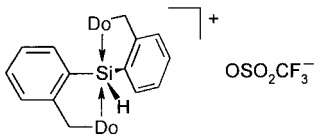
Stabilization of Organosilicenium Ions by means of Intramolecular Coordination of O, S, or P Ligands

Uwe-H. Berlekamp, Peter Jutzi,* Andreas Mix, Beate Neumann, Hans-Georg Stammler, and Wolfgang W. Schoeller

Dedicated to Professor Edgar Niecke on the occasion of his 60th birthday

Organosilicenium ions, R_3Si^+, are very strong electrophiles which can be stabilized by various donors.[1, 2] An intramolecular coordination of N donors was described first by Corriu et al.[3] and then by other authors;[4] it leads to trigonal-bipyramidal siliconium ions. Surprisingly, other donors have not yet been employed in these systems. We now present compounds of the type **1b–d**, in which oxygen, sulfur, or phosphorus donors are used for the first time for stabilization purposes, compare them with each other and with the known N donor compound **1a**,[4] and describe interesting differences with regard to structure and reactivity. Furthermore, we present quantum-chemical calculations on model systems.



1a-d

1	a	b	c	d
Do	NMe_2	OMe	SMe	PMe_2

The compounds **1b–d** (Table 1) are produced in excellent yield in the reaction of the corresponding chlorosilanes $(C_6H_4CH_2Do)_2Si(H)Cl$[5] (Do = donor) with trimethylsilyl triflate ($Me_3SiOSO_2CF_3$) at −80 °C in hexane. They are obtained as colorless solids (**1b, d**) or as a colorless oil (**1c**). The presence of 1:1 electrolytes in solution is confirmed by conductivity measurements. Statements concerning structure and bond type are made according to X-ray structure and multinuclear NMR data.

The molecular structure of an enantiomer of **1b** in the solid state is represented in Figure 1, together with important bond lengths and angles.[6] The geometry at the silicon atom is almost perfect trigonal bipyramidal; the Si–O distances of 192 pm are comparatively short for donor–acceptor interactions.

According to the DNMR data, **1b–d** also have a trigonal-bipyramidal structure in solution. It is particularly interesting that dynamic processes in the sense of coordination equilibria (Scheme 1; "flip-flop" coordination[7]) are observed for the

Table 1. Physical data for **1b–d**.

1b: ^{1}H NMR (500.1 MHz, CD_2Cl_2, RT): $\delta = 4.19$ (s, 6H, OCH_3), 5.18 (s, 1H, Si-H); 5.39, 5.63 (AB sys., $^2J(H,H) = 12.2$ Hz, 4H, CH_2), 7.31 (d, $^3J(H,H) = 8.1$ Hz, 2H, Ar-H), 7.41 (t, $^3J(H,H) = 7.5$ Hz, 2H, Ar-H), 7.53 (t, $^3J(H,H) = 7.5$ Hz, 2H, Ar-H), 7.56 (d, $^3J(H,H) = 7.5$ Hz, 2H, Ar-H); ^{13}C{^{1}H} NMR (125.8 MHz, CD_3CN): $\delta = 62.7$, (CH_2), 80.6 (CH_3), 124.1, 125.4, 129.7, 133.1, 135.1, 143.5 (arom. C); ^{29}Si NMR (99.4 MHz, [D_6]DMSO, RT): $\delta = -47.2$ ($^1J(Si,H) = 272$ Hz); ^{19}F{^{1}H} NMR (470.6 MHz, CD_3CN): $\delta = 142.78$; IR (KBr): $\tilde{\nu} = 2170$ cm^{-1}; C,H analysis (%) calcd for $C_{17}H_{19}F_3O_5SiS$ (420.5): C 48.60, H 4.55; found: C 48.59, H 4.60

1c: ^{1}H NMR (500.1 MHz, CD_2Cl_2, RT): $\delta = 1.36$ (s, 6H, SMe), 3.89, 3.94 (br, AB sys., 4H, CH_2), 6.10 (s, 1H, Si-H), 6.97 (m, 4H, Ar-H), 7.05 (d, $^3J(H,H) = 7.32$ Hz, 2H, Ar-H), 7.79 (d, $^3J(H,H) = 6.98$ Hz, 2H, Ar-H); ^{1}H NMR (500.1 MHz, C_7D_8, 90 °C): $\delta = 1.47$ (s, 6H, CH_3), 3.57 (s, 4H, CH_2), 6.19 (s, 1H, Si-H), 7.31–7.39 (m, 4H, Ar-H), 7.45 (t, $^3J(H,H) = 7.40$ Hz, 2H, Ar-H), 7.77 (d, $^3J(H,H) = 7.40$ Hz, 2H, Ar-H); ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): $\delta = 14.9$ (SMe), 38.8 (CH_2), 119.5 (q, $^1J(C,F) = 318.3$ Hz, CF_3), 127.4, 129.6, 130.8, 130.9, 136.1, 143.3 (arom. C); ^{29}Si NMR (99.4 MHz, C_6D_6, RT): $\delta = -47.9$ ($^1J(Si,H) = 278.4$ Hz); ^{29}Si NMR (99.4 MHz, C_7D_8, 90 °C): $\delta = -41.4$ ($^1J(Si,H) = 275$ Hz); ^{19}F{^{1}H} NMR (470.6 MHz, C_6D_6): $\delta = 132.7$; IR (KBr): $\tilde{\nu} = 2199$ cm^{-1}; C,H analysis (%) calcd for $C_{17}H_{19}F_3O_3S_3Si$ (452.6): C 45.11, H 4.23; found: C 44.99, H 5.76

1d: ^{1}H NMR (500.1 MHz, CD_2Cl_2, −80 °C): $\delta = 1.54$ (br s), 12H, CH_3), 3.30, 3.41 (AB sys., $^2J(H,H) = 9.98$ Hz, 4H, CH_2), 5.92 (t, $^2J(P,H) = 72.5$ Hz, 1H, Si-H), 7.32 (m, 4H, Ar-H), 7.41 (m, 2H, Ar-H), 7.47 (m, 2H, Ar-H); ^{1}H NMR (500.1 MHz, CD_2Cl_2, RT): $\delta = 1.54$ (t, $^2J(P,H) = 3.5$ Hz, 12H, PMe_2), 3.45 (t, $^2J(P,H) = 3.7$ Hz, 4H, CH_2), 5.98 (t, $^2J(P,H) = 55.1$ Hz, 1H, Si-H), 7.35 (t, $^3J(H,H) = 7.3$ Hz, 2H, Ar-H), 7.42 (m, 4H, Ar-H), 7.52 (t, $^3J(H,H) = 7.5$ Hz, 2H, Ar-H); ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, −80 °C): $\delta = 5.8$ (CH_3), 7.50 (CH_3), 30.1 (CH_2), 119.8 (q, $^1J(F,C) = 320$ Hz, CF_3), 127.0, 129.3, 131.3, 134.8, 142.7 (arom. C); ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, RT): $\delta = 14.9$ (SMe), 38.6 (CH_2), 127.4, 129.6, 130.8, 130.9, 136.1, 143.3 (arom. C); ^{29}Si NMR (99.4 MHz, CD_2Cl_2, −80 °C): $\delta = -104.3$ (t, $^1J(Si,P) = 37,8$ Hz); ^{29}Si NMR (99.4 MHz, C_6D_6, RT): $\delta = -67.8$ ($^1J(Si,H) = 251$, $^1J(P,Si) = 19.8$ Hz); ^{29}Si{^{1}H} CP-MAS NMR: $\delta = -89.2$;[10] ^{19}F{^{1}H} NMR (470.6 MHz, CD_2Cl_2): $\delta = 131.3$; ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2, −80 °C): $\delta = -17.9$; ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2, RT): $\delta = -22.1$; IR (KBr): $\tilde{\nu} = 2159$ cm^{-1}; C,H analysis (%) calcd for $C_{19}H_{25}ClF_3O_3P_2SiS$ (480.50): C 46.16, H 5.38; found: C 44.00, H, 5.22. A more accurate C,H analysis was impossible owing to the extreme sensitivity.

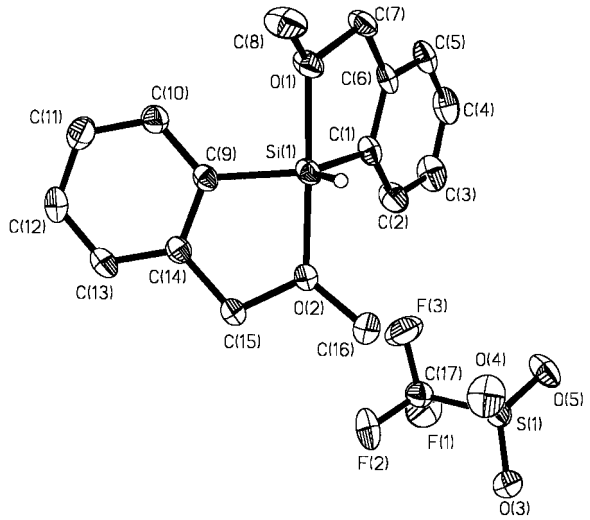


Figure 1. Molecular structure of **1b**; the ellipsoids correspond to a probability level of 50%. The hydrogen atoms were omitted for clarity. Selected bond lengths [pm] and angles [°]: Si(1)–O(1) 191.8(3), Si(1)–O(2) 192.3(3), Si(1)–H 137(4); C(1)-Si(1)-C(9) 120.7(2), C(1)-Si(1)-H(1) 118(2), C(9)-Si(1)-H(1) 121(2), O(1)-Si(1)-O(2) 178.57(12), C(1)-Si(1)-O(1) 84.7(2), C(1)-Si(1)-O(2) 96.6(2), O(1)-Si(1)-H(1) 88(2), O(2)-Si(1)-H(1) 92(2), C(9)-Si(1)-O(1) 94.6(2), C(9)-Si(1)-O(2) 84.3(2).

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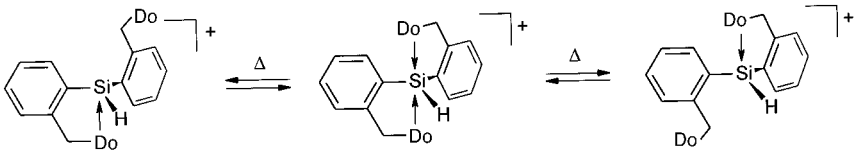

Scheme 1. Molecular dynamics in the cations of **1c, d**.

cations with "soft" ligands (**1c**, **d**), with activation energies of approximately 17 (**1c**) and 11 kcal mol^{-1} (**1d**). These dynamics can be proved by the cancellation of the diastereotopicity of the CH_2 units (**1c** and **1d**) and the PMe_2 unit (**1d**), as well as the temperature dependence of the $\delta(^{31}P)$, $^2J(P,H)$, and $^1J(Si,P)$ values (**1d**).

For a comparison of **1a**–**d**, the SiH units are important NMR spectroscopic probes (Table 2). The $\delta(^{29}Si)$ values are characteristic for trigonal-bipyramidal silicon centers (Table 1); the enormous upfield shift in **1d** is striking. The large

Table 2. Selected NMR data for **1a**–**d.**

	1a	**1b**	**1c**	**1d**
δ(Si)	−51.6	−47.2	−47.9	−104.3[a]
δ(H(Si))	4.60	5.18	6.10	5.92[b]
^1J(Si,H) [Hz]	272	272	279	251

[a] $T = -80\,^\circ$C, $^1J(Si,P) = 37.8$ Hz ($-80\,^\circ$C); [b] $^2J(P,H) = 72.5$ Hz ($-80\,^\circ$C).

^1J(Si,H) coupling constants speak for an increased s proportion in the Si–H bond (towards sp^2 hybridization[8]) in all cases. Significant differences are observed in the δ(H(Si)) values: A downfield shift occurs in the systems with "soft" donors (**1c**, **d**), speaking for a decrease in hydride character. Confirmation of this, as well as for the dynamics in **1c**, **d**, is supplied by quantum chemical calculations.

Ab initio calculations (CCSD(t)/6-311 + g**//MP2/6-31g**) on the model system SiH_3^+[9] speak for clearly different bonding situations in complexes with "hard" (OH_2, NH_3) and with "soft" donors (SH_2, PH_3). A comparison of the bond energies [kcal mol^{-1}] for the tetrahedrally coordinated monoaddition products $[Do \rightarrow SiH_3]^+$ (Do = OH_2 (51.4), NH_3 (72.3), SH_2 (46.4), PH_3 (57.1)) with those for the trigonal-bipyramidal bis-addition products $[Do \rightarrow SiH_3 \leftarrow Do]^+$ (Do = OH_2 (74.3), NH_3 (100.2), SH_2 (59.0), PH_3 (67.8)) shows that the addition of a second donor molecule is less exothermic in the case of the "soft" donors. A comparatively easier dissociation—as in the process according to Scheme 1—thus becomes understandable. The differences in the Do→Si bonds of the bis-adducts $[Do \rightarrow SiH_3 \leftarrow Do]^+$ follow immediately from population analyses, which is documented in Scheme 2 with charge densities at atomic groups (values in square brackets) and of Wiberg bond orders (values in parentheses) according to the NBO method (NBO = natural bond orbital).

Accordingly, a transfer of electron density to the SiH_3^+ ion is much less distinctive for a "hard" donor than for a "soft" donor. Therefore, Do→Si bonds with "soft" donors show a comparatively higher covalent character. GIAO calculations confirm the trend observed for the δ(H(Si)) values (Table 2); population analyses yield comparatively less negative charge densities for the H atoms in **1c**, **d** (SiH_3^+: −0.152, $(NH_3)_2SiH_3^+$: −0.188, $(OH_2)_2SiH_3^+$: −0.183, $(PH_3)_2SiH_3^+$: −0.144, $(SH_2)_2SiH_3^+$: −0.149).

The differences in structure between **1a**–**d** lead to marked differences in reactivity, as preliminary experiments have shown. Therefore, the susceptibility towards hydrolysis and the general reactivity towards nucleophiles increases drastically in the order **1b** < **1c** < **1d**. Surprisingly, **1b** reacts like an oxonium salt with pyridine, under transfer of a methyl group and formation of a neutral five-membered silyl ether; on the other hand, **1c**, **d** react under substitution of a donor molecule. The addition of acetonitrile leads to the exchange of a donor molecule in the case of **1c**, to the formation of a product with an as yet unknown structure in the case of **1d**, and to no reaction in the case of **1b**.

The stabilization of a silicenium ion with O-, S-, or P-donors described here has interesting consequences in terms of structure and bond theory, and also offers the possibility of control of reactivity. This concept should be transferable to other element cations of the type R_xEl^{n+}.

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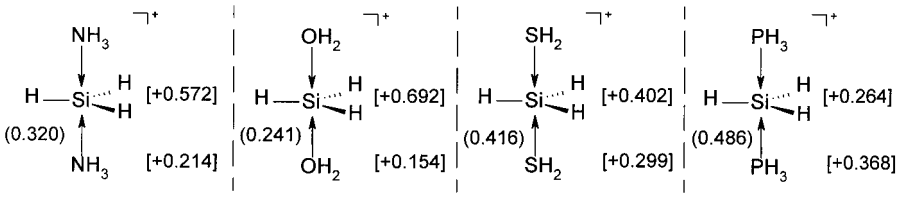

Scheme 2. Charge density at atomic groups (values in square brackets) and Wiberg bond orders (values in parentheses); average values over all H atoms are given for OH_2 and SH_2, respectively.

[1] a) Review: P. Lickiss in *The Chemistry of Organic Silicon Compounds*, *Vol. 2*, *Part 1* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, **1998**, pp. 557–594; b) σ donors: J. Y. Corey, R. West, *J. Am. Chem. Soc.* **1963**, *85*, 4034–4035; B. J. Aylett, J. M. Campbell, *J. Chem. Soc. Chem. Commun.* **1967**, 159; Hensen, T. Zengerly, P. Pickel, G. Klebe, *Angew. Chem.* **1983**, *95*, 739; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 725; c) A. R. Bassindale, T. Stout, *J. Chem. Soc. Chem. Commun.* **1984**, 1387–1389; d) A. R. Bassindale, T. Stout, *Tetrahedron Lett.* **1985**, *26*, 3403–3406; e) J. Chojnowski, W. Stanczyk, *Adv. Organomet. Chem.* **1990**, *30*, 243–307; f) M. Kira, T. Hino, H. Sakurai, *Chem. Lett.* **1993**, 153–156; g) S. R. Bahr, P. Boudjouk, *J. Am. Chem. Soc.* **1993**, *115*, 4514–4519.

[2] π Donors: a) J. B. Lambert, S. Zhang, C. L. Stern, J. C. Huffman, *Science* **1993**, *260*, 1917; b) P. Jutzi, E. A. Bunte, *Angew. Chem.* **1992**, *104*, 1636–1638; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1605; c) H.-U. Steinberger, T. Müller, N. Auner, C. Maerker, P. von R. Schleyer, *Angew. Chem.* **1997**, *109*, 667–669; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 626–628.

[3] C. Chuit, R. J. P. Corriu, A. Mehdi, C. Reyé, *Angew. Chem.* **1993**, *105*, 1372; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1311.

[4] J. Belzner, D. Schär, B. O. Kneisel, R. Herbst-Irmer, *Organometallics* **1995**, *14*, 1840.

[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 CB2 1EZ, 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 $[(Me_3Sn)_3O]Cl$**

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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)].

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

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

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 ^{1}H NMR spectroscopy. Unfortunately, we were not able to obtain single crystals; traces of LiCl probably prevent crystallization. In the ^{1}H 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

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