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Preliminary communication

Unique tin–oxygen coordination bond in a pentacoordinated tetraorganotin compound. First confirmation by X-ray crystal structure of (2-carbomethoxy-1,4-cyclohexadien-1-yl)trimethyltin

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Abstract

The X-ray crystal structure of (2-carbomethoxy-1,4-cyclohexadien-1-yl)trimethyltin reveals the presence of a tin–oxygen coordination bond, unique for a tetraorganotin compound.

In continuation of our studies on vinyltins obtained by Diels–Alder reaction of alkynyltin derivatives [1] we reported recently the first examples of halodemetalations in which the usual sequence of reactivity is reversed, i.e. where alkyl groups are cleaved in preference to aryl, vinyl, or benzyl groups in mixed tetraorganotin compounds [2]. The common feature of these derivatives is that the unsaturated substituent have a coordinating group (ketone, ester or amine) in a γ-position with respect to the tin, so that they can form a five-membered ring by intramolecular coordination. We proposed an explanation of these unexpected results in terms of intramolecular nucleophilic assistance by the chelating group during the halodemetalation.

Tetraorganotin derivatives were previously regarded as unable to show a pentacoordinate structure because of the poor acceptor properties of the tin centre [3], but it

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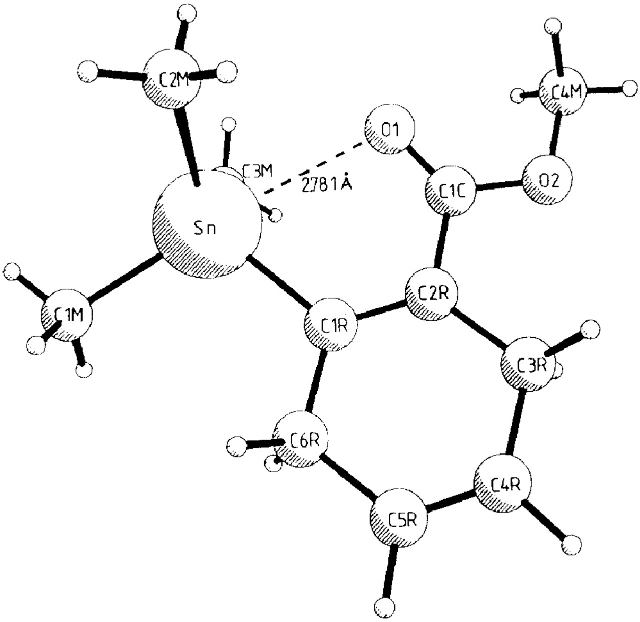

Fig. 1. The X-ray crystal structure of **1**. Some important distances (Å) and angles (°): Sn–O(1) 2.781(3), Sn–C(1M) 2.150(5), Sn–C(2M) 2.146(5), Sn–C(3M) 2.127(6), Sn–C(1R) 2.177(3), C(1R)–C(2R) 1.343(4), C(2R)–C(1C) 1.480(4), C(1C)–O(1) 1.197(4); C(1M)–Sn–C(2M) 106.3(2), C(1M)–Sn–C(3M) 106.0(2), C(1M)–Sn–C(1R) 103.7(2), C(2M)–Sn–C(3M) 113.1(2), C(2M)–Sn–C(1R) 111.0(2), C(3M)–Sn–C(1R) 115.7(2), O(1)–Sn–C(1M) 172.4(2), O(1)–Sn–C(2M) 77.8(2), O(1)–Sn–C(3M) 77.6(2) O(1)–Sn–C(1R) 68.8(1).

has recently been demonstrated that internal chelation by nitrogen can rise the coordination of a tin atom from four to five [4,5], or even six [6].

In our case, though the previous studies based on IR and liquid ^{119}Sn NMR showed no evidence for chelation in the starting materials, we decided to check if such bonding could be detected in the solid state. We prepared (2-carbomethoxy-1,4-cyclohexadien-1-yl)trimethyltin (**1**) *. The IR, ^{13}C, and ^{119}Sn NMR data for solutions of **1** are those expected for an uncoordinated tetraorganotin, but **1** shows the same behaviour towards halodemetalation as the compounds mentioned above i.e. the tin–methyl bond is cleaved first by halogens rather than the vinyl–tin bond, in a 100% regiospecific process. **1** was found to be solid at room temperature so we were able to carry out a single-crystal X-ray diffraction study. The structure of **1** is shown in Fig. 1 along with the most important molecular parameters. The backbone atoms are approximately coplanar, forming two condensed rings.

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* Crystal data: $C_{11}H_{18}O_2Sn$, M = 300.95, triclinic, space group $P\bar{1}$ (no. 2), a 7.528(2), b 9.038(3), c 9.609(1) Å α 92.52(1), β 94.42(2), γ 97.71(3)°, $Z = 2$, $V = 645$ Å^3, λ(Mo-K_α) 0.71069 Å, μ(Mo-K_α) 18.02 cm^{-1}. Data were collected on a Kappa CAD4 diffractometer ($2\theta < 60$°). A total of 3721 independant reflexions was mesured. Only 3050 observed reflexions with $I > 2\sigma(I)$ were used subsequently. The structure was solved by using Patterson and Fourier syntheses and refined by full matrix least squares. Hydrogen atoms were not located. They were introduced in idealized positions and constrained to ride on their carbon atoms. The final R values were $R = 0.042$ and $R_w = 0.050$. Atomic coordinates and a full list of bond lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre.

The five membered ring is made up of three carbons, a tin, and the carbonyl oxygen. The angle between the two planes is 5.6 °. The distance between the tin and oxygen atoms is 2.781(3) Å, which is unambigously shorter than the sum of their Van der Waals radii (3.7 Å) and falls in the range for previously reported tin–oxygen coordination bonds [7] in triorganotin compounds.

The configuration of the tin is between tetrahedral and trigonal bipyramidal, as shown by bond angles, and C(1M) and O(1) are almost aligned. Similar distortions have been reported in the case of nitrogen analogues [4].

Confirmation of this coordination is given by solid state ^{119}Sn NMR (HPD/CP/MAR) results. The spectrum of **1** indicates that the anisotropic chemical shift is -56.6 ppm, shifted upfield by 8.7 ppm with respect to the value in the liquid state (-47.9 ppm). Although very few solid state ^{119}Sn NMR spectra have been measured [8], chemical shifts for tetrahedral four-coordinate tin in solution and the solid state seem to be identical [9]. Thus the observed shielding reflects the weak but significant coordination of the tin atom in **1** in the solid state.

Although caution is necessary in transposing solid state data to the liquid state, this tin–oxygen coordination confirms the nucleophilic assistance at tin that we proposed [2]. The observations indicate that the chelation which is present in the solid state is much weaker in solution, where the equilibrium favours unchelated species.

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