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Synthesis and spectral characterization of medium ring distannacycloalkanes and their Lewis acid derivatives

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Abstract

A study of the syntheses and some properties of several methyl substituted acyclic and cyclic bidentate organotin Lewis acids has been carried out. Of particular interest were cyclic species with 7-, 8-, 9- and 10-membered rings. The distannaalkanes and distannacycloalkanes were converted to the chlorides by chlorodemethylation with tin chlorides or mercuric chloride; this reaction was accompanied by ring cleavage in some cases. Chlorides, in turn, were readily converted to the methanesulfonates and trifluoromethanesulfonates. ^{1}H, ^{13}C and ^{119}Sn NMR and IR spectral data were used to gain information concerning structures, conformations and aggregation behavior. The mesylates are associated in chloroform; the triflates are not.

Introduction

The chemistry of multidentate Lewis acids has received much less attention than that of their base counterparts. Apparently the first explicit example was reported by Shriver and Biallas [1]. They established cooperative binding of a bidentate Lewis acid in the complex of methoxide ion with bis-1,2-difluoroborylethane. Other examples involving boron have been reported by Shore [2] and by Katz [3]. A cyclic trisiladodecane has been shown to promote transfer of halide ions through a liquid membrane [4]. The complexation behavior of organomercurials containing two and four mercury atoms has been studied in some depth [5]. Acyclic ditins have been examined in three laboratories [6–8]. 2,2′-Bis(trimethylstannyl)-1,1′-binaphthyl derivatives have been prepared in racemic and optical form [9]. Newcomb has reported on extensive synthetic and binding studies of macrocyclic [10], macrobicyclic and tricyclic [11] di- and tetratins. The monocyclic tritins with the 1,5,9-tristannacyclododecane ring [12] and the 1,6,11-tristannacyclopentadecane ring [13] have been shown to display interesting complexation properties.

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In this paper we report on the synthesis of cyclic bis-dimethyldistannacycloalkanes with seven to ten atoms in the rings. Reactions with organotin chlorides or mercuric chloride were shown to lead to chlorodemethylation and to ring cleavage. Cyclic chlorostannanes were converted to mesylatees and triflates. The ^{13}C and ^{119}Sn NMR parameters and IR data were obtained and are discussed in terms of structures and conformational properties.

Results and discussion

Terminal bis-trimethylstannylalkanes were prepared by reaction of the dichlorides or dibromides with trimethyltinsodium, and were converted into the bis-chlorodimethylstannaalkanes by reaction with mercuric chloride or methyltin chlorides as shown in eq. 1.

$$\begin{array}{lcl} Cl(CH_2)_nCl + 2\ Me_3SnNa & \longrightarrow & Me_3Sn(CH_2)_nSnMe_3 \\ & & \Big\downarrow MCl \\ Me{-}M & + & ClMe_2Sn(CH_2)_nSnMe_2Cl \\ M = HgCl,\ SnClMe_2,\ SnCl_3 & & (n = 1, 3\text{–}6) \end{array} \quad (1)$$

1,2-Bis(trimethylstannyl)ethane cannot be prepared by this route because 1,2-dichloroethane is dechlorinated by trimethyltinsodium. Hydrostannation of trimethylvinylstannane with trimethyltin hydride yields a mixture of 40% 1,1-bis-(trimethylstannyl)ethane and 60% of 1,2-bis(trimethylstannyl)-ethane [14] which could not be conveniently resolved. However, conversion of these to the chlorodimethylstannyl derivatives provided a mixture which could be readily resolved by recrystallization yielding about 80% of each regioisomer. ^{119}Sn NMR chemical shifts and $^{119}Sn{-}^{119}Sn$ coupling constants were measured for comparison with cyclic analogs and the parameters are presented in Table 1. The values for **2** and **3** agree well with values previously reported [15].

Replacement of a methyl group of tetramethylstannane by either a t-butyl or a trimethylstannyl group moves the chemical shift downfield by about 20 ppm. In the geminal distannyl series **2**, **3**, **4** the chemical shifts decrease slightly. The (presumably negative) values of $^2J(^{119}Sn{-}^{119}Sn)$ fall rapidly from 287 to 162 to 19 Hz in the same series. In the distannylethane **5** the chemical shift moves back upfield to 0.52 ppm, and the three-bond coupling constant is 1107 Hz, while that for **5Cl** is 1281 Hz, consistent with a predominant trans relationship of the stannyl groups. Another parameter of interest is the four-bond coupling seen in **6** which suggests that the molecule preferentially assumes an extended conformation with the methylene carbon–tin bonds forming the outer arms of a W conformation.

Preparation of distannacycloalkane rings was effected by the reaction of eq. 2.

$$ClMe_2Sn(CH_2)_nSnMe_2Cl + BrMg(CH_2)_4MgBr \longrightarrow \underset{(n = 1\text{–}4)}{Me_2Sn\begin{array}{l}\ulcorner\!\!-\!\!(CH_2)_n\!\!-\!\!\urcorner \\ \llcorner\!\!-\!\!(CH_2)_4\!\!-\!\!\lrcorner\end{array}SnMe_2} \quad (2)$$

Table 1

Tin-119 chemical shifts (ppm *versus* Me_4Sn) and tin–tin coupling constants (Hz) in $CDCl_3$

Compound	Structure	$\delta(^{119}Sn)$	$^nJ(Sn-Sn)$ [a]
1	Me_3Sn^tBu [b]	19.5	
2	$(Me_3Sn)_2CH_2$	23.3	$^2(286.7)$
2Cl	$(ClMe_2Sn)_2CH_2$	160.9	$^2(252.2)$
3	$(Me_3Sn)_2CHMe$	27.5	$^2(162.0)$
3Cl	$(ClMe_2Sn)_2CHMe$	171.0	$^2(83.0)$
4	$(Me_3Sn)_2CMe_2$	30.9	$^2(19.0)$
4Cl	$(ClMe_2Sn)_2CMe_2$	167.1	$^2(150.0)$
5	$Me_3Sn(CH_2)_2SnMe_3$	0.52	$^3(1107.6)$
5Cl	$ClMe_2Sn(CH_2)_2SnMe_2Cl$	159.6	$^3(1280.9)$
6	$Me_3Sn(CH_2)_3SnMe_3$	−0.37	$^4(30.3)$
6Cl	$ClMe_2Sn(CH_2)_3SnMe_2Cl$	163.0	
7	$Me_3Sn(CH_2)_4SnMe_3$	−0.3	
7Cl	$ClMe_2Sn(CH_2)_4SnMe_2Cl$	166.7	
8	$Me_3Sn(CH_2)_5SnMe_3$	−0.55	
8Cl	$ClMe_2(CH_2)_5SnMe_2Cl$	167.7	
9	$Me_3Sn(CH_2)_6SnMe_3$	−0.79	
9Cl	$ClMe_2Sn(CH_2)_6SnMe_2Cl$	168.0	

[a] Coupling constants in parentheses with the superscript denoting the number of intervening bonds. $^{119}Sn-^{117}Sn$ coupling constants were measured from ^{119}Sn NMR spectra and multiplied by 1.046 to obtain $^{119}Sn-^{119}Sn$ coupling constants. [b] From ref. 16.

Use of methyltins made it possible to separate the pure distannacycloalkanes from the product mixtures by moderate heating at < 0.02 Torr. A disadvantage emerged when chlorodealkylation with tin or mercury chlorides was found to result in ring cleavage along with replacement of methyl groups as described below.

When bis-(chlorodimethylstannyl)methane **1** was used in reaction 2, 1,1,3,3-tetramethyl-1,3-distannacycloheptane (**10**) was obtained in 38% yield. The ^{13}C and ^{119}Sn NMR data for **10** and other distannacycloalkanes and their chloro derivatives are presented in Table 2. The ^{119}Sn chemical shift and the value of $^2J(^{119}Sn-^{119}Sn)$ of **10** are very similar to those of **2** indicating no significant changes in the bonding parameters or the tin environments upon incorporation of the bis-stannylmethane unit in the seven-membered ring.

Attempted chlorodemethylation of **10** by reaction with 2 mol of mercuric chloride in acetone yielded a mixture with complex ^1H and ^{13}C spectra and a ^{119}Sn spectrum with four signals in the range 154–160 ppm due to the presence of chlorodialkyltin groups, and the ^{199}Hg NMR spectrum showed a signal at 37 ppm (relative to external MeHgCl in $CDCl_3$) due to the presence of methylmercuric chloride. A major signal at −18.5 ppm was assigned to an HgCl group *geminal* to tin because of satellites with the ^{119}Sn, ^{117}Sn pattern and intensity with a $^2J(^{119}Sn-^{199}Hg)$ value of 763.0 Hz. This showed that ring cleavage had occurred at the methylene segment. No effort was made to separate the components of the mixture.

Use of 1,1-bis(chlorodimethylstannyl)ethane (**3Cl**) in the cyclization provided 1,1,2,3,3-pentamethyl-1,3-distannacycloheptane (**11**) in 37% yield. Its ^{119}Sn chemical shift was upfield by 1.7 ppm from that of **3**, but the $^2J(^{119}Sn-^{119}Sn)$ value at 193.4 Hz was larger than that for **3** by 31 Hz, suggesting a slight change in bond angle upon incorporation of the Sn–C–Sn unit into a seven-membered ring.

Table 2

Carbon-13 and tin-119 parameters [a,b,c] for bis-dimethyl-, bis-chloro(methyl)- and bis-dichlorostannacycloalkanes

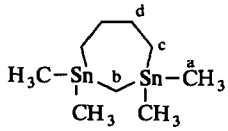
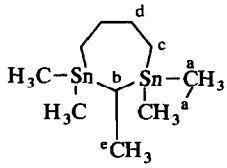
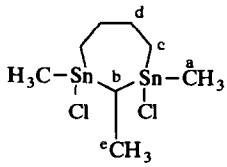
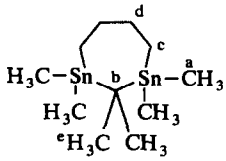
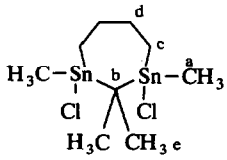
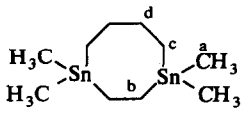
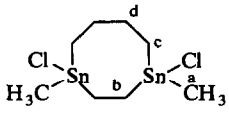
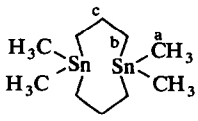
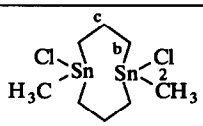
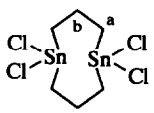
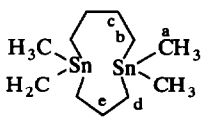
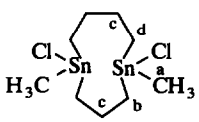
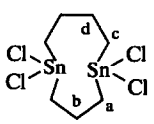
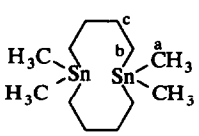
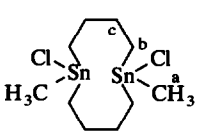
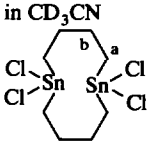
Compound		Chemical shift (ppm)					
		^{13}C					^{119}Sn [d]
		a	b	c	d	e	
10		−8.4 ^{1}(309.5)	−15.2 ^{1}(240.9)	10.2 ^{1}(350.0)	27.5 ^{2}(24.9)		22.4 ^{2}(284.5)
11		a: −11.8 ^{1}(297.0) ^{3}(10.4)	−2.2 ^{1}(278.0)	10.2 ^{1}(341.0)	27.7 ^{2}(23.0) ^{3}(11.0)	14.8 ^{2}(25.6)	25.8 ^{2}(193.4)
		a′: −9.5 ^{1}(285.0) ^{3}(15.4)					
11Cl		−2.1 ^{1}(330.0) ^{3}(16.0)	15.96 ^{1}(270.0)	18.4 ^{1}(367.7)	26.2 ^{2}(28.0) ^{3}(13.0)	12.5 ^{2}(28.0)	175.4
12		−12.1 ^{1}(277.0)	9.7 ^{1}(326.0)	10.2 ^{1}(326.0)	27.8 ^{2}(24.0) ^{3}(10.0)	26.9 ^{2}(20.0)	27.3 ^{2}(36.6)
12Cl		−3.97 ^{1}(292.1)	26.6 ^{1}(n.d.) [e]	18.2 ^{1}(333.0)	26.5 ^{2}(35.0) ^{3}(13.0)	24.4 ^{2}(21.1)	166.0 ^{2}(309.6)
13		−10.6 ^{1}(279.9)	7.0 ^{1}(354.0) ^{2}(15.9)	9.7 ^{1}(341.8)	28.0 ^{2}(19.6) ^{3}(20.8)		4.32 ^{3}(89.0)
13Cl		−1.6 ^{1}(322.0)	13.9 ^{1}(371.0) ^{2}(18.0)	17.8 ^{1}(359.0)	26.8 ^{2}(24.0) ^{3}(17.0)		163.1
14		−11.7 ^{1}(297.6)	17.4 ^{1}(347.5) ^{3}(31.2)	23.1 ^{2}(23.3)			−7.04 ^{4}(34.4)

Table 2 (continued)

Compound		Chemical shift (ppm)					
		^{13}C					^{119}Sn [d]
		a	b	c	d	e	
14Cl		0.01 ^{1}(340.0)	22.2 ^{1}(340.0)	23.6 ^{2}(26.2) ^{3}(n.d.) [e]			148.1
14Cl2		36.7 [f] ^{1}(497.6) ^{3}(35.3)	24.2 ^{2}(23.0) ^{3}(n.d.)				15.0
15		−10.8 ^{1}(295.4)	16.1 ^{1}(351.6)	23.0 ^{2}(24.2) ^{3}(26.9)	10.7 ^{1}(348.0)	28.4 ^{2}(20.0) ^{3}(< 5.0)	−3.21
15Cl		−1.8 ^{1}(319.0)	23.7 ^{1}(364.6) ^{3}(30.0)	21.2 ^{2}(27.0)	19.5 ^{1}(371.7)	27.3 ^{2}(22.0) ^{3}(< 5.0)	156.8
15Cl2		31.9 ^{1}(416.5) ^{3}(38.5)	19.9 ^{1}(30.2)	27.7 ^{1}(432.2)	26.3 ^{2}(24.2) ^{3}(18.1)		118.9
16		−10.8 ^{1}(296.6)	10.2 ^{1}(348.5)	29.3 ^{2}(24.2) ^{3}(36.3)			−3.75
16Cl		1.8 ^{1}(315.0)	18.5 ^{1}(368.7)	28.6 ^{2}(28.1) ^{3}(42.6)			154.5
16Cl2	in CD_3CN 	31.8 ^{1}(501.6)	29.2 ^{2}(402.9) ^{3}(18.2)				36.15

[a] In $CDCl_3$ with solvent signal as an internal standard. [b] Chemical shifts for ^{119}Sn versus external Me_4Sn. [c] Coupling constants $^nJ(^{13}C-^{119}Sn)$ and $^nJ(^{119}Sn-^{13}C)$ given in parentheses below ^{13}C and ^{119}Sn chemical shifts, respectively. [d] $^{119}Sn-^{117}Sn$ coupling constants were measured from ^{119}Sn NMR spectra and multiplied by 1.046 to obtain $^{119}Sn-^{119}Sn$ coupling constants. [e] Not observed: broadened signal.

Treatment of **11** with 2 mol of mercuric chloride afforded the bis-monochlorotin derivative (**11Cl**) in 63% yield. Whereas **11** showed two tin-methyls in the ^{13}C spectrum only one was present in that of **11Cl** revealing that only the isomers with the tin-methyls cis to each other were present or, more probably, that rapid inversion on the NMR time scale occurs at the tins. Attempts to replace the second methyl groups on the tins by reaction with two additional moles of mercuric chloride led to a complex mixture indicating the occurrence of ring cleavage.

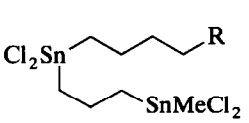
2,2-Bis-(chlorodimethylstannyl)propane (**4Cl**) provided 1,1,2,2,3,3-hexamethyl-1,3-distannacycloheptane (**12**) in 39% yield in the cyclization reaction. Here again the ^{119}Sn chemical shift is higher by 2.6 ppm in the cyclic compound **12** and the value of $^{2}J(^{119}Sn-^{119}Sn)$ is larger by 25.7 Hz than that of **4** suggesting a small difference in the Sn–C–Sn bond angles.

Replacement of a methyl group on each tin by chlorine proceeded smoothly upon reaction of **12** with 2 mol of mercuric chloride in acetone providing **12Cl** in 62% yield. If the less basic solvent tetrahydrofuran (THF) was used in place of acetone a mixture of products was obtained.

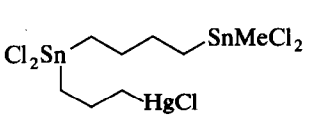
1,1,4,4-Tetramethyl-1,4-distannacyclooctane (**13**) was obtained in 27% yield in the cyclization reaction with 1,2-bis-(chlorodimethyl)stannane. Of particular interest among its NMR parameters is the $^{3}J(^{119}Sn-^{119}Sn)$ value of 89.0 Hz in comparison with the value of 1108 Hz for **5**. Models suggest a preferred dihedral Sn–C–C–Sn angle of about 60° for **13**; and this is consistent with the suggestion of Mitchell [15b] that the value for a dihedral angle of 90° would be less than 100 Hz.

Conversion of **13** to **13Cl** by treatment with mercuric chloride proceeded normally, but attempted conversion to the bis-(dichloro)methylstannacyclooctane provided a mixture of products which was not resolved.

Use of 1,3-bis-(chlorodimethylstannyl)propane (**6Cl**) in reaction 2 provided 1,1,5,5-tetramethyl-1,5-distannacyclononane (**15**) in 28% yield. Its ^{13}C NMR spectrum reveals values for $^{3}J(^{119}Sn-^{13}C)$ of 26.9 Hz to C(b) and < 5.0 Hz to C(d) which are in accord with dihedral angles for Sn–C–C–C of $< 90°$ and about 90°, respectively. Conversion to the bis-chloro*di*methyl derivative (**15Cl**) proceeded in 87% yield. Treatment of **15** with 4 mol of mercuric chloride in acetone provided a mixture of products which could be separated by crystallization and were shown to be **15Cl2** (20%) and a ring-opened product containing the ClSn and HgCl functions. Cleavage could occur at the carbon–tin bond of either the four- or the three-carbon segment of the ring. The structure of this product



20 R = HgCl
21 R = Br
22 R = $SnCl_3$



(20a)

was shown to be **20** on the basis of the ^{13}C and ^{119}Sn NMR spectra of Table 3. Eight types of carbons were present. Of these, carbons a, b, d and e display $^{1}J(^{119}Sn-^{13}C)$ values in the vicinity of 550 Hz indicating that they are bonded directly to tin. Carbon c showed satellites with the tin coupling pattern with $J = 36.6$ Hz and its intensity was that expected for two-bond coupling, reflecting

Table 3

^{13}C NMR spectral data [a] for $Cl_2(\overset{a}{C}H_3)Sn\overset{h}{C}H_2\overset{c}{C}H_2\overset{d}{C}H_2Sn(Cl_2)\overset{c}{C}H_2\overset{f}{C}H_2\overset{g}{C}H_2\overset{h}{C}H_2R$

Carbon	**20** R = HgCl		**21** R = Br		**22** R = $SnCl_3$	
	δ (ppm)	^nJ [b]	δ (ppm)	^nJ [b]	δ (ppm)	^nJ [b]
a	12.9	^{1}(555.0)	12.8	^{1}(542.0)	12.8	^{1}(573.0)
b	31.3	^{1}(546.0)	30.7	^{1}(544.0)	34.8	^{1}(567.2)
c	22.2	^{2}(36.6)	22.0	^{2}(38.3)	22.1	^{2}(40.1)
d	34.4	^{1}(538.0)	34.4	^{1}(506.0)	34.5	^{1}(591.3)
				^{3}(105.0)		^{3}(131.8)
e	34.3	^{1}(577.0)	34.5	^{1}(512.0)	31.3	^{1}(560.0)
f	30.5	^{2}(41.2)	24.4	^{2}(39.4)	28.4	^{2}(39.0)
		^{3}(183.0) [c]				^{3}(215.2)
g	32.2	^{2}(82.0) [d]	34.7	^{3}(112.0)	29.2	^{2}(68.0)
		^{3}(115.0)				^{3}(124.2)
h	32.4	^{1}(1543.0) [e]	35.9		38.9	^{1}(1070.0)

[a] In CD_3CN with the solvent peak as an internal standard. [b] $^nJ(^{13}C-^{119}Sn)$ where n is the number of intervening bonds. [c] $J(^{13}C-^{199}Hg)$. [d] $^2J(^{13}C-^{199}Hg)$. [e] $^1J(^{13}C-^{199}Hg)$.

two-bond coupling to each of two tins. Carbon f shows one coupling of 41.2 Hz with the tin coupling pattern. This carbon also shows a coupling of 183 Hz involving one pair of satellites as expected for coupling to ^{199}Hg which is consistent with $^3J(^{199}Hg-^{13}C)$. Carbon g shows two pairs of tin satellites with $J = 115.0$ Hz consistent with a three-bond coupling. It also displayed a pair of satellites with $J = 82.0$ Hz which fits for a two-bond coupling to mercury. Carbon h also shows only one pair of satellites with $J = 1543$ Hz, revealing its bonding to mercury. For further confirmation of its structure, **20** was treated with bromine in acetonitrile, and the course of the reaction was followed by ^{199}Hg NMR. The signal at -180.0 ppm was replaced by one at -900 ppm due to BrHgCl. The ^{13}C spectral data for the product (**21**) are included in Table 3. Particularly relevant to the structural assignment is the chemical shift of carbon h in **20** which moves downfield by 3.5 ppm and loses the satellites due to coupling with mercury as **21** is formed. Carbon f shows only a two-bond coupling of 39.4 Hz to tin, and carbon g shows a three-bond coupling of 112.0 Hz to tin.

When THF was used as the solvent in the reaction of **15** with mercuric chloride only the ring cleavage product **20** was formed. Treatment of **15** with 4 mol of tetrachlorostannane produced a mixture of products from which 40% of **15Cl2** and 20% of the ring cleavage product were obtained by recrystallization. The direction of cleavage was established by the NMR spectra to have occurred at the four-carbon segment of **15** producing **22**. Definitive parameters, shown in Table 3, were the large one-bond coupling of 1070 Hz of carbon h with $-SnCl_3$ and the two- and three-bond couplings to tin of carbons f and g with the required relative magnitudes, *i.e.* for C(g)–C–$SnCl_3$ (68 Hz); C(f)–C–$SnCl_2$– (39 Hz); and C(f)–C–C–$SnCl_3$ (215 Hz); C(g)–C–C–$SnCl_2$– (124 Hz).

1,1,6,6-Tetramethyl-1,6-distannacyclodecane (**16**) was obtained in 20% yield in the cyclization reaction with 1,4-bis-chlorodimethylstannylbutane. Reaction of **16** with 2 mol of mercuric chloride in acetone provided 80% of 1,6-dichloro-1,6-dimethyl-1,6-distannacyclodecane (**16Cl**) which was also the product of reaction of **16** with dichlorodimethylstannane. When 4 mol of mercuric chloride were used only

the product of chlorodemethylation, 1,1,6,6-tetrachloro-1,6-distannacyclodecane (**16Cl2**) was obtained in 78% yield; no ring cleavage product was found. The same result was obtained when 4 mol of tetrachlorostannane was used. The ^{13}C and ^{119}Sn NMR parameters of **16, 16Cl** and **16Cl2** fell within the ranges observed for analogous acyclic compounds.

The alternative reaction of eq. 3 was used to prepare 1,1,5,5-tetramethyl-1,5-distannacyclooctane (**14**) because of difficulties in preparing reasonably pure

$$(CH_3)_2Sn(Na)(CH_2)_3Sn(Na)(CH_3)_2 + Br(CH_2)_3Br \longrightarrow \underset{\textbf{(14)}}{\text{Me}_2\text{Sn}(\text{CH}_2)_3\text{SnMe}_2} \quad (3)$$

Grignard reagent from 1,3-dibromopropane. The complex product mixture obtained showed three ^{119}Sn signals in the range -100 to -106 ppm which is characteristic for compounds with tin–tin bonds [17], and three minor signals in the desired range of -6.0 to -10.0 ppm. Heating the mixture at 100°C and 0.01 Torr provided 6% of the desired **14**. Use of 1,3-dichloropropane led to an increase in the yield to 11%. Use of 1,3-bis(methanesulfonyloxy)propane provided no improvement. Indeed, the product mixture showed the presence of vinyl groups (^1H: 4.6–4.9 ppm and 5.08–6.01 ppm; ^{13}C: 137.5 and 137.6 ppm) indicating that elimination had occurred. The formation of ditin can therefore be accounted for by the following reaction sequence [18]:

$$R_3SnNa + XCH_2CH_2CH_2X \longrightarrow R_3SnH + XCH_2CH{=}CH_2 + NaX$$

$$R_3SnNa + XCH_2CH{=}CH_2 \longrightarrow R_3SnCH_2CH{=}CH_2 + NaX$$

$$2\,R_3SnH \xrightarrow{R_3SnNa} R_3SnSnR_3 + H_2$$

Treatment of **14** with mercuric chloride as above yielded the bis-(monochlorodistanna)cyclooctane (**14Cl**) and the bis-dichloro analog (**14Cl2**), respectively. Both were extremely soluble in water. Indeed, **14Cl2** was hygroscopic and required prolonged heating *in vacuo* at 85°C to remove the water.

Methanesulfonates and trifluoromethanesulfonates

Mesylates and triflates corresponding to the chlorides described above were prepared in order to obtain compounds with a range of Lewis acidities for quantitative studies on complexation and catalysis. Trimethyl(methanesulfonyloxy)-tin was prepared by reactions 4 [19] and 5 [20]. Reaction 4 proved to be reversible as indicated by the signal in the tin-119 NMR spectrum at 138 ppm which lies

$$Me_3SnG + MeSO_3H \xrightarrow{CH_2Cl_2} \underset{\textbf{(17Ms)}}{Me_3SnO_3SMe} + HG \qquad \begin{matrix} G = Cl & (4) \\ G = Me & (5) \end{matrix}$$

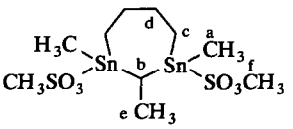
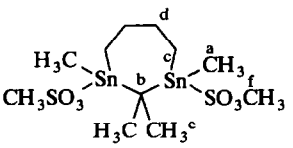
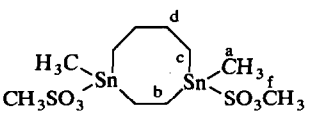
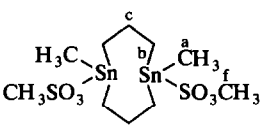
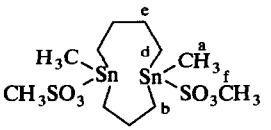
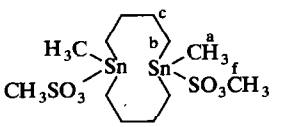
between the values of 164 ppm for **17Cl** and 74 ppm for **17Ms**. (See Table 4 for identifications and ^{13}C and ^{119}Sn NMR spectral data.) This latter value was obtained when the solvent was removed, the residue warmed to 80°C and then

Table 4

Carbon-13 and tin-119 NMR parameters for alkyltinmethanesulfonates with R = $MeSO_3$ [a,b,c]

Compound	Solvent	Chemical shifts (ppm)						
		^{13}C						^{119}Sn
		a	b	c	d	e	R	
$\overset{a}{Me}_3SnR$ **17Ms**	$CDCl_3$	1.57 ^{1}(489.5)					40.2	75.5
	CD_3CN	0.66 ^{1}(485.0)					41.0	69.3
	D_2O	0.83 ^{1}(509.7)					41.0	41.7
$\overset{a}{Me}_2SnR_2$ **18Ms2**	D_2O	12.6 ^{1}(1056.6)					41.0	−346.0
$(\overset{d}{C}H_3\overset{c}{C}H_2\overset{b}{C}H_2\overset{a}{C}H_2)_3SnR$ **19Ms**	$CDCl_3$	20.3 ^{1}(404.7)	27.7 ^{2}(27.0)	25.9 ^{3}(78.6)	13.7		39.9	77.5
$\overset{b}{C}H_2(Sn\overset{a}{Me}_2R)_2$ **2Ms**	$CDCl_3$	2.42 ^{1}(486.2)	6.45 ^{1}(384.1)				40.0	70.9
$\overset{c}{C}H_3\overset{b}{C}H(Sn\overset{a}{Me}_2R)_2$ **3Ms**	$CDCl_3$	0.46 ^{1}(469.0)	20.63 ^{1}(419.0)	13.12 ^{2}(33.0)			39.9	70.3
	CD_3CN	0.68 ^{1}(477.4)	20.75 ^{1}(427.1)	13.6 ^{2}(35.3)			40.39	66.5
$(\overset{c}{C}H_3)_2\overset{b}{C}Sn\overset{a}{Me}_2R$ **4Ms**	$CDCl_3$	0.46 ^{1}(430.0)	33.4 ^{1}(430.1)	23.75 ^{2}(25.2)			40.1	83.0
	CH_3CN	0.86 ^{1}(436.0)	33.7 ^{1}(428.6)	24.56 ^{2}(23.0)			40.95	75.9
$(\overset{b}{C}H_2Sn\overset{a}{Me}_2R)_2$ **5Ms**	$CDCl_3$	0.32 ^{1}(453.2)	16.61 ^{1}(500.6) ^{3}(31.2)				39.6	65.61
	CD_3CN	0.76 ^{1}(449.2)	17.4 ^{1}(498.6) ^{2}(33.3)				40.0	62.2
$\overset{c}{C}H_2(\overset{b}{C}H_2Sn\overset{a}{Me}_2R)_2$ **6Ms**	$CDCl_3$	0.55 ^{1}(447.5)	24.83 ^{1}(591.3) ^{3}(57.2)	21.54 ^{2}(28.0)			40.07	73.3
	CD_3CN	0.96 ^{1}(453.6)	25.7 ^{1}(497.4)	22.6 ^{2}(28.4)			40.7	59.0
	D_2O	0.79 ^{1}(481.4)	26.0 ^{1}(502.0) ^{3}(92.0)	23.8 ^{2}(28.0)			41.0	29.3
$(\overset{c}{C}H_2\overset{b}{C}H_2Me_2\overset{a}{R})_2$ **7Ms**	$CDCl_3$	0.25 ^{1}(435.0)	19.95 ^{1}(484.5)	28.4 ^{2}(32.8) ^{3}(69.8)			46.2	74.0
	CD_3CN	0.34 ^{1}(458.3)	20.58 ^{1}(510.1)	29.08 ^{2}(30.6) ^{3}(70.0)			40.3	61.0

Table 4 (continued)

Compound	Solvent	Chemical shifts (ppm)						
		^{13}C						^{119}Sn
		a	b	c	d	e	f	
11Ms 	$CDCl_3$	0.45 ^{1}(446.2) ^{3}(20.0)	18.2 ^{1}(356.6)	19.95 ^{1}(465.3)	25.5 ^{2}(33.2)	12.64 ^{2}(32.2) ^{3}(14.1)	39.9	75.41
	CD_3CN	−0.35 ^{1}(453.2) ^{3}(16.8)	18.97 ^{1}(362.6)	22.03 ^{1}(477.4)	26.38 ^{2}(33.2)	13.15	40.58	69.4
12Ms 	$CDCl_3$	−0.8 ^{1}(405) ^{3}(16.8)	31.1 ^{1}(352.0)	22.7 ^{1}(445.0)	26.1 ^{2}(32.0)	26.4 ^{2}(23.0)	40.0	69.9
13Ms 	$CDCl_3$	0.5 ^{1}(395.3)	18.2 ^{1}(453.5)	19.73 ^{1}(419.0)	26.3 ^{2}(20.0) ^{3}(25.0)		40.3	60.2
14Ms 	$CDCl_3$	1.1 ^{1}(421.0)	25.8 ^{1}(448.4) ^{3}(n.d.)	22.0 ^{2}(33.2)			40.1	49.4
	CD_3CN	0.34 ^{1}(425.0)	26.0 ^{1}(460.3)	^{2}(30.2)	22.3		40.4	43.7
15Ms 	D_2O	1.7 ^{1}(449.4)	25.4 ^{1}(480.0) ^{3}(33.6)	23.0 ^{2}(24.4)	22.2 ^{1}(486.0)	29.0 ^{2}(19.4) ^{3}(32.6)	41.0	23.6
16Ms 	D_2O	1.5 ^{1}(431.6)	22.5 ^{1}(487.3) ^{3}(31.5)	30.7 ^{2}(31.5)			41.0	25.0

[a] Chemical shifts relative to Me_4Si for ^{13}C. [b] Coupling constants $^nJ(^{13}C-^{119}Sn)$ given in parentheses below ^{13}C chemical shift. [c] Chemical shifts *versus* external Me_4Sn for ^{119}Sn.

dissolved in methylene chloride. Mixing the reactants for reaction 5 at −78°C and warming to room temperature provided a quantitative yield of **17Ms**.

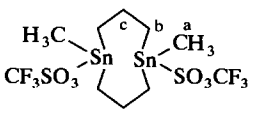
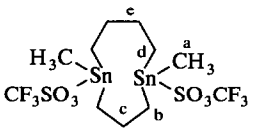
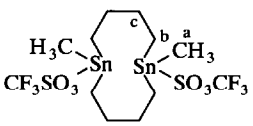
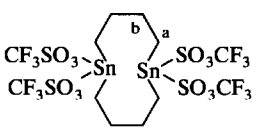
Methanesulfonic acid cleaved the Sn–CH_2 as well as the Sn–CH_3 bonds in mixed tetraalkyltins, making it an unsuitable reagent for general use. Furthermore

Table 5

^{13}C and ^{119}Sn NMR parameters for alkyltin trifluoromethanesulfonates with R = CF_3SO_3 [a,b,c]

Compound	Solvent	Chemical shifts (ppm)					
		^{13}C					^{119}Sn
		a	b	c	d	e	
$\overset{a}{Me}_3SnR$ **17Tf**	$CDCl_3$	15.1 ^{1}(439.9)					166.3
	CD_3CN	0.62 ^{1}(481.6)					74.9
$\overset{a}{Me}_2SnR_2$ **18Tf2**	CD_3CN	17.8 ^{1}(890.1)					−344.1
$(\overset{d}{C}H_3\overset{c}{C}H_2\overset{b}{C}H_2\overset{a}{C}H_2)_3SnR$ **19Tf**	$CDCl_3$	20.93 ^{1}(382.8)	27.3 ^{2}(28.2)	26.8 ^{3}(76.5)	13.44		168.4
	CD_3CN	n.d.	n.d.	n.d.	n.d.	n.d.	70.5
$(\overset{d}{C}H_3\overset{c}{C}H_2\overset{b}{C}H_2\overset{a}{C}H_2)_2SnR_2$ **19Tf2**	CD_3CN	37.8 ^{1}(743.4)	27.4 ^{2}(56.4)	26.2 ^{3}(173.3)	13.8		−361.5
$\overset{b}{C}H_2(Sn\overset{a}{M}e_2R)_2$ **2Tf**	$CDCl_3$	2.53 ^{1}(448.2)	6.84 ^{1}(335.4)				143.2
	CD_3CN	2.23 ^{1}(487.2)	2.79 ^{1}(397.0)				76.1
$C\overset{b}{H}_2(Sn\overset{a}{M}eR_2)_2$ **2Tf2**	CD_3CN	15.45 ^{1}(906.6)	33.6 ^{1}(902.0)				−350.5
$C\overset{b}{H}_2(Sn\overset{a}{M}e_2R2)_2$ **5Tf**	CD_3CN	−0.7 ^{1}(443.2)	16.4 ^{1}(485.5)				69.45
$(C\overset{b}{H}_2Sn\overset{a}{M}eR_2)_2$ **5Tf2**	CD_3CN	18.4 ^{1}(n.d.)	33.9				n.d.
$C\overset{c}{H}_3C\overset{b}{H}(Sn\overset{a}{M}e_2R)_2$ **3Tf**	$CDCl_3$	0.94 ^{1}(437.2)	21.8 ^{1}(368.7)	12.6 ^{2}(30.2)			154.3
	CD_3CN	0.8 ^{1}(457.3)	19.5 ^{1}(415.0)	13.4 ^{2}(30.2)			85.7
$(\overset{c}{C}H_3)_2\overset{b}{C}(Sn\overset{a}{M}e_2R)_2$ **4Tf**	CD_3CN	0.6 ^{1}(419.9)	32.97 ^{1}(419.0)	24.72 ^{2}(27.3)			105.7
$\overset{c}{C}H_2(\overset{b}{C}H_2Sn\overset{a}{M}e_2R)_2$ **6Tf**	CD_3CN	−0.14 ^{1}(451.2)	25.01 ^{1}(482.5) ^{3}(95.7)	22.24 ^{2}(26.2)			67.3
$\overset{d}{C}H_2(\overset{c}{C}H_2\overset{b}{C}H_2Sn\overset{a}{M}e_2R)_2$ **8Tf**	CD_3CN	0.23 ^{1}(445.1)	21.1 ^{1}(494.0)	25.4 ^{2}(31.2)	37.6 ^{3}(80.1)		76.6
$(R\overset{a}{M}e_2Sn\overset{b}{C}H_2\overset{c}{C}H_2\overset{d}{C}H_2)_2$ **9Tf**	CD_3CN	−0.03 n.d.	21.07 n.d.	25.7 n.d.	33.31 n.d.	n.d.	77.7

Table 5 (continued)

Compound	Solvent	Chemical shifts (ppm)					
		^{13}C					^{119}Sn
		a	b	c	d	e	
14Tf 	$CDCl_3$	0.38 ^{1}(375.9)	26.5 ^{1}(397.9) ^{3}(n.d.)	21.4 ^{2}(32.2)			132.5
15Tf 	CD_3CN	0.75 ^{1}(405.2)	24.6 ^{3}(38.3)	21.8 ^{2}(28.3)	21.8 ^{1}(444.4)	27.0 ^{2}(32.0) ^{3}(20.0)	66.0
16Tf 	CD_3CN	0.84 ^{1}(413.0)	21.9 ^{1}(455.3)	29.2 ^{2}(37.3) ^{3}(30.5)			60.0
16Tf2 	CD_3CN	31.0 ^{1}(668.0)	28.69 ^{2}(33.0) ^{3}(18.0)				−99.7

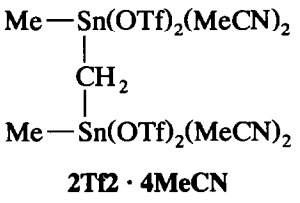
[a] Chemical shifts *versus* Me_4Si for ^{13}C. [b] Coupling constants $^nJ(^{13}C-^{119}Sn)$ given in parentheses below ^{13}C chemical shifts. [c] Chemical shifts *versus* external Me_4Sn for ^{119}Sn.

both reactions 4 and 5 could yield product with residual protic acid which would complicate studies on the Lewis acidities of the mesylates. Therefore, the reaction of the tin chlorides with silver mesylate [21] was used for the preparation of most of the remaining mesylates.

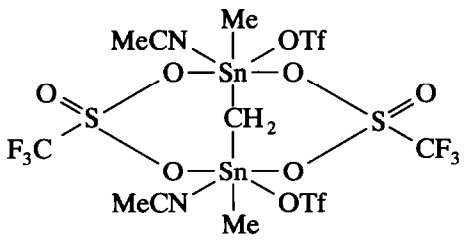
Whereas the chlorides described above were moderately soluble in solvents like dichloromethane and chloroform, the mesylates varied somewhat in solubility. Thus those of lower molecular weight such as **2Ms–6Ms** and **19Ms** were conveniently prepared in the chlorocarbon. Others such as **7Ms, 11Ms–16Ms** displayed low solubility in methylene chloride as well as in donor solvents such as acetonitrile and tetrahydrofuran. These were prepared in methanol in which they were quite soluble and easily separated from the silver chloride. This suggests that they may be oligomeric in the solid state and that these aprotic solvents are not sufficiently strong as donors to the tin atoms to break down the oligomers; solvents such as methanol and water do this effectively by hydrogen bonding to the oxygens of the sulfonyloxy groups.

Triflates were prepared by the reaction of the organotin chlorides with silver triflate. (See Table 5 for identifications and ^{119}Sn and ^{13}C NMR spectral parameters.) Trimethyltin triflate (**17Tf**) and tri-n-butyltin triflate (**19Tf**), prepared in

dichloromethane, proved to be low-melting, moderately hygroscopic solids. The corresponding ditriflates (**18Tf2**) and (**19Tf2**) were insoluble in the chlorocarbons and were prepared in diethyl ether. These were extremely hygroscopic and turned brown upon exposure to the air. In acetonitrile, they showed ^{119}Sn chemical shifts of −344.0 and −316.0 ppm, respectively, clearly indicating hexacoordinate tins [17]. The bis-ditriflate (**2Tf2**) prepared in nitromethane, from bis[dichloro(methyl) stannyl]methane (**2Cl2**) also revealed the high-field (−350.1 ppm) chemical shift expected for hexacoordinate tin. Such coordination could be achieved in a normal 1:4 complex **2Tf2 · 4MeCN** below with two independently coordinated tins, or a 1:2 complex **2Tf · 2MeCN** (arbitrary stereochemistry) with the tins joined by two sulfonate bridges. The acyclic triflates **5Tf, 8Tf, 9Tf** and **5Tf2** were prepared in



2Tf2 · 4MeCN



2Tf2 · 2MeCN

nitromethane while **6Tf** required the use of t-butyl alcohol as solvent.

The ^{119}Sn chemical shifts and the $^{13}C-^{119}Sn$ coupling constants of the mesylates and triflates shown in Tables 4 and 5 follow trends which reveal differences in

Table 6

SO_3 stretching frequencies of alkyltin methanesulfonates

Compound	1% in KBr (cm^{-1})		2–5% in $CHCl_3$ (cm^{-1})	
	Asymmetric	Symmetric	Asymmetric	Symmetric
AgOMs	1195	1050		
17Ms	1200	1050	1150	1040
	1190		1130	
19Ms	1200	1075	1150	985
		1060		
18Ms2	1205	1050		
	1190			
5Ms	1150	1035	1150	1025
	(neat)			
3Ms	1210	1060	1150	1000
	1195			
4Ms	1205	1055		
	1195			
6Ms	1190	1035		
	1150	(neat)		
11Ms	1205	1105	1135	1025
	1190			
14Ms	1210	1060	1155	1050
	1195			1030
16Ms	1205	1050		
	1198	1040		

their structures in solution. In chloroform the tin chemical shifts for the triflates fall in the range 132–168 ppm while those for the mesylates appear at higher fields (49–83 ppm). However, the $^1J(^{13}C-^{119}Sn)$ values are uniformly smaller for the triflates (335–440 Hz) than for the mesylates (400–490 Hz). These trends are seen in the data for **2, 3, 14, 17** and **19** mesylates and triflates. In acetonitrile, on the other hand, the chemical shifts and coupling constants for these sulfonates are very similar, falling in the range 60–75 ppm and 415–485 Hz, respectively. These observations are consistent with the notion that the mesylates are associated through S=O–Sn coordination in chloroform, leading to the lowered S=O stretching frequencies seen in Table 6 and to high J values due to increased s-orbital character of equatorial Sn–C bonds in the trigonal-bipyramidal structure. The triflates are not associated in chloroform but become pentacoordinate upon coordination with acetonitrile; this results in higher field chemical shifts and larger ^1J values. The pentacoordination of the mesylates in acetonitrile may be due to association or coordination with the solvent.

Dimethyltin ditriflate (**18Tf2**), and di-n-butyltin ditriflate (**19Tf2**) and bis(methylditrifluoromethanesulfonyloxy)stannylmethane (**2Tf2**) show ^{119}Sn chemical shifts near -350 ppm in acetonitrile indicating hexacoordinate species. By contrast 1,6-distannacyclodecane ditriflate (**16Tf2**) shows the ^{119}Sn chemical shift at -100 ppm which indicates pentacoordination. This reveals that hexacoordination at the tins in the ten-membered ring is not achieved, presumably due to angle and steric strains which would result.

Experimental section

General

^1H NMR spectra were recorded on Varian EM-360A at 60 MHz and Varian XL-300 instruments at 300 MHz. Chemical shifts are reported in parts per million relative to internal tetramethylsilane $(CH_3)_4Si$ 0.0 when organic solvents were used, or to sodium 4-4-dimethylsilapentanesulfonate (DSS, 0.0) when D_2O was the solvent. Values for chemical shifts are followed in parentheses by the multiplicity, number of protons, coupling constant and assignment. Proton-tin-119 coupling constants are reported as $^nJ(^{119}Sn-C-H)$ with the first superscript denoting the number of bonds intervening between nuclei. Unless otherwise noted ^{13}C, ^{119}Sn and ^{199}Hg NMR were recorded on a Varian XL-300 instrument with a 5 mm tunable probe at 75.4 MHz, 111.86 MHz and 53.6 MHz, respectively. ^{13}C NMR spectra were obtained in $CDCl_3$ or CD_3CN with the solvent peak as an internal standard. Chemical shifts for ^{119}Sn spectra were recorded in parts per million relative to external tetramethylstannane. For tetraalkyltins ^{13}C and ^{119}Sn spectra were obtained at a sweep width of 16 500 Hz with an acquisition time of 0.9 s, 32K data points were collected. A pulse width of 13 μs was employed. Satisfactory signal-to-noise ratios were normally obtained after 100–400 transients. The fast relaxation times of the methyl carbons on the tin and the tin nuclei in substituted organotin compounds R_3SnX and R_2SnX_2 (X = Cl, OTf, OMs), allowed use of acquisition times of 0.3–0.5 s. As a result it was possible to obtain decoupled spectra of moderately concentrated samples with satisfactory signal-to-noise ratio after 10 000–20 000 transients in a matter of hours; with inverse gated decoupling and line broadening, fewer transients were needed. ^{199}Hg chemical shifts are

reported in parts per million relative to an external saturated $CDCl_3$ solution of CH_3HgCl. Typical experimental parameters were: 16K data points, 0.3 s acquisition time, 50000 Hz spectral width, 20 s (90°) pulse width, number of scans 10000 with no relaxation delay. Infrared spectra were obtained on a Perkin–Elmer 283-B instrument. Gas chromatographic analyses were performed using a 12 ft × 1.4 in column of 15% SE30 on Chromosorb W 60–80 mesh. Melting points and boiling points are uncorrected. Carbon-hydrogen analyses were done by Galbraith Laboratories, Inc., Knoxville, TN, and Desert Analytics, Tucson, AZ. All operations involving air and moisture-sensitive materials were conducted under dry nitrogen.

1,n-Bistrimethylstannylalkanes and their chloro(methyl)stannyl analogs were prepared by previously described methods and had the expected spectral properties [7].

Preparation of distannacycloalkanes

Distannacycloalkanes were prepared by the reaction of the di-Grignard reagent of 1,4-dibromobutane and the 1,*n*-bis(chlorodimethylstannyl)alkane in THF. The procedure used here differs from that described in earlier work [12]. We have employed moderate dilution conditions which resulted in 5–10% improvement in product yields. Using a motor driven syringe a solution of di-Grignard reagent and a solution of chlorostannane in THF were added simultaneously over a period of 3–4 h. A representative procedure follows.

1,1,4,4-Tetramethyl-1,4-distannacyclooctane (13). Into a flame dried, 250-mL, 3 neck, round-bottom flask equipped with a mechanical stirrer, water condenser and an addition funnel was placed 5.0 g (205.5 mmol) of magnesium turnings under nitrogen. A solution of 1,4-dibromobutane (17.7 g, 82.2 mmol) in THF (150 mL) was added dropwise with stirring over a period of 0.4 h. After the solution was stirred for 3 h at room temperature an aliquot was titrated for active base. The solution was filtered and was diluted to 300 mL with THF. The di-Grignard reagent (300 mL, 66.0 mmol) and a solution of 1,2-bis(chlorodimethylstannyl)-ethane (23.4 g, 59.0 mmol) in 50 mL of THF were added simultaneously under nitrogen over a period of 3 h, to a 1-L flask containing 100 mL of THF with stirring. After 24 h at room temperature, the solution was hydrolyzed with saturated aqueous NH_4Cl solution (150 mL). The organic layer was separated, the aqueous layer was extracted with petroleum ether (2 × 200 mL). The organic layer was washed with water (3 × 400 mL), dried over anhydrous magnesium sulfate, filtered and the solvent rotary evaporated to give a viscous liquid, which was heated at 0.01 Torr to 100°C to afford 6.2 g (16.2 mmol, 27%) of **10**. ^1H NMR (CH_2Cl_2): δ 0.03 (s, 12H, $^2J(^{119}Sn–C–H) = 49.0$ Hz, $-Sn(CH_3)_2$), 1.2 (s, 4H), 0.62–1.17 (m, 4H, $-SnCH_2-$), 1.22–1.87 (m, 4H, $-Sn–C–CH_2-$). Anal. Found: C, 31.66; H, 6.69. $C_{10}H_{24}Sn_2$ calc.: C, 31.47; H, 6.34%.

1,1,3,3-Tetramethyl-1,3-distannacycloheptane (10). Yield 38%. ^1H NMR (CH_2Cl_2): δ 0.10 (s, 12H, $^2J(^{119}Sn–C–H) = 52.0$ Hz, $Sn(CH_3)_2$), −0.2 (s, 2H, $^2J(^{119}SnH) = 50.0$ Hz, $SnCH_2Sn$), 0.61–1.01 (m, 4H, $Sn–CH_2–C$), 1.55–1.95 (m, 4H, $Sn–C–CH_2$). Anal. Found: C, 29.63; H, 6.48. $C_9H_{22}Sn_2$ calc.: C, 29.40; H, 6.04%.

1,1,2,3,3-Pentamethyl-1,3-distannacycloheptane (11). Yield 37%. ^1H NMR ($CDCl_3$): δ 0.10 (s, 12H, $^2J(^{119}Sn–CH_3) = 48.9$ Hz, $-Sn–CH_3$), 0.89 (t, 4H, $Sn–CH_2–C$), 1.8 (t, 4H, $SnCH_2CH_2$), 1.63 (q, 1H, $^2J(^{119}Sn–H) = 50$ Hz,

SnC*H*(CH_3)), 1.45 (d, 3H, $^3J(^{119}Sn-CH) = 75$ Hz, SnCH(CH_3)). Anal. Found: C, 31.29; H, 6.47. $C_{10}H_{24}Sn_2$ calc.: C, 31.47; H, 6.34%.

1,1,2,2,3,3-Hexamethy-1,3-distannacycloheptane (12). Yield 39%. ^{1}H NMR (CH_2Cl_2): δ 0.08 (s, 12H, $^2J(^{119}SnCH) = 46.5$ Hz, Sn(CH_3)$_2$), 1.49 (s, 6H, $^3J(^{119}SnCCH) = 72.0$ Hz, SnC(CH_3)$_2$), 0.69–1.13 (m, 4H, SnCH_2–C), 1.64–1.94 (m, 4H, SnCCH_2). Anal. Found: C, 33.68; H, 6.97. $C_{11}H_{26}Sn_2$ calc.: C, 33.38; H, 6.64%.

1,1,5,5-Tetramethyl-1,5-distannacyclononane (15). Yield 28%. ^{1}H NMR (CH_2Cl_2): δ 0.03 (s, 12H, $^2J(^{119}SnCH) = 50.0$ Hz, Sn(CH_3)$_2$), 0.73–1.33 (m, 10H, SnCH_2CCSn, SnCCH_2CSn and SnCH_2CCCSn), 1.47–2.08 (m, 4H, SnCCH_2CH_2CSn). Anal. Found: C, 33.98; H, 6.82. $C_{11}H_{26}Sn_2$ calc.: C, 33.39; H, 6.62%.

1,1,6,6-Tetramethyl-1,6-distannacyclodecane (16). Yield 20%. ^{1}H NMR ($CDCl_3$): δ 0.02 (*s*, 12H, $^2J(^{119}SnCH) = 49.3$ Hz, Sn(CH_3)$_2$), 0.69 (t, 8H, –SnCH_2), 1.64 (m, 8H, SnCCH_2). Anal. Found: C, 35.66; H, 6.98. $C_{12}H_{28}Sn_2$ calc.: C, 35.78; H, 6.89%.

1,1,5,5-Tetramethyl-1,5-distannacyclooctane (14). 1,3-Bis-(chlorodimethylstannyl) propane (30.0 g, 73.1 mmol) and 250 mL of THF were transferred into a 1-L, 3-neck flask, fitted with a mechanical stirrer, dry ice cold finger and nitrogen bubbler. Ammonia (0.4 L) was then condensed into the flask. The mixture was stirred rapidly while sodium (6.7 g, 290 mmol) in small pieces was added over a period of 35 min. The mixture was stirred 25 min longer, resulting in a pale yellow solution. 1,3-Dichloropropane (8.26 g, 73.1 mmol) was added slowly by a syringe through a septum while stirring. Ammonia was then allowed to evaporate, and the resulting mixture was extracted with 150 mL of petroleum ether and 350 mL of water. The organic layer was washed with water (3 × 350 mL), dried over anhydrous magnesium sulfate, filtered, and the solvent rotary evaporated to give a viscous liquid which was heated at 0.01 Torr to 100°C to afford 3.0 g (11%) of **14**. ^{1}H NMR ($CDCl_3$): δ 0.01 (s, 12H, $^2J(^{119}SnCH) = 50.0$ Hz, Sn(CH_3)), 1.08 (t, 3H, SnCH_2CCSn), 2.14 (quintet, 4H, SnCCH_2CCH_2Sn). Anal. Found: C, 31.96; H, 6.55. $C_{10}H_{24}Sn_2$ calc.: C, 31.48; H, 6.34%.

Preparation of bis-chlorodistannacycloalkanes

Bis-chlorodistannacycloalkanes were prepared by the reaction of mercuric chloride and the corresponding distannacycloalkane in acetone. A typical procedure follows.

1,3-Dichloro-1,2,2,3-tetramethyl-1,3-distannacycloheptane (12Cl). Into a 3-neck, 50-mL flask equipped with a magnetic stirrer and cooled in an ice bath were placed 1.6 g (4.1 mmol) of 1,1,2,2,3,3-hexamethyl-1,3-distannacycloheptane (**5**) and 7.0 mL of acetone. To this was added 2.2 g (8.2 mmol) of mercuric chloride. The reaction mixture was stirred at the bath temperature for 0.5 h, then at room temperature for 1 h. The by-product methylmercuric chloride was removed at 0.01 Torr and 85°C. The residue in the flask was dissolved in hot hexanes, cooled, then filtered. The hexanes were evaporated under reduced pressure to afford 1.1 g (62%) of the product as a colorless oil. ^{1}H NMR (CH_2Cl_2): δ 0.57 (s, 6H, $^2J(^{119}SnCH) = 51.0$ Hz, SnCH_3), 1.62 (s, 6H, $^3J(^{119}SnCCH) = 89.0$ Hz, Sn–C–CH_3), 2.0–1.23 (m, 8H, SnCH_2CCCSn, and SnCCH_2CCSn). Anal. Found: C, 24.55; H, 4.38. $C_9H_{20}Cl_2Sn_2$ calc.: C, 24.77, H, 4.60%.

1,3-Dichloro-1,2,3-trimethyl-1,3-distannacycloheptane (11Cl). Yield 62%; colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.62 (s, 6H, $^2J(^{119}Sn-CH_3) = 53.0$ Hz, $Sn(CH_3)$), 1.62 (d, 3H, $SnCH(CH_3)$), 1.98–1.3 (m, 9H, ($SnCH(CH_3)$, $SnCH_2CCCSn$, and $SnCCH_2CCSn$). Anal. Found: C, 22.29; H, 4.49. $C_8H_{18}Cl_2Sn_2$ calc.: C, 22.74; H, 4.29%.

1,4-Dichloro-1,4-dimethyl-1,4-distannacyclooctane (13Cl). Crystallized from methylene chloride and hexanes in 70% yield; m.p. 106–109°C. ^{1}H NMR ($CHCl_3$): δ 0.63 (s, 6H, $^2J(^{119}SnCH) = 51.7$ Hz, $SnCH_3$), 1.82 (s, 4H, $SnCH_2CSn$), 1.49 (m, 4H, $SnCH_2CCCSn$), 1.93 (m, 4H, $SnCCH_2CCSn$). Anal. Found: C, 23.19; H, 4.07. $C_8H_{18}Cl_2Sn_2$ calc.: C, 22.74; H, 4.29%.

1,5-Dichloro-1,5-dimethyl-1,5-distannacyclooctane (14Cl). Yield 91%; m.p. 37–140°C. ^{1}H NMR ($CDCl_3$): δ 0.6 (s, 6H, $^2J(^{119}SnCH) = 55.4$ Hz, $SnCH_3$), 1.5 (t, 8H, $Sn-CH_2CCSn$), 2.35 quintet, 4H, $SnCCH_2CSn$). Anal. Found: C, 22.91; H, 4.32. $C_8H_{18}Cl_2Sn_2$ calc.: C, 22.74; H, 4.29%.

1,5-Dichloro-1,5-dimethyl-1,5-distannacyclononane (15Cl). Crystallized from carbon tetrachloride in 87% yield; m.p. 135–137°C. ^{1}H NMR (CH_2Cl_2): δ 0.63 (s, 6H, $^2J(^{119}SnCH) = 52.0$ Hz, $SnCH_3(Cl)$), 1.11–2.13 (m, 14H, $Sn(CH_2)_3Sn(CH_2)_4Sn$). Anal. Found: C, 24.63; H, 4.72. $C_9H_{20}Cl_2Sn_2$ calc.: C, 24.76; H, 4.62%.

1,6-Dichloro-1,6-dimethyl-1,6-distannacyclodecane (16Cl). Crystallized from methylene chloride and hexane to give 1.2 g (82%) of product; m.p. 180–182°C. ^{1}H NMR (CH_2Cl_2): δ 0.62 (2, 6H, $^2J(^{119}SnCH) = 52.4$ Hz, $SnCH_3(Cl)$), 1.56 (t, 8H, $SnCH_2CCCSn$), 1.87 (t, 8H, $SnCH_2CCCSn$). Anal. Found: C, 26.90; H, 5.01. $C_{10}H_{22}Cl_2Sn_2$ calc.: C, 26.66; H, 4.92%.

DMSO complex of 16Cl (16Cl · 2DMSO). 1,6-Dichloro-1,6-dimethyl-1,6-distannacyclodecane (0.4931 g, 1.1 mmol) and dimethylsulfoxide (0.1711 g, 2.2 mmol) were placed in a 50-mL Erlenmeyer flask. To this was added 0.3 mL of dichloromethane and the mixture was then warmed to allow dichloromethane to evaporate; the remaining colorless solid was crystallized from carbon tetrachloride to give 0.5 g (77%) of colorless crystals; m.p. 109–111°C. ^{1}H NMR ($CDCl_3$): δ 0.62 (s, 6H, $^2J(^{119}SnCH) = 62.0$ Hz, $SnCH_3$), 1.52 (t, 8H, $SnCH_2CH_2$), 1.8 (t, 8H, $SnCH_2CH_2$), 2.64 (s, 12H, Me_2SO). Anal. Found: C, 27.68; H, 5.79. $C_{12}H_{36}Cl_2O_2S_2Sn_2$ calc.: C, 27.71; H, 5.65%.

1,1,5,5-Tetrachloro-1,5-distannacyclooctane (14Cl2). Into a 50 mL, 3-neck flask equipped with a magnetic stirrer, reflux condenser and cooled in an ice bath were placed 0.91 g (2.4 mmol) of 1,1,5,5-tetramethyl-1,5-distannacyclooctane and 15 mL of dry acetone under nitrogen. To this was added 2.59 g (9.5 mmol) of mercuric chloride. The reaction mixture was stirred at the bath temperature for 10 min, then warmed to room temperature, and refluxed for 48 h until the first formed bis-monochloride had completely disappeared. Acetone was removed under reduced pressure. Methylmercuric chloride was removed at 0.01 Torr and 65°C. The product, a colorless solid proved to be hygroscopic. Water was then removed by heating at 82°C and < 0.002 Torr for 24 h. This afforded 0.6 g (54%) of product; m.p. 286–289°C. H NMR (CD_3CN): δ 2.16 (8H, t, $SnCH_2$), 2.71 (4H, quintet, $SnCH_2CH_2$). Anal. Found: C, 15.82; H, 2.81. $C_6H_{12}Cl_4Sn_2$ calc.: C, 15.55; H, 2.61%.

Reaction of 1,1,5,5-tetramethyl-1,5-distannacyclononane (15) with 4 mol of tetrachlorostannane. Into a 3-neck, 50-mL flask equipped with a magnetic stirrer,

reflux condenser and cooled in an ice bath, were placed 1.264 g (3.2 mmol) of 1,1,5,5-tetramethyl-1,5-distannacyclononane and 10.0 mL of chloroform. To this was added by a syringe 1.52 mL (3.3878 g, 13.0 mmol) of tetrachlorostannane. The flask was warmed to room temperature, and refluxed for 96 h. The disappearance of the bis-monochloride derivative was monitored by ^{1}H NMR. After the reaction was completed, the solvent was removed on the rotary evaporator. The byproduct trichloromethylstannane was removed at 0.01 Torr and 100°C. The crude product was crystallized from methylene chloride to give the acyclic product (**22**). The acyclic (**22**) was recrystallized from methylene chloride and hexanes to give 0.5 g (22%) of colorless crystals; m.p. (dec.) 137–140°C. Anal. Found: C, 12.96; H, 2.27. $C_8H_{17}Cl_7Sn_3$ calc.: C, 13.39; H, 2.39%.

The filtrate from the crude product was rotary evaporated to give crude (**15Cl2**) which was recrystallized from carbon tetrachloride to give 0.5 g (33%); m.p. 191–193°C. Anal. Found: C, 17.86; H, 2.93. $C_7H_{14}Cl_4Sn_2$ calc.: C, 17.61; H, 2.95%.

Reaction of 1,1,5,5-tetramethyl-1,5-distannacyclononane (15) with 4 mol mercuric chloride. Into a 50-mL, 3-neck flask equipped with a magnetic stirrer, reflux condenser and cooled in an ice bath, were placed 1.24 g (3.1 mmol) of 1,1,5,5,-tetramethyl-1,5-distannacyclononane and 10 mL of acetone. To this was added 3.80 g (12.5 mmol) of mercuric chloride. The flask was warmed to room temperature, and then refluxed for 96 h. The disappearance of the bis-monochloride derivative was monitored by ^{1}H NMR. After the reaction was completed, the solvent was removed on a rotary evaporator. Methylmercuric chloride was removed by heating at 75°C and 0.01 Torr. The residue was crystallized from dichloromethane to give 1.2 g (53%) of the acyclic product (**20**); m.p. 96–99°C. Anal. Found: C, 13.34; H, 2.36. $C_8H_{17}Cl_5HgSn_2$ calc.: C, 13.19; H, 2.35%.

The filtrate was rotary evaporated and the residue was recrystallized from carbon tetrachloride to give 0.3 g (20%) of the cyclic product (**15Cl2**); m.p. 191–193°C. ^{1}H NMR ($CDCl_3$): δ 2.15–1.96 (m, 12H, $SnCH_2CCH_2$ and $Sn(CH_2CH_2CH_2CH_2Sn)$, 2.55 (quintet, 2H, $SnCCH_2CSn$).

Reaction of 1,1,5,5-tetramethyl-1,5,-distannacyclononane (15) with 4 mol of mercuric chloride in THF. The procedure was the same as that described above yielding the acyclic chloride (**20**) as the only product which was crystallized from dichloromethane to yield 65%; m.p. 96–99°C.

1,1,6,6-Tetrachloro-1,6-distannacyclodecane (16Cl2). Into a 3-neck, 50-mL flask equipped with a magnetic stirrer, reflux condenser and cooled in an ice bath, were placed 1.0769 g (2.6 mmol) of 1,1,6,6-tetramethyl-1,6-distannaycyclodecane and 14 mL of acetone. To the reaction flask was added 2.8456 g (10.0 mmol) of mercuric chloride. The reaction mixture was stirred at the bath temperature for 30 min, then warmed to room temperature and was refluxed for 36 h. After the reaction was completed, the solvent was removed on the rotary evaporator. The byproduct methylmercuric chloride was removed at 0.01 Torr and 85°C. The crude product was crystallized from methylene chloride to give 1.0 g (78%) of product; m.p. 236–240°C. ^{1}H NMR (CD_3CN): δ 7.0 (m, 16 H, $Sn-CH_2CH_2$). Anal. Found: C, 19.85; H, 3.16. $C_8H_{16}Sn_2Cl_4$ calc.: C, 19.55; H, 3.28%.

Alkyltin mesylates

Trimethyl(methanesulfonyloxy)stannane (17Ms). Into a 3-neck, 50-mL flask

equipped with a magnetic stirrer, were placed 1.6029 g (8.0 mmol) of chlorotrimethylstannane and 25 mL of methylene chloride. To this was added (1.6323 g, 8.0 mmol) of silver methanesulfonate. The reaction mixture was stirred at room temperature for 1 h, then filtered. The solvent was removed at reduced pressure and the residue product was heated to 70°C at 0.01 mmHg to afford 1.9 g (95%) of product as a colorless solid; m.p. 157–159°C. ^{1}H NMR ($CDCl_3$): δ 0.72 (s, 9H, $^2J(^{119}Sn–C–H) = 68.0$ Hz, $Sn(CH_3)_3$), 2.74 (s, 3H, $SnOSO_2CH_3$).

Tributyl(methanesulfonyloxy)stannane (19Ms). The above procedure was used; yield 90% of product as a viscous oil. ^{1}H NMR ($CDCl_3$): δ 1.34 (m, 12H, $SnCH_2CH_2CC$), 1.66 (m, 2H, $SnCCCH_2CH_3$), 0.90 (t, 9H, $SnCCCCH_3$), 2.73 (s, 3H, $SnSO_3CH_3$). Anal. Found: C, 40.40; H, 7.82. $C_{13}H_{30}O_3SSn$ calc.: C, 40.54; H, 7.85%.

Bis[dimethyl(methanesulfonyloxy)stannyl]methane (2Ms). The same procedure as above was used with **2Cl** yielding 85% of product as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.79 (s, 12H, $^2J(^{119}SnCH) = 67.0$ Hz, $SnCH_2Sn$), 2.81 (s, 6H, $SnOSO_2CH_3$). Anal. Found: C, 16.20; H, 4.27. $C_7H_{20}O_6S_2Sn_2$ calc.: C, 16.76; H, 4.02%.

1,2-Bis[dimethyl(methanesulfonyloxy)stannyl]ethane (5Ms). The same procedure using **5Cl** (0.49 g, 1.3 mmol) and silver methanesulfonate (0.5095 g, 2.5 mmol) in dichloromethane (15 mL) to give 0.55 g (79%) of product as a colorless solid; m.p. 82–86°C. ^{1}H NMR ($CDCl_3$): δ 0.67 (s, 12H, $^2J(^{119}SnCH) = 64.0$ Hz, $Sn–CH_3$), 1.88 (s, 4H, $^2J(^{119}SnCH) = 61.04$ Hz, $^3J(^{119}SnCH) = 125.0$ Hz, $SnCH_2Sn$). Anal. Found: C, 18.48; H, 4.33. $C_8H_{22}O_6S_2Sn_2$ calc.: C, 18.63; H, 4.30%.

1,1-Bis[dimethyl(methanesulfonyloxy)stannyl]ethane (3Ms). The same procedure was used with **3Cl** to afford 83% of product as a white solid; m.p. 76–78°C. ^{1}H NMR ($CDCl_3$): δ 0.75 (s, 12H, $^2J(^{119}SnH) = 65.0$ Hz, $SnCH_3$), 1.56 (q, 1H, $SnCH(CH_3)$), 1.93 (d, 3H, $^3J(^{119}SnCH) = 100.0$, $SnCH(CH_3)$), 2.82 (s, 6H, $SnSO_3CH_3$). Anal. Found: C, 18.76; H, 4.49. $C_8H_{22}O_6S_2Sn_2$ calc.: C, 18.63; H, 4.30%.

2,2-Bis[dimethyl(methanesulfonyloxy)]propane (4Ms). The above procedure with **4Cl** was used to afford 81% of product as a colorless solid; m.p. 159–164°C. ^{1}H NMR ($CDCl_3$): δ 0.81 (s, 12H, $^2J(^{119}SnCH) = 62.0$ Hz, $SnCH_3$), 1.81 (s, 6H, $^3J(^{119}SnC–CH) = 99.6$ $SnCCH_3$), 2.82 9s, 6H, $SnSO_3CH_3$). Anal. Found: C, 20.14; H, 4.86. $C_9H_{24}O_6S_2Sn_2$ calc.: C, 20.40; H, 4.57%.

1,3-Bis[dimethyl(methanesulfonyloxy)stannyl]propane (6Ms). The same procedure with **6Cl** afforded 83% of product as a colorless gum. ^{1}H NMR ($CDCl_3$): δ 0.70 (s, 12H, $^2J(^{119}SnCH) = 63.0$ Hz, $–Sn–CH_3$), 1.52 (t, 4H, $SnCH_3$), 1.52 (t, 4H, $SnCH_2CCH_3$), 2.29 (quintet, 2H, $SnCCH_2CH_3$), 2.78 (s, 6H, $SnSO_3CH_3$). Anal. Found: C, 20.53; H, 4.85. $C_9H_{24}O_6S_2Sn_2$ calc.: C, 20.40; H, 4.57%.

1,4-Bis[dimethyl(methanesulfonyloxy)stannyl]butane (7Ms). The above procedure was followed with 1.26 g (2.9 mmol) of **7Cl** and 1.20 g (5.9 mmol) of silver methanesulfonate in 15 mL of dry methanol. Workup as above provided 1.5 g (94%) of **7Ms** as a colorless gum. ^{1}H NMR ($CDCl_3$): δ 0.69 (s, 12H, $^2J(^{119}SnCH) = 62.5$ Hz, $SnCH_3$), 1.5 (t(br), 4H, $SnCH_2–CH2–$), 1.92 (t(br), 4H, $SnCH_2CH_2$), 2.77 (s, 6H, $SnSO_3CH_3$). Anal. Found: C, 22.58; H, 4.52. $C_{10}H_{26}O_6S_2Sn_2$ calc.: C, 22.09; H, 4.82%.

Dimethylbis(methanesulfonyloxy)stannane (18Ms2). Into a 50-mL, 3-neck flask equipped with a magnetic stirrer and a reflux condenser were placed 1.15 g (11.95

mmol) of methanesulfonic acid and 5 mL of dichloromethane. **2Ms** (1.3 g, 5.9 mmol) dissolved in dichloromethane (10 mL) was added dropwise to the reaction flask while stirring. The reaction mixture was refluxed for 15 h. The disappearance of the starting material from the supernatant was monitored by PMR. Workup as above gave a colorless solid 2.0 g (99%) of product; m.p. (dec.) 315–317°C. ^{1}H NMR (D_2O): δ 0.71 (s, 6h, $^2J(^{119}SnCH) = 108.2$ Hz, $SnCH_3$), 2.56 (s, 6H, $SnSO_3CH_3$).

*1,2,3-Trimethyl-1,3-bis(methanesulfonyloxy)-1,3-distannacycloheptane (**11Ms**).* Into an oven-dried, 50-mL, 3-neck flask under nitrogen were placed dry methanol (20 mL) and **11Cl** (0.77 g, 1.8 mmol). Silver methanesulfonate (0.74 g, 3.7 mmol) was added quickly and the mixture stirred for 1 h at room temperature during which time silver chloride precipitates. The reaction mixture was filtered quickly through a Buchner funnel. Methanol was removed under reduced pressure and the residue in the flask was heated to 70°C at 0.01 mmHg to afford 0.8 g (82%) of product as a colorless solid; m.p. (dec.) 220°C. ^{1}H NMR ($CDCl_3$): δ 0.67 (s, 6H, $^2J(^{119}SnCH) = 65.4$ Hz, $SnCH_3$), 1.6–1.37 (m, 8H, $SnCH_2CH_2$), 1.92 (d, 3H, $SnCHCH_3$), 2.1 (q(br), 1 H, $SnCH(CH_3)$). Anal. Found: C, 21.92; H, 4.23. $C_{10}H_{24}O_6S_2Sn_2$ calc.: C, 22.17; H, 4.46%.

*1,2,2,3-Tetramethyl-1,3-bis(methanesulfonyloxy)-1,3-distannacycloheptane (**12Ms**).* The same procedure was used with **12Cl** yielding 95% of a colorless solid; m.p. (dec.) 170°C. ^{1}H NMR ($CDCl_3$): δ 0.7 (s, 6H, $^2J(^{119}SnCH) = 60.6$ Hz, $SnCH_3$), 1.64 (t(br), 4H, $SnCH_2CCCH_2$), 2.09 (t(br), 4H, $SnCCH_2CH_2C$), 1.87 (s, 6H, $^3J(^{119}SnCCH) = 91.2$ Hz, $SnCCH_3$), 2.86 (s, 6H, $SnSO_3CH_3$). Anal. Found: C, 23.39; H, 4.60. $C_{11}H_{26}O_6S_2Sn_2$ calc.: C, 23.77; H, 4.71%.

*1,4-Dimethyl-1,4-bis(methanesulfonyloxy)-1,4-distannacyclooctane (**13Ms**).* The same procedure as that described for the preparation of **11Ms** was used to afford 74% of product as a colorless gum. ^{1}H NMR ($CDCl_3$): δ 0.64 (s, 6H, $^2J(^{119}SnCH) = 60.0$ Hz, $SnCH_3$), 1.57 (4H, s, $SnCH_2CH_2Sn$), 2.01 (m, 8H, $SnCH_2CH_2CH_2CH_2Sn$). Anal. Found: C, 21.92; H, 4.43. $C_{10}H_{24}O_6S_2Sn_2$ calc.: C, 22.17; H, 4.46%.

*1,5-Dimethyl-1,5-bis(methanesulfonyloxy)-1,5-distannacyclooctane (**14Ms**).* The preparation of **14Ms** was carried out in methanol with ***14Cl*** using a procedure similar to that described for the preparation of the above mesylates. This afforded 80% of product as a colorless solid; m.p. 155–159°C. ^{1}H NMR ($CDCl_3$): δ 0.57 (s, 6H, $^2J(^{119}SnCH) = 62.0$ Hz, $SnCH_3$), 1.7 (t(br), 8H, $SnCH_2CH_2CH_2CH_2$), 2.47 (quintet (br), 4H, $SnCH_2CH_2Sn$), 2.79 (6H, s, $SnSO_3CH_3$). Anal. Found: C, 21.79; H, 4.62. $C_{10}H_{24}O_6S_2Sn_2$ calc.: C, 22.17; H, 4.46%.

*1,5-Dimethyl-1,5-bis(methanesulfonyloxy)-1,5-distannacyclononane (**15Ms**).* The procedure using **15Cl** yielded 86% of **15Ms** as a colorless solid; m.p. (dec.) 275–290°C. ^{1}H NMR (D_2O): δ 0.35 (s, 6H, $^2J(^{119}SnCH) = 63.5$, $SnCH_3$), 1.9–1.17 (m, 14H), 2.6 (s, 6H, $SnOSO_2CH_3$). Anal. Found: C, 23.64; H, 4.87. $C_{11}H_{26}O_6S_2Sn_2$ calc.: C, 23.77; H, 4.71%.

*1,6-Dimethyl-1,6-bismethanesulfonyloxy-1,6-distannacyclodecane (**16Ms**).* Into a 3-neck, 50-mL flask equipped with a magnetic stirrer, and a reflux condenser were placed 0.3 g (3.2 mmol) of methanesulfonic acid and 5.0 mL of methylene chloride. To this was added 1,6-dimethyl-1,6-dichloro-1,6-distannacyclodecane (0.7 g, 1.6 mmol) in 10.0 mL of methylene chloride. The reaction mixture was refluxed for 12 h. The disappearance of the starting material from the supernatant was monitored by PMR. After the completion of the reaction, the solvent was de-

canted, the residue in the flask was washed with methylene chloride (2 × 10 mL), then heated to 70°C at 0.01 mmHg for 1 h to afford 0.9 g (96%) of product; m.p. (dec.) 200°C. ^{1}H NMR (D_2O): δ 0.31 (s, 12H, $^2J(^{119}SnCH) = 62.4$ Hz, 6H, $SnCH_3$), 1.27 (t, 8H, $SnCH_2CCCH_2$), 1.67 (t, 8H, $SnCCH_2C$), 2.6 (s, 6H, $SnOSO_2CH_3$). Anal. Found: C, 25.23; H, 5.05. $C_{12}H_{28}O_6S_2Sn_2$ calc.: C, 25.29; H, 4.95%.

Alkyltin trifluoromethanesulfonates

Trimethyl(trifluoromethanesulfonyloxy)stannane (17Tf). Into a 3-neck, 50-mL flask equipped with a magnetic stirrer, were placed 0.83 g (4.2 mmol) of chlorotrimethylstannane and 20 mL of methylene chloride. To this was added (1.07 g, 4.2 mmol) of silver trifluromethanesulfonate. The reaction mixture was stirred at room temperature for 1 h, then filtered. Methylene chloride was removed under reduced pressure and an inert atmosphere. The residue was heated to 65°C and 0.01 mmHg to afford 0.7 g (88%) of a colorless solid; m.p. 74–76°C. ^{1}H NMR ($CDCl_3$): δ 0.8 (s, 9H, $^2J(^{119}SnCH) = 65.0$ Hz, $SnCH_3$).

Tri-n-butyl(trifluoromethanesulfonoyloxy)stannane (19Tf). Using the above procedure provided 88% of a colorless mushy product. ^{1}H NMR ($CDCl_3$): δ 0.92 (t, 9H, $SnCCCCH_3$), 1.3–1.4 (m, 12H, $SnCH_2CH_2CCH_3$), 1.64 (m, 6H, $SnCCCH_2CH_3$).

Bis-[dimethyl(trifluoromethanesulfonyloxy)stannyl]methane (2Tf). 1,1-Bis(chlorodimethylstannyl)methane (0.4231 g, 1.1 mmol) and dichloromethane (10 mL) were placed in a flame dried, 3-neck flask equipped with a magnetic stirrer under nitrogen. To the flask was added 0.57 g (2.2 mmol) of silver trifluoromethane sulfonate. The mixture was stirred for 1 h at room temperature. Silver chloride was removed quickly by vacuum filtration. The solvent was removed under reduced pressure and inert atmosphere. The residue in the flask was heated to 60°C at 0.01 mm to give 0.6 g (90%) of product as a colorless solid; m.p. 48–50°C. ^{1}H NMR ($CDCl_3$): δ 0.98 (s, 12H, $^2J(^{119}SnCH) = 66.0$ Hz $SnCH_3$), 1.16 (s, 2H, $^2J(^{119}SnCH) = 65.0$ Hz, $SnCH_2Sn$). Anal. Found: C, 13.65; H, 2.75. $C_7H_{14}F_6O_6S_2Sn_2$ calc.: C, 13.79; H, 2.30%.

1,2-Bis[dimethyl(trifluoromethanesulfonyloxy)stannyl]ethane (5Tf). The same procedure using 0.45 g (1.1 mmol) of **15Cl** and 0.59 g (2.3 mmol) of silver trifluoromethanesulfonate in 15 mL of nitromethane provided 0.52 g (74%) of product as a colorless solid; m.p. 158–160°C. ^{1}H NMR (CD_3CN): δ 0.53 (s, 12H, $^2J(^{119}SnCH) = 63.5$ Hz, $SnCH_3$), 1.62 (s, 4 H, $SnCH_2CH_2Sn$). Anal. Found: C, 15.79; H, 2.75. $C_8H_{16}F_6O_6S_2Sn_2$ calc.: C, 15.41; H, 2.58%.

1,1-Bis[dimethyl(trifluoromethanesulfonyloxy)stannyl]ethane (3Tf). Following the procedure for **5Tf**, 0.41 g (1.04 mmol) of 1,1-bis(chlorodimethylstannyl)ethane reacted with silver trifluoromethanesulfonate (0.54 g, 2.08 mmol) to give 0.5 g (84%) of product as a brownish gum. ^{1}H NMR ($CDCl_3$): δ 0.85 (s, 12H, $^2J(^{119}SnCH) = 62.5$ Hz, $SnCH_3$), 1.50 (q, 1H, $SnCH(CH_3)$), 1.93 (d, 3H, $SnCHCH_3$). Anal. Found: C, 15.98; H, 2.75. $C_8H_{16}F_6O_6S_2Sn_2$ calc.: C, 15.49; H, 2.58%.

2,2-Bis[dimethyl(trifluoromethanesulfonyloxy)stannyl]propane (4Tf). Into a 50-mL, 3-neck flask equipped with a magnetic stirrer, were placed 0.88 g (2.1 mmol) of 2,2-bis(chlorodimethylstannyl)propane and 20 mL of t-butyl alcohol. To this was added (1.09 g, 4.3 mmol) of silver trifluromethanesulfonate. The reaction mixture

was stirred at room temperature for 1 h, then filtered rapidly. t-Butyl alcohol was first removed under reduced pressure and an inert atmosphere, then the product residue was heated to 90°C at 0.01 mmHg to give 1.1 g (85%) of a brownish solid; m.p. 118–122°C. ^{1}H NMR (CD_3CN): δ 0.76 (s, 12H, $^2J(^{119}SnCH) = 63.5$ Hz, $SnCH_3$), 1.75 (s, 6H, $^3J(^{119}Sn(CH_3)_2) = 97.8$ Hz). Anal. Found: C, 17.23; H, 2.82. $C_9H_{18}F_6O_6S_2Sn_2$ calc.: C, 16.95; H, 2.84%.

1,3-Bis[dimethyl(trifluoromethanesulfonyloxy)stannyl]propane (6Tf). The same procedure as that described above was used with 1,3-bis[chloro(dimethyl)stannyl] propane yielding 87% of **6Tf** as a colorless oil. ^{1}H NMR (CD_3CN): δ 0.64 (s, 12H, $^2J(^{119}SnCH) = 67.0$ Hz, $SnCH_3$), 1.41 (t, 4H, $SnCH_2$), 1.93 (quintet, 2H, $SnCCH_2CH_3$). Anal. Found: C, 17.02; H, 2.84. $C_9H_{18}F_6O_6S_2Sn_2$ calc.: C, 16.95; H, 2.84%.

1,5-Bis[dimethyl(trifluoromethanesulfonyloxy)stannyl]-pentane (8Tf). To a solution of **8Cl** (0.35 g, 0.80 mmol) in nitromethane (15 mL), silver trifluoromethanesulfonate (0.41 g, 1.6 mmol) was added under nitrogen. The reaction mixture was stirred at room temperature and worked up as above providing 0.49 g (92%) of product as a colorless viscous oil. ^{1}H NMR (CD_3CN): δ 0.65 (s, 12H, $^2J(^{119}SnCH) = 67.4$ Hz, $SnCH_3$), 1.37 (t, 8H, $SnCH_2CCCCH_2Sn$), 1.44 (quintet, 8H, $SnCCH_2CCH_2C$), 1.73 (quintet, 4H, $SnCCCH_2CCSn$). Anal. Found: C, 19.30; H, 3.55. $C_{11}H_{22}F_6O_6S_2Sn_2$ calc.: C, 19.85; H, 3.33%.

1,6-Bis[dimethyl(trifluoromethanesulfonyloxy)stannyl]hexane (9Tf). The above procedure with **9Cl** provided 87% of product as a colorless oil. ^{1}H NMR (CD_3CN): δ 0.65 (s, 12H, $^2J(^{119}SnCH) = 65.9$ Hz, $SnCH_3$), 1.5–1.3 (m, 16H, $SnCH_2CCH_2CH_2CCH_2Sn$), 1.7 (quintet, 8H, $SnCCH_2CCCH_2C$). Anal. Found: C, 21.21; H, 3.82. $C_{12}H_{24}F_6O_6S_2Sn_2$ calc.: C, 21.26; H, 3.57%.

Dimethylbis(trifluoromethanesulfonyloxy)stannane (18Tf). Into a 100-mL, 3-neck flask equipped with a magnetic stirrer were placed 0.42 g (1.0 mmol) of dichlorodimethylstannane and 15 mL of diethyl ether. To this was added 0.99 g (3.8 mmol) of silver trifluoromethanesulfonate. The reaction mixture was stirred for 1 h at room temperature and worked up as above to afford 0.7 g (82%) of product as a colorless solid; m.p. 330–335°C. ^{1}H NMR (CD_3CN): δ 1.4 (s, 6H, $^2J(^{119}SnCH) = 107.0$ Hz, $SnCH_3$).

Bis[methyldi(trifluoromethanesulfonyloxy)stannyl]methane (2Tf). Into a 50-mL, 3-neck flask equipped with a stirring bar were placed bis[dichloro(methyl)stannyl]-methane (0.31 g, 0.74 mmol) and dry nitromethane (15 mL) and 0.76 g (2.9 mmol) silver trifluoromethanesulfonate. The solution was stirred for 3 h at room temperature and the product worked up as usual yielding 0.5 g (78%) of product as a colorless solid; m.p. (dec.) 210°C. ^{1}H NMR (CD_3CN): δ 1.06 (s, 6H, $^2J(^{119}SnCH) = 117.7$ Hz, $SnCH_2Sn$). Anal. Found: C, 9.21; H, 1.02. $C_7H_8O_{12}S_4F_{12}Sn_2$ calc.: C, 9.58; H, 0.92%.

1,2-Bis[methylbis(trifluoromethanesulfonyloxy)stannyl]ethane (5Tf2). Following the above procedure, 0.35 g (0.80 mmol) of **5Cl2** reacted with silver trifluoromethanesulfonate (0.83 g, 3.2 mmol) to give 0.5 g (70%) of product as a slightly brownish solid; m.p. (dec.) 380°C. ^{1}H NMR (CD_3CN): δ 1.38 (s, 6H, $^2J(^{119}SnCH) = 102.0$ Hz, $SNCH_3$), 2.44 (s, 4H, CH_2CH_2Sn). Anal. Found: C, 10.53; H, 1.29. $C_8H_{10}O_{12}S_4F_{12}Sn_2$ calc.: C, 10.77; H, 1.13%.

Cyclic alkyltin trifluoromethanesulfonates

A typical procedure is that used for the preparation of 1,5-dimethyl-1,5-bis(trifluoromethanesulfonyloxy)-1,5-distannacyclononane (**15Tf**).

Into a 100-mL, 3-neck flask equipped with a magnetic stirrer were placed 0.45 g (1.04 mmol) of 1,5-dimethyl-1,5-dichloro-1,5-distannacyclononane and 50 mL of t-butyl alcohol. To this was added 0.53 g (2.07 mmol) of silver trifluoromethanesulfonate. The reaction mixture was stirred at room temperature for 2 h, then filtered rapidly. t-Butyl alcohol was removed under reduced pressure and an inert atmosphere. The residual product was heated to 75°C at 0.01 mm to give a brownish solid; m.p. 175°C. ^{1}H NMR (CD_3CN): δ 0.59 (s, 6H, $^2J(^{119}SnCH) = 61.0$ Hz $SnCH_3$), 1.43 (t(br), 4H, $SnCH_2CCH_2Sn$), 1.56 (t, 4H, $SnCH_2CCCH_2Sn$), 2.18–1.83 (9m, 6H, $SnCCH_2CSn$, $SnCCH_2CH_2CSn$). Anal. Found: C, 20.49; H, 2.83. $C_{11}H_{20}F_6O_6S_2Sn_2$ calc.: C, 19.91; H, 3.04%.

*1,6-Dimethyl-1,6-bis(trifluoromethanesulfonyloxy)-1,6-distannacyclodecane (**16Tf**).* Using the above procedure with 1,6-dichloro-1,6-dimethyl-1,6-distannacyclodecane afforded 85% of product as a colorless solid; m.p. (dec.) 178°C. ^{1}H NMR (CD_3CN): δ 0.65 (s, 6H, $^2J(^{119}SnCH) = 63.5$ Hz, $SnCH_3$), 1.59 (t, 8H, $SnCH_2CCCH_2Sn$), 1.93 (t, 8H, $SnCCH_2CH_2C$–). Anal. Found: C, 20.97; H, 3.31. $C_{12}H_{22}F_6O_6S_2Sn_2$ calc.: C, 21.26; H, 3.27%.

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