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TRIMETHYLENE-BRIDGED TETRAORGANODISTANNOXANES $\{[Me_3SiCH_2(RCOO)Sn(CH_2)_3Sn(OOCR)CH_2SiMe_3]O\}_n$ ($R = Ph, 2,4\text{-}Me_2C_6H_3$): CONTROL OF STRUCTURE BY VARIATION OF R*

B. Costisella[1], D. Dakternieks[2], K. Jurkschat[1], M. Mehring[1], I. Paulus[1], M. Schürmann[1]

*The synthesis of trimethylene-bridged, carboxylate-substituted tetraorganodistannoxanes $\{[Me_3SiCH_2(RCOO)Sn(CH_2)_3Sn(OOCR)CH_2SiMe_3]O\}_n$ (**1**, $R = Ph$; **2**, $R = 2,4\text{-}Me_2C_6H_3$) is reported. Depending on the structure of R, in the solid state these compounds are either dimers (**1**, $n = 2$, cis-isomer) with a ladder-type structure or tetramers (**2**, $n = 4$) with a double ladder-type structure.*

Keywords: distannoxanes, X-ray structure.

Tetraorganodistannoxanes $[R_2(X)SnOSn(X)R'_2]_2$ (X = halogen, OH, RCOO, NCS; R, R' = alkyl, aryl) [1-7] have been reported to be efficient homogeneous catalysts in various organic reactions, such as transesterification under virtually neutral conditions [8], highly selective acylation of alcohols [9], polyurethane synthesis [10, 11], urethane formation [12], polymerization of butyrolactones [13, 14], and alkyl carbonate synthesis [15]. Nevertheless, for all applications it still remains uncertain whether monomers or dimers are the catalytically active species. Single crystal X-ray crystallography and NMR-spectroscopic studies have evidenced the dimeric structure (**A**-type) in the solid state and in solution of a great number of tetraorganodistannoxanes [1-7, 16, 17]. However, a few monomeric species have also been reported [2, 4, 18-21]. In general, compounds of the type $[R_2(X)SnOSn(X)R'_2]_2$ show intramolecular and intermolecular dynamics in solution, e.g., the acetate-substituted distannoxanes $[R_2(AcO)SnOSn(OAc)R_2]_2$ (R = Bu, Et, Me) partially dissociate into monomeric species at low concentration, as was evidenced by cryoscopic molecular weight determination and ^{119}Sn NMR spectroscopy [2, 18, 19]. Based on multinuclear NMR spectroscopy, intramolecular rearrangements in solution and in the solid state of monofunctional tetraorganodistannoxanes $[R_2(X)SnOSn(X)R_2]_2$ (X = F, Cl, OAc, OMe, OPh, $OSiMe_3$) have been described [4, 17, 22].

Several single crystal X-ray structure analyses of dimeric carboxylate-substituted tetraorganodistannoxanes have been reported and led to the elucidation of five structural types which are all based on a central four-membered Sn_2O_2 ring but differ in the coordination mode of the carboxylate ligands [23]. In the most common structure type both the endo- and the exocyclic tin atoms of the $Sn_4(OOCR)_4O_2$ layers

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* Dedicated to Professor Dr. Edmunds Lukevics on the occasion of his 65th birthday.

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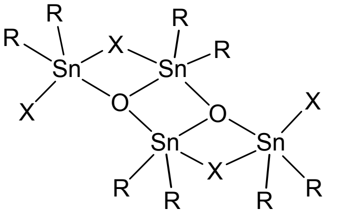
[1] Lehrstuhl fur Anorganische Chemie II der Universitat Dortmund, D-44221 Dormund, Germany; e-mail: kjur@platon.chemie.uni-dormund.de. [2] Centre for Chiral and Molecular Technologies, Deakin University, Geelong, Victoria 3217, Australia. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1535-1548, November, 2001. Original article submitted October 26, 2001.

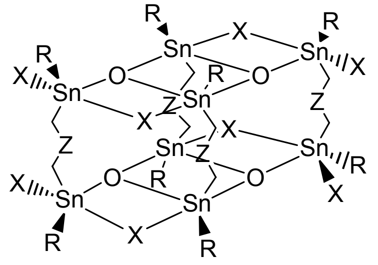
are five-coordinate and they are linked *via* bidentate bridging carboxylate ligands. The other carboxylate groups are bound in a monodentate fashion. In contrast, a crystal structure analysis of $\{[Ph_2Sn(OOCCCl_3)]_2O\}_2$ shows all carboxylate ligands to be bidentate leading to six-coordinate tin atoms [24]. In $\{[Me_2Sn(OOCMe)]_2O\}_2$ three intramolecular and one intermolecular bidentate acetate ligands are present giving two penta- and two hexacoordinate tin centers [25]. The only carboxylate-substituted double ladder structures $\{[Me_3SiCH_2(AcO)Sn(CH_2)_nSn(OAc)CH_2SiMe_3]O\}_4$ (n = 3, 4) reported so far show five-coordinate tin atoms [26, 27].

We are interested in the synthesis, structure, and catalytic activity of spacer-bridged tetraorganodistannoxanes of the type $\{[R(X)Sn–Z–Sn(X)R]O\}_n$ Recently, we have reported compounds containing the spacers Z = $–(CH_2)_3–$, $–(CH_2)_4–$, $–CH_2SiMe_2CH_2–$, and $–CH_2SiMe_2CCSiMe_2CH_2–$ and the electronegative substituents X = Cl, F, OH, OAc [27-31]. In the solid state the latter exhibit either a double ladder-type structure (**B**, tetramer), a dimeric ladder-type structure **C**, or a monomeric diorganostannoxane **D** (Chart 1). In solution, most of the reported spacer bridged distannoxanes retain their solid state structure, but in the cases of Z = $–(CH_2)_4–$ and X = Cl, and Z = $–(CH_2)_3–$ and X = OAc equilibria between **B**- and **C**-type structures have been observed. These kinetically labile species show higher catalytic activity in acylation reactions than kinetically inert double ladder-type compounds [27, 32].

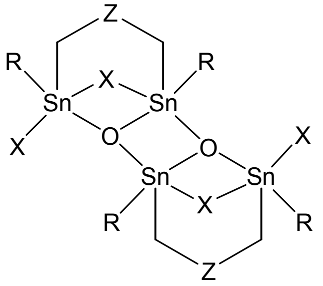
Here we report the synthesis of trimethylene bridged carboxylate-substituted compounds of the type $\{[Me_3SiCH_2(RCOO)Sn(CH_2)_3Sn(OOCR)CH_2SiMe_3]O\}_n$ (**1** R = Ph, **2** R = 2,4-$Me_2C_6H_3$) and show that rather small differences of the substituents R cause substantial changes in the solid state structures.



A



B



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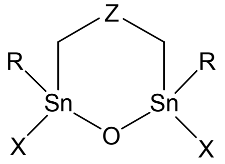

D

The trimethylene-bridged carboxylate-substituted organostannoxanes $\{[Me_3SiCH_2(RCOO)Sn(CH_2)_3Sn(OOCR)CH_2SiMe_3]O\}_n$ (**1,** R = C_6H_5; **2,** R = 2,4-$Me_2C_6H_3$) have been prepared by the reaction of the polymeric organotin oxide $[Me_3SiCH_2(O)Sn(CH_2)_3Sn(O)CH_2SiMe_3]_n$ [26, 27] with two molar amounts of the corresponding carboxylic acids PhCOOH and 2,4-$Me_2C_6H_3COOH$, respectively (Scheme, Method 1). Alternatively, compound **1** has also been synthesized by reaction of the double ladder-type compound $\{[Me_3SiCH_2(Cl)Sn(CH_2)_3Sn(Cl)CH_2SiMe_3]O\}_4$ with eight molar amounts of silver benzoate (Method 2), and by reaction of the polymeric organotin oxide $[Me_3SiCH_2(O)Sn(CH_2)_3Sn(O)CH_2SiMe_3]_n$ with equimolar amounts of $Me_3SiCH_2(PhCOO)_2Sn(CH_2)_3Sn(OOCPh)_2CH_2SiMe_3$ (Method 3).

Method 1

$$1/n\ [\mathrm{Me_3SiCH_2(O)Sn(CH_2)_3Sn(O)CH_2SiMe_3}]_n \ + \ 2\ \mathrm{RCOOH} \ \xrightarrow[-\ \mathrm{H_2O}]{\text{toluene}}$$

$$\longrightarrow \ 1/n\ \{[\mathrm{Me_3SiCH_2(RCOO)Sn(CH_2)_3Sn(OOCR)CH_2SiMe_3}]\mathrm{O}\}_n$$

1, R = Ph, **2**, R = $2,4\text{-}\mathrm{Me_2–C_6H_3}$

Method 2

$$\{[\mathrm{Me_3SiCH_2(Cl)Sn(CH_2)_3Sn(Cl)CH_2SiMe_3}]\mathrm{O}\}_4 \ + \ 8\ \mathrm{RCOOAg} \ \xrightarrow[-\ 8\ \mathrm{AgCl}]{\text{toluene}}$$

$$\longrightarrow \ 4/n\ \{[\mathrm{Me_3SiCH_2(RCOO)Sn(CH_2)_3Sn(OOCR)CH_2SiMe_3}]\mathrm{O}\}_n$$

1, R = Ph

Method 3

$$\begin{array}{c} 1/n\ [\mathrm{Me_3SiCH_2(O)Sn(CH_2)_3Sn(O)CH_2SiMe_3}]_n \\ + \\ \mathrm{Me_3SiCH_2(RCOO)_2Sn(CH_2)_3Sn(OOCR)_2CH_2SiMe_3} \end{array} \ \xrightarrow{\text{toluene}}$$

$$\longrightarrow \ 2/n\ \{[\mathrm{Me_3SiCH_2(RCOO)Sn(CH_2)_3Sn(OOCR)CH_2SiMe_3}]\mathrm{O}\}_n$$

1, R = Ph

Both compounds **1** and **2** are colorless crystalline solids which are well soluble in common organic solvents such as chloroform, toluene, and tetrahydrofuran.

The association factors as determined by osmometric molecular weight measurements in toluene at $T = 60°\mathrm{C}$ amount to $n = 1.94/1.98$ (**1**, $c = 0.037/0.079$ mol/l) and $n = 1.68/1.88$ (**2**, $c = 0.038/0.076$ mol/l). The ^{119}Sn NMR spectrum (111.92 MHz, $\mathrm{C_6D_6}$, room temperature) of **1** ($c = 0.57$ mol/l) and **2** ($c = 0.60$ mol/l) each shows two major signals of equal integral ratio at $\delta = -155.6$ [$^2J(^{119}\mathrm{Sn–O–}^{117/119}\mathrm{Sn}) = 191$ Hz] and -207.6 [$^2J(^{119}\mathrm{Sn–O–}^{117/119}\mathrm{Sn}) = 194$ Hz] for **1**, and $\delta = -155.0$ [$^2J(^{119}\mathrm{Sn–O–}^{117/119}\mathrm{Sn}) = 185$ Hz] and -208.1 ppm [$^2J(^{119}\mathrm{Sn–O–}^{117/119}\mathrm{Sn}) = 182$ Hz] for **2**. Furthermore, additional signals of minor intensity (total integral approximately 4%) appear at $\delta = -127.3$, -160.8, -176.0, -199.4 and -211.9 (**1**), and $\delta = -150.6$ and -200.1 ppm (**2**) for which no unambiguous assignment was made. Notably, no minor intense signals were present in the ^{119}Sn NMR spectrum of a sample of compound **1** which had been prepared by reaction of the tetraorganodistannoxane derivative $\{[\mathrm{Me_3SiCH_2(Cl)Sn(CH_2)_3Sn(Cl)CH_2SiMe_3}]\mathrm{O}\}_4$ with silver benzoate.

No change of the spectra of compounds **1** and **2** was observed upon dilution of the samples to $c = 0.028$ mol/l and $c = 0.033$ mol/l, respectively. In addition, the spectrum of compound **1** was measured at $T = 60°\mathrm{C}$ showing the signals to become broader ($\nu_{1/2} = 68\text{-}76$ Hz) and the $^2J(^{119}\mathrm{Sn–O–}^{117/119}\mathrm{Sn})$ couplings to be no longer visible, indicating dynamic behavior. Most remarkably and in contrast to the corresponding acetate derivative $\{[\mathrm{Me_3SiCH_2(AcO)Sn(CH_2)_3Sn(OAc)CH_2SiMe_3}]\mathrm{O}\}_n$ and to the 1,3-dichlorotetrabutyldistannoxane dimer $[(n\text{-}\mathrm{Bu_2ClSn})_2\mathrm{O}]_2$ for which the signal-to-satellite integral ratios amount to approximately 16:68:16 (exocyclic tins) and 20:60:20 (endocyclic tins) (Fig. 1), the signal-to-satellite integral ratios for the signals of both compounds **1** and **2** are approximately 8:84:8 resembling AXX'-type spectra (A = ^{119}Sn, X = ^{119}Sn, X' = ^{117}Sn) (Fig. 1) resulting from **D**-type monomers but containing two chemically nonequivalent tin atoms.

A close inspection of the spectrum of compound **1** reveals shoulders at both the higher and lower frequency signals which might be a coupling of about 53 Hz (Fig. 1). The $^{119}\mathrm{Sn}–^{119}\mathrm{Sn}$ COSY 2D-NMR spectrum of the benzoate derivative **1** confirms this assumption and unambiguously indicates for both signals two $^2J(^{119}\mathrm{Sn–O–}^{117/119}\mathrm{Sn})$ couplings (Fig. 2) and rules out that the corresponding resonances originate from a monomeric **D**-type structure.

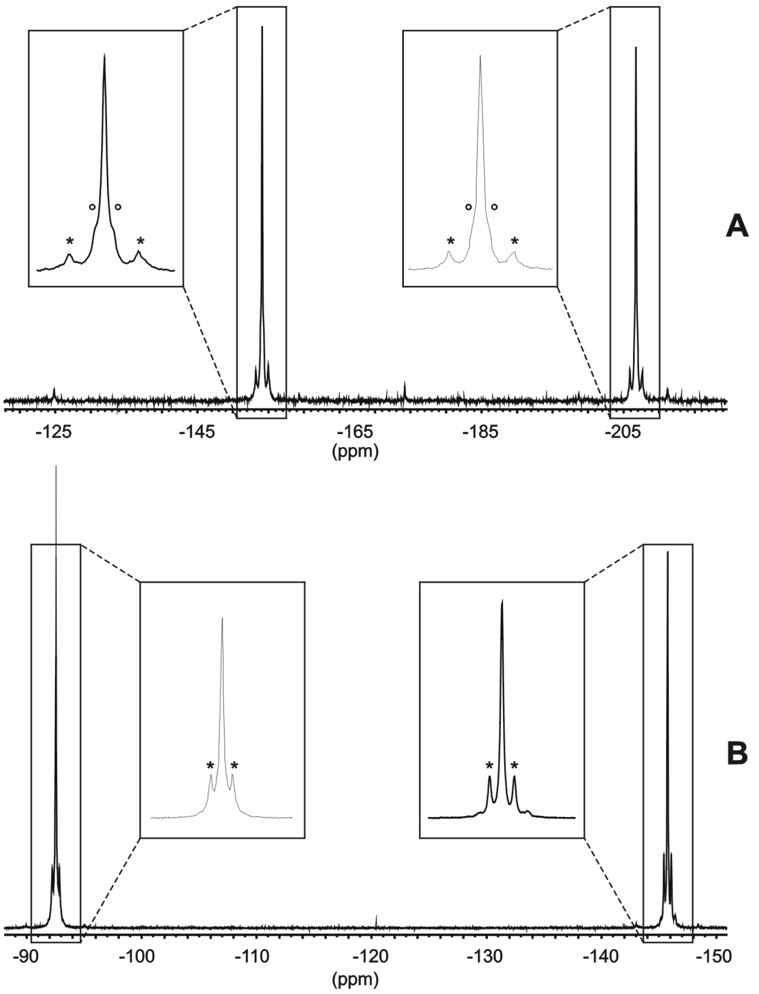

Fig. 1. ^{119}Sn NMR spectra of compound **1** (**A**, C_6D_6, 111.92 MHz, °53 Hz, *191, 194 Hz) and of [*n*-Bu$_2$(Cl)SnOSn(Cl)*n*-Bu]$_2$ (**B**, toluene/D_2O-capillary, 111.92 MHz, *72 Hz).

The ^{13}C NMR spectrum (100.61 MHz, toluene-d$_8$) of compound **1** shows two sets of resonances of rather different intensities, with two equally intense signals each for the carbonyl carbons, the phenyl carbons, the silicon-bonded methylene carbons, and the methyl carbons, and with single resonances for each of the trimethylene carbons. At T = 90°C coalescence of the corresponding signals of both the major and the minor species is observed. The high-intensity resonances are assigned to compound **1** whereas in analogy to the ^{119}Sn NMR spectra, no assignment was made for the low-intensity resonances.

The temperature-dependent NMR spectra and the molecular weight determination indicate for compounds **1** and **2** the existence of equilibria between **C**-type dimers and **D**-type monomers with the former dominating. At ambient temperature (i) the population of the monomer can be neglected and (ii) the rate of monomer-dimer exchange is slow on both the ^{13}C and ^{119}Sn NMR time scales but becomes faster on these time scales at elevated temperatures.

For {[Me_3SiCH_2(OAc)Sn(CH_2)$_3$Sn(AcO)CH_2SiMe_3]O}$_4$, an equilibrium between **B**- and **C**-type structures has been observed in the same concentration range [27] whereas {[(Me_3Si)$_2$CH(Cl)Sn(CH_2)$_3$Sn(Cl)CH($SiMe_3$)$_2$]O} is exclusively monomeric [30]. Apparently, in solution

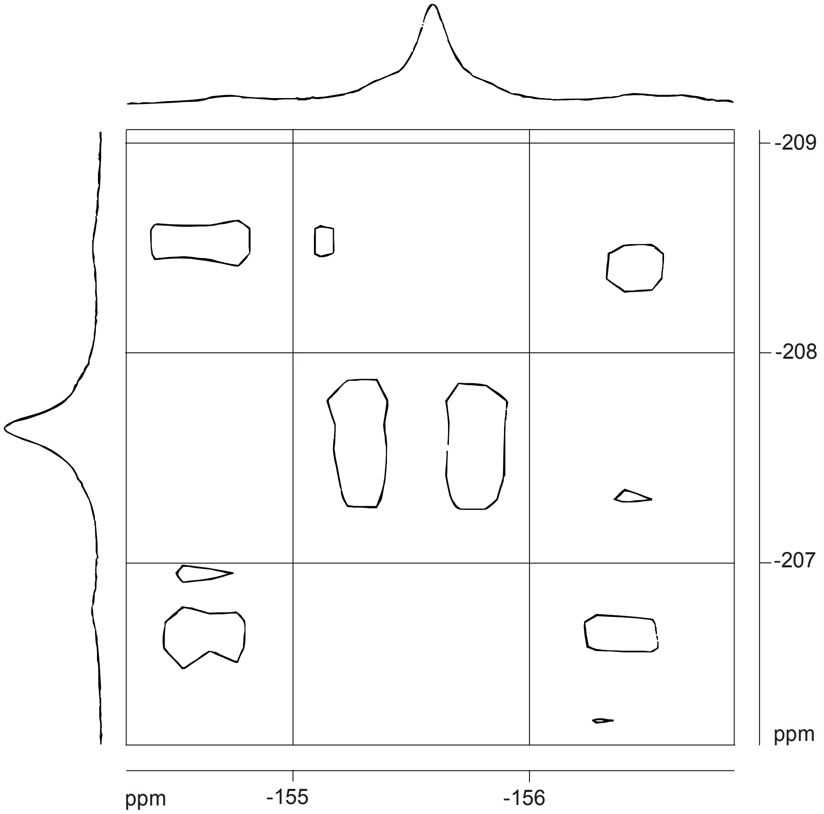

Fig. 2. ^{119}Sn–^{119}Sn COSY NMR spectrum of compound **1** (C_6D_6, c = 0.5686 mol/l) showing two distinct J(^{119}Sn–O–^{119}Sn) couplings. Bruker DPX 300: 111.9003 MHz, NS = 112, TD = 128.

compounds of the general formula $\{[R(X)Sn(CH_2)_3Sn(X)R]O\}_n$ show equilibria between **B**-, **C**-, and **D**-type structures (Chart 1) the position of which depends on the organic substituents R, the electronegative substituents X, the concentration, and the temperature.

The molecular structure of the benzoate-substituted trimethylene-bridged tetraorganodistannoxane **1** is shown in Fig. 3 and selected bond lengths and bond angles are listed in Tables 1 and 2.

Compound **1** crystallizes as a dimer with **C**-type structure. Both trimethylene bridges are on the same side of the ladder core, *i.e.*, **1** adopts the *cis*-configuration similar to that recently reported for an acetylene-bridged tetraorganodistannoxane [29]. A spacer-bridged tetraorganodistannoxane with the higher symmetry *trans*-configuration has also been reported [30]. At first approximation, the exocyclic Sn(1) (geometrical goodness [33-35] $\Delta\Sigma\vartheta$ 81.1°; ΔSn (plane) 0.143(2) Å) and Sn(4) ($\Delta\Sigma\vartheta$ 81.1°; ΔSn (plane) 0.129(1) Å) atoms show distorted trigonal bipyramidal configurations with O(51), O(62), and O(72), O(81), respectively, occupying the axial positions, and O(1), C(1), C(11), and O(2), C(6), C(41), respectively, occupying the equatorial positions. The distortion from the ideal trigonal bipyramidal configuration becomes apparent from the deviation of the axial O(51)–Sn(1)–O(62) and O(72)–Sn(4)–O(81) angles of 167.5(1) and 170.1(1)°, respectively, from 180°. Furthermore, the equatorial C(1)–Sn(1)–C(11) and C(6)–Sn(4)–C(41) angles are opened to 147.8(1) and 149.8(1)°, respectively. This is the result of intramolecular Sn(1)–O(52) and Sn(4)–O(82) distances of 2.689(2) Å and 2.608(2) Å, respectively, which are far shorter than the sum of the van der Waals radii [36] of tin (2.20 Å) and oxygen (1.50 Å). These interactions proceed via the face defined by C(1), C(11), O(51) and C(6), C(41), O(81), respectively. Taking these interactions into account, both Sn(1) and Sn(4) are typical examples for [5+1]-coordinated tins.

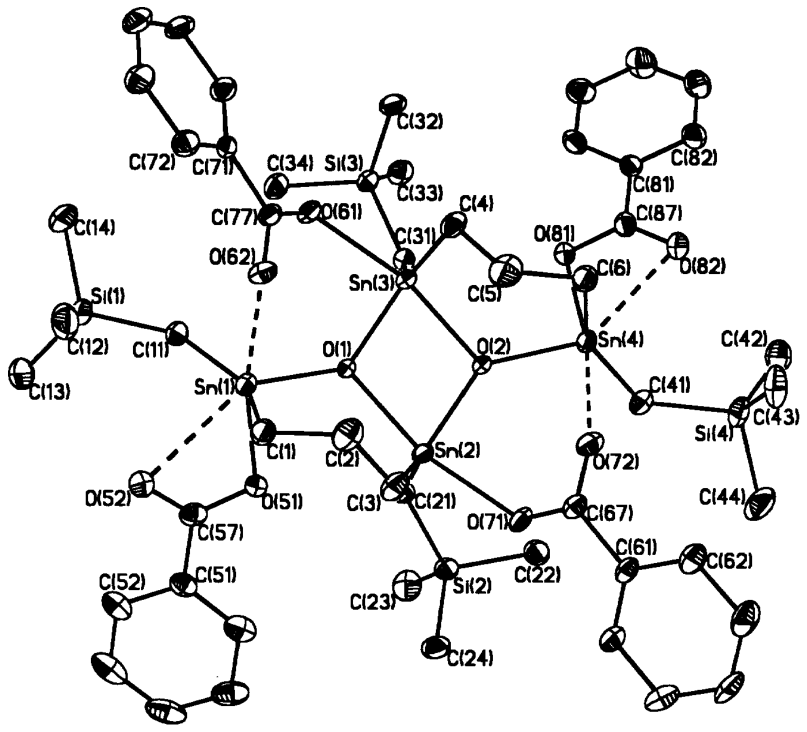

Fig. 3. General view (SHELXTL) of **1** showing 30% probability displacement ellipsoids and the atom numbering scheme.

The endocyclic Sn(2) ($\Delta\Sigma\vartheta$ 89.9°; ΔSn (plane) 0.006(1) Å) and Sn(3) ($\Delta\Sigma\vartheta$ 90.9°; ΔSn (plane) 0.025(1) Å) atoms are also five-coordinate but the trigonal bipyramidal configuration is less distorted. The axial positions are occupied by O(2), O(61), and O(1), O(71), respectively, and the equatorial ones by O(1), C(4), C(31), and O(2), C(3), C(21), respectively. In addition, there are intramolecular Sn(2)$\cdots$O(51) and Sn(3)$\cdots$O(81) distances of 3.372(2) and 3.247(2) Å, respectively, being also shorter than the sum of the van der Waals radii of the corresponding atoms.

Two of the four benzoate groups coordinate in a bidentate fashion bridging each two tin atoms with Sn(1)–O(62) 2.313(2), Sn(3)–O(61) 2.236(2), and Sn(2)–O(71) 2.218(2), Sn(4)–O(72) 2.365(2) Å, respectively. The two other benzoate groups coordinate in an unisobidentate mode with Sn(1)–O(51) 2.168(2), Sn(1)–O(52) 2.689(2), and Sn(4)–O(81) 2.174(2), Sn(4)–O(82) 2.608(2) Å, respectively. These different coordination modes are also reflected in the IR spectra showing two absorptions at $\nu(COO)_{as}$ = 1570, 1537 cm^{-1}.

The ^{119}Sn CP MAS spectrum of an amorphous sample of compound **1** shows four signals of equal integral ratio at δ = -158, -171, -215, and -220 ppm and reflects the nonequivalence of the four tin atoms as observed by the single crystal X-ray analysis.

The molecular structure of the 2,4-dimethylbenzoate-substituted trimethylene-bridged tetraorganodistannoxane **2** is shown in Fig. 4 and selected bond lengths and bond angles are listed in Tables 3 and 4.

Compound **2** crystallizes as a centrosymmetric tetramer with a double ladder-type structure (**B**) in which two $Sn_4O_2(OOCC_6H_3Me_2\text{-}2,4)_4$-layers are bridged by four trimethylene spacers. For the sake of clarity one layer is shown in Fig. 5. The configuration of the tin atoms ($\Delta\Sigma\vartheta$ 80.8° (Sn1), 90.1 (Sn2), 90.3° (Sn3), 84.1° (Sn4); ΔSn (plane) 0.135(3) Å (Sn1), 0.034(3) Å (Sn2), 0.016(3) Å (Sn3), 0.110(4) Å (Sn4)) resembles that of the corresponding tins in compound **1** as do the coordination modes of the four 2,4-dimethylbenzoate moieties.

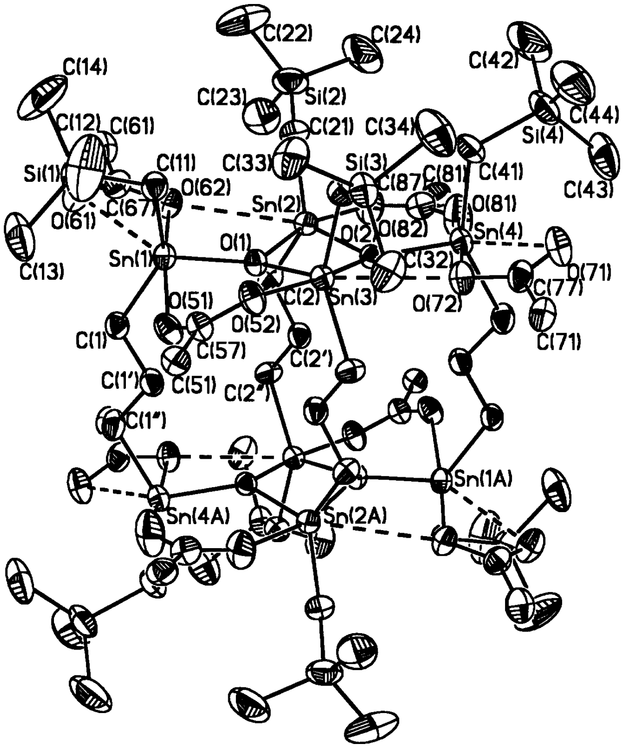

Fig. 4. General view (SHELXTL-PLUS) of **2** showing 30% probability displacement ellipsoids and the atom numbering scheme. Only the C *ipso* atoms of 2,4-$Me_2C_6H_3$ groups are shown for clarity. (Symmetry transformations used to generate equivalent atoms: a = -*x*, -*y* + 1, -*z* + 1).

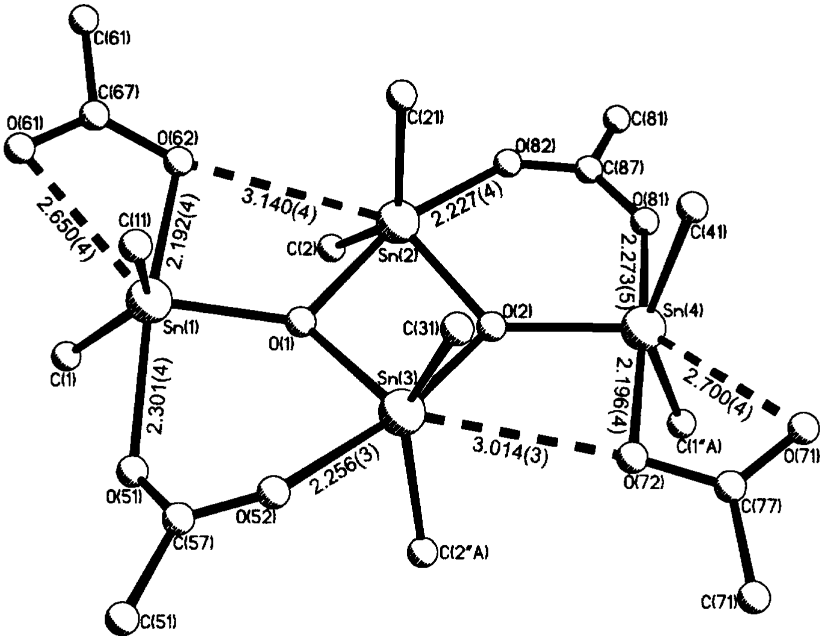

Fig. 5. View on the $Sn_4(OCOR)_4O_2$ layer of compound **2**. For clarity only the *ipso* carbons of the phenyl groups and the methylene carbons of the trimethylsilylmethyl groups are shown.

TABLE 1. Selected bond distances for structure **1**

Bond	*d*, Å	Bond	*d*, Å
Sn(1)–C(1)	2.113(3)	Sn(3)–C(4)	2.139(3)
Sn(1)–C(11)	2.109(2)	Sn(3)–C(31)	2.111(3)
Sn(1)–O(1)	2.026(2)	Sn(3)–O(1)	2.030(2)
Sn(1)–O(51)	2.168(2)	Sn(3)–O(2)	2.159(2)
Sn(1)–O(62)	2.313(2)	Sn(3)–O(61)	2.236(2)
Sn(1)–O(52)	2.689(2)	Sn(3)–O(81)	3.247(2)
Sn(2)–C(3)	2.143(3)	Sn(4)–C(6)	2.116(3)
Sn(2)–C(21)	2.110(2)	Sn(4)–C(41)	2.099(3)
Sn(2)–O(1)	2.152(2)	Sn(4)–O(2)	2.034(2)
Sn(2)–O(2)	2.036(2)	Sn(4)–O(81)	2.174(2)
Sn(2)–O(71)	2.218(2)	Sn(4)–O(72)	2.365(2)
Sn(2)–O(51)	3.230(2)	Sn(4)–O(82)	2.608(2)

The reason why the benzoate derivative **1** crystallizes as a dimer with ladder-type structure (Fig. 3) whereas the rather similar 2,4-dimethylbenzoate derivative **2** gives a tetramer with double ladder structure (Fig. 4) is not quite obvious but indicates a rather small difference in energy between both forms.

TABLE 2. Selected bond angles for structure **1**

Angle	ω, deg.	Angle	ω, deg.
O(1)–Sn(1)–C(1)	103.18(8)	O(2)–Sn(3)–C(4)	93.20(9)
O(1)–Sn(1)–C(11)	107.40(8)	O(2)–Sn(3)–C(31)	99.87(8)
O(1)–Sn(1)–O(51)	84.57(7)	O(61)–Sn(3)–C(4)	87.13(9)
O(1)–Sn(1)–O(62)	84.66(6)	O(61)–Sn(3)–C(31)	91.68(9)
C(1)–Sn(1)–C(11)	147.8(1)	C(4)–Sn(3)–C(31)	134.9(1)
C(1)–Sn(1)–O(62)	83.73(9)	O(2)–Sn(4)–O(72)	85.56(6)
C(1)–Sn(1)–O(51)	92.58(9)	O(2)–Sn(4)–O(81)	84.78(6)
C(11)–Sn(1)–O(51)	100.08(9)	O(2)–Sn(4)–C(6)	101.40(8)
C(11)–Sn(1)–O(62)	89.18(9)	O(2)–Sn(4)–C(41)	106.61(8)
O(51)–Sn(1)–O(62)	167.50(6)	O(81)–Sn(4)–O(72)	170.08(6)
O(1)–Sn(2)–O(2)	75.76(6)	O(81)–Sn(4)–C(6)	95.8(1)
O(1)–Sn(2)–O(71)	165.04(6)	O(81)–Sn(4)–C(41)	97.80(9)
O(1)–Sn(2)–C(3)	93.00(9)	O(72)–Sn(4)–C(6)	83.9(1)
O(1)–Sn(2)–C(21)	98.63(8)	O(72)–Sn(4)–C(41)	87.14(9)
O(2)–Sn(2)–O(71)	91.32(6)	C(6)–Sn(4)–C(41)	149.8(1)
O(2)–Sn(2)–C(3)	118.96(9)	Sn(1)–O(1)–Sn(3)	131.99(8)
O(2)–Sn(2)–C(21)	106.34(9)	Sn(1)–O(1)–Sn(2)	118.72(8)
O(71)–Sn(2)–C(3)	86.63(9)	Sn(3)–O(1)–Sn(2)	104.41(6)
O(71)–Sn(2)–C(21)	92.16(8)	Sn(4)–O(2)–Sn(2)	132.34(8)
C(3)–Sn(2)–C(21)	134.7(1)	Sn(4)–O(2)–Sn(3)	118.34(7)
O(1)–Sn(3)–O(2)	75.74(6)	Sn(2)–O(2)–Sn(3)	104.41(6)
O(1)–Sn(3)–O(61)	89.33(6)	O(51)–C(57)–O(52)	122.1(3)
O(1)–Sn(3)–C(4)	118.59(9)	O(61)–C(67)–O(62)	124.0(3)
O(1)–Sn(3)–C(31)	106.52(9)	O(71)–C(77)–O(72)	124.0(3)
O(2)–Sn(3)–O(61)	163.18(6)	O(81)–C(87)–O(82)	121.0(3)

TABLE 3. Selected bond distances for structure **2**

Bond	*d*, Å	Bond	*d*, Å
Sn(1)–C(1)	2.122(5)	Sn(3)–C(2"a)	2.117(5)
Sn(1)–C(11)	2.104(5)	Sn(3)–C(31)	2.106(5)
Sn(1)–O(1)	2.036(3)	Sn(3)–O(1)	2.038(3)
Sn(1)–O(51)	2.301(4)	Sn(3)–O(2)	2.190(3)
Sn(1)–O(62)	2.193(4)	Sn(3)–O(52)	2.255(3)
Sn(1)–O(61)	2.648(4)	Sn(3)–O(72)	3.014(3)
Sn(2)–C(2)	2.104(5)	Sn(4)–C(41)	2.117(6)
Sn(2)–C(21)	2.120(5)	Sn(4)–C(1"a)	2.125(5)
Sn(2)–O(1)	2.196(3)	Sn(4)–O(2)	2.051(3)
Sn(2)–O(2)	2.036(3)	Sn(4)–O(71)	2.699(4)
Sn(2)–O(82)	2.228(4)	Sn(4)–O(72)	2.196(4)
Sn(2)–O(62)	3.139(4)	Sn(4)–O(81)	2.271(5)

TABLE 4. Selected bond angles for structure **2**

Angle	ω, deg.	Angle	ω, deg.
O(1)–Sn(1)–C(1)	113.7(2)	O(2)–Sn(3)–C(2"a)	94.7(2)
O(1)–Sn(1)–C(11)	102.2(2)	O(2)–Sn(3)–C(31)	95.9(2)
O(1)–Sn(1)–O(51)	89.3(1)	O(52)–Sn(3)–C(2"a)	89.6(2)
O(1)–Sn(1)–O(62)	84.4(1)	O(52)–Sn(3)–C(31)	87.2(2)
C(1)–Sn(1)–C(11)	142.8(2)	C(2"a)–Sn(3)–C(31)	139.7(2)
C(1)–Sn(1)–O(62)	93.6(2)	O(2)–Sn(4)–O(72)	83.7(1)
C(1)–Sn(1)–O(51)	81.3(2)	O(2)–Sn(4)–O(81)	93.6(2)
C(11)–Sn(1)–O(51)	89.6(2)	O(2)–Sn(4)–C(1"a)	108.3(2)
C(11)–Sn(1)–O(62)	99.9(2)	O(2)–Sn(4)–C(41)	104.0(2)
O(51)–Sn(1)–O(62)	169.6(1)	O(81)–Sn(4)–O(72)	172.9(2)
O(1)–Sn(2)–O(2)	76.1(1)	O(81)–Sn(4)–C(1"a)	83.3(2)
O(1)–Sn(2)–O(82)	164.8(2)	O(81)–Sn(4)–C(41)	87.0(3)
O(1)–Sn(2)–C(2)	94.1(2)	O(72)–Sn(4)–C(1"a)	91.2(2)
O(1)–Sn(2)–C(21)	99.5(2)	O(72)–Sn(4)–C(41)	100.1(2)
O(2)–Sn(2)–O(82)	91.2(1)	C(1"a)–Sn(4)–C(41)	146.7(2)
O(2)–Sn(2)–C(2)	117.4(2)	Sn(1)–O(1)–Sn(3)	128.2(2)
O(2)–Sn(2)–C(21)	108.6(2)	Sn(1)–O(1)–Sn(2)	126.0(2)
O(82)–Sn(2)–C(2)	84.4(2)	Sn(3)–O(1)–Sn(2)	102.3(1)
O(82)–Sn(2)–C(21)	92.3(2)	Sn(4)–O(2)–Sn(2)	130.1(2)
C(2)–Sn(2)–C(21)	133.9(2)	Sn(4)–O(2)–Sn(3)	121.8(2)
O(1)–Sn(3)–O(2)	76.2(1)	Sn(2)–O(2)–Sn(3)	102.6(1)
O(1)–Sn(3)–O(52)	93.1(1)	O(51)–C(57)–O(52)	123.3(5)
O(1)–Sn(3)–C(2"a)	112.2(2)	O(61)–C(67)–O(62)	120.9(6)
O(1)–Sn(3)–C(31)	108.1(2)	O(71)–C(77)–O(72)	121.4(6)
O(2)–Sn(3)–O(52)	169.2(1)	O(81)–C(88)–O(82)	121.7(6)

EXPERIMENTAL

All solvents were dried and purified by standard procedures. Bruker DPX-300, DRX-400, DRX-500, CP-MAS MSL-400, and Varian INOVA-600 spectrometers were used to obtain ^{1}H, ^{13}C, and ^{119}Sn NMR spectra. ^{1}H, ^{13}C, and ^{119}Sn chemical shifts δ are given in ppm and were referenced against Me$_4$Si and Me$_4$Sn. The molecular weight determinations were performed on a Knauer Osmometer K7000 in freshly distilled toluene at

60°C and were referenced against Benzil. The organotin chloride $Me_3SiCH_2(Cl)_2Sn(CH_2)_3Sn(Cl)_2CH_2SiMe_3$, the organotin oxide $[Me_3SiCH_2(O)Sn(CH_2)_3Sn(O)CH_2SiMe_3]_n$ and the tetraorganodistannoxane derivative $\{[Me_3SiCH_2(Cl)Sn(CH_2)_3Sn(Cl)CH_2SiMe_3]O\}_4$ were prepared according to literature procedures [28, 31].

Synthesis of $\{[Me_3SiCH_2(PhCOO)Sn(CH_2)_3Sn(OOCPh)CH_2SiMe_3]O\}_n$ (1). Method 1. Benzoic acid (0.367 g, 3.00 mmol) was added to a suspension of $[Me_3SiCH_2(O)Sn(CH_2)_3Sn(O)CH_2SiMe_3]_n$ (0.730 g, 1.50 mmol) in toluene (80 ml). The reaction mixture was heated at reflux in a Dean Stark apparatus for 7 h giving a cloudy solution. The solution was filtered and concentrated to 30 ml. Crystallization at 0°C gave 0.850 g (80%) of **1** as colourless crystals of mp 179-183°C.

^1H NMR spectrum ($CDCl_3$, 400.13 MHz), δ, ppm: -0.11 (s, 18H, $SiMe_3$); 0.26 (s, 18H, $SiMe_3$); 0.36, 0.58 (AB-pattern established by ^1H–^1H COSY experiment, $^2J(H_A–H_B)$ = 13 Hz, 4H, $SiCH_2$); 0.97, 1.25 (AB-pattern, $^2J(H_A–H_B)$ = 13 Hz, 4H, $SiCH_2$); 1.56 (complex pattern, 4H, CH_2Sn); 1.95 (complex pattern, 4H, CH_2Sn); 2.55 (complex pattern, 4H, CH_2); 7.30-7.56 (complex pattern, 8H, H_{aryl}); 7.98 (d, $^3J(^1H–^1H)$ = 7 Hz, 2H, H_{aryl}); 8.04 (d, $^3J(^1H–^1H)$ = 7 Hz, 2H, H_{aryl}). ^{13}C NMR spectrum (toluene-d_8, 100.61 MHz), δ, ppm: 1.1, 1.6 ($SiMe_3$), 12.0, 13.6 ($SiCH_2$), 22.4 (CH_2), 30.6, 30.8 (CH_2Sn), 127.8, 128.0, 130.0, 130.2, 131.8, 132.4, 133.2, 133.6 (C_{aryl}), 174.0, 175.8 (COO), additional resonances at δ = 1.3, 1.4, 11.3, 14.2, 21.8, 29.6, 29.8, 131.6, 132.3, 133.8, 134.0, 171.8, 172.4. ^{119}Sn NMR spectrum (C_6D_6, 111.92 MHz), δ, ppm: -127.3 (~1%), -155.6 (48%; $^2J(^{119}Sn–^{117/119}Sn)$ = 191 Hz), -160.8 (~1%), -176.0 (~1%), -199.4 (~1%), -207.6 (48%, $^2J(^{119}Sn–^{117/119}Sn)$ = 194 Hz), -211.9 (~1%). IR spectrum (KBr): $\nu(COO)_{as}$ = 1571, 1535 cm^{-1}; $\nu(COO)_{sym}$ = 1393, 1364 cm^{-1}. IR spectrum ($CHCl_3$): $\nu(COO)_{as}$ = 1570, 1537 cm^{-1}; $\nu(COO)_{sym}$ = 1394, 1364 cm^{-1}. Molecular weight determination: 1385 $g \cdot mol^{-1}$ (c = 0.037 mol l^{-1}), 1408 $g \cdot mol^{-1}$ (c = 0.079 $mol \cdot l^{-1}$). Found, %: C 42.3; H 5.8. $C_{50}H_{76}O_{10}Si_4Sn_4$ (1424.5). Calculated, %: C 42.17; H 5.38.

Method 2. To a solution of $\{[Me_3SiCH_2(Cl)Sn(CH_2)_3Sn(Cl)CH_2SiMe_3]O\}_4$ (1.800 g, 0.83 mmol) in toluene (190 ml) silver benzoate (1.520 g, 6.66 mmol) was added and the mixture was stirred for 360 h at room temperature. The precipitate of AgCl was separated by filtration and the filtrate evaporated in *vacuo* to give 2.330 g (98%) of **1** as colourless solid.

Method 3. $Me_3SiCH_2Cl_2Sn(CH_2)_3SnCl_2CH_2SiMe_3$ (0.500 g, 0.84 mmol) and silver benzoate (0.770 g, 3.36 mmol) were dissolved in toluene (70 ml) and stirred for 48 h at room temperature. The precipitate was separated by filtration and the solvent evaporated in *vacuo* to give 0.570 g (72%) of $Me_3SiCH_2(PhCOO)_2Sn(CH_2)_3Sn(OOCPh)_2CH_2SiMe_3$ as yellow oil (^{119}Sn NMR (toluene, D_2O-capillary, 111.92 MHz) δ = -142.6 ($^2J(^{119}Sn–^{117/119}Sn)$ = 296 Hz)) which was not purified further. The yellow oil (0.410 g, 0.44 mmol) and $[Me_3SiCH_2(O)Sn(CH_2)_3Sn(O)CH_2SiMe_3]_n$ (0.212 g, 0.44 mmol) were added to CH_2Cl_2 (10 ml) and stirred for 12 h at room temperature. The solvent of the clear solution was evaporated in *vacuo* to give **1** almost quantitatively.

Synthesis of $\{[Me_3SiCH_2(2,4\text{-}Me_2C_6H_3COO)Sn(CH_2)_3Sn(OOCC_6H_3Me_2\text{-}2,4)CH_2SiMe_3]O\}_n$ (2). 2,4-Dimethyl benzoic acid (0.309 g, 2.06 mmol) was added to a suspension of $[Me_3SiCH_2(O)Sn(CH_2)_3Sn(O)CH_2SiMe_3]_n$ (0.500 g, 1.03 mmol) in toluene (55 ml). The reaction mixture was heated at reflux in a Dean–Stark apparatus for 6 h giving a cloudy solution. The solution was filtered and the filtrate evaporated *in vacuo*. The residual colorless oil was crystallized from CH_2Cl_2 to give 0.703 g (89%) of **2** as a colorless solid; mp 138-152°C.

^1H NMR spectrum ($CDCl_3$, 400.13 MHz), δ, ppm: -0.11 (s, 18H, $SiMe_3$); 0.10 (s, 18H, $SiMe_3$); 0.35, 0.66 (AB-pattern, $^2J(H_A–H_B)$ = 13 Hz, 4H, $SiCH_2$); 0.85, 0.99 (AB-pattern, $^2J(H_A–H_B)$ = 13 Hz, 4H, $SiCH_2$); 1.51 (complex pattern, 4H, CH_2Sn); 1.90 (complex pattern, 4H, CH_2Sn); 2.29, 2.31, 2.33 (s, 12H, Me); 2.51 (complex pattern, 4H, CH_2); 6.97 (complex pattern, 8H, H_{aryl}); 7.66 (d, $^3J(^1H–^1H)$ = 7 Hz, 2H, H_{aryl}); 7.75 (d, $^3J(^1H–^1H)$ = 7 Hz, 2H, H_{aryl}). ^{119}Sn NMR spectrum (C_6D_6, 111.92 MHz), δ, ppm: -150.6 (~1%), -155.0 (49%; $^2J(^{119}Sn–^{117/119}Sn)$ = 185 Hz), -200.1 (~1%), -208.1 (49%, $^2J(^{119}Sn–^{117/119}Sn)$ = 182 Hz). IR spectrum (KBr): $\nu(COO)_{as}$ = 1590, 1536 cm^{-1}; $\nu(COO)_{sym}$ = 1382, 1345 cm^{-1}. IR spectrum ($CHCl_3$): $\nu(COO)_{as}$ = 1595, 1532 cm^{-1}; $\nu(COO)_{sym}$ = 1379, 1355 cm^{-1}. Molecular weight determination: 1294 $g \cdot mol^{-1}$ (c = 0.038 $mol \cdot l^{-1}$), 1447 $g \cdot mol^{-1}$ (c = 0.076 $mol \cdot l^{-1}$). Found, %: C 45.30; H 6.20. $C_{116}H_{184}O_{20}Si_8Sn_8$ (3073.3). Calculated, %: C 45.33; H 6.04.

TABLE 5. Crystal data for compounds **1** and **2**

Compound number	**1**	**2**
Empirical formula	$C_{50}H_{76}O_{10}Si_4Sn_4$	$C_{116}H_{184}O_{20}Si_8Sn_8{\cdot}2C_7H_8$
Formular weight	1424.45	3257.14
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	P-1
Cell constants, Å and °		
a	17.9120(3)	15.6877(4)
b	14.7076(3)	17.6756(7)
c	24.1362(5)	17.7484(7)
α	90	74.709(1)
β	103.136(1)	63.809(2)
γ	90	74.651(2)
Volume, Å^3	6192.1(2)	4196.8(3)
Z	4	1
Density(calculated), mg·m^{-3}	1.528	1.289
Absorption coefficient, mm^{-1}	1.720	1.278
Crystal size, mm^3	0.25 × 0.15 × 0.12	0.25 × 0.13 × 0.13
Theta range for data collection	2.94 to 27.47°	3.46 to 27.50°
Reflections collected	58061	55116
Independent reflections	14090 [R_{int} = 0.0490]	17335 [R_{int} = 0.0440]
Data/restraints/parameters	14090/0/613	17335/12/670
Goodness-of-fit on F^2	0.767	0.835
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0298$, $wR_2 = 0.0359$	$R_1 = 0.0402$, $wR_2 = 0.0943$
R indices (all data)	$R_1 = 0.0922$, $wR_2 = 0.0402$	$R_1 = 0.1254$, $wR_2 = 0.1055$
Largest diff. peak and hole (e/Å^3)	0.640 / -0.470	0.673 / -0.553

Crystallography. Intensity data for the colorless crystals were collected on a KappaCCD diffractometer with graphite-monochromated MoKα radiation (0.71069 Å) at 173 K (**1**) and 291 K (**2**), respectively. The data collection covered almost the whole sphere of reciprocal space with 303 (**1**, 3 sets at different κ-angles) and 360 (**2**) frames *via* ω-rotation (Δ/ω= 1°) at two times 10s per frame. The crystal-to-detector distance was 3.4 cm (**1**) and 2.8 cm (**2**), with a detector-θ-offset of 5° (**2**). Crystal decay was monitored by repeating the initial frames at the end of data collection. Analyzing the duplicate reflections, there was no indication for any decay for both **1** and **2**. The structures were solved by direct methods SHELXS97 [37] and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods SHELXL97[38].

The H atoms were placed in geometrically calculated positions using a riding model with U_{iso} constrained at 1.2 for non-methyl groups and 1.5 for methyl groups times U_{eq} of the carrier C atom.

Solvent molecules (toluene, **2**) were refined isotropically with a common U_{iso} (C(91) > C(97) 0.172(3) Å^2, C(101) > C(107) 0.184(4) Å^2), and with an occupancy of 0.5 and a set of restraints to aid in modelling the disorder (AFIX 66 for aromatic rings and DFIX 1.540(1) for methyl aryl distances). One 2,4-$Me_2C_6H_3$ group in **2** (C62 > C66, C68, C69) was refined isotropically.

Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from reference [39]. Figures were created by SHELXTL [40]. Crystallographic data are given in Table 3, and selected bond distances and bond angles are listed in Tables 1, 2 (**1**) and 3, 4 (**2**).

Supplementary Material Available. A complete description of the X-ray crystallographic structure determina-tions of compounds **1** and **2** have been deposited with Cambridge Crystallo-graphic Data Centre as supplementary publication Nos. CCDC 148994 (**1**), CCDC 148995 (**2**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-(0)12 23-33 60 33 or e-mail: deposit@ccdc.cam.ac.uk).

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