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A simplified, high-yield synthesis, and crystal structure of [tris{bis(2,4,6-triisopropylphenyl)tin}]

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Abstract

The species $[\{Sn(C_6H_2{}^iPr_3\text{-}2,4,6)_2\}_3]$ has been obtained in a simple, essentially quantitative, synthesis from $SnCl_2$ and ArLi in diethyl ether at low temperature. The crystal structure analysis confirms the trimeric nature of the molecular units but reveals some unusual features. The crystal contains the unusual feature of an asymmetric unit that consists of three units of $[\{SnAr_2\}_3]$ in $P2_1/c$; the molecular unit is a scalene triangle, showing high consistency between the three molecules, in contrast to analogous trimeric species of silicon or germanium. The Sn–Sn bonds are lengthened (average value 2.942 Å) owing to steric crowding.

Introduction

The title compound was first obtained by Masamune and Sita [1], via arylation of $SnCl_4$ followed by hydrolysis of the triaryltin chloride to give the corresponding stannoxane, treatment with chlorine to give the diaryltin dichloride, and a two-stage reduction with lithium naphthalenide. These authors formulated the compound as a cyclotristannane, on the basis of NMR coupling data, but no structural data were reported.

Results and discussion

We now report that a simpler, essentially quantitative preparation can be achieved directly from anhydrous stannous chloride in diethyl ether by slow addition of the aryllithium to a suspension of $SnCl_2$ at −80 °C. If the reaction temperature is kept below −30 °C the product is the monomeric tin(II) species, whereas if the product mixture is allowed to warm to ambient temperature with partial removal of the solvent under vacuum orange crystals of the trimer are obtained. It is also possible to use the Grignard reagent, but yields are somewhat lower, and there is some evidence for complexation with the solvent, which is not easily removed completely from the product obtained in this way.

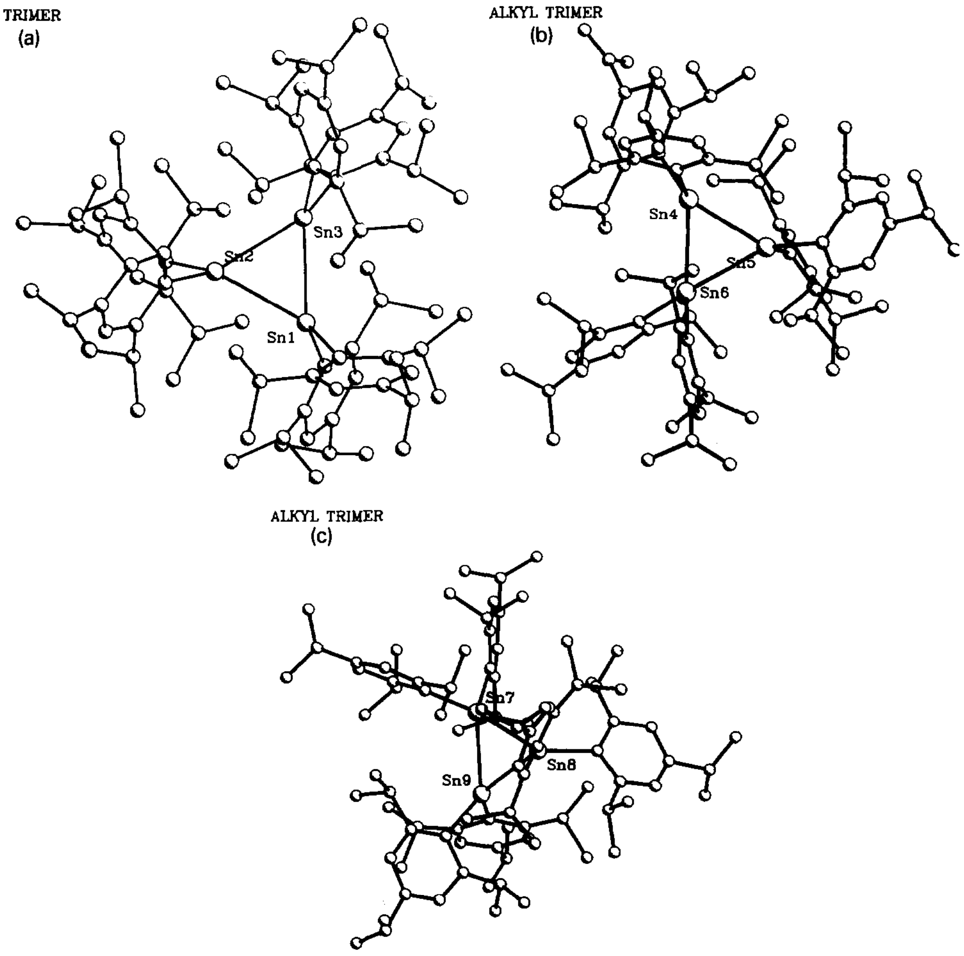

Fig. 1.

Crystals of the trimer, which are stable in air for extended periods, were grown at −20 °C from an anaerobic hexane solution. The purpose of the initial crystallographic measurements was simply to confirm the state of aggregation by a cell volume determination, which yielded the surprisingly high value of 25,889 $Å^3$. Since this high value implied an asymmetric unit containing nine or possibly ten SnR_2 units, it seemed worthwhile to proceed with the analysis, even though it presented a considerable structural problem.

The analysis revealed three trimeric units [Fig. 1, (a)–(c)], differentiated from each other principally by the arrangement of the peripheral isopropyl ligands, and remarkably similar in their overall geometry and conformation, showing no evidence of serious disorder. The overall packing (Fig. 2) may be thought of as a repeating stack, but with no major intermolecular interactions that give rise to the threefold repeat in the long-range order. Each molecule is essentially globular (Fig. 3).

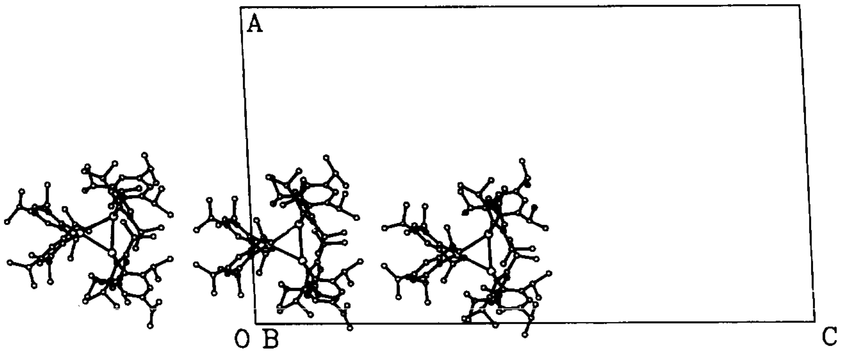

Fig. 2. The trimer asymmetric unit shown relative to the unit cell, projected down the *b*-axis.

As shown in Fig. 1, the three tin atoms of [$\{SnAr_2\}_3$] form a scalene triangle with average tin–tin bond lengths of 2.963, 2.947, and 2.916 Å. The average angles at the tin atoms are 60.16, 59.13, and 60.73 °. In the analogues hexakis(2,6-dimethylphenyl)cyclotrisilane [2], hexakis(2,6-diethylphenyl)cyclotrigermane [3], and hexakis(2,6-diethylphenyl)cyclotristannane [4], the three core atoms form isosceles triangles. This difference is probably associated with the greater steric demands of the present ligand. This is demonstrated by (i) the greater tin–tin bond lengths (the longest reported for a compound of this type) in the title trimer compared with those in the 2,6-diethylphenyl analogue, and (ii) by the greater barriers to rotation of the ligands for the present compound as derived from NMR data [1]. Also noteworthy is the lack of orthogonality between the Sn_3 planes in the three molecules and the C–Sn–C planes (Table 1), which could be expected to result in considerable weakening of the Sn–Sn bonds by reduced orbital overlap.

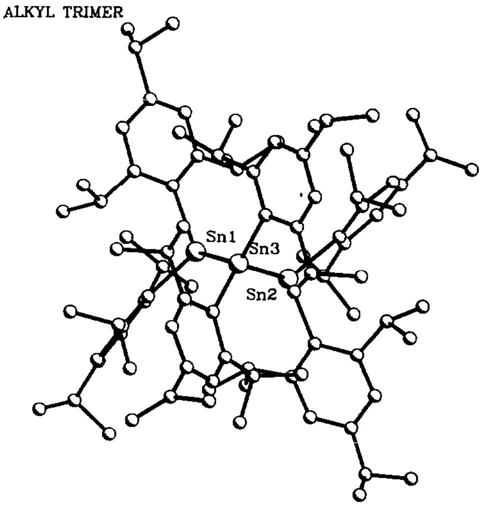

Fig. 3. Projection of a single molecule orthogonal to the metal plane.

Table 1

Angles between Sn–Sn–Sn planes and C–Sn–C planes (°)

	Sn1–Sn2–Sn3	Sn4–Sn5–Sn6	Sn7–Sn8–Sn9
C–Sn–C [a]	81.68	80.62	80.11
	80.8	81.08	81.94
	78.49	79.03	78.61

[a] Corresponding dihedral angles maintaining comparability around each ring.

Experimental

All manipulations of the tin species were carried out under pure dry nitrogen by vacuum line or Schlenk techniques.

Synthesis of the cyclotristannane

a. Synthesis of the monomer / dimer mixture. (i) From the lithium reagent. A solution of the aryllithium reagent (55 cm^3, 0.15 *M*, 8.25 mmol) in ether was added dropwise to a solution of $SnCl_2$ (0.86 g, 4.53 mmol) in ether (50 cm^3) at −90 °C. The solution was warmed to −65 °C, at which the deep red colour of the product developed. To ensure completion of the reaction the mixture was warmed briefly to −40 °C, then cooled to −80 °C and stored at that temperature until required. The yield was essentially quantitative.

(ii) From the Grignard reagent. The Grignard reagent (40 cm^3, 0.135 *M*, 5.4 mmol) in ether was added dropwise to $SnCl_2$ (0.51 g, 2.7 mmol) in ether (50 cm^3) at −85 °C. The mixture was warmed to −70 °C and kept there for 1 h, then warmed to −60 °C, and finally briefly to −30 °C to ensure completion of the reaction. It was finally cooled to −80 °C and stored at that temperature until used.

b. Oligomerisation of the products from above. An ether solution of the equilibrium mixture was made, preferably by route (i) above, and allowed to warm with stirring to between 0 and −10 °C. About two-thirds of the solvent were removed under vacuum, the latent heat of evaporation resulting in cooling of the mixture, which was then allowed to warm to near ambient temperature. Three or four repetitions of the cycle of evacuation with cooling followed by warming produced the trimer as orange yellow crystals. When the crystals started to form the solution was reduced in volume to ca. 20 cm^3 and kept at −20 °C. The trimeric product was filtered off, and recrystallised from the minimum quantity of hexane. The yield was quantitative.

Crystal data

$C_{90}H_{138}Sn_3$, $M_r = 1460.244$. Monoclinic, $P2_1/c$, $a = 24.515(3)$, $b = 24.366(3)$, $c = 43.357(7)$ Å; $\beta = 91.55°$. $U = 25889.07$ Å^3, $D_c = 1.124$ g cm^{-3}, $Z = 12$; $F(000) = 9936$, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 8.17$ cm^{-1}.

Data collection and structure solution

An orange rhomb-shaped crystal of approximate size $0.3 \times 0.3 \times 0.2$ mm^3 was mounted on an Enraf–Nonius CAD4 diffractometer, and the intensities of 25688 reflections in the range $1 \leqslant \theta \leqslant 20°$ were measured using Mo-K_α radiation with a graphite monochromator. Owing to the large size of the unit cell, the stationary background measurement technique was used. The data were measured to 22°, but virtually nothing was observed beyond 20°, and so only these data were used in structure solution and refinement. The data were reduced to give 23679 reflections (merging $R = 4.15\%$) of which 10891 had $|F_{obs}| > 4\sigma(F_{obs})$ and were used in structure solution and refinement.

The structure was solved by the direct method (SHELXS), which revealed the positions only of the three Sn triangles. All 270 carbon atoms were located by the difference Fourier method, and refined by blocked full-matrix least squares to a conventional R-factor of 9.4%. Unit weights were used with the aromatic and tertiary aliphatic hydrogen atoms in calculated positions. Only the Sn atoms were given anisotropic temperature factors. The goodness of fit was 1.75, and the highest peak in the final difference map was 0.594 e $Å^{-3}$. Comparatively high thermal motion was associated with the 108 methyl carbon atoms in the structure, and no attempt was made to place the associated 324 methyl hydrogen atoms in calculated positions. However, 60 aromatic and 30 tertiary aliphatic hydrogens were placed in calculated positions and refined with a fixed temperature factor of 0.07.

The three separate molecules of the final structure are shown in Fig. 1. The packing of the trimeric units is shown in Fig. 2, and Fig. 3 shows a projection of the trimer orthogonal to the metal plane. Full data have been deposited with the Cambridge Crystallographic Data Centre *. The programs SHELXS and SHELX-76 are used by kind permission of Professor G.M. Sheldrick (University of Göttingen).

Acknowledgements

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* *Editor's note:* The table of atomic coordinates, which we usually include in ordinary papers, is omitted in this case because of its unusual length.