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Formation of a Unique 'Unsupported' Hydridic Sn(II) Stannate

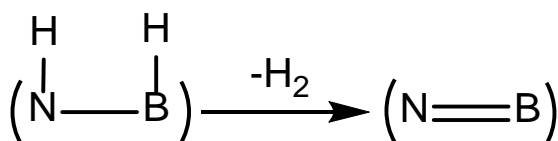
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The reaction of the Sn^{II} amido-stannate LiSn(NMe₂)₃ with the phosphine-borane ^tBu₂PHBH₃ gives the Sn^{II} hydride [(Me₂NH)₂Li{BH₃P(^tBu)₂}₂Sn(H)]; the first example of a hydridic stannate that is not supported by transition metal or ligand bonding.

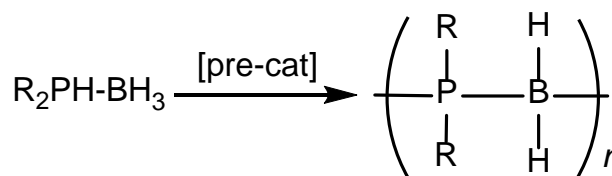
Transition-metal- and, more recently, main-group-metal-catalysed dehydrogenation (dehydrocoupling) of amine boranes has been an area of increasing interest in the past decade, owing particularly to potential applications in H₂-storage and in the synthesis of BN-polymers (Scheme 1).¹ Extensive mechanistic studies have revealed that metal hydrides are the likely active catalytic intermediates in the majority of transition-metal- and main-group-metal-mediated amine-borane dehydrocoupling reactions. Experimental evidence for this has come from a range of sources, most commonly from *in situ* NMR spectroscopic studies and the isolation of selected intermediates.² However, the potential to exploit this as a synthetic method for the preparation of low-oxidation state main group metal hydrides has not previously been explored.



Scheme 1 Dehydrogenation of an amine borane

In contrast to amine boranes, very few related studies of the dehydrocoupling of closely related phosphine boranes have appeared and, to our knowledge, the only reported examples involving metals are based on transition-metal catalysis.³ Manners and co-workers showed that catalytic

dehydrocoupling of primary (RPH₂BH₃) and secondary (R₂PHBH₃) phosphine boranes gives a range of B-P bonded acyclic and cyclic oligomers and polymers depending on the reaction conditions (Scheme 2).⁴

Scheme 2 Oligomerisation and polymerisation of phosphine boranes ([pre-cat] = [Rh(1,5-cod)Cl]₂, [Rh(1,5-cod)₂][O₃SCF₃]).

As part of our ongoing studies of the applications of main group (*d*⁰) catalysts in bond-forming reactions, we have recently initiated studies of a range of *p*-block metal reagents with phosphine boranes. Although our studies so far have revealed that such reagents are not effective at catalysing the oligomerisation or polymerisation of phosphine boranes,⁵ we show here that stoichiometric reactions can be employed in the synthesis of unusual low-oxidation state main group hydrides, as exemplified by the novel Sn^{II} hydride [(Me₂NH)₂Li{BH₃P(^tBu)₂}₂Sn(H)] (1). To our knowledge, this is the first report of a hydridic stannate that is not supported by coordination to a transition metal.

As part of our broader studies of the activity of main group bases as pre-catalysts in this area, we investigated the stoichiometric reactions of the Sn^{II} reagent Sn(NMe₂)₂ with the phosphine borane ^tBu₂PHBH₃. An *in situ* NMR spectroscopic investigation of the 1 : 1 room-temperature reaction in *d*₈-toluene in a sealed NMR tube showed the presence of a complicated mixture of decomposition products after 1 week at room temperature, including ^tBu₂PH, HB(NMe₂)₂ and Me₂NH. The reaction was also accompanied by the formation of H₂ and Sn metal (the former also being observed by ¹H NMR). Repeating this NMR study at -78°C shows that this latter reaction occurs through a single intermediate. Scaling up the reaction using the *same* batch of Sn(NMe₂)₂, followed by

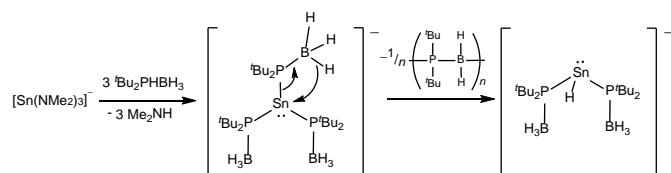
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^c † Electronic Supplementary Information (ESI) available: Multinuclear NMR and IR. See DOI: 10.1039/x0xx00000x.

immediate storage of the reaction solution at -25°C , resulted in the formation of colourless crystals of this intermediate (**1**).

In addition to obtaining the single-crystal X-ray structure of **1** (see later), an extensive array of sophisticated 1D and 2D multinuclear (^1H , ^{11}B , ^{31}P , ^{119}Sn) NMR spectroscopic analyses provided unambiguous evidence that **1** is the Sn^{II} hydride $[(\text{Me}_2\text{NH})_2\text{Li}\{\text{BH}_3\text{P}(\text{tBu})_2\}_2\text{Sn}(\text{H})]$ (see the structure in the inset to Figure 1, and ESI for full details). The unexpected appearance of Li^+ in the structure of **1** is explained by the involvement of $\text{LiSn}(\text{NMe}_2)_3$ (the active base in this reaction) as a contaminant in $\text{Sn}(\text{NMe}_2)_2$. Closer inspection of the $\text{Sn}(\text{NMe}_2)_2$ used in the original reaction, and of several other batches prepared by the literature method (from the reaction of SnCl_2 with Me_2NLi in Et_2O),⁷ revealed the presence of an intense ^7Li NMR resonance at $\delta 0.26$ (in d_8 -thf). It has been shown previously that the *tris*-amido stannate $\text{LiSn}(\text{NMe}_2)_3$ is a potential by-product in the synthesis of $\text{Sn}(\text{NMe}_2)_2$,⁸ and a subsequent *in situ* multinuclear NMR spectroscopic study of the 1 : 1 : 3 stoichiometric reaction of $\text{Me}_2\text{NLi} : \text{Sn}(\text{NMe}_2)_2 : \text{tBu}_2\text{PHBH}_3$ at -78°C [using a recrystallized, Li-free sample of $\text{Sn}(\text{NMe}_2)_2$] shows that **1** is formed in *ca.* 50% yield. Scaling up this reaction gave a 21% crystalline yield of **1**.[‡] A possible mechanism of formation of the stannate anion in **1** involves a deprotonation/ β -H elimination pathway (Scheme 3).



Scheme 3 Proposed mechanism of formation of the stannate anion of **1**. The $\text{tBu}_2\text{P}=\text{BH}_2$ may oligomerise or polymerise into $(\text{tBu}_2\text{PHBH}_2)_n$.⁴

The ^{119}Sn and ^1H NMR spectra of **1** both show the presence of a $[\text{P}-\text{Sn}^{\text{II}}(\text{H})-\text{P}]$ unit in **1**; with the Sn-H resonance in the ^1H NMR spectrum appearing as a triplet ($\delta 8.14$, $^2J_{\text{HP}} = 6.8$ Hz) with $^{119,117}\text{Sn}$ satellites ($^1J_{\text{SnH}} = 102$ Hz, $^1J_{\text{SnH}} = 98$ Hz) (see Figure 1a) and the ^{119}Sn NMR consisting of a triplet of doublets ($\delta -276.7$, $^1J_{\text{SnP}} = 1708$ Hz, $^1J_{\text{SnH}} = 102$ Hz) (Figure 1b). The ^1H chemical shift and $^1J_{\text{SnH}}$ coupling constant of the Sn-H hydride are similar to those found in the Sn-(μ -H)-Sn bridged dimeric hydrides $[\text{4-X-Ar}'\text{Sn}(\text{m-H})_2]$ [$\text{X} = \text{Me}_3\text{Si}$, F; $\text{Ar}' = \text{C}_6\text{H}_3-2,6-(\text{C}_6\text{H}_3-2,6-\text{Pr}_2)_2$] ($\delta 9.12$, $^1J_{\text{SnH}} = 87$ Hz).^{6e} The ^1H , ^{31}P and ^{11}B NMR spectra of **1** show that the BH_3 groups present in the precursor $\text{tBu}_2\text{PHBH}_3$ are retained in **1**. The coordination environment of the Li ion was also probed by a $^7\text{Li}-^1\text{H}$ HOESY experiment, which shows that the Me and NH protons of the Me_2NH ligands are in close proximity to the Li^+ cation.

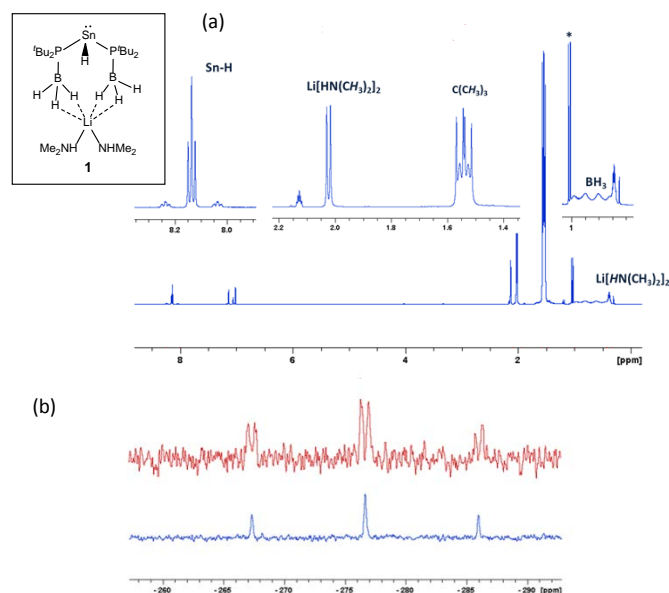


Figure 1 Room-temperature NMR spectra of isolated crystals of **1** dissolved in d_8 -toluene (a) ^1H (500.1 MHz) and (b) ^{119}Sn (186.56 MHz), ^1H -coupled (red), ^1H -decoupled (blue).

The crystal structure of **1** (Figure 2a) confirms that it is a Sn^{II} stannate complex of formula $[(\text{Me}_2\text{NH})_2\text{Li}\{\text{BH}_3\text{P}(\text{tBu})_2\}_2\text{Sn}(\text{H})]$, resulting from the ion-pairing of the stannate anion $[\{\text{BH}_3\text{P}(\text{tBu})_2\}_2\text{Sn}(\text{H})]^-$ with a *bis*- Me_2NH coordinated Li^+ cation.[§] All of the atoms within the $\text{SnP}_2\text{B}_2\text{Li}$ ring of **1** are in the same plane (lying in a crystallographic mirror plane). The hydridic H-atom was located in the difference map, and is disordered above and below the mirror plane. The H atoms on B and on N were also located in the difference map and refined freely. Although a number of transition-metal phosphide-boranes have been structurally characterised previously,⁹ far fewer main-group-metal complexes of this type are known¹⁰ and only a handful of these involve *p*-block metals.^{10a,e,g} Many of the structural features of **1**, the B-P bond lengths [$1.954(4)$ Å] and the presence of B-H...Li interactions linking the $[\{\text{BH}_3\text{P}(\text{tBu})_2\}_2\text{Sn}(\text{H})]^-$ to the Li^+ cation [B-H...Li $2.02(2)$ Å], are similar to those found in alkali metal complexes of phosphide-boranes.¹⁰ However, more importantly, of the various classes of Sn^{II} hydrides that have been reported [containing terminal $\text{Sn}^{\text{II}}-\text{H}$ (**A**),¹¹ bridging $\text{Sn}^{\text{II}}(\mu\text{-H})\text{Sn}^{\text{II}}$ (**B**)⁶ or ligand- or transition metal-stabilised Sn^{II} -hydrides (**C**)¹² (Figure 2)], **1** is the first species to contain an 'unsupported' Sn^{II} hydridic stannate anion, i.e., that is not stabilised by Sn-bonding to a transition metal (the only reported examples of stannates being transition metal bonded SnH_3 complexes, $\text{H}_3\text{Sn}[\text{Tm}]$ ¹³).

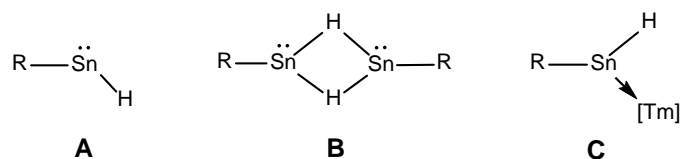


Figure 2 Major types of Sn^{II} hydrides reported so far; **A** monomer with terminal Sn-H, **B** dimer with bridging Sn-(μ -H)-Sn, **C** transition metal [Tm]-stabilised monomer.

The steric stabilisation of the hydridic H-atom by the surrounding ^tBu groups in **1** can be seen in the space-filling representation of the structure shown in Figure 2b. A degree of electrostatic stabilisation is also conceivable in this situation, bearing in mind the shortness of the associated Sn-H^{δ-}...H^{δ+}-C contacts (range 2.06-3.10 Å; cf 2.40 Å for the sum of the van der Waals radii¹⁴). The importance of dispersion forces in the stabilisation of main group metal compounds has also been noted recently. Significantly, the room-temperature ¹H-¹H NOESY NMR spectrum of **1** in *d*₈-toluene proves the near proximity of the Sn-H and ^tBu groups (Figure 2c). Also of interest, the ³¹P/¹¹B-decoupled ¹H NMR spectrum shows that the initially complicated ^tBu resonance in **1** (see Figure 1a) is resolved into two 1 : 1 singlets (see ESI). Their magnetic inequivalence suggests that the stannate anion of **1** is retained in solution and results from the orientation of the Sn-H bond (*cis* or *trans*) to either ^tBu group.

In summary, the formation of the unique hydridic stannate [(Me₂NH)₂Li{BH₃P(^tBu)₂}₂Sn(H)] (**1**) illustrates a soft approach to low-oxidation-state main group hydrides. In the case of **1**, this is the first discrete Sn^{II} stannate containing a hydride ligand. The stabilisation of this complex is largely steric in origin, but may also be due to H^{δ-}...H^{δ+} interactions with the surrounding ligands. Further studies will be aimed at assessing the potential of other main group bases as precursors to low-oxidation-state hydrides.

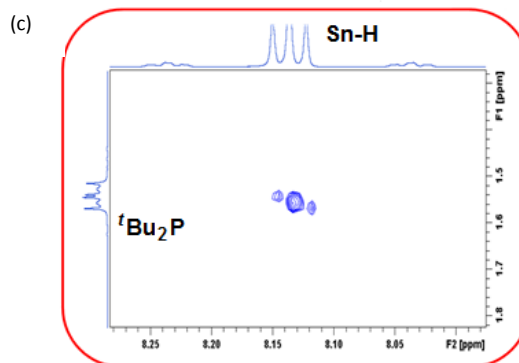
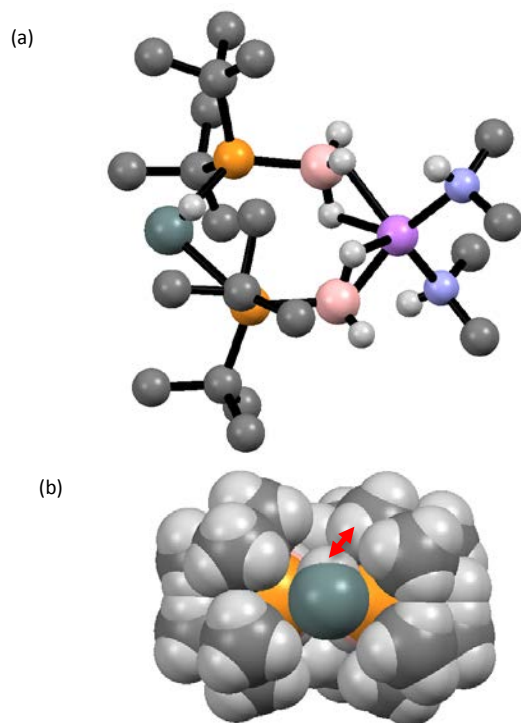


Figure 2 (a) The crystal structure of **1**. Only one of the two disordered components of the ^tBu groups and the Sn-H proton are shown for clarity. Selected bond lengths (Å) and angles (°); Sn(1)-H(1) 0.89, Sn(1)-P(1) 2.6460(6), P(1)-B(1) 1.954(4), B-H...Li(1) 2.02(2) [B(1)...Li(1) 2.442(5)], Li(1)-N(1) 2.097(5), P(1)-Sn(1)-H(1) 73.9, P(1)-Sn(1)-P(1A) 104.98(3), Sn(1)-P(1)-B(1) 122.6(1), P(1)-B(1)...Li(1) 132.6(2). Sn (green), B (pink), Li (magenta), N (violet). (b) Space-filling representation of **1**, viewed down the Sn...Li axis, illustrating the sterically-shielded 'pocket' in which the hydridic H-atom resides, H...H contacts range 2.06-3.10 Å (the red arrow indicates the shortest of the four H...H contacts). (c) The ¹H-¹H NOESY spectrum of **1** in *d*₈-toluene, confirming the near proximity of the ^tBu and Sn-H protons in solution.

Notes and references

‡ Synthesis of **1**; In the glovebox, a Schlenk tube was charged with ^tBu₂PH-BH₃ (0.164 g, 0.91 mmol), Sn(NMe₂)₂ (0.064 g, 0.30 mmol) and LiNMe₂ (0.016 g 0.30 mmol). Upon cooling to -78 °C, 1 mL of toluene was added to the tube, and the mixture was stirred for 10 min. The solution was then placed in the freezer overnight (-25 °C). After one day colourless crystals of compound **1** were observed. The crystals were isolated and washed with *n*-hexane to remove the finely-divided (colloidal) elemental Sn (yield of **1** 31 mg, 0.06 mmol, 21 %). ¹H NMR (500 MHz, 298 K, *d*₈-toluene): δ 8.14 (t, *J*_{HP} = 6.8 Hz, *J*_{HSn} = 101 Hz, 1H, Sn-H), 2.02 (d, ³*J*_{HH} = 6.45 Hz, 12H, NCH₃), 1.54 (m, 36H, C(CH₃)₃), 1.00-0.42 (br, 6H, BH₃), 0.38 (sept, ³*J*_{HH} = 6.45 Hz, 2H, HN CH₃). ¹³C{¹H} NMR (125.65 MHz, 298 K, *d*₈-toluene): δ 37.8 (NCH₃), 33.5 (C(CH₃)₃), 29.7, 29.5 (C(CH₃)₃). ¹¹B{¹H} NMR (160.35 MHz, 298 K, *d*₈-toluene): δ -35.8 (br, ¹*J*_{BH} = 87.0 Hz, ¹*J*_{BP} = 64.5 Hz). ³¹P{¹H} NMR (202.47 MHz, 298 K, *d*₈-toluene): δ 18.9 (br, ¹*J*_{PB} = 64.5 Hz, ¹*J*_{PSn} = 1708.0 Hz). ⁷Li NMR (194.40 MHz, 298 K, *d*₈-toluene): δ 0.599. ¹¹⁹Sn NMR (186.50 MHz, 298 K, *d*₈-toluene): δ -276.7 (td, *J*_{SnH} = 101 Hz, ¹*J*_{SnP} = 1708.0 Hz). IR: (Nujol, cm⁻¹) 2390., 2354, 2277 (BH₃) 1643 (Sn-H). Elemental Analysis (%): C₂₀H₅₇B₂LiN₂P₂Sn (534.34): *calcd*: C = 44.9, N = 5.2, H = 10.7, *found*: C = 44.6, N = 5.5, H = 10.6.

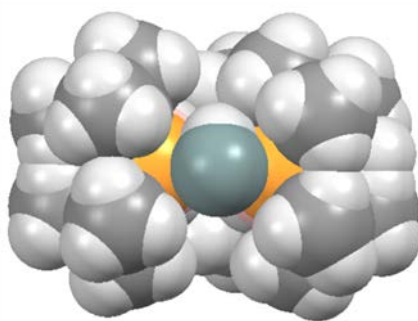
§ Crystal data for **1**: *M* = 534.86, orthorhombic, space group *Cmcm*, *Z* = 4, *a* = 18.9850(8), *b* = 10.8911(5), *c* = 14.8749(7) Å, *V* = 3075.6(2) Å³, μ(Cu-Kα) = 7.625 mm⁻¹, ρ_{calc} = 1.155 g cm⁻³, *T* = 180(2) K. Total reflections 18658, unique 1576 (*R*_{int} = 0.035). *R*₁ = 0.023 [*I* > 2σ(*I*)] and *wR*₂ = 0.056, (all data). The complex lies on a site of crystallographic *m2m* (*C_{2v}*) symmetry. The H atoms associated with the unique B and N atoms were located in the difference Fourier map and refined freely with isotropic displacement parameters. The H atom on Sn was also visible in the difference map, but is disordered above and below the SnP₂B₂Li ring; it was retained in the position identified from the difference map and set to ride on the Sn atom for subsequent refinement. The assignment as one disordered H atom (rather than two H atoms occupying both symmetry-related positions) is made by consideration of the spectroscopic data and the requirement for charge balance. CCDC 1454030 contains the supplementary crystallographic data for **1**.

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