corresponding value for the dimethyl sulfoxide complex;[3] k^{f}_{1} is some 75 times smaller. This significant difference of the trans effect on the forward and the backward reaction means that a change from dimethyl sulfoxide to dimethyl sulfide strongly affects the equilibrium constant which increases from 3.1×10^{2} to 3.2×10^{3}. This is not an isolated observation and it is clear that the minimum value for the equilibrium constant for the analogous reaction with the 3,4-dimethylpyridine complex, 5.1×10^{5}, is considerably greater than that measured for the corresponding dimethyl sulfoxide complex (1.6×10^{4}).[3] It is therefore not possible to explain the difference in the trans effects of Me_2S and Me_2SO solely in terms of transition-state effects.

It would now be of interest to compare the trans effects of Me_2S and Me_2SO in the reaction *cis*-$Pt(L)(am)Cl_2$ + am = *cis*-$Pt(L)(am)_2Cl^+ + Cl^-$ to see whether the difference between sulfides and sulfoxides is even more marked in cationic substrates.

Acknowledgment. R.G. thanks the Science Research Council for a studentship. K_2PtCl_4 was generously loaned by Johnson, Matthey and Co. Ltd.

Registry No. $Et_4N[Pt(Me_2S)Cl_3]$, 62571-71-5; *trans*-$Pt(Me_2S)(3,4\text{-}Me_2py)Cl_2$, 62571-72-6; *trans*-$Pt(Me_2S)(py)Cl_2$, 31203-93-7; *trans*-$Pt(Me_2S)(3\text{-}Cl\text{-}py)Cl_2$, 62571-73-7; *trans*-$Pt(Me_2S)_2Cl_2$, 17457-51-1; $Pt_2Cl_4(C_2H_4)_2$, 15905-87-0; piperidine, 110-89-4; *n*-butylamine, 109-73-9; ethylenediamine, 107-15-3; cyclohexylamine, 108-91-8; piperazine, 110-85-0; ethanolamine, 75-39-8; cyclopropylamine, 765-30-0; morpholine, 110-91-8; 3,4-dimethylpyridine, 583-58-4; 4-methylpyridine, 108-89-4; pyridine, 110-86-1; 3-chloropyridine, 626-60-8; 3-bromopyridine, 626-55-1; 4-cyanopyridine, 100-48-1; 3,5-dichloropyridine, 2457-47-8.

Supplementary Material Available: A table of observed first-order rate constants, k_{obsd}, for the reaction $Pt(Me_2S)Cl_3^-$ + am = *trans*-$Pt(Me_2S)(am)Cl_2 + Cl^-$ in methanol at 30.0 °C, [LiCl] = 0.015 M, and $\mu = 0.505$ and a table of specific rate constants for the approach to equilibrium for the process $Pt(Me_2S)Cl_3^- + MeOH = Pt(Me_2S)(MeOH)Cl_2 + Cl^-$ at $\mu = 0.50$ ($LiClO_4$ in methanol), 30.0 °C, and [complex] = 6.0×10^{-4} M (3 pages). Ordering information is given on any current masthead page.

References and Notes

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N-Organotin Aziridines and Other Cyclic Amines and Their Adducts

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N-Trimethyltin aziridine is shown to possess an associated solid-state structure involving nitrogen→tin coordination on the basis of its crystalline state at ambient temperature and larger ^{119m}Sn Mössbauer quadrupole splitting (QS), a dimeric structure in benzene from osmometry and the identical QS in frozen *n*-butylbenzene, and the retention of these structures in the gas phase from the observation of 12 ditin fragments larger than the parent molecular ion in the mass spectrum. 2-Methyl and 2,2-dimethyl substitution or use of cyclic amines with rings of four to seven members disrupts the association. *N*-Trimethyltin aziridine is synthesized by trans- and lithioamination reactions and undergoes hydrolysis, methanolysis, carbonylation, acid cleavage with hydrogen chloride and cyclopentadiene, and transamination reactions with higher amines as well as insertion reactions with the dipolar, unsaturated substrates carbon dioxide and disulfide, phenyl isocyanate and isothiocyanate, acetone, and diethylacetylene dicarboxylate and with tetrasulfur tetranitride. Boron trifluoride is removed from its etherate as a 1:1 complex which is inert to refluxing triethylamine. The 1:1 carbon dioxide insertion product has the aziridine ring intact in an axially associated, trigonal-bipyramidal structure, but 2 mol of carbon disulfide reacts to form a solid thiazolidone which is associated through sulfur→tin axial bridging. The carbon dioxide adduct is converted to the carbon disulfide adduct by treatment with CS_2. Heating the 1:1 adduct with phenyl isocyanate which is bonded through nitrogen yields the corresponding imidazolin-2-one, while the analogous 1:1 thio adduct is bonded through sulfur, the acetone adduct is bonded through oxygen, and the acetylene adduct contains a cis tin enamine. Reaction with tetrasulfur tetranitride yields bis(1-aziridinyl) sulfide and *N*,*N'*-bis(trimethylstannyl)sulfur diimide. Complete infrared and ^{1}H and ^{13}C NMR assignments are made. The absence of the two-bond $|^{2}J(^{119}Sn\text{-}N\text{-}^{13}C)|$ couplings in all but the *N*-trimethyltin cyclic amines with ring sizes of greater than five is interpreted in terms of bimolecular exchange of NR_2 groups in the concentrated solutions studied.

Introduction

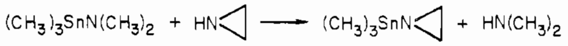
Aziridine (ethylenimine) holds an especial place among amines[2] because of its small steric bulk and the exceptional electrical properties of its three-membered ring. Aziridine is a weaker base than dimethylamine, and the possibility of ring opening provides another dimension to its chemistry. The poorer proton-acceptor ability reflects the diminished availability of the lone electron pair on nitrogen owing to its interaction with the ring. The order of pK_a and hydrogen-bonding values among the cyclic imines $(CH_2)_nNH$ and $(CH_2)_nNCH_3$ is $n = 3 << 6 < 5 < 4$.[2]

N-Trimethyltin aziridine has been synthesized by transamination,[3] and the germanium analogue, by lithioamination.[4] The triethylgermyl analogue[5] and over 30 triorganosilylaziridines[5-11] are known, in addition to nearly a dozen diorganosilyl derivatives[6,8,9,11] synthesized by the direct amination of a chlorosilane in the presence of a strong base to take up the HCl liberated,[6-8] by dehydrocondensation with an organosilicon hydride,[8,10] by lithioamination,[5] or by silicon–carbon bond cleavage in 2-furyl-, 2-thienyl-, benzyl-, and allylsilanes in the presence of an alkali metal catalyst.[11] Triethylgermylaziridine inserts acetone into the Ge–N bond to give triethyl(1-methyl-1-ethyleniminoethoxy)germane, which unlike the addition product of the corresponding dimethylamine derivative is stable against decomposition to bis(triethylgermanium) oxide and dimethylisopropenylamine.[5] *N*-Silylaziridines add phenyl isocyanate[9] to form urea derivatives and aldehydes to form 1-organo-1-ethyleniminomethyloxysilanes[12] and undergo cyclodimerization on heating to 250 °C to give the corresponding *N,N*-bis(silyl)piperazines.[13] It is known, however, that the same reagents which insert into the fourth group element–nitrogen bond also add to the aziridine ring,[2] and it is, therefore, of interest to determine under what conditions each will take place.

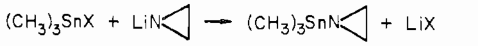
We report in this paper the synthesis of *N*-trimethyltin aziridines by transamination and lithioamination reactions and their characterization by infrared, proton and carbon-13 NMR, and tin-119m Mössbauer spectroscopies. The products are used in hydrolysis, methanolysis, carbonylation, acid cleavage, and transamination reactions with higher imines as well as insertion reactions with dipolar unsaturated substrates and the formation of adducts with Lewis acids. The 2-methyl- and 2,3-dimethylaziridine derivatives are synthesized for comparison, as well as the analogous saturated cyclic imine derivatives with four to seven members.

Results and Discussion

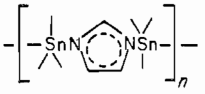
N-Trimethyltin aziridine is prepared by the transamination of trimethyltin dimethylamine with aziridine[3]


(1)

as well as by the lithioamination of trimethyltin chloride or acetate by *N*-lithioaziridine


(2)

The latter named is the method of choice. The product had been reported as a liquid, bp 53–56 °C (16 Torr),[3] like its silicon[9-11] and germanium[4] analogues, but careful sublimation at room temperature on the vacuum manifold gave long, white needle crystals, mp 28.5 °C. By contrast, the dimethylamino analogue, which differs in molecular weight by only two units, is reported to melt at –79 °C,[14] and all other trialkyltin amines are liquids at room temperature.[15,16] An exception is the class of *N*-triorganotin derivatives of heterocycles in which nitrogen atoms are in 1,3 positions in a conjugated ring, as in the imidazole, 1,2,3- and 1,2,4-triazole, benzimidazole, and 1,2,3-benztriazole derivatives,[17-20] in which association in the solid state arises through *inter*molecular coordination by the second nitrogen atom to give a one-dimensional polymer with five-coordinated tin atoms surrounded by planar alkyl groups

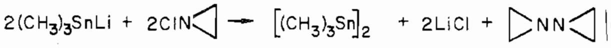


The melting points of the *N*-trimethyl derivatives are 235–280 °C,[17-20] and the Mössbauer quadrupole splitting (QS) values are in the range 2.5–3.0[21,22] vs. only 1.0 mm/s for the open-chain diethylamino derivative.[23] The solid-state association is also reflected in chemical stabilization, so that the *N*-trimethyltin imidazole can be recrystallized from boiling water, and the viscous solutions in organic solvents contain oligomeric species.[20-24]

Colligative property measurements have indicated the monomeric nature of the stannylamines in solution,[15,16,25] but *N*-trimethyltin aziridine is dimeric in benzene by osmometry, and probably more highly associated in the solid state since fragments of higher mass than the dimer are seen in the mass spectrum.

The formulas of the *N*-trimethyltin aziridine, its 2-methyl and 2,2-dimethyl analogues, and homologues containing cyclic imines with ring sizes of three to seven members are listed in Table I together with their adducts. The 1-piperidinyl derivative is known;[25] the remainder of the *N*-trimethyltin imines were synthesized by trans- and lithioamination reactions.

N-Chloroaziridine[26,27] reacted with trimethyltin lithium to give hexamethylditin

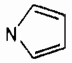

(3)

a reaction similar to that observed for chloroazide.[28] *N*-Bromoaziridine, prepared by a similar procedure[27] from sodium hypobromite and aziridine, decomposed rapidly after distillation and in several cases exploded. Other workers have experienced similar difficulties.[29] *N*-Chloroaziridine also fails to cleave the phenyl group from phenyltrimethyltin, even after prolonged heating at 110 °C.

N-Trimethyltin aziridine undergoes hydrolysis with liquid water to give trimethyltin hydroxide,[30] methanolysis to give trimethyltin methoxide,[31] carbonylation with aqueous carbon dioxide solution to give bis(trimethyltin) carbonate,[32-34] acidic hydrogen cleavage of the tin–nitrogen bond with cyclopentadiene to give trimethyltin cyclopentadiene,[35,36] and transamination with pyrrole to give *N*-trimethyltin pyrrole[19]


(4)

where A = OH, OCH_3, CO_3, C_5H_5, and

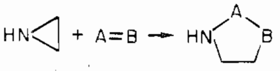


N-Trimethyltin pyrrole, which was also prepared by an alternative method from potassium pyrrole[37] and trimethyltin chloride, proved to be unstable, rapidly darkening, even under vacuum in the absence of light. The action of hydrogen chloride results in ring opening of the aziridine.

Insertion reactions of tin–nitrogen compounds involving unsaturated substrates have been known since 1962[38] and many examples of aminostannolysis have now been worked out.[39]

$$R_3SnNR'_2 + A{=}B \rightarrow R_3SnA{-}BNR'_2 \qquad (5)$$

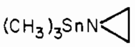
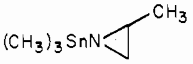
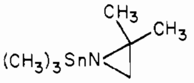
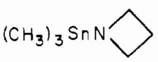
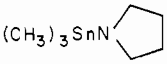
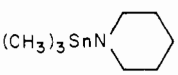
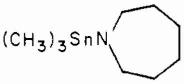
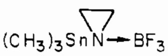
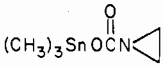
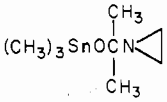
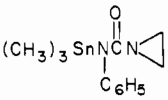
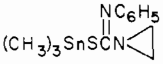
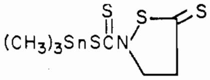
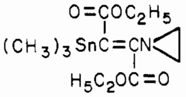
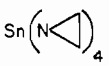
N-Trimethyltin aziridine was subjected to treatment with a selected number of reagents known to react with the dimethylamino analogue[40,41] to provide a comparison. Some of the reagents chosen are also capable of insertion into the aziridine ring, as well[2]


(6)

However, in only one case, that of carbon disulfide, was 2 mol of the insertion reagent consumed. The question of whether the unsaturated substrate had added to the tin–nitrogen bond or to the aziridine ring could be easily answered in the other cases with reference to the characteristic ring breathing mode at ca. 1240 cm^{-1} in the infrared spectrum,[2] which was used to indicate that the aziridine ring system was intact.

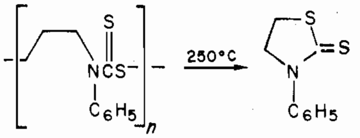
Carbon dioxide brings about the rapid polymerization of aziridine at room temperature,[2] but the *N*-phenyl derivative must be in the form of the quaternary ion in order to take up CO_2.[42] With carbon disulfide, a copolymer forms which can

Table I. Tin-119m Mössbauer Parameters for N-Trimethyltin Cyclic Imines and Adducts[a]

Compd	No.	IS[b]	QS[c]	Γ_1[b]	Γ_2[b]
	I	1.21 1.20[d]	2.27 2.35[d]	1.38 0.84	1.39 1.17
	II	1.17	1.43	1.16	1.29
	III	1.18	1.04	1.06	1.06
	IV	1.23	1.35	1.16	1.19
	V	1.24	0.91	1.12	1.02
	VI	1.19	0.86	0.75	1.01
	VII	1.19	1.05	1.25	1.04
$(CH_3)_3SnN(CH_3)_2$	VIII	1.29	0.81	1.02	1.02
$(CH_3)_3SnN(C_2H_5)_2$[e]	IX	1.25	0.92	1.19	1.29
	X	1.28	3.03	1.33	1.46
	XI	1.31	3.26	1.37	1.41
	XII	1.21	2.22	1.44	1.16
	XIII	1.33	2.69	1.05	1.10
	XIV	1.28	2.04	1.05	1.11
	XV	1.28	3.32	1.21	1.27
	XVI	1.23	2.38	1.09	1.75
$(CH_3)_3SnOCH_3$	XVII	1.23	3.04	1.28	1.32
$[(CH_3)_3Sn]_2CO_3$[f]	XVIII	1.20[f]	3.00[f]	0.87	1.04
$(CH_3)_3SnN{=}S{=}NSn(CH_3)_3$	XIX	1.23	2.39	1.16	1.44
	XX	0.50	0	1.66	

[a] Recorded at 77 K vs. a $Ba^{119m}SnO_3$ (New England Nuclear Corp.) source at ambient temperature by published techniques.[77] [b] ±0.06 mm/s. [c] ±0.12 mm/s. [d] Frozen solution 33% v/v in n-butylbenzene. [e] From ref 23. [f] Listed as 1.34 ± 0.06 and 3.05 ± 0.12 mm/s vs. $Ba^{119m}SnO_3$ in ref 34.

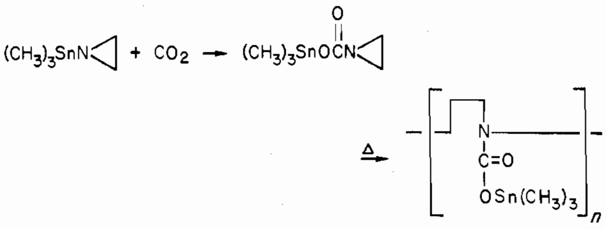
be thermally depolymerized to the 3-phenylthiazolid-2-one[42]



(7)

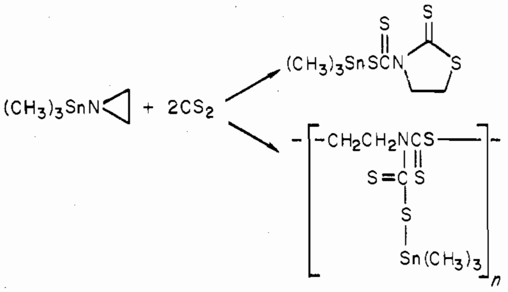
Aminostannylation of carbon dioxide and disulfide is effected under mild conditions to give the carbamato- and dithiocarbamatoorganostannanes. The former contains planar trimethyltin groups in the solid as shown by the absence of the $\nu_{sym}(Sn—CH_3)$ in the infrared spectrum and bidentate carbamato groups as shown by the lowered $\nu(C{=}O)$.[40] In the sulfur analogue, by contrast, both ν_{asym} and ν_{sym} tin–carbon stretching frequencies are present, and a monomeric, *intra*molecularly coordinated structure was postulated.

N-Trimethyltin aziridine takes up carbon dioxide and carbon disulfide in exothermic reactions to give solids which melt with decomposition. Carbon dioxide reacts in a 1:1 mole ratio, and the aziridine ring is preserved in the product (eq 8), but heating



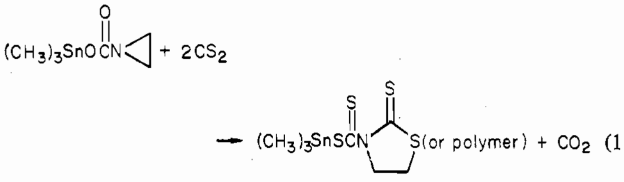
(8)

to 105 °C gives a thermosetting polymer; 2 mol of CS_2 reacts to give the thiazolidone or a ring-opened polymer (eq 9). The



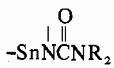
(9)

greater affinity of tin for sulfur is shown by the conversion of the CO_2 adduct by CS_2 (eq 10).



(10)

Isocyanates and isothiocyanates insert into the aziridine ring to give the corresponding 2-amino-2-oxazolines and 2-amino-2-thiazolines but only when the aziridine is in the form of the quaternary ion.[2] Aminostannylation of phenyl isocyanate and isothiocyanate occurs exothermically under mild conditions to give the ureido- and thioureidostannanes. In the absence of crystallographic data, the structural problem remains unsolved, but it is likely that the oxygen-containing derivative takes the

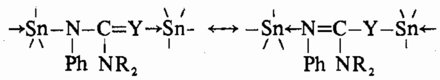


$$-\mathrm{Sn}\overset{|}{\mathrm{N}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{NR_2}$$

ureido form, while the isothiocyanate product contains a tin–sulfur bond

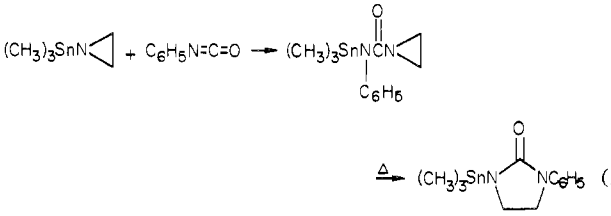
$$-\mathrm{SnS}\overset{\mathrm{N^-}}{\overset{\|}{\mathrm{C}}}\mathrm{NR_2}$$

Interconversion of the two forms through *inter*molecular association complicates the analysis[43]



$$\rightarrow\mathrm{Sn{-}\underset{Ph}{N}{-}\underset{NR_2}{C}{=}Y{\rightarrow}Sn{-}} \longleftrightarrow \mathrm{{-}Sn{\leftarrow}\underset{Ph}{N}{=}\underset{NR_2}{C}{-}Y{-}Sn{\leftarrow}} \qquad (11)$$

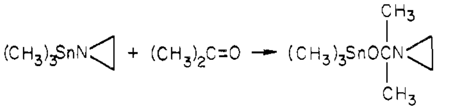
N-Trimethyltin aziridine forms 1:1 adducts with both phenyl isocyanate and isothiocyanate, in reactions preserving the ring. The liquid, sulfur-containing adduct decomposes on attempted distillation as its dimethylamino analogue,[40] but slow sublimation of the solid phenyl isocyanate adduct at 112 °C (0.02 Torr) gives a low-melting (60–62 °C) solid in which the aziridine ring has been expanded (eq 12). An analogous



(12)

imidazolidin-2-one has been produced by the thermolysis of the phenyl isocyanate insertion product of trimethylsilylaziridine at 140 °C.[9]

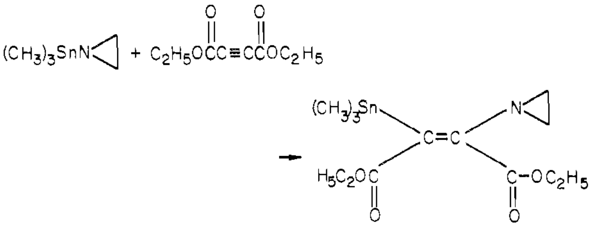
The acetone adducts of both triethylgermyl-[5] and trimethylstannyldimethylamine[44] are unstable, forming the bis(trialkylelement) oxide and liberating dimethylisopropenylamine in the former and dimethylamine and mesityl oxide in the latter case. The acetone insertion product of triethylgermylaziridine is, however, stable. *N*-Trimethyltin aziridine forms a colorless liquid adduct with acetone which is distillable at 63–64 °C under reduced pressure and contains the intact aziridine ring



(13)

No decomposition products as formed in the acetone reactions with the open-chain amine derivatives[5,44] were detected.

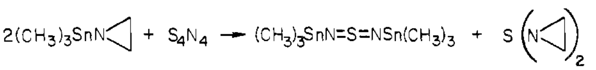
Aziridines undergo a ring-opening reaction involving cleavage of the carbon–carbon bond with substituted acetylenes to give mixtures of products depending on the substituents.[2] Aminostannolysis of disubstituted acetylenes results in the 1,2-insertion product in cases where powerfully electron-withdrawing groups are present.[41] *N*-Trimethyltin aziridine adds diethyl acetylenedicarboxylate under mild conditions to give a 1:1 adduct which has cis geometry, by analogy (vide supra) to the product from the open-chain, dimethylamino derivative[41] (see eq 14). The initial step in the mechanism



(14)

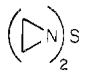
of formation has been postulated to be nucleophilic attack at an acetylenic carbon by the imine nitrogen.[41]

Trimethyl(1-aziridinyl)stannane reacts with tetrasulfur tetranitride to give the yellow, solid *N*,*N*′-bis(trimethylstannyl)sulfur diimide, $(CH_3)_3SnN{=}S{=}NSn(CH_3)_3$ (XIX), in moderate yield in a reaction analogous to that observed for trimethyl(dimethylamino)stannane[46]

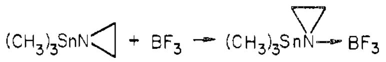


(15)

Identification was made by comparing the ^1H NMR and infrared spectra and melting point of the present preparation to the values observed for an authentic sample. The melting point of both samples proved to be near 61 °C in contrast to the published value[45] of 69–71 °C, but the ^1H NMR spectrum shows the trimethyltin protons in both preparations at 0.32 ppm with $|^2J(^{119}Sn{-}C^1H)| = 58.5$ Hz in complete agreement with ref 45 and the infrared spectrum shows $\nu(N{=}S{=}N)$, asymmetric at 1175 cm^{-1} and symmetric at 1060 cm^{-1}, as previously reported.[45] Mössbauer data on the authentic sample show IS = 1.23 ± 0.06 mm/s and QS = 2.39 ± 0.12 mm/s. A red, viscous liquid was isolated whose infrared spectrum shows a strong band at 1259 cm^{-1} which presumably is the symmetrical ring breathing mode in



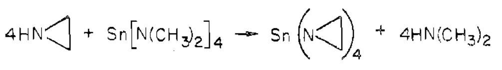
The basicity of the group 4 amines has been much discussed in terms of $(p{\rightarrow}d)\pi$ bonding from spectroscopic studies, but little evidence is available from chemical investigations. *N*-Trimethyltin aziridine removes boron trifluoride from its etherate to form a 1:1 adduct



(16)

The solid adduct does not react with refluxing triethylamine, but undergoes hydrolysis to liberate aziridine which is found as the BF_3 adduct and gives trimethyltin hydroxide. The analogous aziridine–borane is known.[46]

Tetrakis(dimethylamino)tin undergoes transamination with excess aziridine to liberate dimethylamine and precipitate the tetrakis(1-aziridinyl)tin

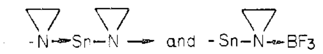


(17)

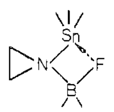
Tin-119m Mössbauer Data. Mössbauer QS values for the open-chain amine and cyclic imine derivatives with ring sizes greater than four, listed in Table I, are in the 0.8–1.1-mm/s range, while the *N*-trimethyltin aziridine exhibits a QS value well over 2.0 mm/s. The substitution of a methyl group on the aziridine ring or increasing the ring size to four reduces the QS to an intermediate value. 2,2-Dimethyl substitution further reduces the QS value to within the 0.8–1.1-mm/s range.

This behavior can have at least two possible interpretations: (i) strong polarization of the electric field at tin by the three-membered aziridine ring and (ii) solid-state association through *inter*molecular nitrogen bridging to form a one-dimensional polymer. Both effects would be expected to fall off with either alkyl substitution on the aziridine ring or an increase in ring size, but the mass spectral evidence discussed below indicates that some weak association is present in all of the *N*-trimethyltin imines studied, and I is a dimer in benzene as shown by osmometry.

The QS value of *N*-trimethyltin aziridine is much increased on adduct formation with BF_3. There is no reason to doubt that the adduct molecules exist as separate units in the solid. Thus, the increase of 1 mm/s arises between the structural units

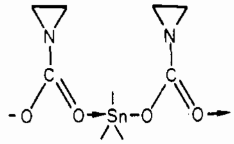


The dipole moment of the aziridine–borane adduct has been determined to be 4.45 ± 0.01 D,[46] and the electric field gradient at tin must then presumably have its origin in the single, strongly polar tin–nitrogen bond present in the BF_3 adduct, as opposed to the five-coordinated, distorted axial trigonal-bipyramidal arrangement in solid *N*-trimethyltin aziridine itself. An alternative explanation for the magnitude of the QS would involve *intra*molecular association between fluorine and tin

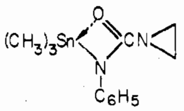


which would raise the coordination number at tin to 5. Similar suggestions of *intra*molecular fluorine–tin coordination have been discussed for (perfluoroethyl)trimethyltin[47] and (*o*-(perfluoroethyl)phenyl)trimethyltin.[47,48] No other Lewis acid adducts of organotin amines have been reported.[15,16]

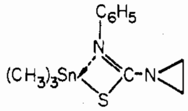
The QS data for the other adducts of the organotin amines are more easily interpreted. The QS values are in the range 2.0–3.32 mm/s for the products in which tin is bonded to oxygen, sulfur, or nitrogen. These compounds may contain tin in a higher coordinated state, and if so, they can adopt an *intra*molecularly coordinated cis or an *inter*molecularly coordinated trans configuration in the solid state. Model compounds of each type, for which structural[49] and Mössbauer data[50] are available, show that derivatives with cis or equatorial configurations have QS values of ca. 2 mm/s,[51] while the trans or axial configuration gives rise to QS values of greater than 3 mm/s.[20] The QS values of the carbon dioxide (3.26 mm/s) and carbon disulfide (3.32 mm/s) insertion products suggest the axial trigonal-bipyramidal, associated structure



The phenyl isocyanate and isothiocyanate adducts, on the other hand, have QS values of 2.69 and 2.04 mm/s, respectively. The analogous triphenyltin *N*-phenyl-*N*-benzoylhydroxylamine has been shown by infrared[51] and x-ray crystallographic[52] studies to be *intra*molecularly coordinated through the carbonyl group. The isocyanate adducts may enjoy weak *intra*molecular coordination through the carbonyl group

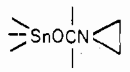


or, in the case of the isothiocyanate, through the imido system



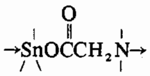
The latter is much more difficult to decide since the infrared evidence (vide infra) is less certain here and because the rather small QS value does not serve to distinguish among the possible coordination numbers at tin. The QS of triethyltin thiobutoxide (1.80 mm/s) is raised to only 1.94 mm/s in pyridine solution, for example, where the tin is presumably higher coordinated, while that of triethyltin thiophenol (2.07 mm/s) becomes 2.85 mm/s.[53]

The acetone insertion product has the backbone structure



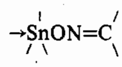
$$\geq SnO\overset{|}{\underset{|}{C}}N\lhd$$

which gives rise to a QS value of 2.22 mm/s. Previous studies have been conducted on trimethyltin glycinate (3.14 mm/s)[54,55]



$$\rightarrow\overset{|}{\underset{/\ \backslash}{Sn}}O\overset{\overset{O}{\|}}{C}CH_2\overset{|}{\underset{|}{N}}\rightarrow$$

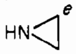
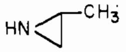
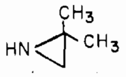
and *o*-trimethyltin cyclohexanone oxime (2.93 mm/s)[56]



$$\rightarrow\overset{|}{\underset{/\ \backslash}{Sn}}ON{=}C\genfrac{}{}{0pt}{}{/}{\backslash}$$

both of which are five-coordinated in the solid state, the former through nitrogen and the latter through oxygen bridges, while our acetone adduct is a liquid. The QS value of only 2.22 mm/s suggests a four-coordinated structure, especially in comparison with trimethyltin methoxide which exhibits a QS of over 3 mm/s (see Table I).

Table II. Proton Chemical Shifts and Coupling Constants for the *N*-Trimethyltin Aziridines and Other Cyclic Imines and Their Adducts

Compd[a]	$\|^2J(^{119}Sn-C-^1H)\|$[b]	$\delta(Sn(C^1H_3)_3)$[c]	$\delta(N-CH_2)$[c]	Solvent
I[d]	56.6	0.08	1.68	10% w/v benzene
II	56.0	0.14	0.16 or 1.24	20% v/v benzene
III	54.8	0.16	2.96	50% v/v benzene-d_6
IV	55.8	0.14	3.81	10% v/v benzene-d_6
V	56.0	0.13	3.00	20% v/v benzene
VI	54.4	0.12	2.91	50% v/v benzene-d_6
VII	56.4	0.11	3.05	Neat
XII	57.8	0.22	1.41	10% v/v benzene
XIII	55.8	0.27	1.72	Satd in benzene-d_6
XIV	54.2	0.35	1.72	Neat
XVI	55.8	0.28	1.92	50% v/v benzene-d_6
XVII	56.6	0.32		22% w/v CCl_4
 HN [e]			1.62	*e*
 HN, CH_3			1.00 or 1.07	Neat
 HN, CH_3, CH_3			2.53	Neat
XIX	58.5	0.32		*f*

[a] Compound number designation given in Table I. [b] ±0.2 Hz. [c] ±0.01 ppm. [d] Listed as 55.2 Hz for $|^2J(^{119/117}Sn-C-^1H)|$ and 0.11 ppm for δ in ref 3. [e] From ref 2 for a dilute solution in $CDCl_3$ 1.37 ppm is given for the neat liquid. [f] See ref 45.

The lack of resolvable QS for the diethyl acetylenedicarboxylate adduct is expected from known behavior of triorganotin vinyl systems[50] and serves to rule out a structure in which carbonyl or ester oxygens are coordinated to tin.

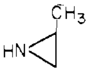
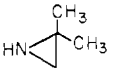
The near-zero isomer shift (IS) and lack of resolvable QS is expected for the tetrakis(1-aziridinyl)tin, but the rather large line width indicates departure from tetrahedral coordination or from perfect octahedral symmetry in an associated lattice. The room-temperature Mössbauer spectrum suggests an associated solid and the IS value reflects an electronic environment similar to that in tin(IV) oxide.[50]

NMR Data. Chemical Shifts. The methylene bridge protons of *N*-trimethyltin aziridine and the 2,2-dimethylaziridinyl analogue give rise to single, sharp resonances at ambient temperature indicating rapid inversion about the pyramidal nitrogen atoms in solution. The methylene bridge portions of the spectra of the higher imine homologues are complex multiplets owing to mutual coupling. The proton data are tabulated in Table II.

The carbon-13 data are tabulated in Table III. The $N-CH_2$ ring carbon resonances in the tin derivatives do not change appreciably from those in the parent aziridines. The assignments of the ring carbons in the methyl derivatives were made on the basis of the data for the parent aziridines and upon expected intensity ratios for the secondary and tertiary carbon atoms. The methyltin carbon chemical shifts are similar to those previously reported for other trimethyltin derivatives.[54]

Coupling Constants. Two-bond $|^2J(^{119}Sn-C-^1H)|$ coupling constants in methyltin derivatives have been applied extensively as a probe to the structure of these species in solution. The tin–proton couplings listed in Table II lie in the range 54.8–56.6 Hz for the *N*-trimethyltin aziridines and higher cyclic amines, the highest named being for *N*-trimethyltin aziridine itself. The magnitude of $|^2J(^{119}Sn-C-^1H)|$ in the dimethylamino analogue is 55.3 Hz.[58] The one-bond $|^1J(^{119}Sn-^{13}C)|$ values fall in the range 372.0–382.2 Hz for the

Table III. Carbon-13 Chemical Shifts and Coupling Constants for the *N*-Trimethyltin Aziridines and Other Cyclic Imines[a]

Compd	$\|^1J(^{119}\mathrm{Sn}-^{13}\mathrm{C})\|^b$	$\delta(\mathrm{Sn^{13}CH_3})^c$	$\delta(\mathrm{N^{13}CH_2})^c$	$\delta(\mathrm{NC^{13}CH_2})^c$	$\delta(\mathrm{NC_2{}^{13}CH_2})^c$	$\|^2J(^{119}\mathrm{Sn}-\mathrm{N}-\mathrm{C})\|^b$	$\|^3J(^{119}\mathrm{Sn}-\mathrm{N}-\mathrm{C}-^{13}\mathrm{C})\|^b$
I	374.4	−8.2	21.0				
II	372.0	−6.6	21.5[d]				
III	378.0	−7.2	40.7[e]				
IV	382.0	−8.3	54.2	25.7			
V	380.8	−8.5	51.2	26.6			
VI	378.6	−8.2	52.1	29.6	26.3	10.0	25.8
VII	382.2	−7.3	54.5	34.7	27.4	10.6	16.2
VIII	381.2	−8.7	43.4				
XIII[f]	372.1	−4.0	27.0				
XVII	398.0	−5.9	52.8[g]				
$\mathrm{CH_3N}$			28.7[h]				
$\mathrm{C_6H_5N}$			25.7[h]				
			19.5[i]				
			36.6[j]				

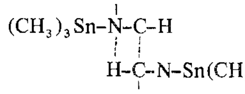
[a] Values determined vs. TMS in 50% v/v solution in benzene-d_6 except XIII and XVII which were measured in saturated $\mathrm{CDCl_3}$ solution. [b] ±0.7 Hz. [c] ±0.1 ppm. [d] The remaining two resonances at 27.9 and 29.2 ppm cannot be assigned with certainty. [e] The remaining resonances centered near 56.5 ppm cannot be assigned with certainty. [f] Additional assignments for this compound include the carbonyl resonance at 149.8 ppm and the aromatic ring C_1, C_2, C_3, and C_4 resonances at 142.5, 128.2, 127.2 and 124.7 ppm, respectively. [g] $\mathrm{O^{13}CH_3}$. [h] From ref 2. [i] The 2-methyl and remaining ring carbon resonances are centered near 25.6 ppm. [j] The 2-methyl carbon resonance is at 52.0 ppm and the remaining ring carbon resonance is at 56.0 ppm.

same set of seven compounds and are similar to the value in trimethyltin bromide (380 ± 2 Hz)[59] which is not altogether unexpected.

No tin satellites were observed on the singlet methylene bridge proton resonance of *N*-trimethyltin aziridine at temperatures down to −50 °C. Similarly no tin satellites were found on the *N*-methyl proton resonance of the neat dimethylamine analogue to −50 °C or on the corresponding carbon-13 resonances at ambient temperature in concentrated solution. The $|^3J(^{119}\mathrm{Sn}-\mathrm{N}-\mathrm{C}-^1\mathrm{H})|$ couplings are present, however, in ambient-temperature proton spectra of the diethylamino derivatives, and the tin-117 and tin-119 satellites of the *N*-methyl proton resonance in triethyltin dimethylamine coalesce at 90 °C and are no longer detected at 130 °C. These and other observations of temperature-variable proton spectra were used to postulate a bimolecular exchange of amino groups involving the breaking of the Sn–N bond in the neat aminostannane liquids and the consequent decoupling of the $|^3J(^{119}\mathrm{Sn}-\mathrm{N}-\mathrm{C}-^1\mathrm{H})|$.[60] Likewise, in this case, it is possible to ascribe the absence of proton– and carbon–tin couplings through the nitrogen linkage to exchange processes.

Examination of Table III reveals that the two-bond $|^2J(^{119}\mathrm{Sn}-\mathrm{N}-^{13}\mathrm{C})|$ couplings are resolved only in ring derivatives containing greater than five members. These couplings are also observed in the straight-chain di-*n*-butyl derivative,[61] and two-bond $|^2J(^{119}\mathrm{Sn}-\mathrm{N}-^{29}\mathrm{Si})|$ coupling has been observed in bis[*N*,*N*-bis(trimethylsilyl)amino]tin(II)[62] in which bulky groups are also present.

Recently, however, van den Berghe and van der Kelen[58] have detected the proton $|^3J(^{119}\mathrm{Sn}-\mathrm{N}-\mathrm{C}-^1\mathrm{H})|$ couplings in dilute solutions of the dimethylaminostannanes in which the postulated bimolecular exchange processes[60] would be expected to be slowed, but these workers rejected the exchange postulate in favor of one involving line broadening arising from interaction of the observed proton with the quadrupolar nitrogen-15. The interaction was said to take place *inter*molecularly, through hydrogen bridges in concentrated solution



$$\begin{array}{l} (\mathrm{CH_3})_3\mathrm{Sn}{-}\overset{|}{\mathrm{N}}{-}\mathrm{C}{-}\mathrm{H} \\ \qquad\qquad\;\vdots\;\;\;\vdots \\ \qquad\qquad\mathrm{H}{-}\underset{|}{\mathrm{C}}{-}\mathrm{N}{-}\mathrm{Sn}(\mathrm{CH_3})_3 \end{array}$$

This hypothesis also calls for association in a bimolecular process, but it replaces the exchange postulate with hydrogen bonding and rationalizes the disappearance of the tin satellites on their being lost in quadrupolar line broadening. The exchange of amino groups at tin is, of course, the basis of the transamination method for synthesizing aminostannanes,[15,16] which is generally thought to proceed through an S_N2 mechanism involving nucleophilic attack at tin.[63] The nitrogen to tin bridging in crystalline trimethyltin glycinate[55] and that suggested for *N*-trimethyltin aziridine by its dimeric nature in benzene, large Mössbauer QS, and basicity sufficient to remove $\mathrm{BF_3}$ from its etherate make the hydrogen-bonding hypothesis[58] untenable. Indeed, the same dependence of the two-bond $|^2J(^{119}\mathrm{Sn}-\mathrm{E}-^{13}\mathrm{C})|$ coupling upon steric bulk is observed in the trimethyltin methyl and ethyl sulfides,[61] but sulfur lacks a quadrupolar isotope in high natural abundance (sulfur-33; $I = {}^3/_2$; 0.76%).

Mass Spectral Data. Tin has the largest number of stable isotopes of any element (10), and tin-bearing fragments are thus easy to identify in the mass spectrum. Mass distributions for polytin species have been worked out,[64] and the number of tin atoms is indicated for each fragment listed in Table IV in which are tabulated the cracking pattern data for the *N*-trimethyltin aziridines and higher cyclic homologues.

Examination of Table IV reveals that ditin fragments of mass above that for the parent molecular ion are found in the spectra of all of the cyclic compounds. The three-membered ring derivatives are thermodynamically less stable than their polymers, but aziridine is polymerized readily only by acids. A second, and probably correct, interpretation involves portions of a nitrogen-bridged, associated solid-state structure that survives transfer to the gas phase. Ditin fragments are similarly observed in the mass spectra of the trialkyltin hydroxides[34] which are known to have an oxygen-bridged solid-state structure.[30]

Parent molecular ion peaks are detected in the spectra of only the *N*-trimethyltin aziridine, 2-methylaziridine, and azetidine derivatives, but all show peaks at *m*/*e* 120 for $\mathrm{Sn^+}$, at *m*/*e* 135 for $\mathrm{SnNH^+}$, and at *m*/*e* 165 for $\mathrm{(CH_3)_3Sn^+}$, $\mathrm{(CH_3)_2SnNH^+}$, or, more interestingly, $\mathrm{CH_3Sn(NH)_2{}^+}$.

The spectrum of *N*-trimethyltin aziridine is the richest above the parent molecular ion (*m*/*e* 207) with 12 ditin peaks, including a weak $\mathrm{Sn_2{}^+}$ (*m*/*e* 238) peak. The molecular ion

Table IV. Mass Spectrometric Data for Tin-Containing Fragments of *N*-Trimethyltin Aziridines and Higher Cyclic Homologues^a

m/e	Ion^f	Rel intens		
		I^c	II^c	III^c
534^b	?	0.03		
491^b	?	0.03		
439^d	$2P + NCH^+$	0.01		
400^d	$2P - CH_2^+$	0.02		
356^d	$[(CH_3)_2SnNCH_3]_2^+$	0.02		
328^d	$[(CH_3)_2SnNH]_2^+$	1.00	1.00	1.00
313^d	$(CH_3)_2Sn(NH)_2SnCH_3^+$	0.01		
298^d	$[CH_3SnNH]_2^+$	0.45	0.46	0.49
283^d	$CH_3Sn(NH)_2Sn^+$	0.02		
268^d	$[SnNH]_2^+$	0.15	0.15	0.31
253^d	Sn_2NH^+	0.13	0.07	0.17
238^d	Sn_2^+	0.02		
235^e	P^+			0.22
220^e	$P - CH_3^+$			0.05
208^e	$P - NCH^+$			0.11
207^e	P^+	0.01		
185^e	?	0.19	0.31	0.23
165^e	$(CH_3)_3Sn^+$, $CH_3Sn(NH)_2^+$, or $(CH_3)_2SnNH^+$	0.31	0.77	0.83
150^e	$Sn(NH)_2^+$	0.08		0.24
135^e	$SnNH^+$	0.11	0.22	0.54
120^e	Sn^+	0.01	0.08	0.18

m/e	Ion^f	Rel intens			
		IV^c	V^c	VI^c	VII^c
328^d	$[(CH_3)_2SnNH]_2^+$	1.00	0.40	0.90	0.08
298^d	$[CH_3SnNH]_2^+$	0.31	0.10	0.30	1.00
268^d	$[SnNH]_2^+$	0.17			0.14
265^d	$[Sn_2NCH]^+$		0.08		
252^d	Sn_2N^+	0.08			
241^e	?			0.46	
229	?		0.13	0.62	0.12
221^e	P^+	0.04			
206^e	$P - CH_3^+$	0.08			
185^e	?	0.26	0.78	0.42	0.34
165^e	$(CH_3)_3Sn^+$, $CH_3Sn(NH)_2^+$, or $(CH_3)_2SnNH^+$	0.91	1.00	1.00	0.65
150^e	$Sn(NH)_2^+$	0.20	0.18	0.24	
135^e	$SnNH^+$	0.37	0.26	0.26	0.20
120^e	Sn^+	0.20	0.09	0.12	0.11

[a] Recorded on an AEI MS-902 mass spectrometer at 70 eV. [b] These fragments contain at least two tin atoms. [c] Compound number designation given in Table I. [d] A fragment which contains two tin atoms. [e] A fragment which contains one tin atom. [f] P = parent ion.

Table V. Infrared Fundamentals and Their Tentative Assignments in Aziridines

Freq, cm^{-1}			
Aziridine^a	2-Methyl-aziridine^b	2,2-Dimethyl-aziridine^b	Assignment
3338	3243 s, br	3295 s, br	ν(N-H)
3079	Complex	Complex	$\nu_{asym}(CH_2)$
3015	region	region	$\nu_{sym}(CH_2)$
1481.5	1456 s	1478	$\delta(CH_2)$
1462.5	1409 s	1451	$\delta(CH_2)$
1268	~1280 w, sh	1296 w, sh	CH_2 twist
1237	1248 s, br	1284 m	δ(NH)
1210.5	1221 m	1259 m	Ring breathing
1131	1141 m–w	1156 s	CH_2 wag
~1095	1096 s	1124 s	CH_2 twist
1089.5	1072 m, sh	1112 s	CH_2 wag
997.5	1025 m, br	~1044 m, br	δ(NH)
903	952 s	1019 m	Asym ring def
856	879 w	888 m, br, sh	Sym ring def
(~817)^c	826 vs	~780 vs, vbr^d	CH_2 rock
772.5	753 m	~780 vs, vbr	CH_2 rock

[a] Vapor phase–from ref 66. [b] Liquid film. [c] Band not observed; deduced from arguments in ref 66. [d] Band not resolved.

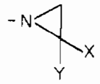
of the dimer is not seen, but three fragments with greater mass are detected, presumably portions of the oligomeric or polymeric structure of the solid. Observation of three fragments with masses above that of the dimer implies that *N*-trimethyltin aziridine is more highly associated than the dimer in the solid, although this is the predominant form in solution from osmometry. Several fragments with masses between those of the monomer and dimer can be rationalized easily on the basis of nitrogen-bridge, cyclic ditin species. These include $[(CH_3)_2SnNCH_3]_2^+$ (m/e 356; intensity 2%), $[(CH_3)_2SnNH]_2^+$ (328; 100%), $(CH_3)_2Sn(NH)_2SnCH_3^+$ (313; 1%), $[CH_3SnNH]_2^+$ (298; 45%), $(CH_3Sn)_2NH^+$ (283; 2%), $[SnNH]_2^+$ (298; 45%), $(CH_3Sn)_2NH^+$ (283; 2%), and $[SnNH]_2^+$ (268; 15%). The noncyclic Sn_2NH^+ (254; 13%) must derive similarly.

The m/e 328 peak is not only the most prominent for the parent tin aziridine but in the spectra of the two methyl-substituted aziridines and the azetidine as well. These spectra are less rich than that of the parent compound in ditin peaks above the mass of the parent molecular ion, but the four symmetrical, nitrogen-bridged fragments mentioned above—$[(CH_3)_2SnNH]_2^+$ (328), $[CH_3SnNH]_2^+$ (298), $[SnNH]_2^+$ (268), and Sn_2NH^+ (253)—appear in each, except that the last named appears as Sn_2N^+ (252; 8%) in the spectrum of the azetidine derivative.

The spectra of the three remaining cyclic amine derivatives contain the $[(CH_3)_2SnNH]_2^+$ (328) and $[CH_3SnNH]_2^+$ (298) peaks only, but the intensities are somewhat reduced although the m/e 328 peak is 90% in the six-membered and the m/e 298 peak is 100% in the seven-membered ring.

An additional monotin peak at m/e 185 which appears in all spectra could not be assigned.

Infrared Data. The assignments of the spectra of trimethyl(1-aziridinyl)stannanes can be approached by considering the molecules to consist of two separate parts, i.e., the $(CH_3)_3Sn–N$ framework and the



system. The overall spectra should be a superimposition of the spectra of these two units. Among the lowest frequencies in the far-infrared region are those belonging to the $–Sn(CH_3)_3$ deformation and rocking modes, but these fall near 150 cm^{-1} [65] and were not recorded in this study. The remaining low-frequency vibrations of the $–Sn(CH_3)_3$ group are the symmetric and asymmetric $Sn–CH_3$ stretches which are found near 510 and 530 cm^{-1}, respectively. The arrangement of the heavy atoms of the $–Sn(CH_3)_3$ skeleton can be deduced from these modes since a trigonal-planar $–SnC_3$ structure (local D_{3h} symmetry) will give rise to an infrared-active $\nu_{asym}(Sn–C)$ but infrared-inactive $\nu_{sym}(Sn–C)$. In cases in which there are significant deviations from planarity (local C_{3v} symmetry), the ν_{sym} absorption is also generally much less intense, since the dipole change is much less in symmetric stretching.

The infrared spectrum of aziridine itself has been carefully assigned,[66,67] and the spectrum of the *N*-trimethylsilyl derivative has been assigned by analogy.[68] The infrared spectrum of *N*-triethylsilylaziridine is shown in ref 8a but is not assigned there. The symmetry of aziridine is quite low (C_s), and all 18 fundamentals are infrared active. The spectra of the tin derivatives are dominated by the characteristic, moderately intense, symmetric ring breathing mode at ca. 1240 cm^{-1}, which can, along with the asymmetric and symmetric ring deformation modes at ca. 905 and 880 cm^{-1}, respectively, be used as a convenient, diagnostic probe for the presence of the aziridine ring. The infrared band assignments in aziridine itself[66,67] are shown in Table V as well as the infrared bands observed for the 2-methyl and 2,2-dimethyl derivatives. Shown

Table VI. Infrared Absorptions ($\mathrm{cm^{-1}}$) and Partial Assignments of *N*-Trimethyltin Aziridines

Assignment	I[a]	II[a]	III[a]
$\nu_{\mathrm{asym}}(\mathrm{CH_2})$	2976 vs	2976 vs	2889 m
$\nu_{\mathrm{sym}}(\mathrm{CH_2})$	2912 m, sh	2912 vs	2916 s, br
$\nu(\mathrm{CH_3})$	2880 s	2897 s	2813 s, br
		1725 w	1718 w
	1688 vw	1700 w	
	1639 vw	1522 w, sh	
$\delta(\mathrm{CH_2})$	1477 ms	1470 ms	1461 m
$\delta(\mathrm{CH_2})$		1456 ms	1443 m
		1445 vw	1420 w, sh
		1396 s	
	1378 w	1364 m	1343 m
		1262 w, sh	1289 w
Sym ring breathing	1237 s	1242 s	1194 s
$\delta(\mathrm{CH_3})$	1189 ms	1191 s	1150 w, sh
$\mathrm{CH_2}$ wag	1130 w	1131 ms	1107 s
$\mathrm{CH_2}$ twist	1096 m	1094 ms	1048 m
$\mathrm{CH_2}$ wag	1065 m	1070 ms	
		977 vs	989 w, sh
Asym ring def	908 s	895 s	961 ms
Sym ring def	884 s	859 s	876 w, sh
$\mathrm{CH_2}$ rock	770 vs, br	780 vs, br	764 vs, br
$\mathrm{SnCH_3}$ rock	737 s, sh	740 s, sh	740 w, sh
			710 vw, sh
$\nu_{\mathrm{asym}}(\mathrm{Sn{-}C_3})$	534 vs	533 vs	532 vs
$\nu_{\mathrm{sym}}(\mathrm{Sn{-}C_3})$	509 s	510 mw	509 m
	454 m	468 w	480 vvw

[a] Liquid film. Compound number given in Table I.

Table VII. Nujol Mull Spectrum for Compound X in the 1350–400-$\mathrm{cm^{-1}}$ Range

Freq, $\mathrm{cm^{-1}}$	Intens	Assignment
1307	w	
1265	ms, br	
1213	m	Sym ring breathing
1170	m	$\delta(\mathrm{CH_3})$
1152	m, br	$\nu(\mathrm{B{-}N})$
1040–1130	m, vbr	B-F vib
968	m, br	Asym ring def
917	w, sh	Sym ring def
780	s, vbr	$\mathrm{Sn(CH_3)_3}$ def + B-F str
727	s	$\mathrm{CH_2}$ rock
594	m	$\mathrm{SnCH_3}$ rock
558	m	
544	m	$\nu_{\mathrm{asym}}(\mathrm{Sn{-}C_3})$
518	mw	$\nu_{\mathrm{sym}}(\mathrm{Sn{-}C_3})$
483	vw	

Table VIII. Nujol and Halocarbon Mull Spectrum for Compound XI

Freq, $\mathrm{cm^{-1}}$	Intens	Assignment
2984	ms, br	$\nu_{\mathrm{asym}}(\mathrm{CH_2})$
2912	ms, br	$\nu_{\mathrm{sym}}(\mathrm{CH_2})$
1578	s, br	$\nu(\mathrm{C{=}O})$
1464	s, br	$\delta(\mathrm{CH_2})$
1370	m, br, sh	
1274	m	Sym ring breathing
1228	ms	
1190	ms	$\delta(\mathrm{CH_3})$
1156	ms	$\mathrm{CH_2}$ wag
1092	m	$\mathrm{CH_2}$ twist
1030	m	$\mathrm{CH_2}$ wag
~985	s, br	
872	ms	Asym ring def
843	ms	Sym ring def
776	s, br	$\mathrm{CH_2}$ rock
724	vs, br	$\mathrm{SnCH_3}$ rock
627	m	
542	vs, br	$\nu_{\mathrm{asym}}(\mathrm{Sn{-}C_3})$
511	vw, sh	$\nu_{\mathrm{sym}}(\mathrm{Sn{-}C_3})$
449	m	

Table IX. Liquid-Film Spectrum of Compound XII

Freq, $\mathrm{cm^{-1}}$	Intens	Assignment
3062	m	$\nu(\mathrm{CH_3})$
2976	s	$\nu_{\mathrm{asym}}(\mathrm{CH_2})$
2912	m	$\nu_{\mathrm{sym}}(\mathrm{CH_2})$
~1430	w, vbr	$\delta(\mathrm{CH_2})$
1369	m	
1358	s	
1262	m	
1218	s	Sym ring breathing
1190	w, sh	$\delta(\mathrm{SnCH_3})$
1171	m	
1139	ms	$\mathrm{CH_2}$ wag
1088	m	$\mathrm{CH_2}$ twist
987	s	
948	s	Asym ring def
941	vw, sh	
853	s	Sym ring def
780	vs, br	$\mathrm{CH_2}$ rock
735	s	$\mathrm{SnCH_3}$ rock
609	w	
572	vw	
534	vs	$\nu_{\mathrm{asym}}(\mathrm{Sn{-}C_3})$
509	m, sh	$\nu_{\mathrm{sym}}(\mathrm{Sn{-}C_3})$
430	m	

Table X. Saturated Solution Spectra of Compound XIII

Freq, $\mathrm{cm^{-1}}$		
In $\mathrm{CCl_4}$	In benzene	Assignment
3062 s	3065 m	$\nu(\mathrm{CH})_{\mathrm{Ar}}$
3020 s	3017 w, sh	$\nu(\mathrm{CH})_{\mathrm{Ar}}$
2999 s	3001 s	$\nu_{\mathrm{asym}}(\mathrm{CH_2})$
2917 s	2918 s	$\nu_{\mathrm{sym}}(\mathrm{CH_2})$
1715 vs	1716 vs	$\nu(\mathrm{C{=}O})_{\mathrm{ester}}$
1673 s	1676 vs	
1622 vs	1623 vs	
1591 vs	1593 vs	$\nu(\mathrm{C{=}C})_{\mathrm{coord}}$
1542 mw	1547 w	
1523 m	1522 mw	
1497 vs	1499 vs	$\delta(\mathrm{CH_2})$
1419 ms	1421 s, br	
1367 vs	1369 vs	
1330 s	1331 s	
1288 m	1290 m	
1263 m	1265 m	$\nu(\mathrm{C_{Ar}{-}N})$
1218 s	1219 ms	Sym ring breathing
1190 ms	1191 m	$\delta(\mathrm{CH_3})$
1153 m	1156 w	$\mathrm{CH_2}$ wag
1072 m	1073 m	$\mathrm{CH_2}$ wag + $\nu_{\mathrm{asym}}(\mathrm{CNC})$
1025 m	1028 mw	$\delta(\mathrm{CH})_{\mathrm{ar}}$
1002 ms	1001 s	Ring def
983 ms	985 ms	
939 s	940 s	$\nu_{\mathrm{sym}}(\mathrm{CNC})$
899 m	900 mw	Asym ring def
[a]	817 w, sh	Sym ring def
[a]	778 vs, br	$\mathrm{CH_2}$ rock
[a]	740 m, sh	$\mathrm{SnCH_3}$ rock
700 vs	[a]	$\delta(\mathrm{CH})_{\mathrm{Ar}}$
591 s	591 s	
542 s	545 s	$\nu_{\mathrm{asym}}(\mathrm{Sn{-}C_3})$
510 ms	512 ms	$\nu_{\mathrm{sym}}(\mathrm{Sn{-}C_3})$
417 mw	415 m	

[a] Solvent interference.

in Tables VI–XIII are the assignments for *N*-trimethyltin aziridines and their adducts. For the *N*-trimethylsilyl derivative, only three assignments have been reported: the $\nu_{\mathrm{asym}}(\mathrm{CH_2})$ and $\nu_{\mathrm{sym}}(\mathrm{CH_2})$ absorptions which now appear at 2976 and 2912 $\mathrm{cm^{-1}}$, respectively, $\delta(\mathrm{CH_2})$ at 1477 $\mathrm{cm^{-1}}$, and the prominent $\mathrm{CH_2}$ rock which falls at 770 $\mathrm{cm^{-1}}$. The asymmetric and symmetric ring deformations appear as a characteristic, partially resolved doublet at 980 and 884 $\mathrm{cm^{-1}}$.

Infrared studies on the *C*-alkyl-substituted aziridines have concentrated on the NH modes,[69,70] and no assignments are available. The symmetric ring breathing mode appears as a strong band at 1194 $\mathrm{cm^{-1}}$ in the 2,2-dimethyl derivative (III), but the $\delta(\mathrm{CH_3})$ mode, which appears as a sharp absorption

Table XI. Liquid-Film Spectrum of Compound XIV

Freq, cm^{-1}	Intens	Assignment
3072	s	$\nu(CH)_{Ar}$
2994	vs	$\nu(CH_2)$
2917	s	$\nu(CH_2)$
1700	vw, br	Aromatic overtones and combinations
1609	s, sh	$\nu(CC)_{Ar}$ and $\nu(CN)$
1591	vs	$\nu(C{=}N)$
1578	s, sh	$\nu(CC)_{Ar}$
1486	s	$\nu(CN_2)$ and $\delta(CH_2)$
1449	m	$\delta(CH_2)$
1402	s, br	$\delta(CH_3)$
1321	m, sh	$\delta(CH)_{Ar}$ and $\delta(CH_3)$
1304	s	$\delta(CH)_{Ar}$
1265	m, sh	$\nu(C_{Ar}\text{-}N)$
1233	m, sh	
1221	m	Sym ring breathing
1211	m, sh	$\nu_{asym}(NCN)$
1187	w	$\delta(CH_3)$
1150	s, br	CH_2 wag
1098	w, sh	CH_2 twist
1085	vs	CH_2 wag
1072	w, sh	
1023	ms	
954	vw	
930	s	$\nu(Sn\text{-}S)$
902	ms	Asym ring def
867	m	Sym ring def
790	w, sh	
778	w, sh	
764	vs, br	CH_2 rock and $SnCH_3$ rock
696	s	
667	s	
644	w, sh	
593	m	
535	vs	$\nu_{asym}(Sn\text{-}C_3)$
510	s	$\nu_{sym}(Sn\text{-}C_3)$
452	m	

Table XII. Nujol and Halocarbon Mull Spectrum for Compound XV

Freq, cm^{-1}	Intens	Assignment
2990	s, br	$\nu_{asym}(CH_2)$
2921	s, br	$\nu_{sym}(CH_2)$
2815	s, br	$\nu(CH_3)$
1569	ms, br	$\nu(S_2C\text{-}N)$
1557	ms, br, sh	$\nu(S_2C\text{-}N)$
1475	s, br	$\delta(CH_2)$
1428	m, sh	
1378	m, br	
1310	m, sh	
1268	mw	
1188	ms	$\delta(CH_3)$
1152	m	$\nu_{asym}(CS_2)$
1071	m	CH_2 twist
1028	m	CH_2 wag
977	ms	$\nu_{sym}(CS_2)$
924	m	$\nu(Sn\text{-}S)$
~780	vs, vb	CH_2 rock
728	m, sh	$SnCH_3$ rock
544	vs, br	$\nu_{asym}(Sn\text{-}C_3)$
515	m, sh	$\nu_{sym}(Sn\text{-}C_3)$

at 1189 cm^{-1} in the parent tin aziridine, must also be accounted for. Two strong absorptions appear in this region in the 2-methyl derivative (II), and it is not possible to assign the symmetric ring breathing mode with confidence.

All three *N*-trimethyltin aziridines exhibit very strong ν_{asym}(Sn–C) and strong to medium ν_{sym}(Sn–C) absorptions, as do all of the cyclic aminostannanes studied. These data rule out a precisely planar trimethyltin group in the phase studied. The spectrum of *N*-trimethyltin aziridine itself (I), mp 28.5 °C, was recorded in 15% solution in hexane, as a liquid smear, and in a Nujol mull and KBr pellet and proved nearly identical in all cases. Osmometry has established that in benzene trimethyl(1-aziridinyl)stannane exists as a dimer, and Mössbauer studies in 33% frozen *n*-butylbenzene also indicate association in solution.

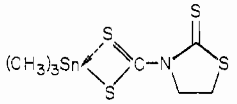
Table XIII. Liquid-Film Spectrum of Compound XVI

Freq, cm^{-1}	Intens	Assignment
3004	s	$\nu(CH_3)$
~2950	m, br	$\nu(CH_2)$
1738	vs	$\nu_{asym}(C{=}O)$
1714	m, sh	$\nu_{sym}(C{=}O)$
1608	s	$\nu(C{=}C)$
1592	w, sh	$\nu(C{=}C)$
1471	m	$\delta(CH_2)$
1448	m	$\delta(CH_2)$
1373	m	
1327	m, sh	
1260	vs, br	Sym ring breathing
1215	m, sh	
1158	m	CH_2 wag
1112	m, br	CH_2 twist
1040	s	
~860	m, br	Sym ring def
791	s	
770	w, sh	CH_2 rock
532	s	$\nu_{asym}(Sn\text{-}C_3)$
516	w	$\nu_{sym}(Sn\text{-}C_3)$

The spectrum of the *N*-trimethyltin aziridine–boron trifluoride complex (X), contains the symmetrical ring breathing mode at 1213 cm^{-1} and the asymmetric and symmetric ring deformations at 968 and 917 cm^{-1}, respectively, showing that the ring is intact. Boron trifluoride would be expected to catalyze the polymerization of aziridines,[28] but in this case, the reaction stops at the complexation step. The ν(B–N) stretching mode is generally assigned in the 1100–1250-cm^{-1} region and should show the isotopomeric doublet structure expected for a vibration involving motion of the boron-10 and boron-11 atoms. A broad absorption is seen at 1130–1040 cm^{-1} and another centered at 1152 cm^{-1}. It is possible to assign a high-frequency, sharp absorption to the tin–methyl group deformation at 1170 cm^{-1} and the ν_{asym}(Sn–C) and ν_{sym}(Sn–C) to 544 and 518 cm^{-1}, respectively, in this presumably tetrahedral tin compound. The ν(B–N) absorption is found at 1112 cm^{-1} in the solid pyridine adduct and at 1249 cm^{-1} in the trimethylamine adduct in solution[71] and is assigned here as the 1152-cm^{-1} band with the ν(B–F) vibrations under the broad envelope at 1130–1140 cm^{-1}.

The spectrum of the CO_2 adduct of *N*-trimethyltin aziridine (XI) contains the symmetrical ring breathing mode at 1274 cm^{-1} and asymmetric and symmetric ring deformations at 872 and 843 cm^{-1}, respectively. The question of association in the solid state can be addressed with reference to the C=O stretching frequencies which can help to distinguish coordinated from free carbonyl groups.[54] Carboxylate groups in organotin structures generally adopt a bridged structure in the solid state unless the organic groups at tin are bulky or the carboxylate group is branched at the α carbon.[49] Trimethylsilyl acetate, on the other hand, possesses a normal ester structure in which the carbonyl stretching frequency occurs at 1725 cm^{-1}. The corresponding absorption at 1576 cm^{-1} in trimethyltin acetate[72] is typical of the associated tin carboxylates, and the x-ray structure of the tribenzyltin acetate,[73] in which the absorption is at 1565 cm^{-1},[74] confirms the bridged arrangement of the carboxylate group, whereas the corresponding infrared absorption in tricyclohexyltin acetate is at 1645 cm^{-1} and the structure as revealed by x-ray study is more ambiguous.[74] The CO_2 insertion product (XI) has a high melting point (101–102 °C) like the tribenzyltin acetate (112–113 °C)[73] and the adduct from the analogous dimethylamino derivative[40] and like the latter exhibits a severely lowered ν(C=O) (1578 cm^{-1} for XI vs. 1555 cm^{-1}).[40] On this basis, we assign a one-dimensional, bridged acetate structure incorporating an axially most electronegative, trigonal-bipyramidal arrangement at tin, but the appearance of a very weak shoulder at 511 cm^{-1}, which is assigned to ν_{sym}(Sn–C), rules out precisely planar trimethyltin groups.

The spectrum of the CS_2 adduct (XV), by contrast, lacks the symmetric ring breathing and asymmetric and symmetric ring deformation modes. It is possible to account for several of the bands which do appear as the $\nu_{asym}(S_2C)$ and $\nu_{sym}(S_2C)$ modes at 1152 and 977 cm^{-1}, but the second $\nu(S_2C–N)$ arising from the group in the expanded aziridine ring also gives rise to a broad absorption at 1569 cm^{-1}. *Intra*molecular sulfur→tin coordination is most likely occurring through a chelated SnS_2C structure



as in the corresponding dimethylamino adduct of CS_2, but in this case the thiocarbonyl group in the ring is also available for additional *inter*molecular coordination to tin reflected in the insolubility of the adduct.

The spectrum of the phenyl isocyanate insertion product (XIII) is complicated by the addition of the phenyl group absorption, but the symmetric ring breathing mode can be assigned at 1218 cm^{-1} and the asymmetric and symmetric ring deformations at 902 and 821 cm^{-1}, respectively. Both ν_{asym}(Sn–C) and ν_{sym}(Sn–C) are observed at 539 and 511 cm^{-1}, respectively, ruling out precisely planar trimethyltin groups. The other absorption of interest is the ureido ν(C=O). By analogy with the corresponding dimethylamino–phenyl isocyanate adduct,[40] it is straightforward to assign the carbonyl stretching modes in this substituted urea to strong bands at 1715, 1673, and 1628 cm^{-1}, the first observed in the Nujol mull and the latter two in CCl_4 solution. As in the dimethylamino analogue,[40] the principal form is probably that which gives rise to the strong, normal carbonyl stretching mode at above 1650 cm^{-1}, while a chelated monomeric or polymeric form which gives rise to the coordinated carbonyl absorption at 1628 cm^{-1} may also be present.

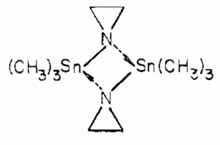
The phenyl isothiocyanate insertion product (XIV) is a liquid at ambient temperatures, like its dimethylamino analogue.[40] The latter adduct was assigned a tin–nitrogen bonded structure, by analogy with its oxygen analogue, but its infrared spectrum exhibited a very strong band at 1605 cm^{-1} which was assigned to a ν(CC) (A_1) mode.[40] It is more likely that this absorption arises from a ν(C=N) mode, a possibility apparently only considered later.[41] The ν(SnS) is assigned to a strong absorption at 930 cm^{-1}. The pronounced ν_{sym}(SnC) at 510 cm^{-1} rules out planar trimethyltin groups. The ν(C=N) absorption was observed at 1582 cm^{-1} in the adduct $(CH_3)_3SnN{=}C(C_6H_5)N(CH_3)_2$.[40]

The infrared spectrum of the acetone insertion product (XII) contains the symmetric ring breathing mode as a strong band at 1218 cm^{-1} and the asymmetric and symmetric ring deformation modes as strong bands at 948 and 853 cm^{-1}, respectively. Both ν_{asym}(Sn–C) and ν_{sym}(Sn–C) are observable at 534 and 509 cm^{-1}, respectively. The spectrum of the triethylgermyl analogue was not listed in ref 5.

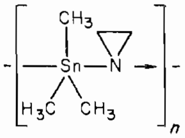
The infrared spectrum of the adduct of diethyl acetylenedicarboxylate contains the symmetrical ring breathing mode at 1260 cm^{-1} and the symmetrical ring deformation mode at ca. 860 cm^{-1}, but the position of the asymmetric deformation is obscured. The ν_{asym}(SnC) mode gives rise to a strong absorption at 532 cm^{-1}, but the ν_{sym}(SnC) is much weaker at 516 cm^{-1}, yet ruling out precisely planar trimethyltin groups. As observed before for the dimethylamino analogue,[41] the bands arising from the ν(C=O) and ν(C=C) modes are split into two, with the former at 1738 and 1714 cm^{-1} and the latter at 1608 and 1592 cm^{-1}. This has been interpreted in terms of *intra*molecular coordination by one of the carbonyl groups to the tin atom, but the absence of a resolvable Mössbauer QS makes the suggestion less plausible. The splitting of the ν(C=C) mode is likely due to the conjugation in the enamine C=C–N system which would be expected to give rise to an asymmetric and symmetric vibration in the ν(C=C) range, as is observed in the related vinyl ethers.[75]

Structural Conclusions

The conventional physical and chemical as well as Mössbauer and mass spectral data force the conclusion that *N*-trimethyltin aziridine takes an oligomeric or polymeric structure with weak nitrogen interaction with the atoms in adjacent molecules to give five-coordination at tin in the solid state. The higher melting point for the parent aziridine derivative reflects the increased lattice forces in this solid. In addition, while *N*-trimethyltin aziridine is only moderately sensitive to hydrolysis by moist air, its liquid dimethylamino analogue fumes in the atmosphere. Osmometric molecular weight determination gives a dimeric formula in benzene solution. The associated structure is weakened by successive 2-methyl substitution on the aziridine ring or by increasing the ring size. Infrared data rule out precisely planar trimethyltin groups but do not serve by themselves to distinguish between dimeric (A), trimeric, or oligomeric or linear polymeric (B) forms in the solid although fragments greater than the dimer in the mass spectrum suggest that the solid consists of higher oligomers or is polymeric. The compound remains associated in the melt and dissolves in benzene as a dimer, unlike other aminostannanes.[25] The dimeric structure proposed above, based upon the trigonal bipyramid, is commonly found for tin in cases where oxygen is the bridging atom[49] and is analogous to the nitrogen-bridged structure of trimethyltin glycinate which we have recently solved.[55]



A



B

Experimental Section

Transfer manipulations requiring anhydrous conditions were carried out in a Vacuum/Atmospheres Dri-Lab glovebox equipped with a HE-193-1 Dri-Train or in polyethylene glovebags (Instruments for Industry and Research). Reactions were performed under dry nitrogen or argon or on a vacuum manifold maintained below 5 × 10^{-3} Torr. Carbon and hydrogen analyses were carried out by Instranal Laboratory, Inc., Rensselaer, N.Y. Tin analyses were performed in this laboratory gravimetrically. Mass spectra were recorded on an AEI MS-902 instrument operating at an ionizing energy of 70 eV and a source temperature of 150 °C. Infrared spectra were recorded in the 4000–200-cm^{-1} range on a Beckman IR-12 grating infrared spectrophotometer and calibrated with polystyrene and water vapor. Samples were run as liquid smears or Nujol mulls on potassium bromide plates (4000–400 cm^{-1}) or in polyethylene cells (450–200 cm^{-1}), as potassium bromide pellets, or as vapors contained in a 10-cm path length cell fitted with potassium bromide windows. Tin-119m Mössbauer spectra were recorded on a constant-acceleration cam-drive spectrometer with the sample mounted in a cryostat at liquid nitrogen temperature[76] vs. a $Ba^{119m}SnO_3$ source (New England Nuclear Corp.) held at ambient temperature. Spectra were calibrated against an NBS 5-mil β-tin foil having an absolute value of 2.56 mm/s. ^{1}H NMR spectra were recorded on a Varian A-60 instrument with tetramethylsilane (TMS) as the internal standard. Natural-abundance, proton noise decoupled ^{13}C NMR spectra were recorded at 25.14 MHz on a Varian HA-100D equipped with a Digilab FTS/NMR-3 pulse and data system. Carbon chemical shifts were measured in parts per million (ppm) relative to internal TMS or the center peak of the deuteriochloroform triplet. Solution concentrations approached 50% (v/v or w/v), solubilities permitting. Less soluble compounds were run in saturated solution. Samples were contained in 8-mm o.d. tubes which held 2-mm o.d. coaxial inner cells filled with C_6F_6, the ^{19}F lock compound. Probe temperature was maintained at ca. 40 °C during proton-decoupled experiments utilizing the Digilab 50-80 decoupler by a continuous flow of nitrogen circulated through cooling coils held in dry ice. Coupling constants were either read directly from teletype print-out or measured from calibrated chart paper. Molecular weight measurements (osmometry in benzene) were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Trimethyl(1-aziridinyl)stannane via Transamination. Trimethyl(1-aziridinyl)stannane was prepared by the transamination method of Kostyanovskii and Prokof'ev.[3] Trimethyl(dimethylamino)stannane (bp 125–127 °C (758 Torr)) was synthesized by a published lithioamination method.[23] Into a four-neck polymerization flask was placed 1.8 g (0.009 mol) of trimethyl(dimethylamino)stannane, and excess aziridine (Dow Chemical Co.), 1.6 g (0.04 mol), was added with magnetic stirring at room temperature. A gas was evolved which was trapped at −77 °C and proved to be dimethylamine as identified by its vapor-phase infrared spectrum (compared to the infrared spectrum of a commercial sample of dimethylamine). A white solid formed, and the solution was warmed to 57 °C for 1.5 h to complete the reaction. Excess aziridine was removed under vacuum at 0 °C, and the product was sublimed at ambient temperature on the vacuum manifold to yield 0.65 g (39%) of product, mp 28.5 °C, as long, white needles. The use of ammonium sulfate as a transamination catalyst or use of a solvent did not alter the yield. Anal. Calcd for $C_5H_{13}NSn$: Sn, 57.7. Found: Sn, 57.0. ^1H NMR (10% w/v solution in benzene): $\delta = 0.08$ ppm (CH_3–Sn) (s), $\delta = 1.68$ ppm (ring) (s); $^2J(^{119}Sn\text{–}C\text{–}^1H) = 56.6$ Hz; proton integration calcd 2.25:1, found 2.4:1.

Trimethyl(1-aziridinyl)stannane via Lithioamination. Into a round-bottom flask were added 140 mL of dry hexane and 6.6 g (0.15 mol) of aziridine. The vessel was cooled to 0 °C and 90 mL (0.15 mol) of *n*-butyllithium was added dropwise with vigorous stirring. A white precipitate of lithium aziridine formed. The suspension was warmed to room temperature for 2 h to expel *n*-butane. The dropwise addition of 28 g (0.14 mol) of trimethyltin chloride in 50 mL of hexane resulted in a slightly exothermic reaction. Lithium chloride precipitated and was filtered using a Büchner funnel packed with diatomaceous earth. The solvent was removed under reduced pressure to leave a white solid. Sublimation at ambient temperature (0.02 Torr) resulted in 8.1 g (28% yield) of product. The melting point and infrared and ^1H NMR spectra were identical with those of a sample prepared by transamination.

Trimethyl(1-aziridinyl)stannane via Trimethyltin Acetate. *n*-Butyllithium, 100 mL (0.16 mol), was added at 0 °C to 7.5 g (0.17 mol) of aziridine in 100 mL of petroleum ether to give a suspension of lithium aziridine. After stirring of the suspension at ambient temperature for 2 h, 30 g (0.15 mol) of solid trimethyltin acetate (M & T Chemical Co.) was added directly, and the mixture stirred for 48 h. Lithium acetate precipitated and was removed by filtration through diatomaceous earth. The solvent was removed under vacuum, and the product sublimed at 30 °C (0.02 Torr) to give 13.5 g (45% yield) based on the acetate. The physical properties and spectral data were identical with those of samples of the first two preparations. Trimethyl(1-aziridinyl)stannane can be stored at −10 °C for several months without decomposition.

Attempted Preparation of Trimethyl(1-aziridinyl)stannane via Trimethyltin Lithium and *N*-Chloroaziridine. *N*-Chloroaziridine was prepared by the method of Graefe and Meyer[26,27] from sodium hypochlorite and aziridine. Trimethyltin lithium was prepared by two methods.

(a) Hexamethylditin, 16.4 g (0.05 mol), was added to 60 mL of tetrahydrofuran in a three-necked, round-bottom flask equipped with a glass-covered magnetic stirring bar. Excess lithium metal ribbon, 2.5 g (0.35 g-atom), was washed with hexane, cleaned to expose a bright surface, and added to the flask in small pieces at 0 °C. After 2 h of stirring, a dark-green solution of trimethyltin lithium resulted which was filtered and transferred by syringe to a second flask.

(b) Lithium wire, 2.31 g (0.33 g-atom), was added to a reaction flask containing 75 mL of dry tetrahydrofuran and a glass-covered stirring bar. Trimethyltin chloride, 9.0 g (0.045 mol), was dissolved in 25 mL of tetrahydrofuran and added dropwise to the flask at 0 °C. The contents were stirred 20 h. The resulting dark green solution was filtered and transferred to a second flask.

A solution [7.8 g (0.1 mol) (a) or 3.9 g (0.05 mol) (b)] of *N*-chloroaziridine in 25 mL of tetrahydrofuran was added dropwise at 0 °C to the trimethyltin lithium solution. At the end of the addition, the dark green color was dispelled in favor of a light straw-colored solution with some tan precipitate. The solution was concentrated under vacuum and 100 mL of petroleum ether was added to extract the tin-containing product. The ether layer was filtered and the solvent removed. Vacuum distillation of the residue on the manifold gave hexamethylditin, mp 22–23 °C, in 7.3 g (23%) and 4.7 g (29%) yields, respectively, for methods a and b above. The infrared spectrum was identical with an authentic sample (M & T Chemical Co.). No trace of trimethyl(1-aziridinyl)stannane was found in the workup.

Attempted Preparation of Trimethyl(1-aziridinyl)stannane via Tin–Phenyl Cleavage of Phenyltrimethyltin by *N*-Haloaziridines. Phenyltrimethyltin, 3.0 g (0.013 mol), was degassed on the vacuum manifold and 1.1 g (0.014 mol) of *N*-chloroaziridine[26,27] was distilled from KOH onto the solid at −77 °C. The mixture was warmed to room temperature and stirred 48 h under vacuum. Infrared analysis showed that no reaction had occurred as evidenced by the strong ν(N–Cl) stretch at 563 cm^{-1}.[27] The solution was heated to 75 °C for 2 h and finally to 110 °C for 4 h with no change in the infrared spectrum. Vacuum distillation of the residue resulted in the isolation of starting reagents: phenyltrimethyltin (90% recovery), bp 93 °C (17 Torr) [lit.[57] bp 98 °C (20 Torr)], and *N*-chloroaziridine (93% recovery), bp 27 °C (0.05 Torr). Starting materials recovered were identified by their infrared spectra. No other volatile tin-containing products could be isolated. Cleavage of the phenyl–tin bond could not be effected under these conditions.

Attempts to prepare *N*-bromoaziridine by a method involving the reaction of aziridine with sodium hypobromite[26] were unsuccessful as the desired product either exploded during purification or decomposed rapidly immediately after distillation. The instability of the *N*-bromo compound was not unexpected, as previous researchers experienced similar difficulties.[26,29] Thus, *N*-bromoaziridine is not suitable as a reagent for this cleavage reaction.

Hydrolysis of Trimethyl(1-aziridinyl)stannane. Trimethyltin(1-aziridinyl)stannane, 0.65 g (0.003 mol), was degassed on a vacuum manifold. Excess distilled water, 0.1 g (0.0056 mol), was distilled onto the stannane. A white solid formed. The volatile products were condensed at −77 °C and an infrared spectrum of the vapor revealed aziridine and a small amount of water. The solid was dried at ambient temperature for 2 days and was identified as trimethyltin hydroxide, 0.6 g (89% yield), mp 114–115 °C [lit.[77] mp 118 °C, although the melting point of an authentic sample (M & T Chemical Co.) proved to be 115 °C in our laboratory]. The infrared spectrum of this preparation was the same as that of the commercial sample.

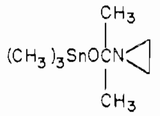
Methanolysis of Trimethyl(1-aziridinyl)stannane. Trimethyl(1-aziridinyl)stannane, 1.3 g (0.0063 mol), was distilled on the vacuum manifold, and excess methanol, 0.32 g (0.01 mol), was distilled onto the stannane at −77 °C. A white solid appeared upon warming and aziridine was evolved. The product was dried 48 h at 0.03 Torr to give a solid, mp 89–99 °C dec (lit.[31] mp 45–75 °C with decomposition depending upon the rate of heating). Infrared analysis shows an Sn–O–C group vibration at 1035 cm^{-1} in the mull which is characteristic of the methoxide.[31] The ^1H NMR spectrum (20% in CCl_4) shows $\delta = 0.33$ ppm (CH_3–Sn) (s) and $\delta = 3.45$ ppm ($-OCH_3$) (s) in agreement with ref 53.

Reaction of Trimethyl(1-aziridinyl)stannane with Aqueous Carbon Dioxide. Freshly distilled trimethyl(1-aziridinyl)stannane, 1.5 g (0.007 mol), was placed in a two-neck flask equipped with a rubber septum, and 5 mL of water saturated with gaseous carbon dioxide was added. Free aziridine (identified by its infrared spectrum) was released and a white solid formed. Excess carbon dioxide was bubbled through the suspension for several minutes, the solution was removed by syringe, and the powdery white solid was dried under dynamic vacuum (0.03 Torr) to give 1.3 g (94% yield) of trimethyltin carbonate, mp >265 °C (lit.[54] values give melting point as infusible above 210 °C). The Mössbauer spectrum shows IS = 1.20 ± 0.06 and QS = 3.00 ± 0.12 mm/s (lit.[54] values 1.34 and 3.05 mm/s, respectively). The infrared spectrum was identical with that published.[33]

Transamination of Trimethyl(1-aziridinyl)stannane with Pyrrole. Redistilled trimethyl(1-aziridinyl)stannane, 0.7 g (0.0034 mol), was mixed with excess pyrrole, 1.0 g (0.015 mol), at −77 °C on the vacuum manifold. Upon warming of the mixture with stirring at room temperature, free aziridine was released as identified by its infrared spectrum. The solution was pumped 15 min at 0 °C to remove excess pyrrole and aziridine to give a colorless viscous liquid which darkened to black in several hours, even under vacuum in the absence of light. The product, trimethyl(1-pyrrolyl)stannane, was distilled at 116–116.5 °C (45 Torr) [lit.[19] value 101.5–102 °C (17 Torr)] to yield 0.5 g (64% yield). An authentic sample was prepared by a published method[19] using potassium pyrrole and trimethyltin chloride, bp 115 °C (44 Torr), 11.8-g yield (35%). The infrared spectra of the two preparations proved identical: 3391 (w), 3112 (m), 3060 (w), 2992 (m), 2921 (m), 2869 (vw), 1705 (w, br), 1530 (m, br), 1467 (s), 1444 (w, sh), 1382 (w), 1297 (w), 1247 (vw, sh), 1231 (m), 1193 (m), 1166 (s), 1082 (s), 1060 (w), 1050 (vw), 1035 (s), 1016 (m), 980 (w, br), 920 (vw), 780 (vs, br), 730 (vs, br), 631 (m), 542 (vs), 515 (m, sh) cm^{-1}.

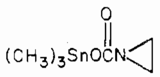
Reaction of Trimethyl(1-aziridinyl)stannane with Cyclopentadiene. To a flask containing 10 mL of petroleum ether (bp 45–60 °C) and 0.80 g (0.013 mol) of cyclopentadiene monomer was added 2.4 g (0.012 mol) of trimethyl(1-aziridinyl)stannane by sublimation on the vacuum manifold at −77 °C. A pinkish solution resulted which turned colorless upon standing. Vapor-phase infrared analysis confirmed aziridine release upon warming to ambient temperature. The solvent was removed under vacuum (5×10^{-2} Torr). The residue consisted of pure trimethylcyclopentadienylstannane, 1.6 g (60%). The infrared and ^1H NMR spectra of the product are identical with published data.[35,36] The ^1H NMR spectrum shows the methyl protons lie 1 Hz downfield from TMS with $|^2J(^{119}Sn–C–^1H)| = 55.8$ Hz while $-C_5H_5$ is found at 5.93 ppm with $|^2J(^{119}Sn–C–^1H)| = 22$ Hz.

Insertion Reaction of Trimethyl(1-aziridinyl)stannane with Acetone. Acetone, 1.0 mL, was dried over calcium chloride and vacuum-distilled into a flask containing 0.24 g (0.001 mol) of trimethyl(1-aziridinyl)stannane at −77 °C. Warming to room temperature resulted in a colorless solution. The reaction vessel was held at 0 °C while excess acetone was removed under vacuum and the colorless liquid product


$(CH_3)_3SnO\overset{CH_3}{\underset{CH_3}{C}}N\lhd$

trimethyl(1-methyl-1-ethyleniminoethoxy)stannane distilled at 26 °C (0.1 Torr) or 63–64 °C (5 Torr) to give a yield of 0.3 g (98%). The density was approximately 1.3 g/mL. Anal. Calcd for $C_8H_{19}NOSn$: Sn, 44.9. Found: Sn, 44.2. ^1H NMR data for 10% v/v solution in benzene: $(CH_3)_3Sn-$, $\delta = 0.22$ ppm (s), $|^2J(^{119}Sn–C–^1H)| = 57.8$ Hz; $CH_3C(O)CH_3$, $\delta = 1.21$ ppm (s); aziridine ring, $\delta = 1.41$ ppm; proton integration calcd 1:1.5:2.25, found 1:1.5:2.6.

Reaction of Trimethyl(1-aziridinyl)stannane with Carbon Dioxide. Freshly sublimed trimethyl(1-aziridinyl)stannane, 3.5 g (0.017 mol), was dissolved in 15 mL of dry petroleum ether in a pear-shaped flask equipped with a side arm and rubber septum. Dry CO_2 gas was bubbled through the solution for a period of 15 min by means of a syringe needle inserted through the septum. A white precipitate formed immediately in an exothermic reaction while the reaction flask was cooled to 10 °C. The solvent was removed under vacuum and the fine white powder


$(CH_3)_3SnO\overset{O}{\overset{\|}{C}}N\lhd$

(1-aziridinylcarbonyloxy)trimethylstannane, 4.0 g (95%), was washed twice with petroleum ether (bp 45–60 °C) to give a material melting at 101–102 °C with decomposition. The compound was not sufficiently soluble for NMR spectroscopy. Anal. Calcd for $C_6H_{13}O_2NSn$: C, 28.84; H, 5.29; Sn, 47.53. Found: C, 29.16; H, 5.92; Sn, 48.2. The product (0.5 g) was placed in a closed, evacuated system (0.05 mm) which was connected to a vapor-phase infrared cell and was heated 30 min each at 65, 85, and 105 °C. No carbon dioxide or aziridine was released at these temperatures. The sample fused into an intractable, dark yellow solid which was insoluble in water, carbon tetrachloride, petroleum ether, tetrahydrofuran, and chlorobenzene. The residue showed no trace of trimethyl(1-aziridinyl)stannane.

Reaction of Trimethyl(1-aziridinyl)stannane with Carbon Disulfide. Carbon disulfide, dried over P_2O_5, 1.5 g (0.02 mol), was vacuum distilled at −77 °C into a reaction tube which was connected to the vacuum manifold containing trimethyl(1-aziridinyl)stannane, 1.5 g (0.008 mol), to give a yellow solid. No aziridine was evolved upon warming to room temperature. Removal of excess carbon disulfide under vacuum at 0 °C left a sticky, yellow solid (stench!). The solid was washed three times with 15 mL of petroleum ether and once with benzene to extract the product (sparingly soluble) as a fine, yellow-white powder, mp 85–95 °C dec, in 0.8-g yield (36%). In some preparations, a solvent such as hexane or petroleum ether was used. Use of a solvent did not alter the nature of the product or the yield of this reaction. Anal. Calcd for $C_6H_{13}NS_2Sn$ (single insertion): Sn, 42.1. Calcd for $C_7H_{13}NS_4Sn$ (double insertion): Sn, 33.2. Found: Sn, 33.9. The product was too insoluble in common organic solvents for NMR measurements.

Reaction of (1-Aziridinylcarbonyloxy)trimethylstannane with Carbon Disulfide. To 0.8 g (0.003 mol) of trimethyl(1-aziridinyl)stannane was added excess carbon disulfide, 1.0 mL, by distillation at −77 °C. An exothermic reaction took place with the rapid evolution of carbon dioxide, identified by its infrared spectrum, and the development of a yellow slurry. The solid was washed with a small amount of petroleum ether (bp 45–60 °C), and the yellow-white solid product, 0.55 g (51% yield), was dried under vacuum. The product decomposed upon melting at ca. 90 °C and proved only slightly soluble in petroleum ether and benzene and insoluble in carbon tetrachloride and chlorobenzene. The infrared spectrum proved to be the same as in the preparation above.

Reaction of Trimethyl(1-aziridinyl)stannane with Phenyl Isocyanate. Phenyl isocyanate, 2.1 g (0.018 mol), was vacuum-distilled into a vessel containing 3.6 g (0.018 mol) of trimethyl(1-aziridinyl)stannane at −77 °C. Upon warming to ambient temperature, an exothermic reaction occurred, and a white solid formed. The volatiles were pumped away, and the dry residue was dissolved in benzene. The addition of petroleum ether (bp 45–60 °C) to the benzene solution brought about precipitation of 5.1 g of pure 1-aziridinyl-*N*-phenylureidotrimethylstannane, in 87% yield. The solvents were removed by means of a syringe, and the product, mp 99–101 °C dec, was washed twice with hexane. This material did not sublime at 112 °C (0.02 Torr), decomposition occurring instead. Anal. Calcd for $C_{12}H_{18}N_2OSn$: Sn, 36.5. Found: Sn, 35.4. ^1H NMR (saturated solution in benzene-d_6): $-CH_3$, $\delta = 0.27$ ppm (s), $|^2J(^{119}Sn–C–^1H)| = 55.8$ Hz; aziridine ring, $\delta = 1.72$ ppm (s); phenyl ring, $\delta = 7.05$ ppm (s); proton integration calcd 1:1.25:2.25, found 1:1.2:2.2. The very strong ν-(N=C=O) vibration found in phenyl isocyanate near 2300 cm^{-1} is absent in the product. Air hydrolysis of this material produced trimethyltin hydroxide after 1-h exposure.

Reaction of Trimethyl(1-aziridinyl)stannane with Phenyl Isothiocyanate. To 3.4 g (0.016 mol) of trimethyl(1-aziridinyl)stannane in 15 mL of hexane was added 2.2 g (0.016 mol) of phenyl isothiocyanate at 0 °C. No observable reaction occurred upon addition, but after being stirred for 24 h at room temperature, the solution became cloudy with decomposition product. The solvent and volatiles were removed under vacuum, to give an oil which decomposed upon attempted distillation. The oil lacked the very characteristic ν-(N=C—S) vibration in the infrared spectrum found in phenyl isothiocyanate near 2100 cm^{-1}. The oil was dissolved in benzene, and the addition of hexane caused the decomposition product to precipitate from solution. The solution was decanted and, after removal of the solvent, was isolated as a colorless liquid, 4.2-g yield (77%). Anal. Calcd for $C_{12}H_{18}N_2SSn$: Sn, 34.8. Found: Sn, 34.1. ^1H NMR spectrum: $-CH_3$, $\delta = 0.35$ ppm (s), $|^2J(^{119}Sn–C–^1H)| = 54.2$ Hz; aziridine ring, $\delta = 1.72$ ppm (s); phenyl ring, $\delta = 7.07$ ppm (m). A small decomposition band appeared at 2.08 ppm.

Reaction of Trimethyl(1-aziridinyl)stannane with Diethyl Acetylenedicarboxylate. In a three-neck flask under argon flow, 4.22 g (0.021 mol) of trimethyl(1-aziridinyl)stannane was dissolved in 20 mL of hexane, and diethyl acetylenedicarboxylate, 3.5 g (0.021 mol), in 10 mL of hexane was added dropwise at 0 °C. A pale yellow solution developed which darkened to orange-red upon stirring for 72 h at room temperature. The solution was filtered, and the solvent removed by pumping under vacuum for 2 h. The liquid was not distillable, turning into a sticky tar at high temperature, but the infrared and ^1H NMR spectra of the liquid, [1,2-dicarbethoxy(1-aziridinyl)vinyl]trimethylstannane, 6.3 g (80% yield), showed no spurious peaks. Anal. Calcd for $C_{13}H_{23}NO_4Sn$: Sn, 31.6. Found: Sn, 31.1. ^1H NMR (50% v/v solution in benzene-d_6): $-Sn(CH_3)_3$, $\delta = 0.28$ ppm (s), $|^2J(^{119}Sn–C–^1H)| = 55.8$ Hz; $-CH_3$ (ethyl), $\delta = 1.13$ ppm (m), overlapping triplets; $-CH_2-$ (ethyl); $\delta = 4.08$ ppm (m), overlapping quartets; aziridine ring, $\delta = 1.92$ ppm (s).

Reaction of Trimethyl(1-aziridinyl)stannane with Tetrasulfur Tetranitride. *N*-Trimethyltin aziridine, 2.25 g (0.01 mol), was dissolved in 8 mL of benzene and added dropwise at 10 °C to a solution of 0.5 g (0.0027 mol) of tetrasulfur tetranitride in 10 mL of benzene. A deep red color developed immediately. Upon stirring overnight at ambient temperature, the color lightened to straw yellow. The solvent was removed and yellow crystals developed amid a red liquid. The liquid was decanted; the crystals were washed with benzene, dissolved in hexane, and recrystallized. The orange-yellow solid *N,N'*-bis(trimethylstannyl)sulfur diimide could be sublimed at 63 °C (0.3 Torr); mp 60–61 °C (mixture melting point with an authentic sample proved to be 60–61 °C). Infrared and ^{1}H NMR data are in complete agreement with published results.[45]

Reaction of Trimethyl(1-aziridinyl)stannane with Boron Trifluoride. Trimethyl(1-aziridinyl)stannane, 4.0 g (0.019 mol), was dissolved in 25 mL of petroleum ether and added dropwise at 0 °C to 3.0 mL (0.027 mol) of boron trifluoride etherate (45% in diethyl ether) dissolved in 25 mL of petroleum ether to give immediate white precipitation. After the mixture stood for 2 h at room temperature, the solvent and excess BF_3 were removed under vacuum. The adduct, which formed in nearly quantitative yield was a soft, white solid (mp 98–101 °C, with decomposition to a red-brown solid), insoluble in hexane, benzene, chloroform, carbon tetrachloride, and acetonitrile, which undergoes hydrolysis to yield trimethyltin hydroxide and aziridine. Anal. Calcd for $C_5H_{13}BF_3NSn$: Sn, 43.4. Found: Sn, 42.9. The infrared spectrum (KBr pellet) contained prominent peaks at 3310 (w), 2920 (vs, br), 1455 (w, sh), 1378 (m), 1345 (vw, sh), 1305 (vw), 1262 (m, br), 1213 (m), 1170 (m), 1154 (m, br), 1100 (m, vbr), 970 (m, vbr), 918 (m), 780 (s, br), 723 (s), 592 (m), 558 (m, sh), 545 (s), 518 (m), 485 (vw) cm^{-1}.

The adduct, 1.0 g, was heated to reflux with excess triethylamine for 2 h. The adduct darkened to a brown color, but no observable reaction occurred. The triethylamine solvent was decanted and evaporation gave no solid residue. The adduct was vacuum-dried and its infrared spectrum showed no change.

Trimethyl(2-methyl-1-aziridinyl)stannane via Transamination. Following the method described above, 3.5 g (0.017 mol) of trimethyl(dimethylamino)stannane was allowed to react with an excess, 1.9 g (0.03 mol), of 2-methylaziridine (Pfaltz and Bauer). The product, trimethyl(2-methyl-1-aziridinyl)stannane, was vacuum-distilled at 24 °C (0.01 Torr) which gave a colorless liquid, 2.0 g (55% yield), that was very sensitive to moisture. Anal. Calcd for $C_6H_{15}NSn$: Sn, 54.1. Found: Sn, 54.6. ^{1}H NMR spectrum (20% v/v in benzene): $-Sn(CH_3)_3$, $\delta = 0.14$ ppm (s), $|^2J(^{119}\mathrm{Sn{-}C{-}}^1\mathrm{H})| = 56$ Hz; aziridine ring protons and ring methyl protons, 1.16 ppm (s) and 1.24 ppm (s) (which integrate at nearly 1:1) compared to the parent aziridine which exhibits these protons at 1.00 and 1.07 ppm.

Trimethyl(2-methyl-1-aziridinyl)stannane via Trimethyltin Acetate. Following the procedure outlined above, trimethyl(2-methyl-1-aziridinyl)stannane was prepared in 63% yield. The product was distilled, 56–57 °C (20 Torr). Infrared and ^{1}H NMR spectra were identical with those of the material prepared by transamination.

Trimethyl(2,2-dimethyl-1-aziridinyl)stannane. Following the transamination procedure given above, 4.2 g (0.020 mol) of trimethyl(dimethylamino)stannane was allowed to react with excess 2,2-dimethylaziridine (Pfaltz and Bauer) to give the desired product, 2.9-g yield (62%), as a colorless liquid, which was distilled at 29 °C (0.02 Torr) on the vacuum manifold. Anal. Calcd for $C_7H_{17}NSn$: Sn, 50.8. Found: Sn, 51.5. ^{1}H NMR spectrum (50% v/v in benzene-d_6): $-Sn(CH_3)_3$, $\delta = 0.16$ ppm (s), $|^2J(^{119}\mathrm{Sn{-}C{-}}^1\mathrm{H})| = 54.8$ Hz; ring methyl, $\delta = 2.70$ ppm (s); ring protons, $\delta = 2.96$ ppm (s).

Methanolysis of Trimethyl(2-methyl-1-aziridinyl)stannane. Following the procedure described above, trimethyl(2-methyl-1-aziridinyl)stannane (0.01 mol) was allowed to react with excess methanol to give trimethyltin methoxide, 1.7-g yield (87%), mp (sealed capillary) 60–62 °C dec. The infrared and ^{1}H NMR spectra were used for identification.

Trimethyl(1-azetidinyl)stannane via Transamination. The transamination reaction described above was employed to yield trimethyl(1-azetidinyl)stannane, 1.1 g (25% yield), from azetidine (Eastman Chemicals). The product was a colorless liquid which was distilled on the vacuum manifold at 26 °C (0.04 Torr). Anal. Calcd for $C_6H_{15}NSn$: Sn, 54.0. Found: Sn, 54.8. ^{1}H NMR spectrum (ca. 10% solution in C_6D_6): $-CH_3$, $\delta = 0.14$ ppm (s), $^2J(^{119}\mathrm{Sn{-}C{-}}^1\mathrm{H}) = 55.8$ Hz; $-C(1)H_2-$, $\delta = 3.81$ ppm (t); $-C(2)H_2-$, $\delta = 2.38$ ppm (m). Prominent peaks in the infrared spectrum: 2976 (s), 2948 (s), 2915 (s), 2880 (s), 2804 (s), 2756 (s), 1710 (vw, br), 1487 (w), 1463 (w), 1442 (w), 1303 (m), 1261 (m), 1233 (m), 1188 (m), 1167 (m), 1054 (s), 1013 (s), 947 (m), 924 (s), 770 (vs, br), 740 (s, br), 531 (vs), 509 (m) cm^{-1}.

Trimethyl(1-pyrrolidinyl)stannane via Transamination. Following the procedure outlined above, trimethyl(1-pyrrolidinyl)stannane was isolated as a colorless liquid from 5.2 g (0.025 mol) of trimethyl(dimethylamino)stannane and 1.8 g (0.025 mol) of pyrrolidine in 3.1-g yield (53%). The product distilled at 57–58 °C (6 Torr). Anal. Calcd for $C_7H_{17}NSn$: Sn, 50.7. Found: Sn, 50.1. Mössbauer spectrum: IS = 1.24 ± 0.06 mm/s, QS = 0.91 ± 0.12 mm/s. ^{1}H NMR data (20% v/v in benzene): $-SnCH_3$, $\delta = 0.13$ ppm (s), $|^2J(^{119}\mathrm{Sn{-}C{-}}^1\mathrm{H})| = 56.0$ Hz; $-C(1)H_2-$, $\delta = 3.00$ ppm (t); $-C_{ring}H_2-$, $\delta = 1.61$ ppm (m).

Trimethyl(1-piperidinyl)stannane via Transamination. The transamination reaction described above was used to produce trimethyl(1-piperidinyl)stannane from 5.11 g (0.25 mol) of trimethyl(dimethylamino)stannane and 2.1 g (0.025 mol) of piperidine as a colorless liquid, bp 68–69 °C (9 Torr), in 65% yield (4.0 g). Anal. Calcd for $C_8H_{19}NSn$: Sn, 47.8. Found: Sn, 47.2. ^{1}H NMR data (50% v/v in benzene-d_6): $-SnCH_3$, $\delta = 0.12$ ppm (s), $|^2J(^{119}\mathrm{Sn{-}C{-}}^1\mathrm{H})| = 54.4$ Hz; ring protons, $\delta = 1.52$ ppm (m) and 2.91 ppm (m).

Trimethyl(1-piperidinyl)stannane from Trimethyltin Acetate. The reaction of trimethyltin acetate, 28.7 g (0.12 mol), and the lithium salt of the imine (0.13 mol) described above was used to obtain trimethyl(1-piperidinyl)stannane, 7.2 g, 34% yield. The infrared and ^{1}H NMR spectra were identical in all respects with those of the material obtained by transamination.

***N*-(Trimethylstannyl)hexamethylenimine via Transamination.** Transamination of trimethyl(dimethylamino)stannane, 4.7 g (0.023 mol), and hexamethylenimine, 2.3 g (0.023 mol), gave *N*-(trimethylstannyl)hexamethylenimine, 3.6 g, in 60% yield. The colorless liquid was distilled at 88–90 °C (8 Torr). Anal. Calcd for $C_9H_{21}NSn$: Sn, 45.4. Found: Sn, 45.6. ^{1}H NMR spectrum (neat): $-SnCH_3$, $\delta = 0.11$ ppm (s), $|^2J(^{119}\mathrm{Sn{-}C{-}}^1\mathrm{H})| = 56.4$ Hz; ring protons at 1.59 ppm (m) and 3.05 ppm (m).

Tetrakis(1-aziridinyl)tin via Transamination from Tetrakis(dimethylamino)tin. Into a polymerization flask was placed 4.8 g (0.016 mol) of tetrakis(dimethylamino)tin (Alfa Inorganics), and excess aziridine, 1.38 g (0.032 mol), was added at room temperature with stirring to give immediate precipitation of a white solid and evolution of gaseous dimethylamine, identified by its infrared spectrum. Additional aziridine, 0.5 mL, was added after 1 h to complete the reaction. Excess aziridine was removed in vacuo, but the insoluble product, mp 104–105 °C dec, could not be vacuum-distilled on the manifold. Anal. Calcd for $C_8H_{16}N_4Sn$: Sn, 54.0. Found: Sn, 54.8.

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Unsymmetrical Bis-Phosphorus Ligands. 9. Group 6 Metal Carbonyl Complexes and Other Derivatives of Various (Phosphinomethyl)phosphine Sulfides[1]

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Some chemistry of a new class of compounds, (phosphinomethyl)phosphine sulfides, $Ph_2P(S)CH_2PR^1R^2$, is described. Reaction with sulfur gives disulfides, $Ph_2P(S)CH_2P(S)R^1R^2$, with sodium gives unsymmetrical di(tertiary phosphines), $Ph_2PCH_2PR^1R^2$, with alkyl halides gives phosphonium salts, $[Ph_2P(S)CH_2PR^1R^2R^3]X$, and with group 6 metal carbonyls gives a complex with phosphorus and sulfur bonded to the metal in a five-membered chelate ring, $[Ph_2P(S)CH_2PR^1R^2]M(CO)_4$; heating causes the sulfur to transfer to the more basic phosphorus atom, producing $Ph_2PCH_2P(S)R^1R^2$. Extensive phosphorus and proton NMR data are given.

Studies of various unsymmetrical bis-phosphorus ligands have been of considerable interest to us recently,[1c,2-4] since these compounds contain, in the same molecule, two phosphorus atoms which are nonequivalent. These types of molecules allow for the direct measurement of phosphorus–phosphorus coupling, which has received considerable