Chelate and Open Structures in Complexes of Bis(stannyl)methanes with Dimethyl Sulfoxide

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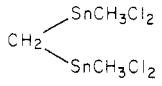
Summary: Structures are given for the complexes bis(dichloromethylstannyl)methane–bis(dimethyl sulfoxide), (chlorodimethylstannyl)(dichloromethylstannyl)methane–dimethyl sulfoxide, and bis(trichlorostannyl)methane–tetrakis(dimethyl sulfoxide).

Organic derivatives of tin(IV) bearing at least one electronegative group have long been known to form complexes with a wide variety of ligands.[1-3] Among the halomethyltins the number of ligands depends upon the number of halogen atoms on the tin atom. For example, trimethylchlorostannane forms a complex with one molecule of dimethyl sulfoxide (Me_2SO),[4] while dimethyldichlorostannane[5] and methyltrichlorostannane[6] form complexes with two molecules of Me_2SO. No studies appear to have been made with compounds containing more than one Lewis acid tin center in the molecule. In such species the possibility for chelation by the acceptor molecule, by analogy with the abundant examples of chelation by donor molecules, exists. We are examining systems in which this phenomenon might be observed and report here on the first examples of chelation by organotin acceptors, bis(chloromethylstannyl)methanes, with Me_2SO.

Bis(dichloromethylstannyl)methane, **1**, (chlorodimethylstannyl)(dichloromethylstannyl)methane, **2**, and bis(trichlorostannyl)methane, **3**, each reacted with excess dimethyl sulfoxide (Me_2SO) to form crystalline solids which were characterized by NMR spectroscopy and elemental analysis.[7] Their compositions were as follows: $1(Me_2SO)_2$, $2(Me_2SO)$, and $3(Me_2SO)_4$. Thus the ratios Sn/Me_2SO are 1, 0.5, and 2, respectively, reflecting substantial differences in coordinative behavior.



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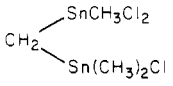

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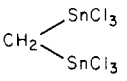

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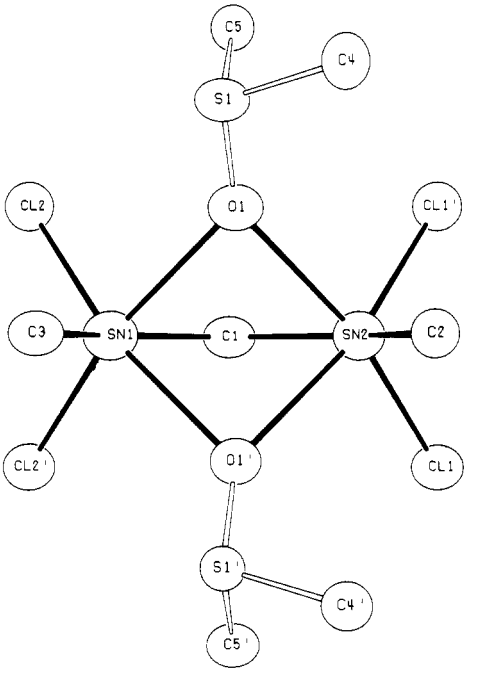
The structures of the complexes were shown by X-ray diffraction to be **4**, **5**, and **6**. As illustrated in the structures, they consist of discrete molecules. In **4** each tin atom is found in a pseudooctahedral environment (supplementary material), face sharing through the bridging methylene carbon and the oxygens of the Me_2SO groups with the adjacent Sn polyhedron. A crystallographic mirror plane passes through Sn1, Sn2, the bridging methylene carbon



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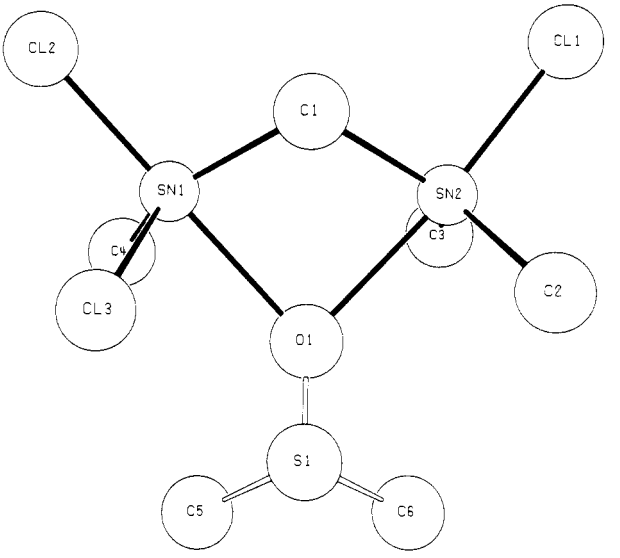

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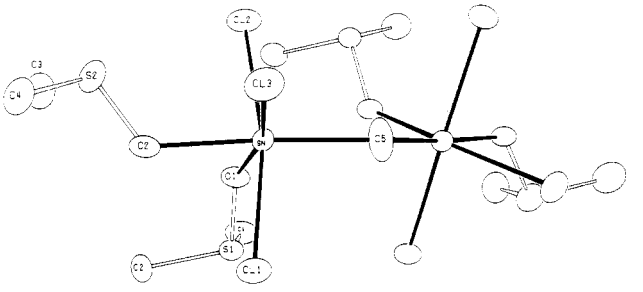

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(7) Experimental details on the preparation and properties of the complexes and their precursors will be described in another manuscript. In general the complexes were prepared by addition of excess Me_2SO to a solution of chlorostannane in carbon tetrachloride. Melting points were as follows: **4**, 150–153 °C; **5**, 107–108 °C; **6**, 169–172 °C.

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C1, and the terminal methyl carbons C2 and C3.

The geometry about the tin atoms in structure **5**, on the other hand, is distorted trigonal bipyramidal, with edge sharing between tin polyhedra provided by the bridging methylene carbon and Me_2SO oxygen atoms. The bridging methylene group occupies an equatorial position in both the Sn1 and Sn2 polyhedra while O1 is found in an apical position in both cases. The tin environments are nonequivalent: Sn1 bound to a methyl carbon, C4, and C13 in the equatorial plane, in addition to the bridging C1, while the trigonal plane about Sn2 is defined by C1 and two methyl carbons C2 and C3. As anticipated, the Sn1–C13 distance of 2.372 (4) Å is significantly shorter than the Sn1–C12 and Sn2–C11 distances, 2.434 (4) Å average, reflecting the equatorial and axial occupancies, respectively.

The crystallographically identical tin atoms in **6** enjoy pseudooctahedral geometry, with a single bridging group, the methylene carbon C5, connecting the vertex-sharing polyhedra. A noteworthy feature of the structure is the short terminal Sn–O(Me_2SO) bond length of 2.118 (6) Å (average) in contrast to bridging Sn–O(Me_2SO) distances of 2.588 (6) and 2.572 (8) Å in **4** and **5**, respectively.

In comparing the structures, the tin–tin distances increase from 3.426 (1) Å in the triply-bridged structure **4** to 3.529 (1) Å in the doubly bridged **5** to 3.760 (1) Å in the singly bridged case **6**, a trend reflected in the Sn–methylene carbon–Sn valence angle which opens from 108.5 (4)° in **4** to an exceptionally large value of 130.8 (6)° in **6**.

These results show that the composition and structure of the most readily formed complexes are strongly dependent on the number of chlorines on the tin atoms. Presumably the high Lewis acidity of the trichlorostannyl groups of **3** leads to pseudooctahedral coordination in **6**. But this occurs at the expense of expanding the Sn–C–Sn bond angle to the remarkably large value of 130.8°. In **4** a more distorted octahedral configuration is achieved by two bridging oxygens of Me_2SO molecules. But **5** finds both tins pentacoordinate. Further studies should reveal structure/composition patterns and may lead to some understanding of the driving forces involved.

Crystal Data. $Sn_2(CH_2)(CH_3)_2Cl_4(Me_2SO)_2$, **4**, crystallizes in the orthorhombic space group *Pbnm* with a = 9.821 (2) Å, b = 12.411 (2) Å, c = 15.540 (3) Å, V = 1894.2 Å^3, D_{calcd} = 2.03 g cm^{-3}, Z = 4, and μ = 34.2 cm^{-1} (Mo Kα, λ = 0.71073 Å).[8] A total of 1498 independent reflections were measured on a Nicolet R3/m diffractometer and 1109 reflections with $F_o \geq 6\sigma(F_o)$ were used in the subsequent solution and least-squares refinement, which have produced current discrepancy factors of 0.048 and 0.047 for R and R_w, respectively.

$Sn_2(CH_2)(CH_3)_3Cl_3(Me_2SO)$, **5**, crystallizes in the triclinic space group $P\bar{1}$ with a = 7.551 (2) Å, b = 7.945 (2) Å, c = 13.354 (3) Å, α = 80.63 (2)°, β = 89.13 (3)°, γ = 72.96 (2)°, and V = 755.3 Å^3 to give D_{calcd} = 2.11 g cm^{-3} for Z = 2 (μ = 39.6 cm^{-1}, Mo Kα). A total of 1932 reflections were collected as above of which 1609 with $F_o \geq 6\sigma(F_o)$ were used in the structure solution and refinement. The current discrepancy factors are R = 0.045 and R_w = 0.055.

$Sn_2(CH_2)Cl_6(Me_2SO)_4$, **6**, crystallizes in the monoclinic space group $C2/c$ with a = 20.998 (5) Å, b = 7.925 (3) Å, c = 16.535 (4) Å, β = 98.79 (3)°, and V = 2719.3 Å^3 with D_{calcd} = 1.90 g cm^{-3} for Z = 4 (μ = 27.5 cm^{-1}, Mo Kα). The structure solution and least-squares refinement are based on 1277 reflections with $F_o \geq 6\sigma(F_o)$, collected on the Nicolet R3/m diffractometer. The current residuals are 0.034 and 0.038 for R and R_w, respectively.

All data was collected on a Nicolet R3/m automated four-circle diffractometer, in the range $0° \geq 2\theta \geq 50°$, and processed on a Nova 3 computer, using local versions of the SHELXTL crystallographic computing package. Lorentz and polarization corrections and absorption corrections were carried out in the usual fashion. Details of the usual procedures may be found in ref 9 and 10.

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Registry No. 1, 79992-66-8; 2, 79992-67-9; 3, 79992-68-0; 4, 79992-48-6; 5, 79992-49-7; 6, 79992-50-0.

Supplementary Material Available: Tables of bond distances, angles, final fractional coordinates, thermal parameters, and observed and calculated structure factors are available (28 pages). Ordering information is given on any current masthead page.

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A New Organometallic Photoreaction: Interconversion of Metal–Alkylidene Geometric Isomers

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Summary: Benzylidene complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]^+PF_6^-$ (**1**), which exists as a >99:1 mixture of anticlinal (**1t**, "thermodynamic") and synclinal (**1k**, "kinetic") Re=C bond geometric isomers at room temperature, is isomerized when irradiated between −20 and −78 °C in CD_2Cl_2, CD_3CN, or $(CD_3)_2CO$ to a (55 ± 3):(45 ± 3) **1t/1k** photostationary state. Propylidene $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH_2CH_3)]^+PF_6^-$ (**2**), which exists as a (95±1):(5±1) mixture of anticlinal (**2t**) and synclinal (**2k**) isomers at room temperature, is similarly isomerized to a (59 ± 2):(41 ± 2) photostationary state. Absorption spectra of **1t** and **2t** and unsuccessful attempts to photosensitize **1t** → **1k** (azulene, rose bengal, eosin Y) are reported. Thermal isomerization rates for **1k** → **1t**, measured between 4 °C ($t_{1/2}$ = 443 min) and 29.5 °C ($t_{1/2}$ = 17 min), yield $\Delta H^{\ddagger}$ = 20.9 ± 0.4 kcal/mol and $\Delta S^{\ddagger}$ = −3.8 ± 0.2 eu. The benzylidene complex $[(\eta\text{-}C_5H_5)Fe(CO)(PPh_3)(=CHC_6H_5)]^+CF_3CO_2^-$ (**3**) decomposes upon low-temperature irradiation.

We recently reported the synthesis of a series of rhenium–alkylidene complexes $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=$

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