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Article

Alkali Metal Complexes of Phosphine−Borane-Substituted Benzyl Ligands and Their Application in the Synthesis of B−H···Sn Stabilized Dialkylstannylenes

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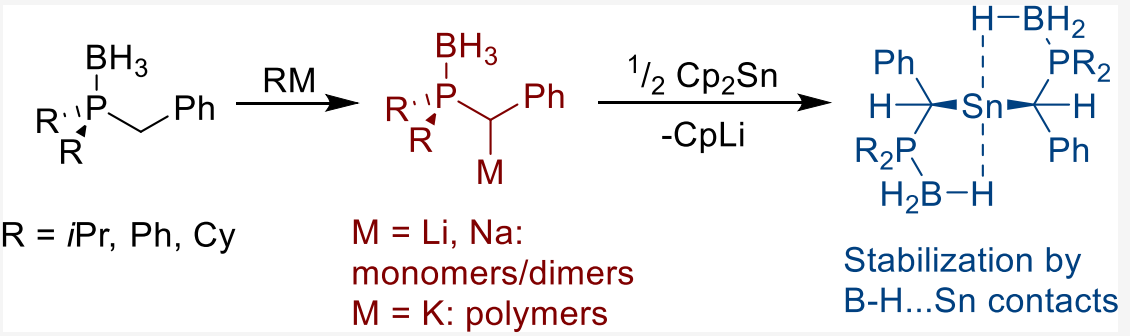

ABSTRACT: The benzyl-substituted phosphine−boranes $PhCH_2P(BH_3)R_2$ [R = *i*Pr (**1H**), Ph (**2H**), Cy (**3H**)] are accessible through either the reaction between R_2PCl and $PhCH_2MgBr$, followed by treatment with $BH_3{\cdot}SMe_2$ or the reaction between $R_2P(BH)_3Li$ and $PhCH_2Br$. Treatment of **1H**, **2H**, or **3H** with *n*BuLi, $PhCH_2Na$, or $PhCH_2K$ gave the corresponding alkali metal complexes $[\{iPr_2P(BH_3)CHPh\}Li(THF)]_2$ (**1Li**), $[\{Ph_2P(BH_3)CHPh\}Li(OEt_2)_2]$ (**2Li**), $[\{Cy_2P(BH_3)CHPh\}Li(TMEDA)]$ (**3Li**), $[iPr_2P(BH_3)CHPh]Na$ (**1Na**), $[\{Ph_2P(BH_3)CHPh\}Na(THF)_2]_2$ (**2Na**), $[Cy_2P(BH_3)CHPh]Na(THF)_{0.5}$ (**3Na**), $[\{iPr_2P(BH_3)CHPh\}K]_\infty$ (**1K**), $[\{Ph_2P(BH_3)CHPh\}K(THF)]_\infty$ (**2K**), and $[\{Cy_2P(BH_3)CHPh\}K.0.5PhMe]_\infty$ (**3K**). X-ray crystallography revealed that, while **2Li** and **3Li** crystallize as monomers, **1Li** and **2Na** crystallize as borane-bridged dimers. The potassium complexes **1K**, **2K**, and **3K** all crystallize with polymeric structures, in which the monomer units are linked to each other through a range of both bridging BH_3 groups and multihapto interactions between the potassium cations and the aromatic rings. The reactions between two equivalents of either **1Li** or **3Li** and Cp_2Sn gave the corresponding dialkylstannylenes $[\{R_2P(BH_3)CHPh\}_2Sn]$ [R = *i*Pr (**1Sn**), Cy (**3Sn**)]. These compounds were isolated as mixtures of the *rac* and *meso* diastereomers. X-ray crystallography reveals that *rac*-**1Sn** and *rac*-**3Sn** crystallize as discrete monomers each exhibiting two agostic-type B−H···Sn contacts.

INTRODUCTION

Although phosphine−borane-stabilized carbanions (PBCs) are key intermediates in the synthesis of commercially important phosphines and diphosphines, well-characterized examples of their complexes remain relatively scarce.[1] The first PBC complex, the separated ion pair $[Li(TMEDA)_2][Me_2P(BH_3)CHP(BH_3)Me_2]$,[2] was reported by Weiss and coworkers in 1979, but it was not until over two decades later that interest in these species began to develop (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine). This is rather surprising, given that the $R_2P(BH_3)$ group is isoelectronic and isosteric with the corresponding silyl group R_2MeSi, and given the importance of silicon-stabilized carbanions in the synthesis of numerous ground-breaking compounds.[3]

Over the last 15 years, we, and others, have studied the synthesis, structures, and reactions of PBCs and have isolated complexes of these ligands with group 1,[4,5] group 2,[6] lanthanide,[7] and group 14 element centers.[8−10] These studies have shown that PBCs may adopt a variety of coordination modes, including C-donation, BH_3-donation, and various bridging modes. In large part, our own studies have focused on ligands possessing a silyl or phosphine substituent at the carbanion center in addition to the phosphine-borane group [i.e., ligands of the form $[R_2P(BH_3)CR'R'']^-$; R′ = H, R″; R″ = $SiMe_3$, PR_2, $PR_2(BH_3)$]. In a relatively small number of cases, we have reported PBC complexes where there is an aryl substituent directly bonded to the carbanion center, but these have been

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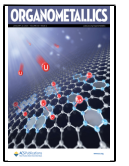
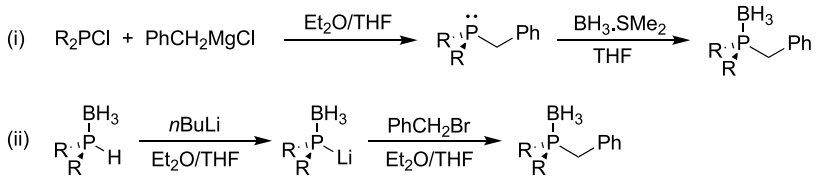


Scheme 1. Syntheses of $R_2P(BH_3)CH_2Ph$ (R = *i*Pr (1H), Ph (2H), Cy (3H))



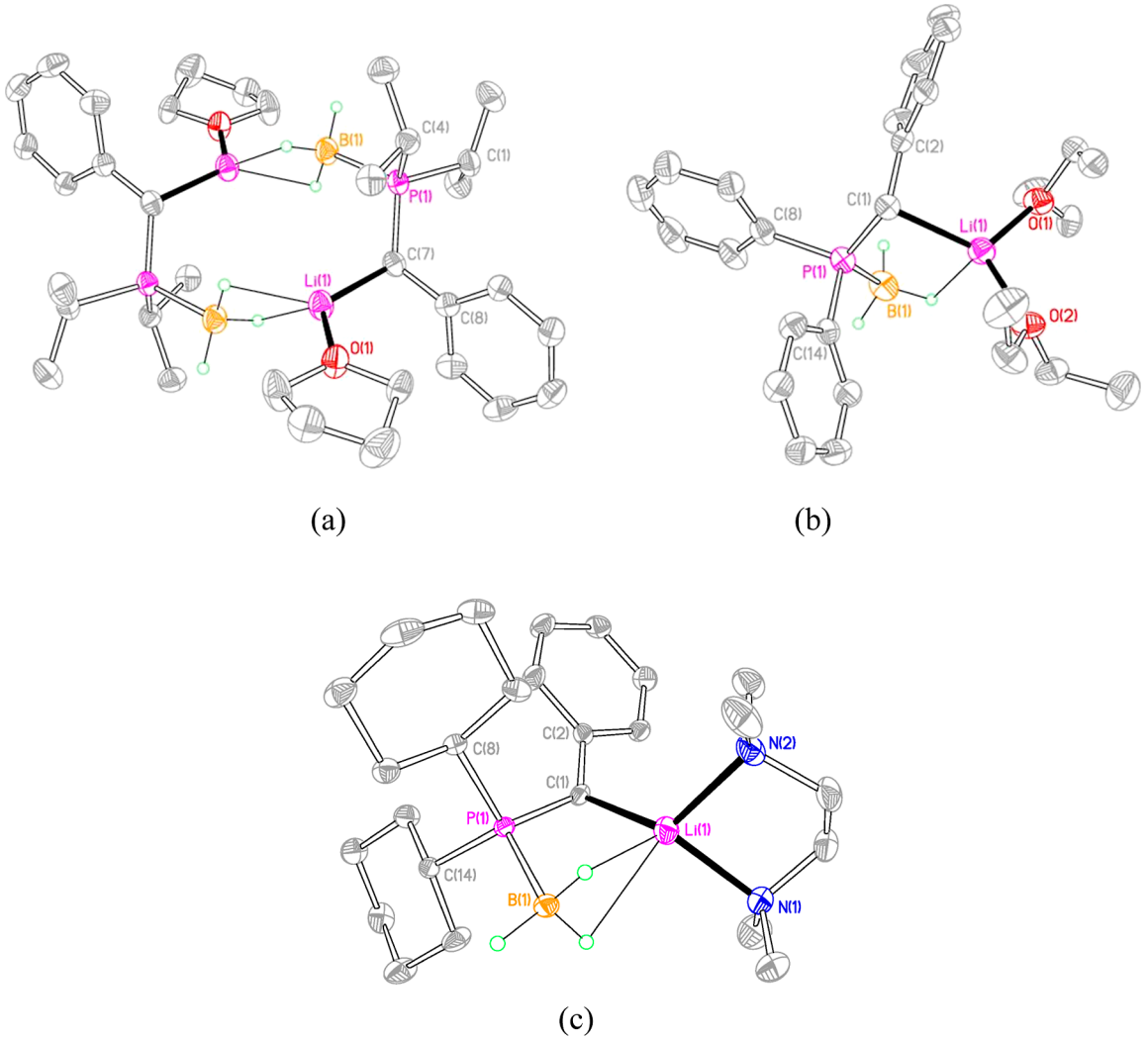


Figure 1. Molecular structures of (a) **1Li**, (b) **2Li**, and (c) **3Li**, with C-bound H atoms and minor disorder components omitted for clarity and with 40% probability ellipsoids; B-bound H atoms were refined isotropically. Selected bond lengths (Å) and angles (deg): **1Li** Li(1)−C(7) 2.167(4), Li(1)−O(1) 1.916(4), Li(1)−H(1A) 1.96(3), Li(1)−H(1B) 2.03(3), Li(1)···B(1A) 2.336(4), P(1)−B(1) 1.924(2), P(1)−C(7) 1.7433(19), P(1)−C(1) 1.8478(19), P(1)−C(4) 1.8548(18), C(7)−C(8) 1.453(3); **2Li** Li(1)−C(1) 2.259(3), Li(1)−O(1) 1.937(2), Li(1)−O(2) 1.957(3), Li(1)−H(1A) 2.17(2), Li(1)···B(1) 2.901(3), P(1)−B(1) 1.9313(17), P(1)−C(1) 1.7430(13), P(1)−C(8) 1.8359(15), P(1)−C(14) 1.8224(14), C(1)−C(2) 1.4536(18), C(1)−Li(1)···B(1) 73.07(7); **3Li** Li(1)−C(1) 2.267(3), Li(1)−N(1) 2.104(3), Li(1)−N(2) 2.082(3), Li(1)−H(1A) 2.328(16), Li(1)−H(1B) 2.035(16), Li(1)···B(1) 2.443(3), P(1)−B(1) 1.9349(16), P(1)−C(1) 1.7403(14), P(1)−C(8) 1.8409(13), P(1)−C(14) 1.8466(13), C(1)−C(2) 1.4458(19), C(1)−Li(1)···B(1) 77.35(9), N(1)−Li(1)−N(2) 87.78(10).

somewhat complex systems involving 1,3- or 1,4-dicarbanions.[5,9]

We were interested to observe the impact of a phenyl substituent on the structures of simple monoanionic PBC ligands, particularly the impact of the reduced steric bulk (compared to silyl and phosphine/phosphine−borane substituents), and the effect of charge delocalization into the phenyl ring, which might be expected to stabilize the PBC anion and thus reduce the nucleophilicity of the carbanion center. With this in mind, we now report the synthesis and structural characterization of a series of alkali metal PBC complexes possessing a phenyl substituent directly bonded to the carbanion center and their use in the synthesis of two new dialkylstannylenes.

RESULTS AND DISCUSSION

The benzyl-substituted phosphine−borane precursors $R_2P(BH_3)CH_2Ph$ [R = *i*Pr (**1H**), Ph (**2H**), Cy (**3H**)] were

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synthesized straightforwardly by one of two routes: (i) the reaction of the chlorophosphine R_2PCl with $PhCH_2MgX$, followed by treatment with $BH_3{\cdot}SMe_2$, or (ii) the reaction of $[R_2P(BH_3)]Li$ with $PhCH_2Br$ (Scheme 1). These compounds were isolated as colorless crystals; the solid-state structures of **1H** and **2H** were obtained for comparison with their metalated derivatives (see the Supporting Information).

Treatment of **1H** or **2H** with *n*BuLi in tetrahydrofuran (THF) or diethyl ether, respectively, gave the corresponding lithium PBC complexes $[\{iPr_2P(BH_3)CHPh\}Li(THF)]_2$ (**1Li**) and $[\{Ph_2P(BH_3)CHPh\}Li(OEt_2)_2]$ (**2Li**). Similar treatment of **3H** with *n*BuLi in THF gave the corresponding lithium complex, according to NMR spectroscopy, but we were unable to obtain crystals suitable for X-ray crystallography; this compound was eventually crystallized as the TMEDA complex $[\{Cy_2P(BH_3)CHPh\}Li(TMEDA)]$ (**3Li**). The structures of **1Li**, **2Li**, and **3Li** are shown in Figure 1, along with selected bond lengths and angles.

Both **2Li** and **3Li** crystallize as discrete monomers in which the ligand binds the lithium cation through the carbanion center and the BH_3 hydrogen atoms to give a pseudo-four-membered chelate ring. In **2Li** the BH_3 group binds in a κ^1 manner and the coordination of the lithium ion is completed by two molecules of diethyl ether, whereas in **3Li** the BH_3 group binds in a κ^2 fashion and the coordination of the lithium ion is completed by the two nitrogen atoms of the TMEDA coligand. In contrast, **1Li** crystallizes as a centrosymmetric head-to-tail dimer, in which each Li cation is coordinated by the carbanion center of one ligand and a κ^2-BH_3 group of the second ligand in the dimer, along with one molecule of THF, generating a $\{Li{-}C{-}P{-}(BH_3)\}_2$ pseudo-eight-membered ring.

The Li−C distances in **1Li** and **3Li** [2.259(3) and 2.267(3) Å, respectively], are longer than the corresponding distance in **2Li** [2.167(4) Å], most likely due to the presence of a strained pseudo-four-membered chelate ring in the former compounds. Nevertheless, each of these distances lies within the range of Li−C distances reported for other lithium PBC complexes.[4]

The reactions between **1H**, **2H**, or **3H** and $PhCH_2Na$ in THF similarly gave the metalated products $[iPr_2P(BH_3)\ CHPh]Na$ (**1Na**), $[\{Ph_2P(BH_3)CHPh\}Na(THF)_2]_2$ (**2Na**), and $[Cy_2P{-}(BH_3)CHPh]Na(THF)_{0.5}$ (**3Na**), according to NMR spectroscopy. Unfortunately, we were unable to obtain crystals of **1Na** and **3Na** suitable for X-ray crystallography, but single crystals of **2Na** were obtained from toluene/THF. Compound **2Na** crystallizes as head-to-tail dimers containing a central $\{Na{-}C{-}P{-}(BH_3)\}_2$ pseudo-eight-membered ring (Figure 2). Each sodium ion is coordinated by the carbanion center of one ligand and by a κ^2-BH_3 group from the second ligand in the dimer, along with two molecules of THF. The Na−C distances of 2.629(3) and 2.657(3) Å are similar to the corresponding distances in related sodium PBC complexes; for example, the Na−C distance in $[[\{Me_2P(BH_3)\}(Me_3Si)_2C]Na(THF)_2{\cdot}0.5PhMe]_\infty$ is 2.640(3) Å.[4h]

The reaction between **1H**, **2H**, or **3H** and $PhCH_2K$ in THF gave the metalated products $[\{iPr_2P(BH_3)CHPh\}K]_\infty$ (**1K**), $[\{Ph_2P(BH_3)CHPh\}K(THF)]_\infty$ (**2K**), and $[\{Cy_2P(BH_3)CHPh\}K.0.5PhMe]_\infty$ (**3K**). All three compounds crystallize with extended structures due to extensive K···Ph and BH_3···K interactions, but with significantly different metal−ligand contacts in each case.

There are two crystallographically distinct ligands and two distinct potassium ions in the asymmetric unit of solvent-free **1K** (Figure 3). K(1) is coordinated by the phenyl ring of one PBC ligand in a η^6 manner and has a relatively long contact to the carbanion center of the same ligand [K(1)−C(1) 3.5343(19) Å]. In addition, K(1) has short contacts to one H atom from the BH_3 group of this ligand and two H atoms from a BH_3 group in an adjacent ligand and has a further η^2 contact with two carbon atoms from the phenyl ring of a third PBC ligand in the sheet, along with a short contact to the carbanion center of this ligand [K(1)−C(1A) 3.0128(19) Å]. The second potassium ion K(2) has a similar η^6 contact with the phenyl ring of one PBC ligand and a long contact with the carbanion center of this ligand [K(2)−C(14) 3.5384(18) Å], along with a κ^1 contact with the BH_3 group in the same ligand, but has a κ^3 contact with a BH_3 group from the first PBC ligand. In addition, K(2) has an η^3 contact with two carbon atoms from the phenyl ring and the carbanion center in a further PBC ligand; the K−C distance to this second carbanion center is significantly shorter than the K(2)−C(14) distance [K(2)−C(14B) 3.0720(18) Å]. Thus, the two distinct BH_3 groups act as μ-κ^1:κ^2 and μ-κ^1:κ^3 bridges between the two different potassium ions.

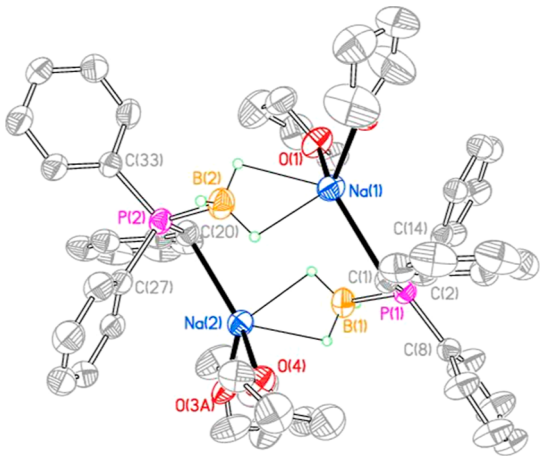

Figure 2. Molecular structure of **2Na** with C-bound H atoms and disorder components omitted for clarity and with 40% probability ellipsoids; B-bound H atoms were refined isotropically. Selected bond lengths (Å): Na(1)−C(1) 2.629(3), Na(1)−O(1) 2.311(2), Na(1)−O(2A) 2.255(7), Na(1)−H(2A) 2.40(7), Na(1)−H(2B) 2.41(7), Na(1)···B(2) 2.862(4), Na(2)−C(20) 2.657(3), Na(2)−O(3B) 2.279(13), Na(2)−O(4) 2.309(2), Na(2)−H(1B) 2.32(7), Na(2)−H(1C) 2.35(7), Na(2)···B(1) 2.831(3), P(1)−B(1) 1.930(3), P(1)−C(1) 1.722(3), P(1)−C(8) 1.832(2), P(1)−C(14) 1.839(2), P(2)−B(2) 1.937(4), P(2)−C(20) 1.723(3), P(2)−C(27) 1.835(3), P(2)−C(33) 1.832(2).

Compound **3K** also crystallizes as a sheet polymer (Figure 4). However, in this compound, there is no significant contact between the potassium ion and the carbanion center [the K(1)···C(1) distance is 3.7154(12) Å]. The potassium cation has a κ^1 contact with a BH_3 group from one ligand and a κ^2-BH_3 contact with an adjacent ligand, forming a $K{-}BH_3{-}K{-}BH_3$ parallelogram. The coordination of each potassium cation is completed by two η^6 phenyl rings, one from the first ligand and the other from a third ligand in the sheet. Thus, each phenyl ring acts as a μ-η^6:η^6 bridge between two potassium ions.

The asymmetric unit of **2K** contains a single potassium cation coordinated by the carbanion center and the *ipso*- and one *ortho*-carbon atoms of the same PBC ligand, along with a molecule of THF (Figure 5). These units form dimers through μ-κ^1:κ^2-BH_3 bridges between adjacent potassium ions to form $K{-}BH_3{-}K{-}BH_3$ parallelograms. The coordination of each potassium ion is completed by a η^3 contact with a *P*-phenyl ring from a further

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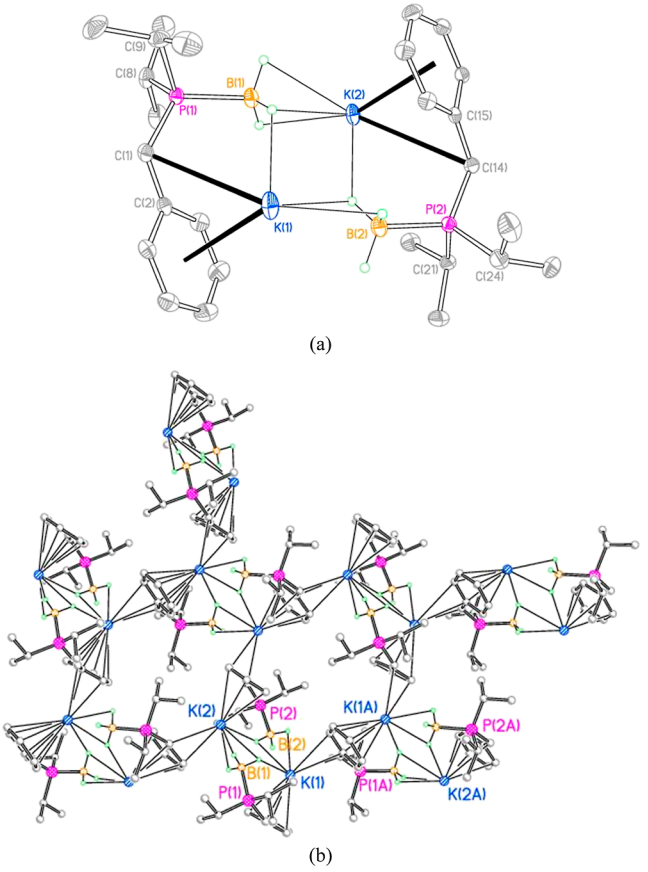

Figure 3. Solid-state structures of (a) the asymmetric unit and (b) the extended network of **1K**, with C-bound H atoms omitted for clarity and with 40% probability ellipsoids; B-bound H atoms were refined isotropically. Selected bond lengths (Å): K(1)−C(1) 3.5343(19), K(1)−C(1A) 3.0128(19), K(1)−H(2A) 2.82(2), K(1)−H(2C) 2.72(2), K(1)···B(1) 3.546(2), K(1)···(B2) 3.043(2), K(2)−C(14) 3.5384(18), K(2)−C(14B) 3.0720(18), K(2)−H(1A) 2.95(2), K(2)−H(1B) 3.05(2), K(2)−H(1C) 2.59(3), K(2)···B(2) 3.739(2), K(2)···B(1) 3.023(2), P(1)−B(1) 1.931(2), P(1)−C(1) 1.7418(18), P(1)−C(8) 1.8498(19), P(1)−C(11) 1.8367(19), P(2)−B(2) 1.936(2), P(2)−C(14) 1.7426(17), P(2)−C(21) 1.8359(19), P(2)−C(24) 1.8505(19).

PBC ligand in the network, leading to the formation of ribbon polymers. The K(1)−C(1) distance of 3.0294(19) Å lies within the range of typical K−C distances.

In each case, metalation of the free phosphine−boranes **1H** and **2H** leads to a significant decrease in the C(carbanion)−P and C(carbanion)−C(Ph) distances; for example, the C(7)−P(1) distances in **1H** and **1Li** are 1.8295(16) and 1.7433(19) Å, respectively, while the C(7)−C(8) distances in these two compounds are 1.506(2) and 1.453(3) Å. This is consistent with both the rehybridization of the benzylic carbon from sp^3 to sp^2 and significant delocalization of the carbanion lone pair into both the phenyl ring and the P−C(*i*Pr) σ^* orbitals (negative hyperconjugation). In accord with this, the P−C(*i*Pr) distances increase from 1.8342(16) and 1.8378(19) Å in **1H** to 1.8478(19) and 1.8548(18) Å in **1Li**. Similar changes in bond lengths are observed for the lithium, sodium and potassium derivatives of **1H** and **2H** in comparison to their free phosphine-borane precursors (Table 1). However, there is little change in the P−B distances in the metalated species in comparison to their protonated precursors, consistent with limited delocalization of the carbanion lone pair into the P−B σ^* orbitals in the

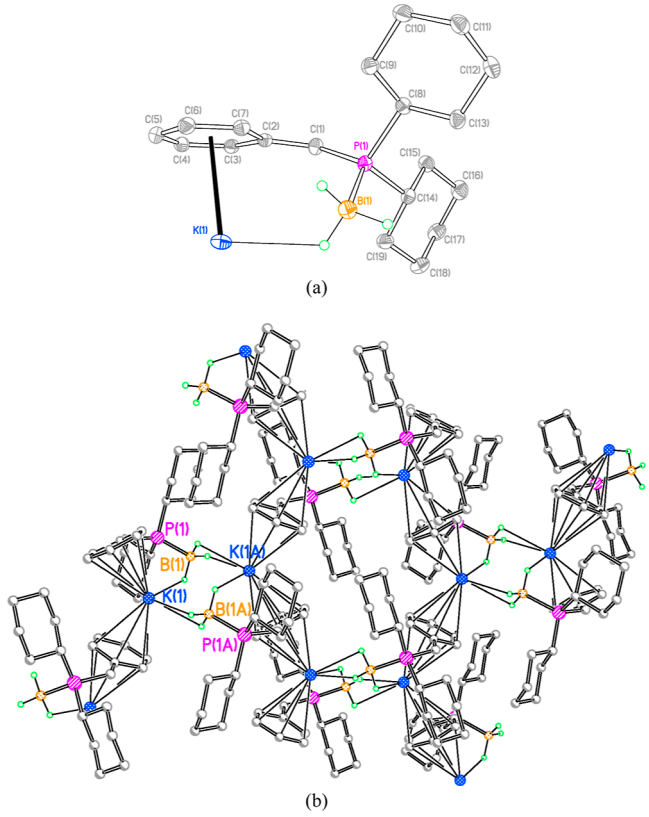

Figure 4. Solid-state structure of (a) the asymmetric unit and (b) the extended network of **3K** with C-bound H atoms and solvent of crystallization omitted for clarity and with 40% probability ellipsoids; B-bound H atoms were refined isotropically. Selected bond lengths (Å): K(1)−H(1A) 2.846(19), K(1)−H(1C) 2.68(2), K(1A)−H(1B) 2.82(2), K(1)···B(1) 3.6071(14), K(1A)···B(1) 3.0152(13), P(1)−B(1) 1.9365(13), P(1)−C(1) 1.7424(11), P(1)−C(8) 1.8537(12), P(1)−C(14) 1.8436(12).

PBC complexes.[4g] The P−C(carbanion) and C(Ph)−C(carbanion) distances decrease slightly with decreasing electronegativity of the metal centers; for example, the P−C(carbanion) distances in **2Li**, **2Na**, and **2K** are 1.743(13), 1.722(3)/1.723(3), and 1.7147(18) Å, respectively. It is possible that this is due to the decreasing charge localizing nature of the metal cations (and hence increasing negative hyperconjugation) as group 1 is descended.

Metalation of the free phosphine-boranes **1H**, **2H**, and **3H** also leads to a significant upfield shift in the ^{31}P and a small downfield shift in the ^{11}B NMR resonances (Table 2); for example, the $^{31}P\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectra of **1H** exhibit a broad quartet at 34.0 and a broad doublet at −43.2 ppm, respectively, while the $^{31}P\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectra of **1Li** exhibit a broad quartet at 17.8 and a broad doublet at −39.4 ppm, respectively). While it is necessary to exercise caution when comparing the ^{31}P and ^{11}B chemical shifts for a given ligand, due to the potential impact of the different solvents used on the ligand coordination mode and aggregation state of the complex, it is noticeable that, for each ligand, decreasing electronegativity of the metal center is associated with a small downfield shift of the ^{31}P signal and a small upfield shift of the ^{11}B signal.

In addition, metalation causes a significant increase in the $^{11}B-^{31}P$ coupling constant such that, for example, J_{PB} increases from 58.1 Hz in **1H** to 96.5 Hz in **1Li**. This is consistent with our

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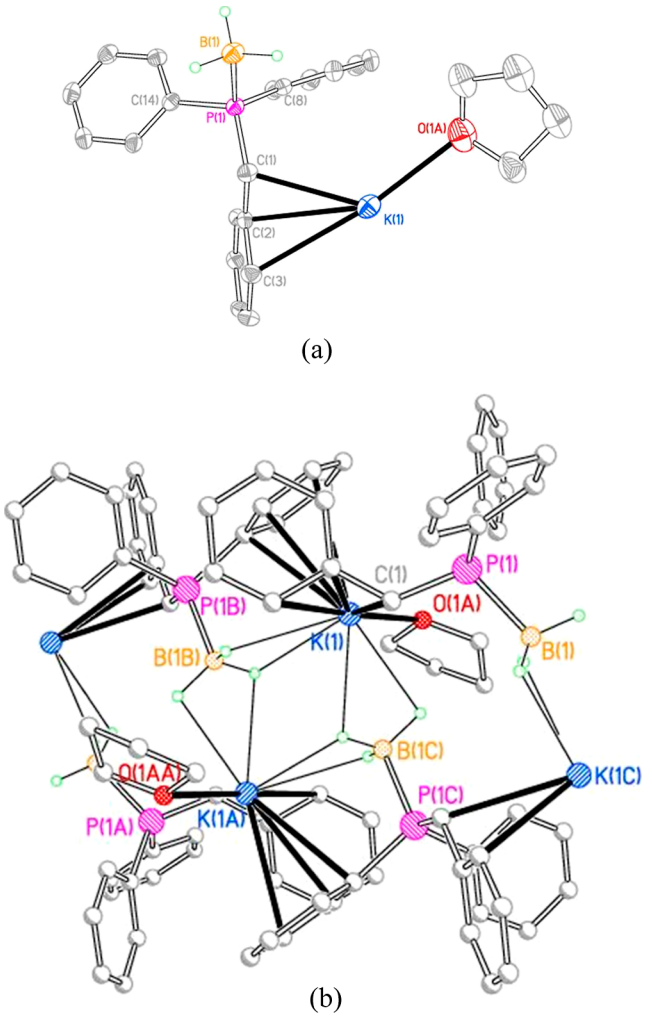

Figure 5. Solid-state structures of (a) the asymmetric unit and (b) the extended ribbon polymer network of **2K**, with C-bound H atoms and disorder component omitted for clarity and with 40% probability ellipsoids; B-bound H atoms were refined isotropically. Selected bond lengths (Å): K(1)−C(1) 3.0294(19), K(1)−H(1A) 2.80(3), K(1)−H(1B) 2.70(3), K(1A)−H(1C) 2.87(3), K(1A)−H(1A) 2.94(2), K(1)···B(1B) 3.325(2), K(1)···B(1C) 3.087(2), K(1)−O(1) 2.820(5), P(1)−B(1) 1.928(2), P(1)−C(1) 1.7147(18), P(1)−C(8) 1.8326(19), P(1)−C(14) 1.8311(18).

previous observation that α-deprotonation of phosphine-boranes by organo-alkali metal reagents typically leads to an increase in the $^{11}B-^{31}P$ coupling constant of between 30 and 50 Hz.[4]

In previous reports, we have shown that dialkylstannylenes may be isolated from the reaction between either $SnCl_2$ or Cp_2Sn and two equivalents of the corresponding lithium PBC complex.[8] We have isolated several complexes of this type using PBC ligands possessing additional stabilization by silyl substituents (**I**–**III**, Chart 1). However, until now, we have isolated only a single example of a stannylene possessing a benzylic PBC ligand: the reaction between $SnCl_2$ and one equivalent of the dicarbanion complex $[1,2\text{-}C_6H_4\{CHPCy_2(BH_3)\}_2]Li_2$ unexpectedly gave the unusual bridged stannyl−stannylene $[1,2\text{-}C_6H_4\{CHPCy_2(BH_3)\}_2]_2Sn_2{\cdot}0.5PhMe$ (**IV**).[9]

The reaction between 2 equiv of either **1Li** or **3Li** and Cp_2Sn in toluene gave yellow crystals of the stannylenes $[\{R_2P(BH_3)\text{-}CHPh\}_2Sn]$ [R = *i*Pr (**1Sn**), Cy (**3Sn**)] (Scheme 2); unfortunately, we were unable to isolate a clean product from the corresponding reaction between 2 equiv of **2Li** and Cp_2Sn, under the same conditions. Compound **1Sn** is soluble in hydrocarbon solvents, including methylcyclohexane, whereas **3Sn** has limited solubility in these solvents, once crystallized, but is sufficiently soluble in THF for characterization by NMR spectroscopy. Both **1Sn** and **3Sn** are sensitive to air and moisture and decompose on exposure to natural daylight or at elevated temperatures (>50 °C) to give elemental tin and the free phosphine−boranes **1H** and **3H**.

Both **1Sn** and **3Sn** are chiral at the central carbon atoms of the PBC ligands and these compounds are isolated as approximately 1:1 mixtures of the *rac* and *meso* diastereomers, according to NMR spectroscopy. This is most clearly shown in the $^{119}Sn\{^1H\}$ NMR spectrum of **3Sn**, which exhibits two broad singlets at rather similar chemical shifts [374 and 376 ppm; separate signals are not resolved in the $^{119}Sn\{^1H\}$ NMR spectrum of **1Sn**]. The similarity in ^{119}Sn chemical shifts between the *rac* and *meso* diastereomers of **3Sn** is in marked contrast to **I**, for which the ^{119}Sn chemical shifts are 587 and 787 ppm for the *rac* and *meso* diastereomers, respectively.[8a] We attribute the greater difference in ^{119}Sn chemical shift in the latter compound to the presence of a five-membered heterocycle, which would likely constrain the geometry at the Sn center more than would be the case in the acyclic compound **3Sn**, where the PBC ligands are free to rotate.

Table 1. Selected Bond Lengths (Å) for 1H, 2H, 1M, 2M, and 3M

	1H	1Li	1K	2H	2Li	2Na	2K	3Li	3K
P−C(H/M)	1.8295(16)	1.7433(19)	1.7418(18) 1.7426(14)	1.8248(16)	1.7430(13)	1.722(3) 1.723(3)	1.7147(18)	1.7403(14)	1.7424(11)
C(H/M)−C(Ph)	1.506(2)	1.453(3)	1.422(3) 1.424(2)	1.509(2)	1.4536(18)	1.440(4) 1.435(4)	1.433(3)	1.4458(19)	1.4314(14)
P−C(R)	1.8342(16) 1.8378(19)	1.8478(19) 1.8548(18)	1.8367(19) 1.8498(19) 1.8359(19) 1.8505(19)	1.8140(17) 1.8152(17)	1.8359(15) 1.8224(14)	1.839(2) 1.832(2) 1.835(3) 1.832(2)	1.8326(19) 1.8311(18)	1.8409(13) 1.8466(13)	1.8537(12) 1.8437(12)
P−B	1.9217(19)	1.924(2)	1.931(2) 1.936(2)	1.919(2)	1.9313(17)	1.930(3) 1.937(4)	1.928(2)	1.9349(16)	1.9365(13)
C−M		2.167(4)	3.5343(19) 3.0128(19) 3.0720(18) 3.5384(18)		2.259(3)	2.629(3) 2.657(3)	3.029(19)	2.267(3)	

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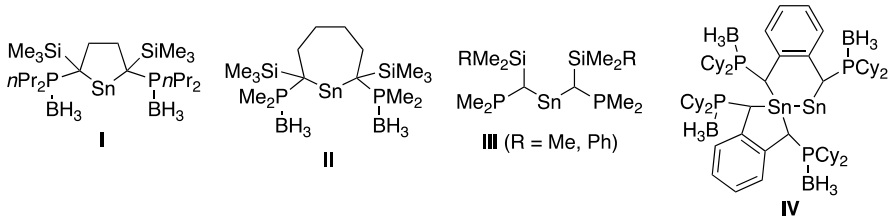
Table 2. Selected NMR Data for 1H, 2H, 3H, and Their Metalated Derivatives

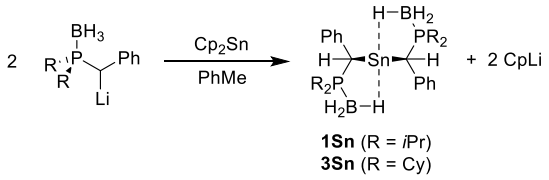
	1H	1Li	1Na	1K	2H	2Li	2Na	2K	3H	3Li	3Na	3K
solvent	$CDCl_3$	C_6D_6	d_8-toluene	d_8-THF	$CDCl_3$	d_8-toluene	d_8-toluene	C_6D_6	$CDCl_3$	d_8-toluene	C_6D_6/d_8-THF	d_8-THF
δ_P (ppm)	34.0	17.8	14.8	13.7	18.0	−2.0	−1.5	3.1	26.6	11.7	9.6	8.3
δ_B (ppm)	−43.2	−39.4	−39.8	−41.6	−39.1	−39.5	−35.0	−35.5	−42.5	−38.5	−38.6	−39.7
$J(^{11}B-^{31}P)$ (Hz)	58	97	[a]	81	58	76	[a]	78	57	87	89	80

[a]Coupling not resolved.

Chart 1. Previously Isolated Phosphine−Borane-Substituted Dialkylstannylenes



Scheme 2. Synthesis of the Stannylenes 1Sn (R = *i*Pr) and 3Sn (R = Cy)



The ^{119}Sn chemical shifts of **1Sn** and **3Sn** lie to significantly higher field than the chemical shifts of similarly sterically hindered dialkylstannylenes which are strictly two-coordinate; for example the ^{119}Sn chemical shift of the cyclic dialkylstannylene $\{(Me_3Si)_2(CH_2)C\}_2Sn$ is 2323 ppm.[11] This, along with the similarity in the ^{119}Sn chemical shifts of **1Sn** and **3Sn**, despite the difference in solvent (d_8-toluene for **1Sn**, d_8-THF for **3Sn**) suggests that the B−H···Sn contacts observed in the solid state (see below) persist in solution, even in the presence of the strong donor solvent THF. The presence of two diastereomers for each compound is confirmed by ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy. The ^{1}H NMR spectra of **1Sn** and **3Sn** each exhibit a pair of doublets due to the benzylic CH group at 2.87 and 3.42 ppm (**1Sn**) and 2.77 and 2.91 ppm (**3Sn**) (satellites due to coupling to $^{117/119}$Sn are partially resolved on the signals for **1Sn**), consistent with the presence of both *rac* and *meso* diastereomers, while the corresponding $^{13}C\{^1H\}$ NMR spectra exhibit broad doublets at 21.7 and 23.2 ppm (**1Sn**) and 42.5 and 43.2 ppm (**3Sn**), although none of these exhibit satellite signals.

While both **1Sn** and **3Sn** crystallized as a mixture of diastereomers, only the *rac*-diastereomer of each compound was obtained in a form suitable for X-ray crystallography. Both *rac*-**1Sn** and *rac*-**3Sn** crystallize as discrete monomers; the shortest Sn···Sn distances are 5.886 and 7.613 Å for **1Sn** and **3Sn**, respectively (Figure 6). In each case, the tin atom and the methine hydrogen atoms of the central alkyl carbon are disordered over two positions, with similar occupancies in

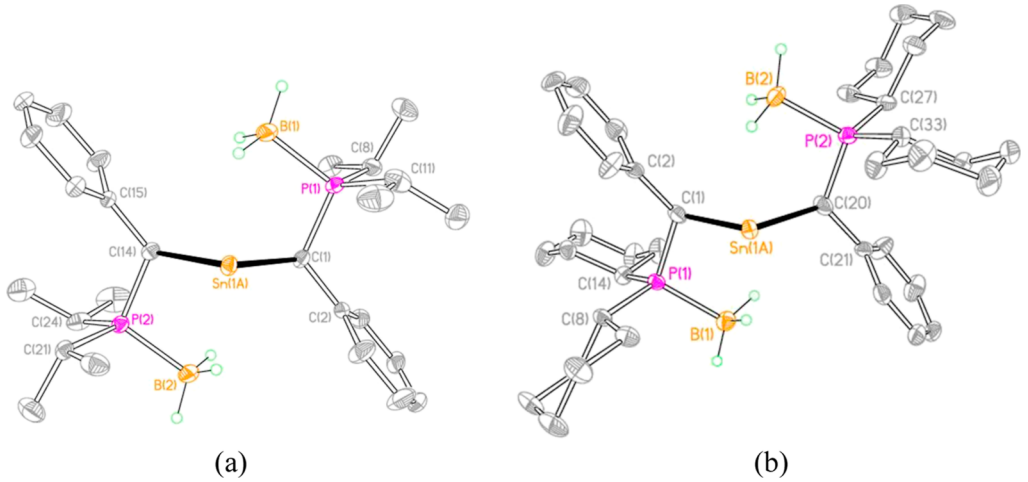


Figure 6. Molecular structures of (a) **1Sn** and (b) **3Sn** with disorder components and C-bound H atoms omitted for clarity and with 40% probability ellipsoids; B-bound H atoms were refined isotropically. Selected bond lengths (Å) and angles (deg): **1Sn** Sn(1A)−C(1) 2.268(5), Sn(1A)−C(14) 2309(5), C(1)−C(2) 1.500(6), C(14)−C(15) 1.501(7), C(1)−P(1) 1.807(5), C(14)−P(2) 1.805(5), C(8)−P(1) 1.847(6), C(11)−P(1) 1.830(8), C(21)−P(2) 1.830(7), C(24)−P(2) 1.845(6), P(1)−B(1) 1.924(7), P(2)−B(2) 1.915(7), C(1)−Sn(1A)−C(14) 95.09(18); **3Sn** Sn(1A)−C(1) 2.176(5), Sn(1A)−C(20) 2.274(4), C(1)−C(2) 1.488(6), C(20)−C(21) 1.499(6), C(1)−P(1) 1.798(4), C(20)−P(2) 1.806(5), C(8)−P(1) 1.835(4), C(14)−P(1) 1.836(4), C(27)−P(2) 1.829(4), C(33)−P(2) 1.836(5), P(1)−B(1) 1.921(5), P(2)−B(2) 1.924(5), C(1)−Sn(1A)−C(20) 101.39(17).

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each structure [Sn1A/Sn1B occupancy: 0.69/0.31 (**1Sn**), 0.62/0.38 (**3Sn**)]. In both structures the tin atoms are coordinated by the carbanion centers of two PBC ligands with a bent geometry at tin (the C−Sn−C angles for the major disorder components are 95.09(18)° (**1Sn**) and 101.39(17)° (**3Sn**)); these angles are similar to the C−Sn−C angles in the acyclic compounds *rac*-**III** [99.60(17)° (R = Ph) and 98.26(6)° (R = Me)]. The Sn−C distances [**1Sn**: 2.268(5), 2.309(5) Å; **3Sn**: 2.176(5), 2.274(4) Å] are similar to the Sn−C distances in other Sn PBC complexes;[8] for example, the Sn−C distances in *rac*-**I** and *rac*-**III** (R = Me) are 2.2984(14) and 2.3046(14) Å, and 2.3149(16) and 2.2864(16) Å, respectively.[8a,d] In addition, each tin atom has short contacts to one H atom within each BH_3 group [**1Sn**: Sn(1)···H(1C) 2.39(8), Sn(1)···H(2A) 2.57(7); **3Sn**: Sn(1)···H(1A) 2.40(4), Sn(1)···H(2C) 2.35(4) Å]. Thus, it appears that the presence of the significantly charge-delocalizing phenyl ring adjacent to the carbanion centers has little impact on the structures of the corresponding stannylenes, in comparison to their triorganosilyl-substituted analogues.

CONCLUSIONS

The benzyl-substituted phosphine−boranes **1H**, **2H**, and **3H** are readily metalated by *n*BuLi, $PhCH_2Na$, or $PhCH_2K$ to give the corresponding alkali metal complexes. While the presence of a benzyl substituent has little impact on the structures of the lithium and sodium derivatives **1Li**, **2Li**, **3Li**, and **2Na**, which crystallize as monomers or dimers, the structures of the potassium complexes **1K**, **2K**, and **3K** are dominated by multihapto interactions between the potassium cations and the phenyl rings of the benzyl groups in each case. The lithium complexes **1Li** and **3Li** are useful reagents for the synthesis of the dialkylstannylenes [$\{R_2P(BH_3)CHPh\}_2Sn$] (R = *i*Pr (**1Sn**), Cy (**3Sn**)). Both **1Sn** and **3Sn** were isolated as a mixture of *rac* and *meso* diastereomers, although only the *rac* isomers were amenable to structural characterization in each case. The solid-state structures of *rac*-**1Sn** and *rac*-**3Sn** reveal two agostic-type B−H···Sn interactions for both compounds; the presence of the phenyl substituent at the central carbon of the ligand appears to have little impact on the structures of these compounds in comparison to their triorganosilyl-substituted analogues.

EXPERIMENTAL PROCEDURE

General. All manipulations were carried out using standard Schlenk and drybox techniques under an atmosphere of dry nitrogen or argon. THF, diethyl ether, toluene, *n*-hexane, methylcyclohexane, 1,4-dioxane, and light petroleum (bp 40−60 °C) were dried prior to use by distillation under nitrogen from sodium, potassium, or sodium/potassium alloy, as appropriate. THF was stored over activated 4A molecular sieves; all other solvents were stored over a potassium film. Deuterated benzene, toluene, and THF were distilled from potassium and $CDCl_3$ was distilled from CaH_2 under argon; all NMR solvents were deoxygenated by three freeze−pump−thaw cycles and were stored over activated 4A molecular sieves. Benzylsodium,[12] benzylpotassium,[13] Cp_2Sn,[14] $iPr_2P(BH_3)H$,[15] $Ph_2P(BH_3)H$,[16] and $Cy_2P(BH_3)H$[17] were prepared according to previously published procedures. *n*-Butyllithium was purchased from Aldrich as a 2.5 M solution in hexanes and its concentration accurately determined by titration before use; *i*PrMgBr and $PhCH_2MgBr$ were purchased from Aldrich as 1.0 M solutions in diethyl ether; $BH_3{\cdot}SMe_2$ was purchased from Aldrich as a 2.0 M solution in THF. All other compounds were used as supplied by the manufacturer.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Avance III 500 spectrometer operating at 500.16 and 125.65 MHz, respectively, or a Bruker Avance III 300 spectrometer operating at 300.13 and 75.48 MHz, respectively; chemical shifts are quoted in ppm relative to tetramethylsilane. ^7Li, $^{31}P\{^1H\}$, $^{11}B\{^1H\}$ and $^{119}Sn\{^1H\}$ NMR spectra were recorded on a Bruker Avance III 500 spectrometer operating at 194.38, 202.35, 160.47, and 186.59 MHz, respectively; chemical shifts are quoted in ppm relative to external 0.1 M LiCl, 85% H_3PO_4, $BF_3{\cdot}OEt_2$, and Me_4Sn, respectively. Due to the air sensitivity of **1Li**, **2Li**, **3Li**, **1Na**, **2Na**, **3Na**, **1K**, **2K**, **3K**, **1Sn**, and **3Sn** consistent elemental analyses were not obtained; evidence of purity for these compounds is furnished by their comprehensive NMR spectroscopic characterization.

*$iPr_2P(BH_3)CH_2Ph$ (**1H**). Method 1.* To a solution of *i*PrMgBr (160 mL, 1.0 M in Et_2O, 160 mmol) was added 1,4-dioxane (7.04 g, 80.0 mmol) and this mixture was stirred for 15 min. The solution was filtered and the filtrate was added dropwise to a solution of PCl_3 (10.98 g, 80.0 mmol) in Et_2O (100 mL) and this mixture was stirred for 2 h. To this solution was added $PhCH_2MgBr$ (80 mL, 1.0 M in Et_2O, 80.0 mmol) dropwise, and this mixture was stirred for 2 h. To this solution was added $BH_3{\cdot}SMe_2$ (40 mL, 2.0 M solution in THF, 80.0 mmol) and this mixture was stirred for 2 h. Water (150 mL) was added and the organic phase was extracted into Et_2O (3 × 100 mL), the combined organic extracts were washed with brine (100 mL), dried over $MgSO_4$, filtered, and the solvent was removed in vacuo from the filtrate to give **1H** as a white oily solid. Crystallization from cold (−30 °C) light petroleum gave colorless crystals suitable for X-ray crystallography. Yield 11.54 g, 65%.

Method 2. To a solution of $iPr_2PH(BH_3)$ (2.66 g, 20.1 mmol) in THF (30 mL) was added *n*BuLi (8.54 mL of a 2.35 M solution in hexanes, 20.1 mmol) and this mixture was stirred for 1 h at room temperature. The resulting solution was added dropwise to a solution of benzyl bromide (2.39 mL, 20.1 mmol) in THF (30 mL) and the mixture was stirred for 16 h at room temperature. To this mixture was added water (30 mL) and the organic phase was extracted into Et_2O (3 × 20 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and the solvent was removed in vacuo from the filtrate to give a colorless oily solid. Yield: 3.26 g, 73%. Anal. Calcd: C, 70.3; H, 10.9%. Found: C, 69.7; H, 9.7%. $^1H\{^{11}B\}$ NMR ($CDCl_3$, 25 °C): δ 0.42 (d, J_{PH} = 15.0 Hz, 3H, BH_3), 1.10 (dd, J_{PH} = 7.2, J_{HH} = 1.2 Hz, 6H, $CHMe\mathit{Me}$), 1.14 (dd, J_{PH} = 7.2, J_{HH} = 1.5 Hz, 6H, $CH\mathit{Me}Me$), 1.97 (m, 2H, $C\mathit{H}Me_2$), 3.03 (d, J_{PH} = 11.4 Hz, 2H, CH_2P), 7.15−7.28 (m, 5H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 17.0, 17.1 ($CH\mathit{Me}Me$), 21.7 (d, J_{PC} = 31.6 Hz, $CHMe_2$), 28.3 (d, J_{PC} = 27.8 Hz, CH_2P), 126.8 (d, J_{PC} = 2.2 Hz, Ph), 128.5 (d, J_{PC} = 1.8 Hz, Ph), 129.9 (d, J_{PC} = 3.8 Hz, Ph), 133.5 (d, J_{PC} = 5.4 Hz, Ph). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ −43.2 (d, J_{PB} = 58.1 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 34.0 (q, J_{PB} = 58.1 Hz).

*$Ph_2P(BH_3)CH_2Ph$ (**2H**).* To a solution of $Ph_2PH(BH_3)$ (5.0 g, 25.0 mmol) in Et_2O (100 mL) was added *n*BuLi (10.2 mL, 2.45 M solution in hexane, 25.0 mmol) and this mixture was stirred for 15 min. This solution was added to a solution of $PhCH_2Br$ (4.27 g, 25.0 mmol) in Et_2O (20 mL) and this mixture was stirred for 2 h. Water (50 mL) was added and the organic phase was extracted into Et_2O (3 × 60 mL). The organic extract was washed with brine (50 mL), dried over $MgSO_4$, filtered, and the solvent was removed in vacuo from the filtrate to give **2H** as a white solid. Crystallization from hot ethanol gave colorless block crystals suitable for X-ray crystallography. Yield 6.16 g, 85%. Anal. Calcd: C, 78.7; H, 7.0%. Found: 77.9; H, 7.2%. $^1H\{^{11}B\}$ NMR ($CDCl_3$, 25 °C): δ 0.99 (d, J_{PH} = 15.9 Hz, 3H, BH_3), 3.62 (d, J_{PH} = 12.0 Hz, 2H, CH_2P), 6.94−7.68 (m, 15H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 34.2 (d, J_{PC} = 32.1 Hz, CH_2P), 127.0 (d, J_{PC} = 3.0 Hz, Ph), 128.13 (d, J_{PC} = 2.5 Hz, Ph), 128.7 (d, J_{PC} = 9.8 Hz, Ph), 128.8 (d, J_{PC} = 54.0 Hz, Ph), 130.3 (d, J_{PC} = 4.5 Hz, Ph), 131.4 (d, J_{PC} = 2.3 Hz, Ph), 131.9 (d, J_{PC} = 4.4 Hz, Ph), 132.7 (d, J_{PC} = 8.8 Hz, Ph). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ −39.1 (d, J_{PB} = 57.9 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 18.0 (q, J_{PB} = 57.9 Hz).

*$Cy_2P(BH_3)CH_2Ph$ (**3H**).* To a solution of Cy_2PH (4.20 mL, 19.2 mmol) in THF (30 mL) was added $BH_3{\cdot}SMe_2$ (9.58 mL, 19.2 mmol) and this mixture was stirred for 1 h at room temperature. To this mixture was added *n*BuLi (7.67 mL of a 2.5 M solution in hexanes, 19.2 mmol) and this solution was stirred for 1 h at room temperature. This solution was added dropwise to a solution of benzyl bromide (2.29 mL, 19.2 mmol) in THF (30 mL) and this mixture was stirred for 16 h at room temperature. To this mixture was added water (30 mL) and the organic phase was extracted into dichloromethane (3 × 20 mL). The

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combined organic extracts were dried over $MgSO_4$, filtered, and the solvent was removed in vacuo from the filtrate to give a colorless solid. Single crystals suitable for X-ray crystallography were obtained from cold (0 °C) toluene. Isolated yield: 4.89 g, 84%. Anal. Calcd: C, 75.5; H, 10.7%. Found: C, 75.8; H, 10.1%. $^1H\{^{11}B\}$ NMR ($CDCl_3$, 25 °C): δ 0.40 (d, J_{PH} = 15.0 Hz, 3H, BH_3), 1.19−1.84 (m, 22H, PCy_2), 3.04 (d, J_{PH} = 11.4 Hz, 2H, CH_2P), 7.21−7.32 (m, 5H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 26.1, 26.9, 27.0, 27.1, 27.1 (Cy), 28.2 (d, J_{PC} = 30.9 Hz, CH_2P), 31.7 (d, J_{PC} = 28.2 Hz, Cy), 126.9 (d, J_{PC} = 2.2 Hz, Ph), 128.5 (d, J_{PC} = 1.7 Hz, Ph), 130.0 (d, J_{PC} = 15.0 Hz), 133.8 (d, J_{PC} = 5.5 Hz, Ph). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ −42.5 (d, J_{PB} = 57.3 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 26.6 (m).

*[{iPr$_2$P(BH$_3$)CHPh}Li(THF)]$_2$ (**1Li**).* To a solution of **1H** (0.88 g, 4.0 mmol) in THF (30 mL) was added *n*BuLi (1.6 mL, 2.47 M solution in hexane, 4.0 mmol) and this mixture was stirred for 30 min. The solvent was removed in vacuo to give a red oily solid, which was crystallized from cold (−25 °C) methylcyclohexane (10 mL) to give red crystals suitable for X-ray crystallography. Yield 0.4 g, 33%. $^1H\{^{11}B\}$ NMR (C_6D_6, 25 °C): δ 0.70 (d, J_{PH} = 15.9 Hz, 3H, BH_3), 1.23−1.34 (m, 16H, Me_2CH + THF), 1.74 (m, 4H, THF), 2.17 (d, J_{PH} = 1.2 Hz, 1H, PhC*H*), 2.21 (m, 2H, Me_2CH), 3.48 (m, 4H, THF), 6.63 (m, 1H, Ph), 7.14 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 18.0 (*Me*MeCH), 18.4 (Me*Me*CH), 25.0 (MeMe*CH*), 25.3 (THF), 27.4 (d, J_{PC} = 47.9 Hz, *CH*Ph), 68.6 (THF), 115.1 (Ph), 121.3 (d, J_{PC} = 9.5 Hz, Ph), 129.4, 151.0 (Ph). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ 17.8 (m). $^{11}B\{^1H\}$ NMR (C_6D_6, 25 °C): δ −39.4 (d, J_{PB} = 96.5 Hz). $^7Li\{^1H\}$ NMR (C_6D_6, 25 °C): δ 1.0 (s).

*[{iPr$_2$P(BH$_3$)CHPh}Na(THF)] (**1Na**).* A solution of $PhCH_2Na$ (0.35 g, 3.0 mmol) in THF (20 mL) was added to a solution of **1H** (0.66 g, 3.0 mmol) in THF (20 mL) and this mixture was stirred for 30 min. The solvent was removed in vacuo to give **1Na** as an orange solid. Yield 0.85 g, 90%. $^1H\{^{11}B\}$ NMR (d_8-toluene, 25 °C): δ 0.35 (d, J_{PH} = 15.6 Hz, 3H, BH_3), 1.09−1.19 (m, 12H, *Me*Me*CH*), 1.40 (m, 4H, THF), 1.94−2.064 (m, 3H, Me_2CH + PhC*H*), 3.44 (m, 4H, THF), 6.21 (m, 1H, Ph), 6.87−6.88 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (d_8-toluene, 25 °C): δ 17.7 (*Me*MeCH), 18.3 (Me*Me*CH), 25.5 (d, J_{PC} = 36.8 Hz, MeMe*CH*), 25.5 (THF), 30.0 (d, J_{PC} = 62.8, *CH*Ph), 68.2 (THF), 111.3 (Ph), 119.1 (d, J_{PC} = 9.8 Hz, Ph), 129.2, 152.8 (Ph). $^{31}P\{^1H\}$ NMR (d_8-toluene, 25 °C): δ 14.8 (m). $^{11}B\{^1H\}$ NMR (d_8-toluene, 25 °C): δ −39.8 (br).

*[{iPr$_2$P(BH$_3$)CHPh}K]$_\infty$ (**1K**).* To a solution of **1H** (0.50 g, 2.24 mmol) in THF (20 mL) was dropwise added a solution of $PhCH_2K$ (0.34 g, 2.61 mmol) in THF (20 mL) and this mixture was stirred for 45 min at room temperature. The solvent was removed in vacuo and the resulting solid was crystallized from cold (−20 °C) toluene to yield orange crystals which were washed with cold (0 °C) light petroleum (3 × 5 mL). Yield: 0.28 g, 48%. ^1H NMR (d_8-THF, 25 °C): δ 0.42 (br. m, 3H, BH_3), 1.05 (br d, J_{PH} = 7.2 Hz, 6H, CHMe*Me*), 1.09 (dd, J_{PH} = 6.4, J_{HH} = 2.4 Hz, 6H, CH*Me*Me), 1.81 (m, 2H, C*H*Me$_2$), 1.92 (d, J_{PH} = 4.0 Hz, 1H, CHK), 5.68 (m, 1H, Ph), 6.48 (m, 2H, Ph), 6.57 (m, 2H. Ph). $^{13}C\{^1H\}$ NMR (d_8-THF, 25 °C): δ 17.7 (CHMe*Me*), 18.6 (CH*Me*Me), 26.8 (d, J_{PC} = 36.6 Hz, *C*HMe$_2$), 35.0 (d, J_{PC} = 74.1 Hz, CHK), 108.0 (Ph), 118.2 (br. Ph), 128.9 (Ph), 155.0 (d, J_{PC} = 8.9 Hz, Ph). $^{11}B\{^1H\}$ NMR (d_8-THF, 25 °C): δ −41.6 (d, J_{PB} = 81.1 Hz). $^{31}P\{^1H\}$ NMR (d_8-THf, 25 °C): δ 13.7 (q, J_{PB} = 81.1 Hz).

*[{Ph$_2$P(BH$_3$)CHPh}Li(OEt$_2$)$_2$] (**2Li**).* To a solution of **2H** (1.16 g, 4.0 mmol) in Et_2O (40 mL) was added *n*BuLi (1.6 mL, 2.47 M solution in hexane, 4.0 mmol) and this mixture was stirred for 30 min. The solvent was removed in vacuo to give an orange solid, which was crystallized from cold (−25 °C) Et_2O (10 mL) to give orange crystals of **2Li** suitable for X-ray crystallography. Yield 1.20 g, 65%. $^1H\{^{11}B\}$ NMR (d_8-toluene, 25 °C): δ 0.88 (t, 12H, Et_2O), 1.47 (d, J_{PH} = 14.4 Hz, 3H, BH_3), 2.69 (br d, J_{PH} = 1.8 Hz, 1H, C*H*Ph), 3.08 (q, 8H, Et_2O), 6.49 (m, 1H Ph), 6.95 (m, 2H, Ph, 7.05 (m, 8H, Ph), 7.93 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (d_8-toluene, 25 °C): δ 14.7 (Et_2O), 30.5 (d, J_{PC} = 51.5 Hz, CHPh), 65.5 (Et_2O), 115.5 (Ph), 121.6 (d, J_{PC} = 12.0 Hz, Ph), 128.2 (d, J_{PC} = 9.3 Hz, Ph), 129.0, 129.4 (Ph), 132.6 (d, J_{PC} = 8.9 Hz, Ph), 136.6 (d, J_{PC} = 51.6 Hz, Ph), 149.0 (Ph). $^{31}P\{^1H\}$ NMR (d_8-toluene, 25 °C): δ −2.0 (m). $^{11}B\{^1H\}$ NMR (d_8-toluene, 25 °C): −39.5 (d, J_{PB} = 76 Hz). $^7Li\{^1H\}$ NMR (d_8-toluene, 25 °C): δ −4.5 (s).

*[{Ph$_2$P(BH$_3$)CHPh}Na(THF)$_2$]$_2$ (**2Na**).* A solution of $PhCH_2Na$ (0.46 g, 4.0 mmol) in THF (20 mL) was added to a solution of **2H** (1.16 g, 4.0 mmol) in THF (20 mL) and this mixture was stirred for 30 min. The solvent was removed in vacuo to give an oily solid which was crystallized from toluene containing a few drops of THF at room temperature to give orange crystals of **2Na** suitable for X-ray crystallography. Yield 0.9 g, 48%. $^1H\{^{11}B\}$ NMR (d_8-toluene, 25 °C): δ 1.27 (br s, 3H, BH_3), 1.35 (m, 8H, THF), 2.73 (d, J_{PH} = 10.8 Hz, 1H, *CH*Ph), 3.35 (m, 8H, THF), 6.35 (m, 1H, Ph), 6.92 (m, 4H, Ph), 6.71 (m, 6H, Ph), 7.95 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (d_8-toluene, 25 °C): δ 25.5 (THF), 33.0 (d, J_{PC} = 71.0 Hz, *CH*Ph), 68.0 (THF), 112.9 (Ph), 119.8 (d, J_{PC} = 12.2 Hz, Ph), 128.2 (d, J_{PC} = 9.5 Hz, Ph), 129.1 (m, Ph), 132.5 (d, J_{PC} = 9.2 Hz, Ph), 137.3 (d, J_{PC} = 53.3 Hz, Ph), 150.1 (d, J_{PC} = 2.5 Hz, Ph). $^{31}P\{^1H\}$ NMR (d_8-toluene, 25 °C): δ −1.5 (m). $^{11}B\{^1H\}$ NMR (d_8-toluene, 25 °C): δ −35.0 (br).

*[{Ph$_2$P(BH$_3$)CHPh}K(THF)]$_\infty$ (**2K**).* A solution of $PhCH_2K$ (0.52 g, 4.0 mmol) in THF (20 mL) was added to a solution of **2H** (1.16 g, 4 mmol) in THF (20 mL) and this mixture was stirred for 30 min. The solvent was removed in vacuo to give an oily solid, which was crystallized from toluene containing a few drops of THF at room temperature to give yellow crystals of **2K** suitable for X-ray crystallography. Yield 1.5 g, 90%. $^1H\{^{11}B\}$ NMR (d_8-THF, 25 °C): δ 1.00 (d, J_{PH} = 14.1 Hz, 3H, BH_3), 1.78 (m, 1H, THF), 2.37 (d, J_{PH} = 13.8 Hz, 1H, C*H*Ph), 3.62 (m, 1H, THF), 5.84 (m, 1H, Ph), 6.43 (m, 2H, Ph), 6.54 (m, 2H, Ph), 7.20 (m, 6H, Ph), 7.76 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 26.4 (THF), 37.0 (d, J_{PC} = 83.3 Hz, CHPh), 68.3 (THF), 109.5, 118.8, 119.0 (Ph), 128.0 (d, J_{PC} = 9.1 Hz, Ph), 128.8 (d, J_{PC} = 9.0 Hz, Ph), 133.0 (d, J_{PC} = 9.0 Hz, Ph), 139.9 (d, J_{PC} = 50.3 Hz, Ph), 152.1 (d, J_{PC} = 7.2 Hz, Ph). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ 3.1 (m). $^{11}B\{^1H\}$ NMR (C_6D_6, 25 °C): δ −35.5 (d, J_{PB} = 78 Hz).

*[[Cy$_2$P(BH$_3$)CHPh]Li(TMEDA)] (**3Li**).* To a solution of **3H** (1.00 g, 3.3 mmol) in THF (30 mL) was added *n*BuLi (1.43 mL of a 2.3 M solution in hexanes, 3.3 mmol) followed by TMEDA (0.49 mL, 3.3 mmol) and this mixture was stirred for 1 h at room temperature. The solvent was removed in vacuo and the resulting solid was crystallized from cold (−5 °C) methylcyclohexane to yield yellow crystals of **3Li** suitable for X-ray crystallography. Yield: 1.07 g, 77%. ^1H NMR (d_8-toluene, 25 °C): δ 0.84 (m, 3H, BH_3), 1.17−2.12 (m, 39H, PCy_2 + CHLi + NMe_2 + NCH_2), 6.49 (m, 1H, Ph), 7.00−7.08 (m, 4H, ArH). $^{13}C\{^1H\}$ NMR (d_8-toluene, 25 °C): 26.9 (d, J_{PC} = 1.4 Hz, PCy_2), 27.8 (d, J_{PC} = 3.0 Hz, PCy_2), 27.9, 28.0 (PCy_2), 28.2 (d, J_{PC} = 2.3 Hz, PCy_2), 28.4 (PCy_2), 35.6 (d, J_{PC} = 30.9 Hz, CHLi), 45.5 (NMe_2), 56.5 (CH_2N), 113.4 (Ph), 120.7 (d, J_{PC} = 9.7 Hz, Ph), 128.9, 152.4 (Ph). $^7Li\{^1H\}$ NMR (d_8-toluene, 25 °C): δ 0.5. $^{11}B\{^1H\}$ NMR (d_8-toluene, 25 °C): δ −38.5 (d, J_{PB} = 87 Hz). $^{31}P\{^1H\}$ NMR (d_8-toluene, 25 °C): δ 11.7 (q, J_{PB} = 87 Hz).

*[Cy$_2$P(BH$_3$)CHPh]Na (**3Na**).* To a solution of **3H** (0.5 g, 1.6 mmol) in THF (20 mL) was added a solution of $PhCH_2Na$ (0.18 g, 1.6 mmol) in THF (10 mL) and this mixture was stirred for 1 h. The solvent was removed in vacuo, the resulting solid was washed with light petroleum (5 mL), and the residual solvent was removed in vacuo to give **3Na** as a yellow powder. Yield 0.41 g, 79%. $^1H\{^{11}B\}$ NMR (C_6D_6/d_8-THF, 25 °C): δ 0.85 (d, J_{PH} = 12.6 Hz, 3H, BH_3), 1.14−1.32 (m, 7H, Cy), 1.60−2.18 (m, 18H, Cy + C*H*Ph), 6.28 (m, 1H, Ph), 6.92−7.02 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (C_6D_6/d_8-THF, 25 °C): δ 27.1 (Cy CH_2), 27.6 (d, J_{PC} = 2.3 Hz, Cy CH_2), 27.9 (d, J_{PC} = 6.0 Hz, Cy CH_2), 28.0 (d, J_{PC} = 5.7 Hz, Cy CH_2), 28.3 (Cy CH_2), 31.2 (d, J_{PC} = 60.3 Hz, CHPh), 36.1 (d, J_{PC} = 34.6 Hz, Cy CH), 110.7 (Ph), 119.1 (d, J_{PC} = 9.7 Hz, Ph), 128.4, 153.9 (Ph). $^{11}B\{^1H\}$ NMR (C_6D_6/d_8-THF, 25 °C): δ −38.6 (d, J_{PB} = 89.2 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6/d_8-THF, 25 °C): δ 9.6 (m).

*[{Cy$_2$P(BH$_3$)CHPh}K(PhMe)]$_n$ (**3K**).* To a solution of **3H** (0.50 g, 1.6 mmol) in THF (20 mL) was dropwise added a solution of $PhCH_2K$ (0.30 g, 2.30 mmol) in THF (20 mL) and this solution was stirred for 45 min at room temperature. The solvent was removed in vacuo and the resulting solid was extracted into warm (50 °C) toluene (30 mL) and filtered. The filtrate was concentrated in vacuo to approximately 10 mL and this solution was cooled to −30 °C for 2 days to yield yellow crystals of **3K**, which were washed with cold (0 °C) petrol (3 × 5 mL). Isolated yield: 0.62 g, 91%. ^1H NMR (d_8-THF, 25 °C): δ 0.44 (m, 3H, BH_3), 1.10−1.90 (m, 23H, PCy_2 + CHK), 2.31 (s, 1.5H, Ph*Me*), 5.67 (m, 1H,

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Ph), 6.45−6.57 (m, 4H, Ph), 7.06−7.31 (m, 2.5H, *Ph*Me). $^{13}C\{^1H\}$ NMR (d_8-THF, 25 °C): δ 27.4 (d, J_{PC} = 2.3 Hz, PCy_2), 27.7, 28.4, 28.4, 28.5 (PCy_2), 35.8 (d, J_{PC} = 73.5 Hz, CHK), 37.3 (d, J_{PC} = 36.9 Hz, *CH*PCy_2), 107.2, 126.1, 129.0, 129.7, 151.3 (Ph), 154.9 (d, J_{PC} = 9.7 Hz, Ph). $^{11}B\{^1H\}$ NMR (d_8-THF, 25 °C): δ −39.7 (d, J_{PB} = 80 Hz). $^{31}P\{^1H\}$ NMR (d_8-THF, 25 °C): δ 8.3 (q, J_{PB} = 80 Hz).

*[{iPr$_2$P(BH$_3$)CHPh}$_2$Sn] (**1Sn**).* To a solution of **1H** (3.1 g, 14 mmol) in Et_2O (50 mL) was added *n*BuLi (5.7 mL, 2.45 M solution in hexane, 14 mmol) and this mixture was stirred for 30 min. The solvent was removed in vacuo and the red solid was dissolved in toluene (40 mL). This solution was added to a solution of Cp_2Sn (1.75 g, 7 mmol) in toluene (30 mL) and this mixture was stirred for 10 min. The solution was filtered and the solvent was removed in vacuo from the filtrate to give an orange solid which was crystallized from warm (40 °C) methylcyclohexane (20 mL) to give orange crystals of a mixture of *rac*- and *meso*-**1Sn**. Yield 2.4 g, 61%. $^1H\{^{11}B\}$ NMR (C_6D_6, 25 °C): δ 0.61 (d, J_{PH} = 8.7 Hz, 12H, BH_3), 0.66−1.15 (m, 48H, *MeMe*CH), 1.70 (m, 4H, MeMe*CH*), 2.01 (m, 2H, MeMe*CH*), 2.12 (m, 2H, MeMe*CH*), 2.87 (d, J_{PH} = 12.6 Hz, 2H, *CH*Ph), 3.42 (d, J_{PH} = 11.1 Hz, 2H, *CH*Ph), 6.93−7.37 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 16.9 (d, J_{PC} = 1.2 Hz, *Me*MeCH), 17.2 (d, J_{PC} = 1.9 Hz, *Me*MeCH), 17.5, 18.3, 19.1 (*Me*MeCH), 21.7 (d, J_{PC} = 33.5 Hz, MeMeCH), 23.2 (d, J_{PC} = 30.2 Hz, MeMeCH), 25.6 (d, J_{PC} = 25.2 Hz, MeMeCH), 25.7 (d, J_{PC} = 25.6 Hz, MeMeCH), 41.0 (d, J_{PC} = 17.6 Hz, CHPh), 41.3 (d, J_{PC} = 13.9 Hz, CHPh), 124.6 (d, J_{PC} = 2.6 Hz, Ph), 124.9 (d, J_{PC} = 2.9 Hz, Ph), 128.8 (d, J_{PC} = 2.5 Hz, Ph), 128.9 (d, J_{PC} = 2.0 Hz, Ph), 129.6 (d, J_{PC} = 5.0 Hz, Ph), 130.3 (d, J_{PC} = 4.5 Hz, Ph), 139.8 (d, J_{PC} = 7.8 Hz, Ph), 140.3 (d, J_{PC} = 10.5 Hz, Ph). $^{31}P\{^1H\}$ NMR (d_8-toluene, 25 °C): δ 27.8 (m). $^{11}B\{^1H\}$ NMR (d_8-toluene, 25 °C): δ −43.6 (d, J_{PB} = 55.8 Hz). $^{119}Sn\{^1H\}$ NMR (d_8-toluene, 25 °C): δ 365 (s), and δ 366 (s).

*[{Cy$_2$P(BH$_3$)CHPh}$_2$Sn] (**3Sn**).* To a solution of **3H** (0.71 g, 2.33 mmol) in THF (20 mL) was added *n*BuLi (0.97 mL of a 2.4 M solution in hexanes, 2.33 mmol) and this mixture was stirred for 1/2 h at room temperature. The solvent was removed in vacuo and the sticky yellow solid was dissolved in toluene (20 mL). This solution was quickly added to a solution of Cp_2Sn (0.29 g, 1.17 mmol) in toluene (20 mL) and this mixture was stirred for 10 min. This mixture was filtered, the solvent was removed in vacuo from the filtrate, and the resulting sticky yellow solid was crystallized from cold (5 °C) diethyl ether as a mixture of *rac*- and *meso*-**3Sn**. Yield: 0.46 g, 54%. $^1H\{^{11}B\}$ NMR (d_8-THF, 25 °C): δ 0.19 (d, J_{PH} = 10.0 Hz, 6H, BH_3), 0.44 (d, J_{PH} = 11.0 Hz, 6H, BH_3), 1.05−2.25 (m, 44H, Cy), 2.77 (d, J_{PH} = 11.0 Hz, 2H, *CH*Ph), 2.91 (d, J_{PH} = 12.5 Hz, 2H, *CH*Ph), 6.92 (m, 2H, Ph), 7.00−7.15 (m, 14H, Ph), 7.23 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (d_8-THF, 25 °C): δ 27.1, 27.2 (Cy), 27.8−28.3 (m, Cy), 28.9, 29.5, 29.6 (Cy), 32.7 (d, J_{PC} = 30.4 Hz, Cy CH), 34.1 (d, J_{PC} = 29.6 Hz, Cy CH), 36.6 (d, J_{PC} = 26.3 Hz, Cy CH), 36.9 (d, J_{PC} = 29.1 Hz, Cy CH), 42.5 (d, J_{PC} = 15.0 Hz, CHPh), 43.2 (d, J_{PC} = 13.5 Hz, CHPh), 124.6, 124.6, 128.9, 129.1 (Ph), 130.4 (d, J_{PC} = 5.0 Hz, Ph), 130.8 (d, J_{PC} = 4.5 Hz, Ph), 141.6 (d, J_{PC} = 7.4 Hz, Ph), 142.0 (d, J_{PC} = 10.3 Hz, Ph). $^{11}B\{^1H\}$ NMR (d_8-THF, 25 °C): δ −39.2 (br). $^{31}P\{^1H\}$ NMR (d_8-THF, 25 °C): 27.3 (m, br). $^{119}Sn\{^1H\}$ NMR (d_8-toluene, 25 °C): δ 376 (br), 374 (br).

X-Ray Crystallography. Crystal structure data sets for all compounds except **3K** were collected on an Oxford Diffraction Gemini A Ultra diffractometer using an Enhance Ultra X-ray Source ($\lambda_{CuK\alpha}$ = 1.54184 Å for **1Li**, **1Sn**, **2H**, **2Li**, **2Na**, and **2K**, and $\lambda_{MoK\alpha}$ = 0.71073 Å for **1H**, **1K**, **3Li**, and **3Sn**). Using an Oxford Cryosystems CryostreamPlus open-flow N_2 cooling device, data for all structures, except **3K**, were collected at 150 K; cell refinement, data collection, and data reduction were undertaken using CrysAlisPro.[18] For **3K**, data were collected at 100 K on a Crystal Logics kappa diffractometer with a Rigaku Saturn 724+ detector using synchrotron radiation (λ = 0.6889 Å); data processing used Rigaku CrystalClear and Bruker APEX2 software.[19] Analytical numeric absorption correction using a multi-faceted crystal model based on expressions derived by Clark and Reid[20] and/or semiempirical absorption corrections using spherical harmonics[21] were applied in each case. The structures were solved using SHELXT[22] and refined by SHELXL[23] through the Olex2 interface.[24] Carbon-bound hydrogen atoms were positioned with idealized geometry and their displacement parameters were constrained using a riding model; boron-bound hydrogen atoms were located in the Fourier difference map and refined freely.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.3c00468.

Details of structure determination, atomic coordinates, bond lengths and angles, and displacement parameters in CIF format. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of all compounds and ^7Li and $^{119}Sn\{^1H\}$ NMR spectra where applicable (PDF)

Accession Codes

CCDC 2305192−2305202 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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