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Allyl- and allyllike-tin derivatives

IV *. The crystal structure of 2-methylallyltriphenyltin: a comparison with other methyl-substituted derivatives of allyltriphenyltin

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Abstract

The crystal structure of $(C_6H_5)_3SnCH_2C(CH_3)=CH_2$ has been determined. The asymmetric unit consists of two molecules of 2-methylallyltriphenyltin. The compound crystallizes in the orthorhombic space group *Pbca* with *a* 31.232(12), *b* 20.890(9), and *c* 11.835(7) Å. The molecular geometry is controlled by σ(C–Sn)–π orbital mixing and by hyperconjugative stabilization involving the σ orbitals of C–H bonds. Any p_π–d_π bonding between the metal and the allyl double bond, or inductive effects in the allyl group are shown to be unimportant. The structural parameters are analyzed and compared with those of various methylated derivatives of triphenylallyltin.

Introduction

The stereochemistry of allyl or allyl-like systems in organometallic complexes of tin has attracted considerable interest in recent years, and has been the subject of

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* For Part III, see ref 16.

numerous reports [1–4]. It is of importance for synthesis and mechanistic studies [5–12]. At present, electrophilic additions to carbon–carbon bonds [4] and additions of unsaturated species to tin–carbon bonds are being used increasingly in synthetic chemistry [13]; and this has stimulated interest into the relevant stereochemical aspects.

As part of a systematic investigation on these problems, we have synthesized and structurally characterized the complex $Ph_3SnCH_2C(CH_3)=CH_2$. Having collected structural data on several similar compounds [14–17], we decided to seek further information about the phenomena responsible for the structural features in allyl systems in order to attempt to rationalize them. It has been shown that the conformation of the allyl or allyl-like group in these complexes is controlled by ground state effects, such as σ(C–Sn)–π orbital mixing, hyperconjugative resonance involving C–H and C=C bonds, change in hybridization of the carbon atoms, and inductive effects [18]. These all seem to contribute to the molecular geometry, though the different extents, but in some cases we believe that the hyperconjugative effect predominates. The data in terms of which the problem has been discussed so far, provide only indirect evidence for or against the phenomenon [19–21], and some authors believe that it is not significant in the ground state of neutral molecules [18,22]. It is noteworthy that the earlier structural arguments were based only on electron diffraction data [18], and the results of recent X-ray studies, to our knowledge, seem not to have been discussed in terms of hyperconjugation. We show below that there is evidence to indicate that hyperconjugation plays an important rôle in determining the molecular geometry of allyl groups. The results of the structural determination described here, provide some of the arguments.

Experimental

Preparation of 2-methylallyltriphenyltin

2-Methylallyltriphenyltin was prepared as previously described [23]. Well formed, colourless, prismatic crystals, suitable for analysis were obtained from petroleum ether (40–60 °C), m.p. 69.5–70 °C (Lit. 70–71 °C [23]).

Crystal and intensity data

Crystal data and an outline of the experimental details of the structural determination of $Ph_3SnCH_2C(CH_3)=CH_2$ are given in Table 1. A single crystal (0.2 × 0.2 × 0.4 mm) was mounted on a Philips PW 1100 computer-controlled four circle diffractometer with graphite monochromator. The crystal was protected after mounting. Standard centering and auto-indexing procedures indicated a primitive orthorhombic lattice, space group *Pbca*. Orientation matrices and accurate unit cell dimensions were determined at 25 °C from a least-squares fit of 25 reflections ($10° \leqslant 2\vartheta \leqslant 23°$). Intensity data were collected by the ϑ–2ϑ scan method; 2 standard reflections, monitored every 150 measuraments, showed only statistical fluctuations. Owing to the small size of the crystal and the small linear absorption coefficient, absorption corrections were judged unnecessary. The intensities were corrected for the usual geometrical factors and scaled to give 3347 independent F_{hkl} values with $I > 3\sigma(I)$.

Solution and refinement of the structure

The positions of the two tin atoms of the asymmetric unit were determined from a three-dimensional Patterson synthesis. The carbon atoms were located from

Table 1

Crystal data and details of intensity and structure refinement for 2-methylallyltriphenyltin

Molecular weight ($C_{22}H_{22}Sn$)	405.11
Space group	*Pbca*
Cell constants: *a*, Å	31.232(12)
b Å	20.890(9)
c Å	11.835(7)
Cell volume, Å^3	7721.6
Z	16
ρ(calcd.) g cm^{-3}	1.393
ρ(meas.) g cm^{-3}	1.39
Radiation	Mo-K_α(0.7107) (graphite monochromator)
μ, cm^{-1}	12.08
2ϑ range, deg	45
Decay of standard reflections	± 2%
Reflections collected	4739
Reflections with $I \geqslant 3\sigma(I)$	3347
R, factor	0.041
t, °C	24

subsequent Fourier synthesis. The hydrogen atoms were located from a final difference synthesis and were included in the calculations but not refined. Anisotropic thermal parameters were used for all the non-hydrogen atoms. The thermal

Table 2

Fractional atomic coordinates ($\times 10^4$) for non hydrogen atoms, with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Sn	678(0)	6234(0)	130(1)	Sn′	7907(0)	6480(0)	4826(0)
C(1)	312(2)	6356(3)	−1384(5)	C(1)′	8409(2)	5785(2)	4911(5)
C(2)	250(2)	5833(3)	−2097(5)	C(2)′	8639(2)	5692(2)	5907(5)
C(3)	−13(2)	5890(3)	−3044(5)	C(3)′	8958(2)	5225(2)	5954(5)
C(4)	−215(2)	6471(3)	−3277(5)	C(4)′	9047(2)	4852(2)	5005(5)
C(5)	−153(2)	6995(3)	−2564(5)	C(5)′	8816(2)	4945(2)	4009(5)
C(6)	110(2)	6937(3)	−1617(5)	C(6)′	8497(2)	5412(2)	3962(5)
C(7)	1003(2)	5336(2)	58(6)	C(7)′	7533(2)	6427(3)	6349(4)
C(8)	874(2)	4831(2)	750(6)	C(8)′	7298(2)	6960(3)	6694(4)
C(9)	1111(2)	4265(2)	772(6)	C(9)′	7055(2)	6933(3)	7682(4)
C(10)	1476(2)	4204(2)	103(6)	C(10)′	7047(2)	6373(3)	8325(4)
C(11)	1605(2)	4709(2)	−589(6)	C(11)′	7283(2)	5841(3)	7979(4)
C(12)	1368(2)	5276(2)	−611(6)	C(12)′	7526(2)	5868(3)	6991(4)
C(13)	223(2)	6198(4)	1492(5)	C(13)′	7513(2)	6216(3)	3405(4)
C(14)	−211(2)	6126(4)	1243(5)	C(14)′	7634(2)	6370(3)	2303(4)
C(15)	−510(2)	6086(4)	2116(5)	C(15)′	7380(2)	6180(3)	1395(4)
C(16)	−375(2)	6118(4)	3238(5)	C(16)′	7003(2)	5837(3)	1588(4)
C(17)	59(2)	6190(4)	3487(5)	C(17)′	6882(2)	5684(3)	2689(4)
C(18)	358(2)	6230(4)	2615(5)	C(18)′	7137(2)	5873(3)	3598(4)
C(19)	1212(4)	6927(5)	396(11)	C(19)′	8141(3)	7470(5)	4629(8)
C(20)	1107(3)	7580(5)	214(9)	C(20)′	8545(3)	7504(5)	4070(8)
C(21)	1240(5)	7907(7)	−675(12)	C(21)′	8891(3)	7485(6)	4720(10)
C(22)	869(5)	7900(7)	1067(15)	C(22)′	8564(4)	7700(8)	2908(10)

parameters of hydrogen atoms were taken to be the same as the U_{eq}'s of the attached atoms. Full-matrix least-squares refinements were used, and converged to the conventional R index of 0.041. Scattering factors for the atoms were taken from Cromer and Waber [24]; the scattering factor for the tin atoms was corrected for the real and imaginary parts of anomalous dispersion by use of Cromer's values [25].

All computations were carried out on a CDC Cyber 76 computer by use of the programmes described in ref. [26]. The final positional parameters of the non hydrogen atoms are listed in Table 2. Thermal factors (Table 4), hydrogen atom coordinates (Table 5) and the list of the structure factors (Table 6) are available from the authors.

Description of the structure and comments

The structure involves two independent molecules of 2-methylallyltriphenyltin. Figure 1 shows a view down the Sn–C(19) axes with the molecules arbitrarily oriented so as to show their structural relationship: the conformation of the methylallyl groups is almost unchanged, while the paddle-wheel configurations of the Ph_3Sn groups in **A** and **B** are mutually opposed. Such a feature has been discussed previously [14,15].

Table 3 lists the most interesting geometrical parameters (for the labelling scheme see Fig. 1). It will be seen that, apart from the feature noted above, the molecular geometries in **A** and **B** are almost identical.

The coordination about the tin atoms is close to ideal tetrahedral except for a significant lengthening of the Sn–C(19) bonds (2.21 Å) beyond the normal value of ~ 2.15 Å. This lengthening is present in all allyl- and allyllike-triphenyltin derivatives [14–16].

The bonds C(19)–C(20) 1.42(1) Å, C(20)–C(22) 1.42(1) Å for **A**, and 1.43(1) and 1.44(2) Å for **B**, respectively, are remarkably short. In contrast, the double bonds C(20)=C(21) and C(20)′=C(21)′ ~ 1.32(2) Å are quite normal; the atoms C(20) [C(20)′] and C(21) [C(21)′] were located with precision, and so any statistical disorder involving the adjacent C–CH_3 bonds must be excluded. (The hydrogen atoms bonded to C(21) [C(21)′] and to C(22) [C(22)′] were unambiguously, even if only approximately, located from the final difference Fourier synthesis, confirming the positions of the double bonds). The intramolecular distance from tin to the mid point of the allyl double bond is about 3.5–3.6 Å, so that p_π–d_π interaction between them is ruled out.

The structural data obtained, considered together with those of other methyl-substituted derivatives of allyl- and allyllike-tin compounds [14–17], allow the following conclusive descriptions of the two main features of the observed molecular geometries.

On one hand, we must accept that as a general rule that a definite σ(C–Sn)–π interaction is always involved in these compounds [15]; it imposes a skew conformation on the allyl groups: i.e., a torsion angle Sn–C–C=C in the range of 90–120°. This angle is |107°| for **A** and |84°| for **B** in this structure. It has been shown that such geometry is that for the best overlap of the relevant orbitals and hence for a minimum conformational energy [4]. The lenghtening of the bonds Sn–C(19) can be though as a consequence of a contribution from a canonical form $Ph_3Sn^+CH_2^-$–R, which has the effect of drawing the electrons of the Sn–C bond closer to C(19) than they would be in its absence, and thus able to facilitates resonance with the π

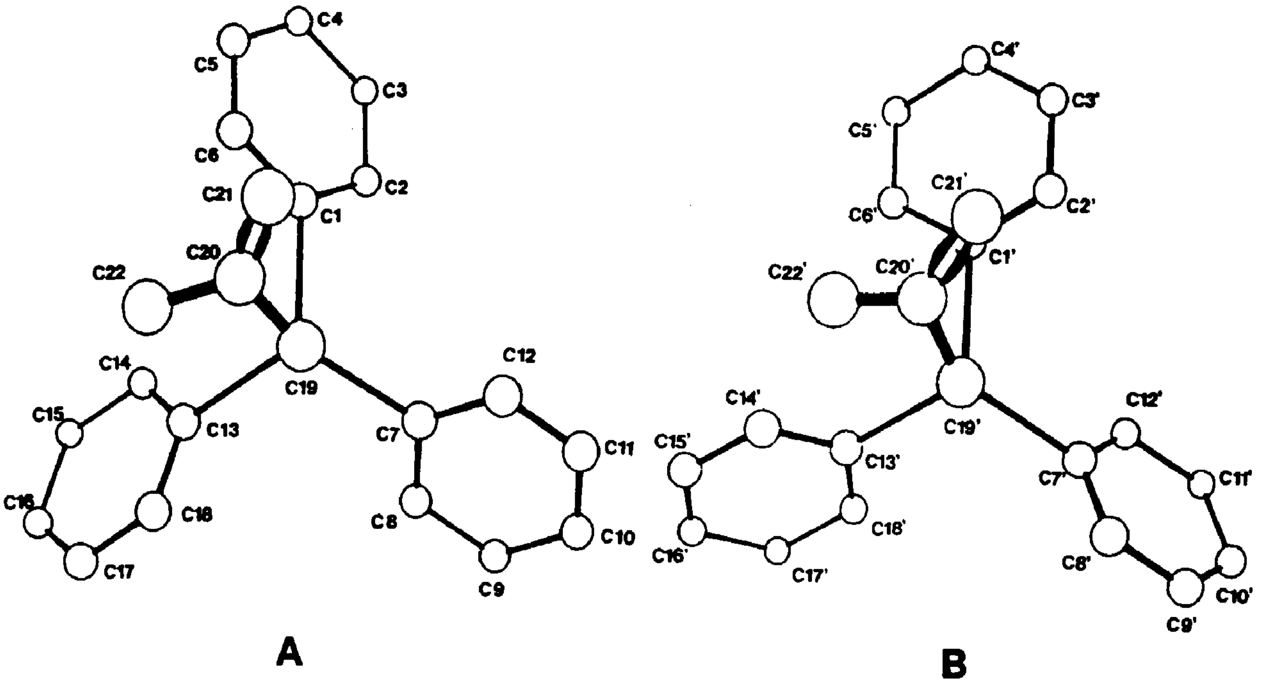


Fig. 1. The two molecules **A** and **B** of 2-methylallyltriphenyltin forming the asymmetric unit as viewed down the Sn–C(19) [Sn′–C(19)′] axis. The projections are arbitrary, and show the mutual relation between **A** and **B**. Since the conformation of the allyl group is retained the Ph_3Sn groups have opposite paddle-wheel configurations.

Table 3

Selected structural parameters for 2-methylallyltriphenyltin, with estimated standard deviations in parentheses

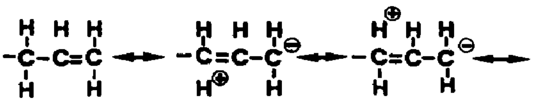
	Molecule A	Molecule B
Bond lengths (Å)		
Sn–C(1)	2.141(6)	2.140(5)
Sn–C(7)	2.132(5)	2.150(6)
Sn–C(13)	2.152(6)	2.155(5)
Sn–C(19)	2.23(1)	2.200(9)
C(19)–C(20)	1.42(1)	1.43(1)
C(20)–C(21)	1.32(2)	1.33(2)
C(20)–C(22)	1.42(2)	1.44(2)
Bond angles (°)		
C(1)–Sn–C(7)	109.0(3)	108.9(2)
C(1)–Sn–C(13)	106.1(2)	106.3(2)
C(1)–Sn–C(19)	116.1(4)	113.1(3)
C(7)–Sn–C(13)	108.3(3)	109.3(2)
C(7)–Sn–C(19)	102.8(3)	108.8(3)
C(13)–Sn–C(19)	114.2(4)	110.4(3)
Sn–C(19)–C(20)	115.5(7)	115.0(7)
C(19)–C(20)–C(21)	123(1)	117(1)
C(19)–C(20)–C(22)	118(1)	120(1)
C(21)–C(20)–C(22)	119(1)	122(1)
Torsion angles (°)		
C(6)–C(1)–Sn–C(19)	−57	−102
C(12)–C(7)–Sn–C(19)	−47	−147
C(18)–C(13)–Sn–C(19)	−40	−138
Sn–C(19)–C(20)–C(21)	−107	−84
Sn–C(19)–C(20)–C(22)	77	95

electrons of the double bond [27]. This feature can be regarded as the result of a hyperconjugative effect as this is commonly described [18,28].

On the other hand, there is also evidence for an hyperconjugative effect involving the $CH_3(CH_2)$ groups adjacent to the allyl double bond.

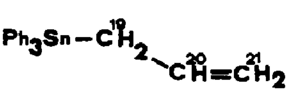
Since hyperconjugation must in general be regarded as an overlap of σ orbitals of C–H and π orbitals of the C=C bonds, the corresponding effect will depend to some extent on the number of available C–H bonds, on their location in the molecule so as to allow the so-called no-bond resonance [18,28], and on stereochemical requirements (see below) [29,30].

For an allylic system, we assume that the following canonical forms contribute to the actual molecular structure [18]:



$$-\overset{H}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{\underset{H}{C}} \longleftrightarrow -\overset{H}{\underset{H^{\oplus}}{C}}=\overset{H}{C}-\overset{H}{\underset{H}{C}}{}^{\ominus} \longleftrightarrow -\overset{H^{\oplus}}{\underset{H}{C}}=\overset{H}{C}-\overset{H}{\underset{H}{C}}{}^{\ominus} \longleftrightarrow$$

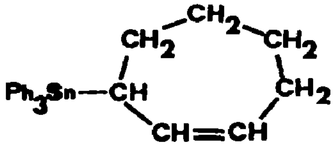
In the case of the parent compound, 1, we have shown [14] that there is



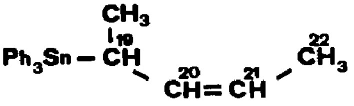
(1)

substantial hyperconjugation; thus we found that C(19)–C(20) 1.36 Å, C(20)=C(21) 1.25 Å and the angle C(19)–C(20)=C(21) 140°, indicating that the geometry about C(20) approaches that for *sp* hybridization. In this case the effect is mainly (or exclusively) due to conjugation of the Sn–C bond with the double bond, and the geometrical parameters are also largely determined by the change in hybridization [31], which is not hindered by molecular constraints [29,30].

The geometry of **1** undergoes interesting and predictable changes when methyl-substitution is carried out stepwise. Compound **2** [16] can reasonably be used as a molecular model for **2′**.



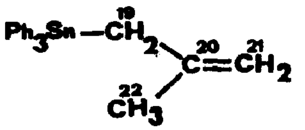
(**2**)



(**2′**)

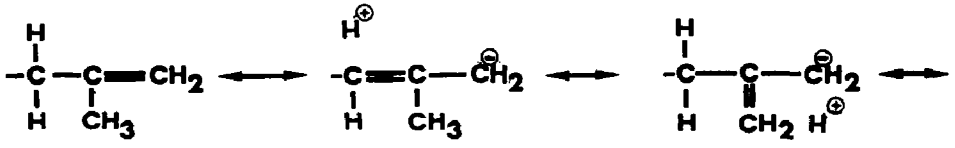
In the case of **2**, we found, as expected, a diminished but still appreciable effect on the bond lengths and angles: in particular the bond angles C–C=C and C=C–C are both about 130°. The widening of these angles is very important in view of the requirements for ring-closure in the molecule **2** and the consequent molecular strain [32,33]. In addition, we pointed out that the effect is almost the same on either side of the double bond; this might indicate that the observed effects produced to the same extent by Ph_3SnCH or RCH_2 groups are in this case due to a hyperconjugative effect and to a partial change in hybridization rather than to inductive effects.

In the case of the structure of compound **3** described in the present paper, there



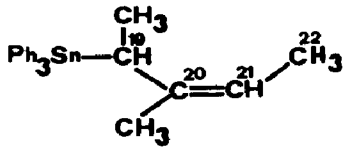
(**3**)

are different features. The presence of a methyl group inhibits an $sp^2 \rightarrow sp$ change in hybridization of C(20) (in contrast to the situation for **1**), so that there is no appreciable effect on the double bond length and all the bond angles around C(20) are about 120°. Here the following canonical forms are conceivable:

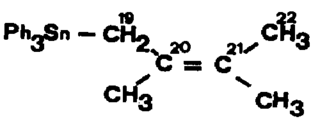


These mainly give rise to shortening of the bonds C(19)–C(20), 1.42–1.43 Å, and C(22)–C(20), 1.42–1.44 Å, as unambigously found for both of the independent molecules **A** and **B** of the structural unit. This cannot be merely coincidental. The effects of the Ph_3SnCH_2 and CH_3 groups are once again almost the same, implying either that inductive effects must be insignificant, or, improbably, that these groups have similar inductive effects.

When more methyl groups are present, as in compouds **4** and **5**, [17] none of



(4)

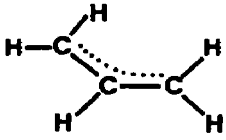


(5)

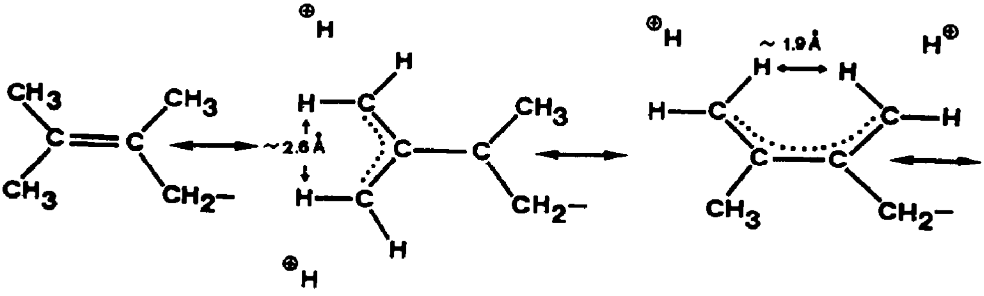
relevant effects are observed, except for the large bond angle C(20)=C(21)–C(22), ~ 128° in **4**, which is similar to that found in **2**, and can be explained in the same way. Therefore a gradual increase of methyl substitution on the allyl group seems to result in a decrease in the hyperconjugative effect.

We suggest the following explanation for such behaviour. In order to have a maximum hyperconjugation involving canonical forms such as:

the negative charged molecular portion must tend towards a planar conformation:



When several methyl groups are bonded to the allyl group, and provided that each of them acts in the same way, we can expect a limiting situation such as the following:



Some of the forms shown would be inhibited by short intramolecular H...H interactions, and so the higher the number of methyl groups the greater is the hindrance to hyperconjugation.

The structural features by themselves do not exclude the possibility that the phenomena observed could be of mesomeric and inductive origin, or that both resonance effects and changes in hybridization operate at the same time but it is sometimes possible to decide whether one or the other of these effects predominates, as was shown in particular for compounds **1**, **2**, and for **3**, described here.

The relevant results can be summarized as follows:

(a) In **1**, both hyperconjugation and change in hybridization are operative to the same extent [31]; inductive effects are absent as previously demonstrated [14,34].

(b) In **2**, hyperconjugation predominates over change in hybridization and inductive effects are probably absent.

(c) In 3, hyperconjugation is virtually the only factor determining the molecular geometry.

In all these cases, the structural parameters have been determined with fairly high accuracy. We believe that the observed deviations from normally expected values are so great as to form a sound basis for our arguments.

Acknowledgements

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