On the existence of trivalent stannyl cations in solution

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It is shown by NMR spectroscopy that no free trigonal stannyl cations in solution have been observed to date as also expected from theoretical *ab initio* IGLO calculations.

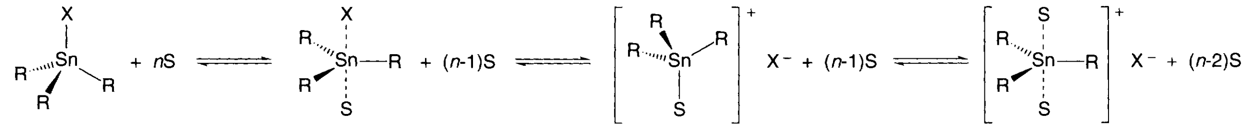
The dispute whether trivalent organosilyl cations can be observed in solution has recently led to increased attention to the whole area of group 14 cations in condensed phases,[1] especially so for the corresponding tin species. One would expect stannyl cations to be less highly electrophilic than the silylium ions and therefore facilitate the observation of an uncomplexed state.[2] As for the silyl complexes, solvation, the role of counter anion and the degree of alkyl substitution of the tin atom can be expected to be important parameters in this context. Based on similar solvation studies on silyl complexes it is also likely that the steric demand of the ligands in the first coordination sphere is of importance for the actual coordination number.[3] By studying trialkylstannyl chlorides, perchlorates and fluoroborates in various solvents it was earlier found that ^{119}Sn chemical shifts and SnC couplings could be explained in terms of an equilibrium situation shown in Scheme 1 where the equilibrium towards trigonal bipyramidal structures was favoured by low temperature, increasing donicity of the solvent or if the counter anion is a weaker Lewis base.[2] However, in two independent reports it was recently claimed that trivalent tributylstannyl cations have been prepared under ambient conditions using weakly nucleophilic counter anions like hydrotris(pentafluorophenyl)borate[4] or tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate (tfpb$^-$).[5] The observed tin chemical shift was the sole evidence of a free trigonal cation in these studies using benzene or dichloromethane as solvents with δ_{Sn} of 360[4] and 356,[5] respectively. The reported observation that the fluorine chemical shift of the counter anion is unaffected relative to the values obtained for uncoordinated counter anions is but poor evidence of a free stannyl cation.[5] If solvent complexation to tin takes place this can not be expected to induce any shift or linewidth changes of the counter anion nuclei. In these previous reports the observed ^{119}Sn values were compared to the early observations in HSO_3F,[6] where chemical shift values of δ *ca.* 322 [$(Me_3Sn)(SO_3F)$] were reported. Lambert and Kira therefore suggested trigonal free tin cations in these experiments, contrary to the earlier proposals.[6]

By using an empirical shift correlation between tin and silicon,[7] as shown in Fig. 1, one should be able to derive a crude prediction of chemical shifts of new complexes as well as obtain an estimate of the Sn chemical shift of the free trigonal stannyl ion. No major change is noticed from the earlier empirical Si–Sn correlation model when more positively charged Si and Sn species are included. The obtained correlation model ($\delta_{Sn} = 5.2$; $\delta_{Si} - 46$, $r^2 = 0.97$, $N = 70$) is approximately the same as the one obtained for 48 neutral four-coordinate stannyl compounds. From this model, the values for the claimed 'free' stannyl cation in benzene is close to what could be expected from the arene complex, the Wheland complex of the silyl ion.[8] The pyridine and Me_2SO values deviate somewhat since the stannyl chemical shift values,[2] contrary to the silyl values,[3] are equilibrium values involving some contribution of five-coordinate structures (**IV**), having two donors in the first coordination sphere. Therefore, these stannyl values are slightly more upfield than those expected from the silicon data for four-coordinate complexes as the tin species more easily form five-coordinate structures.

Similarily we obtained for trimethylplumbyl perchlorate a Pb chemical shift value of δ 694 which then, according to the established Sn–Pb correlation model,[7] predicts the tin chemical shift for the corresponding stannyl compound to be δ 212 *i.e.* close to the found value (δ 220). For trimethylplumbyl fluorosulfate at low temperature we obtained a chemical shift of δ 980 which predicts the corresponding tin shift to be δ *ca.* 370 (*cf.* experimental value of 322). Using the chemical shift for trimethylplumbyl tetrakis(pentafluorophenyl)borate (tpfpb$^-$) in benzene we predict a chemical shift for the corresponding stannyl compound at δ 262. Hence, similar structural and bonding situations seem to prevail for both plumbyl and stannyl species. To summarize, empirical correlation models seem to predict Sn chemical shifts of stannyl complexes quite well. The observed values of the claimed trigonal stannyl cations for instance by Lambert in benzene (δ 360) are best described as due to covalent arene complexes according to the agreement with the observed silicon chemical shift of the Wheland complex of δ 83.6 (δ *ca.* 80 by IGLO calculations).[8]

The solid-state CP MAS data of stannyl perchlorate shows three peaks with δ_{Sn} 178, 204 and 244 reflecting the proposed bipyramidal polymeric structure of stannyl perchlorate.[9] As expected, the solution value (δ 220, $^1J_{SnC}$ 353 Hz) seems to be in the same range as those obtained from the solid experiment, which indicates predominantly five-coordination. The corresponding silicon chemical shift value of δ *ca.* 50 is close to that of the covalent perchlorate but also close to the calculated value of a bipyramidal complex having oxygen donor atoms [for $Me_3Si(OH_2)_2^+$, δ 58.2].[3] The observed scalar coupling in solution is also consistent with such an arrangement around tin as discussed below.

We repeated the earlier solution Sn studies[4,5] using another weakly coordinating counter anion (tpfpb$^-$) in dichloromethane. Indeed we found a Sn chemical shift value of δ 349, *i.e.* close to the value reported by Kira[5] and Lambert.[4] However, we also measured the one-bond SnC coupling to be significantly smaller ($^1J_{SnC}$ 278 Hz) than the couplings observed in FSO_3H ($^1J_{SnC}$ 388 Hz)[6] or those obtained for a tributylstannyl triflate ($^1J_{SnC}$ 375 Hz) or perchlorate in dichloromethane. For covalent complexes, having weakly coordinating ligands, values of *ca.* 300 Hz are typical for four-coordinate complexes (**III**) or *cis*-



I **II** **III** **IV**

Scheme 1

trigonal-bipyramidal arrangements, while higher values of *ca.* 400 Hz indicate sp^2 character of the SnC bond *i.e.* like in bipyramidal arrangements (**II**, **IV**).[10] The fluorosulfates have earlier been claimed to have a trigonal-bipyramidal arrangement around tin.[6] However, the scalar coupling is affected not only by hybridization of the orbitals to the coupled nuclei but also by the effective nuclear charge at tin.[11] More electronegative substituents on the tin atom should increase the orbital electron density of tin producing larger values of $|J|$. According to the observed shifts of fluorosulfates and 'non-coordinating' borates, the effective charge is approximately the same. An additional support for this conclusion is that the measured C-1 shifts of the butyl substituents are within 2 ppm in all studied complexes and similar to those earlier reported by Kira. Hence, the low value of the SnC scalar coupling observed in solution for the stannyl–tpfpb complex can only be consistent with a significant pyramidalization of the SnC framework, *i.e.* a four-coordinate solvent complex (**III**) is formed. In summary, dissolving the weakly interacting borates affords, according to their chemical shifts and their scalar coupling, four-coordinate solvent structures similar to those observed in the silyl cases.

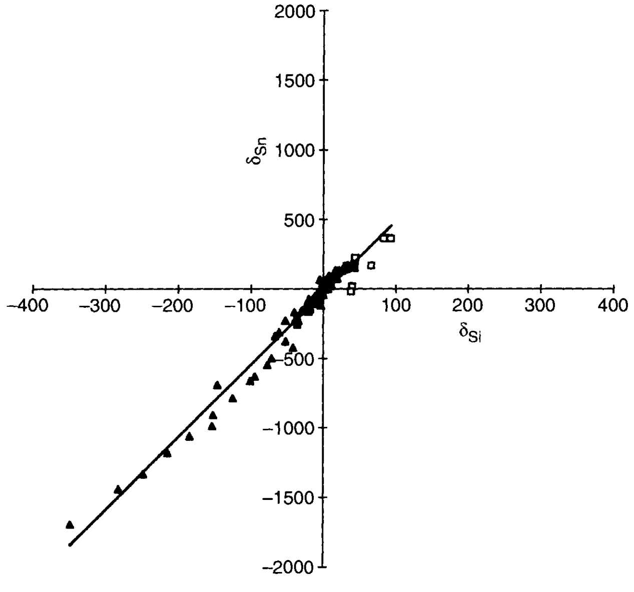


Fig. 1 Correlation between ^{29}Si and ^{119}Sn chemical shifts including positively charged solvent complexes (shown as □)

Table 1 ^{119}Sn and ^{29}Si chemical shifts of organostannyl and organosilyl species

Solvent	X	Bu_3SnX	R_3SiX	R
CH_2Cl_2	ClO_4^-	220[a]	45[a]	Bu
CH_2Cl_2	Cl	156	33	Bu
Et_2O	tfpb$^-$	165[b]	67[c]	Me
CH_2Cl_2	OTf$^-$	172	44	Me
CH_2Cl_2	tpfpb$^-$	349	94[d]	Bu
Me_2SO	ClO_4^-	12	41	Bu
Pyridine	ClO_4^-	−24	39	Bu

[a] ^{119}Sn and ^{29}Si chemical shifts related externally to $SnMe_4$ and $SiMe_4$ respectively. Experimental details are given in refs. 2 and 3. [b] Data from ref. 5. [c] Data from ref. 14. [d] Measured in C_6D_6.

It is of interest to compare these experimental findings with recent *ab initio* IGLO/DZ calculations without f-type polarization functions at Sn.[12] The truly trigonal trimethylstannyl cation has a calculated chemical shift δ significantly > 1000, which is supported by the prediction from Fig. 1 (by extrapolation, δ_{Sn} = 1500–2000) using the IGLO shift value for the trimethylsilylium ion of δ 356.[3] The experimental shifts reported for the claimed free stannyl cations of δ *ca.* 300–360 compare nicely, however, to the IGLO-calculated values for such species having one oxygen donor (approximated by H_2O) in the first coordination shell.[12] Preliminary calculations on a Wheland complex of the trialkylstannyl cation afford values of δ *ca.* 400, *i.e.* close to the experimental values in benzene.[13]

To conclude, the experimental findings based on observed Sn chemical shifts and scalar SnC couplings strongly suggest that no free trialkylstannyl cations have been observed in solution, not even in nonpolar solvents using 'non-coordinating' counter anions. The situation is almost identical to the silyl case where the observed species are covalent solvent complexes. Our findings are supported by data on similar plumbyl species as well as Sn–Si shift correlations and *ab initio* IGLO calculations.

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