</td>
<td>10 %</td>
</tr>
<tr>
<td>n = 7 (31)</td>
<td>85 %</td>
<td>15 %</td>
</tr>
<tr>
<td>n = 8 (32)</td>
<td>75 %</td>
<td>25 %</td>
</tr>
<tr>
<td>n = 10 (33)</td>
<td>67 %</td>
<td>33 %</td>
</tr>
<tr>
<td>n = 12 (34)</td>
<td>60 %</td>
<td>40 %</td>
</tr>
</tbody>
</table>

4.3.2 ESMS of Oxygen-Functionalised Double Ladder with Added Cations
The complexation ability of 112 with various metal cations (Na⁺, Li⁺, Mg²⁺, Cu²⁺) was investigated using the Electrospray Mass Spectrometry (ESMS) technique. The concentration of the 112 solution (acetonitrile) was approximately 0.1 mM. In order to avoid potential halide exchange reactions, ESMS studies were only performed using metal chlorides. In each case species were assigned by comparison of experimental and calculated isotopic patterns.

At low voltage (50V) the positive ESMS of 112 plus one drop of aqueous NaCl shows the cationic species \([1/2M - 3Cl + O]^+\) (m/z = 1107.0) as the most abundance species (80%). The other singly charged species \([1/2M - 4Cl + OH + O]^+\) (m/z = 1089.0) is present in relative abundance of 19.0%. Increasing the cone voltage (100V) causes the relative intensity of \([1/2M - 3Cl + O]^+\) to decrease while the intensity of \([1/2M - 4Cl + OH + O]^+\) increases. In addition, there are three new but very low intensity peaks at m/z = 2418.8 (1%), m/z = 2476.8 (2%) and m/z = 2534.7 (2%) which are indicative for the presence of \([M + Na]^+\), \([M + NaCl + Na]^+\) and \([M + 2NaCl + Na]^+\).

The positive mode spectrum of 112 plus one drop of aqueous LiCl in acetonitrile solution at a cone voltage of 200V shows peaks at m/z = 605.0 (16%) for \([1/4M + Li]^+\), m/z = 646.0 (15%) for \([1/4M + Li + MeCN]^+\), m/z = 1149.0 for \([1/2M - Cl + NaCl]^+\) and m/z = 1204.9 which is assigned to the presence of \([1/2M + Li]^+\). At this stage there is some evidence for formation of complexes.

Interactions of 112 with divalent metal cations were also investigated. The positive mode spectrum of 112 plus one drop of aqueous MgCl₂ in acetonitrile/THF solution at a cone voltage of 100V shows peaks at m/z = 1107.3 (16%), m/z = 1143.0 (7%) and m/z = 2359.9 (9%) which are indicative for the presence of \([1/2M - 3Cl + O]^+\), \([1/2M - 2Cl + OH]^+\) and \([M - Cl]^+\). The identifiable species in the positive mode spectrum of 112 plus one drop of aqueous CuCl₂ in acetonitrile/THF solution at a cone voltage of 200V are similar to 112 plus one drop of aqueous MgCl₂.

The positive mode spectra of solutions of 112 with various metal cations did indicate the formation of complexes only with Na and of very low abundance. However, the spectra indicate the presence of both monomer and dimer of 112 as the dominant species. It was therefore speculated that 112 undergo extensive
dissociation in solution, a property that reduces its potential to complex with metal cations.

4.4 Cationic Double Ladders

4.4.1 Reaction of $\{[R(O)Sn]_2(CH_2)_3\}_m$ with Triflic Acid

Slow addition of triflic acid, TfOH to a suspension of polymeric 1,3-bis(trimethylsilylmethyloxostannyl)propane $\{[R(O)Sn]_2(CH_2)_3\}_m$ ($R = CH_2SiMe_3$ (98c)) (Scheme 35) in acetonitrile gave a clear solution. Removal of solvent resulted in an oil. The $^{119}\text{Sn}$ NMR (MeCN) of the crude oil shows only one sharp signal at $\delta -316.3$ consistent with the formation of $[RSn(CH_2)_3SnR](OTf)_4$. The crude oil was then exposed to air moisture in a mixture of acetonitrile/chloroform (4:1) for 14 days. Exposure of crude oil to air moisture gives rise to a colourless precipitate (113c), which was filtered off and dried in the air.

\[
\begin{align*}
4 \ [R(O)Sn(CH_2)_3Sn(O)R]_m & \xrightarrow{TfOH, CH_3CN, rt} 4 \ [RSn(CH_2)_3SnR](OTf)_4 \\
\text{R} &= CH_2SiMe_3
\end{align*}
\]

Scheme 35
Slow evaporation of an acetonitrile/chloroform solution (75:25) of \(113c\) gave crystals suitable for X-ray analysis. The molecular structure of \(113c\) is shown in Figure 30, and Table 20 lists important geometric parameters. The structure resembles closely the trimethylene-bridged double ladder, \(\{[\text{RSn(Cl)}][(\text{CH}_2)_3[\text{RSn(Cl)}]}\text{O}_4\} (17)^{98,173}\). Each of the two \(\text{Sn}_4\text{Cl}_4\text{O}_2\) planes are nearly planar (mean deviations of 1.31 and 1.30 Å, respectively) and approximately parallel, forming a dihedral angle of 2.83°. The average separation between the two layers of 5.9 Å of \(113c\) is marginally shorter than the comparable distance found for \(17\) of 6.0 Å.\(^{98}\) The tin atoms exits in distorted trigonal bipyramidal geometries with trigonal \(\text{C}_2\text{O}\) and axial \(\text{O}\) atoms donor sets for \(\text{Sn}(1), \text{Sn}(2), \text{Sn}(3)\) and \(\text{Sn}(4)\).

<p>| Table 20. Selected interatomic (Å, deg.) parameters for ({[(\text{Me}_3\text{SiCH}_2)\text{Sn(OH)}][(\text{CH}_2)_3[(\text{Me}_3\text{SiCH}_2)\text{Sn(\text{H}_2\text{O})]}\text{O}_4}4\text{OTf} (113c).) |
|-----------------|-------|-----------------|-------|
| (\text{Sn}(1)-\text{O}(2)) | 2.165 | (\text{Sn}(3)-\text{O}(4)) | 2.154 |
| (\text{Sn}(1)-\text{O}(1)) | 2.171 | (\text{Sn}(3)-\text{O}(5)) | 2.181 |
| (\text{Sn}(1)-\text{C}(1)) | 2.126 | (\text{Sn}(3)-\text{C}(3)) | 2.119 |
| (\text{Sn}(1)-\text{C}(7)) | 2.117 | (\text{Sn}(3)-\text{C}(15)) | 2.122 |
| (\text{Sn}(2)-\text{O}(1)) | 2.123 | (\text{Sn}(4)-\text{O}(4)) | 2.000 |
| (\text{Sn}(2)-\text{O}(2)) | 2.004 | (\text{Sn}(4)-\text{O}(5)) | 2.119 |
| (\text{Sn}(2)-\text{O}(3)) | 2.329 | (\text{Sn}(4)-\text{O}(6)) | 2.317 |
| (\text{Sn}(2)-\text{C}(4)) | 2.131 | (\text{Sn}(4)-\text{C}(6)) | 2.124 |
| (\text{Sn}(2)-\text{C}(11)) | 2.116 | (\text{Sn}(4)-\text{C}(19)) | 2.106 |
| (\text{C}(1)-\text{Sn}(1)-\text{O}(2)i) | 97.32(82) | (\text{C}(15)-\text{Sn}(3)-\text{O}(5)i) | 96.32(63) |
| (\text{C}(1)-\text{Sn}(1)-\text{O}(2)) | 116.75(82) | (\text{C}(15)-\text{Sn}(3)-\text{O}(4)) | 114.92(32) |
| (\text{C}(1)-\text{Sn}(1)-\text{C}(7)) | 132.66(98) | (\text{C}(15)-\text{Sn}(3)-\text{O}(4)i) | 96.1(3) |
| (\text{C}(1)-\text{Sn}(1)-\text{O}(1)) | 97.34(78) | (\text{C}(15)-\text{Sn}(3)-\text{C}(3)) | 128.42(100) |
| (\text{O}(2)-\text{Sn}(1)-\text{O}(2)i) | 74.13(55) | (\text{O}(5)i-\text{Sn}(3)-\text{O}(4)) | 146.58(72) |
| (\text{O}(2)-\text{Sn}(1)-\text{C}(7)) | 93.97(39) | (\text{O}(4)i-\text{Sn}(3)-\text{O}(4)) | 73.23(44) |
| (\text{O}(2)-\text{Sn}(1)-\text{O}(1)) | 148.00(44) | (\text{C}(3)-\text{Sn}(3)-\text{O}(4)) | 98.63(114) |
| (\text{C}(7)-\text{Sn}(1)-\text{O}(2)) | 110.56(41) | (\text{O}(5)i-\text{Sn}(3)-\text{C}(3)) | 97.65(126) |
| (\text{C}(7)-\text{Sn}(1)-\text{O}(1)) | 96.72(29) | (\text{O}(4)i-\text{Sn}(3)-\text{C}(3)) | 116.66(114) |
| (\text{O}(1)-\text{Sn}(1)-\text{O}(2)) | 73.87(48) | (\text{O}(5)i-\text{Sn}(3)-\text{O}(4)i) | 73.39(74) |
| (\text{C}(4)-\text{Sn}(2)-\text{O}(1)) | 100.14(29) | (\text{C}(19)-\text{Sn}(4)-\text{O}(4)) | 112.92(34) |</p>
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<td>131.66(5)</td>
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<td>130.17(5)</td>
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Symmetry operation i : x, y, z.
Figure 30. Molecular structure (25% probability ellipsoids) and crystallographic numbering scheme employed for \{([RSn(OH)](CH_2)_3[RSn(H_2O)]O)_4\cdot4OTf\} (R = CH_2SiMe_3 (113c)). Some triflic groups have been omitted for clarity.

The infrared spectrum in KBr of 113c shows two absorptions at 3250.0 and 3365.3 cm$^{-1}$, which have been assigned to the bridging hydroxyl and coordinated water. The $^{119}$Sn NMR (MeCN) of an analytically pure sample of 113c shows two
equally intense signals at δ -119.0 and -128.5 with a total integral of 64.0%. Furthermore, two pairs of signals are observed at δ –110.0 (5.1%) / –152.0 (4.2%) and –115.8 (13.1%) / –126.5 (10.2%), which are tentatively assigned to the cis and trans isomer of dimer of 113c (Chart 1). This observation is in agreement with the electrospray mass spectrometry showing cluster patterns that are consistent with dimeric as well as tetrameric species.

Table 21 shows the species assigned in both the positive and negative ions ESMS of 113c in acetonitrile at a cone voltage of 20V. The species were assigned by comparison of experimental and calculated isotopic patterns.

Table 21. Speciation in the positive and negative modes ESMS of {{[(Me₃SiCH₂)Sn(OH)](CH₂)₃[(Me₃SiCH₂)Sn(H₂O)]}O}_4·4OTf (113c) in MeCN.

<table>
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<th>n</th>
<th>m/z</th>
<th>Assignment</th>
<th>% Abundance</th>
</tr>
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<td>3</td>
<td>486.9</td>
<td>[1/2M]^2+</td>
<td>97</td>
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<tr>
<td></td>
<td>507.5</td>
<td>[1/2M + MeCN]^2+</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>1122.9</td>
<td>[1/2M + OTf]^+</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>1140.9</td>
<td>[1/2M + H₂O + OTf]^+</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>2280.8</td>
<td>[M + 2OTf + Cl]^−</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>2394.8</td>
<td>[M + 3OTf]^−</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>916.8</td>
<td>[1/4M – OH + 3OTf]^−</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>1420.8</td>
<td>[1/2M + 3OTf]^−</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>1553.8</td>
<td>[1/2M – OH + 4OTf]^−</td>
<td>5</td>
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</table>
The positive mode spectrum of 113c is comparatively simple. The dominant peaks at m/z = 486.9 (97%) is assigned to the doubly charged species \([1/2M]^2+\). The peak at m/z = 1122.9 (81%) is assigned to the ion-pair \([1/2M + OTf]^+\) and m/z = 2394.8 is assigned to the presence of \([M + 3OTf]^+\). Experimental and calculated isotopic cluster patterns are in excellent agreement (Figure 31). The presence of chloride in \([M + 2OTf + Cl]^+\) and \([M + 4OTf + Cl]^−\) of sample 113c is due to the omnipresence of chloride ions in the spectrometer.

The negative mode spectrum of 113c contains major peaks at m/z = 916.8 (89%), m/z = 1420.8 (13%) and m/z = 2691.9 (16%) which are indicative for the presence of \([1/4M – OH + 3OTf]^−\), \([1/2M + 3OTf]^−\) and \([M + 5OTf]^−\) (Figure 32).

Figure 31. The calculated (top) and experimental (bottom) isotopic tin pattern of \([1/2M + OTf]^+\) (m/z = 1122.9) and \([1/2M + H_2O + OTf]^+\) (m/z = 1140.9).
Figure 32. The calculated (top) and experimental (bottom) isotopic pattern of $[1/4M - \text{OH} + 3\text{OTf}]^-$ (m/z = 916.8) and $[M + 5\text{OTf}]^-$ (m/z = 2691.9).

4.4.2 Reactions of $\{[\text{R(O)Sn}]_2(\text{CH}_2)_n\}_m$ ($n = 4, 8, 10$) with Triflic Acid
Slow addition of triflic acid, TfOH to a suspension of polymeric α,ω-
bis(trimethylsilylmethyloxostannyl)alkanes \{[R(O)Sn]_2(CH_2)_n\}_m (R = CH_2SiMe_3; n = 4 (98d), n = 8 (98h), n = 10 (98i)) in acetonitrile at room temperature gave clear
solutions. In each case removal of solvent resulted in an oil the \(^{119}\text{Sn}\) NMR (MeCN) of which show only one sharp signal at \(\delta -332.7, -326.4\) and \(-326.0\), respectively,
assigned to the species \([RSn(CH_2)_nSnR](OTf)_4\). The chemical shifts in acetonitrile
are consistent with six coordinate tin environments suggesting that the tin atoms are
coordinate to the strong donor solvent.

In each case, exposure to air moisture in a mixture of acetonitrile/chloroform
(4:1) gives rise to a colourless precipitate. In one case, \textbf{113d} slow evaporation of an
acetonitrile/chloroform solution (75:25) gave crystals suitable for X-ray analysis. It
is worth mentioning that \textbf{113d} was isolated as its dihydrate adduct
\{[(H_2O)(OH)RSn]_2(CH_2)_4\}·2OTf·2H_2O (\textbf{113d}·2H_2O). The molecular structure of
\textbf{113d}·2H_2O is shown in Figure 33, and Table 22 lists important geometric parameter.
The structure is comprised of hydrated polymeric chains of
\{[(H_2O)(OH)RSn]_2(CH_2)_4\}·2OTf·2H_2O with the repeat units illustrated in Figure 33.
The repeat unit comprises two tin centres linked via a tetramethylene bridge. Each
tin atom is also coordinated by one carbon atom and an oxygen atom derived from a
water molecule. The remaining positions in the distorted trigonal bipyramidal
coordination geometry about each tin atom are occupied by two \(\mu_2\)-hydroxide
groups. The crystallographic asymmetric unit is completed by two triflic anions and
two water molecules of crystallisation.

The linkage of the tin atoms via four-membered Sn_2OH_2 rings observed in the
structure of \textbf{113d}·2H_2O is analogous to that found in the hydrated polymeric chains
of \{[(H_2O)(OH)Cl_2Sn]_2(CH_2)_3\}·2H_2O\}\textsuperscript{167} except that in the latter the tin atoms exist in
a distorted octahedral geometry defined by a CCl_2O_3 donor set. The hydrated
polymeric chains of \{[(H_2O)(OH)Cl_2Sn]_2(CH_2)_3\}·2H_2O is derived from the
hydrolysis of a similar di-tin compound, [Cl_3Sn]_2(CH_2)_3.

<table>
<thead>
<tr>
<th>Table 22.</th>
<th>Selected interatomic (Å, deg.) parameters for {[(H_2O)(OH)(Me_3SiCH_2)Sn]_2(CH_2)_4}·2OTf·2H_2O (\textbf{113d}·2H_2O).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn(1)-O(1)</td>
<td>2.085(28)</td>
</tr>
<tr>
<td>Bond Type</td>
<td>Distance (Å)</td>
</tr>
<tr>
<td>----------------</td>
<td>-------------</td>
</tr>
<tr>
<td>Sn(1)-O(2)</td>
<td>2.186(22)</td>
</tr>
<tr>
<td>Sn(1)-O(3)</td>
<td>2.263(24)</td>
</tr>
<tr>
<td>Sn(1)-C(1)</td>
<td>2.179(33)</td>
</tr>
<tr>
<td>Sn(1)-C(5)</td>
<td>2.146(43)</td>
</tr>
<tr>
<td>O(1)-Sn(1)-O(2)</td>
<td>71.43(99)</td>
</tr>
<tr>
<td>O(1)-Sn(1)-O(3)</td>
<td>86.22(116)</td>
</tr>
<tr>
<td>O(1)-Sn(1)-C(1)</td>
<td>108.37(102)</td>
</tr>
<tr>
<td>O(1)-Sn(1)-C(5)</td>
<td>118.23(133)</td>
</tr>
<tr>
<td>O(2)-Sn(1)-O(3)</td>
<td>157.65(92)</td>
</tr>
<tr>
<td>O(2)-Sn(1)-C(1)</td>
<td>97.28(105)</td>
</tr>
<tr>
<td>O(2)-Sn(1)-C(5)</td>
<td>100.59(136)</td>
</tr>
<tr>
<td>O(3)-Sn(1)-C(1)</td>
<td>90.01(120)</td>
</tr>
<tr>
<td>O(3)-Sn(1)-C(5)</td>
<td>89.41(152)</td>
</tr>
<tr>
<td>C(1)-Sn(1)-C(5)</td>
<td>133.246(121)</td>
</tr>
</tbody>
</table>

![Diagram of molecule with Sn-O-C bonds](image-url)
Figure 33. Molecular structure (30% probability ellipsoids) and crystallographic numbering scheme employed for \{[(H_2O)(OH)(Me_3SiCH_2)Sn]_2(CH_2)_4\cdot2OTf\cdot2H_2O\}_m (113d\cdot2H_2O). Some triflic groups have been omitted for clarity.

The infrared spectrum in KBr of 113d shows two distinguishable hydroxyl absorptions i.e. the bridging and coordinated water at 3233.3 / 3334.1 cm\(^{-1}\). The \(^{119}\)Sn NMR spectrum (MeCN) of an analytically pure sample of 113d shows two signals at \(\delta \approx 165.5\) (broad, 26.0%) / \(-185.7\) (sharp, 74.0%), indicating four coordinated tin centres and that the coordinated water found in the crystal structure has dissociated in solution.

Attempted crystallisation from an acetonitrile/chloroform (75:25) solutions of the crude compounds of 113h and 113i afforded white crystalline solids unsuitable for X-ray study. However, both compounds have elemental analysis consistent with their formulation as \{[(H_2O)(OH)(R)Sn]_2(CH_2)_n\cdot2OTf\cdot2H_2O\}_m. The infrared spectra in KBr of these compounds show two distinguishable hydroxyl absorptions i.e. the bridging and coordinated water at 3215.0 / 3363.8 cm\(^{-1}\) for 113h and 3225.0 / 3353.8 cm\(^{-1}\) for 113i, respectively. The \(^{119}\)Sn NMR spectra (MeCN) of analytically pure samples of 113h and 113i each show two signals at \(\delta \approx 166.6\) (broad, 39.0%) / \(-170.5\) (broad, 61.0%) and \(-132.0\) (broad, 5.5%) / \(-178.2\) (broad, 94.5%) for 113h and 113i, respectively.

The reaction between \{[R(O)Sn]_2(CH_2)_n\}_m and triflic acid afforded in the first instance [RSn(CH_2)_nSnR](OTf)_4 which are easily hydrolysed (Scheme 36). For \(n = 3\) self-assembly leads to discrete double ladder type structure, 113c. For \(n > 3\) hydrolysis gives polymeric products, as demonstrated by the crystal structure of 113d. The relationship between structures 113c and 113d can be viewed as addition of two acidified water molecules (Scheme 37).
\[ [R(O)\text{Sn}(\text{CH}_2)_n\text{Sn}(O)\text{R}]_{m} \]

\[ \xrightarrow{\text{TfOH}} \]

\[ [\text{RSn}(\text{CH}_2)_n\text{SnR}(\text{OTf})_4]_4 \]

n = 4, 8, 10  

n = 3

\[ \text{air moisture} \]

\[ \text{Scheme 36} \]
4.4.3 ESMS Studies of \{[(H_2O)(OH)RSn]_2(CH_2)_n2OTf_2H_2O\}_m

The positive mode spectrum of **113d** in acetonitrile solution is comparatively simple. The dominant fragments, \(m/z = 632.9\) (100%) and \(m/z = 1432.9\) (56%) contain two and four tin atoms respectively, and their assignments are shown in Chart 2. The presence of clusters patterns \(m/z = 632.9\) and \(m/z = 1432.9\) are consistent with the species formed by dehydration of dicationic and tetracationic **113d**, respectively. Analogous fragments are observed in the positive mode spectra of **113h** and **113i** (Chart 2).

---

Chart 2
The negative mode spectrum of 113d contains major peaks at m/z = 948.9 (38%) and 1732.8 (50%), which are in agreement with the species formed by dehydration of dicationic and tetracationic 113d, respectively (Chart 3). Species in the negative mode spectrum of 113i shows peaks at m/z = 1164.9 (100%) for [1/4M – OH – 2H2O + 4OTf]− and m/z = 1296.9 (70%) which is assigned to the presence of [1/4M – 2OH – 2H2O + 5OTf]−. The isotopic patterns associated with these peaks are totally consistent with the formulations of the five anionic species.

4.5 Summary
The synthesis and characterisation of a heteroatom-bridged di-tin tetrachloride \([\text{R(Cl)}_2\text{Sn(CH}_2)_3\text{]}_2\text{O} \ (\text{R} = \text{CH}_2\text{SiMe}_3, \text{(110)})\) and its corresponding polymeric oxide \([[\text{R(O)}\text{Sn(CH}_2)_3\text{]}_2\text{O}]_m \text{(111)}\) are described. Reaction of \([\text{R(Cl)}_2\text{Sn(CH}_2)_3\text{]}_2\text{O}\) with \([[\text{R(O)}\text{Sn(CH}_2)_3\text{]}_2\text{O}]_m\) results in a unique functionalised double ladder \([[\text{RSn(Cl)}](\text{CH}_2)_3\text{O(CH}_2)_3[\text{RSn(Cl)}])\text{O}]_4 \text{(112)}\) whose structure in the solid state was determined by X-ray analysis. Identification of tetrameric functionalised double ladder as well as dimeric and monomeric species suggest the existence of an equilibrium in solution. The feasibility of the functionalised double ladder to form host-guest complexes with a variety of metal cations is investigated using electrospray mass spectrometry (ESMS). Evidence for such complexes is found only for sodium cations.

The reaction between \([\text{R(O)}\text{Sn}]_2(\text{CH}_2)_n]_m \ (n = 3, 4, 8, 10)\) and triflic acid is described. The initial formed products \([\text{RSn(CH}_2)_n\text{SnR]}(\text{OTf})_4\) are easily hydrolysed. For \(n = 3\), self-assembly leads to discrete double ladder type structure, \([[\text{RSn(OH)}](\text{CH}_2)_3[\text{RSn(H}_2\text{O)}])\text{O}]_4\cdot4\text{OTf}\), which is the first example of a cationic double ladder. For \(n > 3\), hydrolysis gives polymeric products, as demonstrated by the crystal structure of \([[\text{H}_2\text{O)(OH)}\text{RSn}]_2(\text{CH}_2)_4\cdot2\text{OTf}\cdot2\text{H}_2\text{O}]_m\).
Chapter 5

Higher-Order Ladders
5.1 Introduction

The use of a spacer-bridged di-tin precursor, RX₂Sn−Z−SnX₂R, makes it possible to introduce a third dimension by linking two ladder units to give a double ladder type structure.⁹⁸,⁹⁹,¹⁷³ This idea has been repeated with the formation of triple ladder¹⁰⁵ from appropriate tri-tin precursor. Quadruple ladder has been suggested based on NMR information however no structure has been reported.¹⁷⁴ The first attempted synthesis of a quadruple ladder, using a tetra-tin precursor [R(Cl)₂Sn−Z−(Cl)₂Sn]₂(Z − Z') (where R = CH₂SiMe₃; Z = (CH₂)₃, Z' = CH₂SiMe₂CH₂) (44), was reported in 1997.¹⁰⁵ It was found that the reaction of 44 with (t-Bu₂SnO)₃ afforded a “folded” double ladder (45) instead of a quadruple ladder. This observation was believed to be due to the additional gain of entropy by formation of the Si−CH₂Sn−O−Sn−CH₂ six-membered chelate intermediate, which prevented association to the anticipated quadruple ladder structure.

The synthesis of higher-order ladders is complicated by the ability of the tin atoms within each precursor chain to behave independently, capable of reacting both intra- and inter-molecularly. It has been shown that for double ladders having organic spacers with tri- and tetramethylene groups, yields of double ladder are almost quantitative.⁹⁸,⁹⁹,¹⁷³ However, with longer methylene spacers, the yield of double ladder decreases, for example for n = 8 (52% yield), n = 10 (43% yield) and

---

The text includes chemical structures and images of molecular structures relevant to the discussion on the synthesis of higher-order ladder compounds.
for $n = 12$ (35% yield), this arises presumably because of polymer formation such as shown in Figure 34 (where some R groups have been omitted for clarity). Furthermore in Chapter 4 it was demonstrated that hydrolysis product of $[\text{RSn(CH}_2\text{)}_n\text{SnR}]_4(\text{OTf})$ were dependent on the length of spacer joining the two tin atoms. For $n = 3$ discrete double ladder structures were obtained whereas for $n > 3$ polymeric materials were formed.

![Figure 34](image)

With this in mind we designed new tetra-tin precursors (122 and 123), which possess a “clip-art” configuration. These trimethylene “clips” i.e. double ladders with trimethylene spacer increase the probability of the chains of the quadruple ladder aligning in the correct way. Therefore, it was hoped that the hydrolysis reaction at these trimethylene “clip” ends might go fast enough to favour the formation of a quadruple ladder configuration.

This Chapter describes the synthesis and characterisation of spacer-bridged tetra-tin octachlorides $[\text{R(Cl)}_2\text{Sn(CH}_2\text{)}_3\text{Sn(Cl)}_2]_2(\text{CH}_2)_n (\text{R} = \text{CH}_2\text{SiMe}_3; n = 1 \ (122), n = 8 \ (123))$ and their corresponding polymeric oxides
Chapter 5

\[[R(O)Sn(CH_2)_3Sn(O)]_2(CH_2)_n\]_m (n = 1 (124), n = 8 (125)). The attempted syntheses of quadruple ladders from these precursors are also described in this Chapter.

5.2 Preparation of Tetra-tin Precursors

Tetra-tin precursors \([R(Cl)_2Sn(CH_2)_3Sn(Cl)_2]_2(CH_2)_n\) (R = CH_2SiMe_3; n = 1 (122), n = 8 (123)) and their corresponding polymeric oxides \{[R(O)Sn(CH_2)_3Sn(O)]_2(CH_2)_n\}_m (R = CH_2SiMe_3; n = 1 (124), n = 8 (125)) were synthesised as described below. (3-Hydroxypropyl)triphenyltin, Ph_3Sn(CH_2)_3OH (114) was obtained in 80\% yield through hydrostannylation of allyl alcohol with Ph_3SnH in the presence of AIBN; ^{119}\text{Sn} NMR (CDCl_3): \(\delta -97.6\). Reaction of 1.2 molar equivalents of triphenylphosphine, Ph_3P with 114 in carbon tetrachloride affords Ph_3Sn(CH_2)_3Cl (115) (Scheme 38); ^{119}\text{Sn} NMR (CDCl_3): \(\delta -98.3\).

The slow addition of one molar equivalent of iodine to 115 at 0 \(^{\circ}\)C gave IPh_2Sn(CH_2)_3Cl (116a) in 95\% yield. The addition of saturated aqueous NH_4Cl solution to 116a resulted in halide exchange to give ClPh_2Sn(CH_2)_3Cl (116b) in 80\% yield; ^{119}\text{Sn} NMR (CDCl_3): \(\delta -6.77\). Reaction of one molar equivalent of the Grignard reagent, Me_3SiCH_2MgCl, with 116b afforded (Me_3SiCH_2)Ph_2Sn(CH_2)_3Cl (117) as a yellow oil in 80\% yield.

\[
\begin{align*}
\text{Ph}_3\text{Sn} & \quad \text{CCl}_4, \quad \text{Ph}_3\text{P} \\
\quad & \quad \text{reflux} \\
\text{Ph}_3\text{Sn} & \quad \text{Cl} \\
\quad & \quad 1. \ I_2 (1.0 \text{ eq}), \text{CH}_2\text{Cl}_2, \ 0 \ ^{\circ}\text{C} \\
& \quad 2. \ \text{Sat. aq. NH}_4\text{Cl}, \text{Et}_2\text{O}, \text{rt} \\
\text{RPh}_2\text{Sn} & \quad \text{RMgCl} (1.2 \text{ eq}) \\
\quad & \quad \text{THF}, \quad \text{reflux} \\
\text{XPh}_2\text{Sn} & \quad \text{Cl} \\
\quad & \quad \text{R} = \text{CH}_2\text{SiMe}_3 \\
\text{116a; X = I} & \quad \text{116b; X = Cl}
\end{align*}
\]

\text{Scheme 38}

Reaction of 2.4 molar equivalents of the Grignard reagent of 117, (Me_3SiCH_2)Ph_2Sn(CH_2)_3MgCl, with one molar equivalent of [ClPh_2Sn]_2(CH_2)_n (n =
1 (118), n = 8 (119)) in a mixture of diethyl ether/THF (1:1) afforded [RPh2Sn(CH2)3SnPh2]2(CH2)n (R = CH2SiMe3; n = 1 (120), n = 8 (121)) in 70% and 50% yields for 120 and 121, respectively (Scheme 39). The 119Sn NMR spectra (CDCl3) of 120 and 121 each contain two signals at δ −49.3 \[2^4J(119\text{Sn}_{\text{endo}}-117\text{Sn}_{\text{endo}}) = 230 \text{ Hz} \]
\[4^4J(119\text{Sn}_{\text{exo}}-117/119\text{Sn}_{\text{endo}}) = 62 \text{ Hz} \]
\[−61.7 \[4^4J(119\text{Sn}_{\text{endo}}-117/119\text{Sn}_{\text{exo}}) = 49 \text{ Hz} \] \] and
\[−61.7 \[4^4J(119\text{Sn}_{\text{exo}}-117/119\text{Sn}_{\text{endo}}) = 51 \text{ Hz} \] \] respectively. Attempts to remove the by-product, (Me3SiCH2)Ph2Sn(CH2)2CH3 using column chromatography and crystallisation were not successful.

Addition of excess concentrated hydrochloric acid to 120 and 121 gave [R(Cl)2Sn(CH2)3Sn(Cl)2]2(CH2)n (R = CH2SiMe3; n = 1 (122), n = 8 (123)) as brown oils, which solidified on standing (Scheme 40). The 119Sn NMR spectra (CDCl3) of 122 and 123 each contain two signals at δ 61.7, 128.4 and 116.8, 131.9 respectively. Purification by crystallisation afforded analytically pure 122 and 123, in 65% and 60% yields, respectively.
The subsequent hydrolysis of 122 and 123 with excess aqueous potassium hydroxide resulted in \{[R(O)Sn(CH_2)_3Sn(O)]_2(\text{CH}_2)_n\}_m \ (R = \text{CH}_2\text{SiMe}_3; \ n = 1 (124), n = 8 (125)) as insoluble white solids (Scheme 41).

\[
\text{KOH} / \text{H}_2\text{O} \\
\text{Toluene, } 100 \degree \text{C}
\]

**Scheme 41**
5.3 Attempted Synthesis of Quadruple Ladders

The reaction of 122 with a suspension of 124 in toluene at 100 °C for 24 h (Scheme 42), resulted in the formation of a cloudy solution. Filtration of the cloudy reaction mixture afforded a white solid, which decomposes above 310 °C indicating absence of starting material 122 (note m. p. of 122 is 56-58 °C). $^{119}\text{Sn}$ NMR could not be performed on this material because of the poor solubility. Elemental analysis of this solid does not fit for starting oxide 124 (calculated: C, 22.2; H, 4.5; found: C, 18.7; H, 3.8.) but was indeed close to the result expected for the quadruple ladder (126) (calculated: C, 19.6; H, 3.9). The $^{119}\text{Sn}$ NMR spectrum (toluene) of the filtrate revealed one minor signal at δ 131.8 (12.0%) and two broad major signals at δ −88.3 (W$_{1/2}$ = 2.8 KHz, 39.0%) and −130.7 (W$_{1/2}$ = 2.8 KHz, 49.0%) indicating absence of starting material 122. The latter two broad signals are in the region usually associated with tetraorganodistannoxanes adopting ladder-type structures. The assignment for the minor signal at δ 131.8 was not conclusive. Inspection of the proposed model structure for a quadruple ladder (126 in Scheme 42) implies the existence of four tin signals. This was indeed reported by Schulte as δ −96.6, −99.0, −137.3 and −140.0.$^{174}$

Longer reaction times and slower rates of addition of 124 to 122 gave no substantial change in reaction product.

An alternative approach to the synthesis of the target quadruple ladder, 126, was by utilisation of the soluble oxide source (t-Bu$_2$SnO)$_3$. Reaction of 122 with (t-Bu$_2$SnO)$_3$ (Scheme 42) in toluene at 100 °C resulted in a cloudy solution (within a few minutes) and was further reacted for 24 h. The $^{119}\text{Sn}$ NMR spectrum (toluene) of the cloudy reaction mixture revealed two broad signals at δ −92.3 (14.6%) and −136.7 (21.3%), in addition to the signal at δ 57.7 (64.2%). The latter signal is assigned to t-Bu$_2$SnCl$_2$, indicative of successful oxygen transfer. Evidence for the reaction was apparent in the $^{119}\text{Sn}$ NMR spectrum of the reaction mixture, which shows the absence of 122 and the presence of t-Bu$_2$SnCl$_2$.

Filtration of the reaction mixture afforded a white solid, which was insoluble in most common organic solvent. Elemental composition of this solid (found: C, 18.4; H, 3.6) is similar to the insoluble solid obtained from the reaction of 122 and
This observation further supported the conclusion drawn earlier that the insoluble solid collected was not due to the oxide 124 but a new product of unknown structure. Attempts to crystallise the quadruple ladder 126 from a mixture of CHCl₃/hexane as well as other solvents were unsuccessful.

Four signals should be observed if the quadruple ladder was synthesised cleanly. Only two broad signals are apparent and consequently no firm conclusion can be made about these signals except that they may indicate the presence of a ladder compound. With each attempt at synthesising the quadruple ladder (126), a
significant amount of insoluble material that has same elemental composition as 126 was made. This led to the conclusion that rather than forming the molecular quadruple ladder, this tetra-tin octachloride (122) preferentially formed ill-defined polymers and/or oligomers.

Similar investigations were undertaken between tetra-tin precursor 123 and its corresponding oxide 125 as well as different oxide transfer reagent, (t-Bu₂SnO)₃. The reaction of 123 with a suspension of 125 in benzene at 100 °C for 24 h (Scheme 42), resulted in a cloudy solution. The ¹¹⁹Sn NMR spectrum (C₆H₆) of the reaction mixture revealed two sets of broad signals at δ −92.7 (27.0%), −98.4 (24.0%) and −135.7 (26.2%), −142.2 (23.0%). These chemical shifts are consistent with the formation of the quadruple ladder (127). Schulte¹⁷⁴ assigned signals at δ −96.6, −99.0, −137.3 and −140.0 to quadruple ladder containing trimethylene bridges. Elemental analysis of the reaction product was consistent with the quadruple ladder (127). (calculated: C, 25.9; H, 4.9. found: C, 25.9; H, 4.9.)

The reaction between 122 and a solution of (t-Bu₂SnO)₃ in toluene at 100 °C gave similar results (Scheme 42). The ¹¹⁹Sn NMR spectrum (toluene) of the reaction mixture revealed two sets of broad signals at δ −93.4 (12.3%), −99.2 (10.0%) and −136.4 (11.6%), −142.8 (10.0%), in addition to the signal at δ 57.8 (53.0%, assigned to t-Bu₂SnCl₂). Attempts to crystallise the quadruple ladder 127 from a mixture of CHCl₃/hexane as well as other solvents were unsuccessful.
5.4 Summary

The synthesis and characterisation of two spacer-bridged tetra-tin octachlorides \([R(Cl)_{2}Sn(CH_{2})_{3}Sn(Cl)_{2}]_{2}(CH_{2})_{n}\) (\(R = \text{CH}_{2}\text{SiMe}_{3}\); \(n = 1\) (122), \(n = 8\) (123)) and their corresponding polymeric oxides \([{[R(O)Sn(CH_{2})_{3}Sn(O)]_{2}(CH_{2})_{n}}]_{m}\) (\(n = 1\) (124), \(n = 8\) (125)) are described. Subsequently attempted syntheses of quadruple ladders from these precursors were also described. Reactions of \([R(Cl)_{2}Sn(CH_{2})_{3}Sn(Cl)_{2}]_{2}CH_{2}\) with \([{[R(O)Sn(CH_{2})_{3}Sn(O)]_{2}CH_{2}}]_{m}\) or \((t-\text{Bu}_{2}\text{SnO})_{3}\) result in, mostly insoluble, amorphous solids. Reactions of \([R(Cl)_{2}Sn(CH_{2})_{3}Sn(Cl)_{2}]_{2}(CH_{2})_{8}\) with \([{[R(O)Sn(CH_{2})_{3}Sn(O)]_{2}(CH_{2})_{8}}]_{m}\) or \((t-\text{Bu}_{2}\text{SnO})_{3}\) result in new tin-containing species which are presumably oligomeric.
Chapter 6

Organotin-Oxo Oligomers
6.1 Introduction

Oligomeric organotin-oxo clusters have application as catalysts for a range of organic synthesis\textsuperscript{106,107} and polymerisation reactions\textsuperscript{106} as well as in the field of new materials science.\textsuperscript{108,113,177,178} Nevertheless, the number of organotin-oxo clusters currently known is comparatively small, probably due to the absence of rational synthetic pathways.

Discrete oligomeric organotin-oxo clusters have been most usually synthesised by hydrolysis reaction of RSnX\textsubscript{3}. The most interesting of these organotin-oxo clusters is [(RSn)\textsubscript{12}O\textsubscript{14}(OH)\textsubscript{6}]X\textsubscript{2} (R = i-Pr, n-Bu; X = Cl, OH)\textsuperscript{108,129-131} because of their potential for further oligomerisation to gives new materials. The current trend is to attempt oligomerisation/polymerisation by use of i) unsaturated functions capable for further polymerisation into “Sn\textsubscript{12}”clusters,\textsuperscript{179} ii) bifunctional anions, such as dicarboxylates, which allow assembly of “Sn\textsubscript{12}” via strong electrostatic interactions,\textsuperscript{109,180} and iii) anions, X, which have functionality, e.g., methacrylate.\textsuperscript{177,178} The strategy described in this Chapter involves use of linked di-tin precursors α,ω-bis[tris(carboxy)stannyl]alkanes, [(RCO\textsubscript{2})\textsubscript{3}Sn]\textsubscript{2}(CH\textsubscript{2})\textsubscript{n}, in place of RSnX\textsubscript{3} as starting materials for the synthesis of “Sn\textsubscript{12}” compounds. It was hoped that the use of linked di-tin precursors could lead to further linkage of “Sn\textsubscript{12}” units (133).
To the best of our knowledge there are no reports for the use of [(RCO₂)₃Sn]₂(CH₂)ₙ as precursors for the preparation of linked “Sn₁₂” clusters. Furthermore, there is only one report on the synthesis of precursors of the type [(CH₃CO₂)₃Sn]₂CH₂.¹⁸¹

This Chapter describes the preparation and characterisation of a series of alkyl-bridged di-tin hexacarboxylates [(RCO₂)₃Sn]₂(CH₂)ₙ (n = 3 (c), n = 4 (d); R = Ph (128), c-C₆H₁₁ (129), CH₃ (130), ClCH₂ (131)). Attempts to use the di-tin precursors for the synthesis of organotin-oxo oligomers are also described.

### 6.2 Preparation of α,ω-Bis[tri(carboxy)stannyl]alkanes, [(RCO₂)₃Sn]₂(CH₂)ₙ

The lability of tin-phenyl bonds against carboxylic acids is well known¹⁵⁵ and was used as a starting point for the synthesis of a new type of precursor for the synthesis of linked “Sn₁₂” clusters. The synthesis of α,ω-bis(triphenylstannyl)alkanes, [Ph₃Sn]₂(CH₂)ₙ (94c) was described in Chapter 3. The reaction of [Ph₃Sn]₂(CH₂)ₙ (n = 3 (94c), n = 4 (94d)) with 6.5 molar equivalents of the appropriate carboxylic acid afforded the related α,ω-bis[tri(carboxy)stannyl]alkanes, [(RCO₂)₃Sn]₂(CH₂)ₙ (n = 3 (c), n = 4 (d); R = Ph (128), c-C₆H₁₁ (129), CH₃ (130), ClCH₂ (131)) in good to moderate yields (Scheme 43).

![Scheme 43](image)

Compounds 128c, 128d, 131d and 130c, 130d are solids, whereas 131c and 129c, 129d are highly viscous oils all have satisfactory elemental analysis. The compounds are hygroscopic and require storage in a moisture-free environment. All of the [(RCO₂)₃Sn]₂(CH₂)ₙ except [(ClCH₂CO₂)₃Sn]₂(CH₂)₃ are readily soluble in
common organic solvents. $^{119}$Sn NMR spectra ($d_8$-toluene) of the compounds gave chemical shifts within the region of $\delta$ −532.7 to −543.9. The chemical shifts are similar to that of the known compound [(CH$_3$CO$_2$)$_3$Sn]$_2$CH$_2$, $\delta$ −530.0$^{181}$ and are consistent with seven coordinate tin environments.$^{182}$ Large $^nJ(119$Sn−$^{117/119}$Sn) couplings of 944 Hz for 128c, 961 Hz for 130c, 876 Hz for 129c and 881 Hz for 129d were observed. The magnitude of these couplings may result from several contributions i) $^4J$ coupling through carboxylate as well as ii) $^4J$ or $^5J$ coupling through methylene bridge (Figure 35).

$$\text{Sn(CO}_2\text{R)}_2(\text{RCO}_2\text{Sn)}_2$$

Figure 35

6.3 Hydrolysis of α,ω-Bis[tri(carboxy)stannyl]alkanes, [(RCO$_2$)$_3$Sn]$_2$(CH$_2$)$_n$

[(PhCO$_2$)$_3$Sn]$_2$(CH$_2$)$_3$ (128c) and [(PhCO$_2$)$_3$Sn]$_2$(CH$_2$)$_4$ (128d) ($\delta(119$Sn) −537.8 and −532.7, respectively) were exposed to air moisture in a mixture of CHCl$_3$/hexane (3:1) (Scheme 44). After exposure for three days, the $^{119}$Sn NMR (toluene) of 128c' showed seven additional signals occurring at $\delta$ −491.0 (15.3%), −505.3 (24.0%), −512.6 (14.0%), −516.33 (16.0%), −518.9 (2.7%), −529.3 (14.0%), −446.1 (14.0%). The $^{119}$Sn NMR (toluene) of 128d after exposure to air moisture for three days showed five additional signals at $\delta$ −507.5 (16.0%), −508.5 (16.0%), −530.6 (18.0%), −532.2 (14.0%), −619.5 (36.0%). The $^{119}$Sn chemical shift positions of these signals are indicative of hexa- and heptacoordinate tin. The number of tin signals indicates a mixture of a number of organotin-oxo carboxylate species.
Alternatively, a product containing a number of tin atoms with different chemical environments could cause the additional signals to occur. Further exposure of these compounds to air moisture afforded white solid materials (128c" and 128d"), which decompose above 310 °C. $^{119}$Sn NMR could not be performed because of the insolubility of these materials in common organic solvents. Attempts to characterise 128c" and 128d" using solid state $^{119}$Sn NMR spectroscopy were unsuccessful. The infrared spectra in KBr of these compounds show three absorptions at 1540.0 / 1599.1, 3405 cm$^{-1}$ for 128c" and 1543.2 / 1598.5, 3100 cm$^{-1}$ for 128d", which have been assigned to the ν(CO$_2$) and ν(OH). Elemental analysis performed on 128c" and 128d" are consistent with the hydrolysis of four PhCO$_2$ groups (calculated: C, 34.6; H, 3.4; found: C, 35.1; H, 3.8 for 128c" and calculated: C, 35.8; H, 3.7; found: C, 36.1; H, 3.9 for 128d").

\[
\text{(RCO}_2\text{)}_3\text{Sn(CH}_2\text{)}_n\text{Sn(RCO}_2\text{)_3} \xrightarrow{\text{air moisture}} \text{1/m} \left[ \frac{(\text{RCO}_2\text{)\_3-xSn(CH}_2\text{)_nSn(RCO}_2\text{)_3-x}}{(\text{OH})_x (\text{OH})_x} \right]_m
\]

| 128c, d; R = Ph | 128c', d'; R = Ph |
| 129c, d; R = c-C$_6$H$_{11}$ | 129c', d'; R = c-C$_6$H$_{11}$ |
| 130c, d; R = CH$_3$ | 130c', d'; R = CH$_3$ |
| 131c, d; R = ClCH$_2$ | 131c', d'; R = ClCH$_2$ |

Similar hydrolysis investigations were undertaken with [(RCO$_2$)$_3$Sn]$_2$(CH$_2$)$_n$ (n = 3 (c), 4 (d); R = c-C$_6$H$_{11}$ (129), CH$_3$ (130), ClCH$_2$ (131)). After exposure to air moisture for four days, $^{119}$Sn NMR of 129c' showed a spectrum with additional signals occurring at δ −507.3 (33.0%), −520.0 (3.0%), −531.8 (36.0%), −543.5 (3.0%) and −645.3 (24.0%), indicating hexa- and possibly heptacoordinated tin atoms. Upon further contact with air moisture over several days, compound 129c' slowly transform to an insoluble amorphous material (129c"), which decompose above 310 °C. Elemental analysis performed on 129c" is consistent with the hydrolysis of two c-C$_6$H$_{11}$CO$_2$ groups (calculated: C, 45.3; H, 6.4; found: C, 44.0; H, 5.9). The hydrolysis of the tetramethylene analogue 129d, gave similar results.

The $^{119}$Sn NMR spectrum (toluene) of 130c, after exposure to air moisture for two days shows additional signals occurring in the range of δ −499.8 to −584.6. Further exposure of the mixture (130c') to air moisture yielded a glass-like solids.
(130c''), which turned opaque when heated to 80 °C and decomposed at 150 °C. Characterisation of 130c'' by 119Sn NMR was not possible, as the product was insoluble in common organic solvent. Similar observations hold for the hydrolysis of 130d. Elemental analysis performed on 130c'' and 130d'' are consistent with the hydrolysis of four CH₃CO₂ groups (calculated: C, 18.0; H, 3.5; found: C, 18.5; H, 3.8 for 130c'' and calculated: C, 20.0; H, 3.8; found: C, 18.9; H, 4.0 for 130d'').

All attempts to crystallise hydrolysis products of [(RCO₂)₃Sn]₂(CH₂)ₙ were unsuccessful.

Compound [(ClCH₂CO₂)₃Sn]₂(CH₂)₄ (131d) is a yellow solid which shows good solubility in common organic solvents compared to the trimethylene analogue [(ClCH₂CO₂)₃Sn]₂(CH₂)₃ (131c). Investigations were performed on exposure of 131d in a mixture of CHCl₃/hexane (3:1) to air moisture (Scheme 44). After exposure for three days, 119Sn NMR (toluene) showed a spectrum with six additional signals occurring at δ −504.3 (19.0%), −504.7 (15.0%), −531.9 (19.0%), −532.5 (15.0%), −614.3 (12.0%) and −618.3 (20.0%), indicating hexa- and heptacoordinated tin. Further exposure of 131d' to air moisture afforded a yellow solid (131d''), which melts at 280-284 °C. 119Sn NMR spectrum could not be obtained, due to poor solubility of 131d'' in common organic solvents.

The previously reported isolation of the “Sn₁₂” cluster [Sn(CH₂)₃Sn]₆(ClCH₂CO₂)₁₄(OH)₂O₁₀ (56) (Figure 36) from the controlled hydrolysis of 131c as reported by co-workers was repeated. The X-ray structure analysis of 56 revealed a completely new motif for “Sn₁₂” clusters. The tin-oxo core as shown in Figure 36 contains 12 tin atoms in two types of coordination geometries. One of the tin atoms, Sn(2) as well as Sn(2’), is pentacoordinated with distorted trigonal bipyramidal geometry, the remaining tin atoms, Sn(1), Sn(3), Sn(4), Sn(5) and Sn(6) as well as Sn(1’), Sn(3’), Sn(4’), Sn(5’) and Sn(6’), are hexacoordinated with distorted octahedral geometry. Compound 56 was successfully synthesised and further characterised by solid state ¹¹⁹Sn NMR spectroscopy (Figure 37). The ¹¹⁹Sn MAS NMR spectrum of 56 shows four signals at δ −322.0, −491.9 −514.0 and −523.6 with a total manifold integration of 1 : 1 : 3 : 1. The number of signals is consistent with the number of crystallographically independent tin sites present in the solid state structure of 56 (Figure 36). In addition, the ¹¹⁹Sn MAS chemical shifts
of $-322.0$ (pentacoordinate tin), $-491.9$–$514.0$ and $-523.6$ (hexacoordinate tins) are in agreement with the coordination number observed in the X-ray analysis. The four large sideband manifolds in the spectrum (Figure 37) were used to perform a tensor analysis according to the method of Herzfeld and Berger.\textsuperscript{162,163} The isotropic chemical shift ($\delta_{\text{iso}}$), anisotropy ($\zeta$) and asymmetry ($\eta$), represented in the Haeberlen convention\textsuperscript{164} are listed in Table 23. It is worth emphasising that the $^{119}$Sn NMR parameters of $\delta -514.0$ are the average of three independent tin sites.

![Figure 36](image)

**Figure 36.** Schematic representation of $[\text{Sn(CH}_2)_3\text{Sn}]_6(\text{ClCH}_2\text{CO}_2)_{14}(\text{OH})_2\text{O}_{10}$ (56). Some organic groups have been omitted for clarity.
Figure 37. $^{119}\text{Sn}$ MAS NMR spectrum of $[\text{Sn(CH}_2\text{)}_3\text{Sn}]_6(\text{ClCH}_2\text{CO}_2)_{14}(\text{OH})_2\text{O}_{10}$ (56) ($\nu_{\text{max}} = 5.5$ KHz). Isotropic chemical shifts are indicated by arrows.

Table 23. Selected $^{119}\text{Sn}$ MAS NMR parameters for $[\text{Sn(CH}_2\text{)}_3\text{Sn}]_6(\text{ClCH}_2\text{CO}_2)_{14}(\text{OH})_2\text{O}_{10}$ (56).

<table>
<thead>
<tr>
<th>$\delta_{\text{iso}}$</th>
<th>$\zeta$ (ppm)</th>
<th>$\eta$</th>
<th>$%$</th>
<th>$\sigma_{11}$ (ppm)</th>
<th>$\sigma_{22}$ (ppm)</th>
<th>$\sigma_{33}$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-322.0$</td>
<td>$472$</td>
<td>$0.80$</td>
<td>$15.3$</td>
<td>$-102$</td>
<td>$275$</td>
<td>$794$</td>
</tr>
<tr>
<td>$-491.9$</td>
<td>$410$</td>
<td>$0.25$</td>
<td>$15.3$</td>
<td>$236$</td>
<td>$338$</td>
<td>$902$</td>
</tr>
<tr>
<td>$-514.0$</td>
<td>$395$</td>
<td>$0.20$</td>
<td>$55.0$</td>
<td>$268$</td>
<td>$356$</td>
<td>$909$</td>
</tr>
<tr>
<td>$-523.6$</td>
<td>$521$</td>
<td>$0.20$</td>
<td>$14.5$</td>
<td>$211$</td>
<td>$315$</td>
<td>$1045$</td>
</tr>
</tbody>
</table>

6.4 Summary
The synthesis of a series of alkyl-bridged di-tin hexacarboxylates \([\text{RCO}_2\text{Sn}]_2\text{(CH}_2)_n\) \((n = 3, 4; R = \text{Ph, } c\text{-C}_6\text{H}_{11}, \text{CH}_3, \text{ClCH}_2)\) is reported. The hydrolysis of these compounds is facile and complex. There appears to be no correlation between spacer chain length and hydrolysis product. However, the conjugate acid strength of the carboxylate does appear to be important. In general only insoluble amorphous polymeric organotin-oxo compounds were obtained.
Chapter 7

Experimental
7.1 General Methods

$^{119}$Sn (inverse-gated and proton coupled) (100.74 MHz) and $^{19}$F NMR (254.19 MHz) spectra were obtained using a JEOL-GX 270 MHz FT NMR spectrometer and are referenced to Me$_4$Sn and CFCl$_3$ respectively. $^1$H (299.98 MHz) and $^{13}$C (75.44 MHz) NMR were obtained on a Varian 300 MHz Unity Plus NMR spectrometer, referenced to tetramethylsilane. $^{119}$Sn MAS NMR spectra of 56, 76b, 89a-H:O and 93 were obtained using a JEOL Eclipse Plus 400 MHz FT NMR spectrometer, referenced to Me$_4$Sn. The $^{119}$Sn MAS and CP-MAS NMR spectra of 61b and 85b were determined by Dr François Ribot at the Université Pierre et Marie Curie (Paris, France) on a Bruker MSL300 MHz spectrometer (300.13 and 111.92 MHz for $^1$H and $^{119}$Sn, respectively). A pulse angle of 30°, recycle delay of 10 s and 4 $\mu$s (90°) pulse, 2 ms contact time, recycle delay of 2 s were used for 85b and 61b, respectively. Chemical shifts are quoted relative to Me$_4$Sn, using solid c-Hex$_4$Sn ($\delta_{\text{iso}} = -97.35$ ppm) as a secondary external reference. Typically 15000 transient were recorded in order to achieve a reasonable signal-to-noise ratio. At least two experiments with sufficiently different spinning rates were recorded in order to determine the isotropic chemical shift. Analysis of the principal components of the $^{119}$Sn shielding tensors was performed with WINFIT software using the method of Herzfeld and Berger. They are reported using Haeberlen’s notation$^{164}$ as the isotropic chemical shift ($\delta_{\text{iso}} = -\sigma_{\text{iso}}$), the anisotropy ($\zeta = \sigma_{33} - \sigma_{\text{iso}}$) and the asymmetry ($\eta = \mid \sigma_{22} - \sigma_{11} \mid / \mid \sigma_{33} - \sigma_{\text{iso}} \mid$), $\sigma_{11}$, $\sigma_{22}$ and $\sigma_{33}$ being the three components of the shielding tensor expressed in its principal axis system with the following convention: $\zeta$ is a signed value expressed in ppm and $\eta$ is a dimensionless parameter, the value of which varies between 0 and 1.

Uncorrected melting points were determined on a Reichert hot stage. Microanalyses were performed at the Australia National University (Canberra, Australia), at CMAS (Geelong, Australia) or at Dortmund University (Germany). Electrospray mass spectra were obtained with a Platform II single quadrupole mass spectrometer (Micromass, Altrincham, UK) using an acetonitrile mobile phase. Acetonitrile solutions (0.1 mM) of the compounds were injected directly into the spectrometer via a Rheodyne injector equipped with a 50 $\mu$L loop. A Harvard 22 syringe pump delivered the solutions to the vaporisation nozzle of the electrospray ion source at a flow rate of 10 $\mu$Lmin$^{-1}$. Nitrogen was used as both a drying gas and for nebulisation with flow rates of approx. 200 mLmin$^{-1}$ and 20 mLmin$^{-1}$ respectively. Pressure in the mass analyser region was usually about $4 \times 10^{-5}$ mbar. Typically 10 signal averaged spectra were collected. X-ray Crystallography was performed at the National University of Singapore (Singapore) by Assoc. Prof.
Edward R. T. Tiekink. The powder X-ray diffraction profiles were determined by Dr François Ribot at the Université Pierre et Marie Curie (Paris, France) on a Philips PW1830 diffractometer.

All solvents and reagents used were Analytical Reagent grade. Reactions were generally carried out under an atmosphere of dry nitrogen or argon. Ph₃SnH was prepared based on the literature procedure.¹⁸³

7.2 Syntheses

General procedure for the reaction of (R₂SnO)ₘ with NH₄X. The organotin oxide, (R₂SnO)ₘ, (10.0 mmol, 1.65 g for R = Me, 1.93 g for R = Et, 2.49 g for R = n-Bu, 3.61 g for R = n-Oct, 3.01 g for R = c-Hex, 2.21 g for R = i-Pr, 2.89 g for R = Ph) was suspended in 1,4-dioxane (50 mL) and a saturated aqueous solution (50 mL) of the appropriate NH₄X (X = F, Cl, Br, I, OAc) was added. The reaction mixture was heated under reflux until all of the (R₂SnO)ₘ had dissolved (c.f. Table 1). Then, the solvent mixture was almost entirely removed in vacuo and the resulting residue was extracted with CHCl₃ (2 × 100 mL). The combined organic extracts were dried over Na₂SO₄. After removal of the solvent, a crude product was obtained, which was recrystallised from chloroform / hexane.

For (Me₂SnO)ₘ / NH₄F a complex mixture was obtained (0.33 g). No pure product could be isolated (see text).

For (Et₂SnO)ₘ / NH₄F a complex mixture was obtained (0.49 g). No pure product could be isolated. The ¹¹⁹Sn NMR (CDCl₃) shows 10 signals between the range of δ −82.0 and −140.7 (see text).

Bis[1,3-difluoro-1,1,3,3-tetrakis(butyl)distannoxane] [(n-Bu₂SnF)₂O]₂ (59b). White solid (1.95 g, 75 %). m. p. 180-185 °C (Lit. m. p. 115-117 °C).¹⁵² ¹H NMR (CDCl₃): δ 0.91-0.97 (m, 24H), 1.35-1.51 (m, 32H), 1.63-1.73 (m, 16H). ¹³C NMR (CDCl₃): δ 13.52, 23.10 [¹J(¹³C-¹¹⁷/¹¹⁹Sn) = 591/618 Hz], 24.00 [¹J(¹³C-¹¹⁷/¹¹⁹Sn) = 567/594 Hz], 26.72, 26.81. ¹⁹F NMR (CDCl₃): δ −132.4 [¹J(¹⁹F-¹¹⁷/¹¹⁹Sn) = 741 Hz, ¹J(¹⁹F-¹¹⁷/¹¹⁹Sn) = 1763 Hz]. ¹¹⁹Sn NMR (CDCl₃): δ −142.2 [t, ¹J(¹¹⁹Sn-¹⁹F) = 771 Hz], −159.4 [t, ¹J(¹¹⁹Sn-¹⁹F) = 1795 Hz]. Anal. Calcd. for C₃₂H₇₂F₄O₂Sn₄: C, 37.0; H, 7.0. Found: C, 37.4; H, 7.6.
For \((n\text{-Oct}_2\text{SnO})_m / \text{NH}_4\text{F}\) a complex mixture was obtained (2.50 g). No pure product could be isolated. The \(^{119}\text{Sn}\) NMR (CDCl\(_3\)) shows 12 signals between the range of \(\delta -140.0\) and –190.0 (see text).

**Bis[1,3-difluoro-1,1,3,3-tetrakis(cyclohexyl)distannoxane]** \([(c\text{-Hex}_2\text{SnF})_2\text{O}]_2\) (61b). Colourless solid (2.68 g, 86 %). m. p. >295 °C (decomp.). \(^1\text{H}\) NMR (d\(_8\)-toluene, r.t.): \(\delta 1.20-2.50\) (m, 88H). \(^{13}\text{C}\) NMR (d\(_8\)-toluene, 100 °C): \(\delta 26.80, 28.75, 28.92, 30.19, 30.35, 41.98, 42.18. \(^{19}\text{F}\) NMR (d\(_8\)-toluene, r.t.): \(\delta -144.9\) \([^{1}J(19\text{F}-117/119\text{Sn}_{\text{endo}}) = 723, ^{1}J(19\text{F}-117/119\text{Sn}_{\text{exo}}) = 822\text{ Hz}], 1^{1}J(19\text{F}-117/119\text{Sn}_{\text{exo}}) = 1875/1956\text{ Hz}\] \(^{119}\text{Sn}\) NMR (d\(_8\)-toluene, 100 °C): \(\delta -237.6\) \([t, ^{1}J(119\text{Sn}-19\text{F}) = 1950\text{ Hz}], -212.0\) \([t, ^{1}J(119\text{Sn}-19\text{F}) = 778\text{ Hz}]\). \(^{119}\text{Sn}\) CP-MAS NMR: \(\delta -232.4\) \([t, ^{2}J(119\text{Sn}-119\text{Sn}) = 1700\text{ Hz}], -270.5\) \([t, ^{2}J(119\text{Sn}-19\text{F}) = 1280\text{ Hz}]\). Anal. Calcd. for C\(_{48}\)H\(_{88}\)F\(_4\)O\(_2\)Sn\(_4\): C, 46.2; H, 7.1. Found: C, 46.3; H, 7.2.

For \((i\text{-Pr}_2\text{SnO})_m / \text{NH}_4\text{F}\) a complex mixture was obtained (1.80 g). No pure product could be isolated. The \(^{119}\text{Sn}\) NMR (CDCl\(_3\)) shows 17 signals between the range of \(\delta -15.0\) and –25.5 (see text).

For \((\text{Ph}_2\text{SnO})_m / \text{NH}_4\text{F}\) a complex mixture was obtained (0.58 g). No pure product could be isolated (see text).

**Bis[1,3-dichloro-1,1,3,3-tetrakis(methyl)distannoxane]** \([(\text{Me}_2\text{SnCl})_2\text{O}]_2\) (64b). White solid (1.58 g, 82 %). m. p. >280 °C (Lit. m. p. >300 °C). \(^{119}\text{Sn}\) NMR (CDCl\(_3\)): \(\delta -62.6, -114.4\).

**Bis[1,3-dichloro-1,1,3,3-tetrakis(ethyl)distannoxane]** \([(\text{Et}_2\text{SnCl})_2\text{O}]_2\) (65b). White solid (1.32 g, 60 %). m. p. 168-170 °C (Lit. mp. 175.5-176.5 °C). \(^{119}\text{Sn}\) NMR (CDCl\(_3\)): \(\delta -89.1, -137.6\).

**Bis[1,3-dichloro-1,1,3,3-tetrakis(butyl)distannoxane]** \([(n\text{-Bu}_2\text{SnCl})_2\text{O}]_2\) (66b). White solid (2.65 g, 96 %). m. p. 110-111 °C (Lit. mp. 112-114 °C). \(^{119}\text{Sn}\) NMR (CDCl\(_3\)): \(\delta -91.4\) \([^{2}J(119\text{Sn}-117/119\text{Sn}) = 74\text{ Hz}], -140.3\) \([^{2}J(119\text{Sn}-117/119\text{Sn}) = 71\text{ Hz}]\).

**Bis[1,3-dichloro-1,1,3,3-tetrakis(octyl)distannoxane]** \([(n\text{-Oct}_2\text{SnCl})_2\text{O}]_2\) (67b). White solid (3.58 g, 92 %). m. p. 94-95 °C. \(^1\text{H}\) NMR (CDCl\(_3\)): \(\delta 0.88\) (broad s, 12H), 1.29 (broad s, 34H), 1.78 (broad s, 4H), 1.81 (broad s, 18H). \(^{13}\text{C}\) NMR (CDCl\(_3\)): \(\delta 14.02, 14.04, 22.60, 22.64, 24.95, 25.16, 29.08, 29.19, 29.24, 31.81, 31.89, 33.06, 33.18, 33.46, 33.61. \(^{119}\text{Sn}\) NMR (CDCl\(_3\)): \(\delta -90.8\) \([^{2}J(119\text{Sn}-117/119\text{Sn}) = 69\text{ Hz}]\),
\[ ^2J(^{119}\text{Sn}-\text{O}^{117/119}\text{Sn}) = 71 \text{ Hz} \]. \(^{119}\text{Sn} \) MAS NMR: \( \delta = -84.0, -141.0 \). Anal. Calcd. for C\(_{64}\)H\(_{136}\)Cl\(_4\)O\(_2\)Sn\(_4\): C, 49.5; H, 8.8. Found: C, 48.5; H, 9.0.

**Bis[1,3-dichloro-1,1,3,3-tetrakis(cyclohexyl)distannoxane]** [(e-Hex\(_2\)SnCl\(_2\))O\(_2\)] (68b). Colourless solid (2.76 g, 84 %). m. p. >250 °C (decomp.). \(^1\text{H} \) NMR (CDCl\(_3\)): \( \delta = 1.20-2.50 \) (m, 88H). \(^{13}\text{C} \) NMR (CDCl\(_3\)): \( \delta = 26.20, 26.65, 26.80, 29.03, 29.89, 30.52, 31.25 \). \(^{119}\text{Sn} \) NMR (CDCl\(_3\)): \( \delta = -139.0, -202.7 \) [\( ^2J(^{119}\text{Sn}-\text{O}^{117/119}\text{Sn}) = 89 \text{ Hz} \)]. Anal. Calcd. for C\(_{48}\)H\(_{88}\)Cl\(_4\)O\(_2\)Sn\(_4\): C, 43.9; H, 6.8. Found: C, 43.0; H, 6.5.

For (Me\(_2\)SnO\(_n\)) / NH\(_4\)Br a complex mixture was obtained (0.85 g). No pure product could be isolated. The \(^{119}\text{Sn} \) NMR (CDCl\(_3\)) shows 12 signals between the range of \( \delta = -131.5 \) and -153.5 (see text).

**Bis[1,3-dibromo-1,1,3,3-tetrakis(ethyl)distannoxane]** [(Et\(_2\)SnBr\(_2\))O\(_2\)] (72b). White solid (1.59 g, 60 %). m. p. 178 °C (Lit. m. p. 172-173 °C). \(^1\text{H} \) NMR (CDCl\(_3\)): \( \delta = 1.41-1.52 \) (m, 24H), 1.86-1.97 (t, 16H). \(^{13}\text{C} \) NMR (CDCl\(_3\)): \( \delta = 9.55, 10.4, 27.8 \) [\( ^1J(^{13}\text{C}-^{117/119}\text{Sn}) = 535/561 \text{ Hz} \)], 29.44 [\( ^1J(^{13}\text{C}-^{117/119}\text{Sn}) = 586/612 \text{ Hz} \)]. \(^{119}\text{Sn} \) NMR (CDCl\(_3\)): \( \delta = -79.3 \) [\( ^2J(^{119}\text{Sn}-\text{O}^{117/119}\text{Sn}) = 79 \text{ Hz} \)], -128.9 [\( ^2J(^{119}\text{Sn}-\text{O}^{117/119}\text{Sn}) = 79 \text{ Hz} \)]. Anal. Calcd. for C\(_{16}\)H\(_{40}\)Br\(_4\)O\(_2\)Sn\(_4\): C, 18.2; H, 3.8. Found: C, 18.5; H, 3.7.

**Bis[1,3-dibromo-1,1,3,3-tetrakis(butyl)distannoxane]** [(n-Bu\(_2\)SnBr\(_2\))O\(_2\)] (73b). White solid (3.05 g, 95 %). m. p. 104 °C (Lit. m. p. 107-108 °C). \(^1\text{H} \) NMR (CDCl\(_3\)): \( \delta = 0.93-0.99 \) (broad s, 24H), 1.29 (broad s, 34H), 1.86 (broad s, 4H), 1.90 (broad s, 18H). \(^{13}\text{C} \) NMR (CDCl\(_3\)): \( \delta = 14.07, 14.09, 22.63, 22.68, 25.07, 25.63, 29.11, 29.20, 29.28, 31.83, 31.92, 33.29, 33.49, 36.39, 33.52 \). \(^{119}\text{Sn} \) NMR (CDCl\(_3\)): \( \delta = -81.3 \) [\( ^2J(^{119}\text{Sn}-\text{O}^{117/119}\text{Sn}) = 79 \text{ Hz} \)], -129.8 [\( ^2J(^{119}\text{Sn}-\text{O}^{117/119}\text{Sn}) = 79 \text{ Hz} \)]. \(^{119}\text{Sn} \) MAS NMR: \( \delta = -58.4, -136.4 \). Anal. Calcd. for C\(_{32}\)H\(_{72}\)Br\(_4\)O\(_2\)Sn\(_4\): C, 30.0; H, 5.7. Found: C, 30.5; H, 5.9.

**Bis[1,3-dibromo-1,1,3,3-tetrakis(octyl)distannoxane]** [(n-Oct\(_2\)SnBr\(_2\))O\(_2\)] (74b). Colourless solid (3.90 g, 90 %). m. p. 63-64 °C. \(^1\text{H} \) NMR (CDCl\(_3\)): \( \delta = 1.29 \) (broad s, 12H), 1.29 (broad s, 34H), 1.86 (broad s, 4H), 1.90 (broad s, 18H). \(^{13}\text{C} \) NMR (CDCl\(_3\)): \( \delta = 14.07, 14.09, 22.63, 22.68, 25.07, 25.63, 29.11, 29.20, 29.28, 31.83, 31.92, 33.29, 33.49, 36.39, 33.52 \). \(^{119}\text{Sn} \) NMR (CDCl\(_3\)): \( \delta = -82.0 \) [\( ^2J(^{119}\text{Sn}-\text{O}^{117/119}\text{Sn}) = 79 \text{ Hz} \)], -130.1 [\( ^2J(^{119}\text{Sn}-\text{O}^{117/119}\text{Sn}) = 79 \text{ Hz} \)]. \(^{119}\text{Sn} \) MAS NMR: \( \delta = -74.0, -134.0 \). Anal. Calcd. for C\(_{64}\)H\(_{136}\)Br\(_4\)O\(_2\)Sn\(_4\): C, 44.4; H, 7.9. Found: C, 44.3; H, 8.1.

**Bis[1,3-dibromo-1,1,3,3-tetrakis(isopropyl)distannoxane]** [(i-Pr\(_2\)SnBr\(_2\))O\(_2\)] (76b). Colourless solid (2.34 g, 80 %). m. p. >270 °C (decomp.). \(^1\text{H} \) NMR (CDCl\(_3\)): \( \delta = 1.24-
1.73 (m, 48H), 2.20-2.54 (m, 8H). ¹³C NMR (CDCl₃): δ 20.06, 21.45 [²J(¹³C-¹¹⁷/¹¹⁹Sn) = 18 Hz], 40.46. ¹¹⁹Sn NMR (CDCl₃): δ −91.9 [²J(¹¹⁹Sn-O-¹¹⁷/¹¹⁹Sn) = 98 Hz], −144 [²J(¹¹⁹Sn-O-¹¹⁷/¹¹⁹Sn) = 98 Hz]. ¹¹⁹Sn MAS NMR: δ −72.0, −148.0. Anal. Calcd. for C₂₄H₅₆Br₄O₂Sn₄: C, 24.6; H, 4.8. Found: C, 24.7; H, 4.8.

For (Et₂SnO)ₙ / NH₄I a complex mixture was obtained (0.65 g). No pure product could be isolated. The ¹¹⁹Sn NMR (CDCl₃) shows 7 signals between the range of δ −31.9 and −176.5 (see text).

Bis[1,3-diacetato,1,1,3,3-tetrakis(methyl)distannoxane] {[Me₂Sn(OAc)]₂O}₂ (85b). Colourless solid (1.64 g, 76 %). m. p. 206-210 °C (Lit. m. p. 240 °C (decomp.)). ¹H NMR (CDCl₃): δ 0.64-0.92 (m, 24H), 1.95 (s, 12H). ¹³C NMR (CDCl₃): δ 5.92 [¹J(¹³C-¹¹⁷/¹¹⁹Sn) = 715/750 Hz], 8.72 [¹J(¹³C-¹¹⁷/¹¹⁹Sn) = 766/800 Hz], 22.94 (CH₃), 177.54 (C=O). ¹¹⁹Sn NMR (CDCl₃): δ −171.4 [²J(¹¹⁹Sn-O-¹¹⁷/¹¹⁹Sn) = 103 Hz], −184.6 [²J(¹¹⁹Sn-O-¹¹⁷/¹¹⁹Sn) = 101 Hz]. ¹¹⁹Sn MAS NMR (CDCl₃): δ −169.1, −207.8, −294.9, −300.0. Anal. Calcd. for C₁₆H₃₆O₁₀Sn₄: C, 22.3; H, 4.2. Found: C, 22.6; H, 4.1.

Bis(acetatodioctyltin(IV)) n-Oct₂Sn(OAc)₂ (88a). Colourless oil (3.71 g, 80 %). ¹H NMR (CDCl₃): δ 0.88 (broad s, 6H), 1.29 (broad s, 28H), 1.67 (broad s, 6H). ¹³C NMR (CDCl₃): δ 13.90, 22.52, 24.25, 25.01, 25.52, 29.89, 31.65, 33.11, 181.42 (C=O). ¹¹⁹Sn NMR (CDCl₃): δ −148.1.

Bis(acetatodicyclohexyltin(IV)hydrate c-Hex₂Sn(OAc)₂⋅H₂O (89a⋅H₂O). Colourless solid (1.27 g, 91 %). m. p. 50-54 °C. ¹H NMR (CDCl₃): δ 0.80-1.99 (m, 22H), 2.10 (s, 6H). ¹³C NMR (CDCl₃): δ 20.48 (CH₃), 26.28 [¹J(¹³C-¹¹⁷/¹¹⁹Sn) = 12 Hz], 28.35 [³J(¹³C-¹¹⁷/¹¹⁹Sn) = 100/104 Hz], 29.56 [²J(¹³C-¹¹⁷/¹¹⁹Sn) = 23 Hz], 42.82 [¹J(¹³C-¹¹⁷/¹¹⁹Sn) = 517/540 Hz], 181.40 (C=O). ¹¹⁹Sn NMR (CDCl₃): δ −215.3. ¹¹⁹Sn MAS NMR δ: −401. IR (KBr) ν(H₂O): 3394.7 cm⁻¹. Anal. Calcd. for C₁₆H₃₀O₅Sn: C, 45.6; H, 7.2. Found: C, 45.7; H, 7.3.

Bis[1-chloro-3-fluoro-1,1,3,3-tetrakis(cyclohexyl)distannoxane] [c-Hex(Cl)SnOSn(F)c-Hex₂]: (93). A solution of 61b (0.114 g, 0.091 mmol) in toluene (2.0 mL) was added to a solution of 68b (0.120 g, 0.091 mmol) in toluene (2.0 mL) and the mixture was heated at 100 °C for 12 h. The solvent was removed in vacuo and the resulted residue was recrystallised from CHCl₃/hexane to afford 92 as colourless crystals (0.111 g, 95 %). m. p. >230 °C(decomp.). ¹H NMR (CDCl₃): δ 1.20-2.50 (m, 88H). ¹³C NMR (CDCl₃): δ 26.75, 26.89, 28.85, 29.10, 30.72, 30.85,
43.91 \[2J(\text{13C}-\text{19F}) = 6 \text{ Hz}\], 44.32 \[2J(\text{13C}-\text{19F}) = 11 \text{ Hz}\]. \(^{19}\text{F} \text{NMR} (\text{CDCl}_3): \delta -124.1 \[1J(\text{19F}-\text{117/119Sn}) = 1220 \text{ Hz}\], 1J(\text{19F}-\text{117/119Sn}) = 1489 \text{ Hz}\]. \(^{119}\text{Sn} \text{NMR} (\text{CDCl}_3): \delta -175.3 \text{ [d, } 1J(\text{19F}-\text{117/119Sn}) = 1240 \text{ Hz}\], 2J(\text{19F}-\text{117/119Sn}) = 1489 \text{ Hz}\]. \(^{19}\text{F} \text{NMR} (\text{CDCl}_3): \delta -124.1 \[1J(\text{19F}-\text{117/119Sn}) = 1220 \text{ Hz}\], 2J(\text{19F}-\text{117/119Sn}) = 1489 \text{ Hz}\]. \(^{119}\text{Sn} \text{NMR} (\text{CDCl}_3): \delta -175.3 \text{ [d, } 1J(\text{19F}-\text{117/119Sn}) = 1240 \text{ Hz}\], 2J(\text{19F}-\text{117/119Sn}) = 1489 \text{ Hz}\]. 

\(\text{1,3-Bis(triphenylstannyl)propane } [\text{Ph}_3\text{Sn}]_2(\text{CH}_2)_3 (94c)\). Ammonia (800 mL) was condensed into a mechanically stirred solution of triphenyltin chloride (200 g, 519 mmol) at \(-78^\circ\text{C}\). Sodium (23.9 g, 1.04 mol) was added in portions to form an orange solution and the mixture was stirred for 2 h at \(-78^\circ\text{C}\). A solution of dichloropropane (29.3 g, 259 mmol) in THF (800 mL) was added dropwise over 1 h which produced a grey solution. The solution was stirred for an additional 2 h at \(-78^\circ\text{C}\) and then allowed to warm to room temperature. The remaining ammonia and THF were removed in vacuo. The crude product was placed in a Soxhlet apparatus and extracted with diethyl ether (500 mL) for 12 h. After removing the diethyl ether in vacuo the crude product was crystallised from ethanol to give pure 94c as a white powder (119 g, 62 \%). m. p. 104 \text{C}. \(^1\text{H} \text{NMR} (\text{CDCl}_3): \delta 1.42 \text{ (t, } 4\text{H, SnCH}_2\text{)}, 1.74 \text{ (quint, } 2\text{H, CH}_2\text{)}, 7.26-7.55 \text{ (m, } 30\text{H)}. \(^{13}\text{C} \text{NMR} (\text{CDCl}_3): \delta 16.25 \text{ [SnCH}_2\text{, } 1J(\text{13C}-\text{117/119Sn}) = 365/382 \text{ Hz}\], 2J(\text{13C}-\text{117/119Sn}) = 66 \text{ Hz}\], 24.32 \text{ [CH}_2\text{, } 2J(\text{13C}-\text{117/119Sn}) = 21 \text{ Hz}\], 128.43, 128.75, 136.99 \[2J(\text{13C}-\text{117/119Sn}) = 66 \text{ Hz}\], 24.32 \[\text{CH}_2\text{, } 2J(\text{13C}-\text{117/119Sn}) = 21 \text{ Hz}\], 128.43, 128.75, 136.99 \[2J(\text{13C}-\text{117/119Sn}) = 66 \text{ Hz}\], 24.32. \(^{119}\text{Sn} \text{NMR} (\text{CDCl}_3): \delta -102.9 \[1J(\text{119Sn}-\text{13Ci}) = 482 \text{ Hz}\]. Anal. Calcd. for C\(_{94}\)H\(_{88}\)Cl\(_2\)F\(_2\)O\(_2\)Sn\(_4\): C, 45.0; H, 7.4. Found: C, 45.9; H, 7.4.

\(\text{1,4-Bis(triphenylstannyl)butane } [\text{Ph}_3\text{Sn}]_2(\text{CH}_2)_4 (94d)\). In a similar manner to 94c, compound 94d was prepared from triphenyltin chloride (200 g, 519 mmol), sodium (23.9 g, 1.04 mol) and dichlorobutane (56.0 g, 259 mmol) and was obtained as a white powder (150 g, 77 \%). m. p. 150 \text{C}. \(^1\text{H} \text{NMR} (\text{CDCl}_3): \delta 1.47 \text{ (t, } 4\text{H, SnCH}_2\text{)}, 1.77 \text{ (quint, } 2\text{H, CH}_2\text{)}, 7.26-7.55 \text{ (m, } 30\text{H)}. \(^{13}\text{C} \text{NMR} (\text{CDCl}_3): \delta 10.56 \text{ [SnCH}_2\text{, } 1J(\text{13C}-\text{117/119Sn}) = 376/393 \text{ Hz}\], 31.25 \text{ [CH}_2\text{, } 2J(\text{13C}-\text{117/119Sn}) = 22 \text{ Hz}\], CH\(_2\), \[3J(\text{13C}-\text{117/119Sn}) = 66 \text{ Hz}\], 128.43, 128.75, 136.99 \[2J(\text{13C}-\text{117/119Sn}) = 66 \text{ Hz}\], 128.43, 128.75, 136.99. \(^{119}\text{Sn} \text{NMR} (\text{CDCl}_3): \delta -99.1 \[1J(\text{119Sn}-\text{13Ci}) = 482 \text{ Hz}\]. Anal. Calcd. for C\(_{40}\)H\(_{38}\)Sn\(_2\): C, 63.1; H, 4.9. Found: C, 63.2; H, 4.8.

\(\text{1,5-Bis(triphenylstannyl)pentane } [\text{Ph}_3\text{Sn}]_2(\text{CH}_2)_5 (94e)\). A solution of BrMg(CH\(_2\))\(_3\)MgBr [prepared from magnesium (12.6 g, 519 mmol) and 1,5-
dibromopentane (29.8 g, 130 mmol) in THF (200 mL) was added to a solution of 
Ph3SnCl (100 g, 259 mmol) in THF (250 mL) and the reaction mixture was 
maintained at reflux for 24 h. The reaction mixture was hydrolysed with satd. 
ammonium chloride (200 mL), extracted with diethyl ether (3 x 200 mL) and the 
combined extracts washed with a solution of KF (10 g) in water (200 mL), dried 
(Na2SO4) and the solvent removed in vacuo. The residue was recrystallised from 
chloroform/hexane (30/70) to afford 94e as a white solid (27.1 g, 90 %). m. p. 75 °C. 

1H NMR (CDCl3): \( \delta \) 1.42-1.72 (m, 10H), 7.26-7.56 (m, 30H). 13C NMR (CDCl3): \( \delta \) 10.80 \( \text{[SnCH}_2 \text{,} \text{1} \text{J(13C-117/119Sn) = 386 Hz]} \), 25.87 \( \text{[CH}_2 \text{,} \text{2} \text{J(13C-117/119Sn) = 22 Hz]} \), 38.70 \( \text{[CH}_2 \text{,} \text{3} \text{J(13C-117/119Sn) = 62 Hz]} \), 128.41, 128.75 \( \text{[4} \text{J(13Cp-117/119Sn) = 11 Hz]} \), 137.00 \( \text{[2} \text{J(13Co-117/119Sn) = 35 Hz]} \), 139.02. 119Sn NMR (CDCl3): \( \delta \) -99.3 \( \text{[1} \text{J(119Sn-13Ci) = 480 Hz]} \). Anal. Calcd. for C41H40Sn2: C, 63.9; H, 5.4. Found: C, 63.8; H, 5.5.

1,6-Bis(triphenylstannyl)hexane [Ph3Sn]2(CH2)6 (94f). In a similar manner to 94e, 
compound 94f was prepared from magnesium (12.6 g, 518 mmol) and 1,6-
dichlorohexane (31.7 g, 130 mmol) and Ph3SnCl (100 g, 259 mmol). Crystallisation 
from chloroform/hexane (30/70) afforded 94f as a white solid (77.1 g, 76 %). m. p. 
84 °C. 1H NMR (CDCl3): \( \delta \) 1.23-1.68 (m, 12H), 7.26-7.64 (m, 30H). 13C NMR 
(CDCl3): \( \delta \) 10.99 \( \text{[SnCH}_2 \text{,} \text{1} \text{J(13C-117/119Sn) = 380/397 Hz]} \), 26.34 \( \text{[CH}_2 \text{,} \text{2} \text{J(13C-117/119Sn) = 22 Hz]} \), 33.50 \( \text{[CH}_2 \text{,} \text{3} \text{J(13C-117/119Sn) = 60 Hz]} \), 128.39, 128.72, 137.06 \( \text{[2} \text{J(13Co-117/119Sn) = 35 Hz]} \), 139.06. 119Sn NMR (CDCl3): \( \delta \) -99.3 \( \text{[1} \text{J(119Sn-13Ci) = 480 Hz]} \). Anal. Calcd. for C42H42Sn2: C, 64.3; H, 5.4. Found: C, 64.5; H, 5.2.

1,7-Bis(triphenylstannyl)heptane [Ph3Sn]2(CH2)7 (94g). In a similar manner to 94e, 
compound 94g was prepared from magnesium (3.80 g, 155 mmol) and 1,7-
dibromoheptane (10.0 g, 38.8 mmol) and Ph3SnCl (29.9 g, 77.5 mmol). Crystallisation 
from chloroform/hexane (30/70) afforded 94g as a white solid (23.1 g, 74 %). m. p. 
131-132 °C. 1H NMR (CDCl3): \( \delta \) 1.25-1.66 (m, 14H), 7.27-7.60 (m, 30H). 13C NMR 
(CDCl3): \( \delta \) 11.28 \( \text{[SnCH}_2 \text{,} \text{1} \text{J(13C-117/119Sn) = 380/397 Hz]} \), 26.71 \( \text{[CH}_2 \text{,} \text{2} \text{J(13C-117/119Sn) = 22 Hz]} \), 34.29 \( \text{[CH}_2 \text{,} \text{3} \text{J(13C-117/119Sn) = 61 Hz]} \), 28.68, 128.63, 128.96 \( \text{[4} \text{J(13Co-117/119Sn) = 10 Hz]} \), 137.23 \( \text{[2} \text{J(13Co-117/119Sn) = 35 Hz]} \), 139.34 \( \text{[1} \text{J(13Co-117/119Sn) = 459/480 Hz]} \), 119Sn NMR (CDCl3): \( \delta \) -98.4 \( \text{[1} \text{J(119Sn-13Ci) = 479 Hz]} \), \( \text{1} \text{J(119Sn-13C) = 399 Hz]} \). Anal. Calcd. for C42H42Sn2: C, 64.7; H, 5.5. Found: C, 64.9; H, 5.2.

1,8-Bis(triphenylstannyl)octane [Ph3Sn]2(CH2)8 (94h). In a similar manner to 94e, 
compound 94h was prepared from magnesium (9.30 g, 383 mmol) and 1,8-
dibromoocctane (26.0 g, 957 mmol) and Ph3SnCl (73.8 g, 191 mmol) and was
obtained as a colourless oil which crystallised on standing (44.7 g, 57 %). m. p. 101 °C. 1H NMR (CDCl3): δ 1.19-1.73 (m, 16H), 7.27-7.64 (m, 30H). 13C NMR (CDCl3): δ 11.07 [SnCH2, 1J(13C-117/119Sn) = 380/397 Hz], 26.46 [CH2, 2J(13C-117/119Sn) = 22 Hz], 28.82, 34.12 [CH2, 3J(13C-117/119Sn) = 60 Hz], 128.40, 128.73, 137.00 [2J(13C-C-117/119Sn) = 35 Hz], 139.11 [1J(13C-117/119Sn) = 459/480 Hz]. 119Sn NMR (CDCl3): δ -98.9 [1J(119Sn-13Ci) = 478 Hz]. Anal. Calcd. for C 44H46Sn2: C, 65.1; H, 5.7. Found: C, 65.0; H, 5.8.

1,10-Bis(triphenylstannyl)decane [Ph3Sn]2(CH2)10 (94i). In a similar manner to 94e, compound 94i was prepared from magnesium (12.6 g, 518 mmol) and 1,10-dibromodecane (38.9 g, 130 mmol) and Ph3SnCl (100 g, 259 mmol) and was obtained as a colourless oil (54.8 g, 50 %). 1H NMR (CDCl3): δ 1.18-1.76 (m, 22H), 7.40-7.65 (m, 30H). 13C NMR (CDCl3): δ 11.13 [SnCH2, 1J(13C-117/119Sn) = 379/396 Hz], 26.51 [CH2, 2J(13C-117/119Sn) = 22 Hz], 28.94, 29.32, 34.10 [CH2, 3J(13C-117/119Sn) = 58 Hz], 128.39, 128.70, 136.95 [2J(13C-C-117/119Sn) = 35 Hz], 139.04 [1J(13C-C-117/119Sn) = 459/480 Hz]. 119Sn NMR (CDCl3): δ -98.9 [1J(119Sn-13Ci) = 479 Hz]. Anal. Calcd. for C46H50Sn2: C, 65.7; H, 6.0. Found: C, 65.5; H, 6.2.

1,12-Bis(triphenylstannyl)dodecane [Ph3Sn]2(CH2)12 (94j). In a similar manner to 94e, compound 94j was prepared from magnesium (9.70 g, 399 mmol) and 1,12-dibromododecane (32.7 g, 99.7 mmol) and Ph3SnCl (76.8 g, 199 mmol) and was obtained as a colourless oil (48.4 g, 56 %). 1H NMR (CDCl3): δ 1.18-1.78 (m, 24H), 7.26-7.66 (m, 30H). 13C NMR (CDCl3): δ 11.14 [SnCH2, 1J(13C-117/119Sn) = 379/397 Hz], 26.55 [CH2, 2J(13C-117/119Sn) = 22 Hz], 29.03, 29.43, 34.19 [CH2, 3J(13C-117/119Sn) = 59 Hz], 128.39, 128.71, 136.98 [2J(13C-C-117/119Sn) = 35 Hz], 139.08 [1J(13C-C-117/119Sn) = 459/480 Hz]. 119Sn NMR (CDCl3): δ -98.9 [1J(119Sn-13Ci) = 479 Hz]. Anal. Calcd. for C48H54Sn2: C, 66.4; H, 6.3. Found: C, 66.1; H, 6.4.

General procedure for the synthesis of α,ω-Bis(iododiphenylstannyl)alkanes [IPh2Sn]2(CH2)n (95). A solution of iodine in dichloromethane (1000 mL) was added to a solution of 94 in chloroform (100 mL) at 0 °C over 12 h. Removal of the solvent and by-product in vacuo afforded 95.

1,3-Bis(iododiphenylstannyl)propane [IPh2Sn]2(CH2)3 (95c). Compound 95c was prepared from 94c (30.0 g, 40.4 mmol) and iodine (20.5 g, 80.9 mmol) and was obtained as a brown oil (33.3 g, 98 %) of sufficient purity for further use. 1H NMR (CDCl3): δ 1.90-2.12 (m, 4H), 2.25-2.53 (m, 2H), 7.22-7.80 (m, 20H). 13C NMR (CDCl3): δ 20.56 [SnCH2, 1J(13C-117/119Sn) = 380 Hz, 3J(13C-C-117/119Sn) = 79 Hz],
24.84 \([\text{CH}_2, \ ^2J(^{13}\text{C-}^{117/119}\text{Sn}) = 40 \text{ Hz}]\), 128.86 \([\ ^3J(^{13}\text{C}_	ext{m-}^{117/119}\text{Sn}) = 59 \text{ Hz}]\), 129.94 \([\ ^4J(^{13}\text{C}_	ext{p-}^{117/119}\text{Sn}) = 13 \text{ Hz}]\), 135.93 \([\ ^2J(^{13}\text{C}_	ext{o-}^{117/119}\text{Sn}) = 47 \text{ Hz}]\), 136.24. \(^{119}\text{Sn} \text{NMR (CDCl}_3\)): \(\delta -58.5 \left[\ ^1J(\^{119}\text{Sn-}^{13}\text{C}) = 505 \text{ Hz}\right]\)

1,4-Bis(iodomiphenylstannyl)butane \([\text{IPh}_2\text{Sn}_2(\text{CH}_2)_4\] (95d). Compound 95d was prepared from 94d (30.0 g, 39.7 mmol) and iodine (20.1 g, 79.4 mmol) and was obtained as a brownish residue (32.6 g, 96 %) of sufficient purity for further use. \(^1\text{H} \text{NMR (CDCl}_3\)): \(\delta 1.40-2.12 \text{ (m, 8H)}\), 7.22-7.80 \text{ (m, 20H, Ph)}\).

\(^{13}\text{C} \text{NMR (CDCl}_3\)): \(\delta 17.20 \left[\text{SnCH}_2, \ ^1J(^{13}\text{C-}^{117/119}\text{Sn}) = 379/389 \text{ Hz}\right]\), 26.84, 128.72, 129.94 \([\ ^4J(^{13}\text{C}_	ext{m-}^{117/119}\text{Sn}) = 13 \text{ Hz}]\), 135.93 \([\ ^2J(^{13}\text{C}_	ext{o-}^{117/119}\text{Sn}) = 47 \text{ Hz}]\), 137.01. \(^{119}\text{Sn} \text{NMR (CDCl}_3\)): \(\delta -52.6\).

1,5-Bis(iodomiphenylstannyl)pentane \([\text{IPh}_2\text{Sn}_2(\text{CH}_2)_5\] (95e). Compound 95e was prepared from 94e (30.0 g, 39.0 mmol) and iodine (19.8 g, 77.9 mmol) and was obtained as a brown oil (31.8 g, 94 %) of sufficient purity for further use. \(^1\text{H} \text{NMR (CDCl}_3\)): \(\delta 1.40-2.00 \text{ (m, 10H, (CH}_2)_5\), 7.30-7.80 \text{ (m, 20H, Ph)}\).

\(^{13}\text{C} \text{NMR (CDCl}_3\)): \(\delta 16.64 \left[\text{SnCH}_2, \ ^1J(^{13}\text{C-}^{117/119}\text{Sn}) = 377/395 \text{ Hz}\right]\), 25.95 \([\text{CH}_2, \ ^2J(^{13}\text{C-}^{117/119}\text{Sn}) = 27 \text{ Hz}]\), 36.77 \([\text{CH}_2, \ ^3J(^{13}\text{C-}^{117/119}\text{Sn}) = 73 \text{ Hz}]\), 128.79 \([\ ^4J(^{13}\text{C}_	ext{m-}^{117/119}\text{Sn}) = 58 \text{ Hz}]\), 129.85, 135.95 \([\ ^2J(^{13}\text{C}_	ext{o-}^{117/119}\text{Sn}) = 46 \text{ Hz}]\), 137.31 \([\ ^1J(^{13}\text{C}_	ext{o-}^{117/119}\text{Sn}) = 353/456 \text{ Hz}]\).

\(^{119}\text{Sn} \text{NMR (CDCl}_3\)): \(\delta -51.5\).

1,6-Bis(iodomiphenylstannyl)hexane \([\text{IPh}_2\text{Sn}_2(\text{CH}_2)_6\] (95f). Compound 95f was prepared from 94f (30.0 g, 38.3 mmol) and iodine (19.4 g, 76.5 mmol) and was obtained as a brown oil (31.8 g, 94 %) of sufficient purity for further use. \(^1\text{H} \text{NMR (CDCl}_3\)): \(\delta 1.30-2.00 \text{ (m, 12H, (CH}_2)_6\), 7.40-7.80 \text{ (m, 20H, Ph)}\).

\(^{13}\text{C} \text{NMR (CDCl}_3\)): \(\delta 16.92 \left[\text{SnCH}_2, \ ^1J(^{13}\text{C-}^{117/119}\text{Sn}) = 379/398 \text{ Hz}\right]\), 26.14, 32.21 \([\text{CH}_2, \ ^3J(^{13}\text{C-}^{117/119}\text{Sn}) = 69 \text{ Hz}]\), 128.66 \([\ ^3J(^{13}\text{C}_	ext{m-}^{117/119}\text{Sn}) = 57 \text{ Hz}]\), 129.72, 135.76 \([\ ^2J(^{13}\text{C}_	ext{o-}^{117/119}\text{Sn}) = 46 \text{ Hz}]\), 137.06. \(^{119}\text{Sn} \text{NMR (CDCl}_3\)): \(\delta -49.1 \left[\ ^1J(^{119}\text{Sn-}^{13}\text{C}) = 499 \text{ Hz}\right]\).

1,8-Bis(iodomiphenylstannyl)octane \([\text{IPh}_2\text{Sn}_2(\text{CH}_2)_8\] (95h). Compound 95h was prepared from 94h (30.0 g, 36.9 mmol) and iodine (18.7 g, 73.9 mmol) and was obtained as a brown oil (31.0 g, 92 %) of sufficient purity for further use. \(^1\text{H} \text{NMR (CDCl}_3\)): \(\delta 1.20-2.00 \text{ (m, 16H, (CH}_2)_8\), 7.40-7.80 \text{ (m, 20H, Ph)}\).

\(^{13}\text{C} \text{NMR (CDCl}_3\)): \(\delta 17.20 \left[\text{SnCH}_2, \ ^1J(^{13}\text{C-}^{117/119}\text{Sn}) = 380/398 \text{ Hz}\right]\), 26.55 \([\text{CH}_2, \ ^2J(^{13}\text{C}_	ext{m-}^{117/119}\text{Sn}) = 27 \text{ Hz}]\), 28.63, 33.15 \([\text{CH}_2, \ ^3J(^{13}\text{C}_	ext{m-}^{117/119}\text{Sn}) = 68 \text{ Hz}]\), 128.78 \([\ ^3J(^{13}\text{C}_	ext{o-}^{117/119}\text{Sn}) = 58 \text{ Hz}]\), 129.83 \([\ ^4J(^{13}\text{C}_	ext{o-}^{117/119}\text{Sn}) = 13 \text{ Hz}]\), 135.99 \([\ ^2J(^{13}\text{C}_	ext{o-}^{117/119}\text{Sn}) = 47 \text{ Hz}]\), 137.36 \([\ ^1J(^{13}\text{C}_	ext{o-}^{117/119}\text{Sn}) = 476/498 \text{ Hz}]\).

\(^{119}\text{Sn} \text{NMR (CDCl}_3\)): \(\delta -48.9 \left[\ ^1J(^{119}\text{Sn-}^{13}\text{C}) = 398 \text{ Hz}\right]\).
1,10-Bis(iododiphenylstannyl)decane \([\text{IPh}_2\text{Sn}]_2(\text{CH}_2)_10\) (95i). Compound 95i was prepared from 94i (30.0 g, 35.7 mmol) and iodine (18.1 g, 71.4 mmol) and was obtained as a brown oil (23.6 g, 70 %) of sufficient purity for further use. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 1.20-2.00 [m, 20H, \((\text{CH}_2)_10\)], 7.40-7.80 (m, 20H, Ph). \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 17.26 [SnCH\(_2\), \(^1J\text{(C-117/119Sn)} = 380/398\) Hz], 26.62 [CH\(_2\), \(^2J\text{(C-117/119Sn)} = 27\) Hz], 28.82, 29.21, 33.25 [CH\(_2\), \(^3J\text{(C-117/119Sn)} = 70\) Hz], 128.77 [\(^3J\text{(Cm-117/119Sn)} = 58\) Hz], 129.81 [\(^2J\text{(Cp-117/119Sn)} = 12\) Hz], 135.98 [\(^2J\text{(Co-117/119Sn)} = 47\) Hz], 137.44 [\(^1J\text{(Ci-117/119Sn)} = 475/497\) Hz]. \(^{119}\)Sn NMR (CDCl\(_3\)): \(\delta\) \(-48.2\) [\(^1J\text{(119Sn-13Ci)} = 497\) Hz].

1,12-Bis(iododiphenylstannyl)dodecane \([\text{IPh}_2\text{Sn}]_2(\text{CH}_2)_12\) (95j). Compound 95j was prepared from 94j (30.0 g, 34.5 mmol) and iodine (17.5 g, 69.1 mmol) and was obtained as a brown oil (30.1 g, 90 %) of sufficient purity for further use. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 1.30-2.10 [m, 24H, \((\text{CH}_2)_12\)], 7.40-7.90 (m, 20H, Ph). \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 17.28 [SnCH\(_2\), \(^1J\text{(C-117/119Sn)} = 380/398\) Hz], 26.60 [CH\(_2\), \(^2J\text{(C-117/119Sn)} = 27\) Hz], 28.86, 29.28, 29.37, 33.25 [CH\(_2\), \(^3J\text{(C-117/119Sn)} = 70\) Hz], 128.73 [\(^3J\text{(Cm-117/119Sn)} = 58\) Hz], 129.77 [\(^2J\text{(Cp-117/119Sn)} = 13\) Hz], 135.95 [\(^2J\text{(Co-117/119Sn)} = 47\) Hz], 137.40 [\(^1J\text{(Ci-117/119Sn)} = 475/497\) Hz]. \(^{119}\)Sn NMR (CDCl\(_3\)): \(\delta\) \(-48.5\) [\(^1J\text{(119Sn-13Ci)} = 497\) Hz].

**General procedure for the synthesis of \(\alpha,\omega\)-Bis[(trimethylsilylmethyl)diphenylstannyl]alkanes \([(\text{Me}_3\text{SiCH}_2)\text{Ph}_2\text{Sn}]_2(\text{CH}_2)_n\) (96).** A solution of 95 in THF (250 mL) was added to a solution of Me\(_3\)SiCH\(_2\)MgCl [prepared from magnesium and Me\(_3\)SiCH\(_2\)Cl in THF (200 mL)] the mixture was stirred at reflux for 24 h. The reaction was quenched by the addition of satd. ammonium chloride (100 mL) at 25 °C. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (2 x 100 mL). The combined organic solutions were dried (Na\(_2\)SO\(_4\)) and the solvent was removed *in vacuo* to yield 96.

1,3-Bis[(trimethylsilylmethyl)diphenylstannyl]propane \([(\text{Me}_3\text{SiCH}_2)\text{Ph}_2\text{Sn}]_2(\text{CH}_2)_3\) (96c). Compound 96c was prepared from magnesium (1.93 g, 79.2 mmol), Me\(_3\)SiCH\(_2\)Cl (9.72 g, 79.2 mmol) and 95c (33.3 g, 39.6 mmol) and was obtained as a brown oil (27.1 g, 90 %) of sufficient purity for further use. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) \(-0.02\) (s, 18H), 0.20 (s, 4H), 1.23-1.65 (m, 6H), 7.27-7.59 (m, 20H). \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) \(-5.37\) [SiCH\(_2\), \(^1J\text{(C-117/119Sn)} = 240/251\) Hz], 1.60 [SiMe\(_3\), \(^3J\text{(C-117/119Sn)} = 16\) Hz, \(^3J\text{Cm-117/119Sn} = 16\) Hz], 17.21 [SnCH\(_2\), \(^1J\text{(C-117/119Sn)} = 367/384\) Hz, \(^3J\text{(C-117/119Sn)} = 65\) Hz], 24.41 [CH\(_2\), \(^2J\text{(C-117/119Sn)} = 20\) Hz], 128.20 [\(^3J\text{(Cm-117/119Sn)} = 46\) Hz], 128.40 [\(^2J\text{(Cp-117/119Sn)} = 11\) Hz], 136.61
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\[ J^{13}(^{117/119}\text{Sn}) = 36 \text{ Hz}, \ 140.69 \ \left[ J^{13}(^{117/119}\text{Sn}) = 433/453 \text{ Hz} \right]. \ 119\text{Sn} \text{ NMR (CDCl}_3\text{): } \delta -61.8 \ \left[ J^{119}(^{13}\text{Sn}-^{13}\text{C}) = 456 \text{ Hz} \right]. \]

1,4-Bis[(trimethylsilylmethyl)diphenylstannyl]butane

\[(\text{Me}_3\text{SiCH}_2\text{PhSn})_2(\text{CH}_2)_4 (96d)\]. Compound 96d was prepared from magnesium (1.85 g, 76.2 mmol), Me\textsubscript{3}SiCH\textsubscript{2}Cl (9.34 g, 76.2 mmol) and 95d (32.6 g, 38.1 mmol). Removal of solvent \textit{in vacuo} yielded 96d as a brown oil (25.4 g, 86%) of sufficient purity for further use. \(^1\text{H NMR (CDCl}_3\text{): } \delta -0.03 \text{ (s, 18H)}, 0.20 \text{ (s, 4H)}, 1.22-1.69 \text{ (m, 8H)}, 7.26-7.59 \text{ (m, 20H)}. \n\)

\[ J^{13}(^{117/119}\text{Sn}) = 240/251 \text{ Hz}, \ 3J^{13}(^{13}\text{C}-^{29}\text{Si}) = 51 \text{ Hz}, 11.44 \text{ [SnCH}_2\text{, } J^{13}(^{117/119}\text{Sn}) = 360/371 \text{ Hz}, 31.35 \text{ [CH}_2\text{, } J^{13}(^{117/119}\text{Sn}) = 21 \text{ Hz}, 3J^{13}(^{117/119}\text{Sn}) = 65 \text{ Hz}, 11.44 \text{ [SnCH}_2\text{, } J^{13}(^{117/119}\text{Sn}) = 360/371 \text{ Hz}, 31.35 \text{ [CH}_2\text{, } J^{13}(^{117/119}\text{Sn}) = 21 \text{ Hz}, 3J^{13}(^{117/119}\text{Sn}) = 65 \text{ Hz}, 11.44 \text{ [SnCH}_2\text{, } J^{13}(^{117/119}\text{Sn}) = 360/371 \text{ Hz}]. \n\]

1,5-Bis[(trimethylsilylmethyl)diphenylstannyl]pentane

\[(\text{Me}_3\text{SiCH}_2\text{PhSn})_2(\text{CH}_2)_5 (96e)\]. Compound 96e was prepared from magnesium (1.78 g, 73.2 mmol), Me\textsubscript{3}SiCH\textsubscript{2}Cl (8.98 g, 73.2 mmol) and 95e (31.9 g, 36.6 mmol). and was obtained as a brown oil (24.6 g, 85%) of sufficient purity for further use. \(^1\text{H NMR (CDCl}_3\text{): } \delta -0.02 \text{ (s, 18H)}, 0.21 \text{ (s, 4H)}, 1.20-1.64 \text{ (m, 10H)}, 7.26-7.60 \text{ (m, 20H)}. \n\)

\[ J^{13}(^{117/119}\text{Sn}) = 239/250 \text{ Hz}, 1.66 \text{ [SiMe}_3, 3J^{13}(^{13}\text{C}-^{117/119}\text{Sn}) = 15 \text{ Hz}, 1.63 \text{ [SiMe}_3, 3J^{13}(^{13}\text{C}-^{117/119}\text{Sn}) = 15 \text{ Hz}, 11.63 \text{ [SnCH}_2, J^{13}(^{117/119}\text{Sn}) = 362/379 \text{ Hz}, 25.90 \text{ [CH}_2, 2J^{13}(^{117/119}\text{Sn}) = 21 \text{ Hz}, 38.73 \text{ [CH}_2, J^{13}(^{117/119}\text{Sn}) = 63 \text{ Hz}, 128.18 \text{ [J}^1(\text{C}_r^{117/119}\text{Sn}) = 46 \text{ Hz}, 128.41 \text{, 136.63 [J}^1(\text{C}_r^{117/119}\text{Sn}) = 35 \text{ Hz}, 140.83 \text{ [J}^1(\text{C}_r^{117/119}\text{Sn}) = 433/453 \text{ Hz}. \n\]

1,6-Bis[(trimethylsilylmethyl)diphenylstannyl]hexane

\[(\text{Me}_3\text{SiCH}_2\text{PhSn})_2(\text{CH}_2)_6 (96f)\]. Compound 96f was prepared from magnesium (1.75 g, 71.9 mmol), Me\textsubscript{3}SiCH\textsubscript{2}Cl (8.82 g, 71.9 mmol) and 95f (31.8 g, 36.0 mmol) and was obtained as a brown oil (24.0 g, 83%) of sufficient purity for further use. \(^1\text{H NMR (CDCl}_3\text{): } \delta -0.04 \text{ (s, 18H)}, 0.19 \text{ (s, 4H)}, 1.22-1.56 \text{ (m, 12H)}, 7.25-7.58 \text{ (m, 20H)}. \n\)

\[ J^{13}(^{117/119}\text{Sn}) = 239/250 \text{ Hz}, 1.67 \text{ [SiMe}_3, 3J^{13}(^{13}\text{C}-^{117/119}\text{Sn}) = 15 \text{ Hz}, J^{13}(^{13}\text{C}-^{19}\text{Si}) = 50 \text{ Hz}, 11.83 \text{ [SnCH}_2, J^{13}(^{13}\text{C}-^{117/119}\text{Sn}) = 363/380 \text{ Hz}, 26.49 \text{ [CH}_2, 2J^{13}(^{13}\text{C}-^{117/119}\text{Sn}) = 21 \text{ Hz}, 33.62 \text{ [CH}_2, J^{13}(^{13}\text{C}-^{117/119}\text{Sn}) = 363/380 \text{ Hz}. \n\]
\[ ^{117/119}\text{Sn} = 48 \text{ Hz} \], \[ 128.18 \left[ ^3J(^{13}\text{C}_m-^{117/119}\text{Sn}) = 45 \text{ Hz} \right], 128.41, 140.81 \left[ ^1J(^{13}\text{C}_r-^{117/119}\text{Sn}) = 434/455 \text{ Hz} \right], ^{119}\text{Sn} \text{ NMR (CDCl}_3\right): \delta -58.4 \left[ ^1J(^{119}\text{Sn}-^{13}\text{C}_i) = 455 \text{ Hz} \right], ^1J(^{119}\text{Sn}-^{13}\text{CH}_2\text{Sn}) = 382 \text{ Hz}, ^1J(^{119}\text{Sn}-^{13}\text{CH}_2\text{Si}) = 250 \text{ Hz}].

1,8-Bis[(trimethylsilylmethyl)diphenylstannyl]octane

[(MeSiCH\(_2\)]Ph\(_2\text{Sn}\)](CH\(_2\))\(_8\) (96h). Compound 96h was prepared from magnesium (1.65 g, 68.0 mmol), Me\(_3\)SiCH\(_2\)Cl (8.34 g, 68.0 mmol) and 95h (31.0 g, 34.0 mmol) and was obtained as a brown oil (22.9 g, 81 \%) of sufficient purity for further use. \(^1\text{H}\) NMR (CDCl\(_3\)): \(\delta -0.02\) (s, 18H), 0.21 (s, 4H), 1.20-1.64 (m, 16H), 7.26-7.60 (m, 20H). \(^{13}\text{C}\) NMR (CDCl\(_3\)): \(\delta -5.53\) [SiCH\(_2\), \(^1J(^{13}\text{C}-^{117/119}\text{Sn}) = 239/250 \text{ Hz}\), \(^1J(^{13}\text{C}-^{19}\text{Si}) = 50 \text{ Hz}\)], 1.62 [SiMe\(_3\), \(^3J(^{13}\text{C}-^{117/119}\text{Sn}) = 15 \text{ Hz}\), \(^1J(^{13}\text{C}-^{19}\text{Si}) = 51 \text{ Hz}\)], 11.85 [SnCH\(_2\), \(^1J(^{13}\text{C}-^{117/119}\text{Sn}) = 364/382 \text{ Hz}\)], 26.56 [CH\(_2\), \(^2J(^{13}\text{C}-^{117/119}\text{Sn}) = 21 \text{ Hz}\)], 28.91, 34.21 [CH\(_2\), \(^3J(^{13}\text{C}-^{117/119}\text{Sn}) = 63 \text{ Hz}\)], 128.16 \left[ ^3J(^{13}\text{Cm}-^{117/119}\text{Sn}) = 46 \text{ Hz} \right], 128.38 \left[ ^1J(^{13}\text{C}r-^{117/119}\text{Sn}) = 11 \text{ Hz} \right], 136.62 \left[ ^2J(^{13}\text{Co}-^{117/119}\text{Sn}) = 35 \text{ Hz} \right], 140.91 \left[ ^1J(^{13}\text{Cr}-^{117/119}\text{Sn}) = 433/453 \text{ Hz} \right]. ^{119}\text{Sn} NMR (CDCl\(_3\)): \(\delta -58.4\) \left[ ^1J(^{119}\text{Sn}-^{13}\text{C}_i) = 453 \text{ Hz} \right], ^1J(^{119}\text{Sn}-^{13}\text{CH}_2\text{Sn}) = 382 \text{ Hz}, ^1J(^{119}\text{Sn}-^{13}\text{CH}_2\text{Si}) = 250 \text{ Hz}].

1,10-Bis[(trimethylsilylmethyl)diphenylstannyl]decane

[(MeSiCH\(_2\)]Ph\(_2\text{Sn}\)](CH\(_2\))\(_{10}\) (96i). Compound 96i was prepared from magnesium (1.22 g, 50.1 mmol), Me\(_3\)SiCH\(_2\)Cl (6.15 g, 50.1 mmol) and 95i (23.6 g, 25.1 mmol) and was obtained as a brown oil (17.3 g, 80 \%) of sufficient purity for further use. \(^1\text{H}\) NMR (CDCl\(_3\)): \(\delta -0.03\) (s, 18H), 0.20 (s, 4H), 1.22-1.69 (m, 20H), 7.26-7.59 (m, 20H). \(^{13}\text{C}\) NMR (CDCl\(_3\)): \(\delta -5.52\) [SiCH\(_2\), \(^1J(^{13}\text{C}-^{117/119}\text{Sn}) = 239/251 \text{ Hz}\), \(^1J(^{13}\text{C}-^{19}\text{Si}) = 48 \text{ Hz}\)], 1.60 [SiMe\(_3\), \(^3J(^{13}\text{C}-^{117/119}\text{Sn}) = 15 \text{ Hz}\), \(^1J(^{13}\text{C}-^{19}\text{Si}) = 51 \text{ Hz}\)], 11.87 [SnCH\(_2\), \(^1J(^{13}\text{C}-^{117/119}\text{Sn}) = 365/382 \text{ Hz}\)], 26.56 [CH\(_2\), \(^2J(^{13}\text{C}-^{117/119}\text{Sn}) = 21 \text{ Hz}\)], 28.91, 34.21 [CH\(_2\), \(^3J(^{13}\text{C}-^{117/119}\text{Sn}) = 63 \text{ Hz}\)], 128.16 \left[ ^3J(^{13}\text{Cm}-^{117/119}\text{Sn}) = 46 \text{ Hz} \right], 128.38 \left[ ^1J(^{13}\text{C}r-^{117/119}\text{Sn}) = 11 \text{ Hz} \right], 136.62 \left[ ^2J(^{13}\text{Co}-^{117/119}\text{Sn}) = 35 \text{ Hz} \right], 140.94 \left[ ^1J(^{13}\text{Cr}-^{117/119}\text{Sn}) = 433/453 \text{ Hz} \right]. ^{119}\text{Sn} NMR (CDCl\(_3\)): \(\delta -58.5\) \left[ ^1J(^{119}\text{Sn}-^{13}\text{C}_i) = 453 \text{ Hz} \right], ^1J(^{119}\text{Sn}-^{13}\text{CH}_2\text{Sn}) = 382 \text{ Hz}, ^1J(^{119}\text{Sn}-^{13}\text{CH}_2\text{Si}) = 250 \text{ Hz}].

1,12-Bis[(trimethylsilylmethyl)diphenylstannyl]dodecane

[(MeSiCH\(_2\)]Ph\(_2\text{Sn}\)](CH\(_2\))\(_{12}\) (96j). Compound 96j was prepared from magnesium (1.51 g, 62.2 mmol), Me\(_3\)SiCH\(_2\)Cl (7.63 g, 62.2 mmol) and 95j (30.1 g, 31.1 mmol) and was obtained as a brown oil (22.1 g, 80 \%) of sufficient purity for further use. \(^1\text{H}\) NMR (CDCl\(_3\)): \(\delta -0.02\) (s, 18H), 0.20 (s, 4H), 1.23-1.65 (m, 24H), 7.27-7.59 (m, 20H). \(^{13}\text{C}\) NMR (CDCl\(_3\)): \(\delta -5.51\) [SiCH\(_2\), \(^1J(^{13}\text{C}-^{117/119}\text{Sn}) = 240/250 \text{ Hz}\), \(^1J(^{13}\text{C}-^{19}\text{Si}) = 48 \text{ Hz}\)], 1.50 [SiMe\(_3\), \(^3J(^{13}\text{C}-^{117/119}\text{Sn}) = 15 \text{ Hz}\), \(^1J(^{13}\text{C}-^{19}\text{Si}) = 51 \text{ Hz}\)], 11.89 [SnCH\(_2\), \(^1J(^{13}\text{C}-^{117/119}\text{Sn}) = 365/382 \text{ Hz}\)], 26.63 [CH\(_2\), \(^2J(^{13}\text{C}-^{117/119}\text{Sn}) = 21 \text{ Hz}\),

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29.54, 34.25 [\text{CH}_2, ^3 J(^{13}\text{C}-^{117}/^{119}\text{Sn}) = 63 \text{ Hz}], 29.60, 34.29 [\text{CH}_2, ^3 J(^{13}\text{C}-^{117}/^{119}\text{Sn}) = 62 \text{ Hz}], 128.16 [^3 J(^{13}\text{Cm}-^{117}/^{119}\text{Sn}) = 45 \text{ Hz}], 128.38 [^4 J(^{13}\text{Cp}-^{117}/^{119}\text{Sn}) = 11 \text{ Hz}], 136.64 [^2 J(^{13}\text{Co}-^{117}/^{119}\text{Sn}) = 35 \text{ Hz}], 140.97 [^1 J(^{13}\text{Ci}-^{117}/^{119}\text{Sn}) = 433/453 \text{ Hz}].^{119}\text{Sn} \text{ NMR (CDCl}_3): \delta \sim -58.6 [^1 J(^{119}\text{Sn}-^{13}\text{C}) = 454 \text{ Hz}, ^1 J(^{119}\text{Sn}-^{13}\text{CH}_2\text{Sn}) = 382 \text{ Hz}, ^1 J(^{119}\text{Sn}-^{13}\text{CH}_2\text{Si}) = 250 \text{ Hz}].

General procedure for the synthesis of \(\alpha,\omega\)-Bis[(trimethylsilylmethyl)dichlorostannyl]alkanes \([(\text{Me}_3\text{SiCH}_2)(\text{Cl})_2\text{Sn})_2(\text{CH}_2)_n\] (97). To a solution of \text{96} in chloroform (100 mL) was added excess conc. HCl (200 ml, 32%). The reaction mixture was stirred and maintained at 70 °C for 24 h. The organic layer was separated, and the aqueous layer was extracted with chloroform (3 x 100 mL). The combined organic extracts were dried (CaCl\(_2\)) and the solvent was removed \textit{in vacuo}. The residue was crystallised from chloroform/hexane (30/70) to afford \text{97}.

1,3-Bis[(trimethylsilylmethyl)dichlorostannyl]propane \([(\text{Me}_3\text{SiCH}_2)(\text{Cl})_2\text{Sn})_2(\text{CH}_2)_3\] (97c). Compound \text{97c} was prepared from conc. HCl (200 ml, 32%) and \text{96c} (27.1 g, 35.6 mmol). Crystallisation from chloroform/hexane (30/70) afforded \text{97c} as a white fluffy solid (16.5 g, 78 %). m. p. 93-94 °C (Lit. m. p. 88-90 °C).\(^{1}^\text{H} \text{NMR (CDCl}_3): \delta 0.18 (s, 18H, Me\_3\text{Si}), 0.89 (s, 4H, SiCH}_2, 1.83 [t, 4H, SnCH}_2, ^2 J(^{13}\text{C}-^{117}/^{119}\text{Sn}) = 88/92 \text{ Hz}], 2.32 (quin, 2H, CH\_2). ^{13}\text{C} \text{NMR (CDCl}_3): \delta 1.24 [\text{SiMe}_3, ^3 J(^{13}\text{C}-^{117}/^{119}\text{Sn}) = 26 \text{ Hz}, ^1 J(^{13}\text{C}-^{29}\text{Si}) = 52 \text{ Hz}], 12.31 [\text{SiCH}_2, ^1 J(^{13}\text{C}-^{117}/^{119}\text{Sn}) = 281/294 \text{ Hz}], 29.73 [^2 J(^{13}\text{C}-^{117}/^{119}\text{Sn}) = 33 \text{ Hz}], 430/450 \text{ Hz}, ^3 J(^{13}\text{C}-^{117}/^{119}\text{Sn}) = 98/103 \text{ Hz}]. ^{119}\text{Sn} \text{ NMR (CDCl}_3): \delta 132.0. Anal. Calcd. for C\_11\text{H}_{28}\text{Cl}_2\text{Si}_2\text{Sn}_2: \text{C, 22.2; H, 4.7. Found: C, 22.0; H, 4.6.}

1,4-Bis[(trimethylsilylmethyl)dichlorostannyl]butane \[[\text{Me}_3\text{SiCH}_2(\text{Cl})_2\text{SnCH}_2]_2(\text{CH}_2)_2\] (97d). Compound \text{97d} was prepared from conc. HCl (200 ml, 32%) and \text{96d} (25.4 g, 32.8 mmol). Crystallisation from chloroform/hexane (30/70) afforded \text{97d} as a white solid (13.9 g, 69 %). m. p. 65-66 °C (Lit. m. p. 64-65 °C).\(^{1}^\text{H} \text{NMR (CDCl}_3): \delta 0.18 (s, 18H, Me\_3\text{Si}), 0.88 (s, 4H, SiCH}_2, ^2 J(^{13}\text{H}-^{117}/^{119}\text{Sn}) = 87/91 \text{ Hz}, ^2 J(^{13}\text{H}-^{29}\text{Si}) = 35 \text{ Hz}], 1.91 [t, 4H, SnCH}_2, ^1 J(^{13}\text{C}-^{117}/^{119}\text{Sn}) = 26 \text{ Hz}, ^1 J(^{13}\text{C}-^{29}\text{Si}) = 52 \text{ Hz}], 12.21 [\text{SiCH}_2, ^1 J(^{13}\text{C}-^{117}/^{119}\text{Sn}) = 275/289 \text{ Hz}], 26.37 [^2 J(^{13}\text{C}-^{117}/^{119}\text{Sn}) = 443/464 \text{ Hz}], 27.96 [^2 J(^{13}\text{C}-^{117}/^{119}\text{Sn}) = 36 \text{ Hz}, ^3 J(^{13}\text{C}-^{117}/^{119}\text{Sn}) = 95/97 \text{ Hz}]. ^{119}\text{Sn} \text{ NMR (CDCl}_3): \delta 137.3. Anal. Calcd. for C\_12\text{H}_{30}\text{Cl}_2\text{Si}_2\text{Sn}_2: \text{C, 23.6; H, 5.0. Found: C, 23.4; H, 5.1.}
1,5-Bis[(trimethylsilylmethyl)dichlorostannyl]pentane

\[[(\text{Me}_3\text{SiCH}_2)(\text{Cl})_2\text{Sn}]_2(\text{CH}_2)_5 (\text{97e})\]. Compound \text{97e} was prepared from conc. HCl (200 ml, 32%) and \text{96e} (24.6 g, 31.1 mmol) and was obtained as a white solid (18.0 g, 93 %). m. p. 40-43 °C after crystallisation from chloroform/hexane (30/70). \(^1\)H NMR (CDCl\(_3\)): \(\delta 0.18\) (s, 18H, Me\(_3\)Si), 0.86 (s, 4H, SiCH\(_2\)), \(2J(\text{H}-\text{117/119Sn}) = 88\) Hz], 1.55 (m, 2H), 1.74 (t, 4H), 1.86 (t, 4H). \(^1\)C NMR (CDCl\(_3\)): \(\delta 1.26 [\text{SiMe}_3, 3J(\text{13C}-\text{117/119Sn}) = 26\) Hz], \(1J(\text{13C}-\text{29Si}) = 52\) Hz], 12.15 [SiCH\(_2\), \(1J(\text{13C}-\text{117/119Sn}) = 272/284\) Hz, \(1J(\text{13C}-\text{29Si}) = 42\) Hz], 24.27 [CH\(_2\), \(2J(\text{13C}-\text{117/119Sn}) = 37\) Hz], 27.00 [SnCH\(_2\), \(1J(\text{13C}-\text{117/119Sn}) = 444/462\) Hz], 35.92 [CH\(_2\), \(3J(\text{13C}-\text{117/119Sn}) = 85/89\) Hz]. \(^{119}\)Sn NMR (CDCl\(_3\)): \(\delta 138.9\). Anal. Calcd. for C\(_{13}\)H\(_{32}\)Cl\(_2\)Si\(_2\)Sn\(_2\): C, 25.0; H, 5.2. Found: C, 25.0; H, 5.3.

1,6-Bis[(trimethylsilylmethyl)dichlorostannyl]hexane

\[[(\text{Me}_3\text{SiCH}_2)(\text{Cl})_2\text{Sn}]_2(\text{CH}_2)_6 (\text{97f})\]. Compound \text{97f} was prepared from conc. HCl (200 ml, 32%) and \text{96f} (24.1 g, 29.9 mmol). Crystallisation from chloroform/hexane (30/70) afforded \text{97f} as a white solid (15.3 g, 80 %). m. p. 39-44 °C. \(^1\)H NMR (CDCl\(_3\)): \(\delta 0.16\) (s, 18H, Me\(_3\)Si), 0.85 (s, 4H, SiCH\(_2\)), \(2J(\text{H}-\text{117/119Sn}) = 86/89\) Hz], 1.46 (m, 4H), 1.74 (m, 4H), 1.82 (m, 4H). \(^1\)C NMR (CDCl\(_3\)): \(\delta 1.24 [\text{SiMe}_3, 3J(\text{13C}-\text{117/119Sn}) = 26\) Hz], \(1J(\text{13C}-\text{29Si}) = 52\) Hz], 12.13 [SiCH\(_2\), \(1J(\text{13C}-\text{117/119Sn}) = 268/281\) Hz, \(1J(\text{13C}-\text{29Si}) = 44\) Hz], 24.57 [CH\(_2\), \(2J(\text{13C}-\text{117/119Sn}) = 36\) Hz], 27.27 [SnCH\(_2\), \(1J(\text{13C}-\text{117/119Sn}) = 444/466\) Hz], 32.21 [CH\(_2\), \(3J(\text{13C}-\text{117/119Sn}) = 88\) Hz]. \(^{119}\)Sn NMR (CDCl\(_3\)): \(\delta 138.9\). Anal. Calcd. for C\(_{14}\)H\(_{34}\)Cl\(_2\)Si\(_2\)Sn\(_2\): C, 26.4; H, 5.4. Found: C, 26.3; H, 5.2.

1,8-Bis[(trimethylsilylmethyl)dichlorostannyl]octane

\[[(\text{Me}_3\text{SiCH}_2)(\text{Cl})_2\text{Sn}]_2(\text{CH}_2)_8 (\text{97h})\]. Compound \text{97h} was prepared from conc. HCl (200 ml, 32%) and \text{96h} (22.9 g, 27.5 mmol) and was obtained as a white solid (17.5 g, 95 %). m. p. 27-28 °C after crystallisation from chloroform/hexane (30/70). \(^1\)H NMR (CDCl\(_3\)): \(\delta 0.18\) (s, 18H, Me\(_3\)Si), 0.84 (s, 4H, SiCH\(_2\)), \(2J(\text{H}-\text{117/119Sn}) = 85/89\) Hz], 1.30-1.45 (m, 8H), 1.65-1.85 (m, 8H). \(^1\)C NMR (CDCl\(_3\)): \(\delta 1.22 [\text{SiMe}_3, 3J(\text{13C}-\text{117/119Sn}) = 25\) Hz], \(1J(\text{13C}-\text{29Si}) = 52\) Hz], 12.11 [SiCH\(_2\), \(1J(\text{13C}-\text{117/119Sn}) = 267/280\) Hz, \(1J(\text{13C}-\text{29Si}) = 42\) Hz], 24.74 [CH\(_2\), \(2J(\text{13C}-\text{117/119Sn}) = 36\) Hz], 27.49 [SnCH\(_2\), \(1J(\text{13C}-\text{117/119Sn}) = 444/466\) Hz], 28.74, 32.88 [CH\(_2\), \(3J(\text{13C}-\text{117/119Sn}) = 86\) Hz]. \(^{119}\)Sn NMR (CDCl\(_3\)): \(\delta 138.9\). Anal. Calcd. for C\(_{16}\)H\(_{38}\)Cl\(_2\)Si\(_2\)Sn\(_2\): C, 28.9; H, 5.8. Found: C, 28.8; H, 5.9.
1,10-Bis[(trimethylsilylmethyl)dichlorostannyl]decan 
\[(\text{Me}_3\text{SiCH}_2)(\text{Cl})_2\text{Sn}]_2(\text{CH}_2)_10\] (97i). Compound 97i was prepared from conc. HCl (200 ml, 32%) and 96i (21.6 g, 25.1 mmol). Crystallisation from chloroform/hexane (30/70) afforded 97i as a white solid (18.3 g, 85 %). m. p. 45-46 °C. ¹H NMR (CDCl₃): δ 0.18 (s, 18H, Me₃Si), 0.84 (s, 4H, SiCH₂, ³J(¹H-¹¹⁷/¹¹⁹Sn) = 85/89 Hz), 1.23-1.45 (m, 10H), 1.65-1.86 (m, 10H). ¹³C NMR (CDCl₃): δ 1.21 [SiMe₃, ³J(¹³C-¹¹⁷/¹¹⁹Sn) = 26 Hz, ¹J(¹³C-²⁹Si) = 52 Hz], 12.06 [SiCH₂, ¹J(¹³C-¹¹⁷/¹¹⁹Sn) = 266/278 Hz, ¹J(¹³C-²⁹Si) = 43 Hz], 24.79 [CH₂, ²J(¹³C-¹¹⁷/¹¹⁹Sn) = 36 Hz], 27.54 [SnCH₂, ¹J(¹³C-¹¹⁷/¹¹⁹Sn) = 444/466 Hz], 28.96, 29.26, 32.02 [CH₂, ³J(¹³C-¹¹⁷/¹¹⁹Sn) = 85/88 Hz]. ¹¹⁹Sn NMR (CDCl₃): δ 139.8. Anal. Calcd. for C₁₈H₄₂Cl₂Si₂Sn₂: C, 31.2; H, 6.1. Found: C, 31.4; H, 6.1.

1,12-Bis[(trimethylsilylmethyl)dichlorostannyl]dodecan 
\[(\text{Me}_3\text{SiCH}_2)(\text{Cl})_2\text{Sn}]_2(\text{CH}_2)_12\] (97j). Compound 97j was prepared from conc. HCl (200 ml, 32%) and 96j (22.1 g, 24.9 mmol) and was obtained as a white solid (15.3 g, 85 %). m. p. 36-37 °C after crystallisation from chloroform/hexane (30/70). ¹H NMR (CDCl₃): δ 0.17 (s, 18H, Me₃Si), 0.83 (s, 4H, SiCH₂, ³J(¹H-¹¹⁷/¹¹⁹Sn) = 86/89 Hz), 1.22-1.43 (m, 12H), 1.65-1.85 (m, 12H). ¹³C NMR (CDCl₃): δ 1.21 [SiMe₃, ³J(¹³C-¹¹⁷/¹¹⁹Sn) = 25 Hz, ¹J(¹³C-²⁹Si) = 52 Hz], 12.07 [SiCH₂, ¹J(¹³C-¹¹⁷/¹¹⁹Sn) = 266/278 Hz, ¹J(¹³C-²⁹Si) = 43 Hz], 24.81 [CH₂, ²J(¹³C-¹¹⁷/¹¹⁹Sn) = 37 Hz], 27.60 [SnCH₂, ¹J(¹³C-¹¹⁷/¹¹⁹Sn) = 444/466 Hz], 28.96, 29.26, 32.02 [CH₂, ³J(¹³C-¹¹⁷/¹¹⁹Sn) = 83/88 Hz]. ¹¹⁹Sn NMR (CDCl₃): δ 139.3. Anal. Calcd. for C₂₀H₄₂Cl₂Si₂Sn₂: C, 31.2; H, 6.4. Found: C, 33.5; H, 6.5.

**General procedure for the synthesis of α,ω-Bis[(trimethylsilylmethyl)oxostannyl]alkanes \([(\text{Me}_3\text{SiCH}_2)(\text{O})\text{Sn}]_2(\text{CH}_2)_n\) (98).** A solution of KOH in water (100 mL) was added to a solution of 97 in toluene (100 mL) and the mixture stirred at 100 °C for 24 h. The white precipitate which formed was collected by filtration. The collected precipitate was then stirred with water (400 mL), filtered and further dried by heating at 80 °C (0.01 mmHg) for 48 h to give 98 as a white solid.

1,3-Bis[(trimethylsilylmethyl)oxostannyl]propane \{"((\text{Me}_3\text{SiCH}_2)(\text{O})\text{Sn})_2(\text{CH}_2)_3\}_m\] (98c). Compound 98c was prepared from KOH (5.94 g, 106 mmol) and 97c (7.88 g, 13.2 mmol) and was obtained as a white solid (5.91 g, 92 %). m. p. > 350 °C(decomp.). Anal. Calcd. for C₁₁H₂₉O₂Si₂Sn₂: C, 27.2; H, 5.8. Found: C, 27.1; H, 6.2.
1,4-Bis[(trimethylsilylmethyl)oxostannyl]butane \{[(Me₃SiCH₂)(O)Sn]₂(CH₂)₄\}_m (98d). Compound 98d was prepared from KOH (4.92 g, 87.7 mmol) and 97d (6.68 g, 11.0 mmol) and was obtained as a white solid (5.14 g, 94 %). m. p. > 350 °C(decomp.) (Lit. m. p. > 350 °C(decomp.)). Anal. Calcd. for C₁₂H₃₀O₂Si₂Sn₂: C, 28.8; H, 6.0. Found: C, 28.4; H, 6.1.

1,5-Bis[(trimethylsilylmethyl)oxostannyl]pentane \{[(Me₃SiCH₂)(O)Sn]₂(CH₂)₅\}_m (98e). Compound 98e was prepared from KOH (6.22 g, 111 mmol) and 97e (8.65 g, 13.9 mmol) and was obtained as a white solid (6.30 g, 88 %). m. p. > 350 °C(decomp.). Anal. Calcd. for C₁₃H₃₂O₂Si₂Sn₂: C, 30.4; H, 6.3. Found: C, 30.2; H, 6.2.

1,6-Bis[(trimethylsilylmethyl)oxostannyl]hexane \{[(Me₃SiCH₂)(O)Sn]₂(CH₂)₆\}_m (98f). Compound 98f was prepared from KOH (4.72 g, 84.1 mmol) and 97f (6.71 g, 10.5 mmol) and was obtained as a white solid (4.34 g, 78 %). m. p. > 270 °C(decomp.). Anal. Calcd. for C₁₄H₃₄O₂Si₂Sn₂: C, 31.8; H, 6.5. Found: C, 32.0; H, 6.2.

1,8-Bis[(trimethylsilylmethyl)oxostannyl]octane \{[(Me₃SiCH₂)(O)Sn]₂(CH₂)₈\}_m (98h). Compound 98h was prepared from KOH (5.25 g, 93.6 mmol) and 97h (7.79 g, 11.7 mmol) and was obtained as a white solid (5.97 g, 92 %). m. p. > 350 °C(decomp.). Anal. Calcd. for C₁₆H₃₈O₂Si₂Sn₂: C, 34.6; H, 6.9. Found: C, 34.3; H, 6.6.

1,10-Bis[(trimethylsilylmethyl)oxostannyl]decane \{[(Me₃SiCH₂)(O)Sn]₂(CH₂)₁₀\}_m (98i). Compound 98i was prepared from KOH (5.73 g, 102 mmol) and 97i (8.85 g, 12.8 mmol) and was obtained as a white solid (7.20 g, 97 %). m. p. > 350 °C(decomp.). Anal. Calcd. for C₁₈H₄₂O₂Si₂Sn₂: C, 37.0; H, 7.2. Found: C, 36.7; H, 7.0.

1,12-Bis[(trimethylsilylmethyl)oxostannyl]dodecane \{[(Me₃SiCH₂)(O)Sn]₂(CH₂)₁₂\}_m (98j). Compound 98j was prepared from KOH (4.56 g, 81.2 mmol) and 97j (7.33 g, 10.2 mmol) and was obtained as a white solid (5.83 g, 94 %). m. p. > 350 °C(decomp.). Anal. Calcd. for C₂₀H₄₆O₂Si₂Sn₂: C, 39.2; H, 7.6. Found: C, 38.9; H, 7.2.

\{[(Me₃SiCH₂)Sn(Cl)]₂(CH₂)₃\}_O₄·C₇H₈ (17-C₇H₈). Solid 97c (0.10 g, 0.17 mmol) was added to a suspension of 98d (0.08 g, 0.17 mmol) in toluene (2 mL) and stirred
at 100 °C for 24 h. $^{119}$Sn NMR (toluene): $\delta$ −66.0 (integral 33.0 %), −76.1 (integral 2.5 %), −76.3 (integral 3.5 %), −77.9 (integral 5.0 %), −92.7 (integral 3.0 %), −93.0 (integral 2.0 %), −95.5 (integral 2.0 %), −129.4 (integral 3.0 %), −134.8 (integral 3.5 %), −135.2 (integral 3.5 %), −136.6 (integral 3.5 %), −137.1 (integral 2.0 %), −140.9 (integral 32.0 %). The clear solution was then allowed to cool to room temperature, after which crystals formed. m. p. 300-301 °C (Lit. m. p. 304-305 °C). $^{119}$Sn NMR (toluene): $\delta$ −97.9 [2$^3$$^J$(119Sn-O-117/119Sn) = 69 Hz], −137.2 [2$^3$$^J$(119Sn-O-117/119Sn) = 69 Hz]. $^1$H NMR ($d_8$-toluene): $\delta$ 0.13 (s, 36H, Me$_3$Si), 0.19 (s, 36H, Me$_3$Si), 0.72-1.28 (m, 16H, CH$_2$Si), 1.59-1.89 (m, 16H, CH$_2$Sn), 2.13-2.29 (m, 8H). $^{13}$C NMR ($d_8$-toluene): $\delta$ 1.02, 1.68 (Me$_3$Si) 11.50 [SiCH$_2$, $^1$$^J$(13C-117/119Sn) = 424 Hz], 14.9 [SiCH$_2$, $^3$$^J$(13C-117/119Sn) = 424 Hz], 21.32, 21.7, 31.41 [CH$_2$Sn, $^1$$^J$(13C-117/119Sn) = 632 Hz, $^3$$^J$(13C-117/119Sn) = 143 Hz], 33.65 [CH$_2$Sn, $^3$$^J$(13C-117/119Sn) = 647 Hz, $^3$$^J$(13C-117/119Sn) = 131 Hz]. Anal. Calcd. for C$_{44}$H$_{112}$O$_4$Cl$_8$ Si$_8$Sn$_8$: C, 24.4; H, 5.2. Found: C, 24.4; H, 6.0.

For reaction of [(Me$_3$SiCH$_2$)(Cl)$_2$Sn]$_2$(CH$_2$)$_4$ (97d) with [[(Me$_3$SiCH$_2$)(Cl)$_2$Sn]$_2$(CH$_2$)$_3$]$_m$ (98c). Solid 97d (0.06 g, 0.11 mmol) was added to a suspension of 98c (0.05 g, 0.11 mmol) in toluene (2 mL) and stirred at 100 °C for 24 h. $^{119}$Sn NMR (toluene, 25 °C): $\delta$ −66.0 (integral 33.0 %), −76.1 (integral 2.5 %), −76.3 (integral 3.5 %), −77.9 (integral 5.0 %), −92.7 (integral 3.0 %), −93.0 (integral 2.0 %), −95.5 (integral 2.0 %), −129.4 (integral 3.0 %), −134.8 (integral 3.5 %), −135.2 (integral 3.5 %), −136.6 (integral 3.5 %), −137.1 (integral 2.0 %), −140.9 (integral 32.0 %). $^{119}$Sn NMR (toluene, 100 °C): $\delta$ −71.4 (integral 11.0 %), −80.0 (integral 15.0 %), −95.4 (integral 11.0 %), −98.3 (integral 12.0 %), −137.6 (integral 14.0 %), −141.8 (integral 10.0 %), −142.3 (integral 27.0 %).

For reaction of [(Me$_3$SiCH$_2$)(Cl)$_2$Sn]$_2$(CH$_2$)$_5$ (97e) with [[(Me$_3$SiCH$_2$)(Cl)$_2$Sn]$_2$(CH$_2$)$_3$]$_m$ (98c). Solid 97e (0.07 g, 0.11 mmol) was added to a suspension of 98c (0.05 g, 0.11 mmol) in toluene (2 mL) and stirred at 100 °C for 24 h. $^{119}$Sn NMR (toluene, 100 °C): $\delta$ −71.4 (integral 11.0 %), −80.0 (integral 15.0 %), −95.4 (integral 11.0 %), −98.3 (integral 12.0 %), −137.6 (integral 14.0 %), −141.8 (integral 10.0 %), −142.3 (integral 27.0 %).

For reaction of [(Me$_3$SiCH$_2$)(Cl)$_2$Sn]$_2$(CH$_2$)$_6$ (97f) with [[(Me$_3$SiCH$_2$)(Cl)$_2$Sn]$_2$(CH$_2$)$_3$]$_m$ (98c). Solid 97f (0.07 g, 0.11 mmol) was added to a suspension of 98c (0.05 g, 0.11 mmol) in toluene (2 mL) and stirred at 100 °C for 24 h. $^{119}$Sn NMR (toluene, 100 °C): $\delta$ −74.5 (integral 6.0 %), −76.7 (integral 34.0 %),
−98.1 (integral 11.0 %), −137.5 (integral 8.0 %), −140.6 (integral 34.0 %), −142.3 (integral 6.0 %).

For reaction of \([\text{Me}_3\text{SiCH}_2\text{Cl}_2\text{Sn}]_2(\text{CH}_2)_8\) (97h) with \([\text{Me}_3\text{SiCH}_2\text{O}2\text{Sn}]_2(\text{CH}_2)_3\) (98c). Solid 97h (0.07 g, 0.11 mmol) was added to a suspension of 98c (0.05 g, 0.11 mmol) in toluene (2 mL) and stirred at 100 °C for 24 h. $^{119}\text{Sn}$ NMR (toluene, 100 °C): $\delta$ −82.5 (integral 7.0 %), −84.1 (integral 21.0 %), −87.0 (integral 13.0 %), −101.5 (integral 9.0 %), −140.9 (integral 9.0 %), −144.0 (integral 27.0 %), −145.4 (integral 14.0 %).

For reaction of \([\text{Me}_3\text{SiCH}_2\text{Cl}_2\text{Sn}]_2(\text{CH}_2)_10\) (97i) with \([\text{Me}_3\text{SiCH}_2\text{O}2\text{Sn}]_2(\text{CH}_2)_3\) (98c). Solid 97i (0.08 g, 0.11 mmol) was added to a suspension of 98c (0.05 g, 0.11 mmol) in toluene (2 mL) and stirred at 100 °C for 24 h. $^{119}\text{Sn}$ NMR (toluene, 100 °C): $\delta$ −80.8 (integral 4.0 %), −81.7 (integral 11.0 %), −84.0 (integral 29.0 %), −97.0 (integral 10.0 %), −136.4 (integral 10.0 %), −139.4 (integral 12.0 %), −140.2 (integral 24.0 %).

For reaction of \([\text{Me}_3\text{SiCH}_2\text{Cl}_2\text{Sn}]_2(\text{CH}_2)_12\) (97j) with \([\text{Me}_3\text{SiCH}_2\text{O}2\text{SnCH}_2]_2(\text{CH}_2)_3\) (98c). Solid 97j (0.08 g, 0.11 mmol) was added to a suspension of 98c (0.05 g, 0.11 mmol) in toluene (2 mL) and stirred at 100 °C for 24 h. $^{119}\text{Sn}$ NMR (toluene, 100 °C): $\delta$ −85.4 (integral 35.0 %), −98.1 (integral 11.0 %), −136.2 (integral 4.0 %), −137.3 (integral 13.0 %), −140.8 (integral 18.0 %), −141.9 (integral 18.0 %).

For reaction of \([\text{Me}_3\text{SiCH}_2\text{Cl}_2\text{Sn}]_2(\text{CH}_2)_5\) (97e) with \([\text{Me}_3\text{SiCH}_2\text{O}2\text{Sn}]_2(\text{CH}_2)_4\) (98d). Solid 97e (0.07 g, 0.10 mmol) was added to a suspension of 98d (0.05 g, 0.10 mmol) in toluene (2 mL) and stirred at 100 °C for 24 h. $^{119}\text{Sn}$ NMR (toluene, 25 °C): $\delta$ −66.8 (integral 1.6 %), −71.8 (integral 1.7 %), −75.6 (integral 1.5 %), −83.4 (integral 8.0 %), −87.3 (integral 3.9 %), −89.1 (integral 9.3 %), −135.0 (integral 5.8 %), −138.7 (integral 5.0 %), −147.1 (integral 8.3 %), −148.4 (integral 5.8 %), −153.2 (integral 1.2 %), −268.1 (integral 31.0 %), −450.6 (integral 16.0 %). $^{119}\text{Sn}$ NMR (toluene, 100 °C): $\delta$ −70.8 (integral 1.7 %), −74.5 (integral 1.9 %), −78.0 (integral 2.3 %), −81.7 (integral 1.8 %), −85.0 (integral 7.8 %), −88.3 (integral 8.0 %), −89.4 (integral 20.0 %), −135.5 (integral 7.0 %), −135.9 (integral 3.0 %), −140.0 (integral 10.0 %), −141.7 (integral 1.0 %), −147.6 (integral 13.0 %), −148.8 (integral 8.7 %), −152.3 (integral 1.5 %), −270.0 (integral 8.0 %), −450.8 (integral 3.8 %).
For reaction of \([(\text{Me}_3\text{SiCH}_2)(\text{Cl})_2\text{Sn}]_2(\text{CH}_2)_6\) (97f) with \{[(\text{Me}_3\text{SiCH}_2)(\text{O})\text{Sn}]_2(\text{CH}_2)_4\}_m (98d). Solid 97f (0.07 g, 0.11 mmol) was added to a suspension of 98d (0.05 g, 0.11 mmol) in toluene (2 mL) and stirred at 100 °C for 24 h. $^{119}\text{Sn NMR}$ (toluene, 25 °C): δ −66.4 (integral 2.0 %), −80.8 (integral 14.0 %), −81.3 (integral 15.0 %), −85.7 (integral 13.0 %), −131.5 (integral 9.0 %), −135.5 (integral 3.0 %), −143.1 (integral 4.0 %), −144.5 (integral 4.0 %), −146.0 (integral 9.0 %), −150.0 (integral 2.0 %), −269.0 (integral 13.0 %), −451.0 (integral 6.6 %).

$^{119}\text{Sn NMR}$ (toluene, 100 °C): δ −71.6 (integral 2.0 %), −72.0 (integral 2.0 %), −76.8 (integral 0.8 %), −81.8 (integral 18.0 %), −82.4 (integral 16.0 %), −86.2 (integral 16.0 %), −131.8 (integral 16.0 %), −135.3 (integral 2.0 %), −140.5 (integral 0.4 %), −143.7 (integral 8.0 %), −145.7 (integral 6.0 %), −146.0 (integral 10.0 %), −148.7 (integral 1.0 %), −149.1 (integral 1.0 %), −270.0 (integral 6.0 %), −450.0 (integral 4.0 %).

For reaction of \([(\text{Me}_3\text{SiCH}_2)(\text{Cl})_2\text{Sn}]_2(\text{CH}_2)_8\) (97h) with \{[(\text{Me}_3\text{SiCH}_2)(\text{O})\text{Sn}]_2(\text{CH}_2)_4\}_m (98d). Solid 97h (0.06 g, 0.08 mmol) was added to a suspension of 98d (0.04 g, 0.08 mmol) in toluene (2 mL) and stirred at 100 °C for 24 h. $^{119}\text{Sn NMR}$ (toluene, 25 °C): δ −66.4 (integral 2.0 %), −80.8 (integral 14.0 %), −81.3 (integral 15.0 %), −85.7 (integral 13.0 %), −131.5 (integral 9.0 %), −135.5 (integral 3.0 %), −143.1 (integral 4.0 %), −144.5 (integral 4.0 %), −146.0 (integral 9.0 %), −150.0 (integral 2.0 %), −269.0 (integral 13.0 %), −451.0 (integral 6.6 %).

$^{119}\text{Sn NMR}$ (toluene, 100 °C): δ −132.5 (integral 19.0 %), −66.5 (integral 1.9 %), −75.4 (integral 2.9 %), −81.7 (integral 5.3 %), −84.0 (integral 11.0 %), −89.9 (integral 6.0 %), −90.5 (integral 5.2 %), −134.7 (integral 6.0 %), −135.1 (integral 4.0 %), −140.2 (integral 18.0 %), −148.1 (integral 4.0 %), −160.0 (integral 3.0 %), −267.7 (integral 3.3 %), −449.6 (integral 8.7 %).

$^{119}\text{Sn NMR}$ (toluene, 100 °C): δ −131.9 (integral 10.0 %), −83.4 (integral 35.0 %), −139.8 (integral 38.0 %), −267.7 (integral 8.0 %), −450.4 (integral 9.0 %).

For reaction of \([(\text{Me}_3\text{SiCH}_2)(\text{Cl})_2\text{Sn}]_2(\text{CH}_2)_10\) (97i) with \{[(\text{Me}_3\text{SiCH}_2)(\text{O})\text{Sn}]_2(\text{CH}_2)_4\}_m (98d). Solid 97i (0.07 g, 0.10 mmol) was added to a suspension of 98d (0.05 g, 0.10 mmol) in toluene (2 mL) and stirred at 100 °C for 24 h. $^{119}\text{Sn NMR}$ (toluene, 25 °C): δ −129.0 (integral 5.0 %), −81.9 (integral 31.0 %), −139.8 (integral 35.0 %), −269.0 (integral 14.0 %), −451.9 (integral 12.0 %).

$^{119}\text{Sn NMR}$ (toluene, 100 °C): δ −130.0 (integral 10.0 %), −71.0 (integral 2.0 %), −84.5 (integral 37.0 %), −140.7 (integral 39.0 %), −267.9 (integral 4.0 %), −270.5 (integral 6.0 %), −450.6 (integral 2.0 %).
For reaction of \([(\text{Me}_3\text{SiCH}_2)(\text{Cl})_2\text{Sn}]_2(\text{CH}_2)_12\) (97j) with \{[(\text{Me}_3\text{SiCH}_2)(\text{O})\text{Sn}]_2(\text{CH}_2)_4\}_m\) (98d). Solid 97j (0.07 g, 0.10 mmol) was added to a suspension of 98d (0.05 g, 0.10 mmol) in toluene (2 mL) and stirred at 100 °C for 24 h. $^{119}\text{Sn}$ NMR (toluene, 25 °C): $\delta$ −132.3 (integral 6.0 %), −74.5 (integral 1.0 %), −82.7 (integral 39.0 %), −140.6 (integral 41.0 %), −267.5 (integral 7.0 %), −450.7 (integral 7.0 %). $^{119}\text{Sn}$ NMR (toluene, 100 °C): $\delta$ 129.0 (integral 2.0 %), 142.0 (integral 11.0 %), −74.5 (integral 2.0 %), −88.9 (integral 39.0 %), −144.0 (integral 28.0 %), −145.5 (integral 14.0 %), −274.2 (integral 1.4 %), −454.7 (integral 2.8 %), −590.0 (integral 1.3 %).

1.7-Bis(triphenylstannyl)dipropyl ether [Ph$_3$Sn(CH$_2$)$_3$]$_2$O (107). A solution of Ph$_3$SnH (58.2 g, 166 mmol) in dried toluene (80 mL) was added slowly over an 3 h period to a solution of allyl ether (6.51 g, 66.3 mmol) in dried toluene (40 mL) and Pd(OH)$_2$/C (0.002 g) at 80 °C. The reaction mixture was stirred at 80 °C for 72 h and the solvent removed in vacuo to afford a slightly yellow residue. To the residue, chloroform (80 mL), H$_2$O$_2$ (40 mL) and a solution of KF (5.00 g) in water (40 mL) were added and stirred at room temperature for 6 h, after which the solvent was removed in vacuo. The residue was extracted with diethyl ether (3 x 80 mL), dried (Na$_2$SO$_4$) and the solvent was removed in vacuo to yield a greenish residue. The by-product was removed by Kugelrohr apparatus (230 °C, 0.01 mmHg). Further purification of the crude product was achieved by column chromatography (silica gel 60, 70-230 mesh) using hexane as the eluent. The solvent was removed in vacuo to give 107 as a colourless oil (46.5 g, 70 %). $^1$H NMR (CDCl$_3$): $\delta$ 0.85 (t, 4H), 1.23 (m, 4H), 7.25-7.64 (m, 30H). $^{13}$C NMR (CDCl$_3$): $\delta$ 7.77 [$^1J(^{13}\text{C}-^{117/119}\text{Sn})$ = 382/401 Hz], 26.97 [$^2J(^{13}\text{C}-^{117/119}\text{Sn})$ = 21 Hz], 74.02 [CH$_2$, $^3J(^{13}\text{C}-^{117/119}\text{Sn})$ = 64 Hz], 128.92, 129.27, 137.50 [$^2J(^{13}\text{C}_\text{m}-^{117/119}\text{Sn})$ = 35 Hz], 139.58 [$^1J(^{13}\text{C}_\text{p}-^{117/119}\text{Sn})$ = 467/490 Hz]. $^{119}\text{Sn}$ NMR (CDCl$_3$): $\delta$ −98.4 [$^1J(^{119}\text{Sn-}^{13}\text{C})$ = 487 Hz]. Anal. Calcd. for C$_{42}$H$_{42}$OSn$_2$: C, 63.0; H, 5.3. Found: C, 63.8; H, 5.1.

1.7-Bis(iododiphenylstannyl)dipropyl ether [IPh$_2$Sn(CH$_2$)$_3$]$_2$O (108). A solution of iodine (9.96 g, 39.2 mmol) in dichloromethane (1.0 L) was added to a solution of 107 (15.7 g, 19.6 mmol) in dichloromethane (100 mL) at 0 °C over 10 h. Removal of the solvent and by-product in vacuo and crystallisation from chloroform/hexane afforded 108 as a white crystalline solid (16.8 g, 95 %). m. p. 98-100 °C. $^1$H NMR (CDCl$_3$): $\delta$ 1.58 (t, 4H), 1.82 (m, 4H), 7.26-7.63 (m, 20H). $^{13}$C NMR (CDCl$_3$): $\delta$ 14.41 [$^1J(^{13}\text{C}-^{117/119}\text{Sn})$ = 420/439 Hz], 25.80 [$^2J(^{13}\text{C}_\text{m}-^{117/119}\text{Sn})$ = 27 Hz], 72.10 [$^3J(^{13}\text{C}_\text{p}-^{117/119}\text{Sn})$ = 63 Hz], 128.54, 129.56 [$^2J(^{13}\text{C}_\text{m}-^{117/119}\text{Sn})$ = 13 Hz], 135.73 [$^3J(^{13}\text{C}_\text{p}-^{117/119}\text{Sn})$ = 47 Hz], 137.14 [$^1J(^{119}\text{Sn-}^{13}\text{C})$ = 531/554 Hz]. $^{119}\text{Sn}$

1,7-Bis[(trimethylsilylmethyl) diphenyl stannyl]dipropyl ether [(Me3SiCH2)2Ph2Sn(CH2)3]2O (109). A solution of 108 (10.4 g, 11.6 mmol) in THF (100 mL) was added to a solution of Me3SiCH2MgCl [prepared from magnesium (2.47 g, 102 mmol) and Me3SiCH2Cl (3.12 g, 25.4 mmol) in THF (150 mL)] and the mixture stirred at reflux for 48 h. The reaction was quenched by the addition of satd. ammonium chloride at 25 °C. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (3 x 100 mL). The combined organic extracts dried (Na2SO4) and the solvent was removed in vacuo. The residue was purified by column chromatography (silica gel 60, 70-230 mesh) using a hexane solvent system. Removal of the solvent in vacuo yielded 109 as a colourless oil (7.57 g, 80 %). 1H NMR (CDCl3): δ 0.18 (s, 18H, SiMe3), 0.89 (s, 4H, SiCH2), 1.29 (s, 4H), 1.85 (s, 4H, SnCH2), 3.30 (s, 4H), 7.27 (m, 20H). 13C NMR (CDCl3): δ −9.97 [SiCH2, 1J(13C-117/119Sn) = 245/257 Hz], −2.92 [SiMe3, 3J(13C-117/119Sn) = 16 Hz, 1J(13C-29Si) = 51 Hz], 3.22 [3J(13C-117/119Sn) = 363/380 Hz], 22.11 [2J(13C-117/119Sn) = 19 Hz], 69.32 [3J(13C-117/119Sn) = 72 Hz], 123.71, 123.97, 132.15 [2J(13C-117/119Sn) = 39 Hz], 136.22 [1J(13C-117/119Sn) = 440/461 Hz]. 119Sn NMR (CDCl3): δ −56.5 [1J(119Sn-13C) = 463 Hz]. Anal. Calcd. for C38H54OSi2Sn2: C, 55.6; H, 6.6. Found: C, 55.4; H, 6.7.

1,7-Bis[(trimethylsilylmethyl) dichloro stannyl]dipropyl ether [(Me3SiCH2)(Cl)2Sn(CH2)3]2O (110). To a solution of 109 (6.00 g, 7.31 mmol) in chloroform (100 mL) was added excess Conc. HCl (200 ml, 32 %). The reaction mixture was stirred and maintained at 70 °C for 24 h. The organic layer was separated, and the aqueous layer was extracted with chloroform (3 x 100 mL). The combined organic extracts were dried (CaCl2) and the solvent was removed in vacuo to afford 110 as a brown oil (3.35 g, 70 %) of sufficient purity for further use. 1H NMR (CDCl3): δ 0.15 (s, 18H, SiMe3), 0.83 (s, 4H, SiCH2), 1.69 (t, 4H), 2.08-2.10 (m, 4H), 3.57 (t, 4H). 13C NMR (CDCl3): δ 1.02 [SiMe3, 3J(13C-117/119Sn) = 28 Hz, 1J(13C-29Si) = 52 Hz], 12.39 [SiCH2, 1J(13C-117/119Sn) = 327/342 Hz], 23.36 [2J(13C-117/119Sn) = 503/526 Hz], 24.03 [2J(13C-117/119Sn) = 36 Hz], 71.06 [3J(13C-117/119Sn) = 73 Hz]. 119Sn NMR (CDCl3): δ 79.1.

1,7-Bis[(trimethylsilylmethyl)oxostannyl]dipropyl ether [(Me3SiCH2)(O)Sn(CH2)3]2O (111). A solution of KOH (0.24 g, 4.28 mmol) in water (50 mL) was added to a solution of 110 (0.70 g, 1.07 mmol) in toluene (50 mL) and the mixture stirred at 100 °C for 24 h. The white precipitate which formed...
was collected by filtration. The collected precipitate was then stirred with water (400 mL), filtered and further dried by heating at 80 °C (0.01 mmHg) for 48 h to give 111 as a white solid (0.50 g, 86 %). m. p. > 300 °C (decomp.). Anal. Calcd. for C_{14}H_{34}O_3Si_2Sn_2: C, 30.9; H, 6.3. Found: C, 29.8; H, 6.1.

\{[(Me_3SiCH_2)Sn(Cl)](CH_2)_3O(CH_2)_3[(Me_3SiCH_2)Sn(Cl)]O\}_4 (112). A solution of 110 (0.09 g, 0.13 mmol) in toluene (2 mL) was added to a suspension of 111 (0.07 g, 0.13 mmol) in toluene (2 mL) and stirred at 100 °C for 24 h. Removal of the solvent in vacuo and crystallisation from chloroform/hexane (30:70) afforded 112 as a colourless crystals (0.17 g, 92 %). m. p. 268-270 °C. 

1H NMR (CDCl_3): δ 0.13 (s, 36H, Me_3Si), 0.191 (s, 36H, Me_3Si), 0.72-1.28 (m, 16H, CH_2Si), 1.59-1.89 (m, 16H), 2.13-2.29 (m, 16H), 3.47-3.62 (m, 16H). 

119Sn NMR (CDCl_3): δ 23.0 (integral 9.4 %), −80.1 (integral 1.4 %), −84.0 (integral 4.5 %), −93.4 (integral 14.0 %), −96.0 (integral 5.0 %), −100.1 (integral 1.0 %), −103.6 (integral 8.0 %), −123.9 (integral 8.1 %), −127.6 (integral 5.8 %), −133.8 (integral 24.3 %), −136.0 (integral 1.0 %), −137.8 (integral 1.4 %), −148.7 (integral 2.8 %), −150.2 (integral 11.0 %), −153.5 (integral 0.5 %), −154.5 (integral 0.5 %), −155.5 (integral 0.5 %), −157.5 (integral 0.5 %). Anal. Calcd. for C_{56}H_{136}O_8Cl_8 Si_8Sn_8: C, 28.1; H, 5.7. Found: C, 28.2; H, 5.5.

\{[(Me_3SiCH_2)Sn(OH)](CH_2)_3[(Me_3SiCH_2)Sn(H_2O)]O\}_4\cdot 4OTf (113c). A suspension of 98c (0.50 g, 1.03 mmol) and TfOH (0.62 g, 4.16 mmol) in acetonitrile (80 mL) was stirred at room temperature for 12 h. Removal of solvent in vacuo yielded the crude product as a pale yellow oil (0.57 g, 85 %). 

119Sn NMR (MeCN): δ −316.3. A sample of the crude product was crystallised from acetonitrile/chloroform (75:25) to give 113c as a colourless crystals. m. p. 193-195 °C. 

IR (KBr) ν(OH): 3250.0, 3365.3 cm\(^{-1}\). Anal. Calcd. for C_{48}H_{124}F_{12}S_4O_{24}Si_8Sn_8: C, 22.0; H, 4.8. Found: C, 22.3; H, 4.8.

\{[(H_2O)(OH)(Me_3SiCH_2)Sn]_2(CH_2)_4\cdot 2OTf\}_m (113d). A suspension of 98d (1.00 g, 2.00 mmol) and TfOH (1.20 g, 8.00 mmol) in acetonitrile (160 mL) was stirred at room temperature for 12 h. Removal of solvent in vacuo yielded the crude product as a yellow solid (1.08 g, 82 %). 

119Sn NMR (MeCN): δ −332.7. A sample of the crude product was recrystallised from acetonitrile/chloroform (75:25) to give 113d as a colourless solid. m. p. 188-190 °C. 

IR (KBr) ν(OH): 3233.3, 3334.1 cm\(^{-1}\). ESMS: m/z = 632.9

{(H2O)(OH)(Me3SiCH2)Sn]2(CH2)8⋅2OTf}m (113h). A suspension of 98h (1.00 g, 1.80 mmol) and TfOH (1.08 g, 7.19 mmol) in acetonitrile (160 mL) was stirred at room temperature for 12 h. Removal of solvent in vacuo left the crude product as a pale yellow oil (0.96 g, 80%). 119Sn NMR (MeCN): δ −326.4. A sample of the crude product was crystallised from acetonitrile/chloroform (75:25) to give 113h as a colourless solid. m.p. 150-152 °C. 119Sn NMR (MeCN): δ −166.6 (integral 39.0 %), −170.5 (integral 61.0 %). IR (KBr) ν(OH): 3245.6, 3363.8 cm−1. ESMS: m/z = 689.0 (63%) for [1/4M − OH + OTf]+, 706.5 (30%) for [1/2M − 2OH + 2OTf + H2O]2+, 1527.0 (15%) for [1/2M − 2OH + 3OTf]+, 1545.0 (100%) for [1/2M − 2OH + 3OTf + H2O]+, 1563.0 (25%) for [1/2M − 2OH + 3OTf + 2H2O]+, 986.9 (20%) for [1/4M − OH + 3OTf]+, 1004.9 (71%) for [1/4M − OH + 3OTf + H2O]−, 1136.9 (30%) for [1/4M + 2OTf]−, 1154.9 (18%) for [1/4M + 2OTf + H2O]−, 1860.9 (18%) for [1/2M + 3OTf + 2H2O]−. Anal. Calcd. for C18H48F6S2O12Si2Sn2: C, 23.3; H, 5.2. Found: C, 23.8; H, 5.6.

{(H2O)(OH)(Me3SiCH2)Sn]2(CH2)10⋅2OTf}m (113i). A suspension of 98i (1.00 g, 1.71 mmol) and TfOH (1.03 g, 6.85 mmol) in acetonitrile (160 mL) was stirred at room temperature for 12 h. Removal of solvent in vacuo left the crude product as a pale yellow oil (0.98 g, 84%). 119Sn NMR (MeCN): δ −326.0. A sample of the crude product was crystallised from acetonitrile/chloroform (75:25) to give 113i as a colourless solid. m.p. 145-148 °C. 119Sn NMR (MeCN): δ −132.0 (integral 5.5 %), −178.2 (integral 94.5 %). IR (KBr) ν(OH): 3225.0, 3353.8 cm−1. ESMS: m/z = 717.0 (63%) for [1/4M − OH + OTf]+, 867.0 (25%) for [1/4M − O + 2OTf]+, 908.0 (42%) for [1/4M − O + 2OTf + MeCN]+, 998.9 (100%) for [1/4M − OH − O + 3OTf]+, 1040.0 (21%) for [1/4M − OH − O + 3OTf + MeCN]+, 1058.0 (30%) for [1/4M − OH − O + 3OTf + MeCN + H2O]+, 1733.0 (20%) for [1/2M − OH − O + 4OTf]+, 1751.0 (19%) for [1/2M − OH − O + 4OTf + H2O]+, 1882.9 (50%) for [1/2M − 2OH + 5OTf]+, 1033.0 (19%) for [1/4M − O + OH + 3OTf]−, 1164.9 (60%) for [1/4M − O + 4OTf]−, 1296.9 (100%) for [1/4M − OH + 5OTf]−. Anal. Calcd. for C20H52F6S2O12Si2Sn2: C, 25.1; H, 5.5. Found: C, 25.6; H, 6.0.
(3-Hydroxylpropyl)triphenyltin Ph$_3$Sn(CH$_2$)$_3$OH (114). Ph$_3$SnH (88.2 g, 251 mmol) and allyl alcohol (43.8 g, 754 mmol) were heated at 85 °C for 72 h. The excess allyl alcohol was removed in vacuo and crystallisation from petroleum ether/chloroform (50/50) afforded 114 as a white crystalline solid (82.2 g, 80 %). m. p. 102-104 °C (Lit. m. p. 105 °C). 1H NMR (CDCl$_3$): δ 1.64 (m, 2H), 2.01 (m, 2H), 2.08 (t, 2H), 7.48-7.75 (m, 15H). 13C NMR (CDCl$_3$): δ 6.45 [SnCH$_2$, $^1$J(C-117/119Sn) = 380/398 Hz], 29.10 [CH$_2$, $^2$J(C-117/119Sn) = 22 Hz], 65.26 [CH$_2$, $^3$J(C-117/119Sn) = 67 Hz], 128.36, 128.72, 136.86 [^2$J(Cm-117/119Sn) = 35 Hz], 138.81 [^3$J(Cp-117/119Sn) = 467/490 Hz]. 119Sn NMR (CDCl$_3$): δ −97.6 [^1$J(C-119Sn-13C) = 490 Hz]. Anal. Calcd. for C$_{21}$H$_{22}$OSn: C, 61.7; H, 5.4. Found: C, 61.5; H, 5.3.

(3-Chloropropyl)triphenyltin Ph$_3$Sn(CH$_2$)$_3$Cl (115). Solid 114 (82.1 g, 201 mmol) was added to a suspension of triphenylphosphine (63.2 g, 241 mmol) in carbon tetrachloride (500 mL) and the mixture stirred at reflux for 24 h. The white precipitate of Ph$_3$PO which formed was filtered and the solvent removed in vacuo. The residue was purified by column chromatography (silica gel 60, 230-400 mesh) using toluene as the eluent. Removal of solvent left 115 as a white solid (61.9 g, 72 %). m. p. 68-70 °C. 1H NMR (CDCl$_3$): δ 1.60 (m, 2H), 2.13 (m, 2H), 3.54 (t, 2H), 7.39-7.75 (m, 15H). 13C NMR (CDCl$_3$): δ 7.85 [SnCH$_2$, $^1$J(C-117/119Sn) = 364/381 Hz], 29.78 [CH$_2$, $^2$J(C-117/119Sn) = 16 Hz], 47.99 [CH$_2$, $^3$J(C-117/119Sn) = 86 Hz], 128.54 [^2$J(Cm-117/119Sn) = 48 Hz], 128.98 [^3$J(Cm-117/119Sn) = 11 Hz], 136.90 [^2$J(Cp-117/119Sn) = 36 Hz], 138.08 [^3$J(Cp-117/119Sn) = 476/497 Hz]. 119Sn NMR (CDCl$_3$): δ −98.3 [^1$J(C-119Sn-13C) = 492 Hz]. Anal. Calcd. for C$_{21}$H$_{21}$ClSn: C, 59.0; H, 5.0. Found: C, 59.0; H, 5.0.

(3-Chloropropyl)diphenyltin iodide IPh$_2$Sn(CH$_2$)$_3$Cl (116a). A solution of iodine (35.6 g, 140 mmol) in dichloromethane (2000 mL) was added over an 12 h period to a solution of 115 (60.0 g, 140 mmol) in dichloromethane (100 mL) at 0 °C. The solvent and by-product were removed in vacuo to afford 116a as a brown oil of sufficient purity for further use. 1H NMR (CDCl$_3$): δ 1.90 (m, 2H), 2.40 (m, 2H), 3.64 (t, 2H), 7.44-7.67 (m, 10H). 13C NMR (CDCl$_3$): δ 13.78 [SnCH$_2$, $^1$J(C-117/119Sn) = 375/392 Hz], 29.60, 47.24 [CH$_2$, $^3$J(C-117/119Sn) = 90 Hz], 128.84 [^3$J(Cm-117/119Sn) = 59 Hz], 129.99 [^4$J(Cp-117/119Sn) = 13 Hz], 135.90 [^2$J(Cp-117/119Sn) = 47 Hz], 138.08. 119Sn NMR (CDCl$_3$): δ −56.2 [^1$J(C-119Sn-13C) = 522 Hz].

(3-Chloropropyl)diphenyltin chloride ClPh$_2$Sn(CH$_2$)$_3$Cl (116b). A saturated aqueous solution of NH$_4$Cl (150 mL) was added to a solution of 116a (60.0 g, 140 mmol) in diethyl ether (150 mL) and the solution was stirred at room temperature for
3 h. The aqueous layer was removed and satd. ammonium chloride (150 mL) was added. The reaction mixture was stirred at room temperature for 3 h and above step was repeated. The two layers were separated and organic layer was washed with water (300 mL), dried (Na₂SO₄) and the solvent removed in vacuo to afford the crude as a yellow oil. The residue was distilled using a Kugelrohr apparatus (200 °C, 0.01 mmHg) to give 116b as a colourless oil (43.2 g, 80 %). ¹H NMR (CDCl₃): δ 1.81 (m, 2H), 2.30 (m, 2H), 3.64 (t, 2H), 7.44-7.67 (m, 10H). ¹³C NMR (CDCl₃): δ 14.82 [SnCH₂, ¹J¹³C₁⁻¹¹⁷/¹¹⁹Sn = 411/430 Hz], 28.37 [CH₂, ²J¹³C₁⁻¹¹⁷/¹¹⁹Sn = 24 Hz], 47.87 [CH₂, ³J¹³C₁⁻¹¹⁷/¹¹⁹Sn = 76 Hz], 128.94 [⁴J¹³Cm₁⁻¹¹⁷/¹¹⁹Sn = 61 Hz], 130.16 [⁵J¹³C₀⁻¹¹⁷/¹¹⁹Sn = 13 Hz], 135.79 [²J¹³C₀⁻¹¹⁷/¹¹⁹Sn = 49 Hz], 138.39. ¹¹⁹Sn NMR (CDCl₃): δ −6.77 [¹J¹¹⁹Sn⁻¹³C = 578 Hz]. Anal. Calcd. for C₁₅H₁₆Cl₂Sn: C, 46.7; H, 4.2. Found: C, 46.7; H, 4.2.

(3-Chloropropyl)(trimethylsilylmethyl)diphenyltin (Me₃SiCH₂)Ph₂Sn(CH₂)₃Cl (117). A solution of 116b (43.0 g, 111 mmol) in THF (100 mL) was added to a solution of Me₃SiCH₂MgCl [prepared from magnesium (6.50 g, 267 mmol) and Me₃SiCH₂Cl (16.4 g, 134 mmol) in THF (200 mL)]. The reaction mixture was stirred at reflux for 24 h and the solvent was removed in vacuo. To the residue, diethyl ether (200 mL) and satd. ammonium chloride (200 mL) were added and the resultant mixture stirred at room temperature for 1 h. The mixture was extracted with diethyl ether (3 x 100 mL) and the combined organic extracts were dried (Na₂SO₄) and the solvent removed in vacuo to yield 117 as pale yellow oil (38.9 g, 80 %). ¹H NMR (CDCl₃): δ 0.04 (s, 9H, Me₃Si), 0.30 (s, 4H, SiCH₂), 1.38 (m, 2H), 2.10 (m, 2H), 3.54 (t, 2H), 7.39-7.62 (m, 10H). ¹³C NMR (CDCl₃): δ −5.53 [SiCH₂, ¹J¹³C⁻¹¹⁷/¹¹⁹Sn = 249/251 Hz], 1.55 [SiMe₃, ³J¹³C⁻¹¹⁷/¹¹⁹Sn = 16 Hz, ¹J¹³C⁻²⁹Si = 51 Hz], 8.72 [SnCH₂, ¹J¹³C⁻¹¹⁷/¹¹⁹Sn = 346/364 Hz], 29.94, 48.03 [CH₂, ³J¹³C⁻¹¹⁷/¹¹⁹Sn = 85 Hz], 128.32, 128.64, 136.54 [²J¹³C₀⁻¹¹⁷/¹¹⁹Sn = 36 Hz], 139.89. ¹¹⁹Sn NMR (CDCl₃): δ −57.2. Anal. Calcd. for C₁₉H₂₇ClSiSn: C, 52.1; H, 6.2. Found: C, 52.3; H, 6.2.

Bis(iododiphenylstannyl)methane [IPh₂Sn]₂CH₂ (95a).¹⁸¹ A solution of iodine (21.6 g, 85.0 mmol) in dichloromethane (1500 mL) was added over an 12 h period to a solution of 94a (30.3 g, 42.5 mmol) in dichloromethane (50 mL) at 0 °C. The solvent and by-product were removed in vacuo to afford 95a as a yellow oil (32.9 g, 95 %) of sufficient purity for further use. ¹¹⁹Sn NMR (CDCl₃): δ −66.8.

Bis(chlorodiphenylstannyl)methane [ClPh₂Sn]₂CH₂ (118). A saturated aqueous solution of NH₄Cl (150 mL) was added to a solution of 95a (32.0 g, 39.3 mmol) in
diethyl ether (150 mL) and the solution was stirred at room temperature for 3 h. The aqueous layer was removed and satd. ammonium chloride (150 mL) was added. The reaction mixture was stirred at room temperature for 3 h and the above step was repeated. The two layers were separated and the organic layer was washed with water (300 mL), dried (Na₂SO₄) and the solvent removed in vacuo. The residue was recrystallised from chloroform/hexane to afford **118** as a white crystalline solid (22.7 g, 90 %). m. p. 100-102 °C. ¹H NMR (CDCl₃): δ 1.56 (s, 2H), 7.26-7.80 (m, 20H). ¹³C NMR (CDCl₃): δ 0.02 [SnCH₂, ¹J(¹³C-¹¹⁷/¹¹⁹Sn) = 296/309 Hz], 128.96 [ ³J(¹³Cm-¹¹⁷/¹¹⁹Sn) = 65 Hz], 130.34 [⁴J(¹³Cp-¹¹⁷/¹¹⁹Sn) = 14 Hz], 135.64 [²J(¹³Co-¹¹⁷/¹¹⁹Sn) = 51 Hz], 138.16. ¹¹⁹Sn NMR (CDCl₃): δ 22.2 [¹J(¹¹⁹Sn-¹³C) = 212 Hz].

1,8-Bis(chlorodiphenylstannyl)octane [ClPh₂Sn]₂(CH₂)₈ (119). A saturated aqueous solution of NH₄Cl (150 mL) was added to a solution of 95h (21.7 g, 23.8 mmol) in diethyl ether (150 mL) and the solution was stirred at room temperature for 3 h. The aqueous layer was removed and satd. ammonium chloride (150 mL) was added. The reaction mixture was stirred at room temperature for 3 h and the above step was repeated. The two layers were separated and the organic layer was washed with water (300 mL), dried (Na₂SO₄) and the solvent removed in vacuo to yield **119** as a yellow oil (16.0 g, 92 %). ¹H NMR (CDCl₃): δ 1.27-1.79 (m, 16H), 7.26-7.70 (m, 20H). ¹³C NMR (CDCl₃): δ 17.60 [SnCH₂, ¹J(¹³C-¹¹⁷/¹¹⁹Sn) = 409/428 Hz], 25.37 [²J(¹³Cm-¹¹⁷/¹¹⁹Sn) = 28 Hz], 28.65, 33.45 [⁴J(¹³Cp-¹¹⁷/¹¹⁹Sn) = 71 Hz], 128.90 [²J(¹³Co-¹¹⁷/¹¹⁹Sn) = 58 Hz], 130.06 [⁴J(¹³Cp-¹¹⁷/¹¹⁹Sn) = 13 Hz], 135.73 [²J(¹³Co-¹¹⁷/¹¹⁹Sn) = 47 Hz], 138.95. ¹¹⁹Sn NMR (CDCl₃): δ 17.3 [¹J(¹¹⁹Sn-¹³C) = 535 Hz]. Anal. Calcd. for C₃₂H₃₆Cl₂Sn₂: C, 52.7; H, 5.0. Found: C, 52.6; H, 4.9.

1,1-Bis{diphenyl[3'-(diphenyl[(trimethylsilyl)methyl]stannyl)propyl]stannyl}methane [(Me₃SiCH₂)Ph₂Sn(CH₂)₃SnPh₂]CH₂ (120).⁷⁴ A solution of **119** (14.4 g, 22.8 mmol) in diethyl ether/THF (100/50 mL) was added to a solution of Me₃SiCH₂Ph₂Sn(CH₂)₃MgCl [prepared from magnesium (4.44 g, 183 mmol) and **117** (20.0 g, 45.7 mmol) in diethyl ether (150 mL)]. The reaction mixture was stirred at 40 °C for 24 h and the solvent was removed in vacuo. To the residue, hexane (200 mL) was added and stirred at 60 °C for 1 h. The reaction mixture was filtered and the solvent removed in vacuo. To the yellow residue, acetone (100 mL) and H₂O₂ (50 mL) and a solution of KF (2.00g) in water (50 mL) were added and the resultant mixture stirred at room temperature for 1 h. The mixture was filtered through a thin layer of filter aid and the solvent removed in vacuo. Diethyl ether (150 mL), and water (150 mL) were added to the residue. The mixture was extracted with diethyl ether (3 x 100 mL), the combined extracts dried (Na₂SO₄) and the solvent removed
in vacuo to yield 120 as a bright yellow oil (22.4 g, 72 %) of sufficient purity for further use. $^1$H NMR (CDCl$_3$): $\delta$ –0.11 (s, 18H, Me$_3$Si), 0.09 (s, 4H, SiCH$_2$), 1.16-1.36 (m, 12H, SnCH$_2$CH$_2$CH$_2$), 1.80 (s, 2H, SnCH$_2$Sn), 7.21-7.39 (m, 40H). $^{13}$C NMR (CDCl$_3$): $\delta$ –5.46 [SiCH$_2$, $^1$J($^{13}$C-$^{117/119}$Sn) = 239/250 Hz], 1.53 [SiMe$_3$, $^3$J($^{13}$C-$^{117/119}$Sn) = 16 Hz, $^1$J($^{13}$C-29Si) = 51 Hz], 16.92 [$^1$J($^{13}$C-$^{117/119}$Sn) = 348/366 Hz], 17.24 [$^1$J($^{13}$C-$^{117/119}$Sn) = 355/373 Hz], 24.26, 128.17, 128.41, 136.54 [$^2$J($^{13}$C-117/119Sn) = 35 Hz], 140.69 [$^1$J($^{13}$C-$^{117/119}$Sn) = 435/460 Hz]. $^{119}$Sn NMR (CDCl$_3$): $\delta$ –49.3 [$^1$J($^{119}$Sn-13C$_i$) = 458 Hz, $^2$J($^{119}$Sn-$^{117}$Sn) = 230 Hz, $^4$J($^{119}$Sn-$^{117/119}$Sn) = 0 Hz, $^6$J($^{119}$Sn-$^{117/119}$Sn) = 62 Hz] –61.7 [$^1$J($^{119}$Sn-13C$_i$) = 455 Hz, $^4$J($^{119}$Sn-$^{117/119}$Sn) = 63 Hz].

1,8-Bis{diphenyl[3'-{diphenyl[(trimethylsilyl)methyl]stannyl}propyl]stannyl} octane [(Me$_3$SiCH$_2$)Ph$_2$Sn(CH$_2$)$_3$SnPh$_2$](CH$_2$)$_8$ (121). A solution of 119 (16.0 g, 22.0 mmol) in diethyl ether/THF (100/50 mL) was added to a solution of Me$_3$SiCH$_2$Ph$_2$Sn(CH$_2$)$_3$MgCl [prepared from magnesium (4.27 g, 176 mmol) and 117 (19.2 g, 43.9 mmol) in diethyl ether (150 mL)]. The reaction mixture was stirred at 40 °C for 24 h and the solvent was removed in vacuo. To the residue, hexane (200 mL) was added and stirred at 60 °C for 1 h. The reaction mixture was filtered and the solvent removed in vacuo. To the yellow residue, acetone (100 mL) and H$_2$O$_2$ (50 mL) and a solution of KF (1.50 g) in water (50 mL) were added and the resultant mixture stirred at room temperature for 1 h. The mixture was filtered through a thin layer of filter aid and the solvent removed in vacuo. Diethyl ether (150 mL), and water (150 mL) were added to the residue. The mixture was extracted with diethyl ether (3 x 100 mL), the combined extracts dried (Na$_2$SO$_4$) and the solvent removed in vacuo to yield 121 as a bright yellow oil (16.1 g, 50 %) of sufficient purity for further use. $^1$H NMR (CDCl$_3$): $\delta$ –0.12 (s, 18H, Me$_3$Si), 0.09 (s, 4H, SiCH$_2$), 1.17-1.42 (m, 16H, SnCH$_2$CH$_2$CH$_2$), 7.25-7.57 (m, 40H). $^{13}$C NMR (CDCl$_3$): $\delta$ –5.46 [SiCH$_2$, $^1$J($^{13}$C-$^{117/119}$Sn) = 239/250 Hz], 1.53 [SiMe$_3$, $^3$J($^{13}$C-$^{117/119}$Sn) = 16 Hz, $^1$J($^{13}$C-29Si) = 51 Hz], 10.61 [$^2$J($^{13}$C-$^{117/119}$Sn) = 350/367 Hz], 15.82, 17.15 [$^3$J($^{13}$C-$^{117/119}$Sn) = 59 Hz], 24.41 [$^4$J($^{13}$C-$^{117/119}$Sn) = 20 Hz], 26.62 [$^2$J($^{13}$C-$^{117/119}$Sn) = 21 Hz], 28.96, 34.24 [$^3$J($^{13}$C-$^{117/119}$Sn) = 57 Hz], 128.14, 128.16, 128.34, 136.55, 136.69, 140.14, 140.65. $^{119}$Sn NMR (CDCl$_3$): $\delta$ –61.7 [$^4$J($^{119}$Sn-$^{117/119}$Sn) = 51 Hz], –73.9 [$^4$J($^{119}$Sn-$^{117/119}$Sn) = 49 Hz].

1,1-Bis{dichloro[3'-{dichloro[(trimethylsilyl)methyl]stannyl}propyl]stannyl} methane [(Me$_3$SiCH$_2$)(Cl)$_2$Sn(CH$_2$)$_3$Sn(Cl)$_2$]::(CH$_2$) (122). To a solution of 120 (22.4 g, 16.4 mmol) in chloroform (100 mL) was added excess Conc. HCl (200 ml, 32%). The reaction mixture was stirred and maintained at 70 °C for 24 h. The organic layer
was separated, and the aqueous layer was extracted with chloroform (3 x 100 mL). The combined organic extracts were dried (CaCl$_2$) and the solvent was removed in vacuo. Crystallisation from chloroform/hexane (30/70) gave 122 as a white solid (11.0 g, 65 %). m. p. 56-58 °C. $^1$H NMR (CDCl$_3$): δ 0.20 (s, 18H, Me$_3$Si), 0.09 (s, 4H, SiCH$_2$), 1.84 (t, 4H), 1.88 (s, 2H, SnCH$_2$Sn), 2.18 (t, 4H), 2.42 (t, 4H). $^{13}$C NMR (CDCl$_3$): δ 0.20 [SiMe$_3$, $^3J$(13C-117/119Sn) = 27 Hz, $^1J$(13C-29Si) = 52 Hz], 12.55 [SiCH$_2$, $^1J$(13C-117/119Sn) = 281/294 Hz], 20.71 [$^2J$(13C-117/119Sn) = 32 Hz], 29.55 [$^1J$(13C-117/119Sn) = 428/448 Hz, $^2J$(13C-117/119Sn) = 123 Hz], 32.83 [$^3J$(13C-117/119Sn) = 516/540 Hz, $^3J$(13C-117/119Sn) = 100 Hz]. $^{119}$Sn NMR (CDCl$_3$): δ 61.7 [$^4J$(119Sn-13C) = 266 Hz], 128.4 [$^4J$(119Sn-13C) = 278 Hz]. Anal. Calcd. for C$_{15}$H$_{36}$Cl$_8$Si$_2$Sn$_4$: C, 17.5; H, 3.5. Found: C, 17.5; H, 3.7.

1,1-Bis{oxo{3'-{oxo[(trimethylsilyl)methyl]stannyl}propyl}stannyl}methane

{[(Me$_3$SiCH$_2$)(O)Sn(CH$_2$)$_3$Sn(O)]$_2$CH$_2}$m (124). A solution of KOH (17.4 g, 310 mmol) in water (100 mL) was added to a solution of 122 (5.00 g, 4.85 mmol) in toluene (100 mL) and the mixture stirred at 100 °C for 24 h. The white precipitate which formed was collected by filtration. The collected precipitate was then stirred with water (400 mL), filtered and further dried by heating at 80 °C (0.01 mmHg) for 48 h to give 124 as a white solid (3.39 g, 86 %). m. p. > 250 °C(decomp.). Anal. Calcd. for C$_{22}$H$_{50}$Cl$_8$Si$_2$Sn$_4$: C, 23.4; H, 4.5. Found: C, 23.4; H, 4.5.
1,8-Bis{oxo{3'-{oxo[(trimethylsilyl)methyl]stannyl}propyl}stannyl}octane

[(Me3SiCH2)(O)Sn(CH2)3Sn(O)]2(CH2)8m (125). A solution of KOH (15.9 g, 283 mmol) in water (100 mL) was added to a solution of 123 (5.00 g, 4.43 mmol) in toluene (100 mL) and the mixture stirred at 100 °C for 24 h. The white precipitate which formed was collected by filtration. The collected precipitate was then stirred with water (400 mL), filtered and further dried by heating at 80 °C (0.01 mmHg) for 48 h to give 125 as a white solid (3.43 g, 85 %). m. p. > 300 °C (decomp.). Anal. Calcd. for C22H50O4Si2Sn4: C, 29.0; H, 5.5. Found: C, 29.5; H, 5.2.

[(Me3SiCH2)Sn(Cl)](CH2)3[Sn(Cl)]CH2[Sn(Cl)](CH2)3[(Me3SiCH2)Sn(Cl)]O2 (126). Method 1: Solid 122 (0.15 g, 0.14 mmol) was added to a suspension of 124 (0.11 g, 0.14 mmol) in toluene (2 mL) and stirred at 100 °C for 24 h. 119Sn NMR (toluene): δ 131.8 (integral 12.0 %), −88.3 (W1/2 = 2.8 KHz, integral 39.0 %), −130.7 (W1/2 = 2.8 KHz, integral 49.0 %). The cloudy solution was filtered and a white solid was obtained (0.10 g, 75 %). m. p. > 310 °C (decomp.). Anal. Calcd. for C60H144O8Cl16 Si8Sn16: C, 19.6; H, 3.9. Found: C, 18.7; H, 3.8.

Method 2: Solid 122 (0.10 g, 0.10 mmol) was added to a solution of (t-Bu2SnO)3 (0.05 g, 0.19 mmol) in toluene (2 mL) and stirred at 100 °C for 24 h. 119Sn NMR (toluene): δ 56.7 (integral 50.0 %), −90.3 (W1/2 = 2.7 KHz, integral 20.0 %), −132.7 (W1/2 = 2.7 KHz, integral 25.0 %). The cloudy solution was filtered and a white solid was obtained (0.06 g, 70 %). m. p. > 310 °C (decomp.). Anal. Calcd. for C60H144O8Cl16 Si8Sn16: C, 19.6; H, 3.9. Found: C, 18.4; H, 3.6.

[(Me3SiCH2)Sn(Cl)](CH2)3[Sn(Cl)](CH2)3[(Me3SiCH2)Sn(Cl)]O2 (127). Method 1: Solid 123 (0.15 g, 0.14 mmol) was added to a suspension of 125 (0.11 g, 0.14 mmol) in benzene (2 mL) and stirred at 80 °C for 24 h. 119Sn NMR (C6H6): δ −92.7 (27.0%), −98.4 (24.0%), −135.7 (26.2%), −142.2 (23.0%). The solvent was removed and a white precipitate was obtained (0.11 g, 82 %). Anal. Calcd. for C88H200O8Cl16 Si8Sn16: C, 25.9; H, 4.9. Found: C, 25.9; H, 4.9.

Method 2: Solid 123 (0.10 g, 0.09 mmol) was added to a solution of (t-Bu2SnO)3 (0.04 g, 0.18 mmol) in toluene (2 mL) and stirred at 100 °C for 24 h. 119Sn NMR (toluene): δ 57.7 (integral 53.3 %), −93.4 (integral 12.3 %), −99.2 (integral 10.0 %), −136.4 (integral 11.6 %), −142.8 (integral 10.0 %). The solvent was removed and a white precipitate was obtained (0.07 g, 80 %). Anal. Calcd. for C88H200O8Cl16 Si8Sn16: C, 25.9; H, 4.9. Found: C, 25.5; H, 5.0.
General procedure for the synthesis of $\alpha,\omega$-Bis[tris(carboxylate)stannyl]alkanes $[(\text{RCO}_2)_3\text{Sn}]_2(\text{CH}_2)_n$ (128). A solution of 94 and the appropriate carboxylic acid in dry toluene (100 ml) was heated under reflux for 168 h. The solvent was removed in vacuo and the excess carboxylic acid was sublimed using a Kugelrohr apparatus (180 °C, 0.01 mmHg) to afford the product.

1,3-Bis[tris(benzoate)stannyl]propane $[(\text{C}_6\text{H}_5\text{CO}_2)_3\text{Sn}]_2(\text{CH}_2)_3$ (128c).

Compound 128c was prepared from 94c (3.00 g, 4.04 mmol) and benzoic acid (3.21 g, 26.3 mmol) and was obtained as a white solid (3.66 g, 90 %). 1H NMR (CDCl$_3$): $\delta$ 1.59-1.89 (m, 4H, SnCH$_2$), 2.13-2.29 (m, 2H, SnCH$_2$CH$_2$), 7.49-8.14 (m, 30H, C$_6$H$_5$COO). 13C NMR ($d_8$-toluene): $\delta$ 21.17, 32.02, 128.75, 131.46, 134.08, 137.55, 178.20 (C=O). $^{119}$Sn NMR ($d_8$-toluene): $\delta$ $-537.8$ [4 $J(^{119}\text{Sn}-^{117}\text{Sn}) = 944$ Hz]. Anal. Calcd. for C$_{45}$H$_{36}$O$_{12}$Sn$_2$: C, 53.7; H, 3.6. Found: C, 53.2; H, 3.7.

1,3-Bis[tris(cyclohexanoate)stannyl]propane $[(\text{C}_6\text{H}_{11}\text{CO}_2)_3\text{Sn}]_2(\text{CH}_2)_3$ (129c).

Compound 129c was prepared from 94c (3.00 g, 4.04 mmol) and cyclohexanecarboxylic acid (3.37 g, 26.3 mmol) and was obtained as a yellow viscous oil (3.58 g, 85 %). 1H NMR (CDCl$_3$): $\delta$ 1.20-2.50 (m, 72H). 13C NMR ($d_8$-toluene): $\delta$ 20.84, 25.76, 26.32, 29.71, 31.47, 41.94, 188.10 (C=O). $^{119}$Sn NMR ($d_8$-toluene): $\delta$ $-535.0$ [4 $J(^{119}\text{Sn}-^{117}\text{Sn}) = 876$ Hz]. Anal. Calcd. for C$_{45}$H$_{72}$O$_{12}$Sn$_2$: C, 51.9; H, 7.0. Found: C, 51.7; H, 7.2. 129c was dissolved in a mixture of CHCl$_3$/hexane (3:1) (150 ml) and exposed to air moisture for 4 days. The solvent was removed in vacuo to afford a yellow oil 129c'. $^{119}$Sn NMR (toluene): $\delta$ $-491.0$ (integral 15.3 %), $-505.3$ (integral 24.0 %), $-512.6$ (integral 14.0 %), $-516.33$ (integral 16.0 %), $-518.9$ (integral 2.7 %), $-529.3$ (integral 14.0 %), $-446.1$ (integral 14.0 %). Further exposure of 129c' to air moisture afforded a white solid 129c''. m.p. > 310 °C (decomp.). IR (KBr) $\nu$(CO$_2$): 1540.0, 1599.1 cm$^{-1}$; $\nu$(OH): 3405.0 cm$^{-1}$. Anal. Calcd. for C$_{31}$H$_{52}$O$_{10}$Sn$_2$: C, 45.3; H, 6.4. Found: C, 44.0; H, 5.9.

1,3-Bis[tris(acetato)stannyl]propane $[(\text{CH}_3\text{CO}_2)_3\text{Sn}]_2(\text{CH}_2)_3$ (130c).

Compound 130c was prepared from 94c (3.00 g, 4.04 mmol) and a mixture of acetic
acid/acetic anhydride (3/1) (1.58 g, 26.3 mmol) and was obtained as a yellow solid (2.18 g, 85 %). $^1$H NMR (CDCl$_3$): $\delta$ 1.59-1.86 (m, 4H, SnCH$_2$), 2.10-2.20 (m, 2H, SnCH$_2$CH$_2$), 2.20 (s, 18H, CH$_3$COO). $^{13}$C NMR (d$_8$-toluene): $\delta$ 15.90, 16.28, 26.98, 175.26 (C=O). $^{119}$Sn NMR (d$_8$-toluene): $\delta$ –532.7 [$^4J(^{119}$Sn-$^{117}$Sn) = 961 Hz]. Anal. Calcd. for C$_{15}$H$_{24}$O$_{12}$Sn$_2$: C, 28.4; H, 3.8. Found: C, 28.6; H, 3.6. 130c was dissolved in a mixture of CHCl$_3$/hexane (3:1) (150 ml) and exposed to air moisture for 2 days. The solvent was removed in vacuo to afford a yellow oil 130c'. $^{119}$Sn NMR (toluene): $\delta$ –499.8 (integral 18.0 %), –517.1 (integral 18.0 %), –525.7 (integral 19.0 %), –543.7 (integral 15.0 %), –584.6 (integral 30.0 %). Further exposure of 130c' to air moisture afforded a glass-like solid 130c''. m.p. > 150 °C (decomp.). Anal. Calcd. for C$_7$H$_{16}$O$_8$Sn$_2$: C, 18.0; H, 3.5. Found: C, 18.5; H, 3.8.

1,3-Bis[tris(chloroacetato)stannyl]propane [(ClCH$_2$CO$_2$)$_3$Sn]$_2$(CH$_2$)$_3$ (131c). Compound 131c was prepared from 94c (3.00 g, 4.04 mmol) and chloroacetic acid (2.48 g, 26.3 mmol) and was obtained as a yellow viscous oil. The resulting yellow oil was stirred for 12 h with CH$_2$Cl$_2$ (100 ml) under the exclusion of air moisture affording a white suspension, which appeared to be completely insoluble. Stirring the white suspension for a further 3 h under the influence of air moisture resulted in a clear solution. The solvent was removed in vacuo to afford a yellowish solid (2.99 g, 88 %). m.p. 248-268 °C (Lit. m. p. 250-270 °C). $^1$H NMR (CDCl$_3$): $\delta$ 1.21-2.89 (m, 6H, CH$_2$CH$_2$CH$_2$), 4.17 (s, 8H, CH$_2$Cl). $^{119}$Sn NMR (CDCl$_3$): $\delta$ –497.6 (s, integral 23 %), –520.8 (s, integral 27 %), –549.8 (s, integral 25 %), –591.3 (s, integral 25 %). Anal. Calcd. for C$_{15}$H$_{18}$Cl$_6$O$_{12}$Sn$_2$: C, 21.4; H, 2.2. Found: C, 21.2; H, 2.3.

1,4-Bis[tris(benzoate)stannyl]butane [(C$_6$H$_5$CO$_2$)$_3$Sn]$_2$(CH$_2$)$_4$ (128d). Compound 128d was prepared from 94d (3.00 g, 3.97 mmol) and benzoic acid (3.15 g, 25.8 mmol) and was obtained as a white solid (3.73 g, 92 %). $^1$H NMR (CDCl$_3$): $\delta$ 1.56-1.87 (m, 4H, SnCH$_2$), 2.10-2.26 (m, 4H, SnCH$_2$CH$_2$), 7.45-8.10 (m, 30H, C$_6$H$_5$COO). $^{13}$C NMR (d$_8$-toluene): $\delta$ 21.10, 32.00, 128.74, 131.42, 134.06, 137.52, 178.18 (C=O). $^{119}$Sn NMR (d$_8$-toluene): $\delta$ –532.7. Anal. Calcd. for C$_{46}$H$_{38}$O$_{12}$Sn$_2$: C, 54.2; H, 3.8. Found: C, 54.4; H, 3.5. 128d was dissolved in a mixture of CHCl$_3$/hexane (3:1) (150 ml) and exposed to air moisture for 3 days. The solvent was removed in vacuo to afford a yellow oil 128d'. $^{119}$Sn NMR (toluene): $\delta$ –507.5 (integral 16.0 %), –508.5 (integral 16.0 %), –530.6 (integral 18.0 %), –532.2 (integral 14.0 %), –619.5 (integral 36.0 %). Further exposure of 128d' to air moisture afforded a white solid 128d''. m.p. > 310 °C (decomp.). IR (KBr) v(CO$_2$):
1,4-Bis[tris(cyclohexanooate)stannyl]butane [(C\textsubscript{6}H\textsubscript{11}CO\textsubscript{2})\textsubscript{3}Sn]\textsubscript{2}(CH\textsubscript{2})\textsubscript{4} (129d). Compound 129d was prepared from 94d (3.00 g, 3.97 mmol) and cyclohexanecarboxylic acid (3.31 g, 25.8 mmol) and was obtained as a yellow viscous oil (3.44 g, 82 %). \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \( \delta 1.24-2.56 \) (m, 74H). \textsuperscript{13}C NMR (\textit{d}\textsubscript{6}-toluene): \( \delta 20.82, 25.70, 26.34, 29.70, 31.47, 41.90, 186.10 \) (C=O). \textsuperscript{119}Sn NMR (\textit{d}\textsubscript{8}-toluene): \( \delta -537.0 \) [\( J^{(119}\text{Sn}-117\text{Sn}) = 886 \) Hz]. Anal. Calcd. for C\textsubscript{46}H\textsubscript{74}O\textsubscript{12}Sn\textsubscript{2}: C, 52.3; H, 7.1. Found: C, 52.4; H, 7.0. 129d was dissolved in a mixture of CH\textsubscript{3}Cl/hexane (3:1) (150 ml) and exposed to air moisture for 4 days. The solvent was removed \textit{in vacuo} to afford a yellow oil 129d'. \textsuperscript{119}Sn NMR (toluene): \( \delta -510.3 \) (integral 23.0 %), \( -530.0 \) (integral 13.0 %), \( -551.8 \) (integral 36.0 %), \( -573.5 \) (integral 3.0 %), \( -650.3 \) (integral 24.0 %). Further exposure of 129d' to air moisture afforded a white solid 129d''. m.p. > 310 °C (decomp.). Anal. Calcd. for C\textsubscript{32}H\textsubscript{54}O\textsubscript{10}Sn\textsubscript{2}: C, 46.0; H, 6.5. Found: C, 47.0; H, 6.8.

1,4-Bis[tris(acetato)stannyl]butane [(CH\textsubscript{3}CO\textsubscript{2})\textsubscript{3}Sn]\textsubscript{2}(CH\textsubscript{2})\textsubscript{4} (130d). Compound 130d was prepared from 94d (3.00 g, 3.97 mmol) and a mixture of acetic acid/acetic anhydride (3/1) (1.55 g, 25.8 mmol) and was obtained as a yellow solid (2.06 g, 80 %). \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \( \delta 1.58-1.80 \) (m, 4H, SnCH\textsubscript{2}), \( 2.14-2.24 \) (m, 4H, SnCH\textsubscript{2}CH\textsubscript{2}), \( 2.35 \) (s, 18H, CH\textsubscript{3}COO). \textsuperscript{13}C NMR (\textit{d}\textsubscript{8}-toluene): \( \delta 15.89, 16.24, 26.96, 175.20 \) (C=O). \textsuperscript{119}Sn NMR (\textit{d}\textsubscript{8}-toluene): \( \delta -528.1 \). Anal. Calcd. for C\textsubscript{16}H\textsubscript{26}O\textsubscript{12}Sn\textsubscript{2}: C, 29.7; H, 4.0. Found: C, 29.5; H, 4.2. 130d was dissolved in a mixture of CHCl\textsubscript{3}/hexane (3:1) (150 ml) and exposed to air moisture for 2 days. The solvent was removed \textit{in vacuo} to afford a yellow oil 130d'. \textsuperscript{119}Sn NMR (toluene): \( \delta -501 \) (integral 18.0 %), \( -517.1 \) (integral 18.0 %), \( -525.7 \) (integral 29.0 %), \( -553.7 \) (integral 15.0 %), \( -590.6 \) (integral 20.0 %). Further exposure of 130d' to air moisture afforded a glass-liked solid 130d''. m.p. > 150 °C (decomp.). Anal. Calcd. for C\textsubscript{8}H\textsubscript{18}O\textsubscript{8}Sn\textsubscript{2}: C, 20.0; H, 3.8. Found: C, 18.9; H, 4.0.

1,4-Bis[tris(chloroacetato)stannyl]butane [(ClCH\textsubscript{2}CO\textsubscript{2})\textsubscript{3}Sn]\textsubscript{2}(CH\textsubscript{2})\textsubscript{4} (131d). Compound 131d was prepared from 94d (3.00 g, 3.97 mmol) and chloroacetic acid (2.44 g, 25.8 mmol) and was obtained as a yellow solid (2.88 g, 85 %). \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \( \delta 1.21-1.67 \) (m, 4H, SnCH\textsubscript{2}), \( 2.08-2.40 \) (m, 4H, SnCH\textsubscript{2}CH\textsubscript{2}), \( 4.17 \) (s, 12H, CH\textsubscript{2}ClCOO). \textsuperscript{13}C NMR (\textit{d}\textsubscript{8}-toluene): \( \delta 21.08, 31.80, 128.70, 131.40, 134.00, 137.50, 178.14 \) (C=O). \textsuperscript{119}Sn NMR (\textit{d}\textsubscript{8}-toluene): \( \delta -531.4 \). Anal. Calcd. for C\textsubscript{16}H\textsubscript{26}O\textsubscript{12}Cl\textsubscript{6}Sn\textsubscript{2}: C, 22.5; H, 2.4. Found: C, 22.7; H, 2.2. 131d was dissolved in a mixture of
CHCl$_3$/hexane (3:1) (150 ml) and exposed to air moisture for 3 days. The solvent was removed *in vacuo* to afford a yellow oil 131d'. $^{119}$Sn NMR (toluene): $\delta$ −504.3 (integral 19.0 %), −504.7 (integral 15.0 %), −531.9 (integral 19.0 %), −532.5 (integral 15.0 %), −614.3 (integral 12.0 %), −618.3 (integral 20.0 %) Further exposure of 130d' to air moisture afforded a yellow solid 131d''. m.p. 280-284 °C.
References


References


References


References


