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Reductive dehydrocoupling of diphenyltin dihydride with LiAlH₄, selective synthesis and structures of the first bicyclo[2.2.1]heptastannane-1,4-diide and bicyclo[2.2.2]octastannane-1,4-diide
Reductive dehydrocoupling of diphenyltin dihydride with LiAlH₄: selective synthesis and structures of the first bicyclo[2.2.1]heptastannane-1,4-diiide and bicyclo[2.2.2]octastannane-1,4-diide†

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The reaction of diphenyltin dihydride with LiAlH₄ gives access to a set of charged tin cages as their lithium salts. Variation in the ratio of reactants provides a perstannabicyclooctane dianion and a perstannabicyclooctane as the di- and monoanions. These compounds can be synthesised selectively by careful stoichiometric control and have been characterised by single crystal X-ray diffraction, NMR and UV-vis spectroscopy. Computational exploration of the electronic structures of these compounds was undertaken and, in agreement with structural and spectroscopic features, indicated significant σ-delocalisation in the tin skeletons.

The chemistry of anionic oligo-tin cage and cluster compounds is dominated by a plethora of Zintl phases, discrete Zintl ions,1 [Sn₉]⁺, or their derivatisation products, [R₉Sn₉]⁻.² Derivatisation reactions of the Zintl ion Sn₉⁺ have led to the trianionic RSn₉⁻,⁴ the monoanion Sn₉⁻[Si(SiMe₃)₃]⁻⁴, the monocation [Sn₁₀(Si(SiMe₃)₃)₅]⁺⁵ and the dianions Sn₉[Si(SiMe₃)₃]⁻⁶,⁷ and Sn₁₀[Si(SiMe₃)₃]⁻⁸,⁹,¹⁰ Moreover, the anionic cluster Sn₉R₇(NH₂)⁻ (R = CH(SiMe₃)₂, NH₂ = 1,2,3,4-tetra-methylimidazol-2-ylidene) was isolated from the reaction of the trihydride RSnH₃ with the corresponding NHC.⁸ Alongside these, several neutral metalloid clusters of the form Sn₉R₉ⁿ⁺ (n > m) have been obtained from reductive or dehydrogenating coupling methods.⁹ Closely related to metalloid compounds,¹⁰αβ albeit with a superstoichimetric ratio of substituents to tin, are the elementoid¹⁰β [1.1.1]pentastannapropellanes, Sn₉R₉⁺,¹¹ tetra-cyclic Sn₉R₉⁺,¹² and the hexastannabenzene isomer, Sn₉R₉⁺.¹³ The aforementioned compounds share a non-classical, i.e. 3D-delocalised, bonding situation. This confers a narrow energy gap between frontier orbitals which facilitates interesting addition chemistry and reoxidation behaviour.¹⁴ In contrast to the well represented class of simple monocyclic rings, (R₈Sn)₉,¹⁵ purely σ-bonded tin cages, (RSn)₉, are sparse. Examples include tricyclo- and pentacycloprismanes of the stoichiometry, R₈Sn₉ and R₁₀Sn₉⁻,⁸,¹⁶ cubanes, R₉Sn₉⁻,¹⁷ and a tetrahedral cage molecule with edge-bridging methandiyl substituents.¹⁸ Anionic, covalent, oligotin cages include Sn₉R₉⁻ (R = Si-alkyl)¹⁶c and Sn₉(CH₃)R₉⁻ and the radical anion Sn₉R₉⁻ (R = 2,6-Et₂C₆H₃). The latter species originate from the addition of methyl lithium to, and the electrochemical one-electron reduction of, a [1.1.1]pentastannapropellane.¹⁴b Organotindihydrides are common starting materials in the synthesis of oligotin compounds. Their dehydrogenating coupling has also been widely applied in the synthesis of linear tin polymers and cyclic oligomers (R₂Sn)₉⁻ whilst the reaction of a tin dihydride with sodium in liquid ammonia led to the formation of Ph₃SnHNa and NaPh₂SnPh₂Na.²⁰

Diphenyltin dihydride can be synthesised by the reaction of LiAlH₄ with diphenyltin dichloride.²¹ During our repetition of this literature method, we noted the reaction mixture would often acquire a deep red or yellow colour upon the use of large excesses of LiAlH₄. This resulted in a significant decrease in yield of the desired diphenyltin dihydride. Thus, in order to elucidate the nature of possible over-reaction products, analytically pure Ph₂SnH₂ was reacted with LiAlH₄.²²

In an initial reaction, an equimolar mixture of the two reagents in THF was observed to provide a persistent bubbling and the formation of a dark red solution, as well as a flocculent white precipitate, identified as AlH₃ by IR spectroscopy. Addition of 12-crown-4 (hereafter, 12-Cr-4) and storage at −30 °C yielded a small amount of an intensely yellow material that was thought to be a single, crystalline product. X-ray diffraction analysis, however, indicated this material to be a disordered mixture of two oligostannane dianions (1 and 2). In order to access analytically
pure samples of 1 and 2, the ratio of LiAlH₄ to Ph₂SnH₂ was optimised.

The reaction of 7 equivalents of diphenyltin dihydride with two equivalent of LiAlH₄ in THF or DME gave access to crystalline, analytically pure [Ph₂Sn]²⁻[Li(12-Cr-4)]₂, 1, in moderate yields after the addition of 12-Cr-4 and storage at −30 °C. Similarly, [Ph₂Sn]²⁻[Li(12-Cr-4)]₂, 2, was obtained by applying analogous conditions albeit with a 8:2 ratio of Ph₂SnH₂:LiAlH₄. These optimised conditions yielded material suitable for X-ray crystallography as orange and red crystals, respectively. Higher tin to alumane ratios of 8:1 and above yielded the bicyclo[2.2.2]heptastannane-1-ide [Ph₂Sn]₃⁻[Li(12-Cr-4)]₃, 3. 3 was characterised by NMR and UV-vis spectroscopy as well as X-ray crystallography.²³ A Ph₂SnH₂:LiAlH₄ ratio of 1:0.75 and 1:2 led to the formation of elemental tin and compounds 4 and 5 which contain discrete [Ph₃AlH]⁻ and [Ph₃AlH]⁻ anions and charge separated [Li[(12-Cr-4)])²⁻ or [Li(DME)(12-Cr-4)]⁻ counterions. The formation of 4 and 5 demonstrates net phenyl group transfer from tin to aluminium which provides the tertiary tin bridgeheads in 1–3 with less than the original two phenyl groups per tin. NMR spectroscopic interrogation of the reaction mixtures indicated the initial formation of benzene and of the anion [HP₃Sn]⁻ (¹¹⁹Sn: −180.5 ppm, J_H⁻¹¹⁹Sn = 152 Hz),²⁰ which undergoes subsequent dehydrative coupling with excess Ph₂SnH₂ to cause the intermediate formation of various unidentified oligostannyl anions. Isotopic labelling experiments showed the predominant formation of H₂ in the reaction of Ph₂SnH₂ with LiAlH₄, while treatment of Ph₃SnD₂ with LiAlH₄ gave D₂ (see ESIF page S31).

1 and 2 constitute the first reports of a bicyclo[2.2.1]-heptastannane-1,4-diide and bicyclo[2.2.2]octastannane-1,4-diide, respectively, and both crystallise in the presence of 2 [Li(12-Cr-4)]⁻ counterions as charge separated structures. In the solid state structure of the bicyclo[2.2.1]heptastannane-1,4-diide 1 (Fig. 1) the anionic bridgeheads Sn1 and Sn7 are separated by an intramolecular distance of 5.04 Å. The angles around Sn1 and Sn7 sum to 265.8° (Sn1) and 264.6° (Sn7), suggesting high p-orbital contribution in bonding orbitals at Sn1 and Sn7 and implying significant s-orbital character for the lone pair at these anionic tin atoms.

The bicyclo[2.2.2]octastannane-1,4-diide 2 (Fig. 1), features a less constrained geometry in the solid state with angles around the bridgehead atoms Sn1 and Sn8 just above 90° (sum of angles around Sn1 = 276.05° and Sn8 = 274.08°). The monoanion 3 displays two distinctly different environments for the bridgehead tin atoms with a highly pyramidalised anionic tin atom Sn1 (sum of angles 287.69°) and a more tetrahedral geometry at the phenyl substituted, formally neutral bridgehead Sn4 (sum of Sn–Sn–Sn angles 318.62°). The bridgehead atoms, Sn1 and Sn4, are separated by 5.27 Å in 3, which is ca. 0.67 Å less than in 2. In contrast to 1, compounds 2 and 3 are both twisted in the solid state (see ESIF Fig. S2.2, page S7 and S2.3, page S8). Compounds 4 and 5 (Fig. 1) containing discrete [Ph₃AlH]⁻ and [Ph₃AlH]⁻ anions and charge separated [Li[(12-Cr-4)])²⁻ or [Li(DME)(12-Cr-4)]⁻ counterions, respectively, display tetrahedral aluminium atoms with Al–C distances slightly greater than 2.0 Å.

The ¹¹⁹Sn{¹H} NMR spectra of 1, 2 and 3 indicate that these cages persist in solution, as evidenced by chemical shifts and the observed ¹¹⁹Sn/¹₁⁷Sn couplings (Fig. 2, ESIF Section 4 pages S-14–S-26). 1 displays three resonances at 200.3 (Ph₃Sn), 35.7 (Ph₂Sn₃SnPh₃) and −857.3 (Sn⁻) ppm for which the coupling pattern is in full agreement with the bicyclo[2.2.1]heptastannane-1,3-diide framework in solution. J_{¹¹⁹Sn⁻¹¹³Sn} coupling constants originating from the anionic bridgehead atoms are large with values of 4640/4430 Hz for the interaction with the mononitride. In the case of coupling between the bridgehead tin atoms and the ditin bridges, values of 5990/5710 Hz for the J_{¹¹⁹Sn⁻¹¹³Sn} coupling and 1130/1080 Hz for the J_{¹¹³Sn⁻¹¹³Sn} coupling are observed. The relatively large J values compare to a smaller J_{¹¹³Sn⁻¹¹⁷Sn} coupling constant of 3940 Hz for chemically equivalent tin atoms within the same ditin bridge.

![Fig. 1](image-url) Formation of anionic oligotin cages 1–3 and phenyl aluminium hydrides 4 and 5. Metal atoms are drawn at 30% probability level, only hydrogen atoms attached to Al are shown, all other H atoms are omitted for clarity. For full geometric parameters, see ESIF pages S-7–S-9. Selected bond angles (°) 1: Sn2–Sn1–Sn6 94.37(2); Sn2–Sn1–Sn6 86.75(1); Sn5–Sn1–Sn6 84.67(1); Sn3–Sn7–Sn4 93.52(2); Sn3–Sn7–Sn6 85.41(1); Sn4–Sn7–Sn6 85.69(1). 2: Sn2–Sn1–Sn3 91.29(2); Sn2–Sn1–Sn4 91.41(2); Sn3–Sn1–Sn4 93.35(2); Sn5–Sn8–Sn6 90.95(2); Sn5–Sn8–Sn7 89.00(2); Sn6–Sn8–Sn7 94.13(2). 3: Sn2–Sn1–Sn6 96.92(8); Sn2–Sn1–Sn7 95.47(8); Sn6–Sn1–Sn7 95.30(8); Sn3–Sn4–Sn5 106.93(8); Sn3–Sn4–Sn8 105.22(8); Sn5–Sn4–Sn8 106.47(8).
ng to its higher molecular symmetry, only two resonances are observed in the $^{119}\text{Sn}^{1}H$ NMR spectrum of 2, with peaks at $-316.8$ (Ph$_2$SnSnPh$_3$) and $-583.0$ (Sn$^-$) ppm. The $J$ and the $J_{119\text{Sn}-119\text{Sn}}$ coupling constants between the bridgehead tin atoms and the Ph$_2$SnSnPh$_2$ bridges are 5020/4800 Hz and 807/770 Hz, respectively. Again, a smaller $J_{119\text{Sn}-119\text{Sn}}$ coupling constant of 3610 Hz is observed for neighbouring diphenyltin fragments. The monoanion $3$ displays four distinct signals in the $^{119}\text{Sn}^{1}H$ NMR spectrum at $-183.1$ (Ph$_2$SnSn$^-$), $-238.6$ (Ph$_2$SnSnPh), $-470.8$ (SnPh) and $-757.9$ (Sn$^-$) ppm. Notably, the coupling constant of the tricoordinate, anionic tin atom in 3 is larger ($J_{119\text{Sn}-119\text{Sn}}=6410/6090$ Hz) in comparison to the signal of the neutral tin bridgehead, which is only 1150/1090 Hz.

Experimentally observed NMR chemical shifts were replicated by DFT calculations. To support the bonding model proposed based on the structural analysis of 1–3, the anions in these compounds were interrogated by DFT calculations employing different methods and basis sets. (For computational details and references see ESI† page S-84). The highest occupied molecular orbitals of 1–3 are shown in Fig. 3. These orbitals are in each case associated with the lone pairs on the anionic bridgehead tin atom(s) with contribution of the tin skeleton and show significant s-character.

This supports the conclusion of significant p-orbital involvement in the Sn–Sn bonding of the bridgehead tin atoms inferred from their experimental solid state structures. The frontier orbitals of 1–3 (Fig. 3 and ESI† pages S-37–S-40) display distinct groupings into sets of orbitals with $\sigma_1$, $\sigma^*$- and $\pi$-character interpreted as the onset of band-like behaviour. The HOMO to HOMO–$8$ ($\Delta E_{\text{HOMO-HOMO-8}}=1.78$ eV) for 2 and HOMO to HOMO–$7$ orbitals for 1 ($\Delta E_{\text{HOMO-HOMO-7}}=2.03$ eV) and 3 ($\Delta E_{\text{HOMO-HOMO-7}}=1.66$ eV) essentially represent the $\sigma$-bonded tin cores with only minor orbital contributions from the phenyl substituents. Within HOMO–LUMO energy gaps of only 2.33 eV (1), 2.15 eV (2) and 2.47 eV (3), the character of the frontier orbitals changes to phenyl based $\pi$-character.

The LUMO to LUMO+ $n$ orbitals ($n=20$ in 1, $n=23$ in 2, $n=25$ in 3) are similar in orbital energy and all localised on the phenyl substituents. This manifold of $\pi$-orbitals is then followed by a set of orbitals with predominant $\sigma$ character of the tin framework, which span energy ranges of 0.78 eV (1), 0.81 eV (2) and 1.34 eV (3). These closely spaced MOs are reflected in the electronic absorptions displayed by 1–3. The UV-visible spectra of these species do not display distinct absorption maxima and are instead broad and tailing, suggestive of weak but extensive absorptions. Nevertheless, the visibly observed colours for crystals of 1 (orange-yellow), 2 (orange-red) and 3 (bright yellow) are consistent with the expected effects of cage size and charge upon $\sigma$-delocalisation inferred from the DFT calculations.

In summary, the reaction of Ph$_2$SnH$_2$ with LiAlH$_4$ provides facile access to the charge-separated species, 1, 2 and 3, comprising an unprecedented set of structural motifs in anionic oligostannane cages. 1 and 2 constitute new dianionic covalent tin cages and we propose that they will provide convenient synthons in further transformations because of their charged nature and solution integrity. The electronic structure of 1–3 was interrogated computationally and support the presence of $\sigma$-delocalisation.

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Conflicts of interest
The authors declare no conflict of interest.

Notes and references


