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Synthesis and Molecular Structure of Diphenylgallium and -indium Stannanethiolates: {$Ph_2M[\mu\text{-}SSn(C_6H_{11})_3]$}$_2$. Potential Precursors to Ternary Materials

Shahid U. Ghazi, Mary Jane Heeg, and John P. Oliver*

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

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The reaction of triphenylgallium and -indium derivatives, Ph_3M (M = Ga, In), with bis(tricyclohexyltin) sulfide, $[(C_6H_{11})_3Sn]_2S$, yields {$Ph_2M[\mu\text{-}SSn(C_6H_{11})_3]$}$_2$ (M = Ga, **1**; In, **2**) and the corresponding organotin compound, $PhSn(C_6H_{11})_3$. The resulting derivatives have been characterized by analysis and by ^1H, ^{13}C, and ^{119}Sn NMR spectroscopy. The structures of **1** and **2** were determined by single-crystal X-ray diffraction techniques and found to be isomorphous in the triclinic space group $P\bar{1}$(No. 2) with cell constants $a = 10.825(2)$ Å, $b = 11.465(3)$ Å, $c = 13.615(3)$ Å, $\alpha = 80.68(2)°$, $\beta = 77.95(2)°$, and $\gamma = 63.78(1)°$ for **1** and $a = 11.198(4)$ Å, $b = 11.441(4)$ Å, $c = 13.612(3)$ Å, $\alpha = 80.15(2)°$, $\beta = 79.16(2)°$, and $\gamma = 62.36(2)°$ for **2** with $Z = 1$ (dimer). The structure for **1** refined to a final $R = 5.0\%$ ($R_w = 5.2\%$) based on 3634 ($I > 3\sigma(I)$) observed reflections and for **2** to a final $R = 3.0\%$ ($R_w = 3.6\%$) based on 4107 ($I > 3\sigma(I)$) observed reflections. The compounds are dimeric with the $Sn(C_6H_{11})_3$ moieties in the *anti* configuration. The Ga−S and Sn−S bond distances in **1** are 2.34(3) and 2.40(3) Å. In **2** the In−S and Sn−S bond distances are 2.55(2) and 2.44(2) Å.

Introduction

Indium−tin oxide thin films are important because of their high transparency and low electrical resistivity, and they are useful in a number of applications such as transparent electrodes, display panels, radiation insulation, and solar energy collection.[1−4] The chemistry of the heavier group 13 organometallic compounds, their group 15 derivatives, and their alkoxides has been extensively studied.[5]

Nomura, et al.,[6] have carried out studies in which they reacted $Bu_2In(OCOEt)$ with Bu_2SnO and then pyrolized the product to obtain $InSnO_x$. They have also investigated the reaction of $i\text{-}Bu_2In(S\text{-}n\text{-}Pr)$ with $Cu(S_2CN\text{-}n\text{-}Bu_2)_2$ to form a mixed copper−indium complex used in the formation of $InCuS_2$ thin films. Some work has been reported also on the heavier chalcogens.[7,8] The preparation of ternary compounds containing a group 13 element, a second metal, and a chalcogen has been very limited. We recently reported the synthesis and structures of organoaluminum and -gallium stannoxanes.[9] The chemistry of the related organogallium and -indium stannanethiolates is unknown. The development of procedures for the synthesis of these materials and the related III−IV−VI (13−14−16) materials is of importance if they are to become of value industrially.

This study is an extension of our previous work.[9] In this paper we report the synthesis and characterization of the first heterobimetallic complexes, {$Ph_2M[\mu\text{-}SSn(C_6H_{11})_3]$}$_2$ (M = Ga, In), formed by the reaction of bis(tricyclohexyltin) sulfide, $[(C_6H_{11})_3Sn]_2S$, with triphenylgallium and -indium. No reaction was observed with the saturated derivatives, R_3Al (R = Me, *i*-Bu), under similar conditions. The crystal and molecular structures of the organogallium stannanethiolates, {$Ph_2Ga[\mu\text{-}SSn(C_6H_{11})_3]$}$_2$, and organoindium stannanethiolates, {$Ph_2In[\mu\text{-}SSn(C_6H_{11})_3]$}$_2$ are reported.

Experimental Section

General Experimental Procedures. All solvents were purified and dried by standard techniques.[10] Argon gas was purified by passing it through a series of columns containing Deox catalyst (Alfa), phosphorus pentaoxide and calcium sulfate. Ph_3Ga and Ph_3In were prepared by literature methods.[11] Aluminum alkyls (Aldrich: Me_3Al, 2 M solution in toluene, *i*-BuAl, 1 M solution in toluene) and $[(C_6H_{11})_3Sn]_2S$ (Aldrich)—$^{13}C\{^1H\}$: C1, $\delta = 32.83$, $^1J_{Sn-C} = 322, 309$ Hz; C2, 6, $\delta = 32.56$, $^2J_{Sn-C} = 13$ Hz; C3, 5, $\delta = 29.74$, $^3J_{Sn-C} = 62$ Hz; C4, $\delta = 27.42$) were used as received. All of the glassware used in the synthetic work was oven dried. The compounds are both oxygen and water sensitive so standard Schlenk line techniques or an argon-filled drybox were employed throughout this work. ^1H and ^{13}C NMR spectra were recorded either on a General Electric QE-300 NMR or on a GN-300 NMR spectrometer. The chemical shifts were referenced to the residual proton line from benzene-d_6 ($\delta = 7.15$ ppm for ^1H; $\delta = 128.0$ ppm for ^{13}C). The ^{119}Sn NMR spectra were obtained on the GN-300 NMR spectrometer with a ^1H gated decoupling sequence (no NOE) with a tin center band frequency of 111.91 MHz, delay time of 4 s, and pulse width of 9.30 μs. The temperature was maintained at 60 °C because of the limited solubility of the compounds in benzene. Chemical shifts were referenced with Me_4Sn as standard.

Preparation of {$Ph_2Ga[\mu\text{-}SSn(C_6H_{11})_3]$}$_2$ (1). Bis(tricyclohexyltin) sulfide (0.64 g, 0.83 mmol) was mixed with Ph_3Ga (0.25 g, 0.83 mmol) in hexane (ca. 60 mL). After a few minutes of stirring the reactants dissolved, and a precipitate was deposited from the solution. The precipitate was dissolved by addition of 10 mL of toluene and warming to 70 °C. When this solution was allowed to stand at room temperature for 24 h, crystals were deposited which were isolated at 0 °C, washed

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Table 1. Selected Experimental Parameters for the X-ray Diffraction Study of $\{Ph_2Ga[\mu\text{-}SSn(C_6H_{11})_3]\}_2$, **1**, and $\{Ph_2In[\mu\text{-}SSn(C_6H_{11})_3]\}_2$, **2**

	1	**2**
compound	$\{Ph_2Ga[\mu\text{-}SSn(C_6H_{11})_3]\}_2$	$\{Ph_2In[\mu\text{-}SSn(C_6H_{11})_3]\}_2$
formula	$C_{30}H_{43}GaSnS$	$C_{30}H_{43}InSnS$
space group	$P1$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	10.825(2)	11.198(4)
b, Å	11.465(3)	11.441(4)
c, Å	13.615(3)	13.612(3)
α, deg	80.68(2)	80.15(2)
β, deg	77.95(2)	79.16(12)
γ, deg	63.78(1)	62.36(2)
Z	1 (dimer)	1 (dimer)
vol, $Å^3$	1477.8(5)	1510.4(7) $Å^3$
density (calcd), g cm^{-3}	1.403	1.472
radiation type	Mo $K\bar{\alpha}$; λ = 0.710 73 Å; graphite monochromator	Mo $K\alpha$; λ = 0.710 73 Å; graphite monochromator
temp, °C	22	22
linear abs coeff (μ), cm^{-1}	18.39	16.63
R,[a] %	5.0	3.0
R_w,[b] %	5.2	3.6

[a] $R = (\Sigma|\Delta F|)/\Sigma|F_o|$. [b] $R_w = [(\Sigma w|\Delta F|^2)/\Sigma wF_o^2]^{1/2}$; $w^{-1} = \sigma F^2 + 0.00005F^2$.

Table 2. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $\{Ph_2Ga[\mu\text{-}SSn(C_6H_{11})_3]\}_2$, **1**

atom	*x*	*y*	*z*	U_{eq},[a] $Å^2$
Sn1	0.12274(5)	0.65284(5)	0.77095(4)	0.0645(2)
Ga1	0.14012(7)	0.46995(7)	1.04120(5)	0.0599(4)
S1	0.0000(2)	0.6418(2)	0.9387(1)	0.075(1)
C1	0.2561(9)	0.4658(7)	0.7121(5)	0.074(4)
C2	0.184(1)	0.421(1)	0.663(1)	0.22(1)
C3	0.278(2)	0.288(1)	0.621(2)	0.25(1)
C4	0.399(1)	0.284(1)	0.5574(7)	0.125(6)
C5	0.473(1)	0.328(1)	0.607(1)	0.172(8)
C6	0.383(1)	0.461(1)	0.648(1)	0.163(8)
C7	−0.0455(8)	0.7613(8)	0.6848(5)	0.079(4)
C8	0.0061(9)	0.8097(8)	0.5852(7)	0.102(5)
C9	−0.106(1)	0.883(1)	0.5181(7)	0.120(6)
C10	−0.230(1)	0.984(1)	0.5712(8)	0.127(6)
C11	−0.2831(9)	0.936(1)	0.6702(8)	0.124(6)
C12	−0.1701(9)	0.8641(9)	0.7359(6)	0.105(5)
C13	0.230(1)	0.766(1)	0.7914(9)	0.128(7)
C14	0.166(2)	0.851(1)	0.8672(9)	0.19(1)
C15	0.234(2)	0.945(1)	0.876(1)	0.18(1)
C16	0.340(3)	0.923(3)	0.811(2)	0.35(3)
C17	0.384(2)	0.881(2)	0.719(1)	0.21(1)
C18	0.322(1)	0.785(1)	0.714(1)	0.20(1)
C19	0.1444(7)	0.5494(7)	1.1571(5)	0.064(3)
C20	0.0693(8)	0.6816(9)	1.1730(6)	0.090(5)
C21	0.083(1)	0.733(1)	1.2527(9)	0.177(6)
C22	0.173(1)	0.654(1)	1.3183(8)	0.121(7)
C23	0.247(1)	0.527(1)	1.3043(7)	0.110(6)
C24	0.2326(8)	0.4744(8)	1.2242(6)	0.083(4)
C25	0.3234(7)	0.3535(6)	0.9754(5)	0.058(3)
C26	0.3605(8)	0.2246(7)	0.9543(6)	0.073(4)
C27	0.494(1)	0.1469(7)	0.9111(6)	0.084(4)
C28	0.5929(9)	0.1954(9)	0.8853(6)	0.094(5)
C29	0.56158)	0.3182(9)	0.9059(6)	0.084(4)
C30	0.4275(7)	0.3970(7)	0.9507(5)	0.066(3)

[a] $U_{eq} = {}^1/_3\Sigma_i\Sigma_j\mathbf{U}_{ij}a_i^*\cdot a_j^*\bar{a}_i\cdot\bar{a}_j$.

with pentane, and dried under vacuum. The compound was identified from its ^1H, ^{13}C, and ^{119}Sn NMR spectra and by chemical analysis as $\{Ph_2Ga[\mu\text{-}SSn(C_6H_{11})_3]\}_2$. Yield: 60%. Mp: 196 °C dec. Anal. Calcd for $C_{30}H_{43}GaSnS$: C, 57.7; H, 6.94; Found: C, 57.51; H, 6.88. ^1H NMR (C_6D_6, δ, ppm): 7.15−8.31 (m, 10H, Ph); 2.16−2.19 (m, 3H); 1.0−1.79 (m, 30H); $^{13}C\{^1H\}$ NMR (C_6D_6, δ, ppm): 147.9, 137.4, 137.2, 128.5, Ph; 33.3, 32.5 32.2, 32.1, 29.7, 29.2, 27.4, 27.1 , $^3J_{Sn-C} = 65$ Hz (two $Sn(C_6H_{11})_3$ groups). ^{119}Sn $\{^1H$, no NOE$\}$ NMR (C_6D_6, δ, ppm): 43.14, 22.63. Mass spectral data (EI mode): peaks at *m/e* 363, 281, 196, 120, 78, and 55 corresponding to fragments $(C_6H_{11})_3Sn^{\cdot+}$, $(C_6H_{11})_2Sn^{\cdot+}$, $C_6H_{11}Sn^{\cdot+}$, $Sn^{\cdot+}$, $C_6H_{11}{}^{\cdot+}$, and $C_4H_7{}^+$ were observed.

Preparation of $\{Ph_2In[\mu\text{-}SSn(C_6H_{11})_3]\}_2$ (2). Bis(tricyclohexyltin) sulfide (1.04 g, 1.35 mmol) was mixed with Ph_3Ga (0.47 g, 1.35 mmol) in pentane (ca. 60 mL). The reaction proceeded as described for **1** and was worked up in an identical manner. The compound was identified from its ^1H, ^{13}C, and ^{119}Sn NMR spectra and by chemical analysis as $\{Ph_2In[\mu\text{-}SSn(C_6H_{11})_3]\}_2$. Yield: 60%. Mp: 230 °C dec. Anal. Calcd for $C_{30}H_{43}InSnS$: C, 53.84; H, 6.47; Found: C, 54.76; H, 6.73. ^1H NMR (C_6D_6, δ, ppm): 7.22−8.21 (m, 10H, Ph); 2.16−2.19 (m, 3H); 0.99−1.86 (m, 30H). $^{13}C\{^1H\}$ NMR (C_6D_6, δ, ppm): 139.1, 138.9, 138.7, 128.4, Ph; 33.1, 32.6, 32.2, 29.7, 29.1, 27.4, 27.0, $^3J_{Sn-C} = 63$ Hz (two $Sn(C_6H_{11})_3$ groups). ^{119}Sn $\{^1H$, no NOE$\}$ NMR (C_6D_6, δ, ppm): −126.5, 87.0. Mass spectral data (EI mode): peaks at *m/e* 363, 281, 196, 120, 78, and 55 corresponding to fragments $(C_6H_{11})_3Sn^{\cdot+}$, $(C_6H_{11})_2SnS^{\cdot+}$, $C_6H_{11}Sn^{\cdot+}$, $Sn^{\cdot+}$, $C_6H_{11}{}^{\cdot+}$, and $C_4H_7{}^+$ were observed.

Attempted Reactions of Bis(tricyclohexyltin) Sulfide with Trialkylaluminum and -gallium Derivatives. No reactions of $[(C_6H_{11})_3Sn]_2S$ with alkylaluminum, R_3Al (R = Me, *i*-Bu), and trimethylgallium were observed in pentane, hexane, and diethyl ether at 22 °C or under reflux conditions as shown by the quantitative recovery of the starting material bis(tricyclohexyltin) sulfide.

Structure Determination of $\{Ph_2Ga[\mu\text{-}SSn(C_6H_{11})_3]\}_2$ (1) and $\{Ph_2In[\mu\text{-}SSn(C_6H_{11})_3]\}_2$ (2). Crystals of **1** and **2** were grown from a pentane/toluene solution at room temperature. In each case a crystal suitable for X-ray diffraction studies was mounted in a thin-walled capillary tube in a drybox, and the tube was plugged with grease, removed from the drybox, flame sealed, mounted on a goniometer head, and placed on a Nicolet $P2_1$ diffractometer for data collection. Crystal and data collection parameters are presented in Table 1.

The crystals of **1** and **2** were found to be triclinic. Lattice constants were verified by axial photographs. **1** and **2** were assigned to the space group $P\bar{1}$ (No. 2), which was later confirmed by successful refinement of the structure. Data reduction and calculations were carried out using the SHELXTL program.[12] Direct method routines produced acceptable solutions for the structures, yielding positions for some of the non-hydrogen atoms while other atoms were located during subsequent refinement. Full-matrix least-squares refinement was carried out using SHELX-76.[13] The data were corrected for Lorentz and polarization effects, and scattering factors for neutral carbon, sulfur, tin, gallium, and indium atoms were used. No correction for secondary extinction was made. Disorder in the cyclohexyl rings resulted in large thermal parameters for some carbon atoms and some unreasonably short C−C distances. Hydrogen atomic positions were observed or calculated, riding on the carbon atoms to which they were bound. Additional cycles of refinement of the data led to a convergence with *R* = 5.0% (R_w = 5.2%) for **1**, and *R* = 3.0% (R_w = 3.6%) for **2**. The atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms of **1** and **2** are presented in Tables 2 and 3.

Results and Discussion

The bis(triorganotin) sulfides have bent structures with minimal $p\pi(S)-d\pi(Sn)$ bonding.[14] As a consequence, the sulfur atom of stannanethiolates may act as a basic site and form adducts with Lewis acids. We took advantage of this and the reactivity of the Sn−S bonds in our effort to prepare mixed metal chalcogenides of the form $[R_2M(\mu\text{-}SSnR'_3)]_n$ (R = alkyl, Ph; M = Ga, In; R′ = cyclohexyl). A general scheme for the reaction is shown in eq 1 and is similar to that proposed for the $(R_3Sn)_2O$ reaction discussed previously.[9] The complexes, $\{Ph_2M[\mu\text{-}SSn(C_6H_{11})_3]\}_2$ (M = Ga, In), are formed in high yield

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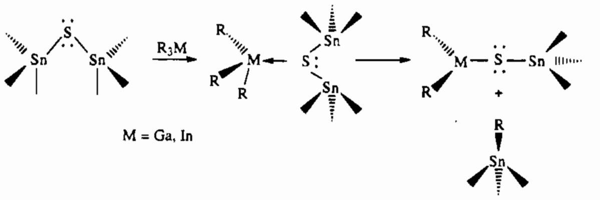
Table 3. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $\{Ph_2In[\mu\text{-}SSn(C_6H_{11})_3]\}_2$, **2**

atom	x	y	z	U_{eq},[a] Å^2
In1	0.15093(3)	0.46783(3)	1.04875(2)	0.0551(2)
Sn1	0.10953(3)	0.67073(3)	0.76616(2)	0.0561(1)
S1	−0.0078(1)	0.6547(1)	0.93490(8)	0.0566(5)
C1	0.2528(5)	0.4778(4)	0.7175(3)	0.064(2)
C2	0.1837(6)	0.3962(6)	0.7160(5)	0.101(3)
C3	0.2832(8)	0.2598(6)	0.6788(6)	0.114(4)
C4	0.3572(7)	0.2729(6)	0.5784(5)	0.100(3)
C5	0.4319(7)	0.3489(6)	0.5843(5)	0.113(4)
C6	0.3358(6)	0.4881(6)	0.6190(5)	0.100(3)
C7	−0.0568(5)	0.7711(5)	0.6761(4)	0.074(2)
C8	−0.0145(6)	0.8218(7)	0.5754(5)	0.117(4)
C9	−0.1306(7)	0.8941(8)	0.5090(5)	0.132(5)
C10	−0.2490(7)	0.9939(7)	0.5600(5)	0.125(4)
C11	−0.2929(6)	0.9484(8)	0.6597(5)	0.128(4)
C12	−0.1806(6)	0.8770(7)	0.7249(4)	0.112(3)
C13	0.1969(6)	0.8003(6)	0.7779(5)	0.094(3)
C14	0.1807(8)	0.8397(8)	0.8759(5)	0.117(5)
C15	0.2375(9)	0.9391(7)	0.8781(6)	0.121(5)
C16	0.374(1)	0.894(1)	0.8221(8)	0.150(7)
C17	0.3849(8)	0.8652(9)	0.7188(7)	0.137(6)
C18	0.3280(7)	0.7690(7)	0.7180(5)	0.113(4)
C19	0.1537(5)	0.5572(5)	1.1738(3)	0.062(2)
C20	0.0799(5)	0.6933(6)	1.1811(4)	0.082(3)
C21	0.0951(6)	0.7510(7)	1.2579(6)	0.107(4)
C22	0.1824(9)	0.674(1)	1.3247(5)	0.121(6)
C23	0.2566(9)	0.5404(9)	1.3198(5)	0.115(5)
C24	0.2421(6)	0.4814(6)	1.2442(4)	0.086(3)
C25	0.3454(4)	0.3431(4)	0.9730(3)	0.054(2)
C26	0.3830(5)	0.2153(5)	0.9523(4)	0.066(2)
C27	0.5091(5)	0.1391(5)	0.9060(4)	0.077(3)
C28	0.6012(5)	0.1893(6)	0.87954)	0.084(3)
C29	0.5676(5)	0.3156(6)	0.8979(4)	0.077(3)
C30	0.4413(4)	0.3906(5)	0.9444(4)	0.064(2)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j \mathbf{U}_{ij} a_i^* \cdot a_j^* \bar{a}_i \cdot \bar{a}_j$.



(1)

and are isolated as colorless crystalline materials. Attempted reactions, under the same conditions with saturated alkyls, were unsuccessful with recovery of all of the starting materials. The products, **1** and **2**, are very reactive, decomposing rapidly upon exposure to air.

Crystal Structures of $\{Ph_2Ga[\mu\text{-}SSn(C_6H_{11})_3]\}_2$ (1) and $\{Ph_2Ga[\mu\text{-}SSn(C_6H_{11})_3]\}_2$ (2). The crystals of **1** and **2** are isomorphous. The molecular structure of **1** with atoms labeled is shown in Figure 1; the diagram for **2** with 50% thermal ellipsoids is shown in Figure 2. The orientation and numbering for the two molecules is the same. The molecule has an inversion center, requiring the $(MS)_2$ (M = Ga, In) unit to be rigorously planar. The gross features of the molecular structure are similar to related dimeric organogallium and -indium thiolates. Each metal atom has a quasi-tetrahedral geometry, the sulfur atom is trigonal pyramidal, and the M—S bond distances are similar to those found in other dimeric four-coordinate gallium and indium thiolates. The average M—C bond distance and the exocyclic C—M—C angle are also in the normal ranges for dimeric gallium and indium derivatives.[15–20]

Table 4. Selected Bond Distances (Å) and Angles (deg) for $\{Ph_2Ga[\mu\text{-}SSn(C_6H_{11})_3]\}_2$, **1**, and $\{Ph_2In[\mu\text{-}SSn(C_6H_{11})_3]\}_2$, **2**

$\{Ph_2Ga[\mu\text{-}SSn(C_6H_{11})_3]\}_2$, **1**		$\{Ph_2In[\mu\text{-}SSn(C_6H_{11})_3]\}_2$, **2**	
	Bond Distances		
Sn1—S1	2.405(3)	Sn1—S1	2.446(2)
Sn1—C1	2.16(1)	Sn1—C1	2.167(6)
Sn1—C7	2.158(9)	Sn1—C7	2.164(6)
Sn1—C13	2.16(2)	Sn1—C13	2.160(9)
Sn1··Ga1	3.926(1)	Sn1··In1	4.125(1)
Ga1··Ga1′	3.203(1)	In1··In1′	3.574(1)
S1···S1′	3.406(2)	S1···S1′	3.619(2)
Ga1—S1	2.342(3)	In1—S1	2.551(2)
Ga1—C19	1.96(1)	In1—C19	2.141(7)
Ga1—C25	1.956(7)	In1—C25	2.149(5)
	Bond Angles		
Sn1—S1—Ga1	111.59(9)	Sn1—S1—In1	111.26(9)
S1—Sn1—C1	114.6(3)	S1—Sn1—C1	112.2(2)
S1—Sn1—C7	102.3(3)	S1—Sn1—C7	102.3(3)
S1—Sn1—C13	100.4(4)	S1—Sn1—C13	103.3(2)
S1—Ga1—C19	105.9(3)	S1—In1—C19	106.4(2)
S1—Ga1—S1′	93.5(1)	S1—In1—S1′	90.72(5)
Ga1—S1—Ga1′	86.5(1)	In1—S1—In1′	89.28(6)
S1—Ga1—C25	116.5(3)	S1—In1—C25	114.5(2)
C19—Ga1—C25	114.5(3)	C19—In1—C25	116.3(2)
C1—Sn1—C7	110.6(4)	C1—Sn1—C7	112.0(3)
C1—Sn1—C13	115.0(4)	C1—Sn1—C13	115.4(2)
C7—Sn1—C13	112.8(5)	C7—Sn1—C13	110.5(3)

Table 5. Reported Structures of Gallium and Indium Thiolates and Related Compounds

compound	M—S, Å	S—M—S, deg	M—S—M, deg	sum of angles around S, deg
$\{(Ph_2Ga[\mu\text{-}SSn(C_6H_{11})_3]\}_2$[a]	2.342	93.5	86.5	312.99
$[Me_2Ga(\mu\text{-}SC_5H_9)]_2$[b]	2.388	93.81	86.19	300.19
$[Ph_2Ga(\mu\text{-}SC_5H_9)]_2$[b]	2.388	92.1	87.9	297.9
$[Ph_2Ga(\mu\text{-}SEt)]_2$[c]	2.378	93.58	86.42	294.92
$[t\text{-}Bu_2Ga(\mu\text{-}SH)]_2$[d]	2.432	90.5	89.5	282.5
$[Me_2Ga(\mu\text{-}SC_6F_5)]_2$[e]	2.449	89.45	87.75	301.75
		88.59	87.99	304.89
$[I_2Ga(\mu\text{-}SMe)]_2$[f]	2.379	94.5	85.5	
$[I_2Ga(\mu\text{-}S\text{-}i\text{-}Pr)]_2$[g]	2.329	89.1	84.7	
$\{Ga[\mu\text{-}S(2,4,6\text{-}t\text{-}Bu_3C_6H_2)]\}_3$[h]	2.205	119.8		
$[Ph_2In(\mu\text{-}SSn(C_6H_{11})_3]_2$[a]	2.551	90.72		
$[(Mes_2In(\mu\text{-}SCMe_2CH_2CH_3)]_2$[i]	2.595	82.4		
	2.587	85.9		
$[Mes_2In(\mu\text{-}SSiPh_3)]_2$[i]	2.698	77.82		
$In(SPh)_3 \cdot 2Py$[j]	2.458	119.2		

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The Sn—S bond distances range from 2.405 to 2.446 Å and are similar to distances found in two- or three-coordinate bridging sulfur atoms in linear[21–23] and polycyclic[24,25] orga-

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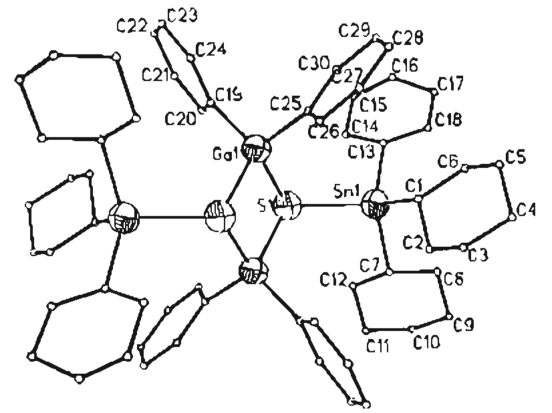


Figure 1. Diagram of $\{Ph_2Ga[\mu\text{-}SSn(C_6H_{11})_3]\}_2$, **1**, with the atom numbering scheme. The sulfur, tin, and gallium atoms are shown as thermal ellipsoids with 50% probability. The hydrogen atoms are omitted.

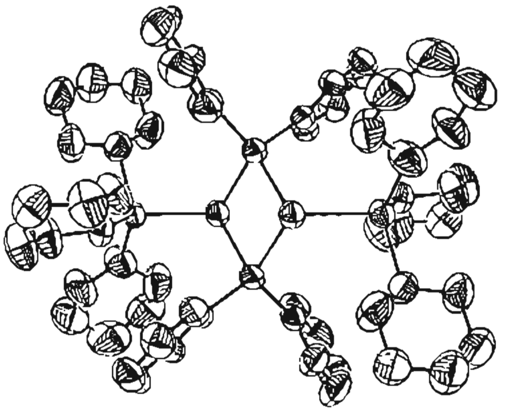
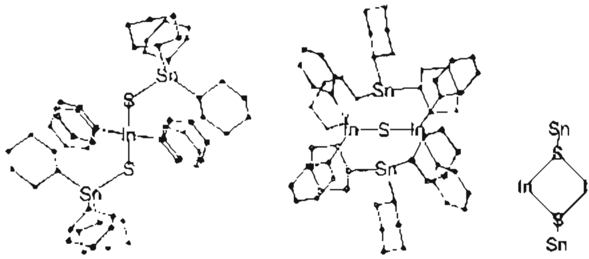


Figure 2. Diagram of $\{Ph_2In[\mu\text{-}SSn(C_6H_{11})_3]\}_2$, **2**, with all heavy atoms shown as thermal ellipsoids with 50% probability. The numbering scheme is identical to that of compound **1**.

Chart 1



nostannanethiolates. The Sn—C bond distances (2.158—to 2.167 Å) and the C—Sn—C angles (110.6—115.00°) are comparable to those found in the related organotin compounds.[21–25]

The structural features of the $(MS)_2$ ring and the orientation of the groups around the ring merit additional comment. Three views of this core are shown in Chart 1. The first view along the In···In vector shows the *trans* orientation of the tricyclohexyl tin moieties. The angles between the $(MS)_2$ plane and the S—Sn bonds are 57.2 and 57.0° in **1** and **2** respectively. (Note the corresponding angle in the oxygen derivative is 23.3°.)[9] The second view along the S···S vector shows the orientation of the cyclohexyl groups. This arrangement appears to minimize interaction between them and the phenyl groups attached to the metal atom, but no detailed analysis of these interactions has been made. Finally, the $(MS)_2$ ring is shown. In both complexes this is nearly square as a result of the planarity of the ring, the equivalent bond distances, and the near 90° internal angles.

Table 6. ^{119}Sn NMR Data for Group 13 Organostannyl Oxides and Organostannanethiolates

compound	$\delta(^{119}Sn)$
$\{Ph_2Ga[\mu\text{-}SSn(C_6H_{11})_3]\}_2$[a]	43.1, 22.6
$\{Ph_2In[\mu\text{-}SSn(C_6H_{11})_3]\}_2$[a]	−126.4, 87.0
$[(C_6H_{11})_3Sn]_2S$[a]	22.6
$[Ph_2Ga(\mu\text{-}OSnPh_3)]_2$[a]	−82.8
$[Me_2Al(\mu\text{-}OSnPh_3)]_2$[a]	−83.3
$[Et_2Al(\mu\text{-}OSnPh_3)]_2$[a]	−82.2
$[i\text{-}Bu_2Al(\mu\text{-}OSnPh_3)]_2$[a]	−82.4
$(Ph_3Sn)_2O$[b]	−83.1

[a] This work. [b] Reference 14.

A comparison of these structures with the oxygen-bridged structures we recently reported[9] shows the major difference between them is the nearly planar oxygen versus the pyramidal sulfur. The difference in the size of the chalcogen also leads to a shift from the nearly square arrangement observed here to a diamond-shaped central ring in the oxygen derivatives.

NMR Studies. The ^1H, ^{13}C, and ^{119}Sn NMR spectral data for the complexes $\{Ph_2M[\mu\text{-}SSn(C_6H_{11})_3]\}_2$ (M = Ga, In) are presented in the Experimental Section. The ^1H NMR spectra of **1** and **2** are very complex with overlapping lines making any detailed analysis difficult and obscuring the tin—proton coupling to the cyclohexyl groups but are consistent with the structures reported. There was no observable tin—proton coupling to the phenyl groups. The ^{13}C spectra support the structural assignment and show two sets of signals that indicate the formation of two conformations or complexes in solution. These spectra also show Sn—C coupling to the cyclohexyl groups. The assignments given in the Experimental Section were based on the magnitude of the observed coupling constants.[26–28] The values for ^1J in **1** and **2** were not recorded because of the low solubility of these compounds in benzene. The ^{119}Sn spectra confirm the presence of Sn in the complexes, and the observation of two signals for compounds **1** and **2** confirms the existence of different species in solution. Table 6 lists the ^{119}Sn chemical shifts for **1** and **2** and the values for structurally-related tin oxides and the starting materials. The observed chemical shifts fall in the general range expected for these derivatives.[14]

In the oxygen derivatives, $[Ph_2Ga(\mu\text{-}OSnPh_3)]_2$ and $[R_2Al(\mu\text{-}OSnPh_3)]_2$ (R = Me, Et, *i*-Bu),[9] only a single resonance was observed for each of the compounds. The chemical shift range is very narrow (−82.2 to −83.3 ppm) and within experimental error of the tin oxide, $(Ph_3Sn)_2O$. These results, the known structures of both **1** and **2** and of the oxygen derivatives as well as our understanding of the dynamic and equilibrium behavior of Group 13 derivatives suggest that in solution, **1** and **2** exist as dimeric complexes with *syn* and *anti* conformers in equilibrium or that the sulfur derivatives form other aggregates such as trimers in equilibrium with dimers. The low solubility of these compounds in aromatic solvents precludes a concentration study in these solvents, and a change to more polar solvents

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will likely alter the equilibrium with formation of adducts. The difference between the behavior of the oxygen and sulfur derivatives is similar to that for the simple alkoxides where dimers predominate and for the thiolates where dimer–trimer equilibria are widely observed for the thiolates.[29–32] Therefore, we conclude that the most likely equilibrium is between dimers and trimers in **1** and **2**.

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Supplementary Material Available: Complete listings of crystal and X-ray data collection parameters, bond distances and bond angles, anisotropic thermal parameters for the heavy atoms and hydrogen atom positional parameters (7 pages). See any current masthead page for ordering information.

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