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Preliminary communication

SYNTHESIS (VIA REDUCTIVE ELIMINATION OR METATHESIS) AND X-RAY CRYSTAL STRUCTURE OF A TETRAMERIC *meso*-TIN(II) METALLOCYCLE $\overline{\mathrm{Sn(CHSiMe_3C_6H_4C}}\mathrm{HSiMe_3}\text{-}o)$, AND CHARACTERISATION OF *meso,meso*-$\overline{\mathrm{Sn(CHSiMe_3C_6H_4C}}\mathrm{HSiMe_3}\text{-}o)_2$ *

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Summary

A yellow, diamagnetic tin(II) metallocycle, *meso*-$\overline{\mathrm{Sn(CHSiMe_3C_6H_4C}}\mathrm{HSiMe_3}\text{-}o)$ (I) showing a monomeric parent ion in its mass spectrum and a first ionisation energy at 7.6 eV in its photoelectron spectrum, is tetrameric in the solid with an $\mathrm{Sn_4}$ ring (Sn—Sn 2.852(3) Å), as determined by X-ray structure analysis, and was isolated as a minor product on treating $\mathrm{SnCl_4}$ with $[\{o\text{-}\mathrm{C_6H_4(CHSiMe_3)_2}\}\text{-}\{\mathrm{Li(tmeda)}\}_2]$ (II) at —78°C (but not +30°C) [tmeda = $\mathrm{Me_2NCH_2CH_2NMe_2}$] in $\mathrm{OEt_2}$. The major product is the spirocyclic complex $\overline{\mathrm{Sn(CHSiMe_3C_6H_4C}}\mathrm{HSiMe_3}\text{-}o)_2$ in which both ligands are in the *meso* configuration; compound I was more conveniently obtained from II and $\mathrm{Sn(OC_6H_2Me\text{-}4\text{-}Bu^t_2\text{-}2,6)_2}$

Only five bis(hydrocarbyl)tin(II) compounds $(\mathrm{SnR_2})_n$ have been authenticated (X-ray) [1]: (a) R = $\mathrm{CH(SiMe_3)_2}$ and $n = 1$ (in the vapour or in $\mathrm{C_6H_{12}}$) or $n = 2$ (crystal) [2], (b) R = $\mathrm{CH_2SiMe_3}$ and $n = 4$ (in the crystal or in $\mathrm{C_6H_6}$) [3], (c) R = Ph and $n = 6$ (crystal or solution) [4], and (d)/(e) R = $\eta\text{-}\mathrm{C_5H_5}$ or $\eta\text{-}\mathrm{C_5Me_5}$ [5]; of these only (a) is coloured (red). The cyclostannanes $(\mathrm{SnR_2})_n$ $(n \geqslant 4)$ have previously been found to have strong Sn—Sn bonds, unlike (a). Indeed their degree of aggregation n was often determined by identification of the iodinolysis product $\mathrm{I(SnR_2)_nI}$: e.g., for R = $\mathrm{Bu^t}$ ($n = 4$) [6] or R = $\mathrm{C_6H_{11}}$

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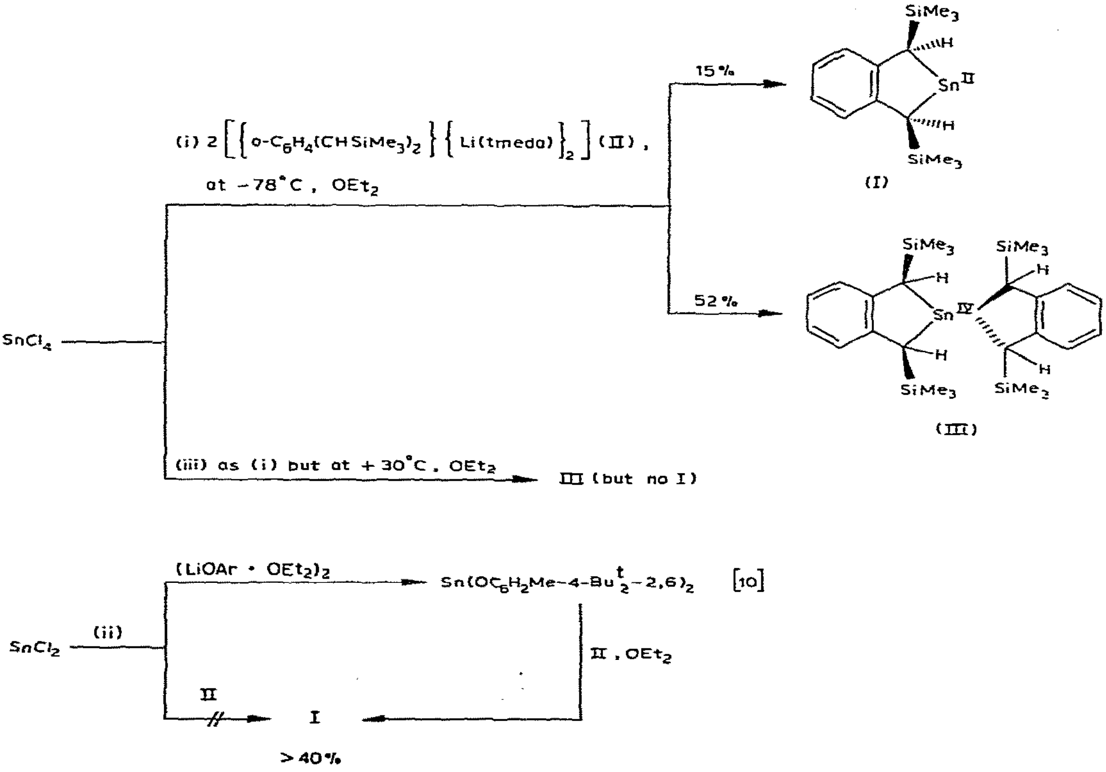
($n = 5$) [7], although (b) with Cl_2 or Br_2 in CCl_4 afforded SnR_2X_2 [3]. Recent ^{119}Sn Mössbauer data for $[Sn\{C_6H_3(CF_3)_2\text{-}2,6\}_2]_n$ have been interpreted as implying that $n = 1$ in the crystal [8].

We now report the synthesis and characterisation (see Scheme 1) of the yellow, diamagnetic, crystalline *meso*-$\overline{\mathrm{Sn[CH\,SiMe_3C_6H_4CH}}\mathrm{SiMe_3}$-*o*] (I), *the first* tin(II) metallocycle (a stannaindene), obtained from either (i) $SnCl_4$ and $[\{o\text{-}C_6H_4(CHSiMe_3)_2\}\{Li(tmeda)\}_2]$ (tmeda = $Me_2NCH_2CH_2NMe_2$) (II) [9] at −78°C in OEt_2 with the *meso,meso*-spiro-metallobicycle $\overline{\mathrm{Sn[CHSiMe_3C_6H_4CH}}$-$\mathrm{SiMe_3}$-*o*]$_2$ (III) as co-product, or (ii) $Sn(OC_6H_2Me\text{-}4\text{-}Bu^t_2\text{-}2,6)_2$ [10] and II. It is also a tetramer in C_2Cl_6 as shown by vapour phase osmometry. Reactions (i) and (ii) are noteworthy, not least because complex I proved to be inaccessible from $SnCl_2$ and the dilithium reagent II, and because of their stereospecificity. Complex III is a rare example of a spirocyclic organotin compound, cf. ref. 11. When reaction (i) was carried out at +30°C (reaction iii) III was the sole product. Evidently the lithium reagent II reacts as a more effective reducing than alkylating agent at low temperature.

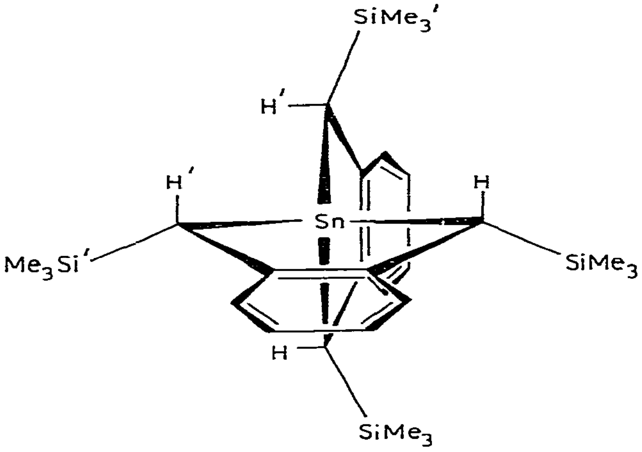
The He(I) photoelectron (PE) spectrum of gaseous *meso*-1,3-bis(trimethylsilyl)-2-stannaindane (I) at 130—136°C, is dominated by the features character-



SCHEME 1. The formation and characterisation of the tin(II) metallocycle (I), [(yellow, dec. > 210°C, tetramer (*meso*)$_4$ in the crystal (see Fig. 1)] and spirotin(IV) metallocycle (II) [colourless, m.p. 115°C, (*meso, meso*)$_4$]. The percentage yields refer to isolated pure compounds, which gave satisfactory analytical, ^{1}H NMR, and mass (monomeric P^+ ions) spectral results, as well as single crystal X-ray data (for III, cf. ref. 13).

istic of the ligand, as shown by comparison with the PE spectrum of o-C_6H_4-$(CH_2SiMe_3)_2$ (first ionisation energy at ca. 8.2 eV) with, however new bands at 7.6, 9.5, and 11.8 eV. The first of these is almost certainly due to ionisation from the metal-centred lone pair orbital of the monomer, cf. ref. 12: 7.42 eV for $Sn[CH(SiMe_3)_2]_2$. Further evidence for the monomer in the gas phase derives from (i) the mass spectrum, which shows the monomer parent ion P^+, as well as $(P-Me)^+$, and $[C_6H_4\{CH(SiMe_3)\}_2]^+$, and (ii) the increase in colour intensity of the vapour compared with the solid.

Compound III shows NMR 1,1-doublets in C_6D_6 for each of (a) the α-C^1H's, (b) the $Si(C^1H_3)_3$'s, (c) the α-^{13}CH's, and (d) the $Si(^{13}CH_3)_3$'s. These data are suggestive of magnetically distinct environments: H/H' (δ 2.58 and 1.75 for ^1H and 28.08 and 26.32 for ^{13}C) and $SiMe_3/SiMe_3'$ (δ 0.18 and 0.03 for ^1H and 2.60 and 1.38 for ^{13}C), which differ in their relative proximity to the aromatic π-cloud, as shown in IV a conclusion confirmed as far as conformation in the crystal is concerned by X-ray diffraction [13].



(IV)

The molecular structure of the tin(II) metallocycle, *meso*-1,3-bis(trimethylsilyl)-2-stannaindane (I) consists of a Sn_4 ring with each tin, of distorted tetrahedral environment, coordinated by the chelating alkyl with the trimethylsilyl substituents in the *meso* configuration (Fig. 1); the overall symmetry is $\bar{4}$. The low "fold angle" [14] (20.8°) and near-tetrahedral Sn—C—C angles [105(3), (101(2)°] demonstrate an η^2-bound o-xylidene ligand as opposed to an intermediate η^2—η^4 situation as found in $[W(CH_2C_6H_4CH_2\text{-}o)_3]$ [15]. In comparison to the only other structurally characterised alkyltin(II) complexes, the Sn—Sn distance is somewhat longer at 2.852(3) Å, cf., 2.78 in $(SnPh_2)_6$ [4], 2.764(2) in $[Sn\{CH(SiMe_3)_2\}_2]_2$ [2], and 2.835(3) Å in $[Sn(CH_2SiMe_3)_2]_4$ [3].

Crystal data. $(C_{14}H_{24}Si_2Sn)_4 \equiv C_{56}H_{96}Si_8Sn_4$, M = 1468.8, tetragonal, space group $I\bar{4}$, a = 17.684(8), c = 11.239(7) Å, Z = 2. The specimen was mounted

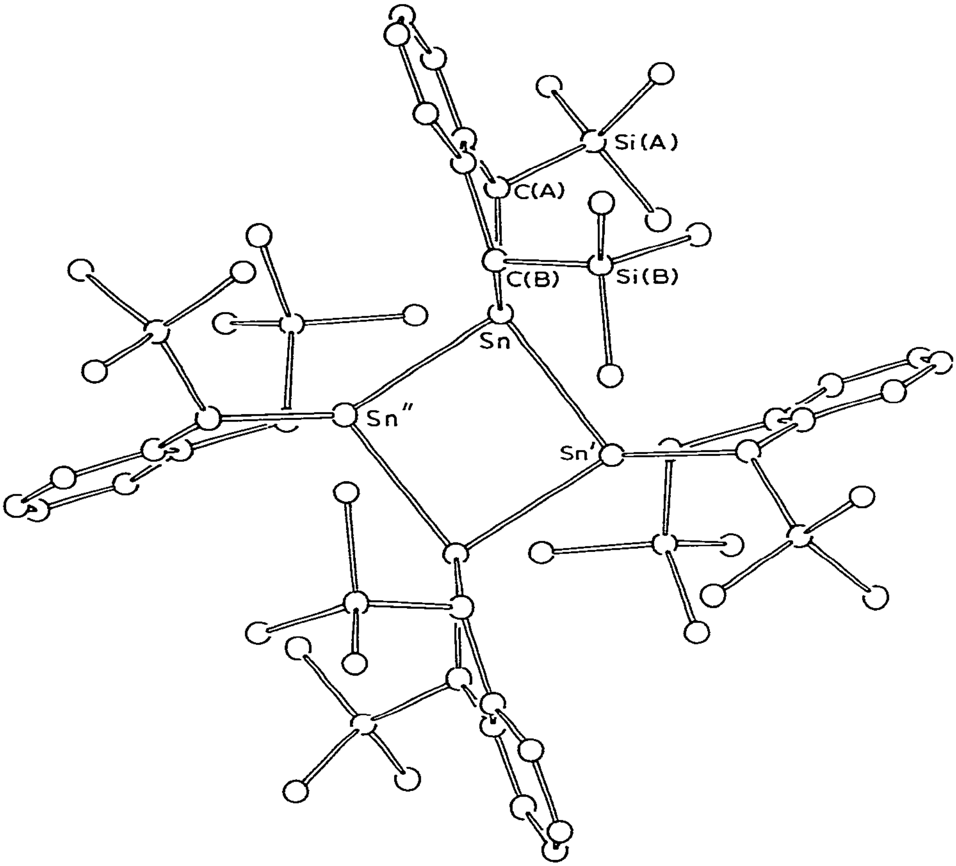


Fig. 1. Projection of $[meso\text{-}\overline{\mathrm{Sn}(\mathrm{CHSiMe_3C_6H_4C}}\mathrm{HSiMe_3}\text{-}o)]_4$ (I) onto the Sn_4 plane; the molecule has $\bar{4}$ symmetry. Important distances (Å) and angles (degrees) are as follows: Sn—Sn, 2.852(3); Sn—C(A), 2.15(3); Sn—C(B), 2.09(4); Sn′—Sn—Sn″, 88.21(8); C(A)—Sn—C(B), 88(1); C(A)—Sn—Sn′, 134(1); C(A)—Sn—Sn″, 117(1); C(B)—Sn—Sn′, 121(1); C(B)—Sn—Sn″, 111(1).

in a capillary under argon and the structure was solved from 615 "observed" diffractometer reflections (Mo-K_α radiation) and refined to $R = 0.066$*.

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*Atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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