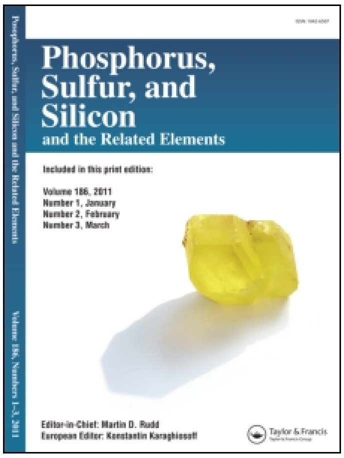

**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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**To cite this Article** Dakternieks, Dainis , Lim, Allan E. K. and Lim, Kieran F.(1999) 'Electrospray Mass Spectrometric Studies on the Solution Chemistry of Triorganostannyl Trifluoromethanesulfonates', Phosphorus, Sulfur, and Silicon and the Related Elements, 150: 1, 339 — 356

**To link to this Article: DOI:** 10.1080/10426509908546403

**URL:** http://dx.doi.org/10.1080/10426509908546403

*Phosphorus, Sulfur and Silicon*, 1999, Vol. 150-151, pp. 339-356
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# Electrospray Mass Spectrometric Studies on the Solution Chemistry of Triorganostannyl Trifluoromethanesulfonates

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Compounds of the type $R_3Sn(OSO_2CF_3)$ (triorganostannyl trifluoromethanesulfonates, R = Me, Bu, Ph) were synthesized and investigated in solution using electrospray mass spectrometry. The mono-acetonitrile adduct $[R_3Sn{\bullet}(CH_3CN)]^+$ is the dominant ionic species in acetonitrile solution, with a weaker signal owing to $R_3Sn^+$. The relative intensity of $R_3Sn^+$ increases significantly upon the use of dichloromethane as a solvent. Variable temperature $^{119}Sn$ NMR studies were also undertaken on the trimethylstannyl and triphenylstannyl trifluoromethanesulfonates in dichloromethane solution. The $^{119}Sn$ chemical shifts and Lewis-base adduction studies reveal that the triorganostannyl trifluoromethanesulfonates are only slightly more Lewis-acidic than the corresponding triorganostannyl chlorides. These solutions are too labile to be studied on the NMR timescale.

*Keywords:* organotin; cations; mass spectrometry; solution chemistry

## INTRODUCTION

### Triorganostannyl Cations

The nature of cationic organotin species in solution has been the subject of extensive discussion in recent years.[1,2] The first report on the formation of triorganostannyl cations was published in 1923,[3] but interest in this area only intensified after the advent of multinuclear NMR techniques.

The detection of $SnH_3^+$ in fluorosulfonic acid at low temperatures by $^{119}Sn$ NMR spectroscopy was reported by Webster and Jolly in 1971.[4] This study was extended to incorporate the detection of the entire $SnMe_{3-n}H_n^+$ (n = 0 - 3) series by Birchall and Manivannan in 1985,[5] who found that these solutions were only stable at very low temperatures and that warming to room temperature resulted in hydrogen or methane evolution to afford Sn(II) species.

The supposed formation of tricoordinate tin cations in solution in ambient conditions was reported by Lambert and Kuhlmann in 1992.[6] Perchlorate and tetrakis(pentafluorophenyl)borate were used as counter-anions and the low field $^{119}Sn$ chemical shifts (150 – 360 ppm) for these species led them to conclude that axial interactions were low or nonexistent and that they had managed to prepare true tricoordinate tin cations.

The following reaction (Scheme 1) was used by Kira *et al.* to generate tributylstannyl tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate (TFPB):[7]

$$Bu_3SnH + Ph_3C^+(TFPB)^- \xrightarrow[-70\ ^\circ C]{CD_2Cl_2} Bu_3Sn(TFPB) + Ph_3CH$$

SCHEME 1

Reaction monitoring by NMR spectroscopy showed this reaction to progress quantitatively to afford a tin species that resonated at 356 ppm.[7] This shift is close to the $^{119}$Sn chemical shift of 360 ppm obtained for tributylstannyl tris(pentafluorophenyl)borate.[6] Kira *et al.* concluded that the low field shift obtained for $Bu_3Sn$(TFPB) was "indicative of no significant interaction between the tin cation and the counterion".[7]

The publication of theoretical $^{119}$Sn NMR shift calculations in 1993 by Cremer *et al.*[8] sparked the debate on whether tricoordinate $R_3Sn^+$ could really be observed in solution. Individual gauge for localized orbitals (IGLO) calculations gave chemical shift values in the neighborhood of +1000 ppm for trigonal planar $R_3Sn^+$. They concluded that the naked cations do not exist in solution and what were previously observed were, in fact, donor-acceptor complexes with solvent molecules.[8]

In 1996, Arshadi *et al.*[1] employed $^{119}$Sn/$^{29}$Si NMR shift correlations to argue also that no naked triorganostannyl cations had been observed in solution to date.

## Electrospray Mass Spectrometry (ESMS)

ESMS is a relatively new technique originally designed for the analysis for large biomolecules.[9] The precise mechanism of ion production is not known, but is believed to involve evaporation of solvent from the droplets of sample solutions, releasing individual ions and ion clusters.[10] Large proteins like Carbonic Anhydrase II (MW ~ 29000) have been successfully analyzed using ESMS, attesting to the gentle nature of the ionization process.[10]

Pioneering work by Colton *et al.*[11] has demonstrated that this new technique shows great promise as an investigative tool in organometallic solution chemistry. The analysis of large biomolecules entails multiply protonating the molecule and then identifying it from the mass spectrum using the signals corresponding to the series of $[(\text{Protein})H_n]^{n+}$ species. In contrast, solutions of organometallic compounds can be analyzed and the raw spectrum used without the need for deconvolution as the charges on organometallic species in solution are invariably of small magnitude. In fact, organometallic species detected in this fashion are usually singly charged, as multiply-charged organometallic ions tend to associate with counterions in solution to afford singly-charged aggregates.[11] As a direct consequence, the quadrupole mass analyzer can resolve the often characteristic isotopic distribution pattern of the analyte, paving the way for unambiguous identification of these organometallic ions.

Colton *et al.* also stressed an important point that pre-existing ions in solution are observed directly in the gas phase, owing to the soft transfer of ions from solution to the gas phase: no external ionization mechanism is employed in ESMS.[11] His experiments have shown that ESMS characterization of solution species is in excellent agreement with results obtained by other methods like NMR spectroscopy and electrochemistry. It is therefore possible to employ ESMS to study new solution chemistry.[11] This has proven benefits in studying complexes that are labile on the NMR timescale[12] or complexes which cannot be studied using NMR, such as paramagnetic complexes.[11]

The ESMS technique has many potential uses in studying organotin solution chemistry: Henderson and Taylor have studied the hydrolysis of the triorganostannyl halides in 1:1 acetonitrile / water.[13] Dakternieks *et al.* have successfully employed ESMS to demonstrate that the organotin oligomer $[(BuSn)_{12}O_{14}(OH)_6]Cl_2 \cdot 2H_2O]$ retains its structure in solution, as well as to examine the reactivity of the oligomer towards alcohols and phosphines.[14]

The current work has used ESMS to study the solution chemistry of cationic triorganostannyl species in solution. The faster timescale and greater sensitivity of the technique compared to NMR is useful in detecting small components of the solution equilibria.

The target compounds for study were the triorganostannyl trifluoromethanesulfonates (triflates). The triflate functionality is known to be a good leaving group and the target compounds could be easily synthesized using the following scheme:

$$R_3SnCl + Ag(trif) \xrightarrow[RT]{CH_2Cl_2} R_3Sn(trif) + AgCl\,(s)$$

SCHEME 2

The ESMS studies were conducted with the trimethyl-, tri-n-butyl- and the triphenylstannyl triflates in order to determine the effects of the organic group on the solution chemistry of the triflates. The reaction of these triorganostannyl triflates with various Lewis bases was monitored in order to gain some knowledge about the Lewis acidity of these species compared to the Lewis acidity of the triorganostannyl halides. The ESMS studies were supplemented with variable-temperature NMR studies.

## RESULTS AND DISCUSSION

### ESMS Experiments at a Low Cone Voltage (20 V)

In ESMS, the cone voltage draws ions into the MS analyzer. At sufficiently low cone voltages (e.g. 20 V), collision-induced dissociation of the analyte ions does not occur, therefore the detected ions must have been present in the analyte solution. Indeed, Colton *et al.* assert that "there are now numerous examples where there is complete correlation between the observed ions and the species known to be present in solution."[11]

Positive-ion ESMS analyses of the triorganostannyl triflate solutions in dichloromethane at a cone voltage of 20 V revealed that uncomplexed $R_3Sn^+$ cations and the di-tin-mono-triflate cluster $[R_3Sn(trif)SnR_3]^+$ were the predominant cationic species present. Smaller signals corresponding to the acetonitrile adduct $[R_3Sn{\bullet}NCCH_3]^+$ and, occasionally, the protonated distannoxane $[R_3SnOHSnR_3]^+$ were also observed.

The acetonitrile adduct arises from the use of acetonitrile as the carrier solvent. Therefore, as some mixing of the analyte solution with the carrier within the sample loop is inevitable, the formation of a small amount of the acetonitrile adduct is expected. With our instrumentation it is not currently possible to use dichloromethane as a carrier solvent as it degrades the tubing used to convey the carrier solvent from the syringe pump to the sample loop. The protonated distannoxane is a known hydrolysis product of triorganostannyl systems[15] and arises from trace amounts of water present in the solvent or the sample delivery capillary.

The negative-ion spectra of the dichloromethane solutions at 20 V revealed the presence of the triflate anion and the mono-tin-di-triflate $[R_3Sn(trif)_2]^-$ cluster.

Positive-ion analyses on the acetonitrile solutions of the triorganostannyl triflates revealed significant changes in the speciation in solution. The mono-acetonitrile adduct was the predominant cationic species, and small amounts of the uncomplexed cation and di-acetonitrile adduct were detected. Small signals owing to the di-tin-mono-triflate cluster and, occasionally, the protonated distannoxane are also detected.

The negative-ion spectra of the acetonitrile solutions at 20 V also had the triflate anion as the base peak, while the signal arising from the mono-tin-di-triflate cluster was smaller than that found in dichloromethane solution. These results are summarized in Table 1.

| Solvent | Positive ions | Negative ions |
|---|---|---|
| Acetonitrile | $[R_3Sn{\bullet}CH_3CN]^{+a}$<br>$R_3Sn^+$<br>$[R_3Sn{\bullet}2CH_3CN]^+$<br>$[(R_3Sn)_2trif]^+$<br>$[(R_3Sn)_2OH]^{+b}$ | $CF_3SO_3^{-a}$<br>$[R_3Sn(CF_3SO_3)_2]^-$ |
| Dichloromethane | $[(R_3Sn)_2trif]^{+a}$<br>$R_3Sn^{+a}$<br>$[(R_3Sn)_2OH]^{+b}$<br>$[R_3Sn{\bullet}CH_3CN]^{+c}$ | $CF_3SO_3^{-a}$<br>$[R_3Sn(CF_3SO_3)_2]^-$ |

[a]Predominant species; [b]Occasional hydrolysis product; [c]From acetonitrile carrier.

TABLE 1: Ions detected using ESMS at 20 V cone voltage

Note that in the ESMS spectra of triphenylstannyl triflate in acetonitrile, signals from $Ag^+$ cations as well as the mono- and di-acetonitrile adducts of $Ag^+$ were also observed. It was found that interference from $Ag^+$ signals could be countered to a large extent by the use of a small excess (approximately 10%) of triphenylstannyl chloride in the reaction mixture.

The $R_3Sn^+$ signals were very small when acetonitrile solutions were analyzed, but became much larger in magnitude when dichloromethane solutions were used. We are therefore confident that these observations are not artifacts of the transfer to the gas-phase, but instead may be viewed as evidence for the existence of uncomplexed triorganostannyl cations in solution. Given the calculated $^{119}Sn$ chemical shifts by Cremer *et al.*[8] and the fact that *ab initio* calculations by

Schleyer *et al.*[16] show that triorganosilyl cations can interact with methane and noble gases, we cannot claim that the $R_3Sn^+$ we observe is completely uncoordinated.

Instead, we view these results as evidence of an equilibrium between uncomplexed solvated $R_3Sn^+$ and solvent-complexed solvated $R_3Sn^+$ in acetonitrile solution, and an equilibrium between uncomplexed, solvated $R_3Sn^+$ and solvated $[(R_3Sn)_2(trif)]^+$ in dichloromethane solution.

While gas-phase calculations have demonstrated that $R_3Sn^+$ binds very strongly to various Lewis bases,[8] a strong binding energy does not preclude kinetic lability in solution. For example, whilst the enthalpy of proton transfer to water is 723 kJ $mol^{-1}$,[17] it is also well known that protons are extremely mobile in water.[17]

It must be borne into consideration that ESMS can only detect the charged components of a solution. Conductivity measurements performed on trimethylstannyl triflate[18] in nitrobenzene and dimethyl sulfoxide have shown that the compound is only a weakly dissociating electrolyte and that the following equilibrium lies mainly to the left:

$$R_3Sn(trif) \rightleftharpoons R_3Sn^+ (solvated) + trif^-$$

SCHEME 3

The conductance of trimethylstannyl triflate in dimethyl sulfoxide is nearly an order of magnitude higher than that in nitrobenzene, but interestingly enough, is still indicative of a relatively weak electrolyte.[18]

It can therefore be surmised that in non-coordinating solvent systems like dichloromethane, while the overall ion concentration is low, the cationic species in solutions of triorganostannyl triflates are primarily uncomplexed (but solvated) triorganostannyl cations and the di-tin-mono-triflate clusters. However, in coordinating solvents like acetonitrile, while there are more ionic species present in solution, they are predominantly solvent adducts of the triorganostannyl cation.

Re-analysis after addition of a few drops of water to the acetonitrile solutions did not significantly change the ESMS spectra apart from an increase in the intensity of the peak arising from the protonated distannoxane hydrolysis product. Peaks arising from $R_3Sn^+$ and the mono-acetonitrile adduct of the cation were still present. At first, this result appears to be surprising as it would be expected that water, being a relatively strong Lewis base, would scavenge the cationic organotin species to afford mainly hydrated triorganostannyl cations, i.e. $[R_3Sn\bullet 2H_2O]^+$. However, the hydrolysis of triorganostannyl compounds is known to be pH dependent[19] and the quantities of water added were probably insufficient to allow hydrolysis to progress beyond the distannoxane stage.

Positive-ion ESMS analysis of a mixture of the triorganostannyl triflate solutions (R = Me, n-Bu) in dichloromethane revealed the presence of mixed di-tin-mono-triflate cations, $[R_3Sn(trif)SnR'_3]^+$. Small signals arising from mixed protonated distannoxanes $[R_3Sn(OH)SnR'_3]^+$ were also detected.

In the negative-ion spectrum of the mixture, small signals arising from mixed di-tin-tri-triflate anionic species $[R_3Sn(trif)_3SnR'_3]^-$ were also detected, (R, R' = Me, n-Bu). Re-analysis after the addition of a few drops of water to the solution revealed a large increase in intensity of the signals due to the presence of mixed protonated distannoxanes.

These results attest to the lability of these systems in solution and are in agreement with results obtained by Blunden and Hill,[20] who reported $^{119}Sn$ NMR evidence for the formation of mixed distannoxanes in solutions containing mixtures of pure distannoxanes.

## Comparative ESMS Studies of the Triorganostannyl Chlorides

Solutions of the triorganostannyl halides in acetonitrile were analyzed to compare the spectra of the triorganostannyl halides and the triorganostannyl triflates.

No discernible signals resulting from the triorganostannyl halides could be observed in the ESMS analysis of the anhydrous acetonitrile and dichloromethane solutions. However, adding a few drops of water and re-analyzing the samples afforded the detection of ionic species.

In the positive-ion spectra, the main cationic species detected were the uncomplexed triorganostannyl cation, the mono-acetonitrile adduct and the protonated distannoxane. Very small signals corresponding to $[R_3Sn{\bullet}OH_2]^+$ and $[R_3Sn{\bullet}OH_2{\bullet}NCCH_3]^+$ could also be detected for all three triorganostannyl chloride samples.

In the negative-ion mode, the five-coordinate triorganostannyl dihalide anion was the predominant species. A small signal arising from free chloride aniion was also present.

These results are in agreement with potentiometric and conductivity studies by Prince,[21] who concluded that the presence of an electron donor is necessary for the dissociation of an triorganostannyl halide. Acetonitrile is an electron donor, and NMR studies have shown that it does coordinate with the triorganostannyl halides in solution.[2] It is therefore believed that acetonitrile does not have sufficient Lewis basicity to completely displace the chloride ion from a triorganostannyl chloride.

The hydrolysis product ES mass spectra obtained differ somewhat from those obtained by Henderson and Taylor[13] at 20 V cone voltage: along with the signals reported here, they detected significant quantities of the $[(R_3Sn)_{n+1}(OH)_n]^+$ series in the positive-ion mode and higher hydrolysis products like $[R_3SnCl(OH)]^-$ and $[R_3SnOSnR_3Cl]^-$ in the negative-ion mode. This discrepancy is due to the addition of only a few drops of water to the samples studied in this section, whereas

Henderson and Taylor used a 1:1 v/v mixture of acetonitrile and water as a solvent. Therefore, it is to be expected that their samples are much further along the hydrolysis equilibria than the samples analyzed here.

It is of interest to note that even at such high water concentrations, they observed very weak signals owing to the presence of $R_3Sn^+$.[13] Again, their samples were probably not at a sufficiently high pH to cause complete hydrolysis of the triorganostannyl cations present.

## Variable Temperature $^{119}$Sn NMR Studies

Variable temperature $^{119}$Sn studies were performed on solutions of trimethylstannyl and triphenylstannyl triflate in dichloromethane. The observed chemical shifts are shown in Table 2.

| Compound | Temperature | δ $^{119}$Sn (ppm) | $W_{1/2}$ (Hz) |
|---|---|---|---|
| $Me_3Sn(trif)$ | 25 °C | 168.09 | 65 |
| $Me_3Sn(trif)$ | -95 °C | 172.00 | 240 |
| $Ph_3Sn(trif)$ | 25 °C | -46.54 | 55 |
| $Ph_3Sn(trif)$ | -95 °C | -46.58 | 45 |
| $Me_3SnCl$ | 25 °C | 164.2[22] | - |
| $Ph_3SnCl$ | 25 °C | -44.7[22] | - |

TABLE 2: Variable temperature $^{119}$Sn NMR chemical shifts

Trimethylstannyl triflate has a slightly higher $^{119}$Sn resonance than the corresponding chloride; the resonance is seen to shift slightly further downfield upon cooling and the line width broadens significantly. Triphenylstannyl triflate resonates slightly downfield from triphenylstannyl chloride and no significant change occurs upon cooling to -95 °C.

In light of the theoretical NMR shifts calculated by Cremer *et al.*,[8] the triorganostannyl triflates in dichloromethane solution appear to be rather far from the ideal uncoordinated trigonal planar $R_3Sn^+$, which would resonate downfield from 1000 ppm.[8] Indeed, we know this to be the case as conductivity measurements[18] have demonstrated that the triorganostannyl triflates are far from being completely dissociated in solution.

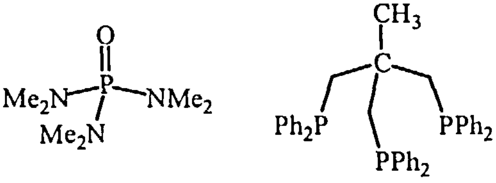
Although the trimethylstannyl triflate resonance broadens significantly upon cooling, it is apparent that variable temperature NMR could not sufficiently slow the exchange rates to permit identification of the individual equilibrium components.

Interestingly, the NMR shifts of the triorganostannyl triflates do not appear to be significantly different from the NMR shifts of the corresponding triorganostannyl halide, implying that the average electronic shielding environment about the tin atoms in the triorganostannyl triflates and the tin atoms in the corresponding triorganostannyl halides are not dissimilar.

## Studies on the Lewis Acidity of the Triorganostannyl Triflates

ESMS was used to analyze mixtures of triorganostannyl triflate (R = Me, n-Bu, Ph) solutions with the Lewis bases: 1,1,1-tris(diphenylphosphinomethyl)ethane (TRIPHOS) and hexamethylphosphoramide (HMPA).

These Lewis bases have different donor properties and steric requirements. Their structures are shown in Figure 1:



**HMPA**

**TRIPHOS**

FIGURE 1: Structures of HMPA and TRIPHOS

The phosphine moieties are expected to be weak bases while the phosphine oxide functionality in HMPA is predicted to be a strong Lewis base.

Addition of half an equivalent of TRIPHOS to the triorganostannyl triflate solutions afforded positive-ion spectra that were virtually identical to those previously acquired without the addition of base. Only very weak signals due to protonated TRIPHOS and a 1:1 TRIPHOS to triorganostannyl cation adduct were observed. The intensity of these signals increased slightly when the base to triorganostannyl triflate ratio was raised to 2:1. It has to be noted that for these samples the TRIPHOS adduct peak was noticeably stronger for the triphenylstannyl triflate solutions than the TRIPHOS adduct peaks in the other two samples: it is expected that triphenylstannyl triflate exhibits stronger Lewis acidic character than the trialkylstannyl triflates.

Addition of HMPA to the triorganostannyl triflate solutions afforded both 1:1 and 1:2 stannyl cation to HMPA adducts from the very outset. Increasing the proportion of HMPA caused the 1:2 HMPA adduct signal to increase in intensity. It is apparent that the phosphine oxide moiety is substantially more Lewis basic than the phosphine compounds.

Addition of excess tributylphosphine oxide to the triorganostannyl triflate solutions also resulted in the formation of 1:2 stannyl cation to base adducts while addition of excess pyridine to trimethylstannyl triflate formed the mono-pyridine adduct of the trimethylstannyl cation cleanly.

Preliminary adduction studies using 1,2-bis-(diphenylphosphino)ethane (DPE) and bis(diphenylphosphino)-methane (DPM) have also been performed within our research group.[23] It was found that (DPE) and (DPM) form small amounts of 1:1 adducts with $R_3Sn^+$. Small amounts of both mono- and bis-adducts (and oxygen adducts thereof) were detected when tris(diphenylphosphinoethyl)phosphine (TETRAPHOS) was added to the triorganostannyl triflate solutions.

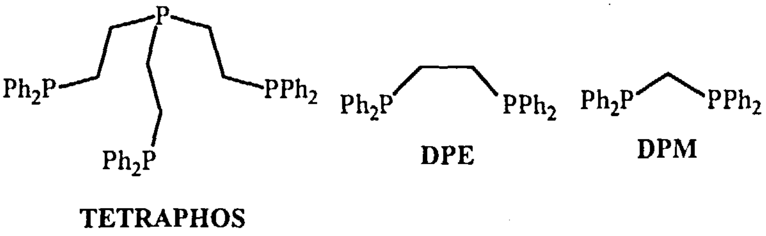


FIGURE 2: Structures of TETRAPHOS, DPE and DPM

$^{119}$Sn NMR studies by Colton and Dakternieks[24] have shown that triorganostannyl chlorides do not react with phosphines but form 1:1 adducts with phosphine oxides. The ESMS results presented hint at a very weak interaction between the triorganostannyl triflates and phosphine compounds. This is in concordance with the present NMR results which suggest that the triorganostannyl triflates are only slightly more Lewis acidic than the triorganostannyl halides. The triorganostannyl triflates very readily form 1:2 adducts with phosphine oxides while triorganostannyl halides only form 1:1 adducts. Colton and Dakternieks[23] have established that phosphine oxides are stronger Lewis bases than halide anions, therefore, given the more ionic character of the tin-triflate bond, the triflate moiety would be easily displaced to afford the 1:2 adducts.

While it was possible to gain some information about the reactivity of the triorganostannyl triflates using ESMS, a major shortcoming of this technique is that only-charged species are detected. For a more complete understanding on the reactivity of the triorganostannyl triflates towards Lewis bases, it would be advantageous to couple the ESMS results with NMR studies.

## CONCLUSION

ESMS analysis of triorganostannyl triflate solutions provided evidence for the existence of uncomplexed triorganostannyl cations in solution. In solution, the solvation equilibria occur too quickly to observed using NMR.

Variable temperature studies of the triorganostannyl triflates afforded chemical shifts not significantly different from those of the corresponding triorganostannyl halides. Therefore, it can be concluded that the average electronic environment about the triorganostannyl triflates and the triorganostannyl halides are similar.

Results obtained from ESMS studies on the reactivity of the triorganostannyl triflate solutions towards Lewis bases implied that the triorganostannyl triflates are only slightly more Lewis acidic than the corresponding triorganostannyl halides. This is in agreement with the NMR results.

It has been shown overall that ESMS demonstrates considerable power as an investigative tool in ionic solution chemistry. Further work relevant to our group's interests would entail monitoring the speciation of the diorganostannyl dihalides and the monoorganostannyl trihalides with respect to pH. This knowledge would be especially useful in planning syntheses involving poly-tin clusters.

## EXPERIMENTAL

### General Procedure

Electrospray mass spectra were obtained with a Platform II single quadrupole mass spectrometer (Micromass, Althrincham, UK) using an acetonitrile mobile phase. Acetonitrile or dichloromethane solutions (~1 mM) of the compounds were injected directly into the spectrometer via a Rheodyne injector equipped with a 50 μL sample loop. A Harvard 22 syringe pump delivered the solutions to the vaporization nozzle of the electrospray ion source at a flow rate of 10 μL min$^{-1}$. Nitrogen was used both as a drying gas and for nebulization with flow rates of approximately 200 mL min$^{-1}$ and 20 mL min$^{-1}$ respectively. Pressure in the mass analyzer region was typically $4 \times 10^{-3}$ Pa. Typically, 10 signal-averaged spectra were collected.

$^{119}$Sn NMR spectra were obtained using a Jeol JNM-GX 270 FT NMR spectrometer. Chemical shifts were referenced to tetramethylstannane. Temperatures were maintained using a Jeol GTV3 control system.

Acetonitrile and dichloromethane were distilled over calcium hydride under an atmosphere of dry nitrogen gas.

### Preparation of Triorganostannyl Triflates for ESMS Analysis

The triorganostannyl triflates were generally prepared immediately before use via Scheme 2. A molar equivalent of silver triflate was added to the relevant triorganostannyl chloride (typically about 100 mg) and the resultant mixture was then taken up in 10 mL of dichloromethane and stirred. The reaction mixtures were protected from light and moisture as the triorganostannyl triflates are susceptible to hydrolysis while both silver triflate and silver chloride are light sensitive. It was found that upon standing in light the white silver chloride precipitate in the product mixture gradually turned purple.

The reaction between $R_3SnCl$ and Ag(trif), (R = Me, n-Bu), was fast, affording clear solutions with the silver chloride precipitate settling within 10 minutes. The reaction between triphenylstannyl chloride and silver triflate was substantially slower, requiring stirring in excess of 45 minutes. The resultant product solution was cloudy and had to be set aside for a further 10 minutes to allow the silver chloride precipitate to settle. The prepared solutions were diluted by a factor of approximately 20 with either acetonitrile or dichloromethane for ESMS analysis. All peak identifications were consistent with the calculated isotope distributions.

### Preparation of Triorganostannyl Triflates for VT $^{119}Sn$ NMR Analysis

The triorganostannyl triflates were prepared in dichloromethane using the aforementioned procedure but on a larger scale. The reaction mixture was stirred for 3 hours to ensure complete reaction. The silver chloride precipitate in the reaction mixtures was then allowed to settle and the supernatant liquid transferred into NMR tubes. Spectra were acquired at both room temperature and -95 °C.

## ACKNOWLEDGMENTS

We thank the Australian Research Council for financial support and Deakin University and Department of Education, Training, and Youth Affairs (DETYA), Australia, for the award of an Overseas Postgraduate Research Scholarship to A. E. K. L.

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