Tetraorganodistannoxanes: formation of a novel *cis*-ladder†

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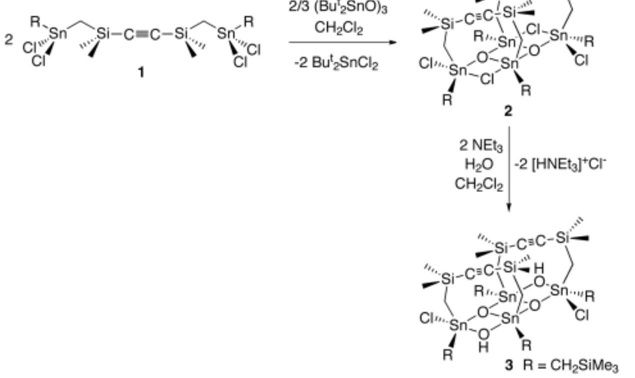
Reaction of the acetylenic-bridged ditin precursor [$Me_3SiCH_2(Cl_2)SnCH_2(Me_2)Si]_2C_2$ 1 with the oxygen source ($Bu^t_2SnO)_3$ results exclusively in formation of the dimeric tetraorganodistannoxane {[$Me_3SiCH_2(Cl)SnCH_2(Me_2)SiC\equiv CSi(Me_2)CH_2Sn(Cl)CH_2SiMe_3]O\}_2$ 2 which has the hitherto unknown *cis*-configuration; this is retained during the quantitative conversion of 2 into the hydroxy-substituted analogue {[$Me_3SiCH_2(OH)SnCH_2(Me_2)SiC\equiv CSi(Me_2)CH_2Sn(Cl)CH_2SiMe_3]O\}_2$ 3.

Dimeric tetraorganodistannoxanes $[R_2(X)SnOSn(X)R_2]_2$ (X = halogen, OH, $R'CO_2$, NCS; R, R′ = alkyl, aryl)[1–5] have been 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]

We recently reported the syntheses and structures of tetraorganodistannoxanes $\{[R(X)SnCH_2ZCH_2Sn(X)R]O\}_n$ which contain tri- or tetra-methylene bridges between the two tin atoms. These compounds exhibit either a double ladder or a dimeric structure (n = 4; R = CH_2SiMe_3; X = Cl, OH; Z = CH_2),[10] [n = 2, 4; R = CH_2SiMe_3, CH_2CMe_3, CH_2CHMe_2; X = Cl, OAc; Z = CH_2, $(CH_2)_2$, $SiMe_2$],[11] [n = 2; R = $CH(SiMe_3)_2$; X = F; Z = CH_2].[12] Also recently reported was the first triple ladder $\{[R(Cl)Sn(CH_2)_3Sn(Cl)(CH_2)_3Sn(Cl)R]O_{1.5}\}_4$ (R = CH_2SiMe_3),[13] in this case three tin atoms are connected by trimethylene bridges.

In the double ladders $\{[R(Cl)SnCH_2ZCH_2Sn(Cl)R]O\}_4$ [R = CH_2SiMe_3; Z = CH_2, $(CH_2)_2$] the distance between the two $Sn_4Cl_4O_2$ layers is 6.04 and 7.07 Å, respectively, which is too small to contemplate any host–guest chemistry. With the goal to increase the $Sn_4Cl_4O_2$ interlayer separation, we synthesised the precursor of a double ladder containing a rigid acetylene spacer, $[Me_3SiCH_2(Cl_2)SnCH_2(Me_2)Si]_2C_2$, **1**.‡

However, reaction of **1** with $(Bu^t_2SnO)_3$ resulted in quantitative formation of the dimeric tetraorganodistannoxane **2**§ rather than the anticipated tetrameric double ladder compound (Scheme 1).



Scheme 1 Synthesis of the tetraorganodistannoxanes **2** and **3**.

Somewhat surprisingly, the crystal structure (Fig. 1) of **2**¶ shows that both acetylenic spacer groups are on the same side of the tetraorganodistannoxane ladder core, *i.e.* **2** adopts the lower symmetry *cis*-configuration as compared to the usual *trans*-configuration.[12] The origin of this geometric disposition is not clear. Each tin atom has a distorted trigonal bipyramidal geometry. For the exocyclic tin atoms, two carbons and one oxygen occupy the equatorial positions and two chlorines occupy the axial positions, while for the endocyclic tin atoms the equatorial positions are occupied by two carbons and one oxygen and the axial positions by one oxygen and one chlorine. The shortest Sn–O bond lengths are found for the exocyclic tins [Sn(1)–O(1) 2.024(3) Å, Sn(4)–O(2) 2.018(2) Å] and the longest Sn–O bonds exist in the Sn_2O_2 ring [Sn(2)–O(2) 2.132(3) Å, Sn(3)–O(1) 2.159(3) Å]. It is worth noting that the Sn(2)–O(2) bond corresponds to the longer Sn(2)–Cl(2) bond [2.641(1) Å] whereas the Sn(3)–O(1) bond corresponds to the shorter Sn(3)–Cl(4) bond [2.512(2) Å]. The chlorine atoms Cl(1) and Cl(3) are non-bridging [Sn(2)–Cl(3) 3.490(1) Å, Sn(3)-Cl(1) 3.497(1) Å]. The torsion angles involving the bridging chlorine atoms [Sn(1)–O(1)–Sn(2)–Cl(2) 7.93(7)°,

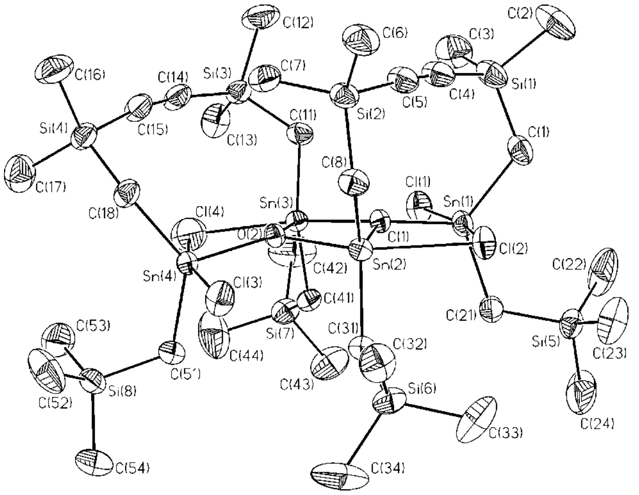


Fig. 1 Crystal structure of *cis*-{[$Me_3SiCH_2(Cl)SnCH_2(Me_2)SiC\equiv CSi(Me_2)CH_2Sn(Cl)CH_2SiMe_3]O\}_2$ **2**, showing 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Sn(1)–O(1) 2.024(3), Sn(1)–Cl(1) 2.453(1), Sn(1)–Cl(2) 2.740(1), Sn(2)–O(1) 2.058(3), Sn(2)–O(2) 2.132(3), Sn(2)–Cl(2) 2.641(1), Sn(2)–Cl(3) 3.490(1), Sn(3)–O(1) 2.159(3), Sn(3)–O(2) 2.049(3), Sn(3)–Cl(1) 3.497(1), Sn(3)–Cl(4) 2.512(2), Sn(4)–O(2) 2.018(2), Sn(4)–Cl(3) 2.507(1), Sn(4)–Cl(4) 2.503(2), O(1)–Sn(1)–Cl(1) 88.29(8), O(1)–Sn(1)–Cl(2) 76.28(8), O(1)–Sn(1)–C(1) 122.7(2), O(1)–Sn(1)–C(21) 112.5(2), Cl(1)–Sn(1)–Cl(2) 164.57(4), O(1)–Sn(2)–O(2) 74.4(1), O(1)–Sn(2)–Cl(2) 78.11(8), O(1)–Sn(2)–C(8) 121.0(1), O(1)–Sn(2)–C(31) 106.6(1), O(2)–Sn(2)–Cl(2) 152.36(7), O(1)–Sn(3)–O(2) 74.0(1), O(2)–Sn(3)–Cl(4) 77.72(8), O(2)–Sn(3)–C(11) 114.0(2), O(2)–Sn(3)–C(41) 108.4(1), O(1)–Sn(3)–Cl(4) 151.59(8), O(2)–Sn(4)–Cl(3) 86.29(8), O(2)–Sn(4)–Cl(4) 78.46(9), O(2)–Sn(4)–C(18) 113.7(2), O(2)–Sn(4)–C(51) 113.7(2), Cl(3)–Sn(4)–Cl(4) 163.50(6), Si(1)–C(4)–C(5) 173.7(5), Si(2)–C(5)–C(4) 176.0(5), Si(3)–C(14)–C(15) 171.8(4), Si(4)–C(15)–C(14) 169.9(4), Sn(1)–O(1)–Sn(2)–Cl(2) 7.93(7), Sn(3)–O(2)–Sn(4)–Cl(4) 6.74(8), Sn(2)–O(1)–Sn(3)–O(2) 8.0(1).

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† This work contains part of the intended PhD thesis of M. Schulte.

Sn(3)–O(2)–Sn(4)–Cl(4) 6.74(8)°] and the $\mathrm{Sn_2O_2}$ ring [Sn(2)–O(1)–Sn(3)–O(2) 8.0(1)°] reveal a distortion from planarity which originates from ring strain in the two nine-membered Sn–O–Sn–C–Si–C≡C–Si–C rings. This ring strain is also manifested in the deviation of the Si–C≡C angles from the ideal value of 180° [Si(1)–C(4)–C(5) 173.7(5)°, Si(2)–C(5)–C(4) 176.0(5)°, Si(3)–C(14)–C(15) 171.8(4)°, Si(4)–C(15)–C(14) 169.9(4)°]. All four Sn–C–Si frameworks are bent into the same direction which results in an intramolecular stacking of the two nine-membered rings. There is no intramolecular or intermolecular interaction between two spacers [shortest intramolecular distance C(7)···C(18) 3.827(7) Å].

The dimeric nature of the material is retained in solution as was verified by molecular weight determination (calc. for **2**: M = 1334 g $\mathrm{mol^{-1}}$, found in $\mathrm{CH_2Cl_2}$: M = 1383 g $\mathrm{mol^{-1}}$). The ^{119}Sn NMR spectrum in $\mathrm{CDCl_3}$ contains two signals of equal integral ratio at δ −132.4 ($\mathrm{C_2}\mathit{Sn}\mathrm{O_2Cl}$) and at δ −75.8 ($\mathrm{C_2}\mathit{Sn}\mathrm{OCl_2}$) indicating the presence of a single isomer in solution. However, these data do not provide unambiguous information about which of the two possible isomers is present in solution.

The tetrachloro-substituted distannoxane **2** reacts almost quantitatively with triethylamine–water to give the dihydroxy-substituted distannoxane **3**.‖ Again, the *cis*-isomer of **3** is formed exclusively in the solid state‡ (Scheme 1).

In aqueous solution compound **3** does not undergo further hydrolysis. Also for **3** the dimeric structure is retained in solution as was verified by molecular weight determination (calc. for **3**: M = 1297 g $\mathrm{mol^{-1}}$, found in $\mathrm{CH_2Cl_2}$: M = 1349 g $\mathrm{mol^{-1}}$). The ^{119}Sn NMR spectrum in $\mathrm{CDCl_3}$ shows two signals of equal integral ratio at δ −153.1 and −152.2 revealing the presence of a single isomer only, but as stated for compound **2** it is not evident which of the two isomers is actually present.

These preliminary results reveal that the silicon containing acetylenic spacer $\mathrm{CH_2(Me_2)SiC{\equiv}CSi(Me_2)CH_2}$ plays an essential role in controlling the structure of the distannoxane dimers **2** and **3**. Further studies on this class of compounds will focus on the catalytic activity of spacer bridged distannoxanes such as **2** and **3**.

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Notes and references

‡ The detailed synthesis of **1** and the crystal structure of **3** will be presented in a forthcoming full paper.

§ *Synthesis and selected spectroscopic data* for **2**: to a solution of **1** (500 mg, 0.69 mmol) in dry $\mathrm{CH_2Cl_2}$ (10 ml) was added dropwise a solution of $\mathrm{(Bu^t{}_2SnO)_3}$ (172 mg, 0.23 mmol) in dry $\mathrm{CH_2Cl_2}$ (10 ml). The mixture was stirred for 3 h at room temp. The solvent and the resulting $\mathrm{Bu^t{}_2SnCl_2}$ were removed *in vacuo* to afford **2** as an amorphous colourless solid with mp 158–160 °C in quantitative yield (461 mg, 0.35 mmol). Single crystals were grown from hexane at 4 °C. Anal. Calc. for $\mathrm{C_{32}H_{76}O_2Cl_4Sn_4Si_8}$: C, 28.80, H, 5.74. Found: C, 29.10, H, 5.60% ^{1}H NMR ($\mathrm{CDCl_3}$, 400.13 MHz, 25 °C) δ 0.13 (s, 18H, $\mathrm{SiMe_3}$), 0.18 (s, 18H, $\mathrm{SiMe_3}$), 0.26 (s, 6H, $\mathrm{SiMe_2}$), 0.31 (s, 6H, $\mathrm{SiMe_2}$), 0.32 (s, 6H, $\mathrm{SiMe_2}$), 0.34 (s, 6H, $\mathrm{SiMe_2}$), 0.63 [d, 2H, $^2J(^1\mathrm{H}-^1\mathrm{H})$ 12 Hz, $\mathrm{CH_2}$], 0.81 [d, 2H, $^2J(^1\mathrm{H}-^1\mathrm{H})$ 12 Hz, $\mathrm{CH_2}$], 0.92 [d, 2H, $^2J(^1\mathrm{H}-^1\mathrm{H})$ 12 Hz, $\mathrm{CH_2}$], 0.93 [d, 2H, $^2J(^1\mathrm{H}-^1\mathrm{H})$ 13 Hz, $\mathrm{CH_2}$], 0.94 [d, 2H, $^2J(^1\mathrm{H}-^1\mathrm{H})$ 12 Hz, $\mathrm{CH_2}$], 1.02 [d, 2H, $^2J(^1\mathrm{H}-^1\mathrm{H})$ 12 Hz, $\mathrm{CH_2}$], 1.05 [d, 2H, $^2J(^1\mathrm{H}-^1\mathrm{H})$ 13 Hz, $\mathrm{CH_2}$], 1.19 [d, 2H, $^2J(^1\mathrm{H}-^1\mathrm{H})$ 13 Hz, $\mathrm{CH_2}$]. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$, 100.63 MHz, 25 °C) δ 0.00 ($\mathrm{SiMe_2}$), 0.95 ($\mathrm{SiMe_2}$), 1.22 ($\mathrm{SiMe_3}$), 1.61 ($\mathrm{SiMe_2}$), 1.82 ($\mathrm{SiMe_3}$), 2.18 ($\mathrm{SiMe_2}$), 17.32 ($\mathrm{CH_2}$), 19.45 ($\mathrm{CH_2}$), 20.23 ($\mathrm{CH_2}$), 20.58 ($\mathrm{CH_2}$), 114.54 (C≡C), 117.81 (C≡C). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$, 79.49 MHz, 25 °C) δ −19.4 [2Si, $^2J(^{117/119}\mathrm{Sn}-^{29}\mathrm{Si})$ 67 Hz, $\mathrm{SiMe_2}$], −19.2 [2Si, $^2J(^{117/119}\mathrm{Sn}-^{29}\mathrm{Si})$ 72 Hz, $\mathrm{SiMe_2}$], 1.1 [2Si, $^2J(^{117/119}\mathrm{Sn}-^{29}\mathrm{Si})$ 19 Hz, $\mathrm{SiMe_3}$], 1.2 [2Si, $^2J(^{117/119}\mathrm{Sn}-^{29}\mathrm{Si})$ 24 Hz, $\mathrm{SiMe_3}$]. $^{119}\mathrm{Sn}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$, 149.21 MHz, 25 °C) δ −132.4 [2Sn, $^2J(^{117/119}\mathrm{Sn}-^{119}\mathrm{Sn})$ 63, 109/114 Hz, $\mathrm{C_2SnO_2Cl}$], −75.8 [2Sn, $^2J(^{117/119}\mathrm{Sn}-^{119}\mathrm{Sn})$ 63, 111/116 Hz, $\mathrm{C_2SnOCl_2}$].

¶ *Crystal data* for **2**: $\mathrm{C_{32}H_{76}Cl_4O_2Si_8Sn_4}$, M_r = 1334.21, triclinic space group $P\bar{1}$, a = 13.240(1), b = 15.536(1), c = 16.387(1)Å, α = 78.643(1), β = 75.868(1), γ = 68.096(1)°, V = 3011.7(4) $\mathrm{Å^3}$, Z = 2, D_c = 1.471 Mg $\mathrm{m^{-3}}$, F(000) = 1328, λ(Mo-Kα) = 0.71069 Å, μ = 2.000 $\mathrm{mm^{-1}}$, T = 291(1)K, final R = 0.032 for 7455 unique observed [$F > 4.0\sigma(F)$] diffractometer data. CCDC 182/1274. See http://www.rsc.org/suppdata/cc/1999/1291/ for crystallographic files in .cif format.

‖ *Synthesis and selected spectroscopic data for* **3**: to a solution of **2** (400 mg, 0.30 mmol) in $\mathrm{CH_2Cl_2}$ (10 ml) was added water (10 ml) and $\mathrm{Et_3N}$ (61 mg, 0.60 mmol). The mixture was stirred for 3 h at room temperature. After addition of $\mathrm{CH_2Cl_2}$ (20 ml) and water (20 ml) the phases were separated. The organic phase was washed with saturated $\mathrm{NH_4Cl}$ (20 ml) and water (20 ml), dried over $\mathrm{Na_2SO_4}$, filtered and evaporated *in vacuo* to give **3** as an amorphous colourless solid with mp 207–208 °C in 97% yield (378 mg, 0.29 mmol). **3** can be recrystallized from $\mathrm{CH_2Cl_2}$–hexane (1 : 1) to afford a crystalline colourless solid. Anal. Calc. for $\mathrm{C_{32}H_{78}O_4Cl_2Sn_4Si_8}$: C, 29.62, H, 6.06. Found: C, 29.60; H, 6.10%. ^{1}H NMR ($\mathrm{CDCl_3}$, 400.13 MHz, 25 °C) δ 0.11 (s, 18H, $\mathrm{SiMe_3}$), 0.12 (s, 18H, $\mathrm{SiMe_3}$), 0.21 (s, 6H, $\mathrm{SiMe_2}$), 0.24 (s, 6H, $\mathrm{SiMe_2}$), 0.33 (s, 6H, $\mathrm{SiMe_2}$), 0.39 (s, 6H, $\mathrm{SiMe_2}$), 0.40 [d, 2H, $^2J(^1\mathrm{H}-^1\mathrm{H})$ 12 Hz, $\mathrm{CH_2}$], 0.44 [d, 2H, $^2J(^1\mathrm{H}-^1\mathrm{H}]$ 12 Hz, $\mathrm{CH_2}$), 0.50 [d, 2H, $^2J(^1\mathrm{H}-^1\mathrm{H})$ 12 Hz, $\mathrm{CH_2}$], 0.58 [d, 2H, $^2J(^1\mathrm{H}-^1\mathrm{H})$ 13 Hz, $\mathrm{CH_2}$], 0.59 [d, 2H, $^2J(^1\mathrm{H}-^1\mathrm{H})$ 13 Hz, $\mathrm{CH_2}$], 0.66 [d, 2H, $^2J(^1\mathrm{H}-^1\mathrm{H})$ 13 Hz, $\mathrm{CH_2}$], 0.77 [d, 2H, $^2J(^1\mathrm{H}-^1\mathrm{H})$ 12 Hz, $\mathrm{CH_2}$], 1.02 [d, 2H, $^2J(^1\mathrm{H}-^1\mathrm{H})$ 13 Hz, $\mathrm{CH_2}$], 2.96 [s, 2H, $^2J(^{117/119}\mathrm{Sn}-^1\mathrm{H})$ 8 Hz, OH]. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$, 100.63 MHz, 25 °C) δ 0.32 ($\mathrm{SiMe_2}$), 1.28 ($\mathrm{SiMe_2}$), 1.33 ($\mathrm{SiMe_2}$), 1.40 ($\mathrm{SiMe_3}$), 1.61 ($\mathrm{SiMe_2}$), 1.85 ($\mathrm{SiMe_3}$), 11.44 ($\mathrm{CH_2}$), 13.17 ($\mathrm{CH_2}$), 15.29 ($\mathrm{CH_2}$), 15.57 ($\mathrm{CH_2}$), 117.65 (C≡C), 117.74 (C≡C). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$, 79.49 MHz, 25 °C) δ −19.1 [2Si, $^2J(^{117/119}\mathrm{Sn}-^{29}\mathrm{Si})$ 55 Hz, $\mathrm{SiMe_2}$], −18.7 [2Si, $^2J(^{117/119}\mathrm{Sn}-^{29}\mathrm{Si})$ 49 Hz, $\mathrm{SiMe_2}$], 1.2 [2Si, $^2J(^{117/119}\mathrm{Sn}-^{29}\mathrm{Si})$ 52 Hz, $\mathrm{SiMe_3}$], 1.4 [2Si, $^2J(^{117/119}\mathrm{Sn}-^{29}\mathrm{Si})$ 52 Hz, $\mathrm{SiMe_3}$]. $^{119}\mathrm{Sn}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$, 149.21 MHz, 25 °C) δ −153.1 [2Sn, $^2J(^{117/119}\mathrm{Sn}-^{119}\mathrm{Sn})$ 50, 88/92 Hz], −152.2 [2Sn, $^2J(^{117/119}\mathrm{Sn}-^{119}\mathrm{Sn})$ 50, 90/94 Hz].

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