[5] The chlorosilanes were obtained from the reaction of the corresponding aryllithium compounds with trichlorosilane (see Supporting Information).

[6] Suitable crystals of **1b** were obtained from CH_2Cl_2/diethyl ether at $-30\,^{\circ}C$. Siemens P2(1) diffractometer, SHELXTL plus, SHELXL-93, direct methods. Crystal data: triclinic, space group $P\bar{1}$; $a = 8.226(7)$, $b = 10.249(7)$, $c = 12.059(13)$ Å; $\alpha = 111.21(7)$, $\beta = 99.04$, $\gamma = 94.97^{\circ}$, $Z = 2$, $V = 924.6(14)$ Å^3, $\rho_{calcd} = 1.510\ g\,cm^{-3}$, $\mu = 0.296\ mm^{-1}$, $F(000) = 436$, Siemens diffractometer, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, graphite monochromator, Wyckoff scans; $1.85 \le \theta \le 27^{\circ}$; 4324 reflections, 4036 independent reflections, $R_F = 0.0677$ ($wR_{F^2} = 0.1381$) for 2831 reflections with $I > 2\sigma I$ 249 parameters, max./min. residual electron density $0.5/-0.3$ e Å^{-3}. All non-hydrogen atoms were refined anisotropically, all hydrogen atoms—with the exception of H(1), which was refined anisotropically—on calculated positions. Crystallographic Data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-113253. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[7] N. Auner, R. Probst, F. Hahn, E. Herdtweck, *J. Organomet. Chem.* **1993**, *459*, 25–41.

[8] a) B. Becker, R. J. P. Corriu, C. Guérin, B. Henner, Q. Wang, *J. Organomet. Chem.* **1989**, *368*, C25; b) C. Maerker, J. Kapp, P. von R. Schleyer in *Organosilicon Chemistry: From Molecules to Materials, Vol. 2* (Eds.: N. Auner, J. Weis), VCH, Weinheim, **1996**, pp. 329–359.

[9] Calculations have already been carried out on some base adducts of SiH_3^+. Review: C. Maerker, P. von R. Schleyer in *The Chemistry of Organic Silicon Compounds, Vol. 2, Part 1* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, **1998**, pp. 513–555.

[10] The ^{29}Si-CP-MAS spectrum of **1d** was kindly recorded by Dr. A. Sebald, Bayerisches Geoinstitut der Universität Bayreuth (Germany).

Synthesis and Structural Characterization of Graphite-Like $[(Me_3Sn)_3O]Cl$**

Bodo Räke, Peter Müller, Herbert W. Roesky,* and Isabel Usón

Dedicated to Professor Hubert Schmidbaur
on the occasion of his 65th birthday

In our investigations on weakly coordinating cations and anions, we were interested in the properties of the sterically demanding oxonium cation $[(Me_3Sn)_3O]^+$. We have already isolated tris(trimethylsilyl)methylaluminum compounds which exhibit weak cation–anion interactions. In the anions of both $[Ag(toluene)_3]^+[\{[(SiMe_3)_3C]_2Al_2F_5\}_2Li]^-$ and $[AlF_2(thf)_4]^+[\{(SiMe_3)_3C\}_2Al_2F_5]^-$ the fluorine atoms bridge the aluminum atoms. Weak ionic interactions are the result of the efficient shielding of the anionic centers by the tris(trimethylsilyl)methyl ligands.[1]

Dehnicke et al. have already described trimethylstannyl-substituted ammonium salts that exhibit an interesting ionic arrangement. In $[NH_2(SnMe_3)_2][SnMe_3Cl_2]$, the chlorine atoms bridge two tin atoms and one hydrogen atom, which leads to a symmetrical three-dimensional lattice.[2, 3]

Interactions of alkyltin compounds with Lewis bases are not rare. The tin atoms in SnF_4 and Me_2SnF_2 as well as in the $[SnCl_6]^{2-}$ dianion are surrounded by their ligands in an octahedral arrangement.[4, 5]

There is an almost trigonal-bipyramidal configuration of tin and oxygen in $Me_3SnN(SO_2Me)_2 \cdot Me_3SnOH$, whereby the oxonium ion $[(Me_3Sn)_2OH]^+$ is formed.[6] The synthesis and properties of $[(Me_3Sn)_3O]I$ have already been discussed by Harada, however, without a structural investigation of this compound.[7]

H_3O^+ and the cation of the Meerwein salt are the best known oxonium ions. Our work is directed to the synthesis and the structural characterization of the oxonium salt $[(Me_3Sn)_3O]Cl$ (**1**). This compound was synthesized by refluxing $(Me_3Sn)_2O$[8] and Me_3SnCl in THF for 12 h. After concentration of the solution and storage at $-23\,^{\circ}C$, **1** precipitated as colorless crystals [Eq. (1)]. Compound **1** was investigated by single-crystal X-ray structural analysis, NMR and IR spectroscopy as well as mass spectrometry. Compound **1** is also accessible by the treatment of Me_3SnCl with Li_2O in refluxing THF [Eq. (2)].

$$Me_3SnCl + (Me_3Sn)_2O \longrightarrow [(Me_3Sn)_3O]Cl \quad \mathbf{1} \tag{1}$$

$$3\,Me_3SnCl + Li_2O \xrightarrow[-2\,LiCl]{} [(Me_3Sn)_3O]Cl \quad \mathbf{1} \tag{2}$$

The solvent was removed under vacuum after 15 h of heating. Excess starting material was removed during the workup of **1**: Me_3SnCl was removed with the solvent under vacuum, and Li_2O was removed by filtration. The formation of **1** was confirmed by ^1H NMR spectroscopy. Unfortunately, we were not able to obtain single crystals; traces of LiCl probably prevent crystallization. In the ^1H NMR spectrum there is a singlet at $\delta = 0.21$. Coupling with the ^{117}Sn and ^{119}Sn nuclei gives a satellite pair with a coupling constant of 56 Hz, which is, however, not split.[8] There is only one signal in both the ^{13}C NMR spectrum ($\delta = -2.40$) and in the ^{119}Sn NMR spectrum ($\delta = 120.02$). The satellite pair in the ^{13}C NMR spectrum is hidden by background noise. The elemental analysis only deviates slightly from the calculated values. The mass spectrum only exhibits fragments of the starting materials, namely, $(Me_3Sn)_2O$ and Me_3SnCl, which are produced on heating **1** in the mass spectrometer. The molecular peak of $(Me_3Sn)_2O$ minus a methyl group (*m/z* 331) and the molecular peak of Me_3SnCl (*m/z* 200) are observed in the mass spectrum.

The single-crystal X-ray structural analysis of **1** reveals that it crystallizes in the hexagonal space group $P6_3/m$ with a sixth of the molecule in the asymmetric unit; the remaining five sixths are produced by a threefold axis and the mirror plane. The structure consists of a positively charged oxygen center that is surrounded by three $SnMe_3$ groups in a trigonal-planar manner as well as a chlorine atom (Figure 1). In the crystal, each chloride ion is coordinated to three Sn atoms to produce an infinite two-dimensional hexagonal structure. Each of these hexagons is formed by a 12-membered $Sn_6Cl_3O_3$ ring

---

[*] Prof. Dr. H. W. Roesky, Dipl.-Chem. B. Räke, Dipl.-Chem. P. Müller, Dr. I. Usón
Institut für Anorganische Chemie der Universität
Tammannstrasse 4, D-37077 Göttingen (Germany)
Fax: (+49)551-39-3373
E-mail: hroesky@gwdg.de

[**] This work was supported by the Deutsche Forschungsgemeinschaft.

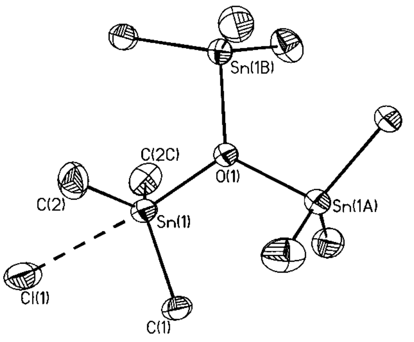

Figure 1. Crystal structure of **1** (the H atoms have been omitted for clarity. The vibration ellipsoids represent 50% probability levels). Selected bond lengths [Å] and angles [°]: Sn(1)–O(1) 2.0999(4), Sn(1)–C(1) 2.124(5), Sn(1)–C(2) 2.125(4), Sn(1)–Cl(1) 3.0856(6); O(1)-Sn(1)-C(1) 103.7(2), O(1)-Sn(1)-C(2) 96.4(1), C(1)-Sn(1)-C(2) 113.2(1), C(2)-Sn(1)-C(2C) 126.8(2), Sn(1)-O(1)-Sn(1A) 120.0(0), O(1)-Sn(1)-Cl(1) 174.37(1).

(Figure 2). Two of these hexagonal layers lie over one another so that the chlorine atoms are positioned over the chlorine atoms of the next layer and the oxygen atoms of one layer lie over the center of the hexagon of the next as well as the previous layer (Figure 3). In this way a hexagonal AB layer structure is formed (distance between two neighboring layers 6.32 Å), which is very similar to the α modification of graphite (graphite: space group $P6_3mc$, hexagonal AB layer structure).[9] The carbon atoms do not participate in the formation of the lattice layers. Each tin atom is in a distorted trigonal-bipyramidal environment, and the three equatorial methyl groups are bent away from the axial oxygen atom, which is placed opposite to the chloride ion in the pyramid (the Sn atom lies 0.319(4) Å outside the plane through the three C atoms), so that the original tetrahedral coordination of the Me_3SnO unit is still recognizable.

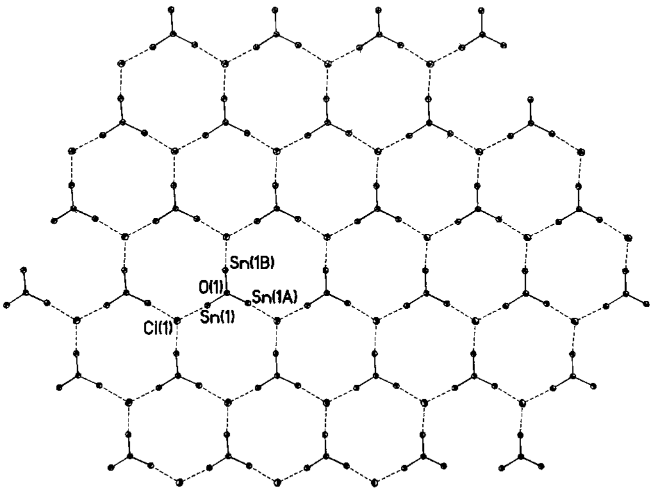

Figure 2. Honeycomb structure of the $Sn_6Cl_3O_3$ rings in **1**. The C and H atoms have been omitted for clarity.

Thus, we have demonstrated that in $[(Me_3Sn)_3O]Cl$ there are strong cation–anion interactions in the solid state. Our results provide many possibilities for the investigation of corresponding systems by exchange of the anion. The prediction of possible structures is, however, risky.

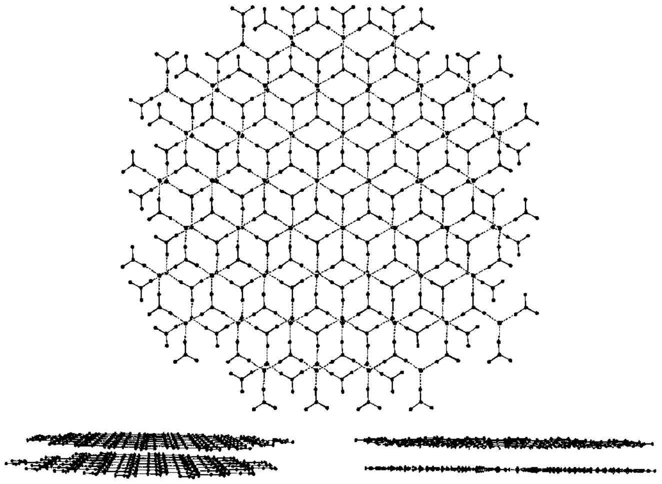

Figure 3. The AB layer structure in **1**. The C and H atoms have been omitted for clarity.

Experimental Section

1. Me_3SnCl (0.12 g, 1 mmol) was refluxed with $(Me_3Sn)_2O$ (0.34 g, 1 mmol) in THF (50 mL) for 12 h. The solution was concentrated (5 mL) and left to stand at −23 °C to give compound **1** as colorless crystals. Yield: 0.2 g (37%).

2. Me_3SnCl (1.39 g, 7 mmol) was refluxed with Li_2O (0.06 g, 2 mmol) in THF (80 mL) for 15 h under reflux. The solid residue was filtered off, and volatile components were removed under vacuum. Yield **1**: 0.3 g (28%).

M.p. 94 °C; ^1H NMR (250 MHz, C_6D_6, TMS): $\delta = 0.21$ (s, 27 H, $Sn(CH_3)$, $J_{SnCH} = 56$ Hz); ^{13}C NMR (62 MHz, C_6D_6, TMS): $\delta = -2.40$ (s, 9 C); ^{119}Sn NMR (149 MHz, C_6D_6, $SnMe_4$): $\delta = 120.02$ (s, 3 Sn); IR (KBr, Nujol): $\tilde{\nu} =$ 3360, 3187, 2359, 1305, 1261, 1194, 1184, 1170, 1155, 1031, 975, 919, 772, 736, 723, 546, 516, 455 cm^{-1}; MS (EI): m/z (%): 331 (67, $M^+ - Me_3SnCl - Me$), 200 (3, $M^+ - (Me_3Sn)_2O$), 165 (100, $M^+ - (Me_3Sn)_2O - Cl$); elemental analysis calcd for $C_9H_{27}ClOSn_3$: C 19.91, H 5.01, Cl 6.53; found: C 19.46, H 5.27, Cl 6.80.

Structural analysis of $C_9H_{27}ClOSn_3$: $M_r = 542.83$, crystal dimensions: 0.70 × 0.70 × 0.60 mm, hexagonal, space group $P6_3/m$, $a = b = 8.971(1)$, $c = 12.646(3)$ Å, $V = 881.4(3)$ Å^3, $\rho_{calcd} = 2.045$ g cm^{-3}, $Z = 2$, absorption coefficient $\mu = 4.348$ mm^{-1}, maximum resolution $2\Theta = 57.4°$; of 15939 reflections measured, 794 were independent ($R_{int} = 0.0719$). Data/restraints/parameter ratio: 794/11/29, final R values: $R1 = 0.0263$, $wR2 = 0.0648$ for reflections with $I > 2\sigma(I)$ and $R1 = 0.0274$, $wR2 = 0.0654$ for all reflections, goodness of fit $S = 1.229$; ($R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $S = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(n-p)]^{1/2}$); weighting scheme: $w^{-1} = \Sigma^2(F_o)^2 + (0.0226\,P)^2 + 1.9493\,P$; $P = [F_o^2 + 2\,F_c^2]/3$; max./min. residual electron density 0.734/−0.474 e A^{-3}.

The crystal was removed from the Schlenk flask under an inert gas, mounted on a glass fiber with perfluoro-polyether, and shock-frozen.[10] The data was collected at $T = 133$ K on a Stoe–Siemens–Huber four-circle diffractometer equipped with a Siemens CCD area detector, with graphite monochromatic $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) performing φ and ω scans. The structure was solved by direct methods (SHELXS-97[11]) and refined against F^2 (SHELXL-97[12]) in a full-matrix least-squares procedure. All the non-hydrogen atoms were anisotropically refined, and the hydrogen atoms were added to the model in calculated geometric positions and refined with a riding model. Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114479. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Received: 12. February 1999 [Z13028IE]
German version: *Angew. Chem.* **1999**, *111*, 2069–2071