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Direct NMR spectroscopic evidence for solvated triorganostannyl cations

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Abstract

Solutions of tributyl- and triphenylstannyl perchlorates have been studied by NMR spectroscopy. Solvent-induced changes in ^{119}Sn, and ^{37}Cl line widths as well as Sn–C scalar couplings indicate the existence of an equilibrium between tetrahedral and trigonal bipyramidal arrangements. Bipyramidal forms are favoured if the solvent donicity is increased, including structures in which the solvent molecules occupy the two axial positions of the five-coordinate trigonal bipyramid. This situation is unequivocally demonstrated by the presence of ^{119}Sn–^{31}P coupling using hexamethylphosphoramide-d_{18} as solvent.

1. Introduction

The question of whether triorganosilyl perchlorates undergo ionization in organic solvents is probably one of the most discussed topics in organometallic chemistry [1]. The role of solvation and the geometry of silicon are important issues in this context, and have recently been addressed [1b,c]. A major problem in these studies has been the insensitivity of the silicon nucleus in NMR spectroscopy, and so the lack of a direct NMR probe. This limitation is especially obvious in low donicity solvents, *i.e.* under precisely the solvent conditions in which a truly trivalent silylenium ion might exist. The present understanding of the structure of these silyl complexes is thus to a large extent based on other NMR and conductivity measurements, and the indirect nature of the evidence is in part responsible for the current controversy.

Since the behaviour of triorganosilyl anions in organic solvents could to a large extent be predicted from the behaviour of other more stable and suitable Group IV element anions [2] we thought that a similar approach could be used to throw light on the structures of silylenium species by performing a study of solutions of compounds such as triorganostannyl perchlorates and fluoroborates.

Effects of solvents on tri-n-butyl- and triphenyltin(IV) compounds, mostly halides or carboxylic esters, have been been studied previously by NMR [3] or far-infrared spectroscopy [4]. Generally it was found that these structures were converted from a tetrahedral into a trigonal bipyramidal form as the donor strength of the solvent was increased. These changes in tin coordination were generally associated with upfield shifts in the tin resonance of the order of 200 ppm and in an increase in the Sn–C one-bond coupling of *ca.* 160–200 Hz. The thermodynamic parameters were calculated from the temperature and concentration dependence of the ^{119}Sn chemical shifts and it was found that the stability of the formed bipyramidal solvent complexes increased on replacing alkyl by phenyl substituents [3d]. A far-infrared investigation of trimethylstannyl-chloride suggested that a continous range of molecular geometries existed between the tetrahedral and bipyramidal arrangements, the latter being more closely approached as the solvent donicity increases [4]. In no case so far has a solvated ionic stannyl species been detected in organic solvents.

2. Results and discussion

The stannyl perchlorates and fluoroborates were generated in solution from the hydride by reaction with a trityl salt by analogy with the preparations of silyl perchlorates [1a,b]. The stannyl fluoroborates were

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TABLE 1. ^{119}Sn chemical shifts and one-bond Sn–C scalar couplings for tributyl- and triphenylstannyl derivatives in various solvents [a].

	CH_2Cl_2	sulfolane	MeCN	pyridine	DMPU	DMSO	HMPA
Bu_3SnCl	156 (339)	130	119	14 (449)	18	2 (464)	−47 (491)
Bu_3SnClO_4	220 (353)	139	54 (424)	−24	6	12 (465)	−43
Bu_3SnBF_4	160	168	44	1	4	11	−44
Ph_3SnCl	−44 (614) [b]	−93	−98	−213 (783)	−223	−227 (810)	−242 (840)
Ph_3SnClO_4	–	−157	−211	−232	−263	−236 (813)	−275
Ph_3SnBF_4	–	−152	−216	−229	−261	−236 (809)	−276

[a] Chemical shifts for ^{119}Sn measured relative to tetramethyltin at room temperature. Concentration of tin derivative 0.4 M. [b] One-bond Sn–C coupling in Hz. Values are missing for solvents in which the *ipso* carbon signals were too broad (exchange) for detection of coupling to tin.

quite stable in solution, in contrast to the corresponding silyl species, which rapidly gave silyl fluorides.

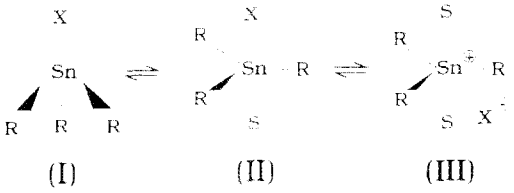
In Table 1 are shown the ^{119}Sn chemical shifts for tributylstannyl (**1**) and triphenylstannyl perchlorate (**2**) as in various solvents. In general there is an upfield shift as the donicity of the solvent increases. The magnitude and the size of the solvent induced shift changes for **1** and **2** are quite similar to those reported earlier for the corresponding halides or other derivatives. Changes from inert to dipolar media are also accompanied by an increase in the ^1J(Sn–C) scalar coupling by *ca.* 200 Hz at the most (Table 1) [3]. The increase in ^1J is expected if the triorganostannyl species are converted from a tetrahedral into a trigonal bipyramid arrangement as the s-character of the tin bonding orbitals increases (sp^2) [3a,3b,5]. Better donor solvents will also increase the s-character of the Sn–C bond as the electron density increases on the tin atom. An interesting observation is also that the ^{119}Sn chemical shifts for **2** are practically the same as those for the fluoroborates (Table 1), a feature that strongly supports an ionic structure. This is also true for the corresponding tributyl complexes in high donicity solvents.

The changes in the ^{13}C chemical shifts for the phenyl carbons of **2** upon variation of the donicity of the solvent are rather minor except for the *ipso* carbon. This resonance is typically shifted by 5 ppm upfield on going from methylene chloride to a high donicity solvent. The corresponding *para* carbon shift is of the order of 2 ppm downfield. The absolute shift values as well as the shift changes are very similar to those observed for the corresponding chlorides [3a,c] and can be satisfactorily explained in terms of a change in π-polarization of the phenyl rings caused by the variation in the donor–acceptor interaction.

It is also possible to probe the solvation by measuring the $^{35(37)}$Cl line widths [1a,b]. For both perchlorates a ^{37}Cl line narrowing is observed as the donicity of the solvent is increased, *i.e.* there is a change in line widths from more than 100 Hz in dichloromethane/acetonitrile (ACN) to less than 4 Hz in dipolar protophilic solvents like N,N-dimethylpropylenurea (DMPU), dimethylsulphoxide-d_6 (DMSO), or hexamethylphosphoramide-d_{18} (HMPA). This value is close to those observed for perchloric acid (60%) or trityl perchlorate in DMSO (*ca.* 3 Hz). Although a narrow line-width of the chlorine signal strongly indicates the presence of perchlorate ions, it does not exclude the possibility that the Group 4 element atom is complexed, even possibly covalently, with other nucleophilic ligands such as solvent molecules. Even weak donors such as ethers, ketones and acetonitrile may take part in such complexation, as recently shown for the trimethylsilyl cation [6]. Hence, hydrolysis of the silyl perchlorate may not be the only explanation for the presence of free perchlorate [1a].

The presence of more than one solvated form in equilibrium was demonstrated by a DMSO or DMPU titration of a dichloromethane solution of the triorganostannyl perchlorates (0.8 M). Addition of DMSO or DMPU at low temperature caused the tin resonance to shift upfield. At approximately equimolar ratio of solute to donor solvent, the signal broadened and split into two resonances (δ(^{119}Sn): Bu_3SnClO_4 (**1**) = +90 and −7 ppm, Ph_3SnClO_4 (**2**) = −208 and −267 ppm at 200 K), which then collapsed into a single line upon further addition of the donor solvent. Representative spectra are shown in Fig. 1. The intensity of the high field signal is increased if R = Ph or if X is a weak Lewis base such as ClO_4^-.

The results reported so far strongly favour the existence of an equilibrium between tetrahedral and two solvated trigonal bipyramidal structures as shown below:



(I) (II) (III)

When the same experiments were performed with HMPA, the most powerful ionizing solvent, it could be

clearly observed as can be seen from Fig. 2, that the high field signal corresponds to a structure in which both axial positions are occupied by HMPA molecules. The chemical shift of this signal is independent of the X ligand and the splitting pattern (^2J(Sn–P) = 163 Hz) is unaffected by a temperature change for the triphenyl derivative, but for **1** the triplet (^2J(Sn–P) = 146 Hz) collapses to a singlet when the temperature is raised. No resolved signal could be detected for the low field signal at low temperature. A decrease in the HMPA concentration only caused a further downfield shift and increased broadening of the signal. Only in the case of triphenylstannyl chloride at low temperature could such slow exchange conditions be reached such that a doublet [(^2J(Sn–P) = 139 Hz, Fig. 2(d)] from the singly solvated bipyramidal form (II) could be seen.

The equilibrium positions and exchange rates are clearly dependent on the nature of R and X. The doubly solvated species III is favoured if the cation coordinating ability (donicity) of the solvent increases,

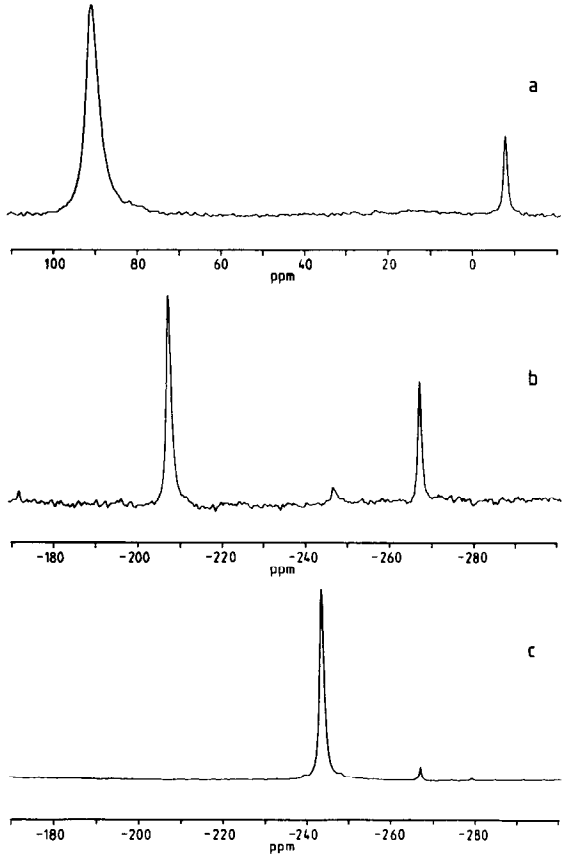


Fig. 1. Representative ^{119}Sn NMR spectra of (a) tributylstannyl- (**1**) and (b) triphenylstannyl perchlorates (**2**) obtained at 200 K in DMPU/methylene chloride. For comparison the corresponding spectrum (c) of triphenylstannyl chloride is included. Equimolar concentrations of stannyl derivative and DMPU (0.8 M:0.8 M) were used.

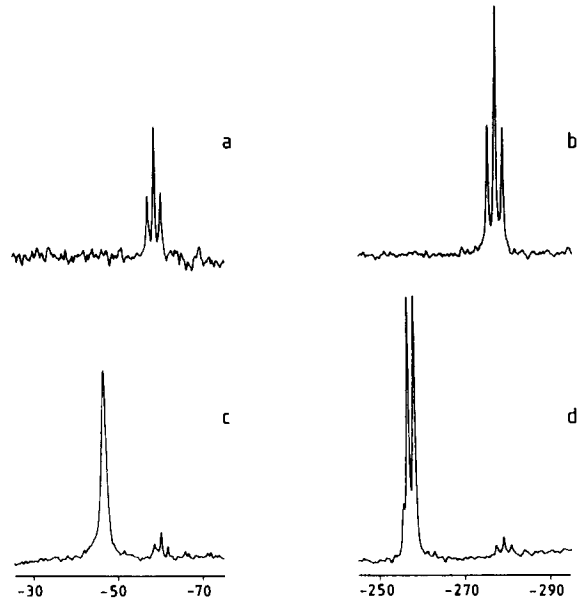


Fig. 2. ^{119}Sn NMR spectra of **1** and **2** (a and b, respectively) and the corresponding chlorides (c and d, respectively) in HMPA/methylene chloride at 200 K. The relative concentrations stannyl derivative: HMPA were 0.2 M:0.8 M.

if the ligand is changed from alkyl to aryl, or if X^- is a weaker Lewis base [4]. A variable temperature study clearly demonstrated these features. Lowering the temperature causes an upfield shift as the solvation of the positively charged tin atom is favoured. This temperature-induced shift change is small in those systems in which the doubly solvated species III is already strongly favoured at high temperature ($\Delta\delta$ (350–230 K; DMPU); Bu_3SnCl = 57 ppm, Bu_3SnClO_4 (**1**) = 26 ppm and Ph_3SnClO_4 (**2**) = 8 ppm).

Birchall *et al.* [7] previously reported the value of the ^{119}Sn chemical shift of trimethylstannyl fluorosulphate in HSO_3F of 322 ppm at low temperature (−60°C). We were able to confirm this observation using both tetramethyltin and trimethylstannyl-chloride as precursors. The shift value and a scalar Sn–C coupling of 390 Hz favour a non-planar trimethylstannyl ion under these conditions. Very recently, conductivity data and ^{119}Sn chemical shifts for trimethyl- and tributyl-stannyl cations were reported using perchlorate and tetrakis(pentafluorophenyl)borate as counterions [8]. Shifts as low as 360 ppm, *i.e.* close to that in HSO_3F, were obtained in solvents of low nucleophilicity, and it was suggested that these low shift values were consistent with a truly trivalent tin cation. The shift values reported for **1** in dichloromethane and sulfolane were close to those given here.

Solvents used in the previous silylenium studies were generally of dipolar protophobic nature such as sulfolane or MeCN [1]. When we used such dissociating

media as solvents for these stannyl complexes we found, as expected, that the equilibrium is shifted to the left in the scheme above. Nevertheless slow exchange conditions could be reached for **2** in MeCN/dichloromethane at low temperature, two signals again appearing in the range −200 to −230 ppm. The intensity of the high field signal increases upon increased addition of MeCN in dichloromethane and this intensity change is accompanied by a line-narrowing and a shift in the ^{37}Cl signal. Similar changes were observed up on dilution in MeCN; thus the ^{37}Cl signal was shifted from −0.3 ppm to +6.0 ppm (relative to dilute $HClO_4$ in D_2O) with line widths of 140 Hz and 3 Hz, respectively, when the concentration of **2** was changed from 1.2 to 0.005 M. The similarity to the earlier reported studies of silyl perchlorates is thus striking, although the stannyl species are, as expected, more easily ionized.

The possibility of a tetrahedral arrangement as (I) but with a solvent molecule in the first coordination sphere must also be considered ($(R_3SnS)^+X^-$). However, the large upfield ^{119}Sn chemical shifts and the significant increase in $^1J(Sn–C)$ for the perchlorates and fluoroborates on going to a more nucleophilic solvent than methylene chloride do not favour a tetrahedral structure. In the corresponding silyl case, the acetonitrile monodentate adduct of the trimethylsilylenium ion was recently reported [6], but the ^{29}Si chemical shift was very close (38.5 ppm) to that of the corresponding perchlorate in methylene chloride (45.1 ppm).

In conclusion we note that an equilibrium involving Sn rehybridization and change in solvent coordination is firmly established for the studied iongenic triorganostannyl compounds in nucleophilic solvents. As judged from earlier data for silyl perchlorates [1], the stannyl perchlorates are better ionogens than the corresponding silyl species. A similar situation as for stannyl species, involving exchange between R_3SiX and solvated structures might explain the difficulty of observing any ^{29}Si resonance except for predominantly solvent- or counterion-coordinated tetravalent forms. The inability to record shifts for truly trigonal silylenium ions can also be seen in this light. So far the reported ^{29}Si chemical shifts in solution can, in our opinion, be ascribed to various counterion- or solvent-coordinated silyl cations, and the need for less nucleophilic solvents and counterions will remain a fundamental problem, since solubility will be a limiting factor.

3. Experimental section

The stannyl chlorides and hydrides were commercially available (Aldrich). Triphenylstannyl hydride was distilled prior to use. Glassware was dried overnight at 145°C and all solvents were carefully purified and dried by standard methods, such as those used for solvents employed in preparation of the corresponding silyl compounds [1a,b]. For the NMR measurements, the stannyl perchlorates and fluoroborates were prepared by hydride abstraction using the corresponding trityl salts as reported previously. For the NMR measurements, stock solutions of trityl salts and stannyl hydride were introduced from a syringe into a 5 mm NMR tube fitted with a septum. The cooled NMR tube was flushed with argon through needles. Solute concentrations were kept relatively high (0.4–0.8 M) in order to avoid interference from hydrolysis. NMR spectra were recorded on Bruker AM-500 and AC-P 250 spectrometers; the ^{119}Sn chemical shifts are reported relative to external tetramethyltin, and the ^{37}Cl shifts, relative to 0.4 M $HClO_4$ in D_2O.

Acknowledgements

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