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The reaction of 1 with $(tBu_2SnO)_3$ leads in quantitative yield to 3 as colorless crystals [Eq. (a)]. The X-ray structure analysis

$$1 + 3/2 (tBu_2SnO)_3 \xrightarrow{CH_2Cl_2} -2 tBu_2SnCl_2$$
(a)

 $1/4 {[R(CI)Sn(CH_2)_3Sn(CI)(CH_2)_3Sn(CI)R]O_{3/2}}_4$

3

 $R = CH_2SiMe_3$

Trimethylene-Bridged Tri- and Tetratin Compounds as Building Blocks for Unusual Double and Triple Ladders

Michael Mehring, Markus Schürmann, Hans Reuter, Dainis Dakternieks, and Klaus Jurkschat*

Dedicated to Professor Adolf Zschunke on the occasion of his 60th birthday

Controlled hydrolysis of diorganotin dichlorides usually affords dimeric tetraorganodistannoxanes $[R_2XSnOSnXR_2]_2$ (X = Cl, OH) of type **A**. These compounds attract attention



because of their interesting structural features^[1-5a] and their applications as catalysts in organic chemistry.^[6-11] The characteristic structural feature of this class of compounds is a planar Sn₄Cl₄O₂ layer with a centrosymmetric Sn₂O₂ ring, known as a ladder-type structure.^[5]

We have been working for some time on the linkage of dimeric ladder units of type **A**. We have shown that the trimethylene-bridged double ladder of type **B** is formed on reaction of 1,3-bis[(trimethylsilylmethyl)dichlorostannyl]propane $[Me_3SiCH_2(Cl_2)SnCH_2]_2CH_2$ with di-*tert*-butyltin oxide $(tBu_2SnO)_3$. This result led to the question whether pillar-shaped triple and quadruple ladders can be constructed from the tri- and tetratin compounds 1 and 2.

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Institut für Anorganische Chemie, Universität Osnabrück (Germany) Prof. Dr. D. Dakternieks ^[13] of **3** shows a triple ladder structure (Figure 1) in which three almost planar Sn₄Cl₄O₂ layers are linked by four trimethylene chains. The average deviation of the atoms from the central plane (0.024 Å) is smaller than that of the outer layers (0.182 Å). In analogy to **B**^[12] all tin atoms are pentacoordinate and have a distorted trigonal-bypyramidal coordination environment. The solid-state structure is retained in solution. The ¹¹⁹Sn{¹H} NMR spectrum in CH₂Cl₂/D₂O_{Cap.} shows four signals at $\delta = -94.0, -114.4, -134.0, \text{ and } -142.8$ with an integral ratio of 2:1:2:1. The ²J(¹¹⁹Sn,¹¹⁷Sn) coupling constants (61–65 Hz) are of the same order of magnitude as those of the dimeric



Figure 1. Molecular structure of 3 (SHELXTL-Plus, thermal ellipsoids for 50% probability). Selected bond lengths [Å] and angles [°]: Sn-Cl_{terminal} 2.428(5)–2.434(6), Sn-Cl_{bridging} 2.616(5)–2.783(6), Sn-O_{eq} 2.003(11)–2.032(11), Sn-O_{ex} 2.127(11)–2.155(11); O_{ax}-Sn-Cl_{ax} 150.2(3)–151.8(3), Cl_{ax}-Sn-Cl_{ax} 164.9(2)–166.1(2), Sn₂O₂ rings: O-Sn-O 73.2(4)–73.8(4), Sn-O-Sn 105.6(5)–106.3(5), Sn₂ClO rings: Sn-O-Sn 122.6(5)–130.6(6), Sn-Cl-Sn 81.53(14)–83.7(2), O-Sn-Cl 74.8(3)–78.1(3), C-Sn(1,2,3,4)-C 130.8(7)–136.4(6), C-Sn(5,6)-C 122.3(7)–123.7(7).

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tetraorganodistannoxanes^[14] and of the double ladder **B**. The ¹³C{¹H} NMR spectrum, which shows two sets of five signals, is also in agreement with the triple-ladder structure.

The reaction of 2 with $(tBu_2SnO)_3$ affords 4 as a colorless solid [Eq. (b)]. The crystal structure of 4 is shown in Figure 2.

 $2 + 2/3 (tBu_2SnO)_3 \xrightarrow{CH_2Cl_2}_{-2 tBu_2SnCl_2} (b)$ $1/2 \{ [(R(Cl)Sn(CH_2)_3Sn(Cl)CH_2)_2SiMe_2]O_2\}_2 (c)$ $4 R = CH_2SiMe_3$ $R = CH_2SiMe_3$

Figure 2. Molecular structure of 4 (SHELXTL-Plus, thermal ellipsoids for 50% probability). Selected bond lengths [Å] and angles [°]: Sn-Cl_{terminal} 2.448(3)–2.463(3), Sn-Cl_{bridging} 2.673(3)–2.781(3), Sn-O_{eq} 2.016(5)–2.055(5), Sn-O_{ax} 2.119(5)–2.145(5); O_{ax}-Sn-Cl_{ax} 148.45(14)–150.9(2), Cl(1)-Sn(1)-Cl(2) 169.02(8), Cl(3)-Sn(4)-Cl(4) 160.48(8), Sn₂O₂ ring: O-Sn-O 73.6(2), 74.1(2), Sn-O-Sn 104.0(2), 105.0(2), Sn₂ClO rings: Sn-O-Sn 115.7(2), 123.5(3), Sn-Cl-Sn 79.27(8), 82.19(8), O-Sn-Cl 75.0(2)–79.8(2), C-Sn-C 131.9(4)–141.4(3).

As in the double ladder of type **B**, in **4** two Sn₄Cl₄O₂ layers are interconnected by four trimethylene chains. Bond lengths and bond angles are similar to those in **B** and **3**. A feature of the structure of **4** is the additional linkage of two tin atoms of one Sn₄Cl₄O₂ layer by a CH₂-SiMe₂-CH₂ bridge. This results in greater distortion of the Sn₄Cl₄O₂ layers (average deviation of the atoms from the plane 0.260 Å) than in **3**. As with **3**, the solid-state structure of **4** is retained in solution, as is evidenced by the ¹H, ¹³C{¹H}, and ¹¹⁹Sn{¹H} NMR spectra. The ¹¹⁹Sn{¹H} NMR spectrum shows four signals of equal integral ratio at $\delta = -91.2, -106.7, -129.4,$ and -141.7. The ¹³C{¹H} NMR spectrum shows two equally intense sets of seven signals. Formally the formation of **4** can be interpreted as shown in Scheme 1. After formation of the bicycle **C** head-totail dimerization of **C** leads to **4**.

So far, the head-to-head dimer 5, which is also expected, could only be detected by ¹¹⁹Sn{¹H} and ¹³C{¹H} NMR spectroscopy as a by-product of 4. Thus, the ¹¹⁹Sn{¹H} NMR spectrum of the crude mixture after the reaction according to Equation (b) displays, in addition to the four signals assigned to 4, four further signals of equal integral ratio at $\delta = -99.4$, -121.3, -133.7, and -141.3. The ¹³C{¹H} NMR spectrum of the same sample shows the signals assigned to 4 and in addition,

two equally intense sets of seven signals. A solution of single crystals of 4 in $CDCl_3$ at room temperature does not show any conversion into 5, even after several days. Thus 4 is kinetically stable and not in equilibrium with C.

The formation of the new ladder-type structures 3 and 4 shows the capability and limits of the concept of spacer-bridged ladders. The fact that 4 forms a "folded" double ladder instead of a quadruple ladder could be a result of additional gain of entropy by formation of the Si-CH₂-Sn-O-Sn-CH₂ six-membered chelate in the intermediate C (Scheme 1). We are currently investigating the influence of R and of the chain length on the formation of ladder structures of types B and C.



Scheme 1. Possible mode of formation of 4 and 5

Experimental Section

1: A solution of Ph₂SnCl₂ (5.15 g, 15 mmol) in Et₂O/THF (3/1, 60 mL) was added dropwise to a Grignard solution prepared from (Me₃SiCH₂)Ph₂Sn(CH₂)₃Cl (20 g, 41 mmol) [16] and Mg (1.21 g, 49 mmol) in Et₂O (130 mL). The reaction mixture was heated at reflux for 12 h and then hydrolyzed. The organic layer was separated, dried over Na2SO4, and filtered, and the solvent was evaporated to yield an oil. This was kept for several hours at 130 °C and 10⁻⁵ Torr to remove all volatile by-products. The oily residue (10.6 g) was dissolved in acetone and treated dropwise under ice cooling with a solution of HgCl₂ (15.34 g, 56 mmol) in acetone (120 mL). The resulting PhHgCl was filtered off. The filtrate was evaporated in vacuo, and the residue recrystallized several times from hexane/CH2Cl2 to give 1 as a colorless solid (2.50 g, 20% yield). ¹¹⁹Sn{¹H} NMR (111.92 MHz, CHCl₃/D₂O_{cap}): $\delta = 90.4$ [⁴J(¹¹⁹Sn,¹¹⁷Sn) = 169 Hz], 125.6 [⁴J(¹¹⁹Sn,¹¹⁷Sn)] = 171 Hz; ¹H NMR (400.13 MHz, CDCl₃): $\delta = 0.22$ (s, 18 H, SiMe₃), 0.93 [s, ²J(¹H, ¹¹⁹Sn) = 92 Hz, 4H, SnCH₂], 1.86 (t, 4H, CH₂Sn), 1.99 (t, 4H, CH₂Sn), 2.39 (quint, 4H, CH₂); ¹³C{¹H} NMR (100.63 MHz, CDCl₃): $\delta = 1.07$ [¹J(¹³C,²⁹Si) = 52 Hz, ⁴J(¹³C,²⁹Si) = 27 Hz, Me₃Si], 12.08 [¹J(¹³C,¹¹Sn) = 295 Hz, SnCH₂Si], 20.87, 29.25, 29.38 (CH₂). M.p. 81-82 °C. Analysis calcd. for C₁₄H₃₄Cl₆Si₂Sn₃: C 20.33, H 4.11; found: C 20.40, H 4.28%.

2: A Grignard reagent was prepared from $(Me_3SiCH_2)Ph_2Sn(CH_2)_3Br$ [16] (20 g, 46 mmol) and Mg (4.5 g, 185 mmol) in Et₂O (150 mL). Excess Mg was filtered off, and $(Ph_2FSnCH_2)_2SiMe_2$ [17] (11.70 g, 18 mmol) was added in small portions. Heating at reflux for 12 h and workup analogous to 1 gave an oil, which was kept for several hours at 160 °C and 10⁻⁵ Torr to remove all volatile by-products. This gave [(Me_3SiCH_2)Ph_Sn(CH_2)_3SnCH_2]_SiMe_2 as yellow oil [¹¹⁹Sn{¹H} NMR (111.92 MHz, CDCl_3): $\delta = -63.7, -64.9$]. This oil (4 g, 2.79 mmol) was dissolved in acetone (30 mL), followed by dropwise addition at 0 °C of a solution of HgCl₂ (6.36 g, 23.44 mmol) in acetone (30 mL). The reaction mixture was stirred for 12 h, PhHgCl filtered off, and the solvent evaporated. The resulting residue was extracted for 18 h in a Soxhelt extractor with *n*-pentane (50 mL) to give a pentane-insoluble precipitate, which was filtered off, dissolved in diethyl ether, and filtered. The filtrate was evaporated in vacuo to give 2 (2.00 g, 65%) as a colorless solid.

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¹¹⁹Sn{¹H} NMR (111.92 MHz, CDCl₃): $\delta = 118.0$ [⁴J(¹¹⁹Sn,¹¹⁷Sn) = 159 Hz], 131.1 [⁴J (¹¹⁹Sn,¹¹⁷Sn) = 169 Hz]; ¹H NMR (400.13 MHz, CDCl₃): $\delta = 0.18$ (s, 18H, SiMe₃), 0.37 (s, 6H, SiMe₂), 0.89 [s, ²J(¹H,¹¹⁹Sn) = 91 Hz, 4H, SnCH₂Si], 1.04 [s, ²J(¹H,¹¹⁹Sn) = 79 Hz, 4H, SnCH₂Si], 1.82 (t, 4H, CH₂Sn), 1.93 (t, 4H, CH₂Sn), 2.33 (quint, 4H, CH₂); ¹³C{¹H} NMR (100.63 MHz, CDCl₃): $\delta = 1.00$ (SiMe₃), 1.19 (SiMe₂), 12.04, 12.44 (SnCH₂Si), 20.80 (CH₂), 29.27, 30.42 (CH₂Sn); ²⁵si(¹H} NMR (59.63 MHz, CDCl₃): $\delta = 2.66$ [²J(²⁹Si,¹¹⁹Sn) = 35 Hz, SiMe₃], 5.55 [²J(²⁹Si,¹¹⁹Sn) = 49 Hz, SiMe₂]. M.p. 79-81°C. Analysis calcd. for C₁₈H₄₄Cl₉Si₃Sn₄: C 19.60, H 3.99; found: C 19.20, H 3.92%.

3: $(tBu_2SnO)_3$ (225 mg, 0.30 mmol) was added in small portions to a solution of **1** (500 mg, 0.60 mmol) in CH₂Cl₂ (20 mL). After heating at reflux for 15 min, the solvent was distilled off. The residue was washed several times with *n*-hexane and recrystallized from chloroform to give **3** as colorless crystals (430 mg, 96%). 11⁹Sn(¹H} NMR (111.92 MHz, CH₂Cl₂/D₂O_{cm₂}): $\delta = -94.0$ [²/(¹¹⁹Sn, ¹¹⁷Sn) = 65 Hz], -114.4 [²/(¹¹⁹Sn, ¹¹⁷Sn) = 62 Hz], -134.0 [²/(¹¹⁹Sn, ¹¹⁷Sn) = 65 Hz], -142.8 [²/(¹¹⁹Sn, ¹¹⁷Sn) = 61 Hz]; ¹H NMR (400.13 MHz, CDCl₃): $\delta = 0.17$ (s, 36H, Me₅Si), 0.23 (s, 36H, Me₅Si), 0.85 [s, ²/(¹H, ¹¹⁹Sn) = 120 Hz, 8H, SnCH₂Si], 0.96 [s, ²/(¹H, ¹¹⁹Sn) = 122 Hz, 8H, SnCH₂Si], 1.73 (m, 16H, CH₂); 2.02 (t, 8H, CH₂), 2.11 (t, 8H, CH₂), 2.47 (m, 8H, CH₂), 2.58 (m, 8H, CH₂); ¹³C{¹H} NMR (100.63 MHz, CDCl₃): $\delta = 1.21$, 1.74 (Me₅Si), 1.748, 20.34, 20.48, 20.92 (SnCH₂Si), 34.96, 35.56 (CH₂Sn), 35.93, 39.56 (CH₂). M.p. 297-299 °C. Analysis calcd. for C₅₆H₁₃₆Cl₁₂O₆Si₈Sn₁₂: C 22.58, H 4.56; found: C 23.12, H 4.76%.

4: $(tBu_2SnO)_3$ (273 mg, 0.37 mmol) and **2** (607 mg, 0.55 mmol) were allowed to react analogously to the procedure described for the synthesis of **3** to give 180 mg (37%) **4** as colorless crystals after recrystallization from toluene. ¹¹⁹Sn[¹H] NMR (111.92 MHz, CDCl₃): $\delta = -91.2$, -106.7, -129.4, -141.7; ¹H NMR (400.13 MHz, CDCl₃): $\delta = 0.12$ (s, 36H, Me₃Si), 0.19 (s, 36H, Me₃Si), 0.26, 0.35 (s, 24H, SiMe₂), 0.86, 0.95, 0.97, 0.98 (s, 32H, SiCH₂), 2.05, 2.15 (t, 16H, SnCH₂), 2.64 (m, 8H, CH₂); ¹³C[¹H] NMR (100.63 MHz, CDCl₃): $\delta = -118$, 1.67 (Me₃Si), 4.06, 5.96 (SiMe₂), 14.71, 16.96, 17.00, 20.37 (SnCH₃Si), 20.64, 20.98 (CH₂), 30.90, 34.27, 37.90, 38.01 (CH₂Sn). M.p. 259–261 °C. Analysis calcd. for C₃₆H₈₈Cl₈O₄Si₆Sn₈: C 21.77, H 4.43; found: C 21.21, H 4.25%.

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- [13] Crystal structure data for 3: C₅₆H₁₃₆Cl₁₂O₆Si₈Sn₁₂, M_r = 2980.05, monoclinic, space group C2/c, a = 31.4100(17), b = 24.100(13), c = 21.602(12) Å, β = 125.34(4)°, V = 13 339(15) Å³, Z = 4, ρ_{caled} = 1.484 gcm⁻³, 2θ_{max} = 20.5°, Mo_{Ks} radiation, λ = 0.71073 Å, ω/2θ measurement, T = 200 K, 7428 reflections measured with a Siemens-P4 diffractometer, 5858 independent reflections (R_{int.} = 0.0464), refinement based on 5858 reflections, no σ limits, no absorption corrections, Lp corrections, structure solution with direct methods (SHELXTL), all non-hydrogen atoms were refined anisotropically, 426 parameters, H atoms were refined in idealized positions, R1 = 0.0889, wR2 = 0.1942, R1 = 0.0673, wR2 = 0.01772 (I>2σI corresponding to 4535 reflections), full-matrix least-squares refinement against F² with SHELXL-93, largest positive and negative difference peaks 1.300 and -1.029 eÅ⁻³.

- [15] Crystal structure data for 4: $C_{36}H_{88}Cl_8O_4Si_6Sn_8 \cdot 2C_7H_8$, $M_r = 2170.99$, triclinic, space group P1, a = 12.724(3), b = 13.002(13), c = 14.334(11) Å, 1.771 gcm⁻³, $2\theta_{max} = 25.0^\circ$, Mo_{ka} radiation, $\lambda = 0.71073$ Å, $\omega/2\theta$ measurement, T = 291 K, 7480 reflections measured with an Enraf Nonius CAD4 diffractometer, 7128 independent reflections ($R_{int.} = 0.0334$), refinement based on 7128 reflections, no σ limits, no absorption corrections, Lp corrections, structure solution with direct methods (SHELXTL), all non - hydrogen atoms except toluene were refined anisotropically, 311 parameters, H atoms were refined in idealized positions, R1 = 0.1260, wR2 = 0.0960, R1 = 0.0473, wR2 = 0.0802 (I>2 σ I corresponding to 3483 reflections), full-matrix leastsquares refinement against F^2 with SHELXL-93, largest positive and negative difference peaks 0.747 and -0.558 eÅ⁻³. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-171. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: Int. code +(1223)336-033; e-mail: deposit@chemcrys.cam.ac.uk).
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- [17] (Ph₃SnCH₂)₂SiMe₂ (m.p. 91-92 °C, ¹¹⁹Sn{¹H} NMR (111.92 MHz, CDCl₃): $\delta = -$ 89.7) is prepared by the reaction of Me₂Si(CH₂MgCl)₂ with Ph₃SnCl. It is converted into almost insoluble (Ph₂FSnCH₂)₂SiMe₂ by subsequent reaction with two equivalents of iodine and aqueous KF solution.

Application of the Langmuir-Blodgett Technique to Polyoxometalates: Towards New Magnetic Films**

Miguel Clemente-León, Christophe Mingotaud,* Béatrice Agricole, Carlos J. Gómez-García, Eugenio Coronado,* and Pierre Delhaès

Soluble metal-oxide clusters (polyoxometalates) are receiving increasing interest in materials science owing to their chemical, structural, and electronic versatility.^[1] Thus, because of the ability of these polyoxoanions to act as electron acceptors and to accommodate magnetic transition metal centers in their structures, they are being used as the inorganic component of conducting radical salts based on tetrathiafulvalene-type organic donors. Of particular interest is the preparation of organic-inorganic composites in which the localized magnetic moments of the polyoxometalate cluster coexist with the mobile conducting electrons of the organic network.[2-5] Other properties of these materials, such as electrochromism^[6] and electrocatalysis, have been recently exploited in the preparation of conducting catalytic electrodes based on conducting polymers such as polypyrrole,^[7] polyaniline,^[8, 9] polythiophene^[10] and poly(3-methylthiophene).^[11, 12] More recently, the use of poly(N-methylpyrrole) with Fe³⁺-containing polyoxometalates has provided a sensitive electrode for detection of nitrite.^[13]

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