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Impact of a Rigid Backbone on the Structure of an Agostically-Stabilised Dialkylstannylene: Isolation of an Unusual Bridged Stanny-Stannylene

Keith Izod, Casey M. Dixon, Ross W. Harrington, Michael R. Probert

The reaction between the phosphine-borane-stabilised dicarbanion complex [1,2-C₄H₄(CHP(BH₃)Cy₂)₂]Li(THF)_n and Cp₂Sn gives the unusual stannyl-stannylene [(1,2-C₄H₄(CHP(BH₃)Cy₂)₂)Sn]₂. This permits the phosphine-borane group to tilt towards the tin centre, maximising overlap between the B-H σ-orbital and the vacant p-orbital at tin and so providing the greatest possible stabilisation of the electron-poor tin(II) centre.

Recently we have begun to explore the chemistry of phosphine-borane-stabilised dicarbanions in which the two carbanion centres are linked by an ortho-phenylene spacer. We were interested to explore the impact of such a rigid ligand backbone on the strength of the B-H...Sn agostic-type interactions in the corresponding dialkylstannylene derivatives, since the rigidity of the ligand should limit the degree to which the borane group can position itself close to the tin atom and so moderate the strength of the stabilising B-H...Sn interactions. We report herein our initial studies in this area and the unexpected isolation of an agostically-stabilised, bridged stannyl-stannylene.

The reaction between in situ-generated [1,2-C₄H₄(CHP(BH₃)Cy₂)₂][Li(THF)_n] and one equivalent of Cp₂Sn in toluene gives a yellow solution containing pale solids of CpLi (Scheme 3). Removal of these solids by filtration, followed by concentration and cooling of the filtrate, yields pale yellow crystals of [(1,2-C₄H₄(CHP(BH₃)Cy₂)₂)Sn]₂.1½PhMe (5) after 1 week.

Somewhat surprisingly, once isolated in the solid state, 5 has limited solubility in aromatic and ethereal solvents and reacts rapidly with chlorinated solvents. Compound 5 is also air-sensitive, decomposes on exposure to ambient light or temperatures above ca 50 °C, and, over a period of several hours, stabilising contacts (Scheme 2) the supporting ligand is either monodentate (1, 4), or else has a flexible spacer group linking the two “carbanion” centres (2, 3). This permits the phosphine-borane group to tilt towards the tin centre, maximising overlap between the B-H σ-orbital and the vacant p-orbital at tin and so providing the greatest possible stabilisation of the electron-poor tin(II) centre.

We have recently shown that agostic-type B-H...E interactions stabilise monomeric dialkylstannylanes, significantly disfavours dimerisation to the corresponding distannene. For example, [(Me₂Si)(Me₂P(BH₃)]ClSn (1), which exhibits two stabilising B-H...Sn contacts, adopts a monomeric structure, whereas, (Me₂Si)₂CHSn, which is isoelectronic and isosteric with 1, but which lacks such agostic-type interactions, dimerises to the corresponding distannene in the solid state. In all of the dialkylstannylanes we have isolated which exhibit these
begins to decompose in THF solution at room temperature. Nonetheless, 5 is sufficiently soluble and stable in THF for limited characterisation by NMR spectroscopy (see below). Single crystals of 5 suitable for X-ray crystallography were obtained from a freshly-prepared sample in toluene.

![Scheme 3](image)

**Figure 1.** Molecular structure of 5 with solvent of crystallisation and H atoms omitted for clarity. Selected bond lengths (Å): Sn(1)–Sn(2) 2.8153(17), Sn(1)–C(1) 2.1887(17), Sn(1)–C(8) 2.0201(18), Sn(1)–C(33) 2.2518(17), Sn(2)–C(40) 2.3250(18), Sn(2)–H(2B) 2.49(2), P(1)–B(1) 1.931(2), P(1)–C(1) 1.8373(18), P(1)–C(9) 1.8404(19), P(1)–C(15) 1.8332(19), P(2)–B(2) 1.927(2), P(2)–C(8) 1.8290(18), P(2)–C(21) 1.8413(18), P(2)–C(27) 1.8406(19), P(3)–B(3) 1.939(2), P(3)–C(33) 1.8218(17), P(3)–C(41) 1.8550(19), P(4)–C(47) 1.841(2), P(4)–B(4) 1.934(2), P(4)–C(40) 1.8103(18), P(4)–C(53) 1.8462(19), P(4)–C(59) 1.8368(19).

Compound 5 crystallises as a discrete molecular species containing two distinct tin centres joined by a formal Sn-Sn σ-bond and with 1\(\frac{1}{2}\) molecules of toluene in the asymmetric unit (Figure 1).\(^\text{1}\) The formal Sn(III) centre is bonded to the two carbon atoms of a chelating dicarbanion ligand [Sn(1)–C(1) 2.1887(17), Sn(1)–C(8) 2.0201(18)] Å and to a single carbon atom of the second dicarbanion ligand [Sn(1)–C(33) 2.2518(17)] Å, along with the short Sn-Sn contact. In contrast, the formal Sn(I) centre is bonded to the adjacent tin atom and a carbon atom of the second dicarbanion ligand [Sn(2)–C(40) 2.3250(18)] Å. In addition, Sn(2) has a short contact to a hydrogen atom of one of the BH\(_3\) groups of the ligand which chelates Sn(1) [Sn(2)–H(2B) 2.49(2)] Å. Although the location of H atoms by X-ray crystallography is rather imprecise, this distance is substantially shorter than the sum of the van der Waals radii of Sn and H (3.37 Å), suggesting that there is a significant, agostic-type B-H…Sn interaction. This distance is similar to the H…Sn distances in 1–4, which fall in the range 2.03(5)–2.41(8) Å.\(^\text{6}\)

Thus, one phosphine-borane-stabilised carbanion ligand chelates Sn(1), generating a five-membered C\(_5\)Sn heterocycle, while the second bridges Sn(1) and Sn(2), generating a C\(_6\)Sn\(_2\) six-membered heterocycle; each of these ligands adapts a meso-configuration. The Sn(1)-Sn(2) distance [2.81531(17) Å] is substantially shorter than the Sn-Sn distances in the few previously reported stannyl-stannylenes, which range from 2.865 to 2.9688(5) Å,\(^\text{3,9}\) and is similar to the Sn-Sn distance in grey tin (2.80 Å).\(^\text{10}\) We attribute the shortness of this distance to the incorporation of the Sn-Sn bond into a rigid six-membered ring.

DFT calculations on the model complex [[1,2-C\(_5\)H\(_6\)ClCHP(BH\(_3\))Me\(_2\)]\(_2\)Sn\(_2\) (5’), in which the cyclohexyl groups have been replaced by smaller methyl substituents, reproduce well the core structure of 5 observed in the solid state (Figure 2). In particular, one of the borane hydrogen atoms lies close to the divalent Sn centre (Sn…H 2.13 Å). Natural Bond Orbital (NBO) analysis indicates that this interaction stabilises 5’ by 28.8 kcal mol\(^{-1}\), similar to the stabilisation energies calculated for 1–4 (in spite of the unusual bridging mode of the ligand in 5’).

**Figure 2.** Optimised geometries of 5’, meso-6’ and rac-6’ with C-bound H atoms omitted for clarity [B3LYP/6-31G(d,p)[LanL2DZ on Sn]] (C dark grey, H white, B pink, P orange, Sn light grey).

In order to estimate the stability of the stannylen-stannylene 5’ in comparison to the putative monomer meso-[1,2-C\(_5\)H\(_6\)ClCHP(BH\(_3\))Me\(_2\)]Sn (meso-6’) we have calculated the energy of both this species and the corresponding rac isomer (Figure 2). The optimised geometries for both meso- and rac-6’ exhibit a single short B-H…Sn contact with Sn…H distances of 2.15 and 2.13 Å, respectively. While for meso-6’ this interaction...
leaves the C₅Sn five-membered ring essentially planar, for rac-6’ it results in a twisting of both the five-membered ring and the aromatic ring, such that the C-Sn-C plane lies at approximately 8° to the mean plane of the aromatic backbone. NBO analysis suggests that the B-H...Sn interactions stabilise meso- and rac-6’ by 41.4 and 33.1 kcal mol⁻¹, respectively. Nonetheless, rac-6’ is calculated to be 1.8 kcal mol⁻¹ more stable than meso-6’. Comparison of the energy of meso-6’ with that of the stannyl-stannylene 5 suggests that the latter is favoured by just 1.1 kcal mol⁻¹.

A ³¹P{¹H} NMR spectrum of the crude reaction solution, prior to the isolation of 5, consists of multiple broad and overlapping signals. This suggests that, in addition to 5, the solution contains the corresponding rac isomer, either as a monomeric or dimeric species; however, we have, as yet, been unable to isolate this species. The ¹H NMR spectrum of 5 is complex and rather uninformative, due to the overlap of signals from the eight chemically inequivalent cyclohexyl groups (within which pairs of CH₂ groups are diastereotopic) and the signals from the four chemically inequivalent benzylic and borane groups. However, the ³¹P{¹H} NMR spectrum of 5 exhibits four broad, approximately equal intensity signals at 27.2, 28.6, 30.0, and 35.4 ppm, while the ¹¹B{¹H} NMR spectrum exhibits two broad signals at -43.5 and -38.8 ppm in an approximately 1:3 ratio; in the latter case, we assign the unique high field signal to the phosphine-borane group associated with the short B-H...Sn interaction. These spectra indicate that the dinuclear structure of 5 observed in the solid state persists in solution. Consistent with this, the ¹¹¹Sn{¹H} NMR spectrum of 5 exhibits broad, featureless signals at -103 and 339 ppm, which we attribute to the stannyl and stannylene centres, respectively; coupling between the two Sn centres is not resolved, due to the broad nature of these signals. The former signal is typical of tetravalent tin centres, while the latter is similar to the chemical shifts of the previously reported agostically-stabilised dialkylstannylene 1-4, which fall into the range 320-787 ppm.

In summary, while phosphine-borane-stabilised dicarbamions linked by a flexible aliphatic spacer group give the corresponding stannylene derivatives, the incorporation of a rigid ortho-phenylene spacer leads to the isolation of the stannyl-stannylene complex 5. Nonetheless, 5 exhibits an agostic-type B-H...Sn interaction which stabilises this complex by 28.8 kcal mol⁻¹.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Details of the synthesis of 5; details of the DFT studies of 5, rac-6’, and meso-6’. See DOI: 10.1039/b000000x.

‡ Crystal data for 5: C₁₁H₁₂,B₂P₅Sn₃; 1.5CH₂Cl₂, MW = 1424.36, monoclinic, P₂₁/c, a = 14.885(1), b = 26.577(2), c = 20.050(2) Å, β = 95.273(10)°, V = 7475.89(11) Å³, Z = 2, µ = 0.793 mm⁻¹, final R₁ = 0.028 for I > 2σ(I), wR₂ = 0.060 for all data, GoF = 1.051. CCDC 1011284.

§ The relatively low isolated yield of 5 (28%) is a reflection of the mixture of isomers produced in this reaction; if an equal ratio of rac to meso isothers is assumed, then this equates to an isolated yield of 56% of the total meso diastereomer.