2788 *Organometallics* **1993,** *12,* 2788–2793

Synthesis, Structure, and Exchange Reactions of New Stannaadamantanes Containing Chalcogenides

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Received January 26, 1993

Reaction of bis(organostannyl)alkanes $(RSnCl_2)_2CH_2$ (**1**, R = Ph; **2**, R = CH_2SiMe_3) and $(MeCl_2Sn)_2CMe_2$, respectively, with sulfide, selenide, and telluride sources, respectively. *i.e.* Na_2X or $(^tBu_2SnX)_2$ (X = S, Se, Te) results in the formation of 1,3,5,7-tetraorgano-2,4,6,8-tetrachalcogena-1,3,4,5-tetrastannaadamantanes $[(RSnX)_2CR'_2]_2$ (**3**, R = Ph, R′ = H, X = S; **4**, R = CH_2SiMe_3, R′ = H, X = S; **5**, R = Ph, X = Se; **6**, R = Ph, R′ = H, X = Te; **13**, R = R′ = Me, X = Se). Cross experiments between **3** and **4** or **3** and **5** gives rise to the formation of all possible isomers and reveal the lability of the tin–chalcogen bonds. Crystal structure determinations of **3** and **13** confirm the adamantane-like structures inferred from the NMR data. Crystal data for **3**: space group $P2_{1/c}$, $a = 10.881(1)$ Å, $b = 20.561(3)$ Å, $c = 14.931(3)$ Å, $\beta = 112.55(1)°$, 5829 reflections, $R_w = 0.027$. Crystal data for **13**: space group *Pbcn*, $a = 14.618(3)$ Å, $b = 10.455(2)$ Å, $c = 14.974(3)$ Å, 3098 reflections, $R_w = 0.050$.

Introduction

Bis(organostannyl)alkanes of the type $R_nCl_{(3-n)}Sn(CH_2)_mSnCl_{(3-n)}R_n$ (m, n = 1–3) have been known for several years and show interesting behavior as mono- and bidentate Lewis acids.[1-3] However little is known about their potential as precursors for tin-containing heterocycles and less about their reaction with chalcogenide anions.[2,4,5] Such compounds may be useful building blocks for new organotin clusters which may have a variety of materials applications including intercalation agents for clays.

As part of an ongoing study of the Lewis acidity of main group elements and of the stereochemistry of such complexes in the solid state and in solution,[6] we now report results of reactions between $(RCl_2Sn)_2CH_2$ (**1**, R = Ph; **2**, R = CH_2SiMe_2) and sulfide, selenide and telluride sources such as Na_2X and $(^tBu_2SnX)_2$ (X = S, Se, Te). Also reported are NMR data for a variety of exchange reactions involving these new stannaadamantanes.

Results and Discussion

Compounds **1** and **2** are easily obtained by treatment of bis(organodiphenylstannyl)methanes $(RPh_2Sn)_2CH_2$ with mercury(II) chloride in acetone (eq 1). Compound

$$(RPh_2Sn)_2CH_2 + 4HgCl_2 \xrightarrow[0\ °C]{acetone} (RCl_2Sn)_2CH_2 + 4PhHgCl \quad (1)$$

1: R = Ph
2: R = CH_2SiMe_3

1 is a colorless, low-melting crystalline solid whereas **2** is an oil. Both compounds are quite soluble in common organic solvents.

The reaction of **1**, **2**, and $(MeCl_2Sn)_2CMe_2$[1] with either Na_2X or $(^tBu_2SnX)_2$ (X = S, Se, Te) results in almost quantitative formation of the corresponding organotin sulfides **3**, **4**, selenides **5**, **13**, and telluride **6** (eq 2).

$$2(RCl_2Sn)_2CR'_2 \xrightarrow{4Na_2X \text{ or } 2(^tBu_2SnX)_2} \underset{3-6,\ 13}{[(RXSn)_2CR'_2]_2} \quad (2)$$

3: R = Ph, R′ = H, X = S

4: R = CH_2SiMe_3, R′ = H, X = S

5: R = Ph, R′ = H, X = Se

6: R = Ph, R′ = H, X = Te

13: R = Me, R′ = Me, X = Se

$(^tBu_2SnX)_2$ (X = S, Se, Te) are useful alternative chalcogenide sources as they allow the reactions to be performed in aprotic solvents. Furthermore they can be handled more conveniently than $(Me_3Si)_2X$ (X = S, Se), the latter also having been employed for the synthesis of organotin chalcogenides.[9,10]

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Table I. Summary of ^{119}Sn NMR Data for Compounds 3–6 and 13

compd	$\delta(^{119}Sn)$	$J(^{119}Sn–X–^{117}Sn)$	$J(^{119}Sn–CH_2–^{117}Sn)$
3	106.4	195	638
4	159.4	195	723
5^a	3.1	220	537
6^b	−278.9	217	391
13^c	42.9	195	

^{a} $J(^{119}Sn–^{77}Se)$ = 1274 Hz; $\delta(^{77}Se)$ −323 ppm. ^{b} Measured in the presence of $^tBu_2SnCl_2$. $J(^{119}Sn–^{125}Te)$ = 3134 Hz; $\delta(^{125}Te)$ −323 ppm. ^{c} $J(^{119}Sn–CMe_2–^{117}Sn)$ not detected. $J(^{119}Sn–^{77}Se)$ = 1255 Hz; $\delta(^{77}Se)$ −362 ppm.

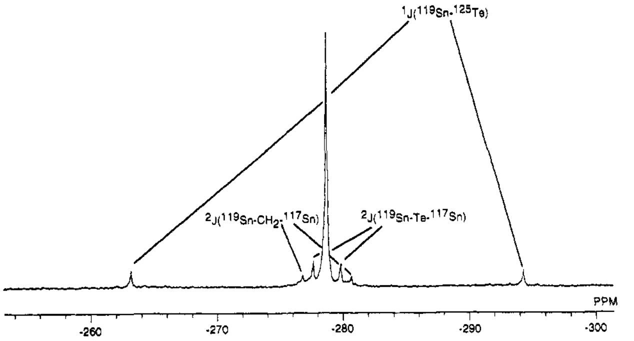


Figure 1. ^{119}Sn NMR spectrum of $[(PhSnTe)_2CH_2]_2$, **6**, in CH_2Cl_2.

Compounds **3** and **4** are colorless crystals which are very soluble in organic solvents. Compounds **5** and **6** form yellow and light green crystals, respectively, which are only poorly soluble in organic solvents.

Tin-119 NMR data for compounds **3**–**6** and **13** are summarized in Table I. The ^{119}Sn NMR spectrum of **3** in CH_2Cl_2 displays a single resonance at 106.4 ppm accompanied by two sets of satellites; the satellites with the smaller coupling are twice the intensity of the satellites with the larger coupling constant. These couplings are assigned to $^2J(^{119}Sn–S–^{117}Sn)$ (195 Hz) and $^2J(^{119}Sn–CH_2–^{117}Sn)$ (638 Hz), respectively. Similarly, the ^{119}Sn NMR spectrum (CH_2Cl_2) of **4** also exhibits a single resonance (159.4 ppm) with two sets of coupling constants (Table I); again, the intensity of the satellites with the smaller coupling are twice the intensity of the satellites with the larger coupling.

The ^{119}Sn NMR spectrum (CH_2Cl_2) of **6** (Figure 1) displays a singlet with $^2J(^{119}Sn–CH_2–^{117}Sn)$, $^2J(^{119}Sn–Te–^{117}Sn)$, and $^1J(^{119}Sn–^{125}Te)$ couplings. The NMR data, and especially the 2:1 intensity ratio observed for the $^2J(^{119}Sn–X–^{117}Sn)$ and $^2J(^{119}Sn–CH_2–^{117}Sn)$ couplings (X = S, Se, Te), indicate that compounds **3**–**6** to have the adamantane-type structure, A rather than the alternative possible structures, B–D (Scheme I). In structure A each tin atom is coupled to two other tin atoms via the bridging X group and to only one other tin via the methylene bridge. This arrangement accounts for the observation that the intensity of the $^2J(^{119}Sn–X–^{117}Sn)$ couplings are twice the intensity of the $^2J(^{119}Sn–CH_2–^{117}Sn)$ couplings.

Adamantane-like structures (A) previously have been reported for $(CH_3Sn)_4S_6$,[7] $(CH_3Sn)_4Se_6$,[8] $(C_6F_5Sn)_4S_6$,[9] $[\{Cp(CO)_2Fe\}_4Sn_4Se_6]$,[10] and 1,3,5-triphenyl-2,4,6-trithia-1,3,5-tristannadamantane.[11] However, an isomer with the B-type structure has recently been reported for $(^tBuGe)_4S_6$.[12] This isomer can be converted to the A-type structure on heating, which suggests that compounds $[(RXSn)_2CH_2]_2$ with B- and/or C-type structures could also be obtained, probably by appropriate variation of the R group. This will be a subject of further studies.

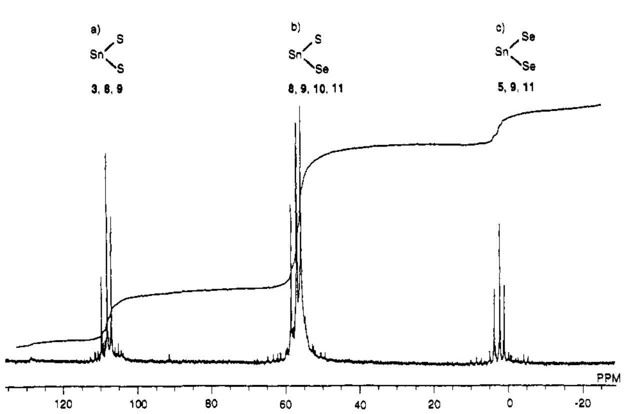
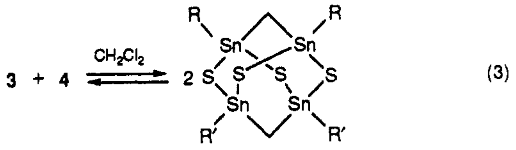


Figure 2. ^{119}Sn NMR spectrum of an equimolar mixture of **3** and **5** (generated *in situ* from $(PhSnCl_2)_2CH_2$ and $(^tBu_2SnSe)_2$). The bold numbers refer to the structures in Scheme I. The signal for $^tBu_2SnCl_2$ arising from the *in situ* preparation of **5** is superimposed by the signals of the SnSSe (b) tin atoms.

Organotin chalcogenides $(R_2Sn)_2X$ (X = O, S) and $(R_2SnX)_n$ (X = S, Se, n = 2, 3) are known to undergo exchange reactions to form mixed species,[13–15] but such reactions involving stannaadamantanes have previously not been investigated. When an equimolar ratio of **3** and **4** is mixed in CH_2Cl_2, the ^{119}Sn NMR spectrum contains only the resonances for the starting materials. After 48 h two additional signals of equal intensity appear at 98.4 ppm [$^2J(^{119}Sn–S–^{117/119}Sn)$ 200 Hz, $^2J(^{119}Sn–CH_2–^{117}Sn)$ 747 Hz] and 168.8 ppm [$^2J(^{119}Sn–S–^{117/119}Sn)$ 205 Hz, $^2J(^{119}Sn–CH_2–^{117}Sn)$ 747 Hz]. These new resonances are each approximately 50% as intense as those of the starting compounds **3** and **4** and are assigned to the mixed adamantane derivative **7** (eq 3) with the low-frequency signal belonging to the phenyltin moiety and the high-frequency signal belonging to the [(trimethylsilyl(methyl]tin moiety.



7: R = Ph, R' = CH_2SiMe_3

When a small amount of Bu_4NCl is added to a freshly prepared solution containing an equimolar ratio of **3** and **4**, the equilibrium shown in eq 3 is established virtually instantaneously and a statistical distribution of **3**, **4**, and **7** is observed in the ^{119}Sn spectrum. This observation implies that the intermolecular exchange is catalyzed by the chloride ion, possibly via formation of a hypervalent tin species involving chloride as a Lewis base. Interestingly addition of a trace amount of chloride to **3** has no observable

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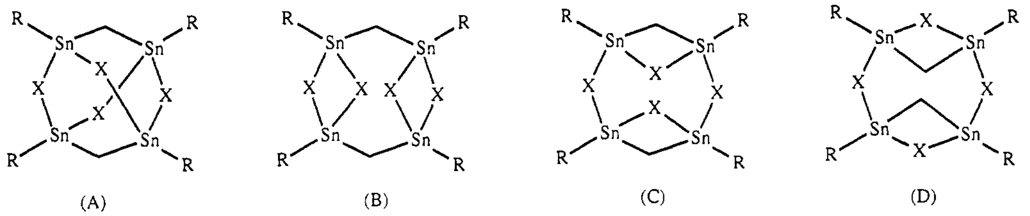
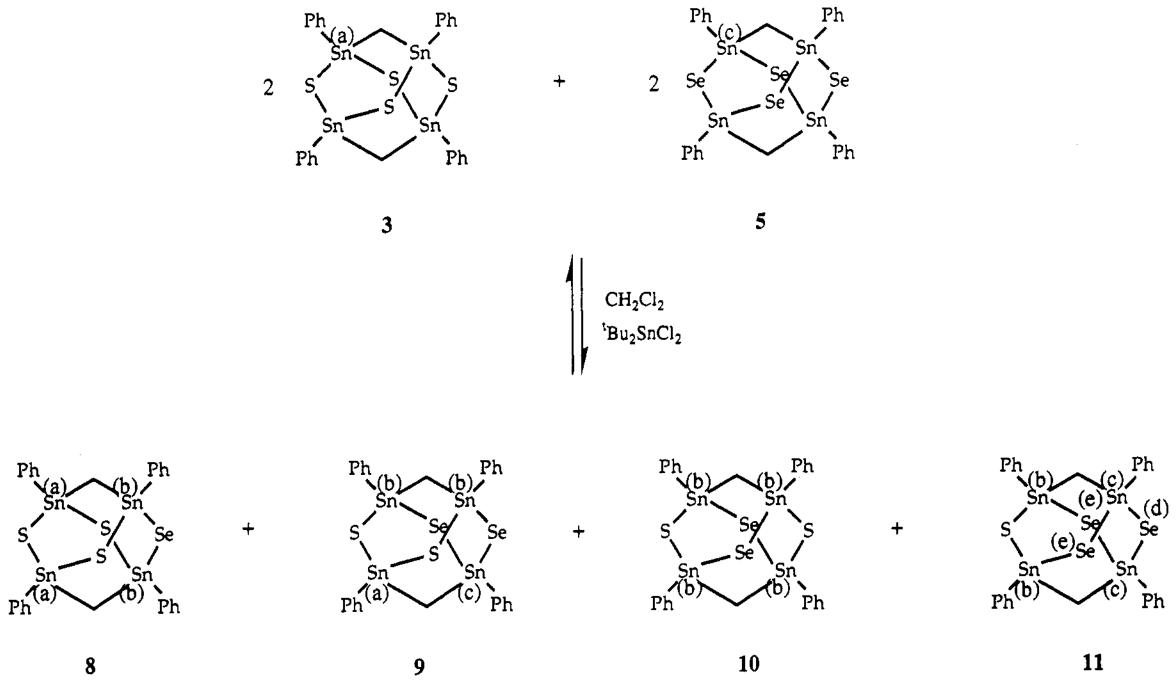
Scheme I



Scheme II



effect on the position of the ^{119}Sn resonance. Addition of stoichiometric amounts of chloride to **3** results in shifts of the ^{119}Sn resonance to lower frequency such that when the chloride to tin ratio is 2:1 the overall chemical shift change is 50 ppm to lower frequency. However, after each addition of chloride the intensity and magnitude of the $^{2}J(^{119}\text{Sn–S–}^{117}\text{Sn})$ and $^{2}J(^{119}\text{Sn–CH}_2\text{–}^{117}\text{Sn})$ couplings remains virtually unchanged. Furthermore these couplings are still clearly evident in a toluene solution of **3** at 100 °C. The mechanism for exchange continues to be studied.

When an equimolar ratio of **3** is added to a methylene chloride solution of **5** [generated *in situ* from $(\text{PhCl}_2\text{Sn})_2\text{CH}_2$ and $(^t\text{Bu}_2\text{SnSe})_2$] the ^{119}Sn NMR spectrum (Figure 2) displays 10 sharp resonances of various intensities, consistent with statistical formation of mixed chalcogenide species **8**, **9**, **10**, and **11**.

The three signals at 0.9 ppm ($^{1}J(^{119}\text{Sn–}^{77}\text{Se})$ 1271 Hz), 2.0 ppm ($^{1}J(^{119}\text{Sn–}^{77}\text{Se})$ 1273 Hz), and 3.6 ppm ($^{1}J(^{119}\text{Sn–}^{77}\text{Se})$ 1274 Hz are assigned to the SnSe_2 tin atoms (c) in **5**, **9**, and **11**. The four signals at 55.6 ppm ($^{1}J(^{119}\text{Sn–}^{77}\text{Se})$ 1291 Hz), 56.7 ppm ($^{1}J(^{119}\text{Sn–}^{77}\text{Se})$ 1314 Hz, 56.9 ppm ($^{1}J(^{119}\text{Sn–}^{77}\text{Se})$ 1279 Hz), and 58.3 ppm ($^{1}J(^{119}\text{Sn–}^{77}\text{Se})$ 1299 Hz) represent the SnSSe tin atoms (b) in **8**, **9**, **10**, and **11**. Finally, the three signals at 106.9 ppm ($^{2}J(^{119}\text{Sn–C–}^{117}\text{Sn})$ 638 Hz, $^{2}J(^{119}\text{Sn–S–}^{117/119}\text{Sn})$ 195 Hz), 108.1 ppm ($^{2}J(^{119}\text{Sn–C–}^{117}\text{Sn})$ 612 Hz, $^{2}J(^{119}\text{Sn–S–}^{117/119}\text{Sn})$ 195 Hz) and 109.6 ppm ($^{2}J(^{119}\text{Sn–C–}^{117}\text{Sn})$ 589 Hz, $^{2}J(^{119}\text{Sn–S–}^{117/119}\text{Sn})$ 194 Hz) can be assigned to the SnS_2 tin atoms (a) of **3**, **8**, and **9**. A further assignment within these three groups of signals is difficult due to lack of clear patterns for the $^{2}J(^{119}\text{Sn–S–}^{117/119}\text{Sn})$, $^{2}J(^{119}\text{Sn–Se–}^{117/119}\text{Sn})$, and $^{2}J(^{119}\text{Sn–CH}_2\text{–}^{117}\text{Sn})$ couplings. The $^t\text{Bu}_2\text{SnCl}_2$ present in solution gives rise to a broad resonance at about 55 ppm superimposed with the resonances for the SnSSe tin atoms (b).

The ^{77}Se NMR spectrum of the same solution (Figure 3) displays six resonances of different intensity and is consistent with the presence of **5** and **8–11** in the equilibrium shown in Scheme I. The signals at −319 and −320.9 ppm, respectively, each show two sets of $^{1}J(^{117/119}\text{Sn–}^{77}\text{Se})$ couplings of normal intensity of 1270, 1302 and 1267, 1300 Hz, respectively,[16] *i.e.* the selenium atoms are bonded to two different tin atoms. Thus, the signals belong to **9** and the selenium atom (e) in **11**. The remaining four signals show each one set of $^{1}J(^{117/119}\text{Sn–}^{77}\text{Se})$ satellites with double intensity, *i.e.* they are each bonded to two equivalent tin atoms (δ^{77}Se(ppm), $^{1}J(^{119}\text{Sn–}^{77}\text{Se})$ (Hz): −311.8, 1278; −313.6, 1276; −326.2, 1294; −328.1, 1291). These signals belong to **5**, **8**, **10**, and selenium atom (d) in **11**. Similarly, mixing an equimolar ratio of **5** and **6** results in the statistical formation of all possible Se and Te chalcogenide compounds having the adamantane structure.

The possibility of forming adamantane-type structures containing at least some oxygen was investigated. Addition of $(^t\text{Bu}_2\text{SnO})_3$ to a dichloromethane solution of **3** results in precipitation of $[(\text{PhOSn})_2\text{CH}_2]_n$, **12**, and formation of $(^t\text{Bu}_2\text{SnS})_2$. There is no evidence for the formation of a stannaadamantane containing both sulfur and oxygen regardless of the ratio of **3** and $(^t\text{Bu}_2\text{SnO})_3$ used.

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(16) Only the $^{119}\text{Sn–}^{77}\text{Se}$ couplings are given.

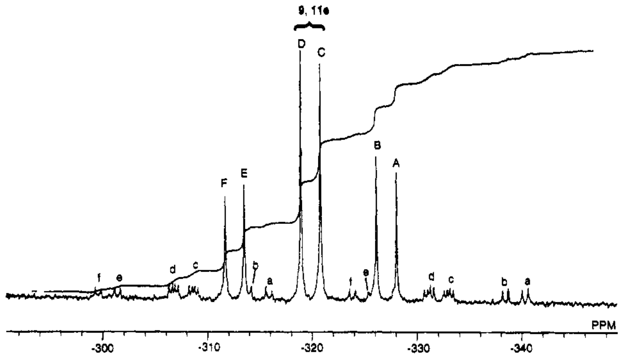

Figure 3. ^{77}Se NMR spectrum of an equimolar mixture of **3** and **5** in CH_2Cl_2 (same sample as used for the ^{119}Sn NMR spectrum shown in Figure 2). The small letters label the $^1J(^{77}Se-^{119/117}Sn)$ satellites of the signals labeled by capital letters. The bold numbers refer to the structures in Scheme I.

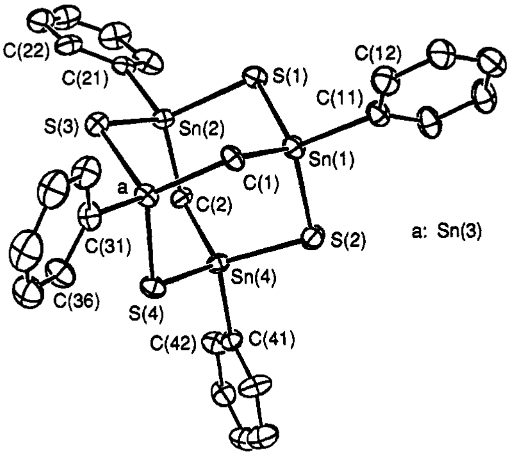

Figure 4. ORTEP diagram showing molecular structure and crystallographic numbering scheme for $[(PhSnS)_2CH_2]_2$, **3**.

Molecular Structure of 3. Unit cell data and refinement details for **3** and **13** are given in Table II, and fractional atomic coordinates for the two structures are listed in Tables III and IV, respectively. The molecular structure of **3** is illustrated in Figure 4 showing the crystallographic numbering scheme and selected interatomic parameters are listed in Table V. The structure of **3** confirms the adamantane-like conformation and supports the conclusions made on the basis of the solution NMR studies.

In **3** each of the Sn atoms exists in a distorted tetrahedral geometry defined by two bridging S atoms, a bridging CH_2 group, and a terminal phenyl group which is directed away from the central core. The Sn–S, Sn–C(methylene), and Sn–C(phenyl) bond distances lies in the relatively narrow ranges 2.388(2) to 2.425(1), 2.130(5) to 2.139(5), and 2.109(5) to 2.133(5) Å, respectively, with no systematic variations being apparent. The distortions from ideal tetrahedral geometry are not significant given the disparate nature of the donor atoms about the Sn centers; the range of tetrahedral angles is 106.0(1) to 114.5(1)°. The angles at the bridging groups fall into two classes with those at the bridging S atoms being more acute (Sn–S–Sn 102.2(1) to 104.0(1)°) than those at the bridging methylene groups (115.4(2) and 116.6(2)°).

Table II. Crystallographic Data

	3	13
formula	$C_{26}H_{24}S_4Sn_4$	$C_{10}H_{24}Se_4Sn_4$
fw	939.49	934.93
cryst size, mm	0.16 × 0.18 × 0.60	0.15 × 0.21 × 0.23
crystal color	colorless	colorless
cryst syst	monoclinic	orthorhombic
space group	$P2_1/c$	*Pbcn*
a, Å	10.881(1)	14.618(3)
b, Å	20.561(3)	10.455(2)
c, Å	14.931(3)	14.974(3)
β, deg	112.55(1)	
V, Å^3	3085.0	2288.6
Z	4	4
ρ_{calcd}, g cm^{-3}	2.023	2.713
F(000)	1800	1680
μ, cm^{-1}	32.31	106.64
transm factors	0.618–0.408	1.456–0.907[a]
data collcd	$\pm h,+k,-l$	$+h,+k,+l$
no. of data collcd	5829	3098
no. of unique data	5427	3098
R_{amal}[b]	0.020	
no. of unique data with $I \geq n\sigma(I)$	3730, $n = 2.5$	1379, $n = 3.0$
R[b]	0.024	0.043
g	0.0025	n/a
R_w[c]	0.027	0.050
residual density, e Å^{-3}	0.33	1.07

[a] Transmission coefficients. [b] $R_{amal} = (\Sigma\{N\Sigma[w(F_{mean} - |F_o|)^2]\}/\Sigma[(N - 1)\Sigma(w|F_o|^2)])^{1/2}$ where the inner summation is over N equivalent reflections averaged to give F_{mean}, the outer summation is over all unique reflections, and the weight w, is taken as $[\sigma(F_o)]^{-2}$.

Table III. Fractional Atomic Coordinates and Their Estimated Standard Deviations for 3

atom	x	y	z
Sn(1)	0.09735(3)	0.57862(2)	0.17058(2)
Sn(2)	0.35175(3)	0.63406(2)	0.41049(2)
Sn(3)	0.42095(3)	0.50247(2)	0.26248(2)
Sn(4)	0.18945(4)	0.47763(2)	0.39459(2)
S(1)	0.1716(1)	0.6752(1)	0.2682(1)
S(2)	0.0041(2)	0.5011(1)	0.2457(1)
S(3)	0.5264(1)	0.5936(1)	0.3646(1)
S(4)	0.3601(1)	0.4240(1)	0.3564(1)
C(1)	0.2579(5)	0.5387(2)	0.1398(3)
C(2)	0.2689(5)	0.5634(2)	0.4764(3)
C(11)	–0.0590(5)	0.6085(3)	0.0421(3)
C(12)	–0.0341(6)	0.6231(3)	–0.0408(4)
C(13)	–0.1323(6)	0.6463(3)	–0.1226(4)
C(14)	–0.2580(7)	0.6552(3)	–0.1262(4)
C(15)	–0.2868(6)	0.6397(3)	–0.0463(4)
C(16)	–0.1890(5)	0.6158(3)	0.0376(4)
C(21)	0.4361(5)	0.7117(2)	0.5098(3)
C(22)	0.5729(5)	0.7265(3)	0.5403(4)
C(23)	0.6313(6)	0.7681(3)	0.6178(4)
C(24)	0.5611(7)	0.7956(3)	0.6641(5)
C(25)	0.4322(7)	0.7835(3)	0.6366(5)
C(26)	0.3661(6)	0.7401(3)	0.5588(4)
C(31)	0.5604(4)	0.4539(3)	0.2182(3)
C(32)	0.5942(6)	0.4801(3)	0.1452(4)
C(33)	0.6722(6)	0.4449(4)	0.1076(5)
C(34)	0.7145(6)	0.3833(4)	0.1421(5)
C(35)	0.6860(6)	0.3577(3)	0.2160(5)
C(36)	0.6088(5)	0.3932(3)	0.2537(4)
C(41)	0.1158(5)	0.4061(3)	0.4647(4)
C(42)	0.1227(5)	0.4166(3)	0.5567(4)
C(43)	0.0798(5)	0.3678(3)	0.6033(4)
C(44)	0.0273(6)	0.3111(3)	0.5555(5)
C(45)	0.0202(7)	0.3015(3)	0.4645(6)
C(46)	0.0644(6)	0.3491(3)	0.4169(4)

The Sn–S and Sn–C bond distances found in **3** are comparable to the corresponding values reported for 1,3,5-triphenyl-2,4,6-trithia-1,3,5-tristannaadamantane[11] and $[(MeSn)_4S_6]$.[17] The Sn–S–Sn bond angles are similar to those found in the structure of $[Ph_2SnS]_3$[14] but significantly larger than those found in 1,3,5-triphenyl-2,4,6-

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Table IV. Fractional Atomic Coordinates and Their Estimated Standard Deviations for 13

atom	x	y	z
Sn(1)	0.09509(7)	0.05572(11)	0.67104(7)
Sn(2)	−0.07971(9)	0.32401(12)	0.65712(7)
Se(1)	0.0221(1)	0.1969(2)	0.5571(1)
Se(2)	0.1975(1)	0.1854(2)	0.7701(1)
C(1)	0.1782(11)	−0.0690(20)	0.6011(11)
C(2)	−0.1517(16)	0.4394(25)	0.5728(15)
C(3)[a]	0	−0.0483(21)	3/4
C(4)[a]	0	0.4363(23)	3/4
C(31)	0.0576(12)	−0.1327(16)	0.8121(11)
C(41)	−0.0651(14)	0.5131(18)	0.8064(14)

[a] Atom has a site occupancy factor = 0.5.

Table V. Selected Bond Lengths (Å) and Bond Lengths (deg) for 3

S(1)–Sn(1)	2.412(1)	S(2)–Sn(1)	2.388(2)
C(1)–Sn(1)	2.134(5)	C(11)–Sn(1)	2.109(5)
S(1)–Sn(2)	2.425(1)	S(3)–Sn(2)	2.403(1)
C(2)–Sn(2)	2.139(5)	C(21)–Sn(2)	2.132(4)
S(3)–Sn(3)	2.410(1)	S(4)–Sn(3)	2.391(1)
C(1)–Sn(3)	2.137(4)	C(31)–Sn(3)	2.122(4)
S(2)–Sn(4)	2.409(1)	S(4)–Sn(4)	2.408(1)
C(2)–Sn(4)	2.130(5)	C(41)–Sn(4)	2.133(5)
S(2)–Sn(1)–S(1)	111.7(1)	C(1)–Sn(1)–S(1)	109.6(1)
C(1)–Sn(1)–S(2)	112.0(1)	C(11)–Sn(1)–S(1)	106.0(1)
C(11)–Sn(1)–S(2)	106.4(2)	C(11)–Sn(1)–C(1)	110.9(2)
S(3)–Sn(2)–S(1)	109.4(1)	C(2)–Sn(2)–S(1)	107.4(1)
C(2)–Sn(2)–S(3)	114.5(1)	C(21)–Sn(2)–S(1)	109.6(1)
C(21)–Sn(2)–S(3)	106.3(1)	C(21)–Sn(2)–C(2)	109.5(2)
S(4)–Sn(3)–S(3)	109.0(1)	C(1)–Sn(3)–S(3)	108.0(1)
C(1)–Sn(3)–S(4)	114.4(1)	C(31)–Sn(3)–S(3)	109.8(1)
C(31)–Sn(3)–S(4)	104.9(2)	C(31)–Sn(3)–C(1)	110.8(2)
S(4)–Sn(4)–S(2)	108.8(1)	C(2)–Sn(4)–S(2)	112.1(1)
C(2)–Sn(4)–S(4)	109.5(1)	C(41)–Sn(4)–S(2)	104.6(1)
C(41)–Sn(4)–S(4)	105.6(1)	C(41)–Sn(4)–C(2)	115.8(2)
Sn(2)–S(1)–Sn(1)	102.3(1)	Sn(4)–S(2)–Sn(1)	102.2(1)
Sn(3)–S(3)–Sn(2)	102.3(1)	Sn(4)–S(4)–Sn(3)	104.0(1)
Sn(3)–C(1)–Sn(1)	115.4(2)	Sn(4)–C(2)–Sn(2)	116.6(2)

trithia-1,3,5-tristannaadamantane,[11] indicating less ring strain in 3 compared to the latter compound. Nevertheless, the presence of some ring strain in 3 is indicated by the magnitude of the Sn–C(methylene)–Sn angles (see above).

Despite the regular nature of the strucutre found for 3, the molecule comprises four independent Sn centers which exist in similar, but crystallographically distinct, chemical environments. This feature is highlighted in the solid-state ^{119}Sn NMR spectrum recorded for a sample of 3. The resolution of this spectrum is remarkable in that four resonances at 83.1, 94.6, 101.6, and 107.8 ppm are observed, indicating four different tin atom environments, a result consistent with the solid-state structure determined crystallographically.

Molecular Structure of 13. The molecular structure of 13 is shown in Figure 5. Selected bond lengths and angles are listed in Table VI. The structure of 13 is similar to a first approximation to that of 3. The molecule is situated about a crystallographic 2-fold axis such that the C(3) and C(4) atoms lie on this axis. The Sn–Se as well as the Sn–CH$_3$ bond lengths are shorter than those measured in (MeSn)$_4$Se$_6$.[8] The bond angles around Se and Sn do not show any abnormal features.

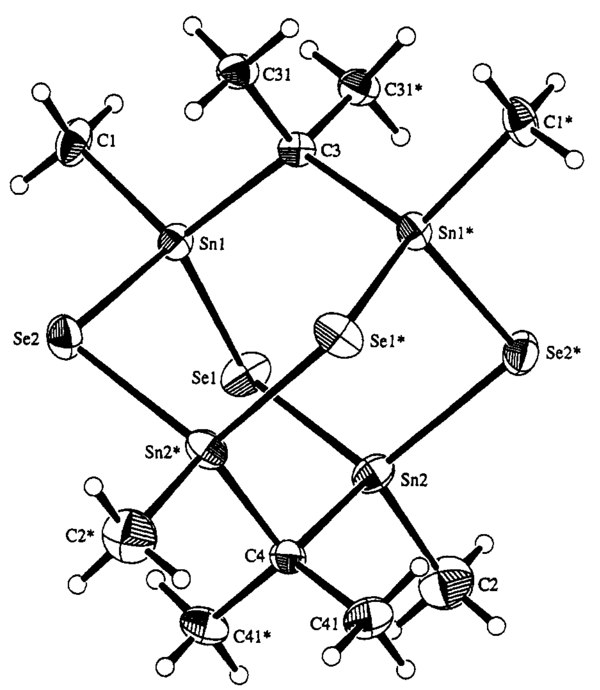

Figure 5. ORTEP diagram showing the molecular structure and crystallographic numbering scheme for [(MeSnSe)$_2$CMe$_2$]$_2$, 13.

Table VI. Selected Bond Lengths (Å) and Bond Angles (deg) for 13[a]

Sn(1)–Se(1)	2.496(2)	Sn(2)–C(2)	2.04(2)
Sn(1)–Se(2)	2.506(2)	Sn(2)–C(4)	2.16(1)
Sn(1)–C(1)	2.07(2)	C(3)–C(31)	1.53(2)
Sn(1)–C(3)	2.12(1)	C(3)–C(31)*	1.53(2)
Sn(2)–Se(1)	2.495(2)	C(4)–C(41)	1.50(2)
Sn(2)–Se(2)*	2.500(2)	C(4)–C(41)*	1.50(2)
Se(1)–Sn(1)–Se(2)	109.89(8)	Sn(1)–Se(2)–Sn(2)*	99.24(7)
Se(1)–Sn(1)–C(1)	106.2(5)	Sn(1)–C(3)–Sn(1)*	118(1)
Se(1)–Sn(1)–C(3)	113.8(3)	Sn(1)–C(3)–C(31)	105.8(6)
Se(2)–Sn(1)–C(1)	106.9(5)	Sn(1)–C(3)–C(31)*	108.4(6)
Se(2)–Sn(1)–C(3)	109.8(2)	Sn(1)*–C(3)–C(31)	108.4(6)
C(1)–Sn(1)–C(3)	110.1(7)	Sn(1)*–C(3)–C(31)*	105.8(6)
Se(1)–Sn(2)–Se(2)*	111.31(9)	C(31)–C(3)–C(31)*	110(2)
Se(1)–Sn(2)–C(2)	104.6(7)	Sn(2)–C(4)–Sn(2)*	114(1)
Se(1)–Sn(2)–C(4)	110.7(2)	Sn(2)–C(4)–C(41)	108.1(8)
Se(2)*–Sn(2)–C(2)	104.9(7)	Sn(2)–C(4)–C(41)*	105.6(9)
Se(2)*–Sn(2)–C(4)	113.9(3)	Sn(2)*–C(4)–C(41)	105.6(9)
C(2)–Sn(2)–C(4)	110.8(9)	Sn(2)*–C(4)–C(41)*	108.1(8)
Sn(1)–Se(1)–Sn(2)	99.18(7)	C(41)–C(4)–C(41)*	116(2)

[a] Atoms marked with an asterisk are related to the respective atoms without an asterisk by a 2-fold axis.

Experimental Section

All solvents were distilled prior to use. The synthesis of (Ph$_3$Sn)$_2$CH$_2$,[18] (Ph$_2$ClSn)$_2$CH$_2$,[19] and (^{t}Bu$_2$SnX)$_2$, (X = S, Se, Te)[20] have been described elsewhere. Elemental analyses were carried out by the Microanalytical Laboratory of the Australian National University, Canberra. Solution NMR spectra were recorded on a JEOL GX 270 FT NMR spectrometer at 270.17 (^{1}H), 67.84 (^{13}C), 51.525 (^{77}Se), 85.385 (^{125}Te), and 100.75 (^{119}Sn) MHz. The chemical shifts are relative to external Me$_4$Si (^{1}H, ^{13}C), Me$_2$Se (^{77}Se), Me$_2$Te (^{125}Te), and Me$_4$Sn (^{119}Sn). The solid-state ^{119}Sn MAS NMR spectrum was accumulated on a Bruker MSL 400 spectrometer operating at 149.16 MHz, using 2-μs (× π/4) pulses with a 10-s recycle delay.

Synthesis of Bis(dichlorophenylstannyl)methane (1). A 7.69-g (28.3-mmol) sample of HgCl$_2$ was added in small portions to an ice-cooled magnetically stirred solution of 5.05 g (7.1 mmol) (Ph$_3$Sn)$_2$CH$_2$ in acetone. After 30 min the ice bath was removed and the solution was stirred at room temperature for a further 2 h. The precipitate (PhHgCl) was filtered off and the solvent

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removed *in vacuo*. A 50-mL portion of ether was added to the residue and the reaction mixture stirred for 5 min followed by filtration. The filtrate was stored at −15 °C to yield 3.3 g (85%) of 1 as colorless crystals of mp 48 °C. ^{1}H NMR ($CDCl_3$): δ $SnCH_2$ 2.07 ppm, $^2J(^{119}Sn-^1H)$ 72 Hz. ^{13}C NMR ($CDCl_3$): δ $SnCH_2$ 17.4 ppm, $^1J(^{119}Sn-^{13}C)$ 72 Hz (C_i 138.6, C_o 134.7) ^2J(119Sn−13C) 62 Hz (C_m 129.6), $^3J(^{119}Sn-^{13}C)$ 95 Hz (Cp 131.7 ppm). ^{119}Sn NMR (0.22 g in 3 mL of $CDCl_3$): δ 8.5 ppm. Anal. Found: C, 28.27; H, 2.23; Cl, 25.20. $C_{13}H_{12}Cl_4Sn_2$ (547.44) Calcd: C, 28.52; H, 2.21; Cl, 25.90.

Synthesis of Bis(dichloro(trimethylsilyl)methylstannyl)methane (2). In analogy of the synthesis of 1 the treatment of 10.6 g (14.4 mmol) $(Me_3SiCH_2Ph_2Sn)_2CH_2$, prepared from $(Ph_2ClSn)_2CH_2$ and Me_3SiCH_2MgCl, with 15.6 g (57.4 mmol) of $HgCl_2$ yields 7.0 g (95%) of 2 as colorless crystals which were not further purified. ^{1}H NMR ($CDCl_3$): δ $SiCH_3$ 0.23, $SiCH_2$ 1.09 ($^2J(^{119}Sn-^1H)$ 104 Hz), $SnCH_2$ 1.73 ppm ($^2J(^{119}Sn-^1H)$ 64 Hz). ^{119}Sn NMR (CH_2Cl_2): δ 118.3 ppm ($^2J(^{119}Sn-C-^{117}Sn)$ 290 Hz).

Synthesis of 1,3,5,7-Tetraorgano-2,4,6,8-tetrachalcogena-1,3,4,5-tetrastannaadamantanes (3–6, 13). For 5, 6, and 13 the reactions and recrystallizations were performed under nitrogen and in the dark.

Method A. A 3.5-g sample of $(RCl_2Sn)_2CR'_2$ (R = Me, Ph, CH_2SiMe_3; R′ = H, Me) was dissolved in 30 mL of acetone and added dropwise to a magnetically stirred ice-cooled solution of the appropriate amount (2 equiv) of sodium chalcogenide Na_2X (X = S, Se, Te) in water. The reaction mixture was stirred overnight at room temperature, and the precipitate was filtered off, dried in vacuo, and recrystallized from dichloromethane/ether (X = S) and dichloromethane (X = Se, Te), respectively. The yields were approximately 80%.

Method B. A 2-g sample of $(RCl_2Sn)_2CR'_2$ (R = Me, Ph, CH_2SiMe_3; R′ = H, Me) and 1 equiv of $(^tBu_2SnX)_2$ (X = S, Se, Te) are dissolved in 15 mL of dichloromethane and stirred for 10 min at room temperature. The ^{119}Sn NMR spectra taken from these solutions revealed an almost quanitative formation of 3–6. Compounds 5 and 6 crystallized directly from these solutions. Precipitation of 3 and 4 was achieved by addition of ether, whereas 13 was recrystallized from dichloromethane/hexane. Mp (°C): 3, 265–268; 4, 80–84; 5, 291–296; 6, 200 dec; 13, 248 dec.

Anal. for 3. Found: C, 33.15; H, 2.52. $C_{26}H_{24}S_4Sn_4$ (939.52) Calcd: C, 33.24; H, 2.58. Anal. for 4. Found: C, 24.81; H, 5.47. $C_{18}H_{48}S_4Sn_4$ (867.64) Calcd: C, 24.92; H, 5.58. Anal. for 5. Found: C, 27.41; H, 2.02. $C_{26}H_{24}Se_4Sn_4$ (1127.10) Calcd: C, 27.71; H, 2.15. Anal. for 6. Found: C, 23.24; H, 1.41. $C_{26}H_{24}Te_4Sn_4$ (1321.66) Calcd: C, 23.63; H, 1.83. Anal. for 13. Found: C, 13.00; H, 2.40. $C_{10}H_{24}Se_4Sn_4$ (934.98) Calcd: C, 12.85; H, 2.59.

^{1}H NMR ($CDCl_3$, δ) (3) 1.30 ($SnCH_2$, $^2J(^{119}Sn-^1H)$ 54 Hz), 7.67 (*o*-Ph), 7.45 (*m*,*p*-Ph); (4) 0.15 ($SiCH_3$), 0.57 ($SiCH_2$, $^2J(^{119}Sn-^1H)$ 91 Hz), 0.82 ($SnCH_2$, $^2J(^{119}Sn-^1H)$ 51 Hz); (5) 1.37 ($SnCH_2$, $^2J(^{119}Sn-^1H)$ 54 Hz), 7.68 (*o*-Ph), 7.50 (*m*,*p*-Ph); (6) 1.34 ($SnCH_2$, ($^2J(^{119}Sn-^1H)$ 53 Hz), 7.58 (*o*-Ph), 7.42 (*m*,*p*-Ph); (13) 0.79 ($SnCH_3$, $^2J(^{119}Sn-^1H)$ 50 Hz), 1.74 (CH_3, $^3J(^{119}Sn-^1H)$ 115 Hz).

^{13}C NMR ($CDCl_3$, δ ($^nJ(^{119}Sn-^{13}C)$) (3) 4.5 (324 Hz) $SnCH_2$, 142.1 (655, 29) C_i, 134.2(55) C_o, 129.1(72) C_m, 130.4 C_p; (4) 1.43 $SiCH_3$, 12.6 (296) $SiCH_2$, 8.3 (297) $SnCH_2$; (6) 29.9 (179) $SnCH_2$, 138.6(430) C_i, 134.2 (55) C_o, 128.8 (61) C_m, 130.0 C_p; (13) 21.9 (352) $SnCH_3$, 22.6 CH_3, −2.2 (308) SnC.

Reaction of 3 with $(^tBu_2SnO)_3$. $[(PhSSn)_2CH_2]$ (0.17 g, 0.18 mmol) was dissolved in 5 mL of dichloromethane. To the solution was added $(^tBu_2SnO)_3$ (0.18 g, 0.24 mmol), and the reaction mixture was stirred for 5 min. The precipitate formed was filtered off, washed with dichloromethane, and dried to give 0.145 g (92%) of $[(PhOSn)_2CH_2]_n$, 12, as an amorphous solid, mp 279 °C dec. Anal. Found: C. 33.98; H, 2.99. $C_{13}H_{12}O_2Sn_2$ Calcd: C, 35.67; H, 2.76.

Crystallography. Intensity data for transparent crystals of 3 and 13 were measured on an Enraf-Nonius CAD4F (Rigaku AFC6R) diffractometer fitted with graphite monochromatized Mo Kα radiation, λ = 0.7107 Å. The ω:2θ scan technique was employed to measure 5829 (details for 13 follow those for 3 in parentheses, 3098) data up to a maximum Bragg angle of 25.0° (27.5°). The data set was corrected for Lorentz and polarization effects[21,22] and an analytical absorption correction was applied for 3[23] and an empirical absorption correction for 13.[24] Relevant crystal data are given in Table II.

The structures were solved by direct methods[25] and refined by a full-matrix least-squares procedure based on *F*[23] for 13.[22] Non-H atoms were refined with anisotropic thermal parameters, and H atoms were included in the model in their calculated positions. After the inclusion of a weighting scheme of the form $w = [\sigma^2(F) + |g|F^2]^{-1}$ for 3 (unit weights were employed in the refinement of 13), the refinements were continued until convergence ($g = 0.003$ for 3); final refinement details are listed in Table II. The analysis of variance showed no special features, indicating that an appropriate weighting scheme had been applied for 3. Fractional atomic coordinates for 3 and 13 are listed in Tables III and IV, and the numbering schemes employed are shown in Figures 4 and 5 which were drawn with ORTEP[26] at 25% (20%) probability ellipsoids. For 3, the scattering factors for all atoms were as incorporated in the SHELX76 program,[23] and the refinement was performed on a SUN4/280 computer. For 13, the Texsan[22] package, installed on an Iris Indigo workstation, was employed.

Acknowledgment. We are grateful to the Australian Research Council (A.R.C.) and the Stifterverband für die Deutsche Wissenschaft, Essen, for financial assistance and we thank Dr. T. J. Bastow, CSIRO Division of Materials Science and Technology, for recording the solid-state ^{119}Sn NMR spectra.

Supplementary Material Available: Listings of thermal parameters, H atom parameters, and bond distances and angles (6 pages). Ordering information is given on any current masthead page.

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