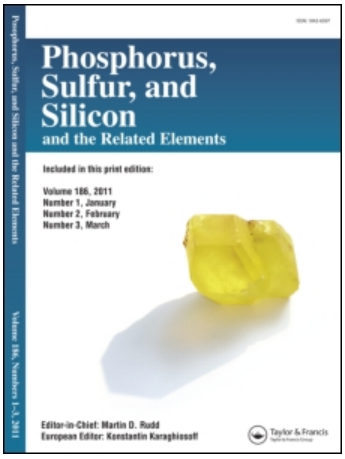

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UNEXPECTED FORMATION AND MOLECULAR STRUCTURE OF 2,2,6,6-TETRA-*t*-BUTYL-4,8-DIMETHYL-1,5,9-TRIOXA-4,8-DISILA-2,6-DISTANNABICYCLO[3.3.1]NONANE

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UNEXPECTED FORMATION AND MOLECULAR STRUCTURE OF 2,2,6,6-TETRA-*t*-BUTYL-4,8-DIMETHYL-1,5,9-TRIOXA-4,8-DISILA-2,6-DISTANNABICYCLO[3.3.1]NONANE

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Dedicated to Professor J. G. Verkade on the occasion of his 60th birthday

(Received January 11, 1996; in final form March 5, 1996)

The title compound **2** has been prepared by treatment of $(i\text{-PrO})_2MeSiCH_2(t\text{-Bu})_2SnCl$ **1** with potassium fluoride/water. Multinuclear NMR and X-ray studies reveal **2** adopts bicyclo[3.3.1]nonane structure. **2** crystallizes in the monoclinic space group P2(1)/n with unit cell dimensions a = 12.880(3), b = 16.949(4), c = 13.472(4) Å, β 93.04(2)°, Z = 4. The structure was refined to a final R value of 0.065.

Key words: X-ray structure, NMR spectra, Lewis acids, organosilicon compound, stannanes.

INTRODUCTION

Alkylidene bridged di- and multitins such as $(Ph_2XSn)_2(CH_2)_n$[1] (X = F, Cl, Br, I; *n* = 1–3), $[Me(Cl)Sn(CH_2)_3]_3$[2] and $ClSn[(CH_2)_8SnCl$[3] behave as bidentate Lewis acids towards anions and neutral donor molecules. $(PhCl_2Sn)_2CH_2$[4] and $ClSn[(CH_2)_3SnMe_2Cl]_3$[5] exhibit high selectivity toward dihydrogen phosphate when used as carriers in anion sensitive electrodes. To the best of our knowledge $o\text{-}C_6H_4(SiPhF_2)_2$[6] is the only organosilicon compound acting in a bidentate mode toward fluoride.

In the course of an ongoing study on multidentate Lewis acids we are interested in investigating compounds containing both tin and silicon as Lewis acidic sides. However, as shown below, when attempting the synthesis of a simple representative of this class of compounds, i.e. $t\text{-}Bu_2FSnCH_2SiF_2Me$, we obtained the hydrolysis product **2** instead.

RESULTS AND DISCUSSION

The reaction of [(diisopropoxy)methylsilyl]methylmagnesium chloride[7] with di-*t*-butyldichlorostannane afforded [(diisopropoxy)methylsilyl]methyl-di-*t*-butylchlorostannane **1** in high yield (Equation 1).

$$(i\text{-PrO})_2MeSiCH_2MgCl + t\text{-}Bu_2SnCl_2 \xrightarrow[-MgCl_2]{thf} \underset{\mathbf{1}}{(i\text{-PrO})_2MeSiCH_2(t\text{-Bu})_2SnCl} \quad (1)$$

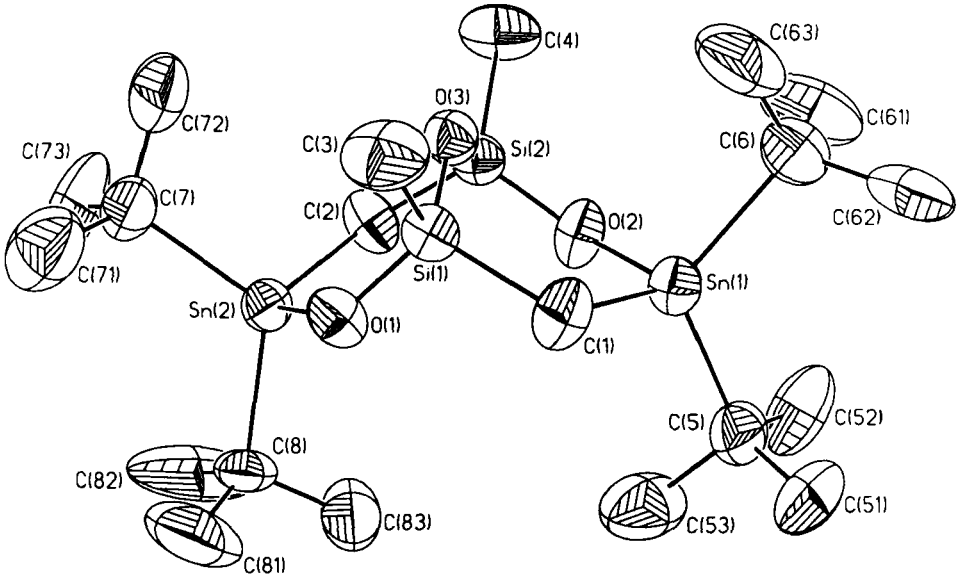
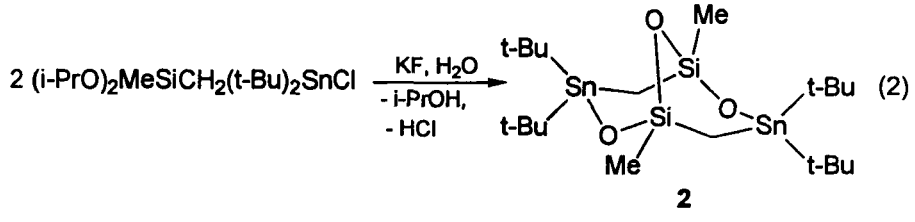


FIGURE 1 Molecular structure (SHELXTL-PLUS) and atom-numbering scheme with thermal ellipsoids at the 50% probability level. H atoms are omitted for clarity.

1 is a distillable liquid which was fully characterized by elemental analysis and NMR spectroscopy.

Surprisingly, its reaction with aqueous potassium fluoride did not result in chloride/fluoride exchange at tin and precipitation of the corresponding organotin fluoride. Instead, complete hydrolysis at both tin and silicon took place with formation of 2,2,6,6-tetra-*t*-butyl-4,8-dimethyl-1,5,9-trioxa-4,8-disila-2,6-distannabicyclo[3.3.1]-nonane **2** (Equation 2).



2

2 is a colourless, sharp melting crystalline solid which is well soluble in common organic solvents such as chloroform, toluene and thf. Its ^{1}H NMR (499.81 MHz, C_6D_6) spectrum displays a singlet for the methyl protons at 0.47 ppm. The methylene protons show an AB pattern, i.e., a doublet at 0.08 ppm with $^2J(^{119}\text{Sn-}^1\text{H})$ 45 Hz and a doublet at 0.37 ppm with $^2J(^{119}\text{Sn-}^1\text{H})$ 57.5 Hz. The $^2J(^1\text{H-}^1\text{H})$ coupling amounts to 13.4 Hz. The AB pattern was confirmed by recording a spectrum at 250.133 MHz. The *t*-butyl protons are not equivalent and appear as a pair of singlets of equal intensity at 1.28 ($^3J(^{119}\text{Sn-}^1\text{H})$ 77 Hz) and 1.29 ($^3J(^{119}\text{Sn-}^1\text{H})$ 79 Hz) ppm.

The ^{13}C NMR (62.896 MHz, C_6D_6) spectrum displays singlets at −2.0 ($SnCH_2Si$) and 4.1 ($SiCH_3$) ppm, two resonances for the quarternary carbons at 30.7 and 30.8 ppm, and two resonances for the methyl carbons at 33.0 and 33.2 ppm. The ^{29}Si(15.92

TABLE I

Selected bond distances (Å) in **2**

Sn(1)	- O(2)	2,006(7)	Sn(2)	- C(7)	2,150(12)	Si(1)	- C(3)	1,869(11)
Sn(1)	- C(5)	2,170(12)	Sn(2)	- C(8)	2,189(10)	Si(2)	- O(2)	1,635(8)
Sn(1)	- C(1)	2,186(10)	Si(1)	- O(1)	1,607(7)	Si(2)	- O(3)	1,654(7)
Sn(1)	- C(6)	2,206(12)	Si(1)	- O(3)	1,659(7)	Si(2)	- C(2)	1,843(11)
Sn(2)	- O(1)	2,009(7)	Si(1)	- C(1)	1,844(11)	Si(2)	- C(4)	1,870(11)
Sn(2)	- C(2)	2,141(10)						

TABLE II

Selected bond angles (°) in **2**

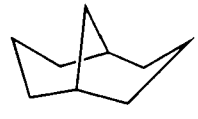
O(2)	- Sn(1)	- C(5)	104,9(4)		O(1)	- Si(1)	- C(3)	112,4(5)
O(2)	- Sn(1)	- C(1)	103,2(3)		O(3)	- Si(1)	- C(3)	108,0(5)
C(5)	- Sn(1)	- C(1)	112,5(5)		C(1)	- Si(1)	- C(3)	109,1(6)
O(2)	- Sn(1)	- C(6)	104,5(4)		O(2)	- Si(2)	- O(3)	108,0(4)
C(5)	- Sn(1)	- C(6)	115,6(5)		O(2)	- Si(2)	- C(2)	110,6(5)
C(1)	- Sn(1)	- C(6)	114,5(5)		O(3)	- Si(2)	- C(2)	109,2(4)
O(1)	- Sn(2)	- C(2)	104,7(4)		O(2)	- Si(2)	- C(4)	112,1(5)
O(1)	- Sn(2)	- C(7)	105,6(4)		O(3)	- Si(2)	- C(4)	106,8(5)
C(2)	- Sn(2)	- C(7)	108,6(5)		C(2)	- Si(2)	- C(4)	110,0(6)
O(1)	- Sn(2)	- C(8)	101,3(4)		Si(1)	- O(1)	- Sn(2)	127,6(4)
C(2)	- Sn(2)	- C(8)	116,8(5)		Si(2)	- O(2)	- Sn(1)	126,0(4)
C(7)	- Sn(2)	- C(8)	118,0(5)		Si(2)	- O(3)	- Si(1)	127,9(4)
O(1)	- Si(1)	- O(3)	108,3(4)		Si(1)	- C(1)	- Sn(1)	113,3(5)
O(1)	- Si(1)	- C(1)	109,4(5)		Si(2)	- C(2)	- Sn(2)	114,1(5)
O(3)	- Si(1)	- C(1)	109,6(4)					

MHz, C_6D_6) and ^{119}Sn(186.409 MHz, C_6D_6) show both single resonances at −11.0 and 47.7 ppm, respectively. The NMR data are fully consistent with the bicyclic structure of **2**.

The molecular structure of **2** is shown in Figure 1. Selected bond lengths and bond angles are listed in Tables I and II, and the torsion angles are summarized in Table III.

Usually, bicyclo[3.3.1]nonanes exhibit more or less distorted twin chair conformations of type (A).[8-10] The twin boat conformation of type (B) is energetically less favoured.

(A)



(B)

TABLE III

Selected torsion angles (°) in **2**

C(1)	- Si(1)	- O(3)	- Si(2)	65,5(7)	O(1)	- Si(1)	- O(3)	- Si(2)	-53,8(6)
Si(1)	- O(3)	- Si(2)	- O(2)	-54,5(6)	Si(1)	- O(3)	- Si(2)	- C(2)	65,8(7)
O(3)	- Si(2)	- O(2)	- Sn(1)	-5,6(6)	O(3)	- Si(2)	- C(2)	- Sn(2)	-22,1(8)
Si(2)	- O(2)	- Sn(1)	- C(1)	34,7(6)	Si(2)	- C(2)	- Sn(2)	- O(1)	-11,4(7)
O(2)	- Sn(1)	- C(1)	- Si(1)	-20,5(7)	C(2)	- Sn(2)	- O(1)	- Si(1)	25,5(7)

However, in case of **2** the bulky *t*-butyl groups prevent a twin chair conformation and force the six-membered rings to turn into distorted boat conformations. The torsion angles (Table III) show that the latter are flattened in the C(1)—Sn(1)—O(2) and C(2)—Sn(2)—O(1) parts, respectively. In fact, **2** represents a real structure along the pathway (A) ... (B).

The configuration of Si(1) as well as Si(2) is tetrahedral with mean angles of 109.5 and 109.4°. The same holds for Sn(1) and Sn(2) (mean angles 109.2°). However, here the configuration is more distorted due to the steric hindrance of the *t*-butyl groups. The latter is especially expressed by the C(5)—Sn(1)—C(6) and C(7)—Sn(2)—C(8) angles of 115.6(5) and 118.0(5)°, respectively, which are nevertheless smaller than the corresponding angle of 133.1° found in *t*-Bu_2SnCl_2.[11] Remarkable are the Si(1)—O(1)—Sn(2), Si(2)—O(2)—Sn(1) and Si(1)—O(3)—Si(2) angles of 127.6(4), 126.0(4) and 127.9(4)°, respectively, which are greater than the values of *ca* 110° expected from the VSEPR model. Nevertheless these angles are smaller compared to those reported for 1,3-bis(triphenylstannoxy)-1,1,3,3-tetraphenyl-1,3-disiloxane (Si—O—Si 165.4, Si—O—Sn 140.0/142.7°).[12] That the corresponding angles in **2** lie in between 110° and those of the latter compound reflects the steric requirements of the bicyclo[3.3.1]nonane skeleton as well as the Si(1) ... Sn(2) (3.249 Å), Si(2) ... Sn(1) (3.250 Å) and Si(1) ... Si(2) (2.976 Å) repulsions. Although these distances are longer than the sums of the covalent radii[13] of Si (1.18 Å) and Sn (1.40 Å) they are shorter than the sums of the corresponding van der Waals radii[13] (Si 2.10 Å, Sn 2.20 Å). Last but not least the Si(1)—C(1)—Sn(1) and Si(2)—C(2)—Sn(2) angles of 113.3(5) and 114.1(5)°, respectively, reflect the ring strain in **2**. As expected for tetrahedral environments the Si—C, Si—O, Sn—C and Sn—O bond lengths do not show any particularities.

EXPERIMENTAL

Solvents were dried by standard procedures and distilled before used. Argon was used as inert atmosphere for Grignard reactions. The ^1H, ^{13}C, ^{29}Si and ^{119}Sn NMR spectra were recorded in $CDCl_3$ on Bruker AC 80 and Varian Unity 500 spectrometers using TMS and tetramethyltin as external references. The mass spectrum was recorded on a Finnigan 8230 spectrometer.

[(Diisopropoxy)methylsilyl]methyl-di-t-butylchlorostanne, t-$Bu_2ClSnCH_2Si(OiPr)_2Me$ (**1**): The Grignard reagent Me(*i*-PrO)$_2$SiCH$_2$MgCl,[7] prepared from magnesium (1.5 g, 62.7 mmol) and Me(*i*-PrO)$_2$SiCH$_2$Cl (13.0 g, 62.7 mmol) in 150 ml thf was added dropwise and under magnetic stirring to a cooled solution (−40°C) of di-*t*-butyldichlorostannane (18.7 g, 67.2 mmol) in 200 ml thf. The reaction mixture was then stirred for additional 3 h. The thf was removed in vacuo and the residue extracted with hexane in order to separate the product from magnesium chloride. The hexane was distilled off and the residue was fractionated to yield 24.3 g (89%) **1**, b.p. 102–105°C (0.01 Torr). Found: C 43.37, H 7.99. $C_{16}H_{37}O_2ClSiSn$. Calcd.: C 43.31, H 8.35%.

TABLE IV

Experimental details of structure determination

CRYSTAL DATA			
Chemical formula	$C_{20}H_{46}O_3Si_2Sn_2$	Crystal system	monoclinic
M_r	628.13	Space group	P2(1)/n
a (Å)	12.880(3)	α (°)	90
b (Å)	16.949(4)	β (°)	93.04(2)
c (Å)	13.472(4)	γ (°)	90
Z	4	D_m (Mg m^{-3})	1.463(1)
V (Å^3)	2937(1)	D_x (Mg m^{-3})	1.421
Radiation	Mo Kα	30 reflections for lattice parameters	
Wavelength (Å)	0.71073	θ range for lattice parameters (°)	7.7 - 10.8
Absorption coefficient (mm^{-1})	1.797	Temperature (K)	291(1)
Crystal size (mm)	0.20 x 0.20 x 0.22	F(000)	1272
Crystal colour	colourless	Crystal description	block
Crystal source	Recrystallisation from aceton.		
DATA COLLECTION			
Diffractometer type	Nicolet R3m/V	Collection method	ω/2θ (2.0-50.0 °)
Absorption correction	empirical	Absorption correction	0.862/0.818
6296 reflections measured		R_{int}	0.0654
5212 independent reflections		θ_{max}(°)	25.05
2665 observed reflections		4 standard reflections every 300 reflections	
Criterion for observed	[I > 2 σ(I)]	Variation of standards	< ± 2.2 %
h_{min}	-1	h_{max}	15
k_{min}	-1	k_{max}	20
l_{min}	-16	l_{max}	16
REFINEMENT			
Refinement on F^2		245 parameters refined	
R	0.0652 (F > 4 σ(F))	5212 reflections used in refinement	
wR	0.1483 (based on F^2)	$(\Delta/\sigma)_{max}$	< 0.001
wR	0.1483 (based on F^2)	$(\Delta/\rho)_{max}$ (e Å^{-3})	1.022 near Sn(1)
S	1.08 (based on F^2)	$(\Delta/\rho)_{min}$ (e Å^{-3})	-1.475

Weighting scheme: calc $w=1/[\sigma^2 (Fo^2)+(0.0867P)^2+2.1411P]$; where $P=(Fo^2+ 2Fc^2)/3$

Source of atomic scattering factors International Tables Vol C, Tables 4.2.6.8 and 6.1.1.4

^{1}H NMR (80.13, MHz $CDCl_3$, δ): 0.22 (s, 3H, $SiCH_3$), 0.27 (s, 2H, $SiCH_2$), 1.17 (d, 6H, $CH(CH_3)_2$) $^3J(^1H—^1H)$ 6.1 Hz, 1.18 (d, 6H, $CH(CH_3)_2$) $^3J(^1H—^1H)$ 6.1 Hz, 1.34 (s, 18H, $C—(CH_3)_3$) $^3J(^{119}Sn—^1H)$ 85 Hz, 4.14 (m, 2H, CH); ^{13}C NMR (125.706 MHz, $CDCl_3$, δ): −1.45 ($SnCH_2$, $^1J(^{119}Sn—^{13}C)$ 107 Hz), −1.71 ($SiCH_3$), 25.6 ($CH(CH_3)_2$), 29.8 ($C(CH_3)_3$), 34.8 (SnC, $^1J(^{119}Sn—^{13}C)$ 392 Hz), 64.9 (OC); ^{29}Si NMR (99.309 MHz, $CDCl_3$, δ): −9.2; ^{119}Sn NMR (29.881 MHz, $CDCl_3$, δ): 114.3.

2,2,6,6-Tetra-t-butyl-4,8-dimethyl-1,5,9-trioxa-4,8-disila-2,6-distanna-bicyclo[3.3.1]nonane (**2**): [(Di-isopropoxy)methyl-di-*t*-butylchlorostanne (3.3 g, 7.4 mmol) were dissolved in 10 ml dichloromethane. Potassium fluoride (1 g, 17.2 mmol) and water (10 ml) were added and the reaction mixture was stirred for 48 h. After addition of acetone (30 ml) the mixture was kept without stirring for several hours.

TABLE V

Atomic coordinates and equivalent isotropic displacement parameters (Å^2) of **2**. $U_{eq} = (1/3)\ \Sigma_i\Sigma_j\ U_{ij}\ a_i^*a_j^*a_i \cdot a_j$

	X	Y	Z	U_{eq}
Sn(1)	0,19854(6)	0,16804(5)	0,11875(6)	0,0501(3)
Sn(2)	0,19119(6)	0,06325(4)	-0,25000(5)	0,0471(2)
Si(1)	0,3503(2)	0,1149(2)	-0,0663(2)	0,0442(7)
Si(2)	0,1796(2)	0,0073(2)	-0,0126(2)	0,0467(8)
O(1)	0,2966(6)	0,1308(4)	-0,1748(5)	0,053(2)
O(2)	0,1254(6)	0,0762(4)	0,0522(5)	0,056(2)
O(3)	0,3030(5)	0,0315(4)	-0,0231(5)	0,048(2)
C(1)	0,3198(9)	0,1970(7)	0,0171(9)	0,058(3)
C(2)	0,1149(9)	-0,0004(7)	-0,1375(8)	0,059(3)
C(3)	0,4946(8)	0,1044(8)	-0,0687(10)	0,079(4)
C(4)	0,1785(9)	-0,0907(7)	0,0511(10)	0,076(4)
C(5)	0,0811(10)	0,2595(7)	0,1240(9)	0,066(3)
C(51)	0,1355(11)	0,3363(7)	0,1609(11)	0,085(4)
C(52)	-0,0059(11)	0,2361(9)	0,1882(12)	0,105(6)
C(53)	0,0383(12)	0,2751(9)	0,0141(12)	0,114(6)
C(6)	0,2571(10)	0,1215(8)	0,2641(9)	0,066(3)
C(61)	0,1759(12)	0,0648(9)	0,3001(13)	0,116(6)
C(62)	0,2823(11)	0,1914(8)	0,3407(10)	0,086(5)
C(63)	0,3543(13)	0,0758(11)	0,2444(11)	0,118(6)
C(7)	0,2796(10)	-0,0188(7)	-0,3332(9)	0,064(3)
C(71)	0,3528(12)	0,0189(9)	-0,4018(12)	0,106(6)
C(72)	0,3422(13)	-0,0732(10)	-0,2628(10)	0,113(6)
C(73)	0,2029(12)	-0,0705(10)	-0,3983(13)	0,126(7)
C(8)	0,0992(10)	0,1525(6)	-0,3326(9)	0,057(3)
C(81)	0,1628(15)	0,2040(11)	-0,3841(13)	0,153(9)
C(82)	0,0188(14)	0,1134(9)	-0,3995(15)	0,172(11)
C(83)	0,0413(14)	0,1993(11)	-0,2563(11)	0,147(9)

Precipitation of **2** occurred at the interphase. It was filtered off and the upper layer was separated and slowly evaporated to give further **2** as colourless crystals with m.p. 145–147°C, yield 2.1 g (90%). Found: C 38.28, H 7.51. $C_{20}H_{46}O_3Si_2Sn_2$. Calcd.: C 38.24, H 7.33%.

MS: m/e 615 (MP—CH_3), m/e 573 (100% MP—C_4H_9), m/e 517 (MP—C_4H_9—C_4H_8), m/e 459 (MP—C_4H_9—C_4H_8—C_4H_{10}), m/e 403 (MP—C_4H_9—C_4H_8—C_4H_{10}—C_4H_8), m/e 269 ($C_3H_9O_3Si_2Sn$).

Crystal Structure of **2**

The structure was solved by standard Patterson and difference Fourier methods using SHELXTL PLUS[14] and refined satisfactorily with space group $P2_1/n$ by full-matrix least-squares calculations using SHELXL93.[15] The H atoms were placed in geometrically calculated positions and refined with a common isotropic temperature factor [H_{alkyl} C—H 0.96 Å, U_{iso} O.131(9)]. Experimental details of the structure determination are given in Table IV. The final coordinates are given in Table V.

Lists of structure factors, complete bond lengths and angles, shortest intermolecular contacts, thermal parameters, and stereoviews of the unit cell have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, UK, CB2, 1EW.

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