Tricoordinate Tin Cations in Solution under Ambient Conditions

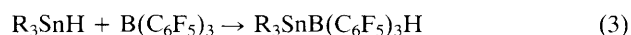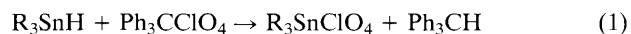## Joseph B. Lambert* and Barbara Kuhlmann

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The tricoordinate form of organotin (R_3Sn^+) has been prepared under ambient conditions in a variety of nonnucleophilic solvents.

The recent reports[1] of stable dicoordinate tin with organic ligands (R_2Sn) have added emphasis to the poorly developed nature of the field of tricoordinate tin. Although known in the gas phase, tricoordinate forms, in which the short apical bonds of pentacoordination are absent, have not been reported in the solid state.[2] There has been only one unambiguous report of tricoordinate tin in solution (Me_3Sn^+ and related species, in highly acidic media), and the observed species decomposed above -30 °C.[3] We now report several procedures for preparing tricoordinate tin under ambient conditions.

We have prepared tin cations by three methods [eqns. (1)–(3)] that encompass three different R groups (Me, Bu, Ph), two anions, and four solvents. Hydride abstraction by trityl (method 1) is analogous to the method used to prepare

$$R_3SnH + Ph_3CClO_4 \rightarrow R_3SnClO_4 + Ph_3CH \qquad (1)$$

$$R_3SnCl + AgClO_4 \rightarrow R_3SnClO_4 + AgCl \qquad (2)$$

$$R_3SnH + B(C_6F_5)_3 \rightarrow R_3SnB(C_6F_5)_3H \qquad (3)$$

silyl perchlorates,[4] and can be carried out at room temperature in dichloromethane, sulfolane, or benzene (the solvent may be evaporated, the triphenylmethane removed by hexane washing, and the same or a new solvent added, including hexane). Chloride removal (method 2) is analogous to the method used by Wannagat for preparation of silyl perchlorates,[5] and is done at room temperature in benzene. The use of the electron deficient borane (method 3) is a novel approach by analogy with Marks's preparation of zirconium cations,[6] and is carried out at room temperature in benzene. These preparations were more successful with alkyl groups (R = Bu or Me) than with phenyl, as presumably free radical reactions led in the latter case largely to precipitation of hexaphenyldi-

tin. Solvents were thoroughly dried and all manipulations were carried out in an inert atmosphere.

The equivalent conductance of tributylstannyl perchlorate produced by method (1) was 10.4 ohm^{-1} cm^2 $equiv^{-1}$ in 10 mmol dm^{-3} CH_2Cl_2, compared with 0.38 for trimethylsilyl perchlorate. Thus the tin species is almost two orders of magnitude more conducting than the analogous silicon species.[4] The two species have similar conductances in sulfolane (*ca.* 100 ohm^{-1} cm^2 $equiv^{-1}$). Under the assumption of two ionic particles, the cryoscopic relative molecular mass of tributylstannyl perchlorate was measured in sulfolane to be 403.9 (3.7% from the actual value of 389.5). If the calculation assumes a one-particle, covalent model, the measured relative molecular mass would be 202.2 (48% error from 389.5). Thus both conductance and cryoscopy require a strongly ionic stucture.

The key diagnostic of tricoordinate tin is the ^{119}Sn chemical shift. The low field resonance of $(Me_3Sn)(FSO_3)$ at δ 322 led Birchall and Manivannan to conclude that the geometry was planar and that apical interactions with solvent or fluorosulfate anions were weak.[3] An increase in coordination to tin invariably results in an upfield shift. One assessment[7] suggests that the range of organotin chemical shifts for hexacoordination is δ -210 to -400, pentacoordination δ $+30$ to -190, and tetracoordination δ $+200$ to -60 (ppm relative to Me_4Sn). The range for dicoordination currently is about δ 2400 to 700.[1]

The ionic species we have prepared exhibit low-field shifts in the range δ 360 to 150, depending on the solvent and counterion. The lowest field shift is observed for the tributylstannyl borate (method 3), δ *ca.* 360 in benzene, compared with δ -84 for Bu_3SnH (0.5 mol dm^{-3} in CH_2Cl_2). This downfield shift of about 450 ppm is strong evidence for a change from tetra- to tri-coordination. Tributylstannyl perchlorate from methods (1) or (2) also resonates at very low

field, but not so extreme as the borate: δ 245 in CD_2Cl_2, 231 in C_6D_6, 150 in sulfolane. To date we have examined trimethyl-stannyl as its perchlorate only by method (2), as manipulation of Me_3SnH is awkward. Its ^{119}Sn shift is δ 249 in CD_2Cl_2 and 234 in benzene, or nearly the same as that for tributylstannyl perchlorate. Similar low-field resonances were observed for triphenylstannyl perchlorate, but these preparations invariably generated mixtures.

The sensitivity to solvent and counterion indicates that the tricoordination is perturbed but not fundamentally altered. Thus even in the most nucleophilic solvent, sulfolane, the resonance is downfield about 250 ppm from tetracoordinate Bu_3SnH (and more so from the pentacoordinate range). Although the low field extreme has not been ascertained, we suggest that the values observed below δ 300 represent very little apical interaction, *i.e.*, true tricoordination. Dynamic interaction with solvent or anion introduces distant apical interactions, intermediate between tri- and penta-coordination, and concomitant upfield shifts from the δ 300 region. Actual bonding to apical ligands is excluded by the low-field shifts even with perchlorate anion and sulfolane solvent (our most nucleophilic conditions).

These ^{119}Sn resonances were accompanied by 0–10% of a resonance about 40 ppm to higher field. We attribute this resonance to a hydrolysis product, from very small amounts of water present in the solvent. Deliberate addition of water resulted ultimately in disappearance of the low-field peak and enhancement of the higher field peak, which may be attributed to protonated distannoxane. This conversion is complex, as it may involve higher coordinated intermediates and is currently under study.

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