

from the trans conformation. This movement of charge is typical for hydrogen bonding. Finally, these charge shifts are balanced by a loss of 0.02 e on the hydrogen bonded to C₆ and a small gain on the ortho carbon.

The charge shifts in *o*-chlorophenol are similar, but chlorine gains more charge than fluorine in the cis conformation. This extra charge comes from the ortho carbon which loses charge in the H-bonded conformation. Whether this reversal in movement of charge is characteristic or an artifact of the basis set is not clear at present.

It appears, therefore, that the trans conformers exhibit the full proximity effect and hence a larger Dq , whereas in the cis conformers the effect is partially compensated owing to H-bonding which allows charge to be transferred from the proton to the proton acceptor. In fluorophenol the charge gained by the proton acceptor just compensates the charge lost in the trans conformation so that $Dq_o(\text{cis})$ is still large. In contrast, $Dq_o(\text{cis})$ for chlorophenol is less because the charge gained overcompensates the loss of charge in the trans conformation.

Conclusions

Ab initio calculations have been carried out on monosubstituted benzenes and phenols using small Gaussian atomic basis sets constructed to preserve the valence-shell description of larger bases.⁵ On the basis of statistical analyses it was shown that these MB's give qualitatively stable values of properties such as the dipole moment and Koopmans' theorem ionization potentials. Such statistical predictability allows the calculated values of a particular property to be scaled to give improved estimates of the observed values. For example, the scaled values of the dipole moment of phenol obtained from the calculated MB and STO-3G values using eq 5 and 6 of Table II, respectively, are 1.39 and 1.48 D, and for benzoic acid they are predicted to be 1.55 and 1.32

D. Naturally the calculated dipole moments of the substituted phenols given in Table VI could also be scaled with these equations. In addition, it is clear that when a given molecular property for a series of molecules is correlated with another observed property, statistical stability is essential if such correlations are to be meaningful. Mulliken charge populations calculated with the MB's or with STO-3G basis sets were found to be qualitatively identical although the atomic net charges differ considerably in absolute value. In contrast to one-electron properties, it was found that isodesmic reaction energies for reactions involving bond breakage on the ring seem to be very basis-set dependent.

A more detailed study of substituent effects was carried out allowing a unified Taft-type dual regression equation to be obtained for the π -HOMO energy which included para, meta, and ortho isomers. An analysis of the additivity of net charge donations by the substituents to the ring showed that the larger deviations from additivity characteristic of ortho substituents are found primarily in the σ -charge distribution, and that deviations were small and not dependent on isomer type for the π electrons. This suggests it should be possible to find unified regression equations for properties which derive primarily from the π -electron charge distribution. It should be noted, however, that most of the substituents studied in this work are σ -electron withdrawing so that the nonadditivity effects arise from the mutual repulsion of excess negative charge on the substituents when bound to the ring. Moreover, since the substituents are relatively small, steric effects are probably not very important.

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Registry No. Benzene, 71-43-2; phenol, 108-95-2.

Structural Analysis of Methyltin(IV) Polymers by Solid-State ¹³C NMR Spectroscopy

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Abstract: High-resolution solid-state ¹³C NMR analysis of 11 crystalline and amorphous polymeric methyltin(IV)s is described. Multiple Sn-methyl resonances observed for linear polymeric trimethyltin acetate and trimethylstannol indicate hindered rotation of the trigonal-planar Me₃Sn group in the crystal lattice. $|^1J(^{119}\text{Sn},^{13}\text{C})|$ values ranging from 470 to 1160 Hz were observed for most of the polymers examined. The magnitude of J of the amorphous polymers methylstannonic acid and bis(trimethyltin) carbonate provides new insight into their bonding and structure. Using an empirical relationship of $|^1J(^{119}\text{Sn},^{13}\text{C})|$ to the Me-Sn-Me angle, an angle of 135° is estimated for microcrystalline, intractable dimethyltin oxide. Chemically bound abundant NMR-active nuclei (¹⁹F, ^{35,37}Cl, ¹⁴N) in the methyltin(IV) solids cause substantial line-broadening that may obscure the ^{117,119}Sn satellites.

Recently we described² the narrow lines that can be obtained in routine cross-polarization magic angle spinning (CPMAS) ¹³C NMR experiments with crystalline methyltin(IV) solids. For example, methyltin(IV) resonances less than 0.5 ppm apart have been resolved at 15.08 MHz, and the ¹¹⁷Sn and ¹¹⁹Sn satellites (both spin-¹/₂, natural abundances 7.6, 8.6%, respectively) are also evident in most spectra. We have investigated the dependence

of these NMR parameters on molecular structure by systematically examining X-ray characterized methyltin(IV) solids and found² that slight differences in the environment of methyls bonded to the same Sn can give rise to multiple, well-separated resonances. Further, the magnitude of $^1J(^{119}\text{Sn},^{13}\text{C})$, $|J|$, is linearly related³ to the Me-Sn-Me bond angle, θ , in tetra-, penta-, and hexa-coordinated di-, tri-, and tetramethyltin(IV)s: $|J|/\text{Hz} = 11.4(\theta) - 875$. This empirical relationship provides a sensitive probe of the structure of uncharacterized methyltin(IV) solids and of methyltin(IV)s in solution.

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Table I. ^{13}C CPMAS NMR of Crystalline Polymeric Methyltin(IV) Solids

compound	chemical shift ^a of Sn-methyl (rel area), ppm	LW, Hz ^b	$ J $, Hz ^c
Me_3SnOAc , 1	1.7, -0.1 (2:1)	7	540
$\text{Me}_2\text{PhSnOAc}$, 2	2.5	15	610
Me_3SnNO_3 , 3	0.9	30	500
Me_3SnOH , 4	6.2, 3.5 (1:2)	18	600
Me_3SnF , 5	2.3	120	550
Me_3SnCl , 6	4.1	160	470
Me_2SnCl_2 , 7	26.8	200	<i>d</i>
Me_2SnF_2 , 8	11.9	250	<i>d</i>

^a Relative to Delrin (89.1 ppm). Values ± 0.3 ppm. ^b Line width at half-height. ^c $|J| = |J(^{119}\text{Sn}, ^{13}\text{C})|$, calculated from center of unresolved $^{119}\text{Sn}, ^{117}\text{Sn}$ satellites ($|J_{\text{obsd}}| \times 1.023$). ^d Not resolved from broad, central resonance.

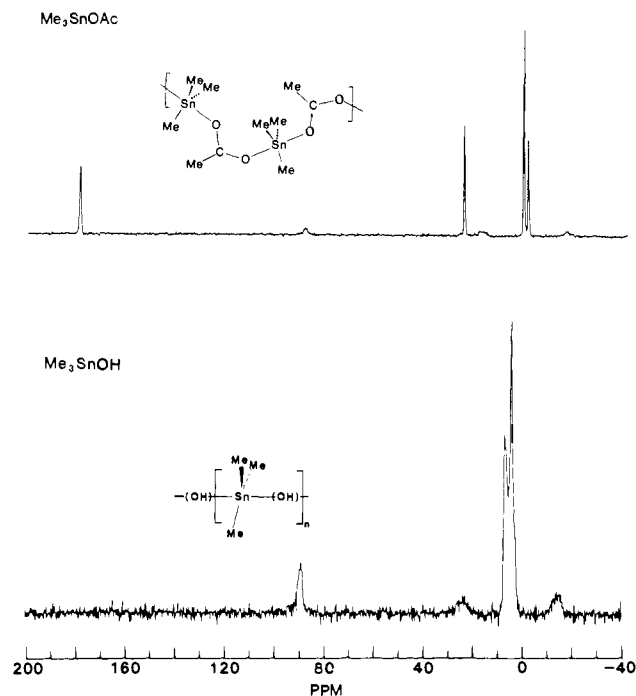


Figure 1. ^{13}C CPMAS NMR spectra of polycrystalline Me_3SnOAc (**1**), top, Me_3SnOH (**4**), bottom. Molecular structures above spectra are based on published X-ray studies (text). Delrin (polyoxymethylene), 89.1 ppm, internal reference.

In this paper we describe the application of CPMAS ^{13}C NMR to the structural characterization of crystalline and amorphous, linear and higher order methyltin(IV) polymers. The structures of several of the crystalline polymers are known, providing the opportunity to compare the NMR and structure data directly. Analysis of the J -resolved spectra of several poorly characterized, amorphous methyltin(IV) polymers provides new insight into their structure and bonding.

Results

^{13}C CPMAS spectra of methyltin(IV) polymers were obtained at 15.08 MHz (1.4 T) with high-power proton decoupling. The presence of a broad Sn-methyl resonance, or a Sn-methyl multiplet, coupled with two spin- $1/2$ isotopes of Sn ($\gamma^{119}\text{Sn}/\gamma^{117}\text{Sn} = 1.046$) gives rise to broadened satellites. The $|J|$ was determined from the distance between the center of the two satellites $\times 1.023$. The NMR spectrum of Me_3SnNO_3 showed an unusual feature: the downfield satellite was broadened considerably relative to either the upfield satellite or the uncoupled central resonance and was not affected by small adjustments of the spinning axis about the magic angle.

Sn-methyl chemical shifts and J coupling constants measured for eight crystalline methyltin(IV) polymers are given in Table I. In Figure 1 the narrow-line spectra observed for two of the

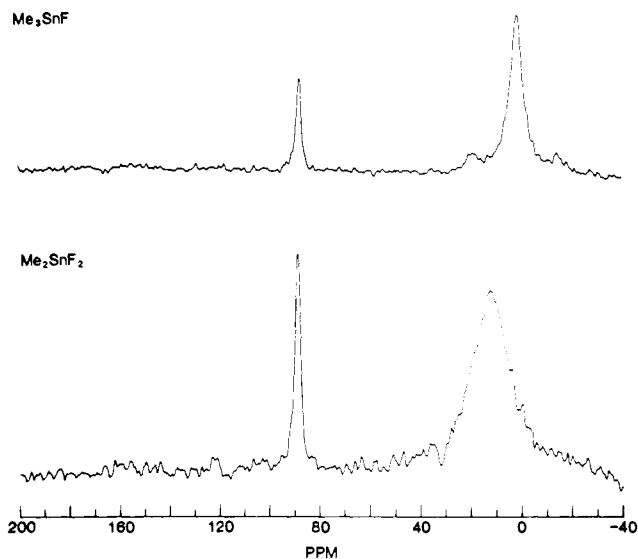


Figure 2. Dipolar line broadening of Sn-methyl resonance caused by abundant spin- $1/2$ nucleus (^{19}F). Top spectrum, Me_3SnF ; bottom, Me_2SnF_2 . Internal reference, Delrin, at 89.1 ppm.

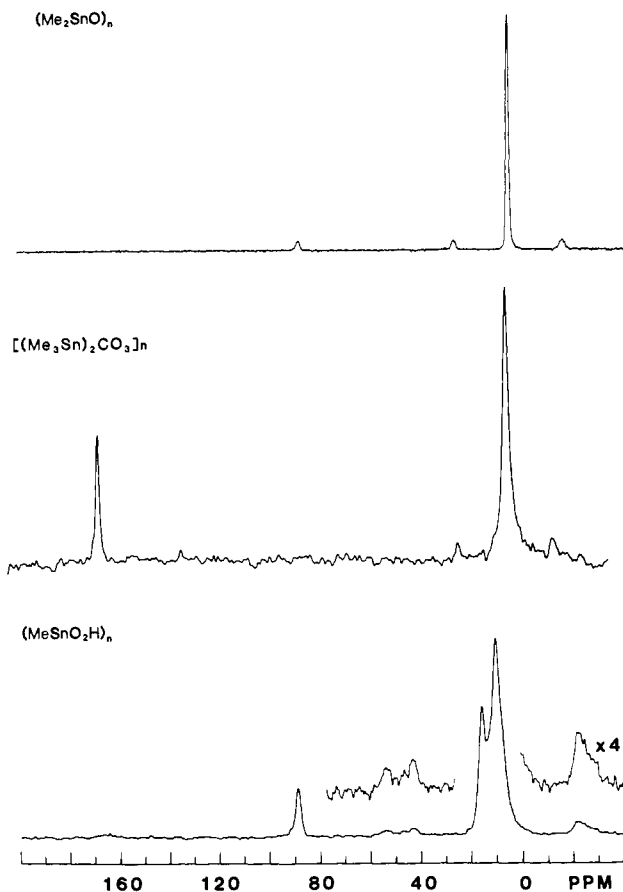


Figure 3. ^{13}C CPMAS NMR spectra of amorphous and microcrystalline methyltin(IV) polymers **9**, **11**, **10**; formulas are given at top of spectra. Internal reference, Delrin, at 89.1 ppm.

crystalline polymers are shown. The $^{117,119}\text{Sn}$ satellites are also visible in the spectra. The line-broadening influence of NMR-active halogen atoms is visible in the spectra of methyltin fluorides (Figure 2); while $^{117,119}\text{Sn}$ satellites can still be identified in the spectrum of Me_3SnF , they are completely obscured for Me_2SnF_2 .

The NMR spectra of amorphous polymeric methylstannonic acid ($[\text{MeSnO}_2\text{H}]_n$), bis(trimethyltin) carbonate ($[(\text{Me}_3\text{Sn})_2\text{CO}_3]_n$), and intractable, microcrystalline dimethyltin oxide ($[\text{Me}_2\text{SnO}]_n$) are shown in Figure 3. Although the resonances are broadened relative to the halogen- and nitrogen-free

Table II. ^{13}C CPMAS NMR of Amorphous Methyltin(IV) Polymers

compound	Sn-methyl chemical shift, ppm ^a	LW, Hz ^a	J , Hz ^a
$[\text{Me}_2\text{SnO}]_n$, 9	6.4	21	660
$[\text{MeSn}(\text{O})\text{OH}]_n$, 10	16.2, 10.0	70	1160, 1030
$[(\text{Me}_3\text{Sn})_2\text{CO}_3]_n$, 11	0.4	45	590

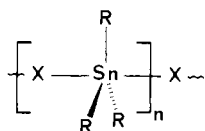
^aSee Table I.

crystalline polymers, the J coupling interaction can still be clearly identified (Table II).

Discussion

The dipolar interaction⁴ between ^{13}C and the abundant NMR-active nuclei (^{19}F , $^{35,37}\text{Cl}$, ^{14}N) in several samples (**3**, **5–8**) produces substantial line-broadening. The line-broadening caused by the single halogen in **5** and **6** is large enough to obscure any methyl resonance multiplicity, but the J coupling interaction can still be observed. The more severe broadening in dihalides **7**⁵ and **8**⁶ (in which each Sn is bonded to four bridging halides) obscures the Sn satellites as well. For the other polymers, line-broadening reflects the structural heterogeneity;⁷ consonant with this, the amorphous polymers gave the broadest resonances.

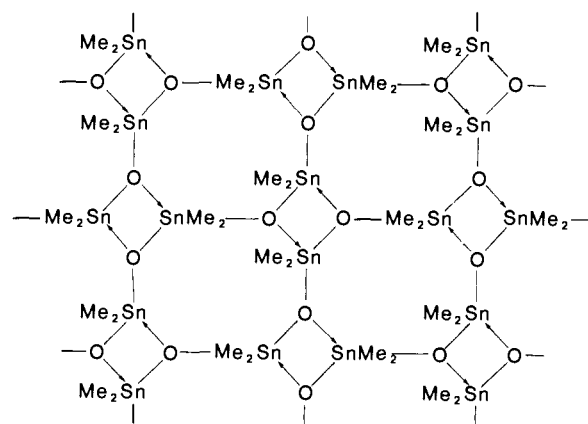
Methyltin(IV)s **1–6** in Table I are linear, crystalline polymers in the solid-state



and all have been examined by single-crystal X-ray diffraction.⁸ For trimethyltin acetate (**1**) a 2:1 Me_3Sn resonance multiplicity was observed (Figure 1). The X-ray structure for this compound⁹ indicates that the polymer chain is formed of pentacoordinated Sn atoms (trigonal-bipyramidal geometry) joined by bridging acetate groups. Two of the Me's bonded to Sn lie on either side of a plane which contains Sn, the acetate C and O atoms, and the third Me bonded to Sn. In this geometry, the two methyls lying out of the Sn-acetate plane are identically related to the other atoms in the molecule but differ from the third methyl, producing the two groups of Sn-methyl resonances. That the Sn-methyl resonances can be resolved must be due to hindered rotation of the Me_3Sn trigonal plane in the crystal lattice and illustrates the sensitivity of the ^{13}C resonances to molecular geometry.

The X-ray structure¹⁰ of dimethylphenyltin acetate (**2**) indicates that it is a linear polymer like **1**, one methyl in the trigonal plane having been replaced by phenyl. In the NMR of the solid, a narrow singlet is observed for the two remaining Sn-methyls which lie on either side of the plane containing Sn, the bridging acetate group, and the phenyl carbon bonded to Sn and occupy magnetically equivalent positions. In this position, steric interactions of the phenyl group with other atoms in the polymer molecule are minimized.

For trimethylstannol (**4**), a 1:2 Me_3Sn ^{13}C multiplicity was found, indicating inequivalence of the methyls in the Me_3Sn trigonal plane. The X-ray structure¹¹ is of low quality but suggests

**Figure 4.** Structure proposed for amorphous $[\text{Me}_2\text{SnO}]_n$ polymer, **9** (ref 15).

that the Me_3Sn plane is inclined about 15° with respect to the linear O-Sn-O fragment (Figure 1), providing one source of magnetic inequivalence. Other asymmetry of the polymer chain such as that in **1** (which removes a C_{3v} axis interconverting the three Sn methyls) may further, or primarily, contribute to the observed inequivalence.

The single Me_3Sn resonance observed for **3**, **5**, and **6** could indicate magnetic equivalence of the three Sn methyls; however, the line broadening in these compounds (particularly **5** and **6**) prevents further analysis.

Although dipolar broadening obscured coupling to Sn in the ^{13}C CPMAS spectra of dihalides **7** and **8**, Sn satellites were evident for the other compounds. $|J|$ for the linear polymers (Table I, **1–6**) falls between 470 and 610 Hz, consistent with approximately trigonal-bipyramidal geometry and pentacoordinated Sn. In CDCl_3 solution, $|J|$ of **1**, **3**, and **4** (see Experimental Section) and **6**¹² are less than about 400 Hz, clearly indicating a change in structure (dissociation to form monomeric, tetraordinated Me_3SnX species) on dissolution.^{2,13}

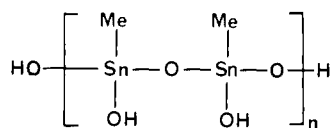
The lack of crystallinity of **10** and **11** and the microcrystallinity of **9** have hampered efforts to determine their molecular structure. The relationship of $|J|$ to the Me-Sn-Me angle,³ and indirectly to the coordination at Sn, provides a new means of determining the bonding and structure of these intractable methyltin(IV) polymers. Solid dimethyltin oxide (**9**) has been studied by IR¹⁴ and Mössbauer¹⁵ spectroscopy and by X-ray powder diffraction.¹⁶ These studies suggested that **9** has considerable crystallinity and that Sn is probably pentacoordinated, composed of cyclic Sn_2O_2 rings which, through additional coordination, produce a reticulated structure (Figure 4). This picture is refined by our solid-state ^{13}C NMR analysis: the single, narrow ^{13}C resonance and single pair of satellites ($|J| = 660$ Hz) indicate a uniform Sn coordination environment and magnetically equivalent methyls in the solid. The Me-Sn-Me angle is estimated to be about 135° , consistent with a distorted trigonal-bipyramidal structure in which the methyl groups are equatorial. The opening of the Me-Sn-Me angle from 120° may reflect orbital rehybridization¹⁷ in the trigonal plane, the Sn bond to oxygen containing more p-orbital character and those to Me having correspondingly greater s character. Alternatively, the large Me-Sn-Me angle raises the possibility of weak coordination to an additional oxygen atom (sixth ligand) similar to that observed for the distorted octahedral $[\text{Me}_2\text{SnCl}_2(\text{salicylaldehyde})_2]$ ($\theta = 131.4^\circ$).¹⁸

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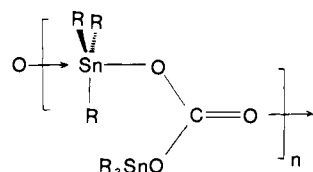
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Mössbauer data¹⁹ for methylstannonic acid, **10** (isomer shift = 0.40, quadrupole splitting (QS) = 1.29), has been interpreted in terms of linear O–Sn(Me)(OH)–O polymer chains with tetrahedral Sn, although the possibility of additional association of Sn was not excluded:



It has been noted,²⁰ however, that the Mössbauer QS is an unreliable indicator of Sn coordination in monoalkyltin(IV)s. The solid-state ¹³C NMR of this polymer shows the presence (Figure 3) of two broad Sn–methyl resonances which have large and different values of J (1160, 1030 Hz). Although substitution at Sn with electronegative substituents can cause an increase in $|J|$ for a given coordination number,¹² it seems very unlikely that the large J coupling found for **10** could arise from tetracoordinated, tetrahedral Sn. Instead, the large $|J|$ is better accommodated by a two- or three-dimensional polymer in which most Sn atoms are hexacoordinated or, possibly, pentacoordinated. The observed multiplicity of the methyl resonance may arise from the presence of different crystalline domains in the polymer or may correspond to different geometric isomers. Annealing the sample under N₂ at 100 °C for 5 h produced no change in the NMR spectrum.

Based on a study of the Mössbauer spectra of Sn carbonates, (R₃Sn)₂CO₃ (R = Me, *n*-Bu), it has been suggested²¹ that these compounds exist as linear polymers with one pentacoordinated R₃Sn group of each carbonate involved in the carbonate-bridged polymeric chain, the second tetracoordinated R₃Sn pendant from the chain:



In the ¹³C solid-state spectrum of **11** (Figure 3), however, only a single, well-resolved set of Sn satellites, $|J| = 570$ Hz, was observed (a second set of satellites of comparable intensity corresponding to tetrahedral Me₃Sn (340 < $|J|$ < 450 Hz) could have been observed easily). $|J|$ of **11** is similar to those observed for the pentacoordinated linear Me₃Sn polymers (Table I) and strongly suggests that Sn is predominantly pentacoordinated in this amorphous polymer. This analysis is reinforced by the single ¹³C resonance of **11**, which is of similar chemical shift to the pentacoordinated Me₃Sn polymers in Table I. If the polymeric carbonate contained a significant number of pendant, tetrahedral Me₃Sn groups, then a second resonance should have been observed [when dissolved in noncoordinating solvents, **1**, **3**, **4**, and **6** are dissociated and approximately tetrahedral at Sn; the solution ¹³C NMR resonances of the tetrahedral Me₃Sn group appear 2.2 to 9 ppm upfield of the solid-state pentacoordinated values (see Experimental Section)]. A structure for this two-dimensional polymer, resembling that of polymeric trimethyltin acetate, is suggested in Figure 5.

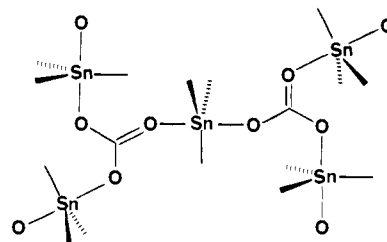


Figure 5. Structure proposed for amorphous (Me₃Sn)₂CO₃ polymer, **11**, based on solid-state ¹³C NMR analysis.

Conclusions

Solid-state ¹³C NMR is sensitive to the bonding and structure of methyltin(IV) polymers and appears to be broadly applicable to their study. Sn–methyl resonance multiplicity was observed for some of the crystalline polymers and provides information about the conformation of the monomeric units. Another powerful probe of structure is provided by the $J(^{117,119}\text{Sn}, ^{13}\text{C})$ coupled interaction which was resolved for most of the polymers examined. The $|J|$ can reveal the Me–Sn–Me bonding geometry and gives insight into the Sn coordination number. Successful application of solid-state ¹³C NMR to poorly characterized or amorphous methyltin(IV) polymers demonstrates the power of the technique to enhance understanding of the structure of refractory organotin(IV) materials.

Experimental Section

Materials. The methyltin(IV)s employed in this study were commercially available, except for **2**, which was provided by Professor J. J. Zuckerman (University of Oklahoma),¹⁰ and **1**,²² **3**,²³ **5**,²⁴ and **11**,²⁵ which were prepared by standard procedures. The crystalline, commercially available compounds were used as received except for **4**, which was freshly sublimed (20 torr, 80 °C). Methylstannonic acid (**11**) was freshly precipitated from aqueous, basic solution²⁶ and dried under vacuum prior to CPMAS analysis. Anal. Calcd for CH₄O₂Sn: C, 7.18; H, 2.41; Sn, 71.24. Found: C, 7.39; H, 2.30; Sn, 71.66 (±1.0).

NMR Spectroscopy. ¹³C CPMAS spectra were obtained at 15.08 MHz on a homebuilt instrument with a probe temperature of 304 K. Spectra were acquired with the following: (1) 60 MHz high power, proton decoupling; (2) spin locking cross-polarization with the ¹H and ¹³C fields matched at 57 kHz for 2 ms; (3) magic angle spinning at 2300 Hz in an Andrew-type rotor with 0.4 g of sample and 5 mg of Delrin (polyoxymethylene) as a secondary chemical shift standard; (4) signal averaging of 3 to 20 K scans at a dwell time of 50 μs and repetition rates ranging from 2 to 20 s.

Solution ¹³C NMR experiments were run at 100 MHz on a Bruker WM-400 spectrometer at 304 K. All solutions (CDCl₃) were <10% by weight in methyltin(IV). Line widths at half-height (LW) were less than 5 Hz except as noted. Chemical shifts (±0.1 ppm) were referenced to Me₄Si internal standard (0 ppm).

The following ¹³C NMR data do not appear elsewhere in the text. **Trimethyltin acetate, 1.** Solid: δ 25.6 (MeC(O)), 178.6 ppm (C(O)). Solution: δ –2.5 (Me₃Sn, $|J(^{119}\text{Sn}, ^{13}\text{C})|$ 401 Hz), 21.4 (MeC(O)), 176.9 ppm (C(O)). **Dimethylphenyltin acetate, 2.** Solid: δ 24.8 (MeC(O)), 131.9, 135 (br), 145.3 (aromatic C), 180.6 ppm (C(O)). **Trimethyltin nitrate, 3.** Solution: δ –1.3 ppm ($|J(^{119}\text{Sn}, ^{13}\text{C})|$ 395 Hz). **Trimethylstannol, 4.** Solution: δ –2.5 ppm (LW 30 Hz, $|J(^{117,119}\text{Sn}, ^{13}\text{C})|$ 388 Hz). **Bis(trimethyltin) carbonate, 11.** Solid: δ 163.7 ppm (CO₃).

Acknowledgment. We thank Professor J.J. Zuckerman (University of Oklahoma) for providing us with a sample of compound **2** and details of its crystal structure prior to publication.

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