The First Spacer-Bridged Tetraorganodistannoxanes with a Mixed Double Ladder Structure[‡]

Michael Mehring,[a] Ingo Paulus,[a] Bernhard Zobel,[a] Markus Schürmann,[a]
Klaus Jurkschat,*[a] Andrew Duthie,[b] and Dainis Dakternieks*[b]

Keywords: Tin / Distannoxanes / Oxo complexes / Electrospray mass spectrometry

The reaction of $Me_3SiCH_2Cl_2Sn(CH_2)_3SnCl_2Ph$ (**6**) with $(tBu_2SnO)_3$ gave a statistical mixture of the corresponding tetraorganodistannoxanes whereas the reaction of the spacer-bridged ditin tetrachlorides $RCl_2Sn(CH_2)_4SnCl_2R$ (**3**, R = Me_3CCH_2; **4**, R = Me_2CHCH_2; **10**, R = Me_3SiCH_2) with the polymeric spacer-bridged ditin oxides $[R(O)Sn(CH_2)_4Sn(O)R]_n$ (**7**, R = Me_2CHCH_2; **8**, R = Me_3CCH_2; **11**, R = Me_3SiCH_2) provided the mixed double ladder compounds $\{[R(Cl)Sn(CH_2)_4Sn(Cl)R][R'(Cl)Sn(CH_2)_4Sn(Cl)R']O_2\}_2$ (**9**, R = Me_3CCH_2, R′ = Me_2CHCH_2; **12**, R = Me_3CCH_2, R′ = Me_3SiCH_2) in almost quantitative yield. In solution, **9** and **12** are in equilibrium with their corresponding dimers, as was evidenced by ^{119}Sn NMR spectroscopy, molecular mass determination, and electrospray mass spectrometry. The molecular structures of **9** and **12** were established by single crystal X-ray diffraction.

Introduction

Currently, there is much interest in dimeric tetraorganodistannoxanes $[R_2(X)SnOSn(X)R_2]_2$ (X = halogen, OH, $R'CO_2$, NCS; R, R′ = alkyl, aryl)[1−5] since these compounds are reported to be efficient homogeneous catalysts in various organic reactions such as transesterification under virtually neutral conditions,[6] highly selective acylation of alcohols,[7] urethane formation,[8] and alkyl carbonate synthesis.[9] X-ray crystallography has illustrated the dimeric nature of a large number of tetraorganodistannoxanes and NMR spectroscopic studies show that this structural arrangement is retained in solution.[1−5] However, only a few examples of monomeric species for both solution and in the solid state have been reported.[2,4,10−13]

In contrast to the symmetrically substituted tetraorganodistannoxanes, unsymmetrically substituted ones, such as $[Bu_2(X)SnOSn(Y)Bu_2]_2$ (X = O_2CMe, Cl, OPh, OMe; Y = Cl, OPh, OMe),[2,4] $[tBu_2(Cl)SnOSn(Cl)R_2]_2$ (R = Me, Et, *i*Pr, *n*Bu),[14] $[tBu_2(OH)SnOSn(Cl)R_2]_2$ (R = *n*Bu, cyclohexyl),[14,15] $[Ph_2(Cl)SnOSn(OH)Ph_2]_2·2(CH_3)_2CO$[16] and $Et_2BrSnOSnBrPr_2$[17] have attracted less attention and only four of these compounds have been characterized by X-ray crystallography.[14−16]

For some time we have been interested in the synthesis, structure, and catalytic activity of the spacer-bridged tetraorganodistannoxanes $\{[R(X)Sn-Z-Sn(X)R]O\}_n$ [X = Cl, F, OH, OAc; R = alkyl; Z = $(CH_2)_3$, $(CH_2)_4$, $CH_2SiMe_2CH_2$, $CH_2SiMe_2CCSiMe_2CH_2$].[18−21] In the solid state, these compounds exhibit either a dimeric (*n* = 2) or a double ladder structure (*n* = 4). Furthermore, the first triple ladder $\{[R(Cl)Sn(CH_2)_3Sn(Cl)(CH_2)_3Sn(Cl)R]O_{1.5}\}_4$ (R = Me_3SiCH_2) was reported, in which three $Sn_4Cl_4O_2$ layers are connected through trimethylene bridges.[22] The most convenient synthetic methodologies for the preparation of compounds of the type $\{[R(Cl)Sn-Z-Sn(Cl)R]O\}_n$ (*n* = 2, 4) are (i) the reaction of a spacer-bridged ditin tetrachloride $RCl_2Sn-Z-SnCl_2R$ with $(tBu_2SnO)_3$ as the oxygen transfer reagent and (ii) the reaction of a spacer-bridged ditin tetrachloride with the corresponding spacer-bridged polymeric ditin oxide $[R(O)Sn-Z-Sn(O)R]_n$.

In solution, most of the spacer-bridged distannoxanes retain their solid-state structure, but in the cases of Z = $(CH_2)_4$ and X = Cl, OAc, and Z = $(CH_2)_3$ and X = OAc, equilibria between dimers and tetramers have been observed. These kinetically labile species show higher catalytic activity in acylation reactions than the kinetically more inert double ladder compounds.[18]

Here we report our attempts to prepare mixed tetraorganodistannoxanes and present the X-ray single crystal structure analyses of $\{[R(Cl)Sn(CH_2)_4Sn(Cl)R][R'(Cl)Sn(CH_2)_4Sn(Cl)R']O_2\}_2$ (**9**, R = Me_3CCH_2, R′ = Me_2CHCH_2; **12**, R = Me_3CCH_2, R′ = Me_3SiCH_2), the first mixed double ladders containing two different organic groups R and R′.

Results and Discussion

The unsymmetrically substituted ditin precursor $Me_3SiCH_2Cl_2Sn(CH_2)_3SnCl_2Ph$ (**6**) was prepared by reac-

---

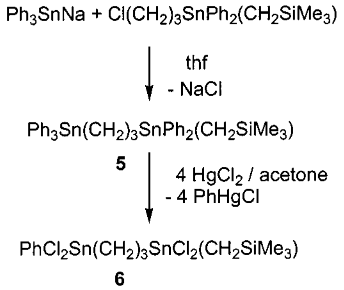
[‡] This work contains parts of the Diploma thesis of M. Mehring, Dortmund University, 1995, and of the planned Ph. D. thesis of I. Paulus.

[a] Lehrstuhl für Anorganische Chemie II der Universität Dortmund,
44221 Dortmund, Germany,
Fax: (internat.) + 49-(0)231/755-5048,
E-mail: kjur@platon.chemie.uni-dortmund.de

[b] Centre for Chiral and Molecular Technologies,
Deakin University,
Geelong, Victoria 3217, Australia

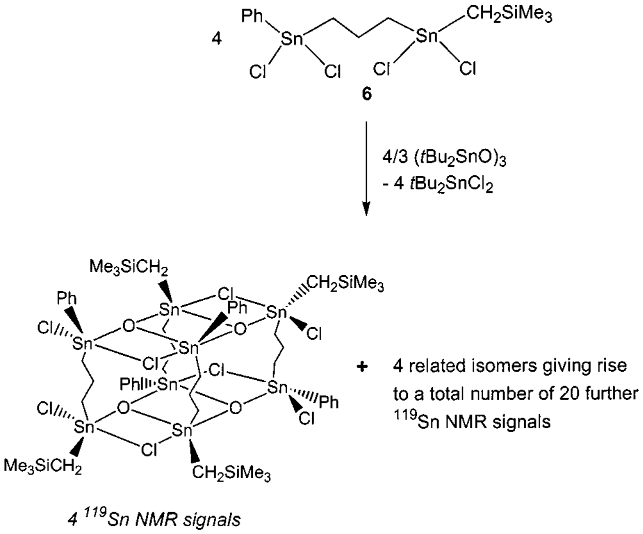
1434−1948/01/0101−0153 $ 17.50+.50/0

tion of Ph_3SnNa (**1**) with $Cl(CH_2)_3SnPh_2CH_2SiMe_3$[22] (**2**) to give $Me_3SiCH_2Ph_2Sn(CH_2)_3SnPh_3$ (**5**) which was converted into its tetrachloro-substituted derivative **6** by reaction with $HgCl_2$ (Scheme 1).



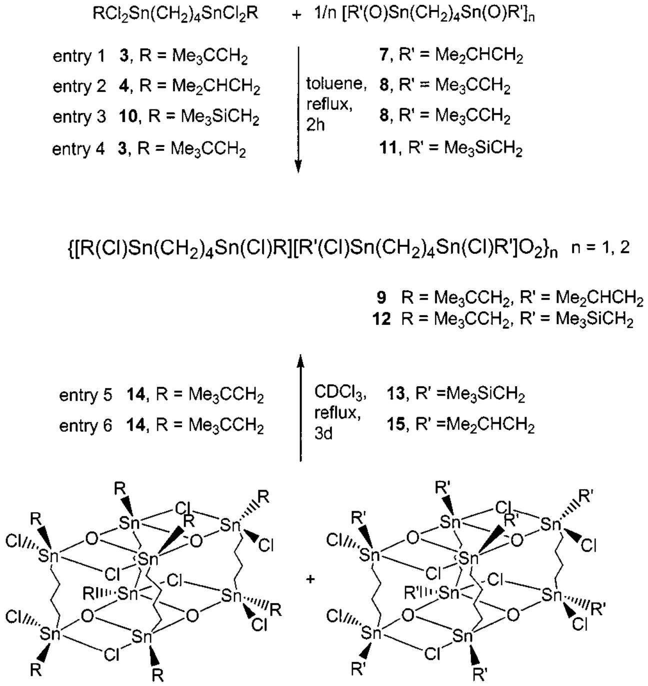
Scheme 1. Synthesis of the unsymmetrically substituted trimethylene-bridged ditin compound **6**

The reaction of compound **6** with one-third molar equivalent $(tBu_2SnO)_3$ gave a complex reaction mixture. The ^{119}Sn NMR spectrum of this mixture displayed 23 signals in the range of $\delta = -90$ to -210, in addition to the resonance at $\delta = 55$ (assigned to tBu_2SnCl_2). This is close to the 24 signals expected for a statistical distribution of 5 possible isomers with a double ladder arrangement (Scheme 2). It is most likely that the missing signal is superimposed with one of the 23 signals. Attempts to isolate a single isomer failed.



Scheme 2. Reaction of compound **6** with $(tBu_2SnO)_3$ giving a statistical mixture of double ladder isomers

However, the reaction of the spacer-bridged ditin tetrachloride $RCl_2Sn(CH_2)_4SnCl_2R$ (**3**, R = Me_3CCH_2) with the spacer-bridged ditin oxide $[R(O)Sn(CH_2)_4Sn(O)R]_n$ (**7**, R = Me_2CHCH_2), as well as the reaction of $RCl_2Sn(CH_2)_4SnCl_2R$ (**4**, R = Me_2CHCH_2) with $[R(O)Sn(CH_2)_4Sn(O)R]_n$ (**8**, R = Me_3CCH_2) in toluene resulted in the almost quantitative formation of the mixed double ladder compound $\{[R(Cl)Sn(CH_2)_4Sn(Cl)R][R'(Cl)Sn(CH_2)_4Sn(Cl)R']O_2\}_2$ (**9**, R = Me_3CCH_2, R′ = Me_2CHCH_2) (Scheme 3). Analogously, the reactions of $RCl_2Sn(CH_2)_4SnCl_2R$ (**10**, R = Me_3SiCH_2) with $[R(O)Sn(CH_2)_4Sn(O)R]_n$ (**8**, R = Me_3CCH_2), and $RCl_2Sn(CH_2)_4SnCl_2R$ (**3**, R = Me_3CCH_2) with $[R(O)Sn(CH_2)_4Sn(O)R]_n$ (**11**, R = Me_3SiCH_2), gave $\{[R(Cl)Sn(CH_2)_4Sn(Cl)R][R'(Cl)Sn(CH_2)_4Sn(Cl)R']O_2\}_2$ (**12**, R = Me_3CCH_2, R′ = Me_3SiCH_2) in almost quantitative yield. The mixed double ladder compounds **9** and **12** were also formed by mixing equimolar amounts of the symmetrically substituted double ladders $\{[R(Cl)Sn(CH_2)_4Sn(Cl)R]O\}_4$, **14** (R = Me_3CCH_2) and **15** (R = Me_2CHCH_2), and **13** (R = Me_3SiCH_2) and **14** (R = Me_3CCH_2), respectively, as was shown by ^{119}Sn NMR experiments in $CHCl_3/CDCl_3$ (Scheme 3). After 2 h of heating at reflux, a complex mixture of different double ladders was observed, whereas after 3 d of heating at reflux, the conversion of the starting double ladders into the mixed ones **9** and **12**, was complete. In contrast to the tetramethylene-bridged double ladders reported here the trimethylene-bridged double ladders $\{[R(Cl)Sn(CH_2)_3Sn(Cl)R]O\}_4$ are kinetically inert and do not show the formation of mixed double ladders.[23]



Scheme 3. Syntheses of the mixed tetramethylene-bridged tetraorganodistannoxanes **9** and **12**

The molecular structure of compounds **9** and **12** are shown in Figure 1 and Figure 2, respectively. Crystallographic data are given in Table 3 and selected geometrical parameters are listed in Table 1. The compounds **9** and **12** form centrosymmetric tetramers in which two $Sn_4Cl_4O_2$ units are linked through four tetramethylene bridges giving a double ladder arrangement. The $Sn_4Cl_4O_2$ layer is almost planar with the greatest deviation from the plane for Cl(2) [0.232(2) Å] in **9** and Cl(3) [0.360(2) Å] in **12**. Each tin atom has a distorted trigonal-bipyramidal geometry. For the exocyclic tin atoms, two carbon atoms and one oxygen atom occupy the equatorial positions and two chlorine atoms the axial positions, while for the endocyclic tin atoms the equat-

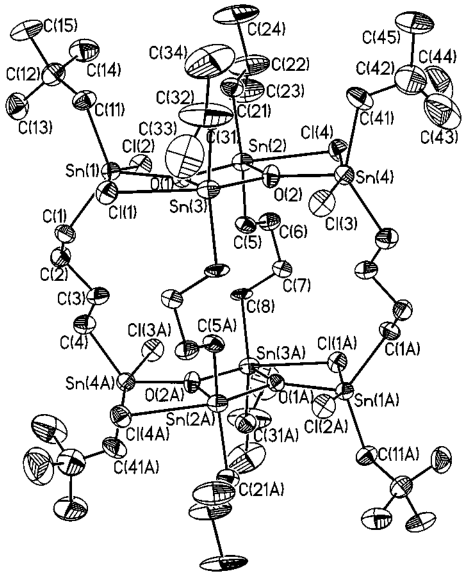


Figure 1. General view (SHELXTL-Plus) of **9** showing 30% probability displacement ellipsoids and the atom numbering scheme (symmetry transformations used to generate equivalent atoms: *a* = $-x + 1$, $-y$, $-z - 1$)

orial positions are occupied by two carbon atoms and one oxygen atom and the axial positions by one oxygen atom and one chlorine atom. In both structures the neopentyl groups Me_3CCH_2 are attached to the exocyclic tin atoms, and the isobutyl groups Me_2CHCH_2 (in **9**) and the trimethylsilylmethyl groups Me_3SiCH_2 (in **12**) are bound to the

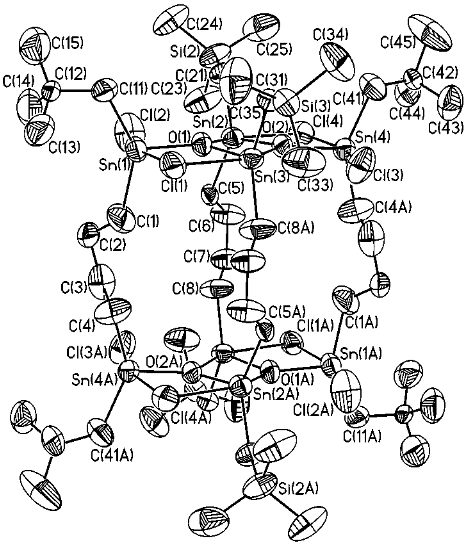


Figure 2. General view (SHELXTL-Plus) of **12** showing 30% probability displacement ellipsoids and the atom numbering scheme (symmetry transformations used to generate equivalent atoms: *a* = $-x + 1$, $-y$, $-z - 1$)

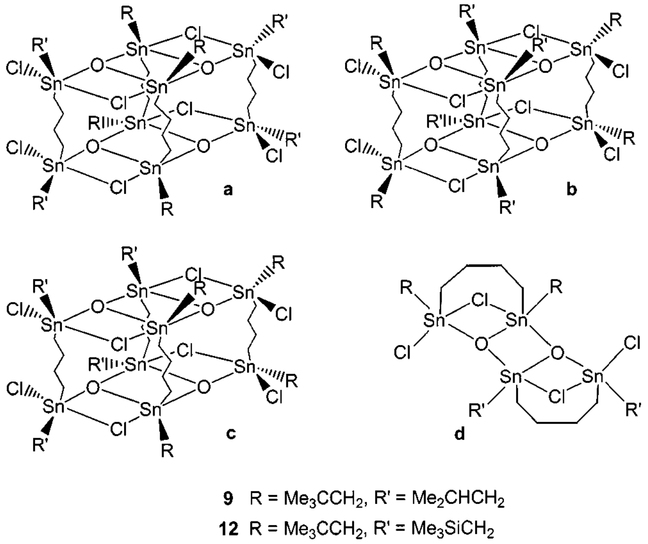
endocyclic ones. The bond lengths and bond angles (Table 1) correspond to those of previously described ladder[14] and double ladder structures.[18,19] The Sn−O bond lengths for the exocyclic tin atoms, Sn(1)−O(1) and Sn(4)−O(2), are 2.021(5) and 2.017(5) Å, respectively, for **9**, and 2.017(3) and 2.009(3) Å, respectively, for **12**. In the four-membered Sn_2O_2 ring the Sn−O bonds are somewhat

Table 1. Selected bond lengths [Å] and angles [°] for **9** and **12**

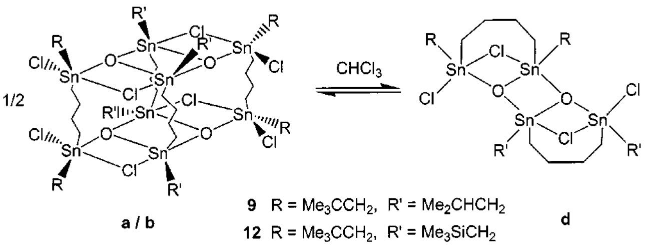
	9	12		9	12
Sn(1)−O(1)	2.021(5)	2.017(3)	Sn(3)−O(1)	2.065(5)	2.052(3)
Sn(1)−Cl(1)	2.809(2)	2.751(2)	Sn(3)−O(2)	2.134(5)	2.140(3)
Sn(1)−Cl(2)	2.434(2)	2.478(2)	Sn(3)−Cl(1)	2.686(2)	2.752(2)
Sn(2)−O(1)	2.125(5)	2.127(3)	Sn(3)−Cl(3)	3.326(3)	3.272(2)
Sn(2)−O(2)	2.051(5)	2.058(3)	Sn(4)−O(2)	2.017(5)	2.009(3)
Sn(2)−Cl(2)	3.320(2)	3.248(2)	Sn(4)−Cl(3)	2.488(2)	2.474(2)
Sn(2)−Cl(4)	2.760(2)	2.724(2)	Sn(4)−Cl(4)	2.733(2)	2.760(2)
O(1)−Sn(1)−C(1)	120.5(3)	106.2(2)	C(31)−Sn(3)−C(8)	144.4(3)	144.5(3)
O(1)−Sn(1)−C(11)	109.6(3)	114.8(2)	O(1)−Sn(3)−Cl(1)	77.3(1)	76.0(1)
C(1)−Sn(1)−C(11)	123.5(3)	136.7(3)	C(31)−Sn(3)−Cl(1)	89.5(3)	88.1(2)
O(1)−Sn(1)−Cl(2)	86.3(2)	85.5(1)	O(2)−Sn(3)−Cl(1)	151.1(1)	150.4(1)
C(11)−Sn(1)−Cl(2)	107.3(3)	96.5(2)	C(8)−Sn(3)−Cl(1)	93.7(2)	92.2(2)
C(1)−Sn(1)−Cl(2)	100.6(2)	99.9(3)	O(2)−Sn(3)−C(8)	97.4(3)	96.0(2)
O(1)−Sn(1)−Cl(1)	75.0(2)	76.5(1)	O(2)−Sn(4)−C(41)	104.3(3)	110.3(2)
C(11)−Sn(1)−Cl(1)	85.4(2)	90.9(2)	O(2)−Sn(4)−C(4)	118.4(3)	109.7(3)
C(1)−Sn(1)−Cl(1)	84.0(2)	85.6(3)	C(41)−Sn(4)−C(4)	136.3(4)	137.9(3)
Cl(2)−Sn(1)−Cl(1)	160.3(1)	162.0(1)	O(2)−Sn(4)−Cl(3)	86.6(2)	85.0(1)
O(2)−Sn(2)−C(5)	107.1(3)	114.9(4)	C(41)−Sn(4)−Cl(3)	95.7(3)	96.4(2)
O(2)−Sn(2)−C(21)	109.6(3)	109.1(2)	C(4)−Sn(4)−Cl(3)	95.3(2)	99.7(3)
C(5)−Sn(2)−C(21)	142.1(3)	135.5(5)	O(2)−Sn(4)−Cl(4)	76.9(2)	76.4(1)
O(2)−Sn(2)−O(1)	74.6(2)	74.6(1)	C(41)−Sn(4)−Cl(4)	90.2(3)	91.0(2)
C(5)−Sn(2)−O(1)	99.5(3)	98.0(5)	C(4)−Sn(4)−Cl(4)	91.1(2)	85.9(3)
C(21)−Sn(2)−O(1)	98.8(3)	99.6(2)	Cl(3)−Sn(4)−Cl(4)	163.4(1)	161.3(1)
O(2)−Sn(2)−Cl(4)	75.7(2)	76.5(1)	Sn(1)−Cl(1)−Sn(3)	82.5(1)	82.0(1)
C(5)−Sn(2)−Cl(4)	89.5(2)	95.2(4)	Sn(2)−Cl(4)−Sn(4)	82.2(1)	82.2(1)
C(21)−Sn(2)−Cl(4)	90.7(3)	88.6(2)	Sn(1)−O(1)−Sn(3)	125.0(2)	125.0(1)
O(1)−Sn(2)−Cl(4)	150.3(1)	151.1(1)	Sn(1)−O(1)−Sn(2)	128.4(2)	128.2(2)
O(1)−Sn(3)−C(31)	109.9(3)	109.6(2)	Sn(3)−O(1)−Sn(2)	105.5(2)	105.6(2)
O(1)−Sn(3)−O(2)	74.1(2)	74.5(1)	Sn(4)−O(2)−Sn(2)	125.2(3)	124.7(2)
C(31)−Sn(3)−O(2)	96.6(3)	101.1(2)	Sn(4)−O(2)−Sn(3)	129.0(3)	129.8(2)
O(1)−Sn(3)−C(8)	105.4(3)	104.9(3)	Sn(2)−O(2)−Sn(3)	105.7(2)	104.9(2)

lengthened, with the longest bonds found for Sn(2)−O(1) [2.125(5) Å] and Sn(3)−O(2) [2.134(5) Å] (**9**), and for Sn(2)−O(1) [2.127(3) Å] and Sn(3)−O(2) [2.140(3) Å] (**12**). Two of the chlorine atoms of each monolayer form Sn−Cl−Sn bridges [Sn(1)−Cl(1)−Sn(3) 82.5(1)° (**9**), 82.0(1)° (**12**), Sn(2)−Cl(4)−Sn(4) 82.2(1)° (**9**), 82.2(1)° (**12**)], with Sn(1)−Cl(1), Sn(3)−Cl(1), Sn(4)−Cl(4) and Sn(2)−Cl(4) bond lengths of 2.809(2), 2.686(2), 2.733(2), and 2.760(2) Å (**9**), respectively, and 2.751(2), 2.752(2), 2.760(2), and 2.724(2) Å (**12**), respectively. The chlorine atoms Cl(2) and Cl(4) can be regarded as non-bridging, although the Sn(2)−Cl(2) [3.320(2) Å (**9**), 3.248 (2) Å (**12**)] and Sn(3)−Cl(3) [3.326(3) Å (**9**), 3.272 (2) Å (**12**)] distances are shorter than the sum of the van der Waals radii of tin and chlorine (3.97 Å).[24] The Sn(1)−Cl(2) and Sn(4)−Cl(3) bond lengths are 2.434(2) and 2.488(2) Å (**9**), respectively, and 2.478(2) and 2.474(2) Å (**12**), respectively, which are slightly longer than the Sn−Cl single bond length of 2.39 Å.[22]

An equilibrium between tetrameric double ladder structures (n = 4) and dimers (n = 2) has been previously reported for $CHCl_3$ solutions of the tetramethylene-bridged tetraorganodistannoxanes $\{[R(Cl)Sn(CH_2)_4Sn(Cl)R]O\}_n$ (**13**, R = Me_3SiCH_2; **14**, R = Me_3CCH_2; **15**, Me_2CHCH_2), which showed degrees of association with n = 3.9, 2.3, and 2.5, respectively.[18] The molecular mass determination of **9** in $CHCl_3$ showed M = 1639 g mol^{-1} (c = 20 mg mL^{-1}), which is indicative of the existence in solution of an equilibrium between double ladder structures (**9a−c**) (calcd. for **9a−c**: M = 2035 g mol^{-1}) and the dimer **9d** (calcd. for **9d**: M = 1018 g mol^{-1}) (Scheme 4). Compound **12** has a molecular mass M = 1191 g mol^{-1} (c = 20 mg mL^{-1}) in $CHCl_3$, showing that the dimer **12d** (calcd. for **12d**: M = 1077 g mol^{-1}) dominates at this concentration (Scheme 4). The molecular mass of **12** increases at higher concentration (M = 1689 g mol^{-1}, c = 145 mg mL^{-1}), showing that the equilibrium is shifted towards formation of double ladders **12a−c** (calcd. for **12a−c**: M = 2155 g mol^{-1}) (Scheme 5).



Scheme 4



Scheme 5. Dimer-tetramer equilibrium in solutions of **9** (R = Me_3CCH_2, R′ = Me_2CHCH_2) and **12** (R = Me_3CCH_2, R′ = Me_3SiCH_2)

The ^{119}Sn NMR spectroscopic data in $CDCl_3$ of the mixed double ladders **9** and **12**, and of the related simple double ladders **13−15** are given in Table 2. A solution of crystalline **9** in toluene shows two pairs of signals of equal integral ratio at δ = −85.2 (26%)/−148.5 (27%) and at δ = −86.4 (15%)/−147.9 (15%) which are assigned with caution to **9a** and **9b**. The resonances at δ = −78.7 (5%),−150.2 (5%), and −85.4 (4%),−152.7 (3%) are assigned with caution to one of the two possible isomers of the dimer **9d**, but we were not able to discriminate the *cis* and the *trans* isomer. In principal, these signals could also be assigned to the tetramer **9c** (Scheme 4), for which four signals of equal integral ratio are expected. However, the molecular mass determination of a solution of **9** in $CHCl_3$ is indicative of an equilibrium between tetramers and dimers, and thus we assign the four signals to the dimer **9d** rather than to the tetramer **9c**. In $CDCl_3$ solution, **9** displays two signals of equal integral ratio at δ = −83.0 (36%) and δ = −145.2 (35%) which are assigned to **9a** and/or **9b,** and three signals for the dimer **9d** [δ = −78.2 (7%), −84.2 (7%), −144.4 (14%)]. The missing signal is likely to be superimposed with the signal at δ = −144.4. Furthermore, one signal of minor intensity was observed at δ = −146.9 (1%).

Table 2. ^{119}Sn NMR spectroscopic data in $CDCl_3$ for compounds of the type $\{[R(Cl)Sn(CH_2)_4Sn(Cl)R][R'(Cl)Sn(CH_2)_4Sn(Cl)R']O_2\}_2$; chemical shifts are given in δ values and coupling constants [$^2J(^{119}Sn-O-^{119/117}Sn)$] in Hz

		Sn_{exo}		Sn_{endo}	
9	R = Me_3CCH_2	−78.2 [74]	7%	−144.4 [66]	14%
	R′ = Me_2CHCH_2	−84.2 [57]	7%		
		−83.0 [61]	36%	−145.2 [70]	35%
				−146.9	1%
12	R = Me_3CCH_2	−68.5	5%	−144.9	5%
	R′ = Me_3SiCH_2	−83.8	5%		
		−70.6	1%	−143.2	2%
		−85.6	1%		
		−84.5 [64]	27%	−140.7 [64]	33%
		−87.0 [60]	11%	−139.5 [62]	10%
13	R = R′ = Me_3SiCH_2	−66.7	50%	−137.3	50%
14	R = R′ = Me_3CCH_2	−83.1	25%	−146.8	25%
		−85.4	25%	−147.3	25%
15	R = R′ = Me_2CHCH_2	−78.7 [62]	8%	−143.1 [70]	8%
		−79.1 [66]	42%	−144.8 [61]	42%

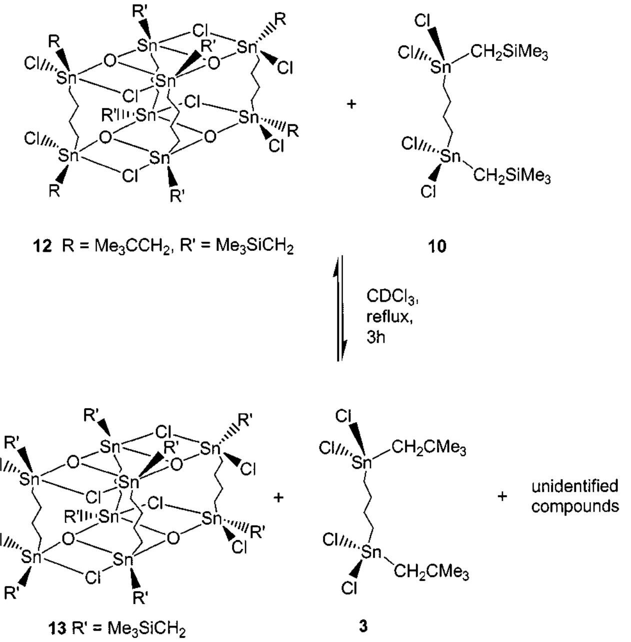
The ^{119}Sn NMR spectrum of **12** in toluene shows two pairs of signals of equal integral ratio at δ = −83.8 (23%)/−145.5 (23%) and at δ = −86.9 (11%)/−144.3 (12%), which are assigned with caution to the tetramers **12a** and **12b**

(Scheme 4). Furthermore, two sets of four signals are observed at $\delta = -68.8$ (5%), -83.3 (5%), -146.2 (5%), and -149.4 (5%) and at $\delta = -71.3$ (2%), -85.4 (3%), -143.0 (3%), and -147.9 (3%), which are assigned to the *cis* and *trans* isomer of **12d** (Scheme 4). The ^{119}Sn NMR spectroscopic experiments of **12** in $CDCl_3$ at concentrations of $c = 145$ mg mL^{-1} and $c = 290$ mg mL^{-1} gave similar results: The tetramers **12a** and **12b** are characterized by two sets of signals at -84.5 (27%)/-140.7 (33%) and at $\delta = -87.0$ (11%)/-139.5 (10%). It is most likely that the signal at $\delta = -140.7$ is superimposed with two resonances of the corresponding dimer. This assumption is supported by the observation of only six additional resonances at $\delta = -68.5$ (5%), -70.6 (1%), -83.8 (5%), -85.6 (1%), -143.2 (2%), and -144.9 (5%) for the *cis* and the *trans* isomer of the dimer **12d** instead of the expected eight signals.

On the basis of the ^{119}Sn NMR spectroscopic experiments in $CDCl_3$ at $c = 145$ mg mL^{-1} the dimer/tetramer ratio of **12** was estimated to be approximately 1:1, which is in accordance with the molecular mass determination at the same concentration. It is worth noting that signals of the symmetrically substituted double ladders **13–15** are not detected in the ^{119}Sn NMR spectra of analytically pure **9** or **12**.

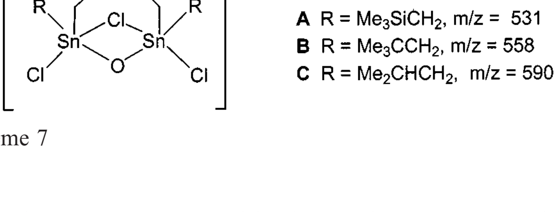
The structure of the double ladders can formally be divided into a spacer-bridged organostannoxane core to which two spacer-bridged ditin tetrachlorides $RCl_2Sn(CH_2)_4SnCl_2R$ are coordinated. The addition of $RCl_2Sn(CH_2)_4SnCl_2R$ (**10**, R = Me_3SiCH_2) to a solution of **12** in a 1:1 molar ratio gave a partial exchange (Scheme 6). The ^{119}Sn NMR spectrum in $CDCl_3$ shows the signals of the starting materials $RCl_2Sn(CH_2)_4SnCl_2R$ (**10**, R = Me_3SiCH_2) and **12**, a resonance at $\delta = -113.0$ assigned to $RCl_2Sn(CH_2)_4SnCl_2R$ (**3**, R = Me_3CCH_2), two resonances at $\delta = -67.7$ and -138.4 assigned to the simple double ladder **13**, and additional resonances at $\delta = -85.7$, -100 ($W_{1/2} = 600$ Hz), and -147 ($W_{1/2} = 600$ Hz), for which no assignment is made.

In the case of the trimethylene-bridged double ladder $\{[R(Cl)Sn(CH_2)_3Sn(Cl)R]O\}_4$ (R = Me_3SiCH_2), no exchange was observed upon addition of a trimethylene-bridged ditin tetrachloride $RCl_2Sn(CH_2)_3SnCl_2R$ (R = Me_3CCH_2), which hints at the higher kinetic stability of the former compound compared with the tetramethylene-bridged double ladders.



Scheme 6. Reaction of the mixed tetramethylene-bridged tetraorganodistannoxane **12** with the tetramethylene-bridged ditin tetrachloride **10**

The electrospray mass spectra of **9** and **12**, in acetonitrile/dichloromethane solution (9:1), show cluster patterns that are consistent with the species formed by ionization of dimers as well as of tetrameric double ladder compounds. The negative ion ESMS spectrum of **9** shows a cluster pattern which is centered at $m/z = 2040$ and which is assigned to the major species $[\mathbf{9a{-}c} + Cl]^-$ (calcd. $m/z = 2071$), $[\mathbf{9a{-}c} + OH]^-$ (calcd. $m/z = 2051$), and $[\mathbf{9a{-}c} - Cl + 2\ OH]^-$ (calcd. $m/z = 2033$). Compound **12** shows a similar cluster pattern centered at $m/z = 2170$ which is indicative of the species $[\mathbf{12a{-}c} + Cl]^-$ (calcd. $m/z = 2191$), $[\mathbf{12a{-}c} + OH]^-$ (calcd. $m/z = 2173$), and $[\mathbf{12a{-}c} - Cl + 2\ OH]^-$ (calcd. $m/z = 2153$). Species corresponding to the symmetrically substituted double ladders $\{[R(Cl)Sn(CH_2)_4Sn(Cl)R]O\}_4$ (**13**, R = Me_3SiCH_2; **14**, R = Me_3CCH_2; **15**, R = Me_2CHCH_2) were not observed, which, in accordance with the NMR spectroscopic experiments discussed above, shows that there is no equilibrium between mixed double ladders and symmetrically substituted double ladders. In the ESMS spectrum of **9** and **12**, additional cluster patterns are observed which are centered at $m/z = 1032$ and $m/z = 1105$, respectively. These patterns are assigned to doubly charged species such as $[\mathbf{9a{-}c} + 2\ OH]^{2-}$ (calcd. $m/z = 1034$) and $[\mathbf{9a{-}c} - Cl + 3\ OH]^{2-}$ (calcd. $m/z = 1025$) and $[\mathbf{12a{-}c} + 2\ OH]^{2-}$ (calcd. $m/z = 1095$) and $[\mathbf{12a{-}c} + 2\ Cl]^{2-}$ (calcd. $m/z = 1113$), rather than to the corresponding anions of the dimers **9d** and **12d**. Nevertheless, we cannot exclude that the cluster patterns of the latter are superimposed by the patterns of the doubly charged species. There are also cluster patterns of low intensity at $m/z = 531$ and $m/z = 558$ (**9**), and $m/z = 558$ and $m/z = 590$ (**12**), which are consistent with the anions **A–C** (Scheme 7). The formation of **A–C** can be explained by the dissociation of the dimers **9d/12d** and the complexation of a chloride.



Scheme 7

In the ESMS spectra of both **9** and **12**, patterns of high intensity were observed, which are assigned to the complexes $[RCl_2Sn(CH_2)_4SnCl_2R + Cl]^-$ (**9**, R = Me_3CCH_2

with *m*/*z* = 613, Me_2CHCH_2 with *m*/*z* = 585; **12**, R = Me_3CCH_2 with *m*/*z* = 613, Me_3SiCH_2 with *m*/*z* = 645). This observation is in agreement with the NMR spectroscopic experiment showing partial exchange of the tetrachloride fragment $RCl_2Sn(CH_2)_4SnCl_2R$ (**3**, R = Me_3CCH_2) in **12** upon addition of $RCl_2Sn(CH_2)_4SnCl_2R$ (**10**, R = Me_3SiCH_2) to a $CHCl_3$ solution of **12** (Scheme 6).

Conclusion

The synthesis of a mixed double ladder starting from the unsymmetrically substituted $(Me_3SiCH_2)Cl_2Sn(CH_2)_3SnCl_2Ph$ (**6**) failed. However, two convenient synthetic methods for the preparation of the first mixed double ladders $\{[R(Cl)Sn(CH_2)_4Sn(Cl)R][R'(Cl)Sn(CH_2)_4Sn(Cl)R']O_2\}_2$ (**9**, R = Me_3CCH_2, R′ = Me_2CHCH_2; **12**, R = Me_3CCH_2, R′ = Me_3SiCH_2) and their characterization by X-ray crystallography are given. In contrast to the previously reported trimethylene-bridged double ladders, the tetramethylene-bridged species are kinetically labile in solution and mixed double ladders are formed by scrambling reactions between the related simple double ladders. Furthermore, the mixed tetramethylene-bridged species seem to be thermodynamically more stable than the related simple species, since no simple double ladders were detected after the quantitative formation of the mixed double ladder compounds. Nevertheless, the partial substitution of fragments such as $RCl_2Sn(CH_2)_4SnCl_2R$ in the mixed double ladders is possible. These observations give an explanation for the fact that tetramethylene-bridged organostannoxanes are more efficient catalysts in transesterification reactions than the trimethylene-bridged analogues.[18] This work is a further step toward the fine tuned catalyst design of spacer-bridged distannoxanes.

Experimental Section

General Remarks: All solvents were dried and purified by standard procedures. − Bruker DPX-300 and DRX-400 spectrometers were used to obtain ^1H and ^{119}Sn NMR spectra. ^1H and ^{119}Sn chemical shifts δ are given in ppm and were referenced against Me_4Si and Me_4Sn, respectively. No integration of the signals in the ^1H NMR spectra is given as a result of their partial superimposition. − Molecular mass determinations were performed with a Knaur osmometer in $CHCl_3$ at 59 °C. − The organotin chlorides $RCl_2Sn(CH_2)_4SnCl_2R$ (**3**, R = Me_3CCH_2; **4**, R = Me_2CHCH_2; **10**, R = Me_3SiCH_2) and oxides $[R(O)Sn(CH_2)_4Sn(O)_2R]_n$ (**8**, R = Me_3CCH_2; **7**, R = Me_2CHCH_2; **11**, R = Me_3SiCH_2) were prepared according to literature procedures.[18] − Electrospray mass spectra were obtained with a Platform II single quadrupole mass spectrometer (Micromass, Altrincham, UK) using an acetonitrile/dichloromethane (9:1) mobile phase. Acetonitrile/dichloromethane solutions (0.1 mM) of the compounds were injected directly into the spectrometer using a Rheodyne injector equipped with a 100 μL loop. A Harvard 22 syringe pump delivered the solutions to the vaporization nozzle of the electrospray ion source at a flow rate of 10 μL min^{-1}. Nitrogen was used as both a drying gas and for nebulization with flow rates of approximately 200 mL min^{-1} and 20 mL min^{-1}, respectively. Pressure in the mass analyzer region was usually about $4 \cdot 10^{-5}$ mbar. Typically, 50 signal-averaged spectra were collected.

Synthesis of $(Me_3SiCH_2)Cl_2Sn(CH_2)_3SnCl_2Ph$ (6): To a solution of hexaphenyldistannane (2.00 g, 2.86 mmol) and naphthalene (100 mg, 1.28 mmol) in THF (30 mL), sodium (0.14 g, 6.09 mmol) was added in small portions. After stirring the resulting solution for 18 h, a solution of (3-chloropropyl)diphenyl(trimethylsilylmethyl)tin (**2**) (1.25 g, 2.86 mmol) in THF (10 mL) was added dropwise at −50 °C. The resulting suspension was stirred for 48 h during which time it was warmed up. The resulting solid material was filtered. After evaporation of the solvent, the resulting crude oily product was dissolved in hot hexane (5 mL) and the solid material was filtered. The solvent was removed in vacuo, giving 2.99 g 1-[diphenyl(trimethylsilylmethyl)stannyl]-3-(triphenylstannyl)propane (**5**) as a yellow oil {^{119}Sn NMR ($CHCl_3/CDCl_3$, 111.92 MHz): δ = −63.5 [$^4J(^{119}Sn-^{117/119}Sn)$ = 56 Hz], −103.9 [$^4J(^{119}Sn-^{117/119}Sn)$ = 54 Hz]}. The intermediate product **5** was dissolved in acetone (20 mL) and a solution of $HgCl_2$ (4.32 g, 15.88 mmol) in acetone (20 mL) was added dropwise at 0 °C. The suspension was stirred overnight and filtered. The solvent was removed in vacuo giving an oily residue, which was suspended in diethyl ether (50 mL). Again, it was filtered and the solvent was evaporated. The resulting solid residue was extracted with hexane (40 mL) in a Soxhlet apparatus for 72 h, giving 1.77 g (53%) of **6** as a beige solid with a m.p. of 74−75 °C. − ^1H NMR (400.13 MHz, $CDCl_3$): δ = 0.17 (s, 9 H, $SiMe_3$), 0.88 [s, 2 H, $SiCH_2$, $^2J(^{119}Sn-^1H)$ = 93 Hz], 1.83 (t, 2 H, $SnCH_2$), 2.07 (t, 2 H, $SnCH_2$), 2.39 (quint, 2 H, CH_2), 7.48−7.63 (m, 5 H, H_{Ph}). − ^{13}C NMR ($CDCl_3$, 100.63 MHz): δ = 1.0 ($SiMe_3$), 11.9 [$^1J(^{13}C-^{119}Sn)$ = 226 Hz, CH_2Si], 20.9 (CH_2), 27.6 [$^1J(^{13}C-^{119}Sn)$ = 369 Hz, CH_2Sn], 29.2 [$^1J(^{13}C-^{119}Sn)$ = 331 Hz, CH_2Sn], 129.6 [$^3J(^{13}C-^{119}Sn)$ = 60 Hz, C_m], 131.7 [$^4J(^{13}C-^{119}Sn)$ = 27 Hz, C_p], 134.6 [$^2J(^{13}C-^{119}Sn)$ = 48 Hz, C_o], 138.6 [$^1J(^{13}C-^{119}Sn)$ = 598 Hz, C_i]. − ^{119}Sn NMR (111.92 MHz, $CHCl_3/CDCl_3$): δ = 38.2 [$^4J(^{119}Sn-^{117/119}Sn)$ = 158 Hz], 130.0 [$^4J(^{119}Sn-^{117/119}Sn)$ = 159 Hz]. − $C_{13}H_{22}Cl_4SiSn_2$ (585.7): calcd. C 26.66, H 3.79; found C 26.30, H 3.80.

Reaction of $(Me_3SiCH_2)Cl_2Sn(CH_2)_3SnCl_2Ph$ (6) with $(tBu_2SnO)_3$ (NMR Spectroscopic Experiment): $(tBu_2SnO)_3$ (140 mg, 0.56 mmol) was added to a solution of $(Me_3SiCH_2)Cl_2Sn(CH_2)_3SnCl_2Ph$ (**6**) (330 mg, 0.56 mmol) in CH_2Cl_2 (3 mL). The resulting solution was heated at reflux for 5 min. The solvent was evaporated, the residue washed with pentane (5 mL) and dissolved in CH_2Cl_2 (2.5 mL). A ^{119}Sn NMR spectrum of this solution was measured. − ^{119}Sn NMR (111.91 MHz, $CH_2Cl_2/D_2O_{capillary}$) δ = −53.7 ($tBu_2SnCl_2$), −84.5 [$^2J(^{119}Sn-^{117/119}Sn)$ = 73 Hz], −86.4 [$^2J(^{119}Sn-^{117/119}Sn)$ = 75 Hz], −90.8 [$^2J(^{119}Sn-^{117/119}Sn)$ = 73 Hz], −92.2 [$^2J(^{119}Sn-^{117/119}Sn)$ = 72 Hz], −94.2, −96.2 [$^2J(^{119}Sn-^{117/119}Sn)$ = 60 Hz], −100.2 [$^2J(^{119}Sn-^{117/119}Sn)$ = 62 Hz], −132.1 [$^2J(^{119}Sn-^{117/119}Sn)$ = 71 Hz], −132.3, −132.5 [$^2J(^{119}Sn-^{117/119}Sn)$ = 72 Hz], −134.5 [$^2J(^{119}Sn-^{117/119}Sn)$ = 68 Hz], −137.6 [$^2J(^{119}Sn-^{117/119}Sn)$ = 63 Hz], −164.1, −165.4, −166.2, −168.5 [$^2J(^{119}Sn-^{117/119}Sn)$ = 78 Hz], −170.5, −209.5, −209.7, −210.9 [$^2J(^{119}Sn-^{117/119}Sn)$ = 83 Hz], −212.2 [$^2J(^{119}Sn-^{117/119}Sn)$ = 88 Hz], −214.0 [$^2J(^{119}Sn-^{117/119}Sn)$ = 73 Hz], −214.9 [$^2J(^{119}Sn-^{117/119}Sn)$ = 82 Hz].

[Synthesis of $\{[R(Cl)Sn(CH_2)_4Sn(Cl)R]_2[R'(Cl)Sn(CH_2)_4Sn(Cl)R']_2O_2\}_2$ (9, R = Me_3CCH_2, R′ = Me_2CHCH_2). − Method A:

$[R(O)Sn(CH_2)_4Sn(O)R]_n$ (R = Me_2CHCH_2) (100 mg, 0.23 mmol) was added to a solution of $RCl_2Sn(CH_2)_4SnCl_2R$ (R = Me_3CCH_2) (131 mg, 0.23 mmol) in toluene (25 mL) at room temperature. The resulting suspension was stirred at room temperature for 1 h and heated at reflux for 2 h until the solution became clear. Crystallization from toluene at room temperature yielded 218 mg (94%) of **9** as colorless crystals with m.p. 214−216 °C. − **Method B:** $[R(O)Sn(CH_2)_4Sn(O)_2R]_n$ (R = Me_3CCH_2) (100 mg, 0.21 mmol) was added to a solution of $RCl_2Sn(CH_2)_4SnCl_2R$ (R = Me_2CHCH_2) (117 mg, 0.21 mmol) in toluene (25 mL) at room temperature. The resulting suspension was stirred at room temperature for 1 h and heated at reflux for 2 h until the solution became clear. Crystallization from toluene at room temperature yielded 203 mg (94%) of **9** as colorless crystals with m.p. 214−216 °C. − **Method C (in situ Preparation, NMR Spectroscopic Experiment):** $\{[R(Cl)Sn(CH_2)_4Sn(Cl)R]O\}_4$ (**15**, R = Me_2CHCH_2) (53 mg, 0.24 mmol) was added to a solution of $\{[R(Cl)Sn(CH_2)_4Sn(Cl)R]O\}_4$ (**14**, R = Me_3CCH_2) (50 mg, 0.24 mmol) in $CDCl_3$ (2 mL), and the resulting solution was heated at reflux for 3 d. A ^{119}Sn NMR spectrum of this solution was recorded after *t* = 4 d. − ^{119}Sn NMR (149.21 MHz, $CDCl_3$) δ = −78.2 [$^2J(^{119}Sn-^{117/119}Sn)$ = 74 Hz, 7%], −83.0 [$^2J(^{119}Sn-^{117/119}Sn)$ = 61 Hz, 36%], −84.2 [$^2J(^{119}Sn-^{117/119}Sn)$ = 57 Hz, 7%], −144.4 [$^2J(^{119}Sn-^{117/119}Sn)$ = 66 Hz, 14%], −145.2 [$^2J(^{119}Sn-^{117/119}Sn)$ = 70 Hz, 35%], −146.9 (1%). − ^{119}Sn NMR (111.92 MHz, toluene/D_2O cap.): δ = −78.7 [$^2J(^{119}Sn-^{117/119}Sn)$ = 67 Hz, 5%], −85.2 [$^2J(^{119}Sn-^{117/119}Sn)$ = 65 Hz, 26%], −85.4 (4%), −86.4 [$^2J(^{119}Sn-^{117/119}Sn)$ = 65 Hz, 15%], −147.9 [$^2J(^{119}Sn-^{117/119}Sn)$ = 66 Hz, 15%], −148.5 [$^2J(^{119}Sn-^{117/119}Sn)$ = 67 Hz, 27%], −150.2 (5%), −152.7 (3%). − ^1H NMR (400.13 MHz, C_6D_6): δ = 1.04 (d, Me_2CH), 1.16 (s, Me_3C), 1.17 (s, Me_3C), 1.23 (d, Me_2CH), 1.24 (d, Me_2CH), 1.40 (s, Me_3C), 1.90−2.42 (complex pattern, CH_2), 2.47 (m, $Me_2\mathit{C}H$), 2.76 (m, Me_2CH). − Molecular mass determination ($CHCl_3$, 20 mg mL^{-1}): 1639 g mol^{-1}. − $C_{52}H_{112}Cl_8O_4Sn_8$ (2035.0): calcd. C 30.69, H 5.55; found calcd. C 30.61, H 5.58%.

Synthesis of $\{[R(Cl)Sn(CH_2)_4Sn(Cl)R]_2[R'(Cl)Sn(CH_2)_4Sn(Cl)R']_2O_2\}_2$ (12, R = Me_3CCH_2, R′ = Me_3SiCH_2). − Method A: In a similar manner to compound **9** the distannoxane **12** was prepared from $RCl_2Sn(CH_2)_4SnCl_2R$ (R = Me_3CCH_2) (347 mg, 0.60 mmol) and $[R(O)Sn(CH_2)_4Sn(O)R]_n$ (R = Me_3SiCH_2) (300 mg, 0.60 mmol), and obtained as a colorless solid (0.62 g, 96%) with m.p. 197−198 °C. − **Method B:** Analogously the reaction of $RCl_2Sn(CH_2)_4SnCl_2R$ (R = Me_3SiCH_2) (456 mg, 0.75 mmol) and $[R(O)Sn(CH_2)_4Sn(O)R]_n$ (R = Me_3CCH_2) (350 mg, 0.75 mmol) gave **12** as a colorless solid (0.79 g, 98%). − **Method C (NMR Spectroscopic Experiment):** $\{[R(Cl)Sn(CH_2)_4Sn(Cl)R]O\}_4$ (**13**, R = Me_3SiCH_2) (53 mg, 0.24 mmol) was added to a solution of $\{[R(Cl)Sn(CH_2)_4Sn(Cl)R]O\}_4$ (**14**, R = Me_3CCH_2) (50 mg, 0.24 mmol) in $CDCl_3$ (2 mL), and the resulting solution was heated at reflux for 3 d. ^{119}Sn NMR spectra of this solution were recorded after *t* = 1 h, 1 d, and 3 d. − ^{119}Sn NMR (149.21 MHz, $CDCl_3$): δ = −68.5 (5%), −70.6 (1%), −83.8 (5%), −84.5 (27%), −85.6 (1%), −87.0 (11%), −139.5 (10%), −140.7 (33%), −143.2 (2%), −144.9 (5%). − ^{119}Sn NMR (111.92 MHz, toluene, D_2O cap.): δ = −68.8 (5%), −71.3 (2%), −83.3 [$^2J(^{119}Sn-^{117/119}Sn)$ = 67 Hz, 5%], −83.8 [$^2J(^{119}Sn-^{117/119}Sn)$ = 66 Hz, 23%], −85.4(3%), −86.9 [$^2J(^{119}Sn-^{117/119}Sn)$ = 66 Hz, 11%], −143.0 (3%), −144.3 [$^2J(^{119}Sn-^{117/119}Sn)$ = 66 Hz, 12%], −145.5 [$^2J(^{119}Sn-^{117/119}Sn)$ = 67 Hz, 23%], −146.2 [$^2J(^{119}Sn-^{117/119}Sn)$ = 67 Hz, 5%], −147.9 (3%), −149.4 [$^2J(^{119}Sn-^{117/119}Sn)$ = 67 Hz, 5%]. − ^1H NMR (400.13 MHz, $[D_8]$toluene): δ = 0.21 (s, Me_3Si), 0.22 (s, Me_3Si), 0.41 (s, Me_3Si), 1.08 (s, Me_3C), 1.11 (s, CH_2Si), 1.15 (s, Me_3C), 1.19 (s, CH_2Si), 1.34 (s, Me_3C), 1.36 (s, CH_2Si), 1.85−2.21 (complex pattern, CH_2). − Molecular mass determination ($CHCl_3$, 20 mg mL^{-1}): 1191 g mol^{-1}, ($CHCl_3$, 145 mg mL^{-1}): 1689 g mol^{-1}. −

Table 3. Crystallographic data for **9** and **12**

	9	**12**
Empirical formula	$C_{52}H_{112}Cl_8O_4Sn_8$	$C_{52}H_{120}Cl_8O_4Si_4Sn_8 \cdot C_6H_6$
Formula mass	2034.54	2233.07
Crystal system	triclinic	triclinic
Crystal size [mm]	0.20 × 0.20 × 0.20	0.30 × 0.25 × 0.20
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	10.996(1)	12.746(1)
b [Å]	12.247(1)	13.529(1)
c [Å]	16.807(1)	16.117(1)
α [°]	69.019(1)	79.424(1)
β [°]	87.145(1)	69.207(1)
γ [°]	65.013(1)	62.388(1)
V [Å³]	1901.7(3)	2301.7(3)
Z	1	1
$\rho_{calcd.}$ [Mg/m³]	1.777	1.611
μ [mm^{-1}]	2.898	2.451
F(000)	992	1098
θ range [°]	2.98 to 25.68	3.16 to 25.37
Index ranges	$-13 \le h \le 13$ $-12 \le k \le 14$ $-20 \le l \le 20$	$-12 \le h \le 12$ $-13 \le k \le 16$ $-18 \le l \le 19$
No. of reflns. collected	18520	26367
Completeness to θ_{max}	85.3	92.3
no. of independent reflns./R_{int}	6156/0.0580	7805/0.0260
no. of reflns. observed with [$I > 2\sigma(I)$]	2780	3885
no. of refined param.	335	406
GooF (F^2)	0.822	0.939
*R*1 (*F*) [$I > 2\sigma(I)$]	0.0431	0.0371
*wR*2 (*F*2) (all data)	0.1312	0.1021
$(\Delta/\sigma)_{max}$	< 0.001	< 0.001
Largest diff peak/hole [e/Å³]	0.714/−0.776	0.539/−0.484

$C_{52}H_{120}Cl_8O_4Si_4Sn_8$ (2155.4): calcd. C 28.98, H 5.61; found calcd. C 29.35, H 5.45.

Reaction of $\{[R(Cl)Sn(CH_2)_4Sn(Cl)R]_2[R'(Cl)Sn(CH_2)_4Sn(Cl)R']_2O_2\}_2$ (12, R = Me_3CCH_2, R′ = Me_3SiCH_2) with $RCl_2Sn(CH_2)_4SnCl_2R$ (3, R = Me_3CCH_2) (NMR Spectroscopic Experiment): Compound **3** (72 mg, 0.34 mmol) was added to a solution of **12** (72 mg, 0.34 mmol) in $CDCl_3$ (2 mL). The resulting solution was heated at reflux for 3 h and a ^{119}Sn NMR spectrum was recorded. − ^{119}Sn NMR (149.21 MHz, $CDCl_3$): $\delta = -131.4$, -113.0, -66.7, -67.5, -69.7, -82.9, $-$ 83.5, -84.7, -85.3, -86.1, -100 ($W_{1/2}$ = 600 Hz), -137.4, -138.5, -139.6, -142.4, -144.8, -147 ($W_{1/2}$ = 600).

Addition of $RCl_2Sn(CH_2)_3SnCl_2R$ (R = Me_3CCH_2) to a Solution of $\{[R(Cl)Sn(CH_2)_3Sn(Cl)R]O\}_4$ (R = Me_3SiCH_2) (NMR Spectroscopic Experiment): $RCl_2Sn(CH_2)_3SnCl_2R$ (R = Me_3CCH_2) (56 mg, 0.10 mmol) was added to a solution of the double ladder (216 mg, 0.10 mmol) in CH_2Cl_2 (3 mL). The resulting solution was heated at reflux for 2 h and a ^{119}Sn NMR spectrum (149.21 MHz, CH_2Cl_2/D_2O cap.) was recorded which showed the signals of the starting materials at $\delta = -96.1$ [$^2J(^{119}Sn-^{117/119}Sn)$ = 67 Hz], -132.9 [$^2J(^{119}Sn-^{117/119}Sn)$ = 69 Hz] and δ = 107.9 [$RCl_2Sn(CH_2)_3SnCl_2R$, R = Me_3CCH_2].

Crystallography: Intensity data for the colorless crystals grown from benzene were collected with a Nonius KappaCCD diffractometer with graphite-monochromated Mo-K_α (0.71069 Å) radiation at 291 K. The data collection covered almost the whole sphere of reciprocal space with 360 frames by ω-rotation (Δ/ω = 1°) at two times 10 s (**9**) and 20 s (**12**) per frame. The crystal-to-detector distance was 2.7 cm (**9**) and 3.0 cm with a detector-θ-offset of 5° (**2**). Crystal decay was monitored by repeating the initial frames at the end of data collection. On analysis of the duplicate reflections, there was no indication for any decay. The data were not corrected for absorption effects. The structure was solved by direct methods SHELXS97[25] (Sheldrick, **1990**) and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods SHELXL97[26] (Sheldrick, **1997**). − The H atoms were placed in geometrically calculated positions using a riding model ($C-H_{prim.}$ 0.96 Å, $C-H_{sec.}$ 0.97 Å; H_{aryl} $C-H$ 0.93), and for **9** refined with a common isotropic temperature factor [U_{iso} 0.148(7) Å^2] and for **12** with isotropic temperature factors constrained to be 1.5 times those of the carrier atom. − Disordered tetramethylene, *tert*-butyl (**12**), and isobutyl (**9**) groups were found with occupancies of 0.3333 [C(43′), C(44′)], 0.5 [C(3), C(5), C(3′), C(5′)], and 0.6666 [C(43), C(44)] in **12** and of 0.15 [C(32′)] and 0.85 [C(32)] in **9**. − Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from International Tables for X-ray Crystallography.[27] The figures were created by SHELXTL[28] (Sheldrick, **1991**). Crystallographic data are given in Table 3 and selected bond lengths and angles in Table 1. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-144264 (**9**) and CCDC-144265 (**12**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the Australian Research Council (ARC) for financial support.

---

[1] R. Okawara, M. Wada, *J. Organomet. Chem.* **1963**, *1*, 81−88.
[2] D. C. Gross, *Inorg. Chem.* **1989**, *28*, 2355−2359.
[3] A. G. Davies, *Organotin Chemistry*, VCH, Weinheim, **1997**.
[4] O. Primel, M.-F. Llauro, R. Pétiaud, A. Michel, *J. Organomet. Chem.* **1998**, *558*, 19−33.
[5] F. Ribot, C. Sanchez, A. Meddour, M. Gielen, E. R. T. Tiekink, M. Biesemans, R. Willem, *J. Organomet. Chem.* **1998**, *552*, 177−186.
[6] J. Otera, N. Dan-oh, H. Nozaki, *J. Org. Chem.* **1991**, *56*, 5307−5311.
[7] A. Orita, A. Mitsutome, J. Otera, *J. Org. Chem.* **1998**, *63*, 2420−2421.
[8] R. P. Houghton, A. W. Mulvaney, *J. Organomet. Chem.* **1996**, *517*, 107−113.
[9] E. N. Suciu, B. Kuhlmann, G. A. Knudsen, R. C. Michaelson, *J. Organomet. Chem.* **1998**, *556*, 41−54.
[10] Y. Meada, R. Okawara, *J. Organomet. Chem.* **1967**, *10*, 247−256.
[11] T. Yano, K. Nakashima, J. Otera, R. Okawara, *Organometallics* **1985**, *4*, 1501−1503.
[12] S. P. Narula, S. K. Bharadwaj, H. K. Sharma, G. Mairesse, P. Barbier, G. Nowogrocki, *J. Chem. Soc., Dalton Trans.* **1988**, 1719−1723.
[13] S. Brooker, F. T. Edelmann, D. Stalke, *Acta Crystallogr.* **1991**, *C47*, 2527−2529.
[14] D. Dakternieks, K. Jurkschat, S. van Dreumel, E. R. T. Tiekink, *Inorg. Chem.* **1997**, *36*, 2023−2029.
[15] U. Baumeister, D. Dakternieks, K. Jurkschat, M. Schürmann, *Main Group Met. Chem.,* manuscript submitted.
[16] J. F. Vollano, R. O. Day, R. R. Holmes, *Organometallics* **1984**, *3*, 745−750.
[17] T. Harada, *Rep. Sci. Res. Inst., Tokyo* **1948**, *24*, 177−181.
[18] M. Mehring, M. Schürmann, I. Paulus, D. Horn, K. Jurkschat, A. Orita, J. Otera, D. Dakternieks, A. Duthie, *J. Organomet. Chem.* **1999**, *574*, 176−192.
[19] D. Dakternieks, K. Jurkschat, D. Schollmeyer, H. Wu, *Organometallics* **1994**, *13*, 4121−4123.
[20] M. Schulte, M. Schürmann, D. Dakternieks, K. Jurkschat, *Chem. Commun.* **1999**, 1291−1292.
[21] B. Zobel, M. Schürmann, K. Jurkschat, D. Dakternieks, A. Duthie, *Organometallics* **1998**, *17*, 4096−4104.
[22] M. Mehring, M. Schürmann, H. Reuter, D. Dakternieks, K. Jurkschat, *Angew. Chem.* **1997**, *109*, 1150−1152; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1112−1114.
[23] M. Mehring, diploma thesis **1996**, University of Dortmund, Germany.
[24] P. G. Harrison, *Compounds of tin: general trends* (Ed.: P. J. Smith,); Blackie Academic & Professional, London, **1998**, vol. 1, pp. 10−61.
[25] G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467−473.
[26] G. M. Sheldrick, University of Göttingen, Germany, **1997**.
[27] *International Tables for Crystallography*, Dordrecht: Kluwer Academic Publishers, **1992**, vol. C.
[28] G. M. Sheldrick, *SHELXTL V5.1* Software Reference Manual, Bruker AXS, Inc., Madison, Wisconsin, USA, **1997**.

Received May 26, 2000
[I00217]