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Synthesis, structure and reactivity of the novel tetratin species bromoheptakis(2,6-diethylphenyl)-cyclotetrastannabutane

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Abstract

Metallation of ArBr (Ar = 2,6-diethylphenyl) with Li powder in diethyl ether, followed by addition of stannous chloride at low temperature does not give the expected oligomeric diarylstannane but an essentially quantitative yield of the novel tetrastannabutane [$\{SnAr_2\}_3SnArBr$]. Some reactions of the new species are reported.

We report the synthesis of the first functionalised cyclotetrastannane, obtained almost quantitatively by treatment of stannous chloride with the product of reaction between fine lithium powder and bromo-2,6-diethylbenzene.

Cyclic configurations are known for several tristannanes [1a–1c], tetrastannanes [2] and hexastannanes [3]. In addition there are some functionalised cage molecules having a germanium skeleton [4]. None of the smaller oligomers, however, has functional groups, which are necessary if the oligomer framework is to be retained in subsequent chemistry.

Treatment of 2,6-diethylphenyl bromide with excess lithium powder (150 mesh) in diethyl ether at ambient temperature, gave a colourless solution which was filtered (Celite) and then reduced in volume substantially under vacuum. When kept for several hours at −20 °C the solution deposited colourless crystals of a lithium reagent, and these were filtered off and redissolved in freshly distilled ether for use. A 2-molar equivalent of this solution was added to a suspension of anhydrous tin(II) chloride (also in ether) at −80 °C to give a deep red solution, which was allowed to warm slowly to room temperature to give an orange suspension. The suspension was filtered and the residue washed with dry ether, and the combined filtrate and washings were evaporated to dryness and extracted with dry hexane. Removal of about two thirds of the hexane from the extract under vacuum and subsequent cooling (12 h, −20 °C) yielded yellow needles in approximately 65% yield. (Further workup of the filtrate gives an essentially quantitative yield.)

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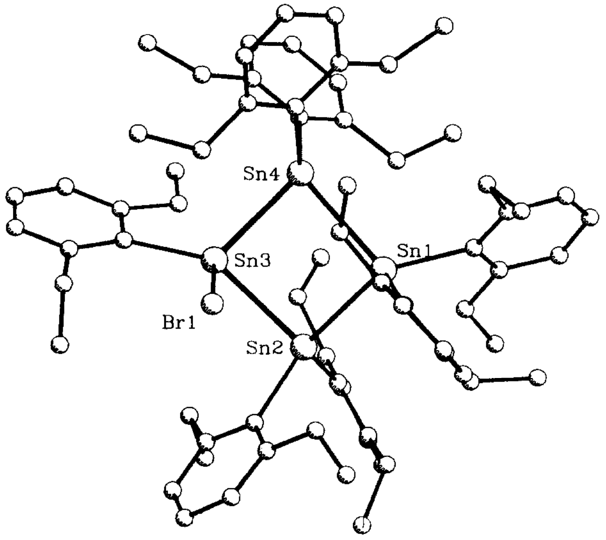

Fig. 1. A single molecule [$\{SnAr_2\}_3SnArBr$]. Salient bond lengths (Å) and angles (°). Sn(1)–Sn(2) 2.910(2), Sn(1)–Sn(4) 2.899(2), Sn(2)–Sn(3) 2.843, Sn(3)–Sn(4) 2.831(2), Sn(3)–Br(1) 2.554(3); Sn(4)–Sn(1)–Sn(2) 90.6(1), Sn(3)–Sn(2)–Sn(1) 84.7(1), Sn(4)–Sn(3)–Sn(2) 93.4(1), Sn(3)–Sn(4)–Sn(1) 85.1(1), C(1)–Sn(1)–C(2) 100.1(5), C(3)–Sn(2)–C(4) 101.0(5), C(5)–Sn(3)–Br(1) 110.9(4), C(6)–Sn(4)–C(7) 100.7(5).

A complicated NMR spectrum *, and elemental analysis did not allow a formulation of the new material. A single crystal was grown anaerobically from hexane, and subjected to structural analysis **. The structure revealed for a single molecule is shown in Fig. 1.

The crystal structure reveals a tetrastannane ring, which is not planar, but has a dihedral angle between the plane defined by Sn(1), Sn(2), Sn(4) and that of Sn(2), Sn(3), Sn(4) of 152.75°, the deviation being such that the bromine atom lies on the

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* ^1H NMR ($CDCl_3$, 300 MHz): δ 7.18 (m), 7.01 (s), 6.99 (s), 2.57 (m), 0.85 (t), 0.65 (q), 0.55 (t), 0.35 (t). Ir (CsI disc): 3051s, 2968s, 2936s, 2878s, 1450s, 1428w, 1377m, 1261w, 1011w, 570w cm^{-1}. M.p.: dec. above 160 °C (in air). Elemental analysis. Found: C, 55.54; H, 5.91. Calc.: C, 56.54; H, 6.12%.

** *Crystal data.* $C_{70}H_{91}BrSn_4$, $M = 1487.162$, triclinic, $a = 11.260(6)$, $b = 12.707(5)$, $c = 23.05(1)$ Å, $\alpha = 85.17(3)$, $\beta = 88.18(3)$, $\gamma = 80.90(3)°$, $U = 3244.1(2.8)$ Å^3 by least squares refinement of the setting angles of 25 independent diffractometric data ($\lambda = 0.71069$ Å), space group $P\bar{1}$ (No. 2). $D_c = 1.522$ g cm^{-3}, $Z = 2$, $F(000) = 1492$. A yellow needle-shaped crystal, approximate dimensions $0.2 \times 0.2 \times 0.2$ mm, $\mu(Mo\text{-}K_\alpha) = 20.36$ cm^{-1}. Data were collected on an Enraf–Nonius CAD-4 diffractometer, using the $\omega - 2\theta$ mode with ω-scan width $= 0.90 + 0.35 \tan\theta$, graphite monochromated Mo-K_α radiation; 6716 reflections measured ($1 < \theta < 20°$), 5183 were unique [merging $R = 0.05$ after decay correction (0.35% per h) and empirical absorption correction (average correction factor 0.8316, average transmission 50.98%)], giving 4185 with $|F_o| \geq 4\sigma(F_o)$. The structure was solved by direct methods followed by difference Fourier synthesis. Refinement used full-matrix least-squares, with heavy atoms and carbons of the aromatic rings anisotropic; the geometry of the rings was constrained placing hydrogen atoms in calculated positions with one temperature factor for each environment [CH $U_{iso} = 0.11(1)$ Å^2, CH_2 $U_{iso} = 0.08(1)$ Å^2, CH_3 $U_{iso} = 0.13(1)$ Å^2]; and unit weights. Final R value 0.0611. The SHELX suite of programmes is used by kind permission of Professor G.M. Sheldrick (Göttingen). A table of atomic coordinates and a complete list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

side having the smaller angle. This non-planarity is presumably associated with the asymmetry at the Sn(Br)Ar atom, and its relative bulk compared with the $SnAr_2$ moieties, an interpretation in harmony with the planarity of $[\{Sn^tBu_2\}_4]$ and slightly non-planar character of $[\{SnR_2\}_4]$ (R = 1,1-dimethylpropyl) [2]. Other noteworthy features of the structures include (i) the Sn–Sn distances between Sn(1) and atoms Sn(2) and Sn(4) which are towards the upper limit for these separations in neutral species, [2.910(2) and 2.899(2)], and similar to these vectors in related small-ring stannanes [1c]; and (ii) the remaining Sn–Sn distances [2,843(2) and 2.831(2)] which are significantly smaller, as expected for bonds to the less bulky SnBrAr group. The angles subtended at the tin atoms Sn(1), Sn(2), and Sn(4) are metal atom in the cyclotristannane $[\{Sn(Ar^\star)_2\}_3]$ ($Ar^\star$ = 2,4,6-triisopropylphenyl) [1c], which has bulkier substituents at the tin atom.

The bromine incorporated in the molecule can only have arisen from the bromophenyl starting material. Since the lithium reagent was crystallised and redissolved we presume that the lithium reagent crystallises with lithium bromide, as has been established for "phenyllithium" prepared from lithium and bromobenzene [5], though we have not investigated this aspect in detail. A lithium reagent can also be prepared from the bromide using butyllithium; this reagent reacts with stannous chloride in either diethyl ether or tetrahydrofuran to give respectively a complex mixture of products or the hexakis(2,6-diethylphenyl)cyclotristannane, albeit in moderate yield (ca 50%) [6].

The new species is thermally stable at 75 °C in toluene for prolonged periods (and possibly at higher temperatures), and in crystalline form is air-stable for extended periods. However ethereal solutions decompose rapidly in air, giving the novel species $[\overline{SnAr_2(SnAr_2)_2O}]$, which has been chemically and structurally characterised [7].

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