Formation of the Novel Six-Coordinate Atrane Cation in $[FMeSn(HMeNCH_2CH_2)_2N(CH_2CH_2NMe)]BF_4$

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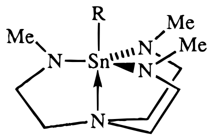
The reaction of the azastannatranes $RSn(NMeCH_2CH_2)_3N$ **1** (R = Me), **2** (R = *n*-Bu), and **3** (R = Ph) with $BF_3{\cdot}Et_2O$ in THF gave the novel six-coordinate tin compounds **4**−**6**, respectively, in which BF_3 adds across one of the three covalent Sn−N bonds to give a $F{-}Sn{\leftarrow}NMe(BF_2)$ linkage. The tricyclic atrane framework retained in the reaction with $BF_3{\cdot}Et_2O$ is preserved under hydrolysis conditions with substoichiometric amounts of water. A hydrolysis product of **4** is the new fluorotin salt $[FMeSn(HMeNCH_2CH_2)_2N(CH_2CH_2NMe)]BF_4$ [**7**(BF_4)] whose structure, determined by X-ray analysis, also features a six-coordinate tin atom. The IR and NMR spectra of **4**−**6** confirm their six-coordinate nature. The ^1H and ^{13}C NMR spectra are assigned using COSY, NOESY, and selectively proton decoupled ^{13}C NMR spectral techniques. Crystallographic parameters for **7**(BF_4) are as follows: triclinic space group $P\bar{1}$, $a = 8.295(2)$ Å, $b = 8.924(2)$ Å, $c = 13.639(2)$ Å, $\alpha = 88.59(2)°$, $\beta = 74.83(2)°$, $\gamma = 79.99(2)°$, and $Z = 2$.

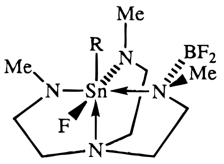
Introduction

We recently described a series of new azastannatranes synthesized by the transamination reaction of $RSn(NMe_2)_3$ with tris(2-aminoethyl)amine (tren) or its tri-*N*-methyl-substituted derivative (Me-tren).[1] The chemistry of the new azastannatranes is dominated by preservation of the tricyclic atrane framework. They were found to undergo facile transmetalation reactions with transition metal alkoxides, transferring their atrane framework intact onto the transition metal.[2] The reaction of the dimethylamino-substituted azastannatrane $Me_2NSn(HNCH_2CH_2)_3N$ with protic species took place exclusively at the Me_2N nitrogen due to the stability of the transannulated framework in which the tin is five-coordinate.[3] Thus, the chemistry of these tricyclic aminostannanes was found to contrast that of their acyclic analogues studied by Lappert et al. in 1965.[4,5]

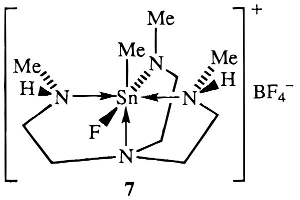
Here we report on the reaction of **1**−**3** (which possess more innocent apical substituents) with $BF_3{\cdot}Et_2O$ to give **4**−**6**. Interestingly the tricyclic atrane framework in **4** was found to be stable under hydrolytic conditions, affording the novel cation **7** stabilized by three coordinating amino functionalities. The IR and NMR characteristics of the new compounds **4**−**7** are described.



	R
1	Me
2	*n*-Bu
3	Ph



4, R = Me
5, R = *n*-Bu
6, R = Ph



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Experimental Section

All manipulations were carried out in an atmosphere of dry argon under strict exclusion of moisture using standard vacuum line techniques. Solvents were purified by standard methods[6] and distilled prior to use. Samples for IR and solid state NMR experiments were prepared in a drybox under an atmosphere of dry and oxygen-free nitrogen. The azastannatranes **1**−**3** were prepared as described earlier.[1] Melting points were determined with a Thomas Hoover capillary melting point apparatus and are uncorrected. Microanalyses were carried out by Galbraith Laboratories. MS measurements were carried out on a Finnigan 4000 instrument using CI (NH_3) and EI techniques. IR spectra were recorded on an IBM98 FT-IR spectrometer. The samples were prepared as KBr pellets (4000−600 cm^{-1}) and as Nujol mulls between polyethylene plates (650−150 cm^{-1}), respectively. Solution NMR spectra were recorded on a Varian VXR500 (^1H, 499.84 MHz; ^{19}F, 470.27 MH), a VXR300 (^1H, 299.95 MHz; ^{11}B, 96.23 MHz; ^{13}C, 75.43 MHz; ^{19}F, 282.20 MHz; ^{119}Sn, 111.92 MHz), and a Bruker WM200 (^{119}Sn, 74.63 MHz; ^{13}C, 50.32 MHz) instrument using deuterated solvents as internal lock and TMS (^1H, ^{13}C), $BF_3{\cdot}Et_2O$ (^{11}B), $CFCl_3$ (^{19}F), and $SnMe_4$ (^{119}Sn) as external standards, respectively. Positive values of δ are downfield of the standard. For solid-state NMR spectra, glycine (^{13}C) and tetracyclohexyltin (^{119}Sn),[7] respectively, were used as secondary references. For the measurement of solid-state NMR spectra, polycrystalline samples (ca. 300−400 mg) were packed in either an airtight insert or directly into a ZrO_2 rotor, which was sealed by a threaded Teflon plunger. Spectra were obtained on a Bruker MSL300 spectrometer (^{13}C, 75.47 MHz; ^{119}Sn, 111.92 MHz) under proton decoupling using the CP/MAS technique, with sweep widths of 10−

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25 (^{13}C) and 100 kHz (^{119}Sn), respectively. A 90° pulse was employed with mixing times for polarization transfer of 2−3 ms followed by a 6 s recycle delay. Spinning rates were in the range 2.0−4.5 kHz. Spectra were generally rerun at different speeds to establish the position of the centerband. The magic angle was set by using the ^{79}Br resonance of KBr.[8]

Synthesis of 4. To a stirred solution of 2.3 g of **1** (7.1 mmol) in 30 mL of tetrahydrofuran (THF) was added dropwise 1.0 equiv (0.87 mL) of neat $BF_3{\cdot}Et_2O$. During the addition the solution warmed to about 40 °C. After the mixture was stirred for 30 min at room temperature, the small amount of white precipitate formed (probably including $B(OH)_3$) was removed by filtration. After removal of the solvent in vacuum, the resulting colorless solid was washed with *n*-pentane and dried in vacuo giving 2.5 g (91%) of product.

Synthesis of 5. After addition of 1.3 mL (11 mmol) of neat $BF_3{\cdot}Et_2O$ adduct to a stirred solution of 3.8 g (11 mmol) of **2** in 50 mL of THF, the temperature of the reaction mixture spontaneously rose to ca. 40 °C. After the mixture was stirred for 45 min at room temperature, the solvent was removed in vacuo. The resulting yellowish solid was redissolved in toluene and filtered to remove the insoluble materials (probably including $B(OH)_3$). Removal of the toluene afforded 4.0 g (88%) of a colorless oil, which upon standing at room temperature slowly solidified, mp dec > 110 °C. Anal. Calcd (found) for $C_{13}H_{30}BF_3N_4Sn$: C, 36.40 (34.64); H, 7.05 (7.65); B, 2.52 (2.12); N, 13.06 (10.94). MS (CI, NH_3): *m/e* 431 ($[M + H]^+$); with EI (70 eV) a weak M^+ peak was observed. IR (cm^{-1}): 264 (w), 320 (vw), 363 (vw), 424 (vw), 438 (vw), 465 (w), 482 (m), 503 (w), 514 (vw), 576 (vw), 604 (vw), 622 (w), 689 (w), 762 (w), 802 (w), 851 (m), 862 (w), 879 (m), 926 (m), 1007 (s), 1020 (vs), 1040 (vs), 1072 (s), 1094 (m), 1113 (m), 1155 (m), 1178 (s), 1196 (m), 1215 (m), 1229 (w), 1252 (w), 1292 (m), 1302 (m), 1312 (m), 1344 (w), 1362 (m), 1377 (m), 1391 (w), 1400 (w), 1423 (w), 1431 (m), 1458 (sh), 1466 (s), 1479 (m), 2673 (m), 2772 (s), 2822 (s), 2843 (s), 2868 (s), 2905 (s), 2949 (vs), 3009 (m).

Synthesis of 6. To a stirred solution of 2.5 g of **3** (6.5 mmol) dissolved in 35 mL of THF was added dropwise 0.80 mL of $BF_3{\cdot}Et_2O$ (6.5 mmol). The temperature of the reaction mixture rose to ca. 40 °C. Stirring was continued for 30 min at room temperature, and then the solvent was removed under reduced pressure. The resulting colorless solid was washed with *n*-pentane and dried in vacuo, affording 2.7 g (93%) of a colorless solid, mp dec > 120 °C. Anal. Calcd (found) for $C_{15}H_{26}BF_3N_4Sn$: C, 40.14 (38.02); H, 5.84 (5.90); F, 12.70 (12.55); N, 12.48 (11.41). MS (CI, NH_3): *m/e* 450 (M^+); with EI no M^+ peak was observed. IR (cm^{-1}): 262 (vw), 282 (vw), 365 (vw), 424 (vw), 439 (sh), 451 (w), 466 (w), 487 (m), 507 (sh), 514 (vw), 576 (vw), 605 (vw), 622 (w), 656 (w), 688 (sh), 704 (m), 737 (m), 760 (w), 802 (w), 847 (m), 862 (w), 879 (m), 928 (m), 1005 (s), 1022 (vs), 1040 (vs), 1070 (s), 1091 (sh), 1115 (m), 1150 (m), 1180 (s), 1195 (sh), 1211 (m), 1267 (w), 1283 (w), 1290 (m), 1305 (w), 1315 (sh), 1339 (w), 1350 (w), 1373 (w), 1389 (sh), 1429 (m), 1458 (sh), 1466 (s), 1481 (m), 1568 (w), 1580 (vw), 2770 (m), 2816 (vs), 2851 (s), 2883 (s), 2908 (s), 2932 (vs), 2943 (s), 2959 (s), 2991 (s), 3013 (m).

X-ray Diffraction Study of 7(BF_4). A triclinic crystal of the colorless compound was attached to the tip of a glass fiber and mounted on a P4/RA diffractometer for a data collection at −50 ± 1 °C. The cell constants for data collection were determined from reflections found by a rotation photograph. Pertinent data collection and reduction information are given in Table 1. Lorentz and polarization corrections were applied. A correction based on decay in the standard reflections was applied to the data. A series of azimuthal reflections was collected in order to apply a semi-empirical absorption correction. The agreement factor for the averaging of reflections was 1.0%. The space group $P\bar{1}$ was not chosen initially, because the intensity statistics had an acentric distribution. A direct-methods solution[9] was generated in $P\bar{1}$ which was later found to be centrosymmetric. The appropriate transformation was made to half of the atomic coordinates to transform to $P\bar{1}$. This assumption proved to be correct as shown by a successful refinement. All non-hydrogen atoms were placed directly from the *E*-map with the exception of the solvent. A set of least-squares and difference-Fourier runs provided the remaining non-hydrogen atoms. These were refined with anisotropic thermal parameters. The hydrogens of the cation were refined as riding atoms with the ideal distance of 0.96 Å from the host atom. This was carried out with individual isotropic thermal parameters for all of the hydrogen atoms with the exception of the amino protons which were refined as isotropic atoms. One solvent molecule of benzene was found for every two complexes. Selected bond lengths and angles are listed in Table 2. The X-ray data collection and structure solution were carried out at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment Corp. MicroVAX 3100/76 computer using the SHELXTL-Plus programs.[9]

Table 1. Crystallographic Data for **7**(BF_4)

formula	$C_{13}H_{29}BF_5N_4Sn$
fw	465.9
space group	$P\bar{1}$
cryst size (mm)	0.40 × 0.30 × 0.18
cryst system	triclinic
a, Å	8.295(2)
b, Å	8.924(2)
c, Å	13.639(2)
α, deg	88.59(2)
β, deg	74.83(2)
γ, deg	79.99(2)
V, $Å^3$	959.4(2)
Z	2
d_{calc}, Mg/m^3	1.613
data collecn instrument	P4/RA
$\mu(Mo, K_\alpha)$, mm^{-1}	1.380
temp, K	223
data collecn range, 2θ, deg	3.5−50.0
scan method	θ−2θ
unique data total	3397
unique data, with $F > 6.0\sigma(F)$	3040
R^a	0.021
$R_w{}^b$	0.025

[a] $R = \sum||F_o| = |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2(|F_o|)$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Cation in **7**(BF_4)

Bond Lengths			
Sn(1)−F(1)	2.038(1)	Sn(1)−C(10)	2.132(3)
Sn(1)−N(1)	2.291(2)	Sn(1)−N(2)	2.049(3)
Sn(1)−N(3)	2.238(3)	Sn(1)−N(4)	2.291(3)
Bond Angles			
F(1)−Sn(1)−C(10)	94.2(1)	F(1)−Sn(1)−N(1)	79.8(1)
C(10)−Sn(1)−N(1)	174.1(1)	F(1)−Sn(1)−N(2)	158.1(1)
C(10)−Sn(1)−N(2)	107.5(1)	N(1)−Sn(1)−N(2)	78.5(1)
F(1)−Sn(1)−N(3)	81.7(1)	C(10)−Sn(1)−N(3)	100.6(1)
N(1)−Sn(1)−N(3)	78.5(1)	N(2)−Sn(1)−N(3)	96.5(1)
F(1)−Sn(1)−N(4)	77.7(1)	C(10)−Sn(1)−N(4)	101.7(1)
N(1)−Sn(1)−N(4)	77.4(1)	N(2)−Sn(1)−N(4)	94.9(1)
N(3)−Sn(1)−N(4)	150.6(1)	Sn(1)−N(1)−C(1)	108.9(2)
Sn(1)−N(1)−C(3)	105.9(2)	C(1)−N(1)−C(3)	111.1(2)
Sn(1)−N(1)−C(5)	107.2(2)	C(1)−N(1)−C(5)	111.3(2)
C(3)−N(1)−C(5)	112.1(2)	Sn(1)−N(2)−C(2)	119.2(3)
Sn(1)−N(2)−C(7)	122.3(2)	C(2)−N(2)−C(7)	118.5(3)
Sn(1)−N(3)−C(4)	110.7(2)	Sn(1)−N(3)−C(7)	113.7(2)
C(4)−N(3)−C(8)	111.9(2)	Sn(1)−N(4)−C(6)	110.0(2)
Sn(1)−N(4)−C(9)	115.3(2)	C(6)−N(4)−C(9)	111.7(3)

Results and Discussion

Synthesis and Hydrolysis Study. The reactions of azastannatranes **1−3** with $BF_3{\cdot}Et_2O$ in tetrahydrofuran at room temperature took place quantitatively to give **4−6**, respectively. These products are soluble in THF, benzene, and toluene. They are stable indefinitely even under refluxing conditions in these solvents as monitored by ^{13}C and ^{119}Sn NMR spectroscopies.

Hydrolysis of **4** with a substoichiometric amount of water in THF yielded a few crystals of the salt **7**[BF_4] which is formally

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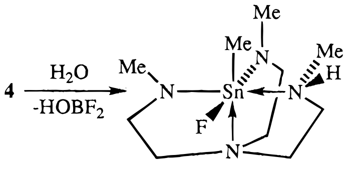
(8) Fry, J. S.; Maciel, G. E. *J. Magn. Reson.* **1982**, *48*, 125.

(9) SHELXTL-PLUS, Siemens Analytical Xray, Inc., Madison, WI.

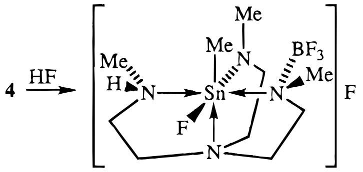
an adduct of **1** with HF and HBF$_4$. The formation of the six-coordinate tin cation **7** is further evidence for the robustness of the tricyclic azastannatrane framework. The first step in the hydrolysis of **4** is probably cleavage of the N−BF$_2$ bond, yielding the formal hydrogen fluoride azastannatrane adduct **8**:



8 (1)

$$HOBF_2 + 2\,H_2O \longrightarrow B(OH)_3 + 2\,HF \quad (2)$$

Further hydrolysis of the HOBF$_2$ liberated in reaction 1 could then occur according to reaction 2. One of the HF molecules formed in this reaction could add to the BF$_2$ group of a second molecule of **4**, thereby affording **9** as a formal BF$_3$ adduct of **8**:



9 (3)

The probable stereochemistries of the equatorial quaternary nitrogens in **9** will be discussed later. The remaining HF molecule could then cleave the B−N bond in **9** yielding **7**[BF$_4$] as the final product with the overall reaction being

$$2\,\mathbf{4} + 3\,H_2O \longrightarrow \mathbf{7} + \mathbf{8} + B(OH)_3 \quad (4)$$

It should be noted that attempts to separate the intermediates and final product in the hydrolysis of **4**−**6** failed. Varying the amount of H$_2$O added also did not facilitate separation. Attempts to isolate more than a few crystals of **7** at a time also were not successful.

The ^{119}Sn, ^{19}F, ^{13}C, and ^{11}B NMR spectra of the hydrolysis reaction mixture of **4** reveal resonances consistent with the presence of the proposed reaction products. In addition to the resonances of **4** (see later), the ^{11}B spectrum contains two additional resonances, one at 1.7 ppm (quintet, $^1J_{BF}$ = 22 Hz) attributable to the BF$_4^-$ of **7** and one at 0.9 ppm (quartet, $^1J_{BF}$ = 18 Hz) probably originating from the BF$_3$ adduct **9**. In the ^{19}F NMR spectrum, four resonances (in addition to those of **4**; see later) are observed, namely, the quartet from the BF$_4^-$ of **7** at 95.2 ppm, a second quartet at 90.2 ppm attributable to the BF$_3$ group of **9**, and two singlets at 87.1 and 99.0 ppm exhibiting ^{119}Sn−^{19}F couplings. The corresponding two new tin resonances appear at −310.7 ($^1J_{SnF}$ = 2340 Hz) and −331.4 ppm ($^1J_{SnF}$ = 2745 Hz). Corresponding resonances [ppm (Hz)] were observed for the hydrolysis mixtures of **5** [^{11}B: BF$_4^-$, 1.6 ($^1J_{BF}$ = 21); BF$_3$, 0.9 ($^1J_{BF}$ = 18). ^{19}F: BF$_4^-$, 94.6; BF$_3$, 90.2, SnF, 86.3 ($^1J_{SnF}$ = 2745); 97.5. ^{119}Sn: could not be observed] and of **6** [^{11}B: BF$_4^-$, 1.5 ($^1J_{BF}$ = 21); BF$_3$, 0.8 ($^1J_{BF}$ = 17). ^{19}F: BF$_4^-$, 94.3; BF$_3$, 90.2; SnF, could not be observed. ^{119}Sn: could not be observed].

The ^{1}H and ^{13}C resonances of **8** and **9** cannot be unambiguously assigned, due to the low concentration of these derivatives and the complexity of the expected spectra; i.e., all the carbons and probably also all the hydrogens are expected to be chemically different. The situation is different for the case of the cation **7** which possesses a virtual mirror plane, thereby reducing the number of expected resonances. Moreover, its observed concentration is significantly higher than that of the other intermediate and final products. Therefore tentative NMR resonance [ppm (Hz)] assignments for the ^{1}H [2.78 (NCH$_3$, $^3J_{SnH}$ = 61), 2.52 (NCH$_3$, $^3J_{SnH}$ = 45), 2.37 (NCH$_2$, the other resonances are covered by those of **4**), SnCH$_3$: 0.61 (SnCH$_3$, $^2J_{SnH}$ = 70), 4.79 (NH, $\Delta\nu_{1/2}$ = 60)] and for the ^{13}C [NMe, 39.2 and 38.2 (both with $\Delta\nu_{1/2}$ = 15), 52.0 (CH$_2$, $\Delta\nu_{1/2}$ = 15), 48.7, 48.2, 47.9 (CH$_2$, $\Delta\nu_{1/2}$ = 20) additional observed *C*H$_2$ at 54.8, 54.7, 50.6, 50.3, −5.7 (SnCH$_3$, $\Delta\nu_{1/2}$ = 18; $^1J_{SnC}$ = 664)] spectra of **7**[BF$_4$] can be made.

Spectroscopic Features. The molecular masses of **5** and **6** were confirmed by the observation of a molecular ion peak in mass spectroscopic experiments using chemical ionization techniques (NH$_3$).

The IR spectra recorded for **5** and **6** show essentially the same absorption bands. The major difference compared with the spectra usually observed for azastannatranes[1,3] is that the lowering of molecular symmetry causes the splitting of degenerate vibrations, thereby affording more observed principal modes. The most important absorption bands for our purposes here concern those associated with the NBF$_2$ moiety. Three of the five absorption bands expected for this fragment in **5** and **6** can be assigned. Thus for **5**, for example, the B−N stretching mode is found at 1466 cm^{-1} ($\Delta\nu_{1/2}$ = 40 cm^{-1}), the symmetric BF$_2$ stretch is at 926 and 928 cm^{-1} for **5** and **6**, respectively, and the out of plane BF$_2$ deformation is at 689 cm^{-1} for **5** and at 688 cm^{-1} for **6**. The remaining two absorptions, namely the antisymmetric BF$_2$ stretching and the in plane BF$_2$ deformation, appear in regions of the spectra where an unambiguous assignment is not possible, i.e., at 1300−1400 and 470−490 cm^{-1}, respectively (as is also the case for Me$_2$NBF$_2$[10]). Whereas the absorption of the symmetric BF$_2$ stretching and the out of plane BF$_2$ deformation modes occur in the expected range compared with Me$_2$NBF$_2$ (980 and 670 cm^{-1},[10] respectively). The B−N stretching mode is shifted significantly to lower wavenumbers compared with Me$_2$NBF$_2$ (1562 cm^{-1} [10]). These observations are in agreement with the structures proposed for **4**−**6**, since the additional coordinative interaction of the N−BF$_2$ nitrogen with the tin atom is expected to decrease the force constant of the B−N bond.

The ^{1}H, ^{11}B, ^{13}C, ^{19}F, and ^{119}Sn NMR data for compounds **4**−**6** are summarized in Tables 3−10. The data are evidence for the presence of SnF and BF$_2$ groups in these molecules. The fact that the two fluorine atoms of the BF$_2$ group are chemically different indicates the presence of a rotation barrier for the boron nitrogen bond. Such a barrier could be imposed by crowding of the methyl groups on opposite sides of the BF$_2$ moiety. The barrier could be augmented by donation of p orbital density from the nitrogen of the adjacent equatorial nitrogen. The ^{11}B chemical shifts are somewhat low compared with literature values for other R$_2$NBF$_2$ compounds (17−18 ppm).[11] The ^{119}Sn chemical shifts are in the expected range for six-coordinate tin compounds,[12] with relatively large $^1J_{SnF}$ coupling constants. The moderate changes of the chemical shifts on going from the solution to the solid state (see Table 3) suggest that the principal structural features of the tin environment are retained.

The ^{13}C NMR spectra of **4**−**6** show that all methylene and methyl cage carbons are chemically different (see Tables 4 and

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(10) Banister, A. J.; Greenwood, N. N.; Straughan, B. P.; Walker, J. *J. Chem. Soc.* **1964**, 995.

(11) Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; NMR Basic Principles and Progress; Springer Verlag: Berlin, Heidelberg, New York, 1978.

(12) Mason, J. *Multinuclear NMR*; Plenum Press: New York, London, 1987.

Table 3. ^{11}B, ^{19}F, and ^{119}Sn NMR Data for **4**−**6**[a]

nucleus	group	**4**	**5**	**6**
^{11}B	BF$_2$	2.2 (40, 52)	2.1 (39, 52)	2.2 (40, 51)
^{19}F	BF$_2$	93.9 (F: 79) (B: 40) 85.3 (F: 79) (B: 52)	94.1 (F: 79) (B: 39) 85.2 (F: 79) (B: 52)	93.8 (F: 79) (B: 40) 85.2 (F: 79) (B: 51)
	SnF	93.9 (2512)	80.8 (2664)	87.4 (2471)
^{119}Sn	SnF	−316.2 (2512)	−344.6 (2664)[b]	−400.9 (2471)[c]

[a] At 293 K in d_6-benzene; chemical shifts are given in ppm. ^{119}Sn−^{19}F, ^{19}F−^{19}F and ^{19}F−^{11}B coupling constants in parentheses (Hz). [b] Solid state: −319.5 (2570). [c] Solid state: −418.2 (2340).

Table 4. ^{13}C NMR Data for the Amino Methyl Groups of **4**−**6**[a]

atom	**4**	**5**	**6**
C1[b]	40.3 (F: 11.7)	40.6 (F: 11.8)	41.4 (F: 11.3)
C2	39.6 (F: 1.5) (Sn: 40.4)	40.0 (F: 1.6) (Sn: 39.2)	40.0 (F: 1.2) (Sn: 38.7)
C3[b]	38.2 (F: 10.2)	38.4 (F: 10.2)	39.5 (F: 9.7)

[a] At 293 K in d_6-benzene; chemical shifts are given in ppm. ^{119}Sn−^{13}C and ^{19}F−^{13}C coupling constants in parentheses (Hz). [b] $\Delta\nu_{1/2} = 2.0$−3.0 Hz; shoulders are indicating a ^{119}Sn−^{13}C coupling constant of about 6 Hz.

Table 5. ^{13}C NMR Data for the Methylene Groups of **4**−**6**[a]

atom	**4**	**5**	**6**
C4	58.5 (Sn: 37.6)	58.6 (Sn: 35.5)	58.6 (Sn: 40.3)
C5	53.0 (Sn: 27.3) (F: 5.0)	53.2 (Sn: 25.3) (F: 5.9)	52.9 (Sn: 30.1) (F: 5.9)
C6[b,c]	52.5 (Sn: 11.0)	52.5 (Sn: 10.0)	53.4 (Sn: 10.0)
C7	50.8 (Sn: 18.3)	51.0 (Sn: 13.4)	51.2 (Sn: 22.0)
C8	49.2 (Sn: 6.0) (F: 3.7)	49.2 (Sn: 5.5) (F: 4.3)	49.3 (Sn: 6.5) (F: 4.3)
C9[b]	47.1 (F: 8.0)	47.1 (F: 8.1)	47.5 (F: 8.1)

[a] At 293 K in d_6-benzene; chemical shifts are given in ppm. ^{119}Sn−^{13}C and ^{19}F−^{13}C coupling constants in parentheses (Hz). [b] $\Delta\nu_{1/2} = 4.5$ Hz. [c] The pattern of this resonance is indicating two ^{19}F−^{13}C coupling constants of 1.1 and 2.2 Hz.

5). The observation of tin satellites for essentially all nine cage related carbons is additional evidence for the closed tricyclic six-coordinate tin structure. The degree of protonation for each individual carbon resonance is established by *J*-modulated spin-echo experiments (APT).[13] For the methyl carbons the resonances of the attached protons was determined by selective proton-decoupled ^{13}C NMR spectra. The identity of the observed fluorine couplings was verified by recording the ^{13}C NMR spectra at a different magnetic field. Moreover, upon raising of the temperature to 350 K the ^{13}C NMR spectra remained virtually unchanged. The solid-state ^{13}C NMR spectra given in Table 4 resemble the pattern found in solution, although the resonances for the methyl and methylene carbons of the atrane tricyclic framework are not resolved, appearing as broad structured peaks in the expected range.

The labeling system for assigning the numbered cage carbon resonances in Tables 4 and 5 is given in Figure 1a. The assignments are based on ^{13}C NMR data known for a series of other azastannatranes.[1,3] The C$_C$ position can be expected to most closely resemble the parent azastannatrane methyl group, so it is assigned to the C2 resonance. Moreover, its coupling behavior is similar to that observed for 1-fluoro-*N*,*N*′,*N*″-trimethylazastannatrane.[1] This is in agreement with the NMR properties of the H1 hydrogens (Table 8) which are attached to C2. The assignment of C1 (with H2 attached) to C$_A$ and of C3 (with H3 attached) to C$_B$, respectively, follows from the assumption that the methyl group at the quarternary nitrogen possessing the BF$_2$ group will be at lower field. The broadening of both the ^{1}H (H2 and H3) and ^{13}C resonances (C1 and C3) may be due to unresolved coupling to either the ^{11}B or the ^{19}F of the BF$_2$ group, thereby indicating that the BF$_2$ group may be between C$_B$ and C$_A$.

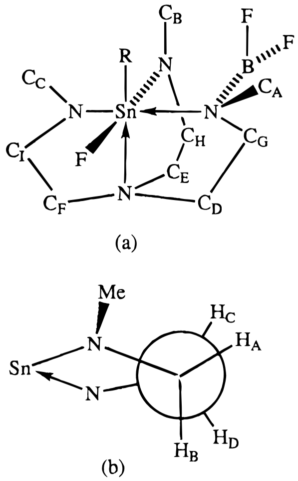

Figure 1. Labeling scheme for the assignment of the ^{13}C resonances in **4**−**6** (a). Newman projection along the carbon carbon bond of the atrane framework with the labeling scheme for the methylene proton assignment in **4**−**6** (b).

Table 6. ^{13}C NMR Data for the Me, *n*-Bu, and Ph Substituents in **4**−**6**, Respectively[a]

4	**5**	**6**
−6.3 (Sn: 849) (F: 22.0)	*β*-C: 28.4 (Sn: 45.7)	*ipso*-C[c]: 140.5 (F: 24.7) (F: 1.6)
	γ-C: 26.9 (Sn: 102)	*meta*-C: 138.1 (Sn: 47.8) (F: 2.7)(F: 1.1)
	α-C[c]: 14.4 (F: 18.3) ($\Delta\nu_{1/2} = 5.0$ Hz)[d]	*para*-C: 129.3 (Sn: 18.3)
	δ-C: 14.1 (Sn: 6.5)	*ortho*-C: 128.6 (Sn: 33.3) (F: 1.1)

[a] At 293 K in d_6-benzene; chemical shifts are given in ppm. ^{119}Sn−^{13}C and ^{19}F−^{13}C coupling constants in parentheses (Hz). [b] Sn−CH$_2^{\alpha}$−CH$_2^{\beta}$−CH$_2^{\gamma}$−CH$_3^{\delta}$. [c] ^{119}Sn−^{13}C coupling not observed. [d] Pattern indicates unresolved coupling.

Table 7. Solid-State ^{13}C NMR Chemical Shifts for **5** and **6**[a]

	5	**6**
R	15.4 25.7 30.5	128.9[b] 139.0 140.0
*C*H$_3$	36.8 39.2[d]	41.5[c]
*C*H$_2$	50.6[e]	52.0[f]

[a] At 293 K, chemical shifts are given in ppm. [b] $\Delta\nu_{1/2} = 350$ Hz. [c] $\Delta\nu_{1/2} = 430$ Hz. [d] A shoulder at 40.0 ppm is observed. [e] $\Delta\nu_{1/2} = 1400$ Hz, shoulder at 58.0 ppm. [f] $\Delta\nu_{1/2} = 1100$ Hz.

The assignments of the ^{1}H and ^{13}C resonances for the R substituents are given in Tables 6 and 10. Noteworthy here are the observed additional fluorine couplings, due to either long-range or through-space coupling to the BF$_2$ group. Either coupling path would be consistent with a closed tricyclic atrane framework.

The assignments of the methylene cage carbons C4−C9 are based on two common properties of azastannatrane ^{13}C resonances associated with the methylene carbons attached to the quarternary axial nitrogen, namely, the low field shift and the larger J_{SnC} coupling constant compared to the second set of methylene cage carbons adjacent to the equatorial nitrogens.

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(13) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy*; Oxford University Press: Oxford, New York, Frankfurt, 1990.

Table 8. ^1H NMR Data for the Amino Methyl Groups of **4**−**6**[a]

	4	**5**	**6**
H1	2.69 (Sn: 51.3) (F: 1.9)	2.79 (Sn: 49.0) (F: 2.0)	2.71 (Sn: 53.4) (F: 1.5)
H2[b]	2.54 (Sn: 37.0)	2.63 (Sn: 36.3)	2.59 (Sn: 40.1)
H3[b]	2.17 (Sn: 29.0)	2.19 (Sn: 29.5)	2.45 (Sn: 28.0)

[a] At 293 K in d_6-benzene; chemical shifts are given in ppm. $^{119}Sn-^1H$ and $^{19}F-^1H$ coupling constants in parentheses (Hz). [b] $\Delta\nu_{1/2} = 7-10$ Hz.

This reasoning leads to the identification of two subsets of three carbons each, namely, C4, C5, and C7 (C_D, C_E, C_F) and C6, C8, and C9 (C_G, C_H, C_I), respectively. Within these subsets the assignments follow the chemical shift sequence and the magnitude of the J_{FC} coupling constants expected for the three corresponding sites. Since the J_{FC} coupling constants can be expected to be small for dihedral angles close to 90°, the C9 resonance is assigned to carbon C_H. The resonances C6 and C8 of this subset are assigned according to their different chemical shifts; i.e., the resonance at lower field is assumed to correspond to the carbon adjacent to the NBF_2 group (C6 = C_G and C8 = C_I). Similar arguments give rise to the assignment of the second subset of methylene carbons as follows: C4 = C_D, C5 = C_F, and C7 = C_E. Probably the most interesting NMR spectral feature of **4**−**6** is the relatively large $^2J_{SnC}$ coupling constant of the C_G carbon and the pattern of the assigned C6 (C_G) resonance, indicating coupling of two fluorines. These observations also support the postulate that the BF_2 group lies between C_A and C_B and that this group experiences restricted rotation as a result of being between these methyl groups.

The ^1H NMR spectral data for the methyl and methylene protons of the tricyclic atrane cage of compounds **4**−**6** are summarized in Tables 8 and 9. The assignments of the observed resonances are based on measurements at different magnetic field, COSY, NOESY, and selectively decoupled ^{13}C NMR spectra. The methyl proton assignment was discussed above. For the methylene protons, twelve well-separated resonances appear in the ^1H spectra, which can be divided into three subsets of four resonances each. COSY and NOESY experiments allowed assignment of the subsets as follows: H4, H5, H12, H14; H6, H7, H9, H11; H8, H10, H13, H15. The first subset can be assigned to the atrane arm with the coordinated BF_2 group, based on the low-field appearance of their chemical shifts and the broadening of resonances H4 and H12, possibly owing to residual coupling to ^{11}B or ^{19}F. The remaining two subsets can be assigned only on the basis of their chemical shifts, assuming similar chemical shift dependencies of the ^1H and ^{13}C resonances on the electron induction/withdrawing properties of neighboring groups. This assumption suggests that H6, H7, H9, and H11 correspond to the pair C_F and C_I, whereas H8, H10, H13, and H15 correspond to C_E and C_H. The labeling scheme for the methylene proton assignment is given in Figure 1b; assuming a dihedral angle defined by H_A and H_D of about 90°, two subsets of protons are expected for each C_2H_4 group in the tricyclic framework. The first, namely H_A and H_D, is expected to show one geminal $^2J_{HH}$ and one vicinal $^3J_{HH}$ coupling, whereas the second subset (H_B and H_C) should exhibit an additional vicinal coupling. From the measured COSY spectra, the expected coupling pattern was extracted. The NOESY spectra gave further evidence for this argumentation, since six cross peaks were observed, namely H_A-H_C and H_B-H_D, following the labeling scheme in Figure 1a. From these considerations the assignment for the methylene protons on C_D and C_G are H_A = H4, H_B = H5, H_C = H12, H_D = H14; on C_E and C_H are H_A = H10, H_B = H8, H_C = H15, H_D = H13; and on C_F and C_I are H_A = H7, H_B = H6, H_C = H9, H_D = H11.

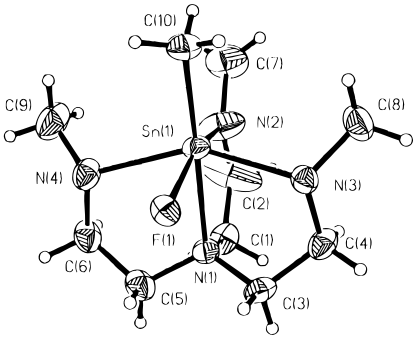
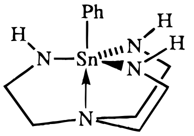


Figure 2. Molecular structure of cation **7** in **7**(BF_4). Ellipsoids are drawn at the 50% probability level except for the hydrogens, which are shown with arbitrary size.

The NOESY spectra of compounds **4**−**6** show additional cross peaks between the three methyl proton resonances of the atrane framework and the protons of the substituents R = Me and *n*-Bu (α-CH_2) and the Ph ortho-H. The observation of these cross peaks is additional evidence for the closed tricyclic structure of these compounds.

Crystal and Molecular Structure of 7(BF_4)·C_6H_6. The molecular structure of cation **7** in Figure 2 is nearly octahedral with a nearly linear vertical axis (174.1°) and an angle sum around the equatorial substituents of 350.8°. In accord with the presence of the meridional array of three tertiary nitrogens (N(1), N(3), N(4)) their corresponding Sn←N coordinate covalent bond lengths are considerably longer (average 2.273(3) Å) than the Sn−N(2) distance (2.049(3) Å) involving the covalent amido nitrogen. The coordinate covalent Sn←N bond lengths are also quite close in magnitude to one another (Table 2). The presence of a hydrogen on N(3) and on N(4), both syn to the fluorine, is also signaled by the average of the non-hydrogen substituent angles around them (112.1(2) and 112.3(2)°, respectively) while the corresponding average is 120.0° for N(2). The transannular bond length Sn−N(1) (2.291(2) Å) is shorter than that found in **10** (2.453(2) and 2.380(2) Å for the two independent molecules in the unit cell[1]) and in **11** (2.368(3) Å[3]). This difference is made reasonable by the presence of a positive charge on **7** compared with the charge neutrality of **10** and **11**. The transannular distance is also large [2.410(6) Å] in neutral **12** which was recently reported to be a tetramer possessing intermolecular Sn-F interactions that render the tin atoms six-coordinate in a geometry that largely retains the atrane structure.[14] Moreover, whereas the Sn−F bonds in **12** are lengthened by about 0.15 Å over a Sn−F single bond (1.96 Å), this distance in cation **7** is lengthened by only about 0.08 Å.



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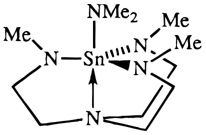

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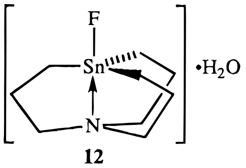

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[14] Kolb, U.; Dräger, M.; Dargatz, M.; Jurkschat, K. *Organometallics* **1995**, *14*, 2827.

Table 9. ^{1}H NMR Data for the Methylene Groups of **4**−**6**[a]

	pattern[b]	**4**	**5**	**6**
H4	*c*	3.39	3.36	3.40
H5	ddd	3.14 (11.0, 7.5, 2.0)	3.14 (11.0, 7.0, 2.0)	3.21 (11.0, 7.0, 2.0)
H6	td	3.09 (11.6, 5.6)	3.11 (11.4, 5.4)	3.24 (11.2, 5.4)
H7	dd	2.76 (11.2, 5.6)	2.77 (11.2, 5.4)	2.87 (11.2, 5.4)
H8	ddd	2.72[d]	2.66 (13.9, 11.6, 5.8)	2.75 (14.6, 6.3)[e]
H9	ddd	2.57[d]	2.53 (11.6, 11.2, 4.8)	2.57[d]
H10	dd	2.49 (11.9, 6.5)	2.45 (11.6, 6.3)	2.47[d]
H11	dd	2.32 (11.2, 4.2)	2.14 (11.2, 4.8)	2.22 (11.2, 4.4)
H12	*f*	2.14	2.10	2.11
H13	dd	2.05[d]	1.97 (11.6, 5.8)	2.07[d]
H14	dd	1.92 (11.0, 7.5)	1.75 (11.0, 7.0)	1.81 (11.0, 7.0)
H15	ddd	1.89 (14.9, 6.5, 2.0)	1.71 (13.9, 6.3, 2.0)	1.76 (14.6, 6.3, 2.0)

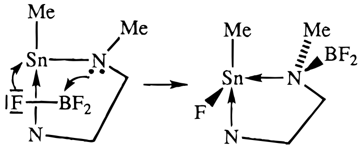
[a] At 293 K in d_6-benzene. Chemical shifts in ppm and ^{1}H−^{1}H coupling constants in parentheses (Hz). [b] Coupling constants are given in decreasing order; d = doublet, t = triplet. [c] $\Delta\nu_{1/2}$ = 40 Hz; shoulders indicate a dd coupling pattern. [d] Overlapped with other resonances. Coupling constants cannot be extracted. [e] The larger two coupling constants have the same value, resulting in a td pattern. [f] $\Delta\nu_{1/2}$ = 30 Hz; shoulders indicate a ddd coupling pattern.

Table 10. ^{1}H NMR Data for the Me, *n*-Bu, and Ph Substituents in **4**−**6**, Respectively[a]

4	**5**	**6**
0.55 (Sn: 82.0) (F: 2.3, 0.7)	β-H: 1.88 (m)	ortho-H: 17 (Sn: 75.3) (dd, H: 7.2, 1.3)
	γ-H: 1.52 (m)	meta-H: 7.27 (Sn: 29.0) (dd, H: 7.2)
	α-H: 1.47 (m, Sn: 70.0)	para-H: 7.16 (Sn: 10.0) (tt, H: 7.2, 1.3)
	δ-H: 0.94 (t, H: 7.2)	

[a] At 293 K in d_6-benzene; chemical shifts are given in ppm. ^{119}Sn−^{1}H, ^{19}F−^{1}H, and ^{1}Hp−^{1}H coupling constants in parentheses (Hz). [b] Sn−CH_2^{α}−CH_2^{β}−CH_2^{γ}−CH_3^{δ}.

Conclusions. Features of the ^{1}H and ^{13}C NMR spectra of **4**−**6** discussed above are consistent with the BF_2 group lying anti to the Sn−F bond. This seems odd at first since cis addition of BF_3 to a Sn−N bond via a four-center intermediate appears more facile as shown schematically in reaction 5. If the stereochemistry shown earlier for structures **4-6** is sterically preferable, however, it could be achieved in an equilibrium of the type shown in reaction 6 for **1**. The stereochemistry shown for the HMeNCH$_2$ group of **9** is supported by the crystallographic X-ray study of **7**(BF$_4$) in which the same stereochemistry is observed for both of these groups. The preservation of this stereochemistry for this group is then also implied for **8** as shown in its structural formulation.



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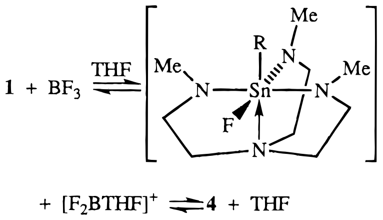

(6)

The stereochemistry shown for the HMeNCH$_2$ groups in **7**(BF$_4$) (and that deduced for **4**−**6**, **8,** and **9**) would not be dictated on steric grounds in a strictly octahedral geometry of the metal. That such a geometry is not achieved, however, is evident from the molecular structure of **7**(BF$_4$) shown in Figure 1. Opening the N(3)−Sn(1)−N(4) angle from 120° in **3** to accommodate the fluorine atom in **7**(BF$_4$) is made difficult by the reluctance of the corresponding C−N−C angle of **3** to open, thus inducing strain in the "front" five-membered rings in the structure of **7**(BF$_4$) in Figure 2. This reluctance is reflected by the equivalence (within 3σ) of the angles around the axial nitrogen of **7**(BF$_4$). The consequent resistance of N(3)−Sn(1)−N(4) to enlargement is registered by the small N(3)−Sn(1)−F(1) and N(4)−Sn(1)−F(1) angles (average = 79.7(1)°) compared with the N(3)−Sn(1)−N(2) and N(2)−Sn(1)−N(4) angles (average = 95.7(1)°). On the basis of this argument the larger exocyclic group on an equatorial quaternary nitrogen in **4**−**6**, **8**, **9**, and **7**(BF$_4$) prefers to be anti rather than syn to the Sn−F bond.

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Supporting Information Available: Text describing X-ray procedures, listings of structural determination parameters, atomic coordinates, bond lengths, bond angles, anisotropic displacement coefficients, and H coordinates, and ORTEP diagrams (12 pages). Ordering information is given on any current masthead page.

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