Journal of Organometallic Chemistry, 349 (1988) 57–63
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Allyl- and allyllike-tin derivatives

II *. The crystal structure of cyclopent-2-enyltriphenyltin

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(Received January 22nd, 1988)

Abstract

The crystal structure of $(C_6H_5)_3Sn$(cyclopent-2-enyl) has been determined. The asymmetric unit consists of two independent molecules of cyclopent-2-enyltriphenyltin, in which the Ph_3Sn groups are bonded to the C_5 rings in an *axial* manner. An interesting feature is the diastereoisomeric relation between the two molecules: the phenyl groups have opposite paddle-wheel configurations with respect to the fixed chirality of the C_5 ring carbon atom bonded to tin.

The geometrical parameters, establishing a preferred quasi-*axial* orientation for the $SnPh_3$ group, exclude $p_\pi-d_\pi$ bonding between the metal and double bond, and may reflect a ground state stabilising effect (of the $\sigma-\pi$ hyperconjugative type) that operates more efficiently from this orientation. A similar phenomenon was suggested to operate in the acyclic $Ph_3SnCH_2CH=CH_2$ on the basis of its crystal structure.

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* Ref. 6 is considered as Part I.

Introduction

There is currently great interest in the utility of unsaturated organic derivatives of tin as synthetic reagents, but full appreciation of their value requires understanding of their structures, preferred conformations, and mechanisms of reaction [1]. We have been employing unsaturated organotin derivatives as synthons in organic chemistry [2–4] as well as for mechanistic and conformational studies [5], but the scantiness of X-ray structural data on allylstannanes led us to commence research in this latter area [6].

We report here the crystal structure analysis of cyclopent-2-enyltriphenyltin, in which the unsaturated ring is formally analogous to the (acyclic) C_3H_5 grouping in $Ph_3SnCH_2CH{=}CH_2$ [6], as far as the so-called β-effect is concerned [7–15]. This effect is generally agreed to be conjugative in nature [16] (mixing of C–Sn (σ) and π systems) and thus has a pronounced angular dependence, and could be a factor in regulating the conformational profiles and crystal structures of allylstannanes, as has been suggested [6]. Although cyclic allylstannanes may pose some problems associated with ring size effects etc. [5,17], they introduce the possibility of two isomers having the Ph_3Sn group either quasi-*axial* or quasi-*equatorial* [5], and it would be anticipated that the orientation in which σ–π mixing was more efficient would be of lower energy [16], and hence observed, provided any non-bonded interactions in such an orientation were not overwhelming. Information on this matter has basic implications for mechanistic and stereochemical studies involving cycloalk-2-enyl derivatives [5,18].

Experimental

Cyclopent-2-enyltriphenyltin: crystal and intensity data

The title compound was prepared from cyclopent-2-enylchloride and triphenyltinlithium in THF. Well formed colourless prismatic crystals suitable for X-ray analysis were obtained by recrystallization from ethanol, m.p. 86 °C. Anal. Found: C, 66.20; H, 5.31. $C_{23}H_{22}Sn$ calcd.: C, 66.09; H, 5.3%. They were not protected after mounting, but there was no evidence of alteration during data collection. A single crystal of Ph_3Sn(cyclopent-2-enyl) ($0.2 \times 0.2 \times 0.4$ mm) was mounted on a Philips PW 1100 computer controlled four-circle diffractometer with graphite monochromator. Standard centering and auto-indexing procedures [19] indicated a primitive orthorhombic lattice, space group *Pbca*. The orientation matrix and accurate unit cell dimensions were determined from a least-squares fit of 25 symmetry-related reflections ($10° \leqslant 2\vartheta \leqslant 23°$). Intensity data were collected at 24 °C using the ϑ–2ϑ scan method. Two standard reflections, monitored every 150 measurements, fluctuated within ±3% of their mean value. The intensities were corrected for Lorentz and polarization effects but not for absorption, owing to the relatively low value of μ (11.9 cm^{-1}). The intensities were scaled to give 2402 independent $F(hkl)$ values for which I was greater than $3\sigma(I)$. A summary of data collection parameters is given in Table 1.

Solution and refinement of the structure

The asymmetric unit consists of two independent molecules of cyclopent-2-enyltriphenyltin, the positions of its two tin atoms being determined from a three-di-

Table 1

Crystal data and details of intensity and structure refinement of Ph_3Sn(cyclopent-2-enyl)

Molecular weight ($C_{23}H_{22}Sn$)	417.12
Space group	*Pbca*
Cell constants: *a*, Å	33.168(12)
b, Å	19.703(9)
c, Å	11.989(7)
Cell volume, Å^3	7834.9
Z	16
ϱ (calcd.) g cm^{-3}	1.414
ϱ (meas.) g cm^{-3}	1.41
Radiation	Mo-K_a (λ 0.7107 Å) (graphite monochromator)
Crystal dimensions, mm	0.2×0.2×0.4
μ, cm^{-1}	11.91
2ϑ range, deg	45
Decay of standard reflections	±3%
Reflections collected	6865
Reflections with $I \geqslant 3\sigma(I)$	2402
R factor	0.059
t, °C	24

mensional Patterson synthesis. The carbon atoms were located from subsequent Fourier synthesis. The hydrogen atoms, except those of the cyclopentenyl rings, were also located from the final difference Fourier synthesis and were included in

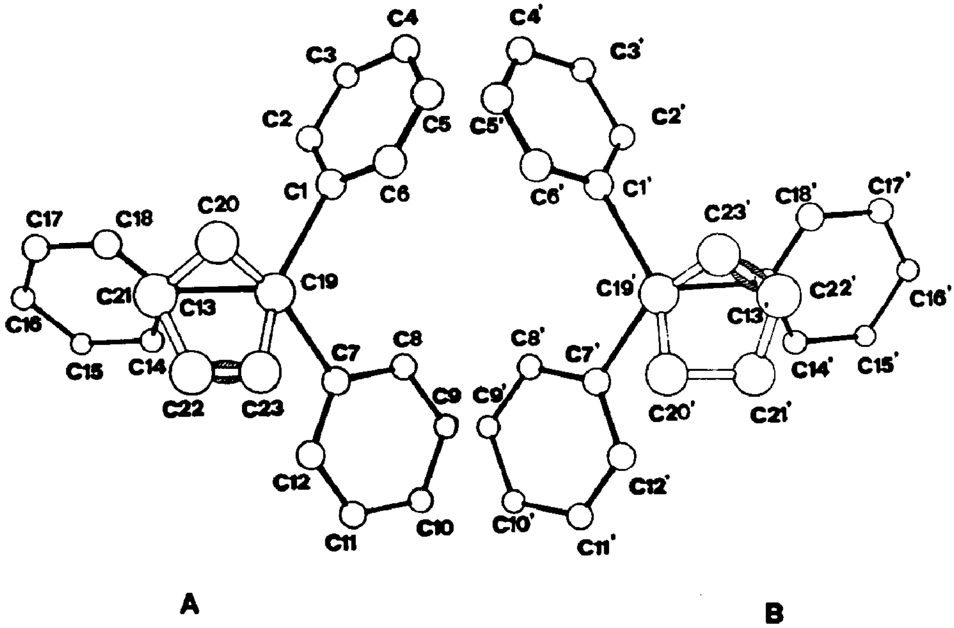

Fig. 1. Structure of cyclopent-2-enyltriphenyltin with atom numbering. The two molecules **A** and **B** forming the asymmetric unit are viewed down the C(19)–Sn (C(19)′–Sn′) axis and suitably oriented in order to show the pseudo-mirror symmetry between the triphenyltin groups. The configurations of the C_5 rings of **A** and **B** are the same.

Table 2

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

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Sn	5471(0)	3593(1)	4961(1)	Sn′	7028(0)	8567(1)	5358(1)
C(1)	5144(5)	3614(9)	3403(20)	C(1)′	7370(5)	8596(8)	3839(18)
C(2)	5145(5)	4194(9)	2735(20)	C(2)′	7361(5)	9159(8)	3134(18)
C(3)	4937(5)	4196(9)	1724(20)	C(3)′	7585(5)	9157(8)	2149(18)
C(4)	4726(5)	3619(9)	1383(20)	C(4)′	7817(5)	8592(8)	1868(18)
C(5)	4725(5)	3039(9)	2051(20)	C(5)′	7825(5)	8028(8)	2573(18)
C(6)	4934(5)	3037(9)	3062(20)	C(6)′	7602(5)	8030(8)	3558(18)
C(7)	5064(5)	3799(9)	6317(13)	C(7)′	7422(4)	8807(11)	6733(17)
C(8)	4656(5)	3897(9)	6092(13)	C(8)′	7829(4)	8936(11)	6520(17)
C(9)	4386(5)	4010(9)	6965(13)	C(9)′	8092(4)	9065(11)	7402(17)
C(10)	4524(5)	4024(9)	8064(13)	C(10)′	7949(4)	9065(11)	8496(17)
C(11)	4933(5)	3926(9)	8289(13)	C(11)′	7543(4)	8937(11)	8709(17)
C(12)	5203(5)	3813(9)	7416(13)	C(12)′	7280(4)	8808(11)	7828(17)
C(13)	5921(5)	4374(10)	5015(12)	C(13)′	6575(6)	9345(10)	5258(13)
C(14)	5874(5)	4914(10)	5756(12)	C(14)′	6515(6)	9801(10)	6133(13)
C(15)	6170(5)	5417(10)	5824(12)	C(15)′	6227(6)	313(10)	6037(13)
C(16)	6512(5)	5379(10)	5150(12)	C(16)′	5998(6)	370(10)	5065(13)
C(17)	6559(5)	4839(12)	4409(12)	C(17)′	6058(6)	9915(10)	4190(13)
C(18)	6263(5)	4337(10)	4341(12)	C(18)′	6346(6)	9402(100	4286(13)
C(19)	5684(10)	2567(22)	5019(33)	C(19)′	6802(7)	7571(13)	5436(26)
C(20)	6059(17)	2366(16)	4290(15)	C(20)′	6710(11)	7362(15)	6620(28)
C(21)	6392(9)	2442(14)	5086(22)	C(21)′	6262(10)	7570(17)	6610(25)
C(22)	6212(12)	2300(21)	6223(16)	C(22)′	6098(6)	7419(15)	5453(23)
C(23)	5807(12)	2372(24)	6199(21)	C(23)′	6428(13)	7398(16)	4852(16)

the calculations but not refined. Anisotropic thermal parameters were used for all the non-hydrogen atoms. Blocked-cascade least squares refinement was used; they converged to the conventional *R* index of 0.059. Scattering factors for the atoms were taken from Cromer and Waber [20]; the scattering factor for the tin atoms was corrected for the real and the imaginary parts of anomalous dispersion using Cromer's values [21].

All computations were carried out on a CDC Cyber 76 computer using the programmes of ref. 22. The final positional parameters of the non-hydrogen atoms are listed in Table 2, the labelling scheme being shown in Fig. 1. Thermal factors (Table 4), hydrogen atom coordinates with their thermal parameters (Table 5) and the list of the structure factors (Table 6) are available from the authors on request.

Description of the structure and comments

The two molecules **A** and **B** of cyclopent-2-enyltriphenyltin forming the asymmetric structural unit are represented in Fig. 1, where they are arbitrarily oriented with respect to each other in order to show their particular and interesting reciprocal relation. The figure together with the structural parameters reported in Table 3 indicate that the molecules **A** and **B** can be considered enantiomorphous only if the Ph_3Sn groups are taken into account (they are pseudo-mirror images of each other) while the configuration of the cyclopentenyl rings is the same. This fact

Table 3

Selected structural parameters for Ph_3Sn(cyclopent-2-enyl), with estimated standard deviations in parentheses

	Molecule *A*	Molecule *B*
Bond lengths (Å)		
Sn–C(1)	2.16(2)	2.15(2)
Sn–C(7)	2.15(2)	2.16(2)
Sn–C(13)	2.14(2)	2.15(2)
Sn–C(19)	2.14(4)	2.10(3)
C(19)–C(20)	1.57(4)	1.51(4)
C(20)–C(21)	1.47(4)	1.54(4)
C(21)–C(22)	1.51(4)	1.51(4)
C(22)–C(23)	1.35(4)	1.32(4)
C(19)–C(23)	1.52(4)	1.47(5)
Bond angles (°)		
C(1)–Sn–C(7)	109.6(7)	108.8(6)
C(1)–Sn–C(13)	111.2(6)	107.6(6)
C(1)–Sn–C(19)	102.2(3)	104.5(5)
C(7)–Sn–C(13)	106.1(6)	108.0(7)
C(7)–Sn–C(19)	111.1(5)	112.7(6)
C(13)–Sn–C(19)	116.5(5)	114.8(6)
Sn–C(19)–C(20)	119(2)	112(2)
Sn–C(19)–C(23)	111(2)	120(2)
C(20)–C(19)–C(23)	104(3)	102(2)
C(19)–C(20)–C(21)	102(2)	97(3)
C(20)–C(21)–C(22)	106(3)	113(3)
C(21)–C(22)–C(23)	111(3)	108(2)
C(22)–C(23)–C(19)	108(4)	115(2)
Torsion angles (°)		
C(6)–C(1)–Sn–C(19)	35	−39
C(12)–C(7)–Sn–C(19)	67	−62
C(18)–C(13)–Sn–C(19)	46	−69
Sn–C(19)–C(23)–C(22)	−111	−92
C(19)–C(23)–C(22)–C(21)	0	−7
C(23)–C(22)–C(21)–C(20)	−20	−20
C(22)–C(21)–C(20)–C(19)	29	30
C(21)–C(20)–C(19)–C(23)	−29	−35
C(20)–C(19)–C(23)–C(22)	18	32

gives rise to some kind of diastereoisomeric relation between **A** and **B**, in which the phenyl groups are in opposite paddle-wheel configuration, whereas the configuration of the chiral carbon atom (bearing tin) is retained. This particular and unusual feature is quite similar to that found in the case of the corresponding allyl derivative [6], though no diastereoisomeric relation could be involved there, and it might be due to the relatively small size of the C_5 ring (and of $CH_2CH{=}CH_2$, respectively) with respect to the Ph_3Sn group. (On this basis, such behaviour will not be observed in the case of the cyclohex-2-, and cyclohept-2-enyl derivatives, because of the increased steric encumbrance of their cycles [23]).

Apart from such a peculiarity the two molecules **A** and **B** show almost identical geometry. The coordination about tin is nearly undistorted tetrahedral, the conformations of the cyclopentenyl rings are the same within the standard deviations: the conformation about the Sn–C(19) and Sn′–C(19)′ bonds is staggered.

Bond lengths and angles of the C_5 rings are similar to those reported for cyclopentene itself [24], but slight deformation may be masked by the uncertainties estimated for the structure. Nevertheless, it would be anticipated that the C_5 ring would resist the deforming effects of strong σ–π interaction, whereas in the simple allyl derivative [6] $CH_2CH=$ and $CH=CH_2$ bonds were significantly shorter. Kuivila and co-workers [17] have described the rates of $S_{E'}$ protonolysis of various cyclic allylic stannanes and the ability of the ring to tolerate the rehybridization effects on the basis of substantial σ–π interaction in the transition state. These results, however, are not directly relevant to the present structural determination, which refers to the ground state arrangement. At the moment, the hypothesis of σ_{C-Sn}–π orbital mixing is the simplest explanation of the observed quasi-*axial* preference of Ph_3Sn in the cyclopent-2-enyl derivative.

It is noteworthy that the standard deviations estimated in this structure are relatively high, as are the thermal factors yielded by the refinement calculations (see Table 4). This is mainly due to the low melting point of this compound, 86 °C (also for Sn are observed U_{eq} values of about 0.09 Å^2) and partially to a relatively high libration of the C_5 rings (they have average U_{eq} values of 0.16 Å^2) about the bonds Sn–C(19). This last fact is also connected with the small size of the cyclopentenyl ring.

The torsion angles Sn–C(19)–C(23)=C(22) and Sn′–C(19)′–C(23)′=C(22)′ are −111° and −92°, respectively, and indicate that both in **A** and **B** the Ph_3Sn groups occupy *axial* position on the rings. These angles would be about 160–180° for an equatiorial position giving completely different molecular geometries. Therefore, we exclude any possibility that statistical disorder involving two such geometries can account for the high thermal factor of the C_5 ring. On the other hand, the possibility of a statistical disorder implying a vicariance of (*R*)- and (*S*)-C_5 rings would be inconsistent with the presence of two molecules in the asymmetric unit; anyway, it would involve a ratio 1/1 of (*R*) and (*S*) stereoisomers and actually, for such an assumption, calculations have been conducted but were unsuccessful, confirming the above justification for the observed thermal factors, the high standard deviations, and the value of the R factor.

The torsion angles for Sn–C–C=C of |111°| and |92°| (Table 3) are similar to those for the allyl derivative ($Ph_3SnCH_2CH=CH_2$) being |118°| and |97°| for the two molecules of the independent structural unit [6]. In other words, the axial conformation in the present case of the cyclopentenyl derivative is energetically more favoured than the equatorial conformation. These values correspond to those theoretically predicted [7,15] for the lowest energy conformation, so that it is likely to be a general phenomenon for allyltriphenyltin derivatives and will have important implications in mechanistic and conformational aspects of such cyclic allylstannanes [5,18].

It is of interest that the distance of the middle point of the double bond from tin is about 3.5–3.6 Å, so that p_π–d_π bonding between the metal and double bond is impossible. The molecular conformations of **A** and **B** show a more spherical and compact shape than that incorporating equatorial conformations, giving rise in this way to more efficient molecular packing, which actually resembles an overall pseudo-tetragonal arrangement.

Acknowledgements

We thank the C.N.R. (Roma) and the Ministero della Pubblica Istruzione, Roma, for financial support. Part of this research was supported by the Australian Research Grants Scheme.

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