Geminal Bis(haloorganostannanes) and Their Complexation as Mono- and Bidentate Lewis Acids with Dimethyl Sulfoxide

Thomas J. Karol, John P. Hutchinson, Jeffrey R. Hyde, Henry G. Kuivila,* and Jon A. Zubieta*

Department of Chemistry, State University of New York at Albany, Albany, New York 12222

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Six (chloromethylstannyl)methanes with structures $CH_2(SnMe_nCl_{3-n})(SnMe_mCl_{3-m})$ with n = 0-3 and m = 0-2 have been prepared by chlorine-methyl exchange from bis(trimethylstannyl)methane or bis-(trivinylstannyl)methane. Four 2,2-bis(chloromethylstannyl)propanes have been similarly prepared from 2,2-bis(trimethylstannyl)propane. Correlations between ¹H and ¹³C magnetic resonance parameters have been examined. The effects of dimethyl sulfoxide (Me₂SO) on the ¹H NMR parameters of the chlorostannanes have been examined as a source of information on complexation. Seven complexes with Me₂SO have been prepared, and the structures of $CH_2(SnMeCl_2)-(SnMe_2Cl)(Me_5SO)^4_{\lambda}$, $CH_2(SnMeCl_2)_2(2Me_2SO)^5_{\lambda}$, and $CH_2(SnCl_3)_2(4Me_2SO)^7_{\lambda}$ have been determined by X-ray diffraction. In the first of these, the oxygen of the Me₂SO bridges the two tins which display distorted trigonal-bipyramidal geometry; in the second, the oxygens of each Me₂SO act as bridges between the tins which display distorted octahedral geometry; in the third, the oxygens do not bridge and the CH₂ group serves as a common apex for the octehedra of two hexacoordinate tins. Pertinent features of the structures are discussed. Compound 4 crystallizes in the space group PI with a = 7.551 (2) Å, b = 7.945 (2) Å, c = 13.354 (3) Å, $\alpha = 80.63$ (2)°, $\beta = 89.13$ (2)°, $\gamma = 72.96$ (2)°, and Z = 2. The structure solution and refinement were based on 1609 reflections with $F_0 > 6\sigma(F_0)$ to give a discrepancy factor of 0.045. Compound 5 crystallizes in the orthorhombic space group Pbnm with a = 9.821 (2) Å, b = 12.411 (2) Å, c = 15.540 (3) Å, and Z = 4. Refinement based on 1109 reflections with $F_0 > 6\sigma(F_0)$ converged at 0.048. Compound 7 crystallizes in the monoclinic space group C2/c with a = 20.998 (5) Å, b = 7.925 (3) Å, c = 16.535 (4) Å, $\beta = 98.79$ (3)°, and Z = 4. Refinement using 1277 reflections with $F_{o} > 6\sigma(F_{o})$ yielded R = 0.034.

A great majority of known organotin compounds contain a single tin atom. The most common of those that contain more than one tin atom have the tins bonded to each other as in the ditins and the polymeric compounds of the formula $(R_2Sn)_{x}$.¹ Those in which the tin atoms are separated by one or more carbon atoms in polymers^{2,3} and in simpler compounds such as distannylmethanes⁴⁻¹⁰ and higher homologues are less familiar. Yet such species should be readily prepared by known synthetic procedures, and they might display novel and useful properties. With this idea in mind we have begun a study of the preparation and properties of compounds containing more than one tin atom separated by one or more carbon atoms. In this paper we report results of studies on the simplest members of this class, namely, those with a single Sn-C-Sn structural unit. Preparations of chlorotins are described along with studies on complexation with dimethyl sulfoxide and physical properties of interest.

Bis(halostannyl)methanes. The obvious precursor of this series compound 1 was first obtained "quantitatively" by Kraus and Neal⁴ by the reaction of (trimethylstannyl)sodium with methylene chloride (eq 1) in liquid

$$2\mathrm{Me}_{3}\mathrm{SnNa} + \mathrm{CH}_{2}\mathrm{Cl}_{2} \rightarrow \mathrm{CH}_{2}(\mathrm{SnMe}_{3})_{2} + 2\mathrm{NaCl} (1)$$

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ammonia. The preparation has been repeated⁵ and has also been carried out in other solvents and by other methods.⁶⁻¹⁰ We have prepared 1 in liquid ammonia routinely in 89% yield and in tetraglyme in 65% yield. Replacement of one or more of the methyl groups of 1 with halogen or other labile group would provide a functional center at tin for elaborating the structure. Kaesz² has reported that treatment of 1 with hydrogen chloride leads to the formation of tetramethylstannane and trimethylchlorostannane (eq 2) by cleavage of a methylene-tin bond rather than the desired methyl-tin bond.

$$CH_2(SnMe_3)_2 + HCl \rightarrow CH_3SnMe_3 + ClSnMe_3 \quad (2)$$

We have found that treatment with bromine in methanol-carbon tetrachloride at -60 °C followed by warming yielded trimethylbromostannane and dibromodimethylstannane as major cleavage products. Iodine similarly yielded a mixture of products.

The desired mode of cleavage was achieved by reaction of 1 with dichlorodimethylstannane (Scheme I). The trimethylchlorostannane formed could be removed at reduced pressure in 95% yield, and the residue was bis(dimethylchlorostannyl)methane (2) of high purity. This dichloride could then be converted in quantitative yield to the diiodide by reaction with potassium iodide in acetone.

Attempted preparation of the monochloride, (trimethylstannyl)(chlorodimethylstannyl)methane (3) by reaction of 1 mol of dichlorodimethylstannane with 1 resulted in a mixture of 1, 2, and 3 in the ratio of about 1:1:2. This was established to be an equilibrium composition, for the same mixture of the three compounds was obtained upon mixing equimolar amounts of 1 and 2. It was possible to obtain 3 as its ammonia complex $(3 \cdot NH_3)$ by extracting the equilibrium mixture in pentane with water and immediately passing ammonia through the pentane solution, whereupon 3.NH3 precipitated. This complex was stable with respect to methyl-chlorine exchange. It lost ammonia if exposed to the air but was stable in an ammonia atmosphere.

Stepwise replacement of a methyl group on each tin atom of 2 could be achieved routinely in 95% yield. (Chlorodimethylstannyl)(dichloromethylstannyl)methane (4) was obtained by reaction of $1 \mod \text{of } 2 \pmod{0.5} \mod \text{of}$ tetrachlorostannane. Replacement of a methyl group on each of the tins of 2 was most easily realized by treatment with excess tetrachlorostannane in methylene chloride to provide bis(dichloromethylstannyl)methane (5).

Exchange of the third methyl group on the tins to form the trichlorostannyl derivatives could not be achieved by simple reaction with tin tetrachloride. It has been shown that vinyl groups undergo exchange with chlorine of chlorostannanes with great facility.¹¹⁻¹³ For example, trichlorovinvlstannane can be prepared from tetravinylstannane by exchange with tetrachlorostannane at temperatures of 100 °C or lower.^{11,12} We exploited these observations by first preparing bis(trivinylstannyl)methane (8) by the reaction of (trivinylstannyl)sodium with methylene chloride in liquid ammonia in 70% yield (Scheme II). Treatment of 8 with tetrachlorostannane provided bis(trichlorostannyl)methane (7) in 87% yield. Treatment of 7, in turn, with 1 mol of trimethylchlorostannane gave (trichlorostannyl)(dichloromethyl)stannane (6).

2,2-Bis(halostannyl)propanes. The "supernucleophilic"9,10 behavior of (trimethylstannyl)sodium as reflected in the facility with which it reacted with methylene chloride prompted an examination of the reaction with the more hindered 2,2-dichloropropane. Reaction occurred readily and in high yield at -33 °C in liquid ammonia providing 2,2-bis(trimethylstannyl)propane (9) (eq 3). Treatment of 9 with 2 mol of dichlorodimethyl-

$$Me_2CCl_2 + 2Me_3SnNa \rightarrow Me_2C(SnMe_3)_2$$
 (3)

stannane at 60 °C yielded 95% of 2,2-bis(chlorodi-

methylstannyl)propane (10) (eq 4). Replacement of a



methyl on each tin was achieved by treatment with excess tetrachlorostannane to form 2,2-bis(dichloromethylstannyl)propane (12). When 1 mol of 10 was treated with 0.5 mol of tetrachlorostannane, the product was 2-(chloromethylstannyl)-2-(dichloromethylstannyl)propane (11) isolated in 75% yield (eq 4).

NMR Spectra. Values of proton chemical shifts and ¹¹⁹Sn⁻¹H coupling constants are given in the Experimental Section and those for ¹³C in Table I for the compounds described above. Both sets of parameters show the expected qualitative trends. Replacement of methyl groups by chlorine atoms decreases chemical shifts and increases the coupling constants. However, simple additivity trends are not discernible.

Comparison of compounds 1-6 shows an unexpected effect of replacing methyl by chlorine. On going from 1 to 5 replacement of two methyls of a trimethylstannyl group by chlorines causes a downfield shift of the methyl carbon by 16.6 ppm, whereas replacement of two trimethylstannyl groups on the methylene by the dichloromethylstannyl groups shifts the carbon signal downfield by 23.5 ppm. But replacement of the third methyls by chlorines causes an additional downfield shift by only 3.8 ppm.

Good correlations between ¹H and ¹³C parameters are observed. For example the chemical shifts for the CH₂ protons of bis(trimethylstannyl)methane, 1, and its chloro analogues are plotted vs. the values for ¹³C in Figure 4. The parameters for the methyl groups do not show a similar correlation.

Previous investigators have examined the relationship between ${}^{2}J({}^{119}Sn-{}^{1}H)$ and ${}^{1}J({}^{119}Sn-{}^{13}C)$ and have reported approximate linear correlations.¹⁵⁻¹⁷ These do not pass through the origin leading to the conclusion that factors other than the Fermi contact interaction are involved in the coupling between the tin and proton or carbon nucleus, or both.¹⁵ In Figure 5 are plotted our data, along with those of Petrosyan et al.,¹⁶ Singh,¹⁷ and Mathiasch.¹⁸ The correlation line drawn for the first three sets of data, excluding that for hexamethylditin, has a correlation coefficient of 0.996 and the intercept on the carbon axis of -98.3 Hz. The Petrosyan data intersect at -51 Hz. The cluster of points that fall above the line at the lower end are for ditins, the diamonds for cyclic derivatives, and the square for hexamethylditin. These deviant data further demonstrate that caution should be used in inferring values of one of the coupling constants from that of the other unless quite similar structures are involved.¹⁷

Complexation of Chlorostannanes with Dimethyl Sulfoxide in Solution. Molecules bearing more than one Lewis base function serve as valuable tools in many aspects of coordination chemistry. The chlorostannanes described above have the potential of playing a complementary role as bidentate Lewis acids. We have examined the behavior of these chlorides in solution with dimethyl sulfoxide

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Figure 1. Effect of Me_2SO on ${}^{2}J({}^{119}Sn_{-}{}^{1}H)$ of methyltin protons in methylene chloride: A, 0.30 M bis(chlorodimethylstannyl)methane, 2; B, 0.63 M chlorotrimethylstannane; C, 0.58 M 2,2bis(chlorodimethylstannyl)propane, 10.



Figure 2. Effect of Me₂SO on chemical shifts of methyltin protons in acetone- d_6 : A, 0.29 M bis(dichloromethylstannyl)-methane, 5; B, 0.25 M 2,2-bis(dichloromethylstannyl)propane, 11.

(Me₂SO), a donor whose complexation with simple organotin halides and other derivatives has been studied from several perspectives during the past two decades. In general the halides R_3SnX tend to form pentacoordinate complexes¹⁹⁻²¹ while R_2SnX_2 and $RSnX_3$ tend to form hexacoordinate complexes.²¹⁻²⁴ We used proton magnetic resonance spectroscopy (¹H NMR) for this study because of its convenience. The observed magnitudes of changes in parameters were not deemed great enough for accurate quantitative work. Nonetheless, the changes in chemical shifts and/or coupling constants on the methyltin protons of the chlorotins upon addition of increments of Me₅SO were sufficient to provide useful information about complexation.

Results for chlorotrimethylstannane, 2, and 10 are shown in Figure 1. In each case a large initial slope in the plot decreases fairly rapidly and approaches zero. The values of the coupling constants are taken to represent weighted

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Figure 3. Effect of Me_2SO on the chemical shifts of the dichloromethyl (MeCl₂Sn) protons in methylene chloride: A, 0.29 M (dichloromethylstannyl)(chlorodimethylstannyl)methane, 4; B, 0.39 M 2-(chlorodimethylstannyl)-2-(dichloromethylstannyl)propane, 10.



Figure 4. Relationship between proton and 13 C chemical shifts in methylene chloride or carbon tetrachloride.

means for species in rapidly established equilibria such as those represented in eq 5 and 6. Extrapolations of the

$$\mathbf{2} + \mathbf{M}\mathbf{e}_2 \mathbf{SO} \rightarrow \mathbf{2}(\mathbf{M}\mathbf{e}_2 \mathbf{SO}) \tag{5}$$

$$2(\text{Me}_2\text{SO}) + \text{Me}_2\text{SO} \rightarrow 2(2\text{Me}_2\text{SO}) \text{ etc.}$$
(6)

nearly linear initial and final portions of the plots for 2 and 10 intersect at a Me_2SO/Sn ratio near 0.5, indicating that 1/1 complexes (2(Me_2SO) and 10(Me_2SO)) are particularly stable, but additional coordination may occur at higher Me_2SO concentrations. By contrast the break in the plot for chlorotrimethylstannane is less pronounced than that in the others, and a similar extrapolation suggests intersection nearer a 1/1 molecular ratio. The chemical shifts of the methyl protons also changes, but the change in the same experiments for 10 was only 2 Hz (0.03 ppm) upfield.

Similar plots for 5 and 11 are shown in Figure 2. Due to the low solubility of the complexes in methylene chloride, acetone- d_6 was used as the solvent. Even then, ¹H NMR data (chemical shifts of the tin methyl protons) could not be obtained when Me₂SO/SN fell between 1 and 7 due to precipitation of the complex. At higher concentrations of Me₂SO the complex was soluble. Inspection

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	w		x		у		Z	
	δ	$n(J)^c$	δ	$n(J)^c$	δ	$n(J)^c$	δ	$n(J)^c$
Me ₃ Sn SnMe ₃	-7.4	¹ (330)			-14.2	¹ (287)		
Me2SnCI SnMe2C	1.5	¹ (400)			4.2	'(295)		
Me ₃ Sn SnMe ₂ Cl	-7.5	¹ (344)	-6.0	¹ (361)	-0.06	^{w1} (236) ^{x1} (287)		
ČH ₂ Me ₂ SnCi SnMeCl ₂	1.1	1(409)	9.7	¹ (508)	10.2	^{w1} (261) ^{x1} (385)		
VeSnCl2 SnCl2Me	9.2	¹ (547)			19.3	'(403)		
MeSnCl ₂ SnCl ₃								
Cl ₃ Sn SnCl ₃					23.1	¹ (698)		
Me Me V Me ₃ Sn SnMe ₃	-18.8	¹ (299)			10.1	'(341)	26.3	²(18)
Me Me C Me ₂ SnCl SnMe ₂ Cl	-1.8	'(340)			29.8	¹ (361)	23.8	²(24)
	-1.9	¹ (365)	7.8	¹ (389)	31.2	е	23.1	^{w2} (15) ^{x2} (29)
11 Me Me MeSnCl ₂ SnMeCl ₂	6.9	¹ (430)			49.2	'(466)	22.6	²(24)

 Table I.
 Carbon-13 Magnetic Resonance Parameters^{a, b}

^a Solvent and internal. ^b Chemical shifts in ppm downfield from Me₄Si obtained by using CH₂Cl₂ as secondary reference (δ 53.486). ^c ⁿ(J) = ⁿJ(¹¹⁹Sn-¹³C); ^{wn}(J) or ^{xn}(J) coupling to carbon w or x. ^d In pyridine. ^e Not detected due to weak signal from tetrasubstituted carbon.

of the plots suggests that the complex with a Me_2SO/Sn ratio of unity or less is particularly stable.

The intermediate trichloro analogues 4 and 13 both yielded plots with somewhat less definite changes in slopes, but indicate intersections near unity. The pentachloro and hexachloro analogues 8 and 7, respectively, formed complexes which were so insoluble that similar ¹H NMR studies could not be made.

Isolation of Me₂SO Complexes. Complexes with Me₅SO were prepared from all of the chlorostannanes except 3. These were obtained by adding the chlorostannane and Me₂SO to carbon tetrachloride. All were crystalline solids but varied in composition as follows: $2(Me_2SO)$; $4(Me_2SO)$; $5(2Me_2SO)$; $8(3Me_2SO)$; $7(4Me_2SO)$; $10(Me_2SO)$; $12(Me_2SO)$; $11(2Me_2SO)$. These may not be the most stable complexes formed but are those whose

stability constants and solubility in carbon tetrachloride are such that they crystallize most readily.

Structures of Me_2SO Complexes. The structures of three of the complexes were determined by X-ray diffraction. That of $6(3Me_2SO)$ could not be solved due to disorder. Schematics of the structures are shown in Figure 6, together with relevant bridging parameters.²⁵ Data on bond lengths and angles are gathered in Table II.

Compound $5(2Me_2SO)$ consists of discrete dimers, each tin atom enjoying pseudooctahedral geometry. The tin

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Figure 5. Plot of coupling constants of ¹¹⁹Sn with protons and ¹³C in methylene chloride or carbon tetrachloride for proton spectra and deuteriochloroform/methylene chloride for ¹³C: O, this work; Δ , ref 16; \Box , ref 17; \diamond , ref 18.



Figure 6. Schematics of structures of Me₂SO complexes.

octahedra share a common face through the bridging methylene groups and the oxygens of the Me₂SO groups. A crystallographic mirror plane passes through Sn1, Sn2, C2, and C3. As anticipated, the average Sn-O(Me₂SO) bridging distance of 2.588 (6) Å is significantly longer than that observed for Sn-O(Me₂SO) terminal bonding in [SnCl₂Ph₂(Me₂SO)₂],²⁵ 2.318 (5) Å, or in 7(4Me₂SO), 2.118 (6) Å. The significant lengthening of the Sn-O(Me₂SO) bond distance in [SnCl₂CH₂(Me₂SO)₂] as compared to 7(4Me₂SO) presumably reflects the steric constraints imposed by the phenyl groups in this species. The (Me₂SO)₂

 Table II.
 Selected Bond Lengths (Å) and Angles (Deg) for the Bis(stannyl)methanes

(a) $[Sn_2(CH_2)(CH_3)_2Cl_4(Me_2SO)_2]$						
	Bond Di	stances				
Sn1…Sn2 Sn1-Cl2 Sn1-C1 Sn1-C3 Sn1-O1 Sn2-Cl1	$\begin{array}{c} 3.426 \ (1) \\ 2.419 \ (3) \\ 2.108 \ (11) \\ 2.115 \ (15) \\ 2.555 \ (6) \\ 2.411 \ (3) \end{array}$	Sn2-C1 Sn2-C2 Sn2-O1 S1-O1 S1-C4 S1-C5	2.112 (10) 2.117 (15) 2.621 (6) 1.527 (6) 1.79 (1) 1.79 (1)			
	Bond A	ngles				
01-Sn1-O1 01-Sn1-C1 01-Sn1-C3 01-Sn1-Cl2 01-Sn1-Cl2 C1-Sn1-Cl2 C3-Sn1-Cl2 Sn1-C1-Cl2 Sn1-C1-Cl2 Sn1-C1-Sn2 Sn1-C1-Sn2	$\begin{array}{c} 82.0 (3) \\ 72.2 (2) \\ 87.1 (3) \\ 88.5 (1) \\ 168.2 (2) \\ 152.3 (5) \\ 98.3 (2) \\ 99.4 (3) \\ 100.1 (1) \\ 82.9 (2) \\ 108.5 (4) \\ 108.5 (4) \end{array}$	01-Sn2-O1' 01-Sn2-C1 01-Sn2-C2 01-Sn2-C11 01-Sn2-C11 C1-Sn2-C2 C1-Sn2-C11 C1-Sn2-C11 C2-Sn2-C11 01-S1-C4	$\begin{array}{c} 79.5 (2) \\ 70.8 (2) \\ 83.1 (3) \\ 90.4 (1) \\ 168.4 (2) \\ 145.7 (5) \\ 100.6 (2) \\ 101.5 (3) \\ 99.1 (1) \\ 105.3 (4) \end{array}$			
Sn1-01-S1 Sn2-01-S1	131.1(3) 145.6(3)	C4-S1-C5	105.8 (4) 97.7 (5)			
(b)	$[Sn_2(CH_2)(CH_2)]$	H ₃)Cl ₃ (Me ₂ SO)]			
	Bond Di	stances				
Sn1Sn2 Sn1-Cl2 Sn1-Cl3 Sn1-O1 Sn1-Cl Sn1-C4 Sn2-Cl1	$\begin{array}{c} 3.529(1)\\ 2.410(4)\\ 2.372(4)\\ 2.572(8)\\ 2.097(13)\\ 2.140(17)\\ 2.453(4) \end{array}$	Sn2-O1 Sn2-Cl Sn2-C2 Sn2-C3 S-O1 S1-C5 S1-C6	$\begin{array}{c} 2.568(8)\\ 2.159(3)\\ 2.136(13)\\ 2.152(18)\\ 1.526(8)\\ 1.82(2)\\ 1.80(2) \end{array}$			
01.0.1.01	Bond A	ngles	55 0 (()			
01-Sn1-Cl 01-Sn1-Cl2 01-Sn1-Cl3 01-Sn1-Cl2 Cl-Sn1-Cl3 Cl-Sn1-Cl3 Cl2-Sn1-Cl3 Cl2-Sn1-Cl3 Cl2-Sn1-C4 Cl3-Sn1-C4 Cl3-Sn1-C4 Sn1-O1-Sn2 Sn1-O1-Sn2 Sn1-O1-Sn2	77.9(4) 174.2(3) 81.5(2) 83.8(4) 99.9(3) 109.6(4) 134.9(6) 94.4(1) 101.4(4) 107.9(4) 86.6(2) 112.0(6)	01-Sn2-C1 01-Sn2-C1 01-Sn2-C2 01-Sn2-C3 C1-Sn2-C1 C1-Sn2-C2 C11-Sn2-C2 C11-Sn2-C3 C11-Sn2-C3 C2-Sn2-C3 01-S1-C5	77.0(4) 175.7(2) 88.4(5) 82.4(5) 98.0(3) 115.2(6) 120.4(6) 97.3(4) 97.1(4) 119.5(6) 106.3(6)			
sn1-01-s1 sn2-01-sn	130.6(5) 134.4(5)	C5-S1-C6	103.4 (6) 97.7 (8)			
(c) $[Sn_2(CH_2)Cl_6(Me_2SO)_4]$						
Bond Distances						
Sn…Sn Sn-Cl1 SnCl2 Sn-Cl3 Sn-O1 Sn-C5	$\begin{array}{c} 3.860(1)\\ 2.46(2)\\ 2.447(2)\\ 2.475(3)\\ 2.109(5)\\ 2.123(5) \end{array}$	$\begin{array}{cccc} S1-O1 & 1 \\ S1-C1 & 1 \\ S1-C2 & 1 \\ S2-O2 & 1 \\ S2-C3 & 1 \\ S2-C4 & 1 \end{array}$.550 (6) .770 (9) .784 (9) .547 (7) .753 (15) .726 (15)			
Bond Angles						
Cl1-Sn-Cl2 Cl1-Sn-Cl3 Cl1-Sn-O1 Cl1-Sn-O2 Cl1-Sn-C5 Cl2-Sn-C1 Cl2-Sn-O1 Cl2-Sn-O2 Cl2-Sn-C5 Cl3-Sn-O1 Cl3-Sn-C5 Cl3-Sn-C5 O1-Sn-O2	$167.2 (1) \\91.5 (1) \\88.9 (1) \\80.9 (2) \\94.8 (1) \\93.0 (1) \\83.9 (2) \\87.6 (2) \\97.0 (1) \\165.9 (2) \\84.9 (2) \\92.3 (3) \\81.2 (2)$	01-Sn-C5 02-Sn-C5 Sn-C5-Sn' Sn-01-S1 01-S1-C1 01-S1-C2 C1-S1-C2 Sn-02-S2 02-S2-C3 02-S2-C4 C3-S2-C4	$\begin{array}{c} 101.8 (3) \\ 174.8 (3) \\ 130.8 (6) \\ 128.7 (3) \\ 100.5 (4) \\ 103.0 (4) \\ 100.2 (4) \\ 123.8 (3) \\ 102.7 (7) \\ 105.1 (6) \\ 97.1 (9) \end{array}$			

compounds of pseudooctahedral Sn adopt cis configurations for the structurally characterized examples $[SnCl_2Me_2(Me_2SO)_2]$,²⁴ $[SnCl_2Ph_2(Me_2SO_2]$, 4(Me₂SO), and 5(2Me_2SO). Steric arguments²⁷ would suggest that pointed monodentate groups preferentially adopt the cis pattern.

In contrast, structure 4(Me₂SO) is doubly bridged by the methylene carbon and the oxygen of the (Me_2SO) group, with each Sn atom displaying distorted trigonal-bipyramidal geometry. The bridging methylene group is in the equatorial position in both the Sn1 and Sn2 coordination while the bridging oxygen atom occupies an axial position in both cases. The equatorial positions for Sn1 are completed by C4 and C13, while the equatorial plane of Sn2 is defined by C2 and C3, in addition to the bridging methylene group. The second apical position is occupied by a Cl atom for both Sn1 and Sn2, Cl2 and Cl1, respectively. The equatorial Sn1-Cl3 distance of 2.372 (4) Å is significantly shorter than the average of the Sn-Cl-axial distances Sn1-Cl2 and Sn2-Cl1, 2.434 (4) Å average. The Sn-O distances, 2.572 (8) Å average, are essentially identical with those observed in 4, where the Me₂SO groups are likewise bridging.

The single bridged compound $7(4Me_2SO)$ displays distorted octahedral geometry about the crystallographically identical Sn atoms. The single-bridged geometry may reflect the coordinative saturation of the Sn atoms, precluding additional bridging through the Me₂SO groups, which would render the Sn atom seven-coordinate.

Figure 6 illustrates the trend in the Sn...Sn distances and the concomitant increase in the Sn–C–Sn angle in passing from triply bridged $5(2Me_2SO)$ to double bridged 4-(Me₂SO) and finally to singly bridged 7(4Me₂SO) species.

Experimental Section

General Data. Proton nuclear resonance spectra were obtained at 60 MHz by using a Varian A-60A or EM360A instrument. Chemical shifts are reported in parts per million downfield from tetramethylsilane followed in parentheses by the multiplicity, number of protons, coupling constant, and assignment. Proton-tin-119 coupling constants are reported as ⁿJ(¹¹⁹Sn-H) with the superscript donoting the number of bonds intervening between nuclei. Carbon-13 NMR spectra were obtained by using a Bruker WH-90 spectrometer with a B-NC-12 data system. All spectra were recorded in chloroform-d as solvent and as internal lock, and chemical shifts are in parts per million from internal tetramethylsilane. Gas chromatographic analyses were performed on an F & M Hewlett-Packard Model 5750 or an F & M 720 instrument using a thermal conductivity detector. All analyses were performed on a 6 ft or 17 ft \times 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 Instranal of Rensselaer, New York. Mass spectra were recorded on an AEI MS 902 mass spectrometer using the heated inlet or direct insertion methods. The spectra were run at 70 eV with an accelerating potential of 8 kV. Values are reported for the peak of highest intensity in the highest m/e cluster observed.

Bis(trimethylstannyl)methane (1). Method I. Trimethylchlorostannane (149 g, 750 mmol) and 100 mL of pentane were transferred into a 1-L, 3-neck flask, fitted with a mechanical stirrer, a Dry ice cooled cold finger, and nitrogen bubbler. Ammonia was condensed into the flask until two-thirds full. The mixture was stirred while sodium (34.6 g, 1.51 mol) in small pieces was added over a period of 5 min. The mixture was stirred 10 min longer. Methylene chloride (31.6 g) was added slowly with stirring by syringe through a septum in one neck of the flask. The ammonia was then allowed to evaporate, and the resulting mixture was extracted with 200 mL of pentane and 500 mL of water. The organic layer was washed with 500 mL of 0.1 M sulfuric acid and then with 500 mL of water. The organic layer was dried over MgSO₄, filtered, concentrated, and distilled into a liquid-nitrogen-cooled trap at 0.01 torr while being stirred at room temperature to yield 97.4 g (89%) of 1: ¹H NMR (CCl₄) δ -0.25 (s, 2, ²J(¹¹⁹Sn-H) = 63.0 Hz, SnCH₂Sn), 0.02 (s, 9, ²J(¹¹⁹Sn-H) = 54.5 Hz, CH₃Sn).

Method II. (Trimethylstannyl)sodium was prepared in a 3-neck, 250-mL round-bottom flask equipped with a wire stirrer by reaction of trimethylchlorostannane (54.9 g, 275.5 mmol) and sodium (17.0 g, 741 mmol) in 225 mL of TG or THF under nitrogen at 0 °C. The yield was 91.5% as determined by reaction of an aliquot with bromobenzene. Methylene chloride (8.81 g, 104 mmol) was added slowly by syringe with stirring at 0 °C. The product was extracted after 5 min by adding 500 mL of water and 100 mL of petroleum ether. The organic layer was washed with 500 mL of water, dried over MgSO₄, and rotary evaporated to afford 29.0 g of crude product which was distilled at 12 torr: bp 70-75 °C; 23.0 g (65%).

3-(Trimethylstannyl)-2,2,4,4,6,6-hexamethyl-2,4,6-tristannaheptane (18). This tetratin compound was isolated as a byproduct in the previous experiments. From method II the residue (6.05 g, 21% total weight) was primarily 18 with roughly 5% of 1 present by GC analysis. From method I, the residue (7.7 g, 7% of total weight, 7% yield overall) was 18 with less than 1% of 1.

Compound 18 was distilled at 0.01 torr through a short path by heating with a steam bath. Compound 1 was an impurity in the distillate and was removed by warming at 50 °C and 0.01 torr with stirring overnight. The residual 18 had the following properties: mp 29-30 °C; mass spectrum, m/e 652 (M - 15), M_2 (calcd) 667; ¹H NMR (CCl₄) $\delta - 0.75$ (s, 1, ²J(¹¹⁹Sn-CH) = 62.0 Hz, SnCH(Sn)₂), -0.25 (s, 2, ²J(¹¹⁹Sn-CH) = 62.0 Hz, SnCH₂Sn), 0.07 (s, 6, ²J(¹¹⁹Sn-CH) = 52.0 Hz, CSn(Me₂)C), 0.12 (s, 18, ²J-(¹¹⁹Sn-CH) = 52.0 Hz, Me_3 SnCSnC(SnMe₃)₂). Anal. Calcd for C₁₃H₃₈Sn₄: C, 23.40; H, 5.45. Found: C, 23.96; H, 5.47.

Bis(chlorodimethylstannyl)methane (2). Bis(trimethylstannyl)methane (3.04 g, 8.9 mmol) was placed in a round-bottom, 1-neck flask with dimethyldichlorostannane (3.91 g, 17.8 mmol). The flask was heated at 60 °C for 12 h. The trimethylchlorostannane formed was collected by distillation by warming with steam at 12–15 torr in 95% yield (98% pure). Following further heating at 0.01 torr, the product remaining contained less than 1% of trimethylchlorostannane.

A portion of the product was recrystallized from benzene for analysis: mp 59–60 °C; ¹H NMR (Cl₂CH₂) δ 0.78 (s, 12, ²J-(¹¹⁹Sn-CH) = 61.0 Hz, SnMe₂), 0.93 (s, 2, ²J(¹¹⁹Sn-CH) = 61.0, SnCH₂Sn). Anal. Calcd for C₅H₁₄Sn₂Cl₂: C, 15.70; H, 3.70. Found: C, 15.49; H, 3.63.

Bis(iododimethylstannyl)methane. Into a 250-mL roundbottom flask were placed bis(dimethylchlorostannyl)methane (7.76 g, 20.29 mmol), potassium iodide (7.94 g, 27.8 mmol), and 100 mL of acetone. The mixture was stirred overnight, concentrated an oil, and then treated with 25 mL of methylene chloride. The solution was filtered to remove sodium chloride and then rotary evaporated. The product was then placed under 0.01 torr by slowly reducing the pressure while the mixture was stirred, leaving an oil which solidified on standing (8.7 g, 98% yield). The H NMR of the product indicated that it contained about 1% trimethyliodostannane. It was further purified by dissolving in petroleum ether (150 mL) with warming, filtered, and concentrated to about 20 mL by rotary evaporation. This afforded a portion of the product recrystallized (5.3 g, 60% yield): mp 33.5–34.0 °C; ¹H NMR (CH₂Cl₂) δ 0.98 (s, 12, ²J(¹¹⁹Sn-CH) = 58.9 Hz, SnMe), 1.30 (s, 2, ²J(¹¹⁹Sn-CH) = 60.0 Hz, SnCH₂Sn).

(Trimethylstannyl)(chlorodimethylstannyl)methane (3). Equimolar amounts of bis(dimethylchlorostannyl)methane (5.5 g, 25 mmol) and bis(trimethylstannyl)methane (8.6 g, 25 mmol) were placed into a 100-mL flask and warmed at 60 °C for 12 h. The product was mixed with 100 mL of pentane and extracted with several 200-mL portions of water to remove unreacted dichloro compound. The pentane solution was then filtered, and ammonia was immediately passed through it with stirring. A white complex which formed was filtered, washed with pentane saturated with ammonia, and dried in a current of ammonia. The unreacted dichloro compound was recovered from the water extract by saturating with sodium chloride and extraction with several 50-mL portions of ether (roughly 80% recovery). The unreacted bis-(trimethylstannyl)methane was recovered quantitatively from the pentane by flash evaporation. The yield of the ammonia complex

Table III.	Summary of Ex	perimental Details and	Crystal Data	for the	Structural	Study
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	$\frac{[\operatorname{Sn}_2(\operatorname{CH}_2)(\operatorname{CH}_3)_2\operatorname{Cl}_4}{(\operatorname{Me}_2\operatorname{SO})_2]}$	$[\operatorname{Sn}_2(\operatorname{CH}_2)(\operatorname{CH}_3)_3\operatorname{Cl}_3 - (\operatorname{Me}_2\operatorname{SO})]$	$[\operatorname{Sn}_2(\operatorname{CH}_2)\operatorname{Cl}_6 - (\operatorname{Me}_2\operatorname{SO})_4]$	
	(A) Crystal Parameters	² at 23 °C		
<i>a</i> . Å	9.821 (2)	7.551 (2)	20.998 (5)	
b. A	12.411(2)	7.945 (2)	7.925 (3)	
c. Å	15.540 (3)	13.354(3)	16.535(4)	
a. deg	90.00	80.63 (2)	90.00	
B. deg	90.00	89.13 (2)	98.79 (3)	
γ deg	90.00	77.96 (2)	90.00	
V. Å ³	1894.2	755.3	2719.3	
space group	Phnm	$P\overline{1}$	C2/c	
Z	4	2	4	
$\tilde{D}(\text{calcd}), \text{ g cm}^{-3}$	2.03	2.11	1.90	
	(B) Measurement of Inten	sity Data		
cryst dimens, mm	$0.20\times0.18\times0.22$	$0.24\times0.16\times0.26$	$0.21 imes ext{ }0.23 imes ext{ }0.20$	
instrument	Nicolet R3m	l i		
radiation	Mo Kα graph	ite monochromator (equa	atorial mode)	
scan mode	$coupled \theta$ (cr	ystal)- 2θ (counter)		
scan rate	variable with	in the limits 3.0°/min and	1 30.0°/min	
scan length, deg	$[2\theta(K\alpha_{1}) - 1.0]$ to $[2\theta(K\alpha_{1}) + 1.0]$			
bkgd measurements	three reflect	ions every 100 data reflec	tions	
no, of reflctns collected	1498	1932	1837	
scan range, deg	$0 < 2 heta \leqslant 45$	$0 < 2 heta \leqslant 45$	$0 \leq 2\theta < 45$	
(C) Treatment of	of Intensity Data, Structure	e Solution, and Refinemer	nt ⁶	
reduction to $F_0{}^2$ and $\sigma(F_0)^2$	data corrected for bac in the usual manner	ekground, attenuators, and	d Lorentz-polarization	
abs coeff, cm ⁻¹	34.2	39.6	27.5	
abs correction	based on Ψ scans for five medium intensity reflections with χ angles near 90°			
obsd unique data	1109	1609	1277	
$F_{\alpha} > 6q(F_{\alpha})$				
structure soln ^{c,d}	tin positions located o non-hydrogen atoms hydrogen atoms wer stages of refinement positional and therm	n three-dimensional Patte: located on subsequent di e introduced as fixed cont ; Block-diagonal least-squa al parameters in the usual	rson maps; all other fference Fourier maps; tributors in the final ares refinement of I fashion	
final discrepancy factors: R, R_w^e	0.048, 0.047	0.045, 0.055	0.034, 0.038	

^a From a least-squares fitting of the setting angle of 25 reflections. ^b All calculations were performed on a Data General Nova 3 computer with 32K of 16-bit words using versions of the Nicolet SHELXTL interactive crystallographic softward package as described in GM Sheldrick, "Nicolet SHELXTL Operations Manual", Nicolet XRD Corp., Cupertino, 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 $R = \Sigma ||F_0| - |F_c||/\Sigma ||F_0|$; $R_w = \{\Sigma w(|F_0| - |F_0|)^2 / \Sigma ||F_0|^2\}^{1/2}$; $w = 1/\sigma^2(F)$.

based on starting bis(dimethylchlorostannyl)methane was 50% assuming a 1:1 complex: ¹H NMR (pyridine) δ 0.28 (s, 9, ²J-(¹¹⁹Sn-CH) = 54.7 Hz, SnMe₃), 0.59 (s, 2, ²J(¹¹⁹Sn-CH) = 73.0 to SnCl and 57.5 to SnMe₃, SnCH₂Sn), 0.90 (s, 6, ²J(¹¹⁹Sn-CH) = 67.2, SnMe₂Cl).

(Chlorodimethylstannyl)(dichloromethylstannyl)methane (4). Into a 100-mL, round-bottom flask was placed 9.6 g (25.1 mmol) of bis(dimethylchlorostannyl)methane with 2 mL of methylene chloride and 3.27 g (12.5 mmol) of tetrachlorostannane. The solution was warmed and the solvent removed by rotary evaporation. The flask was then heated at 60 °C for 36 h. Dimethyldichlorostannane was removed by reducing the pressure to 0.01 torr with stirring and warming to 60 °C, leaving 9.4 g (24.0 mmol, 93% yield) of product of ca. 95% purity by ¹H NMR analysis. A portion was recrystallized from CCl₄ (mp 66-67 °C) for analysis: ¹H NMR (CH₂Cl₂) δ 0.85 (s, 6, ²J(¹¹⁹Sn-CH) = 62.0 Hz, Sn(Cl)Me₂), 1.30 (s, 3, ²J(¹¹⁹Sn-CH) = 73.6 Hz, Sn(Cl₂)Me), 1.40 (s, 2, ²J(¹¹⁹Sn-CH) = 75.9 Hz for CH₂SnCl₂Me and 60.0 Hz for CH₂SnClMe₂). Anal. Calcd C₄H₁₁Sn₂Cl₃: C, 11.92; H, 2.76. Found: C, 11.88; H, 2.78.

2,2-Bis(trimethylstannyl)propane (9). (Trimethylstannyl)sodium was prepared under nitrogen from sodium (15.2 g, 660 mmol) and trimethylchlorostannane (58.59 g, 294.2 mmol) in 100 mL of pentane and 250 mL of liquid ammonia in a 3-neck 1-L round-bottom flask, equipped with a mechanical stirrer and cold finger Dry Ice-acetone cooled condenser. The flask was fitted with a septum through which 2,2-dichloropropane (15.6 g, 139 mmol) was slowly added with stirring by syringe. After the ammonia was allowed to boil off, the product was extracted with 200 mL of pentane and 700 mL of water and the pentane layer washed once with water. The pentane was removed in a rotary evaporator, and the product was treated with a solution of 2 mL of 30% hydrogen peroxide in 100 mL of acetone and stirred for several minutes (to remove hexamethyldistannane). The product was immediately treated with 200 mL of pentane and washed twice with 500-mL portions of water. The pentane layer was dried over MgSO₄, filtered, and concentrated. The product was distilled at room temperature into a liquid-nitrogen-cooled trap at 0.01 torr. This afforded 46.4 g of material (90% yield (98+% purity)): ¹H NMR (CCl₄) δ 0.02 (s, 18, ²J(¹¹⁹Sn-CH) = 50.0 Hz, SnMe₃), 1.47 (s, 6, ³J(¹¹⁹Sn-CH) = 77.5 Hz, SnC(Me₂)Sn). Anal. Calcd for C₉H₂₄Sn₂: C, 29.23; H, 6.56. Found: C, 29.68; H, 6.32.

2,2-Bis(chlorodimethylstannyl)propane (10). 2,2-Bis(trimethylstannyl)propane (46.85 g, 126.7 mmol) was placed in a 200-mL round-bottom flash with dimethyldichlorostannane (56.5 g, 257 mmol). The flask was heated at 60 °C overnight at which time the contents were entirely liquid. The bulk of the byproduct trimethylchlorostannane was removed with stirring at 15-20 torr into an ice-cooled receiver by using a steam bath temperature. The remaining byproduct was removed by warming at 0.01 torr to 100 °C. ¹H NMR analysis of the product indicated 1% or less of the byproduct trimethylchlorostannane remained after the high vacuum treatment. This afforded the product (49.8 g, 120 mmol), a 95% yield on the controversion. Further purification was accomplished by recrystallization from CCl₄: mp 110-111 °C; ¹H NMR (Cl₂CH₂) δ 0.70 (s, 12, ²J(¹¹⁹Sn-CH) = 55.5 Hz, SnMeCl, $1.73 (s, 6, {}^{3}J({}^{119}Sn-CH) = 94.5 Hz, SnC(Me_2)Sn)$. Anal. Calcd for C₇H₁₈Sn₂Cl₂: C, 20.33; H, 5.12. Found: C, 20.23; H, 4.82.

2-(Chlorodimethylstannyl)-2-(dichloromethylstannyl)propane (11). Into a 100-mL, round-bottom flask was placed 13.02 g (31.50 mmol) of 2,2-bis(dimethylchlorostannyl)propane along with 2 mL of methylene chloride and 4.0 g (15.4 mmol) of tetrachlorostannane. The solution was warmed and the solvent removed by rotary evaporation. The flask was warmed and the solvent removed by rotary evaporation. The flask was warmed to 60 °C overnight. Dimethyldichlorostannane was removed at 0.01 torr with stirring at 60 °C, leaving 13.0 g (30.0 mmol, 95%) of product of ca. 95% purity by ¹H NMR analysis. The product was recrystallized from petroleum ether to afford 10.3 g (24.0 mmol, 75%)d of product: mp 50-51 °C; ¹H NMR (Cl₂CH₂) δ 0.78 (s, 6, ²J(¹¹⁹Sn-CH) = 56.0 Hz, Sn(Cl)Me₂), 1.23 (s, 3, ²J(¹¹⁹Sn-CH) = 61.0 Hz, Sn(Cl₂)Me), 1.78 (s, 3, ³J(¹¹⁸Sn-CCH = 139.3 Hz for Me₂CSnCl₂Me and 83.2 Hz for Me₂CSnClMe₂). Anal. Calcd for C₆H₁₅Sn₂Cl₃: C, 16.72; H, 3.56. Found: C, 16.74; H, 3.59.

Bis(dichloromethylstannyl)methane (5) and 2,2-Bis(dichloromethylstannyl)propane (12). Into a 100-mL roundbottom flask were placed 12–13 mmol of bis(dimethylchlorostannyl)methane or 2,2-bis(dimethylchlorostannyl)propane. An excess of tetrachlorostannane (5–7 g, 19–27 mmol) was added slowly after the addition of 5 mL of methylene chloride. The solution was agitated for 5 min and then concentrated by rotary evaporation. The product was heated at 60 °C overnight. The reaction was shown to be complete by the disappearance of methyltin peaks in the region: δ 0.5–0.8 (R–Sn(Me₂)Cl. The dimethyldichlorostannane, methyltrichlorostannane, and unreacted tetrachlorostannane were removed by slowly reducing the pressure to 0.01 torr and warming to 60 °C for 0.5 h. The residue was recrystallized from CCl₄ to afford 70% of product in each case.

2,2-Bis(dichloromethylstannyl)propane (11): mp 96–98 °C; ¹H NMR (Cl₂CH₂) δ 1.38 (s, 6, ²J(¹¹⁹Sn–CH) = 66.0 Hz, SnMe), 1.93 (2, 6, ³J(¹¹⁹Sn–CCH) = 128.0 Hz, (Sn)₂CMe₂). Anal. Calcd for C₅H₁₂Sn₂Cl₄: C, 13.30; H, 2.69. Found: C, 13.20; H, 2.64.

Bis(dichloromethylstannyl)methane (5): mp 62–64 °C; ¹H NMR (Cl₂OH₂) δ 1.44 (s, 6, ²J(¹¹⁹Sn–CH) = 78.0 Hz, SnMeCl₂), 1.93 (s, 2, ²J(¹¹⁹Sn–CH = 68.0 Hz, SnCH₂Sn). Anal. Calcd for C₃H₈Sn₂Cl₄: C, 8.51; H, 1.91. Found: C, 8.43; H, 2.06.

Bis(trivinylstannyl)methane (6). Into a 500-mL, 3-neck, round-bottom flask, equipped with a stirrer, a serum cap, and Dry ice cap, and Dry ice-acetone condenser was placed 25.5 g (108 mmol) of trivinylchlorostannane along with 100 mL of petroleum ether under an atmosphere of nitrogen. Ammonia (200 mL) was condensed into the flask with stirring. Sodium (5.2 g, 226 mmol) was added over a period of 3-5 min as stirring was continued. To the resulting pale yellow solution was added 4 mL (5.2 g, 61 mmol) of methylene chloride slowly by syringe.

The ammonia was allowed to boil off, and 100 mL of petroleum ether was added with stirring. The mixture was filtered and the solvent removed by rotary evaporation, and the product was pot-to-pot distilled into a liquid-nitrogen-cooled receiver at 0.01 torr, with warming with steam. The distillate was stirred for 10 min at 1 torr to remove traces of solvent and lower boiling impurities affording 15.3 g (38 mmol, 70% yield) of product of ca.d 95% purity by GC analysis. A portion of the product was GC purified for characterization: ¹H NMR (CCl₄) δ 0.05 (s, 2, ²J-(¹¹⁹Sn-CH) = 61.0 Hz, SnCH₂Sn), 5.37-6.63 (m, 18, SnCH=CH₂). Anal. Calcd for C₁₃H₂₀Sn₂: C, 37.74; H, 5.03. Found: C, 37.77; H. 5.03.

Bis(trichlorostannyl)methane (7). Into a 250-mL, roundbottom flask was placed 26.1 g (63.1 mmol) of bis(trivinylstannyl)methane along with 200 mL of methylene chloride. The solution was cooled to 0 °C and 25 mL (56.5 g, 217 mmol) of tetrachlorostannane was added cautiously. After 5 min the solvent was removed by rotary evaporation, and the solution was cooled to 0 °C, and 25 mL of SnCl₄ (56.5 g, 217 mmol) was added. It was warmed to 60 °C for 72 h, the flask cooled to room temperature, and the pressure slowly reduced to 0.01 torr and held at this pressure for 15 min with slight warming. The product was removed, treated with 2 g of activated charcoal in 50 mL of CCl₄ with stirring for 10 min, and filtered. Removal of the solvent by rotary evaporation afforded 27.7 g (95 mmol) of crude product. This was treated in 200 mL of warm petroleum ether which was decanted from a dark oil. The solvent was removed by rotary evaporation and the product distilled pot-to-pot at 0.01 torr by

Table IV. Final Positional Parameters for the Structural Studies of Sn₂(CH₂)(CH₃)₂Cl₄(Me₂SO)₂, Sn₂(CH₂)(CH₃)₃Cl₃(Me₂SO), and Sn₂(CH₂)Cl₆(Me₂SO)₄

atom	x	У	z			
(a) $Sn_2(CH_2)(CH_3)_2Cl_4(Me_2SO)_2$						
Sn1 Sn2 Cl1 Cl2 S1 O1 C1 C2 C3 C4 C5	0.81308 (7) 1.15277 (7) 1.2974 (2) 0.7209 (2) 0.9187 (2) 0.9554 (5) 1.0112 (9) 1.1787 (12) 0.6755 (13) 1.0511 (9) 0.9651 (13)	0.59388 (6) 0.65657 (6) 0.6937 (2) 0.4921 (1) 0.7485 (1) 0.7009 (4) 0.5285 (8) 0.8259 (10) 0.7250 (12) 0.8433 (7) 0.6487 (8)	0.75000 0.75000 0.6319 (2) 0.8693 (2) 0.5545 (1) 0.8579 (4) 0.7500 0.7500 0.7500 0.9688 (7) 1.0229 (7)			
	(b) $\operatorname{Sn}_2(\mathbf{C})$	H_2)(CH ₃) ₃ (Me ₂ S	0)			
Sn1 Sn2 Cl1 Cl2 Cl3 S1 O1 C1 C2 C3 C4 C5 C6	$\begin{array}{c} 0.08444 \ (9) \\ 0.29589 \ (10) \\ 0.2836 \ (5) \\ -0.0662 \ (5) \\ 0.3043 \ (5) \\ 0.4048 \ (5) \\ 0.2767 \ (9) \\ 0.2099 \ (16) \\ 0.5865 \ (17) \\ 0.1044 \ (18) \\ -0.1218 \ (18) \\ 0.2594 \ (20) \\ 0.4396 \ (19) \end{array}$	$\begin{array}{c} 0.47585(8)\\ 0.27512(9)\\ 0.4160(5)\\ 0.7816(5)\\ 0.4266(5)\\ 0.0092(5)\\ 0.1558(9)\\ 0.5154(16)\\ 0.1411(18)\\ 0.1262(19)\\ 0.3507(18)\\ -0.0467(20)\\ -0.1879(17)\end{array}$	$\begin{array}{c} 0.29397(7)\\ 0.08809(7)\\ -0.0903(3)\\ 0.3115(3)\\ 0.4287(3)\\ 0.3544(3)\\ 0.2774(6)\\ 0.1544(10)\\ 0.1002(13)\\ 0.0720(13)\\ 0.3484(11)\\ 0.4569(11)\\ 0.2974(12) \end{array}$			
(c) $\operatorname{Sn}_2(\operatorname{CH}_2)\operatorname{Cl}_6(\operatorname{Me}_2\operatorname{SO})_4$						
Sn Cl1 Cl2 Cl3 S1 S2 O1 O2 C1 C2 C3 C4 C5	0.41333(3) 0.4307(1) 0.3807(1) 0.4767(1) 0.2649(1) 0.4440(3) 0.3260(3) 0.4850(5) 0.4114(5) 0.2515(8) 0.2016(7) 0.5000	$\begin{array}{c} 0.29665(7)\\ 0.2167(3)\\ 0.4247(3)\\ 0.0361(3)\\ 0.6078(3)\\ 0.4283(3)\\ 0.5433(5)\\ 0.3901(6)\\ 0.7921(11)\\ 0.6997(16)\\ 0.6430(16)\\ 0.3511(16)\\ 0.1852(15)\\ \end{array}$	$\begin{array}{c} 0.69082(3)\\ 0.5521(1)\\ 0.8127(1)\\ 0.7045(1)\\ 0.5962(1)\\ 0.6622(2)\\ 0.6682(3)\\ 0.6237(3)\\ 0.8598(5)\\ 0.5289(5)\\ 0.5289(5)\\ 0.6401(10)\\ 0.5931(9)\\ 0.7500\\ \end{array}$			

warming with steam, affording 25.2 g (87%) of product: mp 63–65 °C; ¹H NMR (CCl₄) δ 2.28 (s, 2, ²J(¹¹⁹Sn–CH) = 93.0 Hz, Cl₃SnCH₂SnCl₃). Anal. Calcd for CH₂Sn₂Cl₆: C, 2.59; H, 0.44. Found: C, 2.72; H, 0.99.

(Trichlorostannyl)(dichloromethylstannyl)methane (6). Into a 10-mL test tube were placed 3.92 g (8.4 mmol) of bis-(trichlorostannyl)methane, 1.06 (5.34 mmol) of trimethylchlorostannane, and 5 mL of methylene chloride. The mixture was shaken and then allowed to stand 1 week. The solvent was removed by rotary evaporation and the product heated at 75 °C at 0.01 torr for 0.5 h. The residue was recrystallized from petroleum ether to afford 1.0 g (43%) of product: mp 68-70 °C; ¹H NMR (CH₂Cl₂) δ 1.44 (s, 3, ²J(¹¹⁹Sn-CH) = 78.0 Hz, SnMe), 2.08 (s, 2, ²J(¹¹⁹Sn-CH) = 105.5 Hz to CH₂SnCl₃ and 62.5 Hz to CHSnCl₂Me). Anal. Calcd for C₂H₅Sn₂Cl₅: C, 5.41; H, 1.14. Found: C, 4.91; H, 1.40.

¹H NMR Studies of Complexation between the Halotins and Dimethyl Sulfoxide. To 0.50 mL of a solution of the chlorostannane (0.20–0.30 M) in CH₂Cl₂ or acetone- d_6 were added increments of Me₂SO, and the spectra were scanned at the normal probe temperature after each addition. Plots of proton chemical shifts or ²J(¹¹⁹Sn⁻¹H) or both vs. Me₂SO concentration are shown in the figures.

Organohalostannane–Dimethyl Sulfoxide Complexes. In a typical procedure 0.367 g (0.96 mmol) of bis(dimethylchlorostannyl)methane, 2, was dissolved in 3 mL of CCl_4 and 0.068 mL (1 mmol) of Me₂SO was added. An oil which separated solidified upon standing at 5 °C. The solvent was decanted, and 0.5 mL of warm CH_2Cl_2 was used to dissolve the oil. Cooling to room temperature followed by storage at -22 °C provided crystals, mp 72–74 °C. Anal. Calcd for $C_7H_{20}Sn_2Cl_2SO$: C, 18.25; H, 4.39. Found: C, 18.05; H, 4.36.

This general procedure was followed for the other complexes listed below. The products were analytically pure after a single recrystallization, but some isolated yields were low due to the solubility of the complexes.

2,2-Bis(chlorodimethylstannyl)propane-dimethyl sulfoxide: from CH_2Cl_2 ; mp 116-117 °C. Anal. Calcd for $C_9H_{24}Sn_2Cl_2SO$: C, 22.12; H, 4.96. Found: C, 22.21; H, 4.96.

Bis(dichloromethylstannyl)methane-bis(dimethyl sulfoxide): from methanol; mp 150-153 °C. Anal. Calcd for

C₇H₂₀Sn₂Cl₄S₂O₂: C, 14.51; H, 3.49. Found: C, 14.59; H, 3.57. 2,2-Bis(dichloromethylstannyl)propane-bis(dimethyl sulfoxide): from methanol; mp 149-154 °C. Anal. Calcd for

 $C_9H_{24}Sn_2Cl_4S_2O_2$: C, 17.79; H, 3.99. Found: C, 17.86, H, 4.11. (Chlorodimethylstannyl)(dichloromethylstannyl)-

methane-dimethyl sulfoxide: from CCl_4 ; mp 107–108 °C. Anal. Calcd for C₆H₁₇Sn₂Cl₃SO: C, 14.98; H, 3.57. Found: C, 14.76; H, 3.65.

2-(Chlorodimethylstannyl)-2-(dichloromethylstannyl)propane-dimethyl sulfoxide: from CCl₄; 91% yield; mp 112–113 °C. Anal. Calcd for $C_8H_{21}Sn_2Cl_3SO$: C, 18.87; H, 4.17. Found: C, 19.11; H, 4.25.

(Trichlorostannyl)(dichloromethylstannyl)methanetris(dimethyl sulfoxide): from Me_2SO/CH_2Cl_2 , 49%; mp 171-173 °C. Anal. Calcd for $C_8H_{23}Sn_2S_3O_3Cl_5$: C, 14.70; H, 3.4. Found: C, 14.07; H, 3.26.

Bis(trichlorostannyl)methane-tetrakis(dimethyl sulfoxide): from CCl_4/Me_2SO , 4/1; CH_2Cl_2 washing, 42% yield; mp 169-173 °C. Anal. Calcd for $C_9H_{26}Sn_2S_4O_4Cl_6$: C, 14.01; H, 3.38. Found: C, 14.30; H, 3.47.

Crystallographic Data Collection and Structure Refinement and Solution. The details for the crystallographic study of the compounds are summarized in Table III and the supplementary material. Full details of the routine crystallographic procedures are described in ref 28.

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Registry No. 1, 16812-43-4; 2, 83135-39-1; 2 dimethyl sulfoxide, 83135-49-3; 3, 83135-40-4; 4, 79992-67-9; 4 dimethyl sulfoxide, 79992-49-7; 5, 79992-66-8; 5 bis(dimethyl sulfoxide), 83198-38-3; 6, 83135-41-5; 6 tris(dimethyl sulfoxide), 83135-51-7; 7, 79992-68-0; 7 tetrakis(dimethyl sulfoxide), 83198-39-4; 8, 83135-42-6; 9, 83135-43-7; 10, 83135-44-8; 10 dimethyl sulfoxide, 83135-40-0; 12 bis(dimethyl sulfoxide), 83152-02-7; 12, 83135-46-0; 12 bis(dimethyl sulfoxide), 83152-01-6; 18, 83135-47-1; Me₃SnCl, 1066-45-1; CH₂Cl₂, 75-09-2; Me₃SnNa, 16643-09-7; Me₂SnCl₂, 753-73-1; KI, 7681-11-0; SnCl₄, 7646-78-8; 2,2-dichloropropane, 594-20-7; bis(iododimethylstannyl)methane, 83135-48-2; chlorotrivinylstannane, 10008-90-9.

Supplementary Material Available: Tables of anisotropic thermal parameters and calculated and observed structure factors for compounds 4-6 (30 pages). Ordering information is given on any current masthead page.

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Pentacarbonyl[tris(phenylethynyl)phosphine]chromium(0), Cr(CO)₅P(C≡CPh)₃: Spectral, Structural, and MO Characteristics

Axel Hengefeld, Jürgen Kopf, and Dieter Rehder*

Institut für Anorganische Chemie der Universität Hamburg, D 2000-Hamburg 13, Federal Republic of Germany

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The crystal and molecular structures of $Cr(CO)_5P(C = CPh)_3$ have been determined ($R_w = 0.057$). The complex crystallizes in space group $P\overline{1}$ with a = 1095.8 (6) pm, b = 1656.2 (8) pm, c = 1689.4 (8) pm, $\alpha = 101.34$ (4)°, $\beta = 108.97$ (4)°, and $\gamma = 105.76$ (5)°. The ligand strength (σ donor and π acceptor capability) of $P(C = CPh)_3$ relative to that of PPh_3 and $P(OPh)_3$ is discussed on the basis of structural data, spectroscopic parameters (IR, ³¹P NMR of $W(CO)_5P(C = CPh)_3$), and SCCCMO calculations carried out on $C = CH^-$ and $P(C = CH)_3$. $P(C = CPh)_3$ is considered a strong σ -interacting ligand (mainly via $P(3p_z)$) but only a moderate π acceptor for $Cr \rightarrow P(3d)$ delocalization. An approach is made to explain structural and spectral features through direct $\pi^*(CO) \rightarrow \pi^*(C = C)$ interaction.

Introduction

There is continuing interest in correlations between structural data and spectral parameters in a series of similar complexes. In transition-metal carbonyl complexes, variations in ligand properties such as the π -acceptor and σ -donor power induce, inter alias, changes in the π^* occupation of the carbonyl set, which are reflected in the M-(CO) and C-O stretching modes of the vibrational spectra. On the other hand, the extent to which the originally degenerate metal d orbitals are split by varying interactions with ligands of differing integral strengths (and, correspondingly, the quality and quantity of electron population in the resulting molecular orbitals) is parallelled by changes in NMR parameters such as the nuclear shielding and the scalar interaction of the atoms participating in the metal-ligand bond. It is commonly accepted that excessive steric strains are closely related to unusual bond parameters as obtained from an X-ray structural analysis (this has recently again been shown by comparing the two complexes $W(CO)_5PMe_3^1$ and $W(CO)_5P(t-Bu)_3^2$).

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