1,2,3,4,5,6-Hexasila-7,8-distannabicyclo[2.2.2]octanes: A **Novel Approach toward Bicyclo Derivatives of Group 14 Elements**[†]

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Summary: Stannasilanes of the 1,2,3,4,5,6-hexasila-7,8distannabicyclo[2.2.2]octane type ($Me_{10}R_4Si_6Sn_2$: R =Me, 5; R = Ph, 6) were synthesized by the reaction of 1,4-dihalogen-substituted decamethylcyclohexasilanes $(Si_6Me_{10}X_2: X = F, \mathbf{1}; X = Cl, \mathbf{2})$ with diorganodichlorostannanes (R_2SnCl_2 : R = Me, **3**; R = Ph, **4**) in the presence of magnesium. Compounds 5 and 6 were characterized by NMR, MS, and elemental analysis. The solid-state structure of **6** was determined by X-ray crystallography.

Introduction

The chemistry of monocyclic, oligomeric silanes of the type $(R_2Si)_n$ (n = 3-20) has been well-investigated over the past few decades.¹ In contrast, little is known about bicyclic silanes containing only group 14 atoms in the ring skeletons.¹⁻³

Compound A is available as a byproduct from the reaction of Me₂SiCl₂ and MeSiCl₃ with sodium-potassium alloy² or as a rearrangement product in the thermolysis of octadecamethylbicyclo[4.4.0]decasilane (B).³



Recently, we reported the first attempts to synthesize group 14 bicyclo[2.2.2] octanes via multistep synthesis starting from MeSi[SiMe₂Sn(H)-*t*-Bu₂]₃.⁴ However, in rather complex amine-catalyzed bond cleavagecoupling reactions, only monocyclic Si-Sn derivatives were accessible. During the last few years we also reported a number of novel monocyclic compounds exclusively containing tin and silicon atoms in the ring skeleton (Chart 1) in order to investigate the influence of organostannyl groups on the properties of cyclic oligosilanes.5,6

The four-, five-, and six-membered rings C-E were obtained in a stepwise manner by starting from α, ω -

Chart 1: Examples for Monocyclic Six- and Seven-Membered Stannasilanes ($\mathbf{R} = \mathbf{Me}, t$ -Bu, Ph)



bis(di-tert-butylhydridostannyl)silanes followed by halogenation and ring closure metathesis with magnesium.⁵ One-pot reactions of halosilanes with chlorostannanes and magnesium yielded six-, seven-, and eightmembered Si-Sn rings of type E-H (Chart 1), indicating that this synthetic route should also be applicable to the synthesis of bicyclic stannasilanes.⁶ This paper describes the synthesis and structure of novel compounds of the bicyclo[2.2.2]octane type containing only Sn and Si atoms in the ring skeletons.

Results and Discussion

The reaction of equimolar amounts of the 1,4-dihalodecamethylcyclohexasilanes Me(X)Si(Me2SiSiMe2)2Si-(X)Me ($\mathbf{1}, X = F; \mathbf{2}, X = CI$) and diorganodihalogenostannanes R_2SnCl_2 (3, R = Me; 4, R = Ph) with magnesium provided the 1,2,3,4,5,6-hexasila-7,8-distannabicyclo-[2.2.2] octanes **5** and **6** in moderate yields (Scheme 1).

Compounds 5 and 6 are colorless solids which are well soluble in aprotic, polar organic solvents. Reactions in

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Scheme 1. Reactions of

a molar ratio of silane to stannane of 1.5:1 increased the yields of 5 and 6 to 35%. If the exact stoichiometric amounts of 2:1 were used, unidentified byproducts without Si-Sn moieties were observed, preventing the isolation of **5** and **6** from the reaction mixtures.

The starting materials 1 and 2 were used as a 1:1 mixture of the cis/trans isomers. We have no experimental evidence as to whether both or only one of the isomers react toward the cage-like compounds 5 and 6. However, it is well-known from the literature that cis/ trans mixtures of 2 can be converted nearly quantitatively into bicyclo[2.2.1]heptane derivatives.^{7,8}



The tin-silicon moieties in compounds 5 and 6 were confirmed by NMR experiments, with coupling constants for ${}^{1}J({}^{119}Sn - {}^{117}Sn)$ at 1505 Hz (5) and 1170 Hz (6). These values agree well with ${}^{1}J({}^{119}Sn - {}^{117}Sn)$ for monocyclic rings of type E.⁶ The ¹J(¹¹⁹Sn-²⁹Si) (243 Hz (5), 238 Hz (6)) are around 100 Hz smaller than in the related compounds of types E and F. These differences might be explained by the different environments of the silicon atom. ¹J(²⁹Si-²⁹Si) and ²J(²⁹Si-²⁹Si) have been determined at 50.5 and 10 Hz for 5 and 49.5 and 10 Hz for 6 and are therefore significantly smaller (8 and 3 Hz) than in monocyclic cyclohexasilane derivatives 1 and 2. The lack of comparable data does not allow a complete discussion.

The bicyclooctane derivative 6, depicted in Figure 1, crystallizes with two independent molecules in the unit cell, of which only one is shown. Crystallographic data and selected interatomic parameters are listed in Tables 1 and 2, respectively. The central tin-silicon backbone consists of Si₄Sn₂ and Si₆ rings each displaying a "twisted boat" conformation (Figure 1).

The two independent molecules differ only slightly in their bond lengths and angles. The tin and silicon atoms display a slightly distorted tetrahedral geometry, with bond distances of 2.7814(5) and 2.7866(5) Å for Sn-Sn and 2.354(2) and 2.336(2) Å for Si(1)-Si(4). The struc-



Figure 1. General view (SHELXTL-PLUS) of one of the two independent molecules of 6, showing 30% probability displacement ellipsoids and the atom numbering.

Table 1. Crystal Data and Structure Refinement Details for 6

Detuiis ioi v	
formula	$C_{34}H_{50}Si_6Sn_2$
fw	864.66
cryst syst	triclinic
cryst size, mm	$0.\underline{40}\times0.12\times0.10$
space group	<i>P</i> 1
a, A	10.639(1)
b, Å	19.879(1)
<i>c</i> , Å	20.708(1)
α, deg	94.402(1)
β , deg	102.718(1)
γ , deg	94.991(1)
V, Å ³	4256.7(5)
Ζ	4
$ ho_{\text{calcd}}, \text{Mg/m}^3$	1.349
μ , mm ⁻¹	1.363
F(000)	1752
θ range, deg	2.95 - 25.70
index ranges	$-11 \le h \le 11$
-	$-24 \leq k \leq 24$
	$-25 \le l \le 24$
no. of rflns collected	51 901
completeness to θ_{max} , %	91.7
no. of indep rflns/R _{int}	14 853/0.052
no. of rflns obsd with $I > 2\sigma(I)$	6933
no. of refined params	759
$GOF(F^2)$	0.828
$R1(F) (I > 2\sigma(I))$	0.0389
$wR2(F^2)$ (all data)	0.0678
$(\Delta/\sigma)_{\rm max}$	0.001
largest diff peak/hole, e/ų	0.465 / -0.428

tural features of compound 6 compare favorably with those of other heteroatom-substituted silabicyclo[2.2.2]octanes,⁹ cyclic distannanes,¹⁰ or the diphenyltin derivative of **F**.⁶

The synthesis of the bicyclo[2.2.2]octane compounds **5** and **6** indicate not only the potentials but also the limitations of one-pot reactions between halogen silanes and chlorostannanes in the presence of magnesium.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Two Independent Molecules of 6 (6')

6		6′	
Bond Lengths			
Sn(1)-Sn(2)	2.7814(5)	Sn(1')-Sn(2')	2.7866(5)
Sn(1)-Si(1)	2.573(1)	Sn(1')-Si(1')	2.589(1)
Sn(2)-Si(6)	2.576(1)	Sn(2')-Si(6')	2.571(1)
Si(1)-Si(2)	2.341(2)	Si(1')-Si(2')	2.353(2)
Si(2)-Si(3)	2.349(2)	Si(2')-Si(3')	2.362(2)
Si(3)-Si(6)	2.346(2)	Si(3')-Si(6')	2.337(2)
Si(4)-Si(5)	2.360(2)	Si(4')-Si(5')	2.350(2)
Si(5)-Si(6)	2.345(2)	Si(5')-Si(6')	2.345(2)
Si(1)-Si(4)	2.354(2)	Si(1')-Si(4')	2.336(2)
Sn(2) - C(31)	2.147(5)	Sn(2')-C(31')	2.152(5)
Sn(2) - C(41)	2.153(5)	Sn(2')-C(41')	2.146(5)
Sn(1) - C(11)	2.131(5)	Sn(1')-C(11')	2.141(5)
Sn(1) - C(21)	2.146(5)	Sn(1')-C(21')	2.132(5)
Bond Angles			
C(11)-Sn(1)-C(21)	103.7(2)	C(11')-Sn(1')-C(21')	102.9(2)
C(11) - Sn(1) - Si(1)	109.1(1)	C(11')-Sn(1')-Si(1')	111.3(1)
C(21) - Sn(1) - Si(1)	112.0(2)	C(21')-Sn(1')-Si(1')	110.6(2)
C(11) - Sn(1) - Sn(2)	113.6(2)	C(11')-Sn(1')-Sn(2')	111.8(1)
C(21) - Sn(1) - Sn(2)	114.3(1)	C(21')-Sn(1')-Sn(2')	115.3(2)
Si(1)-Sn(1)-Sn(2)	104.32(3)	Si(1') - Sn(1') - Sn(2')	105.03(3)
C(1) - Si(1) - Si(2)	108.4(2)	C(1')-Si(1')-Si(2')	108.0(2)
C(1) - Si(1) - Si(4)	112.6(2)	C(1')-Si(1')-Si(4')	111.3(2)
Si(2) - Si(1) - Si(4)	108.37(7)	Si(2')-Si(1')-Si(4')	109.86(8)
C(1) - Si(1) - Sn(1)	111.0(2)	C(1')-Si(1')-Sn(1')	112.3(2)
Si(2)-Si(1)-Sn(1)	107.35(6)	Si(2') - Si(1') - Sn(1')	108.83(7)
Si(4) - Si(1) - Sn(1)	108.94(6)	Si(4') - Si(1') - Sn(1')	106.51(7)

There is no evidence for the formation of the thermodynamically less favored, more strained bicyclo[2.2.1]heptane 7 (Scheme 1), but the reactions are well suited for the formation of thermodynamically favored products such as six-, seven-, or eight-membered mono- and bicyclic Si–Sn rings.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of inert gas (N₂ or Ar) using Schlenk techniques. All solvents were dried by standard methods and freshly distilled prior to use. The 1,4-dihalodecamethylcyclohexasilanes 1 and 2 were prepared according to published procedures.11 All other chemicals were obtained commercially. 1H and ¹³C NMR spectra were recorded using a Bruker DPX 400 spectrometer (solvent CDCl₃ or C₆D₆, internal reference Me₄-Si). ²⁹Si and ¹¹⁹Sn NMR spectra were recorded using a Bruker DPX 400 spectrometer (solvent CDCl₃ or C₆D₆, internal reference Me_4Si or Me_4Sn , respectively) or a Bruker DRX 300 spectrometer (solvent hexane or THF with D₂O capillary, internal reference Me₄Si or Me₄Sn, respectively). The ^xJ(²⁹Si-²⁹Si) coupling constants were determined as described previously.¹² MS analyses were recorded using a MAT 8200. Molecular mass determinations were performed with a Knauer osmometer at 56 °C. Elemental analyses were performed on a LECO-CHNS-932 analyzer.

General Procedure. In a 250 mL Schlenk tube 10 mmol of **1** or **2** and 10–20 mmol of **3** or **4** were dissolved in 100 mL of THF. A 2 g amount (83 mmol, excess) of magnesium (activated with iodine¹³) was added. The resulting reaction mixture was stirred at room temperature for 3 days (**1**) or 6 days (**2**). After evaporation of the THF the resulting residue was extracted twice with 50 mL portions of a *n*-hexane/Et₂O (1:1) mixture. The extracts were filtered through a frit (G3) to remove magnesium salts. After evaporation of the filtrate, the crude products were purified by recrystallization.

Tetradecamethyl-1,2,3,4,5,6-hexasila-7,8-distannabicyclo[2.2.2]octane, $Me_{14}Si_6Sn_4$ (5). (a) The starting materials used were 3.71 g (10 mmol) of 1 and 2.2 g (10 mmol) of 3. Recrystallization from *n*-hexane/Et₂O (1:1) gave 1.23 g (20%) of 5 as colorless solid. (b) The starting materials used were 3.71 g (10 mmol) of 1 and 3.3 g (15 mmol) of 3. Recrystallization from *n*-hexane/Et₂O (1:1) yielded 2.16 g (35%) of 5 as a colorless solid.

¹¹⁹Sn NMR (111.92 MHz, CDCl₃): δ –227.9, ¹*J*(¹¹⁹Sn–¹¹⁷Sn) = 1505 Hz. ²⁹Si NMR (59.63 MHz, CDCl₃): δ –80.9 (¹*J*(¹¹⁹Sn–²⁹Si) = 243 Hz, ²*J*(¹¹⁹Sn–²⁹Si) = 94 Hz, SiMe), -37.6 (²*J*(¹¹⁹Sn–²⁹Si) = 58 Hz, ³*J*(¹¹⁹Sn–²⁹Si) = 38 Hz, SiMe₂), ¹*J*(²⁹Si–²⁹Si) = 50.5 Hz, ²*J*(²⁹Si–²⁹Si) = 10 Hz.¹³C NMR (100.63 MHz, C₆D₆): δ –9.8 (²*J*(¹¹⁹Sn–¹³C) = 32 Hz, SiMe), -2.8, -3.1 (³*J*(¹¹⁹Sn–¹³C) = 41 Hz, SiMe₂), -5.6 (¹*J*(¹¹⁹Sn–¹³C) = 195 Hz, SnMe₂). ¹H NMR (400.13 MHz, CDCl₃): δ 0.41 (²*J*(¹¹⁹Sn–¹H) = 36 Hz, 12H 2 × SnMe₂). 0.37 (³*J*(¹¹⁹Sn–¹H) = 24 Hz, 6H, SiMe), 0.35 (12H, 2 × SiMe₂). Mp: 208–210 °C. Molecular mass determination (CHCl₃, 20 mg mL⁻¹): 612 g mol⁻¹. Anal. Calcd for C₁₄H₄₂Si₆Sn₂ (616.41): C, 27.28; H, 6.87. Found: C, 27.1; H, 6.6, MS: *m*/*z* 616 (M⁺/80%), 601 (M⁺ – Me/10%), 586 (M⁺ – 2 Me/5%), 318 (Si₆Me₁₀/100%).

7,7,8,8-Tetraphenyldecamethyl-1,2,3,4,5,6-hexasila-7,8-distannabicyclo[2.2.2]octane, $Me_{10}Ph_4Si_6Sn_4$ (6). (a) The starting materials were 4.04 g (10 mmol) of 2 and 3.43 g (10 mmol) of 4. Recrystallization from CHCl₃/Et₂O (1:1) yielded 1.29 g (15%) of 6 as a colorless solid.

(b) The starting materials were 4.24 g (11 mmol) of **1** and 5.5 g (16 mmol) of **4**. Recrystallization from CHCl₃/Et₂O (1:1) gave 2.59 g (27%) of **6** as a colorless solid.

¹¹⁹Sn NMR (149.21 MHz, CDCl₃): δ –206.1, ¹*J*(¹¹⁹Sn⁻¹¹⁷Sn) = 1170 Hz. ²⁹Si NMR (79.49 MHz, CDCl₃): δ –74.4 (¹*J*(¹¹⁹Sn⁻²⁹Si) = 238 Hz, ²*J*(¹¹⁹Sn⁻²⁹Si) = 97 Hz, SiMe), -37.1 (²*J*(¹¹⁹Sn⁻²⁹Si) = 53 Hz, ³*J*(¹¹⁹Sn⁻²⁹Si) = 40 Hz, SiMe₂), ¹*J*(²⁹Si⁻²⁹Si) = 49.5 Hz, ²*J*(²⁹Si⁻²⁹Si) = 10 Hz. ¹³C NMR (100.63 MHz, C₆D₆): δ 139.8(¹*J*(¹¹⁹Sn⁻¹³C) = 298 Hz, C₁), 138.4 (²*J*(¹¹⁹Sn⁻¹³C) = 41 Hz, C₀), 128.0 (³*J*(¹¹⁹Sn⁻¹³C) = 42 Hz, C_m), 127.7 (C_p), -10.7 (²*J*(¹¹⁹Sn⁻¹³C) = 34 Hz, SiMe), -2.3, -2.5 (³*J*(¹¹⁹Sn⁻¹³C) = 39 Hz, SiMe₂), ¹H NMR (400.13 MHz, C₆D₆): δ 7.75 (³*J*(¹¹⁹Sn⁻¹H) = 45 Hz, d, 8H, SnPh), 7.18 (m, 12H, SnPh), 0.64 (³*J*(¹¹⁹Sn⁻¹H) = 23 Hz, SiMe), 0.37, 0.30 (SiMe₂). Mp: 168–170 °C, Anal. Calcd for C₃₄H₅₀Si₆Sn₂ (864.69): C, 47.23; H, 5.82, Found: C, 46.8, H, 5.7, MS: *m*/*z*863 (M⁺/100%), 848 (M⁺ - Me/3%), 786 (M⁺ - Ph/10%), 333 (Si₆Me₁₀/90%), 272 (SnPh₂/60%).

Crystallography. The data of **6** were collected to a θ value of 25.70° with 360 frames via ω -rotation ($\Delta/\omega = 1^\circ$) with a 60 s exposure time per frame on a Nonius KappaCCD diffractometer ($\lambda = 0.71073$ Å) and was corrected for LP but not for absorption effects. The structure was solved by direct methods SHELXS97.¹⁴ Refinement used SHELXL97¹⁵ full-matrix least-squares methods. The H atoms were placed on geometrically calculated positions using a riding model and refined with a common isotropic temperature factor for aliphatic and aromatic H atoms.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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