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Phosphido-borane-supported stannates†

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The reactions between SnCl_2 and three equivalents of the alkali metal phosphido-borane complexes $[\text{R}_2\text{P}(\text{BH}_3)]\text{M}$ yield the corresponding tris(phosphido-borane)stannate complexes $[\text{L}_n\text{M}(\text{R}_2\text{P}(\text{BH}_3))_3\text{Sn}]$ [$\text{R}_2 = \text{iPr}_2$, $\text{L}_n\text{M} = (\text{THF})_3\text{Li}$ (**2Li**), $(\text{Et}_2\text{O})\text{Na}$ (**2Na**), $(\text{Et}_2\text{O})\text{K}$ (**2K**); $\text{R}_2 = \text{Ph}_2$, $\text{L}_n\text{M} = (\text{THF})\text{Li}$ (**3Li**), $(\text{THF})(\text{Et}_2\text{O})\text{Na}$ (**3Na**), $(\text{THF})(\text{Et}_2\text{O})\text{K}$ (**3K**); $\text{R}_2 = \text{iPrPh}$, $\text{L}_n\text{M} = (\text{THF})_4\text{Li}$ (**4Li**)]. In each case X-ray crystallography reveals an anion consisting of a trigonal pyramidal tin centre coordinated by the P atoms of the phosphido-borane ligands. These tris(phosphido-borane)stannate anions coordinate to the alkali metal cations *via* their BH_3 hydrogen atoms in a variety of modes to give monomers, dimers, and polymers, depending on the alkali metal and the substituents at the phosphorus centres. In contrast, reactions between SnCl_2 and three equivalents of $[\text{tBu}_2\text{P}(\text{BH}_3)]\text{M}$ ($\text{M} = \text{Li}, \text{Na}$) gave the known hydride $[\text{M}(\text{tBu}_2\text{P}(\text{BH}_3))_2\text{SnH}]$, according to multinuclear NMR spectroscopy.

Introduction

Phosphido-borane anions $[\text{R}_2\text{P}(\text{BH}_3)]^-$ (also known as phosphanyl-borohydrides or mono(borane)phosphanides) are versatile ligands which are isoelectronic with silanide anions $[\text{R}_2\text{MeSi}]^-$. These anions are also key intermediates in the synthesis of chiral phosphines and in the catalytic dehydrocoupling of phosphine-boranes to give poly(phosphino-borane) materials.^{1,2} However, in spite of this, and the relatively simple synthesis of phosphido-borane ligands, they have received only limited attention.³ While the majority of reported phosphido-borane complexes are of the hard alkali or alkaline earth metals,^{4,5} a small number of late transition metal complexes have been isolated;⁶ only a very few complexes of these ligands with p-block elements are known.^{4a,7,8}

Phosphido-borane anions may bind to metal centres *via* their phosphorus centres and/or their borane hydrogen atoms, leading to a variety of coordination modes. In complexes with hard alkali or alkaline earth metals $\text{BH}_3\cdots\text{M}$ contacts are favoured, whereas with softer late transition metals P–M contacts dominate. Interestingly, it has recently been shown that phosphido-borane anions may exhibit temperature-dependent ditopic character, such that, at low temperatures, $[\text{Ph}_2\text{P}(\text{BH}_3)]\text{Li}$ reacts as a P-nucleophile, whereas at high temperatures this compound acts as a B–H reducing agent towards ketones,

suggesting Li–P coordination at higher temperatures and $\text{Li}\cdots\text{BH}_3$ coordination at low temperatures.⁹

Crystallographically characterised phosphido-borane complexes of the p-block elements are limited to the aluminium complexes $[\text{Li}(\text{TMEDA})_2][\{\text{Me}_2\text{P}(\text{BH}_3)\}_4\text{Al}]$, $[(\text{MeOtBu})\text{Li}[\{\text{Me}_2\text{P}(\text{BH}_3)\}_4\text{Al}]]_\infty$,^{4a} and $[(\text{Et}_2\text{O})_2\text{Li}\{\text{Ph}_2\text{P}(\text{BH}_3)\}\text{Al}(\text{C}_6\text{F}_5)_3]$,⁷ and the recently reported hydridostannate complex $[(\text{Me}_2\text{NH})_2\text{Li}\{\text{tBu}_2\text{P}(\text{BH}_3)\}_2\text{SnH}]$ (**1**) [TMEDA = *N,N,N',N'*-tetramethylethylenediamine].⁸ Compound **1** was formed unexpectedly from the reaction between three equivalents of $\text{tBu}_2\text{P}(\text{BH}_3)\text{H}$ and one equivalent each of $\text{Sn}(\text{NMe}_2)_2$ and $\text{Li}(\text{NMe}_2)$. The formation of **1** was proposed to proceed *via* a deprotonation/ β -hydride elimination from the tris(phosphido-borane)stannate $\text{Li}\{\text{tBu}_2\text{P}(\text{BH}_3)\}_3\text{Sn}$, with concomitant formation of an unidentified P–B bonded poly(phosphino-borane) side-product (Scheme 1).

In an effort to elucidate the stability of such tris(phosphido-borane)stannate anions, and building on our previous work on s-block phosphido-borane complexes,^{4f–i,5a,d} we have explored the 3 : 1 reaction between a selection of alkali metal phosphido-borane complexes and tin(II) chloride. Herein we report the results of this study and comment on the stability of the resulting tris(phosphido-borane)stannate complexes.

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Scheme 1 Isolation of a bis(phosphido-borane)hydridostannate (**1**).



Results and discussion

The reaction between SnCl_2 and three equivalents of the phosphido-borane complexes $[\text{M}\{\text{R}_2\text{P}(\text{BH}_3)\}]$ ($\text{M} = \text{Li}, \text{Na}, \text{K}\})^{4i}$ gave the corresponding tris(phosphido-borane)stannate complexes $[\text{L}_n\text{M}\{\text{R}_2\text{P}(\text{BH}_3)\}_3\text{Sn}]$ as yellow or red crystals in each case [Scheme 2; $\text{R}_2 = i\text{Pr}_2$, $\text{L}_n\text{M} = (\text{THF})_3\text{Li}$ (**2Li**), $(\text{Et}_2\text{O})\text{Na}$ (**2Na**), $(\text{Et}_2\text{O})\text{K}$ (**2K**); $\text{R}_2 = \text{Ph}_2$, $\text{L}_n\text{M} = (\text{THF})\text{Li}$ (**3Li**), $(\text{THF})(\text{Et}_2\text{O})\text{Na}$ (**3Na**), $(\text{THF})(\text{Et}_2\text{O})\text{K}$ (**3K**); $\text{R}_2 = i\text{PrPh}$, $\text{L}_n\text{M} = (\text{THF})_4\text{Li}$ (**4Li**)]. Although the yields of isolated crystalline material were low to moderate, $^{31}\text{P}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$ and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectra of the crude reaction solutions indicated that the reactions were essentially quantitative in each case.

For each of these stannate complexes the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum consists of a singlet exhibiting satellites due to coupling to $^{117}\text{Sn}/^{119}\text{Sn}$, while the ^{119}Sn NMR spectrum consists of a binomial quartet. This clearly indicates that the tris(phosphido-borane)stannate anion persists in solution, even in strong donor solvents such as THF. The $^{31}\text{P}\{^1\text{H}\}$ and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectra of **2Li**, **2Na**, and **2K** were all recorded in d_8 -THF and are remarkably similar, with ^{31}P and ^{119}Sn chemical shifts ranging from 8.7 to 10.3 ppm and -171 to -181 ppm, respectively, and ^{31}P – ^{119}Sn coupling constants of 1910–1915 Hz (Table 1). In contrast, the ^{31}P and ^{119}Sn chemical shifts and ^{31}P – ^{119}Sn coupling constants of **3Li** (-10.4 and -46 ppm, and 1708 Hz, respectively), which were recorded in d_8 -THF, are quite different from those of **3Na** and **3K** (-32.6 – -33.2 and -113 – -87 ppm, and 1428/1461 Hz, respectively), which were recorded in d_8 -toluene. This suggests that a similar structure, possibly a separated ion pair $[\text{M}(\text{THF})_n][\{\text{R}_2\text{P}(\text{BH}_3)\}_3\text{Sn}]$, is adopted by the stannate complexes in the strong donor solvent THF, while a different structure, possibly a contact ion pair, persists in toluene. Similar behaviour has been observed for the tris(phosphido)stannate complex $[(\text{THF})\text{LiSn}\{\text{P}(\text{Ph})\{\text{CH}(\text{SiMe}_3)_2\}_3\}]$, which exists as a cage complex in which the Li cation is coordinated by the three P centres in toluene solution, but as a separated ion pair $[\text{Li}(\text{THF})_4][\text{Sn}\{\text{P}(\text{Ph})\{\text{CH}(\text{SiMe}_3)_2\}_3\}]$ (**5**) in THF.¹⁰ For all of the tris(phosphido-borane)stannate complexes isolated, except **3K**, ^1H NMR spectroscopy indicates that exposure of the crystalline solids to vacuum leads to partial loss of coordinated solvent.

In contrast to the above, the reaction between SnCl_2 and three equivalents of either $[\text{Li}\{t\text{Bu}_2\text{P}(\text{BH}_3)\}]$ or $[\text{Na}\{t\text{Bu}_2\text{P}(\text{BH}_3)\}]$ did not give the corresponding tris(phosphido-borane)stannate complexes. Instead, the $^{31}\text{P}\{^1\text{H}\}$ and ^{119}Sn NMR spectra of the crude reaction mixtures consist of a singlet at

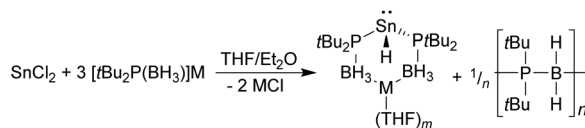
Table 1 ^{11}B , ^{31}P , and ^{119}Sn chemical shifts (ppm) and ^{31}P – ^{119}Sn coupling constants (Hz) for **2M**, **3M**, and **4Li**

	Solvent	$^{11}\text{B}/$ ppm	$^{31}\text{P}/$ ppm	$^{119}\text{Sn}/$ ppm	$J(^{31}\text{P}$ – $^{119}\text{Sn})/$ Hz
2H ^a	CDCl_3	–40.0	1.0	—	—
2Li	d_8 -THF	–39.9	8.7	–181	1910
2Na	d_8 -THF	–38.1	10.3	–176	1915
2K	d_8 -THF	–38.1	9.7	–171	1910
3H ^{a,b}	CDCl_3	–45.3	27.8	—	—
3Li	d_8 -THF	–32.5	–10.4	–46	1708
3Na	d_8 -Toluene	–33.8	–32.6	–113	1428
3K	d_8 -Toluene	–33.2	–20.1	–87	1461
4H ^{a,b}	CDCl_3	–42.8	15.2	—	—
4Li	d_8 -Toluene	–36.8	–14.0	–113	1420

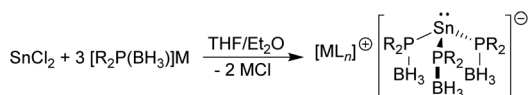
^a **2H**: $i\text{Pr}_2\text{P}(\text{BH}_3)\text{H}$, **3H**: $\text{Ph}_2\text{P}(\text{BH}_3)\text{H}$, **4H**: $i\text{PrPhP}(\text{BH}_3)\text{H}$. ^b Data from ref. 4i.

24.0 ppm, exhibiting ^{119}Sn satellites ($J_{\text{PSn}} = 1700$ Hz), and a 1 : 2 : 1 triplet of doublets at -287 ppm ($J_{\text{PSn}} = 1700$, $J_{\text{HSn}} = 97$ Hz), respectively. These are consistent with the formation of the tin(II) hydrides $[\text{M}\{t\text{Bu}_2\text{P}(\text{BH}_3)\}_2\text{SnH}]$ ($\text{M} = \text{Li}, \text{Na}$; Scheme 3), the lithium derivative of which (**1**) was previously isolated by Wright and co-workers as its Me_2NH complex (for comparison, the ^{31}P and ^{119}Sn chemical shifts of **1** are reported as 18.9 and -276 ppm, respectively, with $J_{\text{PSn}} = 1708$, $J_{\text{HSn}} = 101$ Hz).⁸ This supports Wright's proposal that the formation of **1** from the reaction between $\text{LiSn}(\text{NMe}_2)_3$ and $t\text{Bu}_2\text{P}(\text{BH}_3)\text{H}$ proceeds via the tris(phosphido-borane)stannate intermediate $[\text{Li}\{t\text{Bu}_2\text{P}(\text{BH}_3)\}_3\text{Sn}]$, which undergoes a deprotonation/ β -hydride elimination reaction to give the hydride.

Similar hydride formation was not observed for any of the reactions between three equivalents of the phenyl- or isopropyl-substituted compounds $[\text{M}\{\text{R}_2\text{P}(\text{BH}_3)\}]$ and SnCl_2 , even after extended periods in THF solution, suggesting that the instability of the putative stannate $[\text{Li}\{t\text{Bu}_2\text{P}(\text{BH}_3)\}_3\text{Sn}]$ may be due to steric effects. All of the isolated stannate complexes decomposed on exposure to atmospheric moisture and oxygen; exposure of solutions of **2M** or **3M** in THF to daylight



Scheme 3 Reaction between SnCl_2 and three equivalents of $[\text{M}\{t\text{Bu}_2\text{P}(\text{BH}_3)\}]$ ($\text{M} = \text{Li}, \text{Na}$).



- $\text{R}_2 = i\text{Pr}_2$, $\text{ML}_n = \text{Li}(\text{THF})_3$ (**2Li**)
- $\text{R}_2 = i\text{Pr}_2$, $\text{ML}_n = \text{Na}(\text{OEt}_2)$ (**2Na**)
- $\text{R}_2 = i\text{Pr}_2$, $\text{ML}_n = \text{K}(\text{OEt}_2)$ (**2K**)
- $\text{R}_2 = \text{Ph}_2$, $\text{ML}_n = \text{Li}(\text{THF})$ (**3Li**)
- $\text{R}_2 = \text{Ph}_2$, $\text{ML}_n = \text{Na}(\text{THF})(\text{OEt}_2)$ (**3Na**)
- $\text{R}_2 = \text{Ph}_2$, $\text{ML}_n = \text{K}(\text{THF})(\text{OEt}_2)$ (**3K**)
- $\text{R}_2 = \text{PhiPr}$, $\text{ML}_n = \text{Li}(\text{THF})_4$ (**4Li**)

Scheme 2 Synthesis of tris(phosphido-borane)stannate complexes **2M**, **3M**, and **4Li**.



led to gradual decomposition over a period of several days, yielding elemental tin and a large number of unidentified phosphorus-containing products. However, in one case, in the absence of light and air, we observed a gradual decomposition of **3Li** in THF over three days. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this solution the signal at -10.9 ppm due to **3Li** was gradually

replaced by a broad signal at -14.3 ppm exhibiting tin satellites ($J_{\text{PSn}} = 1555$ Hz) and a sharp triplet at -35.9 ppm, also exhibiting tin satellites ($J_{\text{PP}} = 23.6$ Hz, $J_{\text{PSn}} = 867, 806$ Hz), in an approximately 2:1 ratio (see the ESI†). In the $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum the sharp quartet at -48.5 ppm was gradually replaced over the same period by a sharp triplet of doublets ($J_{\text{PSn}} = 843, J_{\text{P'Sn}} = 1615$ Hz) at -24.8 ppm; the ^{119}Sn and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectra of this solution were identical, precluding the formation of a tin hydride. However, this reaction did not proceed to completion and after 3 days decomposition ceased. Careful inspection of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum revealed the presence of $[\text{Ph}_2\text{P}(\text{BH}_3)]\text{Li}$ as a contaminant in the solution (very broad signal at -32 ppm; the literature value for the ^{31}P chemical shift of $[\{\text{Ph}_2\text{P}(\text{BH}_3)\}_2\text{Li}(\text{OEt}_2)_2\text{Li}]_\infty$ is -32.6 ppm).⁴ⁱ The signal due to this species gradually disappeared, to be replaced by a broad signal at -6.8 ppm, consistent with the formation of the phosphido-bis(borane) complex $[\text{Ph}_2\text{P}(\text{BH}_3)_2]\text{Li}$ (the literature value for the ^{31}P chemical shift of the related complex $[\text{Ph}_2\text{P}(\text{BH}_3)_2]\text{K}(18\text{-crown-6})$ is -11.1 ppm).^{4c} It therefore appears that, in this case, **3Li** reacted with the excess $[\text{Ph}_2\text{P}(\text{BH}_3)]\text{Li}$ present, removing one of the borane groups from **3Li** to give $[\text{Li}\{\text{Ph}_2\text{P}(\text{BH}_3)\}_2(\text{Ph}_2\text{P})\text{Sn}]$ and $[\text{Ph}_2\text{P}(\text{BH}_3)_2]\text{Li}$. In support of this, we have previously observed that alkali metal phosphido-borane complexes are able to abstract BH_3 groups from neutral phosphine-boranes to give phosphido-bis(borane) anions.^{4h}

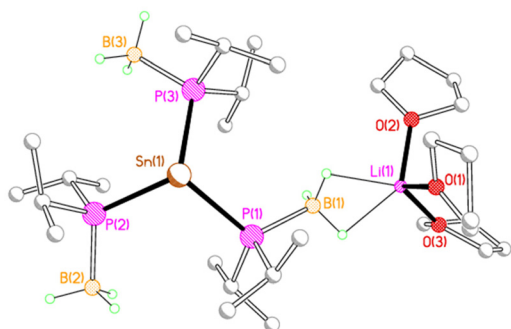


Fig. 1 Molecular structure of **2Li** with C-bound H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Sn(1)–P(2) 2.6349(6), Sn(1)–P(3) 2.6219(6), Sn(1)–P(1) 2.6241(6), P(1)–B(1) 1.956(3), P(2)–B(2) 1.957(3), P(3)–B(3) 1.957(3), Li(1)–B(1) 2.381(5), Li(1)–O(1) 1.916(5), Li(1)–O(2) 1.926(5), Li(1)–O(3) 1.955(5), P(1)–Sn(1)–P(2) 103.459(19), P(1)–Sn(1)–P(3) 103.853(18), P(2)–Sn(1)–P(3) 104.400(19).

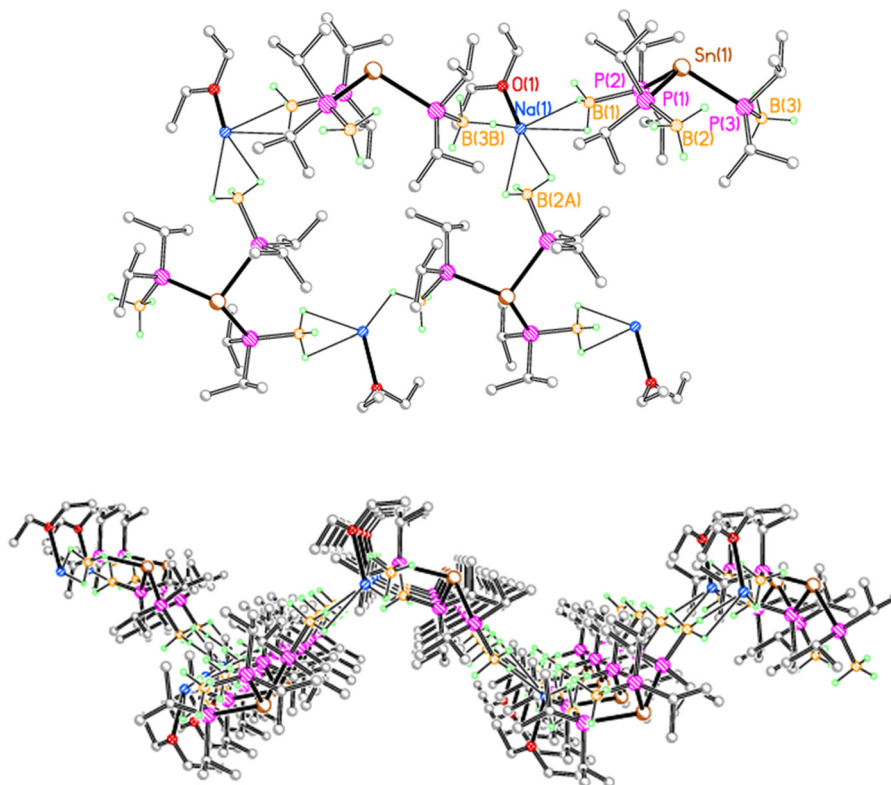


Fig. 2 Polymeric structure of **2Na**, with C-bound H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Sn(1)–P(1) 2.6424(7), Sn(1)–P(2) 2.6325(7), Sn(1)–P(3) 2.6401(7), P(1)–B(1) 1.947(3), P(2)–B(2) 1.956(3), P(3)–B(3) 1.952(3), Na(1)–B(1) 2.742(4), Na(1)–B(2A) 2.779(3), Na(1)–B(3B) 2.814(3), Na(1)–O(1) 2.333(2), P(1)–Sn(1)–P(2) 101.79(2), P(1)–Sn(1)–P(3) 104.78(2), P(2)–Sn(1)–P(3) 102.46(2).



X-ray crystallography reveals that each of **2M**, **3M** and **4Li** crystallises as an alkali metal salt of a tris(phosphido-borane)stannate anion, in which the tin centre is coordinated by the phosphorus atoms of three phosphido-borane anions in a trigonal pyramidal geometry. While the core structure of the tris(phosphido-borane)stannate anion is essentially the same for all compounds, the coordination of the alkali metal cation differs significantly in each case. Compound **2Li** crystallises as a contact ion pair in which the lithium cation is coordinated by three molecules of THF and one of the BH₃ groups of the tris(phosphido-borane)stannate anion in a κ^2 -manner (Fig. 1).

In contrast, **2Na** crystallises as a corrugated sheet polymer, due to multiple BH₃...Na contacts (Fig. 2). Each sodium ion is coordinated by a molecule of diethyl ether, along with three BH₃ groups from three adjacent tris(phosphido-borane)stannate anions, with one κ^1 and two κ^2 BH₃...Na contacts. Thus, each stannate anion is bridged by three sodium ions to give a sheet polymer network. Compound **2K** adopts a similar corrugated sheet structure, in which each stannate anion is bridged by three potassium ions to three adjacent anions (see the ESI†). However, reflecting the increased ionic radius of potassium compared with sodium, each potassium ion is coordinated by one molecule of diethyl ether, along with one κ^3 and two κ^2 BH₃...K contacts.

The three phenyl-substituted tris(phosphido-borane)stannate complexes **3Li**, **3Na**, and **3K**, adopt a rather different structural motif in the solid state, in which each alkali metal ion is coordinated by three BH₃ groups from the same stannate anion. Compounds **3Li** and **3Na** crystallise as discrete monomers (Fig. 3). In **3Li** the lithium ion is coordinated by a molecule of THF and by the three BH₃ groups, with one κ^1 and two κ^2 BH₃...Li contacts. Compound **3Na** crystallises with two independent molecules in the asymmetric unit. In both molecules the sodium ions are coordinated by one molecule each of THF and diethyl ether; in molecule 1 further coordination is provided by three κ^2 BH₃...Na contacts, whereas in molecule 2 the sodium ion is further coordinated by two κ^2 and one κ^1 BH₃...Na contacts.

In contrast, **3K** crystallises as a centrosymmetric dimer (Fig. 4). Each potassium ion is coordinated by one molecule each of THF and diethyl ether and by three κ^2 BH₃ groups from one stannate anion, along with a κ^1 BH₃ group from the second stannate anion in the dimer. Thus, one borane group from each stannate anion bridges the two potassium ions in a μ - κ^2 : κ^1 fashion.

Given the two different structural motifs adopted by the isopropyl- and phenyl-substituted compounds **2M** and **3M**, it seemed of interest to investigate the structure of a compound possessing both phenyl and isopropyl substituents at phosphorus (**4Li**). Unexpectedly, this compound crystallised as a separated ion pair, with no short contacts between the tris(phosphido-borane)stannate anion and the [Li(THF)₄]⁺ cation (Fig. 5).

Across all of the compounds studied there is little variation in the Sn–P and P–B distances, which fall in the ranges 2.6072(7)–2.6455(8) and 1.936(4)–1.963(5) Å, respectively. The Sn–P

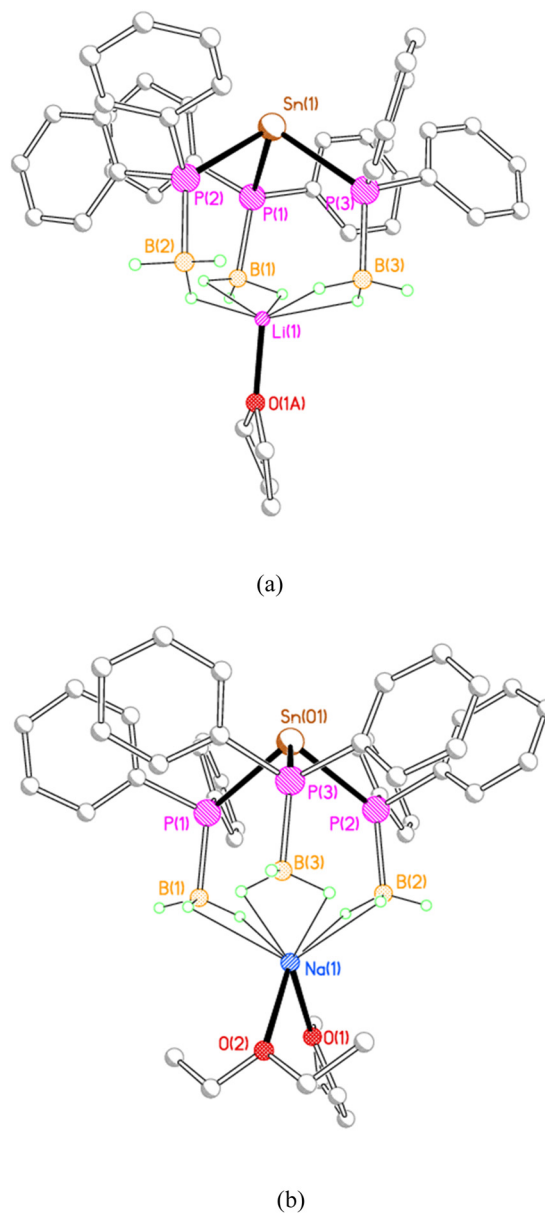


Fig. 3 Molecular structures of (a) **3Li** and (b) one of the two independent molecules of **3Na**, with H atoms and minor disorder components omitted for clarity. Selected bond lengths (Å) and angles (°) [values for the second independent molecule of **3Na** in square brackets]: **3Li** Sn(1)–P(1) 2.6097(14), Sn(1)–P(2) 2.6444(13), Sn(1)–P(3) 2.6288(13), P(1)–B(1) 1.940(7), P(2)–B(2) 1.963(5), P(3)–B(3) 1.954(6), Li(1)–B(1) 2.470(13), Li(1)–B(2) 2.798(14), Li(1)–B(3) 2.477(14), Li(1)–O(1) 1.908(15), P(1)–Sn(1)–P(2) 93.60(4), P(1)–Sn(1)–P(3) 95.56(5), P(2)–Sn(1)–P(3) 95.17(4). **3Na** Sn(01)–P(1) 2.6301(6), Sn(01)–P(2) 2.6072(7), Sn(01)–P(3) 2.6237(7) [Sn(02)–P(4) 2.6457(7), Sn(02)–P(5) 2.6536(7), Sn(02)–P(6) 2.6343(7)], P(1)–B(1) 1.951(3), P(2)–B(2) 1.938(4), P(3)–B(3) 1.945(3) [P(4)–B(4) 1.940(3), P(5)–B(5) 1.949(3), P(6)–B(6) 1.952(3)], Na(1)–B(1) 2.912(4), Na(1)–B(2) 2.931(4), Na(1)–B(3) 2.959(4), Na(1)–O(1) 2.358(2), Na(1)–O(2) 2.386(2) [Na(2)–B(4) 2.882(3), Na(2)–B(5) 2.835(4), Na(2)–B(6) 3.346(4), Na(2)–O(3) 2.414(15), Na(2)–O(4) 2.328(3)], P(1)–Sn(01)–P(2) 94.52(2), P(1)–Sn(01)–P(3) 96.03(2), P(2)–Sn(01)–P(3) 95.93(2) [P(4)–Sn(02)–P(5) 97.53(2), P(4)–Sn(02)–P(6) 94.11(2), P(5)–Sn(02)–P(6) 95.99(2)].



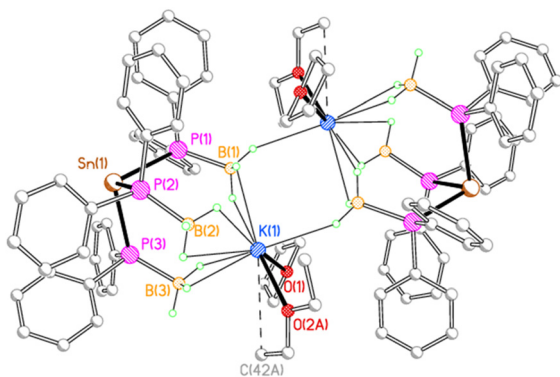


Fig. 4 Molecular structure of **3K** with C-bound H atoms and minor disorder components omitted for clarity. Selected bond lengths (Å) and angles (°): Sn(1)–P(1) 2.6386(7), Sn(1)–P(2) 2.6427(7), Sn(1)–P(3) 2.6455(8), P(1)–B(1) 1.936(4), P(2)–B(2) 1.950(4), P(3)–B(3) 1.941(4), K(1)···B(1) 3.213(4), K(1)···B(2) 3.343(4), K(1)···B(3) 3.241(4), K(1)···B(1A) 3.686(3), K(1)–O(1) 2.704(2), K(1)–O(2A) 2.719(6), P(1)–Sn(1)–P(2) 95.28(2), P(1)–Sn(1)–P(3) 97.54(2), P(2)–Sn(1)–P(3) 96.94(2).

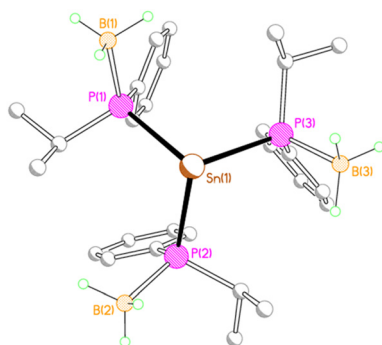


Fig. 5 Solid-state structure of the anion of **4Li** with C-bound H atoms and minor disorder components omitted for clarity. Selected bond lengths (Å) and angles (°): Sn(1)–P(1) 2.6244(7), Sn(1)–P(2) 2.6323(6), Sn(1)–P(3) 2.6324(7), P(1)–B(1) 1.945(4), P(2)–B(2) 1.947(3), P(3)–B(3) 1.951(3), Li(1)–O(1) 1.905(5), Li(1)–O(2A) 1.895(7), Li(1)–O(3A) 1.929(8), Li(1)–O(4A) 1.940(7), P(1)–Sn(1)–P(2) 100.47(2), P(1)–Sn(1)–P(3) 101.73(2), P(2)–Sn(1)–P(3) 100.13(2).

distances are similar to other Sn(II)–P distances;¹¹ for example, the Sn–P distances in [Li(THF)₄][Sn{P(Ph){CH(SiMe₃)₂}}₃] (**5**) are 2.649(2) Å,¹⁰ whereas the Sn–P(terminal) distances in Sn[P{CH(SiMe₃)₂}(C₆H₄-2-CH₂NMe₂)₂] are 2.5906(9) and 2.6061(9) Å for the two independent molecules in the asymmetric unit.¹²

The degree of pyramidalisation at the tin centre within the set of compounds **2Li**, **2Na** and **2K** is also rather similar [sum of P–Sn–P angles = 311.71, 309.03 and 309.65°, respectively], but this differs significantly from the degree of pyramidalisation of tin in **3Li**, **3Na**, and **3K** [sum of P–Sn–P angles = 284.33, 286.48 and 289.76°, respectively]. This clearly reflects the different binding modes between the stannate anions and alkali metal cations within these two sets of compounds. In **2M** the alkali metals are bound at the periphery of the stannate anions and so the P–Sn–P angles are close to those expected for a trigonal pyramid. Whereas, in **3M** the stannate

anion acts as a pseudo-tridentate ligand to the alkali metal centres; this necessarily leads to a reduction in the P–Sn–P angles in **3M** compared with **2M**. Notably, the sum of P–Sn–P angles in **3M** increases as the size of the alkali metal ion increases from Li to Na and K, as expected, but is essentially identical for **2Li**, **2Na** and **2K**. In the separated ion pair compound **4Li** the pyramidalisation of the tin centre [sum of angles at tin = 302.33°] appears to be intermediate between the pyramidalisation of the tin centres in **2M** and **3M**. This is in marked contrast to the sum of P–Sn–P angles in **5**, which crystallises with a discrete tris(phosphido)stannate anion (sum of P–Sn–P angles in **5** = 274.23°).¹⁰

Conclusions

A series of tris(phosphido-borane)stannate complexes [L_nM{R₂P(BH₃)₃]₃Sn] (M = Li, Na; R = Ph, iPr; L = THF, Et₂O) is readily accessible by the simple treatment of SnCl₂ with three equivalents of the corresponding alkali metal phosphido-borane salt. However, similar reactions between three equivalents of the bulky phosphido-borane complexes [M{tBu₂P(BH₃)₃}] (M = Li, Na) and SnCl₂ led to decomposition to the corresponding hydridostannate [M{tBu₂P(BH₃)₂SnH].

Although all of the isolated compounds crystallise as tris(phosphido-borane)stannate salts containing a trigonal pyramidal Sn(II) centre, they adopt three distinct binding modes, depending on the substituents at phosphorus. The isopropyl-substituted complexes [L_nM{iPr₂P(BH₃)₃]₃Sn (**2M**) crystallise as monomers or polymers in which the alkali metal cation is coordinated by BH₃ groups at the periphery of one or more stannate anions. In contrast, the phenyl-substituted compounds [L_nM{Ph₂P(BH₃)₃]₃Sn (**3M**) adopt molecular structures in which the alkali metal cation is coordinated by all three BH₃ groups from a single stannate anion. The mixed substituent complex **4Li** crystallises as a separated ion pair, with no short contacts between the cation and the stannate anion. The preference for one structural motif over another is likely due to the steric bulk of the substituents: in **3M** the phenyl rings are able to rotate in order to minimise steric repulsion and so all three borane groups are able to position themselves close to the alkali metal centre; this appears to be disfavoured for the more bulky isopropyl groups in **2M** and so an alternative structural motif is adopted.

Experimental section

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Diethyl ether, toluene and THF were dried prior to use by distillation under nitrogen from sodium/potassium alloy, sodium or potassium, respectively; THF was stored over activated 4 Å molecular sieves, while toluene and diethyl ether were stored over a potassium film. Deuterated toluene and THF were distilled from potassium under nitrogen and were deoxygenated by



three freeze–pump–thaw cycles and stored over activated 4 Å molecular sieves. Benzylsodium,¹³ benzylpotassium,¹⁴ Ph₂P(BH₃)H (**3H**),¹⁵ iPr₂P(BH₃)H (**2H**),¹⁶ iPrPhP(BH₃)H (**4H**),^{4f} and *t*Bu₂P(BH₃)H^{4i,17} were prepared by previously published procedures; *n*-butyllithium was purchased from Aldrich as a 2.5 M solution in THF and its concentration was accurately determined by titration before use. All other compounds were used as supplied by the manufacturer.

¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker AvanceIII 300 spectrometer operating at 300.13 and 75.48 MHz, respectively, or a Bruker AvanceIII 400 spectrometer operating at 399.78 and 100.54 MHz, respectively; chemical shifts are quoted in ppm relative to tetramethylsilane. ³¹P{¹H}, ¹¹B{¹H}, ⁷Li and ¹¹⁹Sn{¹H} NMR spectra were recorded on a Bruker AvanceIII 300 or a Bruker AvanceIII 400 spectrometer operating at 121.49 [161.83], 96.29 [128.27], 116.64 and 111.91 [149.08] MHz, respectively [values in square brackets correspond to the frequencies on the latter machine]; chemical shifts are quoted in ppm relative to external 85% H₃PO₄, BF₃·Et₂O, 0.1 M LiCl in D₂O, and Me₄Sn, respectively.

We were unable to obtain consistent elemental analyses for the isolated compounds due to their air- and moisture-sensitive nature and to partial loss of coordinated solvent in most cases; however, multinuclear NMR data indicate that all compounds are isolated in good purity.

[Sn{iPr₂P(BH₃)₃Li(THF)₃}]_∞ (**2Li**)

To a solution of iPr₂PH(BH₃) (0.4 g, 3 mmol) in THF (20 mL) was added *n*BuLi (1.2 mL, 2.45 M solution in hexane, 3 mmol) and this mixture was stirred for 30 min. This solution was added, dropwise, to a cold (−78 °C) solution of SnCl₂ (0.19 g, 1 mmol) in THF (20 mL) and this mixture was stirred for 1 h. The solution was allowed to warm to room temperature and the solvent was removed *in vacuo* to give a sticky yellow solid. This was extracted into Et₂O (10 mL) containing a few drops of THF and filtered. The filtrate was cooled to −30 °C overnight to give **2Li** as yellow crystals suitable for X-ray crystallography. Yield of crystalline material 0.25 g, 18%. The coordinated THF is partially lost under vacuum; all NMR data correspond to the formula [Sn{iPr₂P(BH₃)₃Li(THF)_{0.25}}]_∞ (**2Li**). ¹H NMR (399.78 MHz, *d*₈-THF, 25 °C): δ 0.54 (br, 9H, BH₃), 1.16 (m, 18H, *MeMeCH*), 1.23 (m, 18H, *MeMeCH*), 1.78 (m, 1H, THF), 2.41 (m, 6H, *MeMeCH*), 3.61 (m, 1H, THF). ¹³C{¹H} NMR (100.54 MHz, *d*₈-THF, 25 °C): δ 19.2 (*J*_{SnC} = 28.0 Hz, *MeMeCH*), 21.8 (*J*_{SnH} = 26.5 Hz, *MeMeCH*), 24.9 (m, *MeMeCH*), 26.4 (THF), 68.3 (THF). ¹¹B{¹H} NMR (128.27 MHz, *d*₈-THF, 25 °C): δ −39.9 (br). ³¹P{¹H} NMR (161.83 MHz, *d*₈-THF, 25 °C): δ 8.7 (*J*_{PSn} = 1910 Hz). ⁷Li{¹H} NMR (116.64 MHz, *d*₈-THF, 25 °C): δ −0.6 (s). ¹¹⁹Sn{¹H} NMR (149.08 MHz, *d*₈-THF, 25 °C): δ −181 (q, *J*_{PSn} = 1910 Hz).

[Sn{iPr₂P(BH₃)₃Na(THF)}]_∞ (**2Na**)

To a solution of iPr₂PH(BH₃) (0.4 g, 3 mmol) in THF (20 mL) was added a solution of PhCH₂Na (0.35 g, 3 mmol) in THF (20 mL), and this mixture was stirred for 30 min. This solution was added, dropwise, to a cold (−78 °C) solution of SnCl₂

(0.19 g, 1 mmol) in THF (20 mL), and this mixture was stirred for 1 h. The mixture was allowed to warm to room temperature and the solvent was removed *in vacuo* to give a yellow solid. This was extracted into THF/Et₂O (20 mL per 20 mL), filtered, and solvent was removed from the filtrate *in vacuo*. The resulting solid was crystallised from THF (5 mL) layered with Et₂O (20 mL) to give yellow crystals of **2Na** suitable for X-ray crystallography. The coordinated THF is partially lost under vacuum; all NMR data correspond to the formula [Sn{iPr₂P(BH₃)₃Na(THF)_{0.5}}]_∞ (**2Na**). Yield of **2Na** 0.21 g, 39%. ¹H{¹¹B} NMR (300.13 MHz, *d*₈-THF, 25 °C): δ 0.54 (br, 9H, BH₃), 1.15–1.29 (m, 36H, *MeMeCH*), 1.77 (m, 2H, THF), 2.13–2.42 (m, 6H, *MeMeCH*), 3.61 (m, 2H, THF). ¹³C{¹H} NMR (75.48 MHz, *d*₈-THF, 25 °C): δ 19.2 (*J*_{SnC} = 28.3 Hz, *MeMeCH*), 21.8 (*J*_{SnC} = 26.3 Hz, *MeMeCH*), 24.9 (*MeMeCH*), 26.4 (THF), 68.3 (THF). ¹¹B{¹H} NMR (96.29 MHz, *d*₈-THF, 25 °C): δ −38.1 (br). ³¹P{¹H} NMR (121.49 MHz, *d*₈-THF, 25 °C): δ 10.3 (s, *J*_{PSn} = 1915 Hz). ¹¹⁹Sn{¹H} NMR (111.91 MHz, *d*₈-THF, 25 °C): δ −176 (q, *J*_{PSn} = 1915 Hz).

[Sn{iPr₂P(BH₃)₃K(Et₂O)}]_∞ (**2K**)

A solution of PhCH₂K (0.39 g, 3 mmol) in THF (20 mL) was added to a solution of iPr₂PH(BH₃) (0.4 g, 3 mmol) in THF (20 mL) and this mixture was stirred for 30 min. This solution was added, dropwise, to a cold (−78 °C) solution of SnCl₂ (0.19 g, 1 mmol) in THF (20 mL) and this mixture was stirred for 1 h. The reaction was allowed to warm to room temperature and the solvent was removed *in vacuo*. The resulting solid was extracted into THF/Et₂O (20 mL per 20 mL), filtered and solvent was removed *in vacuo* from the filtrate. The resulting solid was crystallised from THF (5 mL) layered with Et₂O (10 mL) to give **2K** as yellow crystals suitable for X-ray crystallography. Yield of crystalline material 0.16 g, 25%. The coordinated diethyl ether is partially lost under vacuum; all NMR data correspond to the formula [Sn{iPr₂P(BH₃)₃K(Et₂O)_{0.5}}]_∞ (**2K**). ¹H NMR (300.13 MHz, *d*₈-THF, 25 °C): δ 0.44–0.46 (br, 9H, BH₃), 1.10 (t, 3H, Et₂O), 1.17–1.24 (m, 36H, *MeMeCH*), 2.41 (m, 6H, *MeMeCH*), 3.38 (q, 2H, Et₂O). ¹³C{¹H} NMR (75.48 MHz, *d*₈-THF, 25 °C): δ 15.8 (Et₂O), 19.3 (*J*_{SnH} = 28.3 Hz, *MeMeCH*), 21.8 (*J*_{SnH} = 26.1 Hz, *MeMeCH*), 25.0 (d, *J*_{PC} = 6.0 Hz, *MeMeCH*), 66.4 (Et₂O). ¹¹B{¹H} NMR (96.29 MHz, *d*₈-THF, 25 °C): δ −38.1 (br). ³¹P{¹H} NMR (121.49 MHz, *d*₈-THF, 25 °C): δ 9.7 (s, *J*_{PSn} = 1910 Hz). ¹¹⁹Sn{¹H} NMR (111.91 MHz, *d*₈-THF, 25 °C): δ −171 (q, *J*_{PSn} = 1910 Hz).

[Sn{Ph₂P(BH₃)₃Li(THF)}]_∞ (**3Li**)

To a solution of Ph₂PH(BH₃) (0.6 g, 3 mmol) in THF (20 mL) was added *n*BuLi (1.2 mL, 2.45 M solution in hexane, 3 mmol) and this mixture was stirred for 30 min. This solution was added, dropwise, to a cold (−78 °C) solution of SnCl₂ (0.19 g, 1 mmol) in THF (20 mL), and this mixture was stirred for 1 h. The reaction was allowed to attain room temperature and the solvent was removed *in vacuo*. The solid was extracted into toluene (20 mL) and filtered. The filtrate was concentrated to 10 mL and cooled (−25 °C) to give **3Li** as pale yellow crystals suitable for X-ray crystallography. Yield of crystalline material



0.3 g, 37%. The coordinated THF is rapidly lost under vacuum; all NMR data correspond to the formula $[\text{Sn}\{\text{Ph}_2\text{P}(\text{BH}_3)\}_3\text{Li}(\text{THF})_{0.5}]$ (**3Li**). $^1\text{H}\{^{11}\text{B}\}$ NMR (300.13 MHz, d_8 -THF, 25 °C): δ 1.18 (br, 9H, BH_3), 1.78 (m, 2H, THF), 3.63 (m, 2H, THF), 6.98–7.11 (m, 24H, Ph), 7.45 (m, 6H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, d_8 -THF, 25 °C): δ 26.4 (THF), 68.4 (THF), 128.1, 128.4, 135.1, 137.7 (m, Ph). $^{11}\text{B}\{^1\text{H}\}$ NMR (96.29 MHz, d_8 -THF, 25 °C): δ –32.5 (br). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.49 MHz, d_8 -THF, 25 °C): δ –10.4 ($J(^{31}\text{P}-^{119}\text{Sn}) = 1708$, $J(^{31}\text{P}-^{117}\text{Sn}) = 1633$ Hz). $^7\text{Li}\{^1\text{H}\}$ NMR (116.64 MHz, d_8 -THF, 25 °C): δ –0.6 (s). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (111.91 MHz, d_8 -THF, 25 °C): δ –46 (q, $J_{\text{PSn}} = 1708$ Hz).

$[\text{Sn}\{\text{Ph}_2\text{P}(\text{BH}_3)\}_3\text{Na}(\text{THF})(\text{Et}_2\text{O})]$ (**3Na**)

To a solution of $\text{Ph}_2\text{PH}(\text{BH}_3)$ (0.60 g, 3 mmol) in THF (20 mL) was added a solution of PhCH_2Na (0.35 g, 3 mmol) in THF (20 mL), and this mixture was stirred for 30 min. This solution was added, dropwise, to a cold (–78 °C) solution of SnCl_2 (0.19 g, 1 mmol) in THF (20 mL) and this mixture was stirred for 1 h. The solution was allowed to warm to room temperature and the solvent was removed *in vacuo*. The resulting solid was extracted into THF/ Et_2O (20 mL per 20 mL), filtered and solvent was removed from the filtrate *in vacuo*. The resulting solid was crystallised from cold (–25 °C) Et_2O (15 mL) containing a few drops of THF to give **3Na** as orange crystals suitable for X-ray crystallography. Yield of crystalline material 0.2 g, 22%. The coordinated diethyl ether is partially lost under vacuum; all NMR data correspond to the formula $[\text{Sn}\{\text{Ph}_2\text{P}(\text{BH}_3)\}_3\text{Na}(\text{THF})(\text{Et}_2\text{O})_{0.5}]$ (**3Na**). $^1\text{H}\{^{11}\text{B}\}$ NMR (300.13 MHz, d_8 -toluene, 25 °C): δ 1.14 (t, 3H, Et_2O), 1.40 (m, 4H, THF), 1.91 (d, $J_{\text{PH}} = 10.5$ Hz, 9H, BH_3), 3.26 (q, 2H, Et_2O), 3.58 (m, 4H, THF), 6.72–6.80 (m, 18H, Ph), 7.61 (m, 12H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, d_8 -toluene, 25 °C): δ 14.5 (Et_2O), 25.6 (THF), 66.0 (Et_2O), 68.1 (THF), 128.3, 128.4, 128.9 (Ph), 133.4 (d, $J_{\text{PC}} = 8.1$ Hz, Ph). $^{11}\text{B}\{^1\text{H}\}$ NMR (96.29 MHz, d_8 -toluene, 25 °C): δ –33.8 (br), $^{31}\text{P}\{^1\text{H}\}$ NMR (121.49 MHz, d_8 -toluene, 25 °C): δ –32.6 (s, $J_{\text{PSn}} = 1428$ Hz), $^{119}\text{Sn}\{^1\text{H}\}$ NMR (111.91 MHz, d_8 -toluene, 25 °C): δ –113 (q, $J_{\text{PSn}} = 1428$ Hz).

$[\text{Sn}\{\text{Ph}_2\text{P}(\text{BH}_3)\}_3\text{K}(\text{THF})_2]$ (**3K**)

A solution of PhCH_2K (0.39 g, 3 mmol) in THF (20 mL) was added to a solution of $\text{Ph}_2\text{PH}(\text{BH}_3)$ (0.60 g, 3 mmol) in THF (20 mL), and this mixture was stirred for 30 min. This solution was added, dropwise, to a cold (–78 °C) solution of SnCl_2 (0.19 g, 1 mmol) in THF (20 mL) and this mixture was stirred for 1 h. The solution was allowed to warm to room temperature and the solvent was removed *in vacuo*. The solid was extracted into THF/ Et_2O (20 mL per 20 mL), filtered and solvent was removed from the filtrate *in vacuo*. The resulting solid was crystallised from a mixture of cold (–25 °C) Et_2O (10 mL) and THF (5 mL) to give red crystals of **3K** suitable for X-ray crystallography. Yield of crystalline material 0.4 g, 44%. $^1\text{H}\{^{11}\text{B}\}$ NMR (300.13 MHz, d_8 -toluene, 25 °C): δ 1.47 (m, 8H, THF), 1.91 (d, $J_{\text{PH}} = 9.9$ Hz, 9H, BH_3), 3.55 (m, 8H, THF), 6.80 (m, 18H, Ph), 7.65 (m, 12H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, d_8 -toluene, 25 °C): δ 25.8 (THF), 67.8 (THF), 128.1 (d, $J_{\text{PC}} = 7.6$ Hz, Ph), 129.0 (d, $J_{\text{PC}} = 10.3$ Hz, Ph), 133.7 (d, $J_{\text{PC}} = 6.2$ Hz, Ph), (*ipso*

carbon not observed). $^{11}\text{B}\{^1\text{H}\}$ NMR (96.29 MHz, d_8 -toluene, 25 °C): δ –33.2 (br). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.49 MHz, d_8 -toluene, 25 °C): δ –20.1 ($J(^{31}\text{P}-^{119}\text{Sn}) = 1461$, $J(^{31}\text{P}-^{117}\text{Sn}) = 1388$ Hz). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (111.91 MHz, d_8 -toluene, 25 °C): δ –87 (q, $J_{\text{PSn}} = 1461$ Hz).

$[\text{Sn}\{\text{iPrPhP}(\text{BH}_3)\}_3][\text{Li}(\text{THF})_4]$ (**4Li**)

To a solution of $\text{iPrPhPH}(\text{BH}_3)$ (0.7 g, 3 mmol) in THF (20 mL) was added *n*BuLi (1.2 mL, 2.45 M solution in hexane, 3 mmol), and this mixture was stirred for 30 min. This solution was added, dropwise, to a cold (–78 °C) solution of SnCl_2 (0.19 g, 1 mmol) in THF (20 mL) and this mixture was stirred for 1 h. The solution was allowed to attain room temperature and the solvent was removed *in vacuo* to give a yellow solid. This was extracted into THF/ Et_2O (20 mL per 20 mL), filtered and solvent was removed *in vacuo* from the filtrate. The resulting solid was crystallised from a cold (–25 °C) mixture of Et_2O (10 mL) and THF (5 mL) to give **4Li** as yellow crystals suitable for X-ray crystallography. Yield of crystalline material 0.3 g, 33%. The coordinated THF is partially lost under vacuum; all NMR data correspond to the formula $[\text{Sn}\{\text{iPrPhP}(\text{BH}_3)\}_3\text{Li}(\text{THF})_2]$ (**4Li**). $^1\text{H}\{^{11}\text{B}\}$ NMR (300.13 MHz, d_8 -toluene, 25 °C): δ 0.71 (dd, $J_{\text{PH}} = 13.8$, $J_{\text{HH}} = 7.2$ Hz, 9H, *MeMeCH*), 0.78 (dd, $J_{\text{PH}} = 15.9$, $J_{\text{HH}} = 6.9$ Hz, 9H, *MeMeCH*), 1.44 (m, 8H, THF), 1.56 (m, 3H, *MeMeCH*), 1.70 (d, $J_{\text{PH}} = 9.6$ Hz, 9H, BH_3), 3.65 (m, 8H, THF), 7.04–7.15 (m, 9H, Ph), 8.05 (m, 6H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, d_8 -toluene, 25 °C): δ 18.2 (*Me_2CH*), 25.7 (THF), 27.1 (m, *Me_2CH*), 68.1 (THF), 128.3, 129.5 (Ph), 135.1 (d, $J_{\text{PC}} = 6.0$ Hz, Ph). $^{11}\text{B}\{^1\text{H}\}$ NMR (96.29 MHz, d_8 -toluene, 25 °C): δ –36.8 (s). $^7\text{Li}\{^1\text{H}\}$ NMR (116.64 MHz, d_8 -toluene, 25 °C): 0.4 (s). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.49 MHz, d_8 -toluene, 25 °C): δ –14.0 ($J_{\text{PSn}} = 1420$ Hz). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (111.91 MHz, d_8 -toluene, 25 °C): –113 (q, $J_{\text{PSn}} = 1420$ Hz).

Crystal structure determinations of **2Li**, **2Na**, **2K**, **3Li**, **3Na**, **3K**, and **4Li**

Measurements were made at 150 K on an Oxford Diffraction (Agilent Technologies) Gemini A Ultra diffractometer, using $\text{CuK}\alpha$ radiation ($\lambda = 1.54184$ Å) for **2Li** and $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å) otherwise. Cell parameters were refined from the observed positions of all strong reflections. For **2K** and **3Li** an analytical numeric absorption correction was applied using a multifaceted crystal model based on expressions derived by R. C. Clark and J. S. Reid.¹⁸ For all other compounds intensities were corrected for absorption empirically using spherical harmonics. The structures were solved by direct or dual-space methods and refined on F^2 values for all unique data; Table S1 in the ESI† gives further details. All non-hydrogen atoms were refined anisotropically, and C-bound H atoms were modelled with idealised geometry, while B-bound H atoms were located using the Fourier difference map; U_{iso} for all hydrogen atoms was constrained to be an appropriate multiple of the U_{eq} value of the parent C atom. Programs were Oxford Diffraction CrysAlisPro for data collection and processing, and programs of the SHELX family for structure solution, refinement, and molecular graphics.¹⁹



Conflicts of interest

There are no conflicts of interest to declare.

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