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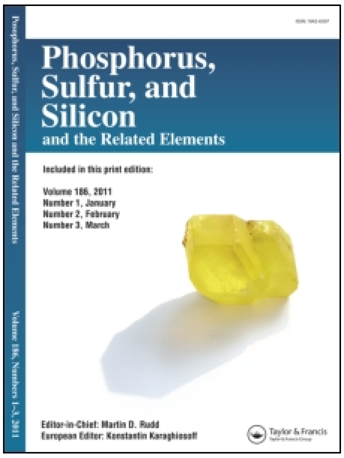

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Recent Developments in the Chemistry of Spacer Bridged Distannoxanes

MARCUS SCHULTE[a], MICHAEL MEHRING[a], INGO PAULUS[a], MARKUS SCHURMANN[a], KLAUS JURKSCHAT[a], DAINIS DAKTERNIEKS[b], ANDREW DUTHIE[b], AKIHIRO ORITA[c] and JUNZO OTERA[c]

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

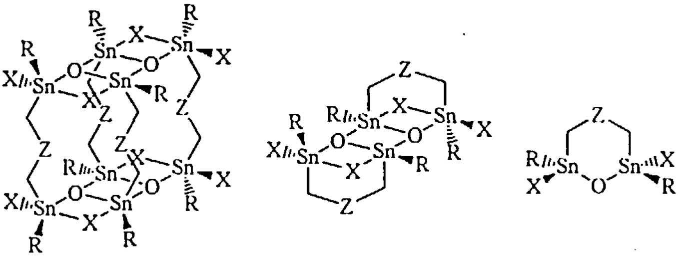
Depending on the identity of Z and R the reaction of the spacer bridged tetrachloroditin compounds $[R(Cl_2)SnCH_2]_2Z$ with $(t\text{-}Bu_2SnO)_3$ or their corresponding organotin oxides $\{[R(O)SnCH_2]_2Z\}_n$ provides either double ladders $\{\{[R(Cl)SnCH_2]_2Z\}O\}_4$ ($Z = CH_2$; $R = CH_2SiMe_3$, CH_2CMe_3), dimeric tetraorganodistannoxanes $\{\{[R(Cl)SnCH_2]_2Z\}O\}_2$ ($Z = Si(Me_2)$, $Si(Me_2)C{\equiv}CSi(Me_2)$, $Si(Me_2)OSi(Me_2)$; $R = CH_2SiMe_3$), or mixtures of both of these structures ($Z = CH_2CH_2$; $R = CH_2SiMe_3$, CH_2CMe_3, CH_2CHMe_2). The chlorine atoms can be replaced stepwise by other electronegative groups such as hydroxide or acetate. Preliminary studies on the catalytic activity of some tetraorganodistannoxanes with alkylidene spacers are reported.

Keywords: tin; distannoxanes; silicon; crystal structure; catalysis

INTRODUCTION

Dimeric tetraorganodistannoxanes $[R_2(X)SnOSn(X)R_2]_2$ (X = halogen, OH, R'COO, NCS; R, R' = alkyl, aryl) hold potential as efficient homogeneous catalysts in various organic reactions, e.g. transesterification under virtually neutral conditions[1], highly selective acylation of alcohols[2], urethane formation[3], and alkyl carbonate synthesis[4]. These compounds feature a planar central Sn_2O_2 four-membered ring and adopt a ladder type structure both in solution and in the solid state[5-7].

In recent publications we reported on the synthesis and structure of the first A-type double ladder $\{[R(Cl)Sn(CH_2)_3Sn(Cl)R]O\}_4$ (Chart 1; Z = CH_2; X = Cl; R = CH_2SiMe_3)[8] and the first triple ladder $\{[R(Cl)Sn(CH_2)_3Sn(Cl)(CH_2)_3Sn(Cl)R]O_{1.5}\}_4$ (R = CH_2SiMe_3)[9].



(A) (B) (C)

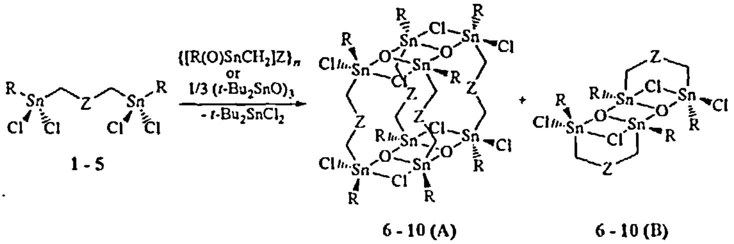
CHART 1

In contrast, $\{[(Me_3Si)_2CH(F)Sn(CH_2)_3Sn(F)CH(SiMe_3)_2]O\}_2$ adopts a dimeric B-type ladder structure (Chart 1; Z = CH_2; X = F; R = $CH(SiMe_3)_2$), whereas $[(Me_3Si)_2CH(Cl)Sn(CH_2)_3Sn(Cl)CH(SiMe_3)_2]O$ forms a C-type monomeric ring species (Chart 1; Z = CH_2; X = Cl; R = $CH(SiMe_3)_2$)[10].

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

RESULTS AND DISCUSSION

The reaction of the α,ω-bis(organodichlorostannyl)propanes **1** and **2** (EQUATION 1; Z = CH_2; R = CH_2SiMe_3, CH_2CMe_3 respectively) with their corresponding organotin oxides or $(t\text{-}Bu_2SnO)_3$ provides exclusively double ladders. Whereas for the α,ω-bis(organodichlorostannyl)butanes **3** - **5** (EQUATION 1; Z = CH_2CH_2; R = CH_2SiMe_3, CH_2CMe_3, CH_2CHMe_2 respectively) a mixture of double ladders and dimers is found in solution (TABLE 1), from which only double ladders crystallize.



(1)

TABLE 1 Alkylidene spacer bridged ladder compounds in solution.

Compound	Z	R	A/%	B/%
6	CH_2	CH_2SiMe_3	100	0
7		CH_2CMe_3	100	0
8	CH_2CH_2	CH_2SiMe_3	92	8
9		CH_2CMe_3	33	67
10		CH_2CHMe_2	67	33

The chlorine atoms in these organodistannoxanes can be completely substituted by acetate groups in a reaction with silver acetate (EQUATION 2). Again, a mixture of double ladders and dimers is found in solution for the three investigated compounds **11** - **13** (TABLE 2), whereas in the solid state these compounds exhibit double ladder structures. The crystal structure of **12** is shown in FIGURE 1.

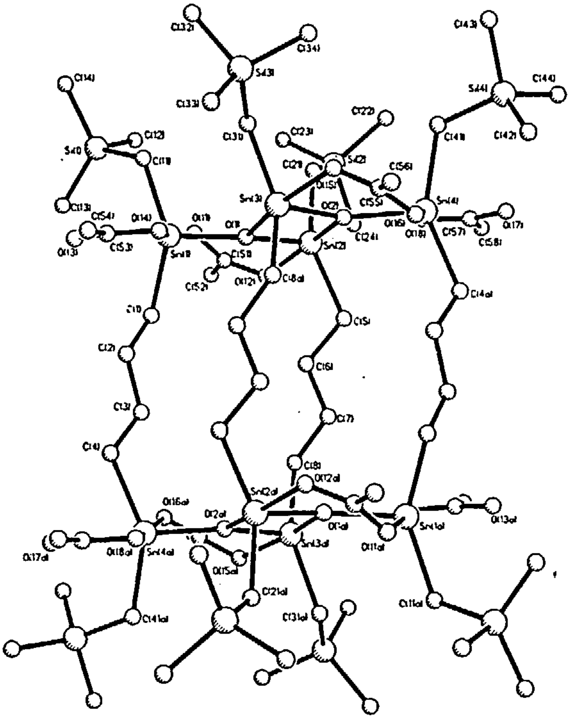
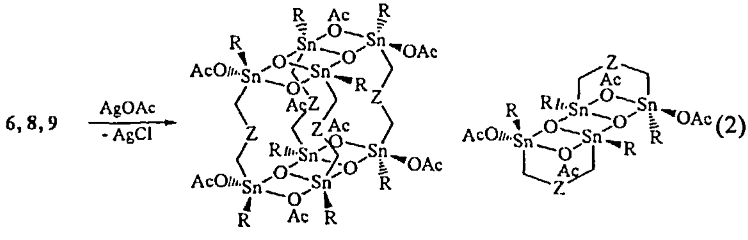


FIGURE 1 Crystal structure of the acetate substituted double ladder **12**; selected bond lengths: O(1)-Sn(1) 2.030(3), O(1)-Sn(2) 2.050(4), O(1)-Sn(3) 2.177(3), O(11)-Sn(1) 2.300(4), O(12)-Sn(2) 2.261(4), O(14)-Sn(1) 2.141(4) Å; the crystal structure is characterized by a crystallographic center of inversion.



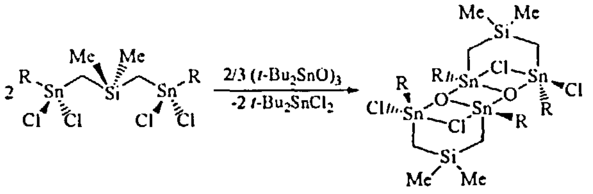
11 - 13 (A) **11 - 13 (B)**

TABLE 2 Alkylidene spacer bridged acetate substituted ladder compounds in solution.

Compound	Z	R	A/%	B/%
11	CH_2	CH_2SiMe_3	5*	95*
12	CH_2CH_2	CH_2SiMe_3	26	74
13		CH_2CMe_3	26	74

*concentration dependent equilibrium

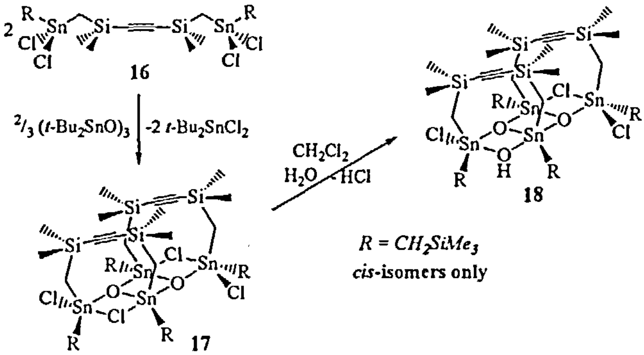
Replacing a methylene group by a dimethylsilyl unit in the trimethylene spacer and reaction of this precursor (14) with (t-$Bu_2SnO)_3$ affords the dimer **15** in quantitative yield (EQUATION 3). Steric hindrance of the dimethylsilyl units prevents this compound from adopting a double ladder structure.



(3)

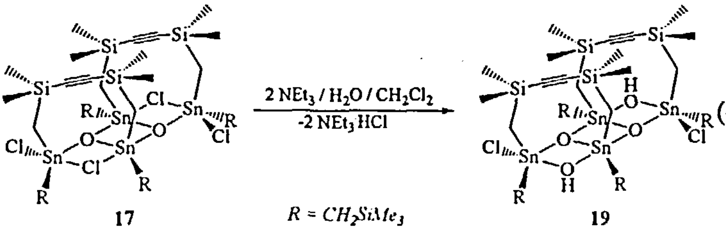
14 $R = CH_2SiMe_3$ **15**

Reaction of the tetrachloroditin compound **16** with $(t\text{-Bu}_2\text{SnO})_3$ provides the dimeric tetraorganodistannoxane **17**. Stirring **17** in a H_2O/CH_2Cl_2-mixture yields **18** with one hydroxy-substituted distannoxane unit (SCHEME 1). The alkyne units force the spacers to adopt a *cis*-configuration, and consequently compound **18** shows asymmetry in both the ladder core and the configuration of the spacers. The crystal structure of **18** is shown in FIGURE 2.



SCHEME 1 Synthesis of the ladder type compounds **17** and **18**.

Both bridging chlorine atoms in **17** can be substituted by hydroxy groups in a reaction with a $NEt_3/H_2O/CH_2Cl_2$-mixture. Again, the *cis*-isomer **19** is formed exclusively (EQUATION 4).



(4)

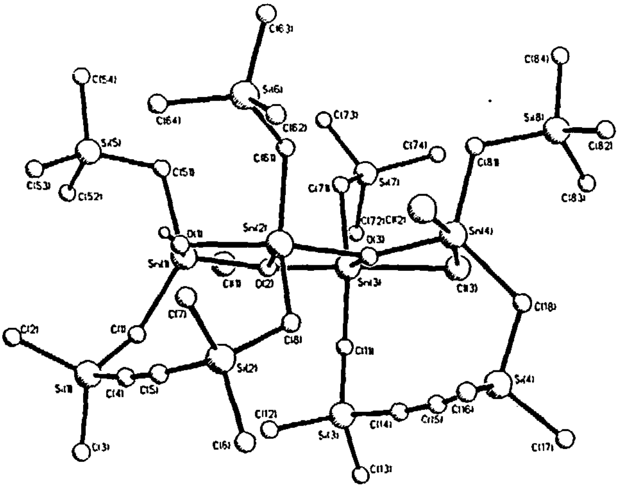
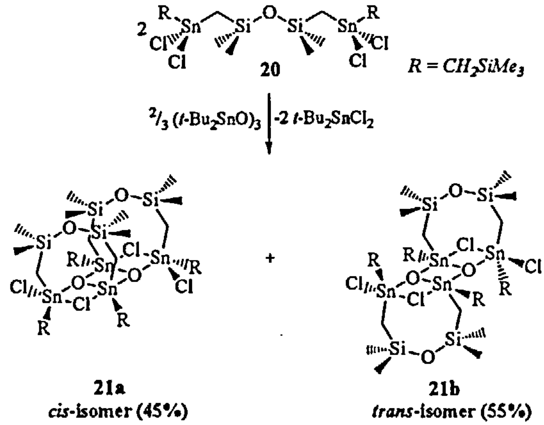


FIGURE 2 Crystal structure of the unsymmetric dimeric distannoxane **18**; selected bond lengths: O(2)-Sn(3) 2.114(2), O(2)-Sn(2) 2.040(2), O(2)-Sn(1) 2.029(2), O(1)-Sn(1) 2.231(3), O(1)-Sn(2) 2.210(3), Cl(1)-Sn(1) 2.118(4), Cl(1)-Sn(3) 3.5668(11) Å.

Reaction of the tetrachloroditin compound **20** with $(t\text{-Bu}_2\text{SnO})_3$ affords the dimeric tetraorganodistannoxanes **21a/21b**. A solution in CH_2Cl_2 consists of a mixture of the *cis*-isomer **21a** (45%) and the *trans*-isomer **21b** (55%) (Scheme 2) from which only the *trans*-isomer **21b** crystallizes. The crystal structure of **21b** is shown in FIGURE 3.

The ladder type compounds **21a/21b** react in a $NEt_3/H_2O/CH_2Cl_2$-mixture under substitution of the bridging chlorine atoms to give the hydroxy-bridged tetraorganodistannoxanes **22a/22b** in a *cis-/trans*-ratio of 37%/63% (EQUATION 5).



SCHEME 2 Synthesis of the ladder type compounds **21a**/**21b**.

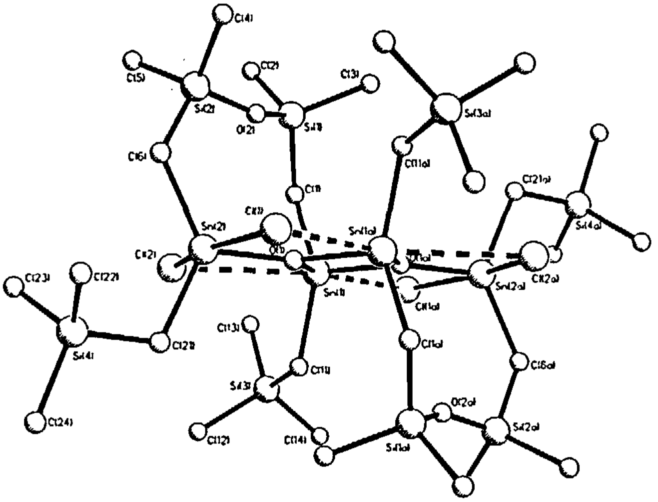
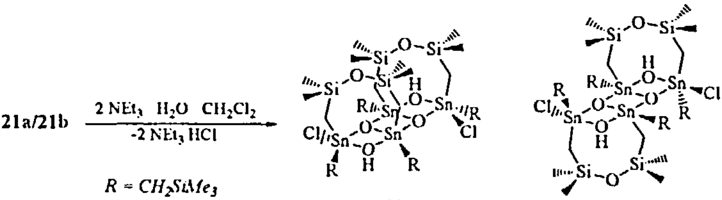


FIGURE 3 Crystal structure of the dimeric distannoxane **21b**; selected bond lengths: O(1)-Sn(1) 2.099(2), O(1)-Sn(1a) 2.069(3), O(1)-Sn(2) 2.013(2), Cl(1)-Sn(2) 2.6328(14), Cl(1)-Sn(1a) 2.9066(14), Cl(2)-Sn(2) 2.5189(14), Cl(2)-Sn(1) 3.1985(17) Å; the crystal structure is characterized by a crystallographic center of inversion.



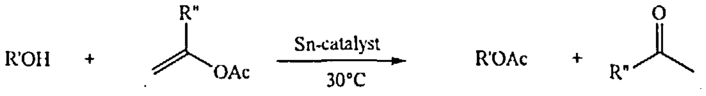
(5)

22a
cis-isomer (37%)

22b
trans-isomer (63%)

CATALYTIC ACTIVITY

Some representative distannoxanes with alkylidene spacers have been investigated with respect to their activity as catalysts in acylation reactions of alcohols with alkenyl acetates (EQUATION 6; TABLE 3).



(6)

TABLE 3 Acylation with alkenyl acetates.[a]

R'	R"	Compound	React. time/h	Yield/%[b]
$PhCH_2CH_2$	H	6	48	57 (20)
		8	24	94 (72)
		9	24	95 (72)
		10	48	92 (66)
		11	48	88
$PhCH_2CH_2$	CH_3	6	48	15
		9	48	85
		10	48	75
		11	48	88
n-C_8H_{17}	CH_3	6	48	67
		9	24	98
		10	48	97
		11	48	76

[a] Reaction conditions: R'OH (5 mmol); compound (0.05 mmol); alkenyl ester (3 ml).
[b] GLC yield; isolated yield after column chromatography in parentheses.

These preliminary results suggest that the tetramethylene bridged compounds **8** - **10** are more efficient catalysts in acylation reactions than the trimethylene bridged compound **6**. Furthermore, the catalytic activity of the trimethylene bridged and acetate containing compound **11** is only slightly lower than the activity of the tetramethylene bridged derivatives **8** - **10**. These differences in catalytic activity seem to correlate with their structures in solution. The double-ladder structure of compound **6** is kinetically inert in solution, whereas the compounds **8** - **11** are kinetically labile and show an equilibrium between **A**- and **B**-type structures in solution[11].

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