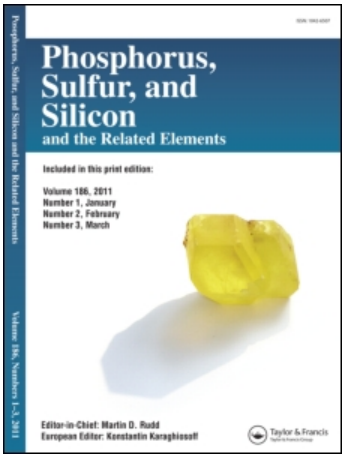

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REACTION OF 1,3-DI-TERT-BUTYL-2,2-DIMETHYL-4,4-DICHLORO-1,3,2,4λ⁴-DIAZASILASTANNETIDINE WITH SILVER TRIFLUOROMETHANESULFONATE. THE CRYSTAL STRUCTURE OF POLYMERIC 1,3-DI-TERT-BUTYL-2,4-DIMETHYL-2,4-DITRIFLUOROMETHANESULFONATE-1,3,2,4λ⁵-DIAZASILASTANNETIDINE

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When 1,3-di-tert-butyl-2,2-dimethyl-4,4-dichloro-1,3,2,4λ²-diazasilastannetidine (**1**) is allowed to react with the chloride abstracting reagent $AgCF_3SO_3$ the chlorides are displaced by triflates forming **2**. At the same time a rearrangement in the molecule takes place, one of the methyl groups on silicon migrating to tin in exchange of a triflate. In the solid the new compound **2** is a coordination polymer with trigonal bi-pyramidal tin centers, which exhibit quite unusual short Sn—N bonds in the axial plane (2.005 Å) [X-ray structure determination, space group $P2_1/n$, a = 10.199(6)Å, b = 13.532(9)Å, c = 17.641(9)Å, β = 99.13(9)°, Z = 4].

Key words: Tin; low coordinate; possible multiple bonding; X-ray.

INTRODUCTION

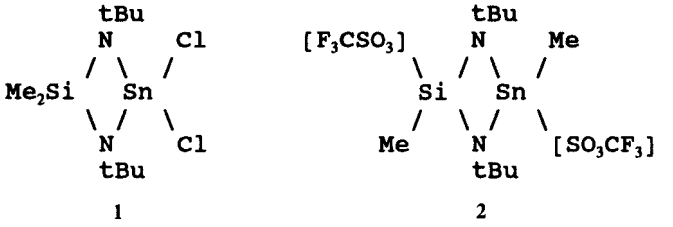
Dicoordinate cationic environments for the heavier pnictogen (Group 15) elements have been the subject of considerable interest in recent years, and are now well characterized.[1,2,3] Subtle structural and electronic differences between phosphorus and its heavier relatives have been revealed both for the salts themselves and for coordination complexes of the cations.[4]

In contrast, despite extensive investigations, especially involving silicon-containing compounds, tricoordinate cationic centers for the heavier Group 14 elements remain elusive and controversial.[5]

Studies into the analogous tin compounds appear to be limited to trialkyl derivates.[6] These compounds, at one time believed to contain discrete tin cations, have been subsequently shown to be polymeric in nature with trigonal bipyramidal tin centers.[6] However, alkyl substituent groups provide, at best, only poor stabilization for such unstable environments. As the bis(*t*-butylamido)dimethylsilane ligand has proved effective in the stabilization of Group 15 dicoordinate cations through a combination of electronic and steric effects[3] we have undertaken a study of the reaction of 1,3-di-tert-butyl-2,2-dimethyl-4,4-dichloro-1,3,2,4λ⁴-diaza-silastannetidine (**1**) with the chloride abstracting agent $AgCF_3SO_3$. Below we report the results of this investigation.

RESULTS AND DISCUSSION

The reaction of **1** with 2 equivalents of $AgCF_3SO_3$ in CH_2Cl_2 has been followed by ^{1}H-NMR and is extremely complex. However if after two hours the precipitated AgCl is removed by filtration of the solvent *in vacuo*, a white residue is obtained. Recrystallization of this residue with diethyl ether gives a coloured crystalline product **2** in 30% yield.



1 **2**

^{1}H-NMR of **2** reveals a dramatic structural adjustment from its precursor **1** with the migration of a methyl group from the silicon across the ring to the tin atom (^{1}H-HMR: tin satellites on the methyl group attached to tin). It is interesting to note that similar methyl transfers have been observed when $Me_2Si(NtBu)_2Li_2$ is allowed to react with $GaCl_3$.[7] Elemental analysis and the mass spectrum of **2** were both consistent with the removal of both chlorine atoms and their replacement by two CF_3SO_3 moieties. In order to ascertain the true structure of **2** a single crystal X-ray structural investigation was carried out. Details of the structure solution and the crystal data are given in Table I. Table II contains the most important bond lengths and angles of **2** and Table III gives the atomic coordinates of the non-hydrogen atoms.[8,9] The quality of the crystal structure determination of **2** is somewhat less than desired because of the serious disorder associated with the CF_3SO_3 group attached to the silicon atom. However, the overall molecular structure is clear and the accuracy of the structural parameters around the tin center is sufficient to allow meaningful discussion.

As can be seen from Figures 1 and 2, **2** is clearly polymeric in structure, with the essentially planar N_2SnC units being bridged by CF_3SO_3 moieties to give a distorted trigonal bipyramid geometry at the tin atom. Two oxygens of the SO_3-group [O(1) and O(2)] are bridging all tin centers. The silicon is at a first sight four coordinate with one terminal F_3CSO_3 ligand, which has no other interactions to neighbouring molecular units and which is highly disordered. Looking more closely at the structure, a very weak interaction can be detected between the SO_3-group of S(1′) and silicon: the Si . . . O(3′) distance is 3.75 Å which is in the order of the sum of the van der Waals radii of Si and O (3.60–3.80 Å). This interaction, which may be merely steric in nature, helps to explain the severe distortion on the silicon-tetrahedron (e.g. Sn . . . Si—C(10) = 138.5° whereas Sn . . . Si—O(4) = 115.3°). It is also interesting to note that the O(4)—Si . . . O(3′) angle is 170.8°.

The lengths of the bonds from tin to the neighbouring atomic centers are worth being discussed more closely. Although the Sn—C bond is standard for trigonal bipyramidal tin, both Sn—O bonds are relatively long [2.41(1), 2.33(1)Å]. In related compounds it is unusual for both such bonds to be so elongated; instead they tend either to be both shorter than those found in **2** (e.g. in $[Ph_3Sn(OPPh_3)(NO_3)]$:

Sn—O 2.22(2), 2.29(2)Å[10] or to have one short and one long bond (e.g. in $[(PhCH_2)_3Sn(CH_3CO_2)]$: Sn—O 2.65(2), 2.14(2)Å).[11] This observation taken together with the relative shortness of the Sn—N bonds [1.99(1), 2.02(1)Å] [typical

TABLE I

Crystal data and details of the X-ray structure determination of **2**

Formula	$C_{12}H_{24}F_6N_2O_6S_2SiSn$
Mol. Weight	617.25 g/mol
Crystal System	monoclinic
Space Group	$P2_1/n$
Lattice Parameters	a 10.199(6)
	b 13.532(9)
[Å] and [°]	c 17.641(9)
	β 99.13(9)
Volume [Å^3]	V = 2404(1)
Number of Molecules per Unit Cell	Z = 4
D_x[g/cm^3]	1.429
μ (MoKα)[cm^{-1}]	1.24
Diffractometer, λ, Temperature	Siemens/Stoe AED 2, MoKα, 290K
Max. and Min. 2θ Values	3° < 2θ < 45°
Number of Independent Reflections	3080
"Observed" Reflections	2916
σ-Limit for F_0	2σ
Structure Solution	direct methods
H-Atoms	fixed with C-H = 0.96Å
Number of Parameters	242
R-Values R	0.072
R_w	0.069
Weighting Scheme	$W = 1/(\sigma_F^2 + 0.000001*F^2)$

TABLE II

Important bond distances (Å), and angles (°) for **2**

N(1)---Sn	1.99(1)	N(2)---Sn	2.02(1)
O(1)---Sn	2.410(9)	O(2)---Sn	2.33(1)
C(11)--Sn	2.13(2)	N(1)---Si	1.70(1)
N(2)---Si	1.71(1)	C(10)--Si	1.80(2)
O(4)---Si	1.75(1)	O(1)---S(1)	1.45(1)
O(3)---S(1)	1.40(1)	C(1)---S(1)	1.86(2)
O(2)---S(1)	1.47(1)	C(2)---N(1)	1.49(2)
C(6)---N(2)	1.44(2)	C(1)---F(1)	1.31(3)
C(1)---F(2)	1.29(3)	C(1)---F(3)	1.29(2)

TABLE II (*Continued*)

N(1)	-Sn	-N(2)	77.2(4)	Si	-Sn	-O(1)	90.1(3)
N(1)	-Sn	-O(1)	88.7(4)	N(2)	-Sn	-O(1)	92.8(4)
N(1)	-Sn	-O(2)	98.3(4)	N(2)	-Sn	-O(2)	97.0(4)
O(1)	-Sn	-O(2)	169.0(4)	N(1)	-Sn	-C(11)	143.8(6)
N(2)	-Sn	-C(11)	138.7(5)	O(1)	-Sn	-C(11)	85.5(5)
O(2)	-Sn	-C(11)	83.8(5)	N(1)	-Si	-N(2)	94.6(6)
N(1)	-Si	-C(10)	121.4(7)	N(2)	-Si	-C(10)	118.6(7)
N(1)	-Si	-O(4)	109.2(6)	N(2)	-Si	-O(4)	106.3(5)
C(10)	-Si	-O(4)	105.8(7)	O(1)	-S(1)	-O(3)	116.9(7)
O(1)	-S(1)	-C(1)	102.6(8)	O(3)	-S(1)	-C(1)	104.2(9)
O(1)	-S(1)	-O(2)	111.8(6)	O(3)	-S(1)	-O(2)	117.3(6)
C(1)	-S(1)	-O(2)	101.0(8)	Sn	-N(1)	-Si	94.8(5)
Sn	-N(1)	-C(2)	130(1)	Si	-N(1)	-C(2)	134(1)
Sn	-N(2)	-Si	93.4(5)	Sn	-N(2)	-C(6)	131.6(9)
Si	-N(2)	-C(6)	135(1)				

TABLE III

Position parameters and isotropic B-values of the atoms in the unit cell of 2

Atom	x	y	z	B[Å²]
Sn	0.2583(1)	0.33033(7)	0.76217(5)	3.11(5)
Si	0.2746(4)	0.3354(3)	0.9177(2)	3.5(2)
S(1)	0.1120(4)	0.0781(3)	0.7214(2)	3.5(2)
N(1)	0.381(1)	0.2983(8)	0.8587(6)	3.3(6)
N(2)	0.154(1)	0.3724(8)	0.8446(6)	3.1(6)
O(1)	0.175(1)	0.1634(7)	0.7605(6)	4.7(6)
O(2)	0.3424(9)	0.4855(7)	0.7394(6)	4.5(6)
O(3)	0.096(1)	0.0786(8)	0.6413(6)	5.2(7)
F(1)	-0.115(1)	0.1665(9)	0.7118(8)	9.1(8)
F(2)	-0.058(1)	0.093(1)	0.8167(9)	11.(1)
F(3)	-0.126(1)	0.010(1)	0.715(1)	11.(1)
C(1)	-0.060(2)	0.086(2)	0.743(1)	7.(1)
C(2)	0.510(1)	0.245(1)	0.8706(9)	4.2(9)
C(3)	0.570(2)	0.249(1)	0.800(1)	6.5(4)
C(4)	0.600(2)	0.294(1)	0.936(1)	6.5(4)
C(5)	0.491(2)	0.138(1)	0.893(1)	7.3(5)
C(6)	0.029(1)	0.424(1)	0.8406(9)	3.9(9)
C(7)	0.053(2)	0.530(1)	0.863(1)	6.9(5)
C(8)	-0.053(2)	0.377(2)	0.893(1)	7.9(5)
C(9)	-0.045(2)	0.420(2)	0.759(1)	8.0(5)
C(10)	0.326(2)	0.420(1)	0.9958(9)	5.6(4)
C(11)	0.231(2)	0.317(1)	0.6406(9)	5.9(4)
S(2a)	0.223(1)	0.2046(8)	1.0468(6)	6.7(2)*
S(2b)	0.248(1)	0.148(1)	1.0176(9)	9.1(3)*
O(4)	0.212(1)	0.2318(8)	0.9589(6)	5.3(2)
O(5)	0.360(2)	0.176(1)	1.0742(9)	10.2(4)
O(6a)	0.131(5)	0.260(4)	1.090(3)	21.(2) *
O(6b)	0.205(4)	0.054(2)	0.979(2)	12.(1) *
C(12a)	0.153(2)	0.068(2)	1.040(1)	19.(2) *
C(12b)	0.099(3)	0.169(2)	1.061(2)	16.(2) *
F(4a)	0.027(2)	0.094(2)	1.010(1)	16.7(8)*
F(5a)	0.181(2)	0.049(2)	1.115(1)	16.6(8)*
F(6a)	0.230(2)	0.027(2)	0.993(1)	13.7(8)*
F(4b)	0.137(3)	0.263(2)	1.083(2)	11.(1) *
F(5b)	0.117(3)	0.099(2)	1.116(2)	19.(1) *
F(6b)	-0.007(3)	0.160(2)	1.006(1)	12.0(9)*

* Site Occupation Factor: 0.5

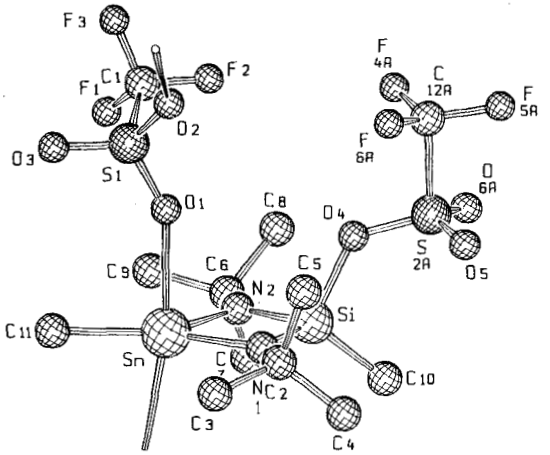


FIGURE 1 The structure and atom numbering of $(F_3C—SO_3)(Me)Sn(NtBu)_2Si(Me)(O_3S—CF_3)$ (**2**).

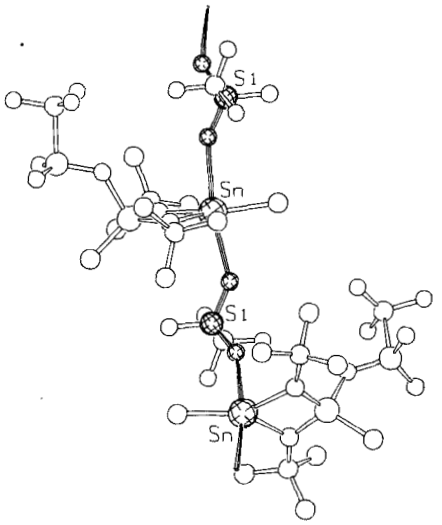
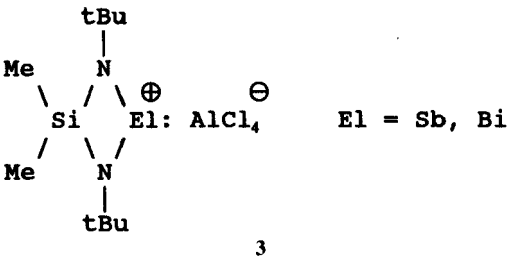


FIGURE 2 The one dimensional arrangement of **2** within the crystal (for atomic numbering see Figure 1).

Sn—N bond lengths are around 2.05–2.10 Å e.g. in $(MeSi)_2(NtBu)_4SnCl_2$: Sn—N 2.052(6), 2.040(16)Å][12] suggest some donation of electron density from the nitrogen centers to the tin atom and a tendency away from a fully covalent system towards one with more ionic character. An interesting comparison to **2** is to be found in the structures of 1,3-di-tert-butyl-2,2-dimethyl-1,3,2,4λ^2-diazastibonium and -bismuthonium tetrachloroaluminates **3**,[3] in which the CF_3SO_3-bridges are replaced by $AlCl_4$-units, the tin center by an antimony or bismuth and the methyl group by a lone pair.

Here, too, we find an association of the cationic and anionic units of the structure and a marginal shortening of the pnictogen-nitrogen bonds, further demonstrating the preference of heavier elements in the main group to accommodate electron



3

deficiency by an increase in coordination number rather than by the formation of multiple bonds to adjacent, electron-donating centers.[13]

EXPERIMENTAL

Nonchlorinated solvents were purified for several days of reflux over $LiAlH_4$ followed by distillation and were stored over Na. CH_2Cl_2 was distilled from P_4O_{10} and CaH_2 (2×) and stored over molecular sieves. Reactions were performed under nitrogen using modified Stock-type vacuum line, ^{1}H-NMR were obtained using a Bruker WP80 (80 MHz) machine, mass spectra using a Finnigen MAT 90 (120 eV), and chemical ionization techniques (reagent gas, iso-butane). 1,3-Di-tert-butyl-2,2-dimethyl-4,4-dichloro-1,3,2,4λ^4-diazasilastannetidine **1** was prepared using the literature method[14] and purified by vacuum sublimation.

1,3-Di-tert-butyl-2,4-dimethyl-2,4-difluoromethanesulfonate-1,3,2,4λ^5-diazasilastannetidine (**2**). A solution of **1** (0.44 g, 1.13 mmol) in CH_2Cl_2 (2.5 ml) was added dropwise to a stirred suspension of $AgCF_3SO_3$ in CH_2Cl_2 (2.5 ml). The reaction vessel was protected from light with aluminium foil. The reaction mixture was stirred at RT for 2 hours and then filtered. The solvent was removed *in vacuo* and the residue recrystallized from Et_2O to give 0.207 g (30%) of **2** as colourless crystals, which decompose at 145°C.

^{1}H-NMR (in CH_2Cl_2/C_6D_6)δ: 0.34(3H, $SiCH_3$), 0.89(3H, $SnCH_3$) 1.08(18H, tBu).

$C_{12}H_{24}F_6N_2O_6S_2SiSn$ (617.25)	calc	C 23.35	H 3.93	N 4.54
	found	C 23.49	H 4.19	N 4.62

MS(CI): (m/z, relative abundance): 619(100; $M^+ + 1$); 603(73; M^+-CH_3) 469(65; M^+-CF_3SO_3) with ^{120}Sn-Isotop.

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