ELECTROPHILIC AND NUCLEOPHILIC ADDITION TO TIN(II) COMPOUNDS

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ABSTRACT

The reactions of aminotin(II) compounds and aminetin(II) halides with trifluoroborane have been investigated. In Part I, the reactions of both a stoichiometric quantity and excess of trifluoroborane with bis(dimethylamino)-tin(II) and bis(diethylamino)tin(II) are described. The reactions were monitored by ^{11}B NMR. The tensimetric titration method was also employed. The first site of BF_3 coordination was found to be the tin lone pair, and additional BF_3 coordinated to the amide nitrogens. In Part II, the reactions of tin(II)halide adducts of trimethylamine and dimethylsulfoxide, and chelated adducts of N,N,N',N'-tetramethylethylenediamine and dipyridyl with BF_3 are described. The nature of the coordinate bonding in the products has been determined by comparison of the results of various possible side-reactions. Whenever the tin(II) halide is participating in an adduct with an electron pair donor, subsequent coordination of BF_3 is on the tin site. The ^{119}Sn, ^{11}B, ^{19}F and ^{1}H NMR spectra of the products confirm the structure. Thus, the tin(II) halides exhibit electrophilic and nucleophilic properties simultaneously and are therefore named amphoadducts. All the BF_3-coordinated tin(II) compounds reported here exhibit lessened reducing characteristics compared to tin(II) halides and may be regarded as psuedotin(II) compounds.

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PART I

ADDUCTS OF AMINOTIN(II) COMPOUNDS WITH TRIFLUOROBORANE

I. INTRODUCTION

The valence electronic structure of tin in its divalent compounds superficially resembles that of carbon in carbene species, but they are quite different in orbital energies, diffuseness of valence electrons and the availability of the d orbitals. These differences influence the chemical behavior of both the types of divalent species and the stability of the products of their reactions.

Burg and Schlesinger[38], in 1937, found that when diborane was treated with excess carbon monoxide the reaction reached equilibrium rapidly at 100 °C and the gaseous product H_3BCO was obtained. In this adduct carbon, formally divalent, acts as donor towards borane. Obviously, diborane will not be expected practically to combine with $SnCl_2$ to form $H_3B\,SnCl_2$ because of the strong reducing potential of the borane group. Trifluoroborane, on the other hand, lacks the reducing capability of borane but has about equal Lewis acid strength[39], suggesting that $BF_3\,SnCl_2$ might be a stable adduct.

The electron acceptor properties of trifluoroborane causes it to be employed in a large number of coordinating compounds[40]. The physical and thermodynamic properties of the coordinated compounds have been widely studied[41]. As an acceptor, BF_3 is weaker than BCl_3. The three fluorines of the BF_3 molecule are bonded to boron in a trigonal planar structure. Three boron sp^2 hybrid orbitals are used to form polar covalent bonds to fluorine and the remaining 2p atomic orbital of boron is available to

accept electrons from any orbitals of the proper symmetry. In free BF_3, p_π-p_π bonding strengthens the B-F bond strength at the expense of the BF_3 acceptor strength. Such concepts have been discussed both in the valence-bond[42] and the molecular orbital pictures[43]. When BF_3 accepts a pair electrons to complete the coordination, its planar structure changes to pyramidal. The planar-pyramidal reorganization energy of the BF_3 molecule is a major factor affecting the acceptor properties.

The important features of the reorganization process include the change of σ bond strength with B-F bond length and F-B-F angle, the change of the electron distribution for each atom (change of the σ and π populations at each atom) and the change in the energy of the highest occupied MO, in turn, influences the energy of the lowest empty orbital. The energy of the lowest vacant MO is related to the ability of the BF_3 molecule to accept a pair of electrons from a donor molecule[41].

The "π energy" term is regarded as the increased bonding energy due to π bonding; in practice, it is the difference between the energy determined by a self-consistent field molecular orbital calculation using a wave function which does not include π basis function on B, and one which does include the π basis function on B. Such a calculation by Schwartz and Allen[44], assuming the π energy to be proportional to total B-F π overlap, gave 59 kcal mol^{-1} as the π energy of BF_3. Armstrong and Perkins[45] calculated the total energies of the different configurations of BF_3 with the result that pyramidal BF_3 was less stable than the planar form by 34.2 kcal mol^{-1}, which is the reorganization energy ($\sigma + \pi$). In another calculation, the lone pair electrons were restricted to localize on the fluorines

of the planar form, i.e., planar localized model, and the calculated energy was less stable than the planar nonlocalized form by 50.4 kcal mol^{-1} which represents the π energy of BF_3. Since the π energy exceeds the reorganization energy, the energy less dispensed during the coordination reaction of BF_3 by changing from planar to pyramidal form would be 16.2 kcal mol^{-1}. These are, however, not the only factors governing the thermodynamics of donor-acceptor complex formation because, in addition to reorganization, the acceptor moiety must recieve negative charges from the donor. Normally, this charge does not amount to one full electron. The stability of the donor-acceptor complex will thus critically depend on the Lewis acid strength of the acceptor molecule and the base strength of the donor molecule. The energy which must be supplied for these hypothetical processes is regained in the form of the intrinsic bond dissociation energy of the coordinate bond.

Trifluoroborane is regarded as a moderate to strong acceptor[39] but the donor properties of tin(II) compounds have not been widely investigated. The effectiveness of the tin(II) lone pair as a donor site will be affected by the substituent, X, in the SnX_2 molecule. A strongly electronegative group bonded to tin should cause the contraction of the lone-pair electron cloud[46]; this effect may slightly enhance the donor ability by increasing the electron density and potentially the overlap. But by Bent's rule[47], electronegative substitutuents usurp p character into the bonds between themselves and tin, thereby leaving more s character in the tin lone pair orbital, making it a weaker donor

because,according to Bent, the base strength generally decreases as the s-character in the orbital occupied by the unshared electron increases. For these reasons, the tin(II) halides are not expected to form stable adducts with acceptors such as BF_3, however, tin(II) compounds with more electron releasing substituents should act as stronger donors.

The aminotin(II) compounds are suggested since, in the amide group, there are polarizable electrons on the nitrogen and they should serve to increase the electron density on tin. Though the electronegativity of N and Cl are generally equal, but the group electronegativities of amides, e.g., $(CH_3)_2N$: 2.37[48], are less than the electronegativity of Cl. Lorberth and Nöth[49] reported that the force constant calculations for the metal-nitrogen bond in $Sn(NMe_2)_4$ clearly indicate that the bond order is greater than one, provided no anomalous structures are present and assuming reasonable force constants for the corresponding metal-nitrogen single bonds. They also calculated the dipole moment of dialkylamino-stannants and indicated that the rather low Sn-N bond partial moments may arise from back-bonding due to the different polarities in the Sn-N σ-bonds and the Sn-N π-bonds.

The field of organotin amine chemistry was opened up in 1962; several reports[50,51,52] presented the preparation of compounds of general formula $R_n Sn(NR'R'')_{4-n}$ covering all possibilities from n=0 to n=3. In 1969, Lorberth[53] reported the alkylaminotin(IV) compounds of the type $R_{4-n} Sn(NR'_2)_n$ (R= Me, Et, Bu, Ph; R'= Me, Et). In 1970, Schumann <u>et</u>

al.[54] described the preparation of $Sn(NR_2)_4$ compounds where R= Me, Et. However, the aminotin(II) compounds have only rarely been studied; report of Foley and Zeldin[3] is an example.

The boron-nitrogen dative bond has been studied extensively[55]. Musgrave[56] and others[57] prepared trifluoroborane-triethylenediamine and reported ν(B-N) absorptions around 1110 cm^{-1}. Fleming and Parry[58] reported $\nu_s(N-^{10}BF_3)$ band in trifluoroborane-trimethylamine at 696 cm^{-1}. Taylor et al.[59] determined the force constant for the B←N bond in F_3BNH_3 to be 3.97 dyne cm^{-1} which corresponds to a stretching frequency of about 740 cm^{-1}.

II. EXPERIMENTAL SECTION

A. Equipments and Materials.

The experiments were carried out either under the dry nitrogen or on the vacuum line, and a LabConCo glovebox was used for transfer of the air sensitive materials. IR spectra were taken on a Beckman Model 4250 spectrophotometer (accuracy ± 4 cm^{-1}). ^{1}H NMR spectra were obtained on a Varian T-60 instrument at 60 MHz, accuracy ± 0.02 ppm. A Varian Model XL-100-15 with Nicolet 1080 data system and NT-440 Mona multinuclear accessory was employed to obtain the Fourier transform NMR spectra of ^{11}B at 32.1 MHz (accuracy ± 0.2 ppm) while a Varian 4412 probe was used for spectra of ^{19}F at 94.1 MHz. The mass spectrum was taken on the Hewlett-Packard Model 5930 GC-MS instrument with a direct probe at 70 eV. Melting points were determined on a Thomas Hoover Capillary melting point apparatus using glass capillaries sealed with wax.

Benzene and n-pentane were nanograde from the Mallinckrodt Co., St. Louis, MO. Trifluoroborane and dimethylamine were obtained in lecture cylinders from the Matheson Co., Cincinnati, OH. Diethylamine was reagent grade from the Aldrich Co., Milwauchee, WI. Butyl lithium was obtained from the Alfa (Ventron Co., Beverly, MA). Anhyfrous tin(II) chloride was prepared fresh in this laboratory[1].

B. Methods of Analysis.

Tin was analyzed by heating a 10 mg-size sample with 4 mL of concentrated HNO_3 in a 40 mL quartz flask over 800 °C and repeating the heating with portions of the acid until constant weight of SnO_2 was obtained. Nitrogen was analyzed by the Dumas method using the Coleman Model 29 nitrogen analyzer. The boron analyses[2] were carried out by digesting a mixture of the sample, which contained approximately 0.3 mmol of boron, and 0.2 g of $CaCl_2$ with concentrated HNO_3. A 1-m-condenser was used and 4 mL of the acid was dropped through the top of the condenser into the 50 mL-flask which contained the sample. The temperature was maintained at 200 °C. When all the brown gas (NO_2) had evolved from the flask, 20 mL of water was added and the digestion was continued 15 min. After this, the solution was diluted to give 2 mg of boron in 100 mL of solution. Concentrated NaOH solution was added to adjust the pH to 7.4. A quantity of mannitol, which corresponded to 8 g per 100 mL of solution, was added and the mixture then titrated with standard NaOH solution back to a pH of 7.4.

C. Synthesis of Tris(trifluoroborane)-Bis(dimethylamino)tin(II),1.

1. Preparation of a Solution of Bis(dimethylamino)tin(II).

Bis(dimethylamino)tin(II) has been previously reported[3]; in this work we have employed it as an intermediate, maintained in solution during a tensimetric titration. The literature synthesis was modified for the purposes of these experiments. The reaction vessel (350 mL) was fitted with a Teflon valve, through which solutions could be transferred using a syringe under a nitrogen atmosphere, and an O-ring connector with Teflon valve adaptor by which the vessel could be attached to the vacuum line. Whenever it was necessary to transfer air sensitive solutions, dry nitrogen was passed through the adaptor into the vessel exiting through the Teflon valve. The solution was withdrawn using a dry, nitrogen-flushed syringe. In a typical reaction 7.77 g (41.0 mmol) of anhydrous $SnCl_2$ was weighed into a dry reaction vessel under N_2 and then 150 mL of anhydrous benzene was added using a syringe. Under N_2, a second vessel was filled with 100 mL of pentane and 82 mmol of a 1.6 M solution of n-buty lithium in n-hexane and then attached to the vacuum line where 82 mmol of dimethylamine was condensed into the vessel at -196 °C. The reaction mixture was warmed slowly to room temperature, stirred for 3 h, and a white solid was obtained after vapor transfer. Finally, the flask was warmed to 50 °C to expel the last trace of volatiles. After back flushing with dry nitrogen, 150 mL of dry benzene was syringed into the vessel; the lithium dimethylamide formed a somewhat gelatinous solution. Under a nitrogen atmosphere, the amide solution was syringed into the

vessel containing the tin(II) chloride. The reaction mixture was stirred for 4 days, after which the precipitate was allowed to settle for 12 h. At this point, treatment of a small quantity of the clear reaction solution with 5% aqueous $AgNO_3$ produced a black color immediately, indicative of divalent tin. Subsequent treatment of the test aliquot with an excess of HNO_3 produced a clear solution indicating that dissolved chloride was absent. The ^1H NMR spectrum of the amine solution consisted of a singlet (δ=2.8 ppm) which coincided with that reported for $Sn[N(CH_3)_2]_2$[3]. The concentration of the solution was determined by two methods. First, 30.0 mL of the solution was placed in a preweighed vessel on the vacuum line and the solvent was thoroughly removed by vapor transfer. A measured portion of the solid was analyzed by heating it with concentrated HNO_3 and weighing the residue as SnO_2. The solid was found to contain 57.3% Sn (theory 57.38% Sn for $Sn[N(CH_3)_2]_2$ which corresponds to a solution concentration of 0.134 M. In an alternate route, 10.0 mL of solution was stirred with an excess of aqueous solution of $HgCl_2$. The white Hg_2Cl_2 precipitate was filtered off, washed with water, and air dried in an oven at 140 °C. From the mass of Hg_2Cl_2, 0.642 g, (1.36 mmol), it was determined that 1.36 mmol of tin was obtained in the sample corresponding to a concentration of 0.136 M. The average concentration was 0.135 M $Sn[N(CH_3)_2]_2$.

2. Tensimetric Titration of Bis(dimethylamino)tin(II) with Trifluoroborane.

A 100 mL reaction vessel containing 52 mL of a 0.135 M $Sn[N(CH_3)_2]_2$ (7.02 mmol) solution in benzene was attached to a section of the vacuum line with a series of calibrated traps. Aliquots of 0.88(±0.01) mmol of

Table I. Tensimetric Titration of $Sn[N(CH_3)_2]_2$ by BF_3[a]

Portions of BF_3 added[b]	1	2	3	4	5
Vapor pressure, torr	96.5	98.0	98.0	93.0	99.0
	6	7	8	9	10
	91.0	91.0	96.0	95.5	95.5
	11	12	13	14	15
	98.5	95.0	95.0	95.5	96.0
	16	17	18	19	20
	97.0	92.0	99.0	84.0	96.5
	21	22	23	24	25
	95.0	90.0	93.5	95.5	102.0
	26	27	28		
	110.0	124.5	140.0		

[a] Solution, 0.135 M, 52 ml.

[b] 0.88 mmol for each portion.

BF_3 were condensed into the reaction vessel at -196 °C; the vessel was closed and allowed to stir until the contents had been at room temperature for two hours. The vessel was then opened to a section of the vacuum line which was fitted with a mercury manometer. The pressure was recorded after 10 min when no further change was evident. A total of 28 portions of BF_3 were thus added, giving pressure values shown in Table I. The initial additions of BF_3 produced a white precipitate which partially redissolved as the titration progressed. After completion of the titration, the volatiles in the reaction mixture were fractionated through two -78° traps and one -196 °C trap. The gas in the last trap (3.46 mmol) was identified as BF_3 by its infrared spectrum. A total of 21.2 mmol of BF_3 was consumed in the reaction which may be compared with 21.06 mmol BF_3 required for a 1:3 complex, $(BF_3)_3.Sn[N(CH_3)_2]_2$, 1. The white solid residue (2.82 g, 97%), which was found to be 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, 29.5 B, 2.57; N, 6.64. The ^1H NMR spectrum of 1 in benzene consisted of a broad singlet at δ1.75 with full width at half height (fwhh) 9.0 Hz. The ^{11}B spectrum of 1 in benzene showed a broad singlet at -20.7 ppm with fwhh 110.2 Hz and a quartet at +0.2 ppm presumably arising from ^{11}B-^{19}F coupling, J_{BF}=14.4 Hz. The reference was external $BF_3{\cdot}O(C_2H_5)_2$. Over a period of time, either in the benzene solution or in the solid state, the singlet diminished in intensity and the quartet shifted to +0.5 ppm (J_{BF}=14.1 Hz). The IR spectrum of 1 in a KBr pellet contained the bands

(cm^{-1}) shown in Table II. A sample of this compound, treated with 5% $AgNO_3$ solution, changed to black within a few minutes. The fact that the color change occured more slowly for the adduct may be the result of the coordination of BF_3 to the lone pair electrons of the tin atom.

In other reactions, the molar ratios of $Sn[N(CH_3)_2]_2$ to BF_3 were set at 1:1 and 1:2. The white solids obtained, 1A and 1B respectively, were for IR spectra only. Their absorption spectra in KBr pellets are listed in Table II.

3. Thermal Decomposition of 1.

Heating 1 to 70-75 °C at a pressure of 10^{-4} torr resulted in its decomposition and the sublimation of a colorless solid (mp 43-45 °C) which was found to contain no tin. The IR bands of the sublimate (1C) in a KBr pellet is listed in Table II. Its ^1H NMR spectrum in benzene consisted of a broad singlet at δ1.70 with fwhh 11.0 Hz. The ^{11}B NMR spectrum in the same solvent was a distorted triplet at +0.03 ppm (J_{BF}=14.7 Hz). The mass spectrum of the sublimate showed a highest mass value at m/e=94, as indicated by the fragment ions summarized in Table III. The decomposition residue (1D) was a gray solid, mp 358-361 °C, sparingly soluble in benzene but more soluble in pyridine where it gave sharp ^1H NMR singlets at δ0.50 and 2.66, respectively. The IR spectral bands obtained in a KBr pellet are listed in Table II. The ^{11}B NMR spectrum of the solid in benzene solution was a very broad resonance centered at -2.6 ppm. The ^{19}F NMR spectrum (solvent, benzene:DMSO=3:1) consisted two complex peaks; one was at +14.4 and the other at +65.3 ppm, referred to external F_3CCOOH. The area ratio

was nearly 3:1. Gravimetric analysis showed it to contain 47.1% tin and qualitative tests indicated the slow color change with $AgNO_3$ solution.

Table II. Relative IR-Absorption Positions of The Group-Compounds of 1[a].

Compounds: 1	1B	1A	1D	1C	Assignment
3290(s)	3280(s)			3290(s)	$\nu(CH_3)$
3190(sb)			3180(sb)		"
3030(w)	3050[b]	3030(s)	3030(sh)	3100[b]	"
2980(w)	2980(m)	2980(s)			"
		2780(w)	2800(w)	2840(w)	"
2420(vw)					
2350(vw)	2360(vw)	2360(vw)	2350(vw)		
1620(m)	1630(m)	1630(m)		1630(vw)	
			1550(w)		$\delta(CH_3)$
1485(s)	1474(s)	1482(s)		1485(s)	"
1450(m)	1460(m)	1465(s)		1465(m)	"
1400(mb)	1400(vw)	1410(w)	1410(sb)	1410(w)	"
1350(s)	1340(w)			1340(m)	
1310(w)					
1250(vsb)	1250(sb)	1250(w)	1290(w)		ν(B-N)
1160(vvsb)	1160(vsb)	1170(vs)		1180(vsb)	$\nu_{as}(NC_2)+\rho(CH_3)$ and $\nu(BF_3)$
1135(vsb)	1103(s)	1135(s)	1130(sh)	1120(s)	"
1085(vsb)[c]	1080(s)[d]	1100(vsb)	1090(vsb)[e]	1090(vsb)	"
1050(vvsb)[c]	1050(vsb)[d]	1055(m)		1065(vs)	"
1010(vsb)[c]	1020(s)[d]	1023(m)	1030(vsb)[e]		"

to be continued.

Table II. Continued.

1	1B	1A	1D	1C	Assignment
960(vvsb)	970(sb)			950(vvs)	$\nu_s(NC_2)$
917(vvsb)	930(sb)	923(vs)	905(sh)	915(m)	"
900(s)	900(s)		900(m)		"
810(w)	810(w)	820(vwb)	810(m)		"
710(w)	710(w)			710(w)	(B-N) mixed mode
			660(w)		$\delta_{as}(BF_3)$
620(m)	610(m)	615(w)			"
565(m)	565(m)	570(m)		575(m)	"
527(mb)	535(m)		530(m)		"
				475(w)	"
460(mb)	470(sb)	500(sb)	425(m)		ν(Sn-B)
420(mb)	420(sb)	430(sb)	370(m)		ν(Sn-N)
350(mb)	350(m)	370(m)	320(m)		$\rho(NC_2)$, $\delta(NC_2)$

[a] ± 5 cm^{-1}.

[b] Spreaded and complex.

[c,d,e] Overlapping.

Table III. Mass Spectral Data of $F_2BN(CH_3)_2$

Mass(m/e)	Relative Abundance	Species Assignment
94	100	p+1
44	54	$N(CH_3)_2^+$
93	28	p
78	24	$F_2BNCH_3^+$
45	21	$[N(CH_3)_2+H]^+$
49	16	F_2B^+
92	10	p-1
42	8	$[N(CH_3)_2-2H]^+$
77	7.5	$[F_2BNCH_3-H]^+$
76	7.5	$[F_2BNCH_3-2H]^+$
60	7	$[FBNCH_3+H]^+$
58	6.5	$[FBNCH_3-H]^+$
15	6.5	CH_3^+
48	5	$^{10}BF_2^+$
43	5	$[N(CH_3)_2-H]^+$
30	4.5	BF^+
95	3	p+2
91	3	p-2

D. Synthesis of Tris(trifluoroborane)-Bis(diethylamino)tin(II), 2.

1. Preparation of a Solution of Bis(diethylamino)tin(II).

The reaction vessels and conditions used for the synthesis of 2 were the same as described for 1. In a typical synthesis 3.60 g (19 mmol) $SnCl_2$ was placed in a vessel along with 100 mL of dry benzene under N_2. In another vessel, 3.94 mL (38 mmol) of reagent grade diethylamine were measured using an accurate syringe and added to 60 mL of n-pentane. An equimolar quantity of n-butyllithium was then syringed into the vessel under N_2. The vessel was closed and stirred for 3 h to produce lithium diethylamide. The volatiles were then removed by vapor transfer; the vacuum was broken with dry N_2 and 200 mL of dry benzene syringed into the vessel to dissolve the solid. The colloidal-like solution was then transferred via a syringe to the vessel containing $SnCl_2$ under N_2 and stirring continued for 4 days at 25 °C. The precipitate was allowed to settle and the brown-colored solution separated for use in the synthesis of 2. At this point, chloride was found to be absent in the solution. The ^1H NMR spectral information for this compound in benzene solution is listed in Table IV and the bands from the solvent compensated IR spectrum are listed in Table V.

2. Synthesis of 2.

A reaction vessel was filled with 100 mL of the $Sn[N(C_2H_5)_2]_2$ solution under N_2 and attached to the vacuum line where 20.5 mmol BF_3 (estimated to be in excess) was condensed into the vessel at -196 °C. The vessel was then closed and allowed to warm slowly to 25 °C with stirring; at which point, the reaction mixture was a light brown solution.

After 24 h, the mixture was fractionated as before, yielding 8.33 mmol BF_3 and leaving 1.84 g of yellow-gray, air-sensitive solid assumed, by analogy to 1, to have the formula $(BF_3)_3.Sn[N(C_2H_5)_2]_2$. It began to decompose at 313 °C. Anal. Calcd for $C_8H_{20}B_3F_9N_2Sn$: Sn, 25.45; B, 2.32; N, 6.01. Found: Sn, 25.13; B, 2.40; N, 5.83. The IR bands of the solid in a KBr pellet are listed in Table V. Its ^1H NMR spectrum consisted of a broad peak at lowfield and a triplet at highfield; the data are given in Table IV. Its ^{11}B NMR spectrum consisted of a broad peak at lowfield and a quartet at highfield; the data are listed in Table VI. The spectra of this compound evidenced changes over a period of time. In the ^1H spectrum, the peaks moved downfield and in the ^{11}B spectrum the broad peak diminished and the quartet moved downfield. Both data are indicated as 2C in the Tables. The ^{19}F NMR spectrum of 2, obtained at moderate resolution, consisted of a small doublet at 60.2 ppm (J=9.7 Hz) and a large quartet at 74.2 ppm (J=18.6 Hz).

In another batch, the molar ratio of $Sn[N(C_2H_5)_2]_2$ to BF_3 was set at 1:1. The brown solid obtained, 2A, was for spectra purpose only. The IR absorptions by KBr pellet are listed in Table V, while the ^1H NMR spectral data is listed in Table IV and the ^{11}B data is in Table VI. A solution with the molar ratio of $Sn[N(C_2H_5)_2]_2$ to BF_3 set to 1:2 was also prepared but the product was not isolated. The ^1H and ^{11}B NMR spectra of this solution are labelled 2B in Tables IV and VI.

Table IV. ^{1}H NMR (60 MHz) Data of the Group Compds of 2[a]

Compd	δ(ppm)[b]	J(Hz)	Mult.	δ	J	Mult.
$Sn[N(C_2H_5)_2]_2$	3.20	7.0	4	1.13	7.5	3
2A	3.00	6.9	4	0.97	7.3	3
2B[c]	3.00	7.4	4	0.97	7.3	3
	2.75	broad		0.86	7.8	3
2	2.75	broad[d]		0.90	7.5	3
2C	2.51	broad[d]		0.80	7.6	3

[a]Solvent, benzene.

[b]±0.02 ppm.

[c]Two sets of peaks overlapped.

[d]peaks overlapped.

Table V. Relative IR-Absorptions Positions of The Group-Compounds of 2[a].

Compounds: $Sn[N(C_2H_5)_2]_2$[b]	2A	2	Assignment
		3265(s)	$\nu(CH_2)$
3000(vs)	3000(vsb)	3000(m)	$\nu(CH_3)$
2960(s)	2960(s)	2960(m)	$\nu(CH_2)$
		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)	$\delta(CH_3)$, $\delta(CH_2)$
	1410(m)	1425(s)	"
1385(s)	1390(w)	1400(s)	"
1350(w)	1350(w)	1380(s)	"
1340(w)	1310(w)	1325(s)	
1300(m)			
		1275(s)	$\nu(B\text{-}N)$
1180(m)	1165(s)[c]	1200(vs)[d]	$\nu_{as}(NC_2) + \rho(C_2H_5)$ and $\nu(BF_3)$
1150(m)	1130(s)[c]	1150(vvs)[d]	"
1080(w)	1090(vs)[c]	1110(s)[d]	"
	1060(vs)[c]	1075(vvs)[d]	"
	1040(vs)[c]	1035(vvs)[d]	"
1030(m)			
1010(s)			

to be continued.

Table V. Continued.

$Sn[N(C_2H_5)_2]_2$	2A	2	Assignment
	940(w)	940(vvs)	$\nu_s(NC_2)$
	900(vw)	915(vvs)	"
880(m)		860(w)	"
		830(w)	"
790(w)	800(m)	800(m)	
740(w)			
		700(mb)	(B-N) mixed mode
		620(mb)	
	570(mb)	530(mb)	ν(Sn-B)
585(m)			ν(Sn-N)
567(m)	470(mb)	450(mb)	"
450(w)	420(m)	430(m)	
380(m)	350(w)	350(m)	

[a] ± 5 cm^{-1}.

[b] By compensated solution cells.

[c,d] Overlapping.

Table VI. ^{11}B NMR (FT 100MHz) Data of the Group Compds of 2[a]

Compd	Shift(ppm)[b]	J(Hz)	Mult.	Shift	J_{BF}	Mult.
2A	-22.4	broad[d]		.....		
2B	-22.0	broad[e]		-0.003	16.4	4
2[c]	-17.5	broad[f]		-0.23	16.7	4
2C	.....			+0.16	17.0	4

[a]Solvemt benzene; reference $BF_3 \cdot OC_2H_5$, up field of reference is counted as positive.

[b]±0.2 ppm.

[c]By integration, the ratio of the lowfield peak to the upfield one is 1:2.

[d]fwhh 6.4 ppm (205.4 Hz).

[e]fwhh 4.85 ppm (155.6 Hz).

[f]fwhh 3.7 ppm (118.7 Hz).

III. RESULTS

A. Formation of $(BF_3)_3 \cdot Sn[N(CH_3)_2]_2$.

Figure 1 shows the tensimetric titration of bis(dimethylamino)tin(II) with 28 portions of 0.88 mmol BF_3. Linear regression treatment of the number of additions(X) versus the observed pressures(Y) from Table I gave the expressions shown below for the two linear areas of the plot.

$$Y = 96.50 - 0.1340X \quad (1)$$

$$Y = -220.2 + 12.80X \quad (2)$$

Solving (1) and (2) simultaneously gave an X coordinate intersection at 24.48 portions or 21.55 mmol BF_3 reacted. This compares well with the value of 21.18 mmol BF_3 consumed which was determined by measuring the BF_3 remaining after the reaction. Taking the average of the values indicates that the formula for the product is $(BF_3)_{3.04} \cdot Sn[N(CH_3)_2]_2$. Elemental analyses were found to be consistent with the 1:3 adduct.

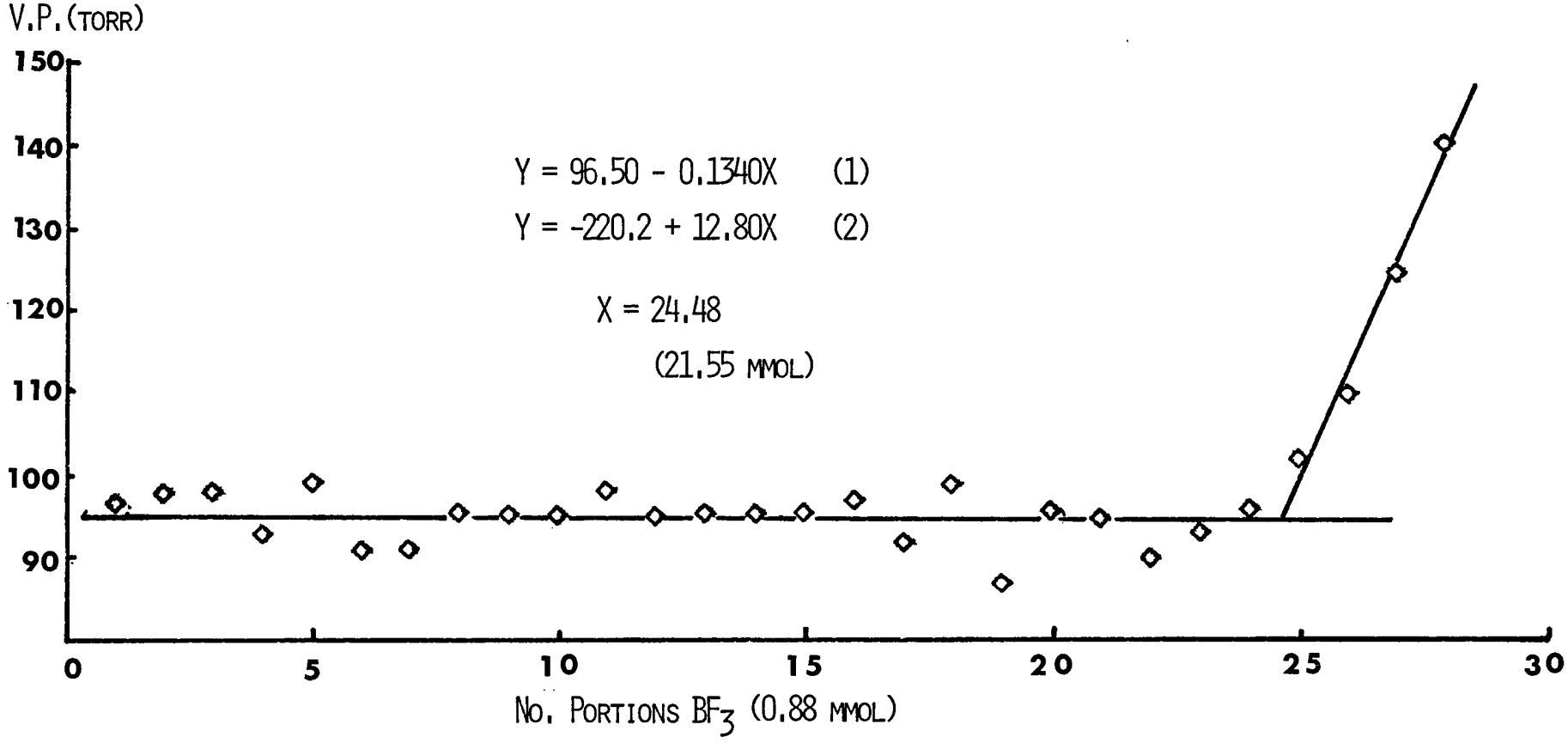


Figure 1. Tensimetric titration of $Sn[N(CH_3)_2]_2$ with BF_3

B. Formation of $(BF_3)_3 \cdot Sn[N(C_2H_5)_2]_2$.

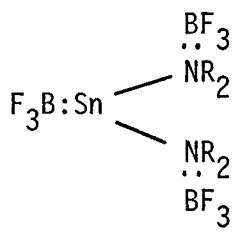
The reaction of $Sn[N(C_2H_5)_2]_2$ in benzene solution with 20.50 mmol of BF_3 left 8.33 mmol of the latter unreacted, indicating that 12.17 mmol were consumed. Elemental analyses were found to be consistent with a 1:3 adduct as expected from the tensimetric titration carried out on bis-(dimethylamino)tin(II). The 1.84 g quantity of product isolated should be 3.95 mmol of the compound; it can be compared with the BF_3 consumed which would be equivalent to 12.17/3=4.05 mmol of the product.

IV. DISCUSSION

A. The Structural Evidence From NMR Spectra.

The ^{11}B NMR spectra of both 1 and 2 showed a broad peak at lowfield and a quartet at highfield (Figure 2). These exhibited two substantially different BF_3 environments in the molecules which could not simply result from the orientations of the BF_3 group owing to the great differences of the chemical shifts, i.e., 20.9 ppm for 1 and 17.3 ppm for 2. The quartet splittings result from ^{19}F-^{11}B spin coupling; J_{BF} values are 14.4 Hz for 1 and 16.7 Hz for 2. The broad peaks may arise from complex spin coupling perhaps involving fluorine and the appropriate isotopes of tin. The small nuclear moment and weak coupling characteristics preclude resolvable ^{11}B-^{14}N coupling of ^{14}N.

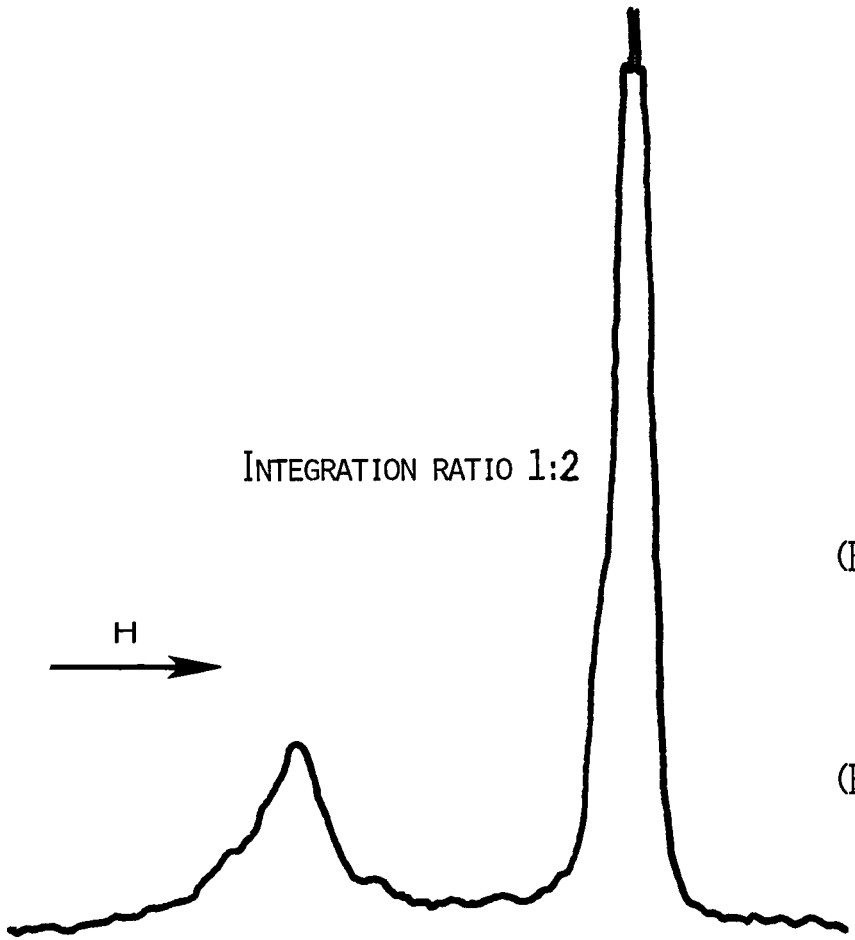
Knowing the composition of these compounds is such that the ratio of BF_3 to $Sn(NR_2)_2$ is 3:1, the integrated 1:2 area ratio of the broad peak and quartet of 2 together with the presence of only three obvious donor sites in $Sn(NR_2)_2$ molecules make the assignment of the coordination apparently straightforward:



The chemical shifts of the quartets can be compared to the ^{11}B NMR data

of similar compounds, e.g., $F_3BN(CH_3)_3$, -0.4 to -0.6 ppm (J not reported) [4,5,6,7] and $F_3BN(C_2H_5)_3$, +0.2 ppm (J=16.4 Hz)[7] compared to 1, +0.2 ppm (J= 14.4 Hz) and 2, -0.23 ppm (J=16.7 Hz). These comparisons indicate that the quartets arise from the BF_3 group coordinated to the amide sites. The reported ^{11}B chemical shift of BF_3 gas was -11.6 to -9.4 ppm[6,8,9], while in typical tetrahedrally coordinated boron adducts, e.g., BF_4^-, the reported shift was ~+2.1 ppm[8,10]. Since the shifts of the broad peak of 1 and 2 are -20.7 and -17.5 ppm, respectively, the positions are very near to the reported shift of $B(OCH_3)_3$ which is -18.3 to-18.1 ppm[4,6,9,11]. The unusually low field shift suggests that the boron is bound to a weak donor site as would be expected for the tin atom. This conclusion coincides with the experimental observations that the BF_3 coordinated to the lone pair of tin(II) gradually dissociated in solution.

On the other hand, the fact that the ^{11}B shift of the BF_3 coordinated to tin is to the low field of free BF_3 and significantly below the normal range for four-coordinated boron suggests that neighborhood anisotropic shift effects arising from the large charge cloud of the tin atom may exert a strong influence on the observed shift. This effect is analogous to the unusually high and low field proton NMR shifts associated with diamagnetic transition metal complexes with hydride ligands.



^{11}B NMR SPECTRA (100 MHz)

REF: $F_3B{\cdot}O(C_2H_5)_2$

SOLVENT: BENZENE

$(BF_3)_3{\cdot}Sn[N(CH_3)_2]_2$ { -20.7 PPM, FWHH = 110 Hz } { +0.2 PPM, J_{BF} = 14.4 Hz }

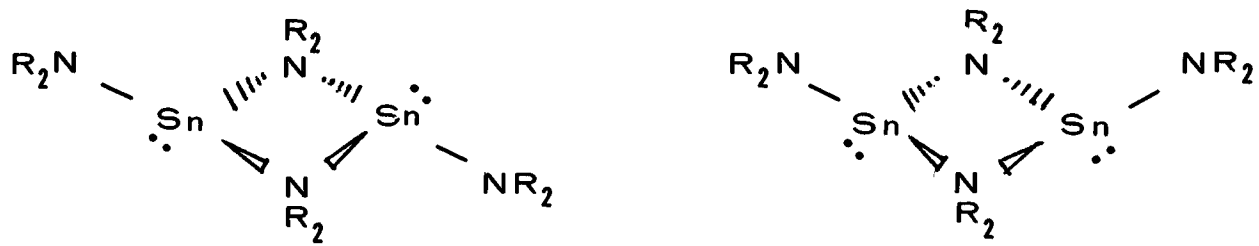
$(BF_3)_3{\cdot}Sn[N(C_2H_5)_2]_2$ { -17.5 PPM, FWHH = 119 Hz } { -0.23 PPM, J_{BF} = 16.7 Hz }

Figure 2. The pattern of the ^{11}B NMR spectra of BF_3 triply coordinated bis(dialkylamino)tin(II) compounds.

When the ^{11}B NMR spectra of 2A and 2B are compared with that of 2 (Table VI), the 1:1 adduct, 2A, exhibits only a broad resonance at -22.4 ppm, while the 2:1 adduct, 2B, shows that the broad peak shifts slightly toward high field and a new quartet resonance (J=16.4 Hz) appears at about 0 ppm. Except for the minor changes of the chemical shifts, the major noticeable difference between the spectra of 2 and 2B is in the integrated area ratios of lowfield to highfield peaks which is 1:2 in the former and 1:1 in the latter. The most reasonable interpretation of these observations is that the first trifluoroborane moiety is coordinated to the tin donor site. In this laboratory, the reaction of BF_3 with $SnCl_2$ in nonpolar solvents such as benzene has been studied without successfully obtaining a product. Birchall *et al.* [12] investigated the reaction of BF_3 with SnF_2; the result was a fluorine-bridged cation with the anion BF_4^-. Zuckerman *et al.* [13] reported dicyclopentadienyltin(II) boron trifluoride adduct in which the tin lone pair acted as the donor site to BF_3. Later, Harrison *et al.* [14] prepared the adducts of dicyclopentadienyltin(II) with aluminium halides. All of the reports indicated that the cyclopentadienyl was pi bonded to tin. In this work, when the more electronegative chlorines of $SnCl_2$ were replaced by the amino group, the electron donating property of tin appeared to be enhanced, making it possible to from an Sn$\longrightarrow$B link similar to that in $(C_5H_5)_2Sn\cdot BF_3$.

The aminotin(II) compounds have been recognized as prone to from associations through the nitrogen bridging. The methyl compound was found to be dimeric in benzene solution (Figure 3)[3]. Amino bridges are not

BIS(DIMETHYLAMINO)TIN(II)



P. FOLEY AND M. ZELDIN, INORG. CHEM., 14, 2264, (1975).

Figure 3. The proposed structures of $Sn[N(CH_3)_2]_2$.

available to serve as donor sites to BF_3 unless the bridges are broken. The terminal amino groups may exhibit N⇌Sn pi bonding which would serve to enhance the donor ability of the tin by increasing the electron density at that site and would decrease the sigma donor capability of the nitrogen. These factors could explain why the first BF_3 in the adduct coordinates to tin rather than to the N-sites. The influence of the BF_3 on tin apparently serves to weaken the dimer,allowing coordination of the second and third BF_3 moieties to amino-sites. However, the coordination of the second and third BF_3 groups to the N-sites destroys any N⇌Sn pi bonding which may have been present in the 1:1 adduct. Since this pi bonding increased the electron density on the tin, its removal should result in the tin becoming a weaker donor site. This rationalizes the gradual loss of BF_3 from the Sn-site observed in the ^{11}B NMR spectra of the 3:1 adduct.

The ^{11}B NMR spectra of 2A is shown in Figure 4. The broadness of the resonance may arise from the coupling of both ^{19}F and the isotopes ^{117}Sn and ^{119}Sn to ^{11}B, however, no resolved ^{11}B-Sn couplings were identified in any spectra of this family of compounds. This failure may result from rapid exchange processes in solution or the small magnitude of the satellites (^{117}Sn, 7.6%; ^{119}Sn, 8.6%) may have precluded their observation.

The ^{1}H NMR spectra supported the conclusions reached from the ^{11}B NMR data. The 1:1 adduct, $BF_3 \cdot Sn[N(C_2H_5)_2]_2$, gave a typical ethyl-group spectrum, a methylene quartet at δ3.00 and a methyl triplet at δ0.97. The apparent equivalence of the ethyl groups in the two amino groups demonstrates that the BF_3 cannot be coordinated to either of the amino nitrogens,

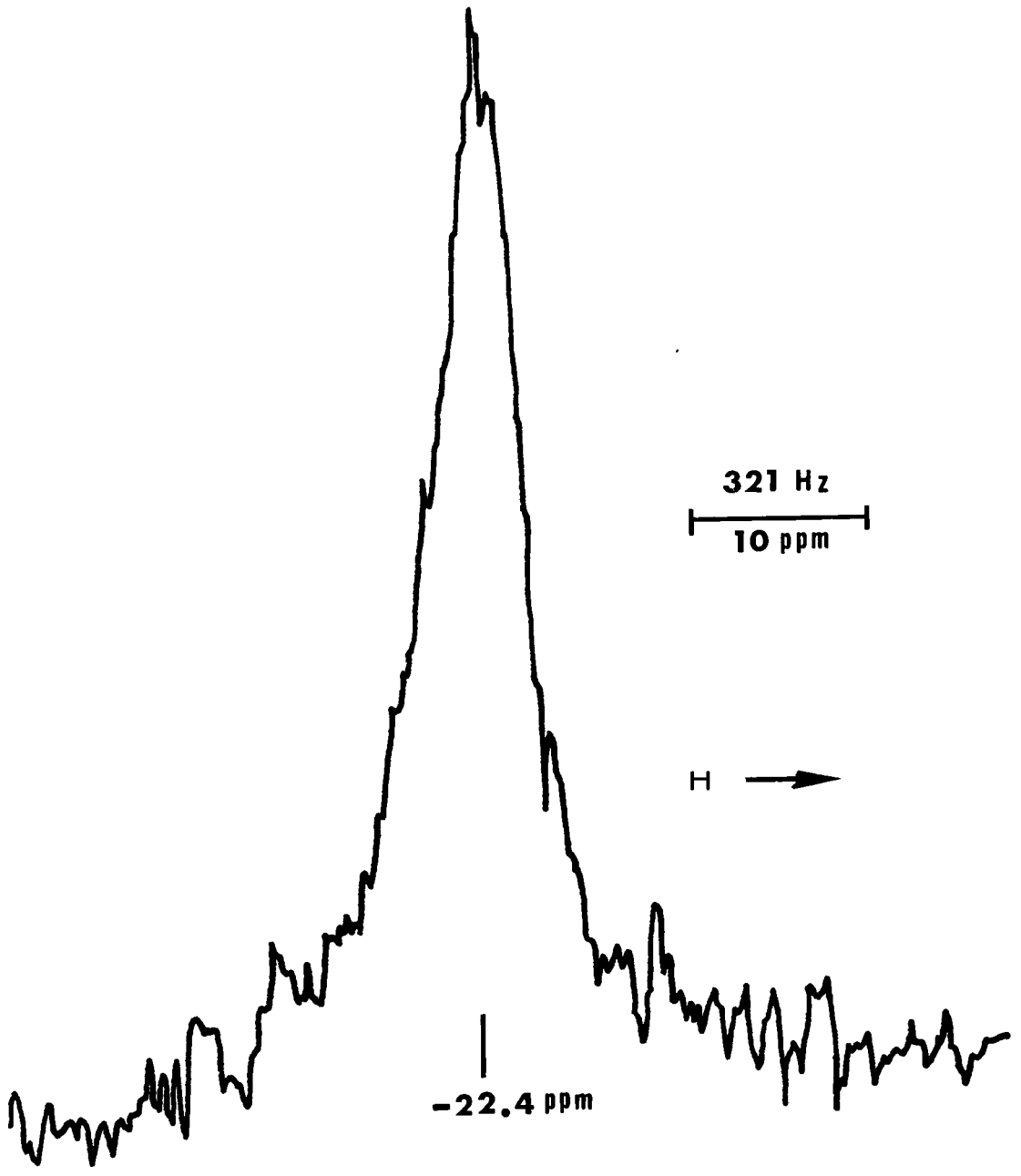


Figure 4. ^{11}B NMR spectrum of $BF_3 \cdot Sn[N(C_2H_5)_2]_2$ in benzene solution.

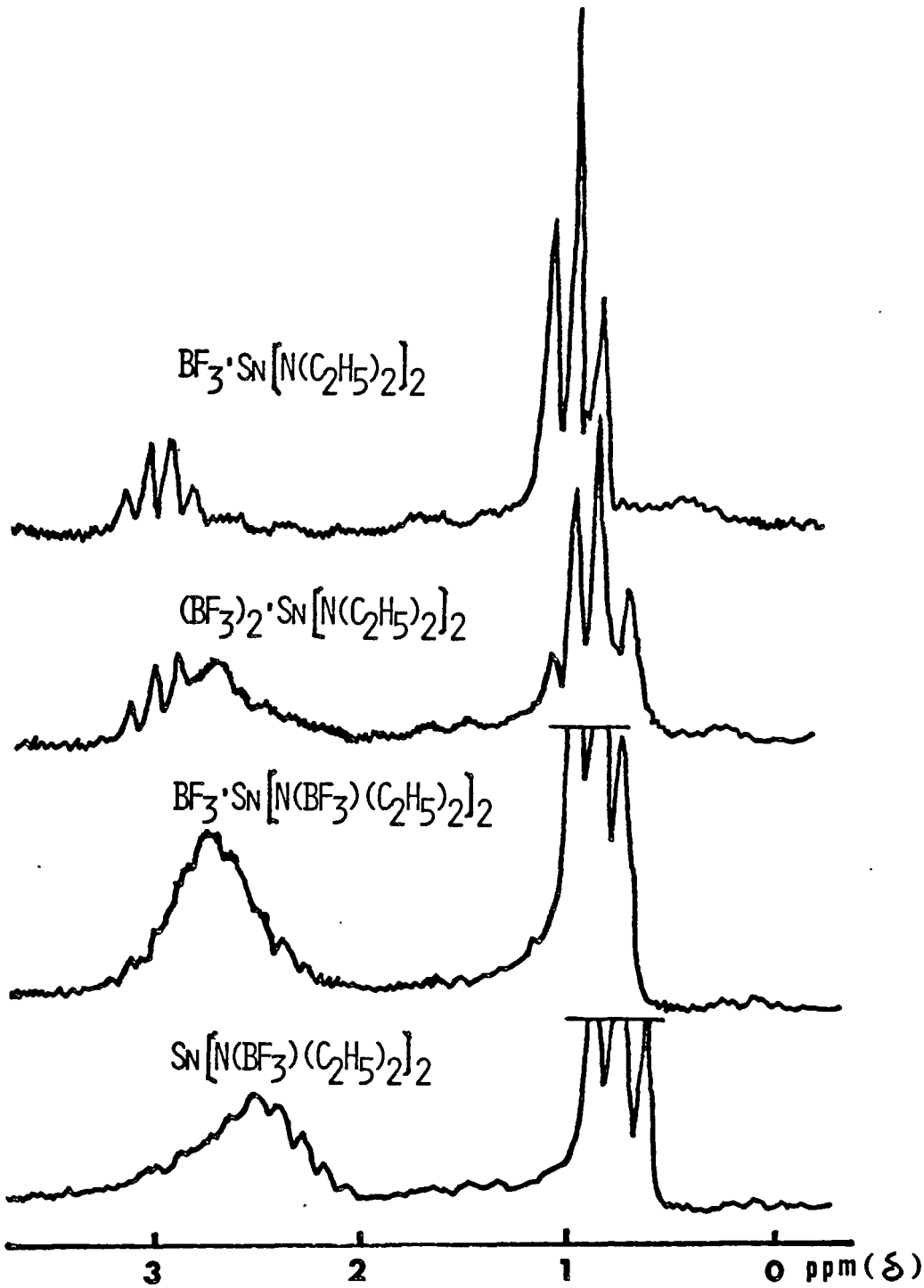
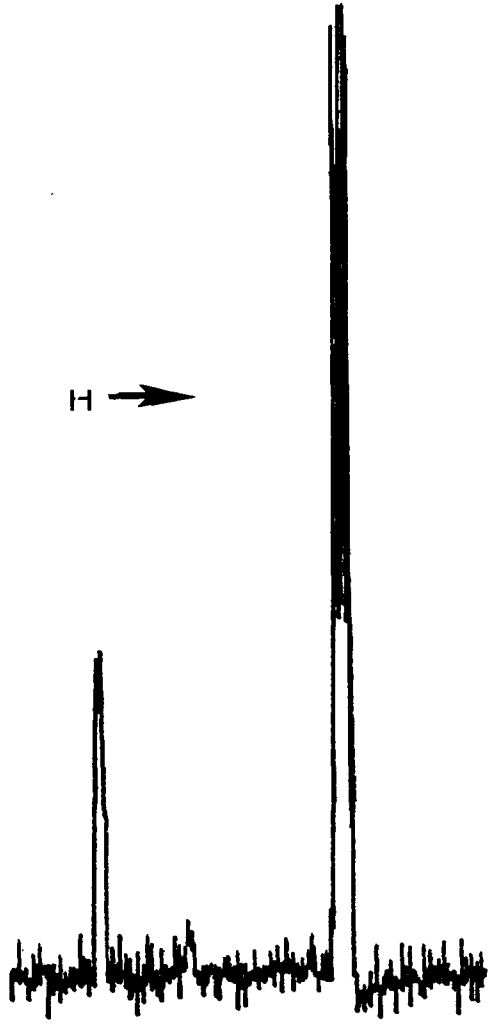


Figure 5. ^{1}H NMR spectra of bis(diethylamino)tin(II) compounds. (60 MHz; in benzene solution)

unless rapid exchange processes are occurring. This leaves only the tin donor site structure as a possibility. Addition of the second mole of BF_3 causes nonequivalence of the ethyl groups as seen by the spectrum of the 2B solution. At this time, one BF_3 is coordinated to Sn and one to an amino nitrogen. The broad peak associated with the methylene quartet represents the methylene groups on the amino group bearing the boron, broadened by long range coupling, presumably, with the ^{11}B nucleus. Coordination of the third mole of BF_3 renders the amino groups equivalent once more and the methylene resonance is completely broadened by the presence of BF_3 coordinated to both amino-sites (Figure 5). Trifluoroborane triethylamine has been prepared and its ^1H NMR spectrum in benzene was obtained for comparison purposes; the data were as follows: $-CH_2$, δ3.63, fwhh 20 Hz; $-CH_3$, δ1.77, fwhh 18 Hz; both were broad peaks. Heitsch reported the complex pattern of the CH_2 and CH_3 resonances of this compound[7]. It seems clear that the long range coupling due to ^{11}B or ^{11}B and ^{19}F causes the broadening of the ^1H resonance. The ^1H chemical shifts of $Sn[N(C_2H_5)_2]_2$ are upfield of those of $F_3BN(C_2H_5)_3$. When those of $Sn[N(C_2H_5)_2]_2$, 2A and 2 were compared, both the CH_2 and CH_3 groups absorptions shifted upfield after the coordination of each new BF_3 group. These shifts are unexpected from inductive considerations. They may represent anisotropic effects resulting from the coordination of the BF_3 on tin. The ethyl protons may approach the fluorines on the trifluoroborane moiety in close proximity.

The ^{19}F NMR spectrum of 2, referred to F_3CCOOH as an external

standard, consisted of a small peak at 60.2 and a large one at 74.2 ppm; while they are 136.7 and 150.7 ppm, respectively, referring to CCl_3F as the standard. From the proposed structure of this molecule, the lesser peak should represent BF_3 group on the tin atom; its shift can be compared with the value of 131.4 ppm which was reported for BF_3 on Sn in dicyclopentadienyltin(II) boron trifluoride[13]. The larger peak is assigned to the BF_3 group coordinated to nitrogen. Quartet coupling with J_{FB}=17.6 Hz is observed in the latter. No Sn-F coupling was observed in the ^{19}F spectrum of either type of BF_3; this may be explained by a rapid exchange of BF_3 groups in solution. On the other hand, the ^{117}Sn and ^{119}Sn satellites, being small, may simply not have been observed (Figure 6).



^{19}F NMR SPECTRUM (100 MHz) (REF. CCl_3F)

$BF_3 \cdot Sn[N(BF_3)(C_2H_5)_2]_2$ (IN BENZENE)

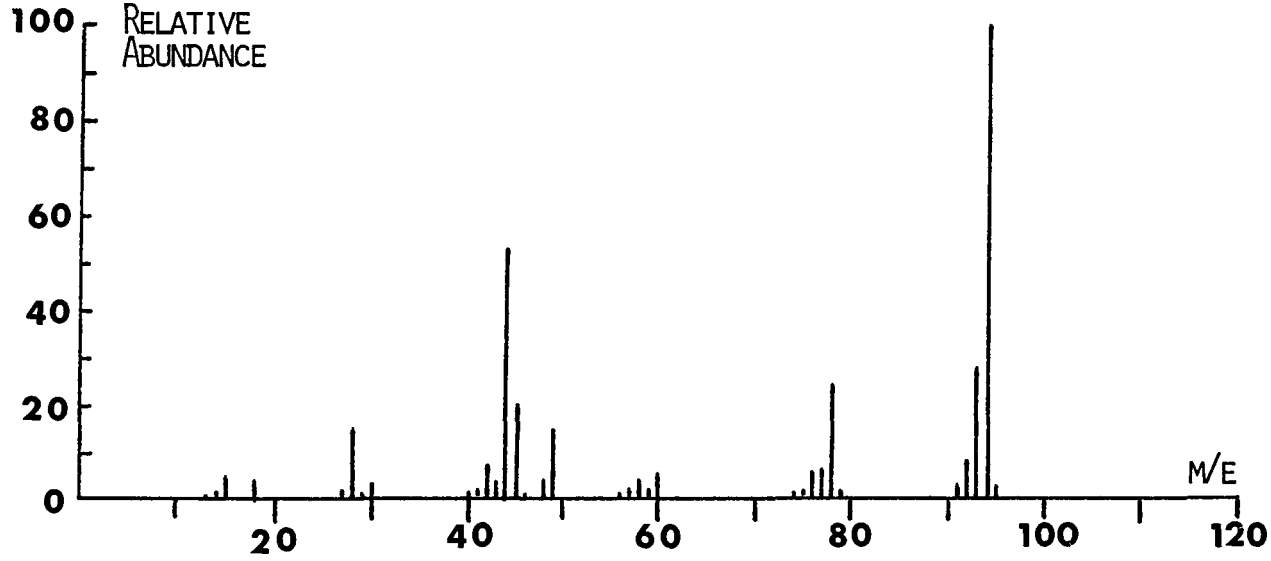
136.7 PPM	150.7 PPM
COMPLEX,	QUARTET,
NOT RESOLVED.	J = 17.6 Hz.

Figure 6. ^{19}F NMR spectrum of $BF_3 \cdot Sn[N(BF_3)(C_2H_5)_2]_2$.

MASS SPECTROMETRY
(70 eV)

$F_2BN(CH_3)_2$

SUBLIMATE



MASS(M/E)	RELATIVE ABUNDANCE	ASSIGNMENT	
95	3	P+2	
94	100	P+1	
93	28	P	$F_2BN(CH_3)_2^+$
92	10	P-1	
78	24		$F_2BNCH_3^+$
49	16		F_2B^+
45	21		$N(CH_3)_2+H^+$
44	54		$N(CH_3)_2^+$

Figure 7. Mass spectrum of $F_2BN(CH_3)_2$.

B. Thermal Decomposition of 1.

The volatile product, 1C, obtained from the pyrolysis of 1 was found contain no tin by element analysis. The distorted triplet seen in its ^{11}B NMR spectrum is consistent with the presence of BF_2 in the product and the similarity in the appearance (broadening) of the ^{1}H resonance to that of $F_3BN(CH_3)_3$ suggests that a B—N linkage is likely in the compound[7]. The mass spectrum of 1C (Figure 7 and Table III) shows the major ions with masses: 94 (100%,p+1), 93(28%, $F_2BN(CH_3)_2^+$), 78(24%, $F_2BNCH_3^+$), 49(16%, F_2B^+) and 44(54%, $N(CH_3)_2^+$). Although it is not clear why the p+1 peak has such a large intensity, probably stemming from the dimer of the compound, the major ions strongly suggest that 1C is $F_2BN(CH_3)_2$ or its dimer. The melting point of the dimer as reported in several literature references[17] ranged from 135 to 165 °C (by sealed capillaries). The low mp of 1C may result from the contact with air. However, the ^{11}B NMR chemical shift coincides with that reported[4,18] and the distorted pattern may indicate the presence of a mixture of dimer with monomer. Therefore, we may conclude that 1C is N,N-dimethylamino-difluoroborane.

The solid product, 1D, shows a sharp ^{1}H NMR peak and a broad ^{11}B peak and, in addition, demonstrates the presence of tin. The spectral characteristics indicate that the boron group is not coordinated to the amino group, but rather to the tin. The qualitative test indicating a slow color change in the reaction of this compound with $AgNO_3$ solution also suggests this conclusion. The ^{19}F NMR spectrum of 1D shows two kinds of fluorine in the ratio of 3:1 which suggests the presence of a single

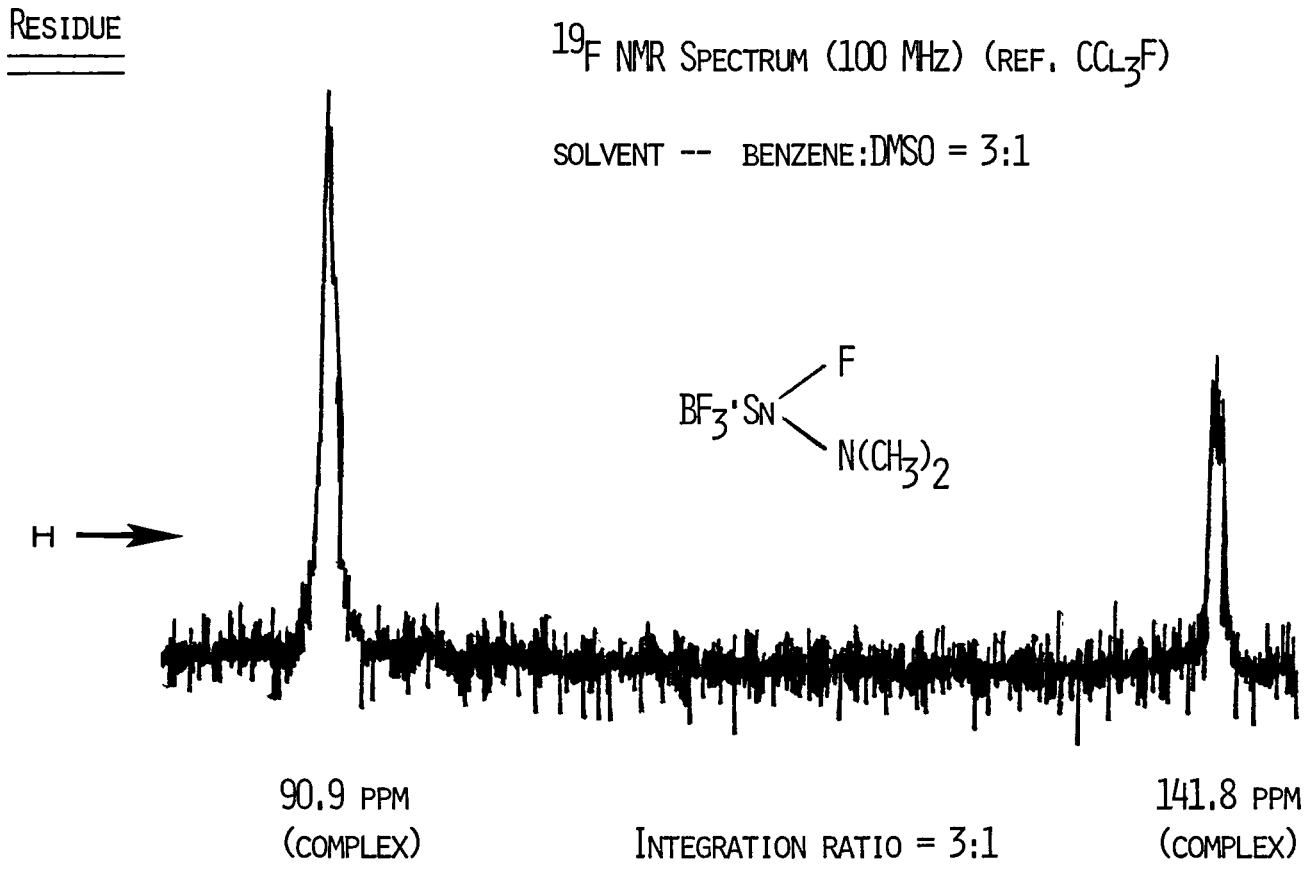
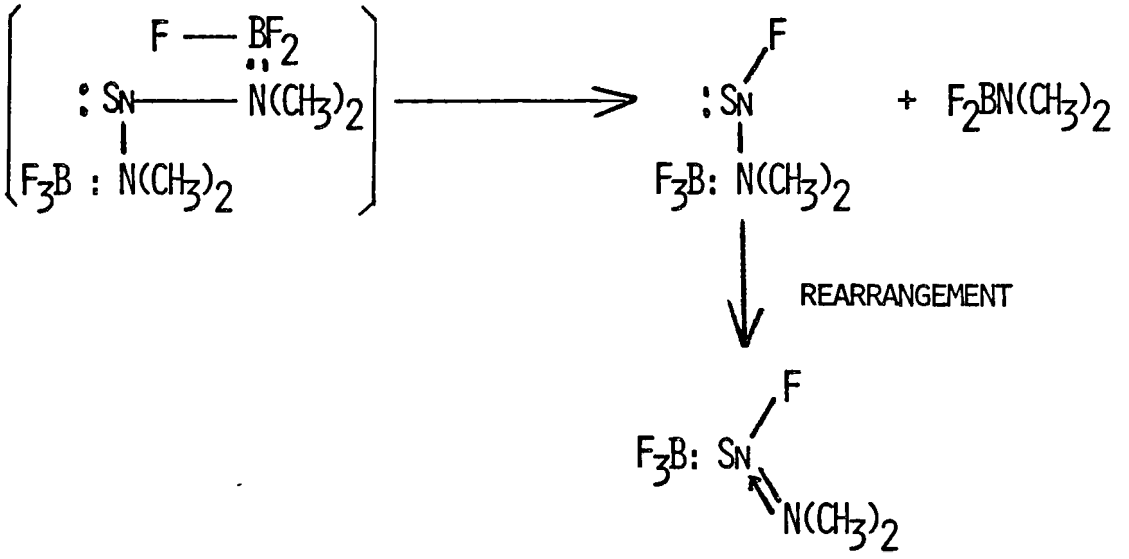


Figure 8. ^{19}F NMR spectrum of $BF_3 \cdot SnF[N(CH_3)_2]$.

F along with BF_3 group (Figure 8). The tin analysis is consistent with the formula $BF_3 \cdot SnF[N(CH_3)_2]$. Anal. Calcd for $C_2H_6BF_4NSn$: Sn, 47.56. Found: Sn, 47.13.

The pyrolysis reaction evidently involves a series of reactions as shown in the following:

$$BF_3 \cdot Sn[NBF_3(CH_3)_2]_2 \xrightarrow[10^{-4}\ \text{TORR}]{70^\circ\ C} Sn[NBF_3(CH_3)_2]_2 + BF_3$$



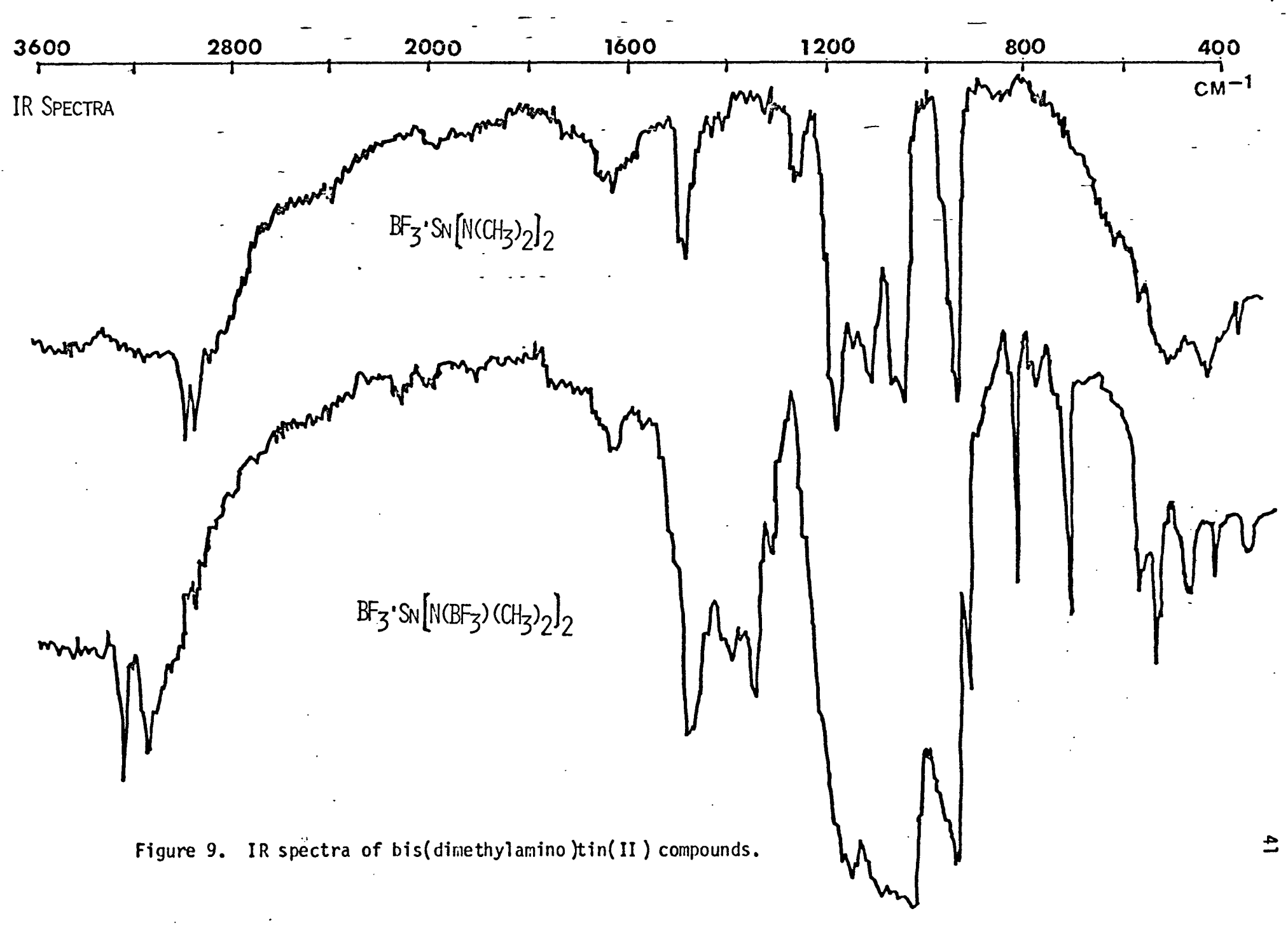


Figure 9. IR spectra of bis(dimethylamino)tin(II) compounds.

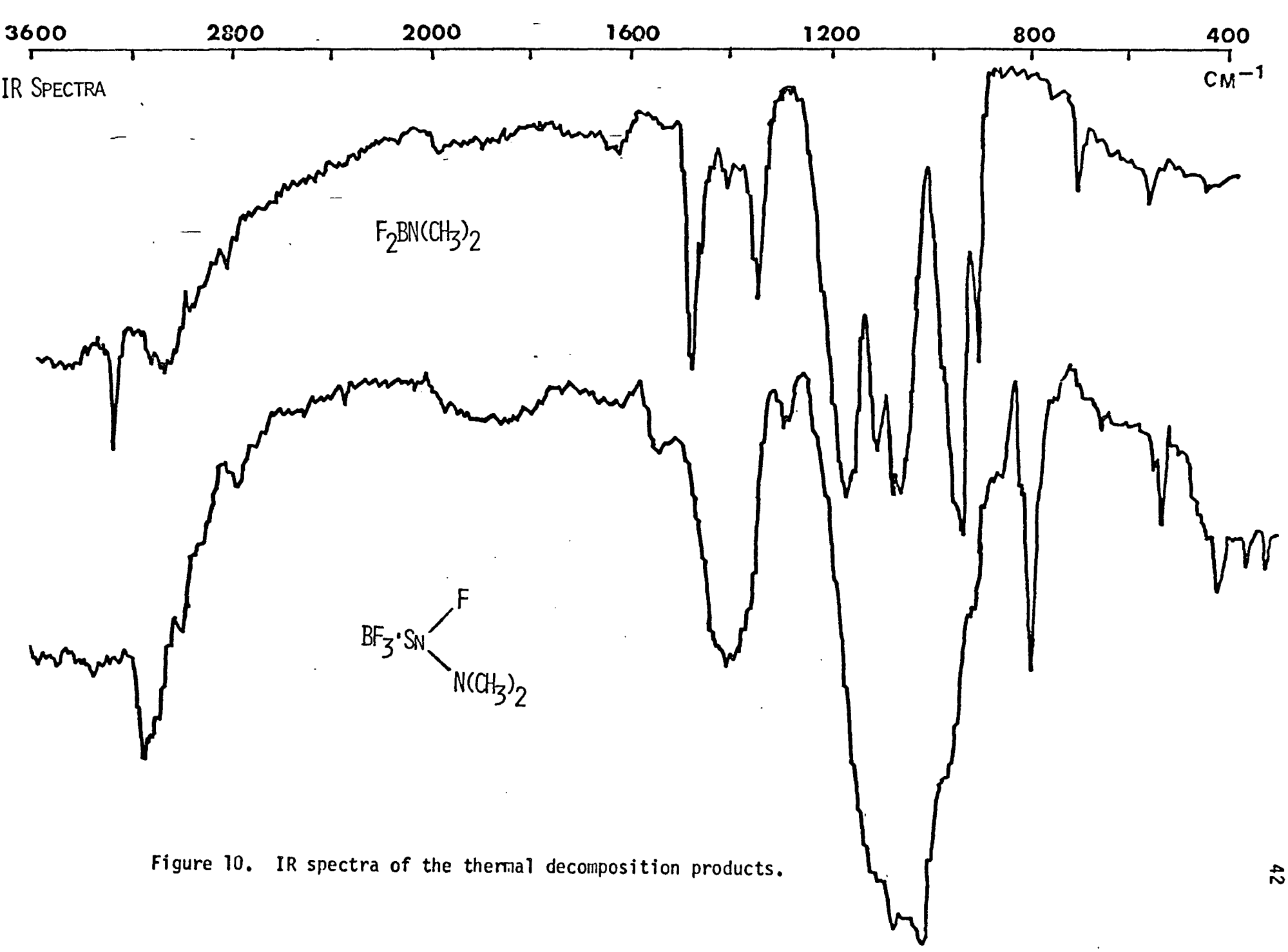


Figure 10. IR spectra of the thermal decomposition products.

C. Infrared Spectra.

The IR spectrum of $Sn[N(CH_3)_2]_2$ has been assigned by Foley and Zeldin[3] by comparing the bands with that of $Sn[N(CH_3)_2]_4$ which was reported by Bürger and Sawodny[19]. There are great similarities between these two, except that ν(Sn-N) is 535 in the Sn(IV) compound and 440 cm^{-1} in the Sn(II) compound. In Bürger's assignment, the absorption were roughly divided into five section: The region 2960-2700 cm^{-1} was ascribed to $\nu(CH_3)$; the region 1460-1400 cm^{-1} to $\delta(CH_3)$; 1260-1000 cm^{-1} to $\nu_{as}(NC_2)+\rho(CH_3)$; 961-800 cm^{-1} to $\nu_s(NC_2)$ and beyound 550 cm^{-1} to ν(Sn-N), $\delta(NC_2)$ and δ(N-Sn-N).

When BF_3 was coordinated on the Sn-site of $Sn[N(CH_3)_2]_2$, the induction effect would be expected to decrease the electron density on tin. The nitrogen atom in the amide group may provide some degree of charge compensation to the tin in order to maintain an overall charge close to zero. This result would affect the C-H bond so the sharp absorptions of $\nu(CH_3)$ in 1A spectrum were moved to 2980 and 3030 cm^{-1}, respectively, while that of $\delta(CH_3)$ was moved to 1465 and 1482 cm^{-1}(Table II and Figure 9). There are other examples as well, e.g., ν(CH): CH_4, 2914[33,34]; CH_3Cl, 3041[35], CH_3CN, 2999[36] cm^{-1}. When the second and third BF_3 groups were coordinated on the N-sites, the effects on $\nu(CH_3)$ were more directly observable than those described for 1A. We find new sharp bands at higher frequencies, i.e., 3280 for 1B, and 3190 and 3290 cm^{-1} for 1. From other data it has been shown that 1C is $F_2BN(CH_3)_2$, and we can also find in its IR spectrum the sharp $\nu(CH_3)$ band at 3290 and the sharp $\delta(CH_3)$ band at 1485 cm^{-1} (Figure 10). Such

bands in these regions appear to be the result of the effect of trifluoroborane bounded to the dimethylamine groups.

Since the most intense absorptions of the BF_3 group fall in the region 1265-870 cm^{-1}, the bands will overlap with that of $\nu_{as}(NC_2)+\rho(CH_3)$ and $\nu_s(NC_2)$. Waddington and Klanberg[20] assigned the BF_3 absorptions in $BF_3 \cdot O(C_2H_5)_2$ to: δ_{as}(520,530), ν_s(876,900), ν_{as}(1025,1065 cm^{-1}); $BF_3 \cdot NC_5H_5$: δ_{as}(517, 525), ν_s(893, 912), ν_{as}(1125, 1165 cm^{-1}). Shriver et al.[32] studied the reaction of BF_3 with $[(CH_3)_4N][SnCl_3]$; they suggested that BF_3Cl^- was formed and the very strong absorptions at 1050 and 1060 were assigned to B-F absorptions. In our work, if BF_3 is coordinated on a Sn-site, or both Sn and N-sites, the absorption in the region of 1085-1010 cm^{-1} are usually very intense and overlapped. A point worth mentioning is if BF_3 is only coordinated to nitrogen, i.e., no BF_3 is on the Sn-site, the overlapped peaks would not extend into the 1040-1010 cm^{-1} region. Waddington also reported the ν(B-N) of $BF_3 \cdot NC_5H_5$ at 1249 cm^{-1}, while Taylor[21] reported the mixed mode of B-N stretch in $BF_3 \cdot N(CH_3)_3$ at 697 cm^{-1}. The great different of these two data may stem from the mixed mode. In the spectrum of 1A, there is a weak band at 1250 cm^{-1} which may arise from $\nu_{as}(NC_2)+\rho(CH_3)$, however, the absorptions at this position in the spectra of 1 and 1B are strong and broad; they apparnetly result from the mixture of ν(B-N) and the others. No such absorption is evident in the spectrum of 1C, perhaps because this compound is dimerized through the coordination of both B and N-sites, making a four-member ring and complex B-N stretching absorptions. Nevertheless, the band at 710 cm^{-1} in the spectrum of 1C would still be

assigned as the B-N stretch by analogy to Taylor, and the same is found in the spectra of 1 and 1B.

The most controversial assignment is the ν(Sn-N). Clark and O'Brien[22] assigned ν(Sn-N) in $(CH_3)_3SnClO_4 \cdot 2NH_3$ to be 490 cm^{-1}. Lappert et al. [23] assigned this absorption in $Me_3SnN(Ph)CO \cdot NMe_2$ to be 510 cm^{-1}. Shishido and Kozima[24] examined the spectra of $(R_3Sn)_3N$, where R= CH_3, C_2H_5 and n-C_3H_7, and assigned the ν_{as}(Sn-N) at 728, 721 and 712 cm^{-1}, respectively. Zuckerman et al. [25] obtained the IR of the isotopomeric pair $(CH_3)_3SnNHC_6H_5$ -^{14}N and -^{15}N, and assigned absorption at 843 and 835 cm^{-1} as ν(Sn-^{14}N) and ν(Sn-^{15}N), respectively. Zuckerman also assigned the 880 cm^{-1} band of $(CH_3)_2Sn[N(C_2H_5)_2]_2$ to ν(Sn-N) in another study[26]. But Brown and Kubota[27] assigned ν(Sn-N) in $SnCl_4 \cdot 2CH_3CN$ at 337 cm^{-1}, while Farona and Grassell[28] assigned it in the same compound at 222 and 207 cm^{-1}. Aggarwal and Singh[29] assigned this absorption in $SnCl_4 \cdot 2DMF$ to be 325 and 310 cm^{-1}. These are the examples of low-frequency assignments, however, the assignments mentioned above all concern tin(IV) compounds. Since the chemistry of tin(II) compounds is less developed, the only similar assignment found is that of Foley and Zeldin[3] who assigned ν(Sn-N) in $Sn[N(CH_3)_2]_2$ at 440 cm^{-1},which can be compared to the assignment of Bürger and Sawodny[19] in $Sn[N(CH_3)_2]_4$ at 535 cm^{-1}. Based on these previous studies, we assign the ν(Sn-N) of 1A at 430 cm^{-1}, which is lower than 440 cm^{-1} since after a BF_3 group has coordinated to the Sn-site, the Sn-amide bonding should be weakened marginally. We find this absorption moves to 420 cm^{-1} in both 1B and 1

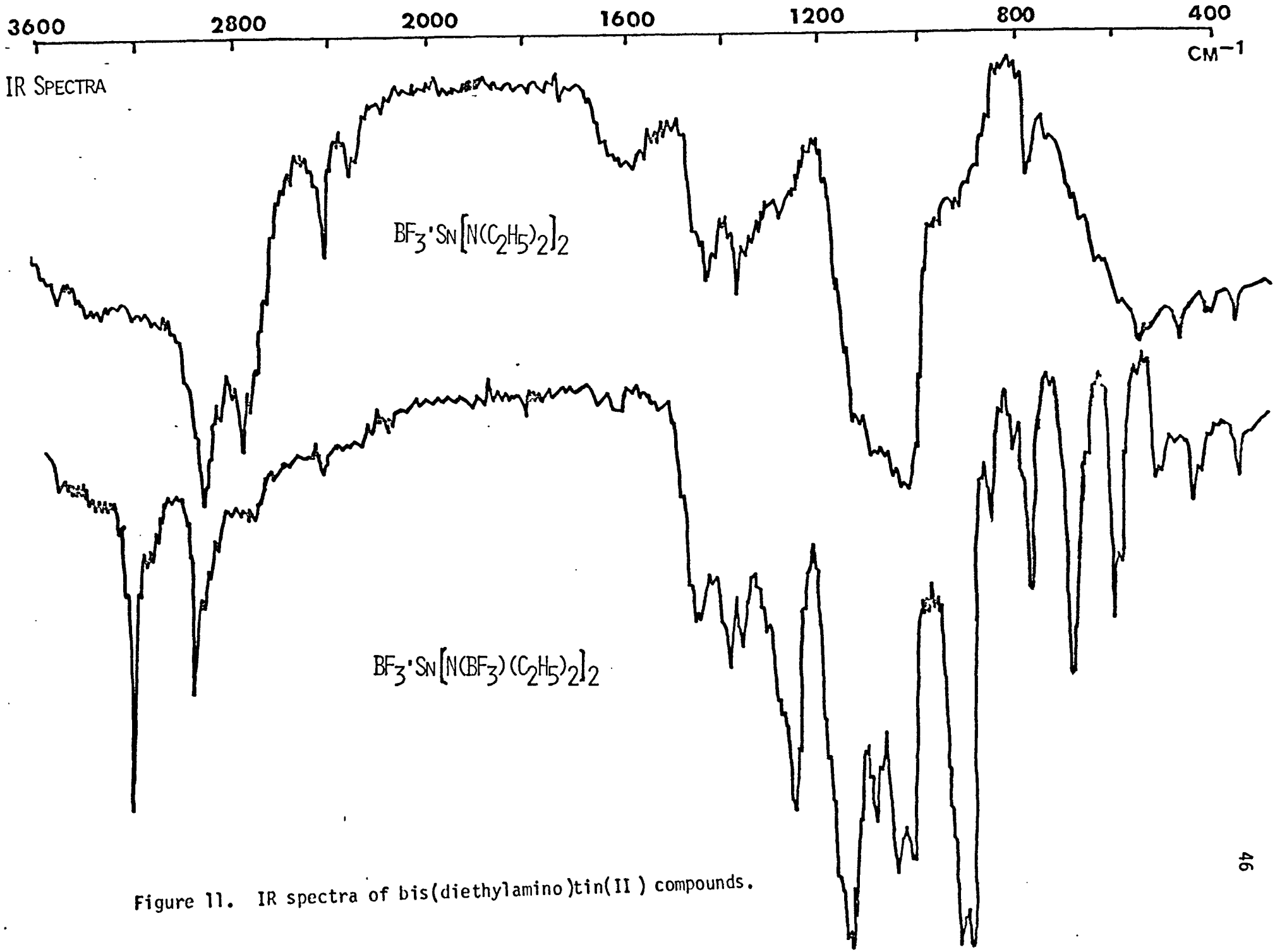


Figure 11. IR spectra of bis(diethylamino)tin(II) compounds.

spectra, a shift which is expected because the second and third BF_3 groups are coordinated on the N-site of the amide and cause further weakening of the Sn-N bond.

The ν(Sn-B) absorption should be near that of ν(Sn-N) owing to the similarity of their atomic masses. We assign the band at 500 cm^{-1} in 1A to this absorption; it moves to 470 cm^{-1} in 1B and to 460 cm^{-1} in 1. This trend is consistent with weakening of the BF_3-Sn(II) bonding observed after the successive addition of BF_3 to the amide-site. In the spectrum of 1D, the 425 cm^{-1} band is assigned to ν(Sn-B); the low-frequency shift is believed to be due to the direct bonding of F to the Sn; and, for the same reason, the ν(Sn-N) band is shifted to 370 cm^{-1}. The absorption at 320 cm^{-1} may be assigned to ν(Sn-F). Wilkins and Haendler[30] have assigned ν(Sn-F) in several SnF_4 coordinated compounds, e.g., in SnF_4·bipy, at 592, 578, 567 cm^{-1}, while Clark and Goel[31] have assigned ν(Sn-F) in $(CH_3)_2SnF_2$ at 373 cm^{-1}. The low-frequency shift of ν(Sn-F) in 1D may result from the mutual weakening of the F and BF_3 bonds to Sn. There is no absorption in this region in 1C spectrum because this compound contains no tin.

When the spectra of the adducts of $Sn[N(C_2H_5)_2]_2$ are examined (Table V and Figure 11), we find the $\nu(CH_3)$ at 3000 cm^{-1} experiences essentially no change among the three compounds ($Sn[N(C_2H_5)_2]_2$, 2A and 2). The intensity diminishes in the region 2900-2820 cm^{-1} when the first BF_3 is coordinated to the Sn-site, 2A. A new sharp band appears at 3265 cm^{-1} when all amide-site are occupied by BF_3, 2, presumably resulting from inductive effects on the CH_2 groups. The 1200-1030 cm^{-1} region exhibits

the overlapping peaks arising from the addition of BF_3 group and the band at 1275 cm^{-1} in 2 shows the apparant ν(B-N) absorption. Also, there is a band at 700 cm^{-1} in the spectrum of 2 which may be attributed to the mixed mode of Sn-N absorption. The ν(Sn-B) band in 2A is assigned at 570 cm^{-1} and that in 2 is at 530 cm^{-1}. The ν(Sn-N) band in $Sn[N(C_2H_5)_2]_2$ is assigned at 585 and 567 cm^{-1}, and it shiftes to lower frequency at 470 cm^{-1} in 2A and at 450 cm^{-1} in 2.

V. CONCLUSION

Evidences from both NMR and IR spectra support the conclusion that when BF_3 is brought into contact with $Sn(NR_2)_2$ (R=CH_3 or C_2H_5),the first donor site to be occupied by this electrophilic molecule is the tin lone pair, giving the product,$BF_3 \cdot Sn(NR_2)_2$, trifluoroborane-bis(dialkylamino)tin(II). Full coordination, i.e., 3:1 for BF_3 and $Sn(NR_2)_2$, gives the product $BF_3 \cdot Sn[NR_2(BF_3)]_2$, trifluoroborane-bis(N-trifluoroborane-dialkylamino)tin(II); wherein the second and third BF_3 groups are bound to the two remaining donor sites, the lone pairs of the amide groups.

Judging by the qualitative tests of the (1:1) and (3:1) adducts, the lone pair electrons on tin, though they are coordinated by BF_3, still can exhibit reducing property but with lessened activity compared to amino tin(II) compounds. By virtue of its position in the periodic table, tin has d valence orbitals which are available for bonding in its compounds. Nominally, tin(II) compounds have a lone pair of electrons in the valence shell(as in $SnCl_2$),which are employed in expanding the valence when tin is tetravalent (as in $(CH_3)_2SnCl_2$). As long as the lone pair electrons are present, the tin is operationally regarded as divalent, regardless of the number of orbitals employed by tin in bonding. For example, a chelated adduct, $SnCl_2 \cdot TMED$, has tetracoordinate, divalent tin. The adducts where BF_3 is coordinated to tin are, in this sense, no longer tin(II) compounds since the lone pair electrons of tin are used in bonding to the BF_3. However, since these compounds exhibit reducing characteristics, the name of pseudotin(II) compounds has been applied.

The aforementioned NMR evidences for the coordination of BF_3 to tin in 1, 1A, 1D, 2 and 2A has permitted the assignment of ν(Sn-B) bands in the IR spectra of these compounds (600-400 cm^{-1} region). Few IR studies of analogous adducts were found in the literature for comparison purposes in making the ν(Sn-B) assignment. Zuckerman[37] has criticized the assumption that a new band arising on complex formation represents a donor acceptor bond, pointing out that a ligand vibration inactive in the free ligand may be activated in the adduct. Thus changes in the spectra on complex formation may be associated with changes of structural configuration. In this instance, major structural changes must occur when BF_3 coordinates and minor changes probably also occur in the amino-tin(II) moiety. Nevertheless, the band assigned to ν(Sn-B) appears reasonably placed in the spectrum and shifts sensibly with changes in the adduct. It is therefore presented as a tentative assignment awaiting more detailed studies through isotopic substitution.

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PART II

DONOR AND ACCEPTOR BEHAVIOR IN DIVALENT TIN COMPOUNDS

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I. INTRODUCTION

The chemical shifts in NMR spectra are directly related to the shielding experienced by the nuclei being studied. Besides the shielding caused by the solvent, a nucleus in a diamagnetic molecule may encounter magnetic field contribution from several sources including effects due to interaction of the local electron cloud with the applied field, quantum mechanical mixing of paramagnetic excited states with the ground state of the molecule and through space fields due to distant groups. These last effects are known as neighbor-anisotropic effects depending on the orientation of the molecule with respect to the direction of the applied magnetic field and produced only by the electron groups which are not spherically symmetrical. Local diamagnetic currents account for the shielding of isolated nuclei and those with no low lying excited states (such as the proton) but in many other nuclei such as ^{19}F, ^{31}P and ^{119}Sn,the local paramagnetic term may overshadow the local diamagnetic contribution. In cases where the charge cloud surrounding the nucleus is not strictly spherical local anisotropic effects, usually paramagnetic, can make a significant contribution to the shift.

One instance of a particular contribution to the chemical shift is due to the intramolecular reaction field. An atom having a spherical electron distribution will experience a distortion of its electron cloud when placed in an electric field and this distortion will normally result in a reduction in the shielding of the nucleus. If the molecule has an electric dipole

moment, the intramolecular electric field may produce significant shielding effects; in molecules with no overall electric dipole moment, local dipoles still occur, and these may have a significant influence on shifts in some nuclei.

According to Drago[38], electron circulations develop about the nucleus of an atom in an applied magnetic field which either produce a secondary magnetic field in the same direction as the applied field or are less effective in producing a diamagnetic field because of restrictions on circulation. This is the condition of local paramagnetic effect.

Until recently, the ^{119}Sn NMR spectra were studied by $^{1}H-\{^{119}Sn\}$ double-resonance experiments. In 1960, Burke and Lauterbur[39] reported ^{119}Sn NMR data of organic and inorganic tin compounds including the type, R_nSnX_{4-n}. The ^{119}Sn spectrum of $SnCl_2$ in tetrahydrofuran also has been reported and the ^{119}Sn chemical shift was +236 ppm with respect to tetramethyltin, a rare example of ^{119}Sn NMR data for a tin(II) compound. They also investigated solvent effects upon the shifts, observing that the chemical shift of $SnCl_2 \cdot 2H_2O$ in aqueous solution is dependent upon the concentration of added HCl. Further, they reported that the spin coupling between methyl protons and tin are affected both by the other substituents and by the solvent used. Longer range spin couplings in tin alkyls are often comparable in magnitude to the shorter range couplings, splitting the tin resonance into a great many closely spaced components so that it appears to be a very broad peak. Davis *et al.*[40] reported ^{119}Sn spectra of 59 tin(IV) compounds. Compounds in which p_π-d_π bonding between the halogen and tin was believed

to be present, exhibited high field shifts which the investigators attributed to an increased paramagnetic contribution to the shielding.[41]. They also mentioned that dispersion forces[42] appear to affect the shift when bulky polarizable groups are present. Berghe and Kelen[43] studied the ^{119}Sn NMR resonance of the compounds, $(CH_3)_n Sn(SCH_3)_{4-n}$, citing the statements of Ebsworth[44] that any p_π-d_π bonding will influence the energy of the d orbitals of the central atom, perhaps causing an increase in that energy with a commensurate decrease in the contribution of the paramagnetic term to the shielding of the nucleus and subsequently contributing to the observed high-field shift. Zuckerman et al.[45] reported ^{119}Sn chemical shifts of 40 organotin compounds and stated that disperson forces and effects due to neighboring polarizable groups appear to result in high-field ^{119}Sn shifts. Berghe and Kelen in another report[46] indicated that, besides the p_π-d_π back-donation effect, an increasing diamagnetic shielding contribution with the increasing halogen size must also be taken into account. Also, the anisotropic effects contributed by the highly polarisable groups arising both from the electric-field effect of the permanent dipole moments in the molecule and from Van der Waals' interactions between the atoms were regarded as important influences on the chemical shift. Clearly, a number of factors are believed to control the ^{119}Sn chemical shifts.

A review of ^{119}Sn spectroscopy has appeared[47] and the application of pulse Fourier transform techniques to direct observation of ^{119}Sn resonance has been described by Lassigne and Wells[48].

Coordination compounds containing Sn-N bonds have been reviewed[49].

It appears that compounds of the type, $RSnX_3$ and R_2SnX_2 (X=halogen), generally form 1:2 adducts with nitrogen donors while compounds of the type, R_3SnX, combine with 1 or 2 moles of ammonia or amines. Thomas and Rochow[50] were the first to suggest that tin is able to expand its valence shell, implying that both the halogen atom and the nitrogen atom are covalently bound to tin. This idea has been confirmed for the trimethyltin chloride-pyridine complex by Beattie et al.[51] Results of infrared measurements and X-ray analysis point to a penta-coordinated trigonal bipyramidal arrangement of groups around the tin atom. The trimethyltin group is planar while the chlorine atom and the pyridine molecule lie on either side of the plane[52].

Complexes of diorganotin dihalides with bidentate ligands like 2,2'-dipyridyl have been described[53,54,55,56]. However, few reports of chelated bivalent tin complexes have appeared; Morrison and Haendler[35] prepared the complex, $SnCl_2 \cdot DP$, but did not give a detailed description of its spectral parameters. Fowles and Khan prepared tin(II) halide dipyridyl complexes[57] and reported their far-infrared spectra and ultraviolet spectra.

The first example of a tin(II) compound coordinated to Group IIIA Lewis acid was reported [58] as $(C_5H_5)_2Sn \rightarrow BF_3$, which was prepared by the reaction of BF_3 with $(C_5H_5)_2Sn$. In the subsequent work[59], $(C_5H_5)_2SnBBr_3$ also reported. The fact that tin(II)dicyclopentadienide is apparently the only divalent tin compound which acts as donor towards BF_3 has led to our investigation of the reaction of BF_3 with several other tin(II) compounds to determine whether other adducts of that type may be formed. It is of particular interest to show under what conditions direct tin-boron bonds are stable.

II. RESULTS

The electronic configuration of tin(II) compounds[4] suggests that the tin may act either as a donor or acceptor site using its valence shell lone pair or orbital, respectively. In a sense, this represents amphoterism in the Lewis acid-base behavior of such molecules, an unusual characteristic. We have studied the reaction of tin(II) species with both electrophiles and nucleophiles, separately and together, to assess the relative donor and acceptor abilities.

A. Investigation of Trifluoroborane-Tin(II)chloride-Trimethylamine Adduct.

Trimethylamine-trifluoroborane is known[5] to be a stable adduct. Its stability has been explained using hard acid-soft base (HSAB) model[6] observing that trimethylamine is regarded as a moderately hard base and that trifluoroborane is a moderately hard acid suggesting a stable adduct. The HSAB character of tin has not yet been elucidated but we may assume that it varies with the number and type of substituents on tin. The direct reaction of BF_3 with $SnCl_2$ was previously studied by Shriver *et al.*[7] who first reported that a simple adduct, $BF_3 \cdot SnCl_2$, was formed. Later, they showed that the product was ionic, probably containing the BF_3Cl^- ion. We have investigated the reaction of BF_3 with the adduct, $SnCl_2 \cdot N(CH_3)_3$[1], and related adducts. The presence of the trimethylamine group was expected to enhance the donor capacity of the tin site. The possibility of an acid displacement reaction giving $BF_3 \cdot N(CH_3)_3$ and $SnCl_2$ was also recognized and subsequently eliminated.

NMR spectra were used to investigate the nature of the product and

no indication was found of trimethylamine-trifluoroborane[3]. Rather, the spectra were consistent with the product, $BF_3 \cdot SnCl_2 \cdot N(CH_3)_3$, where tin is behaving simultaneously as a donor towards BF_3 and an acceptor towards $(CH_3)_3N$. The results are evaluated as follows.

The ^1H NMR spectrum of the product in aniline solution (Table I) consisted of a sharp singlet at δ1.77. In $BF_3 \cdot N(CH_3)_3$, the ^1H resonance is a broad poorly resolved multiplet occuring at δ1.97, while that for $SnCl_2 \cdot N(CH_3)_3$ occured at δ1.83. In our experience, ^1H spectra of methyl and methylene groups on amine nitrogens coordinated to BF_3 appeared as broad, poorly resolved multiplets[4,8] unless rapid exchange involving B-N bond breaking is occuring. In one experiment the product, $BF_3 \cdot SnCl_2 \cdot N(CH_3)_3$, and $BF_3 \cdot N(CH_3)_3$ were mixed together in aniline solution. The ^1H NMR spectrum of the mixture (Figure 4) exhibited peaks characteristic of the individual chemical species showing that BF_3 is not coordinated to $(CH_3)_3N$ in the product and that no obvious exchange processes are occuring between the compounds. When the chemical shifts of ^1H NMR resonance are considered, we can see that the absorption of $BF_3 \cdot N(CH_3)_3$ shifted to the lowfield of that of $(CH_3)_3N$, while $SnCl_2 \cdot N(CH_3)_3$ was at higher field and $BF_3 \cdot SnCl_2 \cdot N(CH_3)_3$ was at higher field yet.

The ^{19}F NMR spectrum of $BF_3 \cdot SnCl_2 \cdot N(CH_3)_3$ in DMSO solution consisted of a 1:1:1:1 quartet at +84.8 ppm (referred to external CF_3COOH). The ^{19}F signal of $BF_3 \cdot N(CH_3)_3$ consisted of a same type of absorption at +64.4 ppm. Again, the presence of $SnCl_2$ in the adduct results in an upfield shift of the NMR signal.

The ^{11}B NMR spectrum of the product in dimethylsulfoxide (DMSO) solution was a broad complex peak at -19.4 ppm from the $BF_3 \cdot O(C_2H_5)_2$. This low-field shift may be compared to those of BF_3 with $Sn(NR_2)_2$ adducts (where BF_3 is believed to be coordinated to tin) which are broad complex in the range of -17 to -23 ppm[8].

Finally, the ^{119}Sn NMR spectrum of the product in DMSO solution consisted of a somewhat broad singlet resonance at +332.8 ppm with respect to $Sn(CH_3)_4$, while that of $SnCl_2 \cdot N(CH_3)_3$ occured at +111.9 ppm. Both spectra were obtained with ^1H decoupling. No clearly defined spin coupling was resolved, although with additional time to vary instrument parameters it may eventually be possible to obtain spin coupling constants. Though $BF_3 \cdot SnCl_2 \cdot N(CH_3)_3$ was somewhat soluble in DMSO and the ^{119}Sn spectrum was reasonably easily obtained, $SnCl_2 \cdot N(CH_3)_3$ exhibited very low solubility and required over 27000 pulses to obtain a spectrum. The fact that these two compounds have such different ^{119}Sn chemical shifts and solubilities argues for a quite strong interaction between BF_3 and $SnCl_2 \cdot N(CH_3)_3$. The additional information is that $SnCl_2$ readily dissolves in DMSO (described in next section) and the ^{119}Sn NMR resonance of the saturated solution occurs at +369.5 ppm. Although the precise nature of $BF_3 \cdot SnCl_2 \cdot N(CH_3)_3$ in solution has not been proven, we may conclude from the evidence cited that the compound does not break down to BF_3 and $SnCl_2 \cdot N(CH_3)_3$ or $SnCl_2$ and $F_3BN(CH_3)_3$ in DMSO solution. Also it is unlikely to exist in an ionic formulation as BF_3Cl^- since the ^{11}B NMR chemical shift of the latter species will be reasonably expected to fall between +2.1 (that of BF_4^-)[9] and -6.7 ppm (that

of BCl_4^-)[10]. Therefore, we can say that the product is doubly coordinated and that it is an amphoteric adduct with respect to tin. The combination word, amphoadduct, will be used to represent this kind of compound in the subsequent descriptions. Amphoadducts of tin(II) compounds with BF_3 **are also regarded as pseudotin(II) compounds since they show a slow color change upon reaction with a $AgNO_3$ solution[8].**

The differences in the IR spectra of $SnCl_2 \cdot N(CH_3)_3$ and its BF_3 adduct reflect the principal components of the compound. The enhanced absorption in the frequencies near 1140, 1070 and 1035 cm^{-1} result from the introduction of BF_3 group[8, 17, 18]. The band at 1035 cm^{-1} is usually indicative of BF_3 coordinated to tin as has been pointed out earlier in the study of the reaction of BF_3 with bis(dimethylamino)tin(II). The environment of the CH_3 group in the dimethylamino group will be very similar to that of the CH_3 group in trimethylamine when they are bound to tin. The result of the earlier investigation indicated that the BF_3 in the bis(dialkylamino)tin(II) adduct reduced the Sn-N bond strength and enhanced the C-H strength and the same effects are seen in the trimethylamine group of this adduct. First, the $\nu(CH_3)$ absorption shifted from 3160 in $SnCl_2 \cdot N(CH_3)_3$[1] to 3170 cm^{-1} in the product and the $\delta(CH_3)$ absorption from 1470 to 1483 cm^{-1}; second, the ν(Sn-N) absorption shifted from 562 to 550 cm^{-1}. The approximately 120 cm^{-1} difference in the ν(Sn-N) absorption between $SnCl_2 \cdot N(CH_3)_3$ (562 cm^{-1}) and $Sn[N(CH_3)_2]_2$ (440 cm^{-1})[8,19] is puzzling since the coordinate Sn←N bond in the former is expected to be weaker than the polar covalent Sn-N bond in the latter. The difference may result from the dimer structure[8,19] of the latter since the

four Sn-N bridging bonds should be weaker than the ordinary Sn-N bond. Although the non-bridging Sn-N bonding can be enhanced by p_π-d_π bonding, the average may still be low, leading to the lower frequency infrared absorption. The absorption at 530 cm^{-1} in the product, which is absent in $SnCl_2 \cdot N(CH_3)_3$, is tentatively assigned as the Sn-B stretch which is also higher than that of $BF_3 \cdot Sn[N(CH_3)_2]_2$. The band at 460(vw) is tentatively assigned to $\delta(NC_2)$ and $\rho(NC_2)$[20] and that at 310 (m) to ν(Sn-Cl)[21,22,23].

Infrared absorptions of BF_3(g) were observed at 1500(s) and 1460(vs, doublet) cm^{-1} [24] and the ν(C-H) absorptions of $(CH_3)_3N$ (g) were found at 3000(vs), 2940(m), 2880(s), 2800(vs) cm^{-1} along with the lower-frequency bands. Upon the formation of adduct $F_3BN(CH_3)_3$, the ν(C-H) absorptions shift to the 3010-2900 range, the BF_3 absorptions occur at 1200-1100(vs, overlapping) and 980-920(vs, Overlapping) cm^{-1} and a new absorption at 680(m) cm^{-1} was assigned to the (B-N) absorption[25] (but as already pointed out[8] it may represent another B-N mode). There is also a band at 1250(m) cm^{-1}, a position which has been proposed by Waddington[18] as the absorption of (B-N) stretch in $BF_3 \cdot NC_5H_5$. The 690(w) cm^{-1} absorption in the spectrum of $BF_3 \cdot SnCl_2 \cdot N(CH_3)_3$ may be assigned to $\nu_s(NC_2)$[20] and there are no other bands in the range of 710-650 cm^{-1} or near 1250 cm^{-1}, regions that are probably due to the absorptions of B-N bonding. Comparing these several ranges of IR absorptions of $F_3BN(CH_3)_3$ with those of the product gives further evidence for the amphoadduct structure in which no direct link of BF_3 with $(CH_3)_3N$ exists. This leads to the conclusion that both BF_3 and $(CH_3)_3N$ are coordinated to $SnCl_2$.

B. Investigation of Trifluoroborane-Tin(II)chloride-Dimethylsulfoxide Adduct.

It is reasonable to assume that $(CH_3)_2SO$ is a weaker donor towards BF_3 or $SnCl_2$ than is $(CH_3)_3N$. Calorimetric studies[11] showed that $(C_2H_5)_3N$ reacts exothermically with tin(II) halides in dimethylsulfoxide suggesting that the displacement reaction shown below occurs:

$$SnX_2 \cdot 2DMSO(solv) + (C_2H_5)_3N(l) \longrightarrow (C_2H_5)_3N \cdot SnX_2 \cdot DMSO(solv) + DMSO(solv)$$

Nevertheless, $F_3B \cdot OS(CH_3)_2$ was readily prepared by direct combination and $SnCl_2$ dissolves in DMSO with evolution of considerable heat.

When BF_3 is reacted with $SnCl_2 \cdot OS(CH_3)_2$, the product is believed to be an amphoadduct, $BF_3 \cdot SnCl_2 \cdot OS(CH_3)_2$. In pyridine solution, the ^1H NMR chemical shift of this amphoadduct was δ1.77, while those for the related species, $SnCl_2 \cdot OS(CH_3)_2$, $BF_3 \cdot OS(CH_3)_2$, and $(CH_3)_2SO$ were δ1.85, 2.30 and 2.30, respectively. It appears from the last two shifts that pyridine displaces DMSO from BF_3. In aniline, a less basic solvent, the shifts were: $(CH_3)_2SO$, δ2.12; $BF_3 \cdot OS(CH_3)_2$, δ2.27; $SnCl_2 \cdot OS(CH_3)_2$, δ1.90; $BF_3 \cdot SnCl_2 \cdot OS(CH_3)_2$, δ1.84. The above sequence indicates that when DMSO was coordinated by BF_3, the ^1H chemical shift moved downfield; when it was coordinated by $SnCl_2$, the signal shifted upfield; and when the intermediate, $SnCl_2 \cdot OS(CH_3)_2$, was coordinated by BF_3, the shift was further upfield. These chemical shift changes can be compared with those of the compounds related to $BF_3 \cdot SnCl_2 \cdot N(CH_3)_3$.

The ^{19}F chemical shift of $BF_3 \cdot SnCl_2 \cdot OS(CH_3)_2$ in DMSO solution is +69.4 ppm which may be compared to the shift of +71.5 ppm which we observed for $BF_3 \cdot OS(CH_3)_2$ in DMSO. Although the shift-difference is small, the

resonances for the two compounds in the same solution can be distinguished, probably indicating that no rapid exchange processes are occurring in that system. The ^{119}Sn chemical shifts of $SnCl_2 \cdot OS(CH_3)_2$ and $BF_3 \cdot SnCl_2 \cdot OS(CH_3)_2$ are +369.6 and 416.1 ppm, respectively, in DMSO solution. The marked difference in these shifts is a strong indication that the amphoadduct remains intact in DMSO solution rather than dissociating to $BF_3 \cdot OS(CH_3)_2$ and $SnCl_2 \cdot OS(CH_3)_2$.

The IR spectra of the amphoadduct and related adducts provide additional evidence on the structure. In $BF_3 \cdot OS(CH_3)_2$, ν(BF) absorptions appear in the range of 1170-1100 cm^{-1}, while in the amphoadduct, they are in the range 1110-1030 cm^{-1}. This difference can be compared to that of $BF_3 \cdot N(CH_3)_3$ with $BF_3 \cdot SnCl_2 \cdot N(CH_3)_3$; the presence of a band around 1030 cm^{-1} appears to be indicative of Sn-BF_3 bonding. A sharp band at 440 cm^{-1} in the spectrum of $SnCl_2 \cdot OS(CH_3)_2$ which was absent in that of $(CH_3)_2SO$ was assigned to ν(Sn-O). In the spectrum of $BF_3 \cdot SnCl_2 \cdot OS(CH_3)_2$, this absorption appeared at 480 cm^{-1}. Clark and Goel[26] assigned ν(Sn-O) in $(CH_3)_2SnSO_4 \cdot DMSO$ at 437 cm^{-1} and in $(CH_3)_2SnCl_2 \cdot 2DMSO$ at 415 cm^{-1}. Aggarwal and Singh[27] assigned this absorption in several $SnCl_4$ adducts, e.g., with dimethyl urea, dimethyl formamide, etc., in a range 575-530 cm^{-1}. Tanaka[28] assigned this absorption in $SnCl_4 \cdot 2DMSO$ at 482 and 477 cm^{-1}. The last assignment is very close to the result of this work. The new absorption of the amphoadduct at 530 cm^{-1} is believed to arise from ν(Sn-B) by analogy to the position of Sn-B absorption in trifluoroborane adducts of aminotin(II) compounds[8]. A band at 570 cm^{-1} in the spectrum of $BF_3 \cdot OS(CH_3)_2$ is difficult to assign. It

does not appear in the spectrum of $(CH_3)_2SO$ (l)[28] nor in the spectrum of free BF_3. This would suggest that it arises from the coordinate B-O link, however, Waddington[18] assigned the B-O stretch in $BF_3 \cdot O(C_2H_5)_2$ at 1166 cm^{-1}, that of $BF_3 \cdot OPCl_3$ at 1150 cm^{-1} and that of $BCl_3 \cdot OPCl_3$ at 1190 cm^{-1}. Accordingly, the 570 cm^{-1} band may represent a B-O-S bending mode or some other mode characteristic of the $BF_3 \cdot OS(CH_3)_2$ structure. There are strong absorptions in the range of 1170-1100 cm^{-1} arising from BF_3 and CH_3 modes which perhaps mask the B-O stretching band.

The characteristic bands of ν(Sn-O) at 480 and ν(Sn-B) at 530 cm^{-1} in the absorption of $BF_3 \cdot SnCl_2 \cdot OS(CH_3)_2$ and the 570 cm^{-1} band in the spectrum of $BF_3 \cdot OS(CH_3)_2$ are mutually exclusive. This is supplementary evidence that no direct combination of BF_3 and DMSO exists in the product, suggesting that these two groups must each be connected to $SnCl_2$ in the amphoadduct structure.

Tanaka[28] assigned the DMSO (l) spectrum: 1045 cm^{-1} to ν(S-O); 954, 931 to $\rho(CH_3)$; 382, 333 to δ(C-S-O) and also assigned the $SnCl_4 \cdot 2DMSO$ spectrum: 1036, 991 cm^{-1} to $\rho(CH_3)$; 923, 907 to ν(S-O); 726, 685 to ν_{as}(C-S); and ν_s(C-S); 482, 477 to ν(Sn-O); 339, 321 to ν(Sn-X). When these bands are compared with those found for $SnCl_2 \cdot OS(CH_3)_2$, there are strong similarities, as expected, except the ν(Sn-O) band which appears at 440 cm^{-1}. We have pointed out that this band shifts to higher frequency at 480 cm^{-1} when BF_3 is coordinated on $SnCl_2 \cdot OS(CH_3)_2$. The high frequency shift of ν(Sn-O) with the increasing electronegativity of substituent on tin also has been seen by Tanaka in his work, i.e., $SnI_4 \cdot 2DMSO$, 459; $SnBr_4 \cdot 2DMSO$, 471; $SnCl_4 \cdot 2DMSO$, 482 cm^{-1}. Wilkins and Haendler[29] in their study of tin(IV) halide complexes

with pyridine N-oxide also indicated that the displacement of Sn-O band to high frequency increased with increasing electronegativity of the halogen on tin. The bond strength increasing is on the contrary way with the Sn-N bonding which we have studied in the bisaminotin(II) compounds[8]; it may be distributed to the polarizable S=O bonding. Curran et al.[16,30], from the study of various donors containing carbonyl groups, have shown that on complexing with metal ions the C=O stretching frequency decreases with increasing strength of the M-O bond. Cotton et al.[31] discussed the coordination reaction of DMSO; first, they pointed out the possibility of back donation of electrons from oxygen to sulfur and that the S-O bond may have partial double-bond character. The second point, in the view of usual kinematic effect, the coupling of the two oscillators, S-O and O-M will tend to raise the (S-O) frequency. Finally, if oxygen is the donor site on DMSO, the electronic structure will change from $R_2S{=}O$ to $R_2S^{+}{-}O^{-}$; if sulfur is the donor site, then the electronic structure may be represented as $R_2S^{-}{\equiv}O^{+}$. Since the overall effect of resonance was supposed to be greater than the kinematic effect, the ν(S-O) absorption should shift to low frequency in the former and to high frequency in the latter case. In our work, the ν(S-O) in $SnCl_2{\cdot}OS(CH_3)_2$ is shifted to the low frequency from 1045 to 920 cm^{-1}, indicating that the coordination of tin is to the oxygen site of the DMSO. The same reasoning can be applied to the spectrum of $BF_3{\cdot}OS(CH_3)_2$; the sharp ν(S-O) peak is at lower frequency, i.e., 875 cm^{-1}. However, the band of ν(S-O) in $BF_3{\cdot}SnCl_2{\cdot}OS(CH_3)_2$ is observed without change from 920 cm^{-1} which gives an evidence that BF_3 is coordinated neither to oxygen nor to sulfur, leaving only the tin-site as a possibility.

C. Investigation of Trifluoroborane-N,N'-Tin(II)chloride-Tetramethylethylenediamine Adduct.

In our previous work[1], it was noticed that tin(II)chloride-bis-(trimethylamine) was air sensitive and somewhat unstable. A related compound, N,N'-tin(II)chloride-tetramethylethylenediamine, SnCl·TMED, was prepared in this work as an intermediate. Since N,N,N',N'-tetramethylethylenediamine (TMED) is a chelating agent, the coordination of the two nitrogens to the tin should lead to a more stable adduct than the bis(trimethylamine) adduct. As hoped, the product did not exhibit air sensitivity for short periods nor did it suffer obvious decomposition. The amphoadduct, $BF_3 \cdot SnCl_2 \cdot TMED$ was prepared by the reaction of the intermediate with BF_3. In order to determine whether the tin acted as both a donor and acceptor, we prepared $BF_3 \cdot TMED$ and reacted that with $SnCl_2$ presumably to form $BF_3 \cdot TMED \cdot SnCl_2$ in which the molecule TMED was believed to act as a nonchelating donor to both BF_3 and $SnCl_2$. The structures of all the compounds mentioned above are listed in Figure 1A.

The ^1H NMR data for this family of compounds are given in Table III. In the spectrum of $BF_3 \cdot TMED$ (Figure 8), methyl and methylene resonances of TMED are split into doublets indicating a static (non-exchange) molecule in aniline solution with the inductive influence of the trifluoroborane changing the shielding of the CH_3 and CH_2 groups associated with the donor nitrogen. The doublet resonance of the methylene group was considerably broadened, a phenomenon regularly observed when BF_3 is coordinated to amine-nitrogens[3,8]. The spectrum of $BF_3 \cdot TMED \cdot SnCl_2$ (Figure 9) shows only one CH_3 and one CH_2

environment presumably due to approximately equal influences of the BF_3 and $SnCl_2$ acceptors, however, the peak of the methylene group is also very broad indicating the BF_3 coordinating on the amine-nitrogen. The spectrum of $SnCl_2 \cdot TMED$ (Figure 6) shows single CH_3 and CH_2 environments with both peaks sharp as expected for a chelating diamine structure. The spectrum of $BF_3 \cdot SnCl_2 \cdot TMED$ (Figure 7) also shows single CH_3 and CH_2 environments with both sharp peaks and, when compared with that of $BF_3 \cdot TMED \cdot SnCl_2$, it is consistent with $BF_3 \cdot SnCl_2 \cdot TMED$ as an amphoadduct.

The differences in the CH_3 and CH_2 chemical shifts (Δ) has been shown to reflect the inductive influence of ethyl group substituents; the greatest separation caused by the most electronegative group[13]. In TMED and its adducts, Δ varies as : $BF_3 \cdot TMED < TMED < BF_3 \cdot TMED \cdot SnCl_2 < SnCl_2 \cdot TMED < BF_3 \cdot SnCl_2 \cdot TMED$ (Figure 1B and Table III). In this series, the effect is apparently not dictated simply by electronegative induction, instead, local anisotropic shielding effects evidently play an important role. The largest Δ of $BF_3 \cdot SnCl_2 \cdot TMED$ may have contributions from both inductive factors and the neighbor-anisotropy effect of Cl and BF_3[14]. The fact that all the CH_3 and CH_2 signals of the TMED adducts are upfield of those in TMED offers further proof that simple inductive factors do not control the ^1H chemical shifts. However, since possible concentration effects and dynamic processes can also affect the shifts, further analysis is probably not justified.

The IR spectra of $BF_3 \cdot TMED$ and $BF_3 \cdot TMED \cdot SnCl_2$ showed B-N stretching absorptions at 685 and 690 cm^{-1}, respectively, and an absorption in the latter at 520 cm^{-1} assigned to a Sn-N stretching mode. In the chelated

adduct, $SnCl_2 \cdot TMED$, bands at 550 and 520 cm^{-1} were tentatively assigned to N-Sn-N modes. Unfortunately, these bands made the area of 540-520 cm^{-1} in which we expected to see the Sn-B absorption somewhat complex. The peaks observed in that range for the tin(II) halide amphoadducts were: $BF_3 \cdot SnCl_2 \cdot TMED$: 565, 540,525 cm^{-1}; $BF_3 \cdot SnBr_2 \cdot TMED$: 565, 540, 520 cm^{-1}; and $BF_3 \cdot SnI_2 \cdot TMED$: 560, 510 cm^{-1}. These were interpreted as Sn-N and Sn-B stretching modes with chance overlap causing only two absorptions to appear in the iodide amphoadduct and the intensity of 510 cm^{-1} was enhanced. The spectrum of $BF_3 \cdot SnCl_2 \cdot TMED$ showed the overlapping in the range of 1130-1030 cm^{-1}, which is usually indicative of BF_3 absorptions. No absorption in the range 650-720 cm^{-1}, ascribable to a B-N mixed mode, appeared in this spectrum and the bands at 325, 300 cm^{-1} will be assigned to ν(Sn-Cl).

D. Investigation of Trifluoroborane-N,N'-Tin(II)chloride-Dipyridyl Adduct.

2,2'-Dipyridyl (DP) also is known to act as a chelating agent. The two rigid pyridine rings restrict the flexibility of this molecule, especially when it is coordinated. With such a donor, the stability of the chelated structure should be enhanced even over that of an α,ω-diamine ligand. The chelated compound, $SnCl_2 \cdot DP$, has been prepared as an intermediate and the coordination of BF_3 to this intermediate to form the amphoadduct, $BF_3 \cdot SnCl_2 \cdot DP$, also has been carried out. When tin(II) chloride was chelated with DP, its color changed to bright yellow, however, when it was further coordinated to BF_3, the product was white. Other compounds prepared as models in studying the amphoadduct were $BF_3 \cdot DP$ and $BF_3 \cdot DP \cdot SnCl_2$. In the latter compound, DP is believed to act as a nonchelating donor to both BF_3 and $SnCl_2$.

The ^1H NMR spectra of the DP adducts is informative, especially when the DP resonances were scrutinized on an expanded scale (Figure 10-14). Figure 10 shows the expanded spectrum of DP with protons labeled showing that the order of chemical shifts is: $H(3) < H(6) < H(5) < H(4)$[12]. The absorptions of the former two appear as doublets and those of the latter two appear as triplets, both with some fine structure. When DP was coordinated to electrophilic groups, i.e., $SnCl_2$ and BF_3, the range of these chemical shifts is compressed as shown in Figure 1C and Table IV. The H(3)-H(6) and H(6)-H(5) differences decrease while H(5)-H(4) difference increases in the order: $SnCl_2 \cdot DP > BF_3 \cdot SnCL_2 \cdot DP > BF_3 \cdot DP \cdot SnCl_2 > BF_3 \cdot DP$. When the whole range is examined, the H(3)-H(4) difference decreases from DP and follows the order indicated above. At the same time there is a gradual downfield shift of the pattern

in this series. In comparing the positions of ^1H resonances in $SnX_2 \cdot DP$ compounds (Table IV), all shift regularly downfield as X changes from Cl to Br to I and the acceptor strength of the tin(II) halide increases. This deshielding trend is as expected from simple inductive effect considerations, although more complex effects arising from pi electron circulation in the DP rings may also be important. Comparison of the positions of ^1H resonances in $SnCl_2 \cdot DP$ and $BF_3 \cdot SnCl_2 \cdot DP$ shows those of the latter all downfield from those of the former perhaps reflecting the additional inductive influence of the trifluoroborane on tin. The bright yellow color of $SnCl_2 \cdot DP$ may be due to the absorption resulting from the conjugation of the lone pair electrons of tin(II) with the pi electrons on the connected two pyridine rings. The electrons can circulate to some extent on both the Sn-DP five-member ring and the DP rings. The coordination of BF_3 on $SnCl_2 \cdot DP$ obviates this conjugation together with the color. In $BF_3 \cdot DP \cdot SnCl_2$, all the ^1H resonances are shifted further yet downfield because of the now direct inductive influence of the BF_3 at its position on the DP. Nevertheless, the positions still stand at slightly higher fields than those of $BF_3 \cdot DP$, possibly indicating neighbor-anisotropic influence on the shifts.

Strukl and Walter[32] assigned the IR absorptions of neat 2,2'-dipyridyl in the range of 3086-3054 cm^{-1} to ring-H stretch, 1579-1240 to ring stretch and ring-H bend, 1210-1063 to ring-H inplane bend, 1039-710 to H out-of-plane bend, 651 and 618 to ring bend and 398 cm^{-1} to ring torsion. They also assigned the absorptions of the complexes of dipyridyl, e.g., $ZnCl_2 \cdot DP$, in which the 3086 cm^{-1} band of DP moved to 3110, 1579 to 1592, 1448 to 1488; etc. Zuckerman *et al.*[33] reported that in the absorptions of

$Me_2SnCl_2 \cdot DP$ and other complexes the ligand bands are generally raised to higher frequency on coordination. In our experiments, when DP was coordinated to $SnCl_2$, the absorptions of the ring stretch part of the spectrum were obviously shifted to the high frequencies, e.g., a sharp absorption appeared at 1613 cm^{-1}, compared to 1579(s) cm^{-1} for the corresponding DP band. When $BF_3 \cdot SnCl_2 \cdot DP$ was formed, the ring-H stretch frequencies appeared to increase; a medium band appeared at 3210 cm^{-1} which was the counterpart of a 3080(w) cm^{-1} DP band. The characteristic overlapped absorptions due to the BF_3 group in the amphoadduct appeared at 1125-1070-1035 cm^{-1}. Tentatively, the ν(Sn-B) absorption in this compound was assigned as the 555-530 (broad) cm^{-1} band which was absent in the spectrum of $SnCl_2 \cdot DP$. The band at 325 cm^{-1} may be assigned to the absorption of ν(Sn-Cl)[34].

Morrison and Haendler[35] prepared the complex $SnCl_2 \cdot DP$ but did not give a detailed description of its spectrum. Clark and Wilkins[21] assigned the absorption at 217 cm^{-1} in $Me_2 \cdot SnCl_2 \cdot DP$ to be ν(Sn-N). Farona and Grasselli[22] reported Sn-N absorptions in $SnCl_4 \cdot DP$ at 254 and 207 cm^{-1}. Strukl and Walter[32] have prepared over ten 1:1 complexes of dipyridyl-coordinated divalent transition metal salts, e.g., $FeCl_2$, $CoCl_2$, $MnCl_2$, $ZnCl_2$, etc., and they assigned metal-N stretch and bend absorptions in the range 307-217 cm^{-1}. The rapidly decreasing transparency of KBr pellets below 300 cm^{-1} prevents us from confidently assigning ν(Sn-N) in our DP adducts.

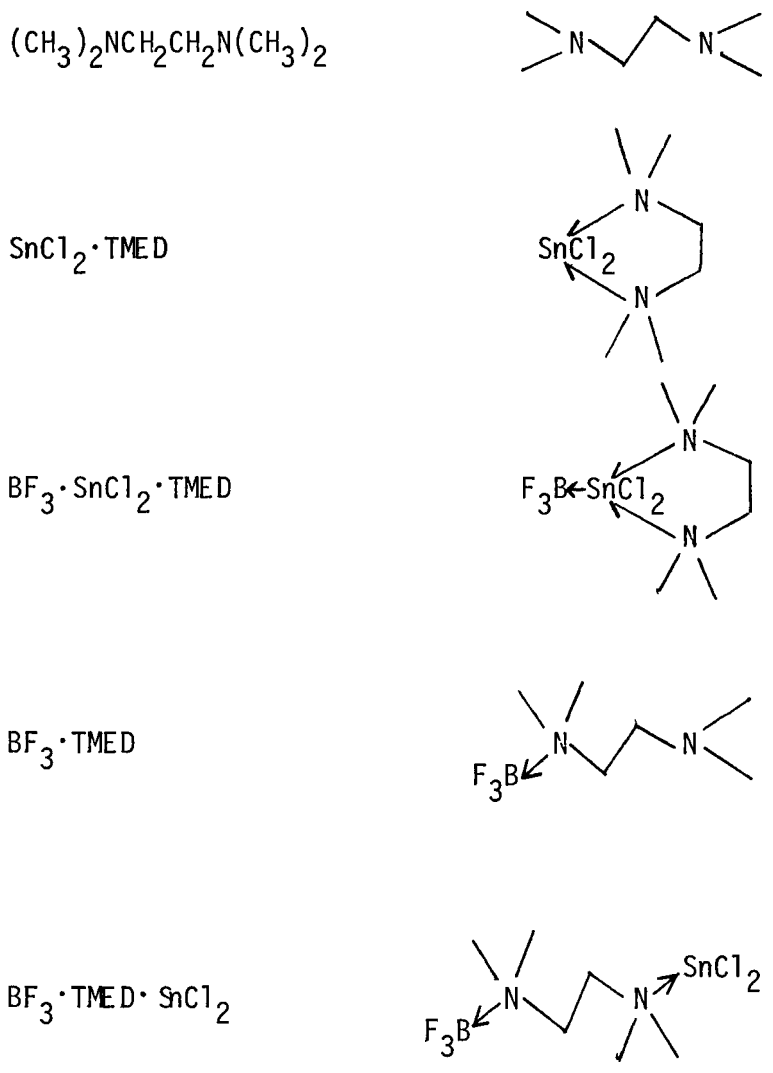

Figure 1A. Simple structures of the TMED-coordinated compounds.

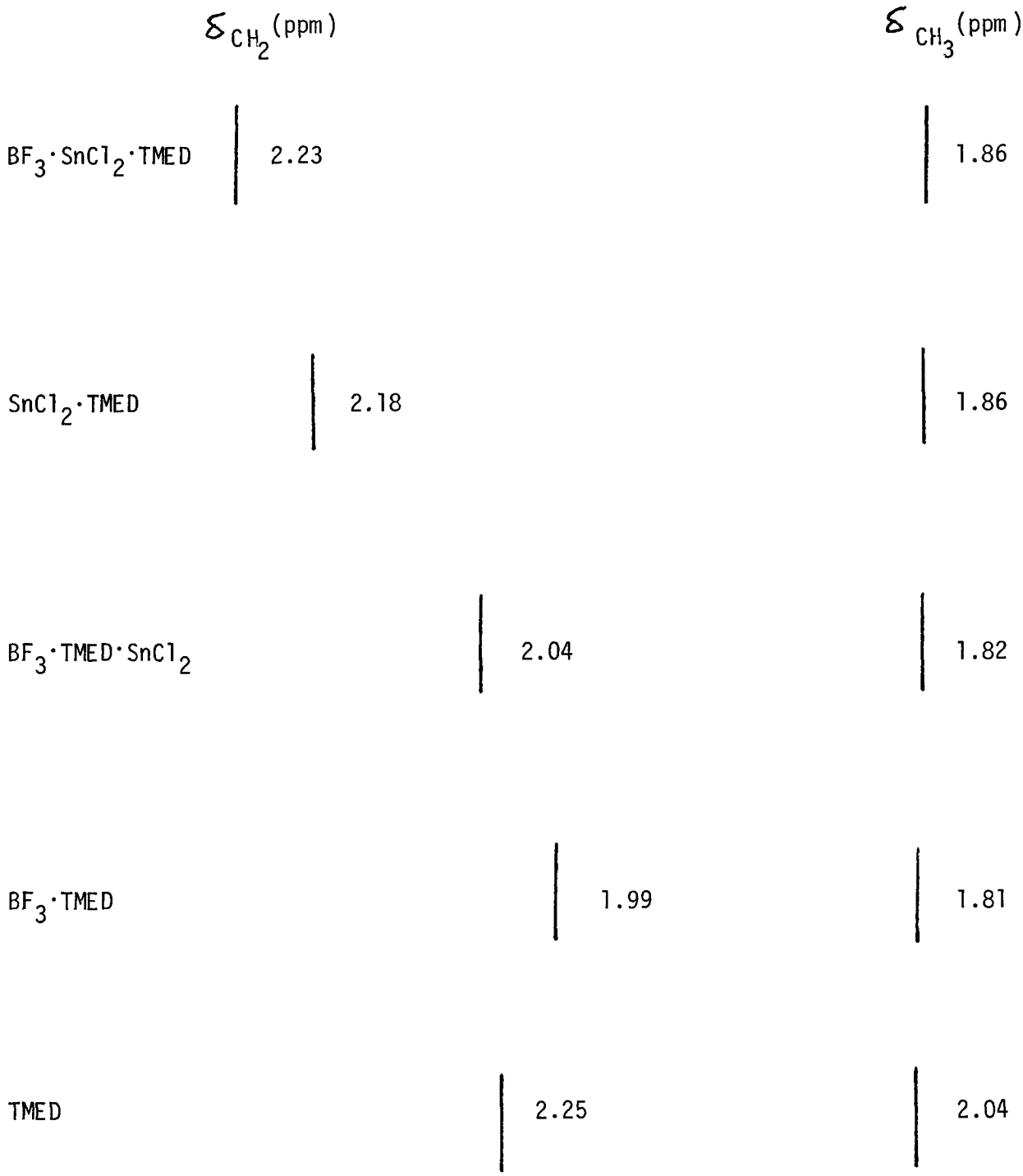

Figure 1B. The ^{1}H NMR chemical shifts of TMED-coordinated compounds in aniline solutions. (The figure does not show the related resonance positions among the compounds.)

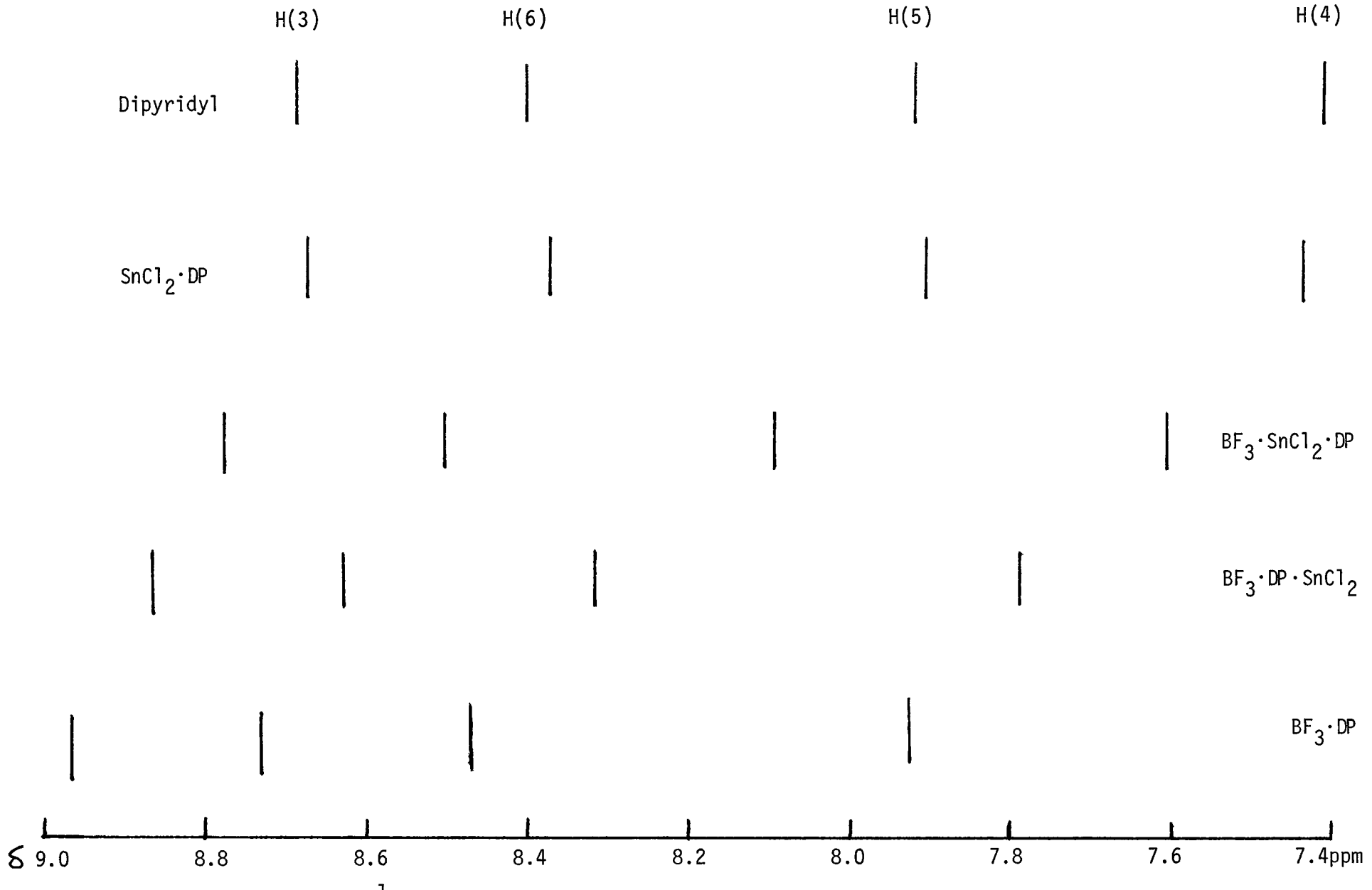

Figure 1C. The ^{1}H NMR chemical shifts of DP-coordinated compounds in DMSO solutions.

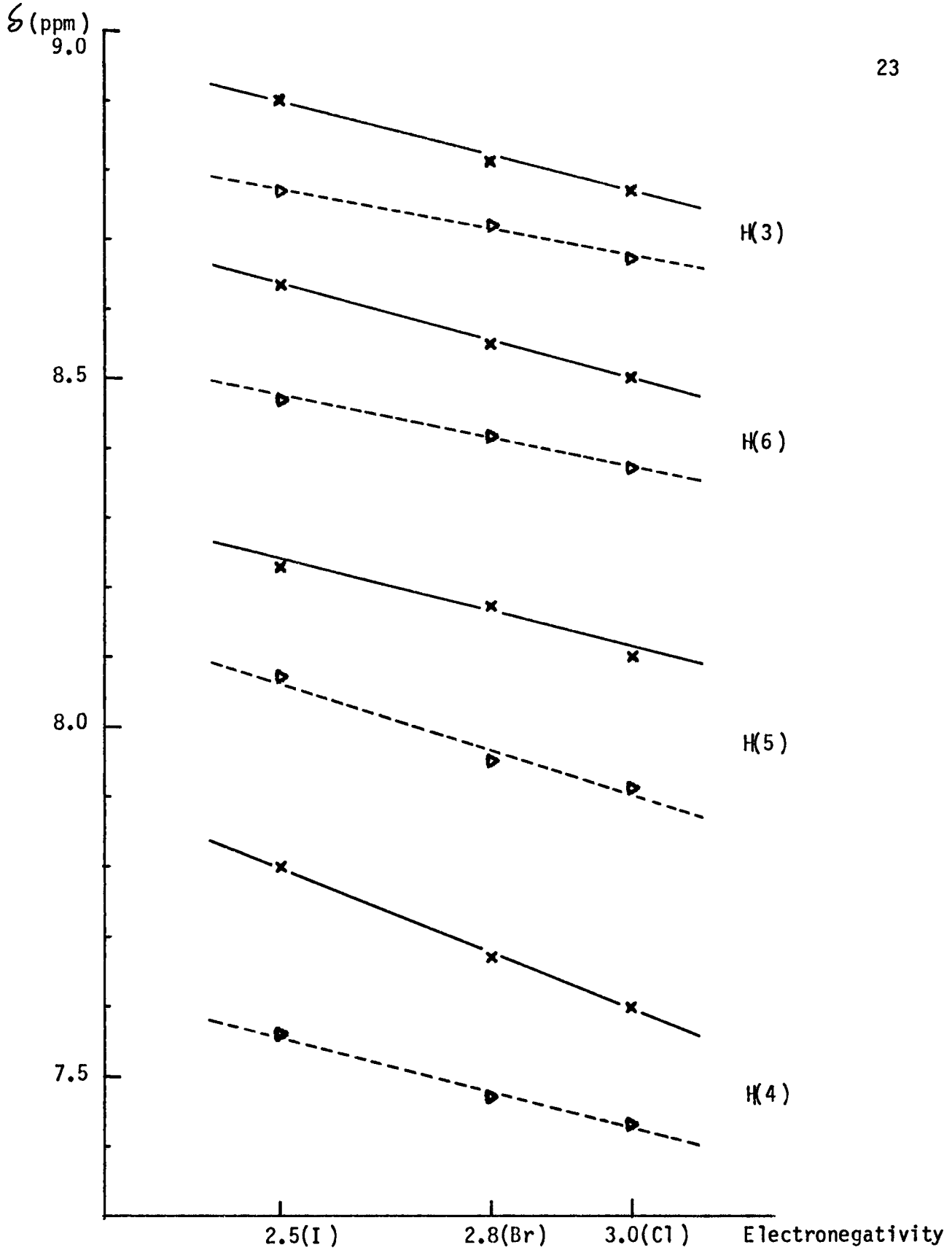

Figure 1D. Proton chemical shifts vs. electronegativities, from dipyridyl coordinated compounds.

—— ✖ —— $BF_3 \cdot SnX_2 \cdot DP$, ---▶---$SnX_2 \cdot DP$.

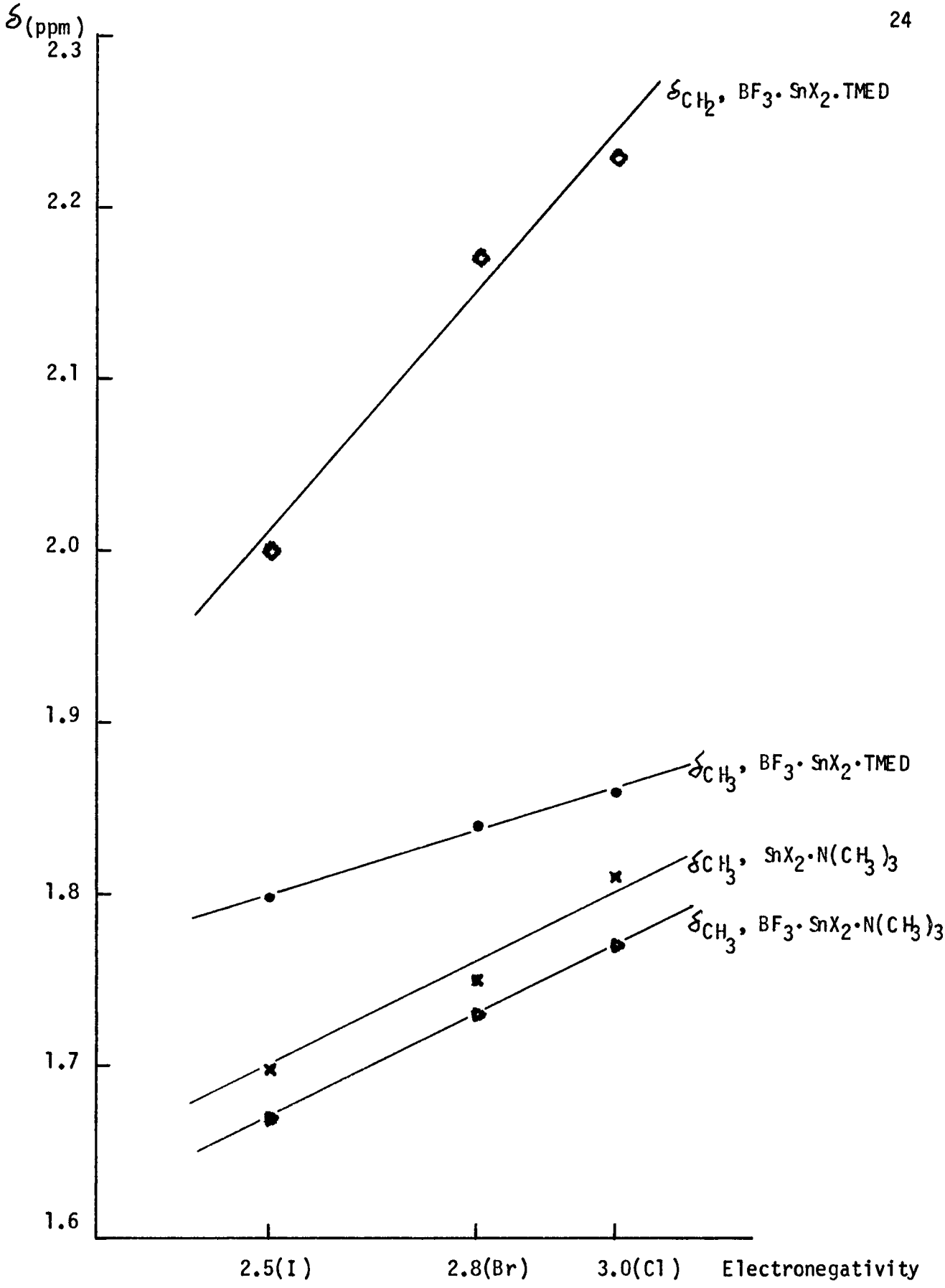

Figure 1E. Proton chemical shifts vs. electronegativities, from $(CH_3)_3N$ and TMED coordinated compounds.

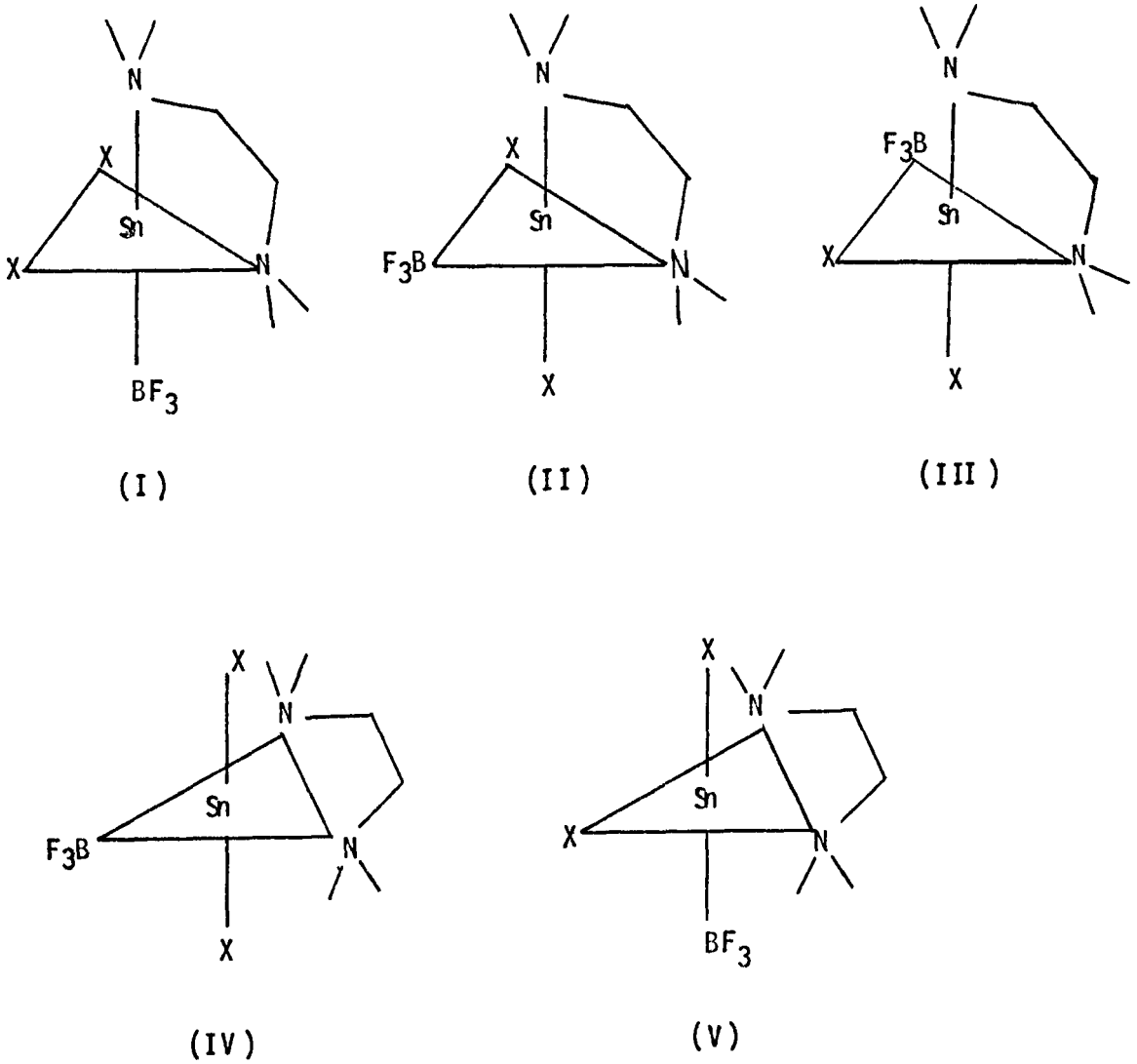

Figure 1F. The possible structures of $BF_3 \cdot SnCl_2 \cdot TMED$.

III. DISCUSSION

The structure of $SnX_2.N(CH_3)_3$, if we assume the presence of discrete species in the solid state, may be trigonal pyramidal with the lone pair of electrons at the apex. The structure of $SnX_2 \cdot OS(CH_3)_2$ should not be greatly different from that of the trimethylamine adducts except that the DMSO group may be bound somewhat more weakly than the trimethylamine. When the BF_3 group is coordinated to the lone pair electrons, only a limited structural change is expected, with the molecules assuming a distorted tetrahedral form. The ^{119}Sn NMR spectral data of these compounds (Table II) show that, except for the iodine compounds, whenever BF_3 is coordinated to $SnCl_2 \cdot N(CH_3)_3$, $SnX_2 \cdot OS(CH_3)_2$ or $SnCl_2 \cdot NC_5H_5$, the resultant amphoadducts exhibit upfield chemical shifts as compared to the precursors. This phenomenon is not expected from consideration of the inductive effect of the BF_3 group, which should decrease the electron density on the tin and cause its resonance to shift downfield. Instead, the shift is probably the result of local paramagnetic contributions to the ^{119}Sn shift induced by the presence of the BF_3. Such contributions are usually regarded to arise from mixing of excited states with the ground state of tin; it is clear that BF_3 could affect such energy levels. The chemical shifts of $SnCl_2 \cdot N(CH_3)_3$, $SnCl_2 \cdot NC_5H_5$ and $SnCl_2 \cdot OS(CH_3)_2$ fall in the order of 111.8 294.0 369.5 ppm; these shifts appear to increase as the base becomes softer or more polarizable, since pyridine has ring pi electrons and DMSO has the $O{=}S\lesssim$ multiple bond.

We have explained the approximately 120 cm^{-1} difference in the IR absorptions of ν(Sn-N) between $SnCl_2 \cdot N(CH_3)_3$ and $Sn[N(CH_3)_2]_2$ by considering the different types of Sn-N bonds involved and the amino bridge bonding in the latter. The ν(Sn-N) absorptions in $BF_3 \cdot SnCl_2 \cdot N(CH_3)_3$, $BF_3 \cdot SnBr_2 \cdot N(CH_3)_3$ and $BF_3 \cdot SnI_2 \cdot N(CH_3)_3$ occur at 550, 570, 563 cm^{-1}, respectively. The similarities of these frequencies probably indicates that the halides do not exert a large influence on the electronic environment of the tin. This may result from the electronegativity effect (greatest for Cl) being counteracted by p_π-d_π back donation to the tin (also greatest for Cl).

The proton chemical shifts of the dipyridyl coordinated compounds (Table IV) have been plotted <u>versus</u> the electronegativities of the halides (Figure 1D). We can see that the chemical shift of every hydrogen, i.e., H(3), H(6), H(5), H(4), is shifted to lower field when BF_3 is coordinated to $SnX_2 \cdot DP$ to form the compound $BF_3 \cdot SnX_2 \cdot DP$. This may be regarded as an inductive effect. However, all the slopes of the lines drawn through the ^1H chemical shifts of corresponding halide compounds are negative; it indicates that, in both $SnX_2 \cdot DP$ and $BF_3 \cdot SnX_2 \cdot DP$, the hydrogen atoms on the pyridine rings become more shielded in the series from iodide to bromide to chloride compounds, in opposition to the obvious inductive effect. Considering the structures of these compounds, the most plausible rationale involves the effect of the halogens on electron distribution in the chelate dipyridyl rings. Pi donation by the halogens to the tin can weaken its interaction with the dipyridyl causing more shielding of hydrogens on the

ring. Ring currents may also be important in determining these chemical shifts.

Figure 1E is also a plot of proton chemical shifts versus the electronegativities of halides in TMED and trimethylamine adducts. All the lines in these plots have positive slopes, indicating that the sequence of shielding of the protons follows the electronegativities of the halogens. When a plot of $SnX_2 \cdot N(CH_3)_3$ is compared with that of $BF_3 \cdot SnX_2 \cdot N(CH_3)_3$, it is seen that the lines are approximately parallel. However, every point on the plot of the BF_3-coordinated compound falls at higher field than that of the corresponding simple adduct. This is again opposite to what is expected from a simple inductive effect of the BF_3 group. In this case, a neighborhood anisotropy produced by the proximity of the BF_3 in the time averaged structure may cause the unexpected upfield shift of the CH_3 resonance. Such anisotropic effects can also be found in the $BF_3 \cdot SnX_2 \cdot TMED$ series when we consider the plots of δ_{CH_2} and δ_{CH_3} of these compounds (Figure 1E). Owing to the stereochemistry of these compounds, the halogens could produce neighborhood anisotropic effects on the CH_2 and CH_3 groups. The steep slope of the δ_{CH_2} plot is in sharp contrast to that of δ_{CH_3} suggesting a considerably different neighborhood anisotropic effect on the two environments. The observation of single resonance absorptions for methyl and methylene protons may result from fluxional behavior of the compound in solution or it may indicate that the methyl and methylene groups each have only one magnetic environment in a static structure. Of the possible static structures, I to V (Figure 1F), the latter scenario

restricts the possibilities to IV and V. The general preference shown by the more electronegative substituents for the axial positions in a trigonal bipyramidal structure[36,37] suggests that structure IV is more favored than structure V. Also the marked effect of halogen substitution on δ_{CH_2} as compared to δ_{CH_3} (Figure 1E) suggests that the CH_2 groups may reside closer in space to the halogens than do the CH_3 groups. This also appears to favor structure IV. McConnell[14] has pointed out that iodine will cause the largest chemical-shift changes due to the anistropy of the halogen which coincides with this data since we can see the δ_{CH_2} plot drops steeply at the left end of the diagram.

Table I. ^{1}H NMR Data of Trimethylamine-Coordinated Compounds[a]

Compound	δ_{CH_3} (ppm)[b]
$BF_3 \cdot SnCl_2 \cdot N(CH_3)_3$	1.77
$BF_3 \cdot SnBr_2 \cdot N(CH_3)_3$	1.73
$BF_3 \cdot SnI_2 \cdot N(CH_3)_3$	1.67
$SnCl_2 \cdot N(CH_3)_3$	1.81[c]
$SnBr_2 \cdot N(CH_3)_3$	1.75[c]
$SnI_2 \cdot N(CH_3)_3$	1.70[c]
$F_3BN(CH_3)_3$	1.97[d]
$(CH_3)_3N$	1.91

[a]Solvent, aniline.

[b]±0.02 ppm.

[c]Reference 1.

[d]Broad multiplet, reference 3.

Table II. Data of ^{119}Sn NMR Spectra[a]

Compound	Shift(ppm)[b]	FWHH(Hz)
$SnCl_2 \cdot N(CH_3)_3$	111.8	27.5
$SnCl_2 \cdot DMSO$	369.5	59.8
$SnBr_2 \cdot DMSO$	833.2	479.0
$SnI_2 \cdot DMSO$	684.2	439.0
$SnF_2 \cdot DMSO$	-56.9	78.7
$SnCl_2 \cdot Py$	294.0	35.9
$BF_3 \cdot SnCl_2 \cdot N(CH_3)_3$	332.8	24.9
$BF_3 \cdot SnCl_2 \cdot DMSO$	416.1	99.8
$BF_3 \cdot SnBr_2 \cdot DMSO$	881.0	279.0
$BF_3 \cdot SnI_2 \cdot DMSO$	625.1	431.0
$BF_3 \cdot SnF_2 \cdot DMSO$	not found	
$BF_3 \cdot SnCl_2 \cdot Py$	303.7	32.5

[a]Solvent, DMSO; all spectra are complex multiplets.

[b]$\pm$0.2 ppm; referred to external $Sn(CH_3)_4$; upfield of standard was counted as positive.

Table III. ^{1}H NMR Data of TMED-Coordinated Compounds[a]

Compound	δ_{CH_2} (ppm)[b]	δ_{CH_3} (ppm)
$SnCl_2 \cdot TMED$	2.18	1.86
$BF_3 \cdot SnCl_2 \cdot TMED$	2.23	1.86
$SnBr_2 \cdot TMED$	2.06	1.81
$BF_3 \cdot SnBr_2 \cdot TMED$	2.17	1.84
$SnI_2 \cdot TMED$	1.93	1.79
$BF_3 \cdot SnI_2 \cdot TMED$	2.00	1.80
$BF_3 \cdot TMED$	1.99[c]	1.81[c]
$BF_3 \cdot TMED \cdot SnCl_2$	2.04[d]	1.82
TMED	2.25	2.04

[a] Solvent, aniline.

[b] ±0.02 ppm.

[c] Split in doublet, the average positions were taken.

[d] Broad.

Table IV. ^{1}H NMR Data of Dipyridyl-Coordinated Compounds

Compound	H(3)			H(6)			H(5)			H(4)		
	δ(ppm)[b]	J(Hz)	Mult.	δ	J	Mult.	δ	J	Mult.	δ	J	Mult.
Dipyridyl	8.69	2.5	2	8.41	3.9	2	7.92	3.8	3	7.37	3.2	3
$SnCl_2 \cdot DP$	8.67	3.0	2	8.37	4.5	2	7.91	4.2	3	7.43	3.0	3
$BF_3 \cdot SnCL_2 \cdot DP$	8.77	2.6	2	8.50	4.0	2	8.10	4.1	3	7.60	3.1	3
$SnBr_2 \cdot DP$	8.72	2.8	2	8.42	3.7	2	7.95	3.9	3	7.47	3.3	3
$BF_3 \cdot SnBr_2 \cdot DP$	8.81	2.8	2	8.55	4.3	2	8.17	3.9	3	7.67	3.1	3
$SnI_2 \cdot DP$	8.77	2.7	2	8.47	4.0	2	8.07	4.0	3	7.56	3.2	3
$BF_3 \cdot SnI_2 \cdot DP$	8.89	2.8	2	8.64	4.0	2	8.23	4.0	3	7.80	3.2	3
$BF_3 \cdot DP$	8.96	2.6	2	8.73	4.0	2	8.47	3.9	3	7.93	3.1	3
$BF_3 \cdot DP \cdot SnCl_2$	8.87	2.8	2	8.63	4.0	2	8.32	3.8	3	7.79	3.0	3

[a] Solvent, DMSO.

[b] ±0.02 ppm.

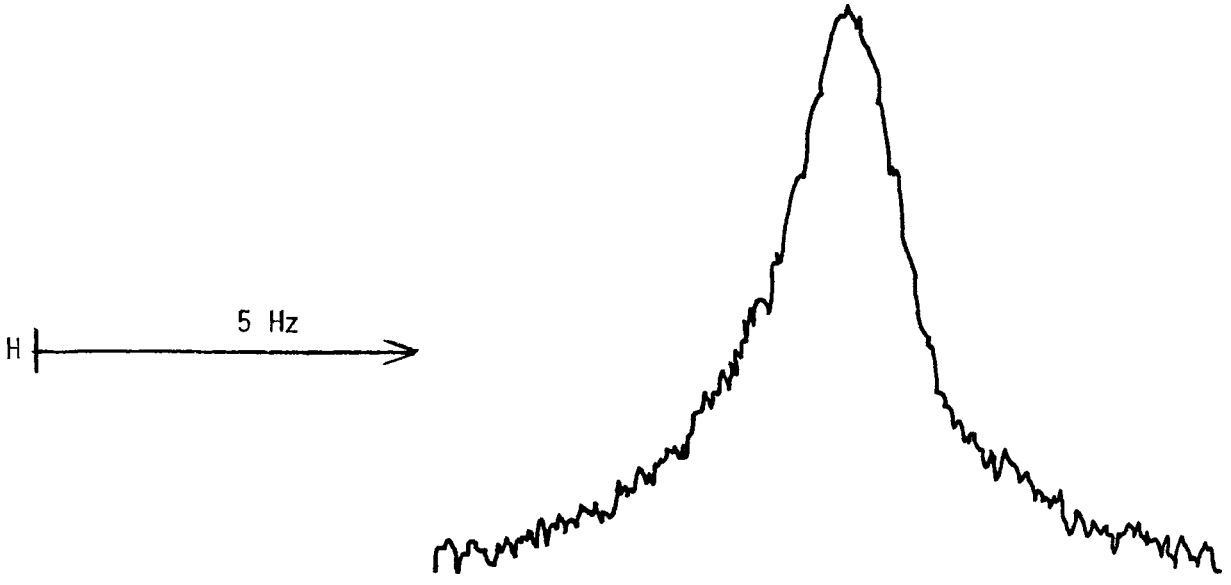

Figure 2. Expanded ^{1}H NMR spectrum of $SnCl_2 \cdot N(CH_3)_3$ (solvent, aniline).

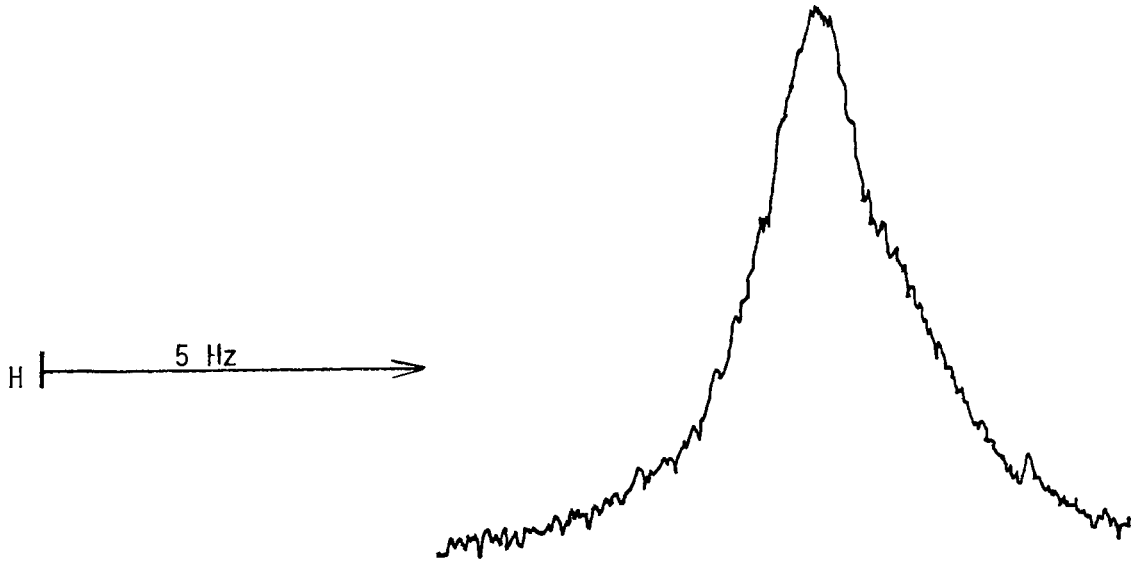

Figure 3. Expanded ^{1}H NMR spectrum of $BF_3 \cdot SnCl_2 \cdot N(CH_3)_3$ (solvent, aniline).

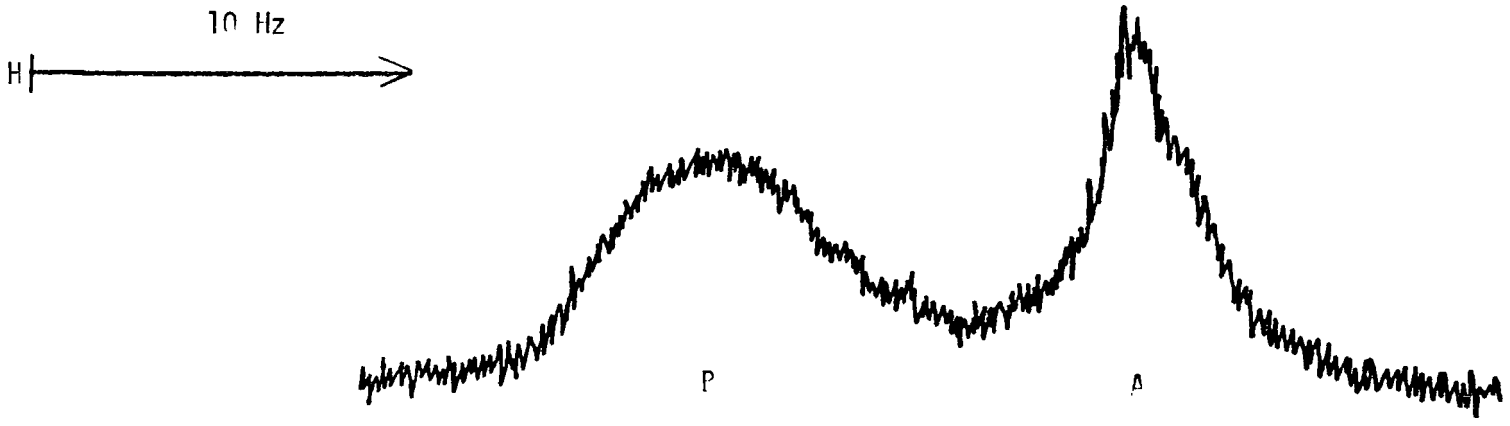

Figure 4. Expanded ^{1}H NMR spectrum of the mixture of $BF_3 \cdot SnCl_2 \cdot N(CH_3)_3$(A) and $F_3BN(CH_3)_3$(B) (solvent, aniline).

IV. EXPERIMENTAL SECTION

A. Equipments and Materials.

The experiments were carried out either under dry nitrogen or on the vacuum line while a LabConCo glovebox was used for transfer of the air sensitive materials. IR spectra were taken on a Beckman Model 4250 spectrophotometer (accuracy ± 4 cm^{-1}). ^{1}H NMR spectra were obtained on a Varian T-60 instrument at 60 MHz (accuracy ± 0.02 ppm). A Varian Model XL-100-15 with Nicolet 1080 data system and NT-440 Mona multinuclear accessory was employed to obtain the Fourier transform NMR spectra of ^{11}B at 32.1 MHz and ^{119}Sn at 37.28 MHz (accuracy ± 0.2 ppm) while a Varian 4412 probe was used for spectra of ^{19}F at 94.1 MHz. X-ray powder diffraction patterns were taken by using a Debye-Scherrer camera of 114.6 mm diameter with a source of hot cathode tube which was fitted with a copper target and nickel filter producing K_{α} radiation. Melting points were determined on a Thomas Hoover Capillary melting point apparatus using glass capillaries sealed with wax.

Benzene and n-pentane were of nanograde qunlity and were obtained from the Mallinckrodt Co., St. Louis, MO. Ethyl ether was deperoxided and distilled before use. Trifluoroborane and trimethylamine were obtained in lecture cylinders; 2,2'-dipyridyl was large crystals and those all were from the Mtheson Co., Cincinnati, OH. N,N,N',N'-Tetramethylethylenediamine and dimethyl sulfoxide were reagent grade from Aldrich Co., Milwauchee, WI and were distilled from barium oxide before use. Anhydrous tin(II) halides were freshly prepared in this laboratory[1].

B. Methods of Analyses.

The tin, boron and nitrogen analyses were the same as described in Part I.

Chlorine, bromine and iodine were determined as halides by potentiometric titration with standard silver nitrate solution after the samples had been treated with dilute sulfuric acid.

C. Syntheses of Trifluoroborane-Tin(II)halide-Trimethylamine.

1. Trifluoroborane-Tin(II)chloride-Trimethylamine, $BF_3 \cdot SnCl_2 \cdot N(CH_3)_2$.

In this method of preparation, tin(II) chloride-trimethylamine was first prepared and isolated, then, it was treated with trifluoroborane.

(a). Formation of tin(II)chloride-trimethylamine, $SnCl_2 \cdot N(CH_3)_3$. This compound has been previously reported[1]. But in this preparation, the synthesis was modified by changing the solvent from p-dioxane to ethyl ether. In a typical preparation, 7.58 g (40 mmol) of anhydrous $SnCl_2$ was weighed into a flask and the latter was connected to the vacuum line via a Teflon valve adaptor. Approximately 50 mL of anhydrous, peroxide-free $(C_2H_5)_2O$ and exactly 40 mmol of $(CH_3)_3N$ were condensed into the reaction vessel. After the mixture reached room temperature, it was stirred for 3 days, then, filtered and washed with ether under N_2, giving a slightly yellow colored solid product. The physical constants were the same as those reported earier. The expanded ^1H NMR spectrum of the product in aniline solution is shown in Figure 2.

(b). Preparation of $BF_3 \cdot SnCl_2 \cdot N(CH_3)_3$. A 7.5 g (30 mmol) portion of freshly prepared $SnCl_2 \cdot N(CH_3)_3$ was transfered into a flask which was then connected to the vacuum line via a Teflon valve adaptor. The vessel was evacuated and approximately 50 mL of anhydrous, peroxide-free ethyl ether was condensed into the flask, followed by a 30 mmol quantity of BF_3. After the mixture obtained the room temperature, it was stirred over 4 days, filtered and washed with ether under N_2. The product was pale yellow colored solid; with a mp of 123-130 °C. Anal.Calcd for $C_3H_9BCl_2F_3NSn$:

Sn, 37.51; B, 3.41; N, 4.42; Cl, 22.44. Found: Sn, 37. 7; B, 3.34; N, 4.25; Cl, 22. 4 Its IR spectrum by KBr pellet contained the following bands (cm^{-1}): 3170(s), 2970(w), 2720(s), 2485(w), 1635(vwb), 1483(s), 1470(s), 1420(m), 1382(m), 1310(m), 1260(w), 1140-1070-1035(vsb, overlapping), 985(s), 820(vw), 690(w), 550(m), 530(mb), 460(vw), 310(m). The ^{1}H NMR data of the product in aniline solution are listed in Table I and the expanded spectrum is shown in Figure 3. The ^{1}H NMR spectrum of the mixture of this compound with $F_3BN(CH_3)_3$ in aniline solution was also obtained and the expanded pattern of the result is displayed in Figure 4. The d spacings in the X-ray powder diffraction pattern were as follows [d, Å (intensity)]: 6.21(vvs), 5.55(s), 4.68(m), 4.59(m), 4.38(vvsb), 4.10(w), 3.93(m), 3.60(s), 3.53(s), 3.42(m), 3.08(s), 2.94(s), 2.77(vs), 2.64(m), 2.57(w), 2.51(m), 2.25(w), 2.19(mb), 2.11(m), 2.05(m), 1.94(w), 1.92(vw), 1.87(vw), 1.84(vw), 1.78(w), 1.72(m). The ^{11}B NMR spectrum of this compound in DMSO solution consisted of a broad complex peak at -19.43 ppm with full width at half height(fwhh)of 305.3Hz referred to $BF_3 \cdot O(C_2H_5)_2$ as the external standard and the upfield of the standard was counted as positive. The ^{19}F NMR spectrum of this compound in DMSO solution consisted of a quartet; centered at +84.86 ppm; J=16.20 Hz referred to CF_3COOH as external standard. We also obtained the ^{19}F NMR spectrum of $F_3BN(CH_3)_3$ in DMSO solution for comparison; the $^{11}BF_3$ part of the spectrum was a 1:1:1:1 quartet (the same as the product) centered at +64.48 ppm; J=15.38 Hz. The ^{119}Sn NMR spectrum of $BF_3 \cdot SnCl_2 \cdot N(CH_3)_3$ in saturated DMSO solution consisted of a complex peak at +332.8 ppm (upfield from $Sn(CH_3)_4$ as the external

reference) with fwhh 24.9 Hz. We also obtained the ^{119}Sn NMR spectrum of $SnCl_2 \cdot N(CH_3)_3$ for comparison; it consisted of a complex peak at +111.8 ppm with fwhh 27.5 Hz.

2. Trifluoroborane-Tin(II)bromide-Trimethylamine, $BF_3 \cdot SnBr_2 \cdot N(CH_3)_3$.

The compound, tin(II)bromide-trimethylamine, $SnBr_2 \cdot N(CH_3)_3$, has been reported previously[1]. This compound was synthesized and used as an intermediate. The procedure and solvent employed for the addition of BF_3 to this intermediate were the same as that used to prepare the chloride compound. The final product, $BF_3 \cdot SnBr_2 \cdot N(CH_3)_3$, was a white hygroscopic solid, mp 150-155 °C dec. The IR spectrum by KBr pellet contained the following bands (cm^{-1}): 3160(s), 2980(w), 2750(m), 2490(w), 1648(wb), 1487(s), 1475(vs), 1425(s), 1385(m), 1315(m), 1262(m), 1170-1090-1035 (vsb, overlapping), 990(s), 918(vw), 815(vw), 570(m), 535(mb), 350(w), 330(w). The proton NMR data for the product in aniline solution are in Table I.

3. Trifluoroborane-Tin(II)iodide-Trimethylamine, $BF_3 \cdot SnI_2 \cdot N(CH_3)_3$.

The intermediate compound, tin(II)iodide-trimethylamine, $SnI_2 \cdot N(CH_3)_3$, has been reported previously[1]. The procedure and solvent used for the addition of BF_3 to this intermediate were the same as that described for the chloride compound. The final product, $BF_3 \cdot SnI_2 \cdot N(CH_3)_3$, was an air sensitive orange solid, mp 220-228 °C dec, which changed to gray in a few minutes in air. The IR spectrum by KBr pellet contained the following bands (cm^{-1}): 3142(s), 2962(s), 2740(s), 2470(w), 1640(w), 1480(s), 1470(s), 1420(m), 1385(m), 1300(m), 1258(m), 1145-1065-1035(vsb, overlapping), 985(s), 800

(vw), 563(m), 530(mb), 450(vw), 310(vw). The proton NMR data for the product in aniline solution are listed in Table I.

D. Synthesis of Trifluoroborane-Tin(II)chloride-Dimethylsulfoxide, $BF_3 \cdot SnCl_2 \cdot OS(CH_3)_2$.

Tin(II)chloride-dimethylsulfoxide was prepared and characterized, then, the adduct was treated with trifluoroborane.

(a). Preparation of tin(II)chloride-dimethylsulfoxide, $SnCl_2 \cdot OS(CH_3)_2$. A quantity(20 mmol(3.8 g)) of anhydrous $SnCl_2$ was weighed into a flask under N_2. An equimolar quantity of dimethylsulfoxide, which had been distilled from barium oxide, was transferred into the flask with a syringe. The flask was capped under N_2 and the reaction took place with the evolution of heat. Later, the flaskwas warmed in boiling water and shaken for 1 h. The whole reaction mixture appeared as a clear liquid which, when cooled, formed colorless slender crystals. The flask and the product were again heated in boiling water and shaken for another hour to insure completion of the reaction. The product melted at 81-83 °C. Anal. Calcd for $C_2H_6OSCl_2Sn$: Sn, 44.33; Cl, 26.48. Found: Sn, 44.3; Cl, 26.5 . The IR spectrum by KBr pellet contained the following bands (cm^{-1}): 3020(s), 2920(s), 1630(vwb), 1430(s), 1403(s), 1322(m), 1300(w), 985(s), 945(sh), 920(vsb), 890(sh), 720(w), 680 (w), 440(sb), 340(m), 320(m). The ^1H NMR spectrum in benzene solution consisted of one sharp peak at δ1.85; in pyridine the sharp peak shifted to δ2.05. The chemical shift of DMSO was measured to be δ2.30 in pyridine solution. The ^{119}Sn NMR spectrum of the product in saturated DMSO solution consisted of one complex peak at +396.5 ppm with fwhh 59.8 Hz. This compound was prepared by a second method whereby $SnCl_2$ was stirred in benzene

under N_2 and an equimolar quantity of DMSO was syringed into the mixture. The flask was closed and stirred for 2 days giving a finely divided white solid product with identical IR and NMR spectra.

(b). Preparation of $BF_3 \cdot SnCl_2 \cdot OS(CH_3)_2$. A 4 g (15 mmol) quantity of freshly prepared $SnCl_2 \cdot OS(CH_3)_2$ was weighed into a flask under N_2 and then 60 mL of benzene was transfered by syringe into this flask. On the vacuum line, a 15 mmol quantity of BF_3 was condensed into the flask and the reaction mixture was stirred for 2 days. The product was a hygroscopic white solid, insoluble in benzene. It was filtered under N_2, washed once with benzene and dried under house vacuum. It began to melt at 117 °C and continued to release gas through 130 °C. Anal. Calcd for $C_2H_6BCl_2F_3OSSn$: Sn, 35.37; Cl, 21.13; B, 3.22. Found: Sn, 35.4 ; Cl, 21.1 ; B, 3.08. The IR spectrum by KBr pellet contained the following bands (cm^{-1}): 3020(s), 2930(s), 2310(vw), 2250(vw), 1622(w), 1590(vw), 1475(s,sh), 1455(sb), 1427 (s), 1415(s), 1400(s), 1330(w), 1307(m), 1200(m), 1110-1070-1030(vvs, overlapping), 990(s), 920(vsb), 800(w), 770(w), 725(w), 650(vw), 540(m), 530(m), 480(s), 425(m), 340-325-305(s, overlapping). The ^1H NMR spectrum in pyridine solution consisted of one sharp peak at δ1.77. The ^1H NMR spectrum of $BF_3 \cdot OS(CH_3)_2$ in pyridine solution was also obtained but the chemical shift of the resultant peak was the same as pure DMSO in pyridine. The DMSO in this molecule thus seems to be totally displaced by pyridine. (The preparation of $BF_3 \cdot OS(CH_3)_2$ is described in the following section.) Aniline was evaluated as an NMR solvent and the results are summarized as follows: $BF_3 \cdot OS(CH_3)_2$, δ2.27; DMSO, δ2.12; $SnCl_2 \cdot OS(CH_3)_2$, δ1.90; $BF_3 \cdot SnCl_2 \cdot OS(CH_3)_2$, δ1.84.

The ^{19}F NMR resonance of $BF_3 \cdot SnCl_2 \cdot OS(CH_3)_2$ in DMSO solution occured at +69.4 ppm, while that of $BF_3 \cdot OS(CH_3)_2$ occured at +71.5 ppm. The ^{119}Sn NMR spectrum of this product in saturated DMSO solution consisted of one complex peak at +416.1 ppm.

(c). Preparation of trifluoroborane-dimethylsulfoxide, $BF_3 \cdot OS(CH_3)_2$. A 2.55 ml(20 mmol)quantity of trifluoroborane-ethylether complex was syringed into a flask which contained 20 mL of pentane under N_2. While the mixture was being stirred, 20 mmol of dimethylsulfoxide was syringed into the mixture, forming a precipitate immediately. The stirring was continued for 20 min and the reaction mixture was filtered by filter paper under N_2, washed once with pentane and dried under house vacuum, giving a white hygroscopic solid, mp 51-52 °C. The ^1H NMR spectrum of the product was reported in the previous section. The IR spectrum in acetonitrile solution with matched liquid cells contained the following bands (cm^{-1}): 3010(m), 2932(w), 1410(wb), 1370(wb), 1333(w), 1170-1100(vvs, overlapping), 1060(vs), 1010(s), 955(s), 875(sb), 720(s), 685(m), 670(w), 570(w), 340(mb), 310(m). This compound has been prepared by Forel et al. and they reported the IR and Raman spectra of the resultants of the isotope substitution of hydrogen and boron [60].

(d). The ^{119}Sn NMR spectra of the tin(II)halide-dimethylsulfoxide and trifluoroborane-tin(II)halide-dimethylsulfoxide compounds. The compounds $SnCl_2 \cdot OS(CH_3)_2$ and $BF_3SnCl_2 \cdot OS(CH_3)_2$, were dissolved in DMSO to form saturated solutions. The ^{119}Sn spectra reported in the previous sections were obtained using these solutions. The other tin(II)halide-DMSO-compounds were not isolated; ^{119}Sn spectra were obtained on saturated solutions of the appropriate tin(II) halide in DMSO. Afterwards, an

equimolar quantity of BF_3 (with respect to the tin) was added into the solution on the vacuum line and the material was stirred thoroughly for 24 h. Then, the ^{119}Sn NMR spectrum of the solution was taken again. The spectral parameters are listed in Table II along with those of the pyridine adducts which were obtained in the similar way using saturated pyridine solutions.

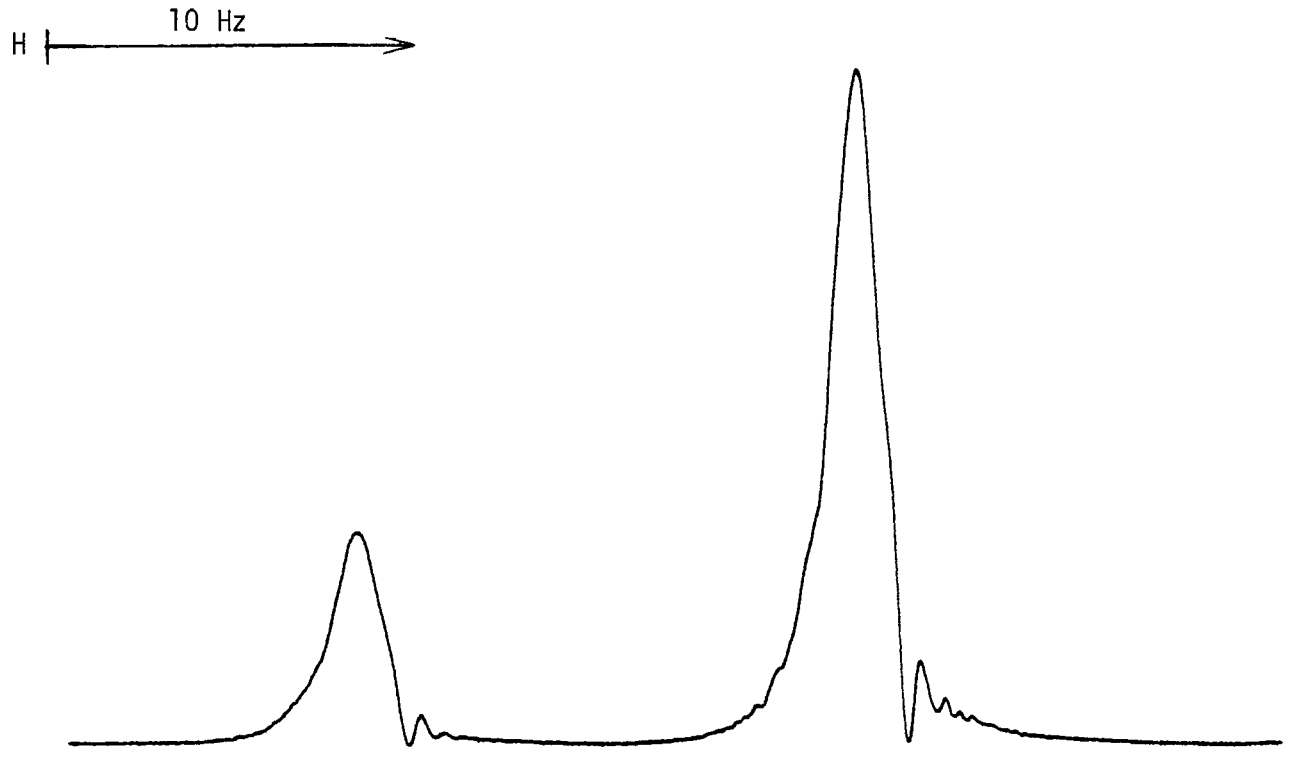

Figure 5. Expanded ^{1}H NMR spectrum of TMED (solvent, aniline).

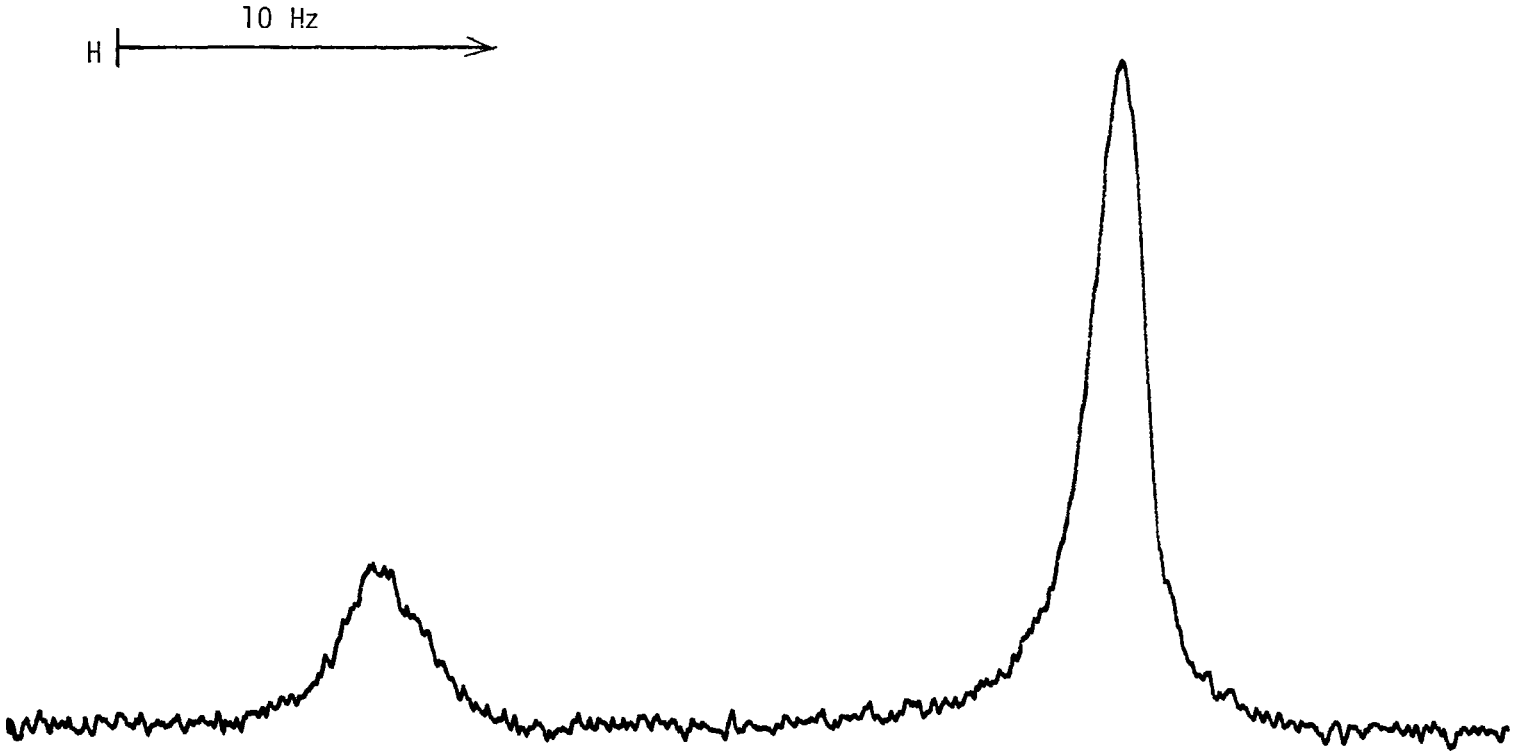

Figure 6. Expanded ^{1}H NMR spectrum of $SnCl_2 \cdot TMED$ (solvent, aniline).

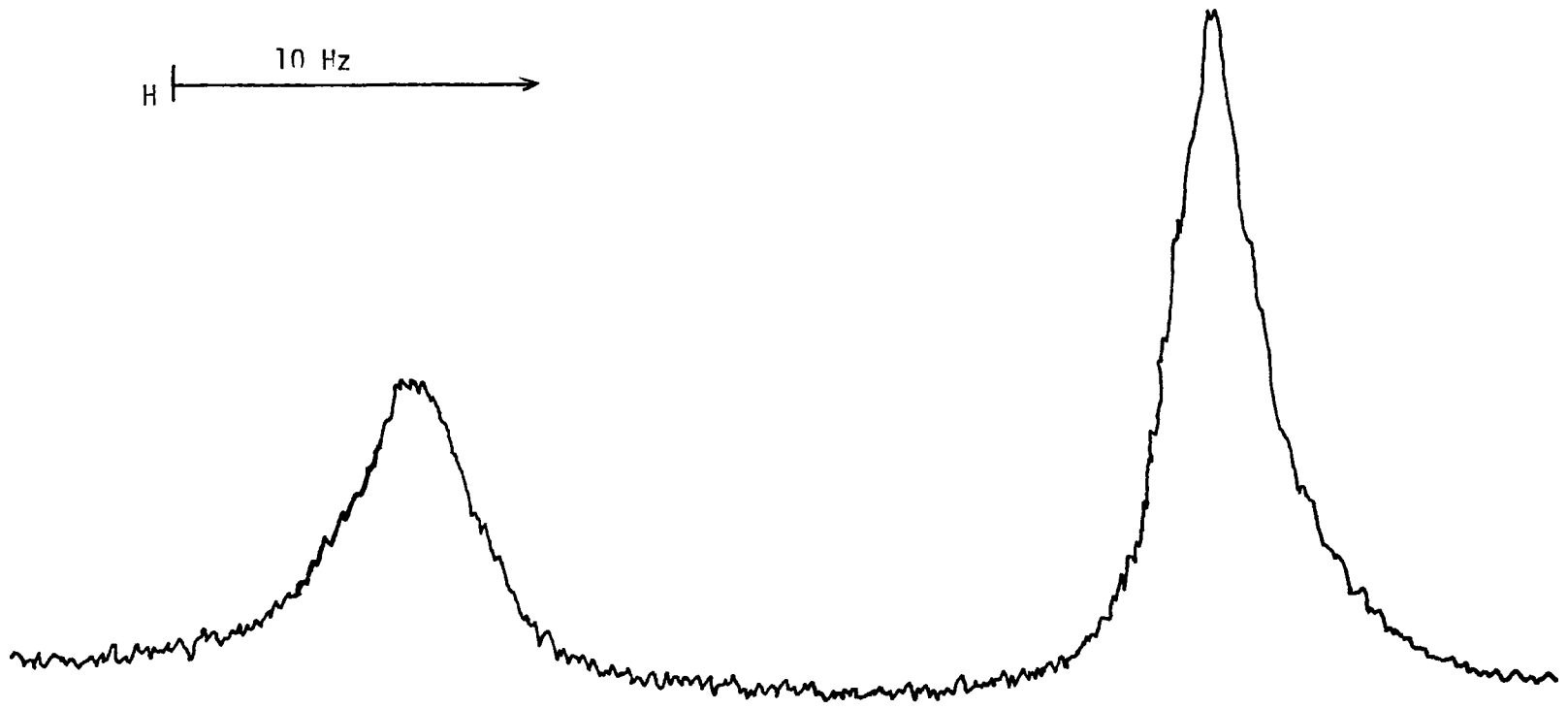

Figure 7. Expanded ^{1}H NMR spectrum of $BF_3 \cdot SnCl_2 \cdot TMED$ (solvent, aniline).

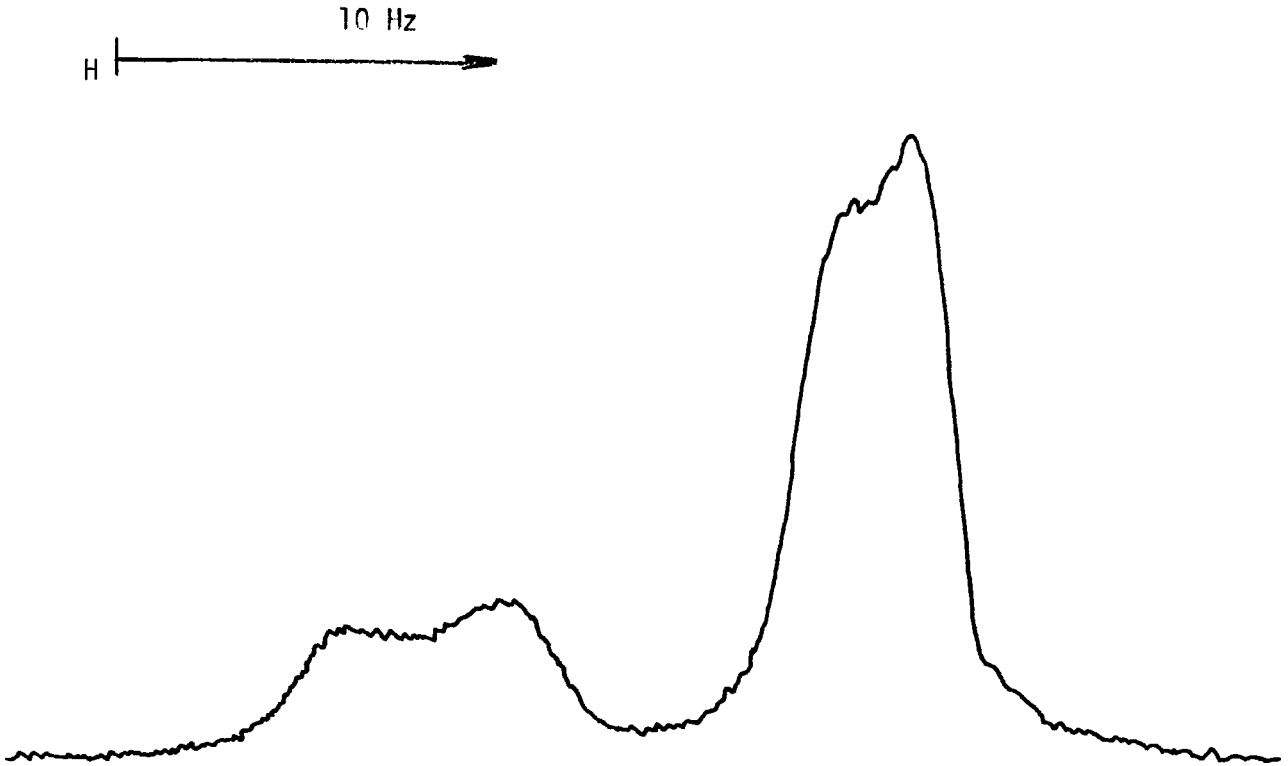

Figure 8. Expanded ^{1}H NMR spectrum of $BF_3 \cdot TMED$ (solvent, aniline).

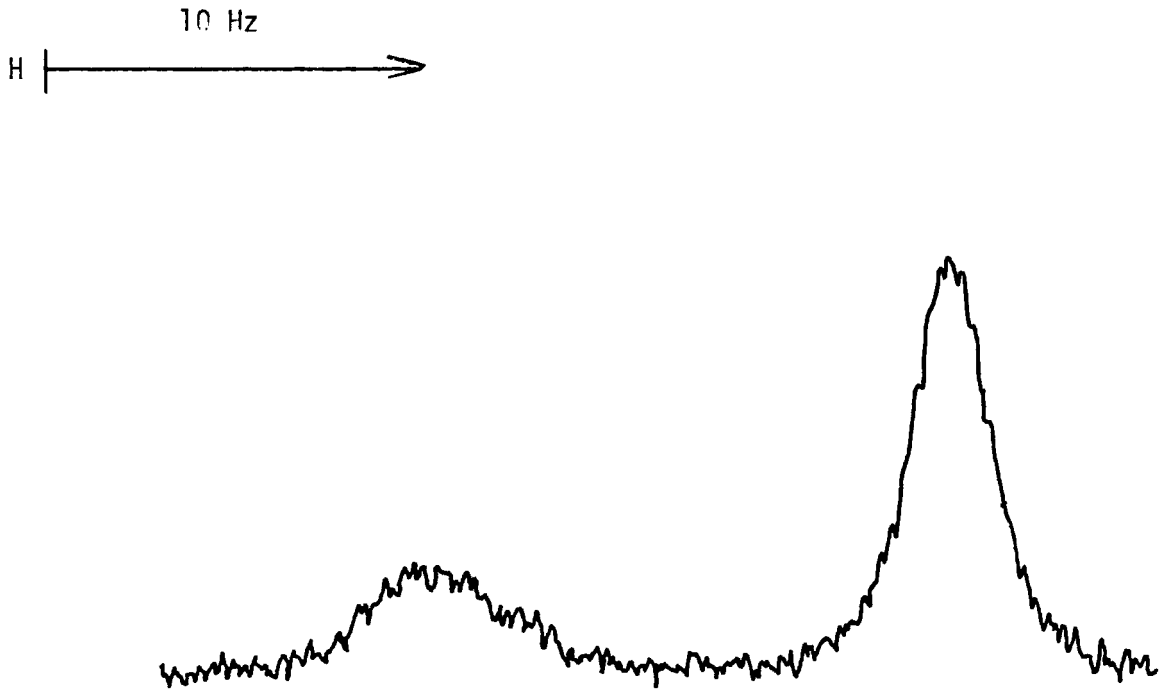

Figure 9. Expanded ^{1}H NMR spectrum of $BF_3 \cdot TMED \cdot SnCl_2$ (solvent, aniline).

E. Syntheses of Trifluoroborane-N,N'-Tin(II)halide-Tetramethylethylenediamine Adducts.

1. Trifluoroborane-N,N'-Tin(II)chloride-Tetramethylethylenediamine, $BF_3 \cdot SnCl_2 \cdot TMED$.

Two steps were employed to prepare this compound. First, $SnCl_2$ was reacted with N,N,N',N'-tetramethylethylenediamine to give the chelated adduct and, secondly, the intermediate was treated with BF_3.

(a). Preparation of N,N'-tin(II)chloride-tetramethylethylenediamine, $SnCl_2 \cdot TMED$. In a typical preparation, 7.58 g (40 mmol) of anhydrous $SnCl_2$ was weighed under a N_2 atmosphere into a flask with a side arm fitted with a septum. A volume of 80 mL of anhydrous, peroxide-free ethyl ether was syringed into the flask and magnetic stirring was begun. Then, a quantity of 5.83 mL (40 mmol) of TMED was added to the mixture via syringe through the septum. The flask was closed and the mixture was stirred for 3 days, then, it was filtered, washed with ether and dried under the house vacuum. The product was a white solid, mp 229-230 °C dec. The yield was 11.5 g (94%). Anal. Calcd for $C_6H_{16}Cl_2N_2Sn$: Sn, 38.81; Cl,23.22; N, 9.16. Found: Sn, 39.2 ; Cl, 22.7 ; N, 8.83. The IR spectrum by KBr pellet contained the bands listed below (cm^{-1}): 3020(m), 2940(m), 2640(vs), 2600(vs), 2580(vs), 2530(w), 2480(vs), 1490(s), 1475(s), 1460(m), 1421(w), 1400(w), 1290(m), 1160(m), 1130(w), 1005(s), 980(s), 795(w), 550(mb), 520(m), 470(w) . Proton NMR data for the product in aniline solution are listed in Table III. The expanded pattern of this spectrum, together with the spectrum of TMED in aniline, are shown in Figure 6 and 5, respectively.

(b). Preparation of $BF_3 \cdot SnCl_2 \cdot TMED$. A portion (9.2 g (30 mmol)) of freshly prepared $SnCl_2 \cdot TMED$ was weighed into a reaction vessel which was fitted with a side arm containing a septum. Then 80 mL of anhydrous, peroxide-free ethyl ether was added under N_2 atmosphere and the vessel was closed. A 3.80 mL (30 mmol) portion of trifluoroborane-ethylether was added to the vessel through the septum by syringe and the mixture was stirred for 4 days. The contents were then filtered and washed with ether under N_2. The product was a pale yellow solid, yield 10.1 g (90%) (mp 224-229 °C). Anal. Calcd for $C_6H_{16}BCl_2F_3N_2Sn$: Sn, 31.76; B, 2.89; Cl, 19.0; N, 7.49. Found: Sn, 30.9 ; B, 3.01; Cl, 18.7 ; N, 7.21. The IR spectrum by KBr pellet contained the bands listed below (cm^{-1}): 3025(m), 2980(sb), 2630(s), 2580(s), 2460(s), 2420(vw), 1620(wb), 1482(s), 1472(s), 1460(s), 1410(m), 1386(w), 1315(w), 1285(m), 1200(m), 1130(s)-1080(vs)-1050(vs)-1030(s) overlapping, 996(s), 980(s), 790(w), 565-540-525(m, overlapping), 325(mb), 300(m). Proton NMR data for the product in aniline solution are listed in Table III, and the expanded spectrum is shown in Figure 7. The ^{11}B NMR spectrum in DMSO solution consisted of a broad, complex peak at -21.1 ppm with fwhh 280.0 Hz. The d spacings in the X-ray powder diffraction pattern were as follows [d, Å (intensity)]: 10.28(w), 9.14(w), 7.22(vw), 6.39(vs), 6.04(m), 5.45(w), 5.11(w), 4.78(w), 4.58(m), 4.41(m), 3.89(m), 3.69(mb), 3.52(w), 3.42(w), 3.17(s), 3.04(m), 2.93(m), 2.84(m), 2.74(w), 2.67(w), 2.57(w), 2.45(wb), 2.31(w), 2.20(s), 2.09(vw), 1.99(m), 1.91(m), 1.81(w), 1.73(vw), 1.69(w), 1.58(w).

2. Trifluoroborane-N,N'-Tin(II)bromide-Tetramethylethylenediamine, $BF_3 \cdot SnBr_2 \cdot TMED$.

The procedure and solvent employed to prepare this compound were the same as that used for the chloride compound. Anhydrous $SnBr_2$ was used. The intermediate product, $SnBr_2 \cdot TMED$, was a pale yellow solid (mp 245-246 °C). The IR spectrum by KBr pellet contained the bands as listed below (cm^{-1}): 3020(m), 2910(sb), 2850(w), 2620(sb), 2560(m), 2450(s), 1635(vwb), 1485(s), 1465(s), 1415(w), 1397(m), 1280(m), 1154(m), 1122(w), 997(s), 975(s), 787(w), 550(m), 520(m), 470(w). Proton NMR data for the product in aniline solution are given in Table III.

The final product, $BF_3 \cdot SnBr_2 \cdot TMED$, was a white solid (mp 180-185 °C). The IR spectrum by KBr pellet contained the bands as listed below (cm^{-1}): 3019(m), 2980(sb), 2730(m), 2640(sb), 2590(s), 2460(m), 2360(w), 2340(w), 1560(wb), 1492(m), 1470(s), 1463(s), 1400(w), 1290(w), 1125(s)-1080(vs)-1035(vs) overlapping, 1005(m), 980(s), 790(vw), 565-540-520(m, overlapping),325(mb), 300(m). Proton NMR data for the product in aniline solution are listed in Table III.

3. Trifluoroborane-N,N'-tin(II)iodide-tetramethylethylenediamine, $BF_3 \cdot SnI_2 \cdot TMED$.

Anhydrous SnI_2 was used for this preparation and all procedures and the solvent were the same as those used for the chloride compound. The intermediate product, $SnI_2 \cdot TMED$, was a yellow solid (mp 228-230 °C dec). Its IR spectrum by KBr pellet contained the bands as listed below (cm^{-1}): 3020(m), 2900(sb), 2832(m), 2760(w), 2660(vsb), 2580(s), 2460(s), 2360(w),

1650(vwb), 1483(s), 1470(s), 1420(m), 1405(m), 1290(m), 1210(w), 1158(m), 1130(vw), 1000(s), 978(s), 830(w), 790(m), 550(m), 520(m), 460(w). The proton NMR data in aniline solution are given in Table III.

The final product, $BF_3 \cdot SnI_2 \cdot TMED$, was an orange solid (mp 207-210 °C dec). Its IR spectrum by KBr pellet contained the bands listed below (cm^{-1}): 3020(m), 2920(sb), 2840(w), 2660(vsb), 2590(s), 2450(s), 2360(w), 1650(wb), 1484(m), 1470(s), 1460(s), 1414(m), 1400(m), 1285(w), 1265(m), 1130(s)-1080(vs)-1040(s) overlapping, 998(s), 975(s), 950(w), 920(m), 870(w), 808(m), 790(m), 560(mb), 510(sb), 460(w), 340(w), 300(m). The proton NMR data for the product in aniline solution are in Table III.

4. Preparation of Auxiliary Compounds.

(a). Trifluoroborane-tetramethylethylenediamine, $BF_3 \cdot TMED$. A 1.46 mL (10 mmol) quantity of N,N,N',N'-tetramethylethylenediamine was dissolved in 30 mL of anhydrous, peroxide-free ethyl ether in a flask under a N_2 atmosphere. An equal molar quantity of trifluoroborane-ethylether was added to the flask which was then closed and the mixture stirred over night. The ethyl ether was then removed by vapor transfer on the vacuum line leaving the product in the flask as a slightly yellow solid (mp 85 °C). Its IR spectrum by KBr pellet contained the bands listed below (cm^{-1}): 3010(w), 2900(sb), 2830(w), 2560(sb), 2450(s), 1450(s), 1415(s), 1375(m), 1280(w), 1130(s)-1075(vs)-1025(vs)-970(s)-910(s) overlapping, 865(m), 788(m), 685(w), 510(vw), 416(s), 395(s), 345(m). The proton NMR data for the product in aniline solution are given in Table III and the expanded spectrum is shown in Figure 8.

(b). N-Trifluoroborane-N'-tin(II)chloride-tetramethylethylenediamine, $BF_3 \cdot TMED \cdot SnCl_2$. A 1.9 g (10 mmol) quantity of anhydrous $SnCl_2$ was reacted with an equimolar quantity of trifluoroborane-tetramethylethylenediamine in 30 mL of anhydrous benzene under an N_2 atmosphere. The mixture was stirred 3 days, then the product was filtered off and washed with benzene under N_2. The product was a white solid which melted in the range 165-172 °C. By virtue of this procedure, the product should have BF_3 coordinated to one TMED nitrogen and $SnCl_2$ coordinated to the other, lacking any subsequent rearrangement. The IR spectrum of the product by KBr pellet contained the bands as listed below (cm^{-1}): 3090(w), 3030(m), 2970(sb), 2720(s), 2650(mb), 2460(m), 1630(wb), 1470(sb), 1410(m), 1355(m), 1300(m), 1140(s)-1110(vs)-1055(vs)-1020(vs) overlapping, 990(s), 970(s), 915(s), 865(m), 790(w), 690(w), 520(mb), 390(m), 350(w). Proton NMR data for the product in aniline solution are listed in Table III and its expanded spectrum is shown in Figure 9.

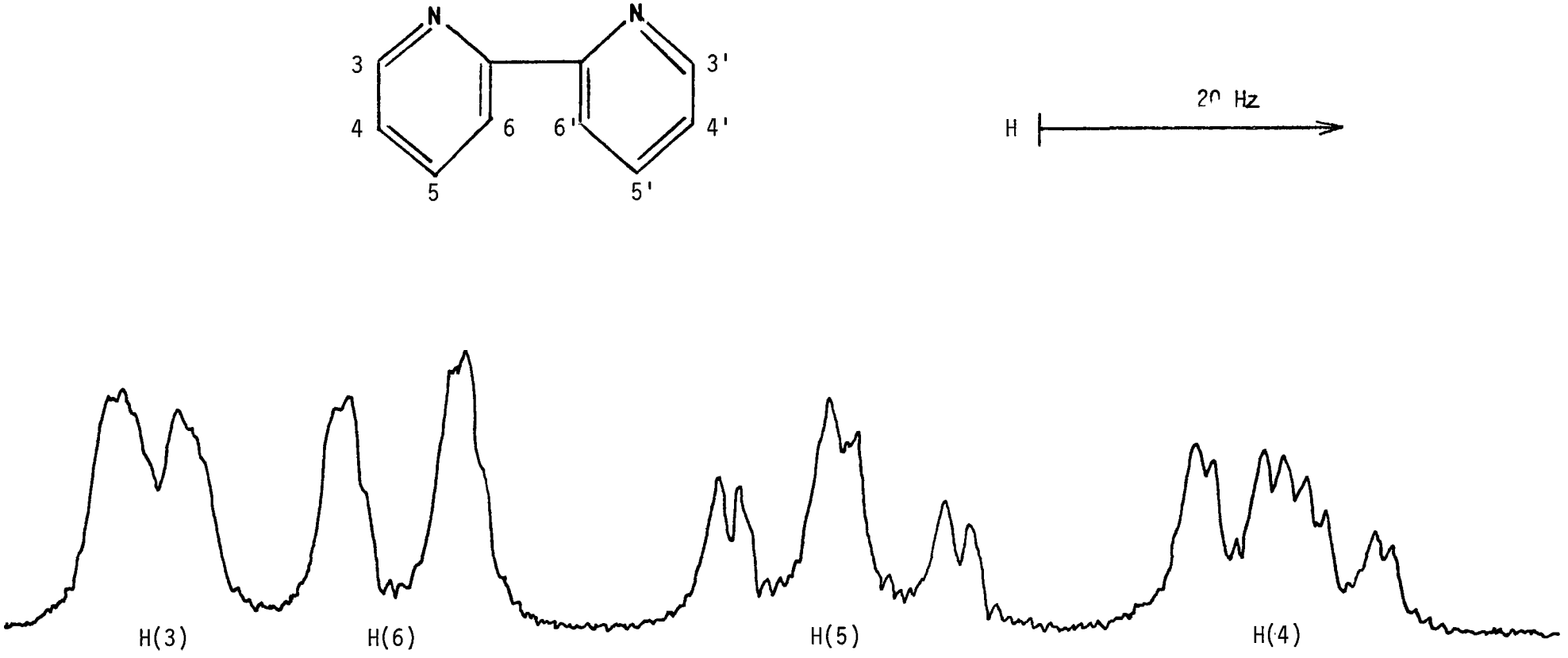

Figure 10. Expanded ^{1}H NMR spectrum of dipyridyl (solvent, DMSO).

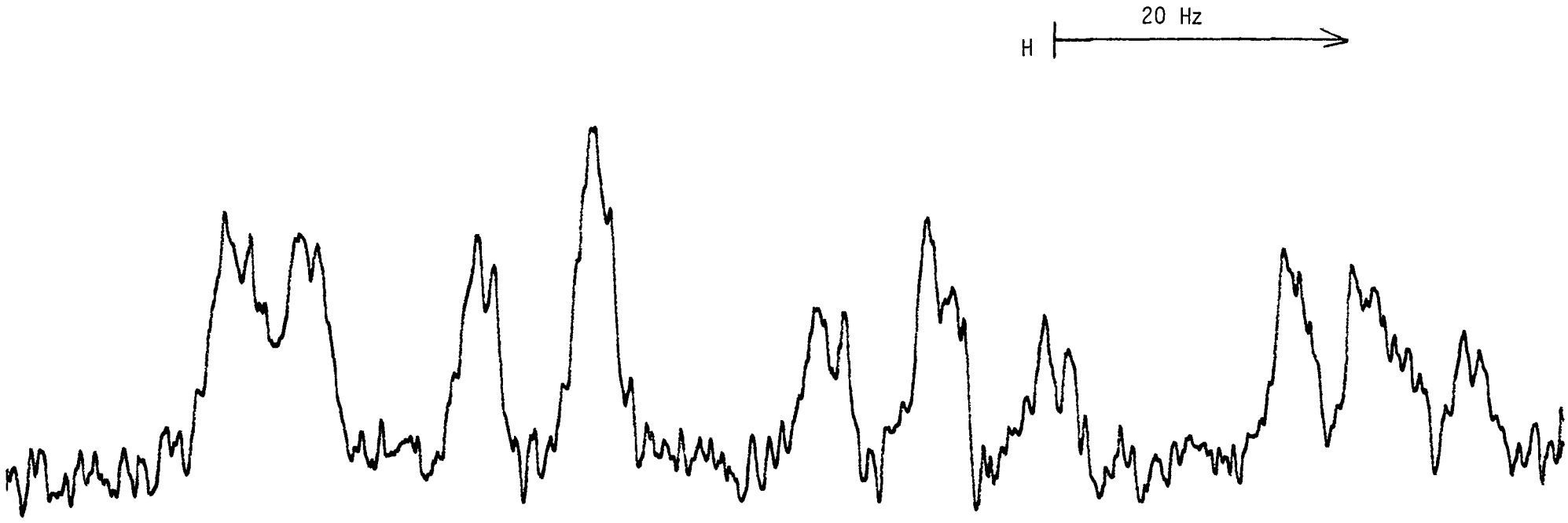

Figure 11. Expanded ^{1}H NMR spectrum of $SnCl_2 \cdot DP$ (solvent, DMSO).

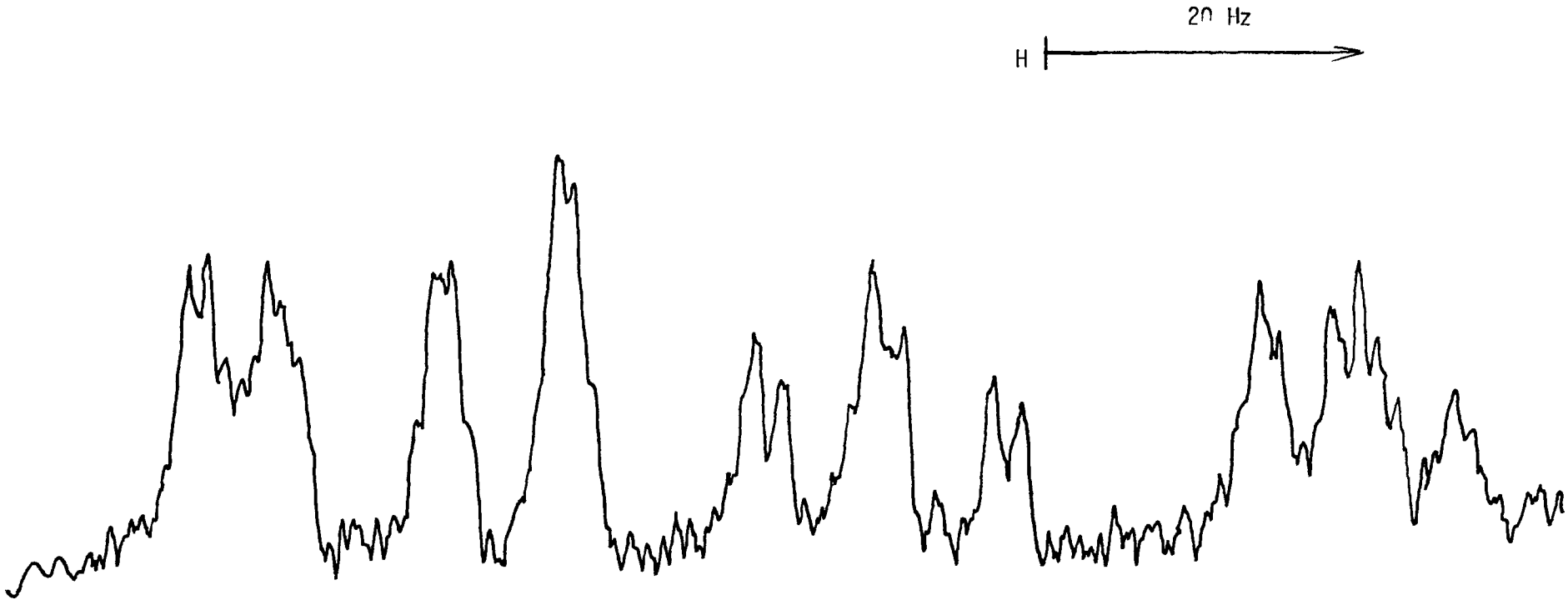

Figure 12. Expanded ^{1}H NMR spectrum of $BF_3 \cdot SnCl_2 \cdot DP$ (solvent, DMSO).

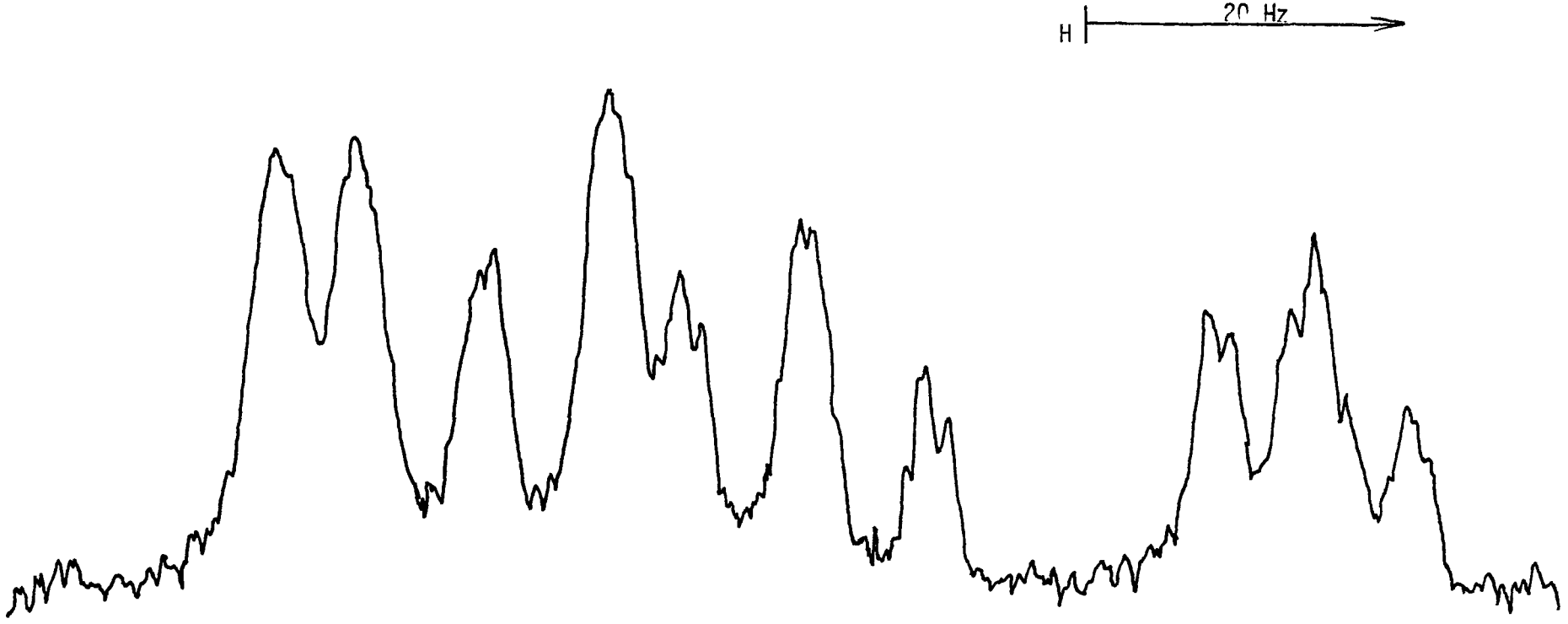

Figure 13. Expanded ^{1}H NMR spectrum of $BF_3 \cdot DP$ (solvent, DMSO).

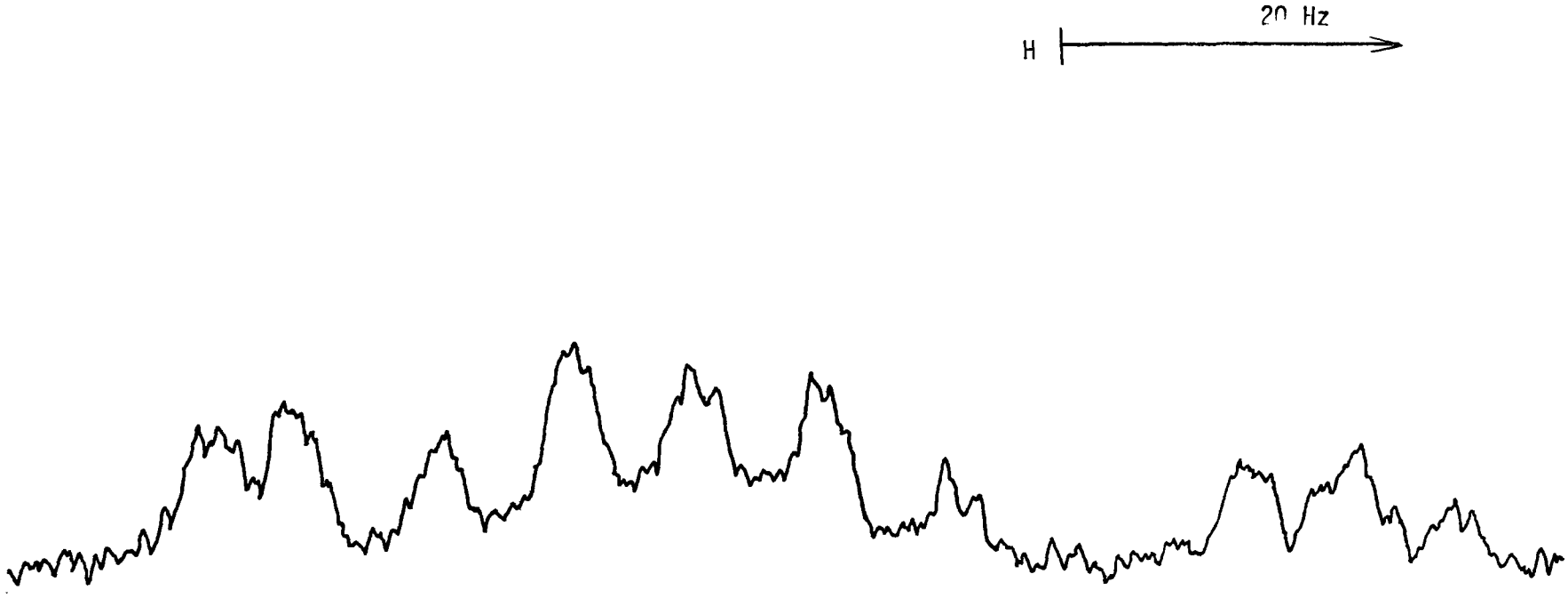

Figure 14. Expanded ^{1}H NMR spectrum of $BF_3 \cdot DP \cdot SnCl_2$ (solvent, DMSO).

F. Syntheses of Trifluoroborane-N,N'-Tin(II)halide-Dipyridyl Adducts.

1. Trifluoroborane-N,N'-Tin(II)chloride-Dipyridyl, $BF_3.SnCl_2.DP$.

The preparation of this compound was carried out in two steps. First, 2,2'-dipyridyl was reacted with tin(II) chloride, forming the chelated adduct, which was then treated with trifluoroborane.

(a). Preparation of N,N'-tin(II)chloride-dipyridyl, $SnCl_2 \cdot DP$. In a typical preparation, 7.58 g (40 mmol) of anhydrous $SnCl_2$ and 80 mL of anhydrous, peroxide-free ethyl ether were placed in a reaction vessel, under the protection of dry nitrogen. A 6.25 g (40 mmol) portion of 2,2'-dipyridyl was added to the vessel which was then closed and the mixture stirred magnetically for 3 days. The product, a yellow solid,was filtered off under nitrogen, washed once with ether and dried under house vacuum. The yield was 13.3 g (96%). Anal.Calcd for $C_{10}H_8Cl_2N_2Sn$: Sn, 34.32; N, 8.10; Cl, 20.51. Found: Sn, 34.9 ; N, 7.85; Cl, 20.4 . (mp 210-211 °C). The IR spectrum of this compound by KBr pellet consisted of the following bands(cm^{-1}): 3070(m), 3030(m), 2430(vw), 1613(s), 1603(s), 1578(mb), 1500(m), 1480(s), 1450(vs), 1420(m), 1320(s), 1250(s), 1220(sh), 1178(m), 1158(s), 1105(vw), 1065(w), 1035(m), 1020(s), 990(vw), 775(s), 726(m), 655(wb), 646(wb), 415(m), 325(mb). The ^1H NMR Spectrum of the product in DMSO solution (Figure 11) resembled the spectrum of 2,2'-dipyridyl (Figure 10) (both are expanded patterns) and the chemical shifts are listed in Table IV.

(b). Preparation of $BF_3 \cdot SnCl_2 \cdot DP$. Under nitrogen, 10.4 g (30 mmol) of freshly prepared $SnCl_2 \cdot DP$ together with 80 mL of ethyl ether were placed

in a flask which was fitted with a sidearm containing a septum. An equimolar quantity of trifluoroborane-ethylether complex was measured with a syringe and transferred into the flask through the septum and the mixture was then stirred for 3 days during which time the color of the mixture changed from yellow to white. The solid product was filtered and washed with ethyl ether under nitrogen and dried under house vacuum. The yield was 11.4 g (92%) (mp 156-160 °C dec). Anal. Calcd for $C_{10}H_8BCl_2F_3N_2Sn$: Sn, 28.69; B, 2.61; N, 6.77; Cl, 17.17. Found: Sn, 29.7 ; B, 2.59; N, 6.74; Cl, 17.0 . The IR spectrum by KBr pellet consisted of the following bands (cm^{-1}): 3210(mb), 3100(w), 2330(vw), 1603(s), 1595(w), 1580(w), 1535(w), 1500(w), 1480(s), 1450(vs), 1325(m), 1255(w), 1220(vw), 1180(m), 1165(m), 1125(s)-1070(vs)-1035(vs) overlapping, 1020(s), 775(s), 650-640-620(w, overlapping), 555-540-530(w, overlapping), 420(m), 325(mb). The ^1H NMR spectrum of the product in DMSO solution, which resembled dipyridyl; the expanded pattern is shown in Figure 12 while the data are listed in Table IV. The ^{11}B NMR spectrum in DMSO solution consisted of a broad complex peak at -20.7 ppm with 254.4 Hz. The d spacings in the X-ray powder diffraction pattern were as follows [d, A (intensity)]: 9.53(vs), 7.61(vs), 6.83(s), 6.01(vvsb), 5.47(w), 5.15(s), 4,76(vw), 4.49(s), 4.26(m), 3.98(m), 3.81(s), 3.65(w), 3.54(vw), 3.43(s), 3.10(vw), 2.97(s), 2.86(vw), 2.63(m), 2.57(w), 2.50(w), 2.44(vw), 2.37(m), 2.29(w), 2.21(w), 2.15(w).

2. Trifluoroborane-N,N'-Tin(II)bromide-Dipyridyl, $BF_3 \cdot SnBr_2 \cdot DP$.

The procedure and solvent for the preparation of this compound were the same as those mentioned in the foregoing section. Anhydrous $SnBr_2$ was used. The intermediate product, $SnBr_2 \cdot DP$, was a bright yellow solid (mp

253-254 °C). The IR spectrum by KBr pellet contained the following bands (cm^{-1}): 3100(m), 3060(m), 2280(vw), 1603(s), 1570(m), 1500(vw), 1475(m), 1445(vs), 1323(s), 1250(m), 1220(w), 1150(m), 1110(w), 1065(w), 1030(s), 770(s), 725(m), 640(w), 415(m), 325(m). The ^1H NMR data from the spectrum of the product in DMSO solution are listed in Table IV. $BF_3 \cdot SnBr_2 \cdot DP$ was obtained by treating freshly prepared $SnBr_2 \cdot DP$ with BF_3. The product was a bright yellow solid (mp 178-185 °C). The IR spectrum by KBr pellet contained the following bands (cm^{-1}): 3210(m), 3170(m), 3080(w), 3060(w), 2270(vw), 1600(s), 1595(s), 1560(w), 1524(w), 1500(m), 1480(s), 1455(vs), 1330(s), 1285(w), 1255(m), 1160(sh), 1125(s)-1070(vs)-1035(vs) overlapping, 770(s), 723(m), 640(w), 540(wb), 415(m), 298(m). The ^1H NMR data from the spectrum of the product in DMSO solution are listed in Table IV.

3. Trifluoroborane-N,N'-Tin(II)iodide-Dipyridyl, $BF_3 \cdot SnI_2 \cdot DP$.

In this preparation, anhydrous SnI_2 was used, and all procedures and solvent were the same as those indicated in the previous sections. The intermediate product, $SnI_2 \cdot DP$, was a deep brown solid (mp 302-303°C). The IR spectrum by KBr pellet contained the following bands (cm^{-1}): 3070(m), 3030(m), 2270(vw), 1600(s), 1590(s), 1556(m), 1525(m), 1490(w), 1475(m), 1450(vs), 1320(m), 1250(m), 1220(w), 1155(w), 1100(vw), 1065(vw), 1040(sh), 1025(s), 900(vw), 765(s), 725(w), 640(w), 420(m), 330(m). The ^1H NMR data of the product in DMSO solution are listed in Table IV. The final product, $BF_3 \cdot SnI_2 \cdot DP$, was a red solid (mp 239-240 °C dec). The IR spectrum by KBr pellet contained the following bands (cm^{-1}): 3200(sb), 3070(m), 3040(m), 1600(s), 1570(w), 1530(vw), 1500(w), 1474(m), 1450(s), 1320(m), 1250(m),

1160(sh), 1110(s)-1070(vs)-1035(vs) overlapping, 1000(sh), 764(s), 720(w), 645(w), 540(wb), 415(w), 295(w). The ^{1}H NMR data from the spectrum of the product in DMSO solution are listed in Table IV.

4. Preparation of the Auxiliary Compounds.

(a). Trifluoroborane-dipyridyl, $BF_3 \cdot DP$. Equimolar quantities, e.g., 10 mmol, of 2,2'-dipyridyl and trifluoroborane-ethylether were reacted in dry ethyl ether solution under N_2 with magnetic stirring for 1 day. The product, $BF_3 \cdot DP$, was a white solid (mp 115 °C). The IR spectrum by KBr pellet contained the following bands (cm^{-1}): 3240(s), 3190(s), 3100(m), 3050(w), 2360(vw), 2270(vw), 1642(sb), 1620(s), 1615(s), 1595(s), 1580(sh), 1543(s), 1480(s), 1468(s), 1442(s), 1380(m), 1320(s), 1285(s), 1245(s), 1180(s), 1160(s), 1120(vs)-1050(vs)-1025(vs) overlapping, 1000(s), 930(m), 900(w), 775(sb), 730(m), 650(mb), 615(mb), 530(m), 470(m), 450(m). Proton NMR data for the product in DMSO solution are listed in Table IV while the expanded spectrum is shown in Figure 13.

(b). N-Trifluoroborane-N'-tin(II)chloride-dipyridyl, $BF_3 \cdot DP \cdot SnCl_2$. A 1.9 g (10 mmol) quantity of anhydrous $SnCl_2$ was reacted with an equimolar quantity of trifluoroborane-dipyridyl in 30 mL of anhydrous benzene solution under an N_2 atmosphere. The mixture was stirred for 3 days, then filtered and washed with ether under N_2 and dried under house vacuum. The product was a pale yellow solid (mp 135-140 °C). It was expected that the product obtained in this way would have both BF_3 and $SnCl_2$ coordinated to the two available DP nitrogens. The IR spectrum by KBr pellet contained the following bands (cm^{-1}): 3220(s), 3170(s), 3100(sh), 3060(sh), 2350(vw),

2270(vw), 1640(sh), 1625(m), 1610(s), 1595(s), 1575(w), 1535(s), 1505(s), 1485(s), 1450(s), 1435(s), 1415(sh), 1325(m), 1312(sh), 1284(w), 1255(m), 1200(m), 1160(s), 1110(vs)-1080(vs)-1040(vs) overlapping, 930(w), 810(w), 775(s), 720(m), 650(wb), 605(w), 530(wb), 450(wb), 420(m), 340-320(m, overlapping). Proton NMR data for the compound in DMSO solution are given in Table IV and the expanded spectrum is displayed in Figure 14.

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