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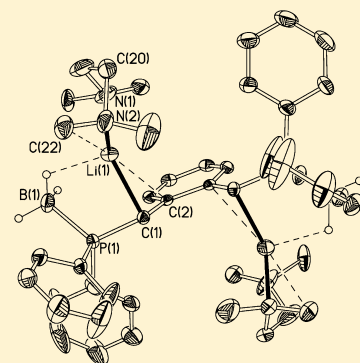
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S Supporting Information

ABSTRACT: The reaction between 1,2- $C_6H_4(CH_2Cl)_2$ and 2 equiv of in situ generated $[R_2P(BH_3)]Li$ in THF gives the corresponding *o*-phenylene-bridged bis(phosphine–boranes) 1,2- $C_6H_4\{CH_2P(BH_3)R_2\}_2$ ($R = iPr$ (**1a**), Ph (**2a**), Cy (**3a**)). Treatment of **1a–3a** with 2 equiv of *n*BuLi and 2 equiv of tmeda yields the corresponding phosphine–borane-stabilized carbanion (PBC) complexes $[1,2-C_6H_4\{CHP(BH_3)R_2\}_2][Li(tmeda)]_2 \cdot nL$ ($R = iPr$, $n = 0$ (**1b**); $R = Ph$, $nL = THF$ (**2b**); $R = Cy$, $nL = 2PhCH_3$ (**3b**)). In contrast, treatment of **1a** with 2 equiv of MeK, followed by 2 equiv of pmdeta, yields the monodeprotonation product $[1,2-C_6H_4\{CHP(BH_3)iPr_2\}\{CH_2P(BH_3)iPr_2\}][K(pmdeta)]$ (**1c**), due to a competing side reaction with the solvent. Treatment of **1a** and **3a** with the less aggressive metalating agent $PhCH_2K$ gives the corresponding dipotassium salts, the latter of which was isolated as the adduct $[1,2-C_6H_4\{CHP(BH_3)Cy_2\}_2][K(pmdeta)]_2$ (**3c**). X-ray crystallography reveals that **1b–3b** adopt similar structures in which the lithium ions are coordinated by the carbanion centers and the borane hydrogen atoms of the phosphine–borane-stabilized carbanions. The potassium ion in **1c** is coordinated by the carbanion center and by B–H...K contacts with both borane groups, whereas the two potassium ions in **3c** exhibit multihapto interactions with the aromatic ring of the PBC ligand, along with B–H...K contacts. The reaction between $ClSiMe_2CH_2CH_2SiMe_2Cl$ and 2 equiv of in situ generated $[R_2P(BH_3)CH_2]Li$ gives the bis(phosphine–boranes) $[CH_2SiMe_2CH_2P(BH_3)R_2]_2$ ($R = Me$ (**4a**), Ph (**5a**)). Treatment of **4a** or **5a** with 2 equiv of *n*BuLi in THF readily yields the 1,6-dicarbanion complexes $[CH_2SiMe_2CHP(BH_3)R_2]_2[Li(THF)_2]_2$ ($R = Me$ (**4b**), Ph (**5b**)). A similar reaction of **5a**, 2 equiv of $PhCH_2K$, and 2 equiv of pmdeta in THF gives the potassium complex $[CH_2SiMe_2CHP(BH_3)Ph]_2[K(pmdeta)]_2$ (**5c**). Complex **5b** adopts a linear structure in the solid state, while **5c** adopts an unusual polycyclic structure by virtue of bridging $K\cdots H-B-H\cdots K$ contacts.



■ INTRODUCTION

Phosphine–borane-stabilized carbanions (PBCs) have been used widely for the synthesis of polyfunctional phosphines, including chiral diphosphines such as DIPAMP, many of which have applications as supporting ligands in catalysis.¹ However, these carbanions are typically generated and used in situ and, until recently, little attention had been paid to their composition and structures. This is particularly notable, given that a $PMe_2(BH_3)$ group is isoelectronic and isosteric with a $SiMe_3$ group and that the latter substituent has played a key role in the development of main-group, transition-metal, and lanthanide organometallic and coordination chemistry, especially in the stabilization of new classes of compounds with, for example, unusually low coordination numbers or $E=M/E=E$ multiple bonds.²

Despite the isoelectronic nature of $SiMe_3$ and $PMe_2(BH_3)$ groups, silicon-stabilized carbanions and PBCs exhibit somewhat different characteristics in their metal complexes. For example, the residual hydridic character of the BH_3 hydrogen atoms in PBCs provides unique opportunities for the interaction of these groups with metal centers. This is evident

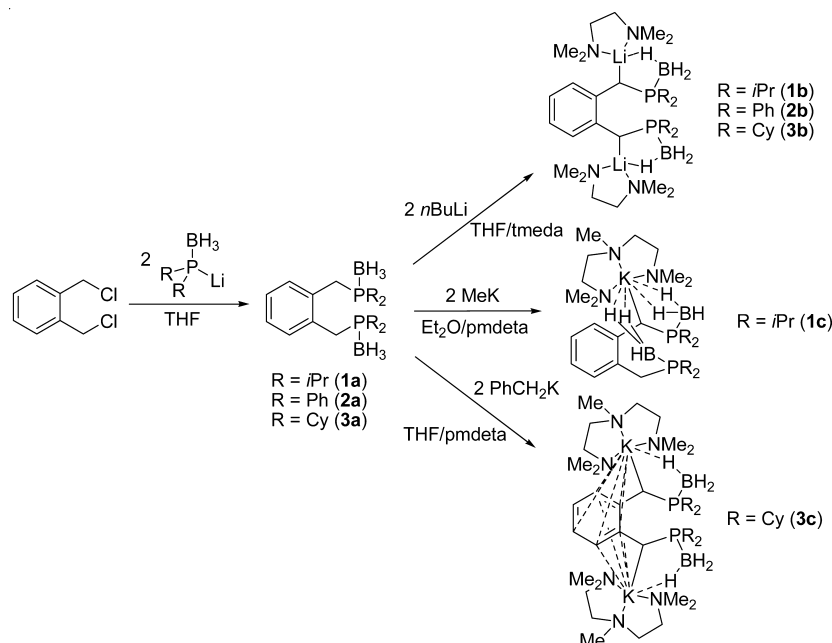
from the diversity of coordination modes adopted by PBC ligands: although a terminal C-donor mode has been observed, in the majority of cases B–H...M contacts are dominant, leading to an array of chelating and bridging coordination motifs.^{3–6} In addition, B–H...E contacts have been shown to significantly stabilize electron-deficient metal centers: DFT calculations suggest that the B–H...Sn and B–H...Pb contacts observed in a series of phosphine–borane-substituted dialkylstannylenes and -plumbylenes stabilize these compounds by around 30 kcal mol^{−1}.⁴ Furthermore, $Me_2P(BH_3)$ substituents stabilize an adjacent carbanion center to a greater degree in comparison to $SiMe_3$ groups by virtue of the more efficient negative hyperconjugation in the former. This has the consequence that C–H groups adjacent to a $PMe_2(BH_3)$ moiety are more acidic than those adjacent to a $SiMe_3$ group. As an illustration of this, $SiMe_4$ undergoes slow metalation with *n*BuLi only in the presence of activating tertiary amine donors such as tmeda,⁷ whereas isoelectronic $PMe_3(BH_3)$ reacts

Received: November 17, 2013

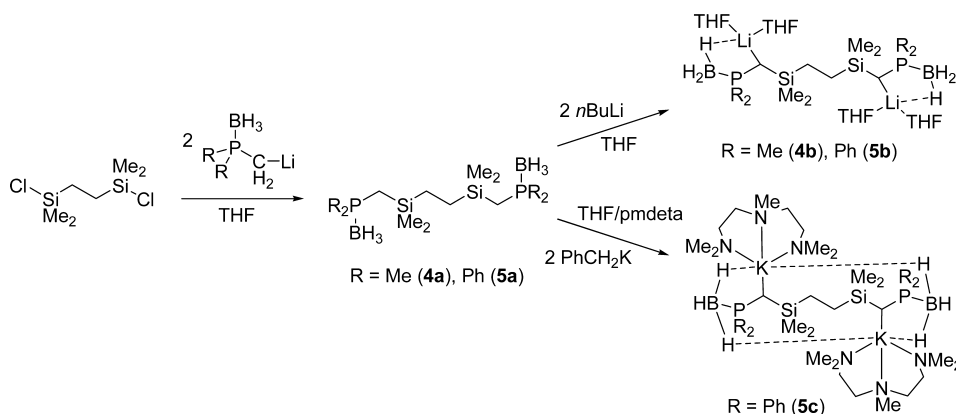
Published: December 19, 2013



Scheme 1



Scheme 2



rapidly with $n\text{BuLi}$ in the absence of such activators to give the corresponding phosphine–borane-stabilized carbanion complex $\text{Me}_2\text{P}(\text{BH}_3)\text{CH}_2\text{Li}$ (tmeda = N,N,N',N' -tetramethylethylenediamine).^{3e} A corollary of this enhanced acidity is that the corresponding PBCs are somewhat less nucleophilic than their silicon-stabilized counterparts and so are less likely to induce unwanted redox processes in their reactions with easily reducible metal centers such as $\text{Pb}(\text{II})$.⁴

Over the past few years we, and others, have developed a range of PBCs and have shown that these are excellent ligands for s-, p-, d-, and f-block metal centers.^{3–6,8} With very few exceptions, the PBCs reported previously fall into three categories: (i) monodentate ligands stabilized by a single phosphine–borane substituent $[\text{R}_2\text{CP}(\text{BH}_3)\text{R}_2]^-$,^{3b–g,1,4d,e,6} (ii) monodentate ligands stabilized by two adjacent phosphine–borane substituents $[\text{R}_2\text{P}(\text{BH}_3)\text{CHP}(\text{BH}_3)\text{R}_2]$,^{3j,k,m,n,5} or (iii) sterically demanding bidentate ligands in which each carbanion center is stabilized by a single phosphine–borane substituent, e.g. $[\text{R}_2\text{P}(\text{BH}_3)\text{CSiMe}_2(\text{SiMe}_3)\text{CH}_2\text{CH}_2\text{SiMe}_2(\text{Me}_3\text{Si})\text{CP}(\text{BH}_3)\text{R}_2]^{2-}$.^{3a,h,4a–c} In each of these cases the monodentate nature of the ligands and/or the flexibility of the linker group allows the phosphine–borane groups to tilt toward the metal

centers where necessary, maximizing the $\text{B}\cdots\text{H}\cdots\text{M}$ contacts; this is of particular importance in compounds where these contacts result in the significant stabilization of an electron-poor metal center (e.g., $\text{Sn}(\text{II})$ or $\text{Pb}(\text{II})$).⁴ We were interested to observe the effect that a rigid backbone might have on these contacts, since this should reduce the degree to which the borane groups can tilt toward the metal and thus substantially affect the nature of the $\text{B}\cdots\text{H}\cdots\text{M}$ interactions, and so have developed a new range of rigid *o*-phenylene-linked PBCs. In this contribution we describe the synthesis of the phosphine–borane precursors to these PBCs, their metalation, and the structures of their alkali-metal derivatives. For comparison, we also describe the synthesis of two new bis(phosphine–boranes) linked by a flexible spacer group and the metalation of these species to give the corresponding 1,6-dicarbanions.

RESULTS AND DISCUSSION

o-Phenylene-bridged bis(phosphine–boranes), $1,2\text{-C}_6\text{H}_4\{\text{CH}_2\text{P}(\text{BH}_3)\text{R}_2\}_2$, with a selection of substituents at phosphorus have previously been prepared as intermediates in the synthesis of *o*-xylyl-bridged diphosphines, ligands which have been successfully exploited in transition-metal-mediated

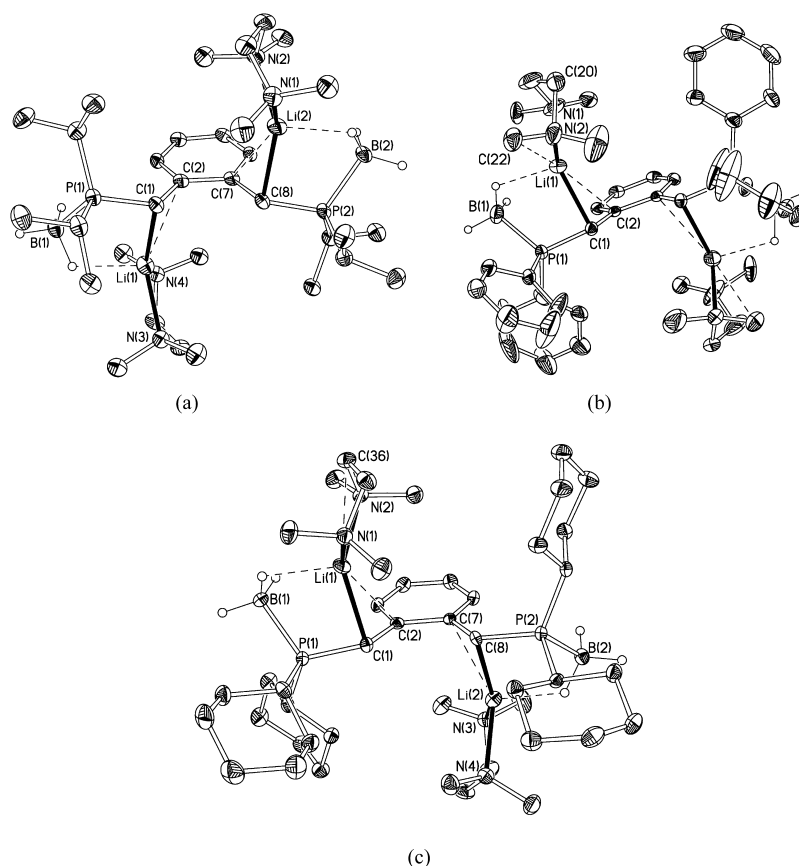


Figure 1. Molecular structures of (a) **1b**, (b) **2b**, and (c) **3b**, with 40% probability ellipsoids and with C-bound H atoms (except those bound to benzylic C atoms) omitted for clarity. Minor disorder components for **2b** and solvent of crystallization for **2b** and **3b** are also omitted for clarity. Selected bond lengths (Å) are as follows. **1b**: Li(1)–C(1) 2.235(5), Li(1)···C(2) 2.636(5), Li(1)–N(3) 2.147(5), Li(1)–N(4) 2.124(5), Li(1)–H(1C) 2.08(3), Li(1)···B(1) 2.763(6), Li(2)–C(8) 2.227(5), Li(2)···C(7) 2.626(5), Li(2)–N(1) 2.146(5), Li(2)–N(2) 2.110(5), Li(2)–H(2C) 2.03(2), Li(2)···B(2) 2.708(6), P(1)–B(1) 1.934(3), P(2)–B(2) 1.929(3). **2b**: Li(1)–C(1) 2.241(4), Li(1)···C(2) 2.701(4), Li(1)–N(1) 2.041(6), Li(1)–N(2) 2.094(5), Li(1)–H(1A) 2.05(2), Li(1)···B(1) 2.635(5), B(1)–P(1) 1.930(2). **3b**: Li(1)–C(1) 2.254(6), Li(1)···C(2) 2.700(6), Li(1)–N(1) 2.118(6), Li(1)–N(2) 2.047(6), Li(1)–H(1B) 2.09(3), Li(1)···B(1) 2.551(7), Li(2)–C(8) 2.271(6), Li(2)···C(7) 2.530(6), Li(2)–N(3) 2.123(6), Li(2)–N(4) 2.134(6), Li(2)–H(2A) 1.96(3), Li(2)···B(2) 2.695(7), P(1)–B(1) 1.937(4), P(2)–B(2) 1.951(4).

catalysis.⁹ However, until now the deprotonation of these compounds to give PBCs has not been investigated. In the current study, we have prepared the previously unreported bis(phosphine boranes) 1,2- $\text{C}_6\text{H}_4\{\text{CH}_2\text{P}(\text{BH}_3)\text{R}_2\}_2$ ($\text{R} = i\text{Pr}$ (**1a**), Ph (**2a**), Cy (**3a**)) according to the method used by Imamoto and co-workers for the synthesis of related bis-(phosphine–boranes) (e.g., $\text{R} = t\text{Bu}$).^{9a} The reactions between 1,2- $\text{C}_6\text{H}_4(\text{CH}_2\text{Cl})_2$ and 2 equiv of in situ generated $\text{R}_2\text{P}(\text{BH}_3)\text{Li}$ in THF gave **1a–3a** as air-stable, colorless solids after a straightforward aqueous workup (Scheme 1). In contrast, similar reactions between 1,2- $\text{C}_6\text{H}_4(\text{CH}_2\text{Br})_2$ and $\text{R}_2\text{P}(\text{BH}_3)\text{Li}$ under the same conditions gave complex mixtures of products, possibly arising from partial quaternization of the phosphorus centers.¹⁰ The linear bis(phosphine–boranes) $[\text{CH}_2\text{SiMe}_2\text{CH}_2\text{P}(\text{BH}_3)\text{R}_2]_2$ ($\text{R} = \text{Me}$ (**4a**), Ph (**5a**)) were prepared by the reaction between $\text{ClSiMe}_2\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Cl}$ and 2 equiv of $\text{R}_2\text{P}(\text{BH}_3)\text{CH}_2\text{Li}$ and were isolated as colorless, crystalline solids (Scheme 2). The ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **1a–5a** are as expected. The ^{31}P signals fall in a reasonably wide range (3.4–35.2 ppm), depending on the nature of the substituents at phosphorus, whereas the $^{11}\text{B}\{^1\text{H}\}$ signals fall in the narrow range –37.5 to –44.3 ppm; where resolved, the ^{31}P – ^{11}B coupling constants lie in the range 49.0–69.5 Hz, as expected for neutral phosphine–

borane adducts.^{1,3–6} In order to enable comparison with the metalated derivatives, compounds **1a** and **4a** were studied by X-ray crystallography; details of the structures of **1a** and **4a** may be found in the Supporting Information.

Treatment of THF solutions of **1a–3a** with 2 equiv of $n\text{BuLi}$, followed by 2 equiv of *tmeda*, gave the complexes $[1,2\text{-C}_6\text{H}_4\{\text{CHP}(\text{BH}_3)\text{R}_2\}_2][\text{Li}(\text{tmeda})]_2 \cdot n\text{Li}$ ($\text{R} = i\text{Pr}$, $n = 0$ (**1b**); $\text{R} = \text{Ph}$, $n\text{Li} = \text{THF}$ (**2b**); $\text{R} = \text{Cy}$, $n\text{Li} = 2\text{PhCH}_3$ (**3b**)) as yellow to orange crystals in good yield (Scheme 1). The ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$, and ^7Li NMR spectra of **1b–3b** are consistent with deprotonation at both of the benzylic sites in each case. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of these compounds consist of broad multiplets at 16.3 (**1b**), 6.2 (**2b**), and 12.3 ppm (**3b**), respectively. We have previously noted that α -metalation of phosphine–borane adducts leads to a significant increase in the ^{31}P – ^{11}B coupling constant of between 20 and 50 Hz. For **2b** no coupling was resolved; however, for **1b** and **3b** the ^{31}P – ^{11}B coupling constants are 78.4 and 105.3 Hz, respectively, consistent with the formation of a phosphine–borane-stabilized carbanion in each case.

In contrast to the foregoing, treatment of **1a** with 2 equiv of MeK in cold (–10 °C) diethyl ether does not result in double deprotonation of the bis(phosphine–borane); $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the crude reaction solution clearly indicate

monodeprotonation of **1a** under these conditions (Scheme 1). Addition of pmdeta to the reaction solution, removal of solvent, and crystallization from *n*-hexane gave the monodeprotonated compound 1,2- $\text{C}_6\text{H}_4\{\text{CHP}(\text{BH}_3)\text{iPr}_2\}\{\text{CH}_2\text{P}(\text{BH}_3)\text{iPr}_2\}[\text{K}(\text{pmdeta})]$ (**1c**) as pale yellow crystals in reasonable yield (pmdeta = *N,N,N',N'',N''*-pentamethyldiethylenetriamine). Since MeK is typically more reactive than *n*BuLi, we attribute the formation of **1c** to the competing reaction between MeK and the diethyl ether solvent.¹¹ This suggests that while the initial deprotonation of **1a** to give **1c** is rapid, deprotonation of the second benzylic site is rather sluggish, allowing the side reaction between MeK and the solvent to compete. In this regard, treatment of either **1a** or **1c** with 2 equiv of PhCH_2K , which does not react rapidly with the THF solvent, results in clean double deprotonation of the bis(phosphine–boranes), as judged by $^{31}\text{P}\{\text{H}\}$ NMR spectroscopy of the crude reaction mixtures, to give the corresponding dipotassium salts, the latter of which was isolated as the adduct $[1,2\text{-C}_6\text{H}_4\{\text{CHP}(\text{BH}_3)\text{-Cy}_2\}_2[\text{K}(\text{pmdeta})]_2$ (**3c**) as a yellow crystalline solid.

Compounds **1b–3b** crystallize as discrete monomers. These compounds adopt similar structures in the solid state but are not isostructural: while **1b** has no solvent of crystallization, **2b** crystallizes with a molecule of THF and **3b** crystallizes with two molecules of toluene in the asymmetric unit. For both **2b** and **3b** the solvent of crystallization is only weakly held and is rapidly lost under vacuum, such that samples of **2b** and **3b** which had been exposed to vacuum for 15 min showed no evidence of THF and toluene, respectively, in their NMR spectra.

The structures of **1b–3b** are shown in Figure 1, along with selected bond lengths. In **1b** each lithium ion is bound to one carbanion center, the two nitrogen atoms of a chelating molecule of tmeda, and one of the borane hydrogen atoms; in addition, each lithium ion has short contacts to one of the two ipso carbon atoms adjacent to a carbanion center of the PBC ligand. The two lithium ions lie on opposite faces of an essentially planar $\text{C}_6\text{H}_4(\text{CP})_2$ fragment. Compounds **2b** and **3b** adopt structures similar to that of **1b**; however, **2b** possesses a crystallographic C_2 axis, which bisects the *o*-phenylene linker group, and exhibits additional short contacts between each lithium ion and one of the methyl carbon atoms of the tmeda coligand ($\text{Li}\cdots\text{C}(22)$ 2.758(9) Å), while **3b** exhibits an additional short contact between one of the lithium ions and one of the methylene carbon atoms of the tmeda coligand ($\text{Li}(1)\cdots\text{C}(36)$ 2.751(5) Å).

The Li–C(carbanion) distances in **3b** (2.254(6) and 2.271(6) Å) are slightly longer than those in **1b** and **2b** (2.235(5) and 2.227(5) Å, and 2.241(4) Å, respectively), possibly due to the somewhat more sterically demanding cyclohexyl substituents in the former compound. Overall, the Li–C(carbanion) distances in **1b–3b** are somewhat longer than the corresponding distances in related benzyllithium compounds¹² but are similar to the Li–C distances in previously reported PBC complexes.³ For example, the Li–C distances in $[\text{Ph}(\text{Me}_2\text{tBuSi})\text{CH}]\text{Li}(\text{tmeda})$ ¹³ and $[\text{Ph}_2(\text{Me}_2\text{PhSi})\text{C}]\text{Li}(\text{THF})_2$ ¹⁴ are 2.141(4) and 2.124(3) Å, respectively, whereas the Li–C distances in $[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{Li}(\text{THF})_3$ ^{3b} and $(\text{THF})_2\text{Li}\{(\text{Me}_3\text{SiCH})_2\text{P}(\text{BH}_3)\text{-Ph}\}\text{Li}(\text{THF})_3$ ³ⁱ are 2.249(8) and 2.252(8) Å, and 2.218(3) and 2.234(3) Å, respectively. The Li–H distances (**1b**, 2.03(2), 2.08(3) Å; **2b**, 2.05(2) Å; **3b**, 1.96(3), 2.09(3) Å) and the Li \cdots B distances (**1b**, 2.763(6), 2.708(6) Å; **2b**, 2.635(5) Å; **3b**,

2.551(7), 2.695(7) Å) are consistent with an $\eta^1\text{-BH}_3\text{-Li}$ contact.

Compound **1c** also crystallizes as a discrete molecular species; the structure of **1c** is shown in Figure 2, along with

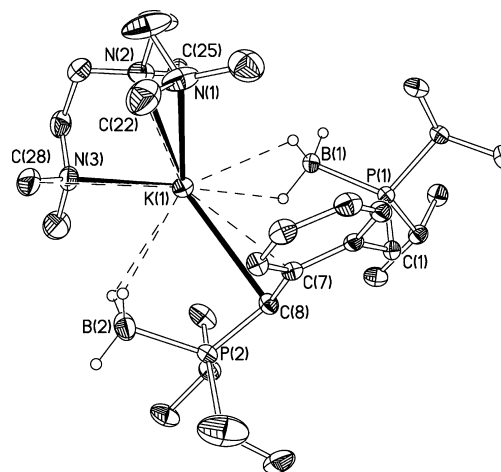


Figure 2. Molecular structure of **1c** with 40% probability ellipsoids and with C-bound H atoms omitted for clarity. Selected bond lengths (Å): K(1)–C(8) 3.211(2), K(1) \cdots C(7) 3.384(2), K(1)–N(1) 2.870(2), K(1)–N(2) 2.946(2), K(1)–N(3) 3.019(2), K(1)–H(1A) 2.75(3), K(1)–H(1C) 2.94(3), K(1)–H(2A) 3.05(3), K(1)–H(2C) 2.86(4), K(1) \cdots B(1) 3.319(3), K(1) \cdots B(2) 3.371(3), K(1) \cdots C(22) 3.535(3), K(1) \cdots C(25) 3.463(3), K(1) \cdots C(28) 3.426(3), P(1)–B(1) 1.924(2), P(2) \cdots B(2) 1.935(3).

selected bond lengths. The potassium ion is coordinated by the carbanion center, by two $\eta^2\text{-BH}_3$ contacts to the PBC ligand, and by the three nitrogen atoms of the pmdeeta coligand. In addition, there are short contacts between the potassium ion and the ipso carbon of the aromatic ring adjacent to the carbanion center and to three of the methyl groups of the pmdeeta coligand. The K–C(8) distance of 3.211(2) Å is at the longer end of previously reported K–C distances involving a benzylic carbanion center;^{12,15} for example, the K–C(carbanion) distance in $[(\text{PhCH}_2)\text{K}(\text{pmdeta})]_\infty$ is 3.171(2) Å,¹⁶ while the K–C(carbanion) distance in $[(\text{Me}_3\text{Si})\text{CH}]\text{-C}_6\text{H}_4\text{-2-NMe}_2[\text{K}]_\infty$ is 2.966(4) Å.¹⁷ However, the K–C(8) distance in **1c** is similar to the K–C distances in other potassium complexes of PBCs; for example, the K–C distances in $[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{K}(\text{tmeda})_2$ and $[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{K}(\text{pmdeta})_2$ are 3.107(3) and 3.440(3) Å, respectively.^{3f}

While $^{31}\text{P}\{\text{H}\}$ NMR spectroscopy of the crude reaction solutions clearly indicates that both **1a** and **1c** undergo double deprotonation at the benzylic sites on treatment with benzyllithium to give the bis(phosphine–boranes) $\text{C}_6\text{H}_4\{\text{CHP}(\text{BH}_3)\text{R}_2\}_2[\text{K}(\text{pmdeta})]_2$ ($\text{R} = \text{iPr}$ (**1d**), Cy (**3c**)), only the latter of these compounds was isolated as single crystals suitable for X-ray crystallography. The structure of **3c** is shown in Figure 3, along with selected bond lengths.

Compound **3c** crystallizes as discrete monomers but adopts a structure somewhat different from those of **1b–3b** and **1c**. As expected, the larger, more polarizable potassium ions in **3c** engender significantly increased multihapto interactions with the ligand. The two potassium ions lie in slightly different coordination environments: both potassium ions are coordinated by the three nitrogen atoms of a molecule of pmdeeta; K(1) has short contacts to one of the carbanion centers and five

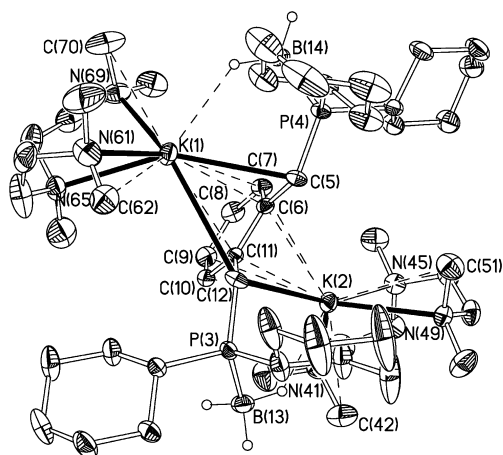


Figure 3. Molecular structure of **3c** with 40% probability ellipsoids. Minor disorder components and C-bound H atoms are omitted for clarity. Selected bond lengths (Å): K(1)–H(14C) 2.81(3), K(1)–C(5) 3.1588(18), K(1)–C(6) 2.8186(16), K(1)–C(7) 3.2770(18), K(1)–C(11) 3.0078(16), K(1)–C(12) 3.5132(19), K(1)–N(61) 2.8642(19), K(1)–N(65) 2.926(5), K(1)–N(69) 2.8168(18), K(1)–C(62) 3.412(4), K(1)–C(70) 3.382(3), K(2)–H(13C) 2.71(3), K(2)–C(6) 3.0262(17), K(2)–C(7) 3.3935(18), K(2)–C(9) 3.5176(19), K(2)–C(10) 3.1475(17), K(2)–C(11) 2.8807(16), K(2)–C(12) 3.446(2), K(2)–N(41) 2.8206(17), K(2)–N(45) 2.8913(17), K(2)–N(49) 2.9092(16), K(2)–C(42) 3.466(3), K(2)–C(51) 3.346(2), P(3)–B(13) 1.943(2), P(4)–B(14) 1.943(2).

of the carbon atoms in the aromatic ring of the ligand, whereas K(2) is coordinated by both carbanion centers and three of the carbon atoms of the aromatic ring. In addition, each potassium ion is coordinated by one H atom of an adjacent BH₃ group and the coordination of each potassium is completed by agostic-type K···Me–N contacts with the pmdeta coligand. The K(1)–C(5) distance of 3.1588(18) Å is similar to the K–C(carbanion) distance in **1c**; however, the K–C distances to the bridging carbanion center (K(1)–C(12) 3.5132(19), K(2)–C(12) 3.446(2) Å) are somewhat longer, as expected. Indeed, these latter distances are significantly longer than some of the K···C contacts to carbon atoms in the aromatic ring of the ligand (the K···C(aromatic) distances range from 2.8186(16) to 3.5176(19) Å).

The linear bis(phosphine–boranes) **4a** and **5a** readily undergo double deprotonation on treatment with 2 equiv of *n*BuLi in THF to give the complexes [CH₂SiMe₂CHP(BH₃)–R₂]₂[Li(THF)₂]₂ (R = Me (**4b**), Ph (**5b**)) (Scheme 2). Similarly, the reaction between **5a** and 2 equiv of PhCH₂K yields the potassium complex [CH₂SiMe₂CHP(BH₃)Ph]₂[K(pmdeta)]₂ (**5c**) after crystallization in the presence of the tertiary amine coligand.

Metalation of **4a** with *n*BuLi leads to a small upfield shift of the ³¹P NMR signal (**4a**, 3.4 ppm; **4b**, –4.8 ppm) and a small downfield shift of the ¹¹B NMR signal (**4a**, –37.5 ppm; **4b**, –33.0 ppm); metalation also leads to a significant increase in the ¹¹B–³¹P coupling constant (**4a**, 58.8 Hz; **4b**, 88.3 Hz). Upon metalation the ³¹P NMR signal of **5a** moves to higher field with decreasing electronegativity of the metal (**5a**, 13.5 ppm; **5b**, 12.5 ppm; **5c**, 11.7 ppm), while the ¹¹B NMR signal moves to slightly lower field with decreasing electronegativity of the metal (**5a**, –38.9 ppm; **5b**, –35.7 ppm; **5c**, –34.7 ppm). The ¹¹B–³¹P coupling constant increases significantly on metalation of **5a** and shows a slight increase with decreasing electronegativity of the metal center (**5a**, 69.5 Hz; **5b**, 107.9

Hz; **5c**, 113.8 Hz). This is consistent with our previous observation that α -metalation of phosphine–borane adducts leads to an increase in the ¹¹B–³¹P coupling constant of between 20 and 50 Hz.³

We have thus far been unable to isolate crystals of **4b** suitable for X-ray crystallography; however, **5b,c** were isolated as colorless blocks and their solid-state structures were obtained. Compounds **5b,c** both crystallize as discrete molecular species, although they adopt quite distinct structures in the solid state; the molecular structures of **5b,c** are shown in Figure 4, along with selected bond lengths. Compound **5b** crystallizes with a center of inversion midway along the C(2)–C(2') vector; the C(2) atoms and their symmetry equivalents are disordered over two positions with equal occupancy. The lithium ions in **5b** are coordinated by the carbanion centers, by an η^1 -BH₃ group, and by the oxygen atoms of two molecules of THF, affording a

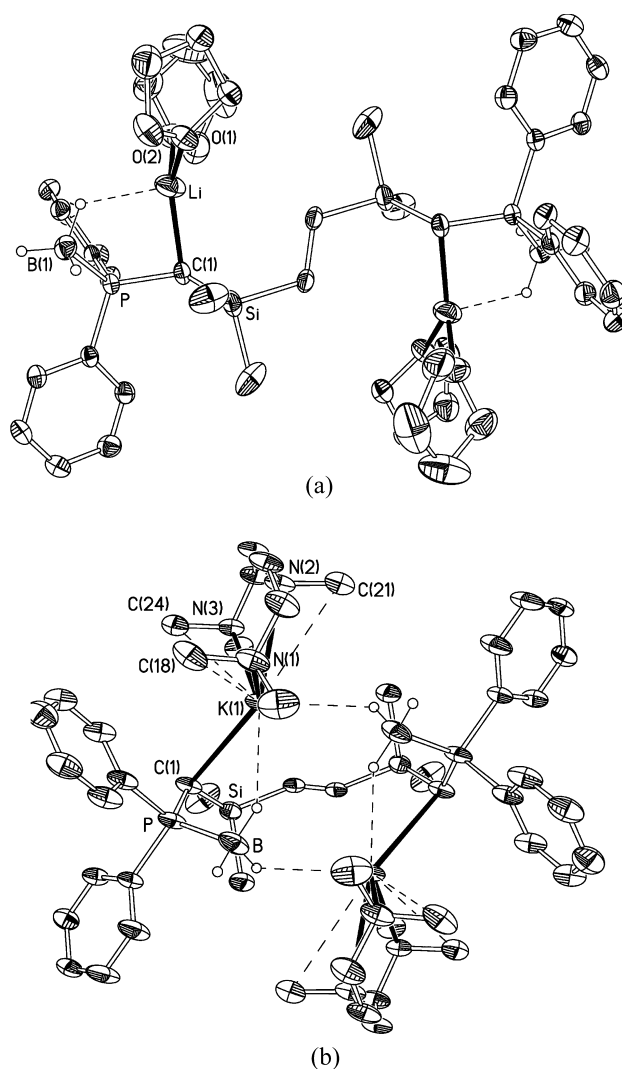


Figure 4. Molecular structures of (a) **5b** and (b) **5c** with 40% probability ellipsoids and with C-bound H atoms and disorder components omitted for clarity. Selected bond lengths (Å) are as follows. **5b**: Li–C(1) 2.194(6), Li–O(1) 1.900(6), Li–O(2) 1.928(6), Li–H(1B) 2.22(3), Li–B(1) 2.888(9), P(1)–B(1) 1.924(3). **5c**: K–C(1) 3.173(4), K–N(1) 2.883(4), K–N(2) 2.966(4), K–N(3) 2.906(4), K–H(1A) 2.82(6), K–H(B) 2.78(6), K···B 3.587(6), K···B' 3.524(7), K···C(18) 3.506(6), K···C(24) 3.392(5), K···C(21) 3.508(5), P–B 1.921(5).

distorted-tetrahedral geometry. The Li–C distance of 2.194(6) Å is somewhat shorter than the corresponding distances in **1b–3b** but lies in the typical range of Li–C distances in alkyl lithium compounds (see above).

Compound **5c** crystallizes with an unusual cyclic structure with a crystallographic C_2 axis perpendicular to the C(2)–C(2A) bond. Each potassium ion is coordinated by the carbanion center and by an H atom of the borane group at one end of the PBC ligand. In addition, each potassium ion is coordinated by the three nitrogen atoms of a molecule of pmdeta and by one H atom of the second BH_3 group in the molecule. Thus, each BH_3 group bridges between the two potassium ions in a $\mu_2-\eta^1:\eta^1$ fashion to generate a (K–H–B–H)₂ cycle. The K–C distance of 3.173(4) Å lies in the typical range for K–C σ bonds (see above). The K–H distances of 2.78(6) and 2.82(6) Å are also typical of such contacts; for example, the K–H distances in $[(Me_3Si)_2\{Me_2P(BH_3)\}C]^-K^+$ range from 2.74(5) to 2.92(5) Å.^{3c}

While compounds **1b–3b**, **1c**, and **3c** possess planar carbanion centers due to extensive delocalization of charge into both the aromatic ring and the P–C σ^* orbitals, compounds **5b,c** crystallize with pyramidal carbanion centers. For **5c** the two carbanion centers adopt an *R,S* configuration, while for **5b** they adopt an *S,S* configuration; however, in solution the C–Li/K contacts are likely to be highly labile and racemization of these centers will be rapid.

Comparison of the structure of the free phosphine–borane **1a** with that of the corresponding lithium complex **1b** reveals that metalation results in contraction of the C(carbanion)–P distances (C(1)–P(1) 1.8392(11) (1a), 1.748(3) Å (1b); C(8)–P(2) 1.8372(11) (1a), 1.755(3) Å (1b)), consistent with extensive delocalization of charge from the carbanion centers into the P–C σ^* orbitals. Similarly, comparison of the structures of **5b,c** with that of the closely related precursor bis(phosphine–borane) **4a** reveals a comparable shortening of the C(carbanion)–P and C(carbanion)–Si distances (C(carbanion)–P 1.8000(19) (4a), 1.729(3) (5b), 1.716(5) Å (5c); C(carbanion)–Si 1.892(2) (4a), 1.830(3) (5b), 1.805(6) Å (5c)).

Compounds **1b–5b**, **5c**, **1d**, and **3c** are potentially excellent ligand transfer reagents for the synthesis of main-group and transition-metal dialkyls. We are currently investigating this chemistry, with a particular focus on the effect of the rigid aromatic backbone in the *o*-phenylene-bridged systems on the structures and stabilities of their main-group-element derivatives.

EXPERIMENTAL SECTION

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. THF, light petroleum (bp 40–60 °C), diethyl ether, toluene, and *n*-hexane were dried prior to use by distillation under nitrogen from sodium, potassium, or sodium/potassium alloy, as appropriate. THF was stored over activated 4 Å molecular sieves; all other solvents were stored over a potassium film. Deuterated THF and benzene were distilled from potassium, and $CDCl_3$ was distilled from CaH_2 under nitrogen; all NMR solvents were deoxygenated by three freeze–pump–thaw cycles and were stored over activated 4 Å molecular sieves. Benzylpotassium,¹⁸ MeK ,^{11b,19} $iPr_2PH(BH_3)$,²⁰ $Ph_2PH(BH_3)$,²¹ $Cy_2PH(BH_3)$,²² $Me_3P(BH_3)$,²³ and $Ph_2MeP(BH_3)$ ²¹ were prepared by previously published procedures; *n*-butyllithium was purchased from Aldrich as a 2.5 M solution in hexanes. tmeda and pmdeta were distilled from CaH_2 under nitrogen and were stored over activated 4 Å molecular sieves. All other compounds were used as supplied by the manufacturer.

¹H and ¹³C{¹H} NMR spectra were recorded on a JEOL ECS500 spectrometer operating at 500.16 and 125.65 MHz, respectively, or a Bruker Avance300 spectrometer operating at 300.15 and 75.47 MHz, respectively; chemical shifts are quoted in ppm relative to tetramethylsilane. ³¹P{¹H}, ¹¹B{¹H}, and ⁷Li NMR spectra were recorded on a JEOL ECS500 spectrometer operating at 202.35, 160.16, and 194.38 MHz, respectively; chemical shifts are quoted in ppm relative to external 85% H_3PO_4 , $BF_3 \cdot Et_2O$, and 0.1 M LiCl, respectively. All NMR spectra were recorded at 295 K. Elemental analyses were obtained by the Elemental Analysis Service of London Metropolitan University.

1,2-C₆H₄(CH₂P(BH₃))₂ (1a). To a solution of $iPr_2PH(BH_3)$ (1.61 g, 12.39 mmol) in THF (20 mL) was added *n*BuLi (4.9 mL, 12.39 mmol), and this mixture was stirred for 1 h. To this solution was added a solution of α,α' -dichloro-*o*-xylene (1.05 g, 6.19 mmol) in THF (20 mL), and this mixture was stirred at room temperature for 16 h. Water (30 mL) was added, and the organic phase was extracted into dichloromethane (3 × 20 mL). The combined extracts were dried over $MgSO_4$, and the solvent was removed under vacuum to give **1a** as a colorless solid. Single crystals suitable for X-ray crystallography were obtained from cold (–30 °C) toluene. Yield: 1.45 g, 67%. ¹H{¹¹B} NMR ($CDCl_3$): δ 0.33 (d, $J_{PH} = 14.5$ Hz, 6H, BH_3), 1.13 (dd, $^3J_{PH} = 13.8$, $^3J_{HH} = 7.1$ Hz, 6H, CHMeMe), 1.20 (dd, $^3J_{PH} = 14.1$, $^3J_{HH} = 7.3$ Hz, 6H, CHMeMe), 2.00 (m, 4H, CHMe₂), 3.32 (d, $^2J_{PH} = 11.6$ Hz, CH_2P), 7.15 (m, 4H, ArH). ¹³C{¹H} NMR ($CDCl_3$): δ 17.2, 17.3 (CHMe₂), 22.0 (d, $J_{PC} = 32.5$ Hz, CHMe₂), 25.9 (d, $J_{PC} = 26.3$ Hz, CH_2P), 127.0, 131.5, 133.4 (Ar). ¹¹B{¹H} NMR ($CDCl_3$): δ –44.3 (d, $J_{PB} = 49.0$ Hz). ³¹P{¹H} NMR ($CDCl_3$): δ 35.2 (m).

1,2-C₆H₄(CH₂P(BH₃))₂ (2a). To a solution of $Ph_2PH(BH_3)$ (1.64 g, 8.2 mmol) in THF (20 mL) was added *n*BuLi (3.3 mL, 8.2 mmol), and this mixture was stirred at room temperature for 1 h. To this solution was added a solution of α,α' -dichloro-*o*-xylene (0.68 g, 4.1 mmol) in THF (20 mL), and this mixture was stirred for 16 h. Water (20 mL) was added, and the organic phase was extracted into dichloromethane (3 × 20 mL). The combined organic extracts were dried over $MgSO_4$, and solvent was removed under vacuum to give **2a** as a colorless solid. Yield: 1.61 g, 82%. ¹H{¹¹B} NMR ($CDCl_3$): δ 0.90 (d, $J_{PH} = 15.5$ Hz, 6H, BH_3), 3.54 (d, $J_{PH} = 11.7$ Hz, 4H, CH_2P), 6.51–7.62 (m, 24H, ArH). ¹³C{¹H} NMR ($CDCl_3$): δ 30.9 (d, $J_{PC} = 30.8$ Hz, CH_2P), 126.7, 128.8, 128.9, 129.3, 131.4, 131.6 (Ar), 132.7 (d, $J_{PC} = 8.6$ Hz, Ar). ¹¹B{¹H} NMR ($CDCl_3$): δ –40.1 (br). ³¹P{¹H} NMR ($CDCl_3$): δ 18.3 (br m).

1,2-C₆H₄(CH₂P(BH₃))₂ (3a). To a solution of $Cy_2PH(BH_3)$ (1.58 g, 7.45 mmol) in THF (20 mL) was added *n*BuLi (3.0 mL, 7.50 mmol), and this mixture was stirred for 1 h. To this mixture was added a solution of α,α' -dichloro-*o*-xylene (0.61 g, 3.73 mmol) in THF (20 mL), and this mixture was stirred at room temperature for 16 h. Water (30 mL) was added, and the organic phase was extracted into dichloromethane (3 × 20 mL). The combined organic extracts were dried over $MgSO_4$ and solvent was removed under vacuum to give **3a** as a colorless solid. Yield: 1.42 g, 77%. ¹H{¹¹B} NMR ($CDCl_3$): δ 0.29 (d, $J_{PH} = 15.1$ Hz, 6H, BH_3), 1.16–1.93 (m, 44H, Cy), 3.29 (d, $J_{PH} = 11.5$ Hz, 4H, CH_2P), 7.09–7.35 (m, 4H, ArH). ¹³C{¹H} NMR ($CDCl_3$): δ 25.8 (d, $J_{PC} = 27.8$ Hz, Cy), 26.1 (Cy), 27.0 (d, $J_{PC} = 7.7$ Hz, CH_2P), 27.1 (Cy), 32.0 (d, $J_{PC} = 30.7$ Hz, Cy), 126.8, 131.5, 133.7 (Ar). ¹¹B{¹H} NMR ($CDCl_3$): δ –43.6 (br m). ³¹P{¹H} NMR ($CDCl_3$): δ 27.8 (br m).

[CH₂SiMe₂CH₂P(BH₃))Me₂]₂ (4a). To a solution of $Me_3P(BH_3)$ (6.31 g, 70.17 mmol) in THF (30 mL) was added *n*BuLi (28.1 mL, 70.17 mmol), and this mixture was stirred for 1 h at room temperature. This solution was added, dropwise, to a solution of 1,2-bis-(chlorodimethylsilyl)ethane (7.55 g, 35.09 mmol) in THF (30 mL), and the resulting mixture was stirred for 1 h at room temperature. Water (30 mL) was added, and the organic phase was extracted into dichloromethane (3 × 30 mL). The combined organic extracts were dried over $MgSO_4$ and filtered and the solvent was removed in vacuo from the filtrate to give a colorless solid, which was crystallized from hot methylcyclohexane (15 mL) to give colorless crystals of **4a**. Isolated yield: 6.97 g, 60%. ¹H{¹¹B} NMR ($CDCl_3$): δ 0.13 (s, 12H, SiMe₂), 0.50 (m, 10H, $CH_2CH_2 + BH_3$), 0.90 (d, $J_{PH} = 15.1$ Hz, 4H,

PCH₂), 1.29 (d, $J_{\text{PH}} = 10.1$ Hz, 12H, PMe₂). ¹³C{¹H} NMR (CDCl₃): δ -1.5 (SiMe₂), 9.0 (CH₂CH₂), 13.5 (d, $J_{\text{PC}} = 24.0$ Hz, PCH₂), 15.6 (d, $J_{\text{PC}} = 38.3$ Hz, PMe₂). ¹¹B{¹H} NMR (CDCl₃): δ -37.5 (d, $J_{\text{PB}} = 58.8$ Hz). ³¹P{¹H} NMR (CDCl₃): δ 3.4 (q, $J_{\text{PB}} = 58.8$ Hz).

[CH₂SiMe₂CH₂P(BH₃)Ph₂]₂ (5a). To a cold (0 °C) solution of Ph₂P(BH₃)Me (4.76 g, 22.24 mmol) in THF (40 mL) was added *n*BuLi (8.9 mL, 22.24 mmol), and this mixture was stirred for 1 h at room temperature. This solution was added, dropwise, to a solution of 1,2-bis(chlorodimethylsilyl)ethane (2.39 g, 11.12 mmol) in THF (30 mL), and the resulting mixture was stirred for 1 h at room temperature. Water (40 mL) was added, and the organic phase was extracted into dichloromethane (3 × 30 mL). The combined organic extracts were dried over MgSO₄ and filtered, and the solvent was removed in vacuo from the filtrate to give a colorless solid, which was crystallized from hot methylcyclohexane/THF (15/5 mL) to give colorless crystals of **5a**. Isolated yield: 4.00 g, 64%. ¹H{¹¹B} NMR (CDCl₃): δ -0.11 (s, 12H, SiMe₂), 0.29 (s, 4H, CH₂CH₂), 1.04 (s, 3H, BH₃), 1.52 (d, $J_{\text{PH}} = 15.0$ Hz, 4H, PCH₂), 7.39 (m, 10H, PPh₂), 7.69 (m, 10H, PPh₂). ¹³C{¹H} NMR (CDCl₃): δ -2.2 (SiMe₂), 8.5 (CH₂CH₂), 11.0 (d, $J_{\text{PC}} = 25.1$ Hz, PCH₂), 128.6 (d, $J_{\text{PC}} = 10.1$ Hz, Ph), 130.9 (Ar), 131.6 (d, $J_{\text{PC}} = 9.1$ Hz, Ph), 132.6 (d, $J_{\text{PC}} = 55.2$ Hz, Ar). ¹¹B{¹H} NMR (CDCl₃): δ -38.9 (br). ³¹P{¹H} NMR (CDCl₃): δ 13.5 (q, $J_{\text{PB}} = 69.5$ Hz).

[1,2-C₆H₄{CHP(BH₃)iPr₂}[Li(tmeda)]₂ (1b). To a solution of **1a** (0.87 g, 2.38 mmol) in THF (30 mL) were added *n*BuLi (2.0 mL, 5.00 mmol) and tmeda (0.77 mL, 5.10 mmol). This mixture was stirred at room temperature for 2 h, and then solvent was removed in vacuo to give a bright yellow solid. This was crystallized from diethyl ether at room temperature to give a large crop of yellow crystals of **1b**. Yield: 1.11 g, 76%. Anal. Calcd for C₃₂H₇₂B₂Li₂N₄P₂ (610.39): C, 62.97; H, 11.89; N, 9.18. Found: C, 62.83; H, 11.79; N, 9.08. ¹H{¹¹B} NMR (*d*₈-THF): δ 0.32 (d, $J_{\text{PH}} = 14.2$ Hz, 6H, BH₃), 1.10–1.17 (m, 24H, CHMe₂), 1.45 (d, $J_{\text{PH}} = 9.7$ Hz, 2H, CHLi), 2.13 (s, 24H, NMe₂), 2.25 (m, 4H, CHMe₂), 2.31 (s, 8H, CH₂N), 5.85 (m, 2H, ArH), 6.61 (m, 2H, ArH). ¹³C{¹H} NMR (*d*₈-THF): δ 18.3 (CHMe₂), 18.5 (CHMe₂), 23.7 (d, $J_{\text{PC}} = 59.5$ Hz, CHLi), 24.3 (d, $J_{\text{PC}} = 34.5$ Hz, CHMe₂), 45.4 (NMe₂), 57.9 (CH₂N), 115.5, 116.7 (Ar), 139.2 (d, $J_{\text{PC}} = 13.4$ Hz, Ar). ⁷Li NMR (*d*₈-THF): δ -1.0. ¹¹B{¹H} NMR (*d*₈-THF): δ -39.3 (d, $J_{\text{PB}} = 78.4$ Hz). ³¹P{¹H} NMR (*d*₈-THF): δ 16.3 (q, $J_{\text{PB}} = 78.4$ Hz).

[1,2-C₆H₄{CHP(BH₃)iPr₂}[CH₂P(BH₃)iPr₂][K(pmdeta)] (1c). To a slurry of MeK (0.70 g, 15.05 mmol) in cold (-10 °C) diethyl ether (20 mL) was added a solution of **1a** (2.43 g, 6.64 mmol) in cold (-10 °C) diethyl ether (20 mL), and this mixture was stirred for 16 h. The solution was filtered, pmdeta (2.77 mL, 13.27 mmol) was added to the filtrate, and this mixture was stirred for 5 min. Solvent was removed in vacuo, and the resulting pale brown solid was crystallized from cold (-30 °C) *n*-hexane (20 mL). The pale yellow crystals of **1c** were isolated by filtration and washed with a small amount of cold light petroleum. Yield 2.69 g, 70%. Anal. Calcd for C₂₉H₆₄B₂KN₃P₂ (577.51): C, 60.31; H, 11.17; N, 7.28. Found: C, 61.03; H, 11.43; N, 7.11. ¹H NMR (*d*₈-THF): δ 0.31 (br m, 6H, BH₃), 1.04–1.81 (m, 24H, CHMe₂), 1.75 (d, $J_{\text{PH}} = 4.4$ Hz, 1H, CHK), 1.84 (m, 2H, CHMe₂), 2.12 (s, 12H, NMe₂), 2.16 (s, 3H, NMe), 2.25 (m, 2H, CHMe₂), 2.27 (m, 4H, CH₂N), 2.38 (m, 4H, CH₂N), 2.83 (d, $J_{\text{PH}} = 10.8$ Hz, 2H, CH₂P), 5.67 (m, 1H, ArH), 6.43 (m, 1H, ArH), 6.53 (m, 1H, ArH), 7.01 (m, 1H, ArH). ¹³C{¹H} NMR (*d*₈-THF): δ 16.7, 16.8, 17.8, 17.6 (CHMe₂), 22.2 (d, $J_{\text{PC}} = 29.8$ Hz, CHMe₂), 25.3 (d, $J_{\text{PC}} = 30.6$ Hz, CH₂P), 25.8 (d, $J_{\text{PC}} = 36.6$ Hz, CHMe₂), 34.8 (d, $J_{\text{PC}} = 76.5$ Hz, CHK), 42.4 (NMe), 45.3 (NMe₂), 56.4, 57.9 (CH₂N), 106.4 (Ar), 115.9 (d, $J_{\text{PC}} = 5.9$ Hz, Ar), 117.7 (dd, $J_{\text{PC}} = 15.0$, $J_{\text{PC}} = 6.6$ Hz, Ar), 126.1, 130.4 (Ar), 151.7 (d, $J_{\text{PC}} = 9.5$ Hz, Ar). ¹¹B{¹H} NMR (*d*₈-THF): δ -43.5 (d, $J_{\text{PB}} = 41.7$ Hz, H₃B-P-CH₂), -40.6 (d, $J_{\text{PB}} = 83.3$ Hz, H₃B-P-CHK). ³¹P{¹H} NMR (*d*₈-THF): δ 16.7 (br q, $J_{\text{PB}} = 83.3$ Hz, H₃B-P-CHK), 34.2 (br q, $J_{\text{PB}} = 41.7$ Hz, H₃B-P-CH₂).

[1,2-C₆H₄{CHP(BH₃)Ph₂}[Li(tmeda)]₂·THF (2b). To a solution of **2a** (0.48 g, 0.96 mmol) in THF (20 mL) were added *n*BuLi (0.77 mL, 1.92 mmol) and tmeda (0.29 mL, 1.92 mmol), and this mixture was stirred at room temperature for 1 h. The solvent was removed in vacuo, and the sticky orange solid was crystallized from cold (-30 °C) toluene as deep orange plates of **2b**. Yield: 0.45 g, 63%. Anal. Calcd for

C₄₄H₆₄B₂Li₂N₄P₂ (746.56): C, 70.80; H, 8.64; N, 7.51. Found: C, 70.61; H, 8.49; N, 7.80. ¹H{¹¹B} NMR (*d*₈-THF) δ 0.99 (d, $J_{\text{PH}} = 14.6$ Hz, 6H, BH₃), 2.12 (s, 16H, NMe₂), 2.20 (d, $J_{\text{PH}} = 14.4$ Hz, 2H, CHLi), 2.27 (s, 8H, CH₂N), 5.74 (m, 2H, ArH), 6.41 (m, 2H, ArH), 7.13 (m, 12H, Ph), 7.72 (m, 8H, Ph). ¹³C{¹H} NMR (*d*₈-THF): δ 27.4 (d, $J_{\text{PC}} = 66.0$ Hz, CHLi), 45.3 (NMe₂), 57.9 (CH₂N), 113.9 (Ar), 126.4 (d, $J_{\text{PC}} = 8.6$ Hz, Ar), 126.9, 128.0, 128.7 (Ar), 132.8 (d, $J_{\text{PC}} = 8.6$ Hz, Ar), 140.2 (d, $J_{\text{PC}} = 47.7$ Hz, Ar). ⁷Li NMR (*d*₈-THF): δ -0.9. ¹¹B{¹H} NMR (*d*₈-THF): δ -34.4 (br m). ³¹P{¹H} NMR (*d*₈-THF): δ 6.2 (br m). N.B.: solvent of crystallization is readily lost under vacuum and was not observed in either the elemental analysis or NMR spectra.

[1,2-C₆H₄{CHP(BH₃)Cy₂}[Li(tmeda)]₂·2PhMe (3b). To a solution of **3a** (1.00 g, 1.90 mmol) in THF (30 mL) was added *n*BuLi (1.52 mL, 3.79 mmol), and this mixture was stirred for 30 min at room temperature. The solvent was removed in vacuo to yield a dark orange oil. This oil was dissolved in toluene (30 mL), and tmeda (0.57 mL, 3.79 mmol) was added. The solution was stirred for 5 min, the solvent was reduced in vacuo to 20 mL, and the solution was cooled to -20 °C for 24 h to give **3b** as yellow crystals, which were washed with a small amount of cold (0 °C) light petroleum. Yield: 1.04 g, 57%. Anal. Calcd for C₄₄H₈₈B₂Li₂N₄P₂ (770.65): C, 68.57; H, 11.51; N, 7.27. Found: C, 68.53; H, 12.23; N, 7.04. ¹H{¹¹B} NMR (*d*₈-THF): δ 0.33 (d, $J_{\text{PH}} = 15.0$ Hz, 6H, BH₃), 1.12–2.02 (m, 46H, PCy₂ + CHLi), 2.16 (s, 24H, NMe₂), 2.31 (s, 8H, NCH₂), 5.86 (br m, 2H, ArH), 6.59 (br m, 2H, ArH). ¹³C{¹H} NMR (*d*₈-THF): δ 23.3 (d, $J_{\text{PC}} = 61.3$ Hz, CHLi), 26.9, 27.7 (PCy₂), 27.8 (d, $J_{\text{PC}} = 10.1$ Hz, PCy₂), 28.1 (d, $J_{\text{PC}} = 10.1$ Hz, PCy₂), 28.5 (PCy₂), 34.8 (d, $J_{\text{PC}} = 34.2$ Hz, PCy₂), 45.4 (NMe₂), 57.9 (CH₂N), 112.5 (Ar), 116.3 (d, $J_{\text{PC}} = 6.0$ Hz, Ar), 139.2 (d, $J_{\text{PC}} = 15.1$ Hz, Ar). ⁷Li NMR (*d*₈-THF): δ -1.0. ¹¹B{¹H} NMR (*d*₈-THF): δ -39.8 (br). ³¹P{¹H} NMR (*d*₈-THF): δ 12.3 (br q, $J_{\text{PB}} = 105.3$ Hz). N.B.: solvent of crystallization is readily lost under vacuum and was not observed in either the elemental analysis or NMR spectra.

[1,2-C₆H₄{CHP(BH₃)Cy₂}[K(pmdeta)]₂ (3c). To a solution of **3a** (0.50 g, 0.95 mmol) in THF (30 mL) were added, dropwise, a solution of benzylpotassium (0.30 g, 2.30 mmol) in THF (30 mL), followed by pmdeta (0.39 mL, 1.90 mmol); this solution was stirred for 1 h at room temperature. The solvent was removed in vacuo, the sticky orange solid was dissolved in diethyl ether (10 mL), and the solution was filtered and left to stand at room temperature for 24 h to yield yellow crystals of **3c**. Isolated yield: 0.37 g, 41%. Anal. Calcd for C₅₀H₁₀₂B₂K₂N₆P₂ (949.15): C, 63.27; H, 10.83; N, 8.85. Found: C, 63.11; H, 11.01; N, 8.76. ¹H{¹¹B} NMR (*d*₈-toluene): δ 0.98 (d, $J_{\text{PH}} = 12.0$ Hz, 6H, BH₃), 1.09–2.23 (m, 67H, PCy₂ + CH₂N + NMe + NMe₂), 6.18 (s, 2H, ArH), 9.96 (s, 2H, ArH). ¹³C{¹H} NMR (*d*₈-toluene): δ 27.2 (PCy₂), 27.6 (PCy₂), 27.8 (d, $J_{\text{PC}} = 10.1$ Hz, PCy₂), 28.0 (d, $J_{\text{PC}} = 10.1$ Hz, PCy₂), 28.5, 33.3 (d, $J_{\text{PC}} = 30.1$ Hz, PCy₂), 37.8 (d, $J_{\text{PC}} = 36.5$ Hz, CHK), 41.8 (NMe), 45.0 (NMe₂), 55.1, 57.0 (NCH₂), 111.2, 113.7 (Ar), 141.9 (d, $J_{\text{PC}} = 3.9$ Hz, Ar). ¹¹B{¹H} NMR (*d*₈-toluene): δ -40.3 (br). ³¹P{¹H} NMR (*d*₈-toluene): δ 12.7 (br).

[CH₂SiMe₂CHP(BH₃)Me₂][Li(tmeda)]₂ (4b). To a solution of **4a** (0.51 g, 1.55 mmol) in THF (30 mL) were added *n*BuLi (1.24 mL, 3.10 mmol) and tmeda (0.46 mL, 3.10 mmol), and this mixture was stirred for 1 h at room temperature. The solvent was removed in vacuo to yield a colorless oil, which was crystallized from cold (-20 °C) methylcyclohexane (10 mL) to give **4b** as colorless crystals that were isolated by filtration and washed with cold (0 °C) light petroleum (3 × 5 mL). Yield: 0.39 g, 74%. Anal. Calcd for C₂₄H₆₈B₂Li₂N₄P₂Si₂ (566.50): C, 50.89; H, 12.10; N, 9.89. Found: C, 50.68; H, 12.15; N, 9.78. ¹H{¹¹B} NMR (*d*₆-benzene): δ -1.05 (d, $J_{\text{PH}} = 6.4$ Hz, 2H, LiCH), 0.30 (s, 12H, SiMe₂), 0.76 (s, 4H, SiCH₂CH₂Si), 1.43 (d, $J_{\text{PH}} = 10.1$ Hz, 12H, PMe₂), 1.78 (s, 8H, CH₂N), 2.05 (s, 24H, NMe₂). ¹³C{¹H} NMR (*d*₆-benzene): δ 2.5 (SiMe₂), 3.2 (d, $J_{\text{PC}} = 17.1$ Hz, LiCH), 14.8 (SiCH₂CH₂Si), 19.7 (d, $J_{\text{PC}} = 33.2$ Hz, PMe₂), 45.8 (NMe₂), 56.3 (CH₂N). ⁷Li NMR (*d*₆-benzene): δ 1.0. ¹¹B{¹H} NMR (*d*₆-benzene): δ -33.0 (d, $J_{\text{PB}} = 88.3$ Hz). ³¹P{¹H} NMR (*d*₆-benzene): δ -4.8 (q, $J_{\text{PB}} = 88.3$ Hz).

[CH₂SiMe₂CHP(BH₃)Ph₂][Li(THF)]₂ (5b). To a solution of **5a** (0.50 g, 0.88 mmol) in THF (40 mL) was added *n*BuLi (0.70 mL, 1.75 mmol), and this mixture was stirred for 1 h at room temperature. The

solvent was removed in vacuo to yield a yellow oil, which was crystallized from cold ($-20\text{ }^{\circ}\text{C}$) diethyl ether (10 mL) to give **5b** as yellow crystals. Yield: 0.41 g, 80%. Anal. Calcd for $\text{C}_{48}\text{H}_{26}\text{B}_2\text{Li}_2\text{O}_4\text{P}_2\text{Si}_2$ (870.74): C, 66.21; H, 8.80. Found: C, 66.11; H, 8.70. $^1\text{H}\{^{11}\text{B}\}$ NMR (d_6 -benzene): δ -0.10 (d, $J_{\text{PH}} = 25.0$ Hz, 2H, LiCH), 0.29 (s, 12H, SiMe_2), 0.86 (s, 4H, $\text{SiCH}_2\text{CH}_2\text{Si}$), 1.33 (m, 16H, THF), 3.52 (m, 16H, THF), 7.00 – 8.10 (m, 20H, PPh_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_6 -benzene): δ -1.2 (d, $J_{\text{PC}} = 16.1$ Hz, LiCH), 2.0 (d, $J_{\text{PC}} = 6.0$ Hz, SiMe_2), 15.2 ($\text{SiCH}_2\text{CH}_2\text{Si}$), 25.2 (THF), 68.0 (THF), 127.6 , 128.4 (Ph), 131.4 (d, $J_{\text{PC}} = 9.1$ Hz, Ph), 141.9 (d, $J_{\text{PC}} = 50.5$ Hz, *ipso*-Ph). ^7Li NMR (d_6 -benzene): δ 1.2 . $^{11}\text{B}\{^1\text{H}\}$ NMR (d_6 -benzene): δ -35.7 (d, $J_{\text{PB}} = 88.2$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (d_6 -benzene): δ 12.5 (q, $J_{\text{PB}} = 88.2$ Hz).

$[\text{CH}_2\text{SiMe}_2\text{CHP}(\text{BH}_3)\text{Ph}_2]_2[\text{K}(\text{pmdeta})]_2$ (**5c**). To a solution of **5a** (0.50 g, 0.88 mmol) in THF (20 mL) were added, dropwise, a solution of benzylpotassium (0.26 g, 2.00 mmol) in THF (10 mL) followed by *pmdeta* (0.37 mL, 1.75 mmol), and this mixture was stirred for 16 h at room temperature. Solvent was removed in vacuo from the resulting orange solution to yield a sticky yellow solid, which was crystallized from hot toluene (20 mL) as yellow blocks. Yield: 0.53 g, 61%. Anal. Calcd for $\text{C}_{50}\text{H}_{90}\text{B}_2\text{K}_2\text{N}_6\text{P}_2\text{Si}_2$ (993.22): C, 60.46; H, 9.13; N, 8.46. Found: C, 60.34; H, 9.06; N, 8.31. $^1\text{H}\{^{11}\text{B}\}$ NMR (d_8 -THF): δ -0.53 (d, $J_{\text{PH}} = 25.0$ Hz, 2H, KCH), -0.15 (s, 12H, SiMe_2), 0.43 (s, 4H, $\text{SiCH}_2\text{CH}_2\text{Si}$), 0.95 (d, $J_{\text{PH}} = 15.0$ Hz, 3H, BH_3), 2.16 (s, 12H, NMe_2), 2.19 (s, 3H, NMe), 2.32 (m, 4H, CH_2N), 2.43 (m, 4H, CH_2N), 7.00 – 8.10 (m, 20H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_8 -THF): δ -2.2 (d, $J_{\text{PC}} = 38.2$ Hz, KCH), -0.1 (SiMe_2), 12.1 (d, $J_{\text{PC}} = 5.0$ Hz, $\text{SiCH}_2\text{CH}_2\text{Si}$), 40.5 (NMe), 43.5 (NMe_2), 54.6 (NCH_2), 56.0 (NCH_2), 124.9 (d, $J_{\text{PC}} = 9.1$ Hz, Ph), 125.0 (Ph), 129.3 (d, $J_{\text{PC}} = 9.1$ Hz, Ph), 129.9 (d, $J_{\text{PC}} = 9.1$ Hz, Ph). $^{11}\text{B}\{^1\text{H}\}$ NMR (d_8 -THF): δ -34.7 (d, $J_{\text{PB}} = 78.3$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (d_8 -THF): δ 11.7 (q, $J_{\text{PB}} = 78.3$ Hz).

Crystal Structure Determinations of 1a–c, 2b, 3b,c, 4a, and 5b,c. Measurements were made at 150 K on an Oxford Diffraction (Agilent Technologies) Gemini A Ultra diffractometer or a Nonius KappaCCD diffractometer, using Cu $K\alpha$ radiation ($\lambda = 1.54178\text{ \AA}$; **4a**) or Mo $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$; **1a–c**, **2b**, **3b,c**, and **5b,c**). Cell parameters were refined from the observed positions of all strong reflections. Intensities were corrected semiempirically for absorption, on the basis of symmetry-equivalent and repeated reflections using SADABS,²⁴ except for **3d**, where analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by Clark and Reid²⁵ was applied on the basis of symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined on F^2 values for all unique data; see Table S1 in the Supporting Information for further details. All non-hydrogen atoms were refined anisotropically, and C-bound H atoms were constrained with a riding model, while B-bound H atoms, having been found directly in a Fourier difference synthesis, were freely refined; $U(\text{H})$ was set at 1.2 (1.5 for methyl groups) times U_{eq} for the parent C atom. Disorder in the *pmdeta* ligand of **1c**, the *tmeda* ligands and solvent molecules of **2b**, one of the *pmdeta* ligands of **3d**, and the two backbone carbon atoms of **5b,c** was successfully modeled with the aid of restraints on geometry and displacement parameters. Programs used were CrysAlisPro and Nonius COLLECT/EvalCC for data collection,²⁴ integration, and absorption corrections, and OLEX2,²⁶ SHELXS/SHELXL, and SHELXTL for structure solution, refinement, and graphics.²⁴

■ ASSOCIATED CONTENT

Supporting Information

For **1a–5a** figures giving ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra and for **1a–c**, **2b**, **3b,c**, **4a**, and **5b,c** tables, figures, and CIF files giving details of structure determination, atomic coordinates, bond lengths and angles, and displacement parameters and details of the molecular structures of **1a** and **4a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are grateful to Newcastle University for financial support.

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