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3,3-Bis(halomethylstannyl)propyl Ethyl Sulfoxides. The Nature of Intramolecular Coordination in the Crystals and in Solution

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The preparations of 3,3-bis(chlorodimethylstannyl)propyl ethyl sulfoxide, (Me$_2$ClSn)$_2$CHCH$_2$CH$_2$S(O)Et, and of 3,3-bis(dichloromethylstannyl)propyl ethyl sulfoxide, (MeCl$_2$Sn)$_2$CHCH$_2$CH$_2$S(O)Et, are described. Structures of these compounds and of their bromo analogues have been determined by single-crystal X-ray diffraction. (Me$_2$ClSn)$_2$CHCH$_2$CH$_2$S(O)Et, **1**, crystallizes in the triclinic space group $P\bar{1}$ with a = 7.002 (3) Å, b = 9.383 (5) Å, c = 13.771 (7) Å, α = 104.35 (4)°, β = 98.67 (4)°, γ = 90.37 (4)°, V = 865.7 (7) Å^3, and D_{calcd} = 1.867 g cm^{-3} for Z = 2. Full-matrix best-squares refinement of positional and anisotropic temperature parameter converged at a conventional residual of 0.068 for 1306 independent reflections. (MeCl$_2$Sn)$_2$CHCH$_2$CH$_2$S(O)Et, **2**, crystallizes in the triclinic space group $P\bar{1}$ with a = 9.099 (3) Å, b = 9.477 (3) Å, c = 10.476 (4) Å, α = 113.34 (2)°, β = 99.68 (2)°, γ = 91.87 (2)°, V = 812.7 (7) Å^3, and D_{calcd} = 2.155 g cm^{-3} for Z = 2; R = 0.032 for 1842 reflections. (MeBr$_2$Sn)$_2$CHCH$_2$CH$_2$S(O)Et, **3**, crystallizes in the space group $P\bar{1}$ with a = 7.074 (2) Å, b = 9.325 (3) Å, c = 14.070 (6) Å, α = 77.45 (2)°, β = 81.03 (3)°, γ = 88.23 (2)°, V = 894.7 (7) A^3, and D_{calcd} = 2.136 g cm^{-3} for Z = 2; R = 0.078 for 1739 reflections. (MeBr$_2$Sn)$_2$CHCH$_2$CH$_2$S(O)Et, **4**, crystallizes in the monoclinic space group $P2_1/n$ with a = 8.965 (3) Å, b = 17.887 (7) Å^3, c = 11.166 (4) Å, β = 102.29 (2)°, V = 1749.5 (6) Å^3, D_{calc} = 2.677 g cm^{-3}, and Z = 4; R = 0.076 for 1128 reflections. The structures of **1** and **3** consist of discrete binuclear units with nonequivalent Sn atoms bridged symmetrically by a carbon of the propyl ethyl sulfoxide group and unsymmetrically by one or two halide atoms, depending on the degree of halide substitution. On the other hand, **2** and **4** exhibit halide bridging between two adjacent binuclear units to produce a loosely associated bimolecular or tetranuclear unit. The propyl ethyl sulfoxide ligand is coordinated through the sulfoxide oxygen donor to one tin atom in all cases. IR, ^{1}H NMR, ^{13}C NMR, and ^{119}Sn NMR studies, coupled with the structural results, suggest that the oxygen of the sulfoxide group undergoes rapid coordinative exchange between the two tin atoms in each compound in solution.

Interest in organostannanes containing organic functional groups (organofunctional organostannanes) has been increasing because of the potential utility of such compounds as synthetic intermediates and because of the specific properties that might result from the presence of two types of functional groups in the same molecule. These are most likely to appear if the molecule contains a tin atom bearing an electronegative group such as a halogen and another group that is an electron pair donor. An appropriate combination can lead to intermolecular coordination or to a coordination polymer if the groups are so disposed that they cannot participate in intramolecular interaction. Early work on this question has been reviewed by Omae,[1,2] and a number of more recent reports have appeared.[3-11] Intramolecular coordination has generally been established by a combination of NMR, IR, and Mössbauer spectroscopy, along with molecular weight determinations. Use of these probes has led to proposals of cyclic structures for halotins in which the donor atom was the oxygen of a ketone,[3] an ester group,[4-7] an amide,[6] a phosphine oxide,[8] an amine nitrogen,[9,10] or a sulfoxide oxygen.[11] Confirmations of the cyclic structures have been obtained in several examples by X-ray diffraction.[4-6,8,10] In each of these cases the ring formed by intramolecular coordination contains five atoms. Our earlier studies on coordination to the ketone carbonyl oxygen showed that the five-membered ring was more stable than the six-membered ring.[3] We recently reported that a six-membered ring is quite stable in solution in compounds in which a sulfoxide oxygen coordinates to bromostannyl and dibromostannyl Lewis acid centers.[11] These studies have now been extended to include the corresponding chloro analogues; and single-crystal X-ray diffraction determinations of the structures of the four compounds are described here, along with some of their spectral properties in solution.

Table I. Infrared S–O Stretching Frequencies (cm^{-1})

compd	KBr	soln
1	958	960[a]
2	940	955[a]
3	952	966[a]
4	953	964[a]
(Me$_3$Sn)$_2$CHCH$_2$CH$_2$SOEt		1052[b]

[a] 10% in CH$_3$CN. [b] Neat.

Results and Discussion

Preparation and Spectral Properties. In the previous paper we described the preparation of 3,3-bis(trimethylstannyl)propyl ethyl sulfoxide.[11] This has been converted into the chlorostannyl derivatives **1** and **2** by the

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(1) Omae, I. *Rev. Silicon, Germanium, Tin Lead Compd.* **1972**, *1*, 59.

(2) Tzschach, A.; Eichmann, W.; Jurkschat, K. *Organomet. Chem. Rev.* **1981**, *12*, 293.

(3) Kuivila, H. G.; Dixon, J. E.; Maxfield, P. L.; Scarpa, N. M.; Topka, T. M.; Wursthorn, K. R. *J. Organomet. Chem.* **1975**, *86*, 89.

(4) Yoshida, M.; Ueki, T.; Yasuoka, N.; Kasai, N.; Kakudo, M.; Omae, I.; Kikkawa, S.; Watsuda, S. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1113.

(5) Kimura, T.; Ueki, T.; Yasuoka, N.; Kasai, N.; Kakudo, M. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2479.

(6) Harrison, P. G.; King, T. J.; Healy, M. A. *J. Organomet. Chem.* **1979**, *182*, 17.

(7) Haigh, R. M.; Davies, A. G.; Tse, M.-W. *J. Organomet. Chem.* **1979**, *174*, 163.

(8) Weichmann, H.; Mugge, C.; Grand, A.; Robert, J. B. *J. Organomet. Chem.* **1982**, *238*, 343.

(9) van Koten, G.; Noltes, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 5393.

(10) van Koten, G.; Jastrzebski, T. B. H.; Noltes, J. G.; Pontenagel, W. M. G. F.; Kroon, J.; Spek, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 5021.

(11) Kuivila, H. G.; Karol, T. J.; Swami, K. *Organometallics* **1983**, *2*, 909.

(12) Harris, R. K.; Mann, B. R. "NMR and the Periodic Table"; Academic Press: New York, 1978; Chapter 10.

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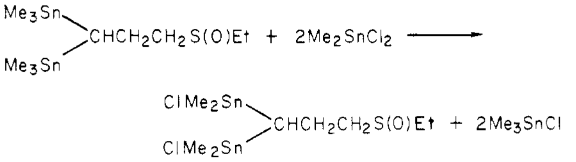
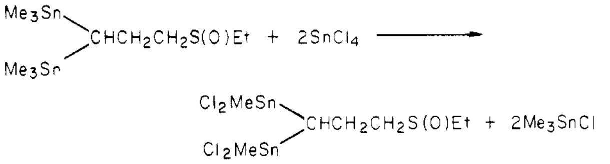
reactions shown in eq 1 and 2. Simple methyl–chlorine exchanges occurred in essentially quantitative yields, 95% being isolated in each case. Molecular weight determinations made in methylene chloride by the isopiestic method indicated both compounds to be substantially monomeric.



$$(Me_3Sn)_2CHCH_2CH_2S(O)Et + 2Me_2SnCl_2 \longrightarrow (ClMe_2Sn)_2CHCH_2CH_2S(O)Et + 2Me_3SnCl \quad (1)$$



$$(Me_3Sn)_2CHCH_2CH_2S(O)Et + 2SnCl_4 \longrightarrow (Cl_2MeSn)_2CHCH_2CH_2S(O)Et + 2Me_3SnCl \quad (2)$$

Preparations of the corresponding bromides **3**, $(Me_2BrSn)_2CHCH_2CH_2S(O)Et$, and **4**, $(MeBr_2Sn)_2CHCH_2CH_2S(O)Et$, using methyl–tin cleavage by bromine were described earlier.[11]

Infrared spectral values for the S–O stretching frequencies in both solid (KBr disk) and solution in acetonitrile are gathered in Table I, along with that for the unhalogenated model compound. In both media it can be seen that the normal band at 1052 cm^{-1} is shifted by about 100 cm^{-1} to lower values. This clearly indicates that the sulfoxide oxygen is coordinated to tin. If the sulfur atom were complexing, the shifts whould be in the opposite direction. Furthermore, the 1052 cm^{-1} band was not present in the spectra, showing that no uncoordinated sulfoxide was present in any of these halostannyls.

^{13}C NMR spectral data are given for **1–4** in Table II. Each shows two kinds of methyl carbons on tin, but their chemical shifts differ from each other by less than 1 ppm. They display different $^1J(^{13}C-^{119}Sn)$ values, but differences are smaller than 40 Hz. Thus very similar environments on the averaged NMR time scale for the tin functions are indicated.

^{119}Sn chemical shift parameters for **1–4** are presented in Table III. The two tin atoms in each compound are in different environments. The chemical shift difference is 47 ppm in the bis(monochloride), while it is 12 ppm in the bis(monobromide). The difference in the bis(dichloride) is 28 ppm, and in the bis(dibromide) it is 10 ppm. Thus the ^{119}Sn NMR is considerably more sensitive than the ^{13}C NMR in revealing the anisochronous nature of the two halomethylstannyl units in these molecules. The signals from the bis(dihalides) appear at higher fields than those in the bis(monohalides) in the ^{119}Sn spectra, but the order is reversed in the ^{13}C signals on the corresponding tin methyls. This effect is particularly dramatic in **1** and **2** in which the values for ^{119}Sn are separated by 47 and 28 ppm, respectively. The values of ^{119}Sn for the trimethyltin halides and dimethyltin dihalides are also shown in Table III and are seen to be at considerably lower fields than those of the corresponding halides of the set **1–4**. On the other hand the values for trimethyltin chloride and dimethyltin dichloride in Me_2SO appear at higher fields than those for **1** and **2**, respectively. These observations, taken together with the infrared spectral data, and the monomeric nature of **1–4**, are indicative of intramolecular bonding between the sulfoxide oxygen and the tin(s). The small differences between the ^{13}C chemical shifts of the methyls on tin as well as the two coupling constants between the methine carbon and the tins suggest that either bridging by the oxygen or rapid exchange between the two tins describe these species in solution as suggested earlier.[11] It was, therefore, of interest to examine the structures of **1–4** in the solid state by X-ray diffraction.

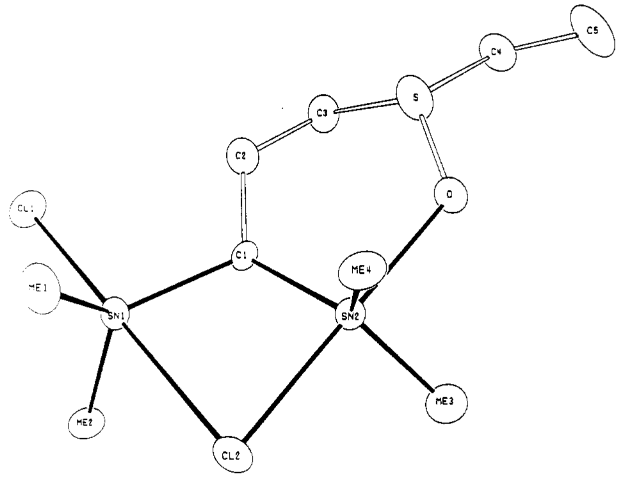


Figure 1. Schematic representation of binuclear 3,3-bis(chlorodimethylstannyl)propyl ethyl sulfoxide $[(ClMe_2Sn)_2CHCH_2CH_2S(O)Et]$, **1**.

Description of the Structures. As illustrated in Figure 1, the structure of $(Me_2ClSn)_2CHCH_2CH_2S(O)Et$ (**1**) consists of discrete binuclear units, with nonequivalent Sn atoms bridged symmetrically by C(1) of the propyl ethyl sulfoxide group and unsymmetrically by Cl(2). Sn(2) displays fairly regular trigonal-bipyramidal geometry, with the oxygen of the chelating sulfoxide group and Cl(2) defining the axial positions while the equatorial plane is occupied by the methyl carbons C(3) and C(4) and C(1) of the propyl arm of the dialkyl sulfoxide group. The Sn–C distances are statistically identical and average 2.12 (3) Å, a value consistent with Sn–C distances observed in pentacoordinate organotin compounds, such as $[SnMe_3Cl_2]^-$[13] and $[SnMe_2Cl_3]^-$,[14] which display average Sn–C distances of 2.12 (1) and 2.12 (5) Å, respectively.

On the other hand, Sn(1) displays distorted pyramidal coordination to Me(1), Me(2), C(1), and Cl(1). Me(1), Me(2), and C(1) generate the basal plane of the pyramid, while Cl(1) occupies the apical position. Sn(1) is displaced ca. 0.4 Å from the base in the direction of the apical group. In addition, Sn(1) enjoys a weak interaction at 2.925 (5) Å with the pseudobridging Cl(2) atom. Since the sum of the van der Waals radii of Sn and Cl falls in the range 3.90–4.10 Å, the observed distance is indicative of a significant Sn(1)–Cl(2) interaction. Unsymmetrical halide bridges are common in the structural chemistry of tin,[15] having been observed for a range of Sn compounds from simple binary halides such as $SnCl_2$[16] to organotin species of the R_2SnCl_2 type, R = CH_3, $ClCH_2$, and C_6H_5.[17-19] The presence of the Cl(2) donor generates overall distorted trigonal-bipyramidal geometry on Sn(1) with Cl(2) occupying an axial position with Cl(1) defining the second axial site; the Cl(1)–Sn(1)–Cl(2) angle is 178.9 (2)°. The major deviation from regular trigonal-bipyramidal geometry is

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(13) Vergamine, P. J.; Vahrenkamp, H.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 6327.

(14) Einstein, F. W. B.; Penfold, B. R. *J. Chem. Soc. A* **1968**, 3019.

(15) Zubieta, J.; Zuckerman, J. J. *Prog. Inorg. Chem.* **1978**, *24*, 251.

(16) Van den Berg, J. M. *Acta Crystallogr.* **1961**, *15*, 509.

(17) Davies, A. G.; Milledge, J. J.; Puxley, D. C.; Smith, P. J. *J. Chem. Soc.* A, **1970**, 2862.

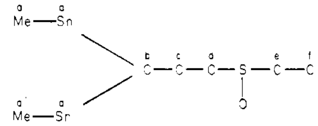
(18) Bokii, N. G.; Struchkov, Ju. T.; Prokfief, A. K. *Zh. Strukt. Khim.* **1972**, *13*, 665.

(19) Greene, P. T.; Bryan, R. F. *J. Chem. Soc. A* **1971**, 2549.

Table II. ^{13}C NMR Chemical Shifts and ^{13}C-^{119}Sn Coupling Constants of 3,3-Bis(halostannyl)propyl Ethyl Sulfoxides[a]

compd	a	a'	b	c	d	e	f
1^c	3.40 ^{1}(466.3)	3.83 ^{1}(500.5)	29.39 ^{1}(418.7), $^{1'}$(394.3)	24.69 ^{2}(22.0)	51.01 ^{3}(58.6), $^{3'}$(33.0)	45.02	6.52
2^d	15.27 ^{1}(747.1)	15.66 ^{1}(720.7)	58.16 ^{1}(700.1)	24.17 ^{2}(32.4)	46.46 ^{3}(61.8)	44.32	6.10
2^e	15.67 ^{1}(742.2)	16.21 ^{1}(717.8)	58.6 ^{1}(681.2), $^{1'}$(651.9)	24.62 ^{2}(34.2)	47.06 ^{3}(58.6)	44.85	6.44
3^f	4.71 ^{1}(471.2)	5.34 ^{1}(439.6)	28.7 ^{1}(400.4), $^{1'}$(382.1)	25.6 ^{2}(20.8)	50.4 ^{3}(54.9), $^{3'}$(34.2)	44.8	6.47
4^d	19.82 ^{1}(703.0)	20.47 ^{1}(714.8)	62.1 ^{1}(644.2), $^{1'}$(638.3)	27.0^g	45.9^g	44.5	6.88
4^e	19.71 ^{1}(693.4)	20.52 ^{1}(688.5)	61.73 $^{1'}$(644.2)^h	26.62 ^{2}(31.7)^h	45.87 ^{3}(73.2)^h	44.47	6.66

[a] Chemical shifts (downfield positive) in ppm from internal Me_4Si; coupling constants (^{13}C-^{119}Sn) (Hz) in parentheses with superscript to denote number of intervening bonds. [b] Carbon atoms are identified on following structure



[c] In $CDCl_3$. [d] In CD_3COCD_3. [e] In CD_3CN. [f] In CH_2Cl_2 with internal $CDCl_3$ lock. [g] Coupling not isolated due to overlap with CD_3 signals. [h] Sn-C satellites broadened, but unresolved.

Table III. ^{119}Sn Chemical Shifts (ppm)[a] of 3,3-Bis(halomethylstannyl)propyl Ethyl Sulfoxides and Simple Halomethylstannanes

1	27.7, 74.7
2	−97.3, −125.6
3	8.22, 20.05
4	−9.02, 2.01
Me_3SnCl	154[b]
Me_2SnCl_2	137[b]
Me_3SnBr	128[b]
Me_2SnBr_2	70[b]
$Me_3SnCl\cdot Me_2SO$	3[b,c]
$Me_2SnCl_2\cdot Me_2SO$	−246[b,c]

[a] Relative to Me_4Sn. [b] Reference 12. [c] In Me_2SO.

the displacement of the Sn(1) atom from the Me(1)–Me(2)–C(1) plane.

The propyl ethyl sulfoxide moiety acts as a donor to Sn(2), bonding through C(1) and O, in addition to bridging the two Sn atoms through C(1). The Sn–C(1) distances are equivalent, the C(1) atom behaving as a symmetric bridge with a Sn(1)–C(1)–Sn(2) bond angle near the tetrahedral ideal. The average Sn–C(1) distance, 2.14 (2) Å, is identical with the average Sn–C(methyl) distance of 2.11 (3) Å. The heteronuclear six-membered ring $\overline{\mathrm{SnC(1)C(2)C(3)SO}}$ displays a chair conformation.

Replacement of a methyl group on each tin by a chlorine atom to produce $(MeCl_2Sn)_2CHCH_2CH_2S(O)Et$ (**2**) results in dramatic structural changes about the tin atoms. The discrete binuclear unit displays a symmetric Sn(1)–C(1)–Sn(2) bridge, similar to that described above for **1**; however, this species displays an additional asymmetric chloride bridge. Thus, Cl(2) is found at distances of 3.578 (2) and 2.371 (2) Å from Sn(1) and Sn(2), respectively, while the Sn(1)–Cl(3) and Sn(2)–Cl(3) distances are 2.375 (2) and 3.631 (2) Å. Once again, the long bond distances Sn(1)–Cl(2) and Sn(2)–Cl(3) are well within the sum of van der Waals radii of Sn and Cl and suggest a real, albeit weak Sn–Cl interaction. The consequences of methyl group replacements at Sn(1) and the concomitant adoption of the semibridging mode by Cl(3) are to generate a distorted pyramidal geometry at Sn(1), with C(1), methyl group Me(1), and Cl(3) defining the basal plane and Cl(1) in the apical position. In contrast to Sn(1) in **1** the tin atom in this derivative is displaced some 0.2 Å from the basal plane in the direction of the apical Cl(1). The Sn(1)–Cl(1) distance in **2** is considerably shorter than that observed for Sn(1)–Cl(1) in **1** 2.364 (3) Å vs. 2.498 (1) Å. This significant bond length contraction is a consequence of the reduction in the interaction with Cl(2) that has been displaced ca. 0.2 Å further from Sn(1), when compared to the single Cl structure **1**. Thus, the Sn(1)–Cl(1) interaction is strengthened as a consequence of displacement of the trans moiety Cl(2), suggesting that in the usual hybridization scheme Cl(1) and Cl(2) compete for the same hybrid orbital in the overall trigonal-bipyramidal geometry of the Sn(1)Cl(1)Cl(2)Me(1)C(1)X grouping, X = Cl (**3**) or Me(2). The dramatic changes in the Sn(1)–Cl(1) distances indicate that the Sn(1)–Cl(2) interaction is a consequence of bonding interactions rather than simply a steric consequence of intramolecular geometric constraints.

The Me(1)–Sn(1)–C(1) valence angle increases from 117.8 (9) Å in **1** to 140.5 (3) Å in **2** as a result of an intermolecular interaction with Cl(4) of a neighboring binuclear unit at 3.578 (2) Å. The overall effect is to produce a bimolecular unit or a loosely interacting tetranuclear unit involving semibridging intramolecular and intermolecular tin-chlorine interactions Sn(1)–Cl(4)···Sn(1)′–Cl(4′), as illustrated in Figure 2b. The geometry at Sn(1) may be viewed as severely distorted octahedral, with Cl(2) and Cl(4) from an adjacent binuclear unit completing the donor set about the tin.

The Sn(2) atom of **2** is distorted toward octahedral geometry, relative to Sn(2) in **1** which displays fairly regular trigonal-bipyramidal geometry. The asymmetrically bridging Cl(3) atom occupies a position pseudotrans to the Me(2) methyl group at 3.631 (2) Å, forcing the C(1)–Sn(2)–Me(2) angle to broaden to 143.9 (3)° from the nearly ideal valence angle of 119.1 (7)° found in **1**.

The bromine derivatives $(Me_2BrSn)_2CHCH_2CH_2S(O)Et$ (**3**) and $(MeBr_2Sn)_2CHCH_2CH_2S(O)Et$ (**4**) exhibit similar geometric characteristics and structural trends. The compound with a single bromine donor to each tin is a discrete binuclear unit, the Sn atoms symmetrically bridged by C(1) of the sulfoxide group and asymmetrically bridged by Br(2). Sn(1) displays a similar distorted trigonal-bipyramidal geometry to that observed for **1** with Me(1), Me(2), and C(1) defining the basal plane and Br(1) and Br(2) in apical positions. The Sn(1)–Br(2) distance of 3.065 (3) Å is well within the sum of the van der Waals radii of Sn and Br, 4.00–4.20 Å. Sn(2) displays trigonal-bipyramidal geometry with Me(3), Me(4), and C(1) in the basal plane and Br(2) and O of the sulfoxide group in the axial positions. The Sn(2)–Br(2) distance of 2.748 (4) Å is significantly longer than the Sn(1)–Br(1) distance of 2.626 (3) Å, presumably a consequence of the bridging

Table IV. Summary of Experimental Details and Crystal Data for the Structural Studies of $[((CH_3)_{2-x}SnX_{1+x})_2CHCH_2CH_2S(O)C_2H_5]$

	1	2	3	4
(A) Crystal Parameters at 23 °C				
a, Å	7.002 (3)	9.099 (3)	7.074 (2)	8.965 (3)
b, Å	9.383 (5)	9.477 (3)	9.325 (3)	17.887 (7)
c, Å	13.771 (7)	10.476 (4)	14.070 (6)	11.166 (4)
α, deg	104.35 (4)	113.34 (2)	77.45 (2)	90.00
β, deg	98.67 (4)	99.68 (2)	81.03 (3)	102.29 (2)
γ, deg	90.37 (4)	91.87 (2)	88.23 (2)	90.00
V, Å^3	865.7 (7)	812.7 (7)	894.7 (7)	1749.5 (6)
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Z	2	2	2	4
D_{calcd}, g cm^{-3}	1.867	2.155	2.136	2.677
(B) Measurement of Intensity Data				
cryst dimens, mm	0.07 × 0.07 × 0.12	0.10 × 0.12 × 0.14	0.06 × 0.09 × 0.09	0.13 × 0.15 × 0.21
instrument	Nicolet R3M			
radiatn	Mo Kα (λ = 0.710 169 Å)			
scan mode	coupled θ(crystal)–2θ(counter)			
scan rate, deg min	variable, 7–30			
scan range, deg	$0 < 2\theta \leqslant 45$			
scan length, deg	[2θ(Mo Kα_1) − 1.0] to [2θ(Mo Kα_2) + 1.0]			
bkgd measurements	stationary crystal–stationary counter at beginning and end of 2 scans, each for half the time of the 2 scans			
stds	three measured every 197 reflections			
no. of reflctns collected	1809	2188	2612	2024
no. of independent reflctns used in soln	1306 with $F_o \geqslant 5\sigma(F_o)$	1842 with $F_o \geqslant 6\sigma(F_o)$	1739 with $F_o \geqslant 6\sigma(F_o)$	1128 with $F_o \geqslant 6\sigma(F_o)$
(C) Reduction of Intensity Data and Summary of Structure Solution and Refinement[b]				
abs coeff, cm^{-1}	33.07 (Mo Kα)	38.47 (Mo Kα)	79.21 (Mo Kα)	120.11 (Mo Kα)
abs correctn	empirical, based on a series of ψ scans for medium intensity reflections with values near 90°			
T_{max}/T_{min}	1.21	1.30	1.43	2.33
structure soln	in all cases, Sn positions were determined from a Patterson map; all other atomic positions were located on subsequent difference Fourier maps			
atomic scattering factors[c]	the analytical scattering factors for neutral Sn, Cl, Br, S, O, C, and H were used			
anomalous dispersion[d]	applied to all non-hydrogen atoms			
final discrepancy factors[e]				
R	0.068	0.032	0.078	0.076
R_w	0.065	0.036	0.074	0.078
goodness of fit[f]	2.33	1.63	2.89	1.97

[a] From a least squares fitting of the setting angle of 25 reflections. [b] Data corrected for background, attentuators, Lorentz, and polarization effects in the usual fashion. All calculations were performed on a Data General Nova 3 computer with 32K of 16-bit words using local versions of the Nicolet SHELXTL interactive crystallographic software package as described in: Sheldrid, G. M. "Nicolet SHELXTL Operations Manual"; Nicolet XRD Corp.: Cupertina, CA, 1979. [c] Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *24A*, 321. [d] "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1962; Vol. III. [e] $R = \Sigma ||F_o| - |F_c|/\Sigma |F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ $w = 1/\sigma^2(F_o) + g(F_o)^2$, and $g = 0.0005$. [f] GOF = $\langle \Sigma w(|F_o| - |F_c|)^2/(NO - NV)\rangle^{1/2}$, where NO is the number of observations and NV is the number of variables.

nature of Br(2) and the trans influence of the sulfoxide oxygen. The six-membered chelate ring SnC(1)C(2)C(3)SO adopts the chair conformation.

Upon replacement of a methyl group on each Sn with a bromine atom, the resultant binuclear species 4 exhibits a triply bridged geometry similar to that observed for 2. The Sn atoms are again symmetrically bridged by C(1) and asymmetrically bridged by Br(2) and Br(3). Sn(2) exhibits a widening of the C(1)–Sn(2)–Me(2) angle to 148.8 (14) Å from the value of 116.3 (9) Å observed in 3, in order to accommodate the steric constraints of the bridging halide, Br(3). The overall geometry at Sn(2) may be described as distorted octahedral with Br(3) occupying the sixth coordination site. The Sn(1) atom is tightly coordinated to C(1), Me(1), Br(1), and Br(3). In addition, Sn(1) enjoys weak interaction with Br(2), an intramolecular asymmetric bridge, and Br(4) from a neighboring binuclear unit. The Sn(1)–Br(1) distance in 4 is ca. 0.1 Å shorter than that observed in 3 as a result of the weakened Sn(1)–Br(2) interaction. Thus, Sn(1) also displays grossly distorted octahedral geometry, with the long Sn(1)···Br(4) intermolecular contact producing a tetranuclear cluster of two weakly interacting binuclear units (Figure 5).

We conclude that substitution of a second bromine atom for a methyl substituent at each tin site has a major consequence an expansion of the tin coordination numbers from five to six, with a consequent stereochemical distortion from fairly regular trigonal-bipyramidal geometries toward severely distorted pseudooctahedra. The availability of a greater number of halido groups appears to allow the tin atoms to exploit the tendency to form both intramolecular and intermolecular halide bridges, thus increasing the degree of association between tin centers and producing a weakly associated tetranuclear unit.

We previously described the structures of intermolecular structures of bis(chlorostannyl)methanes with dimethyl sulfoxide (Me_2SO).[20,21] The complex $ClMe_2SnCH_2SnCl_2Me{\cdot}Me_2SO$ has structure in which the

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(20) Hyde, J. R.; Karol, T. J.; Hutchinson, J. P.; Kuivila, H. G.; Zubieta, J. A. *Organometallics* **1982**, *1*, 404.

(21) Karol, T. J.; Hutchinson, J. P.; Hyde, J. R.; Kuivila, H. G.; Zubieta, J. A. *Organometallics* **1983**, *2*, 106.

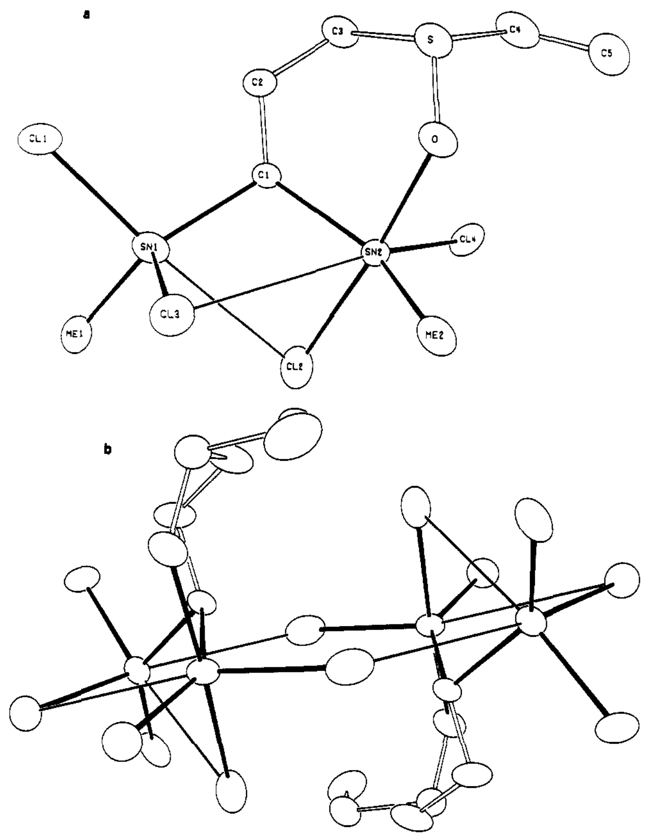

Figure 2. (a) Schemtatic representation of binuclear unit of 3,3-bis(dichloromethylstannyl)propyl ethyl sulfoxide [$(Cl_2MeSn)_2CHCH_2CH_2S(O)Et$], **2**. (b) Schematic representation of the loosely associated bimolecular unit, resulting from the Sn(1)···Cl(4)′ and Sn(1)′···Cl(4) interactions.

Me_2SO molecule bridges the two tins through the oxygen atom. In $(Cl_2MeSn)_2CH{\cdot}2Me_2SO$ both of the Me_2SO molecules bridge the tins forming a bicyclic structure with tin atoms at the bridgeheads. A possible explanation for this difference between the inter- and intramolecular complexation may be found by examination of simple models. A model of the intramolecular species with the oxygen bridging both tins shows considerable angle strain. Presumably this is sufficient to overcome any gain in stability due to bridging, and the simple coordination to one tin atom results. Thus it seems reasonable that compounds 1–4 undergo rapid exchange of sulfoxide oxygen between the two tins in solution as proposed earlier.[11]

Experimental Section

General Data. Proton nuclear magnetic resonance spectra were obtained at 60 MHz by using a Varian EM360A instrument. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane followed in parentheses by the multiplicity, number of protons, coupling constant, and assignment. Proton–tin-119 coupling constants are reported as $^{n}J(^{119}Sn{-}H)$ with the superscript denoting the number of bonds intervening between nuclei. Carbon-13 NMR spectra were obtained by using a Bruker WH-90 spectrometer with a B-NC data system. Spectra were recorded in chloroform-*d* as internal lock and as solvent except where noted; chemical shifts are given in parts per million from internal tetramethylsilane.

^{119}Sn NMR spectra were obtained through the courtesy of Drs. Karl Wursthorn and Keith Mesch. Chemical shifts are relative to external tetramethyltin. Gas chromatographic analyses were performed on an F & M Hewlett-Packard Model F & M 720 instrument using a thermal conductivity detector. Analyses were performed on a 6 ft. or 17 ft. × 0.25 in. copper column packed with 15% SE-30 on Chromosorb W, 60–80 mesh. Melting points and boiling points are uncorrected. Carbon–hydrogen analyses were done by Galbraith Laboratories, Knoxville, TN. Molecular weights were performed by the isopiestic method.

Table V. Final Positional Parameters for the Structural Studies of Complexes [$((CH_3)_{2-x}SnX_{1+x})_2CHC_2H_4SOC_2H_5$]

atom	x	y	z
	(a) **1**		
Sn(1)	411 (2)	1827 (1)	8758 (1)
Sn(2)	1426 (2)	2500 (1)	6496 (1)
Cl(1)	1306 (8)	3116 (8)	10576 (4)
Cl(2)	−718 (8)	331 (6)	6612 (4)
Me(1)	2253 (32)	48 (24)	8826 (18)
Me(2)	−2543 (23)	1559 (26)	8774 (15)
Me(3)	−667 (29)	3047 (24)	5410 (16)
Me(4)	3703 (24)	1112 (22)	6103 (14)
C(1)	1303 (25)	3471 (20)	8075 (12)
C(2)	2995 (27)	4443 (22)	8698 (14)
C(3)	3561 (30)	5800 (22)	8387 (14)
S	4744 (9)	5299 (7)	7316 (5)
O	3192 (20)	4547 (15)	6440 (10)
C(4)	5165 (32)	7042 (22)	7092 (17)
C(5)	6143 (38)	6938 (28)	6213 (22)
	(b) **2**		
Sn(1)	7810 (1)	601 (1)	7935 (1)
Sn(2)	6249 (1)	3227 (1)	6752 (1)
S	3251 (3)	4180 (3)	8422 (3)
Cl(1)	7363 (4)	−114 (4)	9771 (4)
Cl(2)	8043 (3)	1500 (3)	5412 (3)
Cl(4)	4510 (3)	2783 (3)	4638 (3)
Cl(3)	9335 (3)	2978 (3)	9321 (3)
O	4736 (7)	4645 (8)	8095 (8)
Me(2)	7619 (12)	5323 (13)	7396 (13)
Me(1)	9293 (12)	−1018 (12)	7020 (12)
C(1)	5709 (9)	1384 (10)	7353 (10)
C(2)	4713 (12)	1688 (14)	8451 (13)
C(3)	3157 (11)	2113 (12)	7944 (14)
C(4)	1789 (12)	4186 (16)	7043 (14)
C(5)	1853 (16)	5794 (16)	7012 (15)
	(c) **3**		
Sn(1)	529 (2)	1810 (2)	6226 (1)
Sn(2)	1487 (2)	2497 (2)	8473 (1)
Br(1)	1429 (4)	3147 (4)	4370 (2)
Br(2)	−633 (4)	137 (3)	8360 (2)
Me(1)	2459 (34)	49 (23)	6115 (19)
Me(2)	−2476 (29)	1694 (28)	6148 (19)
Me(3)	3819 (29)	1106 (26)	8858 (18)
Me(4)	−662 (38)	3057 (32)	9539 (19)
S	4637 (11)	5291 (7)	7743 (5)
O	3122 (27)	4519 (18)	8582 (11)
C(1)	1353 (28)	3417 (20)	6932 (14)
C(2)	3024 (36)	4384 (23)	6345 (16)
C(3)	3407 (36)	5766 (23)	6690 (17)
C(4)	4944 (36)	6983 (27)	8025 (19)
C(5)	5905 (42)	6912 (29)	8906 (22)
	(d) 4		
Sn(1)	12243 (3)	154 (2)	7245 (3)
Sn(2)	13949 (3)	1551 (2)	9229 (3)
Br(1)	12853 (6)	−323 (3)	5280 (4)
Br(2)	11858 (6)	709 (3)	10010 (5)
Br(3)	11008 (6)	1390 (3)	6510 (5)
Br(4)	15904 (6)	1472 (3)	11231 (5)
O	15442 (37)	2233 (16)	8314 (29)
S	16833 (15)	2007 (8)	7763 (13)
C(1)	14408 (42)	609 (20)	8231 (35)
C(2)	15531 (47)	669 (24)	7438 (39)
C(3)	17068 (47)	1032 (22)	8006 (42)
C(4)	18430 (57)	2365 (27)	8806 (48)
C(5)	18490 (58)	3174 (26)	8858 (48)
Me(1)	10500 (44)	−592 (21)	7462 (37)
Me(2)	12745 (20)	2544 (20)	9280 (36)

3,3-Bis(chlorodimethylstannyl)propyl Ethyl Sulfoxide (1). Into a 50-mL flask equipped with a magnetic stirrer were placed 3.0 g (6.7 mmol) of 3,3-bis(trimethylstannyl)propyl ethyl sulfoxide[11] and 2.95 g (13.5 mmol) of dichlorodimethylstannane in

Table VI. Selected Bond Lengths (Å) and Angles (deg) for [((CH$_3$)$_{2-x}$SnX$_{1+x}$)$_2$CHC$_2$H$_4$SOC$_2$H$_5$] Complexes

(a) 1

Bond Lengths

Sn(1)-Cl(1)	2.478 (5)	Sn(2)-Cl(2)	2.572 (6)
Sn(1)-Me(1)	2.128 (23)	Sn(2)-Me(4)	2.115 (18)
Sn(1)-Me(2)	2.087 (17)	Sn(2)-C(1)	2.154 (15)
Sn(1)-C(1)	2.129 (20)	Sn(2)-O	2.301 (15)
S-O	1.519 (13)	C(1)-C(2)	1.504 (23)
S-C(4)	1.769 (24)	C(20)-C(3)	1.509 (32)
S-C(3)	1.764 (22)	C(4)-C(5)	1.461 (40)
Sn(1)···Sn(2)	3.498 (1)	Sn(1)···Cl(2)	2.925 (5)

Bond Angles

Cl(1)-Sn(1)-Cl(2)	178.9 (2)	Cl(2)-Sn(2)-Me(3)	91.9 (6)
Cl(1)-Sn(1)-Me(1)	95.1 (6)	Cl(2)-Sn(2)-Me(4)	92.1 (6)
Cl(1)-Sn(1)-Me(2)	96.7 (5)	Cl(2)-Sn(2)-C(1)	88.1 (5)
Cl(1)-Sn(1)-C(1)	100.2 (4)	Cl(2)-Sn(2)-O	176.1 (4)
Cl(2)-Sn(1)-Me(1)	85.9 (6)	Me(2)-Sn(2)-Me(4)	122.6 (8)
Cl(2)-Sn(1)-Me(2)	82.4 (5)	Me(3)-Sn(2)-C(1)	118.2 (7)
Cl(2)-Sn(1)-C(1)	79.8 (4)	Me(3)-Sn(2)-O	86.6 (7)
Me(1)-Sn(1)-Me(2)	120.1 (9)	Me(4)-Sn(2)-C(1)	119.1 (7)
Me(1)-Sn(1)-C(1)	117.8 (9)	Me(4)-Sn(2)-O	91.7 (7)
Me(2)-Sn(1)-C(1)	117.3 (8)	C(1)-Sn(2)-O	89.5 (6)
Sn(1)-Cl(2)-Sn(2)	78.8 (1)	Sn(1)-C(1)-Sn(2)	109.5 (7)
Sn(1)-C(1)-C(2)	113.9 (13)	Sn(2)-C(1)-C(2)	118.1 (13)
C(1)-C(2)-C(3)	119.1 (16)	C(2)-C(3)-S	110.0 (13)
C(3)-S-O	105.6 (9)	C(3)-S-C(4)	100.9 (11)
O-S-C(4)	104.0 (10)	Sn(2)-O-S	121.3 (9)
S-C(4)-C(5)	112.2 (16)		

(b) 2

Bond Lengths

Sn(1)-Cl(1)	2.366 (4)	Sn(2)-Cl(2)	2.537 (3)
Sn(1)-Cl(3)	2.374 (2)	Sn(2)-Cl(4)	2.371 (3)
Sn(1)-Me(1)	2.104 (9)	Sn(2)-Me(2)	2.084 (10)
Sn(1)-C(1)	2.148 (8)	Sn(2)-C(1)	2.141 (10)
S-O	1.541 (6)	S-C(4)	1.800 (9)
S-C(3)	1.809 (8)	C(2)-C(3)	1.530 (10)
S-C(4)	1.800 (9)	C(4)-C(5)	1.517 (16)
Sn(1)···Sn(2)	3.440 (1)	Sn(2)···Cl(3)	3.632 (2)
Sn(1)···Cl(2)	3.118 (2)	Sn(1)···Cl(4)′	3.578 (2)

Bond Angles

Cl(3)-Sn(1)-Cl(1)	99.4 (1)	Cl(2)-Sn(2)-Cl(4)	92.7 (1)
Cl(1)-Sn(1)-Me(1)	100.7 (3)	Cl(4)-Sn(2)-Me(2)	109.3 (3)
Cl(1)-Sn(1)-C(1)	102.6 (2)	Cl(4)-Sn(2)-C(1)	106.6 (2)
Cl(3)-Sn(1)-Me(1)	106.0 (2)	Cl(2)-Sn(2)-O	174.0 (2)
Cl(3)-Sn(1)-C(1)	101.1 (2)	Me(2)-Sn(2)-O	86.3 (2)
Me(1)-Sn(1)-C(1)	140.5 (3)	Cl(2)-Sn(2)-Me(2)	95.8 (2)
Sn(1)-C(1)-Sn(2)	107.0 (3)	Cl(2)-Sn(2)-C(1)	85.8 (2)
Sn(1)-C(1)-C(2)	113.8 (5)	Me(2)-Sn(2)-C(1)	143.9 (3)
C(1)-C(2)-C(3)	112.7 (8)	Cl(4)-Sn(2)-O	92.0 (1)
C(3)-S-C(4)	99.9 (4)	C(1)-Sn(2)-O	89.2 (2)
Sn(2)-O-S	131.6 (3)	Sn(2)-C(1)-C(2)	117.5 (5)
		C(2)-C(3)-S	109.9 (5)
		C(3)-S-O	105.3 (3)
		O-S-C(4)	105.9 (4)
		S-C(4)-C(5)	110.5 (5)

(c) 3

Bond Lengths

Sn(1)-Br(1)	2.626 (3)	Sn(1)-Br(2)	2.748 (4)
Sn(1)-Me(1)	2.119 (23)	Sn(1)-Me(2)	2.131 (21)
Sn(2)-Me(3)	2.153 (21)	Sn(2)-Me(4)	2.100 (26)
Sn(2)-C(1)	2.110 (21)	Sn(2)-O	2.167 (19)
S-O	1.532 (27)	C(1)-C(2)	1.526 (28)
S-C(3)	1.800 (27)	C(1)-C(3)	1.518 (34)
S-C(4)	1.736 (29)	C(4)-C(5)	1.492 (44)
Sn(1)···Sn(2)	3.527 (1)	Sn(1)···Br(2)	3.065 (1)

Bond Angles

Br(1)-Sn(1)-Br(2)	177.2 (1)	Br(2)-Sn(2)-Me(3)	91.3 (7)
Br(2)-Sn(1)-Me(1)	84.8 (6)	Me(3)-Sn(2)-Me(4)	122.3 (10)
Br(2)-Sn(1)-Me(2)	84.1 (6)	Me(3)-Sn(2)-C(1)	119.2 (8)
Br(1)-Sn(1)-C(1)	100.6 (5)	Br(2)-Sn(2)-O	177.4 (5)
Me(1)-Sn(1)-C(1)	116.5 (9)	Me(4)-Sn(2)-O	87.0 (9)
Br(1)-Sn(1)-Me(1)	94.4 (7)	Br(2)-Sn(2)-Me(4)	90.8 (8)
Br(1)-Sn(1)-Me(2)	94.0 (6)	Br(2)-Sn(2)-C(1)	89.2 (5)
Me(1)-Sn(1)-Me(2)	123.7 (10)	Me(4)-Sn(2)-C(1)	118.6 (9)
Br(2)-Sn(1)-C(1)	82.1 (5)	Me(3)-Sn(2)-O	91.0 (8)
Me(2)-Sn(1)-C(1)	116.3 (9)	C(1)-Sn(2)-O	90.6 (7)

Table VI (*Continued*)

(d) 4

Bond Lengths

Sn(1)-Br(1)	2.520 (56)	Sn(2)-Br(2)	2.690 (6)
Sn(1)-Br(3)	2.529 (5)	Sn(2)-Br(4)	2.534 (5)
Sn(1)-Me(1)	2.108 (41)	Sn(2)-Me(2)	2.084 (37)
Sn(1)-C(1)	2.174 (34)	Sn(2)-C(1)	2.109 (39)
S-O	1.557 (38)	Sn(2)-O	2.215 (34)
S-C(3)	1.772 (42)	C(1)-C(2)	1.480 (63)
S-C(4)	1.762 (47)	C(2)-C(3)	1.533 (56)
Sn(1)· · ·Sn(2)	3.471 (1)	C(4)-C(5)	1.449 (66)
Sn(1)· · ·Br(2)	3.335 (1)	Sn(2)· · ·Br(3)	3.584 (1)
		Sn(1)· · ·Br(4)′	3.599 (1)

Bond Angles

Br(3)-Sn(1)-Br(1)	100.0 (2)	Br(3)-Sn(1)-C(1)	96.9 (10)
Br(1)-Sn(1)-C(1)	103.4 (11)	Br(3)-Sn(1)-Me(1)	107.9 (10)
Br(1)-Sn(1)-Me(1)	100.9 (12)	C(1)-Sn(1)-Me(1)	141.4 (15)
Br(2)-Sn(2)-Br(4)	94.7 (2)	Br(2)-Sn(2)-C(1)	171.5 (8)
Br(4)-Sn(2)-O	93.7 (2)	Br(2)-Sn(2)-C(1)	87.2 (11)
Br(4)-Sn(2)-C(1)	104.2 (9)	O-Sn(2)-C(1)	89.5 (14)
Br(2)-Sn(2)-Me(2)	93.9 (11)	Br(4)-Sn(2)-Me(2)	106.8 (10)
O-Sn(2)-Me(2)	84.9 (14)	C(1)-Sn(2)-Me(2)	148.8 (14)
Sn(2)-O-S	130.8 (18)	O-S-C(3)	105.9 (21)
O-S-C(4)	104.5 (23)	C(3)-S-C(4)	101.7 (21)
Sn(1)-C(1)-Sn(2)	108.2 (17)	Sn(1)-C(1)-C(2)	111.8 (25)
Sn(2)-C(1)-C(2)	119.5 (27)	C(1)-C(2)-C(3)	116.7 (36)
S-C(3)-C(2)	106.6 (27)	S-C(4)-C(5)	114.0 (34)

5 mL of methylene chloride, and the mixture was refluxed for 12 h. The disappearance of starting materials was monitored by ^{1}H NMR. After the reaction was complete, the solvent was removed on the rotary evaporator. The chlorotrimethylstannane was removed at 0.01 torr and 60 °C leaving crude product in quantitative yield. This was recrystallized from CCl_4 and hexane to yield colorless crystals: 3.11 g, 95%; mp 125–126 °C; ^{1}H NMR ($CDCl_3$) δ 0.75 (s, 6, ^2J(Sn–C–H) = 46.0 Hz); IR (KBr) $\nu_{S=O}$ 958 cm^{-1}, IR (10% in CH_3CN) $\nu_{S=O}$ 960 cm^{-1}; ^{119}Sn NMR (CD_3CN) δ 27.7, 74.7. Anal. Calcd for $C_9H_{22}Cl_2OSSn_2$: C, 22.21; H, 4.57; mol. wt., 486.6. Found: C, 22.29; H, 4.70; mol. wt, 506.6 (isopiestic in CH_2Cl_2 at 22 °C).

3,3-Bis(dichloromethylstannyl)propyl Ethyl Sulfoxide (2). Into a 100-mL flask equipped with a magnetic stirrer, 3.2 g (7.2 mmol) of 3,3-bis(trimethylstannyl)propyl ethyl sulfoxide was dissolved in 5 mL of methylene chloride and cooled to 0 °C. To this was added a solution of 3.74 g (14.4 mmol) of tetrachlorostannane in 10 mL of methylene chloride dropwise while being stirred at 0 °C. After the addition was complete, the reaction mixture was slowly warmed to room temperature and then refluxed for 20 h until the starting materials had completely disappeared (^{1}H NMR analysis). The solvent was removed on the rotary evaporator, and the dichlorodimethylstannane was removed at 0.01 torr and 60 °C to yield crude product. This was recrystallized from methylene chloride and hexane to yield white crystals: 3.7 g, 97%; mp 174–176 °C; ^{1}H NMR (CD_3COCD_3) δ 1.22 (s, 3, ^2J(^{119}Sn–C–H) = 73 Hz), 1.25 (s, 3, J(^{119}Sn–C–H) = 75.0 Hz); IR (KBr) $\nu_{S=O}$ 940 cm^{-1}; IR (10% in CH_3CN) $\nu_{S=O}$ 955 cm^{-1}; ^{119}Sn NMR [$(CD_3)_2CO$] δ −97.3, −125.6. Anal. Calcd for $C_7H_{16}Cl_4OSSn_2$: C, 15.94; H, 3.06; mol wt, 527.46. Found: C, 15.85; H, 3.13; mol wt, 593.27 (isopiestic in CH_2Cl_2 at 22 °C).

Collection and Reduction of X-ray Data. The crystals used in the studies were colorless, regularly shaped blocks or rods with dimensions reported in Table IV. In all cases, unit cell dimensions were obtained by using an autoindexing routine on the angular settings of 25 reflections with 20° < 2θ < 25° aligned in the counter window of a Nicolect R3m diffractometer. Axial photographs and Delauney reductions of the various unit cell dimensions revealed no hidden symmetry. The quality of the data sets was checked by taking $\theta/2\theta$ scans of several strong low-angle reflections in each case. The details of the data collections and reductions are given in Table IV.

Structure Solutions and Refinements. All structures were solved for Sn positions by using conventional Patterson techniques and other non-hydrogen atomic positions located on difference Fourier maps. Hydrogen atoms were introduced as fixed contributions, and all non-hydrogen atoms were refined anisotropically.

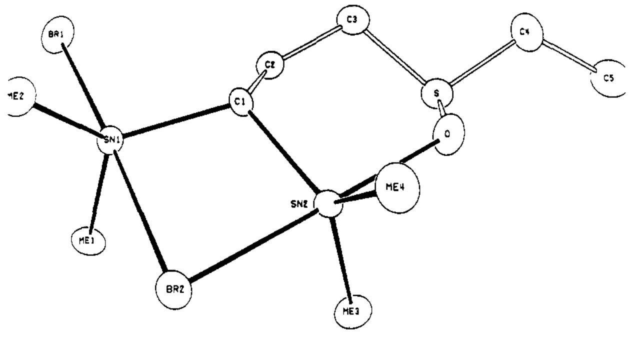

Figure 3. Schematic representation of binuclear 3,3-bis(bromodimethylstannyl)propyl ethyl sulfoxide [$(BrMe_2Sn)_2CHCH_2CH_2S(O)Et$], 3.

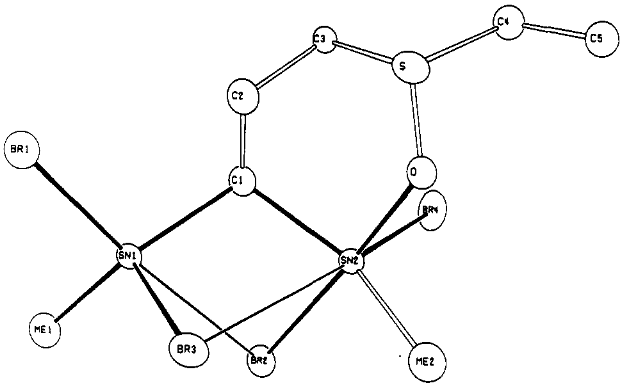

Figure 4. Schematic representation of binuclear 3,3-bis(dibromomethylstannyl)propyl ethyl sulfoxide [$(Br_2MeSn)_2CHCH_2CH_2S(O)Et$], 4.

The final full-matrix least-squares refinements converged at discrepancy values listed in Table IV. In each case, an analysis of variance according to $|F|$ and (sin θ)/γ showed satisfactory consistency, and the weighting scheme was judged satisfactory. In no case did the final difference Fourier map exhibit significant excursions of electron density.

Atomic positional parameters, along with their standard deviations, are given in Table V. Table VI lists interatomic distances

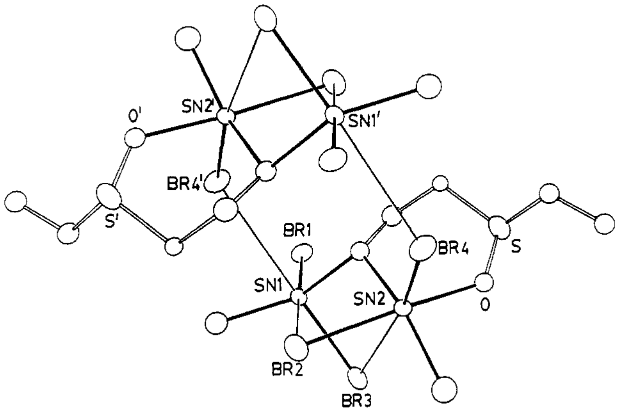

Figure 5. Schematic representation of tetranuclear 3,3-bis(dibromomethylstannyl)propyl ethyl sulfoxide [$(Br_2MeSn)_2CHCH_2CH_2S(O)Et$], 4.

and angles for the four compounds of this study. Tables of anisotropic thermal parameters calculated hydrogen positions, and observed and calculated structure factor amplitude are provided as supplementary materials. Views of the molecular geometries along with the atom-labeling scheme are shown in Figures 1–5.

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Supplementary Material Available: Tables of anisotropic thermal parameters calculated hydrogen positions and isotropic thermal parameters, and calculated and observed structure factors for compounds 1–4 (45 pages). Ordering information is given on any current masthead page.

Reactions of Atomic Cobalt Ions with Aldehydes and Ketones. Observation of Decarbonylation Processes Leading to Formation of Metal Alkyls and Metallacycles in the Gas Phase[†]

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An ion beam apparatus is used to study the reactions of singly charged cobalt positive ions with several aldehydes and ketones as a function of relative kinetic energy. Deuterium labeling is used to provide mechanistic information. Decarbonylation yielding $CoCO^+$ is the dominant process in the reactions of Co^+ with formaldehyde, acetaldehyde, and acetone at low energies. At ~0.5 eV relative kinetic energy cross sections for formation of $CoCO^+$ from these neutrals are 0.25, 29, and 80 Å^2, respectively, indicating that formaldehyde is much less reactive than the alkyl-substituted species. An ion corresponding to $Co(CH_3)_2^+$ is formed as an exothermic product in the reaction of Co^+ with acetone. The analogous product is also observed in the reactions of Fe^+ and Ni^+ with acetone. This indicates that the sum of the first two methyl bond energies to first-row group 8 metal ions is greater than 96 kcal/mol, which exceeds typical C–C single bond energies and supports the conclusion of earlier studies that metal ion insertion into unactivated carbon–carbon bonds of saturated hydrocarbons is an exothermic process. As the alkyl chains of the dialkyl ketones are extended, loss of alkene and aldehyde dominate the product distributions at low energies. If one of the alkyl groups is highly branched, the major product is due to loss of methane. Decarbonylation of cyclopentanone yields $Co(C_4H_8)^+$, suggested to be a metallacycle which further dehydrogenates to yield $Co(C_4H_6)^+$ as the major species formed in exothermic processes at low relative kinetic energies. Analyses of products formed at high relative kinetic energies are used in conjunction with thermochemical estimates to infer mechanistic details and construct qualitative reaction coordinate diagrams for the interaction of metal ions with carbonyl compounds. Some interesting conclusions can be reached from an inspection of these diagrams. For example, reaction of coordinatively unsaturated metal dialkyls and hydrido alkyls with carbon monoxide will lead to the reductive elimination of alkanes rather than formation of ketones and aldehydes. The results of this work are compared to earlier ion cyclotron resonance studies of related reactions at thermal energies.

Introduction

Studies in our laboratory have provided detailed insights into the mechanism and energetics of reactions of atomic transition-metal ions with hydrocarbons.[2-6] These studies have utilized a specially designed ion beam apparatus that permits the relative kinetic energy to be varied over a wide range, making it possible to characterize not only exo-

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[2] Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784.

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