PHOSPHIDO-BORANE COMPLEXES OF GROUP I AND II METALS

by

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Abstract

The synthesis and characterisation of a range of novel phosphine-borane precursors is described: \{(Me_3Si)_2CH\}PH(C_6H_4-2-CH_2OMe)(BH_3) (39), \{(Me_3Si)_2CH\}PH(C_6H_4-2-SMe)(BH_3) (40), \{(Me_3Si)_2CH\}PH(C_6H_4-2-OMe)(BH_3) (41) and \{(Me_3Si)_2CH\}PH(C_6H_5)(BH_3) (42).

Treatment of 39 with \(n\)-BuLi, BnNa or BnK proceeds cleanly to give the corresponding alkali metal complexes, which are crystallised in the presence of THF, tmeda and pmdeta, respectively, to yield the adducts \(\left\{\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P}(\text{BH}_3)(\text{C}_6\text{H}_4-2-\text{CH}_2\text{OMe})\text{ML}\right\}_2 \text{[ML} = \text{Li(THF)}, (49); \text{ML} = \text{Na(tmeda)}, (50); \text{ML} = \text{K(pmdeta)}), (51)\].

Deprotonation of 40 with \(n\)-BuLi, BnNa or BnK, followed by crystallisation in the presence of THF, tmeda or pmdeta, respectively, yields the compounds \(\left\{\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P}(\text{BH}_3)(\text{C}_6\text{H}_4-2-\text{SMe})\text{M(L)}\right\}_n \text{[ML} = \text{Li(THF)}, n = 2 \text{(64); ML} = \text{Na(tmeda)}, n = \infty \text{(65); ML} = \text{K(pmdeta)}, n = 2 \text{(66)}\]. On heating a solution of 64 in the presence of free phosphine-borane 40, concurrent formation of the corresponding phosphine \(\left\{\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{PH}(\text{C}_6\text{H}_4-2-\text{SMe})\text{M}2\text{Li}\right\}\text{[ML} = \text{Li(THF)}, (49); \text{ML} = \text{Na(tmeda)}, (50); \text{ML} = \text{K(pmdeta)}), (51)\].

Treatment of 41 with \(n\)-BuLi, BnNa or BnK, yield the corresponding phosphido-boranes. Heating a solution of the lithium salt \(\left\{\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P}(\text{C}_6\text{H}_4-2-\text{OMe})\text{BH}_3\text{Li(THF)}\right\} \text{(85) in toluene, in the presence of one equivalent of tmeda yields the unexpected phosphine-substituted lithium alkoxide \(\left\{\{\text{(Me}_3\text{Si)}\text{CH}\}\text{PH}(\text{C}_6\text{H}_4-2-\text{O})\text{Li}\right\}_6 \text{(89) and the tertiary phosphine-borane \(\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{PMe(BH}_3\text{)(C}_6\text{H}_4-2-\text{OMe}) \text{(90), and a third unidentified phosphorus-containing compound. Repeating the experiment with the analogue \(\left\{\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P}(\text{C}_6\text{H}_4-2-\text{OMe})\text{BD}_3\text{Li(THF)}\right\}_n \text{(104), and monitoring the reaction using 2D and 3P\{1H\} NMR spectroscopy, indicates that the source of the P-H proton is the borane group. It was also found that heating a solution of 85 in toluene, in the presence of an excess of THF and one equivalent of tmeda results in another thermolytic reaction pathway, generating 90 and a phosphorus-containing compound, proposed to be the alkoxo-phosphido-borane \(\left\{\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P}(\text{BH}_3)(\text{C}_6\text{H}_4-2-\text{O})\text{Li}_2\text{(tmeda)}\right\}_2 \text{(91). Reaction between CaI}_2 \text{and two}

i | P a g e
equivalents of \[
\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P}(\text{C}_6\text{H}_4\text{-2-OMe})(\text{BH}_3)\}\text{K}
\] yields the cluster \[
\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P}(\text{C}_6\text{H}_4\text{-2-O})(\text{BH}_3)\text{Ca}(\text{THF})_4
\] (108) and 90. 108 crystallises with an unusual Ca$_4$O$_4$ core, with two distinct calcium environments.

Reaction between 42 and \text{n-BuLi}, BnNa or BnK proceeds cleanly to give the corresponding alkali metal phosphido-boranes. The lithium salt crystallises in the presence of THF as a polymer \[
\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P}(\text{C}_6\text{H}_5)(\text{BH}_3)\text{Li}(\text{THF})_2\}_{\infty}
\] (115), whilst the sodium salt crystallises in the presence of 12-crown-4 as the solvent-separated ion species \[
\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P}(\text{C}_6\text{H}_5)(\text{BH}_3)\}][\text{Na}(12\text{-crown-4})_2
\] (116). The potassium salt crystallises in the presence of pmdeta as the adduct \[
\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P}(\text{C}_6\text{H}_5)(\text{BH}_3)\text{K}(\text{pmdeta})\}_{2}
\] (117). The reaction between 42 and PhCH$_2$K followed by addition of half an equivalent of either SrI$_2$ or BaI$_2$, generates the corresponding alkaline-earth metal complexes \[
\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P}(\text{C}_6\text{H}_5)(\text{BH}_3)\}_{2}\text{Sr}
\] (119) and \[
\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P}(\text{C}_6\text{H}_5)(\text{BH}_3)\}_{2}\text{Ba}
\] (120).

A series of alkaline and alkaline earth metal phosphido-bis(borane) complexes have been prepared. The reaction between 42 and one equivalent of \text{n-BuLi}, PhCH$_2$Na or PhCH$_2$K, followed by addition of BH$_3$·SMe$_2$, yields the corresponding phosphido-bis(borane) complexes. The lithium salt is crystallised in the presence of one equivalent of 12-crown-4 to yield the monomer \[
\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P}(\text{C}_6\text{H}_5)(\text{BH}_3)\text{Li}(12\text{-crown-4})\}_{2}
\] (123), whilst the sodium and potassium salts are crystallised in the presence of THF to yield the adducts \[
\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P}(\text{C}_6\text{H}_5)(\text{BH}_3)\text{Na}(\text{THF})_2\}_{2}
\] (124) and \[
\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P}(\text{C}_6\text{H}_5)(\text{BH}_3)\text{K}(\text{THF})_2\}_{\infty}
\] (125). Deprotonation of 41 with PhCH$_2$Na followed by reaction with BH$_3$·SMe$_2$ yields the corresponding salt, which is crystallised in the presence of 12-crown-4 as a solvent-separated ion pair \[
\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P}(\text{C}_6\text{H}_4\text{-2-OMe})(\text{BH}_3)\}_{2}[\text{Na}(12\text{-crown-4})_2
\] (126).

Treatment of two equivalents of 42 with one equivalent of either MgBu$_2$, CaBn$_2$ or \{Me$_3$Si)$_2$CH\}_2Sr, followed by addition of BH$_3$·SMe$_2$ yield the corresponding salts, which are crystallised in the presence of THF as the adducts \[[\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P}(\text{BH}_3)_2(\text{C}_6\text{H}_5)]_2\text{Mg}(\text{THF})_4\], (128), \[[\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P}(\text{BH}_3)_2(\text{C}_6\text{H}_5)]_2\text{Ca}(\text{THF})_4\] (129) and \[[\{\text{(Me}_3\text{Si)}_2\text{CH}\]\text{P}(\text{BH}_3)_2(\text{C}_6\text{H}_5)]_2\text{Sr}(\text{THF})_4\] (130), respectively.
Acknowledgements

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Finally, to Lynsey, who has given her support, encouragement and help throughout my PhD. I could not have done this without her, and so it is to my wife that I dedicate this thesis.
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<tr>
<td>Bn</td>
<td>benzyl</td>
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<tr>
<td>d</td>
<td>doublet</td>
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<td>dd</td>
<td>doublet of doublets</td>
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<tr>
<td>dmp</td>
<td>dimesitylphenyl</td>
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<td>{1H}</td>
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<td>mes</td>
<td>mesityl</td>
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<tr>
<td>mes*</td>
<td>2,4,6-tri-(t)-butylphenyl</td>
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<tr>
<td>(\mu_n)</td>
<td>n-bridging</td>
</tr>
<tr>
<td>NMR</td>
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<tr>
<td>pmrta</td>
<td>(N,N,N^<em>,N^{</em>'},N^{*''})</td>
</tr>
<tr>
<td></td>
<td>pentamethyldiethylenetriamine</td>
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![Diagram 108](image)
\[
\begin{align*}
\text{117} & \quad (\text{Me}_3\text{Si})_2\text{HC}^-\text{P}^-\text{K(pmdeta)}\text{BH}_3 \\
\text{119} & \quad (\text{Me}_3\text{Si})_2\text{HC}^-\text{P}^-\text{M(THF)}_n\text{BH}_3 \\
\text{120} & \quad (\text{Me}_3\text{Si})_2\text{HC}^-\text{P}^-\text{CH(SiMe}_3)_2 \\
\text{121} & \quad (\text{Me}_3\text{Si})_2\text{HC}^-\text{P}^-\text{Na(THF)}_2
\end{align*}
\]

\[
\begin{align*}
\text{122} & \quad (\text{Me}_3\text{Si})_2\text{HC}^-\text{P}^-\text{BH}_3 \\
\text{123} & \quad (\text{Me}_3\text{Si})_2\text{HC}^-\text{P}^-\text{Li(12-crown-4)} \\
\text{124} & \quad (\text{Me}_3\text{Si})_2\text{HC}^-\text{P}^-\text{Na(THF)}_2
\end{align*}
\]

\[
\begin{align*}
\text{125} & \quad (\text{Me}_3\text{Si})_2\text{HC}^-\text{P}^-\text{BH}_3 \\
\text{126} & \quad (\text{Me}_3\text{Si})_2\text{HC}^-\text{P}^-\text{OMe}
\end{align*}
\]

\[
\begin{align*}
\text{127} & \quad (\text{Me}_3\text{Si})_2\text{HC}^-\text{P}^-\text{BH}_3 \\
\text{128} & \quad (\text{Me}_3\text{Si})_2\text{HC}^-\text{P}^-\text{Mg(THF)}_2 \\
\text{129} & \quad (\text{Me}_3\text{Si})_2\text{HC}^-\text{P}^-\text{Ca(THF)}_2 \\
\text{130} & \quad (\text{Me}_3\text{Si})_2\text{HC}^-\text{P}^-\text{Ba(THF)}_2
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Chapter 1. Introduction

1.1 Alkali metal organometallics

The first examples of alkali metal organometallic reagents were organolithiums, reported by the pioneer Wilhelm Schlenk in 1914.\textsuperscript{1,2} Since then the numbers of alkali metal organometallics have vastly increased, as have their uses in chemical synthesis as either nucleophilic or basic reagents.\textsuperscript{3,4,5} However, our understanding of the chemistry that governs these compounds has not developed to the same extent. To gain an insight into the mechanistic behaviour of these reagents, it is crucial to know their molecular structures, i.e. the precise location of the atoms, and the level of solvation and aggregation.\textsuperscript{6,7} To this end, advances in X-ray crystallography over the past 30 years, alongside developments in \textit{ab initio} calculations and analytical techniques such as NMR spectroscopy, have resulted in the full characterisation of a large number of organometallic complexes. Nevertheless, despite these advances, organometallic compounds of the heavier alkali metals (sodium, potassium, rubidium and caesium) have been less extensively investigated in comparison to lithium complexes due, at least in part, to the increased difficulty in handling these compounds.

In addition, much less attention has been paid to complexes of the alkali metals with organophosphorus ligands, although the factors that govern their structures and aggregation states are parallel to those observed in organometallics. This section will briefly discuss these factors, and highlight the trends that have been observed.

The behaviour of alkali metal organometallics in solution is very important in rationalising the reactivity of these compounds. Although it was previously assumed that the anionic ligand and cationic metal dissociate in solution, it is now accepted that the ligand is stabilised by the cation and contact ion pairs are often formed. The ion pairing can be divided into two categories: tight contact ion pairs with one solvent shell around the RM unit (\(R = R_3C, M = \text{alkali metal cation}\)) and solvent separated ion pairs, in which the \(R^-\) and \(M^+\) ions each become solvated and are shielded from each other (Scheme 1.1).\textsuperscript{5}
Scheme 1.1. Solvated forms of an organometallic complex.

The structure and aggregation state of RM is most strongly dependent on the charge-to-size ratio of the metal cation $M^+$. As the ionic radius of the alkali metals increases down the group, the charge to size ratio decreases, which affects electronic factors such as lattice energy and electronegativity, as shown in Table 1.1. The size of the cation has a significant effect on the coordination numbers; for example, complexes of lithium, the smallest alkali metal, typically favour a four-coordinated structure, whereas the larger potassium, rubidium and caesium cations can have coordination numbers of up to ten. Consequently complexes of the heavier alkali metals are more likely to undergo extensive aggregation, often leading to insoluble polymers that are difficult to crystallise or to characterise in solution.

<table>
<thead>
<tr>
<th>Ionic radius *(^a) (Å)</th>
<th>Lattice energy (kJ mol(^{-1})) $M^+ (g) + Cl^- (g) \rightarrow MCl$</th>
<th>Pauling Electronegativity (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0.76</td>
<td>-834</td>
</tr>
<tr>
<td>Na</td>
<td>1.02</td>
<td>-769</td>
</tr>
<tr>
<td>K</td>
<td>1.38</td>
<td>-701</td>
</tr>
<tr>
<td>Rb</td>
<td>1.52</td>
<td>-680</td>
</tr>
<tr>
<td>Cs</td>
<td>1.67</td>
<td>-657</td>
</tr>
</tbody>
</table>

Table 1.1. Selected physical and electronic properties of the alkali metals (* for coord. no. 6).

The extent of aggregation also depends on the steric requirements of the organic ligand, with more bulky/branched substituents leading to lower aggregation states; e.g. $^t$BuLi is hexameric in cyclohexane and benzene, whereas the more branched $^i$BuLi is tetrameric in the same solvents. Sterically demanding ligands such as mesityl (2,4,6-trimethylphenyl) and (Me$_3$Si)$_2$CH can counteract the aggregation effects associated with complexes of the larger alkali metals, by blocking the vacant coordination sites. Preventing formation of larger lattices increases the solubility of these complexes, thus allowing characterisation.

The presence of coordinating solvents such as THF and Et$_2$O, and other chelating donors such as pmdeta and tmeda usually results in lower aggregation states, as they can also occupy
the vacant metal coordination sites \[ \text{pmdeta} = N,N',N'',N''',N''''-\text{pentamethyldiethylene-triamine}; \text{tmeda} = N,N',N''-\text{tetramethylethylenediamine} \].

In summary, the structures and reactivities of alkali metal organometallic reagents are a compromise between several factors including cation size, the steric requirements of the ligand and the presence of coligands. Aggregation is often observed in these complexes, with dimmers trimers and ladder structures often observed. The degree of aggregation can be greatly reduced by occupying/blocking the vacant coordination sites of the alkali metal, which becomes more challenging with the larger alkali metals.

### 1.2 Phosphides

The interactions between alkali metal cations and P-donor ligands are expected to be weak and highly disfavoured due to Pearson’s hard-soft acid-base principle.\(^{10}\) Indeed, theoretical calculations suggest that the bonding affinities in complexes between a soft phosphorus-based ligand and a hard alkali metal cation are much lower than those for the corresponding nitrogen-based complexes; the binding energies for the reaction \( \text{M}^+ + \text{PH}_3 \rightarrow [\text{M-PH}_3] \) are calculated to be -26.7 and -17.4 kcal mol\(^{-1}\) for \( \text{Li}^+ \) and \( \text{Na}^+ \), respectively, compared to those of \( \text{Li}^+ \text{NH}_3 \) and \( \text{Na}^+ \text{NH}_3 \), which are calculated to be -40.2 and -28.0 kcal mol\(^{-1}\), respectively.\(^{11,12}\)

The low affinity of the alkali metal cation for phosphorus may be overcome by incorporating the P-donor site in an anionic ligand. Such ligands can be organised into three classes: ligands where the charge is localised on the phosphorus atom, i.e. phosphides (I), ligands where there is charge delocalisation towards phosphorus from an adjacent atom (II), or ligands where the negative charge is localised on an atom distant from the phosphorus (III).

![Diagram of phosphides I, II, and III](image)

The simplest complexes of the alkali metals with P-donor ligands are those of the type \( \text{R}_2\text{P}^\ominus \) (I). The factors that affect the structures adopted by these complexes are parallel to those observed in organometallic compounds as discussed in 1.1.
Due to the importance of alkali metal phosphide species as $R_2P^-$ transfer reagents and nucleophiles in organic synthesis (examples of synthetic uses are shown in Scheme 1.2), interest in their solid-state structures has been growing considerably since the 1980s. However, the number of reports detailing the structures of alkali metal phosphides is still significantly less compared to their alkyl and amido counterparts.

1.2.1 Alkali metal phosphides

The synthesis of alkali metal organophosphides is usually achieved via the direct metalation of a primary or secondary phosphine with a strong base.

$$R_2PH + R'M \rightarrow (R_2P)M + R'H$$

($R'M = \text{e.g. } ^7\text{BuLi, BnK, NaH}$)

Whilst this is the most widely used method to synthesise these species, alternative routes to alkali metal phosphide complexes include:

i) Direct metalation of a phosphine with a heavier alkali metal.$^{13,14}$

$$R_2PH + M \rightarrow (R_2P)M + ^{1/2}H_2 \quad (M = \text{K, Rb, Cs})$$
ii) P-C cleavage of an aryl-substituted tertiary phosphine with an alkali metal in a donor solvent e.g. THF, dioxane, or liquid ammonia.\textsuperscript{15,16,17}

\[
\text{R}_2\text{ArP} + 2\text{M} \rightarrow (\text{R}_2\text{P})\text{M} + \text{MAr}
\]

(Ar = aryl group, M = alkali metal)

The side product MAr can be removed with a proton source e.g. 'BuCl or NH\textsubscript{4}Cl, however the P-C cleavage reactions are not straightforward, and the products depend on the substituents of the aryl group; the presence of electron donating groups (e.g. OMe, NMe\textsubscript{2}, SMe etc.) tends to inhibit cleavage,\textsuperscript{15} although this depends also on the alkali metal.\textsuperscript{17}

iii) P-Si cleavage of a tertiary phosphine with an alkali metal alkoxide, or alkali metal alkyl. This route has proved suitable for (Me\textsubscript{3}Si)\textsubscript{2}PM complexes, avoiding the need for complex synthesis of secondary phosphines.\textsuperscript{18,19,20}

\[
\text{R}_2(\text{R'}_2\text{Si})\text{P} + \text{MR}'' \rightarrow (\text{R}_2\text{P})\text{M} + \text{R'}_2\text{SiR}''
\]

(MR'' = e.g. 'BuOLi, "BuLi)

iv) Metathesis between a lithium phosphide and a heavier alkali metal alkoxide.\textsuperscript{21}

\[
(\text{R}_2\text{P})\text{Li} + \text{MOR}' \rightarrow (\text{R}_2\text{P})\text{M} + \text{LiOR}'
\]

(M = Na-Cs; R' = e.g. 'Bu)

\subsection{1.2.1.1 Lithium organophosphides}

The first structurally characterised alkali metal phosphide was reported by R.A. Jones and co-workers in 1983.\textsuperscript{22} The deprotonation of 'Bu\textsubscript{2}PH with "BuLi in THF, followed by crystallisation from THF gave rise to the complex [Li\textsubscript{2}('Bu\textsubscript{2}P)\textsubscript{2}(THF)]\textsubscript{2} (1), which adopts a four-rung ladder structural motif, where two of the phosphide groups are triply bridging, and two are doubly bridging the lithium atoms (Figure 1.1). The Li-P distances in 1 range from 2.476(10) Å [Li(2)-P(2)] to 2.669(9) Å [Li(1)-P(1)].
A report by Steiglitz ten years later demonstrates that the ladder motif of this compound can be broken down by the addition of the bidentate ligand DME. The modified complex \([\text{Li}^+(\text{tBu}_2\text{P})(\text{DME})]^2 \text{ (2) consists of a dimer with a planar Li}_2\text{P}_2 \text{ core (Figure 1.2)}\) [Li(1)-P(1A) = 2.600(6); Li(1)-P(1) = 2.573(5) Å, P-Li-P' = 97.1(2)°].

Lithium diphenylphosphide was first characterised in 1984 as an adduct with 12-crown-4, and crystallises as a solvent separated ion pair. Since then it has been characterised in a number of adducts with O- or N-donor ligands: [Li(PPh_2)(OEt_2)]_∞ (3) and [Li(PPh_2)(THF)]_∞ (4) both crystallise as a chain of alternating Li^+ and PPh_2^- units, with greater solvation observed in 4 due to the smaller size of THF (Figure 1.3).
The Li-P distances correlate well with the coordination number of Li; P-Li = 2.629-2.634 Å for 3 (4 coordinate Li) and 2.483-2.496 Å for 4 (3-coordinate Li). The tmeda adduct [Li(PPh₂)(tmeda)]₂ adopts a dimeric structure with a planar Li₂P₂ core, whilst the pmdeta adduct [Li(PPh₂)(pmdeta)] crystallises as a monomer.

The simplest lithium phosphide LiPH₂ has been isolated as the polymeric adduct [Li(PH₂)(DME)]ₙ (5, Figure 1.4), which consists of an infinite zig-zag chain of alternating Li and P atoms, with an essentially linear Li-P-Li angle of 176.9(1)° and a P-Li-P angle of 117.0(2)°.²⁶,²⁷ The linearity of the Li-P-Li angle is attributed to the low steric demands of the H atoms in the phosphide.

Figure 1.3. Structures of 3 and 4 [disorder in THFs for 3].²⁵
Chelating or bridging alkali metal bis-phosphide complexes are useful synthons for the preparation of phosphorus macrocycles. For example, the compound \([1,2-C_6H_4(PPh)_2Li(tmeda)]_2\) (6, Figure 1.5) crystallises as a monomer, where each lithium ion is bound equivalently to the two phosphorus atoms. The coordination about each lithium ion is completed by a molecule of tmeda.\(^{28}\)

More recently, Power and co-workers were able to structurally characterise the novel phosphide \([^\{C_6H_3-2,6(C_6H_2-2,4,6-iPr_3)\}PhPLi(THF)_2\}]\) (7, Figure 1.6). The P–C(ipso) bond lengths in 7 were 1.836(2) and 1.830(3) Å for the terphenyl and phenyl linkages, respectively, with a Li–P contact of 2.478(4) Å, which suggests that this is a reasonably strong interaction. The large, bulky terphenyl groups are able to sterically protect the phosphorus, thus reducing the tendency to form P-bridging oligomers.\(^{29}\)
A number of lithium phosphide complexes containing organosilicon substituents have also been synthesised and structurally characterised. Treatment of the secondary phosphine \((\text{Me}_3\text{Si})_2\text{PH}\) with \(~\text{BuLi}\) in cyclopentane yields the solvent-free, hexameric complex \([\text{(Me}_3\text{Si})_2\text{PLi}]_6\) \((\text{8}, \text{Figure 1.7}).\) The hexamer adopts a six-rung ladder motif in the solid state. This is in contrast to earlier reports of the solvated form of this compound when synthesised via the tertiary phosphine \(\text{P(SiMe}_3\text{)}_3\), which forms a tetrameric ladder \([\{\text{Me}_3\text{Si}\}_2\text{P}\text{Li}_2(\text{THF})\}_2\) (Figure 1.8.). The formation of an extended ladder in \(\text{8}\) is inhibited by the steric demands of the \(\text{SiMe}_3\) groups, which occlude the free coordination site on \(\text{Li}(3)\).
Examples of silicon-containing phosphides that adopt a dimeric or tetrameric structure are the compounds \[
\{\text{Ph}_3\text{Si} \}_{2}\text{P} \text{Li}_2 \] (9) and \[
\{\text{PH(Si'Pr}_3\}\{\text{P(Si'Pr}_3\}_{2}\text{P} \text{Li}_4 \] (10, Figure 1.9).\textsuperscript{31} The large steric requirements of the SiPh\textsubscript{3} substituent in 9 prevent oligomerisation beyond a dimer and allow the isolation of a solvent-free complex. In addition to the P-Li contacts in the dimer, there are further contacts between the lithium and the phenyl rings: one phenyl ring from one \text{P(SiPh}_3\}_{2}\text{P} \text{ligand binds in a } \eta^2 \text{- fashion, whilst one ring from the other ligand binds in a } \eta^1 \text{- fashion to the metal. Compound 10 arises from deprotonation of } \{\text{Pr}_3\text{Si}\}_{2}\text{PH} \text{ with } n^\text{-BuLi. Formation of an additional } \{\text{Pr}_3\text{Si}\}_{2}\text{PH subunit is attributed to a Si-P cleavage that occurs on treatment with } n^\text{BuLi.}

1.2.1.2 Heavier alkali metal phosphides

Heavier alkali metal phosphides are important due to their enhanced reactivity over their lithium counterparts, and also with respect to the diversity of their solid state-structures. However, there are relatively few examples of heavier alkali metal phosphides, due to the larger size/charge ratios of the metals compared to lithium, leading to insoluble polymers that are difficult to crystallise and to characterise in solution. This can be counteracted by the use of sterically demanding substituents and/or the use of polydentate coligands (e.g. pmdeta, tmeda) to block or occupy vacant coordination sites.

The first heavier alkali metal phosphides to be structurally characterised were the sodium and potassium complexes \([\{\text{mes}\}{\text{F}^1\text{Bu}_2\text{Si}}\text{P})\text{M(THF)}_2]\) \([\text{M} = \text{Na (11), K (12); mes = mesityl}]\). Compounds 11 and 12 adopt an 8-membered ring motif, where the metal cation is coordinated by a phosphorus atom from one ligand and a fluorine atom from the neighbouring ligand. The M-P and M-F bond distances are 2.890(1) and 2.383(2) Å, respectively, for 11, and 3.230(1) and 2.643(1) Å, respectively, for 12.

![Figure 1.10. Structure of 11.](image)

The first simple sodium phosphide was reported by Raston and co-workers in 1995.33 \([(\text{C}_6\text{H}_{11})\text{PHNa(pmdeta)}_2]\) (13, Figure 1.11) crystallises as discrete centrosymmetric dimers with a planar central \(\text{P}_2\text{Na}_2\) ring. The cyclohexyl substituents adopt a transoid position relative to the \(\text{P}_2\text{Na}_2\) ring with both \(\text{Na}^+\) cations achieving a five-coordinate geometry via
complexation with the tridentate pmdeta ligand, which prevents aggregation. Within the ring
the P-Na distances [P-Na 2.883(8), P’-Na 2.936(7) Å] are comparable to those found in 11.

![Figure 1.11. Structure of compound 13.](image)

There are several reports of caesium and rubidium phosphide complexes. Rabe and co-
workers have isolated several complexes of these heavier alkali metals with mesityl- and
supermesitylphosphides. Two such examples are [{(mes*)PH}Cs(py)]∞ (14, mes* = 2,4,6-tri-tert-butylphenyl, Figure 1.12) and [{(dmp)PH}Rb]4·(toluene) (15, dmp = dimesitylphenyl, Figure 1.13). The caesium complex (14) crystallises as a ladder polymer in
which the squares are alternately bridged and non-bridged by the pyridine ligands. The ladder
also exhibits a twist of ca. 130° in one direction, followed by an equal twist in the opposite
direction. There are several other base adducts of this compound that adopt similar ladder
motifs. 

![Figure 1.11. Structure of compound 13.](image)
Compound 15 crystallises as a tetramer with an unprecedented heterocubane structure, with each Rb atom coordinated by three phosphide ligands, with further coordination by multihapto interactions with two mesityl rings from two different dmp substituents. The NMR spectra of 15 suggest that this structure is retained in solution.
1.2.1.3 Donor-functionalised phosphides

Since the coordination of additional donor ligands to alkali metal complexes enhances reactivity by reducing the extent of aggregation, there have been several reports that have investigated the effects on aggregation of incorporating additional donor functionality into phosphide ligands.\textsuperscript{21,37-39} The first structurally characterised example was the compound \([\{(\text{C}_6\text{H}_4\text{-2-OMe})_2\text{P}\}\text{Na(diglyme)}]\)\textsubscript{2} (16, Figure 1.14).\textsuperscript{37}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.14.png}
\caption{Structure of compound 16 [Dig = diglyme (MeO\{C\text{2H}_4\}O\{C\text{2H}_4\}OMe)].\textsuperscript{37}}
\end{figure}

Compound 16 was prepared by cleavage of (C\textsubscript{6}H\textsubscript{4}-2-OMe)\textsubscript{3}P with Na in liquid ammonia/THF, and was crystallised as its diglyme adduct as discrete dimers. Each Na atom is coordinated to the P and one O atom of the phosphide ligand to give a 5-membered chelate ring; the second O atom of the phosphide ligand does not bind to the metal centre. Coordination to the sodium is completed by the P atom of the second phosphide, and three O atoms of a facially coordinated diglyme. Although 16 possess a P\textsubscript{2}Na\textsubscript{2} core, this is not planar as in compounds 11 and 13.\textsuperscript{31,32}

The related amino-functionalised phosphide complexes \([\{(\text{Me}_3\text{Si})_2\text{CH}\}(\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMMe}_2)\text{PM}(\text{L})]\) \([\text{M = Li, L = (THF)}_2\) (17), \text{M = Na, L = tmeda (18), M = K, L = (pmdeta) (19)]\) have also been isolated and structurally characterised by Izod and co-workers.\textsuperscript{21} In each case, the phosphide ligand binds via its N and P atoms to the metal centres to give a puckered 6-membered chelate ring. However, in compounds 18 and 19, there is a significant M···C contact to the ipso carbon directly attached to the P atom. The Na-P and K-P distances of 2.8396(9) and 3.2326(6) Å, respectively, are short compared to other Na-P and K-P distances.
The same group have also reported examples of amino-functionalised phosphides that have been prepared from the rearrangement of a tertiary phosphine: compounds \([\text{MeP}\{\text{C}_6\text{H}_4\text{-2-CH(C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2\}\text{NMe}_2}\}\text{Li(THF)}_2\] (20) and \([\text{‘PrP}\{\text{C}_6\text{H}_4\text{-2-CH(C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2\}\text{NMe}_2}\}\text{Li (THF)}_2\] (21). Deprotonation of the tertiary phosphine \(\text{MeP(C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2)\) with \(^n\text{BuLi}\) in a solution of THF yields compound 20 exclusively. Similarly, treatment of a THF solution of the related tertiary phosphine \(\text{‘PrP(C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2)\) with \(^n\text{BuLi}\) yields only compound 21. These compounds were formed via an unusual Smiles rearrangement, which is completely dependent on the presence of a strong donor solvent i.e. THF. The mechanism proposed for the formation of 20 (Scheme 1.3) proceeds via a phosphinomethanide intermediate, which is initially formed upon metalation.
**Scheme 1.3.** Formation of compound 20.

In both cases the lithium ion is bound by the P and one of the N atoms of the ligands, generating a six-membered chelate ring with a bite angle of 97.39(15)° and 95.4(2)° for 20 and 21 respectively. These compare to a bite angle of 93.8(3)° observed in compound 17. The coordination sphere of each lithium ion is completed by two molecules of THF to give a distorted tetrahedral geometry.
1.2.2 Alkaline earth metal phosphides

Complexes of the heavier alkaline earth metals (Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$) have been shown to have catalytic activity in the hydrophosphination, hydroamination$^{41,42}$ and hydrosilylation$^{43}$ of alkenes and alkynes, and furthermore, have high reactivity that allows the synthesis of a wide range of derivatives.$^{44,45}$ However, they have a tendency to form aggregates or solvates with neutral donor ligands due to their large ionic radii. Thus, the synthesis of phosphide complexes of group II metals requires sterically demanding substituents that can block the vacant coordination sites and prevent oligomerisation. Phosphide complexes with group II metals usually adopt one of four structural types (Figure 1.17) and are attracting much interest due to their high reactivity.$^{45-47}$
The first example of an alkaline earth metal phosphide to be characterised in the solid-state was reported in 1987 by Raston and co-workers, and has the formula [(PhPH)$_2$Mg(tmeda)] (22, Figure 1.18).\(^{48}\)

The first structurally characterised diorganophosphide derivative of beryllium [(η\(^5\)-C\(_5\)Me\(_5\))Be(PBu\(_t^2\))] (23, Figure 1.19), was reported in 1990.\(^{49}\) Compound 23 crystallises as a monomer due to the steric bulk of the C\(_5\)Me\(_5\) ligand which is bound to the beryllium in a η\(^5\)-fashion. The Be-P bond length of 2.083(6) Å is much shorter than the Mg-P distance in 22 [2.592(5) Å], which is as expected.\(^{48}\) The P-Be-ring centroid angle of 168.3(7)° suggests that there is some steric strain between the 'Bu groups on the phosphorus atom and the methyl substituents of the C\(_5\)Me\(_5\) ligand. Notably, the Be-ring centroid distance [1.48(1) Å] is much shorter than that found in (C\(_5\)H\(_5\))BeMe [1.907(5) Å].\(^{49}\)
The first strontium phosphide to be structurally characterised was the compound \([\{\{\text{Me}_3\text{Si}\}_2\text{P}\} \cdot \text{Sr} \cdot (\text{THF})_4] \cdot \frac{1}{2} \text{THF}\) (24, Figure 1.20), reported by Westerhausen and co-workers.\(^{50}\) The phosphide ligands adopt trans positions and are planar, and the normals of the Si\(_2\)P planes are nearly perpendicular to each other. Heating compound 24 in a vacuum yields \([\text{Sr}_2(\{\text{Si} \cdot \text{Me}_3\}_2) \cdot (\text{THF})_3] \cdot \text{toluene}\) (24a), with three bridging and one terminal phosphide ligands.\(^{50}\)
In 2002 Izod reported a series of alkaline earth metal complexes with the phosphide ligand \[{(\text{Me}_3\text{Si})_2\text{CH}}P(\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2)]\]–.\(^{51}\) Compounds \[{(\text{Me}_3\text{Si})_2\text{CH}}P(\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2)]_2\text{Mg} (25) and \[{(\text{Me}_3\text{Si})_2\text{CH}}P(\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2)]_2\text{Ca} (26) are monomeric in the solid state with a four-coordinate metal centre, which adopts a distorted tetrahedral geometry. Two phosphide ligands are bound to each metal centre through their P and N atoms, forming two puckered 6-membered rings, with larger bite angles observed for 25 [90.89(6)°] compared to 26 [84.27(4)°] which is to be expected, due to the larger ionic radius of Ca\(^{2+}\) compared to Mg\(^{2+}\) (1.00 and 0.72 Å, respectively, for a 6-coordinate centre). The remaining angles about the metal centres are very similar for 25 and 26, illustrating a high degree of flexibility of the phosphide ligands. The Mg-P distance of 2.556(1) Å is similar to Mg-P distances in other magnesium phosphides,\(^{47,48,52}\) which is unexpected due to the steric congestion about the Mg centre. In contrast, the Ca-P distances of 2.824(1) and 2.826(1) Å are the shortest of such distances to be reported.

The related compounds \[\{(\text{Me}_3\text{Si})_2\text{CH}}P(\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2)]_2\text{Sr(THF)}\] (27) and \[\{(\text{Me}_3\text{Si})_2\text{CH}}P(\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2)]_2\text{Ba(THF)}\] (28) crystallise as monomers. Compounds 27 and 28 are isostructural, with the metal centres adopting a five-coordinate, distorted square pyramidal geometry. The ligands bind to the metal centre through their N and P atoms to form the basal plane of the square pyramid, generating two puckered six-membered chelate rings. The coordination spheres of the metals in 27 and 28 are completed by a molecule of THF. A study of the dynamic behaviour of compounds 26, 27 and 28 in solution showed that an equilibrium is established between their monomeric and dimeric forms, with the monomer favoured at low temperatures.

To summarise, complexes of phosphide anions with group I and II metals are a versatile class of compounds that exhibit much structural diversity. However, although there has been strong growth in the number of such complexes that have been isolated in the solid state in the past 30 years, there still remains a dearth of information, particularly with regards to the structures of heavier alkali and alkaline earth metal complexes.
Figure 1.21. Structures of compounds 25 to 28.\textsuperscript{51}
1.3 Phosphine-boranes

1.3.1 Introduction

Phosphine-boranes have several important features that make them interesting synthetic tools, and as such there has been an explosion of their use in organic synthesis over the past 30 years. These features include: a strong P-B bond, which is very stable and protects the phosphorus towards oxidation; reversible adduct formation; and activation of P-H or adjacent C-H bonds towards deprotonation. The air-stable, easy-to-handle properties of phosphine-boranes help overcome the usual problems associated with the handling and storage of air and moisture sensitive trivalent phosphines.

The first example of a phosphine-borane adduct, reported in 1890 by Besson, was the phosphine trichloroborane $\text{H}_3\text{P} \cdot \text{BCl}_3$.\textsuperscript{53} 50 years later, Gamble and Gilmont continued with detailed investigations of phosphine-boranes, and reported the synthesis of the diborane diphosphine compound $\text{B}_2\text{H}_6 \cdot 2\text{PH}_3$, at low temperatures, postulating the formula based on work by Stock on the amine analogue.\textsuperscript{54,55} However it was later found that the data collected was misinterpreted, and in fact the compound was monomeric in nature, and the true formula was the simple phosphine-borane adduct $\text{PH}_3 \cdot \text{BH}_3$.\textsuperscript{56}

The methodology of the synthesis of alkyl-functionalised secondary phosphine-boranes of the general form $\text{R}_2\text{PH} \cdot \text{BH}_3$ (Figure 1.22) has since been greatly developed, and these species now constitute a unique class of compound with widespread application in synthesis.\textsuperscript{55-59}

![Figure 1.22. A secondary phosphine-borane.](image-url)
1.3.2  Preparation

Formation of phosphine-borane adducts via direct reaction of diborane with a phosphine is now rarely used and instead is usually achieved through direct reaction of a phosphine (primary, secondary or tertiary) with BH$_3$·THF or BH$_3$·SMe$_2$, where the weaker Lewis base is displaced by the more strongly donating phosphine, forming a dative covalent bond to the boron (Scheme 1.4).$^{62-66}$

\[
\text{THF} \cdot \text{BH}_3 + \text{R}_2\text{PH} \rightarrow \text{R}_2\text{PH} \cdot \text{BH}_3 + \text{THF}
\]

Scheme 1.4. Synthesis of a secondary phosphine-borane adduct.

Similarly, phosphine/amine exchange reactions are also a well-established route to phosphine-borane adducts, where treatment of an amine-borane adduct with excess phosphine yields the phosphine-borane and free amine via an equilibrium process (Scheme 1.5).$^{67}$ The position of equilibrium in these processes is dependent on the donor abilities of the phosphine and amine and, as such, is defined by the electronic and steric effects of the substituents.

\[
\text{R}_3\text{N} \cdot \text{BH}_3 + \text{R'}_3\text{P} \leftrightarrow \text{R'}_3\text{P} \cdot \text{BH}_3 + \text{R}_3\text{N}
\]

Scheme 1.5. Phosphine-borane and amine-borane equilibrium.

1.3.2.1  Preparation of phosphine-boranes from borohydrides

Alternatively, phosphine-boranes can be synthesised from phosphine oxides in a one pot reaction mixture of LiAlH$_4$, NaBH$_4$ and CeCl$_3$ (Scheme 1.6).$^{68}$ The reaction does not proceed without CeCl$_3$, which is postulated to have a dual role in the mechanism: it activates the phosphine oxide by coordination so that reduction with LiAlH$_4$ occurs readily,$^{69}$ and it activates NaBH$_4$ to facilitate the reaction with the intermediate phosphines to form the phosphine-boranes. This method can be used with secondary and tertiary phosphines, however the reduction step of the mechanism is followed by a rapid pseudorotation, leading to racemisation, so is unsuitable for preparing optically active phosphines.$^{70}$
A more novel approach to accessing phosphine-borane adducts from NaBH₄ has been recently developed. A secondary phosphine can be reacted with NaBH₄ alongside a proton source, generating BH₃ \textit{in situ} and generating the phosphine-borane in high yield (Scheme 1.7).⁷¹

1.3.2.2 Preparation of phosphine-boranes from secondary chlorophosphines

Secondary phosphine-boranes can also be prepared from secondary chlorophosphines in a one pot reaction, by treatment with LiAlH₄ and BH₃·THF (Scheme 1.8)⁷⁰ or with NaBH₄ (Scheme 1.9).⁷²,⁷³
1.3.3 Decomplexation of phosphine-boranes

In section 1.3.1 it was mentioned that in the formation of phosphine-borane adducts, borane acts as a protecting group, thus allowing alternative chemistry to be performed; due to the relative ease in which phosphorus can be oxidised, the use of a protecting group means that selective oxidation can occur elsewhere in the molecule. Another important feature is that the formation of the adduct is reversible. Although a P-B bond is generally more stable than an N-B bond, the equilibrium that exists between phosphine/amine-borane adducts (as shown in Scheme 1.5) can be driven so that the borane group can migrate from phosphorus to nitrogen. This was first reported by Imamoto, who treated phosphine-boranes with a large excess of either diethylamine or morpholine to cleave the P-B bond in a variety of phosphine-boranes; this was found to occur with retention of chirality at phosphorus (Scheme 1.10). However, the use of secondary amines is not always suitable for deprotecting phosphine-boranes that contain other functional substituents. This problem was first solved by Le Corre et al who decomplexed phosphine-boranes containing carbonyl groups by treatment with dabco (1,4-diazabicyclo[2.2.2]octane) or tmeda.

![Scheme 1.10. Decomplexation of a phosphine borane with an amine](image)

Decomplexation can also be achieved through the use of acids, such as methanesulfonic acid or trifluoromethanesulfonic acid, or HBF$_4$, or zeolites in combination with alcoholysis. Mechanistically, the deprotection with acids is more complex. For deprotection with HBF$_4$, it has been shown that the fluoride of the reagent exchanges with the hydride on the borane moiety of the phosphine-borane, thus rendering it more easily attacked by water, leading to hydrolysis.
1.3.4 Reactivity and functionalisation of phosphine-boranes

Phosphine-boranes are very versatile reagents, which is, in part, due to their increased reactivity over their phosphine precursors.\textsuperscript{68,80,81} The activation of phosphine-boranes towards deprotonation has been demonstrated by Le Corre and co-workers via the olefination of carbonyl compounds (Scheme 1.11); treatment of a hydroxy-functionalised phosphine-borane with \textsuperscript{t}BuOK will proceed with elimination of an alkene, whereas the reaction is not observed with free phosphines.\textsuperscript{82}

Due to the wide scope of applications, this section will only focus on the uses of secondary phosphine-boranes in synthesis.

\textbf{Scheme 1.11.} Olefination reaction of phosphine-boranes and carbonyls.

The Imamoto group have investigated the reactions of secondary phosphine-boranes with a range of electrophiles in the presence of a base (e.g. \textsuperscript{t}BuLi, NaH) to provide a variety of functionalised tertiary phosphine-boranes (Scheme 1.12).\textsuperscript{83} In these reactions, the borane acts as both an activating and protecting group, and can be removed with an excess of amine (see also Scheme 1.10)
Livinghouse and Wolfe have synthesised a series of $P$-chiral phosphine-boranes prepared from a racemic secondary phosphine-borane precursor with excellent enantiocontrol via dynamic resolution/alkylation of the corresponding lithium derivative in the presence of (-)-sparteine (Scheme 1.13). This may be followed by borane deprotection to yield chiral phosphines, which are well established as controller ligands for asymmetric processes.

Grubbs and co-workers have synthesised a number of water-soluble aliphatic phosphines via secondary phosphine-borane intermediates. This approach was developed to generate phosphine-boranes that can bear ionic functionalities (Scheme 1.14).
1.3.4.1 Hydrophosphination

The utilisation of phosphine-boranes as a source of P-H bonds for hydrophosphination reactions has recently attracted much interest and was first described by Imamoto and co-workers. Addition of a P-H bond across an unsymmetrical, unsaturated carbon–carbon bond can lead to two different isomers via Markovnikov (α-addition) or anti-Markovnikov (β-addition) addition, and is very challenging to control regioselectivity. However a number of hydrophosphination reactions of alkynes with phosphine-boranes have since been reported with improved yields and regio- and stereoselectivities. For example, it was observed that under thermal conditions, a mixture of alkyne and phosphine-borane yields only the anti-Markovnikov β-adduct, whilst in the presence of a Pd(0) catalyst, only the Markovnikov α-adduct is formed (Scheme 1.15). Subsequently, hydrophosphination reactions of secondary phosphine-boranes with unactivated alkenes have been reported: on heating diphenyl- or methylphenyl phosphine-boranes with a range of alkenes under microwave radiation, clean formation of the hydrophosphination product is observed (Scheme 1.16). These types of reactions have also been shown to proceed catalytically using basic conditions with a number of alkynes and allenyl phosphine-oxides as shown in Scheme 1.17.
1.3.4.2 Cross-coupling functionalisation

Functionalisation of phosphine-boranes can also be achieved by metal-catalysed cross-coupling reactions. Pd-catalyzed coupling of aryl iodides with secondary phosphine-boranes yields tertiary phosphine-borane adducts (Scheme 1.18) in a process that is similar to the Buchwald-Hartwig cross-couplings known for amines and alcohols. Copper complexes have also been successfully utilised as a catalyst in P-C bond formation.
[Cu$^{II}$(OH)-tmeda]$\text{Cl}_2$ is able to cross-couple secondary phosphine-boranes with alkynes, which are believed to undergo subsequent hydrolysis of the triple bond to generate the corresponding ketone and regenerate the catalyst (Scheme 1.19).$^{97}$ Copper-amine adducts, generated \textit{in situ} between Cul and a variety of diazo compounds, can also react with secondary phosphine-boranes. If chiral phosphine-boranes are used, these reactions can proceed with retention of chirality (Scheme 1.20).$^{98}$

\begin{equation}
\text{BH}_3
\begin{array}{c}
\text{Ph} \\
\text{H}
\end{array}
\begin{array}{c}
\text{P} \\
\text{R}^1
\end{array} + \begin{array}{c}
\text{R}^2 \\
\text{I}
\end{array}
\xrightarrow{\text{(dpff)PdCl}_2 (5 \text{ mol\%})}
\begin{array}{c}
\text{BH}_3 \\
\text{Ph} \\
\text{H}
\end{array}
\begin{array}{c}
\text{P} \\
\text{R}^1
\end{array}
\begin{array}{c}
\text{R}^2 \\
\text{I}
\end{array}
\xrightarrow{2 \text{ K}_2\text{CO}_3}
\xrightarrow{\text{MeCN}}
\begin{array}{c}
\text{BH}_3 \\
\text{Ph} \\
\text{H}
\end{array}
\begin{array}{c}
\text{P} \\
\text{R}^1
\end{array}
\begin{array}{c}
\text{R}^2 \\
\text{I}
\end{array}
\xrightarrow{\text{Et}_3\text{N} (20 \text{ mol\%})}
\xrightarrow{\text{MeCN, r.t, 6 h}}
\begin{array}{c}
\text{BH}_3 \\
\text{Ph} \\
\text{H}
\end{array}
\begin{array}{c}
\text{P} \\
\text{R}^1
\end{array}
\begin{array}{c}
\text{R}^2 \\
\text{I}
\end{array}
\xrightarrow{\text{- H}_2\text{O}}
\end{equation}

\textbf{Scheme 1.18.} Pd-catalysed cross-coupling reaction [dpff = 1,1'-bis(diphenylphosphino)ferrocene].

\begin{equation}
\begin{array}{c}
\text{BH}_3
\begin{array}{c}
\text{Ph} \\
\text{H}
\end{array}
\begin{array}{c}
\text{P} \\
\text{R}^1
\end{array} + \begin{array}{c}
\text{R}^2 \\
\text{I}
\end{array}
\xrightarrow{\text{2 Cl}^\text{\text{\footnotesize{2}}}}
\begin{array}{c}
\text{BH}_3
\begin{array}{c}
\text{Ph} \\
\text{H}
\end{array}
\begin{array}{c}
\text{P} \\
\text{R}^1
\end{array} + \begin{array}{c}
\text{R}^2 \\
\text{I}
\end{array}
\end{array}
\xrightarrow{\text{Et}_3\text{N} (20 \text{ mol\%})}
\xrightarrow{\text{MeCN, r.t, 6 h}}
\begin{array}{c}
\text{BH}_3
\begin{array}{c}
\text{Ph} \\
\text{H}
\end{array}
\begin{array}{c}
\text{P} \\
\text{R}^1
\end{array} + \begin{array}{c}
\text{R}^2 \\
\text{I}
\end{array}
\xrightarrow{\text{- H}_2\text{O}}
\end{equation}

\textbf{Scheme 1.19.} Cu-catalysed cross-coupling reaction and oxyfunctionalisation.

\begin{equation}
\begin{array}{c}
\text{BH}_3
\begin{array}{c}
\text{Ph} \\
\text{H}
\end{array}
\begin{array}{c}
\text{P} \\
\text{R}^1
\end{array} + \begin{array}{c}
\text{R}^2 \\
\text{I}
\end{array}
\xrightarrow{\text{Cul (5 mol\%)}}
\begin{array}{c}
\text{BH}_3
\begin{array}{c}
\text{Ph} \\
\text{H}
\end{array}
\begin{array}{c}
\text{P} \\
\text{R}^1
\end{array} + \begin{array}{c}
\text{R}^2 \\
\text{I}
\end{array}
\end{equation}

\textbf{Scheme 1.20.} Stereocontrolled Cu-catalysed cross-coupling reaction.

\subsection*{1.3.5 \textbf{Summary}}

The examples given above demonstrate that phosphine-boranes are extremely useful synthetic intermediates. The stability of the P-B bond and the ability of borane to act as both
an activating and protecting group has been well exploited, particularly in the synthesis of \(P\)-chiral phosphines, with scope for the development of new, more efficacious phosphines. With increasing demand for ligands in asymmetric catalysis, there is no doubt that this area of chemistry will continue to grow.

### 1.4 Phosphido-boranes

Secondary phosphine-boranes are readily deprotonated to yield the corresponding phosphido-boranes. There are very few examples of phosphido-boranes that have been structurally characterised, as they are generally generated *in situ* in the preparation of (chiral) phosphines. However, phosphido-boranes are a unique class of compound which have the potential to form complexes with main group metals that contain unusual bonding modes between the ligand and metal centre. By studying their solid-state structures and the nature of the metal-ligand interactions, it can be possible to ‘fine tune’ their reactivity.

The first examples of phosphido-mono(borane) ligands coordinated to a main group metal were reported by Müller in 2003.\(^9\) The deprotonation of either of the secondary phosphine-boranes \(\text{Me}_2\text{PH(BH}_3\text{)}\) or \(\text{tBuPhPH(BH}_3\text{)}\) with \(\text{tBuLi}\) in the presence of tmeda or (-)-sparteine, respectively (Scheme 1.21), yields the compounds \([\text{Me}_2\text{P(BH}_3\text{)}\text{Li(tmeda)}]\)\(^29\) and \([\text{tBuPhP(BH}_3\text{)}\text{Li(}-\text{-sparteine)}]\) \(^30\), respectively (Figure 1.23). Compound \(29\) crystallises as a polymer due to a series of Li-H-B interactions. The Li-P bond length of 2.620(4) \(\text{Å}\) is typical for lithium coordinated to an anionic phosphide, whilst it was found that the P-B bond lengthened to 1.945(3) \(\text{Å}\) compared to the phosphine-borane (1.898(1) \(\text{Å}\)). Compound \(30\) crystallises as a dimer, where metal-ligand contacts are formed exclusively due to Li-H-B interactions, which generates a central eight-membered ring. No P-Li contact is observed in the structure, which is possibly due to the steric bulk of the (-)-sparteine.

\[\text{R}^1\text{P(BH}_3\text{)}\text{Li}(-\text{-sparteine)}]\]

Scheme 1.21. Preparation of Compounds \(29\) (\(\text{R}^1 = \text{R}^2 = \text{Me}; \text{L} = \text{tmeda}\)) and \(30\) (\(\text{R}^1 = \text{Bu}, \text{R}^2 = \text{Ph}; \text{L} = (-)-\text{sparteine)}\).
Fig. 1.23. Structures of 29 and 30.\textsuperscript{99}

Reaction of AlCl\textsubscript{3} with four equivalents of 29 yields the corresponding lithium aluminate [Al{P(BH\textsubscript{3})Me\textsubscript{2}}\textsubscript{4}Li(MeO\textsubscript{t}Bu)] (31, Fig. 1.24), which was the first homoleptic tetraphosphorus aluminate to be structurally characterised.\textsuperscript{99}

Fig. 1.24. Structure of 31.\textsuperscript{99}
Two examples of phosphido-boranes coordinated to the heavier alkali metal potassium have been reported by Wagner and co-workers.\(^{100}\) The phosphine-boranes \(\text{Ph}_2\text{PH}(\text{BH}_3)\) and \(\text{tBu}_2\text{PH}(\text{BH}_3)\) were deprotonated using KH at low temperatures, and crystallised in the presence of 18-crown-6 to yield compounds \([\text{Ph}_2\text{P}(\text{BH}_3)\text{K}(18\text{-crown}-6)]\) (32) and \([\text{tBu}_2\text{P}(\text{BH}_3)\text{K}(18\text{-crown}-6)]\) (33), respectively (Figure 1.25). In compound 32, a direct bond is formed between the P atom and the metal centre [K-P 3.320(2) Å] and there is an additional \(\eta^2\)-coordination of the borane fragment [K...B 3.162 Å]. In compound 33, there are two crystallographically independent molecules (only one is shown) but in both cases there is no direct P-K contact, most likely due to the fact that the larger \(t\)-butyl groups force the phosphorus away from the plane of the \([\text{K}(18\text{-crown}-6)]\) adduct. In one of the molecules of 33, coordination of the borane fragment to potassium is thought to be somewhere between a \(\eta^2\) and \(\eta^3\) interaction whereas the second ion-pair is linked via an \(\eta^3\)-coordinated \(\text{BH}_3\).

\[ \text{Figure 1.25. Structures of 32 and 33.}\] \(^{100}\)
The same group have also synthesised the bis(phosphido-borane) \([\{\text{P(BH}_3\text{)(Ph)CH}_2\}\text{}_2\text{K}_2(\text{THF})_4\}]_n\) (34), which crystallises as a polymer (meso-diastereoisomer shown in Figure 1.26). Both borane groups in the phosphido-borane ligand are coordinated to an adjacent potassium ion, and in turn, each potassium ion also bound to a borane group from a second ligand, forming a series of BH\(_3\)…K interactions, which forms the polymer. The coordination about each potassium is completed by two molecules of THF.\(^{101}\)

![Figure 1.26. Structure of compound 34.\(^{101}\)](image)

In 2001 Romanenko, Bertrand et al identified two phosphido-poly(boranes), which demonstrated that phosphide anions can be bound to two or three borane groups. The only previous examples of trivalent phosphorus bound to two or three boron atoms that had been characterised in the solid state were limited to polyhedral compounds, neutral diborylphosphines, and heterocyclic compounds.\(^{102}\)

The primary phosphine (mes*)PH\(_2\) was deprotonated with an equimolar amount of \(^n\)BuLi in THF, and subsequent addition of two equivalents of BH\(_3\)·THF gave rise to the compound \([\text{(mes*)PH(BH}_3\text{)}_2\text{Li(THF)}_3]\) (35). The phosphido-bis(borane) ligand is coordinated to lithium
through one of the borane fragments via an η^2-interaction. The coordination sphere of lithium is completed by three molecules of THF. The borane bound to lithium is found to have a shorter P-B distance [P(1)-B(1) 1.955 Å] compared to the P-B distance in the ‘free’ BH₃ group [P(1)-B(2) 1.984 Å]. Further treatment of 35 with an excess of tBuLi and BH₃·THF at low temperature resulted in the formation of a new complex that crystallises as a dimer [(mes*)P(BH₃)(μ-BH₂)₂H Li(THF)₂] (36, Scheme 1.22). Compound 36 is characterised by the presence of a four-membered heterocyclic ring with a hydride that bridges the two BH₂ groups.

Scheme 1.22. Synthesis of compounds 35 and 36 [Ar = 2,4,6-tri-t-butylphenyl].

Figure 1.27. Structures of compounds 35 and 36.¹⁰²
The only example of a phosphido-bis(borane) coordinated to a heavier alkali metal is [Ph₂P(BH₃)₂K(18-crown-6)] (37, Figure 1.28).¹⁰³ Compound 37 crystallises as a monomer with the ligand bound to the potassium ion through the hydrogen atoms of one of the borane groups in an η³ fashion. Short contacts between one of the phenyl carbon atoms and the potassium ion [K(1)...C(34) = 3.372(2) Å] aid stabilisation of the molecular packing in the crystal lattice.

In 2009, Lancaster and co-workers synthesised a number of related phosphido-bis(borane) complexes, which possess (pentafluorophenyl)borane groups.¹⁰⁴ Of particular interest is the compound [Ph₂P{B(C₆F₅)₃}(BH₃)Li(Et₂O)₃] (38, Figure 1.29), which crystallises as a monomer, with the ligand bound to the lithium ion via an η²-type interaction from the BH₃ group. The Li...B distance in 38 of 2.477(3) Å is similar to that of 35, which is consistent with a η²-BH₃-Li interaction. As with 35, the P-B distance for the Li-bound BH₃ group in 38 is considerably shorter than the P-B distance for the ‘free’ borane group.

Figure 1.28. Compound 37.¹⁰³
Although there is only a small number of crystallographically-characterised phosphido-borane complexes with main group metals, there are several reports detailing the structures of phosphido-borane complexes with transition metals, these are discussed in chapter 3.

1.5 Summary

This chapter gives a brief overview of the factors that can affect the reactivity of alkali metal organometallic complexes, and reviews a diverse range of phosphide complexes with alkali and alkaline earth metals, exploring the factors which contribute to the unique structure and chemistry of each complex. The chapter also reviews the synthesis and applications of a wide-range of phosphine-boranes, with particular emphasis on the importance of the structures of the phosphido-borane intermediates, as this can help in our understanding of their reactivity. However, in general, there is a distinct lack of information on the structures of phosphido-boranes.

The work presented in this thesis will focus on the synthesis and solid-state structures of phosphido-boranes coordinated to alkali and alkaline earth metals, expanding upon the limited number examples found in the literature. There is a particular emphasis on the effect of introducing donor-functionality on the phosphorus, which will give a greater insight into the role played by a peripheral donor, and the factors that afford stability and that affect the
extent of aggregation in these species. Several new phosphido-bis(borane) complexes are also reported, including the first examples of alkaline earth metals coordinated to ligands of this type.

1.6 References


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Chapter 2. Synthesis of Phosphine-Borane Precursors

2.1 Introduction

Phosphine-boranes are highly valuable compounds due to their widespread applications in synthesis (see chapter 1.3). Deprotonation of secondary phosphine-boranes yields the corresponding anionic phosphido-boranes which are key intermediates in the synthesis of chiral phosphines. However, little is known about the structures of phosphido-boranes, as they are usually generated in situ, and as a result the factors that govern their structures and reactivities are not well understood.

In this project, several novel phosphine-boranes were prepared, with the general structure shown in Figure 2.1. The P-H group is activated towards deprotonation due to the presence of the BH₃ group directly bonded to phosphorus, thus phosphido-boranes are easily accessible upon treatment with a strong base. The bulky substituent (Me₃Si)₂CH confers several desirable properties, which include increased solubility, thermal stability, lipophilicity, and hindrance of high-order aggregation of the phosphido-borane complexes. Particular focus is paid to the introduction of peripheral donor functionality within the ligand, which can potentially provide additional stabilisation in the phosphido-borane complexes through intramolecular interactions between the peripheral donor atom and metal centre, resulting in the formation of a chelate ring. Changing the nature of the chelate ring i.e. varying the donor atom and ring size, can have a significant effect on the structures and consequently the reactivities of these phosphido-borane complexes. The borane group has also been shown to provide additional stabilisation through agostic-type B-H…M bonding modes with group I metals.¹⁻⁴

![Figure 2.1. General structure of phosphine-borane precursor. X = CH₂OMe, SMe, OMe, H.](image-url)
To probe the effects that peripheral donor groups have on the structures of phosphido-borane complexes, three donor-functionalised phosphine-borane precursors have been synthesised: 
\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{PH}(\text{C}_6\text{H}_4-2-\text{CH}_2\text{OMe})(\text{BH}_3) \ (39), \ \{(\text{Me}_3\text{Si})_2\text{CH}\}\text{PH}(\text{C}_6\text{H}_4-2-\text{SMe})(\text{BH}_3) \ (40), and \ \{(\text{Me}_3\text{Si})_2\text{CH}\}\text{PH}(\text{C}_6\text{H}_4-2-\text{OMe})(\text{BH}_3) \ (41). For comparison, the non-donor-functionalised \{(\text{Me}_3\text{Si})_2\text{CH}\}\text{PH}(\text{C}_6\text{H}_3)(\text{BH}_3) \ (42) was also synthesised.

![Chemical structures of phosphine-boranes](image)

**Figure 2.2.** Donor-functionalised phosphine-boranes.

### 2.2 Synthesis of secondary phosphine-borane precursors

#### 2.2.1 Synthesis of \{(\text{Me}_3\text{Si})_2\text{CH}\}\text{PH}(\text{C}_6\text{H}_4-2-\text{CH}_2\text{OMe})(\text{BH}_3) \ (39)

The preparation of 39 is shown in Scheme 2.1. Synthesis of 1-bromo-2-(methoxymethyl)benzene (BrC₆H₄-2-CH₂OMe) was achieved as previously reported.⁵ Treatment of BrC₆H₄-2-CH₂OMe with "BuLi at low temperatures (0 °C) yields LiC₆H₄-2-CH₂OMe via a lithium-halogen exchange reaction; this compound was not isolated, but was generated and used in situ. The reaction between the lithium salt and a cold solution of \{(\text{Me}_3\text{Si})_2\text{CH}\}\text{PCL}_2 \ (43)⁶ yields the monochlorophosphine \{(\text{Me}_3\text{Si})_2\text{CH}\}\text{PCL}(\text{C}_6\text{H}_4-2-\text{CH}_2\text{OMe}); the steric bulk of the (Me₃Si)₂CH group and low reaction temperature allows for mono-substitution of 43. The monochlorophosphine may be reduced in situ with LiAlH₄ to yield the secondary phosphine \{(\text{Me}_3\text{Si})_2\text{CH}\}\text{PH}(\text{C}_6\text{H}_4-2-\text{CH}_2\text{OMe}) \ (44). After an aqueous work-up, 44 may be isolated as a colourless oil. The phosphine-borane adduct was prepared by addition of BH₃·SMe₂ to a solution of 44 in Et₂O, and crystallised as colourless blocks from hot light petroleum in good yield (60%).
Scheme 2.1 Synthesis of 39. Reagents and conditions: i) NaH, THF, 0°C, 1 h. ii) MeI, 0°C, 0.5 h. iii) "BuLi, Et₂O, 0°C, 2 h. iv) {(Me₃Si)₂CH}PCl₂ (43), -78°C, 16 h. v) LiAlH₄, 35°C, 2 h. vi) Deoxygenated H₂O. vii) BH₃·SMe₂, THF, r.t. 1 h.

2.2.2 Synthesis of {(Me₃Si)₂CH}PH(C₆H₄-2-SMe)(BH₃) (40)

The preparation of 40 is shown in Scheme 2.2. The reaction between a cold solution of 2-bromothioanisole in Et₂O and "BuLi yields (2-(methylthio)phenyl)lithium via a lithium-halogen exchange reaction. The in situ-generated lithium salt is added to a cold solution of 43, to yield the chlorophosphine {(Me₃Si)₂CH}PCl(C₆H₄-2-SMe), which may be reduced in situ with LiAlH₄ to yield the secondary phosphine {(Me₃Si)₂CH}PH(C₆H₄-2-SMe) (45). After an aqueous work-up, 45 is isolated as a colourless oil. Addition of BH₃·SMe₂ to a solution of 45 in Et₂O yields the phosphine-borane {(Me₃Si)₂CH}PH(C₆H₄-2-SMe)(BH₃) (40), which may be crystallised from cold (-30 °C) n-hexane as colourless needles in excellent yield (83%).

Scheme 2.2. Synthesis of 40. Reagents and conditions: i) "BuLi, Et₂O, 0°C, 2 h. ii) {(Me₃Si)₂CH}PCl₂ (43), Et₂O, -78°C, 16 h. iii) LiAlH₄, 35°C, 2 h. iv) Deoxygenated H₂O. v) BH₃·SMe₂, THF, r.t., 1 h.
2.2.3 Synthesis of \{(\text{Me}_3\text{Si})_2\text{C}H\}\text{PH}(\text{C}_6\text{H}_4\text{-2-OMe})(\text{BH}_3) (41)

The synthesis of 41 is shown is Scheme 2.3. The reaction between a cold solution of 43 in THF and one equivalent of (2-methoxyphenyl)lithium\(^7\) yields the corresponding monochlorophosphine \{(\text{Me}_3\text{Si})_2\text{C}H\}\text{PCl}(\text{C}_6\text{H}_4\text{-2-OMe})\), which may be reduced \textit{in situ} with LiAlH\(_4\) to give the secondary phosphine \{(\text{Me}_3\text{Si})_2\text{C}H\}\text{PH}(\text{C}_6\text{H}_4\text{-2-OMe}) (46). After an aqueous work-up, 46 is isolated as a colourless oil. Treatment of a solution of 46 in Et\(_2\)O with BH\(_3\)·SMe\(_2\) gives the phosphine-borane precursor \{(\text{Me}_3\text{Si})_2\text{C}H\}\text{PH}(\text{C}_6\text{H}_4\text{-2-OMe})(\text{BH}_3) (41), which may be crystallised from light petroleum upon cooling (-30 °C), in good yield (73%), as colourless blocks.

\[
\text{Scheme 2.3. Synthesis of 41. Reagents and conditions: i) }^9\text{BuLi, TMEDA, Et}_2\text{O, 16 h. ii) }\{(\text{Me}_3\text{Si})_2\text{C}H\}\text{PCl}_2 (43), \text{THF, -78°C, 16 h. iii) LiAlH}_4, 66°C, 2 h. iv) }\text{Deoxygenated H}_2\text{O. v) BH}_3\cdot\text{SMe}_2, \text{THF, r.t., 1 h.}
\]

2.2.4 Synthesis of \{(\text{Me}_3\text{Si})_2\text{C}H\}\text{PH}(\text{C}_6\text{H}_5)(\text{BH}_3) (42)

The non-donor-functionalised phosphine-borane 42 was synthesised as shown in Scheme 2.4. The reaction between (Me\(_3\)Si\(_2\))\text{C}H\(_2\)Li (47)\(^6\) and one equivalent of phenyldichlorophosphine in Et\(_2\)O at low temperature (-78 °C) yields the monochlorophosphine \{(Me\(_3\)Si\(_2\))\text{C}H\}\text{PCl}(\text{C}_6\text{H}_5)\), which may be reduced with LiAlH\(_4\) \textit{in situ}, to generate the secondary phosphine \{(Me\(_3\)Si\(_2\))\text{C}H\}\text{PH}(\text{C}_6\text{H}_5) (48). After an aqueous work-up, 48 is isolated as a colourless oil. Reaction between a solution of 48 in Et\(_2\)O and one equivalent of BH\(_3\)·SMe\(_2\) yields the
phosphine-borane adduct \{(\text{Me}_3\text{Si})_2\text{CH}\}\text{PH(C}_6\text{H}_5\text{)(BH}_3\} (42), which may be crystallised from cold toluene (-30 °C) as a colourless, air-stable solid in good yield (63%).

\[ \begin{array}{c}
\text{Cl} \quad \text{P} \quad \text{Cl} \quad \xrightarrow{i), ii), iii)} \quad (\text{Me}_3\text{Si})_2\text{CH}^+ \quad \xrightarrow{iv)} \quad (\text{Me}_3\text{Si})_2\text{CH}^- \quad \text{P}^- \quad \text{H} \quad \text{BH}_3 \quad 48 \quad 42
\end{array} \]

**Scheme 2.4.** Synthesis of 42. Reagents and conditions: (i) (\text{Me}_3\text{Si})_2\text{CHLi} (47), Et_2O, -78°C, 16 h. ii) LiAlH_4, 35°C, 2 h. iii) Deoxygenated H_2O. iv) H_3B·SMe_2, THF, r.t., 1 h.

### 2.3 NMR spectroscopic characterisation of 39-42

The $^1\text{H}$, $^{11}\text{B}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of 39-42 are as expected. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra each compound exhibits a broad quartet at -16.2, -15.7 -22.3 and -8.6 ppm for 39-42, respectively, due to coupling of the $^{31}\text{P}$ nucleus to the quadrupolar $^{11}\text{B}$ nucleus ($I = 3/2$, nat. ab. = 80.1%, $^1J_{PB} = 49.0 \text{ Hz}$ in each case); the magnitude of $^{31}\text{P}-^{11}\text{B}$ coupling in secondary phosphine-boranes typically ranges between 38-58 Hz.\(^{8-12}\) The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 41 is shown in Figure 2.3 for illustration. $^{31}\text{P}-^{11}\text{B}$ coupling is confirmed in the corresponding $^{11}\text{B}\{^1\text{H}\}$ NMR spectra, which exhibit broad doublets at -39.8, -40.1, -40.6 and -40.6 ppm for 39-42, respectively [$^1J_{PB} = 49.0 \text{ Hz}$].

The quartets in the $^{31}\text{P}\{^1\text{H}\}$ spectra do not exhibit the expected signal ratio of 1:1:1:1, which may be a consequence of coupling to the $^{10}\text{B}$ isotope, which is also spin active but found in lower abundance than $^{11}\text{B}$ ($^{10}\text{B} I = 3$, nat. ab. = 19.9 %). The $^{10}\text{B}$ nucleus couples to $^{31}\text{P}$ to give a seven line multiplet, however the $^{31}\text{P}-^{10}\text{B}$ coupling constant has a much lower value than for $^{31}\text{P}-^{11}\text{B}$; the coupling of two nuclei is proportional to their magnetogyratic ratios ($J_{ij} \propto \gamma_i \gamma_j$), which is approximately three times larger for $^{11}\text{B}$ than for $^{10}\text{B}$ ($\gamma = 8.58 \times 10^7$ and $2.87 \times 10^7 \text{ rad T}^{-1}\text{s}^{-1}$, respectively).\(^{13}\) Therefore the observed signal in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra is a result of overlying $^{10}\text{B}$ and $^{11}\text{B}$ coupling, which is dominated by the more abundant $^{11}\text{B}$ isotope.
In the $^1$H NMR spectra, the P-H signals are observed as a doublet of quartets of doublets in each compound, except for 42, which has only been resolved as a doublet of quartets, lying at 5.97, 5.83, 6.04 and 5.72 ppm for 39-42 respectively (Figure 2.4). The splitting pattern is a result of the proton coupling to phosphorus, the borane protons and the adjacent C-H proton of the CH(SiMe$_3$) group. The $^1J_{PH}$ coupling constants in 39-42 range from 359.0 to 385.0 Hz, and are consistent with values reported in related compounds;$^{10,14-23}$ for example, for Ph$_2$P(BH$_3$) $^1J_{PH} = 385$ Hz, whilst for $^t$BuPhP(BH$_3$) $^1J_{PH} = 367$ Hz. The borane hydrogen atoms exhibit a broad quartet in the $^1$H NMR spectra, and as a result cannot be easily identified or integrated. Therefore it is necessary to decouple the $^{11}$B nucleus, which collapses the broad quartet into a sharp doublet of doublets, which are observed between 0.89 and 0.94, where $^2J_{PH} = 14.2$, 14.7, 14.9, 15.3 Hz, and $^3J_{HH} = 6.4$, 7.1, 6.6 and 6.6 Hz, for 39-42, respectively. This effect can be seen in Figure 2.5, where the $^1$H and $^1$H{$^{11}$B} NMR spectra of compound 40 have been overlaid.
Figure 2.4. P–H region of the $^1$H NMR spectra of compounds 39–42 in CDCl$_3$. 
Figure 2.5. $^1$H (above) and $^1$H$^{^11}B$ (below) NMR spectra of compound 40 in CDCl$_3$ (*$^{11}B$-decoupled borane hydrogens).

2.4 Solid-state structures of phosphine-boranes

X-ray diffraction studies of compounds 39, 41 and 42 were carried out for comparison with the structures of the corresponding metalated phosphido-borane species (see chapters 3, 5, 6 and 7). The molecular structures of 39, 41 and 42 are shown in Figures 2.6, 2.7 and 2.8 respectively, with selected bond lengths and angles shown in Tables 2.1, 2.2 and 2.3.

The P-B distances of 1.9232(18), 1.925(2) and 1.919(7) Å for 39, 41 and 42 respectively, are very similar, and typical of P-B distances for secondary phosphine-boranes, which lie in the range of 1.91-1.95 Å.\textsuperscript{24-31} The P-H distances in compounds 39, 41 and 42 are identical to within experimental error [1.294(14), 1.32(2) and 1.35(4) Å respectively], and lie within the range of P-H distances that have previously been reported for related phosphine-boranes: 1.26-1.41 Å.\textsuperscript{23-30}
The B-P-H angles for 39, 41 and 42 fall in the typical range for phosphine-boranes [104-120.6°], however, the B-P-H angle is somewhat larger in 42 [118.1(15)°] than in 39 and 41 [110.8(7) and 110.6(9)°, respectively]. There are slight variations between the remaining bond angles about the phosphorus centre, but no significant differences; the sum of angles within the C$_2$PB framework for 39, 41 and 42 are also identical to within experimental error [339.64, 339.68 and 340.07°, respectively].

In summary, the structures of 39, 41 and 42 are unsurprising, with structural parameters, falling within typical values for secondary phosphine-boranes. However the non-donor functionalised 42 has a larger B-P-H bond angle in comparison to the donor-functionalised species.
Figure 2.6. Structure of compound 39. All C-bound H atoms omitted for clarity.

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Table 2.1. Selected bond lengths (Å) and angles (°) of compound 39.
Figure 2.7. Structure of compound 41. All C-bound H atoms omitted for clarity.

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Table 2.2. Selected bond lengths (Å) and angles (°) of compound 41.
Figure 2.8. Structure of compound 42. All C-bound H atoms omitted for clarity.

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Table 2.3. Selected bond lengths (Å) and angles (°) of compound 42.


2.5 References


Chapter 3. Alkali metal complexes of a benzyl-methylether-functionalised phosphido-borane

3.1 Introduction

Phosphido-borane complexes of the alkali metals are highly reactive intermediates, often used in the preparation of synthetically important chiral phosphines, but are usually generated in situ and as a result there are few examples of these compounds that have been characterised in the solid state (chapter 1.4). This is rather surprising given the considerable interest in complexes of organophosphides with main group metals (chapter 1.2), and in complexes of silyl anions of the type (R₂SiMe)⁻, which are isoelectronic with phosphido-boranes.

There have, however, been a small number of reports detailing the solid-state structures of anionic phosphido-borane complexes with transition metals (Figure 3.1). These compounds can be prepared either via metathesis reactions between a transition metal halide and an alkali metal phosphido-borane complex (Scheme 3.1) or via oxidative addition of a phosphine-borane adduct to a low oxidation state transition metal complex. Although these examples rarely demonstrate any B-H...M interactions, such as those observed in the group I complexes, the structures obtained provide an insight into the activity of transition metal-catalysed reactions with phosphine-boranes, such as dehydrogenation, dehydrocoupling or cross-coupling reactions.

It has previously been shown that phosphides containing peripheral donor-functionality can provide additional stabilisation in complexes with group I and II metals through intramolecular interactions between the donor atom and the metal. However, to date there are no examples of donor-functionalised phosphido-borane complexes with main group metals that have been characterised in the solid-state. This chapter details the synthesis and characterisation of a series of phosphido-borane complexes prepared from compound 39 with alkali metals and considers the effects of cation size on structure.
Figure 3.1. Phosphido-borane complexes with transition metals \([\text{Ar}^1 = C_6F_5, \text{Ar}^2 = 1,3,5\text{-tri-} t\text{ert-buty}lphenyl]\).\(^{1-14}\)
3.2 Synthesis of the alkali metal complexes [{(Me$_3$Si)$_2$CH}P(C$_6$H$_4$-2-CH$_2$OMe)(BH$_3$)M(L)]$_2$ [M(L) = Li(THF) (49), Na(tmeda) (50), K(pmdeta) (51)]

Treatment of 39 with one equivalent of $^n$BuLi in THF yields the corresponding phosphido-borane. Removal of the solvent gives a yellow solid, which may be crystallised from methylecyclohexane containing a few drops of THF as colourless needles of the adduct [{(Me$_3$Si)$_2$CH}P(C$_6$H$_4$-2-CH$_2$OMe)(BH$_3$)Li(THF)]$_2$ (49). The reaction between 39 and one equivalent of either BnNa or BnK in THF yields the corresponding heavier alkali metal salts, which upon removal of the solvent yields a yellow and an orange solid, respectively. The sodium compound was crystallised from toluene in the presence of one equivalent of tmeda to yield colourless blocks of the adduct [{(Me$_3$Si)$_2$CH}P(C$_6$H$_4$-2-CH$_2$OMe)(BH$_3$)Na(tmeda)]$_2$ (50), whereas the potassium compound was crystallised from toluene in the presence of pmdeta, also as colourless blocks, as the adduct [{(Me$_3$Si)$_2$CH}P(C$_6$H$_4$-2-CH$_2$OMe)(BH$_3$)K(pmdeta)]$_2$ (51).
Scheme 3.2. Synthesis of compounds 49-51. i) "BuLi, THF, 1 h, r.t. ii) BnNa, THF, 1h, r.t. iii) tmeda, toluene. iv) BnK, THF, 1h, r.t. vi) pmdeta, toluene [R = (Me₃Si)₂CH].

3.3 Solution-phase characterisation of compounds 49-51

Upon metalation, the $^{31}$P{$^1$H} NMR signal shifts significantly from -16.2 ppm for 39 to -66.6, -65.3 and -64.2 ppm for 49, 50 and 51, respectively, consistent with single phosphido-borane ligand environments. The $^{31}$P-$^{11}$B coupling constants decrease with decreasing electronegativity of the cation, which occurs, approximately, in the order of 10 Hz increments \([^{1}J_{PB} = 49.0 \ (39), \ 37.2 \ (49), \ 29.4 \ (50), \ \text{and} \ 19.6 \ \text{Hz} \ (51)]\), which is consistent with increasing ionic character of the P-M interaction.
The $^1$H and $^{13}$C{$^1$H} NMR spectra are as expected. In the $^1$H NMR spectra the BH$_3$ protons exhibit a broad quartet at 0.6-0.8 ppm, which can be collapsed into a sharp doublet [$^2J_{PH} = 14.6$ (49), 5.5 (50), 5.0 Hz (51)] by decoupling the $^{11}$B nucleus appearing at between 0.6 and 0.88 ppm for 49-50. The diastereotopic Me$_3$Si groups appear as two sharp signals, whilst the CHP protons appear as unresolved singlets between 0.3 and 0.4 ppm. In the $^{13}$C{$^1$H} NMR spectra, the SiMe$_3$ groups also appear as two separate signals, whereas the CH carbon adjacent to the phosphorus atom appears as a doublet at 8.01 and 8.26 ppm for 50 and 51 [$^1J_{PC} = 47.9$ (50), 49.8 Hz (51)], respectively, but does not appear in 49.

3.4 Solid-state structures of compounds 49-51

3.4.1 Solid-state structure of 49

Compound 49 crystallises as discrete dimers; the molecular structure of 49 is shown in Figure 3.2 and details of selected bond lengths and angles are shown Table 3.1. Each lithium ion is bound to the P and O atoms of the phosphido-borane ligand, generating a six-membered chelate ring [P-Li-O bite angle 84.8(2)$^\circ$]. The coordination sphere of each lithium ion is completed by a molecule of THF, an $\eta^1$-interaction with one of the borane hydrogen atoms, and an $\eta^3$-BH$_3$ interaction with the borane group from the adjacent phosphido-borane ligand in the dimer, such that each borane group acts as a $\mu_2$-$\eta^1$: $\eta^3$ bridge between the lithium metal centres. The two halves of the dimer thus form a planar, pseudo-six-membered [PLi(BH$_3$)]$_2$ ring.

By comparison, the majority of structurally characterised group I complexes with isoelectronic silyl anions (R$_2$SiMe)$^-\text{crystallise as monomers,}^{18-22}$ although the peripherally donor-functionalised compound [Ph(C$_5$H$_5$NCH$_2$)MeSiLi(THF)]$_2$ (52) crystallises as a dimer with a Si$_2$Li$_2$ core.$^{23}$ However, unlike 49, the two halves of the dimer in 52 are linked by the peripheral donor substituents of each ligand, which coordinate to the adjacent lithium ion in the dimer, thus forming intramolecular bridges (Figure 3.3).
Figure 3.2. Structure of compound 49. All C-bound H atoms omitted for clarity.

Figure 3.3. Structure of compound 52.²³
The P-Li distance of 2.611(6) Å in 49 is only slightly shorter than the corresponding distance reported for [Me₂P(BH₃)Li(tmeda)] (29) [2.620(4) Å] but is typical of Li-P distances of 4-coordinate lithium phosphide complexes. The η³-BH₃...Li distances in 49 [1.98(4) Å] are comparable to similar η³-type borane-lithium interactions. For example, the Li-H distances in [Li(BH₄)(THF)₃] (53) are 2.02(4), 2.10(5) and 2.12(4) Å, and in the complex [Li(η³-BH₄)(NC₅H₄-4-Me)₃] (54) the Li-H distances are 2.10(2), 2.20(2) and 2.10(2) Å (Figure 3.4). The Li-H distances for the bridging borane hydrogen atoms in the dimer are 2.05(4) Å, which is consistent with other μ₂-η¹ bridges; for example, the η¹-BH₃-Li distances in [Li(BH₄)(MeNCH₂)₃] (55) is 2.08(1)Å, while the corresponding distances in [LiBH₄(py-2-Me)₂]₂ (56) are 2.134(6) and 2.184(7) Å.

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Table 3.1. Selected bond lengths (Å) and angles (°) for 49.
3.4.2 Solid-state structure of 50

Compound 50 crystallises as discrete centrosymmetric dimers in which the phosphido-borane ligand adopts a tridentate coordination mode; the structure of 50 is shown in Figure 3.5 and selected bond length and angles are given in Table 3.2. Each phosphido-borane ligand binds the adjacent sodium ion through its P and O atoms to give a six-membered chelate ring [P(1)-Na(1)-O(1) bite angle 76.40(6)°], and in an \( \eta^2 \) fashion through two borane hydrogen atoms, which bridge the two sodium ions in the dimer. The third borane hydrogen of each group is \( \eta^1 \)-bonded to the second sodium ion, such that each borane group acts as a \( \mu_2-\eta^2:\eta^3 \) bridge between the cations, forming a rhombus-shaped pseudo-four-membered ring. The coordination of the sodium ions is completed by the N atoms of a chelating molecule of
The $\eta^2$ and $\eta^3$ nature of the Na...B interactions in 50 is consistent with the bond distances observed [Na(1)-B(1) = 2.989(4), Na(1)-B(1A) = 2.844(3) Å].

The P-Na, O-Na and H-Na distances are longer than the corresponding bond lengths observed in compound 49 [P(1)-Na(1) 3.0528(13), P(1)-Li(1) 2.611(6) Å; O(1)-Na(1) 2.445(2), O(1)-Li(1) 1.988(6) Å; Na(1)-H(1B) 2.44(3), Li(1)-H(1B) 1.97(4) Å], whilst the P-Na-O bite angle of 76.4(6)$^\circ$ is significantly smaller than the P-Li-O angle in 49, all of which are consistent with the greater ionic radius of sodium than lithium. The P-Na bond lengths in 50 lie just outside the range of previously reported P-Na distances (2.8-3.0 Å), however the Na-O distances in 50 of 2.445(2) Å are somewhat shorter than the related Na-O distances in [{(C$_6$H$_4$-2-OMe)$_2$P}Na(diglyme)]$_2$ (16) [2.531(3) and 2.563(3)].

The Na-H distances in 50 [2.32-2.91 Å] are comparable with those in [Na(BH$_4$)(pmdeta)]$_2$ (57) [2.49(3)-2.58(3) Å], which also exhibits a $\mu_2$-$\eta^2$:$\eta^3$ BH$_3$ binding mode. The Na...B distances in 57 [Na(1A)...B(1) 2.727(4), Na(1)...B(1) 2.867(4) Å] are similar to the corresponding $\eta^2$-BH$_3$-Na and $\eta^3$-BH$_3$-Na interactions observed in 50. Similarly, in [Na($\eta^3$-BH$_4$)(15-crown-5)(py)$_0$] (58), the Na-H bond lengths [2.28(2), 2.42(2), 2.74(2) Å] are comparable to those observed in 50, but the Na...B distances [58 2.659(3) Å] are shorter in the former compound.

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Table 3.2. Selected bond lengths (Å) and angles (°) for 50.
Figure 3.5. Structure of compound 50. All C-bound H atoms omitted for clarity.

Figure 3.6. Structures of compounds 57 and 58, which exhibit $\eta^3$-Na-BH$_n$ interactions.
3.4.3 Solid-state structure of 51

Like 50, compound 51 also crystallises as centrosymmetric dimers; the structure of 51 is shown in Figure 3.7, with selected bond lengths and angles shown in Table 3.3. Each potassium ion is bound by the P and O atoms of the adjacent phosphido-borane ligand, forming a six-membered chelate ring, and through the borane hydrogen atoms; the adjacent borane group binds in a \( \eta^2 \)-manner, and the second ligand binds in a \( \eta^3 \)-fashion, such that each borane group acts as a \( \mu_2-\eta^2:\eta^3 \) bridge between the two potassium ions. The coordination of each potassium ion is completed by the three nitrogen atoms and by a short Me...K contact with the central methyl group of a molecule of pmdeta, making the potassium ion pseudo-eight-coordinate.

The K-P bond length in 51 [3.7620(10) Å] is significantly longer than the corresponding distance in the related potassium salt 32 [3.320(2) Å], which also exhibits a \( P,BH_3 \) binding mode. The K(1)...B(1A) distance in 51 [3.322(3) Å] is also somewhat longer than the corresponding distance in 32 [3.162 Å], despite both having \( \eta^2-BH_3 \) coordination modes, whereas the K(1)...B(1) distance in 51 [3.103(3) Å] is slightly shorter than this, consistent with \( \eta^3 \)-coordination. The P-K-O bite angle of 60.74(3)° in 51 is significantly smaller than the bite angles in 49 and 50, which is consistent with the greater ionic radius of potassium than of sodium and lithium.

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</table>

Table 3.3. Selected bond lengths (Å) and angles (°) of compound 51.
Figure 3.7. Structure of compound 51. All C-bound H atoms eliminated for clarity.

The K-H distances in 51 are similar to other reported BHₙ-K distances; for example the η²-BHₙ distances in 51 [2.80(2) and 3.095(20) Å] are comparable to those in [K(H₂BC₅H₁₀)(18-crown-6)] \( (59) \) [K(1)–H(1) 2.58(2), K(1)–H(2) 2.66(2) Å],²⁹ while the η³-type interactions [2.816(18), 2.970(19) and 3.06(2) Å] are similar to those in [K(BH₄)(18-crown-6)] \( (60) \), Figure 3.8) [K(1)–H(11) 2.85(6), K(1)–H(13) 2.61(8), K(1)–H(14) 2.77(7) Å].²⁹

Figure 3.8. Structures of complexes which exhibit η² and η³ K-BHₙ interactions.
3.5 Conclusions

This chapter demonstrates that the alkali metal complexes of the phosphido-borane anion \({\{(\text{Me}_3\text{Si})_2\text{CH}}\text{P(BH}_3\text{)}(\text{C}_6\text{H}_4\text{-2-CH}_2\text{OMe})\}}\) are readily accessible using straightforward synthetic procedures. Compounds 49-51 crystallise as dimers in the presence of THF, tmeda, or pmdeta, respectively, demonstrating ‘tridentate’ coordination of the phosphido-borane ligand, through P-M, B…M and O-M contacts with the metal centre. Compound 50 is the first example of a phosphido-borane complex with sodium.

The dimeric nature of the structures of these complexes is a result of agostic-type B-H-M interactions; within the lithium complex, the two halves of the dimer are bridged by the borane groups in a \(\mu_2\cdot\eta^1\cdot\eta^3\) fashion, whereas the two halves of both the sodium and potassium complexes are bridged in a \(\mu_2\cdot\eta^2\cdot\eta^3\) manner by the borane groups.

As expected, the P-M, O-M and BH-M distances increase with increasing radius of the cation, and likewise, the P-M-O and M-B-P bite angles decrease with increasing ionic radius of the alkali metal.

3.6 References


Chapter 4. Alkali metal complexes of a thioanisole-functionalised phosphido-borane

4.1 Introduction

In previous studies of thioanisole-substituted phosphines, it was found that compound 45 \(\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{PH(C}_6\text{H}_4\text{-2-SMe)}\) exhibits unusual behaviour towards alkyllithium reagents.\(^1\) The reaction between 45 and one equivalent of \(^n\text{BuLi}\) in diethyl ether yields, after crystallisation in the presence of tmeda, half an equivalent of the dianion complex \(\{(\text{Me}_3\text{Si})_2\text{CH}\}P(C_6\text{H}_4\text{-2-S})\{\text{Li(tmeda)}\}_2\) (61) (Scheme 4.1), which results from simultaneous deprotonation and demethylation of the phosphine, leaving half an equivalent of 45 unchanged. Compound 61 may be accessed cleanly by reaction of 45 with two equivalents of \(^n\text{BuLi}\) under the same conditions.

In comparison, reaction of 45 with one equivalent of \(^n\text{BuLi}\) in the presence of tmeda yields the expected lithium phosphide \(\{(\text{Me}_3\text{Si})_2\text{CH}\}P(C_6\text{H}_4\text{-2-SMe})\text{Li(tmeda)}\) (62). However, compound 62 undergoes a rapid isomerisation in toluene upon exposure to ambient light, leading to the formation of the corresponding phosphine-thiolate \(\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{PMe(C}_6\text{H}_4\text{-2-S})\text{Li(tmeda)}\) (63).

To obtain further insight into this unusual behaviour, this chapter considers the deprotonation of the related thioanisole-functionalised phosphine-borane 40, exploring the effect that the borane adduct has on the ligand binding modes, and the photolytic/thermolytic stability of the corresponding phosphido-borane. For a comprehensive overview, a series of complexes with the group I metals (Li, Na and K) have been synthesised to also take into consideration the effect of cation size.
4.2 Synthesis of the alkali metal complexes \([\{(\text{Me}_3\text{Si})_2\text{CH}\}P(C_6\text{H}_4-2-\text{SMe})(\text{BH}_3)\text{M(L)}\}_n\ [\text{M(L)} = \text{Li(THF)}, n = 2 \ (64), \ \text{M(L)} = \text{Na(tmeda)}, n = \infty \ (65), \ \text{M(L)} = \text{K(pmdeta)}, n = 2 \ (66)]\)

The reaction between compound 40 and one equivalent of \(\text{"BuLi}\) in THF proceeds cleanly to give the phosphido-borane complex \([\{(\text{Me}_3\text{Si})_2\text{CH}\}P(C_6\text{H}_4-2-\text{SMe})(\text{BH}_3)\text{Li(THF)}\}_2 \ (64)\), which was crystallised from cold toluene/THF as colourless blocks. Similarly, the reaction between 40 and one equivalent of either BnNa or BnK in THF yields the corresponding alkali metal salts, which were crystallised from cold toluene in the presence of either one equivalent of tmeda or pmdeta, respectively, as the adducts \([\{(\text{Me}_3\text{Si})_2\text{CH}\}P(C_6\text{H}_4-2-\text{SMe})(\text{BH}_3)\text{Na(tmeda)}\}_\infty \ (65)\), and \([\{(\text{Me}_3\text{Si})_2\text{CH}\}P(C_6\text{H}_4-2-\text{SMe})(\text{BH}_3)\text{K(pmdeta)}\}_2 \ (66)\). The syntheses of 64-66 are shown in Scheme 4.2.
Scheme 4.2. Synthesis of compounds 63-65. i) "BuLi, THF, 1 h, r.t. ii) BnNa, THF, 1h, r.t. iii) tmeda, toluene.
iv) BnK, THF, 1h, r.t. vi) pmdeta, toluene [R = (Me₃Si)₂CH].
4.3 Solution-phase characterisation of compounds 64-66

The room temperature $^1$H{${}^{11}$B}, $^{13}$C{${}^1$H}, $^{11}$B{${}^1$H}, and $^{31}$P{${}^1$H} NMR spectra of complexes 64-66 indicate the presence of single phosphido-borane ligand environments. Upon metalation, the $^{31}$P{${}^1$H} NMR signals shift significantly upfield from -15.7 ppm for 40 to between -58.3 and -59.5 ppm for compounds 64-66. The magnitude of the $^{31}$P-$^{11}$B coupling constant decreases steadily with decreasing electronegativity of the cation [$^1J_{PB} = 49.0$ (40), 39.2 (64), 29.4 (65) and 19.6 Hz (66)], which is consistent with increasing ionic character of the P-M interaction.

The $^1$H NMR spectra of 64-66 are as expected, the diastereotopic SiMe$_3$ groups give rise to two sharp singlets between -0.05 and 0.11 ppm, and the BH$_3$ protons give rise to a broad quartet, which collapses into a sharp doublet on decoupling of the $^{11}$B nucleus. The $^{13}$C{${}^1$H} NMR spectra are also as expected. The SiMe$_3$ carbons give rise to two signal, a doublet and a singlet between 1.5 and 2.9 ppm for 64 and 65 [$^3J_{PC} = 6.7$ Hz (64 and 65)], and a pair of doublets at 2.4 and 3.7 ppm [$^3J_{PC} = 6.71$ and 1.9 Hz, respectively] for 66. The adjacent CH carbons appear as doublets between 6.9 and 8.0 ppm [$^1J_{PC} = 48.0$ (64) 43.2 (65) and 47.0 Hz (66)].

4.4 Solid-state structures of compounds 64-66

4.4.1 Solid-state structure of 64

Compound 64 crystallises as discrete centrosymmetric dimers; the molecular structure of 64 is shown in Figure 4.1 and selected bond lengths and angles are given in Table 4.1. Each lithium ion is coordinated by the P and S atoms of a phosphido-borane ligand to give a five-membered chelate ring [P-Li-S bite angle 77.28(7)$^\circ$. The coordination about each Li ion is completed by a molecule of THF, and by an $\eta^2$-BH$_3$ contact with the borane group from the other phosphido-borane ligand in the dimer, resulting in pseudo-tetrahedral geometry at lithium. The two halves of the dimer, therefore, are linked via an essentially planar, pseudo-six-membered [PLi(BH$_3$)]$_2$ ring.
Figure 4.1. Structure of compound 64. All C-bound H atoms omitted for clarity.

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Table 4.1. Selected bond lengths (Å) and angles (°) of compound 64.
The P-Li distance of 2.527(3) Å is slightly shorter than the corresponding distances in 29 [2.620(4) and 2.611(6) Å respectively], and also slightly longer than the P-Li distance in 62 [2.508(3) Å]. The S-Li distance in 64 of 2.608(2) Å is somewhat longer than the corresponding distance in 62 [2.543(3) Å] and is much longer than the related O-Li distance in 49 [1.988(6) Å], which is consistent with the larger atomic radius of sulphur compared to oxygen. The Li-H distances in 64 [2.053(14) and 1.905(14) Å] and the Li(1)...B(1A) distance [2.403(3) Å] are similar to those in 49 [Li-H: 1.97(4), 1.98(4) and 2.05(4) Å; Li...B: 2.453(7)], and are typical of complexes where there is an $\eta^2$-BH$_3$-Li contact. For example, the Li-H distances and Li...B distance in Li[$\eta^2$-BH$_4$](py)$_3$] (67) are 2.06 and 1.90 Å, and 2.401(7) Å, respectively (Figure 4.2); the corresponding distances in the complex Li[$\eta^2$-BH$_4$](HNPr$_2$)] (68) are 2.03(1) and 1.93(1) Å, and 2.358(3) Å, respectively, whilst the compound Li[$\eta^2$-BH$_4$](THF)$_2$(py-2-NH$_2$)] (69) has a Li...B distance of 2.41(1) Å.\textsuperscript{2,3}

![Structures of complexes which exhibit $\eta^2$-BH$_4$-Li interactions.](image)
4.4.2 Solid-state structure of 65

Compound 65 crystallises as a linear polymer with two crystallographically independent molecular units per asymmetric unit. The structure of 65 is shown in Figure 4.3, and selected bond lengths and angles are shown in Table 4.2. The sodium ions are coordinated by the P and S atoms of a phosphido-borane ligand to generate a five-membered chelate ring [P-Na-S bite angles 62.93(4) and 63.43(4)°], and by two N atoms of a chelating molecule of tmeda. The coordination of Na(1) is completed by an \(\eta^2\)-BH\(_3\) interaction from the adjacent phosphido-borane unit in the polymer chain and a short contact to one of the methylene carbon atoms of the tmeda co-ligand [Na(1)...C(17) 3.126(4) Å], whereas the coordination of Na(2) is completed by \(\eta^3\)-coordination of a BH\(_3\) group from the adjacent polymer unit.

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Table 4.2. Selected bond lengths (Å) and angles (°) of compound 65.

The P-Na distances of 2.9661(17) and 2.9474(16) Å are typical of P-Na distances in related sodium phosphide complexes, which range from 2.8-3.0 Å,\(^4\) and are similar to the corresponding distance in compound 50 [3.0528(13) Å]. The S-Na distances in 65 of 3.0441(19) and 3.0735(18) Å are longer than the related distance in 64, which is consistent with the larger ionic radius of sodium. The Na(1)...B(2) distance of 2.646(4) Å is somewhat
Figure 4.3. Structure of compound 65. All C-bound H atoms omitted for clarity.
shorter than typical $\eta^2$-BH$_n$-Na distances, for example, the Na...B distances in Na$_2$(η$^2$-BH$_4$)$_2$(triglyme) (70) and NaBH$_4$(py)$_3$ (71) are 2.830(2) and 2.927(3) Å, respectively (Figure 4.4), whilst the Na(2)...B(1B) distance of 2.694(4) Å is similar to other $\eta^3$-BH$_n$...Na distances; for example, the $\eta^3$-BH$_4$...Na distances in [Na($\eta^3$-BH$_4$)(15-crown-5)(py)$_{0.5}$] (58) are 2.7298 Å.$^5$

\[\textbf{Figure 4.4.} \text{Structures of a section of compound 70 and compound 71.}\]

### 4.4.3 Solid-state structure of 66

The structure of 66 is shown in Figure 4.5, with selected bond lengths and angles given in Table 4.3. Compound 66 crystallises as discrete centrosymmetric dimers in which the phosphido-borane ligands adopt a tridentate coordination mode, each binding to an adjacent potassium ion through its P and S atoms, and in an $\eta^2$ manner, through the BH$_3$ group. The borane groups are also coordinated to the second potassium ion in the dimer through an $\eta^3$ type interaction, such that each borane acts as a $\mu$$_2$-$\eta^2$:η$^3$ bridge between the two potassium ions, forming a rhombus-shaped pseudo-four-membered K$_2$(BH$_3$)$_2$ ring. The coordination about each potassium ion is completed by the three N atoms of a molecule of pmdeta, and by a short K...C contact from the central methyl group of the pmdeta ligand.
**Figure 4.5.** Structure of 66. All C-bound H atoms omitted for clarity.

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</table>

**Table 4.3.** Selected bond lengths (Å) and angles (°) of compound 66.
The K-P distance in 66 of 3.6617(6) Å is significantly longer than the corresponding distance in [Ph₂P(BH₃)K(18-crown-6)] (32) [3.320(2) Å], which supports the argument that K-P interactions in ‘tridentate’ phosphido-boranes, where there is additional coordination to potassium from a peripheral donor-atom, such as in compounds 51 and 66, are considerably weaker than in ‘bidentate’ phosphido-boranes, such as 32. The K-S distance in 66 of 3.7568(7) Å is much longer than the corresponding Li-S and Na-S distances in compounds 64 and 65 [2.608(2) and 3.0441(19) Å, respectively] which is consistent with the larger ionic radius of potassium. Similarly, the P-K-S bite angle [49.666(12)°] is considerably smaller than the corresponding P-M-S angles in 64 and 65 [77.28(7) and 62.93(4)°, respectively], which again is consistent with the larger ionic radius of potassium.

The K(1)...B(1) and K(1)...B(1A) distances in 66 of 3.243(2) and 3.047(2) Å, respectively, are consistent with the relative η²- and η³-BH₃ coordination modes, but are slightly shorter than the related distances in compound 51 [3.322(3) and 3.103(3) Å, respectively]. The K-H distances of 66 [2.74(2)-3.047(2) Å], however, are similar to those observed in compound 51 [2.816(18)-3.095(20)].

4.5 Behaviour of 64 in solution

4.5.1 Photolytic reactivity of 64

In an effort to ascertain if these species undergo S-Me cleavage under photolytic conditions, NMR samples of compounds 64-66 in THF were exposed to both ambient light and a 10 W fluorescent light, whilst being monitored via ³¹P NMR spectroscopy. However, after long periods of exposure to light, compounds 64-66 showed no evidence of rearrangement, which was confirmed by ¹H{¹¹B} NMR spectroscopy. This suggests that these phosphido-borane species are photolytically stable (Scheme 4.3) compared to their phosphide counter-parts, which rapidly rearrange to give the corresponding tertiary phosphine-functionalised thiolate.
4.5.2 Thermolytic reactivity of 64

Although 64 is stable towards photolysis, it was found that the compound can undergo a thermally-induced rearrangement in the presence of phosphine-borane 40. Heating a solution of a 1:1 mixture of 64 and 40 in THF to 50 °C for 16 h results in conversion of the phosphido-borane and 40 into a mixture of the corresponding lithium phosphido-bis(borane) [{(Me₃Si)₂CH}P(C₆H₄-2-SMe)(BH₃)₂Li] (72), which is observed in the $^{31}$P{$^1$H} NMR spectrum as a broad multiplet at -4.6 ppm, and the secondary phosphine 45 in a 1:1 ratio (Scheme 4.4). It is thought that the rearrangement results from the abstraction of borane from 40 by the anionic phosphido-borane, which has greater basic character.

Unfortunately 72 could not be isolated from these thermolysis reactions, however the $^{31}$P{$^1$H}, $^{31}$P, $^1$H and $^{11}$B{$^1$H} NMR spectra of samples taken from the reaction solution are consistent with a mixture of 72 and 45 ($^{31}$P NMR spectra shown in Figure 4.6).
Scheme 4.4. Conversion of 64 in the presence of 40 into 72 and 45 upon thermolysis [R = (Me₃Si)₂CH].

Figure 4.6. Undecoupled $^{31}$P NMR spectrum of 72 and 45, from the thermolysis of 64 in the presence of 40 in THF, after 16 h at 50°C [R = (Me₃Si)₂CH].
4.5.3 Synthesis and solution-phase characterisation of 72·(12-crown-4)

To confirm the identity of 72, this compound was prepared using a direct route. The reaction between a solution of 64 and two equivalents of BH$_3$·SMe$_2$ yields the corresponding phosphido-bis(borane) [\{(Me$_3$Si)$_2$CH\}P(C$_6$H$_4$-2-SMe)(BH$_3$)$_2$Li] (72) upon removal of the solvent. The product was isolated as the adduct [\{(Me$_3$Si)$_2$CH\}P(C$_6$H$_4$-2-SMe)(BH$_3$)$_2$Li(12-crown-4)] (72·(12-crown-4)) as a colourless solid (Scheme 4.5).

Upon addition of the second equivalent of borane, the $^{31}$P{$_1^1$H} NMR signal at -59.5 ppm for 64 is replaced by a new, very broad signal at -4.6 ppm, which is indistinguishable from that of the sample of 72 prepared from the thermolysis of 64. This chemical shift is typical of phosphido-bis(borane) complexes, which have previously demonstrated a relatively downfield shift in comparison to phosphido-boranes. For example, the $^{31}$P{$_1^1$H} NMR spectrum of the potassium complex [Ph$_2$P(BH$_3$)K(18-crown-6)] (32) gives rise to a signal at -28.8 ppm, whereas the related complex [Ph$_2$P(BH$_3$)$_2$K(18-crown-6)] (37) has a $^{31}$P chemical shift of -11.1 ppm. Although the signal observed in the $^{31}$P{$_1^1$H} NMR spectrum of 72 is a very broad multiplet, the P-B coupling can be resolved in the $^{11}$B{$_1^1$H} NMR spectrum where $^1J_{PB}$ is measured as 68.6 Hz, which is significantly larger than the P-B coupling constant in 64 [$^1J_{PB} = 39.2$ Hz].

The $^1$H NMR spectrum of 72·(12-crown-4) in THF is as expected; the six BH$_3$ protons appear as a broad signal at 0.8 ppm, which, upon decoupling of the $^{11}$B nucleus, resolve as a
sharp doublet \[^2J_{PH} = 10.5\ \text{Hz}\]. That all six borane protons appear to be identical would suggest that in solution there is either rapid exchange between the borane groups coordinating with the lithium ion (Scheme 4.6), or that the compound exists as a separated ion pair in THF. In the \[^{13}\text{C}^{1\text{H}}\] NMR spectrum the SiMe\(_3\) carbons appear as a singlet at 3.1 ppm, whilst the adjacent CH carbon appears as a doublet at 7.0 ppm; the magnitude of the P-C coupling in \(72\cdot(12\text{-crown-}4)\) \[^1J_{PC} = 3.8\ \text{Hz}\] is smaller compared to the mono(borane) compounds 64-66 \[^1J_{PC} = 48.0\ \text{Hz}\].

![Scheme 4.6](image_url)

Scheme 4.6. Exchange between borane coordination to lithium in \(72\cdot(12\text{-crown-}4)\) in THF \([R = (\text{Me}_3\text{Si})_2\text{CH}]\).

### 4.6 Conclusions

The lithium, sodium and potassium complexes of the phosphido-borane anion \([\{\text{(Me}_3\text{Si})_2\text{CH}\}\text{P(C}_6\text{H}_4\text{-2-SMe)}\}]^-\) have been successfully prepared via relatively straightforward synthetic procedures. In the solid state, the structures vary significantly with increasing radii of the alkali metal and can adopt unique structural motifs: the structure of complex 64 is a dimer linked through \(\eta^2\)-BH\(_3\) type interactions; compound 65 crystallises as a linear polymer, where each unit is joined by a series of alternating \(\eta^3\)-BH\(_3\) and \(\eta^2\)-BH\(_3\) interactions; and compound 66 is a dimer, where the BH\(_3\) groups bridge the two potassium...
ions in a $\mu_2$-$\eta^2$-$\eta^3$ fashion. As with the previously reported phosphido-boranes, the BH$_3$M interactions in these complexes are an essential feature of their structures.

Unlike the related phosphide, 64 showed no photolytic reactivity upon exposure to ambient or fluorescent light. This would suggest that the formation of a P-B bond sufficiently perturbs the electronics of this system, so that methyl migration is disfavoured.

An investigation of the thermolytic reactivity of 64 in solution led to the observation that a borane migration can occur in the presence of 40, which results in the formation of the corresponding phosphido-bis(borane) complex 72 and the secondary phosphine 45. This behaviour has not previously been reported.

4.7 References


Chapter 5. Alkali metal and calcium complexes of anisole-functionalised phosphido-boranes

5.1 Introduction

The first example of an anisole-functionalised phosphine-borane was the chiral compound PhP(BH$_3$)(CH$_3$)(C$_6$H$_4$-2-OMe) (73) reported by Imamoto and co-workers in 1985. This compound allowed a rapid route to the synthesis of the optically pure 1,2-ethanediylbis[(o-methoxyphenyl)phenylphosphine] (DIPAMP), which is an extremely useful ligand in catalytic asymmetric hydrogenation reactions (Scheme 5.1).

![Scheme 5.1. Synthesis of DIPAMP. i) tBuLi, THF, -78°C, 2 h. ii) CuCl$_2$, 2 h. iii) Et$_2$NH, 50 ºC, 10 h.](image)

To date, the only example of a structurally characterised anisole-functionalised phosphido-borane is the palladium complex [(2-(2-(Ph$_2$P)C$_6$H$_4$)-4-'Pr-4,5-C$_3$NO)Pd(C$_6$F$_5$) (PhP(BH$_3$)(C$_6$H$_4$-2-OMe))] (74, Figure 5.1). There are, however, several examples of anisole-functionalised phosphides coordinated to group I, II and lanthanide metals. These systems have demonstrated that complex stabilisation can be afforded through an intramolecular chelate effect between the oxygen atom and metal centre.
The chemistry of group II and lanthanide metal complexes with the phosphide ligand [(Me₃Si)₂CH]P(C₆H₄-2-OMe)]⁻ has been well established.⁶⁻¹⁰ The compounds [(Me₃Si)₂CH]P(C₆H₄-2-OMe)]₂Sr(THF)₂ (75), [(Me₃Si)₂CH]P(C₆H₄-2-OMe)]₂Ba(THF)₃ (76) and [(Me₃Si)₂CH]P(C₆H₄-2-OMe)]₂Sm(DME)(THF)] (77) crystallise as discrete molecular species in which the phosphide ligands bind the metal centers via their P and O donors to give five-membered chelate rings.⁶,¹⁰ The strontium atom in 75 adopts a distorted trans-octahedral geometry, whilst both the Ba and Sm metal centers in 76 and 77 adopt a distorted pentagonal bipyramidal geometry. Compounds 75-77 are stable in the solid state and in THF solution at room temperature.

In contrast, the related complexes [(Me₃Si)₂CH]P(C₆H₄-2-OMe)]₂Ca(THF)₂ (78) and [(Me₃Si)₂CH]P(C₆H₄-2-OMe)]₂Yb(THF)₂ (79) undergo rapid decomposition to yield [(Me₃Si)₂CH]P(C₆H₄-2-O)Ca(THF)]₄ (80) and [(Me₃Si)₂CH]P(C₆H₄-2-O)Yb(THF)]₄ (81), respectively, and the side product (Me₃Si)₂CH]PMe(C₆H₄-2-OMe) (82).⁷,⁹ Compounds 80 and 81 are isostructural in the solid state, and both crystallise as tetrameric clusters, adopting Ca₄O₄ and Yb₄O₄ cuboidal cores, respectively. They are thought to arise from rapid migration of a methyl group from the oxygen atom of one phosphide ligand to the phosphorus atom of the second ligand in the complex (Scheme 5.2).

Similarly, the compound [(Me₃Si)₂CH]P(C₆H₄-2-OMe)Mg(C₄H₉)]₂ (83) is observed by NMR spectroscopy to undergo rapid decomposition, to yield 82 and a new magnesium phosphide compound.⁸ Although this new compound could not be isolated for full
characterisation, it is proposed to be the magnesium alkoxophosphide \[\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P(C}_6\text{H}_4\text{-2-O})\text{Mg(THF)}\_n\}\_m(84),\] which could arise directly from the Grignard-like compound 83. Alternatively, 83 may be subject to a Schlenk-type equilibrium in solution, generating the homoleptic phosphide \[\{(\text{Me}_3\text{Si})_2\text{CH}\}\{\text{C}_6\text{H}_4\text{-2-OMe}}\text{P}\}_2\text{Mg}\] and one equivalent of \text{Bu}_2\text{Mg}, followed by methyl migration in a similar fashion to that observed in the formation of 80 and 81.

The different reactivities of 75-79 and 83 suggest that the ligand cleavage reactions are dependent upon the Lewis acidity of the metal centre.

\[
\begin{align*}
\text{Scheme 5.2.} & \text{ Formation of 80 and 82 through facile C-O cleavage of compound 78.}
\end{align*}
\]
This chapter discusses the synthesis of several phosphido-borane adducts prepared from the anisole-functionalised phosphine-borane \{(Me_3Si)_2CH\}PH(C_6H_4-2-OMe)(BH_3) \((41)\), and illustrates the effects that varying the metal centre and solvent have on the structures and reactivities of these complexes in solution.

### 5.2 Synthesis of alkali metal complexes \[\{[(Me_3Si)_2CH]P(C_6H_4-2-OMe)(BH_3)M(L)\} \ [M(L) = Li(THF) (85), Na(THF) (86), K(pmdeta) (87)]\]

The synthesis of compounds 85-87 is shown in Scheme 5.4. The reaction between 41 and one equivalent of "BuLi in THF proceeds cleanly to yield the corresponding phosphido-borane \[\{[(Me_3Si)_2CH]P(C_6H_4-2-OMe)(BH_3)Li(THF)\}] \(85\). Unfortunately, single crystals of
85 could not be isolated, and so the crystal structure of this compound could not be determined; its composition was confirmed by NMR spectroscopy. Treatment of 41 with one equivalent of either BnNa\textsuperscript{11} or BnK\textsuperscript{12} in THF yields the corresponding phosphido-boranes, which, upon removal of the solvent, yields yellow and orange solids respectively. The sodium compound may be crystallised from toluene in the presence of one equivalent of THF as the adduct \[\{\text{Me}_3\text{Si})_2\text{CH}\}P(C_6\text{H}_4\text{-2-OMe})(\text{BH}_3)\text{Na}(\text{THF})\] (86), whereas the potassium compound may be crystallised from toluene in the presence of pmdepta, as colourless blocks of the adduct \[\{(\text{Me}_3\text{Si})_2\text{CH}\}P(C_6\text{H}_4\text{-2-OMe})(\text{BH}_3)\text{K}(\text{pmdepta})\]\textsubscript{2} (87). Single crystals of 86 suitable for X-ray crystallography could not be isolated, however, its composition was confirmed by elemental analysis and NMR spectroscopy.

**Scheme 5.4.** Synthesis of 85, 86 and 87. i) BuLi, THF, 1h, r.t. ii) BnNa, THF, 1h, r.t. iii) BnK, THF, 1h, r.t. iv) pmdepta, toluene \([R = \text{Me}_3\text{Si})_2\text{CH}\]\].
5.3 Solution-phase characterisation of 85-87

Upon metalation of 41, the $^{31}$P{$^1$H} NMR signal shifts upfield from -22.3 ppm to between -62.5 and -64.3 ppm for compounds 85-87. Although there are only slight variations in the $^{31}$P{$^1$H} chemical shifts of the metalated compounds, the $^{31}$P-$^{11}$B coupling constants decrease in magnitude by 10 Hz steps between 41, 85 and 86, although this trend does not continue to compound 87 [$J_{PB} = 49.0$ (41), 39.4 (85), 29.8 (86), 29.4 (87) Hz].

The $^1$H and $^{13}$C{$^1$H} NMR spectra of 85-87 are as expected. In the $^1$H NMR spectra of 85-87, the diastereotopic SiMe$_3$ groups each give rise to sharp singlets between -0.3 and 0.5 ppm, whilst the adjacent CH protons appear as sharp doublets at 0.7 ppm for 85 and 86 [$^2J_{PH} = 6.9$ (85) and 7.3 Hz (86), and at 1.1 ppm for 87 [$^2J_{PH} = 7.8$ Hz]. The BH$_3$ protons appear as broad quartets, which collapse upon decoupling of the $^{11}$B nucleus, to give sharp doublets at 0.6 [$^2J_{PH} = 3.2$ Hz], 0.7 [$^2J_{PH} = 6.9$ Hz] and 1.1 ppm [$^2J_{PH} = 5.5$ Hz] for 85, 86 and 87, respectively. In the $^{13}$C{$^1$H} NMR spectra of 85-87, the diastereotopic SiMe$_3$ groups give rise to two signals, a doublet [$^3J_{PC} = 8.6$ Hz for each compound] and a singlet, between 1.4 and 3.4 ppm, and the CH carbons appear as sharp doublets between 6.0-6.2 ppm [$^1J_{PC} = 44.1$ (85) and 41.2 Hz (86 and 87)].

5.4 Solid-state structure of 87

The adduct [{(Me$_3$Si)$_2$CH}P(C$_6$H$_4$-2-CH$_2$OMe)(BH$_3$)K(pmdeta)] (87) crystallises as discrete centrosymmetric dimers in which the phosphido-borane ligand adopts a bidentate coordination mode; the structure of 87 is shown in Figure 5.2 with selected bond lengths and angles shown in Table 5.1. Each phosphido-borane ligand binds to the adjacent potassium ion through its phosphorus atom and an $^2$-BH$_3$ interaction. The potassium ion is also bound by the second ligand in the dimer via an $^2$-BH$_3$ interaction, such that each borane group acts as a $\mu_2$- $^2$: $^3$ bridge between the two cations, forming a pseudo-four-membered K$_2$(BH$_3$)$_2$ ring [B(1)-K(1)-B(1A) 93.94(5)$^\circ$]. Each potassium ion is coordinated by the three nitrogen atoms of a molecule of pmdeta. Unlike the related potassium salts [{(Me$_3$Si)$_2$CH}P(C$_6$H$_4$-2-CH$_2$OMe)(BH$_3$)K(pmdeta)] (51) and [{(Me$_3$Si)$_2$CH}P(C$_6$H$_4$-2-SMe)(BH$_3$)K(pmdeta)] (66), the potassium ions in 87 are not coordinated by the peripheral donor. This is rather unexpected, as a K-O interaction would be considered more favourable than a K-S
interaction, as observed in 66, due to Pearson’s hard-soft acid-base principle. Instead, the OMe groups in 87 are orientated away from the potassium ions, and the coordination about each potassium is completed by three short contacts to the central methyl group, and a methyl from each NMe₂ group of the pmdeta ligand. This is in contrast to 66, which possesses a single K...Me contact to the central methyl of the pmdeta molecule. This shows that there is a fine balance between K-O and agostic type K...Me contacts.

![Figure 5.2](image)

**Figure 5.2.** Molecular structure of compound 87. All C-bound H atoms omitted for clarity.

The K-P bond lengths in 87 [K(1)-P(1) 3.2338(5) Å] are similar to the corresponding distance in 32 [3.320(2) Å], but are significantly shorter than the K-P distances in compounds 51 [3.7620(10) Å] and 66 [3.6617(6) Å]. This suggests that the K-P interactions are stronger when the metal centre is not bound by a peripheral donor atom. The K...B distances of 3.317(2) and 3.1365(8) Å in 87 are similar to the corresponding distances in 51 and 66, and are consistent with η²- and η³-BH₃ coordination modes, respectively.
Compound 87 is very similar to 66, except that the former has O- while the later has S-donor functionality. Both compounds crystallise as dimers, where dimerisation is afforded through $\mu^2$-$\eta^2$-$\eta^3$ bridging borane groups, and both have similar K...B and K-H distances. However, alongside K-P and K-BH$_3$ coordination modes, 66 also possesses coordination to potassium through the sulphur donor atom, to generate a five-membered chelate ring. In contrast, the oxygen donor atom in 87 does not coordinate to the adjacent potassium ion, as discussed above. Consequently, there are some variations between the structures of 66 and 87. A comparison of the sum of angles within the C$_2$PB framework [312.33 and 321.34° for 66 and 87, respectively] reveals that the geometry about the phosphorus anion in 87 is more planar than in 66, whilst the K-P bond in 66 is significantly longer than the corresponding distance in 87.

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (°)</th>
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<tr>
<td>K(1)–P(1)</td>
<td>3.2338(5)</td>
</tr>
<tr>
<td>K(1)–B(1)</td>
<td>3.317(2)</td>
</tr>
<tr>
<td>K(1)–B(1A)</td>
<td>3.1365(18)</td>
</tr>
<tr>
<td>K(1)–H(1C)</td>
<td>3.359(17)</td>
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<tr>
<td>K(1)–H(1B)</td>
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</tr>
<tr>
<td>K(1)–H(1AA)</td>
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</tr>
<tr>
<td>K(1)–H(1BA)</td>
<td>2.845(14)</td>
</tr>
<tr>
<td>K(1)–H(1CA)</td>
<td>2.735(17)</td>
</tr>
<tr>
<td>P(1)–B(1)</td>
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</tr>
<tr>
<td>P(1)–C(8)</td>
<td>1.8375(15)</td>
</tr>
<tr>
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</tr>
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</tr>
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</tr>
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<td>K(1)–P(1)–B(1)</td>
<td>74.97(6)</td>
</tr>
</tbody>
</table>

Table 5.1. Selected bond lengths (Å) and angles (°) of compound 87.
5.5 Thermally-induced reactions of 85

In chapter 4, the stabilities of the analogous phosphido-boranes 64, 65 and 66 on exposure to heat and light were explored, and it was found that these complexes do not undergo any change. Compound 87 is also found to be thermally and photolytically stable in THF solutions over extended periods of time, as is the previously reported phosphide [{(Me₃Si)₂CH}P(C₆H₄-2-OMe)]K (88). ⁷

In contrast, under certain conditions, compound 85 undergoes one of two competing, thermally-induced reactions. Heating a solution of 85 and one equivalent of tmeda in toluene to 60 °C for 72 h resulted in the conversion of the phosphido-borane complex into a mixture of the unusual aryloxide cluster [{(Me₃Si)CH}PH(C₆H₄-2-O)Li]₆ (89) and the tertiary phosphine-borane {(Me₃Si)₂CH}PMe(BH₃)(C₆H₄-2-OMe) (90), which are observed in the ³¹P NMR spectrum as a sharp doublet [¹J_{PH} = 217.6 Hz] and a broad quartet [¹J_{PB} = 58.8 Hz] at -72.7 and 12.5 ppm, respectively, in an approximately 1:1 ratio (Figure 5.3). A broad signal is also observed in the ³¹P NMR spectrum at around 79.0 ppm, due to an unidentified side product (A) (see section 5.10).

The identity of 89 was confirmed by multi-element NMR spectroscopy (see section 5.6) and X-ray crystallography (see section 5.7), which demonstrates unequivocally that the structure of 89 results from elimination of the methyl and BH₃ groups from a phosphido-borane ligand, and concurrent formation of a P-H bond (Scheme 5.5). The cleaved methyl group appears to migrate to a second phosphido-borane ligand, forming a P-Me bond, thus generating 90. It appears that 85 must be coordinated to THF for this thermolysis reaction to proceed; this is usually present as 85 is prepared in THF solutions. THF-free samples of 85 showed no evidence for conversion after heating in toluene for several days.

Alternatively, when a solution of 85 in toluene, in the presence of one equivalent of tmeda and an excess of THF is heated for 16 h at 60 °C, the formation of new phosphorus-containing species results. This compound gives rise to a broad peak in the ³¹P NMR spectrum at -69.7 ppm (Figure 5.4), which is consistent with a phosphido-borane-containing species, and is observed alongside compound 90, which also forms in the reaction. Unfortunately, this new compound could not be separated from 90.
Figure 5.3. Proton-coupled $^{31}$P NMR spectrum of 89 and 90 in THF, from the thermolysis of 85 in the presence of tmeda, after heating at 50°C for 16 h in toluene.
Previous studies have shown that degradation of the related calcium phosphide 78 in THF/ether results in the formation of the corresponding tertiary phosphine 82, and a dianionic phosphide ligand, which forms the novel calcium cluster 80 (Section 5.1). On the basis of these observations and the presence of 90, we propose that, in the presence of excess THF, 85 undergoes a similar ligand degradation to generate an alkoxo-functionalised phosphido-borane dianion, possibly forming the complex \([\{(\text{Me}_3\text{Si})_2\text{CH}\}P(\text{BH}_3)(\text{C}_6\text{H}_4-2-O)\text{Li}_2(\text{tmema})_2]\) (91, Scheme 5.5).

![Scheme 5.5. Thermolysis reactions of compound 85.](image)

The proposed mechanisms for the formation of 89, 90 and 91 are shown in Scheme 5.6. Both processes may occur via an equilibrium to generate an “ate” species, analogous to the proposed mechanism for the formation of 83, which is set up to undergo an intramolecular methyl migration, as also seen for the calcium and ytterbium complexes 80 and 81. The reaction conditions are finely balanced; when THF is present in a stoichiometric amount, reaction pathway 1 is preferred, generating 89 and 90, whilst in the presence of an excess of THF, pathway 2 is favoured, and 91 is generated alongside 90.
In the absence of tmeda, yields of either 89 or 91 and 90 are noticeably lower. This may suggest that tmeda favours the formation of the intermediate ate complex, promoting the methyl-migration reaction.

Diorganolithates were first proposed as intermediates over 50 years ago, although only a few examples of complexes of this type have been characterised in the solid state. Examples include the phosphine-borane-stabilised carbanion complex \([(\text{THF})_3\text{Li}\{(\text{Me}_3\text{Si})_2\text{CPMe}_2(\text{BH}_3)}\}_2\text{Li}\] (92), which crystallizes as a contact ion multiple ate complex. In solution, 92 is subject to a dynamic equilibrium between the ate complex and a second, possibly
monomeric, species (Scheme 5.7). Therefore, it is reasonable to propose that in solution, \( \text{85} \) also exists in equilibrium between the monomeric species and the corresponding ate complex.

\[
2 \text{[RLi(THF)}_n\text{]} \rightleftharpoons [R_2\text{Li}][\text{Li(THF)}_2\text{]}n
\]

**Scheme 5.7.** Equilibrium between a mononuclear and an ate complex.

The conditions for these thermolysis reactions are finely balanced, where a slight variation in THF concentrations appears to be the only factor which determines the reaction pathway that is followed. The extent of aggregation in phosphide complexes with alkali metals in solution is dependent on the nature of donor solvents present e.g. the complex \([\text{Li(}^{t}\text{BuP)}]_n\) is tetrameric in THF (1), but is dimeric in DME (2), and as a consequence, this can have an effect on the reactivities of these species in solution. A well-known organometallic example which demonstrates this is \(^{t}\text{BuLi}, \) which is hexameric in hexanes, but upon complexation with tmeda, the aggregate is broken down, generating a more reactive species. Therefore, it is possible that the reactivity of \( \text{85} \), upon thermolysis, is governed by its aggregation state in solution, which can be affected by changes in THF concentration in solution; an excess of THF may favour the monomeric species over the ate complex.
Figure 5.4. $^{31}$P NMR spectrum of the conversion of 85 into 90 and 91 after heating at 50°C for 16 h in toluene/THF.

5.6 Solution-phase characterisation of compound 89

The $^1$H and $^{13}$C{$^1$H} NMR spectra of 89 in $d_6$-benzene is consistent with a single ligand environment. In the $^1$H NMR spectrum, the P-H proton appears at 4.5 ppm as a doublet of doublets due to coupling of the proton to the $^{31}$P nucleus [$^1J_{PH} = 217.6$ Hz] and coupling to the adjacent PCH proton [$^3J_{HH} = 5.5$ Hz]. The PCH proton gives rise to a doublet of doublets at 0.7 ppm [$^1J_{HH} = 5.5$ Hz, $^2J_{PH} = 1.9$ Hz], whilst the Me$_3$Si groups appear as a singlet at 0.2 ppm due, presumably, to rapid, reversible P-Li cleavage. In the $^{13}$C{$^1$H} NMR spectrum, the Me$_3$Si groups also appear as a singlet at 1.1 ppm, whereas the adjacent CH appears as a doublet at 4.4 ppm due to coupling to the phosphorus nucleus, where $^1J_{PC} = 42.2$ Hz. The $^{31}$P NMR spectrum of 89 exhibits a sharp doublet at -72.7 ppm due to the $^{31}$P-$^1$H coupling [$^1J_{PH} = 217.6$ Hz].

To gain a further understanding of the formation of 89, the kinetics of the thermolysis reaction were studied. NMR samples containing solutions of known concentrations of 85 in toluene and a few drops of THF were prepared; the progress of the thermolysis reaction was then monitored by $^{31}$P{$^1$H} NMR spectroscopy over a 16 h period for a range of
temperatures. Changes in the concentration of 85 were measured against the presence of impure quantities of 41, which remained at a constant concentration throughout the experiment. The experiment was repeated at various temperatures (23.1 to 60 °C), to determine the rate of thermolysis, however, it was impossible to ascertain whether 1st or 2nd order kinetics were being obeyed under the conditions that the data was collected.

5.7 Solid-state structure of compound 89

Compound 89 crystallises as a hexameric phosphine-substituted lithium aryloxide cluster with a puckered-hexagonal prismatic Li₆O₆ core; the structure of 89 is shown in Figure 5.5 (the Li₆O₆ core is shown in Figure 5.6), and selected bond lengths and angles are shown in Table 5.2. The Li and O atoms sit in alternating positions in the hexagonal prism, and are bridged through μ³-type interactions, thus linking the six units. The coordination about each lithium ion is completed by the P atom of an adjacent ligand, to give a five-membered chelate ring [P-Li-O 84.52(17)-85.20(2)°].

<table>
<thead>
<tr>
<th>Bond Description</th>
<th>Range (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P–Li</td>
<td>2.523(5)-2.551(5)</td>
</tr>
<tr>
<td>P–H</td>
<td>1.31(3)-1.48(3)</td>
</tr>
<tr>
<td>Li–O (hexagonal face)</td>
<td>1.870(6)-1.924(6)</td>
</tr>
<tr>
<td>Li–O (edge)</td>
<td>2.051(5)-2.066(5)</td>
</tr>
<tr>
<td>Li–P–H</td>
<td>115.8(12)-118.1(10)</td>
</tr>
<tr>
<td>P–Li–O (bite angle)</td>
<td>84.52(17)-85.2(2)</td>
</tr>
<tr>
<td>O–Li–O (hexagonal face)</td>
<td>124.8(3)-126.9(3)</td>
</tr>
<tr>
<td>Li–O–Li (hexagonal face)</td>
<td>112.2(2)-113.7(2)</td>
</tr>
<tr>
<td>O–Li–O (edge)</td>
<td>94.8(2)-98.4(2)</td>
</tr>
<tr>
<td>Li–O–Li (edge)</td>
<td>81.9(2)-84.9(2)</td>
</tr>
</tbody>
</table>

Table 5.2. Selected ranges of bond lengths (Å) and angles (°) for compound 89.
**Figure 5.5.** Molecular structure of compound 89. All C-bound H atoms omitted for clarity.

**Figure 5.6.** Structure of the core of 89, with all C, Si and H atoms omitted bar phosphine protons.
The P-Li distances in 89 range from 2.523(5) to 2.551(5) Å, and are typical of P-Li distances of Li-PR₃ containing complexes, which range between 2.51 and 3.18 Å.¹⁵ The Li-O distances range from 1.901(5) to 2.055(5) Å, which are similar to Li-O distances observed in related lithium alkoxides.¹⁶⁻²⁰ The O-Li-O angles within the hexagonal face of the Li₆O₆ core, range from 112.5(2) to 125.6(3)°.

Lithium alkoxides have been extensively used as precursors to ceramic and electronic materials²¹,²² and have been investigated in great detail, with many of these compounds being crystallographically characterised. These complexes typically form aggregates, and usually adopt one of the structural motifs I-V, as shown in Figure 5.7. The contributing factors which govern the structures of these compounds include: the Lewis basicity of the solvent, the binding mode of the ligand (mono-, bi-, tri- or polydentate), the steric bulk of the ligand, and crystal packing effects.¹⁶,¹⁹,²⁰

The majority of simple solvent-free lithium alkoxide compounds that have been characterised typically crystallise as hexanuclear clusters.¹⁶,²⁰,²³,²⁴ Three exceptions are polymeric [Li(OMe)]ₙ (93),²⁵,²⁶ dinuclear [Li(OC₃Bu₃)]₂ (94),²⁷ and octanuclear [Li(μ₃-OCH₂CMe₃)]₈ (95), although 95 adopts a hexagon-cube prism structure IV, which maintains a high degree of solubility.¹⁷ The structures observed for these compounds are associated with the degree of steric hindrance introduced by the pendant hydrocarbon chain of the alkoxide ligand. Using less sterically hindered ligands tends to result in insoluble polymer aggregates, such as 93, which limits the utility of these compounds. A number of related lithium-oxygen hexamers such as enolates,²⁸⁻³⁰ azaenolates,³¹,³² and a hydroxylamide³³ have previously been reported.
Figure 5.7. Typical [Li(OR)]₆ structural motifs.

There have also been several reports detailing the structures of related α-amine-stabilised lithium alkoxides, some of which have also adopted the hexameric prism structure IV. The first such example was [(4-methoxybenzaldehyde)(N-methylpiperazide)Li]₆·2PhMe·THF (96), which was reported by Armstrong et al in 1999, in which the lithium ions in the Li₆O₆ core are each coordinated by an N atom from the adjacent ligand, thus affording stable four-membered N-C-O-Li rings. This compound is closely related to the lithium enolate Li₆[OC(OEt)=C(H)NEt₂]₆ (97).  

More recently, a series of lithium quinolates: [Li (NC₆H₅-8-O)] (98), [Li (NC₆H₅-2-Me-8-O)] (99) and [Li(NC₆H₅-2-Ph-8-O)] (100), were synthesised by Rajeswaran and co-workers. It was found that compounds 98 and 99 adopted the hexagonal prism motif IV, whilst 100 crystallises as a tetramer (III). Interestingly, computational studies of these complexes, which were carried out in tandem, showed that the observed tetrameric structure of 100 was less favourable (+1.2 kcal/mol/monomer) than the hexameric prism structure. However, in that particular case the crystal packing effects probably outweighed the small differences in cluster stability.
5.8 Synthesis and solution-phase characterisation of \{(Me_3Si)_2CH\}PMe (BH_3)(C_6H_4-2-OMe) (90)

To confirm the identity of 90, which was isolated from the thermolysis of 85 and characterised using multi-nuclear NMR spectroscopy and mass spectrometry, this compound was also prepared using a direct route.

The reaction between a solution of 85 in THF and one equivalent of MeI yields 90 as a white solid after aqueous work-up (Scheme 5.8); the \(^1\)H, \(^{31}\)P\({}^{1}\)H, and \(^{11}\)B\({}^{1}\)H NMR spectra of this deliberately prepared sample are identical to those observed in the 1:1 mixture of 89 and 90 after thermolysis of 85; in the \(^{31}\)P\({}^{1}\)H NMR spectrum a broad quartet is observed at 11.7 ppm \([^{1}J_{PB} = 58.8 \text{ Hz}]\), whilst in the \(^{11}\)B\({}^{1}\)H NMR spectrum 89 gives rise to a broad doublet at -37.5 ppm \([^{1}J_{BP} = 58.8 \text{ Hz}]\). The \(^1\)H NMR spectrum is as expected; the P-methyl protons are observed as a sharp doublet at 1.7 ppm \([^{2}J_{PH} = 10.1 \text{ Hz}]\) due to coupling to phosphorus, and in the \(^{13}\)C\({}^{1}\)H NMR spectrum, the signal due to the PMe is a doublet \([^{1}J_{PC} = 9.6 \text{ Hz}]\) at 16.7 ppm. The borane protons appear as a broad peak at around 0.9 ppm, but upon \(^{11}\)B decoupling the signal collapses into a sharp doublet \([^{2}J_{PH} = 14.7 \text{ Hz}]\).

5.9 Investigation into the mechanism of formation of 89

Although the mechanisms for the thermolysis reactions of 85 are clearly complex, NMR spectroscopic studies have given some insight into the processes occurring. The chemistry of facile O-Me cleavage is well established for the ligand \[\{(Me_3Si)_2CH\}P(C_6H_4-2-OMe)\]^−, however the borane elimination and P-H formation processes observed in the formation of 89 are highly unusual.
It has already been mentioned in section 5.1 that compound 73 was identified as a key intermediate in the synthesis of DIPAMP. In an attempt by Imamoto et al to develop synthetic routes to prepare enantiomerically pure 73, it was observed that when 73 is prepared by the treatment of \((R_{\alpha},1'R,2'S,5'R)\)-\((2'-2Pr-5-C_6H_5Me)O)MePhP(BH_3)\) with o-anisyllithium in a solution of THF/DME at reflux, it is unexpectedly formed as a racemic mixture. The proposed mechanism for this observed behaviour is shown in Scheme 5.9. It is proposed that, in solution at high temperatures, an equilibrium is established where the oxygen atom can abstract the BH\(_3\) group, breaking the P-B bond, thus allowing phosphorus to undergo an inversion, before the P-B bond is reformed.\(^{34}\) This behaviour may apply to borane elimination observed in the formation of 89; a suggested mechanism is shown in Scheme 5.10.

![Scheme 5.9](image)

**Scheme 5.9.** Racemisation of 73.

![Scheme 5.10](image)

**Scheme 5.10.** Possible mechanism for borane elimination of 85 \([R = (Me_3Si)_2CH]\).  

Perhaps the most intriguing aspect in the formation of 89 is the origin of the hydrogen atom of the P-H group. The hydrogen may be derived from the solvents used in synthesis, or
possibly the methyl or borane group which are cleaved during thermolysis. Several experiments were designed to identify the source from which the P-H proton is derived. These may be divided into two categories: deuterated solvents and deuterated phosphine-boranes. In each case, the potential proton sources were modified by replacing protons with deuterium atoms; the formation of a P-D bond can then be identified by $^{31}$P and $^2$D NMR spectroscopy.

### 5.9.1 Deuterated solvents

Two solvents are used in the overall synthesis of 89: THF in the synthesis of 85 and toluene, which is used in the thermolysis reaction. To determine if the P-H hydrogen atom is derived from one of these solvents, two experiments were performed using deuterated solvents. In the first instance, compound 41 was dissolved in $d_8$-THF and treated with $^n$BuLi, to yield compound 85($d_8$-THF)$_n$. The solvent was removed from the product in vacuo to give 85($d_8$-THF) as a sticky yellow residue. Compound 85($d_8$-THF) was then dissolved in toluene and heated for 16 h at 50 °C (Scheme 5.11). In the second experiment, compound 85 was synthesised using the general method as described in section 5.2. The THF used for the reaction was then removed in vacuo until 85 was left as a sticky residue, which was then dissolved in $d_8$-toluene and heated for 16 h at 50 °C (Scheme 5.12).

Both reactions were monitored by $^{31}$P NMR spectroscopy, which in each case saw the rise of the characteristic sharp doublet at -72.7 ppm associated with the P-H centre of 89, thus eliminating the solvents as the proton source in this rearrangement.

![Scheme 5.11. Thermolysis of 85($d_8$-THF)$_n$[R = (Me$_3$Si)$_2$CH].](image)
Scheme 5.12. Thermolysis of 85 in $d_8$-toluene \[ R = (\text{Me}_3\text{Si})_2\text{CH} \].

5.9.2 Synthesis of \{(\text{Me}_3\text{Si})_2\text{CH}\}\text{PH}(\text{BH}_3)(\text{C}_6\text{H}_4\text{-2-OCD}_3) \ (101) and \{(\text{Me}_3\text{Si})_2\text{CH}\}\text{PH}(\text{BD}_3)(\text{C}_6\text{H}_4\text{-2-OMe}) \ (102)

After it was determined that the P-H proton in 89 is not derived from the solvents used in its preparation, two variants of the precursor phosphine-borane 41, modified with deuterium, were synthesised: \{(\text{Me}_3\text{Si})_2\text{CH}\}\text{PH}(\text{C}_6\text{H}_4\text{-2-OCD}_3)(\text{BH}_3) \ (101) and \{(\text{Me}_3\text{Si})_2\text{CH}\}\text{PH}(\text{C}_6\text{H}_4\text{-2-OMe})(\text{BD}_3) \ (102). The syntheses of phosphine-boranes 101 and 102 are shown in Schemes 5.13 and 5.14, respectively.

The reaction between 2-bromophenol and potassium hydroxide in acetonitrile (MeCN) at low temperatures, followed by the addition of 1 equivalent of CD$_3$I yields BrC$_6$H$_4\text{-2-OCD}_3$, which can be isolated as an oil after aqueous work-up. Treatment of a solution BrC$_6$H$_4\text{-2-OCD}_3$ in Et$_2$O with $^\text{BuLi}$ at 0 °C yields LiC$_6$H$_4\text{-2-OCD}_3$, which is added \textit{in situ} to a cold solution of \{(\text{Me}_3\text{Si})_2\text{CH}\}\text{PCl}_2 \ (43), to yield the monochlorophosphine \{(\text{Me}_3\text{Si})_2\text{CH}\}\text{PCI}(\text{C}_6\text{H}_4\text{-2-OCD}_3), which may then be reduced with LiAlH$_4$ \textit{in situ} to yield the phosphine \{(\text{Me}_3\text{Si})_2\text{CH}\}\text{PH}(\text{C}_6\text{H}_4\text{-2-OCD}_3), which is isolated as a colourless oil after aqueous work-up. Reaction of the phosphine with BH$_3\cdot$SMe$_2$ yields 101, which may be isolated as colourless, crystalline needles from cold light petroleum.

The reaction between \{(\text{Me}_3\text{Si})_2\text{CH}\}\text{PH}(\text{C}_6\text{H}_4\text{-2-OMe}) \ (46) and BD$_3$·THF in a solution of THF yields 102. Upon removal of the solvent \textit{in vacuo}, 102 is isolated as a colourless oil.

Treatment of a THF solution of either 101 or 102 with one equivalent of $^\text{BuLi}$ yields the corresponding phosphido-boranes \[ \{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P(}\text{C}_6\text{H}_4\text{-2-OCD}_3)(\text{BH}_3)\text{Li(THF)) \ (103) and \[(\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P(}\text{C}_6\text{H}_4\text{-2-OMe})(\text{BD}_3)\text{Li(THF)) \ (104), respectively (Schemes 5.13 and 5.14).} \]
The phosphido-boranes were dissolved in toluene and heated to 60 °C. The thermolysis of 103 was monitored by $^{31}$P NMR spectroscopy; after 16 h stirring at 50 °C, the sharp doublet associated with the P-H centre of 89 appeared at -72.7 ppm, simultaneously with the appearance of a broad quartet at 11.7 ppm due to the CD$_3$ analogue of 90 [{(Me$_3$Si)$_2$CH}P(CD$_3$)(BH$_3$)(C$_6$H$_4$-2-OCD$_3$)]. As a consequence the methyl group was eliminated as a potential proton source in the formation of 89.

![Scheme 5.13. Synthesis of 103. i) KOH, MeCN, 0 °C, ½ h ii) CD$_3$I, MeCN, 0 °C, 1 h; r.t., 40 h. iii) $^6$BuLi, Et$_2$O, 0 °C, 2 h. iv) 43, Et$_2$O, -78 °C, 16 h. v) LiAlH$_4$, 35 °C, 2 h. vi) BH$_3$·SMe$_2$, THF, 1 h, r.t. vii) $^6$BuLi, THF, 1 h, r.t. [R = (Me$_3$Si)$_2$CH].](image)

The thermolysis of 104, although not in the presence of tmeda, was also monitored by $^{31}$P NMR spectroscopy. After heating for approximately two hours a new peak began to appear in the $^{31}$P NMR spectrum at around -80.0 ppm. After 16 h hours stirring at 50 °C, the thermolysis of 104 had given rise to a broad quartet at 11.7 ppm (90), whilst the broad signal at -80.0 ppm grew in intensity; the sharp doublet associated with the P-H signal of 89 was not observed. The $^2$D NMR spectrum of the thermolysis of 104 (Figure 5.8) exhibits a peak.
at 3.9 ppm, which suggests the presence of a P-D bond, thus indicating that the complex [([(Me₃Si)CH]PD(C₆H₄-2-O)]₆Li₆ (105) has formed (Scheme 5.15); although the signal is not the expected doublet, this may be due to poorly resolved coupling and/or a small ³¹P-²D coupling constant. It therefore appears that the BH₃ group is the source of the P-H proton in compound 89. Interestingly, a peak also appears at 2.1 ppm in the ²D NMR spectrum, which may possibly be attributed to the unidentified compound A, which will be discussed in the following section.

Scheme 5.15. Thermal rearrangement of compound 104 [R = (Me₃Si)₂CH].

Figure 5.8. ²D NMR spectra of thermolysis of 104 in toluene.
5.10 Identity of unknown compound A

We were, unfortunately, unable to isolate and identify compound A, which gives rise to the broad signal at 79.0 ppm in the $^{31}$P NMR spectra of the thermolysis products of 85. However, it is likely that, since the proton in 89 is derived from a BH$_3$ group, compound A results from elimination of a borane proton from 85. In this regard, it is notable that Romanenko and co-workers recently reported the synthesis of the complex [(mes*)P(BH$_3$)(μ-BH$_2$)$_2$Li(THF)$_2$]$_2$ (36). Compound 36 was prepared by the reaction of the phosphido-bis(borane) [(mes*)PH(BH$_3$)$_2$Li(THF)$_3$] (35) with an excess of $^n$BuLi, followed by addition of excess BH$_3$·THF, and forms as a mixture with LiBH$_4$ (Scheme 5.16). The prominent feature in the structure of 36 (Figure 5.9) is the hydride-bridged μ-B$_2$H$_5$ unit.$^{35}$

![Scheme 5.16. Synthesis of compounds 35 and 36 [Ar = mes*].](image)

![Figure 5.9. Structure of compound 36.](image)
It is tentatively proposed that, should 85 eliminate a proton from its borane group, the resulting species could react with a second borane fragment, possibly arising from BH$_3$ elimination in the formation of 89, and a B$_2$H$_5$ containing species, stabilised by a bridging hydride, could form. That this suggested process is similar to the synthesis of 36 is unlikely, given that the mechanism for the formation of 36 results in the elimination of a hydride ion, whereas in the thermolysis of 85, the P-H centre which arises in compound 89 must be formed by a proton. Scheme 5.17 highlights the possible products from a reaction between 85 and BH$_3$, similar to the synthesis of 36.

![Scheme 5.17. Possible reaction between BH$_3$ and 85 [R = (Me$_3$Si)$_2$CH].](image)

It has been shown previously by Manners and co-workers that phosphine-boranes can undergo a Rh-catalysed dehydrogenation to give H$_2$ and (poly)phosphine-boranes (Scheme 5.18). This process also occurs with elimination of a hydrogen atom from the borane group. It may also be possible that during the thermolysis of 85, proton elimination from two BH$_3$ groups could generate H$_2$, which could then be the source of the P-H proton in compound 89.

Compound A gives rise to a very broad, poorly resolved signal in the $^{31}$P{${^1}$H} NMR spectrum, which is consistent with a phosphido/phosphine-poly(borane) species, whilst the signal observed in the $^2$D NMR spectrum, from the thermolysis of 104, at 2.1 ppm may possibly be attributed to a bridging borane deuteride. Although there is an example of a bridging B-H-B hydride containing species with a $^1$H NMR resonance at 1.97 ppm, other examples have been found to range from 1.1 to 8.2 ppm.

Since we have been unable to isolate A, to confirm its identity would be difficult; to prepare a phosphine/phosphido-borane species containing a hydride-bridged B$_2$H$_5$ group directly would be challenging, and as all previous examples of this type of compound have not been fully characterised by NMR spectroscopy, no comparisons can be drawn.
5.11 Comparison between the stability of 85 and [(Me$_3$Si)$_2$CH]P(C$_6$H$_4$-2-OMe)Li(tmeda)] (106)

5.11.1 Synthesis and solution-phase characterisation of 106

In order to better understand the thermolysis behaviour of 85, the related phosphide was prepared to ascertain if methyl migration is due to borane activation. The reaction between 46 and one equivalent of nBuLi in THF proceeds cleanly to yield the corresponding lithium phosphide, which can be crystallised from cold toluene in the presence of one equivalent of tmeda as the adduct [(Me$_3$Si)$_2$CH]P(C$_6$H$_4$-2-OMe)Li(tmeda)] (106, Scheme 5.18).

The $^1$H, $^{13}$C{$^1$H} and $^{31}$P{$^1$H} NMR spectra of 106 are as expected. The $^{31}$P{$^1$H} NMR spectrum consists of a sharp singlet at -85.1 ppm. In the $^1$H NMR spectra, the diastereotopic Me$_3$Si groups appear as a single peak, due to intermolecular exchange involving P–M bond scission/bond formation which is rapid on the NMR time-scale.

**Scheme 5.18.** Synthesis of compound 106. i) $^n$BuLi, THF, 1 h, r.t. ii) tmeda, toluene. [R = (Me$_3$Si)$_2$CH].
5.11.2 Solid-state structure of 106

Compound 106 crystallises as discrete monomers, the structure of which is shown in Figure 5.10; details of selected bond lengths and angles are given in Table 5.3. Each lithium ion is coordinated by the P and O atoms of the phosphide ligand to give a five-membered chelate ring [P-Li-O bite angle 80.97(19)°]. The coordination about lithium is completed by two nitrogen atoms from a molecule of tmeda, to give the lithium ion a distorted tetrahedral geometry.

The P-Li distance of 2.428(5) Å falls within the range of previously reported lithium phosphides of 2.42-2.67 Å.\textsuperscript{15} The Li-O distance 1.986(6) Å is similar to the related distance reported for compound 49 [1.982(7) Å], whilst the P-Li-O bite angle is somewhat smaller [P-Li-O bite angles: 80.97(19)\textdegree (106) and 89.5(2)\textdegree (49)].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{structure.png}
\caption{Molecular structure of compound 106. All H atoms omitted for clarity.}
\end{figure}
Table 5.3. Selected bond lengths (Å) and angles (°) for compound 106.

<table>
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<th>Value</th>
</tr>
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</tr>
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</tr>
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<tr>
<td>O(1)–Li(1)</td>
<td>1.986(6)</td>
</tr>
<tr>
<td>N(1)–Li(1)</td>
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</tr>
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<td>N(2)–Li(1)</td>
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<td>Si(1)–C(1)</td>
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</tr>
<tr>
<td>P(1)–C(1)–Si(2)</td>
<td>108.14(16)</td>
</tr>
</tbody>
</table>

5.11.3 Reactivity of 106

Samples of 106 in toluene in sealed NMR tubes were monitored by $^{31}$P{¹H} NMR spectroscopy. After heating the sample, and after an extended period at room temperature, there was no evidence of O-Me cleavage. Similarly, heating a solution of 106 in toluene, in the presence of THF, resulted in no change, suggesting that the methyl migration seen in the thermolysis of compound 85 is borane activated.

The chemistry of group II and lanthanide metal complexes with the ligand $[\{(Me_3Si)_2CH\}P(C_6H_{14}-2-OMe)]^-$ has already been discussed, and highlights that O-Me cleavage is dependent on the Lewis acidity of the metal centre. As such, the stability of 106 suggests that lithium is insufficiently Lewis acidic to mediate O-Me cleavage in this ligand. However, the addition of a Lewis acidic borane group, generating 85, may be sufficient enough to promote O-Me cleavage. This reactivity may be attributed to decreased electron density at phosphorus. However, whilst the combined Lewis acidity of a lithium metal centre and a borane substituent may promote O-Me cleavage, the potassium analogue (87) is stable.

Alternatively, it has been shown by Imamoto and co-workers that anisole-functionalised phosphine-boranes undergo racemisation at high-temperatures via a P-BH$_3$/O-BH$_3$ equilibrium (Scheme 5.8). It has already been proposed that borane elimination in the preparation of 89 occurs via this mechanism, but it could also contribute to methyl
migration; the formation of the O-B bond could promote O-Me cleavage, and generate alkoxy-functionality, which is otherwise unobserved in 106 (Scheme 5.19).

Scheme 5.19. Possible mechanism for Me elimination for 85 [R = (Me₃Si)₂CH].

5.12 Synthesis and solution-phase characterisation of [{(Me₃Si)₂CH}P(C₆H₄-2-OMe)(BH₃)₂Li(THF)] (107)

In an analogous manner to that observed for the complex [{(Me₃Si)₂CH}P(C₆H₄-2-SMe)(BH₃)Li(THF)]₂ (64) (see chapter 4), heating a THF solution of 85 in the presence of the free phosphine-borane 41, results in the conversion of 85 into the phosphine-bis(borane) [{(Me₃Si)₂CH}P(BH₃)₂(C₆H₄-2-OMe)Li] and the secondary phosphine 46, due to borane-redistribution.

The formation of [{(Me₃Si)₂CH}P(BH₃)₂(C₆H₄-2-OMe)Li] can be observed by ³¹P{¹H} and ¹¹B{¹H} NMR spectroscopy, however we were unable to isolate a pure sample from the thermolysis reactions. Therefore, in order to confirm the identity of the phosphido-bis(borane), this compound was prepared using a direct route.

The reaction between 85 and one equivalent of BH₃·SMe₂ in THF proceeds cleanly to yield [{(Me₃Si)₂CH}P(BH₃)₂(C₆H₄-2-OMe)Li], which, upon removal of the solvent, is isolated as a viscous, colourless oil. The product may be crystallised from light petroleum in the presence of THF as the adduct [{(Me₃Si)₂CH}P(C₆H₄-2-OMe)(BH₃)₂Li(THF)] (107, Scheme 5.20).

Upon addition of the second equivalent of borane, the ³¹P{¹H} NMR signal for 85 [-62.5 ppm] is replaced by a new, very broad signal at -12.7 ppm, which is indistinguishable from that of the sample of 107 prepared from the thermolysis of 85 in the presence of 41 in solutions of THF.
The $^1$H NMR spectrum of \textbf{107} in $d_8$-THF is as expected; the SiMe$_3$ groups appear as a sharp singlet, whilst the six BH$_3$ protons appear as a broad signal at 0.7 ppm, which, upon decoupling of the $^{11}$B nucleus, resolves as a sharp doublet [$^2J_{PH} = 11.0$ Hz]. As observed in \textbf{72·(12-crown-4)}, all six borane protons appear to be identical. This suggests that in solution there is either rapid exchange between the free and coordinated borane groups, or that the compound exists as a separated ion pair in THF. In the $^{13}$C\{$^1$H\} NMR spectrum the SiMe$_3$ carbons appear as a doublet [$^3J_{PC} = 1.9$ Hz], whilst the adjacent CH carbon also gives rise to a doublet [$^1J_{PC} = 1.9$ Hz].

![Scheme 5.20. Synthesis of \textbf{107}. i) BH$_3$SMe$_2$, THF, 1 h, r.t. [R = (Me$_3$Si)$_2$CH].](image)

5.13 Synthesis of the alkaline earth metal complex [\{(Me$_3$Si)$_2$CH\}P(C$_6$H$_4$-2-O)(BH$_3$)Ca(THF)]$_4$ (108)

To probe the effects of varying the metal centre in complexes with [\{(Me$_3$Si)$_2$CH\}P(C$_6$H$_4$-2-OMe)(BH$_3$)]$^-$, the related calcium compound was prepared. The reaction between \textbf{41} and one equivalent of BnK in THF proceeds cleanly to yield the corresponding phosphido-borane [\{(Me$_3$Si)$_2$CH\}P(C$_6$H$_4$-2-OMe)(BH$_3$)]K, which was added \textit{in situ} to a solution of CaI$_2$ in THF, which yields the adduct [\{(Me$_3$Si)$_2$CH\}P(C$_6$H$_4$-2-O)(BH$_3$)Ca(THF)]$_4$ (108) and the tertiary phosphine-borane \textbf{90} (Scheme 5.21) after 16 hours stirring. Compound \textbf{108} was extracted into hexamethyldisiloxane, and upon cooling, formed as colourless crystals suitable for X-ray crystallography. This is in stark contrast to the related complex [\{(Me$_3$Si)$_2$CH\}P(C$_6$H$_4$-2-O)Ca(THF)]$_4$ (\textbf{80}) which is sparingly soluble in ether solvents, but may be obtained as pale yellow needles by recrystallization from hot THF.
Scheme 5.21. Synthesis of 108. i) BnK, THF, 1 h, r.t. ii) CaI$_2$, THF, 16 h, r.t. [R = (Me$_3$Si)$_2$CH].

5.14 Solution-phase characterisation of 108

The $^{31}$P{$^1$H} NMR spectrum of 108 in $d_8$-toluene at room temperature indicates the presence of several phosphorus-containing species with signals between -62 and -76 ppm, alongside traces of compound 90 at 12.1 ppm, and another compound, which gives rise to a broad signal at -30 ppm, possibly a phosphido-bis(borane) species (Figure 5.11). The peaks between -62 and -76 ppm are very broad, and suggest that in solution, 108 exists as a mixture of species, which are in dynamic equilibrium.

Variable-temperature $^{31}$P{$^1$H} NMR (Figure 5.12) supports the thesis that 108 is subject to dynamic equilibria. At 90 °C, the $^{31}$P{$^1$H} NMR spectrum exhibits a single broad peak at -69.1 ppm, suggesting that the dynamic equilibria are fast on the NMR time scale at
elevated temperatures. As the temperature is decreased to 40 °C, this peak de-coalesces into two very broad peaks at -64.5 and -75.6 ppm, which are of similar intensity. Upon further cooling, a third and a fourth peak begin to emerge, whilst the signals at -64.5 and -75.6 ppm begin to partially de-coalesce into overlapping peaks. Unfortunately, even at the lowest attainable temperature (-90 °C), these signals are very broad and poorly resolved.

In $d_8$-toluene it is possible that 108 fragments into smaller species (possibly dimers and/or monomers). In addition, where two or more ligands are present in a complex, multiple diastereoisomers are possible. Dynamic equilibria between these species would be consistent with the observed NMR spectra. This is in contrast to compound 80, which, in $d_8$-THF, gives rise to a single resonance in the $^{31}$P{\textsuperscript{1}H} NMR spectrum, whilst its $^1$H and $^{13}$C{\textsuperscript{1}H} NMR spectra show only a single set of signals for the ligands, which suggests that either its cubane structure is maintained in solution, or that any equilibria are very rapid.

The $^1$H and $^{13}$C{\textsuperscript{1}H} NMR spectra of 108 consist of many broad and overlapping resonances, consistent with dynamic behaviour in solution, and as such are not amenable to interpretation.
Figure 5.11. $^{31}\text{P} \{^1\text{H}\}$ spectra of 108, 90 and an unknown compound at 0 °C in $d_8$-toluene.
Figure 5.12. Stacked variable-temperature $^{31}$P-$^1$H NMR spectra of 108 in $d_{8}$-toluene.
5.15 Solid-state structure of 108

Compound 108 crystallises as discrete tetramers, with a Ca$_4$O$_4$ core consisting of a square of O atoms with a Ca ion over each face and along two opposing edges; the structure of 108 is shown in Figure 5.13 (with the core structure shown in Figure 5.14), with selected bond lengths and angles given in Table 5.4. The alkoxophosphido-borane ligands in the complex are essentially identical, but the complex contains two independent calcium environments; one set of Ca ions are coordinated by two adjacent ligands via their phosphorus and oxygen atoms, and by an $\eta^1$-BH$_3$ interaction. The coordination sphere of these Ca ions is completed by the alkoxo oxygen atoms of the remaining two ligands. In the second set, the Ca ions are coordinated by two alkoxo oxygen atoms, such that each oxygen is acting as a $\mu_3$ bridge between the calcium ions. The coordination about each of these ions is completed by two adjacent ligands via $\eta^2$-BH$_3$ interactions, so that each borane group acts as a $\mu_2$-$\eta^2$:$\eta^1$ bridge between two Ca ions, and also by two molecules of THF.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca–P</td>
<td>2.8454(12) and 2.8778(11)</td>
</tr>
<tr>
<td>Ca–O</td>
<td>2.297(2)-2.524(2)</td>
</tr>
<tr>
<td>Ca–B</td>
<td>2.873(5)-3.280(5)</td>
</tr>
<tr>
<td>Ca–H</td>
<td>2.33(3)-2.54(4)</td>
</tr>
<tr>
<td>P–B</td>
<td>1.965(5) and 1.980(5)</td>
</tr>
<tr>
<td>P(2A)–Ca(1)–P(1)</td>
<td>120.94(4)</td>
</tr>
<tr>
<td>Ca–P–B</td>
<td>81.03(13)-83.60(15)</td>
</tr>
<tr>
<td>P–Ca–O (bite angle)</td>
<td>67.04(6) and 67.53(6)</td>
</tr>
<tr>
<td>Ca–O–Ca</td>
<td>78.08(7)-102.63(8)</td>
</tr>
<tr>
<td>O–Ca–O</td>
<td>63.51(7)-165.6(10)</td>
</tr>
</tbody>
</table>

Table 5.4. Selected ranges of bond lengths (Å) and angles (°) for compound 108.
Figure 5.13. Molecular structure of compound 108. All C-bound H atoms omitted for clarity.

Figure 5.14. Structure of the central core of 108, with all Si, C and C-bound H atoms omitted for clarity.
To date, only a small number of calcium complexes with phosphides have been structurally characterised.⁴⁴-⁵⁵ These are typically isolated as solvated monomers (e.g. 
\[(\text{Ph}_2\text{P})\text{CaPh(THF)}_4\])⁵¹ although dimers, a trimer, a hexamer and a number of alkaline earth-tin heterometallic clusters have been isolated.

The P-Ca distances of 2.8454(12) Å and 2.8778(11) in 108 are slightly shorter than the corresponding distance in the related alkoxophosphide 80 [2.9612(6) and 29695(7) Å], reported by Izod and co-workers,⁹ and other P-Ca distances that have been reported previously.³²-⁴⁵,⁵¹,⁵⁵ For example, the compound \([(\text{Ph}_2\text{P})\text{CaPh(THF)}_4\)] (109) has a P-Ca distance of 3.010(2) Å. The Ca-O (alkoxo) distances range from 2.369(2) to 2.524(2) Å, which are similar to the Ca-O distances reported for the oxo-alkoxide clusters \([\text{Ca(tmhd)}(\mu_3\text{-OEt})(\text{EtOH})]_4\) (110, thmd = Bis(2,2,6,6-tetramethyl-3,5-heptanedionate) [Ca-O 2.328(6)-2.367(6) Å] and \([\text{Ca}_6(\mu_4\text{-O})_2(\mu_3\text{-OEt})_4(\text{EtOH})]_4\cdot14\text{EtOH}\) (111) [Ca-O 2.312(6)-2.529(5) Å].⁵⁷,⁵⁸ Compound 108 is the first example of a phosphido-borane complex with calcium to be characterised in the solid-state.

5.16 Conclusions

The synthesis of alkali metal and calcium complexes of the phosphido-borane \[\{(\text{Me}_3\text{Si})_2\text{CH}\text{P(C}_6\text{H}_4\text{-2-OMe})(\text{BH}_3)\}^-\] are readily achievable through straightforward synthetic procedures. However, the lithium and calcium compounds were found to undergo unusual thermally-driven rearrangements.

The thermolytic reactivity of 85 in solution is finely balanced, with two possible reaction pathways, which can result in the formation of either complex 89 along with side products 90 and another unidentified compound (A) or complex 91, which is postulated to be an alkoxo-functionalised phosphido-borane, also alongside the formation of 90. The formation of compounds 89, 90 and 91 is thought to arise via the formation of an ate complex intermediate, which is favoured in the presence of tmeda. The formation of 89 involves concurrent O-Me and P-BH₃ cleavage and P-H bond formation.
Through comparison with 87 and the phosphide 106, activation of the O-Me bond in 85 towards cleavage may be attributed to a combination of the Lewis acidity of the lithium metal centre and the borane group.

The reaction between [(Me₃Si)₂CH]P(C₆H₄-2-OMe)(BH₃)K and CaI₂ in THF yields the unusual alkoxophosphido-borane complex 108, which proceeds with intramolecular methyl migration, generating 90 in situ. The structure adopted by 108 is rather unique; it is tetranuclear in the solid-state, with two distinct Ca ion environments. In d₈-toluene 108 is subject to dynamic equilibria, possibly between diastereoisomers and/or oligomers.

5.17 References


Chapter 6. Alkali and alkaline earth metal complexes of a phenyl-functionalised phosphido-borane

6.1 Introduction

Chapters 3, 4 and 5 have explored the effects that varying the peripheral donor-functionalised substituent on phosphido-boranes has on the structures and stabilities of these complexes. In this regard, to gain further insight into the role of the peripheral donor substituent, this chapter discusses the synthesis and characterisation of complexes of the phosphido-borane \[\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P(C}_6\text{H}_5\text{)}(\text{BH}_3)^-\], which does not contain additional donor functionality, and explores the factors which determine the structure of its complexes. For a comprehensive overview of the effects that the cation has on structure, complexes of this ligand with both alkali and alkaline earth metal cations have been synthesised.

It is expected that removing the donor functionality will have a significant effect on the structures adopted by the alkali metal complexes of this phosphido-borane ligand. A similar effect was observed for complexes of the phosphide \[\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P(C}_6\text{H}_5\text{)}\text{M(L)}\], \[\text{M(L)} = \text{Li(THF)}_3\ (112), \text{Na(tmeda)}\ (113), \text{K(pmdeta)}\ (114)\], which were reported in 2010 by Izod and co-workers,\(^1\) and the related N-donor functionalised phosphides \[\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P(C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2\}\text{M(L)}\] \[\text{M(L)} = \text{Li(THF)}_2\ (17), \text{Na(tmeda)}\ (18), \text{K (pmdeta)}\ (19)\], which were reported by the same group.\(^2\) Compounds 113 and 114 crystallise as dimers, each containing a rhombus-shaped \text{M}_2\text{P}_2\ core, whereas the corresponding N-donor-functionalised phosphide complexes 18 and 19 crystallise as monomers (Figure 6.1).
6.2 Synthesis of the alkali metal complexes $\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P(C}_6\text{H}_5\text{)}(\text{BH}_3)\text{M(L)}\}_n$ $\text{M(L)} = \text{Li(THF)}_2$, $n = \infty$ (115), $\text{M(L)} = \text{Na(12-crown-4)}_2$, $n = 1$ (116), $\text{M(L)} = \text{K(pmdeta)}$, $n = 2$ (117)

The reaction between a solution of 42 in THF and $^t$BuLi yields the corresponding phosphido-borane, which may be crystallised from a mixture of toluene and THF as the adduct $\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P(C}_6\text{H}_5\text{)}(\text{BH}_3)\text{Li(THF)}_2\}_\infty$ (115). The sodium and potassium salts were prepared from the reaction between 42 and a solution of either BnNa$^3$ or BnK$^4$ in THF, giving the corresponding phosphido-boranes $\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P(C}_6\text{H}_5\text{)}(\text{BH}_3)\text{Na}$ and $\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P(C}_6\text{H}_5\text{)}(\text{BH}_3)\text{K}$, respectively, in quantitative yield. The sodium salt may be crystallised from a solution of 12-crown-4 and toluene, containing a small amount of THF, as single crystals of the adduct $\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P(C}_6\text{H}_5\text{)}(\text{BH}_3)[\text{Na(12-crown-4)}_2]$ (116), suitable for X-ray crystallography, whilst the potassium salt may be crystallised from toluene containing one equivalent of pmdeta as the adduct $\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P(C}_6\text{H}_5\text{)}(\text{BH}_3)\text{K(pmdeta)}\}_2$ (117).
Scheme 6.1. Synthesis of compounds 115, 116 and 117. Reagents and conditions: i) $n$-BuLi, THF, 1 h, r.t. ii) BnNa, THF, 1 h, r.t. iii) 12-crown-4, toluene. iv) BnK, THF, 1 h, r.t. v) pmde, toluene [R = (Me$_3$Si)$_2$CH].
6.3 Solution-phase characterisation of 115-117

The $^{31}$P{$^1$H} NMR spectra of 115-117 exhibit broad quartets, with chemical shifts that range from -48.2 to -56.8 ppm. The P-B coupling constant in 115 [$^{3}J_{PB} = 49.0$ Hz] is unchanged from that of the phosphine-borane 42, however the coupling constant decreases in magnitude for the sodium and potassium salts [$^{3}J_{PB} = 29.4$ (116), 19.6 Hz (117)].

The $^1$H and $^{13}$C{$^1$H} spectra of 115 and 117 are as expected. In the $^1$H NMR spectra of 115 and 117, the diastereotopic SiMe$_3$ groups give rise to two sharp signals between 0.0 and 0.4 ppm. The PCH proton in 115 and 117 affords a doublet at 0.6 ppm [$^{2}J_{PH} = 7.8$ and 6.0 Hz, respectively], whilst the BH$_3$ protons give rise to broad quartets, which collapse upon decoupling of the $^{11}$B nucleus. The BH$_3$ signals appear as a doublet at 1.1 ppm [$^{2}J_{PH} = 4.1$ Hz] for 117, however, the corresponding signal in the $^1$H{$^{11}$B} NMR spectrum of 115 could only be resolved as a broad singlet at 1.0 ppm. In the $^{13}$C{$^1$H} NMR spectra, the SiMe$_3$ carbons give rise to two signals, a doublet and a singlet between 2.3 and 3.3 ppm for 115 and 117, respectively [$^{3}J_{PC} = 7.7$ Hz (115 and 117)], whilst the adjacent CHP carbon gives rise to a doublet at 8.9 and 9.8 for 115 and 117, respectively [$^{1}J_{PC} = 34.6$ (115) and 43.1 Hz (117)].

In contrast, the $^1$H NMR spectrum of 116 in $d_8$-THF exhibits two rather broad singlets for the diastereotopic SiMe$_3$ groups. At low temperatures these signals sharpen to give two singlets at -0.1 (A) and 0.2 ppm (B), whilst at higher temperatures these signals coalesce to give a broad signal at 0.1 ppm (C) (Figure 6.2).
Figure 6.2. Variable-temperature $^1$H/$^{11}$B NMR spectra of 116 in $d_8$-THF. Only SiMe$_3$ region shown [* free phosphine-borane 42].
The rate of exchange between the SiMe$_3$ groups at each temperature was calculated using simulated $^1$H{$^1$}B NMR spectra (Appendix 1). From the data collected, an Eyring plot could be obtained, from which, the enthalpy of activation, $\Delta H^\ddagger$ and the entropy of activation, $\Delta S^\ddagger$, were calculated: $\Delta H^\ddagger = 52.78$ kJ mol$^{-1}$, $\Delta S^\ddagger = -28.33$ J K$^{-1}$ mol$^{-1}$. The low value of $\Delta S^\ddagger$ suggests that this is an intramolecular exchange process.

Also in the $^1$H NMR spectrum of 116, the PCH proton gives rise to a doublet at 0.2 ppm [$^2J_{PH} = 5.5$ Hz], whilst the borane protons appear as a broad quartet at around 1.0 ppm [$^2J_{PH} = 4.1$ Hz]; these signals do not change with temperature. In the $^{13}$C{$^1$}H spectrum of 116 the SiMe$_3$ groups give rise to two broad signals, which also shows its dynamic behaviour in solution, whilst the adjacent PCH carbon give rise to a sharp doublet at 10.5 ppm [$^1J_{PC} = 47.9$].

The dynamic behaviour observed for 116 is rather surprising, given that the two SiMe$_3$ are diastereotopic due to the chiral P centre, and as such should always give two signals. Hence the exchange process cannot be attributed to rotation about the Si$_2$CH-P bond. Instead, the only way for the two SiMe$_3$ signals to coalesce in the $^1$H NMR spectrum, is if the chiral centre is lost or inverted. For this to happen, there must either be inversion at the P centre (Scheme 6.2),$^5$ or reversible P-B cleavage, which could be facilitated by the THF present in solution (Scheme 6.3).$^6$

\[ \begin{array}{c}
\text{R} \quad \text{P} \quad \begin{array}{c}
\text{Ph} \\
\text{BH}_3
\end{array} \\
\text{R} \quad \text{P} \quad \begin{array}{c}
\text{BH}_3 \\
\text{Ph}
\end{array}
\end{array} \leftrightarrow \begin{array}{c}
\text{R} \quad \text{P} \quad \begin{array}{c}
\text{Ph} \\
\text{BH}_3
\end{array} \\
\text{R} \quad \text{P} \quad \begin{array}{c}
\text{BH}_3 \\
\text{Ph}
\end{array}
\end{array} \leftrightarrow \begin{array}{c}
\text{R} \quad \text{P} \quad \begin{array}{c}
\text{Ph} \\
\text{BH}_3
\end{array} \\
\text{R} \quad \text{P} \quad \begin{array}{c}
\text{BH}_3 \\
\text{Ph}
\end{array}
\end{array} \]

Scheme 6.2. Inversion of the P centre of 116 [R = (Me$_3$Si)$_2$CH].

\[ \begin{array}{c}
\text{R} \quad \text{P} \quad \begin{array}{c}
\text{BH}_3 \\
\text{Ph}
\end{array} \\
\text{R} \quad \text{P} \quad \begin{array}{c}
\text{BH}_3 \\
\text{Ph}
\end{array}
\end{array} \leftrightarrow \begin{array}{c}
\text{R} \quad \text{P} \quad \begin{array}{c}
\text{BH}_3 \\
\text{Ph}
\end{array} \\
\text{R} \quad \text{P} \quad \begin{array}{c}
\text{BH}_3 \\
\text{Ph}
\end{array}
\end{array} \leftrightarrow \begin{array}{c}
\text{R} \quad \text{P} \quad \begin{array}{c}
\text{BH}_3 \\
\text{Ph}
\end{array} \\
\text{R} \quad \text{P} \quad \begin{array}{c}
\text{BH}_3 \\
\text{Ph}
\end{array}
\end{array}
\]

Scheme 6.3. Reversible P-B cleavage of 116 in THF [R = (Me$_3$Si)$_2$CH].
The inversion behaviour of tertiary phosphines has been extensively studied, and there is a substantial amount of information regarding the factors that affect barriers to inversion in these compounds; for phosphorus, the inversion barrier is reduced by i) bulky substituents, and ii) electropositive substituents. For instance, the silyl groups in the compound \((\text{t-Pr}_3\text{Si})_3\text{P}\), have a combination of both steric bulk and electropositivity, which results in near planar geometry of the PSi$_3$ framework in the solid state.\(^7\)

The influence of electropositivity on inversion has been extensively studied by Mislow and co-workers, who have shown that substitution of tertiary phosphines with increasingly electropositive EMe$_3$ groups (E = C, Si, Ge, Sn) leads to progressive reduction of the inversion barrier.\(^8,9,10,11\) For example, variable-temperature NMR experiments reveal that the free energies of inversion of \(\text{t-PrPhP(EMe}_3\) are 136.8, 89.5, and 80.8 kJ mol$^{-1}$ for E = C, Ge, and Sn, respectively.\(^9\)

In contrast, Izod and co-workers have calculated that the barrier to inversion at phosphorus for the phosphagermylenes \{\((\text{Me})\text{P(C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2\}\text{GeX [X = F, Cl , Br, H, Me] decreases with increasing electronegativity of the substituent X, however this is thought to be due to increasing delocalization of the p-type phosphorus lone pair in the transition state. As part of an ongoing study, the same group have also observed by multi-element and variable-temperature NMR analysis, that the related compound \[\{(\text{Me}_3\text{Si})_2\text{CH}\}(\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2)\text{P}\]\]GeCl is highly dynamic in solution, due to rapid interconversion of diastereoisomers most likely due to inversion at phosphorus.

The Pauling electronegativity of Ge (2.01) and B (2.04) are rather similar and so it is tempting to attribute the dynamic behaviour observed for 116 to a similar inversion process. However on the available evidence it is not possible to do so unambiguously.

As mentioned above, the other possible process that may be occurring for 116 is reversible P-B cleavage. It is well documented that the formation of phosphine-borane adducts is reversible, and decomplexation can be achieved using a strong Lewis base. For example, treatment of a phosphine-borane adduct with excess amine yields the amine-borane and free phosphine \textit{via} an equilibrium process.

It has also been previously proposed by Imamoto and co-workers that the methoxy group in the phosphine-borane PhP(BH$_3$)(CH$_3$)(C$_6$H$_4$-2-OMe) (73) can abstract the borane fragment,
cleaving the P-B bond.\(^6\) It is possible therefore that a THF-BH\(_3\) adduct could form in THF solutions of \(\textbf{116}\) in a similar fashion, resulting in rapid conversion between enantiomers, as shown in Scheme 6.3.

### 6.4 Solid-state structures of 115, 116 and 117

#### 6.4.1 Solid-state structure of 115

Compound \(\textbf{115}\) crystallises as essentially linear polymers, in contrast to the donor-functionalised lithium phosphido-boranes \(\textbf{49}\) and \(\textbf{64}\), which crystallise as dimers. The molecular structure of \(\textbf{115}\) is shown in Figure 6.3, with details of selected bond lengths and angles given in Table 6.1. Each lithium ion is coordinated by the P atom of a phosphido-borane ligand and by the oxygen atoms of two molecules of THF. The coordination of Li is completed by an \(\eta^2\)-interaction with the BH\(_3\) group of an adjacent unit in the polymer chain, so that each Li ion is pseudo-four-coordinate. The phosphido-borane ligands thus adopt a bridging coordination mode.

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>Angles (º)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{P(1)--Li(1)})</td>
<td>2.741(3)</td>
</tr>
<tr>
<td>(\text{P(1)--B(1)})</td>
<td>1.9611(17)</td>
</tr>
<tr>
<td>(\text{P(1)--C(1)})</td>
<td>1.8850(14)</td>
</tr>
<tr>
<td>(\text{P(1)--C(8)})</td>
<td>1.8394(14)</td>
</tr>
<tr>
<td>(\text{Li(1)--B(1B)})</td>
<td>2.440(3)</td>
</tr>
<tr>
<td>(\text{Li(1)--H(2A)})</td>
<td>2.182(19)</td>
</tr>
<tr>
<td>(\text{Li(1)--H(3A)})</td>
<td>2.084(18)</td>
</tr>
<tr>
<td>(\text{Li(1)--C(1)})</td>
<td>3.857(30)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Table 6.1. Selected bond lengths (Å) and angles (º) for \(\textbf{115}\). |
The Li-P distance of 2.741(3) Å is slightly longer than the corresponding distances in
\[\text{[Me}_2\text{PH(BH}_3\text{)Li(tmeda)] (29) [2.620(4) Å], \ [\{(\text{Me}_3\text{Si})_2\text{CH}\}_2\text{P(C}_6\text{H}_4\text{-2-CH}_2\text{OMe})(\text{BH}_3)\text{Li(THF)\}_2 (49) [2.611(6) Å], \ [\{(\text{Me}_3\text{Si})_2\text{CH}\}_2\text{P(C}_6\text{H}_4\text{-2-SMe})(\text{BH}_3)\text{Li(THF)\}_2 (64) [2.527(3) Å], but is typical of Li-P distances in lithium phosphides.}^{1,2,12-16}\]

The Li...B distance and Li-H distances in 115 of 2.440(3) Å and 2.182(19) and 2.084(18) Å, respectively, are similar to the corresponding interactions in 29 [Li...B 2.372(4); Li-H 2.03(2) Å] and 64 [Li...B 2.403(3); Li-H 2.053(14) Å], which is consistent with an \(\eta^2\)-BH\(_3\)-Li interaction.

The B-P-Li bridging angle in 115 of 123.04(8)° is comparable to the B-P-Li angle in 29 [120.2(1)°], which also crystallises as a linear polymer.\(^{17}\)

Figures 6.4 and 6.5 show in detail the packing arrangement between two adjacent polymer chains; Figure 6.4 shows how one chain sits above the other, so that the phenyl groups are directed towards each other, and so that the (Me\(_3\)Si)\(_2\)CH substituents are orientated in opposite directions. At first glance it appears that this could be a consequence of aromatic \(\pi-\pi\) stacking, particularly with C...C distances of 3.976 Å, but in Figure 6.5, it can be clearly seen that the phenyl rings are arranged in a staggered manner, such that steric interactions between the two chains are reduced.
Figure 6.3. Part of the polymeric structure of compound 115. All C-bound H atoms omitted for clarity.
Figure 6.4. Structure of compound 115 viewed along a section of two adjacent polymer chains. All C-bound H atoms omitted for clarity.

Figure 6.5. Structure of compound 115 viewed from above a section of two polymer chains. All H atoms omitted for clarity.
6.4.2 Solid-state structure of 116

Compound 116 crystallises as a solvent-separated ion pair; the structure of 116 is shown in Figure 6.6, with selected bond lengths and angles shown in Table 6.2. This is the first example of a phosphido-borane complex that has been isolated as a solvent-separated ion pair; all previous examples of phosphido-boranes that have been characterised in the solid-state demonstrate BH$_3$...M interactions, even when there is no direct contact between the phosphorus atom and the metal centre.

Interestingly, a comparison between 116 and compound 115, which crystallises as a contact ion pair, shows that the P-B and P-C bond distances within the ligand have similar values; for instance, the P-B distances are 1.9611(17) and 1.9688(15) Å for 115 and 116, respectively. Also, the P-C(1) distances are 1.8850(14) and 1.8899(13) Å for 115 and 116, respectively, whilst the P-C(8) distances are 1.8394(14) Å for 115 and 1.8400(14) Å for 116.

The sum of angles within the C$_2$PB framework in 116 is 318.13°, which is similar to the sum of angles about the P atom in compound 115 [319.6°], which demonstrates that the geometry about phosphorus is not appreciably affected by its interaction with the metal centre.

These traits suggest that phosphido-boranes which exist as an isolated anion are likely to possess the same structural parameters as those that form a tight contact ion-pair with the metal cation.

<table>
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Table 6.2. Selected bond lengths (Å) and angles (°) for 116.
6.4.3 Solid-state structure of 117

Compound 117 crystallises as discrete centrosymmetric dimers; the molecular structure of 117 is shown in Figure 6.7 and details of selected bond lengths and angles are shown in Table 6.3. Each phosphido-borane ligand is bound to an adjacent potassium ion via its P atom and an \( \eta^1 \)-BH\(_3\) interaction, generating a pseudo-three-membered B-P-K ring [B-P-K bite angle 72.11(9)°]. The phosphido-borane ligand also coordinates to the second potassium ion in the dimer via its borane group in an \( \eta^3 \)-type fashion such that each BH\(_3\) fragment acts as a \( \mu_2-\eta^1: \eta^3 \) bridge; thus the two halves of the dimer are linked, generating a planar, pseudo-six-membered [PK(BH\(_3\))]\(_2\) ring. The coordination sphere of each potassium ion is completed by the three nitrogen atoms of a molecule of pmdeta, so that each potassium ion is pseudo-six-coordinate.
Figure 6.7. Structure of compound 117. All C-bound H atoms omitted for clarity.

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Table 6.3. Selected bond lengths (Å) and angles (°) for 117.
The K-P distance in 117 of 3.2754(8) Å is somewhat shorter than the corresponding distance in the related phosphide 114 [3.3351(12) Å]. Interestingly, in comparison to related potassium phosphido-borane complexes, the K-P distance in 117 is similar to the corresponding distances in [Ph₃P(BH₃)K(18-crown-6)] (32) [3.320(2) Å] and [{(Me₃Si)₂CH}P(C₆H₄-2-OMe)(BH₃)K(pmdeta)]₂ (87) [3.2338(5) Å], but is far shorter than the K-P distances in [{(Me₃Si)₂CH}P(C₆H₄-2-CH₂OMe)(BH₃)K(pmdeta)] (51) and [{(Me₃Si)₂CH}P(C₆H₄-2-SMe)(BH₃)K(pmdeta)]₂ (66) [3.6617(6) and 3.7620(10) Å, respectively], which have additional intramolecular coordination to potassium through a peripheral donor (the phosphido-borane ligand in 87, although containing donor functionality, does not coordinate to potassium via the donor oxygen atom).

That compounds 51 and 66 have longer P-K distances than 32, 87 and 117 suggests that P-K interactions are weaker in phosphido-boranes where the potassium ion is coordinated by a peripheral donor atom. Interestingly, however, this behaviour is only observed in phosphido-borane complexes with potassium, and not with lithium contact ion pairs.

The K...B(1A) distance in 117 of 3.107(3) Å is comparable to other η³-BH₃-K distances, for example, the K...B distance in [K(BH₄)(18-crown-6)] (60) is 2.964(9) Å. The K-H distances for the bridging borane hydrogen in 117 [2.71(2) Å] are similar to the corresponding distances in the compound [(Et₃BH)K(pmdeta)]₂ (118), which also possesses a μ₂-bridging hydrogen [K-H 2.64(3) and 2.69(3) Å].

The K-P-B(1) angle in 117 [72.11(9)°] is somewhat larger than the corresponding angles in the ‘tridentate’ complexes 51 and 66 [61.79(7) and 62.01(7)° respectively], which may account for the difference in binding mode between the borane group and potassium; 117 adopts an η¹-BH₃-K binding mode, whereas 51 and 66 adopt an η²-BH₃-K coordination mode, which results in shorter B...K distances.

6.5 Synthesis of alkaline earth metal complexes [{(Me₃Si)₂CH}P(C₆H₅) (BH₃)]₂M [M = Sr(119), Ba(120)]

The compounds [{(Me₃Si)₂CH}P(C₆H₅)(BH₃)]₂Sr (119) and [{(Me₃Si)₂CH}P(C₆H₅) (BH₃)]₂Ba (120) were prepared by the addition of two equivalents of
[(Me₃Si)₂CH]₂P(C₆H₅)(BH₃)K] in THF to a cold (-78 °C) slurry of either SrI₂ or BaI₂ in cold toluene (Scheme 6.4). The products were crystallised from cold toluene as an orange and a yellow solid, respectively. Unfortunately, however, single crystals of 119 and 120 could not be isolated, and so the X-ray crystal structures of these compounds could not be determined; the identity of 119 and 120 was confirmed by multi-element NMR spectroscopy and elemental analysis. It is reasonable to assume that 119 and 120 are coordinated by 4 or 5 molecules of THF molecules in THF solutions, as seen with group 2 complexes of related phosphides²¹,²²,²³ and phosphine-borane-stabilised carbanions²⁴. However, NMR spectroscopy of compounds 119 and 120 alongside elemental analysis of 120 show no evidence of THF coordinated to the metal centres, which suggests that THF is easily lost when these compounds are exposed to vacuum.

Scheme 6.4. Synthesis of compounds 119 and 120. Reagents and conditions: i) 2 BnK, THF, 1 h r.t. ii) SrI₂, toluene/THF, -78 °C, 16 h. iii) BaI₂, toluene/THF, -78 °C, 16 h [R = (Me₃Si)₂CH].
6.6 Solution-phase characterisation of 119 and 120

The $^1$H, $^{13}$C{$^1$H}, and $^{31}$P{$^1$H} NMR spectra of 119 and 120 are as expected, and show that in both cases, the phosphido-borane ligands are equivalent. The $^{31}$P{$^1$H} NMR spectra show broad quartets at -46.7 and -48.7 ppm, respectively, whilst the magnitude of the P-B coupling decreases from 39.7 Hz for 119 to 29.8 Hz for 120 (49.0 Hz for 42), which is consistent with the greater ionic character in the P-M bonding interaction in the latter case.

In the $^1$H NMR spectra of 119 and 120, the diastereotopic SiMe$_3$ protons give rise to two sharp singlets between -0.05 and 0.14 ppm. The BH$_3$ protons give rise to a very broad quartet in each case, which collapses upon decoupling of the $^{11}$B nucleus to give sharp doublets [$^2J_{PH} = 4.1$ Hz (119 and 120)] centred at 0.82 and 0.84 ppm for 119 and 120, respectively. In the $^{13}$C{$^1$H} NMR spectra of 119, the SiMe$_3$ groups give rise to two singlets at 1.5 and 2.7 ppm, whilst in 120, they appear as a doublet and a singlet at 1.68 [$^3J_{PC} = 5.8$ Hz] and 2.8 ppm. The adjacent CHP carbon gives rise to a doublet at 9.54 [$^1J_{PC} = 45.1$ Hz] and 6.34 ppm [$^1J_{PC} = 44.1$ Hz] for 119 and 120, respectively.

6.7 Conclusions

Complexes of the phosphido-borane anion [{(Me$_3$Si)$_2$CH}P(C$_6$H$_5$)(BH$_3$)]$^-$ with Li, Na, K, Sr and Ba have been prepared using straightforward synthetic procedures.

Compound 115 adopts a polymeric structure, where each unit is bridged by an η$^2$-BH$_3$-Li interaction, in a comparable fashion to compound 29. This is in stark contrast to the related compounds 49 and 64, which possess a peripheral donor coordination to lithium, and which crystallise as dimers. This suggests that phosphido-borane complexes with lithium are more likely to exist as high-order aggregates if the lithium ion is not coordinated by a peripheral donor, or a sterically demanding co-ligand.

Compound 116 is the first example of a phosphido-borane to be characterised as a solvent-separated ion pair. A study of the phosphido-borane anion in 116 shows that there are no significant structural differences compared with phosphido-borane complexes that crystallise as a contact ion pair, and that coordination of the P and BH$_3$ centres has little influence on ligand structure.
The structure of compound 117 demonstrates that complexes of phosphido-boranes with potassium which do not possess additional chelation from a peripheral donor atom, have shorter P-K distances than the related compounds 51 and 66, which do possess coordination from a peripheral donor. Compound 117 also has a larger M-P-B angle than that of the related ‘tridentate’ phosphido-boranes, and as a result, the borane group in 117 acts as a $\mu_2$-$\eta^1$:$\eta^3$ bridge between the two halves of the dimer, as opposed to a $\mu_2$-$\eta^2$:$\eta^3$ interaction as seen with compounds 51 and 66.

Compounds 119 and 120 are the first examples of phosphido-borane complexes with strontium and barium. The structures of compounds 119 and 120 were deduced by $^1$H, $^1$H{$^{11}$B}, $^{31}$P{$^1$H}, $^{11}$B{$^1$H} and $^{13}$C{$^1$H} NMR spectroscopy, alongside elemental analysis of 120.

### 6.8 References


(22) Westerhausen, M; Digeser, M. H; Nöth, H; Ponikwar, W; Seifert, T; Polborn, K. Inorg. Chem. 1999, 38, 3207.


Chapter 7. Alkali and alkaline earth metal complexes of phosphido-bis(boranes)

7.1 Introduction

The first example of a phosphido-bis(borane), reported by Thompson in 1965, was the compound \([\text{H}_2\text{P(BH}_3)_2\text{K}]\) (121). Compound 121 was prepared by reducing \(\text{PH}_3\) with potassium in liquid ammonia to give the corresponding phosphide, followed by removal of the ammonia and addition of excess diborane in a cold solution of diethylether (Scheme 7.1). The unreacted diborane was recovered and showed that only one equivalent had reacted. That the compound was of empirical formula \([\text{H}_2\text{P(BH}_3)_2\text{K}]\) and not a mixture of potassium borohydride and \((\text{H}_2\text{P·BH}_2)_n\) was shown by a comparison of X-ray powder diffraction patterns.¹

![Scheme 7.1. Preparation of 121.](image)

In 1971 Keller and Schwartz reported the synthesis of lithium dimethylphosphido-bis(borane) (122).² Similar to 121, compound 122 was prepared by reaction of the phosphide with diborane in monoglyme (Scheme 7.2). Interestingly, even when an excess of the phosphide was reacted with diborane only 122 was observed, with no \([\text{Me}_2\text{P(BH}_3)_2\text{Li}]\) present, indicating that diborane reacts directly with the phosphide.

![Scheme 7.2. Preparation of 122.](image)

This type of compound could have applications as reactive intermediates, as seen in their phosphido-borane counterparts. However, to date there are only a handful of examples of
structurally characterised phosphido-bis(borane) compounds (see chapter 1.4), hence a clearer understanding of the relationship between structure and reactivity is needed.

This chapter reports the synthesis and solid- and solution-state characterisation of a series of phosphido-bis(borane) complexes with group I and II metals.

### 7.2 Synthesis and characterisation of the alkali metal complexes

\[
\{\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P}(\text{C}_6\text{H}_5)(\text{BH}_3)_2\text{M(L)}\}_n \quad \text{[M(L) = Li(12-crown-4), } n = 1 \text{ (123), M(L) = Na(THF)}_2, \text{ } n = 2 \text{ (124), M(L) = K(THF)}_2, \text{ } n = \infty \text{ (125)}] \]

Reaction between a solution of compound 42 in THF and \(^{n}\text{BuLi}\), followed by addition of one equivalent of \text{BH}_3\cdot\text{SMe}_2 yields the corresponding phosphido-bis(borane), which can be crystallised from toluene containing one equivalent of 12-crown-4 as the adduct \[
\{\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P}(\text{C}_6\text{H}_5)(\text{BH}_3)_2\text{Li(12-crown-4)}\} \text{ (123, Scheme 7.3)}.
\]

The sodium and potassium salts are prepared from the reaction of a solution of 42 in THF and either a solution of \text{BnNa}^3 or \text{BnK}^4 in THF, followed by addition of \text{BH}_3\cdot\text{SMe}_2 \textit{in situ}. The products may be crystallised in good yield at room temperature, from toluene/methylcyclohexane/THF or toluene/THF, respectively, as the adducts \[
\{\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P}(\text{C}_6\text{H}_5)(\text{BH}_3)_2\text{Na(THF)}_2\}_2 \text{ (124)} \text{ and } \{\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P}(\text{C}_6\text{H}_5)(\text{BH}_3)_2\text{K(THF)}_2\}_\infty \text{ (125)}.
\]

The \(^{31}\text{P}\{^1\text{H}\}, ^1\text{H} \text{ and } ^{13}\text{C}\{^1\text{H}\} \text{ NMR spectra of 123-125 are as expected. The } ^{31}\text{P}\{^1\text{H}\} \text{ NMR spectra of compounds 123-125 exhibit broad signals at -8.8, -14.9 and -14.1 ppm respectively, which is a considerable downfield shift from -56.8, -49.4 and -48.2 ppm in the corresponding phosphido-boranes 115, 116 and 117, respectively. The signals should appear as septets due to coupling to two equivalent } ^{11}\text{B} \text{ nuclei, but the coupling is unresolved due to quadrupolar broadening by } ^{11}\text{B}. \text{ The P-B coupling constant can be measured through } ^{11}\text{B}\{^1\text{H}\} \text{ NMR spectroscopy } [{}^1J_{PB} = 49.0 \text{ (123), 68.6 (124) and 58.8 Hz (125)}]. \text{ It is interesting that in compound 123, only one BH}_3 \text{ resonance is observed in the } ^{11}\text{B} \text{ and } ^1\text{H} \text{ spectra, although the solid-state structure of this compound (see section 7.4.1) shows that the two BH}_3 \text{ groups are distinct. This suggests that in solution, 123 exists in a dynamic equilibrium, or as a solvent-separated ion pair.}
Scheme 7.3. Synthesis of compounds 123, 124 and 125. Reagents and conditions: i) $^6$BuLi, THF, 1 h, r.t. ii) BH$_3$·SMe$_2$, 1 h, r.t. iii) 12-crown-4. iv) BnNa, THF, 1 h, r.t. v) BnK, THF, 1 h, r.t. [R= (Me$_3$Si)$_2$CH].

In the $^1$H NMR spectra, the SiMe$_3$ protons of 123-125 appear as sharp singlets, centred at -0.1 ppm for 123 and 0.1 ppm for 124 and 125, whilst the CHP protons appear as doublets, centred around 0.6 ppm [$^2J_{PH}$ = 13.8, 15.1, 14.7 Hz, for 123-125, respectively]. The six borane hydrogens give rise to a broad signal centred between 0.6-0.8 ppm in each case,
which, upon decoupling of the $^{11}$B nucleus, collapse into sharp doublets [$^2J_{PH} = 10.1$ (123), 8.7 (124) and 9.6 (125) Hz]. The $^{13}$C$_2$H NMR spectrum is as expected; the SiMe$_3$ carbons appear as a singlet at 3.2 ppm for 123, and as doublets at 2.8 and 2.9 ppm for 124 and 125, respectively [$^3J_{PC} = 1.9$ Hz (124 and 125)], whilst the CHP carbon gives rise to a doublet between 10.6 and 11.9 ppm for 123-125 [$^1J_{PC} = 6.7$ (123), 2.9 (124) and 3.8 Hz (125)].

### 7.3 Synthesis and characterisation of the alkali metal complex

[$\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P}($C$_6\text{H}_4$-2-OMe)(BH$_3$)$_2$][\text{Na}(12\text{-crown-4})$_2$] (126)

Reaction between a solution of compound 41 in THF with one equivalent of BnNa, followed by addition of one equivalent of BH$_3$·SMe$_2$ yields the corresponding phosphido-bis(borane), which may be crystallised from light petroleum ether containing two equivalents of 12-crown-4 as the adduct [$\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P}($C$_6\text{H}_4$-2-OMe)(BH$_3$)$_2$][\text{Na}(12\text{-crown-4})$_2$] (126, Scheme 7.4).

![Scheme 7.4. Synthesis of 126. Reagents and conditions: i) BnNa, THF, 1 h, r.t. ii) BH$_3$·SMe$_2$, 1 h, r.t. iii) 12-crown-4. [R= (Me$_3$Si)$_2$CH].](image)

The $^{31}$P$^{\{1\text{H}\}}$, $^1$H and $^{13}$C$^{\{1\text{H}\}}$ NMR spectra of 126 are as expected. The $^{31}$P$^{\{1\text{H}\}}$ NMR spectrum of compound 126 exhibits a broad signal at -8.1 ppm, which is in the same region as those of compounds 123-125. Unfortunately, the P-B coupling could not be resolved by either $^{31}$P or $^{11}$B$^{\{1\text{H}\}}$ NMR spectroscopy; the $^{11}$B$^{\{1\text{H}\}}$ spectrum of 126 gives rise to a broad, poorly resolved signal at -32.7 ppm.

In the $^1$H NMR spectrum, the SiMe$_3$ groups of 126 give rise to a singlet at 0.1 ppm, whilst the PCH hydrogen appears as a doublet, centred at 0.6 ppm [$^2J_{PH} = 10.1$ Hz], whilst the six borane hydrogens generate a broad signal centred at 0.8 ppm, which upon decoupling of the $^{11}$B nucleus, collapses into a sharp doublet [$^2J_{PH} = 9.6$ Hz].
7.4  Solid-state structures of 123-126

7.4.1  Solid-state structure of 123

The lithium complex 123 crystallises as discrete monomers, with two distinct BH$_3$ groups: one shows contacts between all three hydrogen atoms and Li through an η$^3$-type interaction [Li(1)-H(1A) 2.02(4) Å, Li(1)-H(1B) 2.27(5) Å, Li(1)-H(1C) 2.26(5) Å], while the hydrogen atoms of the other borane group have no intra- or intermolecular contacts with the metal. Coordination of the lithium ion is completed by the four oxygen atoms of the crown ether molecule. The Li...B distance in 123 is somewhat shorter than the corresponding interaction in [(mes*)PH(BH$_3$)$_2$Li(THF)$_3$] (35) [Li...B 2.281(7) (123), 2.430(5) (35) Å], which is consistent with their respective η$^3$-BH$_3$-Li and η$^2$-BH$_3$-Li type coordination. The distance between phosphorus and the boron engaged in Li coordination in 123 is slightly shorter than that for the ‘free’ BH$_3$ group [P(1)-B(1) 1.928(4), P(1)-(B2) 1.947(4) Å], as seen for compound 35 [P(1)-B(1) 1.955(3) Å, P(1)-B(2) 1.984(3) Å]. The molecular structure of 123 is shown in Figure 7.1, with details of selected bond lengths and angles given in Table 7.1.

\[\text{Figure 7.1. Structure of compound 123. All C-bound H atoms omitted for clarity.}\]
Table 7.1. Selected bond lengths (Å) and angles (°) for 123.

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</tbody>
</table>

The range of Li-H distances in 123 [2.02(4)-2.27(5) Å] is also similar to other η^3-BH_n-Li distances reported, such as in complexes 49, [Ph_2BuSi(BH_3)Li(THF)_3] (127) and the borohydrides [Li(BH_4)(THF)_3] (53) and [Li(η^3-BH_4)(NC_5H_4-4-Me)_3] (54). For example, the Li-H distances in 127 are 2.07, 2.13 and 2.21 Å.6-10

### 7.4.2 Solid-state structure of 124

Compound 124 crystallises as discrete centrosymmetric dimers and is the first example of a sodium complex of a phosphido-bis(borane) anion to be crystallographically characterised; the molecular structure of 124 is shown in Figure 7.2, with selected bond lengths and angles shown in Table 7.2. Within the phosphido-bis(borane) ligand there are two distinctly different types of borane groups. In the first, the borane group binds to the adjacent sodium ion through two hydrogen atoms in an η^2-manner, with the third hydrogen atom not involved in any Na-H interactions. The second borane group bridges both sodium ions in the dimer via an η^2-type interaction with two hydrogen atoms, which forms a planar pseudo-four-membered Na_2B_2 ring, with the third hydrogen forming an η^1 contact to the second Na atom in the dimer, such that the borane group acts as a μ_2-η^2:η^3 bridge. In all, the sodium ions are coordinated to three BH_3 groups, with coordination completed by two molecules of THF on each ion. The B...Na distances in 124 range from 2.782(3) to 3.011(3) Å, and these values are consistent with η^3 or η^2-BH_n-Na coordination modes, respectively.7,10 For example, the η^3- and η^2-BH_4...Na distances in [NaBH_4(pmdeta)]_2 (57) are 2.727(4) and 2.837(4) Å, respectively. The Na-H distances in 124 [2.42(2)-2.67(3) Å] also lie in the typical range for Na-H-B containing
species; for example, the Na-H distances in \[ \{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P(C}_6\text{H}_4\text{-2-SMe})(\text{BH}_3)\text{Na(tmeda)}\] \(_\infty\) (65) range from 2.35(3) to 2.69(4) Å.

<table>
<thead>
<tr>
<th>Bond Lengths and Angles (Å and °) for 124</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(1)–B(1A)</td>
<td>2.782(3)</td>
</tr>
<tr>
<td>Na(1)–B(1)</td>
<td>3.011(3)</td>
</tr>
<tr>
<td>Na(1)–B(2)</td>
<td>2.864(3)</td>
</tr>
<tr>
<td>Na(1)–H(1A)</td>
<td>2.63(2)</td>
</tr>
<tr>
<td>Na(1)–H(1B)</td>
<td>2.67(3)</td>
</tr>
<tr>
<td>Na(1)–H(2A)</td>
<td>2.42(2)</td>
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<tr>
<td>Na(1)–H(2B)</td>
<td>2.54(3)</td>
</tr>
<tr>
<td>P(1)–B(1)</td>
<td>1.950(3)</td>
</tr>
<tr>
<td>P(1)–C(1)</td>
<td>1.862(2)</td>
</tr>
<tr>
<td>P(1)–B(2)</td>
<td>1.958(3)</td>
</tr>
<tr>
<td>P(1)–C(8)</td>
<td>1.846(2)</td>
</tr>
<tr>
<td>B(1)–P(1)–B(2)</td>
<td>109.59(12)</td>
</tr>
<tr>
<td>B(1)–P(1)–C(1)</td>
<td>114.59(12)</td>
</tr>
<tr>
<td>B(2)–P(1)–C(1)</td>
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</tr>
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<td>B(1)–P(1)–C(8)</td>
<td>104.19(12)</td>
</tr>
<tr>
<td>B(2)–P(1)–C(8)</td>
<td>109.06(12)</td>
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<tr>
<td>C(1)–P(1)–C(8)</td>
<td>104.99(10)</td>
</tr>
<tr>
<td>P(1)–C(1)–Si(1)</td>
<td>113.44(12)</td>
</tr>
<tr>
<td>P(1)–C(1)–Si(2)</td>
<td>113.39(12)</td>
</tr>
<tr>
<td>Si(1)–C(1)–Si(2)</td>
<td>116.56(12)</td>
</tr>
<tr>
<td>B(1)–Na(1)–B(2)</td>
<td>65.79(8)</td>
</tr>
<tr>
<td>Na(1)–B(1)–Na(1A)</td>
<td>91.12(9)</td>
</tr>
<tr>
<td>B(1)–Na(1)–B(1A)</td>
<td>88.88(9)</td>
</tr>
</tbody>
</table>

**Table 7.2.** Selected bond lengths (Å) and angles (°) for 124.
7.4.3 Solid-state structure of 125

Compound 125 crystallises as a linear polymer; the structure of 125 is shown in Figure 7.3, with selected bond lengths and angles shown in Table 7.3. In each polymer unit, the phosphido-bis(borane) ligand is coordinated via both BH$_3$ groups to the potassium centre in an $\eta^2$-manner, thus forming a pseudo-four-membered K(BH$_3$)$_2$P ring. Each borane group also coordinates in an $\eta^3$ fashion to the potassium ion in an adjacent unit, such that the potassium
ions in the polymer are bridged by two $\mu_2$-$\eta^2$-$\eta^3$ borane groups, generating a series of pseudo-four-membered $\text{K}_2(\text{BH}_3)_2$ rings along the polymer chain, thus the polymer adopts a zig-zag ladder structural motif (Figure 7.4). The coordination about each potassium ion is completed by two molecules of THF, making the K ion pseudo-six-coordinate.

The K...B distances in 125 [3.316(4), 3.131(4), 3.417(4) and 3.183(4) Å] are much longer than the corresponding Li...B and Na...B distances in 123 and 124, consistent with the larger ionic radius of potassium, and are similar in length to the K...B distance in the related phosphido-bis(borane) compound 37 [3.205 Å]. The B-P-B angle in 125 [111.48(16)°] is slightly larger than the related angle in 124 [109.59(12)°], which is as expected, due to the larger ionic radius of the potassium ion.

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>Bond Lengths (Å)</th>
<th>Bond Lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K(1)–H(1A) 3.06(3)</td>
<td>P(1)–C(8) 1.838(3)</td>
<td>K(1)–H(1B) 2.76(3)</td>
</tr>
<tr>
<td>K(1)–H(2B) 2.88(3)</td>
<td>B(1)–P(1)–B(2) 111.48(16)</td>
<td>K(1)–B(1) 3.316(4)</td>
</tr>
<tr>
<td>K(1)–B(1) 3.131(4)</td>
<td>K(1)–B(2)–K(1A) 88.35(9)</td>
<td>K(1)–B(1A) 3.131(4)</td>
</tr>
<tr>
<td>K(1)–B(2) 3.417(4)</td>
<td>B(1)–K(1)–B(2) 56.89(9)</td>
<td>K(1)–B(2) 3.183(4)</td>
</tr>
<tr>
<td>K(1)–B(2B) 3.183(4)</td>
<td>B(1)–P(1)–C(8) 104.06(16)</td>
<td>K(1)–B(2B) 3.183(4)</td>
</tr>
<tr>
<td>P(1)–B(1) 1.933(4)</td>
<td>B(2)–P(1)–C(1) 115.12(15)</td>
<td>P(1)–B(2) 1.949(4)</td>
</tr>
<tr>
<td>P(1)–B(2) 1.949(4)</td>
<td>C(1)–P(1)–C(8) 103.45(14)</td>
<td>P(1)–C(1) 1.850(3)</td>
</tr>
</tbody>
</table>

Table 7.3. Selected bond lengths (Å) and angles (°) for 125.
Figure 7.3. Part of the polymeric structure of compound 125. All C-bound H atoms and THF C-atoms omitted for clarity.

Figure 7.4. A section of the polymeric structure of 125, showing only P, B and K atoms for clarity.
7.4.4 Solid-state structure of 126

Compound 126 crystallises with two crystallographically independent molecular ion pairs in the asymmetric unit; the structures of both ion pairs are shown in Figure 7.5, with selected bond distances and angles shown in Table 7.4. In a similar fashion to the related sodium phosphido-borane complex [{(Me₃Si)₂CH}P(C₆H₅)(BH₃)][Na(12-crown-4)₂] (116), 126 crystallises as solvent separated ion pairs; the sodium ions are coordinated by eight oxygen atoms of two molecules of 12-crown-4.

The angles about the phosphorus centre in 126 are similar to those seen in 124; the B-P-B and C-P-C angles are 109.59(12) and 104.99(10)° for 124 and 111.7(3) and 105.0(2)° for 126, respectively, whilst the B-P-C angles lie in the same range of 104-116°. There are no significant differences in the bond distances about phosphorus in 124 and 126, which suggests that phosphido-bis(borane) complexes are likely to possess the same structural parameters whether they exist as a solvent-separated ion species or as a contact ion pair.

\textbf{Figure 7.5}. Structure of compound 126 (both independent molecules shown). All C-bound H atoms omitted for clarity.
\[
\begin{array}{ccc}
P(1)–B(1) & 1.943(7) & C(1)–P(1)–B(1) & 116.3(3) \\
P(1)–B(2) & 1.954(6) & C(8)–P(1)–B(2) & 110.1(3) \\
P(1)–C(1) & 1.858(5) & B(1)–P(1)–B(2) & 111.7(3) \\
P(1)–C(8) & 1.841(5) & C(22)–P(2)–C(15) & 103.5(2) \\
P(2)–B(3) & 1.956(7) & C(22)–P(2)–B(3) & 108.6(3) \\
P(2)–B(4) & 1.963(6) & C(15)–P(2)–B(3) & 110.3(3) \\
P(2)–C(22) & 1.825(5) & C(22)–P(2)–B(4) & 104.9(3) \\
P(2)–C(15) & 1.855(5) & C(15)–P(2)–B(4) & 116.4(3) \\
Na(1)–O(6) & 2.385(6) & B(3)–P(2)–B(4) & 112.4(3) \\
Na(2)–O(18) & 2.507(4) & P(1)–C(1)–Si(2) & 115.3(3) \\
C(8)–P(1)–C(1) & 105.0(2) & P(1)–C(1)–Si(1) & 113.1(3) \\
C(8)–P(1)–B(1) & 103.4(3) & Si(2)–C(1)–Si(1) & 116.4(3)
\end{array}
\]

Table 7.4 Selected bond lengths (Å) and angles (°) for 126.

7.5 Synthesis and characterisation of alkaline earth metal complexes

\[\text{\small{[\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P(C}_6\text{H}_5\text{(BH}_3\text{)}_2\}]\text{M(THF)}_4\}} \quad [\text{M} = \text{Mg} \ (128), \ \text{Ca}(129), \ \text{Sr}(130)]\]

Treatment of a solution of two equivalents of 42 in toluene with one equivalent of MgBu\(_2\) in heptane, followed by addition of one equivalent of BH\(_3\)·SMe\(_2\) \textit{in situ}, yields the corresponding phosphido-bis(borane) (Scheme 7.5), which crystallises from toluene/THF at room temperature as the adduct \[\text{\small{[\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P(BH}_3\text{)}_2\text{(C}_6\text{H}_5\text{)}]\text{Mg(THF)}_4\}}\] (128).

To prepare the related calcium and strontium derivatives, the basic reagents [Bn\(_2\text{Ca(THF)}_4\)] and \[\text{\small{[\{\text{(Me}_3\text{Si)}_2\text{CH}\}_2\text{Sr(THF)}_3\}}}\] were synthesised using previously reported procedures.\textsuperscript{12,13} The reaction between a solution of two equivalents of 42 in toluene and one equivalent of either [Bn\(_2\text{Ca(THF)}_4\)] or \[\text{\small{[\{\text{(Me}_3\text{Si)}_2\text{CH}\}_2\text{Sr(THF)}_3\}}}\] in THF, followed by addition of BH\(_3\)·SMe\(_2\) \textit{in situ}, yields the corresponding alkaline earth metal salts. The compounds may be crystallised from toluene/THF by concentrating the reaction solution \textit{in vacuo}, as the adducts \[\text{\small{[\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P(BH}_3\text{)}_2\text{(C}_6\text{H}_5\text{)}]\text{Ca(THF)}_4\}}\] (129) and \[\text{\small{[\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P(BH}_3\text{)}_2\text{(C}_6\text{H}_5\text{)}]\text{Sr(THF)}_4\}}\] (130).
Scheme 7.5. Synthesis of compounds 128-130. Reagents and conditions: i) MgBu$_2$, 1 h, r.t. ii) BH$_3$·SMe$_2$, THF, 1 h, r.t. iii) [Bn$_2$Ca(THF)$_3$], THF, 1 h, r.t. v) [R$_2$Sr(THF)$_3$], THF, 1 h, r.t. [R= (Me$_3$Si)$_2$CH].

The $^{31}$P{$^1$H} NMR spectra of compounds 128-130 in $d_8$-THF exhibit broad, poorly resolved multiplets at -11.5, -15.9 and -16.4 ppm respectively, due to coupling to two $^{11}$B nuclei.

In the $^1$H NMR spectra, the SiMe$_3$ protons of 128-130 are equivalent, and give rise to a sharp singlet at 0.1 ppm in each case. The twelve borane protons give rise to a broad signal centred around 0.7-0.8 ppm, and, upon decoupling of the $^{11}$B nucleus, the broad signals collapse into sharp doublets due to coupling to the $^{31}$P nucleus [$^2J_{PH} = 10.5$ (128), 12.9 (129) and 11.0 Hz (130)].
That the BH$_3$ groups in compounds 128-130 are equivalent by NMR spectroscopy is rather surprising, given the crystal structures of these complexes in the solid-state show that they are inequivalent (see chapter 7.6). This indicates that, in THF, either there is rapid exchange between the free and bound BH$_3$ groups, or that the complexes exist as solvent separated ion multiples (Scheme 7.6).

![Scheme 7.6. Possible behaviour of compound 130 in solution.](image)

### 7.6 Solid-state structures of compounds 128-130

Compounds 128-130 crystallise as discrete centrosymmetric monomers, and are essentially isostructural in the solid state. The structures of 128-130 are shown in Figures 7.8, 7.9 and 7.10 with selected bond lengths and angles given in Tables 7.6-7.8, respectively.

In each complex, the metal centres are coordinated by two phosphido-bis(borane) ligands via one of the BH$_3$ groups. The coordination about each metal ion is completed by four molecules of THF. This is rather surprising, as it would be assumed that the larger cations would adopt higher coordination numbers. Indeed the ionic radius of Sr$^{2+}$ is over 60% greater than the
radius of Mg$^{2+}$, with coordination numbers, which typically lie in the range of 8-12 compared to four for Mg$^{2+}$. However, in compound 128 the borane groups adopt an η$^1$-BH$_3$-Mg type interaction, whereas compounds 129 and 130 adopt η$^3$-BH$_3$-M binding modes.

<table>
<thead>
<tr>
<th>Cation (2+)</th>
<th>Ionic Radius Å</th>
<th>Coordination No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.78</td>
<td>6</td>
</tr>
<tr>
<td>Ca</td>
<td>1.06</td>
<td>6-9</td>
</tr>
<tr>
<td>Sr</td>
<td>1.27</td>
<td>8-12</td>
</tr>
</tbody>
</table>

Table 7.5. Ionic radii of group 2 metals.

The Mg…B distance of 2.7800(18) Å is slightly longer than related η$^1$-BH$_n$-Mg distances that have been reported. For example the complex [(B$_3$H$_9$)$_2$(Et$_2$O)$_2$Mg] (131) has a Mg…B distance of 2.575(5). However the Mg-H distance of 2.069(19) Å lies in the typical range of 1.9-2.4 Å. For example, in compound 131, the Mg-H distances are 1.99(3) and 2.01(4) Å.

The Ca…B distances in 129 of 2.751(2) Å are similar to the corresponding η$^3$-BH$_n$-Ca interactions in (BH$_4$)$_2$Ca(DME)$_2$ (132)$^{16}$ [2.67(5) and 2.65(4) Å], and the Ca-H distances of 132 [2.637(19) 2.834(19) and 2.374(19) Å] are also similar to those in 129 [2.345(29)–2.577(29)]. As expected the Ca-H distances in 129 [2.637(19), 2.834(19) and 2.374(19) Å] are longer than the corresponding Mg-H distances in 128.

<table>
<thead>
<tr>
<th>Bond/Distance</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(1)–B(1)</td>
<td>2.8700(18)</td>
</tr>
<tr>
<td>Mg(1)–H(1A)</td>
<td>2.069(19)</td>
</tr>
<tr>
<td>Mg(1)–H(1B)</td>
<td>3.020(19)</td>
</tr>
<tr>
<td>Mg(1)–H(1C)</td>
<td>3.209(20)</td>
</tr>
<tr>
<td>P(1)–B(1)</td>
<td>1.9465(18)</td>
</tr>
<tr>
<td>P(1)–B(2)</td>
<td>1.937(2)</td>
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<tr>
<td>P(1)–C(1)</td>
<td>1.8520(16)</td>
</tr>
<tr>
<td>P(1)–C(8)</td>
<td>1.8311(16)</td>
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<tr>
<td>B(1)–Mg(1)–B(1A)</td>
<td>149.24(8)</td>
</tr>
<tr>
<td>B(1)–P(1)–B(2)</td>
<td>114.39(8)</td>
</tr>
</tbody>
</table>

Table 7.6. Selected bond lengths (Å) and angles (°) for 128.
Table 7.7. Selected bond lengths (Å) and angles (°) for compound 129.

<table>
<thead>
<tr>
<th>Bond Lengths/Angles</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(1)–B(1)</td>
<td>2.751(2)</td>
</tr>
<tr>
<td>Ca(1)–H(1A)</td>
<td>2.637(19)</td>
</tr>
<tr>
<td>Ca(1)–H(1B)</td>
<td>2.834(19)</td>
</tr>
<tr>
<td>Ca(1)–H(1C)</td>
<td>2.374(19)</td>
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<tr>
<td>P(1)–B(1)</td>
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</tr>
<tr>
<td>P(1)–B(2)</td>
<td>1.941(2)</td>
</tr>
<tr>
<td>P(1)–C(1)</td>
<td>1.8426(18)</td>
</tr>
<tr>
<td>P(1)–C(8)</td>
<td>1.8286(19)</td>
</tr>
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<td>O(1)–Ca(1)–O(2)</td>
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</tr>
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<td>90.03(7)</td>
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<td>B(1)–Ca(1)–B(1A)</td>
<td>180.00(5)</td>
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<td>B(1)–P(1)–B(2)</td>
<td>111.97(11)</td>
</tr>
<tr>
<td>B(1)–P(1)–C(1)</td>
<td>114.30(10)</td>
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<td>B(1)–P(1)–C(8)</td>
<td>100.73(10)</td>
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<td>B(1)–P(1)–C(8)</td>
<td>113.42(10)</td>
</tr>
<tr>
<td>B(1)–P(1)–C(8)</td>
<td>110.14(10)</td>
</tr>
<tr>
<td>B(1)–P(1)–C(8)</td>
<td>105.22(8)</td>
</tr>
</tbody>
</table>

The Sr-H distances of 2.54(6), 2.78(7) and 2.81(7) Å and the Sr…B distance of 2.871(12) Å in 130 are comparable to the η³-BH₄-Sr distances in the phosphine-borane-stabilised carbanion [(Me₃Si)₂{Me₂(H₃B)P}C]₂Sr(THF)₅ (133)\(^{17}\) [Sr-H 2.65(3), 2.76(3) and 2.89(4) Å; Sr…B 2.893(7) Å] and the tetrahydridoborate complex (BH₄)₂Sr(diglyme)₂ (134)\(^{18}\) [Sr-H 2.64(4), 2.77(4) and 2.65(4) Å; Sr…B 2.916(7) Å].

Figure 7.6. Examples of η³-BH₄-Sr interactions.
Table 7.8. Selected bond lengths (Å) and angles (°) for 130.

From compounds 128-130 it is clear to see that there is a trend of increasing M-H distances with increasing ionic radius of the metal cation [for example: M-H(1) 2.069(19) (128), 2.374(19) (129) and 2.54(6) Å (130)]. However, the overall M...B distances in 128-130 do not exhibit any trend, in fact quite surprisingly, the Mg...B distance in 128 and the Sr...B distance in 130 are identical [2.8700(18) and 2.871(12) Å, respectively].

As seen with compound 123, the P-B distances in compounds 129 [1.926(2) and 1.941(2)] and 130 are shorter for the BH$_3$ group engaged with the metal centre [P-B$_{\text{bound}}$ 1.928(4) (123), 1.926(2) (129) and 1.914(12) Å (130)] than for the free BH$_3$ group [P-B$_{\text{free}}$ 1.947(4) (123), 1.941(2) (129) and 1.957(12) Å (130)]. In contrast to these observations, the P-B distances of the compound 128 are very similar, where the P-B distance for the magnesium-bound borane group is only marginally longer than the P-B distance to the free BH$_3$ group [1.9465(18) and 1.937(2) Å, respectively]. This may be attributed to the η$^1$ binding mode of the metal bound borane group in 128 which closer resembles a separated ion pair, where the P-B distances would be identical.

Interestingly, as you move down the series, the P-B distances for the metal-bound borane groups decrease, whilst the P-B distances for the non-bound BH$_3$ groups increase, which comes with an increasing disparity between the P-B$_{\text{bound}}$ and P-B$_{\text{free}}$ distances.
Figure 7.7. P-B bond lengths in compounds 123, 128, 129 and 130.
Figure 7.8. Structure of compound 128. All C-bound H atoms omitted for clarity.
Figure 7.9. Structure of compound 129. All C-bound H atoms omitted for clarity.
Figure 7.10. Structure of compound 130. All C-bound H atoms omitted for clarity.
7.7 Conclusions

The alkali metal complexes of the phosphido-bis(borane) \[ \{(\text{Me}_3\text{Si})_2\text{CH}\}P(C_6\text{H}_5)(\text{BH}_3)_2^- \] are prepared using straightforward synthetic techniques. The lithium complex may be crystallised as the 12-crown-4 adduct 123, which is monomeric in structure and has similar characteristics to the related complex 35. In contrast to previous reports of phosphido-bis(boranes), the sodium and potassium complexes 124 and 125 are shown to have dimeric and polymeric structures, respectively, in the solid state; where previous reports show that this type of ligand coordinates to the metal ion through only one borane group, in the case of 124 and 125 each ligand is bound to an adjacent metal centre through both BH3 groups.

Similarly, the sodium complex of the phosphido-(bis)borane \[ \{(\text{Me}_3\text{Si})_2\text{CH}\}P(C_6\text{H}_4\text{OMe})(\text{BH}_3)_2^- \], is easily synthesised and can be crystallised as an adduct with 12-crown-4 (126) as a separated ion pair. In comparison to the sodium complex 124, which crystallises as a tight contact ion pair, there are no significant differences in their structural parameters.

Phosphido-bis(borane) complexes with the alkaline earth metals Mg, Ca and Sr have also been prepared and characterised in the solid state. Complexes 128, 129 and 130 are isostructural in the solid state, with each metal adopting a pseudo-coordination number of 6; two ligands are bound to the metal centre through BH3 hydrogen interactions, with coordination completed by four molecules of THF. This is rather surprising, given the markedly different ionic radii of the metal centres. As you move down the series, the P-B distances for the bound borane groups decrease, whilst the P-B distances for the free borane group decrease.

7.7 References

(1) Thompson, N. R. *Journal of the Chemical Society (Resumed)* 1965, 6290.


Chapter 8. Conclusions

The work presented in this thesis has explored the effects that varying the metal centre and peripheral donor have on the structure and stabilities of complexes of phosphido-boranes. A series of phosphido-borane and phosphido-bis(borane) complexes with group I and II metals has been isolated, with the majority of these compounds characterised in the solid-state, using X-ray crystallography. This chapter aims to draw comparisons between the structures of these compounds and highlight the trends that have been observed.

8.1 Effects of varying the peripheral donor on group I complexes of phosphido-boranes

The synthesis, isolation and characterisation of group I complexes with phosphido-boranes illustrates the variety of structures these complexes can adopt (Figure 8.1). The structural motifs and aggregation states of these species are highly dependent on a number of factors, including cation size and polarisability, the nature of the peripheral donor, the presence of coligands, and agostic-type BH$_3$...M interactions.

![Diagram of coordination modes adopted by phosphido-boranes](image)

**Figure 8.1.** Coordination modes adopted by phosphido-boranes.
The P-M distances between lithium, sodium or potassium, and phosphido-borane ligands prepared from either \{(\text{Me}_3\text{Si})_2\text{CH}\}\text{PH}(\text{C}_6\text{H}_4-2-\text{CH}_2\text{OMe})(\text{BH}_3) (39), \{(\text{Me}_3\text{Si})_2\text{CH}\}\text{PH}(\text{C}_6\text{H}_4-2-\text{SMe})(\text{BH}_3) (40) or \{(\text{Me}_3\text{Si})_2\text{CH}\}\text{PH}(\text{C}_6\text{H}_5)(\text{BH}_3) (42), are shown in Figure 8.2. The effect of cation size is as expected, with P-M distances increasing with increasing radius of the alkali metal, where P-Li < P-Na < P-K. Figure 8.2 also shows that phosphido-boranes prepared from compound 39 possess slightly longer P-M distances compared with the corresponding thioanisole-functionalised phosphido-borane complexes prepared from 40. Whether this is a result of the nature of the donor atom or the flexibility of the chelate ring is unclear at this time; an X-ray study of \[(\text{Me}_3\text{Si})_2\text{CH}]\text{P}(\text{C}_6\text{H}_4-2-\text{OMe})(\text{BH}_3)\text{Li}\) (85) would provide further understanding of this trend, however, due to its poor stability tendency to decompose into 89 and 90, the isolation of single crystals of 85 for X-ray analysis has proved to be particularly challenging.

**Figure 8.2.** P-M distances in selected phosphido-borane complexes \[R = (\text{Me}_3\text{Si})_2\text{CH}\].
Compounds \[\{(\text{Me}_3\text{Si})_2\text{CH}\}P(\text{C}_6\text{H}_4\text{-2-CH}_2\text{-OMe})(\text{BH}_3)\text{K}(\text{pmdeta})\] (51) and \[\{(\text{Me}_3\text{Si})_2\text{CH}\}P(\text{C}_6\text{H}_4\text{-2-SMe})(\text{BH}_3)\text{K}(\text{pmdeta})\] (66) are the first examples of potassium complexes with phosphido-boranes to be structurally characterised that contain peripheral donor coordination of the metal centre. Figure 8.3 highlights the drastic increase in P-K bond length observed in these two compounds compared to the corresponding distances in the related complexes \[\text{[Ph}_2\text{P(BH}_3\text{)K(18-crown-6)]}\] (32), \[\{(\text{Me}_3\text{Si})_2\text{CH}\}P(\text{C}_6\text{H}_4\text{-2-OMe})(\text{BH}_3)\text{K}(\text{pmdeta})\] (87) and \[\{(\text{Me}_3\text{Si})_2\text{CH}\}P(\text{C}_6\text{H}_5)\text{K}(\text{pmdeta})\] (117), which do not exhibit intramolecular coordination from a peripheral donor. Interestingly, this trend is not observed for the phosphido-borane complexes with lithium, which possess similar Li-P distances, irrespective of whether the ligand possesses peripheral donor functionality (Figure 8.5).
Figure 8.4. P-K distances of phosphido-boranes.

Figure 8.5. P-Li distances of phosphido-boranes.
An important feature of the structures of group I complexes with phosphido-boranes is the coordination mode adopted by the borane group, which provides additional stabilisation through agostic-type B-H-M interactions. The borane group can adopt a range of coordination modes, illustrated by the structures discussed previously. In addition to straightforward $\eta^1$, $\eta^2$ or $\eta^3$ coordination, the borane group can bridge metal centres in a $\mu_2$-$\eta^1$-$\eta^2$, $\mu_2$-$\eta^1$-$\eta^3$, $\mu_2$-$\eta^2$-$\eta^2$ or $\mu_2$-$\eta^2$-$\eta^3$ manner (Figure 8.6).

The B...M distances in phosphido-boranes are expected to vary depending on the size of the metal centre and hapticity of the BH$_3$ group. It is unsurprising, therefore, that B...M distances increase with increasing radius of the alkali metal and with lower hapticities (Figure 8.7). The M-H distances correlate well with $\eta^1$-, $\eta^2$- and $\eta^3$-BH$_3$ coordination modes.

![Figure 8.6. Examples of BH$_3$...M bridging modes.](image-url)
Aggregation states are markedly affected by the presence of peripheral donor functionalisation. Whereas the lithium salt \(
\{(\text{Me}_3\text{Si})_2\text{CH}\}P(\text{C}_6\text{H}_3)(\text{BH}_3)\text{Li(THF)}_2\) \((115)\) crystallises as a polymer, the donor-functionalised compounds \(\{(\text{Me}_3\text{Si})_2\text{CH}\}P(\text{C}_6\text{H}_4-2-\text{CH}_2\text{OMe})(\text{BH}_3)\text{Li(THF)}_2\) \((49)\) and \(\{(\text{Me}_3\text{Si})_2\text{CH}\}P(\text{C}_6\text{H}_4-2-\text{SMe})(\text{BH}_3)\text{Li(THF)}_2\) \((64)\) crystallise as dimers; both of the latter complexes possess a direct P-Li bond and \(\eta^2\)-type BH\(_3\)-Li coordination. In the absence of a peripheral donor, the lithium ions in \(115\) adopt a four-coordinate geometry, through an additional molecule of THF; however, as a consequence of removing peripheral functionality, \(115\) exhibits a larger B-P-Li angle [the B-P-Li angles of \(49\), \(64\) and \(115\) are 94.28(19), 109.30(8) and 123.04(8)º, respectively], which is an important feature of the polymeric structure, confirming that steric bulk is insufficient to stabilise the species in a dimeric state.

The sodium complex \(\{(\text{Me}_3\text{Si})_2\text{CH}\}P(\text{C}_6\text{H}_4-2-\text{SMe})(\text{BH}_3)\text{Na(tmeda)}\) \((65)\), also crystallises as a polymer, whereas the related complex \(\{(\text{Me}_3\text{Si})_2\text{CH}\}P(\text{C}_6\text{H}_4-2-\text{CH}_2\text{OMe})(\text{BH}_3)\text{Na(tmeda)}\) \((50)\) crystallises as a dimer. Compounds \(65\) and \(50\) (Figure 8.8) are essentially constitutionally identical, except for their donor-functionalities, hence their aggregation states must be attributed to the nature of the chelate ring generated by the
peripheral donor. Compound 50 contains a six-membered chelate ring, and has a Na-P-C(8) angle of 107.31(9)° and a P-Na-O bite angle of 76.40(6)°, whereas 65 has a sulphur-containing five-membered chelate ring, a corresponding Na-P-C(8) angle of 98.10(12)° and a P-Na-S bite angle of 62.93(4)°. As a consequence of these distortions, the B-P-Na angle in 65 is somewhat larger than the corresponding angle in 50 [118.70(15) and 69.21(11)°, respectively], which may be ascribed to the borane-bridged polymer structure in 65.

![Figure 8.8. Structures of compounds 50 and 65.](image)

From this result, it may be expected that the potassium complex 66 would also adopt a higher order aggregate than the related compound 51, which crystallises as a dimer. However, the presence of pmdeta as a co-ligand in 66 provides sufficient coordination about the potassium cation to prevent aggregation beyond a dimer.

A comparison of the sum of angles within the C$_2$PB framework reveals some interesting trends in the geometry of the phosphorus centre in the phosphine- and phosphido-borane structures (Figure 8.8). The phosphido-borane anions adopt a more pyramidal geometry about phosphorus compared with the corresponding phosphine-boranes, which may be expected, as the metal cations are able to localise negative charge on the phosphorus atom. The geometry about the phosphorus centre is dependent upon the nature of each phosphido-borane structure adopted, however, it is apparent that for each metal cation, the phosphorus anion is more pyramidal in complexes with the ligand [{(Me$_3$Si)$_2$CH}P(C$_6$H$_4$-2-CH$_2$OMe)(BH$_3$)]$^-$. The lithium salt [{(Me$_3$Si)$_2$CH}P(C$_6$H$_4$-2-CH$_2$OMe)(BH$_3$)Li(THF)] (49) exhibits the most pyramidal phosphorus centre, although in general, the size of the metal cation does not appear to significantly affect the geometry about the phosphorus atom.
In summary, it appears that there is a fine balance between the formation of dimeric and polymeric structures in these species, which depends on a combination of: the peripheral donor, chelate ring size, the size of the cation, B...M interactions and chelating coligands. The distances between phosphorus and the alkali metal vary with respect to the functionality of the peripheral donor. In particular, P-K distances are substantially longer when the potassium ion is coordinated by a peripheral donor.

![Graph showing sum of angles about phosphorus atoms with C2PB frameworks.](image)

**Figure 8.9.** Sum of angles about phosphorus atoms with C2PB frameworks.
8.2 Comparisons between group I complexes of the ligands \[\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P(C}_6\text{H}_5\text{)}\text{BH}_3\}^-\] and \[\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P(C}_6\text{H}_5\text{)(BH}_3\text{)}_2\}^-\]

Alkali metal complexes of the ligands \[\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P(C}_6\text{H}_5\text{)}\text{BH}_3\}^-\] and \[\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P(C}_6\text{H}_5\text{)(BH}_3\text{)}_2\}^-\] have been prepared from the corresponding phosphine-borane 42; the coordination modes that have been adopted by these ligands are shown in Figure 8.10.

The complexes of the phosphido-mono(borane) ligand with lithium (115) and potassium (117), in the presence of THF and pmdeta, respectively, crystallise as tight contact ion pairs, whilst the sodium complex crystallises as a solvent-separated ion pair in the presence of 12-crown-4 (116).

Alkali metal complexes of the related phosphido-bis(borane) ligand, 123, 124 and 125 crystallise as contact ion pairs; the ligand may coordinate to the metal cation through either one or both borane groups, with no direct contact between the formally anionic phosphorus and the alkali metal (VI, VII).

\[\text{Figure 8.10. Coordination modes adopted by } [\text{RP(C}_6\text{H}_5\text{)(BH}_3\text{)}]^- \text{ and } [\text{RP(C}_6\text{H}_5\text{)(BH}_3\text{)}_2]\text{ complexes with alkali metals } [\text{R = (Me}_3\text{Si})_2\text{CH}].\]
A comparison between the phosphido-boranes 115 and 117 and the related phosphido-bis(boranes) 123 and 125 highlights that the additional P-B bond has no effect on the B...M distances between the borane groups and metal cation; the B...Li distances for 115 and 123 are 2.440(3) and 2.281(7) Å, respectively, whilst the B...K distances are 3.262(3) and 3.107(3) Å for 117 and range between 3.131(4) and 3.417(4) Å for 125. It was observed in compound 123, that the P-B distance for the boron group engaged in bonding to the lithium ion is slightly shorter than the P-B distance for the ‘free’ borane group. In general, however, the P-B distances of the phosphido-(bis)borane complexes are very similar, and differences between these and the corresponding P-B distances in the phosphido-borane complexes are negligible.

8.3 Summary

The structures of a number of phosphido-borane and phosphido-bis(borane) complexes with group I and II metals and the trends that are observed have been discussed. As expected, P-M distances in phosphido-complexes with alkali metals increase with increasing size of the metal cation. Varying the peripheral donor has also been shown to have an effect on P-M distances, where complexes of the ligand \[\{(Me_3Si)_2CH\}P(C_6H_4-2-CH_2OMe)(BH_3)\] have longer P-M distances than the corresponding complexes with \[\{(Me_3Si)_2CH\}P(C_6H_4-2-SMe)(BH_3)\].

The structures of phosphido-borane/bis(borane) complexes have been shown to adopt a variety of coordination modes not previously reported. These may be rationalised by considering the charge/size ratio of the metal cations, which affects the hapticity of the borane groups, peripheral functionality, and the nature of co-ligands used.
Chapter 9. Experimental

9.1 General procedure

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen or in a nitrogen filled MBraun dry-box. Diethyl ether, THF, light petroleum (bp 40-60), toluene, benzene and methylcyclohexane were dried prior to use by distillation under nitrogen from sodium, potassium or sodium/potassium alloy as appropriate. n-Hexane was distilled under nitrogen from sodium/benzophenone, and hexamethyldisiloxane was distilled under nitrogen from calcium hydride. THF and hexamethyldisiloxane were stored over activated 4Å molecular sieves; all other solvents were stored over a potassium film. Deuterated-THF, -toluene and -benzene were distilled from potassium and deoxygenated by three freeze-pump-thaw cycles and were stored over activated 4Å molecular sieves.

n-Butyllithium was purchased from Aldrich as a 2.5 M solution in hexanes. Dibutylmagnesium was purchased as a 1.0 M solution in heptanes from Aldrich. The adduct H$_3$B·SMe$_2$ was obtained as a 2.0 M solution in THF from Aldrich. Potassium t-butoxide and sodium t-butoxide were purchased from Lancaster and were heated under vacuum at 100 °C (0.01 mmHg) for 3 h prior to use. All other compounds were used as supplied by the manufacturer, with the exception of tmeda and pmadena, which were freshly distilled from CaH$_2$, and 12-crown-4, which was dried over activated 4 Å molecular sieves.

The compounds (Me$_3$Si)$_2$CHPCl$_2$ (43), \textsuperscript{1} \{(Me$_3$Si)$_2$CH\}PH(C$_6$H$_4$-2-SMe) (45), \textsuperscript{2} \{(Me$_3$Si)$_2$CH\}PH(C$_6$H$_4$-2-OMe) (46), \textsuperscript{3} \{(Me$_3$Si)$_2$CH\}PH(C$_6$H$_5$) (48), \textsuperscript{4} benzylsodium, \textsuperscript{5} benzylpotassium, \textsuperscript{6} bis-benzylcalcium \textsuperscript{7} and \{(Me$_3$Si)$_2$CH\}$_2$Sr \textsuperscript{8} were prepared by previously published procedures.

9.2 NMR Spectroscopy and elemental analyses

\textsuperscript{1}H and \textsuperscript{13}C{\textsuperscript{1}H} NMR spectra were recorded on a JEOL Lambda500 spectrometer operating at 500.16 and 125.65 MHz, respectively, or a JEOL ECS400 spectrometer operating at
399.78 and 100.53 MHz, respectively; chemical shifts are quoted in ppm relative to
tetramethylsilane. $^{31}P\{^1H\}$, $^7Li\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectra were recorded on a JEOL Lambda500 spectrometer operating at 202.35, 194.25 and 160.35 MHz, respectively; chemical shifts are quoted in ppm relative to external 85% $H_3PO_4$, external 0.1 M LiCl, and external $BF_3(OEt)_2$ respectively. Elemental analyses were obtained by the Elemental Analysis Service of London Metropolitan University.

9.3 Crystal structure determinations

Measurements were made at 150 K on either a Bruker AXS SMART, a Nonius KappaCCD
or an Oxford Diffraction Gemini A Ultra diffractometer using either graphite-
monochromated MoKα or CuKα radiation ($\lambda = 0.71073$ and 1.54184 Å, respectively). Cell
parameters were refined from the observed positions of all strong reflections. Intensities
were corrected semi-empirically for absorption, based on symmetry-equivalent and repeated
reflections. The structures were solved by direct methods and refined on $F^2$ values for all
unique data. All non-hydrogen atoms were refined anisotropically, H atoms bonded to boron
were freely refined isotropically and the remaining H atoms were constrained with a riding
model; $U(H)$ was set at 1.2 (1.5 for methyl groups) times $U_{eq}$ for the parent atom.
Programmes were Oxford Diffraction CrysAlisPro Bruker AXS SMART and SAINT or
Nonius COLLECT and EvalCCD, and SHELXTL for structure solution, refinement, and
molecular graphics.9,10,11

9.4 Preparative methods

{(Me$_3$Si)$_2$CH}PH(C$_6$H$_4$-2-CH$_2$OMe)(BH$_3$) (39):

To a cold (0 °C) solution of 2-BrC$_6$H$_4$CH$_2$OMe (2.39 g, 11.9 mmol) was added one
equivalent of $^n$BuLi (4.8 mL of a 2.5 M solution in hexane, 11.9 mmol). The reaction was
stirred for 2 h at 0 °C, then added in situ to a cold -78 °C solution of 43 (2.85 g, 11.0 mmol)
in THF (30 mL). The mixture was stirred for 16 h and allowed to reach room temperature.
Solid LiAlH$_4$ (0.41 g, 11.0 mmol) was carefully added, and the reaction mixture was stirred
under reflux for 2 h. The reaction mixture was allowed to cool to room temperature, and excess LiAlH$_4$ was quenched by the careful addition of deoxygenated water (30 mL). The organic layer was decanted, and the aqueous layer was extracted into Et$_2$O (3 x 20 mL). The combined organic extracts were dried over 4Å molecular sieves, the solution was filtered, and the solvent was removed in vacuo from the filtrate to give {(Me$_3$Si)$_2$CH}PH(C$_6$H$_4$-2-CH$_2$OMe) 44 as a colourless oil. Isolated yield: 2.62 g, 76%.

To a solution of 44 (4.62 g, 14.88 mmol) in THF (20 mL) was added BH$_3$·SMe$_2$ (7.4 mL of a 2.0 M solution in THF, 14.80 mmol). After one hour stirring the solvent was removed in vacuo to yield a white solid. The product was dissolved in hot petroleum-ether 40-60 (10 mL) and crystallised upon cooling. Isolated yield: 2.91 g, 60%.

$^1$H{$^{11}$B} NMR (CDCl$_3$, 25 °C): δ -0.04 (s, 9H, SiMe$_3$), 0.29 (s, 9H, SiMe$_3$), 0.89 (dd, $^1$J$_{PH}$ = 13.8 Hz, $^3$J$_{HH}$ = 6.4 Hz, 3H, BH$_3$), 1.14 (d, $J_{PH}$ = 20.2 Hz, 1H, CH), 3.41 (s, OMe), 4.48 (d, $J_{HH}$ = 11.9 Hz, 1H, CH$_2$), 4.65 (d, $J_{HH}$ = 11.5 Hz, 1H, CH$_2$), 5.97 (dqd, $^1$J$_{PH}$ = 375.5 Hz, $^3$J$_{HH}$ = 6.4 Hz, $^3$J$_{HH}$ = 4.0 Hz, 1H, PH), 7.41 (m, 2H, ArH), 7.46 (d, $J_{HH}$ = 9.2 Hz, 1H, ArH), 8.05 (dd, $J_{HH}$ = 13.7 Hz, $J_{HH}$ = 7.8 Hz, 1H, ArH).

$^{13}$C{$^1$H} NMR (CDCl$_3$, 25 °C): δ 1.52 (d, $^3$J$_{PC}$ = 2.9 Hz, SiMe$_3$), 2.29 (d, $^3$J$_{PC}$ = 2.9 Hz, SiMe$_3$), 8.85 (d, $^1$J$_{PC}$ = 1.9 Hz, CHP), 58.22 (OMe), 73.47 (CH$_2$), 128.43 (d, $J_{PC}$ = 13.4 Hz, ArC), 128.97 (d, $J_{PC}$ = 47.0 Hz, ArC), 130.37 (d, $J_{PC}$ = 6.7 Hz, ArC), 131.58 (d, $J_{PC}$ = 1.9 Hz, ArC), 135.83 (d, $J_{PC}$ = 18.2 Hz, ArC), 140.37 (ArC). $^{11}$B{$^1$H} NMR (CDCl$_3$, 25 °C): δ -39.8 (d, br, $^1$J$_{PB}$ = 49.0 Hz). $^{31}$P{$^1$H} NMR (CDCl$_3$, 25 °C): δ -16.2 (q, broad, $^1$J$_{PB}$ = 49.0 Hz).

{(Me$_3$Si)$_2$CH}PH(C$_6$H$_4$-2-SMe)(BH$_3$) (40):

To a solution of 45 (6.64 g, 21.11 mmol) in THF (20 mL) was added BH$_3$·SMe$_2$ (10.6 mL of a 2.0 M solution in THF, 21.20 mmol). After one hour stirring the solvent was removed in vacuo to yield an off-white oil. The product was dissolved in n-hexane and crystallised upon cooling (-30 °C). The product was then washed with petrol (3 x 10 mL) and dried in vacuo, to give a white powder. Isolated crystalline yield: 7.22 g, 83%. $^1$H{$^{11}$B} NMR (CDCl$_3$, 25 °C): δ -0.06 (s, 9H, SiMe$_3$), 0.32 (s, 9H, SiMe$_3$), 0.92 (dd, $^2$J$_{PH}$ = 14.9 Hz, $^3$J$_{HH}$ = 6.5 Hz, 3H, BH$_3$), 1.46 (dd, $^2$J$_{PH}$ = 20.6 Hz, $^3$J$_{HH}$ = 2.8 Hz, 1H, CHP), 2.56 (s, 3H, SMe), 6.04 (dqd, $^1$J$_{PH}$ = 375.2 Hz, $^3$J$_{HH}$ = 6.5 Hz, $^3$J$_{HH}$ = 2.8 Hz, 1H, PH), 7.24 (t, $J_{HH}$ = 7.8 Hz, 1H, ArH), 7.29 (d, $J_{HH}$ = 6.9 Hz, 1H, ArH), 7.46 (t, $J_{HH}$ = 7.6 Hz, 1H, ArH), 8.02 (dd, $J_{HH}$ = 13.8 Hz, $J_{HH}$ = 6.0 Hz,
$^{13}$C{$_1^1$H} NMR (CDCl$_3$, 25 °C): $\delta$ 1.53 (d, $^3J_{PC} = 3.8$ Hz, SiMe$_3$), 2.18 (d, $^3J_{PC} = 2.8$ Hz, SiMe$_3$), 6.34 (CHP), 16.59 (SMe), 125.25 (d, $^3J_{PC} = 12.5$ Hz, ArC), 126.02 (d, $J = 4.8$ Hz, ArC), 127.51 (d, $J_{PC} = 49.8$ Hz, ArC), 132.08 (d, $J_{PC} = 1.9$ Hz, ArC), 136.14 (d, $^2J_{PC} = 18.2$ Hz, ArC), 143.08 (ArC).

$^{11}$B{$_1^1$H} NMR (CDCl$_3$, 25 °C): $\delta$ -40.1 (d, br, $^1J_{BP} = 49.0$ Hz).

$^{31}$P NMR (CDCl$_3$, 25 °C): $\delta$ -15.7 (dq, br, $^1J_{PH} = 375.2$ Hz, $^1J_{PB} = 49.0$ Hz).

{(Me$_3$Si)$_2$CH}PH(C$_6$H$_4$-2-OMe)(BH$_3$) (41):

To a solution of 46 (6.55 g, 21.94 mmol) in THF (20 mL) was added BH$_3$·SMe$_2$ (11.0 mL of a 2.0 M solution in THF, 22.0 mmol). After one hour stirring the solvent was removed in vacuo to yield a white solid. The product was dissolved in n-hexane (20 mL) and THF (1 mL) with heating, and crystallised upon cooling (-30 °C). Isolated yield: 5.00 g, 73%. $^1$H{$^{11}$B} NMR (CDCl$_3$, 25 °C): $\delta$ -0.01 (s, 9H, SiMe$_3$), 0.29 (s, 9H, SiMe$_3$), 0.89 (dd, $^2J_{PH} = 14.9$ Hz, $^3J_{HH} = 6.6$ Hz, 3H, BH$_3$), 1.08 (d, $^1J_{PH} = 20.2$ Hz, 1H, CHP), 3.90 (s, 3H OMe), 5.86 (dqd, $^1J_{PH} = 384.0$ Hz, $^3J_{HH} = 1.4$ Hz, 1H, PH), 6.90 (dd, $^1J_{HH} = 7.6$ Hz, $^2J_{HH} = 2.5$ Hz, 1H, ArH), 7.06 (t, $^1J_{HH} = 7.3$ Hz, 1H, ArH), 7.48 (t, $^1J_{HH} = 7.8$ Hz, 1H, ArH), 7.92 (dd, $^1J_{HH} = 13.1$ Hz, $^2J_{HH} = 7.6$ Hz, 1H, ArH). $^{13}$C{$_1^1$H} NMR (CDCl$_3$, 25 °C): $\delta$ 1.25 (d, $^3J_{PC} = 3.8$ Hz, SiMe$_3$), 2.11 (d, $^3J_{PC} = 2.8$ Hz, SiMe$_3$), 6.51 (d, $^1J_{PC} = 4.8$ Hz, CHP), 55.54 (OMe), 110.28 (d, $J_{PC} = 3.8$ Hz, ArC), 116.87 (d, $^3J_{PC} = 12.5$ Hz, ArC), 121.05 (d, $^3J_{PC} = 18.2$ Hz, ArC), 133.50 (ArC), 136.19 (d, $^2J_{PC} = 15.3$ Hz, ArC), 160.78 (ArC). $^{11}$B{$_1^1$H} NMR (CDCl$_3$, 25 °C): $\delta$ -40.6 (d, br, $^1J_{PB} = 49.0$ Hz). $^{31}$P{$_1^1$H} NMR (CDCl$_3$, 25 °C): $\delta$ -22.3 (q, br, $^1J_{PB} = 49.0$ Hz).

{(Me$_3$Si)$_2$CH}PH(C$_6$H$_5$)(BH$_3$) (42):

To a solution of 48 (9.78 g, 36.43 mmol) in THF (20 mL) was added BH$_3$·SMe$_2$ (18.2 mL of a 2.0 M solution in THF, 36.40 mmol). After one hour stirring the solvent was removed in vacuo to yield a white solid. THF was added to a solution of 42 in methylcyclohexane (20 mL), until the product dissolved. Compound 42 was then crystallised upon cooling to -30 °C. Isolated yield: 8.89 g, 63%. $^1$H{$^{11}$B} NMR (CDCl$_3$, 25 °C): $\delta$ 0.36 (s, 9H, SiMe$_3$), 0.29 (s, 9H, SiMe$_3$), 0.76 (d, $^1J_{PH} = 19.3$ Hz, 1H, CHP), 0.94 (dd, $^1J_{PH} = 15.3$ Hz, $^3J_{HH} = 6.4$ 3H, BH$_3$), 5.72 (dq, $^1J_{PH} = 368.9$ Hz, $^3J_{HH} = 6.4$ Hz, 1H, PH), 7.46 (m, 3H, ArH), 0.77 (dd, $^1J_{HH} = 11.2$ Hz, 3H, ArH).
Hz, $J_{HH} = 7.1$ Hz, 2H, ArH). $^{13}$C $\{^1$H$\}$ NMR (CDCl$_3$, 25 °C): $\delta$ 1.26 (d, $^3$J$_{PC}$ = 2.9 Hz, SiMe$_3$), 2.10 (d, $^3$J$_{PC}$ = 2.9 Hz, SiMe$_3$), 9.41 (d, $^1$J$_{PC}$ = 2.9 Hz, CHP), 128.81 (d, $^3$J$_{PC}$ = 10.5 Hz, ArC), 129.21 (d, $J_{PC}$ = 51.8 Hz, ArC), 131.29 (d, $^1$J$_{PC}$ = 2.9 Hz, ArC), 133.16 (d, $^3$J$_{PC}$ = 9.6 Hz, ArC).

$^{11}$B $\{^1$H$\}$ NMR (CDCl$_3$, 25 °C): $\delta$ -40.6 (d, br, $^1$J$_{BP}$ = 49.0 Hz).

$^{31}$P $\{^1$H$\}$ NMR (CDCl$_3$, 25 °C): $\delta$ -8.6 (q, br, $^1$J$_{PB}$ = 49.0 Hz).

\[\text{[(Me}_3\text{Si)}_2\text{CH}]{\text{P(C}_6\text{H}_4\text{-2-CH}_2\text{OMe})(BH}_3\text{)}\text{Li(THF)}\text{]}_2 (49):\]

To a solution of 39 (0.41 g, 1.26 mmol) in THF (15 mL) was added $^n$BuLi (0.5 mL of a 2.5 M solution in hexane, 1.25 mmol). After 1 h stirring the solvent was removed in vacuo to yield an off-white solid. THF was added to a solution of 39 in methylcyclohexane until the product had dissolved. Upon cooling (-30°C) colourless crystals suitable for X-ray crystallography were deposited. Isolated crystalline yield: 0.06g, 18%. Anal. Calcd for \[\text{[(Me}_3\text{Si)}_2\text{CH}]{\text{P(C}_6\text{H}_4\text{-2-CH}_2\text{OMe})(BH}_3\text{)}\text{Li(THF)}\text{]}_2: C 56.43, H 9.72%. Found C 56.29, H 9.62%.

$^1$H $\{^{11}$B$\}$ NMR (d$_8$-THF, 25 °C): $\delta$ -0.05 (s, 9H, SiMe$_3$), 0.25 (s, 9H, SiMe$_3$), 0.75 (d, $^2$J$_{PH}$ = 16.0 Hz, 1H, CHP), 0.83 (d, $^2$J$_{PH}$ = 14.7 Hz, 3H, BH$_3$), 1.69 (m, 4H, THF), 3.54 (m, 4H, THF), 3.38 (s, 3H, OMe), 4.82 (d, $^1$J$_{HH}$ = 11.5 Hz, 1H, ArH), 5.12 (d, $^1$J$_{HH}$ = 11.5 Hz, 1H, ArH), 7.14 (t, $^1$J$_{HH}$ = 7.1 Hz, 1H, ArH), 7.20 (t, $J_{HH} = 7.3$ Hz, 1H, ArH), 7.33 (d, $J_{HH} = 7.3$ Hz, 1H, ArH), 8.08 (d, $J_{HH} = 7.6$ Hz, 1H, ArH). $^{13}$C $\{^1$H$\}$ NMR (d$_8$-THF, 25 °C): $\delta$ 1.98 (SiMe$_3$), 3.23 (SiMe$_3$), 25.44 (THF), 57.08 (OMe), 67.28 (THF), 72.80 (CH$_2$), 125.84 (ArC), 127.83 (ArC), 129.02 (d, $J_{PC} = 5.8$ Hz, ArC), 133.74 (d, $J_{PC} = 17.3$ Hz, ArC), 139.54 (ArC), 145.90 (d, $J_{PC} = 37.4$ Hz).

$^{11}$B $\{^1$H$\}$ NMR (d$_8$-THF, 25 °C): $\delta$ -31.4 (d, br, $^1$J$_{BP}$ = 37.2 Hz).

$^{31}$P $\{^1$H$\}$ NMR (d$_8$-THF, 25 °C): $\delta$ -66.6 (q, br, $^1$J$_{PB}$ = 37.2 Hz).

$^7$Li $\{^1$H$\}$ NMR (d$_8$-THF, 25 °C): $\delta$ -0.7.

\[\text{[(Me}_3\text{Si)}_2\text{CH}]{\text{P(C}_6\text{H}_4\text{-2-CH}_2\text{OMe})(BH}_3\text{)}\text{Na(tmeda)}\text{]}_2 (50):\]

To a solution of 39 (0.37 g, 1.14 mmol) in THF (15 mL) was added a solution of benzylsodium (0.13 g, 1.14 mmol) in THF (15 mL). After 1 h stirring the solvent was removed in vacuo to yield an off-white solid. The product was dissolved in the minimal amount of toluene containing tmeda (0.2 mL, 1.14 mmol). The solvent was then carefully reduced in vacuo until the product began to precipitate slightly. The solution was allowed to
warm to room temperature, dissolving the product, and upon cooling (-30 °C) colourless crystals of 50 suitable for X-ray crystallography were deposited. Isolated crystalline yield: 0.46 g, 43%. Anal. Calcd for [{(Me₃Si)₂CH}P(C₆H₄-2-CH₂OMe)(BH₃)Na(tmeda)]₂: C 54.29, H 10.20, N 6.03%. Found C 54.14, H 10.16, N 5.93%. ¹H{¹¹B} NMR (d₈-THF, 25 °C): δ -0.02 (s, 9H, SiMe₃), 0.06 (s, 9H, SiMe₃), 0.40 (s, 1H, CHP), 0.62 (d, J_{PH} = 5.5 Hz, 3H, BH₃), 3.31 (s, 3H, OMe), 4.61 (d, J_{HH} = 12.4 Hz, 1H, CH₂), 4.92 (d, J_{HH} = 12.4 Hz, 1H, CH₂), 6.90 (t, J = 7.1 Hz, 1H, ArH), 6.95 (t, J = 7.3 Hz, 1H, ArH), 7.18 (d, J = 5.5 Hz, 1H, ArH), 7.68 (dd, J_{HH} = 7.1 Hz, J_{HH} = 3.4 Hz, 1H, ArH). ¹³C{¹H} NMR (d₈-THF, 25 °C): δ 1.27 (d, J_{PC} = 6.7 Hz, SiMe₃), 2.88 (SiMe₃), 8.01 (d, J_{PC} = 47.9 Hz, CHP), 42.29 (NMe₂), 56.86 (OMe), 57.95 (NCH₂), 73.52 (d, J = 32.6 Hz, CH₂), 123.34 (ArC), 125.19 (ArC), 125.81 (d, J_{PC} = 3.8 Hz, ArC), 132.30 (ArC), 139.88 (d, J_{PC} = 18.2 Hz, ArC), 151.69 (d, J_{PC} = 32.6 Hz). ¹¹B{¹H} NMR (d₈-THF, 25 °C): δ -31.9 (d, br, J_{BP} = 29.4 Hz). ³¹P{¹H} NMR (d₈-THF, 25 °C): δ /g3/g3 -65.3 (d, br, J_{PB} = 29.4 Hz).

[{(Me₃Si)₂CH}P(C₆H₄-2-CH₂OMe)(BH₃)K(pmdeta)]₂ (51):

To a solution of 39 (0.39 g, 1.20 mmol) in THF (15 mL) was added a solution of benzylpotassium (157 mg, 1.20 mmol) in THF (10 mL). After 1 h stirring the solvent was removed in vacuo, yielding an orange powder. The product was dissolved in toluene upon addition of pmdeta (0.3 mL, 1.44 mmol). The solvent was then carefully reduced in vacuo until the product began to precipitate slightly. The solution was allowed to warm to room temperature, dissolving the product, and upon cooling (-30 °C) colourless crystals of 51 suitable for X-ray crystallography were deposited. Isolated crystalline yield: 0.25 g, 39%. Anal. Calcd for [{(Me₃Si)₂CH}P(C₆H₄-2-CH₂OMe)(BH₃)K(pmdeta)]₂: C 53.60, H 10.12, N 7.81%. Found C 53.48, H 10.24, N 7.81%. ¹H{¹¹B} NMR (d₈-THF, 25 °C): δ -0.07 (s, 9H, SiMe₃), 0.09 (s, 9H, SiMe₃), 0.43 (s, 1H, CHP), 0.68 (d, J_{PH} = 5.0 Hz, 3H, BH₃), 2.15 (s, 12H, NMe₂), 2.19 (s, 3H, NMe), 2.31 (m, 4H, CH₂N), 2.41 (m, 4H, CH₂N), 3.29 (s, 3H, OMe), 4.53 (d, J_{HH} = 11.9 Hz, 1H, CH₂), 5.00 (d, J_{HH} = 11.9 Hz, 1H, CH₂), 6.92 (t, J = 7.3 Hz, 1H, ArH), 6.98 (t, J = 7.3 Hz, 1H, ArH), 7.17 (d, J = 6.9 Hz, 1H, ArH), 7.71 (d, J = 4.6 Hz, 1H, ArH). ¹³C{¹H} NMR (d₈-THF, 25 °C): δ 2.86 (SiMe₃), 8.26 (d, J_{PC} = 49.8 Hz, CHP), 42.32 (NMe), 45.27 (NMe₂), 56.40 (NCH₂), 56.69 (OMe), 57.86 (NCH₂), 73.48 (d, J_{PC} = 24.0 Hz, CH₂), 123.28 (ArC), 125.38 (ArC), 126.17 (d, J_{PC} = 2.9 Hz, ArC), 132.41 (ArC), 139.88 (d, J_{PC} = 18.2 Hz, ArC),
139.78 (d, $J_{PC} = 18.2$ Hz, ArC), 152.93 (d, $J_{PC} = 32.6$ Hz, ArC). $^{11}$B$^{1}$H NMR ($d_{8}$-THF, 25 °C): δ -29.2 (d, br, $J_{BP} = 19.6$ Hz).

$^{31}$P$^{1}$H NMR ($d_{8}$-THF, 25 °C): δ -64.2 (d, br, $J_{PB} = 19.6$ Hz).

$^{1}$H NMR ($d_{8}$-THF, 25 °C): δ -0.03 (s, 9H, SiMe$_3$), 0.07 (s, 9H, SiMe$_3$), 0.59 (q, $J_{BH} = 87.0$ Hz, $^{3}$J$_{PC} =$ 6.7 Hz, SiMe$_3$), 2.88 (SiMe$_3$), 7.52 (d, $J_{HHi} = 7.3$ Hz, 1H, ArH). $^{13}$C$^{1}$H NMR ($d_{8}$-THF, 25 °C): δ 15.05 (d, $^{3}$J$_{PC} =$ 6.7 Hz, SiMe$_3$), 2.88 (SiMe$_3$), 7.52 (d, $J_{PC} = 48.0$ Hz, CHP), 15.05 (d, $^{4}$J$_{PC} =$ 13.4 Hz, SMe), 122.28 (ArC), 122.52 (ArC), 124.68 (ArC), 133.51 (ArC), 143.35 (d, $^{2}$J$_{PC} =$ 24.0 Hz, ArC), 149.95 (d, $^{1}$J$_{PC} =$ 32.6 Hz, ArC). $^{11}$B$^{1}$H NMR ($d_{8}$-THF, 25 °C): δ -32.9 (d, br, $J_{BP} =$ 39.2 Hz).

$^{31}$P$^{1}$H NMR ($d_{8}$-THF, 25 °C): δ -59.5 (q, br, $J_{PB} =$ 39.2 Hz). $^{7}$Li NMR ($d_{8}$-THF, 25 °C): δ 2.3.

[[{(Me$_3$Si)$_2$CH}P(BH$_3$)(C$_6$H$_4$-2-SMe)Na(tmeda)]$\infty$ (65):

To a solution of 40 (0.47 g, 1.43 mmol) in diethyl ether (15 mL) was added n-BuLi (0.7 mL of a 2.5 M solution in hexanes, 1.75 mmol) and this mixture was stirred at room temperature for 1 h. Solvent was removed in vacuo to yield a white powder, which was crystallized from cold (5 °C) toluene (5 mL) containing a few drops of THF, to yield 64 as colourless blocks suitable for X-ray crystallography. Crude yield: 0.48 g, 100%. Anal. Calcd. For [{(Me$_3$Si)$_2$CH}P(BH$_3$)(C$_6$H$_4$-2-SMe)Li(THF)]$^2$: C 50.29, H 8.74%. Found C 50.40, H 8.65%.

$^{1}$H NMR ($d_{8}$-THF, 25 °C): δ -29.2 (d, br, $J_{BP} =$ 19.6 Hz).

$^{31}$P$^{1}$H NMR ($d_{8}$-THF, 25 °C): δ -64.2 (d, br, $J_{PB} =$ 19.6 Hz).

$^{11}$B$^{1}$H NMR ($d_{8}$-THF, 25 °C): δ -32.9 (d, br, $J_{BP} =$ 39.2 Hz).

$^{31}$P$^{1}$H NMR ($d_{8}$-THF, 25 °C): δ -59.5 (q, br, $J_{PB} =$ 39.2 Hz).

$^{7}$Li NMR ($d_{8}$-THF, 25 °C): δ 2.3.

{{(Me$_3$Si)$_2$CH}P(BH$_3$)(C$_6$H$_4$-2-SMe)Na(tmeda)]$\infty$ (65):

To a solution of 40 (0.47 g, 1.43 mmol) in diethyl ether (15 mL) was added n-BuLi (0.7 mL of a 2.5 M solution in hexanes, 1.75 mmol) and this mixture was stirred at room temperature for 1 h. Solvent was removed in vacuo to yield a white powder, which was crystallized from cold (5 °C) toluene (5 mL) containing a few drops of THF, to yield 64 as colourless blocks suitable for X-ray crystallography. Crude yield: 0.48 g, 100%. Anal. Calcd. For [{(Me$_3$Si)$_2$CH}P(BH$_3$)(C$_6$H$_4$-2-SMe)Li(THF)]$^2$: C 50.29, H 8.74%. Found C 50.40, H 8.65%.

$^{1}$H NMR ($d_{8}$-THF, 25 °C): δ -29.2 (d, br, $J_{BP} =$ 19.6 Hz).

$^{31}$P$^{1}$H NMR ($d_{8}$-THF, 25 °C): δ -64.2 (d, br, $J_{PB} =$ 19.6 Hz).

$^{11}$B$^{1}$H NMR ($d_{8}$-THF, 25 °C): δ -32.9 (d, br, $J_{BP} =$ 39.2 Hz).

$^{31}$P$^{1}$H NMR ($d_{8}$-THF, 25 °C): δ -59.5 (q, br, $J_{PB} =$ 39.2 Hz). $^{7}$Li NMR ($d_{8}$-THF, 25 °C): δ 2.3.
Found C 51.38, H 9.76%. $^1$H{$^{11}$B} NMR (d$_8$-THF, 25 °C): δ -0.05 (s, 9H, SiMe$_3$), 0.11 (s, 9H, SiMe$_3$), 0.72 (d, $^2$J$_{PH}$ = 6.9 Hz, 3H, BH$_3$), 0.87 (d, $^2$J$_{PH}$ = 5.5 Hz, 1H, CHP), 2.15 (s, 12H, NMe$_2$), 2.20 (s, 4H, NCH$_2$), 2.33 (s, 3H, SMe), 6.84 (t, $^1$J$_{HH}$ = 7.1 Hz, 1H, ArH), 6.92 (d, $^1$J$_{HH}$ = 8.3 Hz, 1H, ArH), 6.96 (t, $^1$J$_{HH}$ = 6.7 Hz, 1H, ArH), 7.84 (d, $^1$J$_{HH}$ = 7.3 Hz, 1H, ArH).

$^{13}$C{$^1$H} NMR (d$_8$-THF, 25 °C): δ 1.60 (d, $^3$J$_{PC}$ = 6.7 Hz, SiMe$_3$), 2.90 (s, SiMe$_3$), 6.94 (d, $^1$J$_{PC}$ = 43.2 Hz, CHP), 14.85 (d, $^4$J$_{PC}$ = 10.6 Hz, SMe), 46.20 (NMe), 58.90 (NMe$_2$), 123.57 (d, $^2$J$_{PC}$ = 3.7 Hz, ArC), 124.04, 125.88, 132.72, 134.86 (ArC), 143.45 (d, $^1$J$_{PC}$ = 22.6 Hz, ArC). $^{11}$B{$^1$H} NMR (d$_8$-THF, 25 °C): δ -33.5 (d, br, $^1$J$_{BP}$ = 29.4 Hz).

$^{31}$P{$^1$H} NMR (d$_8$-THF, 25 °C): δ -58.6 (q, br, $^1$J$_{PB}$ = 29.4 Hz).

To a solution of 40 (0.55 g, 1.67 mmol) in diethyl ether (15 mL) was added a slurry of benzylpotassium (224 mg, 1.72 mmol) in diethyl ether (15 mL). This mixture was stirred at room temperature for 1 h and then solvent was removed in vacuo to give a white powder. This powder was dissolved in toluene (5 mL) and pmdeta (0.3 ml, 1.44 mmol). The solvent was then carefully reduced in vacuo until the product began to precipitate slightly. The solution was allowed to warm to room temperature, dissolving the product, and upon cooling to 5 °C colourless crystals of 66 suitable for X-ray crystallography were deposited. Crude yield: 0.57 g, 93%. Anal. Calcd. For [{(Me$_3$Si)$_2$CH}P(BH$_3$)(C$_6$H$_4$-2-SMe)K(pmdeta)]$_2$: C 51.18, H 9.71, N 7.78%. Found C 51.09, H 9.75, N 7.74%. $^1$H{$^{11}$B} NMR (d$_8$-THF, 25 °C): δ 0.01 (s, 9H, SiMe$_3$), 0.04 (s, 9H, SiMe$_3$), 0.73 (d, $^2$J$_{PH}$ = 5.5 Hz, 3H, BH$_3$), 0.83 (d, $^2$J$_{PH}$ = 4.2 Hz, 1H, CHP), 2.16 (s, 12H, NMe$_2$), 2.19 (s, 3H, NMe), 2.31 (m, 4H, CH$_2$N), 2.32 (s, 3H, SMe), 2.42 (m, 4H, CH$_2$N), 6.84 (t, $^1$J$_{HH}$ = 7.4 Hz, 1H, ArH), 6.90 (d, $^1$J$_{HH}$ = 6.9 Hz, 1H, ArH), 6.95 (t, $^1$J$_{HH}$ = 7.55 Hz, 1H, ArH), 7.75 (d, $^1$J$_{HH}$ = 7.8 Hz, 1H, ArH). $^{13}$C{$^1$H} NMR (d$_8$-THF, 25 °C): δ 2.36 (d, $^3$J$_{PC}$ = 6.71 Hz, SiMe$_3$), 3.73 (d, $^3$J$_{PC}$ = 1.9 Hz, SiMe$_3$), 8.03 (d, $^4$J$_{PC}$ = 47.0 Hz, CHP), 15.75 (d, $^4$J$_{PC}$ = 13.4 Hz, SMe), 43.15 (NMe), 46.16 (NMe$_2$), 57.24 (NCH$_2$), 58.70 (NCH$_3$), 122.03 (d, $^2$J$_{PC}$ = 3.8 Hz, ArC), 122.45, 125.78, 134.25 (ArC), 143.48 (d, $^2$J$_{PC}$ = 22.0 Hz, ArC), 150.42 (d, $^1$J$_{PC}$ = 27.8 Hz, ArC). $^{11}$B{$^1$H} NMR (d$_8$-THF, 25 °C): δ -30.6 (d, br, $^1$J$_{BP}$ = 19.6 Hz).

$^{31}$P{$^1$H} NMR (d$_8$-THF, 25 °C): δ -58.3 (q, br, $^1$J$_{PB}$ = 19.6 Hz).
[(Me₃Si)₂CH]P(BH₃)₂(C₆H₄-2-SMe)Li(12-crown-4)] (72·(12-crown-4)):

To a solution of 40 (0.57 g, 1.74 mmol) in THF (10 mL) was added n-BuLi (0.7 mL of a 2.5 M solution in hexane, 1.75 mmol). After 1 h stirring, H₃B·SMe₂ (0.90 mL of 2 M solution in THF, 1.80 mmol) was added to the reaction mixture, turning the solution from yellow to colourless. After 1 h further stirring, the solvent was removed in vacuo to yield a colourless solid, which was promptly dissolved in a solution toluene (10 mL) containing a few drops of Et₂O and 12-crown-4 (0.3 mL, 1.84 mmol). The solution was then filtered, and the compound precipitated from solution at room temperature. Isolated yield: 0.55 g, 60%. Anal. Calcd for [(SiMe₃)₂CH]P(BH₃)₂(C₆H₄-2-SMe)Li(12-crown-4): C 50.29, H 9.40%. Found C 50.13, H 9.39%.

1H{¹¹B} NMR (d₈-THF, 25 °C): δ 0.07 (s, 18H, SiMe₃), 0.34 (d, JPH = 8.3 Hz, 1H, CHP), 0.80 (d, JPH = 10.5 Hz, 6H, BH₃), 2.42 (s, 3H, SMe), 3.74 (s, 16H, 12-crown-4), 6.93 (t, JHH = 7.3 Hz, 1H, ArH), 7.09 (t, JHH = 7.6 Hz, 1H, ArH), 7.22 (d, JHH = 7.8 Hz, 1H, ArH), 8.11 (t, JHH = 8.9 Hz, 1H, ArH).

13C{¹H} NMR (d₈-THF, 25 °C): δ 3.09 (SiMe₃), 6.98 (d, JPC = 3.8 Hz, CHP), 17.40 (SMe), 68.53 (12-crown-4), 123.7 (d, JPC = 8.6 Hz, ArC), 127.32 (ArC), 128.10 (d, JPC = 3.8 Hz, ArC), 135.07 (d, JPC = 12.46 Hz, ArC), 143.23 (ArC), 143.62 (d, JPC = 26.8 Hz, ArC). ¹¹B{¹H} NMR (d₈-THF, 25 °C): δ -32.6 (d, br, JBP = 68.6 Hz).

³¹P{¹H} NMR (d₈-THF, 25 °C): δ -4.6 (m, br, JPB = 68.6 Hz). ⁷Li NMR (d₈-THF, 25 °C): δ -0.7.

[(Me₃Si)₂CH]P(C₆H₄-2-OMe)(BH₃)Li(THF)] (85):

To a solution of 41 (0.20 g, 0.64 mmol) in Et₂O (20 mL) was added n-BuLi (0.4 mL of 1.9 M solution in hexane, 0.76 mmol). After 1 h stirring, the solvent was removed to yield a yellow solid. The product was dissolved in the minimal amount of THF, which was removed in vacuo, leaving a sticky residue. Upon addition of light petroleum, the product precipitated as a white powder. The mother liquor was removed via cannula, isolating the solid, which was then washed with cold light petroleum. Isolated yield: 0.13 g, 54%. ¹H{¹¹B} NMR (d₈-THF, 25 °C): δ -0.11 (s, 9H, SiMe₃), 0.15 (s, 9H, SiMe₃), 0.62 (d, JPH = 3.2 Hz, 3H, BH₃), 0.73 (d, JPH = 6.9 Hz, 1H, CHP), 1.76 (m, 4H, THF), 3.65 (m, 4H, THF), 3.75 (s, 3H, OMe), 6.61 (dd, JHH = 7.8 Hz, JHH = 5.1 Hz, 1H, ArH), 6.65 (t, JHH = 7.6 Hz, 1H, ArH), 6.90 (d, JHH = 7.6 Hz, 1H, ArH), 7.69 (d, JHH = 6.9 Hz, 1H, ArH). ¹³C{¹H} NMR (d₈-THF, 25 °C): δ 1.46 (d, JPC = 8.6 Hz, SiMe₃), 2.82 (SiMe₃), 6.17 (d, JPC = 44.1 Hz, CHP), 25.46 (THF), 54.55
(OMe), 67.40 (THF), 109.25 (ArC), 119.44 (ArC), 124.65 (ArC), 133.76 (ArC), 140.28 (d, \( J_{PC} = 36.4 \) Hz, ArC), 161.39 (d, \( J_{PC} = 10.5 \) Hz, ArC). \(^{11}\)B\{\(^1\)H\} NMR (\( d_8\)-THF, 25 °C): δ -34.3 (d, \( 1 J_{PB} = 39.2 \) Hz).

\[^{31}\]P\{\(^1\)H\} NMR (\( d_8\)-THF, 25 °C): δ -62.5 (d, \( 1 J_{PB} = 39.2 \) Hz).

\(^7\)Li NMR (\( d_8\)-THF, 25 °C): δ -0.58.

\([\{(\text{Me}_3\text{Si})_2\text{CH}\}P(\text{C}_6\text{H}_4-2-\text{OMe})(\text{BH}_3)\text{Na}(\text{THF})]\) (86):

A solution of 41 (0.21 g, 0.67 mmol) and benzylsodium (0.08 g, 0.67 mmol) in Et\(_2\)O (30 mL) was stirred for 1 h. The solvent was removed \textit{in vacuo} to yield a yellow solid. The product was dissolved in the minimal amount of THF, and upon addition of light petroleum ether the product precipitated from solution as a white powder, which was isolated by removing the mother liquor \textit{via} canula and then washed with cold light petroleum. Crude yield: 0.25 g, 96%. Anal. Calcd for \([\{(\text{Me}_3\text{Si})_2\text{CH}\}P(\text{C}_6\text{H}_4-2-\text{OMe})(\text{BH}_3)\text{Na}(\text{THF})]\): C 53.19, H 9.18%. Found C 53.06, H 9.18%.

\[^1\]H\{\(^{11}\)B\} NMR (\( d_8\)-THF, 25 °C): δ -0.07 (s, 9H, SiMe\(_3\)), 0.15 (s, 9H, SiMe\(_3\)), 0.66 (d, \( 2 J_{PH} = 7.3 \) Hz, 1H, CHP), 0.72 (d, \( 2 J_{PH} = 6.9 \) Hz, 3H, BH\(_3\)), 1.79 (m, 4H, THF), 3.63 (m, 4H, THF), 3.77 (s, 3H, OMe), 6.66 (m, 2H, ArH), 6.92 (t, \( J = 7.3 \) Hz, 1H, ArH), 7.72 (m, 1H, ArH). \(^{13}\)C\{\(^1\)H\} NMR (\( d_8\)-THF, 25 °C): δ 1.41 (d, \( 2 J_{PC} = 8.6 \) Hz, SiMe\(_3\)), 2.79 (SiMe\(_3\)), 6.09 (d, \( 1 J_{PC} = 41.2 \) Hz, CHP), 25.46 (THF), 54.57 (OMe), 67.33 (THF), 109.16 (ArC), 119.60 (ArC), 124.91 (ArC), 133.93 (ArC), 139.43 (d, \( 1 J_{PC} = 29.7 \) Hz ArC), 161.08 (d, \( J_{PC} = 9.6 \) Hz).

\[^{31}\]P\{\(^1\)H\} NMR (\( d_8\)-THF, 25 °C): δ -64.3 (d, br, \( 1 J_{PB} = 29.4 \) Hz).

\([\{(\text{Me}_3\text{Si})_2\text{CH}\}P(\text{C}_6\text{H}_4-2-\text{OMe})(\text{BH}_3)\text{K(pmdeta)}]\) (87):

To a solution of 41 (0.88 g, 2.82 mmol) in THF (20 mL) was added a solution of BnK (0.37 g, 2.82 mmol) in THF (20 mL). After 1 h stirring the solvent was removed \textit{in vacuo} to yield a yellow solid. The product was dissolved in the minimal amount of toluene and pmdeta (0.6 mL, 2.87 mmol). The solvent was then carefully reduced \textit{in vacuo} until the product began to precipitate slightly. The solution was allowed to warm to room temperature, dissolving the product, and upon cooling (5 °C) colourless crystals of 87 suitable for X-ray crystallography were deposited. Isolated crystalline yield: 0.54 g, 37%. Anal. Calcd for
\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P}(\text{C}_6\text{H}_4\text{-2-OMe})(\text{BH}_3)\text{K}(\text{pmdeta})\}: \text{C} 52.75, \text{H} 10.01, \text{N} 8.02\%. \text{Found C} 56.69, \text{H} 9.92, \text{N} 7.87\%.

\text{\textsuperscript{1}H\{}^{11}\text{B}\} \text{NMR} (\text{C}_6\text{D}_6, 25 ^\circ\text{C}): \delta -0.27 (s, 9\text{H}, \text{SiMe}_3), 0.45 (s, 9\text{H}, \text{SiMe}_3), 1.05 (d, J_{PH} = 5.5 \text{ Hz}, 3\text{H}, \text{BH}_3), 1.07 (d, J_{PH} = 7.8 \text{ Hz}, 1\text{H}, \text{CHP}), 2.01 (s, 8\text{H}, \text{NCH}_2), 2.05 (s, 3\text{H}, \text{NMe}), 2.11 (s, 12\text{H}, \text{NMe}_2), 3.53 (s, 3\text{H}, \text{OMe}), 6.54 (dd, J = 7.8 \text{ Hz}, J = 2.8 \text{ Hz}, 1\text{H}, \text{ArH}), 6.94 (t, J = 7.3 \text{ Hz}, 1\text{H}, \text{ArH}), 7.06 (d, J = 7.6 \text{ Hz}, 1\text{H}, \text{ArH}), 8.04 (\text{m, br}, 1\text{H}, \text{ArH}). \text{\textsuperscript{13}C\{}^{1}\text{H}\} \text{NMR} (\text{C}_6\text{D}_6, 25 ^\circ\text{C}): \delta 2.21 (d, J_{PC} = 8.6 \text{ Hz}, \text{SiMe}_3), 3.39 (\text{SiMe}_3), 6.00 (d, J_{PC} = 41.2 \text{ Hz}, \text{CHP}), 41.11 (\text{NMe}), 44.93 (\text{NMe}_2), 54.29 (\text{OMe}), 55.74 (\text{NCH}_2), 56.88 (\text{NCH}_2), 108.92 (\text{ArC}), 120.07 (\text{ArC}), 125.76 (\text{ArC}), 133.87 (\text{ArC}), 138.48 (d, J_{PC} = 29.7 \text{ Hz}, \text{ArC}), 161.24 (d, J_{PC} = 9.58 \text{ Hz}, \text{ArC}). \text{\textsuperscript{11}B\{}^{1}\text{H}\} \text{NMR} (\text{C}_6\text{D}_6, 25 ^\circ\text{C}): \delta -32.3 (d, \text{br}, J_{BP} = 29.8 \text{ Hz}). \text{\textsuperscript{31}P\{}^{1}\text{H}\} \text{NMR} (\text{C}_6\text{D}_6, 25 ^\circ\text{C}): \delta -63.0 (d, \text{br}, J_{PB} = 29.8 \text{ Hz}).

\text{To a solution of 41} (0.23 \text{ g}, 0.74 \text{ mmol}) \text{ in THF (20 mL)} \text{ was added} \text{tBuLi (0.4 mL of 2.0 M solution in hexane, 0.80 mmol)}. \text{After 1 h stirring, the solvent was removed to yield 85. The product was dissolved in toluene (20 mL) and tmeda (0.2 mL, 1.30 mmol) was added. After 16 h stirring 85 was fully converted into 89 and other side products. 89 was extracted into hexamthydisiloxane, then the solvent was removed \textit{in vacuo} to yield an oil. Single crystals of 89 were grown from cold (-30 \textdegree \text{C}) methycyclohexane. Isolated yield 0.09 \text{ g}, 38\%. \text{\textsuperscript{1}H NMR} (\text{C}_6\text{D}_6, 25 ^\circ\text{C}): \delta 0.24 (s, 18 \text{H}, \text{SiMe}_3), 0.65 (dd, J_{HH} = 5.5 \text{ Hz}, J_{PH} = 1.9 \text{ Hz}, 1\text{H}, \text{CHP}), 4.51 (dd, J_{PH} = 217.6 \text{ Hz}, J_{HH} = 5.5 \text{ Hz}), 6.47 (d, J_{HH} = 8.3 \text{ Hz}, 1\text{H}, \text{ArH}), 6.79 (t, J_{HH} = 7.3 \text{ Hz}, 1\text{H}, \text{ArH}), 7.20 (t, J_{HH} = 7.3 \text{ Hz}, 1\text{H}, \text{ArH}), 7.47 (t, J_{HH} = 7.3 \text{ Hz}, 1\text{H}, \text{ArH}). \text{\textsuperscript{13}C\{}^{1}\text{H}\} \text{NMR} (\text{C}_6\text{D}_6, 25 ^\circ\text{C}): \delta 1.07 (\text{SiMe}_3), 4.38 (d, J_{PC} = 42.2 \text{ Hz}, \text{CHP}), 109.4 (\text{ArC}), 120.52 (d, J_{PC} = 5.8 \text{ Hz}, \text{ArC}), 129.7 (\text{ArC}), 134.94 (d, J_{PC} = 18.2 \text{ Hz}, \text{ArC}), 160.99 (d, J_{PC} = 6.7 \text{ Hz}, \text{ArC}), 161.20 (d, J_{PC} = 2.9 \text{ Hz}, \text{ArC}). \text{\textsuperscript{31}P NMR} (\text{C}_6\text{D}_6, 25 ^\circ\text{C}): \delta -72.7 (d, J_{PH} = 219.6 \text{ Hz}). \text{\textsuperscript{7}Li NMR} (\text{C}_6\text{D}_6, 25 ^\circ\text{C}): \delta 0.7.

\text{\{(Me}_3\text{Si})_2\text{CH\}}\text{PMe(\text{C}_6\text{H}_4\text{-2-OMe})(\text{BH}_3)} (90):

\text{To a solution of 41} (0.31 \text{ g}, 0.99 \text{ mmol}) \text{ in THF (15 mL)} \text{ was added} \text{tBuLi (0.4 mL of a 2.5 M solution in hexane, 1.00 mmol)}. \text{After ½ h stirring MeI (0.07 mL, 1.12 mmol) was added to
the solution. After a further ½ h stirring, the solvent was removed **in vacuo** to yield a white solid. Isolated yield: 0.32 g, 99%. $^1$H{$^{11}$B} NMR (CDCl$_3$, 25 °C): $\delta$ -0.08 (s, 9H, SiMe$_3$), 0.31 (s, 9H, SiMe$_3$), 0.88 (d, $^2$$J_{PH}$ = 14.7 Hz, 3H, BH$_3$), 1.46 (d, $^2$$J_{PH}$ = 20.2 Hz, 1H, CHP), 1.66 (d, $^2$$J_{PH}$ = 10.1 Hz, 3H, PMe), 3.91 (s, 3H, OMe), 6.88 (dd, $^2$$J_{HH}$ = 8.3 Hz, $^2$$J_{HH}$ = 3.2 Hz, 1H, ArH), 7.06 (t, $^2$$J_{HH}$ = 7.3 Hz, 1H, ArH), 7.48 (t, $^2$$J_{HH}$ = 7.8 Hz, 1H, ArH), 7.92 (dd, $^2$$J_{HH}$ = 13.1 Hz, $^2$$J_{HH}$ = 7.6 Hz, 1H, ArH).$^{13}$C{$^1$H} NMR (CDCl$_3$, 25 °C): $\delta$ 2.40 (d, $^3$$J_{PC}$ = 2.9 Hz, SiMe$_3$), 3.50 (d, $^3$$J_{PC}$ = 1.9 Hz, SiMe$_3$), 10.40 (d, $^J_{PC}$ = 4.8 Hz, CHP), 16.68 (d, $^J_{PC}$ = 39.3 Hz, PMe), 55.17 (OMe), 110.58 (d, $^J_{PC}$ = 3.83 Hz, ArC), 120.93 (d, $^J_{PC}$ = 12.5 Hz, ArC), 121.63 (d, $^J_{PC}$ = 50.8 Hz ArC), 132.90 (ArC), 135.77 (d, $^J_{PC}$ = 15.3 Hz, ArC), 161.33 (ArC).$^{11}$B{$^1$H} NMR (CDCl$_3$, 25 °C): $\delta$ -37.5 (d, br, $^J_{PB}$ = 58.8 Hz). $^{31}$P{$^1$H} NMR (CDCl$_3$, 25 °C): $\delta$ 11.7 (q, br, $^J_{PB}$ = 58.8 Hz).

{(Me$_3$Si)$_2$CH}PH(C$_6$H$_4$-2-OCD$_3$)(BH$_3$) (101):

To a cold (0 °C) solution of KOH (0.63 g, 12.00 mmol) in acetonitrile (10 mL) was added a solution of 2-bromophenol (2.0 mL of 5.0 M solution in acetonitrile, 10.00 mmol) in acetonitrile (10 mL). After ½ h stirring at 0 °C CD$_3$I (0.75 mL, 12 mmol) was added to the solution. The reaction was stirred for 40 h. The solvent was removed in vacuo, and the residue was washed with light petroleum (3 x 20 mL). The solvent was removed to yield a colourless oil (2-bromo-$d_3$-anisole). Yield 1.19 g, 62 %. To a cold (0 °C) solution of 2-bromo-$d_3$-anisole (1.19 g, 6.23 mmol) in Et$_2$O (10 mL) was added $^n$BuLi (2.5 mL of a 2.5 M solution in hexane, 6.25 mmol). After 2 h stirring at 0 °C, the solution was added dropwise to a cold (-78 °C) solution of 43 (1.70 g, 6.51 mmol) in Et$_2$O (20 mL). The reaction was stirred for 16 h and allowed to reach room temperature. Solid LiAlH$_4$ (0.28 g, 7.3 mmol) was added to the solution in situ, then the mixture was heated under reflux for 2 h. When the solution was cool, BH$_3$·SMe$_2$ (3.2 mL of 2 M solution in THF, 6.4 mmol) was added, and the solution stirred for 1 h at room temperature. The reaction was quenched with water. The product was extracted into THF (3 x 20 mL) and the extracts were washed with brine (30 mL). The organic phase was dried with MgSO$_4$, filtered, and then the solvent was removed in vacuo. The product was dissolved in hot $n$-hexane, and crystals of {(Me$_3$Si)$_2$CH}PH(C$_6$H$_4$-2-OCD$_3$)(BH$_3$) (101) were deposited upon cooling to -30 °C. Isolated yield: 0.83 g, 42%. $^1$H{$^{11}$B} NMR (CDCl$_3$, 25 °C): $\delta$ -0.01 (s, 9H, SiMe$_3$), 0.28 (s, 9H, SiMe$_3$), 0.89 (dd, $^3$$J_{HH}$ =
6.6 Hz, $^2J_{PH} = 14.9$ Hz, 3H, BH$_3$), 1.07 (d, $J_{PH} = 20.2$ Hz, 1H, CHP), 5.84 (dq, $^1J_{PH} = 384.0$ Hz, $^3J_{HH} = 12.9$, 1H, PH), 6.89 (dd, $J_{HH} = 8.2$ Hz, $J_{HH} = 2.8$ Hz, 1H, ArH), 7.04 (t, $J_{HH} = 6.9$ Hz, 1H, ArH), 7.47 (t, $J_{HH} = 7.8$ Hz, 1H, ArH), 7.91 (dd, $J_{HH} = 13.3$ Hz, $J_{HH} = 7.3$ Hz, 1H, ArH), 7.84 (dq, $J_{HH} = 384.0$ Hz, $^3J_{HH} = 12.9$, 1H, PH), 5.84 (dq, $J_{HH} = 13.3$ Hz, $J_{HH} = 7.3$ Hz, 1H, ArH), 7.47 (t, $J_{HH} = 7.8$ Hz, 1H, ArH), 7.91 (dd, $J_{HH} = 13.3$ Hz, $J_{HH} = 7.3$ Hz, 1H, ArH).

$^{13}$C{${}^1$H} NMR (CDCl$_3$, 25 °C): δ 1.25 (d, $J_{PC} = 2.9$ Hz, SiMe$_3$), 2.10 (d, $J_{PC} = 2.9$ Hz, SiMe$_3$), 6.49 (d, $^2J_{PC} = 3.8$ Hz, CHP), 110.20 (d, $J_{PC} = 3.8$ Hz, ArC), 116.88 (d, $J = 50.8$ Hz, ArC), 121.07 (d, $J_{PC} = 12.5$ Hz, ArC), 133.47 (ArC), 136.25 (d, $J_{PC} = 15.3$ Hz, ArC), 160.78 (ArC).

$^{11}$B{${}^1$H} NMR (CDCl$_3$, 25 °C): δ -40.4 (d, br, $J_{PB} = 49.0$ Hz).

$^{31}$P{${}^1$H} NMR (CDCl$_3$, 25 °C): δ -22.3 (q, br, $J_{PB} = 49.0$ Hz).

{(Me$_3$Si)$_2$CH}PH(C$_6$H$_4$-2-OMe)(BD$_3$) (102): used in situ

To a solution of 46 (0.37 g, 1.24 mmol) in THF (5 mL) was added BD$_3$-THF (1.2 mL of a 1.0 M solution in THF, 1.20 mmol). After one hour stirring the solvent was removed in vacuo to yield a white solid (102). 102 was dissolved in THF (5 mL) and used in situ.

[{(Me$_3$Si)$_2$CH}P(C$_6$H$_4$-2-OMe)Li(tmeda)] (106):

To a solution of 46 (0.39 g, 1.31 mmol) in THF (20 mL) was added nBuLi (0.5 mL of a 2.5 M solution in hexanes, 1.25 mmol). After 1 h stirring the solvent was removed in vacuo to yield a yellow solid. The product was dissolved in toluene and tmeda (0.2 mL, 1.31 mmol). The solvent was then carefully reduced in vacuo until the product began to precipitate slightly. The solution was allowed to warm to room temperature, dissolving the product, and upon cooling (-30 °C), crystals of the adduct [{(Me$_3$Si)$_2$CH}P(C$_6$H$_4$-2-OMe)Li(tmeda)] suitable for X-ray crystallography were deposited. Isolated crystalline yield: 0.32 g, 58%. Anal. Calcd for [{(Me$_3$Si)$_2$CH}P(C$_6$H$_4$-2-OMe)Li(tmeda)]: C 57.11, H 10.06, N 6.66%. Found C 56.98, H 9.91, N 6.53%. $^1$H NMR (d$_8$-THF, 25 °C): δ 0.11 (s, 18H, SiMe$_3$), 0.18 (s, 1H, CHP), 2.18 (s, 12H, NMe$_2$), 2.31 (s, 4H, NCH$_2$), 3.81 (s, 3H, OMe), 6.19 (t, $J_{HH} = 7.6$ Hz, 1H, ArH), 6.37 (dd, $^1J_{HH} = 6.9$ Hz, $^2J_{HH} = 4.2$ Hz, 1H, ArH), 6.51 (t, $J_{HH} = 7.6$ Hz, 1H, ArH), 6.77 (d, $J_{HH} = 7.7$ Hz, 1H, ArH). $^{13}$C{${}^1$H} NMR (CDCl$_3$, 25 °C): δ 0.53 (d, $^3J_{PC} = 5.8$ Hz, SiMe$_3$), 4.06 (d, $^2J_{PC} = 42.2$ Hz, CHP), 45.30 (NMe$_2$), 55.09 (OMe), 57.95 (NCH$_2$), 107.75 (ArC), 113.07 (d, $J_{PC} = 3.8$ Hz, ArC), 121.84 (ArC), 125.48 (d, $J_{PC} = 2.9$ Hz, ArC), 129.68 (ArC), 154.9 (d,
$^2J_{PC} = 22.0 \text{ Hz, ArC}$. $^{31}P\{^1H\}$ NMR ($d_8$-THF, 25 °C): $\delta$ -85.1. $^7$Li NMR ($d_8$-THF, 25 °C): $\delta$ 3.7.

$[{(\text{Me}_3\text{Si})_2\text{CH}}\text{P}(\text{BH}_3)_2(\text{C}_6\text{H}_4\text{-2-OMe})\text{Li(THF)}]\ (107)$:

To a solution of 41 (0.52 g, 1.67 mmol) in THF (10 mL) was added “BuLi (0.9 mL of a 1.9 M solution in hexane, 1.71 mmol). After 1 h stirring, H$_3$B·SMe$_2$ (0.9 mL, of a 2.0 M solution, 1.80 mmol) was added to the reaction mixture turning the solution from yellow to colourless. After 1 h further stirring, the solvent was removed in vacuo to yield 107. The product was crystallised from light petroleum in the presence of a few drops of THF as a colourless powder. Isolated yield: 0.06 g, 9%. Anal. Calcd for $[{(\text{SiMe}_3)_2\text{CH}}\text{P}(\text{BH}_3)_2(\text{C}_6\text{H}_4\text{-2-OMe})\text{Li(THF)}]$: C 53.48, H 9.97%. Found C 53.03, H 9.82%.

$^1H\{^{11}B\}$ NMR ($d_8$-THF, 25 °C): $\delta$ 0.04 (s, 18H, SiMe$_3$), 0.66 (dd, $^2J_{PH} = 11.0 \text{ Hz, } 6H, \text{BH}_3$), 1.56 (dd, $^2J_{PH} = 15.6 \text{ Hz, } 1H, \text{CHP}$), 1.78 (m, 4 H, THF), 3.62 (m, 4 H, THF), 2.42 (d, $^3J_{HH} = 2.8 \text{ Hz, } 3H, \text{OMe}$), 6.73 (t, $^5J_{HH} = 7.3 \text{ Hz, } 1H, \text{ArH}$), 7.76 (d, $^5J_{HH} = 8.3 \text{ Hz, } 1H, \text{ArH}$), 7.11 (t, $^5J_{HH} = 7.8 \text{ Hz, } 1H, \text{ArH}$), 7.87 (t, $^5J_{HH} = 9.2 \text{ Hz, } 1H, \text{ArH}$). $^{13}C\{^1H\}$ NMR ($d_8$-THF, 25 °C): $\delta$ 3.00 (d, $^3J_{PC} = 1.9 \text{ Hz, SiMe}_3$), 7.52 (d, $^1J_{PC} = 1.9 \text{ Hz, CHP}$), 25.46 (THF), 54.74 (OMe), 67.39 (THF), 110.64 (d, $^3J_{PC} = 2.9 \text{ Hz, ArC}$), 119.33 (d, $^3J_{PC} = 8.6 \text{ Hz, ArC}$), 128.39 (ArC), 132.26 (d, $^3J_{PC} = 29.7 \text{ Hz, ArC}$), 134.55 (d, $^3J_{PC} = 9.6 \text{ Hz, ArC}$), 162.34 (ArC). $^{11}B\{^1H\}$ NMR ($d_8$-THF, 25 °C): $\delta$ -33.3 (d, br, $^1J_{BP} = 68.6 \text{ Hz})$. $^{31}P\{^1H\}$ NMR ($d_8$-THF, 25 °C): $\delta$ -12.7 (m, br, $^1J_{PB} = 68.6 \text{ Hz}$). $^7$Li NMR ($d_8$-THF, 25 °C): $\delta$ -0.8.

$[{(\text{Me}_3\text{Si})_2\text{CH}}\text{P}(\text{C}_6\text{H}_4\text{-2-O})(\text{BH}_3)\text{Ca(THF)}]_4\ (108)$:

To a solution of 41 (0.98 g, 3.14 mmol) in THF (15 mL) was added BnK (0.47 g, 3.30 mmol) in THF (20 mL). After 1 h stirring the solution was added to a slurry of CaI$_2$ (0.48 g, 1.63 mmol) in THF (20 mL). After 16 h stirring the solvent was removed, then the residue was extracted into diethyl ether (50 mL). The solvent was again removed in vacuo, and the product was extracted into hexamethyldisiloxane. The product was crystallised from cold (5 °C) methylcyclohexane. Isolated yield: 0.63 g, 22% Anal. Calcd for $[{(\text{Me}_3\text{Si})_2\text{CH}}\text{P}(\text{C}_6\text{H}_4\text{-2-O})(\text{BH}_3)\text{Ca(THF)}]_4$:
2-O)(BH₃)Ca(THF)₄: C 51.67, H 8.79%. Found C 51.56, H 8.64%. ³¹P{¹H} NMR (d₈-THF, 25 °C): δ -69.1 (m, br).

\[(\text{Me}_3\text{Si})_2\text{CH}]\text{P(C}_6\text{H}_5\text{)}(\text{BH}_3)\text{Li(THF)}_2\]∞ (115):

To a solution of 42 (0.41 g, 1.26 mmol) in THF (15 mL) was added "BuLi (0.5 mL of 2.5 M solution in hexane, 1.25 mmol). After 1 h stirring the solvent was removed in vacuo to yield an off-white solid. THF was added to a solution of 115 in methylecyclohexane until product was dissolved. THF was carefully removed in vacuo, until the point of precipitation. Upon cooling to -30 °C colourless crystals of 115 suitable for X-ray crystallography were deposited. Isolated crystalline yield: 0.19 g, 35%. Anal. Calcd for \[(\text{Me}_3\text{Si})_2\text{CH}]\text{P(C}_6\text{H}_5\text{)}(\text{BH}_3)\text{Li(THF)}_2]\∞: C 58.32, H 10.02%. Found C 58.29, H 9.95%.

\[^{1}\text{H}\{^{11}\text{B}\} NMR (d₈-toluene, 25 °C): δ 0.29 (s, 9H, SiMe₃), 0.39 (s, 9H, SiMe₃), 0.63 (d, J_{PH} = 7.8 Hz, 1H, CHP), 1.04 (s, 3H, BH₃), 1.40 (m, 8H, THF), 3.54 (m, 8H, THF), 6.99 (t, J_{HH} = 7.3 Hz, 1H, ArH), 7.17 (t, J_{HH} = 7.1 Hz, 2H, ArH), 7.78 (t, J_{HH} = 6.9 Hz, 2H, ArH).\]

\[^{13}\text{C}\{^{1}\text{H}\} NMR (d₈-toluene, 25 °C): δ 2.29 (d, J_{PC} = 7.7 Hz, SiMe₃), 3.32 (SiMe₃), 8.86 (d, J_{PC} = 34.6 Hz, CHP), 25.12 (THF), 68.13 (THF), 124.23 (ArC), 127.14 (d, J_{PC} = 4.8 Hz, ArC), 131.84 (d, J_{PC} = 11.5 Hz, ArC), 149.62 (d, J_{PC} = 16.3 Hz, ArC).\]

\[^{11}\text{B}\{^{1}\text{H}\} NMR (d₈-toluene, 25 °C): δ -32.7 (d, br, J_{BP} = 49.0 Hz ).\]

\[^{31}\text{P}\{^{1}\text{H}\} NMR (d₈-toluene, 25 °C): δ -56.8 (q, br, J_{PB} = 49.0 Hz).\]

\[^{7}\text{Li}\{^{1}\text{H}\} NMR (d₈-toluene, 25 °C): δ 3.1.\]

\[(\text{Me}_3\text{Si})_2\text{CH}]\text{P(C}_6\text{H}_5\text{)}(\text{BH}_3)[\text{Na(12-crown-4)}] (116):

A solution of 42 (0.37 g, 1.31 mmol) and benzylsodium (0.15 g, 1.31 mmol) in THF (30 mL) was stirred for 1 h. The solvent was removed to yield a yellow solid. The product was dissolved in the minimal amount of toluene and THF. 12-crown-4 (0.4 mL, 2.62 mmol) was added to the solution, and THF was carefully removed in vacuo, until the product began to precipitate from solution. Upon warming to room temperature, the product had dissolved back into the solution. After cooling (-30 °C) colourless crystals of 116 suitable for X-ray crystallography were deposited. Isolated crystalline yield: 0.73 g, 86%. \[^{1}\text{H}\{^{11}\text{B}\} NMR (d₈-THF, 25 °C): δ -0.05 (s, br, 9H, SiMe₃), 0.14 (s, br, 9H, SiMe₃), 0.20 (d, J_{PH} = 5.5 Hz, 1H, 2-O)(BH₃)Ca(THF)₄: C 51.67, H 8.79%. Found C 51.56, H 8.64%. ³¹P{¹H} NMR (d₈-THF, 25 °C): δ -69.1 (m, br).
CHP), 0.97 (d, \(^2J_{PH} = 4.1\) Hz, 3H, BH\(^3\)), 3.63 (s, 32 H, 12-crown-4), 6.70 (t, \(^1J_{HH} = 7.6\) Hz, 1H, ArH), 6.91 (t, \(^1J_{HH} = 7.1\) Hz, 2H, ArH), 7.55 (m, 2H, ArH). \(^{13}C\{^1H\} \text{NMR} (d_8-\text{THF}, 25\,°C): \delta 1.81 (s, \text{br, SiMe}_3), 2.91 (s, \text{br, SiMe}_3), 10.51 (d, \(^1J_{PC} = 47.9\) Hz, CHP), 66.13 (12-crown-4), 121.11 (ArC), 125.73 (ArC), 131.84 (d, \(^1J_{PC} = 11.5\) Hz, ArC), 157.07 (d, \(^1J_{PC} = 35.5\) Hz, ArC). \(^{11}B\{^1H\} \text{NMR} (d_8-\text{THF}, 25\,°C): \delta -32.4 (s, \text{br}). \(^{31}P\{^1H\} \text{NMR} (d_8-\text{THF}, 25\,°C): \delta -41.0 (d, \text{br, } ^1J_{PB} = 26.1\) Hz).

\[\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P(C}_6\text{H}_5\text{)(BH}_3\})\text{K(pmdeta)}\] \(^2\) (117):

To a solution of 42 (0.45 g, 1.59 mmol) in THF (15 mL) was added a solution of benzylpotassium (0.21 g, 1.59 mmol) in THF (10 mL). After 1 h stirring the solvent was removed \textit{in vacuo} yielding an orange powder. The product was dissolved in toluene and pmdeta (0.3 mL, 1.44 mmol). The solvent was then carefully reduced \textit{in vacuo} until the product began to precipitate slightly. The solution was allowed to warm to room temperature, dissolving the product, and upon cooling (-30 °C) colourless crystals of 117 suitable for X-ray crystallography were deposited. Isolated crystalline yield: 0.41 g, 39%. Anal. Calcd for \[\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P(C}_6\text{H}_5\text{)(BH}_3\})\text{K(pmdeta)}\] \(^2\): C 53.52, H 10.21, N 8.51%. Found C 53.41, H 10.14, N 8.42%.

\(^{1}H\{^{11}B\} \text{NMR} (d_8-\text{toluene}, 25\,°C): \delta 0.28 (s, 9H, SiMe\(^3\)), 0.42 (s, 9H, SiMe\(^3\)), 0.61 (d, \(^2J_{PH} = 6.9\) Hz, 1H, CHP), 1.08 (d, \(^2J_{PH} = 4.1\) Hz, 3H, BH\(^3\)), 1.93 (m, 4H, NCH\(_2\)), 1.95 (m, 4H, NCH\(_2\)), 1.99 (s, 3H, NMe), 2.09 (s, 12H, NMe\(_2\)), 6.98 (t, \(^1J_{HH} = 7.3\) Hz, 1H, ArH), 7.20 (t, \(^1J_{HH} = 7.3\) Hz, 2H, ArH), 7.80 (t, \(^1J_{HH} = 6.4\) Hz, 2H, ArH). \(^{13}C\{^1H\} \text{NMR} (d_8-\text{toluene}, 25\,°C): \delta 2.25 (d, \(^3J_{PC} = 7.7\) Hz, SiMe\(_3\)), 3.20, (SiMe\(_3\)), 9.78 (d, \(^1J_{PC} = 43.1\) Hz, CHP), 41.00 (NMe), 44.80 (NMe\(_2\)), 55.60 (NCH\(_2\)), 56.76 (NCH\(_2\)), 123.42 (ArC), 127.09 (d, \(^{1}J_{PC} = 2.9\) Hz, ArC), 131.83 (d, \(^{1}J_{PC} = 11.5\) Hz, ArC), 153.07 (d, \(^{1}J_{PC} = 25.9\) Hz). \(^{11}B\{^1H\} \text{NMR} (d_8-\text{toluene}, 25\,°C): \delta -31.6 (d, \text{br, } ^{1}J_{BP} = 19.6\) Hz ). \(^{31}P\{^1H\} \text{NMR} (d_8-\text{toluene}, 25\,°C): \delta -50.6 (d, \text{br, } ^{1}J_{PB} = 19.6\) Hz).

\[\{\text{(Me}_3\text{Si)}_2\text{CH}\}\text{P(C}_6\text{H}_5\text{)(BH}_3\})\text{Sr} \] \(^2\) (119):

A solution of 42 (0.97 g, 3.44 mmol) and BnK (0.45 mmol 3.44 mmol) in diethyl ether (20 mL) was stirred for 1 h. The solvent was removed \textit{in vacuo} to yield a yellow/ orange solid.
The product was dissolved in toluene (20 mL) and added to a cold (-78 °C) solution of SrI_2 (0.59 g, 1.72 mmol) in toluene (20 mL). The solution was stirred overnight and allowed to reach room temperature. The solution was filtered through celite to remove KI and the solvent was removed in vacuo. The product was dissolved in methycyclohexane containing a few drops of THF and upon cooling (-30 °C) crystals of 119 were deposited. The product was washed with cold (0 °C) light petroleum and isolated as a yellow powder. Isolated yield: 0.20 g, 18 %. 

1H{^11}B NMR (d8-THF, 25 °C): δ 0.05 (s, 9H, SiMe_3), 0.10 (s, 9H, SiMe_3), 0.25 (d, J_PH = 5.5 Hz, 1H, CHP), 0.82 (d, J_PH = 4.1 Hz, 3H, BH_3), 6.76 (d, J_HH = 7.3 Hz, 1H, ArH), 6.94 (t, J_HH = 7.6 Hz, 2H, ArH), 7.50 (t, J_HH = 6.0 Hz, 2H, ArH). 

13C{^1}H NMR (d8-THF, 25 °C): δ 1.52 (SiMe_3), 2.66 (SiMe_3), 9.54 (d, J_PC = 45.1 Hz, CHP), 121.80 (ArC), 126.88 (d, J_PC = 3.8 Hz, ArC), 131.55 (d, J_PC = 12.5 Hz, ArC), 155.04 (d, J_PC = 30.7 Hz, ArC). 

11B{^1}H NMR (d8-THF, 25 °C): δ -31.8 (m, br, J_PB = 39.7 Hz). 

31P{^1}H NMR (d8-THF, 25 °C): δ -46.7 (q, br, J_PB = 39.7 Hz).

[(Me_3Si)_2CH]P(C_6H_5)(BH_3)_2Ba (120):

A solution of 42 (0.72 g, 2.55 mmol) and BnK (0.33 mmol 2.55 mmol) in diethyl ether (20 mL) was stirred for 1 h. The solvent was removed in vacuo to yield a yellow/ orange solid. The product was dissolved in toluene (20 mL) and added to a cold (-78 °C) solution of BaI_2 (0.50 g, 1.28 mmol) in toluene (20 mL). The solution was stirred overnight and allowed to reach room temperature. The solution was filtered through celite to remove KI and the solvent was removed in vacuo. The product was dissolved in methycyclohexane containing a few drops of THF and upon cooling (-30 °C) crystals of 120 were deposited. The product was washed with cold (0 °C) light petroleum and isolated as a yellow powder. Isolated yield: 0.27 g, 30% Anal. Calcd for [(Me_3Si)_2CH]P(C_6H_5)(BH_3)_2Ba: C 44.62, H 7.78%. Found C 44.72, H 7.88%. 

1H{^11}B NMR (d8-THF, 25 °C): δ 0.01 (s, 9H, SiMe_3), 0.14 (s, 9H, SiMe_3), 0.32 (d, J_PH = 5.5 Hz, 1H, CHP), 0.84 (d, J_PH = 4.1 Hz, 3H, BH_3), 6.84 (d, J_HH = 7.1 Hz, 1H, ArH), 7.01 (t, J_HH = 7.3 Hz, 2H, ArH), 7.53 (t, J_HH = 6.2 Hz, 2H, ArH). 

13C{^1}H NMR (d8-THF, 25 °C): δ 1.68 (d, J_PC = 5.8 Hz, SiMe_3), 2.76 (SiMe_3), 6.34 (d, J_PC = 44.1 Hz, CHP), 126.02 (ArC), 126.25 (d, J_PC = 3.8 Hz, ArC), 131.53 (d, J_PC = 12.5 Hz, ArC), 154.02 (d, J_PC = 28.8 Hz, ArC). 

11B{^1}H NMR (d8-THF, 25 °C): δ -31.5 (m, br, J_PB = 29.8 Hz). 

31P{^1}H NMR (d8-THF, 25 °C): δ -48.7 (q, br, J_PB = 29.8 Hz).
\[
\left\{\left(\text{Me}_3\text{Si}\right)_2\text{CH}\right\}\text{P}\left(\text{C}_6\text{H}_5\right)(\text{BH}_3)_2\text{Li(12-crown-4)}\right\} (123):
\]

To a solution of 42 (0.54 g, 1.91 mmol) in THF (10 mL) was added \[^6\text{BuLi}\] (0.8 mL of a 2.5 M solution in hexane, 2.0 mmol). After 1 h stirring, a solution of BH\(_3\).SMe\(_2\) (1.0 mL, of a 2.0 M solution in THF, 2.0 mmol) was added to the reaction mixture turning the solution from yellow to colourless. After 1 h further stirring, the solvent was removed \textit{in vacuo} to yield a colourless solid. The product was dissolved in toluene (5 mL) and 12-crown-4 (0.3 mL, 1.85 mmol) was added. Colourless crystals suitable for X-ray crystallography were obtained upon cooling this solution to 5 °C. Isolated crystalline yield: 0.46 g, 50%. Anal. Calcd for \[
\left\{\left(\text{Me}_3\text{Si}\right)_2\text{CH}\right\}\text{P}\left(\text{C}_6\text{H}_5\right)(\text{BH}_3)_2\text{Li(12-crown-4)}\right\}:
\]
C 52.73, H 9.69%. Found C 52.67, H 9.81%.

\(^1\text{H}\{^{11}\text{B}\} \text{NMR (d}_8\text{-THF, 25 °C)}: \delta -0.05 \text{ (s, 18H, SiMe}_3\), 0.57 \text{ (d, }^2\text{J}_{\text{PH}} = 13.8 \text{ Hz, 1H, CHP), 0.77 \text{ (d, }^2\text{J}_{\text{PH}} = 10.1 \text{ Hz, 6H, BH}_3\), 3.75 \text{ (s, 16H, 12-crown-4), 7.07 \text{ (t, }^3\text{J}_{\text{HH}} = 7.1 \text{ Hz, 2H, ArH), 7.12 \text{ (t, }^3\text{J}_{\text{HH}} = 7.2 \text{ Hz, 2H, ArH), 7.79 \text{ (t, }^3\text{J}_{\text{HH}} = 10.1 \text{ Hz, 1H, ArH).}^{13}\text{C}\{^{1}\text{H}\} \text{NMR (d}_8\text{-THF, 25 °C): } \delta 3.20 \text{ (SiMe}_3\), 11.85 \text{ (d, }^1\text{J}_{\text{PC}} = 6.7 \text{ Hz, CHP), 67.15 \text{ (12-crown-4), 126.02 \text{ (ArC), 126.31 \text{ (d, }^1\text{J}_{\text{PC}} = 7.7 \text{ Hz, ArC), 132.32 \text{ (d, }^1\text{J}_{\text{PC}} = 6.7 \text{ Hz, ArC), 146.78 \text{ (d, }^1\text{J}_{\text{PC}} = 29.7 \text{ Hz, ArC), 11\text{B}\{^{1}\text{H}\} \text{NMR (d}_8\text{-THF, 25 °C): } \delta -32.5 \text{ (d, br, }^1\text{J}_{\text{BP}} = 49.0 \text{ Hz).}^{3}
\]

\(^3\text{P}\{^{1}\text{H}\} \text{NMR (d}_8\text{-THF, 25 °C): } \delta -8.8 \text{ (m, }^1\text{J}_{\text{PB}} = 49.0 \text{ Hz).}^{7}\text{Li}\{^{1}\text{H}\} \text{NMR (d}_8\text{-THF, 25 °C): } \delta -0.7.\]

\[
\left\{\left(\text{Me}_3\text{Si}\right)_2\text{CH}\right\}\text{P}\left(\text{C}_6\text{H}_5\right)(\text{BH}_3)_2\text{Na(THF)}_2\right\} (124):
\]

To a solution of 42 (0.45 g, 1.59 mmol) in THF (10 mL) was added a solution of BnNa (184 mg, 1.61 mmol). After 1 h stirring, a solution of BH\(_3\).SMe\(_2\) (0.8 mL, of a 2.0 M solution in THF, 1.60 mmol) was added to the reaction mixture, turning the solution from yellow to colourless. After 1 h further stirring, the solvent was removed to yield a colourless solid. The product was dissolved in a mixture of methycyclohexane (10 mL), toluene (2 mL), and THF (5 mL). Colourless crystals suitable for X-ray crystallography were obtained upon cooling this solution to 5 °C. Isolated crystalline yield: 0.46 g, 50%. Anal. Calcd for \[
\left\{\left(\text{Me}_3\text{Si}\right)_2\text{CH}\right\}\text{P}\left(\text{C}_6\text{H}_5\right)(\text{BH}_3)_2\text{Na(THF)}_2\right\}:
\]
C 49.08, H 9.51%. Found C 48.89, H 9.45%.

\(^1\text{H}\{^{11}\text{B}\} \text{NMR (d}_8\text{-THF, 25 °C): } \delta 0.07 \text{ (s, 18H, SiMe}_3\), 0.63 \text{ (d, }^2\text{J}_{\text{PH}} = 8.7 \text{ Hz, 6H, BH}_3\), 0.64 \text{ (d, }^2\text{J}_{\text{PH}} = 15.1 \text{ Hz, 1H, CHP), 1.78 \text{ (m, 8H, THF), 3.61 \text{ (m, 8H, THF), 7.12 \text{ (t, }^3\text{J}_{\text{HH}} = 8.5 \text{ Hz, 1H, ArH), 7.17 \text{ (t, }^3\text{J}_{\text{HH}} = 9.1 \text{ Hz, 2H, ArH), 7.74 \text{ (t, }^3\text{J}_{\text{HH}} = 8.5 \text{ Hz, 2H, ArH).}^{13}\text{C}\{^{1}\text{H}\} \text{NMR (d}_8\text{-THF, 25 °C): } \delta 2.79 \text{ (d, }^3\text{J}_{\text{PC}} = 1.9 \text{ Hz, SiMe}_3\), 10.55 \text{ (d, }^1\text{J}_{\text{PC}} = 2.9 \text{ Hz, CHP), 25.30 \text{ (THF), 67.14 \text{ (THF), 126.58 \text{ (ArC), 126.68 \text{ (d, }^1\text{J}_{\text{PC}} = 7.7 \text{ Hz, ArC), 132.03 \text{ (d, }^1\text{J}_{\text{PC}} = 7.7 \text{ Hz, ArC), 143.84 \text{ (d, }^1\text{J}_{\text{PC}} = 36.4 \text{ Hz, CHP).}
\]
Hz, ArC). $^{11}$B$\{^1$H$\}$ NMR ($d_8$-THF, 25 °C): $\delta$ -33.8 (d, br, $^1J_{BP} = 68.6$ Hz). $^{31}$P$\{^1$H$\}$ NMR ($d_8$-THF, 25 °C): $\delta$ -14.9 (m, $^1J_{PB} = 68.6$ Hz).

$\{[(\text{Me}_3\text{Si})_2\text{CH}]\text{P}(\text{C}_6\text{H}_5)(\text{BH}_3)_2\text{K}(\text{THF})_2\}_\infty$ (125):

To a solution of 42 (0.42 g, 1.49 mmol) in THF (10 mL) was added a solution of BnK (194 mg, 1.49 mmol) in THF (10 mL). After 1 h stirring, a solution of BH$_3$.SMe$_2$ (0.8 mL of a 2.0 M solution in THF, 1.60 mmol) was added to the reaction mixture, turning the solution from yellow/orange to colourless. After 1 h further stirring, the solvent was removed to yield a colourless solid. THF was added to a solution of 125 in toluene (5 mL) until the product was dissolved. THF was carefully removed in vacuo, until the point of precipitation. Upon cooling to 5 °C, colourless crystals of 125 suitable for X-ray crystallography were obtained. Isolated crystalline yield: 1.30 g, 88%. Anal. Caled for $\{[(\text{Me}_3\text{Si})_2\text{CH}]\text{P}(\text{C}_6\text{H}_5)(\text{BH}_3)_2\text{K}(\text{THF})_2\}_\infty$: C 49.71, H 9.05%. Found C 46.78, H 8.95%.

$^{1}$H$\{^{11}$B$\}$ NMR ($d_8$-THF, 25 °C): $\delta$ 0.07 (s, 18H, SiMe$_3$), 0.62 (d, $^2J_{PH} = 14.7$ Hz, 1H, CHP), 0.70 (d, $^2J_{PH} = 9.6$ Hz, 6H, BH$_3$), 1.78 (m, 8H, THF), 3.62 (m, 8H, THF), 7.10 (t, $J_{HH} = 6.8$ Hz, 1H, ArH), 7.14 (t, $J_{HH} = 6.8$ Hz, 2H, ArH), 7.77 (t, $J_{HH} = 8.5$ Hz, 1H, ArH). $^{13}$C$\{^1$H$\}$ NMR ($d_8$-THF, 25 °C): $\delta$ 2.91 (d, $J_{PC} = 1.9$ Hz, SiMe$_3$), 11.37 (d, $J_{PC} = 3.8$ Hz, CHP), 25.01 (THF), 66.85 (THF), 126.38 (ArC), 126.46 (ArC), 132.27 (d, $^3J_{PC} = 6.7$ Hz, ArC), 144.58 (d, $J_{PC} = 34.5$ Hz, ArC), $^{11}$B$\{^1$H$\}$ NMR ($d_8$-THF, 25 °C): $\delta$ -32.9 (d, br, $^1J_{BP} = 58.8$ Hz ). $^{31}$P$\{^1$H$\}$ NMR ($d_8$-THF, 25 °C): $\delta$ -14.1 (m, br, $^1J_{PB} = 58.8$ Hz).

$\{[(\text{Me}_3\text{Si})_2\text{CH}]\text{P}(\text{C}_6\text{H}_4-2-\text{OMe})(\text{BH}_3)_2\}[\text{Na}(12\text{-crown-4})_2]$ (126):

To a solution of 41 (0.38 g, 1.22 mmol) in THF (10 mL) was added a solution of benzylsodium (0.14 g, 1.22 mmol). After 1 h stirring, a solution of BH$_3$.SMe$_2$ (0.6 mL of a 2.0 M solution in THF, 1.20 mmol) was added to the reaction mixture, turning the solution from yellow to colourless. After 1 h further stirring, the solvent was removed to yield a colourless solid. The product was dissolved in a mixture of methylcyclohexane (10 mL), toluene (2 mL), and THF (5 mL). Colourless crystals suitable for X-ray crystallography were obtained at room temperature. Isolated crystalline yield: 0.28 g, 33%. Anal. Caled for
[(Me$_3$Si)$_2$CH]P(C$_6$H$_5$)(BH$_3$)$_2$][Na(12-crown-4)$_2$]: C 51.43, H 9.21%. Found C 52.37, H 8.94%. $^1$H{$^1$B} NMR (d$_8$-THF, 25 °C): δ 0.06 (s, 18 H, SiMe$_3$), 0.68 (d, $^2$J$_{PH}$ = 10.1 Hz, 1H, CHP), 0.78 (d, $^2$J$_{PH}$ = 9.6 Hz, 6H, BH$_3$), 3.65 (s, 32H, 12-crown-4), 6.71 (m, 2H, ArH), 7.05 (t, $^3$J$_{HH}$ = 7.6 Hz, 1H, ArH), 7.90 (t, $^3$J$_{HH}$ = 8.5 Hz, 1H, ArH). $^{13}$C{$^1$H} NMR (d$_8$-THF, 25 °C): δ 3.22 (SiMe$_3$), 7.77 (d, $^1$J$_{PC}$ = 4.8 Hz, CHP), 54.99 (OMe), 67.30 (12-crown-4), 110.96 (ArC), 119.32 (d, $^3$J$_{PC}$ = 8.6 Hz, ArC), 127.59 (ArC), 134.35 (d, $^3$J$_{PC}$ = 25.9 Hz, ArC), 134.99 (d, $^3$J$_{PC}$ = 9.6 Hz, ArC), 162.63 (ArC). $^{11}$B{$^1$H} NMR (d$_8$-THF, 25 °C): δ -32.7 (m, br). $^{31}$P{$^1$H} NMR (d$_8$-THF, 25 °C): δ -8.1 (m, br).

To a solution of 42 (0.50 g, 1.77 mmol) in toluene (10 mL) was added Bu$_2$Mg (0.90 mL of a 1.0 M solution in heptane, 0.9 mmol). After 1 h stirring, a solution of BH$_3$.SMe$_2$ (1.4 mL of a 2.0 M solution in THF, 2.80 mmol) was added to the reaction mixture, turning the solution from pale yellow to colourless. After 1 h further stirring, the solvent volume was reduced in vacuo to 5 mL, and the solution was filtered. Colourless crystals suitable for X-ray crystallography were obtained on standing at room temperature for 16 h. Isolated crystalline yield: 0.36 g, 45%. Anal. Calcd for [(Me$_3$Si)$_2$CH]P(C$_6$H$_5$)(BH$_3$)$_2$Mg(THF)$_4$]: C 55.86, H 10.27%. Found C 55.94, H 10.39%. $^1$H{$^1$B} NMR (d$_8$-THF, 25 °C): δ 0.05 (s, 18H, SiMe$_3$), 0.59 (d, $^2$J$_{PH}$ = 14.2 Hz, 1H, CHP), 0.74 (d, $^2$J$_{PH}$ = 10.5 Hz, 6H, BH$_3$), 1.77 (m, 8H, THF), 3.61 (m, 8H, THF), 7.08 (t, $^3$J$_{HH}$ = 7.5 Hz, 2H, ArH), 7.18 (t, $^3$J$_{HH}$ = 7.5 Hz, 2H, ArH), 7.78 (t, $^3$J$_{HH}$ = 7.5 Hz, 2H, ArH). $^{13}$C{$^1$H} NMR (d$_8$-THF, 25 °C): δ 2.53 (SiMe$_3$), 11.26 (d, $^1$J$_{PC}$ = 4.8 Hz, CHP), 25.44 (THF), 67.24 (THF), 125.10 (ArC), 126.43 (d, $^3$J$_{PC}$ = 7.7 Hz, ArC), 132.33 (d, $^3$J$_{PC}$ = 6.7 Hz, ArC), 137.49 (ArC). $^{11}$B{$^1$H} NMR (d$_8$-THF, 25 °C): δ -32.8 (d, br, $^1$J$_{BP}$ = 58.8 Hz). $^{31}$P{$^1$H} NMR (d$_8$-THF, 25 °C): δ -11.5 (m, br, $^1$J$_{PB}$ = 58.8 Hz).

[(Me$_3$Si)$_2$CH]P(C$_6$H$_5$)(BH$_3$)$_2$Ca(THF)$_4$] (129):

To a solution of 42 (0.77 g, 2.73 mmol) in toluene (10 mL) was added a solution of (4'-butylbenzyl)$_2$Ca (0.85 g, 1.36 mmol) in THF (10 mL). After 1 h stirring, the solution was concentrated, and a solution of BH$_3$.SMe$_2$ (1.4 mL of a 2.0 M solution in THF, 2.80 mmol)
was added to the reaction mixture, turning the solution from yellow to colourless. After 1 h further stirring, the solvent volume was reduced in vacuo until the product crystallised from solution. The solution was warmed until the product re-dissolved. Colourless crystals suitable for X-ray crystallography were obtained on standing at room temperature for 16 h. Isolated crystalline yield: 0.85 g, 80%. Anal. Calcd for \([(\text{Me}_3\text{Si})_2\text{CH}]\text{P(C}_6\text{H}_5)(\text{BH}_3)_2\text{Ca(THF)}_4]\): C 52.72, H 9.89%. Found C 52.69, H 9.77%.

\[\text{^1H\{^11B\} NMR (}\delta\text{): } 0.07 (\text{s, 18H, SiMe}_3), 0.68 (\text{d, }^2J_{\text{PH}} = 15.1 \text{ Hz, 1H, CHP}), 0.72 (\text{d, }^2J_{\text{PH}} = 12.9 \text{ Hz, 6H, BH}_3), 1.79 (\text{m, 8H, THF}), 3.60 (\text{m, 8H, THF}), 7.15 (\text{t, }J_{\text{HH}} = 6.9 \text{ Hz, 1H, ArH}), 7.19 (\text{t, }J_{\text{HH}} = 6.9 \text{ Hz, 2H, ArH}), 7.76 (\text{t, }J_{\text{HH}} = 8.0 \text{ Hz, 2H, ArH}).\]

\[\text{^13C\{^1H\} NMR (}\delta\text{): } 2.55 (\text{d, }^3J_{\text{PC}} = 1.9 \text{ Hz, SiMe}_3), 10.80 (\text{d, }^1J_{\text{PC}} = 1.9 \text{ Hz, CHP}), 25.30 (\text{THF}), 67.15 (\text{THF}), 126.82 (\text{d, }^3J_{\text{PC}} = 7.7 \text{ Hz, ArC}), 127.08 (\text{ArC}), 132.09 (\text{d, }^2J_{\text{PC}} = 7.7 \text{ Hz, ArC}), 143.69 (\text{d, }^1J_{\text{PC}} = 36.4 \text{ Hz, ArC}),\]

\[\text{^11B\{^1H\} NMR (}\delta\text{): -32.4 (d, br, }^1J_{\text{BP}} = 68.6 \text{ Hz}).\]

\[\text{^31P\{^1H\} NMR (}\delta\text{): -16.4 (m, br, }^1J_{\text{PB}} = 58.8 \text{ Hz}).\]

\[\text{[(\{Me}_3\text{Si})_2\text{CH}\}}\text{P(C}_6\text{H}_5)(\text{BH}_3)_2\text{Sr(THF)}_4]\] (130):

To a solution of 42 (0.24 g, 0.84 mmol) in toluene (10 mL) was added a solution of \{\{Me}_3\text{Si})_2\text{CH}\}_2\text{Sr} (0.26 g 0.42 mmol) in THF (10 mL) followed by a solution of BH\text{3}.SMe\text{2} (0.4 mL of a 2.0 M solution in THF, 0.80 mmol). After 1 h stirring, the solvent volume was reduced in vacuo to 10 mL. Upon cooling (5 °C) colourless crystals suitable for X-ray crystallography were deposited. Isolated yield: 0.34 g, 84%. Anal. Calcd for \[\text{[(\{Me}_3\text{Si})_2\text{CH}\}}\text{P(C}_6\text{H}_5)(\text{BH}_3)_2\text{Sr(THF)}_4]\]: C 52.20, H 9.60%. Found C 52.00, H 9.47%.

\[\text{^1H\{^11B\} NMR (}\delta\text{): } 0.08 (\text{s, 18H, SiMe}_3), 0.67 (\text{d, }^2J_{\text{PH}} = 15.1 \text{ Hz, 1H, CHP}), 0.81 (\text{d, }^2J_{\text{PH}} = 11.0 \text{ Hz, 6H, BH}_3), 1.77 (\text{m, 8H, THF}), 3.62 (\text{m, 8H, THF}), 7.16 (\text{t, }J_{\text{HH}} = 6.6 \text{ Hz, 1H, ArH}), 7.19 (\text{t, }J_{\text{HH}} = 7.1 \text{ Hz, 2H, ArH}), 7.77 (\text{t, }J_{\text{HH}} = 8.0 \text{ Hz, 2H, ArH}).\]

\[\text{^13C\{^1H\} NMR (}\delta\text{): } 2.07 (\text{d, }^3J_{\text{PC}} = 1.9 \text{ Hz, SiMe}_3), 10.58 (\text{d, }^1J_{\text{PC}} = 1.9 \text{ Hz, CHP}), 25.45 (\text{THF}), 67.37 (\text{THF}), 126.84 (\text{d, }^1J_{\text{PC}} = 7.7 \text{ Hz, ArC}), 127.14 (\text{ArC}), 132.14 (\text{d, }^1J_{\text{PC}} = 6.7 \text{ Hz, ArC}), 143.31 (\text{d, }^1J_{\text{PC}} = 37.4 \text{ Hz, ArC}),\]

\[\text{^11B\{^1H\} NMR (}\delta\text{): -31.5 (d, br, }^1J_{\text{BP}} = 58.8 \text{ Hz}).\]

\[\text{^31P\{^1H\} NMR (}\delta\text{): -16.4 (m, br, }^1J_{\text{PB}} = 58.8 \text{ Hz}).\]
9.5 References


(10) *COLLECT* software; Nonius BV, Delft, The Netherlands, **2000**.

Appendix 1.

1. Dynamic NMR spectroscopy

In chapter 6.3 it was shown using variable-temperature NMR spectroscopy that the SiMe$_3$ groups in the compound $[(\text{Me}_3\text{Si})_2\text{CH}]\text{P(C}_6\text{H}_5)(\text{BH}_3)][\text{Na}(12\text{-crown-4})_2]$ (116) exhibit dynamic exchange behaviour in solution. As the temperature is increased rate of exchange becomes increasingly rapid. This results in the two signals coalescing into a single peak, so that the two groups can no longer be distinguished.

2. Line-shape analysis

The variable-temperature $^1\text{H}$\{$^1\text{B}$\} NMR spectra for compound 116 were simulated using the programme gNMR. Using this programme, the rate constant, $k$, for the SiMe$_3$ exchange process could be calculated from line-shape analysis at each temperature. As there is no coupling between the exchanging nuclei, the line shape can be calculated using the modified Bloch equations.

For uncoupled exchanging groups which are equally populated, three parameters determine the shape of the NMR peak: i) lifetime of exchanging sites $\tau$ ($1/\tau =$ exchange rate) ii) peak separation $\delta$, (shift difference between exchanging sites in Hz), and iii) signal width.

3. The free enthalpy of activation $\Delta G^\ddagger$

By applying the Eyring equation (1) it is possible to determine the free enthalpy of activation $\Delta G^\ddagger$:

$$k = x \frac{k_BT}{h} e^{-\Delta G^\ddagger/RT}$$  (1)
\[ k_B = \text{Boltzmann constant} = 3.2995 \times 10^{-24} \text{ cal K}^{-1} \]
\[ = 1.3805 \times 10^{-23} \text{ J K}^{-1} \]

\[ x = \text{transmission coefficient (assumed to be exactly 1)} \]

\[ h = \text{Planck constant} = 1.5836 \times 10^{-34} \text{ cal s} \]
\[ = 6.6256 \times 10^{-34} \text{ J s} \]

Equations (2) and (3) describe the relationship between the free enthalpy of activation \( \Delta G^\ddagger \), with enthalpy of activation \( \Delta H^\ddagger \) and the entropy of activation \( \Delta S^\ddagger \), and thermodynamic equilibrium constant \( K \):

\[ \Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (2) \]

\[ \Delta G^\ddagger = -RT\ln K^\ddagger \quad (3) \]

By combining (2) and (3) and solving for \( \ln K^\ddagger \) yields equation (4):

\[ \ln K^\ddagger = \frac{\Delta G^\ddagger}{RT} + \frac{\Delta H^\ddagger}{R} - \frac{T\Delta S^\ddagger}{R} \quad (4) \]

If we insert this expression into the Eyring equation (1), and take the natural log, assuming \( x = 1 \), the following is obtained:

\[ \ln \frac{k}{T} = 23.76 - \frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R} \quad (5) \]

Thus plotting \( \ln(k/T) \) against \( 1/T \) yields \( \Delta H^\ddagger \) and \( \Delta S^\ddagger \). For mononuclear reactions the relationship between enthalpy of activation and the Arrhenius activation energy is:

\[ \Delta H^\ddagger = E_A - RT \quad (6) \]
4. Line shape data for SiMe₂ groups of 116 in $d_8$-THF

<table>
<thead>
<tr>
<th>$T / K$</th>
<th>$k$</th>
<th>$k/T$</th>
<th>$\ln(k/T)$</th>
<th>$1/T, K^{-1} (10^{-3})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>263.15</td>
<td>$6.30 \times 10^9$</td>
<td>0.024</td>
<td>-3.73</td>
<td>3.8</td>
</tr>
<tr>
<td>273.15</td>
<td>$9.30 \times 10^9$</td>
<td>0.034</td>
<td>-3.38</td>
<td>3.7</td>
</tr>
<tr>
<td>283.15</td>
<td>$4.60 \times 10^1$</td>
<td>0.16</td>
<td>-1.82</td>
<td>3.5</td>
</tr>
<tr>
<td>296.25</td>
<td>$1.15 \times 10^2$</td>
<td>0.39</td>
<td>-0.95</td>
<td>3.4</td>
</tr>
<tr>
<td>303.15</td>
<td>$1.66 \times 10^2$</td>
<td>0.55</td>
<td>-0.60</td>
<td>3.3</td>
</tr>
<tr>
<td>313.15</td>
<td>$3.66 \times 10^2$</td>
<td>1.17</td>
<td>0.16</td>
<td>3.2</td>
</tr>
<tr>
<td>323.15</td>
<td>$4.94 \times 10^2$</td>
<td>1.53</td>
<td>0.42</td>
<td>3.1</td>
</tr>
</tbody>
</table>

5. Eyring plot

6. Calculation of $\Delta H^\ddagger$, $\Delta S^\ddagger$ and $\Delta G^\ddagger$ of 116 using (5) and (2)

Where $\Delta H^\ddagger$ can be calculated from the slope ($m = -\Delta H^\ddagger/R$), whilst $\Delta S^\ddagger$ can be calculated from the intercept ($c = \frac{\Delta S^\ddagger}{R} + 23.76$).

$\Delta H^\ddagger = 52.78$ kJ mol$^{-1}$

$\Delta S^\ddagger = -28.33$ J K$^{-1}$ mol$^{-1}$

As $\Delta S^\ddagger$ is so small and has an inherent large degree of error, it can be considered as 0 kJ mol$^{-1}$, thus $\Delta G^\ddagger$ is essentially equal to $\Delta H^\ddagger$. The low value also suggests that the exchange process in 116 is an intramolecular process.
## Appendix 2. X-ray crystallographic data

### List of crystal structures

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>file no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>39</td>
<td>{(Me₃Si)₂CH}PH(C₆H₄-2-CH₂OMe)(BH₃)</td>
<td>ki476</td>
</tr>
<tr>
<td>41</td>
<td>{(Me₃Si)₂CH}PH(C₆H₄-2-OMe)(BH₃)</td>
<td>ki467</td>
</tr>
<tr>
<td>42</td>
<td>{(Me₃Si)₂CH}PH(C₆H₅)(BH₃)</td>
<td>ki367</td>
</tr>
<tr>
<td>49</td>
<td>[{(Me₃Si)₂CH}P(C₆H₄-2-CH₂OMe)(BH₃)Li(THF)]₂</td>
<td>ki316</td>
</tr>
<tr>
<td>50</td>
<td>[{(Me₃Si)₂CH}P(C₆H₄-2-CH₂OMe)(BH₃)Na(tmeda)]₂</td>
<td>ki468</td>
</tr>
<tr>
<td>51</td>
<td>[{(Me₃Si)₂CH}P(C₆H₄-2-CH₂OMe)(BH₃)K(pmdeta)]₂</td>
<td>ki314</td>
</tr>
<tr>
<td>64</td>
<td>[{(Me₃Si)₂CH}P(C₆H₄-2-SMe)(BH₃)Li(THF)]₂</td>
<td>ki397</td>
</tr>
<tr>
<td>65</td>
<td>[{(Me₃Si)₂CH}P(C₆H₄-2-SMe)(BH₃)Na(tmeda)]∞</td>
<td>ki385</td>
</tr>
<tr>
<td>66</td>
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</tr>
<tr>
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<td>ki474</td>
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<tr>
<td>89</td>
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<tr>
<td>106</td>
<td>[{(Me₃Si)₂CH}P(C₆H₄-2-OMe)Li(tmeda)]</td>
<td>ki404</td>
</tr>
<tr>
<td>108</td>
<td>[[{(Me₃Si)₂CH}P(C₆H₄-2-O)]Ca(THF)]₄</td>
<td>ki469</td>
</tr>
<tr>
<td>115</td>
<td>[[{(Me₃Si)₂CH}P(C₆H₅)(BH₃)Li(THF)]₂]∞</td>
<td>ki319</td>
</tr>
<tr>
<td>116</td>
<td>[[{(Me₃Si)₂CH}P(C₆H₅)(BH₃)][Na(12-crown-4)]₂]</td>
<td>ki334</td>
</tr>
<tr>
<td>117</td>
<td>[[{(Me₃Si)₂CH}P(C₆H₅)(BH₃)K(pmdeta)]₂</td>
<td>ki493</td>
</tr>
<tr>
<td>123</td>
<td>[[{(Me₃Si)₂CH}P(C₆H₅)(BH₃)₂Li(12-crown-4)]</td>
<td>ki462</td>
</tr>
<tr>
<td>124</td>
<td>[[{(Me₃Si)₂CH}P(C₆H₅)(BH₃)₂Na(THF)]₂]</td>
<td>ki320</td>
</tr>
<tr>
<td>125</td>
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<td>ki437</td>
</tr>
<tr>
<td>126</td>
<td>[[{(Me₃Si)₂CH}P(C₆H₄-2-OMe)(BH₃)]₂[Na(12-crown-4)]₂]</td>
<td>ki494</td>
</tr>
<tr>
<td>128</td>
<td>[[[{(Me₃Si)₂CH}P(BH₃)₂(C₆H₅)]₂Mg(THF)]₄</td>
<td>ki463</td>
</tr>
<tr>
<td>129</td>
<td>[[[{(Me₃Si)₂CH}P(BH₃)₂(C₆H₅)]₂Ca(THF)]₄</td>
<td>ki461</td>
</tr>
<tr>
<td>130</td>
<td>[[[{(Me₃Si)₂CH}P(BH₃)₂(C₆H₅)]₂Sr(THF)]₄</td>
<td>ki480</td>
</tr>
</tbody>
</table>