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The Reaction of Bis(dialkylamino)tin(II) Compounds with Trifluoroborane

CHUNG-CHUN HSU† and R. A. GEANANGEL*
Department of Chemistry, University of Houston, Houston, Tex. 77004, U.S.A.

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The reactions of the bis(dialkylamino)tin(II) compounds, $Sn(NR_2)_2$ ($R = CH_3, C_2H_5$), with trifluoroborane have been investigated. A tensimetric titration of $Sn(N(CH_3)_2)_2$ with BF_3 indicated formation of a 1:3 adduct, which was confirmed by elemental analyses. Multinuclear NMR spectra of the product showed two boron environments, one with BF_3 coordinated to the amino nitrogens and the other with BF_3 coordinated to tin. Spectra of solutions containing 1:1 and 1:2 donor to acceptor ratios suggested that the initial site of BF_3 coordination was the tin atom and subsequent coordination occurred at the amino nitrogens. A ^{119}Sn Mössbauer spectrum of the air sensitive 1:1 adduct showed larger differences in isomer shift and quadrupole splitting parameters compared to those of the parent amino tin(II) compound.

Introduction

Divalent tin compounds possess the potential of acting as either acceptors or donors of electron pairs [1]. Numerous instances of the former have been reported [1, 2–6]; donor behavior has been only substantiated for a few adducts involving organo-tin compounds. It seems reasonable to expect substituent effects to play an influencial role in determining the electrophilic or nucleophilic character of SnX_2 compounds, however this aspect of the chemistry of divalent tin is nearly unexplored. Treatment of SnF_2 with BF_3 yields a compound [7] containing the fluorine-bridged SnF^+ cation with BF_4^- rather than a simple adduct. Harrison and Zuckerman [8] reported the adduct $(C_5H_5)_2Sn \cdot BF_3$ in which the tin is believed to act as a donor, forming a sigma bond to boron. Later, similar adducts with aluminum trihalides were prepared [9]. Apparently no simple adducts between tin(II) halides and trihaloboranes have been reported.

We have investigated some of the donor properties of two bis(dialkylamino)tin(II) compounds [10] to determine whether the inductive influence and other relevant characteristics of the amino groups permit the compounds to form stable adducts with Lewis acids. We wish to report here the results of the reaction of $Sn(NR_2)_2$ ($R = CH_3, C_2H_5$) with BF_3.

Experimental

Equipment and Materials

All reactions were carried out either on a vacuum line or under flowing dry nitrogen [11]. Trifluoroborane and dimethylamine were obtained in lecture cylinders from Matheson Co. and used as obtained. Diethylamine was reagent grade from Aldrich and butyl lithium was obtained from Alfa (Ventron Co.). Anhydrous tin(II) chloride was prepared fresh [12].

Proton NMR spectra were obtained using a Varian T-60 instrument at 60 MHz (accuracy ±0.02 ppm). A Varian Model XL-100 instrument with Nicholet Model 1080 data system was used to obtain ^{11}B, ^{119}Sn, and ^{19}F spectra, using a Nicholet Model NT-440 multinuclear probe for the first two at 32.1 and 37.0 MHz respectively, and a Varian Model 4412 probe at 94.1 MHz for the ^{19}F spectra. All spectra (except two ^{11}B spectra) were obtained in the Fourier transform mode. IR spectra were obtained using a Beckman Model 4250 spectrophotometer (accuracy ±4 cm^{-1}). Melting points were determined with a Thomas Hoover melting point apparatus with the samples in glass capillaries sealed with wax.

Analytical Methods

Tin content was determined gravimetrically by heating approximately 10 mg of sample repeatedly with 4 mL portions of concentrated nitric acid in a quartz vessel until a constant mass of SnO_2 was obtained. Nitrogen content was determined using a Coleman Model 29 analyzer. Boron analyses were carried out using a modification of a literature method [13]. A sample containing about 0.3 mmol boron was digested at 200 °C with 0.2 g $CaCl_2$ and about 4 ml of concentrated nitric acid in a 50 mL round-bottom flask fitted with a 36 inch water-cooled condenser. When nitrogen dioxide evolution

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*Author to whom correspondence should be addressed.

†Present address: Dept. of Chemistry, Chung-Hsing University, Taichung, Taiwan, Republic of China.

TABLE I. Infrared bands[a] of $Sn[N(CH_3)_2]_2 \cdot nBF_3$ [n = 1 (*1A*), 2(*1B*), 3(*1*)].

Compounds			Compounds		
1	*1B*	*1A*	*1*	*1B*	*1A*
3290(s)	3280(s)		960(vvsb)	970(sb)	
3190(sb)			917(vvsb)	930(sb)	923(vs)
3030(w)	3050[b]	3030(s)	900(s)	900(s)	
2980(w)	2980(m)	2980(s)	810(w)	810(w)	820(vwb)
		2780(w)	710(w)	710(w)	
2420(vw)			620(m)	610(m)	615(w)
2350(vw)	2360(vw)	2360(vw)	565(m)	565(m)	570(m)
1620(m)	1630(m)	1630(m)	527(mb)	535(m)	
1485(s)	1474(s)	1482(s)	460(mb)	470(sb)	500(sb)
1450(m)	1460(m)	1465(s)	420(mb)	420(sb)	430(sb)
1400(mb)	1400(vw)	1410(w)	350(mb)	350(m)	370(m)
1350(s)	1340(w)				
1310(w)					
1240(vsb)	1250(sb)	1250(w)			
1160(vvsb)	1160(vsb)	1170(vs)			
1134(vsb)	1103(s)	1135(s)			
1085(vsb)[c]	1080(s)[d]	1100(vsb)			
1050(vvsb)[c]	1050(vsb)[d]	1055(m)			
1010(vsb)[c]	1020(s)[d]	1023(m)			

[a] ±4 cm^{-1}. [b] Broad and complex. [c,d,e] Overlapping.

ceased, 20 mL of water was added and the digestion was continued for 15 min. After cooling, more water was added to give 2 mg boron per 100 mL of solution and conc. NaOH added to obtain a pH of 7.4. Mannitol (8 g per 100 mL) was added with stirring and the solution was back titrated with standard NaOH solution to a pH of 7.4

Synthesis of Tris(trifluoroborane)bis(dimethylamino)-tin(II), 1

Preparation of a Solution of Bis(dimethylamino)-tin(II)

A modification of the literature procedure [10] was used to prepare a solution of $Sn(N(CH_3)_2)_2$. A two-necked 350 mL flask was fitted with a Teflon valve adapter for attachment to the vacuum line and another Teflon valve into which solutions could be syringed under a flowing nitrogen stream. In a typical synthesis 7.77 g (41.0 mmol) $SnCl_2$ and 150 mL of anhydrous benzene were placed in this vessel after it had been oven-dried and flushed with nitrogen. In another dry flask, under nitrogen flush, was placed 100 mL of pentane and 82 mmol of 1.6 *M* soln. of n-butyl lithium in n-hexane. After attaching the flask to the vacuum line, cooling to −196 °C and evacuating, 82 mmol of dimethylamine was condensed in and the reaction mixture was warmed slowly to room temperature with stirring. After 3 h the volatiles were removed by vapor transfer, first at 25° then up to 50 °C to remove the last traces, leaving a white solid. Nitrogen was admitted to the flask followed by 150 mL of dry benzene forming a gelatinous solution of lithium dimethylamide. Under nitrogen flush, the solution was transferred *via* syringe to the vessel containing the $SnCl_2$ and the mixture was stirred 4 days and then left overnight to allow the precipitate to settle. The ^1H NMR spectrum of the clear reaction solution consisted of a singlet (δ 2.8 ppm) which closely coincided with that reported [10] for $Sn(N(CH_3)_2)_2$ (δ 2.75 at 40 °C). At this point, treatment of a small amount of the clear solution with 5% aqueous $AgNO_3$ gave a black solution indicative of the presence of divalent tin. Addition of excess HNO_3 produced a clear solution demonstrating the absence of chloride.

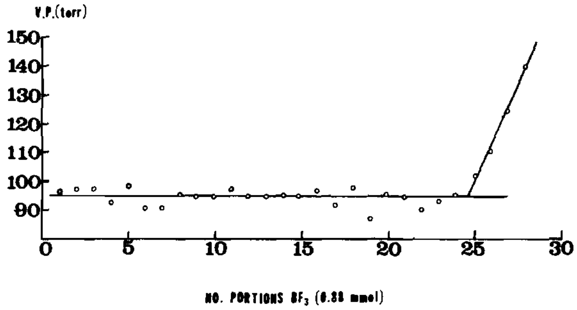


Fig. 1. A tensimetric titration of $Sn[N(CH_3)_2]_2$ with BF_3.

The concentration of the tin(II) amide solution was determined by two methods. First, 30.0 mL of the solution was removed to the vacuum line and the volatiles thoroughly removed by vapor transfer. The

TABLE II. Infrared bands[a] of $Sn[N(C_2H_5)_2]\cdot nBF_3$ [n = 0, 1(*2A*), 3(*2*)].

Compounds		
$Sn[N(C_2H_5)_2]_2^{b}$	*2A*	*2*
		3265(s)
3000(vs)	3000(vsb)	3000(m)
2960(s)	2960(s)	2960(m)
		2930(w)
2900(s)	2900(s)	2910(vw)
2840(s)	2830(m)	
2825(s)		
	2490(m)	2490(w)
	2390(m)	2350(vw)
1460(m)	1470(mb)	1490(s)
	1410(m)	1425(s)
1385(s)	1390(w)	1400(s)
1350(w)	1350(w)	1380(s)
1340(w)	1410(w)	1325(s)
1300(m)		
		1275(s)
1180(m)	1165(s)^{c}	1200(vs)^{d}
1150(m)	1130(s)^{c}	1110(vvs)^{d}
1080(w)	1090(vs)^{c}	1150(s)^{d}
	1060(vs)^{c}	1075(vvs)^{d}
	1040(vs)^{c}	1035(vvs)^{d}
1030(m)		^{d}
1010(s)		
	940(w)	940(vvs)
	900(vw)	915(vvs)
880(m)		860(w)
		830(w)
790(w)	800(m)	800(m)
740(w)		
		700(mb)
		620(mb)
	570(mb)	530(mb)
585(m)		
567(m)	470(mb)	450(mb)
450(w)	420(m)	430(m)
380(m)	350(w)	350(m)

[a] ±4 cm^{-1}. [b] Solution spectra. [c,d] Overlapping.

tin content of a measured portion of the solid was determined as 57.3% Sn (theory 57.4% Sn) for $Sn(N(CH_3)_2)_2$ which corresponded to a solution concentration of 0.134 M. In an alternate approach [10] 10.0 mL of solution was stirred with an excess of aqueous $HgCl_2$. The white Hg_2Cl_2 precipitate was separated by filtration, washed with water and air dried at 140 °C. From the mass of Hg_2Cl_2, 0.642 g (1.36 mmol), it was determined that the tin solution concentration was 1.36 *M*, giving an average concentration of 0.135 *M* $Sn(N(CH_3)_2)_2$.

Synthesis of Tris(trifluoroborane)bis(dimethylamino)tin(II) via *a Tensimetric Titration*

A 100 mL reaction vessel containing 52 mL of 0.135 *M* $Sn(N(CH_3)_2)_2$ (7.02 mmol) was attached to a section of the vacuum line with a series of calibrated volumes. Aliquots of 0.88 (±0.01) mmol BF_3 were condensed sequentially into the reaction vessel at −196 °C. After each addition, the vessel was closed and allowed to stir until the contents had been at room temperature 2 h. The vessel was then opened to a section of the vacuum line fitted with a mercury manometer and the pressure recorded after a 10 minute interval for stabilization. A total of 28 portions of BF_3 were thus added, resulting in the tensimetric titration graph shown in Figure 1. The initial portions of BF_3 produced a white precipitate which partially redissolved as the titration progressed. After completion of the titration, the volatiles were fractionated through two −78 and one −196 °C traps. The gas in the −196 °C trap was identified as BF_3 by its IR spectrum. A total of 21.18 mmol BF_3 was consumed in the reaction which may be compared to 21.06 mmol BF_3 required for the 3:1 complex $(BF_3)_3\cdot Sn(N(CH_3)_2)_2$, *1*. The titration graph was also found to indicate a 3:1 complex.

The white solid residue (2.82 g, 97%), which was very air sensitive, did not melt sharply but rather began to decompose above 190 °C. *Anal.* Calcd for $C_4H_{12}B_3F_9N_2Sn$: Sn, 28.93; B, 2.63; N, 6.83. Found: Sn, 29.46; B, 2.57; N, 6.64. Treated with 5% $AgNO_3$, the solid produced a black solution, but more slowly than was observed for the tin(II) amide. The ^{1}H NMR spectrum of *1* in C_6H_6 consisted of a broad singlet at δ 1.75 (fwhh = 9.0 Hz). The ^{11}B spectrum of *1* also appeared as a broad singlet at δ 20.7 (downfield from $BF_3\cdot O(C_2H_5)_2$) (fwhh = 110 Hz) and a quartet at δ −0.2 (J_{BF} = 14.4 Hz). Over a period of time in solution, changes occurred in the complex such that the singlet in the ^{11}B spectrum diminished and the quartet shifted to δ −0.5 ppm. The IR spectrum of the solid in a KBr disk is listed in Table I.

Other reactions with mole ratios of $Sn(N(CH_3)_2)_2$ to BF_3 of 1:1 and 1:2 were carried out but the products, *1A* and *1B*, were characterized only by their IR spectra which are listed in Table I and by the Mössbauer spectrum of the 1:1 product.

The ^{119}Sn Mössbauer spectrum of the solid product, *1A*, at −180 °C consisted of a broad peak at −0.04 ± 0.05 mm sec^{-1} and an apparent quadrupole split doublet centered at +3.22 ± 0.05 mm sec^{-1} (reference SnO_2) with quadrupole splitting of 1.81 ± 0.1 mm sec^{-1}. The necessity for a slight exposure of the solid to the atmosphere during sample mounting is probably responsible for the peak near zero velocity which almost certainly represents oxidized, Sn(IV) materials.

Synthesis of Tris(trifluoroborane)bis(diethylamino)-tin(II), 2

Using the same procedure as described for *1*, $Sn[N(C_2H_5)_2]_2$ was prepared in benzene solution. Its ^{1}H NMR spectrum consisted of the expected quartet (δ 3.20, J = 7 Hz) and triplet (δ 1.13, J = 7.5 Hz). The IR bands are listed in Table II.

A reaction vessel with 100 mL of the $Sn[(C_2H_5)_2]_2$ solution was attached to the vacuum line where 20.5 mmol BF_3 (excess) was condensed in at −196 °C and the contents were allowed to warm slowly to 25 °C with stirring, producing a brown clear solution. Removal of the volatiles (8.3 mmol BF_3) left 1.84 g of yellow-gray air-sensitive solid, *2*, which decomposed without a clear melting point beginning at 313 °C. *Anal.* Calcd for $C_8H_{20}B_3F_9N_2Sn$: Sn, 25.45; B, 2.32; N, 6.01. Found: Sn, 25.1; B, 2.40; N, 5.83. The IR bands of the product (KBr pellet) are listed in Table II. The ^{1}H NMR spectrum of a freshly prepared solution of *2* in benzene consisted of a broad multiplet (δ 2.75) and a triplet (δ 0.90, J = 7.5 Hz). Over a period of time both resonances shift downfield. The ^{11}B spectrum of a fresh solution in benzene consisted of a broad peak at δ +17.5 (fwhh = 119 Hz) and a quartet at δ +0.23 (J = 16.7 Hz) in the area ratio of 1:2. Over a period of time the low field peak diminished in intensity and the quartet shifted downfield. The ^{19}F spectrum of *2* in benzene consisted of a small, poorly resolved doublet at δ −60.2 (J = 9.7 Hz) ppm (upfield from external CF_3COOH) and a large quartet at δ −74.2 (J = 18.6 Hz).

Two additional reactions were carried out between $Sn(N(C_2H_5)_2)_2$ and BF_3; one with 1:1 and the other with 1:2 mol ratio. The products, *2A* and *2B* respectively, were not analyzed, but their NMR spectra in benzene were obtained. The ^{1}H spectrum of *2A* consisted of quartet (δ 2.89, J = 6.9 Hz) and a triplet (δ 0.97, J = 7.3 Hz) and that of 2B consisted of a quartet (δ 2.97, J = 7.4 Hz) overlapping a broad peak centered near δ 2.75 and two overlapping triplets (δ 0.97, J = 7.3 Hz and δ 0.86, J = 7.8 Hz).

Results and Discussion

Tensimetric Titration of $Sn[N(CH_3)_2]_2$ with BF_3

Solutions of bis(dimethylamino)tin(II) in benzene were prepared by a modification of the literature method [10] and the presence of the desired product was confirmed by its ^{1}H NMR chemical shift (δ 2.8 compared to δ 2.75 reported in reference 10). The concentration of $Sn[N(CH_3)_2]_2$ in the solution used for the tensimetric titration was determined by two independent methods. An aliquot of the solution was then treated successively with measured quantities of trifluoroborane and the pressure-composition relationship is shown in Figure 1. A break in the tensimetric titration plot occurs at $3BF_3$:1 $Sn[N(CH_3)_2]_2$, but any possible deflections at lesser ratios are obscured by scatter in the pressure data. The adduct composition was confirmed by measurement of the uncombined BF_3 as well as by elemental analysis.

The 3:1 adduct of BF_3 with bis(diethylamino)tin(II) was prepared *via* the reaction of excess BF_3 with a benzene solution of the amino-tin compound. Elemental analyses supported the formula $(BF_3)_3 \cdot Sn[N(C_2H_5)_2]_2$. Solutions of analogous 2:1 and 1:1 adducts were prepared for spectroscopic investigation but the products were not isolated.

NMR Spectra

The ^{11}B spectra of both *1* and *2* in benzene solution exhibited a broad peak (relative area 1) at approximately δ +18 (ref. $BF_3 \cdot O(C_2H_5)_2$) and a quartet (relative area 2, J_{B-F} = 14.4 and 16.7 Hz respectively) at about zero shift. The parameters for the upfield peak(s) compare closely with those of $(C_2H_5)_3NBF_3$ (δ −0.2 ppm and J_{B-F} = 16.4 Hz) [14], suggesting that the borons responsible for that signal represent BF_3 groups coordinated to the amino nitrogens of the tin compound.

The low field peaks in the ^{11}B spectra were unsymmetrical and broad (fwhh = 110 and 119 Hz respectively) but no spin coupling was resolved. The relative area ratio of the low to high field resonances was 1:2 only for fresh samples; the low field resonance decreased in intensity and the upfield quartet shifted slightly downfield with time. The chemical shift of the low field signal is significantly lower than those of known BF_3 adducts [15]. The species responsible for the low field resonance was not unequivocally identified, but some possibilities are considered in the following.

Additional evidence concerning the products was obtained from the ^{1}H NMR spectra. The ^{1}H spectrum of bis(diethylamino)tin(II) in benzene solution consisted of the expected triplet (δ 1.13) and quartet (δ 3.20), while that of the 3:1 adduct, *2*, exhibited a triplet (δ 0.90) and a broadened unresolved multiplet centered at δ 2.75 (Fig. 2). The same broadening is seen in the methylene resonance of $(C_2H_5)_3NBF_3$ and has been attributed to long range coupling from the coordinated BF_3 group [14]. If broadening and loss of resolution of the methylene resonance results from the presence of coordinated BF_3, this seems

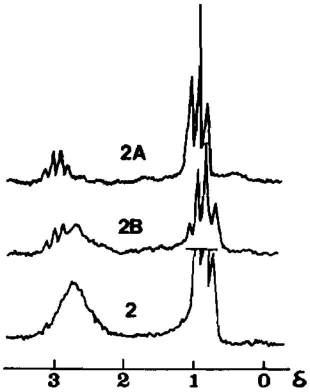


Fig. 2. The ^1H NMR spectrum of $(BF_3)_n \cdot Sn[N(C_2H_5)_2]_2$, (n = 1, *2A*; n = 2, *2B*; n = 3, *2*).

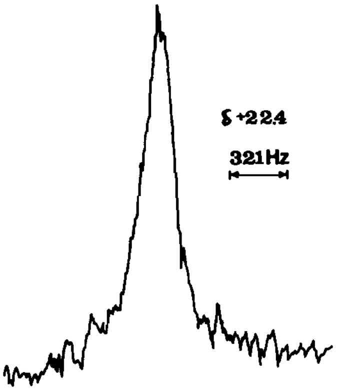


Fig. 3. The ^{11}B NMR spectrum of $BF_3 \cdot Sn[N(C_2H_5)_2]_2$, *2A*.

to confirm the indication from ^{11}B spectra that two BF_3 moieties in the 3:1 adducts are coordinated to the amino nitrogens.

It is interesting to note that the ^1H spectrum (Fig. 2) of a benzene solution containing equivalent amounts of trifluoroborane and bis(diethylamino)-tin(II) (presumably containing $BF_3 \cdot Sn[N(C_2H_5)_2]_2$) does not show appreciable broadening of the methylene resonance. The only significant spectral change in the ^1H spectrum of $Sn[N(C_2H_5)_2]_2$ observed on adding the first equivalent of BF_3 is a small upfield shift of both the methyl and methylene resonances. Significantly, the ^{11}B spectrum of the same solution consisted of a broad singlet at δ +22.4 (Fig. 3). Although no 1:1 adducts were isolated for full characterization, there is an indication from these NMR results that the trifluoroborane initially added does not coordinate to an amino nitrogen.

The ^1H spectrum of the solution containing $2BF_3$:1 $Sn[N(C_2H_5)_2]_2$ shows a methylene quartet (δ ~0.3) overlapping a broadened resonance (δ 2.75) typical of CH_2 adjacent to nitrogen to which BF_3 is coordinated. The areas are about equal, suggesting that one amino group has BF_3 coordinated to it and one remains free at this stage in the addition of BF_3. At this point, the methyl ^1H resonance appears as an unsymmetrical quartet and the ^{11}B spectrum evidences a new peak near 0 ppm, in concert with the above suggestion.

The upfield shifts of the methyl and methylene ^1H resonances upon coordination of BF_3 to the amino groups are unexpected since shifts in the opposite direction occur when BF_3 coordinates to $N(C_2H_5)_3$ [14]. However, the observed shifts for $Sn[N(C_2H_5)_2]_2$ are both significantly downfield from those for triethylamine itself (CH_2, δ 2.46; CH_3, δ 0.95) [16]. Two factors which may contribute to the downfield ^1H shifts are association of $Sn(NR_2)_2$ moieties in benzene solution, as was observed for $Sn[N(CH_3)_2]_2$ [10], and $N \overset{\rightarrow}{\leftarrow} Sn$ pi back-bonding. Both of these effects will be removed or diminished as BF_3 coordinates to the amino nitrogens, possible accounting for the higher ^1H shifts of the 3:1 adduct.

The ^{19}F spectrum of $(BF_3)_3 \cdot Sn[N(C_2H_5)_2]_2$ in benzene consisted of a small complex multiplet at δ –60.2 ppm referred to external CF_3COOH and a larger 1:1:1:1 quartet (J_{F-B} = 18.6 Hz) at δ –74.2 ppm. On the basis of the observed coupling constant, the larger peak may be assigned to the fluorines of the BF_3 groups coordinated to nitrogen while the smaller peak would seem to represent the unique BF_3. It is noteworthy that the ^{19}F chemical shift of the fluorines in $(C_5H_5)_2Sn \cdot BF_3$ is reported to be δ –54.9 ppm with respect to the same reference. The similarity between this shift and that of the smaller peak in the spectrum of the 3:1 product may indicate that the unique BF_3 is coordinated to tin as in the dicyclopentadienyl adduct.

One possible explanation for the fact that the initial BF_3 coordination site is the tin atom rather than the presumably stronger donor amino nitrogens, is that $N \overset{\rightarrow}{\leftarrow} Sn$ pi bonding in the amino tin (II) compound enhances the donor capacity of the tin at the expense of the nitrogens. Such bonding would be greatly attenuated in the 3:1 adduct where the nitrogen lone pairs are involved in coordinate bonding to boron. This interplay of sigma and pi bonding could also account for the observation made earlier that the 3:1 adduct gradually decomposes with loss of BF_3, apparently from the tin site. In the absence of the $N \overset{\rightarrow}{\leftarrow} Sn$ pi bonding, tin is inherently a weaker donor, accounting for the gradual loss of its BF_3 from the 3:1 adduct.

IR Spectra

The IR spectral bands of $Sn[N(CH_3)_2]_2$ have been assigned [10] by comparing them with those of $Sn[N(CH_3)_2]_4$ [17]. Of particular interest are $\nu(CH_3)$ modes, 2780–2920 cm^{-1}, and $\nu(Sn–N)$, 440 cm^{-1}. Coordination of BF_3 to the amino-tin compound results in a progressive shift towards high frequencies of the CH_3 stretching vibrations in the series *1A, 1B, 1*. The direction of the shift is as expected from the inductive influence of the coordinated BF_3 groups. The assignment of ν(Sn–N) is not straightforward. Previous assignments of ν(Sn–N) in amino-tin(IV) compounds include 535 cm^{-1} in $Sn[N(CH_3)_2]_4$ [17] 843 cm^{-1} in $(CH_3)_3SnN(H)C_6H_5$ [18], and 880 cm^{-1} in $(CH_3)_2\ Sn[N(C_2H_5)_2]_2$ [19]. We are not aware of any other Sn^{II}–N stretching frequencies for comparison but find it reasonable that the inductive flow of electrons to the coordinate bond sites in the adduct coupled with the entrainment of the nitrogen lone pairs in sigma coordinate bonds to boron, removing the possibility of tin–nitrogen pi interactions, should cause a lower ν(Sn–N) in the adducts as compared to the parent amino-tin compound. Therefore we tentatively assign ν(Sn–N) in *1A* to the 430 cm^{-1} band and to the 420 cm^{-1} bands in *1B* and *1*.

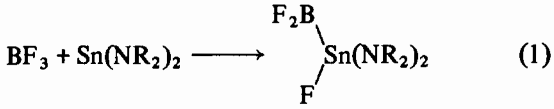
Since intense bands of coordinated BF_3 fall in the region of 870–1265 cm^{-1}, which overlaps NC_2 and CH_3 modes of $Sn[N(CH_3)_2]_2$ [10], we are unable to make convincing assignments of the bands in that range for either the dimethyl or diethylamino-adducts.

Taylor [20] reported B–F bands in $(CH_3)_3NBF_3$ at 1142, 927 (mixed mode with B–N), 547, 458 and 323 cm^{-1} (assignment uncertain). Corresponding bands in the adducts *1, 1A,* and *1B* are found at 1010–1160, 917–930, 565–570, and 460–500 and 350–370 cm^{-1}. Taylor also assigned a band at 697 cm^{-1} as the BN stretch (mixed mode with B–F stretch). Weak bands at 710 cm^{-1} in *1B* and *1* (absent in *1A*) appear to represent the analogous mode in those adducts; if the proposed structures of the adducts are correct, *1A*, has no BF_3 coordinated to nitrogen and therefore should lack a B–N band.

The assignment of the Sn–B stretching band is difficult because no prior assignments of comparable modes have appeared. Since the tin–boron bond represents a relatively weak coordinate interaction, it is probable that the frequency of the stretching vibration lies below 300 cm^{-1}, beyond the effective range of our instrumentation.

The IR spectra of *2*-series adducts were similar, in general, to those just described but with some increase in complexity. Bands at 2960 and 3000 cm^{-1}, attributed to CH_2 and CH_3 modes, appear unchanged when one BF_3 is added, forming *2A*, in general agreement with the idea that the BF_3 coordinates to the tin which, being relatively remote from the alkyl groups, produces negligible changes in their stretching frequencies. In adduct *2* the corresponding bands are shifted to higher frequency presumably due to the coordination of BF_3 to the amino nitrogens. We tentatively assign bands at 450, 420 and 430 cm^{-1} to ν(Sn–N) in $Sn[N(C_2H_5)_2]_2$, *2A*, and *2* respectively, based on considerations mentioned earlier. The band at 700 cm^{-1} in the spectrum of *2* (absent in *2A* and the parent amino-tin compound) is believed to represent B–N stretch.

The available evidence seems to support the proposed structures for the mono, bis, and tris(trifluoroborane) adducts but the known chemistry of divalent tin compounds suggests one other possible mode of attachment of the first BF_3 *via* an insertion reaction (eq. 1)



$$BF_3 + Sn(NR_2)_2 \longrightarrow (F_2B)(F)Sn(NR_2)_2 \qquad (1)$$

While such a product might account for the low field shift of the ^{11}B resonances of *1A* and *2A*, it is inconsistent with the ^{19}F spectrum of *2* and there is no other direct evidence to support it. The fact that the tris(trifluoroborane) adducts reduce silver nitrate, albeit slowly, seems to indicate that the adducts contain divalent tin rather than the tetravalent tin of the insertion product.

Mössbauer Spectrum

The Mössbauer spectral parameters for *1A* exposed briefly to air during mounting, showed a peak at –0.04 mm sec^{-1} (referenced to SnO_2) indicative of some product oxidation to Sn(IV) material. The isomer shift and quadrupole splitting at –170 °C for *1A* were 3.22 ± 0.05 and 1.81 ± 0.05 mm sec^{-1}, respectively, which may be compared to the isomer shift of 2.80 ± 0.05 mm sec^{-1} and quadrupole splitting of 3.17 ± 0.05 mm sec^{-1} reported [10] for $Sn(N(CH_3)_2)_2$. The very large differences in both parameters are consistent with the structure of *1A* in which BF_3 is coordinated directly to the tin. Inasmuch as the product was only characterized by reaction stoichiometry and IR, it is not appropriate to attempt a detailed rationale of the isomer shift and quadrupole splitting at this time. It is interesting to note, however, that the Mössbauer parameters of dicyclopentadienyltin(II) changed in comparatively minor amounts upon coordination of BF_3 to the tin [8]. We plan additional studies of this question.

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