Phosphine-Borane-Stabilised Carbanion Complexes of Main Group Elements

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Abstract

An array of phosphorus-stabilised-carbanion complexes of group 1, 2 and 14 elements and their behaviour in the solid state is reviewed, along with a brief overview of the chemistry of phosphine-boranes, stannyl-stannylenes, heteroleptic stannylenes and oxidative addition. The synthesis and characterisation of a range of novel phosphine-borane precursors is described: [Me₂P(BH₃)CH₂SiMe₂CH₂]₂ (1), [Ph₂P(BH₃)CH₂Si(Me₂)CH₂]₂ (2), 1,2-C₆H₄{CH₂PPr₂(BH₃)}₂ (3), 1,2-C₆H₄{CH₂PPh₂(BH₃)}₂ (4), 1,2-C₆H₄{CH₂PCy₂(BH₃)}₂ (5), C₆H₅CH₂PPr₂(BH₃) (6), C₆H₅CH₂PPh₂(BH₃) (7), C₆H₅CH₂PCy₂(BH₃) (8), C₆H₅{CH₂SiMe₃PCy₂(BH₃)} (9), {CH₂CH₂PCy₂(BH₃)}₂ (10).

Treatment of 1 and 2 with two equivalents of °BuLi and tetramethylethylenediamine (tmdea) in THF yields the corresponding complexes [Li(tmdea)]₂[Me₂P(BH₃)CHSi(Me₂)CH₂]₂ (1a) and [Li(THF)]₂[Ph₂P(BH₃)CHSi(Me₂)CH₂]₂ (2a), respectively, as monomeric units where the metal centre is bound to the carbanion along with agostic-type B-H···Li interactions.

Similarly, the reaction between 2 and two equivalents of BnK (PhCH₂K) in the presence of the pentamethyldiethylenetriamine (pmdeta), followed by recrystallisation from hot toluene yields the potassium complex [K(pmdeta)]₂[CH₂SiMe₂C(H)CH₂]₂ (2b), which has an unusual cyclic structure.

The α-phenylene-bridged bis(phosphine-boranes) 3-5 undergo α-metalation with two equivalents of °BuLi and tmdea to yield the corresponding phosphine-borane-stabilised carbanions [1,2-C₆H₄{CHP(BH₃)R₂}]₂[Li(tmdea)]₂·nL (R = °Pr, n = 0 (3a); R = Ph, nL = THF (4a); R = Cy, nL = 2PhCH₃ (5a)) after recrystallisation. Compounds 3a-5a adopt similar structures where each Li is positioned on the opposite sides of an essentially planar C₆H₄(CP)₂ fragment and has interactions with the carbanion and BH₃ unit. Treatment of 3-5 with two equivalents of PhCH₂K and pmdeta yields the corresponding phosphine-borane-stabilised carbanions [K(pmdeta)]₂[1,2-C₆H₄{CHPR₂(BH₃)}₂] (R = °Pr (3b), Ph (4b) and (5b)). Compound 5b crystallises as a discrete monomer, in which each potassium is bound to the carbanion, the pmdeta co-ligand, an η¹ contact to the BH₃ unit and has additional short contacts with an ipso carbon atom in the α-phenylene linker.

The benzyl-substituted phosphine-boranes 6, 7 and 8 undergo α-metalation with one equivalent of °BuLi and tmdea to yield the corresponding phosphine-borane-stabilised carbanions [C₆H₅CHP(BH₃)R₂][Li(tmdea)] (R = °Pr (6a), Ph (7a) and Cy (8a)). Compound 8a...
crystallises as a discrete molecular species with coordination between the Li and the carbanion centre, BH$_3$ hydrogens in an $\eta^2$-fashion, the hydrogen atom associated with the carbanion centre and with the coordination sphere completed by two contacts to the two nitrogen atoms in one molecule of tmeda. Treatment of compound 8 with an excess of BnK in THF results in the phosphine-borane-stabilised carbanion complex K[C$_6$H$_5$CHP(Cy)$_2$(BH$_3$)] (8b); which crystallises as a sheet polymer,

The synthesis of group 2 complexes of 6 and 8 was investigated using three different methods in which included the use of $^n$BuLi followed by the group 2 halide, BnK followed by the group 2 halide and the use of previously prepared Bn$_2$M (M = Ca, Sr, Ba).

Treatment of in situ-generated 5a with one equivalent of Cp$_2$Sn in toluene yields pale yellow crystals of the unusual agostically-stabilised stannyl-stannylene [[1,2-C$_6$H$_4${CHP(BH$_3$)Cy$_2$}]$_2$Sn]$_2$:1½PhMe (11). Compound 11 crystallises as a discrete molecular species containing two different Sn centres with formal oxidation states of I and III, joined by a formal Sn-Sn $\sigma$-bond.

Treatment of one equivalent of SnCl$_2$ with two equivalents of in situ-generated [Li(tmeda)][C$_6$H$_5$CHPR$_2$(BH$_3$)] (R = $^i$Pr (6a) and Cy (8a)) in diethyl ether yields Sn[C$_6$H$_5$CHPR$_2$(BH$_3$)]$_2$ (R = $^i$Pr (rac-6c) and Cy (rac-8c)). Both rac-6c and rac-8c have interactions between the Sn centre and one H atom from each of two separate BH$_3$ units in an $\eta^1$-fashion.

Treatment of one equivalent of SnCl$_2$ with one equivalent of in situ-generated Li[C$_6$H$_5$CHPR$_2$(BH$_3$)] (R = $^i$Pr (6a), Cy (8a)) in diethyl ether yields SnCl[C$_6$H$_5$CHPR$_2$(BH$_3$)] (R = $^i$Pr (6d), Cy (8d)). Treatment of a diethyl ether solution of 6c with one equivalent of methyl iodide or benzyl bromide yields the corresponding oxidative addition products [C$_6$H$_5$CHPPr$_2$(BH$_3$)]$_2$Sn(Me)I (12) and [C$_6$H$_5$CHPPr$_2$(BH$_3$)]$_2$Sn(Bn)Br (13), respectively. Compound 12 crystallises as a discrete monomer where the tin has contacts with two phosphine-borane fragments via the carbanion centre, a bond to the methyl carbon atom and a contact with an iodide in a distorted tetrahedral geometry; this compound has no agostic-type interactions between the borane hydrogens and the tin. The solution state structure of 12 was determined using multi-element and multi-nuclear NMR spectroscopy.
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Publications from this work

Chapter 3


Chapter 5

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<td>n-butyl</td>
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Table of important compounds

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<td></td>
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</tbody>
</table>
Table of Contents

Abstract ........................................................................................................................................... i
Acknowledgements ......................................................................................................................... iv
Publications from this work .............................................................................................................. v
List of Abbreviations ......................................................................................................................... vi
Table of important compounds ......................................................................................................... vii

Chapter 1. Introduction ....................................................................................................................... 5
  1.1 Group 1 metal organometallics .................................................................................................... 5
  1.2 Phosphorus-stabilised carbanions ............................................................................................ 7
    1.2.1 Phosphinomethanide complexes of the alkali metals ...................................................... 8
  1.3 Phosphine-boranes ................................................................................................................... 9
    1.3.1 Introduction ....................................................................................................................... 9
    1.3.2 Preparation of phosphine-boranes ................................................................................... 10
    1.3.3 Decomplexation of boranes .............................................................................................. 13
  1.4 Phosphine-borane-stabilised carbanions .................................................................................. 14
    1.4.1 Heavier alkali metal complexes ....................................................................................... 21
    1.4.2 Alkaline earth metal complexes ....................................................................................... 23
  1.5 Heavier group 14 carbene analogues [tetrylenes, R₂E (E = Ge, Sn, Pb)] ................................ 26
  1.6 References ................................................................................................................................... 31

Chapter 2. Synthesis of phosphine-borane precursors ....................................................................... 34
  2.1 Introduction ............................................................................................................................... 34
  2.2 Synthesis and characterisation of Group A precursors [linear bis(phosphine-boranes)] .......... 35
    2.2.1 Me₃P(BH₃) (36) ................................................................................................................ 35
    2.2.2 [Me₂P(BH₃)CH₂SiMe₂CH₂]₂ (37) ..................................................................................... 37
2.2.3 $\text{Ph}_2(\text{Me})\text{P(BH}_3\text{)}$ (39) ........................................................................................................... 39

2.2.4 $[\text{Ph}_2\text{P(BH}_3\text{)}\text{CH}_2\text{SiMe}_2\text{CH}_2\text{]}_2$ (40) .................................................................................. 40

2.3 Synthesis and characterisation of Group B precursors [$\sigma$-phenylene-bridged bis(phosphine-boranes)] ........................................................................................................... 41

2.3.1 $\text{R}_2\text{PH(BH}_3\text{)}$ [R = $^3\text{Pr}$ (41), Ph (42) or Cy (43)] ........................................................................... 41

2.3.2 1,2-C$_6$H$_4$\{CH$_2$PR$_2$(BH$_3$)\}_2 [R = $^3\text{Pr}$ (44), Ph (45) and Cy (46)] ........................................ 42

2.4 Synthesis and characterisation of Group C precursors (benzyl-substituted phosphine-boranes) ........................................................................................................... 45

2.4.1 C$_6$H$_5$CH$_2$PR$_2$(BH$_3$) [R = $^3\text{Pr}$ (47), Ph (48) and Cy (49)] .................................................. 45

2.5 Synthesis and characterisation of Group D precursors [SiMe$_3$-substituted and linear bis(phosphine-boranes)] .................................................................................. 49

2.5.1 C$_6$H$_5$\{CH(SiMe$_3$)PCy$_2$(BH$_3$)$\}$ 50 ..................................................................................... 49

2.5.2 {CH$_2$CH$_2$PCy$_2$(BH$_3$)$\}$ 51 ........................................................................................................ 49

2.6 Conclusion ............................................................................................................................................. 50

2.7 References ............................................................................................................................................. 51

Chapter 3. Synthesis and structural characterisation of $\alpha$-metalated phosphine-borane precursors .................................................................................................................. 52

3.1 Introduction .......................................................................................................................................... 52

3.2 Synthesis and characterisation of Group A phosphine-borane-stabilised carbanions ... 53

3.3 Synthesis and characterisation of Group B phosphine-borane-stabilised carbanions ... 60

3.4 Synthesis and characterisation of Group C phosphine-borane-stabilised carbanions ... 69

3.5 Synthesis and characterisation of Group D phosphine-borane-stabilised carbanions ... 76

3.6 Conclusions .......................................................................................................................................... 78

3.7 References .......................................................................................................................................... 80

Chapter 4. Group 2 Phosphine-borane-stabilised carbanions ......................................................... 82

4.1 Introduction .......................................................................................................................................... 82

4.2 Organolithium as a reagent .................................................................................................................. 82

4.3 Benzylpotassium as a reagent ............................................................................................................. 85

4.4 Dibenzylcalcium, -strontium and –barium as a reagent ................................................................. 87
4.5 Conclusion ................................................................. 90
4.6 References ............................................................... 92

Chapter 5. Impact of a rigid backbone on the structure of an agostically-stabilised dialkylstannylene ................................................................. 94
5.1 Introduction .................................................................. 94
5.2 Synthesis of dialkylstannylene ........................................... 96
5.3 DFT Calculations on a model stannyl-stannylene ..................... 104
5.4 Conclusion .................................................................. 105
5.5 References .................................................................. 107

Chapter 6. Replacement of a trimethylsilyl group and its impact on stability of dialkylstannylene ................................................................. 109
6.1 Introduction .................................................................. 109
6.2 Synthesis of dialkylstannylene ........................................... 111
6.2.1 Benzylic dialkylstannylene ........................................... 111
6.2.2 Characterisation of compounds 64 and 65 ......................... 112
6.3 Conclusion .................................................................. 117
6.4 References .................................................................. 118

Chapter 7. Heteroleptic dialkylstannylene ....................................... 119
7.1 Introduction .................................................................. 119
7.2 Synthesis of heteroleptic dialkylstannylene ........................... 120
7.3 Reactivity of heteroleptic alkylstannylene with bulky reagents .......... 121
7.3.1 Carbon-containing groups .......................................... 121
7.3.2 Nitrogen- and oxygen-containing groups ......................... 122
7.3.3 Phosphorus-containing groups .................................... 124
7.4 Reactivity of heteroleptic alkylstannylene with less sterically hindered groups ...... 127
7.5 Conclusions .................................................................. 129

Chapter 8. Oxidation reactions of a phosphine-borane-stabilised dialkylstannylene .... 130
8.1 Introduction .................................................................. 130
8.2 Synthesis of an oxidative addition product using MeI or BnBr ...........................................131
8.3 Oxidation addition reactions using compound 64 .................................................................150
8.4 Conclusion ..........................................................................................................................153
8.5 References ..........................................................................................................................154

Chapter 9. Conclusions ..............................................................................................................155

9.1 Effects on the structures and stabilities on group 1 and 14 phosphine-borane-stabilised carbanions with either a rigid aromatic or flexible backbone. ...........................................155
9.2 Replacement of a SiMe₃ group and its impact on the stability and structure of dialkylstannylenes. ..................................................................................................................159
9.3 Difficulties in the isolation of heteroleptic alkylstannylenes ..............................................160
9.4 Dynamic behaviour of the oxidative addition product [C₆H₅CHPPr₂(BH₃)]₂Sn(Me)I (86) ......................................................................................................................................161
9.5 Possible future work .............................................................................................................162
9.6 References ..........................................................................................................................163

Chapter 10. Experimental ..............................................................................................................164

10.1 General procedures ..............................................................................................................164
10.2 NMR Spectroscopy and elemental analyses .........................................................................165
10.3 Crystal structure determinations .........................................................................................165
10.4 DFT calculations ................................................................................................................165
10.5 Preparative methods ............................................................................................................166
10.6 References ..........................................................................................................................180

Appendix 1. X-ray crystallographic data ......................................................................................182
Appendix 2. Eyring plot data ........................................................................................................182
1.1 Group 1 metal organometallics

Organometallic reagents are very important in synthetic chemistry due to their ability to act as both a base and nucleophile; their use in many reactions is common. The first organolithium was reported by Wilhelm Schlenk\textsuperscript{1,2} in 1914 and its discovery led to the synthesis of an array of group 1 metal organometallics.\textsuperscript{3-5}

It is surprising, however, that even with the widespread use of alkali metal organometallics, the understanding of their reactivity is still relatively limited. In order to better understand the reactivity of these species, the determination of their structures in solution and the solid-state is vital, along with their tendency towards aggregation. Advances in X-ray crystallography have been fundamental to this and now a great deal of structural data is available for this class of compound. In addition to X-ray crystallography, analytical methods such as NMR, UV-Vis and IR spectroscopies have improved the ease with which these compounds may be characterised. However, there is still a lot more work to be done in order to fully understand the reactivity of alkali organometallics; especially with regards to heavier alkali metals such as sodium and potassium. Sodium and potassium organometallics pose a slightly different problem to those of lithium due to their increased sensitivity towards moisture and oxygen; alkali metal organometallics must be handled under an inert atmosphere (usually N\textsubscript{2}) using Schlenk techniques to prevent hydrolysis and/or oxidation via a hydroperoxide salt (Scheme 1.1).

\begin{align*}
\text{(i)} \quad \text{RM} + \text{O}_2 & \quad \rightarrow \quad \text{RO}_2\text{M} \\
\text{(ii)} \quad \text{RO}_2\text{M} + \text{RM} & \quad \rightarrow \quad 2\text{ROM}
\end{align*}

**Scheme 1.1:** Decomposition of alkali metal organometallic compounds with oxygen.

Not only are alkali metal organometallics reactive towards oxygen, but they are also known to deprotonate ethereal solvents, such as diethyl ether and THF; this decomposition has been studied in detail by Maercher and co-workers who used deuterium-labelled ethers.
and witnessed $\alpha$-, $\beta$-, and $\alpha,\beta$-eliminations, as well as Wittig rearrangements, resulting in many products (Scheme 1.2).\(^6\)

\[
\text{Et}_2\text{O} + \text{RLi} \rightarrow \text{RH} + \text{H}_2\text{C=CH}_2 + \text{LiOCH}_2\text{CH}_3
\]

\[
\text{[EtCD}_2\text{CH]} + \text{LiOCH}_2\text{CD}_2\text{Et} \rightarrow \text{EtDC=CDH}
\]

\[
\text{EtD}_2\text{C} = \text{C} - \text{OCH}_2\text{CD}_2\text{Et}
\]

\[
\alpha\text{-C}_6\text{H}_{14} \quad \text{EtDC=CH}_2\text{OCH}_2\text{CD}_2\text{Et} \rightarrow \text{EtDC=CH}_2 + \text{LiOCH}_2\text{CD}_2\text{Et}
\]

\[
\beta\text{-C}_6\text{H}_{13}\text{D} \quad \text{Wittig}
\]

\[
\text{EtD}_2\text{C} = \text{C} - \text{O} - \text{CH}_2\text{CD}_2\text{Et} \rightarrow \text{EtD}_2\text{C} = \text{CHO}_\text{Li}
\]

\[
\text{EtD}_2\text{CDOLi} + \text{EtDC=CH}_2
\]

**Scheme 1.2:** (i) Reaction of diethyl ether with deuterated alkali metal organometallics, (ii) Reaction of THF with $^t\text{BuLi}$.

The factors in alkali metal organometallic compounds which determine structure and reactivity are: i) charge to size ratio, which decreases as the group is descended, ii) ionicity, which generally increases as you go down the group and iii) atomic radii, which increase as you go down the group. The size of the cation is important as it tends to dictate the coordination number of the metal centre; as the cation radius increases, so does the coordination number, leading to a greater tendency towards aggregation.

Overall, now that spectroscopic methods have improved over the last 3 decades, so has our understanding of the reactivity and structure of alkali organometallics. The size of the
cation and aggregation properties are very important as aggregation is a common problem in alkali metal organometallics; this can affect the reactivity of the reagent and so it is quite common to use amines to decrease aggregation and thereby increase the reactivity. As knowledge of alkali metal organometallics increases, so will their uses and the ability to be selective in the use of these types of compounds during synthetic approaches.

1.2 Phosphorus-stabilised carbanions

Phosphorus-stabilised carbanions have been recognised as useful reagents for a variety of important organic reactions, such as variants of the Wittig olefination reaction (Horner or Horner-Wadsworth-Emmons reactions).\(^7\)-\(^10\) It has been found that phosphorus-stabilised carbanions (phosphinomethanides) have increased reactivity compared to neutral ylide species in the Wittig reaction. These phosphorus-stabilised carbanions can be used as ligands, and complexes of metallic elements from groups 1, 2, 13, 14 and 15 are known.\(^10\) The reason why phosphorus (or other third row elements) can stabilise a carbanion is due to a combination of electrostatic interactions (due to the greater electropositivity of the heteroatom); greater polarisability of the 2nd row elements, negative hyperconjugation, which stabilises the carbanion by donation of the carbanion lone pair into a low lying \(\sigma^*\) orbital on the heteroatom (Figure 1.1 (I)), and \(d\pi-p\pi\) interactions (Figure 1.1 (II)). However, \(d\pi-p\pi\) interactions are now thought not to be very stabilising, since the 3d-orbitals are too high in energy for good overlap with the lone pair (l.p.) orbital on the carbanion centre. Also, studies have shown that any stabilisation in the gas phase is lost on complexation with lithium or sodium ions due to these metals localising the charge on the carbanion centre, although this effect is diminished in complexes with the less charge-localising heavier alkali metal cations.\(^10\)

![Figure 1.1: Negative hyperconjugation (I) and \(d\pi-p\pi\) interactions (II) between phosphorus and an adjacent carbanion.](image-url)
Phosphorus(III)-stabilised carbanions can act as monodentate (i and ii), bidentate (iii) and bridging (iv) ligands due to the presence of lone pairs on both the P(III) centre and the carbanion, the similar electronegativities of P and C, and the fact that both atoms are valence isoelectronic (Figure 1.2). These factors enable the two atoms to compete as donor ligands, hence the ability to act as a bidentate and bridging ligand.\textsuperscript{10}

![Diagram](image)

\textbf{Figure 1.2}: Binding modes of phosphinomethanide ligands.

\textbf{1.2.1 Phosphinomethanide complexes of the alkali metals}

The structure adopted by a phosphinomethanide complex depends on the nature of the metal, the nature of the substituents on the carbanion and phosphorus centres and the presence of co-ligands or coordinating solvents. If a charge-delocalising or sterically demanding substituent (e.g. SiMe\textsubscript{3}) is bound to the carbanion, then the nucleophilicity of the centre decreases and so coordination through the phosphorus atom is favoured. There are a number of structures that have been published from the Izod group, such as the α-lithiated phosphinomethanide Li[\(\text{C(SiMe}_{3}\text{)}\text{2}\{\text{P(C}_{6}\text{H}_{4}\text{CH}_{2}\text{NMe}_{2-2}\text{-2}\text{)}\text{2}\}\text{]}\) (I) (Figure 1.3) in which the Li ion is bound to the P and two N atoms of the ligand, but has no short Li-C contacts.\textsuperscript{11}
Figure 1.3: $\alpha$-lithiated phosphinomethanide $\text{Li}[\text{C(SiMe}_3\text{)}_2\{\text{P(C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-2)}_2\}]$ (1).

The first example of a phosphinomethanide with a co-ligand-free lithium ion $[\text{Li}\{\text{C(SiMe}_3\text{)}_2\text{PMe}_2\}]_2$ (2) (Figure 1.4) was reported by Karsch and co-workers in 1990 [this compound exhibits binding modes similar to iv (Figure 1.2)].\(^{12}\) The two lithium cations exhibit a six-membered chair conformation where the lithium cations in the ring are bridged by the phosphinomethanide ligands; the coordination sphere of each lithium ion is completed by additional weak intermolecular and intramolecular Si-Me-\cdots Li interactions.\(^{12}\)

Figure 1.4: Compound 2 in a chair conformation.

1.3 Phosphine-boranes

1.3.1 Introduction

For many years phosphine-boranes have been used extensively for the synthesis of phosphines due to the P-B serving as a protecting group against oxidation. For example, phosphine-borane adducts are important intermediates used to synthesise polyphosphines, such as the chiral diphosphine DIPAMP (Scheme 1.3).\(^{13,14}\) More recently, phosphine-boranes have also become of interest as ligands for transition metal complexes.\(^{15}\) The key features of
phosphine-borane adducts include: (i) the P-B bond shows particular stability, and so the phosphorus atom is protected from oxidation; this enables the easy handling of air-sensitive trivalent phosphines, which would otherwise need to be handled under air- and moisture-free conditions; (ii) the formation of an adduct between a phosphine and a borane is often reversible; and (iii) CH protons a to the phosphorus atom are activated towards deprotonation (using a strong base such as "BuLi), giving highly stabilised carbanions. Surprisingly, relatively little is known about the structures of these carbanions in solution or the solid state.

![Scheme 1.3: Synthesis of DIPAMP using a phosphine-borane-stabilised carbanion. Reaction conditions: i) "BuLi{(-)-sparteine}, ii) Cu(OPiv)₂ and Et₂NH.](attachment:scheme1.3.png)

The first example of a phosphine-borane, phosphine trichloroborane (H₃P·BCl₃) was reported by Besson in 1890. However, detailed investigations were not carried out until the mid-20th century when the next phosphine-borane was published by Gamble and Gilmont in 1940. Based on Stock’s work it was first thought that diborane diphosphine (B₂H₆·2PH₃) had been synthesized, however, on further investigations the simplest example of a phosphine-borane adduct (PH₃·BH₃) was identified. This phosphine-borane was monomeric and a white solid which did not show any decomposition.

### 1.3.2 Preparation of phosphine-boranes

An array of secondary and tertiary alkyl-functionalised phosphine-boranes (R₂PH·BH₃ and R₃P·BH₃) have been synthesised and published (Me₃P·BH₃, Me₂PH·BH₃, MePH₂·BH₃, Me₂PH·BHMMe₂ and Me₂PH·BMe₃). It was found that secondary and tertiary phosphine-borane adducts are significantly more stable than primary phosphine-borane adducts due to the phosphorus centre being much higher in basicity for the secondary and tertiary compounds due to increased electron donation from the alkyl substituents. This donation leads to a much stronger phosphorus-boron bond and so will prevent dissociation, which is a common feature in monoalkyl-substituted phosphine-boranes.
In early synthetic experiments it was common to use diborane (B$_2$H$_6$) and the required phosphine to yield the corresponding phosphine-borane. However, due to the toxicity and pyrophoric nature of diborane, this synthesis is very rarely used today. The modern approach in research labs is to carry out adduct formation via direct addition of primary, secondary or tertiary phosphines to BH$_3$·THF or BH$_3$·SMe$_2$ (Scheme 1.4) where the strongly donating phosphine rapidly displaces the weaker Lewis base; these reactions are usually clean and quantitative.$^{18}$

$$\text{PMe}_3 + \text{BH}_3\cdot\text{L} \rightarrow \text{Me}_3\text{P}-\text{BH}_3 + \text{L}$$

$L = \text{THF, SMe}_2$

**Scheme 1.4**: Preparation of a phosphine-borane using a borane adduct.

In situations where large quantities of reagents are needed a number of procedures have been used to synthesise phosphine-boranes. The first example is reduction of a phosphine oxide with a mixture of LiAlH$_4$, NaBH$_4$ and CeCl$_3$ (Scheme 1.5, Reaction 1).$^{22}$ The cerium trichloride is essential for this reaction to occur as the reduction will not proceed if the cerium complex is not present. The cerium forms a coordination complex with the oxygen on the phosphine oxide to improve the electrophilic nature of the P-centre which will then aid the LiAlH$_4$ to deoxygenate at the phosphorus. A second, widely used method is the use of borohydride reagents with mono/dichlorophosphines to produce the corresponding phosphine-borane adduct (Scheme 1.5, Reaction 2).$^{23, 24}$ The main advantage to this is the elimination of handling reactive primary and secondary phosphines. A third and more recent approach is the reaction of NaBH$_4$ and a proton source with a secondary or tertiary phosphine (Scheme 1.5, Reaction 3).$^{25}$ The NaBH$_4$ and proton source generate BH$_3$ *in situ* which then reacts with the phosphine, producing the phosphine-borane.
Scheme 1.5: Alternative reactions for the synthesis of phosphine-borane adducts. Reaction conditions. Reaction 1, i) LiAlH$_4$, NaBH$_4$, CeCl$_3$, 25 °C, THF. Reaction 2, i) sodium borohydride. Reaction 3, i) NaBH$_4$, THF and HOAc, THF.

The three alternative methods for synthesising phosphine-borane adducts (Scheme 1.5) are advantageous on a much larger scale due to the instability of the adduct (BH$_3$·THF) or the large production of noxious gases (BH$_3$·SMe$_2$). Sodium borohydride is much more readily available due to its low cost and convenient long term storage.

A fourth alternative method for the synthesis of phosphine-borane adducts is via a phosphine-amine exchange reaction where the amine-borane adduct can be treated with a large excess of the phosphine to yield the phosphine-borane adduct. Due to this reaction being an equilibration process, there are a number of factors which will affect the position of the equilibrium, such as the relative donor ability of the amine and phosphine, which depends on its substituents in relation to its sterics and electronic effects. It should be noted that this synthesis would not be ideal for expensive phosphines, such as HPCy$_2$, as a large excess of phosphine is needed to favour the production of the corresponding phosphine-borane adduct.

Many different functionalised tertiary phosphine-borane adducts have been synthesised from secondary phosphine-boranes by the Imamoto group (Chart 1.1).
Chart 1.1: Various reactions of the lithium derivative of diphenylphosphine-borane with a number of different electrophiles to form tertiary phosphine-boranes. Reaction conditions: i) RX. ii) XCH$_2$Y. iii) Br(CH$_2$)$_2$Br, EtOH. iv) R$_1$COR$_2$. v) O(CHO)$_n$, n = 2, 3. vi) RHCCHX. vii) (CH$_2$CH)$_3$PBH$_3$. viii) PhI, Pd(Ph$_3$P)$_4$.

Imamoto and co-workers investigated the reactions of secondary phosphine-boranes where the corresponding phosphine-borane-stabilised-carbanion can be easily made with an organometallic reagent (BuLi). These anions will then react with an array of electrophiles yielding functionalised phosphine-boranes (Chart 1.1). Due to the stability of the P-B bond and the versatility in which these types of compounds can be synthesised and used, these species are starting to show an increasing demand within asymmetric catalysis.$^{13}$

1.3.3 Decomplexation of boranes

As mentioned above, a useful feature of phosphine-boranes is that their formation is often reversible. The use of an excess of an amine such as diethylamine will often drive the reaction so that the BH$_3$ will bind to the nitrogen in preference to phosphorus (Scheme 1.6). This was first reported by Imamato, who used a large excess of diethylamine to cleave the P-B bond in a variety of phosphine-borane compounds.$^{22, 26}$ The limiting factor in the use of secondary amines in this way is that their use is not always suitable for phosphine-boranes that contain other functional groups, such as carbonyl groups. This problem was first
overcome by using DABCO (1,4-diazabicyclo[2.2.2]octane) or tmeda [tmeda = N,N,N′,N′-tetramethylethylenediamine]. Decomplexation can then be achieved under mild conditions, while retaining other functional groups within the newly made phosphine.

\[
\text{Me}_3\text{P} -\text{BH}_3 + \text{R}_2\text{NH} \rightleftharpoons \text{R}_2\text{HN} -\text{BH}_3 + \text{PR}_3
\]

Scheme 1.6: Decomplexation of a phosphine-borane.

Other methods of decomplexation include the use of acids, such as HBF$_4$·OMe$_2$, methane- and trifluoromethanesulfonic acid, or zeolites along with alcoholysis. Although the exact mechanism of decomplexation using acids is not understood, the production of hydrogen gas is observed and it is believed that the BH$_3$ unit may undergo nucleophilic substitution (Scheme 1.7).

Scheme 1.7: Nucleophilic substitution of a generic phosphine-borane. Reaction conditions: i) BH$_3$·SMe$_2$, ii) HBF$_4$·OMe$_2$.

1.4 Phosphine-borane-stabilised carbanions

Deprotonation of a phosphine-borane adduct α- to a P-BH$_3$ group yields the corresponding phosphine-borane-stabilised carbanion. However, until as recently as 2006, only four species of this kind had been isolated and structurally characterised. All of these compounds adopted a different structure in the solid state (Figure 1.5).

\[
[\text{Me}_2\text{P(BH}_3)\text{CHPMe}_2(\text{BH}_3)]\text{[Li(tmeda)]}_2 \ (3) \text{ crystallises as a separated ion pair with no contact between the carbanion centre and the lithium ion.}\]

The dicarbanion complex

\[
[(\text{Me}_3\text{Si})(\text{n-Pr}_2\text{P(BH}_3))\text{CCH}_2]\text{Li(pmdeta)}\text{[Li(pmdeta)]}_2 \ (4) \text{ was synthesised via a Schlenk dimerisation of the alkene } \{\text{Pr}_2\text{P(BH}_3)\}(\text{Me}_3\text{Si})\text{C=CH}_2; \text{ this compound is stabilised by both phosphine-borane and silyl groups [pmdeta = N,N,N′,N′-pentamethyldiethylenetriamine]. Compound 4 crystallises as a contact ion multiple in which the lithium cations are bound at either end of the dicarbanionic ligand by two H atoms of the BH}_3 \text{ moiety rather than the carbanion centres.}\]
The P-C and Si-C distances [1.711(2) and 1.808(2) Å, respectively] are shorter than usual bond lengths for P-C single bonds, which is consistent with a significant degree of negative hyperconjugation.\textsuperscript{32}

The α-metalated phenylphosphine-borane (5) crystallises as a monomeric species with a direct C-Li bond but no Li-BH\textsubscript{3} interactions,\textsuperscript{33} whereas the sterically hindered α-metalated phosphine-borane (THF)\textsubscript{3}Li\{[(Me\textsubscript{3}Si)\textsubscript{2}CPMe\textsubscript{2}(BH\textsubscript{3})]Li (6) crystallises as a contact ion multiple ate complex where one Li ion is bound by two carbanion centres of two phosphine-borane-stabilised carbanions and has a short contact to one of the H atoms of a BH\textsubscript{3} moiety from one ligand, whereas the second lithium cation is bound in an η\textsuperscript{3}-fashion by the H atoms of a BH\textsubscript{3} group. Therefore, the solid state structure exhibits both C-Li and BH\textsubscript{3}-Li contacts (Figure 1.6).
Figure 1.5: Different structural motifs observed for phosphine-borane-stabilised carbanions in the solid state.
During an extended study of the synthesis and structures of $\alpha$-metalated phosphine-boranes, Izod and co-workers found that the structures of these compounds are influenced by a number of different factors, including: (i) the degree of charge delocalisation at the carbanion centre, (ii) the nature of the substituents at the phosphorus, and (iii) the presence of co-ligands such as tmeda and pmdeta.\textsuperscript{34}

Even though the first example of a dialkylolithate complex was reported 50 years ago, very few have been isolated and structurally characterised by X-ray crystallography. The few complexes of this type are limited to tris(trimethylsilyl)methyl derivatives $[\text{Li}(\text{L})_n][\{\text{Me}_3\text{Si}\}_3\text{C}]_2\text{Li}]$ $\text{Li}(\text{THF})_4$ (7),\textsuperscript{35} $\text{Li}(\text{tmeda})_2$ (8),\textsuperscript{36} ($\text{pmdeta})\text{LiClLi(pmdeta)}$\textsuperscript{37}, cyclic systems such as $[\text{Li}(\text{tmeda})_2][(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{CH}_2)_2]\text{Li}]$ (9)\textsuperscript{38} and $[\text{Li}(\text{tmeda})_2][(\text{tmeda})\text{Li}(\text{CH}_2\text{Ph})_2]$ (10).\textsuperscript{39}

In the carbanion complex 6 the negative charge may be delocalised across both the silyl and phosphine-borane groups and so the binding modes adopted may be influenced by the steric and electronic properties of the bulky silyl groups. It is also important to note that $\text{Me}_2\text{PBH}_3$ and $\text{Me}_3\text{Si}$ groups are isoelectronic to each other which is why the dialkylolithate section of compound 6 is very similar to the dialkylolithate anions in compounds 7-10. The lengthening of the Li(2)-C bonds in 6 [2.249(8) and 2.252(8) Å] compared to the
corresponding bonds in compounds 7-10 [2.16(1), 2.20(1), 2.213(5), and 2.156(4) Å] is due to the increased coordination at 7 with a H atom of the BH3 moiety.\textsuperscript{34} Variable-temperature NMR spectroscopy of compound 6 reveals dynamic behaviour (Figure 1.7).

In order to investigate the level of stabilisation that could be achieved by the effect of the phosphine-borane group only, a new phosphine-borane Me\textsubscript{3}P(BH\textsubscript{3}) was examined.\textsuperscript{40} Treatment of Me\textsubscript{3}P(BH\textsubscript{3}) with either one equivalent of \textsuperscript{n}BuLi or MeNa gave the corresponding complexes {Me\textsubscript{2}P(BH\textsubscript{3})CH\textsubscript{2}}M [M = Li (11), Na (12)] (Scheme 1.8).\textsuperscript{40} The sodium derivative crystallises to form a polymeric chain where a sodium cation is bound through a carbanion centre and through one hydrogen on one borane group to give a pseudo-four-membered chelate ring (Figure 1.8 and 1.9).\textsuperscript{40}

\textbf{Figure 1.7}: Variable-temperature \textsuperscript{31}P{\textsuperscript{1}H} and \textsuperscript{7}Li NMR spectra of 6 in \textit{d}\textsubscript{8}-toluene [* Free phosphine-borane (Me\textsubscript{3}Si)\textsubscript{2}CHPMe\textsubscript{2}(BH\textsubscript{3})].
Figure 1.8. Repeat unit of polymeric 12.

Figure 1.9: Polymer chain of 12 with H atoms (except those bound to B) omitted for clarity.
However, the lithium complex 11 undergoes a rapid reaction with silicone grease to give a cluster complex \{\text{Me}_2\text{P(BH}_3\text{)CHSiMe}_2\text{OLi}\}_4\text{Li}_4\text{(Et}_2\text{O)}_{2.75}\text{(THF)}_{1.25} (13), which contains a siloxy-functionalised alkyl ligand (Scheme 1.8 and Figure 1.10). \[20\]

\[
\begin{align*}
\text{Me}_3\text{P(BH}_3\text{)} & \xrightarrow{n-\text{BuLi}} \text{Me}_2\text{P}-\text{C} & \text{Li} & \xrightarrow{(\text{Me}_2\text{SiO})_3} \text{Me}_2\text{P}-\text{C} & \text{Si} & \text{O} & \text{Li} \\
(11) & & & & \text{Me} & & \text{Me}
\end{align*}
\]

\[
\begin{align*}
\{\text{Me}_2\text{P(BH}_3\text{)CHSiMe}_2\text{OLi}\}_4\text{Li}_4 & \xrightarrow{x4} \text{Me}_2\text{P}-\text{C} & \text{Si} & \text{O} & \text{Li} & \text{Li} & \text{Li} & \text{Li} & \text{Li} \\
(13) & & & & \text{Me} & & \text{Me} & & \text{Li} & & \text{Me} & & \text{Me}
\end{align*}
\]

**Scheme 1.8: Synthesis of the cluster complex**

\{\text{Me}_2\text{P(BH}_3\text{)CHSiMe}_2\text{OLi}\}_4\text{Li}_4\text{(Et}_2\text{O)}_{2.75}\text{(THF)}_{1.25} (13).
The greater reactivity of the lithium salt of trimethylphosphine-borane towards the siloxanes in silicone grease compared to [(Me$_3$Si)$_2$(Me$_2$P(BH$_3$))C]$^-$ may be due to an increase in negative charge on the carbanion centre from a decrease in negative hyperconjugation, which leads to an increase in nucleophilicity at the carbanion centre. Attempts to isolate the lithiated complex {Me$_2$P(BH)CH$_2$}Li were unsuccessful.$^{40}$

1.4.1 Heavier alkali metal complexes

In 2006, the Izod group set out to study how the size and polarisability of the metal cation can affect the solid and solution state structure of complexes of the heavier alkali metals with the sterically hindered phosphine-borane-stabilised carbanion [(Me$_3$Si)$_2$(Me$_2$P(BH$_3$))C]$^-$.\textsuperscript{16}

Reactions between (Me$_2$Si)$_2$(Me$_2$P(BH$_3$))CH and one equivalent of either MeNa or MeK in cold diethyl ether gave the compounds [(Me$_3$Si)$_2$(Me$_2$P(BH$_3$))C]M [M = Na (14), K (15)].\textsuperscript{16} It was concluded that the solid state structures of these species varied significantly with increasing ionic radius of the metal. The sodium complex 14 crystallises as a one-
dimensional polymer, where each sodium ion is coordinated by the carbanion centre of one ligand and by an $\eta^2$-$\text{BH}_3$ group of an adjacent ligand, giving a pseudo-four-coordinate sodium ion with a distorted tetrahedral geometry (Figure 1.11). The potassium complex 15, however, crystallises with a complex two-dimensional sheet structure, in which there are two distinct ligand environments. For both structures it was evident that $\text{M-BH}_3$ contacts appeared to be the essential feature along with contacts from the metal cation to the carbanion centre.\(^{16}\)

**Figure 1.11:** Structures of compounds 14 and 15.

It is well known that co-ligands such as tmeda and pmdeta can affect the aggregation state and ligand binding modes of organo-alkali metal complexes. In 2007 Izod and co-workers investigated the effect of changing the co-ligand on the structure of the previously published potassium salt \([\{(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\}C]\text{K}\) (16) and showed that the solid state structures of the potassium complexes 16, \([(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\}C]\text{K(THF)}_{0.5}\) (17), \([(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\}C]\text{K(tmeda)}_2\) (18), \([(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\}C]\text{K(pmdeta)}_2\) (19) and \([(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\}C]\text{K(12-crown-4)}_2\) (20) were defined by the respective co-ligand.\(^{41}\) In each case, except 20, $\text{B-H-K}$ contacts seemed to be the important feature in the structures.

Izod and co-workers have also investigated the influence of aromatic ring substituents on the structures of phosphine-borane-stabilised carbanion complexes (Scheme 1.9).\(^{42}\)
This study concluded that the phenyl substituents affected the coordination mode of the carbanion.\textsuperscript{42} Compound 22 exhibited a preference for coordination through the BH$_3$ hydrogens with no metal-carbanion centre contact. In the presence of the weaker, monodentate diethyl ether ligands in 22 there was significant competition for coordination of the potassium cation by the aryl rings of the respective phosphine-borane-stabilised carbanion.\textsuperscript{42}

1.4.2 Alkaline earth metal complexes

Since the early 20th century, when the first organomagnesium compound was published by Barbier and Grignard, these compounds have been widely exploited in synthetic organic and organometallic chemistry.\textsuperscript{43} However, until recently there were still very few organo-heavier alkaline earth metal complexes and these were largely limited to complexes of cyclopentadienyl and substituted cyclopentadienyl ligands.\textsuperscript{43, 44} This was thought to be due to difficulties with their synthesis and manipulation due to their large ionic radii and the highly polar nature of the M-C σ-bonds.\textsuperscript{45-47} These properties tend to make compounds of this kind highly reactive, even towards the solvents they are prepared in. The first heavier alkaline earth metal analogue of a Grignard reagent was reported in 1905 by Beckmann,\textsuperscript{48} but the first structurally characterised organocalcium, \{(Me$_3$Si)$_2$CH\}_2Ca(1,4-dioxane) was not reported until 1991 by Cloke and co-workers.\textsuperscript{49} Significant progress has recently been made in this area, yielding an array of heavier alkaline earth metal organometallics including benzyl, acetylide, aryl, heteroatom-stabilised alkyl compounds, heterometallic species and organocalcium halides.\textsuperscript{43}

Izod and co-workers have reported some new organo-heavier alkaline earth metal compounds using the ligand \{(Me$_3$Si)$_2$[Me$_2$(BH)$_3$P]C\}.\textsuperscript{43} It was found that heavier alkaline earth metal complexes of the phosphine-borane-stabilised carbanion were easily accessible, however, their stabilities, especially towards THF were dependent on the nature of the cation. Treatment of AeI$_2$ [Ae = Mg, Ca, Sr, Ba] with two equivalents of \{(Me$_3$Si)$_2$[Me$_2$(BH)$_3$P]C\}K
in toluene or THF yielded the complexes \([(\text{Me}_3\text{Si})_2\text{Me}_2(\text{BH}_3)\text{P}]\text{C}\);\text{Ae}(\text{THF})_n\ [\text{Ae} = \text{Mg (23)}, \ n = 0; \ \text{Ca (24)}, \ n = 4; \ \text{Sr (25)}, \ n = 5; \ \text{Ba (26)}, \ n = 5]\) (Scheme 1.10).\(^{43}\)

Scheme 1.10: Synthesis of group 2 complexes of a phosphine-borane-stabilised carbanion.

Compound 23 crystallises solvent-free, with chelating ligands, whereas 24, 25 and 26 crystallise as THF solvates, where the phosphine-borane-stabilised carbanions bind to the metal centres via their borane H atoms only, such that there is no contact between the metal and the carbanion centres in these compounds.\(^{43}\) Compounds 22 and 23 are stable indefinitely in THF, however, 23 and 24 react slowly with THF at room temperature to give the free phosphine-borane as the sole phosphorus-containing product.\(^{43}\)

Westerhausen and co-workers, and Harder and co-workers have independently published the same example of a heavier alkaline earth metal complex of phosphine-borane-stabilised carbanion \([(\text{THF})\text{Ca}\{\text{CH(PPh}_2\text{BH}_3\}_2]\) (27).\(^{50, 51}\) In compound 27 one anion exclusively binds through the hydrogen atoms of the BH\(_3\) unit whereas the other ligand binds via the carbanion centre (Figure 1.12).\(^{50, 51}\)
In summary, it has been shown that phosphine-borane-stabilised carbanions adopt a wide variety of coordination modes in their complexes (Figure 1.13), including (i) a chelating mode (I), (ii) a number of bridging modes (II–V), and (iii) a terminal BH3-donor mode (VI). The coordination mode adopted depends on the nature of the metal, the presence of co-ligands and on the steric and electronic properties of the substituents at the P and C centres.41

Figure 1.12: Structure of 27.

Figure 1.13: Range of ligand binding modes for phosphine-borane-stabilised carbanions.
1.5 Heavier group 14 carbene analogues [tetrylenes, \( R_2E \) (E = Ge, Sn, Pb)]

Carbene chemistry has seen a huge rise in popularity since Arduengo and co-workers reported the first stable \( N \)-heterocyclic carbene (NHC).\(^5\) Over the last 3 decades there has been significant progress with regards to the synthesis of heavier group 14 carbene analogues (tetrylenes) \( R_2E \) (E = Ge, Sn or Pb).\(^5\) The vast majority of these tetrylenes are stabilised by heteroatoms which are adjacent to the tetrel centre, for example the diaminotetrylenes, \((R_2N)_2E\), which are analogues of the Arduengo-type diaminocarbenes. Within these compounds the electron deficient tetrel centre is thermodynamically stabilised by efficient overlap between the heteroatom lone pairs and the vacant tetrylene \( p_\pi \) orbital (Figure 1.14).\(^3\)

![Vacant \( p_\pi \)-orbital](image)

**Figure 1.14:** Molecular orbital diagram illustrating electron donation from the heteroatom into the vacant \( p \)-orbital of the Sn centre.

In comparison to diaminotetrylenes, there are far fewer examples of diorganotetrylenes i.e. diaryl- or dialkyl-tetrylenes.\(^5\) This is due to the fact that thermodynamic stabilisation is absent in these compounds and therefore these compounds solely relied on kinetic stabilisation by stERICALLY bulky groups.\(^5\) In the absence of sufficient steric bulk these species typically dimerise to the corresponding ditetrene analogues \( R_2E=ER_2 \) or else oligomerise to cyclic species (e.g. \([Cy_2Sn]_6\)).

Lappert and co-workers reported the first dialkylstannylene \( ((Me_3Si)_2CH)_2Sn \) (28) in the 1970s (Figure 1.15). Compound 28 exists as a monomeric structure in the gas phase, but dimerises to the corresponding distannene 28a in the solid state; compounds 28 and 28a are in a dynamic equilibrium in solution.\(^5\)

With the ongoing investigation into the chemistry of phosphine-borane-stabilised carbanions Izod and co-workers have recently reported several examples of cyclic and acyclic dialkyltetrylenes which are stabilised by the presence of sterically demanding groups and by agostic-type B-H···E interactions (Figure 1.16).\(^5\) This stabilising effect means that monomeric dialkylstannylene and plumbylene compounds may be isolated even with relatively small alkyl substituents.\(^5\)
The first and second examples of dialkylstannylene shown to exist as a monomer in the solid state that did not contain heteroatoms were reported by Kira and co-workers in 1991 (30), and Eaborn, Smith and co-workers in 2000 (31), respectively (Figure 1.15).59,60 The first example of a B-H···Sn agostic-type interaction involving low oxidation-state main group metal centres was reported by Izod and co-workers (32)53 (Figure 1.16), which is similar to Kira’s dialkylstannylene (30), however, 30 and 32 exhibit different structures and electronic behaviour.

Figures 1.15: An array of cyclic and acyclic heavier group 14 tetrylenes.
Figure 1.16: An array of cyclic and acyclic heavier group 14 phosphine-borane-stabilised tetrylenes.

Kira and co-workers noted difficulties in the isolation of 30 cleanly and in good yields, whereas compound 32 was isolated in very good yields and with high purity. Izod and co-workers attributed this characteristic to compound 32 exhibiting a higher charge delocalisation away from the carbanion centres, which may be due to the R₂P(BH₃) group. This would then decrease the nucleophilic character of the carbanion centres, reducing the tendency towards reduction of Sn(II) to elemental tin. Compound 32 was isolated as a 1:1 mixture of the rac and meso diastereomers (Figure 1.17).
Figure 1.17: Compound 32 existing as rac and meso diastereomers with B-H···Sn agostic-type interactions.

Spectroscopic studies of compound 32 clearly show that the solid state structure is persistent in solution, where the $^{119}\text{Sn}\{^1\text{H}\}$ NMR chemical shifts are more than 1500 ppm lower than the chemical shifts for compound 30, indicating the B-H···Sn interactions have a remarkable influence on the electronic structure.\textsuperscript{53} Multi-element NMR spectroscopy indicated that meso-32 exhibited dynamic behaviour which was clearly seen in the variable-temperature $^{31}\text{P}\{^1\text{H}\}$ and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra and which was attributed to the competitive binding of the two BH$_3$ units to the Sn(II) centre (Figure 1.18) as well as restricted rotation about the highly sterically hindered P-C bond of the phosphine-borane ligands (Figure 1.19).\textsuperscript{53}

Figure 1.18: Competition of the binding of two BH$_3$ units to the Sn(II) centre.
The first acyclic phosphine-borane-substituted dialkylstannylenes (34 and 35) were reported by Izod and co-workers in 2009 (Figure 1.16).\(^{54}\) Compounds 34 and 35 were isolated as the rac diastereomers and \(^{31}\)P{\(^1\)H} NMR spectra showed no evidence for the formation of the meso diastereomer, which is different compared to compound 32 where both the rac and meso diastereomers are formed.\(^{53, 54}\) Izod and co-workers proposed that the formation of only the rac isomer was due to the formation of two B-H agostic-type interactions being much more favourable than in the meso diastereomer, where only one such type of interaction is seen.\(^{54}\) There was also no evidence to suggest that compounds 34 and 35 dimerise in solution and DFT studies show that dimerisation is significantly disfavoured.\(^{54}\)

This chapter has provided a brief overview of the chemistry involved in phosphine-boranes, phosphine-borane-stabilised carbanions of group 1, 2 and heavier group 14, and organometallics, with a particular emphasis on the different structural motifs. It is clear that information regarding \(\alpha\)-metalated phosphine-boranes is scarce, compared to their Si-substituted analogues. The work presented in this thesis is the synthesis of an array of \(\alpha\)-metalated phosphine-boranes and phosphine-borane-substituted heavier group 14 carbene analogues (Sn) with either a flexible backbone or a rigid linker, with particular interest in both the solid and solution-state structures of these complexes. These investigations are vital in order to focus on the extent of the stabilisation effects of the agostic interactions between the heavier group 14 cation and the hydrogen atoms on the BH\(_3\) unit. Also whether the incorporation of a rigid linker yields differences in the solid and solution-state structures compared to their flexible linker analogues.
1.6 References

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Chapter 2. Synthesis of phosphine-borane precursors

2.1 Introduction

Phosphine-borane adducts are important intermediates used to synthesise polyphosphines, such as the chiral diphosphate DIPAMP (Scheme 2.1).\textsuperscript{1,2}

\[ \text{BH}_3 \quad \text{Me} \quad \text{P} \quad \text{CH}_3 \quad \underset{(i)}{\text{BuLi}(-	ext{-sparteine})} \quad \text{Me} \quad \text{P} \quad \text{Ar} \quad \text{Ar} \quad \text{R} \quad \text{R} \quad \text{SiMe}_3 \quad \text{PCy}_2 \quad \text{BH}_3 \]

\textbf{Scheme 2.1:} Synthesis of DIPAMP using a phosphine-borane-stabilised carbanion. Reaction conditions: i) \textsuperscript{t}BuLi\{(-)-sparteine\}, ii) Cu(OPiv)\textsubscript{2} and Et\textsubscript{2}NH.

An array of phosphine-borane adducts and phosphine-borane-stabilised carbanions has been synthesised and characterised over the past century (see sections 1.3.2 and 1.4 for more detail). Despite the widespread use of phosphine-borane-stabilised carbanions, little is known about their reactivity and structure. In order to investigate the incorporation of a rigid backbone linker and its effect on the structure of heavier group 14 tetrelenes, an array of mono- and bis(phosphine-boranes) with flexible and rigid linkers has been prepared, these compounds are described below. The compounds can be classified into 4 groups. Group A includes the linear bis(phosphine-boranes) \([\text{Me}_2\text{P}((\text{BH}_3)\text{CH}_2\text{SiMe}_2\text{CH}_2)]_2\) (37) and \([\text{Ph}_2\text{P}((\text{BH}_3)\text{CH}_2\text{SiMe}_2\text{CH}_2)]_2\) (40), group B includes the bis(phosphine-boranes) with rigid spacers \(1,2-\text{C}_6\text{H}_4\{\text{CH}_2\text{PR}_2((\text{BH}_3))\}_2\) [\(\text{R} = \text{tPr}\) (44), Ph (45) and Cy (46)], group C includes the mono(phosphine-boranes) \(\text{C}_6\text{H}_5\{\text{CH}_2\text{PR}_2((\text{BH}_3))\}\) [\(\text{R} = \text{tPr}\) (47), Ph (48) and Cy (49)] and group D includes the linear phosphine-boranes \(\text{C}_6\text{H}_5\{\text{CH}_2\text{SiMe}_3\text{PCy}_2((\text{BH}_3))\}\) (50) and \{\(\text{CH}_2\text{CH}_2\text{PCy}_2((\text{BH}_3))\)\}_2 (51).
2.2 Synthesis and characterisation of Group A precursors [linear bis(phosphine-boranes)]

2.2.1 Me₃P(BH₃) (36)

There are several methods that have been published which describe the synthesis of this precursor, all of which include the reaction of Me₃P with one of the following: i) NaBH₄ activated with CO₂; ii) diborane; or iii) with the borane adduct BH₃·THF. Work reported in this thesis, however, uses the adduct BH₃·SMe₂ rather than the THF adduct, due to its availability and low cost.

Reaction of one equivalent of BH₃·SMe₂ with one equivalent of Me₃P gives the air stable colourless solid 36 in quantitative yield (Scheme 2.2).

\[
\begin{align*}
\text{Me}_3\text{P} & \overset{(i)}{\longrightarrow} \text{Me}_3\text{P} \text{---BH}_3 \\
\text{36}
\end{align*}
\]

**Scheme 2.2.** Synthesis of 36. Reagents and conditions: i) BH₃·SMe₂, r.t., Et₂O, 1 h.

The preparation of 36 and its α-metalated species must be carried out in a grease-free Schlenk. If the metalation of 36 is carried out in normal silicone-greased Schlenks, an unexpected reaction of the simple phosphine-borane-stabilised carbanion occurs with the siloxanes present within the silicone grease to give an alkyl siloxide cluster (Scheme 2.3).³ It is therefore imperative to exclude silicone grease during the synthesis of 36.
Scheme 2.3. Synthesis of an unusual complex containing [Me₂P(BH₃)CHSiMe₂O]²⁺ siloxy-functionalised carbanions formed via the reaction between intermediate 36a and silicone grease. Reagents and conditions: i) "BuLi, THF, r.t., 2 h. ii) Silicone grease, Et₂O, r.t., 2 h. iii) + 36a, - 36.

The product 36b crystallises as a cluster containing siloxy-functionalised carbanions (Figure 2.1). Izod and co-workers have suggested that the reaction with the silicon grease could be due to increased negative charge around the carbanion centre, due to a decrease in delocalisation around the molecule compared to Si-substituted analogues such as [Me₃SiCHP(BH₃)Me]⁺. This therefore, increases the nucleophilicity of the carbanion centre and so it is more reactive towards silicone grease than its phenyl-substituted analogue 38.
Figure 2.1. Molecular structure of one independent molecule of 36b with all H atoms (except for those bound to boron) omitted for clarity.

2.2.2 $[\text{Me}_2\text{P(BH}_3\text{)CH}_2\text{SiMe}_2\text{CH}_2\text{]}_2$ (37)

One equivalent of $^t\text{BuLi}$ was added to 36 and the resulting mixture was added in situ to half an equivalent of 1,2-bis(chlorodimethylsilyl)ethane to give the linear bis(phosphine-borane) 37 in very good yield (Scheme 2.4).

![Scheme 2.4](image)

Scheme 2.4. Metalation of 36 and synthesis of 37. Reagents and conditions: i) $^t\text{BuLi}$, THF, r.t., 1 h. ii) ClSiMe$_2$CH$_2$CH$_2$SiMe$_2$Cl, THF, r.t., 1 h.

Compound 37 is isolated as an essentially pure compound but can be crystallised from hot methylocyclohexane to form colourless single crystals suitable for X-ray crystallography. The structure of 37 is of interest for comparison of its bond lengths and angles with $\alpha$-
metalated phosphine-borane analogues (see Chapter 3.2 for further information). Below are selected bond lengths and angles for 37 (Table 2.1) along with its molecular structure (Figure 2.2).

![Molecular structure of 37](image)

**Figure 2.2.** Molecular structure of 37 with H atoms (except for those bound to boron) omitted for clarity.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-B</td>
<td>1.917(4)</td>
<td>B-P-C(3)</td>
<td>115.5(1)</td>
</tr>
<tr>
<td>P-C(3)</td>
<td>1.800(2)</td>
<td>B(0A)-P(0A)-C(3A)</td>
<td>115.5(1)</td>
</tr>
<tr>
<td>C(3)-Si</td>
<td>1.892(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-C</td>
<td>1.811(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-C(2)</td>
<td>1.807(2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 2.1.** Selected bond lengths (Å) and angles (°) for 37.

The $^1$H,$^{11}$B,$^{13}$C,$^{31}$P NMR spectra of compound 37 are as expected. In CDCl$_3$ the $^1$H,$^{11}$B NMR spectrum of 37 contains a multiplet at 0.5 ppm which corresponds to the two BH$_3$ moieties and the CH$_2$CH$_2$ backbone, and a broad singlet at 0.51 ppm due to the CH$_2$P protons. The $^{11}$B,$^{1}$H NMR spectrum contains a doublet at -37.5 ppm and the $^{31}$P,$^{1}$H NMR spectrum contains a quartet at 3.4 ppm ($J_{PB} = 58.8$ Hz).

The solid state structure of compound 37 is as expected. The C-Si and P-B distances [C(3)-Si 1.892(2) and B-P 1.917(4) Å] are typical of such compounds, whereas the P-C
distance [P-C(3) 1.800(2) Å] is somewhat shorter than the corresponding P-C distance [P-C 1.826(2) Å] in the previously reported linear bis(phosphine-borane) [Me₂P(BH₃)CH(SiMe₃)SiMe₂CH₂]₂ (38) (Figure 2.3).

![Molecular structure of 38](image)

**Figure 2.3.** Molecular structure of 38 with H atoms (except for those bound to boron) omitted for clarity.¹⁰

### 2.2.3 Ph₂(Me)P(BH₃) (39)

Compound 39 was prepared by a modified literature procedure where the phosphine-borane was made via the chlorodiphenylphosphine rather than diphenylmethylphosphine.¹¹ Chlorodiphenylphosphine was alkylated using methylmagnesium bromide and was then boronated using BH₃·SMe₂ to give 39 as a viscous colourless liquid in excellent yield (Scheme 2.5).

```
Ph₂PCl \rightarrow \text{(i)} \rightarrow \text{Ph₂PMe} \rightarrow \text{(ii)} \rightarrow \text{Ph₂MeP} - \text{BH₃}
```

**Scheme 2.5.** Synthesis of 39. Reagents and conditions: i) MeMgBr, THF, 0 °C, 1 h.  ii) BH₃·SMe₂, THF, r.t., 16 h.

The ¹H, ¹³C{¹H}, ¹¹B{¹H} and ³¹P{¹H} NMR data for compound 39 correspond to the data reported previously.¹¹
2.2.4 \[\text{Ph}_2\text{P}((\text{BH}_3)\text{CH}_2\text{SiMe}_2\text{CH}_2)_2\] (40)

One equivalent of "BuLi was added to 39, resulting in a dark orange solution. This solution was added in situ to 0.5 equivalent of 1,2-bis(chlorodimethylsilyl)ethane. Recrystallisation from hot methylcyclohexane/THF gave 40 as a colourless crystalline solid in good yield (Scheme 2.6).

Scheme 2.6. Synthesis of 40. Reagents and conditions: i) "BuLi, THF, r.t., 1 h.
ii) ClSiMe\_2\text{CH}_2\text{SiMe}_2\text{Cl}, THF, r.t., 1 h.

The \(^1\text{H}\{^{11}\text{B}\}, \text{^{11}\text{B}\{^{1}\text{H}\}, \text{^{13}\text{C}\{^{1}\text{H}\}\ and \text{^{31}\text{P}\{^{1}\text{H}\} NMR spectra of compound 40 are as expected. In CDCl}_3 the \(^1\text{H}\{^{11}\text{B}\} NMR spectrum of 40 contains a doublet at 1.04 ppm which corresponds to the two BH\_3 moieties, a doublet at 0.30 ppm (J\_PH = 5.00 Hz) due to the CH\_3P protons, and, a complex multiplet between 7.39 and 7.44 ppm due to the aromatic protons. The \(^{11}\text{B}\{^{1}\text{H}\} NMR spectrum contains a broad peak at -38.9 ppm on which coupling to \text{^{31}\text{P}} is not resolved and the \text{^{31}\text{P}\{^{1}\text{H}\} NMR spectrum contains a quartet at 13.5 ppm (J\_PB = 69.5 Hz).

It is notable that throughout these investigations with phosphine-boranes, the \text{^{31}\text{P}\{^{1}\text{H}\} NMR spectra do not exhibit a typical quartet (Figure 2.4). The spin of \text{^{11}\text{B}} is I = 3/2 and therefore, the \text{^{31}\text{P}} NMR spectrum of a phosphine-borane obtained should exhibit a quartet with line ratios of 1:1:1:1.\textsuperscript{12} However, the \text{^{31}\text{P}\{^{1}\text{H}\} NMR spectra recorded during these investigations show an increase in line height for the two middle peaks of the quartet. This increase in height is due to low abundant \text{^{10}\text{B}} with a spin of I = 3. With \text{^{10}\text{B}}, the septet produced by this nucleus lies underneath the original \text{^{11}\text{B}} quartet, and so increases the two middle signals of the quartet to give the appearance of a Pascals quartet. There is also a significant amount of line broadening of the \text{^{31}\text{P}\{^{1}\text{H}\} NMR spectra of phosphine-borane compounds due to \text{^{11}\text{B}} and \text{^{10}\text{B}} possessing a relatively large quadrupole moment (4.059 and 8.459 \times 10^{-30} \text{ Q m}^2, respectively).\textsuperscript{12}
2.3 Synthesis and characterisation of Group B precursors [\(o\)-phenylene-bridged bis(phosphine-boranes)]

2.3.1 \(R_2PH(BH_3) \ [R = \text{iPr} (41), \text{Ph} (42) \text{ or Cy} (43)]\)

A solution of diisopropylchlorophosphine in THF was heated under reflux with one equivalent of LiAlH₄ and the resulting product was treated with the adduct BH₃·SMe₂ to give a colourless oil in fairly good yield (Scheme 2.7). An acidic aqueous workup with dilute HCl was needed to dissolve any remaining salts that resulted from the use of LiAlH₄ in order to isolate 41.
When diphenylchlorophosphine was reacted with one equivalent of LiAlH₄ followed by an *in situ* boronation (Scheme 2.7) a mixture of Ph₂PH(BH₃) (42) and other impurities was isolated. Distillation of this mixture gave a pure sample of 42 in an excellent yield. Both 42 and 43 [Cy₂PH(BH₃)] can be made via a straightforward boronation from the relevant phosphine. This, however, is a much more expensive way of making the corresponding phosphine-boranes; however, compound 43 [Cy₂PH(BH₃)] was always made via its phosphine to optimise yield.

**2.3.2 1,2-C₆H₄(CH₂PR₂(BH₃))₂ [R = ’Pr (44), Ph (45) and Cy (46)]**

Compounds 41, 42 and 43 were metalated by treatment with "BuLi and these solutions were added to 0.5 equivalent of α,α-,dichloro-α-xylene to give 44, 45 and 46, respectively as colourless solids after an aqueous workup (Scheme 2.8).¹³

It has been previously reported that similar reactions between 1,2-C₆H₄(CH₂Br)₂ and R₂P(BH₃)Li gave a mixture of products.¹³ This mixture of products was likely due to quaternisation of the resulting phosphine-borane (Scheme 2.9), due to favoured oxidative addition of the benzylic bromide to the phosphorus centre.¹⁴
Scheme 2.9. Possible products formed via quaternisation of tertiary phosphine-boranes with 1,2-C₆H₄(CH₂Br)₂.

The ¹H{¹¹B}, ¹¹B{¹H}, ¹³C{¹H} and ³¹P{¹H} NMR spectra of compounds 44-46 are as expected. In CDCl₃ the ¹H{¹¹B} NMR spectrum of 44 contains a doublet at 0.33 ppm (J₁H = 14.5 Hz) which corresponds to the two BH₃ moieties, a pair of doublet of doublets at 1.13 ppm (J₁H = 13.8, J₁H = 7.1 Hz) and 1.20 ppm (J₁H = 14.1, J₁H = 7.3 Hz) which are due to the CH₃ groups on the ³Pr₂ substituents and a doublet at 3.32 ppm (J₁H = 11.6 Hz) which is due to the CH₂P protons. The ¹¹B{¹H} NMR spectrum contains a doublet at -44.3 ppm (J₁P = 49.0 Hz) and the ³¹P{¹H} NMR spectrum contains a broad peak at 35.2 ppm in which coupling to ¹¹B is not resolved. In CDCl₃ the ¹H{¹¹B} NMR spectrum of 45 contains a doublet at 0.9 ppm (J₁H = 15.5 Hz) which corresponds to the two BH₃ moieties and a doublet at 3.53 ppm (J₁H = 11.7 Hz) due to the CH₂P protons. The ¹¹B{¹H} NMR spectrum contains a broad peak at -40.1 ppm and the ³¹P{¹H} NMR spectrum contains a broad peak at 18.3 ppm. In CDCl₃ the ¹H{¹¹B} NMR spectrum of 46 contains a doublet at 0.29 ppm (J₁H = 15.1 Hz) which corresponds to the two BH₃ moieties and a doublet at 3.29 ppm (J₁H = 11.5 Hz) due to the CH₂P protons. The ¹¹B{¹H} NMR spectrum contains a broad peak at -43.6 ppm and the ³¹P{¹H} NMR spectrum contains a broad peak at 27.8 ppm.

Compound 44 is isolated as an essentially pure compound but can be recrystallised to form single crystals suitable for X-ray crystallography from cold (-30 °C) toluene. Below are selected bond lengths and angles for 44 (Table 2.2) along with its molecular structure (Figure 2.5).
**Figure 2.5.** Molecular structure of 44 with H atoms (except for those bound to boron) omitted for clarity.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(1)-P(1)</td>
<td>1.914(2)</td>
</tr>
<tr>
<td>P(1)-C(1)</td>
<td>1.8392(11)</td>
</tr>
<tr>
<td>P(1)-C(9)</td>
<td>1.8413(12)</td>
</tr>
<tr>
<td>P(1)-C(12)</td>
<td>1.8375(11)</td>
</tr>
<tr>
<td>P(2)-C(8)</td>
<td>1.8372(11)</td>
</tr>
<tr>
<td>P(2)-C(15)</td>
<td>1.8365(13)</td>
</tr>
<tr>
<td>P(2)-C(18)</td>
<td>1.8338(12)</td>
</tr>
<tr>
<td>B(2)-P(1)</td>
<td>1.923(2)</td>
</tr>
<tr>
<td>C(18)-P(2)-B(1)</td>
<td>113.29(6)</td>
</tr>
<tr>
<td>C(16)-P(1)-B(2)</td>
<td>115.34(6)</td>
</tr>
</tbody>
</table>

**Table 2.2.** Selected bond lengths (Å) and angles (°) for 44.

Compound 44 crystallises as a discrete molecular species where the two 'Pr₂P(BH₃) fragments lie on opposites sides of the phenylene linker. The B-P bond lengths [B(1)-P(2), 1.914(2); B(2)-P(1), 1.923(2) Å] for compound 44 are similar to the corresponding B-P distance in compound 37 [B-P, 1.917(4) Å], whereas the P(1)-C(benzyl) bond lengths in 44 [P(1)-C(1), 1.8392(11); P(2)-C(8), 1.8372(11) Å] are significantly longer than the corresponding distances in 37 [P(1)-C(3), 1.800(2) Å].
2.4 Synthesis and characterisation of Group C precursors (benzyl-substituted phosphine-boranes)

2.4.1 C₆H₅CH₂PR₂(BH₃) [R = 'Pr (47), Ph (48) and Cy (49)]

Benzylic-substituted phosphine-boranes C₆H₅{CH₂PR₂(BH₃)} [R = 'Pr (47), Ph (48) and Cy (49)] were made via the corresponding precursors 41, 42 and 43 respectively. Compounds 41, 42 and 43 were reacted with one equivalent of °BuLi followed by one equivalent of benzyl bromide to form a colourless oil (47), and colourless solids (48 and 49) in relatively good yields after an aqueous workup (Scheme 2.10). Compounds 48 and 49 were isolated as essentially pure solids but 48 can be recrystallised from hot toluene to give single crystals suitable for X-ray crystallography. Below are selected bond lengths and angles for 48 (Table 2.3) along with its molecular structure (Figure 2.6).

**Scheme 2.10.** Synthesis of 47, 48 and 49. Reagents and conditions: i) °BuLi, THF, r.t., 1 h. 
ii) Benzyl bromide, THF, r.t., 16 h.

Quantities of the benzyl bromide have to be 1 mol equivalent as this reaction will yield quaternisation products in the presence of an excess of benzyl bromide (Scheme 2.11).

**Scheme 2.11.** Quaternisation of tertiary phosphine-boranes. Reagents and conditions: 
  i) excess benzyl bromide.
The use of benzyl chloride could eliminate this issue, however as long as care is taken using benzyl bromide 47, 48 and 49 may be isolated in excellent purity and yield.

\[ \text{Figure 2.6. Molecular structure of 48 with H atoms (except for those bound to boron) omitted for clarity.} \]

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>Angles (°)</th>
</tr>
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<tbody>
<tr>
<td>P(1)-B(1)</td>
<td>1.918(2)</td>
</tr>
<tr>
<td>P(1)-C(1)</td>
<td>1.825(2)</td>
</tr>
<tr>
<td>B(1)-H(1C)</td>
<td>1.11(2)</td>
</tr>
<tr>
<td>B(1)-H(1D)</td>
<td>1.12(2)</td>
</tr>
<tr>
<td>B(1)-H(1E)</td>
<td>1.14(2)</td>
</tr>
<tr>
<td>B(1)-P(1)-C(1)</td>
<td>113.00(8)</td>
</tr>
</tbody>
</table>

**Table 2.3.** Selected bond lengths (Å) and angles (°) for 48.

The \( ^1 \text{H} \{^{11} \text{B}\}, ^{11} \text{B} \{^1 \text{H}\}, ^{13} \text{C} \{^1 \text{H}\} \) and \( ^{31} \text{P} \{^1 \text{H}\} \) NMR spectra of compounds 47-49 are as expected. In CDCl\(_3\) the \( ^1 \text{H} \{^{11} \text{B}\} \) NMR spectrum of 47 contains a doublet at 0.35 ppm \( (J_{\text{PH}} = 15.0 \text{ Hz}) \), which corresponds to one BH\(_3\) unit, and a pair of doublet of doublets
(Figure 2.7) at 1.07 ppm ($J_{HH} = 3.00$ Hz, $J_{PH} = 9.00$ Hz) due to the methyl protons, as well as a doublet at 2.98 ppm ($J_{PH} = 11.5$ Hz) corresponding to the CH$_2$P protons.

**Figure 2.7.** $^1$H($^{11}$B) NMR spectrum of 47 in CDCl$_3$ showing diastereotopic methyl groups and CH fragment of the isopropyl substituents.

This splitting pattern arises due to the fact that both methyl groups within the isopropyl substituents are diastereotopic so Me$_a$ can never be in the same chemical environment as Me$_b$ (Figure 2.8).
The $^{11}$B{$^1$H} NMR spectrum of 47 contains a doublet at -43.2 ppm ($J_{PB} = 59.7$ Hz) and the $^{31}$P{$^1$H} NMR spectrum contains a quartet at 34.0 ppm ($J_{PB} = 59.7$ Hz). In CDCl$_3$ the $^1$H{$^{11}$B} NMR spectrum of 48 contains a doublet at 0.9 ppm ($J_{PH} = 15.9$ Hz) which corresponds to the BH$_3$ unit, and a doublet at 3.15 ppm ($J_{PH} = 11.8$ Hz) due to the CH$_2$P protons. The $^{11}$B{$^1$H} NMR spectrum contains a doublet at -39.1 ppm ($J_{PB} = 49.3$ Hz) and the $^{31}$P{$^1$H} NMR spectrum contains a quartet at 18.0 ppm ($J_{PB} = 49.3$ Hz). In CDCl$_3$ the $^1$H{$^{11}$B} NMR spectrum of 49 contains a doublet at 0.40 ppm ($J_{PH} = 15.0$ Hz) which corresponds to the BH$_3$ unit, and a doublet at 3.04 ppm ($J_{PH} = 15.0$ Hz) which corresponds to the CH$_2$P protons. The $^{11}$B{$^1$H} NMR spectrum contains a doublet at -43.5 ppm ($J_{PB} = 57.8$ Hz) and the $^{31}$P{$^1$H} NMR spectrum contains a quartet at 27.2 ppm ($J_{PB} = 57.8$ Hz).

Compound 48 crystallises as a discrete molecular species. The B-P bond length [B(1)-P(1), 1.918(2) Å] for compound 48 is similar to the corresponding B-P distances in compounds 37 [B-P, 1.917(4) Å] and 44 [P(1)-B(1), 1.914(2), P(2)-B(2), 1.923(2) Å], whereas the P(1)-C(benzyl) bond length in 48 [P(1)-C(1), 1.825(2) Å] is significantly shorter than the corresponding distances in compound 44 [P(1)-C(1), 1.8392(11); P(2)-C(8), 1.8372(11) Å] and significantly longer than the corresponding distance in 37 [P(1)-C(3), 1.800(2) Å].

**Figure 2.8.** Newman projections along the C-P bond showing the diastereotopic nature of Me$_a$ and Me$_b$ in the isopropyl substituents of 47.
2.5 Synthesis and characterisation of Group D precursors [SiMe$_3$-substituted and linear bis(phosphine-boranes)]

2.5.1 C$_6$H$_5$[CH(SiMe$_3$)PCy$_2$(BH$_3$)] 50

Compound 49 undergoes an α-metalation by $^n$BuLi followed by a silicon-carbon bond formation with chlorotrimethylsilane to form essentially pure 50 as a colourless solid in a relatively good yield (Scheme 2.12).

Scheme 2.12. Synthesis of 50. Reagents and conditions: i) $^n$BuLi, THF, r.t., 30 mins.

ii) Me$_3$SiCl, THF, r.t., 30 mins.

The $^1$H{$^{11}$B}, $^{11}$B{$^1$H}, $^{13}$C{$^1$H} and $^{31}$P{$^1$H} NMR spectra of compound 50 are as expected. In CDCl$_3$ the $^1$H{$^{11}$B} NMR spectrum of 50 contains a doublet at 0.65 ppm ($J_{PH} = 14.2$ Hz) which corresponds to the BH$_3$ unit, and a doublet at 2.72 ppm ($J_{PH} = 20$ Hz) which corresponds to the PCHSi proton. The $^{11}$B{$^1$H} NMR spectrum contains a doublet at -40.3 ppm ($J_{PB} = 64.2$ Hz) and the $^{31}$P{$^1$H} NMR spectrum contains a quartet at 29.2 ppm ($J_{PB} = 64.2$ Hz).

2.5.2 [CH$_2$CH$_2$PCy$_2$(BH$_3$)]$_2$ 51

Two equivalents of 43 underwent an α-metalation with $^n$BuLi followed by addition to one equivalent of 1,4-dibromobutane to form an air stable colourless solid with good purity and yield (Scheme 2.13).
Scheme 2.13. Synthesis of 51. Reagents and conditions: i) "BuLi, THF, r.t., 1 h. ii) 1,4-dibromobutane, THF, r.t., 16 h.

The \(^1\text{H}\{^{11}\text{B}\}, ^{11}\text{B}\{^{1}\text{H}\}, ^{13}\text{C}\{^{1}\text{H}\} \text{ and } ^{31}\text{P}\{^{1}\text{H}\} \text{ NMR spectra of compound 51 are as expected. In CDCl}_3 \text{ the } ^{1}\text{H}\{^{11}\text{B}\} \text{ NMR spectrum of 51 contains a doublet at 0.29 ppm (}J_{PH} = 15.1 \text{ Hz}) \text{ which corresponds to the two BH}_3 \text{ moieties, the } ^{11}\text{B}\{^{1}\text{H}\} \text{ NMR spectrum contains a doublet at -44.3 ppm and the } ^{31}\text{P}\{^{1}\text{H}\} \text{ NMR spectrum contains a quartet at 25.2 ppm (}J_{PB} = 49.0 \text{ Hz}).}

2.6 Conclusion

The phosphine-borane precursors 37, 40, 41-51 have been successfully synthesised and characterised by multi-element NMR spectroscopy. Crystals suitable for X-ray crystallography were isolated for compounds 37 and 48 and the molecular structures are typical for this type of compound. The \(^1\text{H}\{^{11}\text{B}\}, ^{11}\text{B}\{^{1}\text{H}\}, ^{13}\text{C}\{^{1}\text{H}\} \text{ and } ^{31}\text{P}\{^{1}\text{H}\} \text{ NMR spectra of compounds 37, 40, 41-51 are as expected. During the synthesis of compound 37 grease-free apparatus was essential in order to eliminate the competing reaction of Me}_2\text{P(BH}_3\text{)CH}_2\text{Li with silicone grease. During the synthesis of compounds 44-46 1,2-C}_6\text{H}_4(\text{CH}_2\text{Cl})_2 \text{ was used instead of 1,2-C}_6\text{H}_4(\text{CH}_2\text{Br})_2 \text{ in order to eliminate quaternisation as the competing reaction. Problems with low yield and purity of compounds 45 and 48 meant no further investigations into these compounds were carried out.}
2.7 References

Chapter 3. Synthesis and structural characterisation of α-metalated phosphine-borane precursors

3.1 Introduction

Phosphine-borane-stabilised carbanions have been used for many years for the synthesis of chiral diphosphines, such as DIPAMP (bis[(2-methoxyphenyl)phenylphosphine]ethane)\(^1,2\), which have many applications as supporting ligands in catalysis.\(^3-5\) However, it is only recently that phosphine-borane-stabilised carbanions have been of interest in their own right as they are usually prepared and used in situ and so little is known about their structures; this is surprising given that Me\(_2\)P(BH\(_3\)) is isoelectronic with SiMe\(_3\). In order to investigate the extent of the stabilisation afforded by phosphine-borane substituents, Izod and co-workers synthesised the phosphine-borane-stabilised carbanion complex Me\(_2\)P(BH\(_3\))CH\(_2\)Li, which undergoes an unusual reaction with silicone grease to yield a complex with a novel siloxy-functionalised alkyl ligand (discussed further in Chapter 1.4);\(^6\) unfortunately, even with the absence of grease {Me\(_2\)P(BH\(_3\))CH\(_2\)}Li was not isolated cleanly. This greater reactivity towards silicone grease in comparison to [(Me\(_3\)Si)\(_2\)C{Me\(_2\)P(BH\(_3\))}]\(^-\) was attributed to the former exhibiting greater negative charge on the carbanion, due to a decrease in negative hyperconjugation (due to the lack of SiMe\(_3\) groups) which leads to an increase in nucleophilic character on the carbanion.\(^6\) From Izod and co-workers’ ongoing investigations it is apparent that, even though PMe\(_2\)(BH\(_3\)) and SiMe\(_3\) groups are isoelectronic, silicon-stabilised carbanions and phosphine-borane-stabilised carbanions show different characteristics in their metal complexes (discussed further in Chapter 1.4).

This chapter discusses the synthesis and characterisation of an array of structurally different phosphine-borane-stabilised carbanions. Group A (compounds 44-46) are linear and group B (compounds 47-49) are phosphine-boranes that contain a phenylene linker in order to incorporate a rigid backbone (see Chapter 2.2 and 2.3 for a more detailed discussion). The ultimate aim was to synthesise the stannylenes of group A and B ligands and to compare the structures of group B with A in order to determine if the introduction of a rigid linker affects the overall structure; the main point of interest is the B-H···Sn interactions. Group C (compounds 50 and 51) are analogues of the silicon-substituted ligands used in the previously published stannylenes {(Me\(_3\)Si)\(_2\)CH}\(_2\)Sn\(^7\) and [(Me\(_3\)Si){Me\(_2\)(BH\(_3\))P}CH]\(_2\)Sn\(^8\) from Lappert
and Izod, respectively, where SiMe\textsubscript{3} groups are absent in group C. The removal of the sterically demanding trimethylsilyl group and how that affects the structures of the corresponding stannylene will be discussed further in Chapter 6.2. In order to progress towards the stannylene of these phosphine-borane-stabilised carbanions, their alkali metal derivatives must first be investigated. This chapter discusses the synthesis of the phosphine-borane-stabilised carbanions of groups A, B and C along with characterisation; as well as the attempted synthesis of group D complexes and the reasons why investigations into group D were not carried any further.

### 3.2 Synthesis and characterisation of Group A phosphine-borane-stabilised carbanions

Treatment of the linear bis(phosphine-boranes) 37 and 40 with two equivalents of \textsuperscript{a}BuLi and tmeda in THF yields the corresponding doubly-deprotonated complexes [Li(tmeda)]\textsubscript{2}[Me\textsubscript{2}P(BH\textsubscript{3})CHSi(Me\textsubscript{2})CH\textsubscript{2}](37a) and [Li(THF)]\textsubscript{2}[Ph\textsubscript{2}P(BH\textsubscript{3})CHSi(Me\textsubscript{2})CH\textsubscript{2}](40a), respectively, as yellow crystalline solids. Similarly, the reaction between 40 and two equivalents of PhCH\textsubscript{2}K in the presence of the tertiary amine pmdeta, yields the potassium complex [K(pmdeta)]\textsubscript{2}[CH\textsubscript{2}SiMe\textsubscript{2}CHP(BH\textsubscript{3})Ph\textsubscript{2}](40b) as yellow blocks after recrystallisation from hot toluene (Scheme 3.1).

The \textsuperscript{1}H{\textsuperscript{11}B}, \textsuperscript{11}B{\textsuperscript{1}H}, \textsuperscript{13}C{\textsuperscript{1}H} and \textsuperscript{31}P{\textsuperscript{1}H} NMR spectra of compounds 37a, 40a and 40b are as expected. In deuterated benzene the \textsuperscript{1}H{\textsuperscript{11}B} NMR spectrum of 37a contains a doublet at -1.05 ppm (J\textsubscript{PH} = 6.4 Hz) corresponding to the two protons bonded to the carbanion centres and a doublet at 1.05 ppm (J\textsubscript{PH} = 11.5 Hz) which corresponds to the two BH\textsubscript{3} units. The \textsuperscript{11}B{\textsuperscript{1}H} NMR spectrum contains a doublet at -33.0 ppm (J\textsubscript{PB} = 88.3 Hz) and the \textsuperscript{31}P{\textsuperscript{1}H} NMR spectrum contains a quartet at -4.8 ppm (J\textsubscript{PB} = 88.3 Hz) whilst the \textsuperscript{7}Li NMR spectrum contains a singlet at 1.0 ppm. In deuterated benzene the \textsuperscript{1}H{\textsuperscript{11}B} NMR spectrum of 40a contains a doublet at -0.10 ppm (J\textsubscript{PH} = 25.0 Hz) corresponding to the two protons bonded to the two carbanion centres. The \textsuperscript{11}B{\textsuperscript{1}H} NMR spectrum contains a doublet at -35.7 ppm and the \textsuperscript{31}P{\textsuperscript{1}H} NMR spectrum contains a quartet at 12.5 ppm (J\textsubscript{PB} = 88.2 Hz), whilst the \textsuperscript{7}Li NMR spectrum contains a singlet at 1.2 ppm. Once isolated, compound 40b has limited solubility in aromatic solvents, such as toluene, but has good solubility in ethereal solvents, such as THF. In deuterated THF the \textsuperscript{1}H{\textsuperscript{11}B} NMR spectrum of 40b contains a doublet at -0.53 ppm (J\textsubscript{PH} = 25.0 Hz) corresponding to the two protons which are bonded to the two carbanion centres and a doublet at 0.95 ppm (J\textsubscript{PH} = 15.0 Hz) which corresponds to the two
BH$_3$ units. The $^{11}$B{^1H} NMR spectrum contains a doublet at -34.7 ppm ($J_{PB} = 113.8$ Hz) and the $^{31}$P{^1H} NMR spectrum contains a quartet at 11.7 ppm ($J_{PB} = 113.8$ Hz).

Scheme 3.1: Synthesis of 37a, 40a and 40b. Reagents and conditions: i) 2 equivalents of nBuLi, THF, r.t., 1 hr. ii) 2 equivalents of nBuLi, tmeda, THF, r.t., 1 hr. iii) 2 equivalents of BnK, pmdeta, THF, r.t., 16 hr.

Metalation of 37 and 40 with nBuLi results in a small downfield shift of the $^{11}$B{^1H} NMR signal (37, -37.5 ppm; 37a, -33.0 ppm; 40, -38.9 ppm; 40a, -35.7 ppm) and a small upfield shift in the $^{31}$P{^1H} NMR signal (37, 3.4 ppm; 37a, -4.8 ppm; 40, 13.5 ppm; 40a, 12.5 ppm). Metalation also leads to a large increase in the $^{31}$P-$^{11}$B coupling constant (37, 58.8 Hz; 37a, 88.3 Hz; 40, 69.5 Hz; 40a, 107.9 Hz).

With decreasing electronegativity of the metal centre there is also a slight upfield shift in the $^{31}$P{^1H} NMR signal (40a, 12.5 ppm; 40b, 11.7 ppm), while the $^{11}$B{^1H} NMR signal moves very slightly to lower field (40a, -35.7 ppm; 40b, -34.7 ppm). The $^{31}$P-$^{11}$B coupling constant also shows a slight increase with decreasing electronegativity of the metal centre (40a, 107.9 Hz; 40b, 113.8 Hz).
There is a noticeable difference between the $^{31}\text{P}^{11}\text{B}$ coupling constants of compounds 37 and 40, where a 10 Hz increase is observed going from a methyl ($\text{sp}^3$) to a phenyl ($\text{sp}^2$) substituent, respectively. This change in coupling can be explained using Bent’s rule (Figures 3.1 and 3.2).\(^9\)

**Figure 3.1:** Atomic orbitals on P of compounds 37 and 40 indicating the change in s-character along the P-B bond when going from a sp\(^3\) to an sp\(^2\) carbon atom, respectively.

The s/p contribution of bonding in orbitals can be explained with the use of Bent’s rule which proposes that the more electronegative a substituent is, the more s-character that substituent will possess. Therefore, the more electronegative sp\(^2\) carbon centre in compound 40 compared to compound 37 has greater carbon s-character which results in greater phosphorus p-character which will then lead to the P-B bond having less phosphorus p- but greater s-character than the sp\(^3\) carbon atom in 37. Greater s-character leads to an increase in the $^{31}\text{P}^{11}\text{B}$ coupling constant, which can also be seen in the phosphine-borane-stabilised carbanion complexes 37a and 40a ($J_{\text{PB}} = 37$, 58.8 Hz; 40, 69.5 Hz; 37a, 88.3 Hz; 40a, 107.9 Hz).\(^10\)
Figure 3.2: Atomic orbitals of compounds 37, 37a and 40-40b showing the increase in s-character with increase in electropositivity on the carbanion.

With increase in electropositivity on the carbanion centre [C-H (37 and 40), to C-Li (37a and 40a) and then to C-K (40b)] the C-M (M = H, Li and K) bond has more carbon s-character in 37a and 40b compared to 37 and 40. If the C-M bond has more s-character, then this will affect the C-P bond resulting in more carbon p-character; overall leading to greater phosphorus s-character in the P-B bond. This increase in phosphorus s-character across the P-B bond results in an increase in the $J_{PB}$ coupling constants in 37, 37a (37, $J_{PB}$ = 58.8 Hz; 37a, 88.3 Hz) and 40, 40a and 40b (40, $J_{PB}$ = 69.5 Hz; 40a, 88.3 Hz; 40b, 113.8 Hz). This trend is consistent with other examples where an increase of 20-50 Hz in $J_{PB}$ is observed upon $\alpha$-metalation of phosphine-borane compounds.6,11-22

Crystals suitable for X-ray crystallography of 37a have so far not been isolated; however, compounds 40a and 40b have been isolated as colourless crystals and yellow blocks, respectively, and so their solid-state structures have been obtained. Both 40a and 40b crystallise as monomeric units but adopt very different structures; the molecular structures of 40a and 40b are shown in Figures 3.3 and 3.4, respectively, along with selected bond lengths and angles (Tables 3.1 and 3.2).

The Li-C distance in 40a [2.194(6) Å] is similar to that in previously reported examples, such as [CH$_2$SiMe$_2$C(SiMe$_3$)$_2$LiC(SiMe$_3$)$_2$SiMe$_2$CH$_2$][Li(TMEDA)$_2$] (52) which has a Li-C distance of 2.156(4) Å.23 Compound 52 is bulkier than compound 40a, however, in 52, one SiMe$_3$ unit is isoelectronic with the Me$_2$P-BH$_3$ groups in 40a. Although the Li-C bond lengths are similar to each other in 40a and 52, the resulting structures are noticeably
different. Compound 40a crystallises as a linear dicarbanion with an inversion centre midway along the C(2)-C(2') bond; the C(2) atoms and their symmetry equivalents are disordered over two positions with equal occupancy. In contrast, 52 crystallises as a separated ion pair containing a chelating lithate anion and [Li(TMEDA)₂] cation resulting in a bent linear C-Li-C core (C-Li-C = 171.4(7) °)²³ and showing clearly two Li environments in the ⁷Li NMR spectrum. Compound 40a adopts a distorted tetrahedral structure at the lithium centres [O(1)-Li-C(1) = 113.7(3) °, O(2)-Li-C(1) = 137.6(3) °] due to interactions with the carbanion centres, an η¹-BH₃ group and the oxygen atoms of two THF molecules. A potential reason why these dicarbanions are structurally different could be due to the presence of the phosphine-borane unit in 40a, where the η¹ interaction with the BH₃ moieties hinders chelation of the lithium ion by the two carbanion centres.

Figure 3.3: Molecular structure of 40a with H atoms (except for those bound to boron) omitted for clarity.
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Table 3.1: Selected bond lengths (Å) and angles (°) for 40a.

Compound 40b crystallises as discrete molecules with an unusual cyclic structure with a C₂ axis perpendicular to the C(2)-C(2A) bond (Figure 3.4). Each potassium cation has contacts with a carbanion centre, one η¹-BH₃ group at one end of the phosphine-borane-stabilised carbanion, three nitrogen atoms of a molecule of pmdeta and an η¹-BH₃ group of the second half of the molecule. This results in each BH₃ group bridging the two potassium ions in a μ-η¹:η¹ fashion to generate a (K-H-B-H)₂ cycle to each K. The K-C bond length of 3.173(4) Å is significantly longer than the K-C distance in the silicon-substituted examples (C₆H₆)₂KC(SiMe₃)₂SiMe₂CH₂CH₂Me₂Si(Me₃Si)₂CK(C₆H₆)₂ and (THF)₂KC(SiMe₃)₂SiMe₂CH₂CH₂Me₂Si(Me₃Si)₂CK(THF)₂ [2.953(4) Å and 2.937(3) Å, respectively]. This longer bond length could be due to either the increase in the number of metal-ligand contacts in 40b or the two pseudo-four-membered rings being strained enough to lengthen the K-C bond.

Comparison of the structures of 40a and 40b with that of the closely related precursor 37 shows a significant shortening of the C-P bond upon metalation (37, 1.8000(19) Å; 40a, 1.729(3) Å; 40b, 1.716(5) Å), which is consistent with extensive delocalisation of charge from the carbanion centre into the P-C σ* orbital;²⁴ this is also true for the C-Si distances [37, 1.892(2) Å; 40a, 1.829(3) Å; 40b, 1.804(4) Å]. This shortening may also be attributed to the increased electron donation in the agostic-type H-B···M interactions. The P-B distances in compounds 40a and 40b are similar to that in 37 [37, 1.917(3) Å; 40a, 1.924(3) Å; 40b, 1.921(5) Å]. The K···H distances in 40b are significantly longer than the Li···H distances in 40a [40a, 2.22(3) Å; 40b, 2.78(6) and 2.82(6) Å], which may be attributed to the increased ionic radius of a potassium cation compared to lithium.
Figure 3.4: Molecular structure of 40b with H atoms (except for those bound to boron) omitted for clarity.

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Table 3.2: Selected bond lengths (Å) and angles (°) for 40b.
3.3 Synthesis and characterisation of Group B phosphine-borane-stabilised carbanions

1,2-C₆H₄{CH₂P(BH₃)R₂}₂ [R = iPr (44), Ph (45) or Cy (46)] undergo α-metalation with two equivalents of "BuLi and tmeda to yield the corresponding phosphine-borane-stabilised carbanions [1,2-C₆H₄{CHP(BH₃)R₂}₂][Li(tmeda)]₂. nL (R = iPr, n = 0 (44a); R = Ph, nL = THF (45a); R = Cy, nL = 2PhCH₃ (46a)) (Scheme 3.2). Compound 45a was made by a previous research student (Emma McMeekin) but data has been used in order to compare bond lengths and angles.

Scheme 3.2: Synthesis of 44a-46a, 44b and 46b. Reagents and conditions: i) 2 equivalents of "BuLi, THF, tmeda, r.t., 1 hr. ii) 2 equivalents of MeK, pmdeta, Et₂O, r.t., 1hr. ii) 2 equivalents of BnK, pmdeta, THF, r.t., 16 hr.

The ¹H{¹¹B}, ¹¹B{¹H}, ¹³C{¹H}, ⁷Li and ³¹P{¹H} NMR spectra of compounds 44a-46a are as expected. The ¹H{¹¹B} spectra of 44a, 45a and 46a exhibit a doublet at 0.32 ppm (J₈₁₈ = 14.2 Hz), 0.99 ppm (J₈₁₈ = 14.6 Hz) and 0.33 ppm (J₈₁₈ = 15.0 Hz), respectively, which corresponds to the BH₃ protons. In the ¹H{¹¹B} NMR spectrum of compounds 44a and 45a the CHLI proton can be distinguished from the phosphorus substituents as doublets at 1.45 ppm (J₈₁₈ = 9.7 Hz) and 2.20 ppm (J₈₁₈ = 14.4 Hz), respectively; no coupling to Li⁷ is
observed. In the $^1$H-$^{11}$B} NMR spectrum of compound 46a in $d_8$-THF it is not possible to identify the CHLi peak due to the many cyclohexyl protons which occur in the same region. The CHLi peak can, however, be observed in the $^{13}$C-$^1$H} NMR spectrum as a doublet ($J_{PC} = 61.3$ Hz) at 23.3 ppm. The $^7$Li NMR spectra of 44a-46a exhibit singlets in the range -0.9 to -1.0 ppm whilst in the $^{11}$B-$^1$H} NMR spectrum of 44a shows a doublet at -39.3 ppm ($J_{PB} = 78.4$ Hz), whereas 45a and 46a show broad signals at -34.4 ppm and -39.8 ppm, respectively. In the $^{31}$P-$^1$H} NMR spectra, 44a and 46a show quartets at 16.3 ppm ($J_{PB} = 83.4$ Hz) and 12.3 ppm ($J_{PB} = 105.3$ Hz), respectively, whilst 45a shows a broad signal at 6.2 ppm. This large increase in the $^{31}$P-$^{11}$B coupling constant (44, 49.0 Hz; 44a, 78.4 Hz) is consistent with the formation of a phosphine-borane-stabilised carbanion (see above).

In order to compare structural characteristics between the Li and K complexes of compound 44, an attempt to prepare the potassium salt 44b was performed by treating 44 with two equivalents of MeK in cold (-10 °C) diethyl ether. This did not result in double deprotonation at the benzylic centres, but only resulted in monodeprotonation; this was clearly shown in the crude $^{31}$P-$^1$H} NMR spectrum, where two quartets were found at 16.7 ppm ($J_{PB} = 83.3$ Hz) and 34.2 ppm ($J_{PB} = 41.7$ Hz), which are due to the monodeprotonated phosphine-borane-stabilised carbanion site and the phosphine-borane site in 44b, respectively.24 With the addition of pmdeta, the monodeprotonated product 44b was recrystallised as pale yellow single crystals from n-hexane in good yield.

The reactivity of MeK is typically much greater than "BuLi and so it was surprising that double deprotonation did not occur. However, the monodeprotonation may be attributed to the competing reaction of MeK and diethyl ether which would leave only one equivalent of MeK available. Even though the initial deprotonation at one benzylic site is rapid, the second deprotonation is much slower and so the side reaction between MeK and diethyl ether dominates. Benzyl potassium is less basic than MeK and does not react with diethyl ether at room temperature, so an attempt was made to doubly deprotonate 44-46 with this reagent. Treatment of 44-46 with two equivalents of PhCH$_2$K and pmdeta yielded the corresponding phosphine-borane-stabilised carbanions [K(pmdeta)]$_2$[1,2-C$_6$H$_4$(CHPR$_2$(BH$_3$))$_2$] [R = iPr (44b), Ph (45b) and (46b)]. Despite repeated attempts, compounds 44b and 45b could not be isolated cleanly, however, crude $^{31}$P-$^1$H} NMR spectra of the reaction mixtures show a typically large increase in the $^{31}$P-$^{11}$B coupling constant upon formation of the dipotassium salts ($J_{PB} = 85.8$ and 89.6 Hz, for 44b and 45b, respectively). The $^1$H-$^{11}$B}, $^{11}$B-$^1$H}, $^{13}$C-$^1$H} and $^{31}$P-$^1$H} NMR spectra of compound 46b are as expected. In the $^1$H-$^{11}$B} NMR spectrum
of 46b in d₈-toluene it is not possible to identify the CHK proton due to the many cyclohexyl and pmdeta protons, however, the corresponding carbon can be seen in the ¹³C{¹H} NMR spectrum as a doublet (Jpc = 36.5 Hz) at 37.8 ppm; the ¹¹B{¹H} NMR and ³¹P{¹H} spectra of 46b contain broad peaks at -40.3 ppm and 12.7 ppm, respectively, on which ³¹P-¹¹B coupling is not resolved.

Compounds 44a-46a crystallise as discrete monomers which are similar in structure but which are not isostructural. Compound 44a crystallises with no solvent associated with its asymmetric unit, whilst 45a contains a molecule of THF and 46a contains two molecules of toluene in their asymmetric units which are only weakly held in place and which are lost after about 15 minutes of the samples being under vacuum; the ¹H NMR spectrum of 46a shows no solvent peaks. The molecular structures of 44a, 45a and 46a are shown in Figures 3.5, 3.6 and 3.7, along with selected bond lengths and angles (Tables 3.3, 3.4 and 3.5).
Figure 3.5: Molecular structure of 44a with H atoms (except for those bound to boron) omitted for clarity.

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Table 3.3: Selected bond lengths (Å) and angles (°) for 44a.
Figure 3.6: Molecular structure of 45a with H atoms (except for those bound to boron) and solvent of crystallisation omitted for clarity.

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Table 3.4: Selected bond lengths (Å) and angles (°) for 45a.
Figure 3.7: Molecular structure of 46a with H atoms (except for those bound to boron) and solvent of crystallisation omitted for clarity.

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Table 3.5: Selected bond lengths (Å) and angles (°) for 46a.
In 44a each lithium ion has a 5-coordinate geometry where each ion is bound to the carbanion centre, two nitrogen atoms of the tmeda co-ligand, the BH₃ unit in an η¹ fashion and an additional short contact with the ipso carbon atom within the o-phenylene linker adjacent to the carbanion centre; each Li ion is positioned on opposite sides of the essentially planar C₆H₄(CP)₂ fragment forming a distorted pentagonal ring. Compounds 45a and 46a adopt similar structures to 44a but 45a has an additional short contact between the Li cation and one of the methyl carbon atoms within the tmeda co-ligand whereas, 46a has an additional short contact between the lithium ion and one of the methylene carbon atoms of the tmeda co-ligand. Compound 45a also has a crystallographic C₂ axis which bisects the o-phenylene linker group.

The Li-C(carbanion) distances in compound 46a (2.254(6) and 2.271(6) Å) are slightly longer than those in compounds 44a and 45a (2.235(5) and 2.227(5) Å, and 2.241(4) Å, respectively) which could be due to compound 46a having the more sterically demanding cyclohexyl substituents compared to the iPr and Ph groups in compounds 44a and 45a. The Li-C(carbanion) distances in compounds 44a-46a are significantly longer than the corresponding distances in similar benzyl lithium compounds [Li(Et₂O)(CH₂Ph)]₂∞ [2.212(8) Å] and Li(CH₂Ph)(tmeda)(THF) [2.210(5) Å], but are similar to the Li-C distances in other phosphine-borane-stabilised carbanions (see above).6, 11, 13, 14, 16-22

The previously reported linear 1,4-dicarbanions [[Ph₂P(BH₃)](Me₃Si)C(CH₂)₂Li(THF)]₂·2THF (53) and [(pmdeta)Li{⁷Pr₂P(BH₃)}(Me₃Si)C(CH₂)₂]₂ (54) adopt different structures to compounds 44a-46a in the solid state (Scheme 3.3).12, 18 Both 53 and 54 crystallise as discrete molecular species (the same as compounds 44a-46a) and each lithium ion has contacts with the BH₃ hydrogens in an η²-fashion at either end of the molecule. The lithium solvation sphere of 53 contains three molecules of THF whilst 54 has interactions to three nitrogen atoms in one molecule of pmdeta at each lithium ion and a crystallographic centre of inversion midway along the CH₂CH₂ bond; neither example has carbanion contacts with the lithium ion. The Li-H distances in compounds 44a (2.08(3) and 2.03(2) Å), 45a (2.04(2) Å) and 46a (1.96(3) and 2.09(3) Å) are similar to those in 53 (2.13(3) and 1.97(3) Å) and 54 (1.94(3) and 2.05(3) Å).
Scheme 3.3: Examples of Schlenk dimerisation to synthesise 1,4-dicarbanions. i) Li, THF. ii) Li, THF, pmdeta.

Compound 46b also crystallises as a discrete monomer but adopts a different structure to compounds 44a-46a. In compound 46b, each potassium ion is bound to the carbanion centre, three nitrogen atoms and two carbon atoms of two methyl groups within the pmdeta co-ligand, in a η¹ fashion to the BH\textsubscript{3} unit and each potassium ion has additional short contacts with an ipso carbon atom in the o-phenylene linker adjacent to the carbanion centre C(5) and C(12); K(1) is also bound to the other carbanion centre and three carbon atoms of the aromatic ring whilst K(2) has short contacts to five carbon atoms within the phenylene ring and the benzylic carbon atom C(12). The molecular structure of 46b is shown in Figure 3.8, along with selected bond lengths and angles (Table 3.6).
Figure 3.8: Molecular structure of 46b with H atoms (except for those bound to boron) omitted for clarity.

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<th>Bond Lengths (Å)</th>
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<td>50.68(4)</td>
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Table 3.6: Selected bond lengths (Å) and angles (°) for 46b.
Compound 44b crystallises as a discrete molecular species where the potassium ion is coordinated via the carbanion centre, by two BH$_3$ units in an η$_2$-fashion and by three nitrogen atoms of the pmdeta co-ligand. There are additional short contacts between the potassium ion and the ipso carbon atom of the aromatic ring adjacent to the pmdeta co-ligand.

The K(1)-C(5) bond length (3.1588(18) Å) in 46b is similar to the K-C(carbanion) distance (3.211(8) Å) in the monosubstituted analogue [1,2-C$_6$H$_4${CHP(BH$_3$)$_2$iPr$_2$} {CH$_2$P(BH$_3$)$_2$iPr$_2$}][K(pmdeta)] 44b, which are longer than K-C distances in previously reported carbanions which involve a benzylic centre; examples include [(PhCH$_2$)K(pmdeta)]$_\infty$ (K-C, 3.171(2) Å) and [{{(Me$_3$Si)CH}C$_6$H$_4$-2-NMe$_2$}][K]$_\infty$ (K-C, 2.966(4) Å).

3.4 Synthesis and characterisation of Group C phosphine-borane-stabilised carbanions

The benzyl-substituted phosphine-boranes C$_6$H$_5$CH$_2$P(BH$_3$)R$_2$ [R = 'Pr (47) or Cy (49)] undergo α-metalation with one equivalent of n$^\circ$BuLi and tmeda to yield the corresponding phosphine-borane-stabilised carbanions [C$_6$H$_5$CHP(BH$_3$)R$_2$][Li(tmeda)] [R = 'Pr (47a), Cy (49a)] (Scheme 3.4) as judged by the $^{31}$P{¹H} NMR spectra of the crude reaction solutions.

Scheme 3.4: Synthesis of 47a and 49a. Reagents and conditions: i) 1 eq. of n$^\circ$BuLi, THF, tmeda, r.t., 1 hr.

Compound 47a has not been fully characterised due to difficulties with purification, however, the crude $^{31}$P{¹H} NMR spectrum exhibits a quartet at 16.2 ppm ($J_{PB} = 88.5$ Hz) which is significantly different to the precursor 47 (quartet at 34.0 ppm, $J_{PB} = 59.7$ Hz) and
which shows a large increase in the $^{31}\text{P}-^{11}\text{B}$ coupling constant. Crystallisation was attempted with either tmeda or pmdeta as a co-ligand, with different solvents (Et$_2$O, toluene, light petroleum or methylcyclohexane) and solvent layering experiments; all of which have been attempted at different temperatures (r.t., 5 °C and -20 °C). However, unfortunately we were unable to isolate either clean samples or single crystals of 47a. Compound 49a was isolated as yellow single crystals suitable for X-ray crystallography from cold (5 °C) methylcyclohexane in good yield.

The $^1\text{H}$$\{^{11}\text{B}\}$, $^{11}\text{B}$$\{^1\text{H}\}$, $^{13}\text{C}$$\{^1\text{H}\}$, $^7\text{Li}$ and $^{31}\text{P}$$\{^1\text{H}\}$ NMR spectra of compound 49a are as expected. The $^1\text{H}$$\{^{11}\text{B}\}$ NMR spectrum contains a doublet at 0.78 ppm ($J_{\text{PH}} = 9.63$ Hz) which is associated with the BH$_3$ unit; the CHLi proton is not observed in the $^1\text{H}$$\{^{11}\text{B}\}$ NMR spectrum due to the cyclohexyl substituents which give rise to a complex multiplet between 1.15 and 2.19 ppm which obscures the CHLi signal. The $^{13}\text{C}$$\{^1\text{H}\}$ NMR spectrum contains a doublet at 35.3 ppm ($J_{\text{PC}} = 31.0$ Hz) which corresponds to the CHLi carbon atom, the $^7\text{Li}$ NMR spectrum exhibits a singlet at 0.24 ppm and the $^{31}\text{P}$$\{^1\text{H}\}$ and $^{11}\text{B}$$\{^1\text{H}\}$ NMR spectra exhibit a quartet at 12.2 ($J_{\text{PB}} = 81.5$ Hz) and a doublet at -39.5 ppm ($J_{\text{PB}} = 81.5$ Hz), respectively. This large increase in the $^{31}\text{P}-^{11}\text{B}$ constant (49, 57.8 Hz; 49a, 81.5 Hz) is consistent with the formation of a phosphine-borane-stabilised carbanion (see section 3.2 on Bent’s rule).

In order to compare structural differences between complexes of Li and K ions the corresponding K compounds were prepared. Treatment of compounds 47 and 49 with an excess of BnK in THF results in the phosphine-borane-stabilised carbanion complexes K[CsH$_5$CHPR$_2$(BH$_3$)] [$R = ^3\text{Pr}$ (47b), Cy (49b)]. Compounds 47b and 49b were isolated whilst trying to make the group 2 analogues using the method shown in Scheme 3.5; the synthesis of group 2 complexes of phosphine-borane-stabilised carbanions will be discussed in more detail in Chapter 4.
Scheme 3.5: Failed synthesis of group 2 complexes of a phosphine-borane-stabilised carbanion. Reagents and conditions: i) Excess BnK, THF, r.t., 1 hr. ii) AeI$_2$ (Ae = Ca, Sr and Ba), THF, r.t., 16 hr.

The $^1$H{$^{11}$B}, $^{11}$B{$^1$H}, $^{13}$C{$^1$H} and $^{31}$P{$^1$H} NMR spectra of compounds 47b and 49b are as expected. In the $^1$H{$^{11}$B} NMR spectrum compound 47b contains doublets at 0.34 ppm ($J_{PH} = 13.1$ Hz) and 1.83 ppm ($J_{PH} = 4.8$ Hz) which correspond to the BH$_3$ unit and the CHK fragment, respectively; the $^{11}$B{$^1$H} NMR spectrum contains doublets at -41.0 ppm ($J_{PB} = 81.3$ Hz) and the $^{31}$P{$^1$H} contains a quartet at 16.0 ppm ($J_{PB} = 81.3$ Hz).

In the $^1$H{$^{11}$B} NMR spectrum compound 49b contains doublets at 0.28 ppm ($J_{PH} = 13.3$ Hz) and 1.86 ppm ($J_{PH} = 4.8$ Hz) which correspond to the BH$_3$ unit and the CHK fragment, respectively; the $^{11}$B{$^1$H} NMR spectrum contains a doublet at -40.2 ppm ($J_{PB} = 79.2$ Hz) and the $^{31}$P{$^1$H} NMR spectrum contains a quartet at 8.80 ppm ($J_{PB} = 79.2$ Hz). This large increase in the $^{31}$P-$^{11}$B coupling constant (47, 59.7 Hz; 47b, 81.3 Hz; 49, 57.8Hz; 49b, 79.2 Hz) is consistent with the formation of a phosphine-borane-stabilised carbanion in each case.

Compounds 49a and 49b were isolated as single crystals suitable for X-ray crystallography. Compound 49a crystallises as a discrete molecular species with coordination between the Li ion and the carbanion centre, BH$_3$ hydrogens in an $\eta^2$-fashion, the hydrogen atom associated with the carbanion centre and with the coordination sphere completed by two contacts to the two nitrogen atoms in one molecule of tmeda; the molecular structure of 49a is shown in Figure 3.9, along with selected bond lengths (Table 3.7).
Figure 3.9: Molecular structure of 49a with H atoms (except for those bound to boron) omitted for clarity.

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<tr>
<td>P-B</td>
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Table 3.7: Selected bond lengths (Å) and angles (°) for 49a.

The Li-C(carbanion) bond length in compound 49a (2.267(3) Å) is similar to the bond lengths in compound 46a (2.254(6) and 2.271(6) Å); both compounds contain cyclohexyl substituents on the phosphorus atoms. Compound 49a has longer Li-C(carbanion) contacts than compounds 40a, 44a and 45a (all of which contain either phenyl or isopropyl...
substituents on the phosphorus); this longer Li-C distance is consistent with the cyclohexyl groups being much larger and so elongating the Li-C(carbanion) contact.

The P-C and P-B distances in 49b [1.7424(11) and 1.9365(13) Å, respectively] are similar to the corresponding P-C and P-B distances in 49a [1.7403(14) and 1.9349(16) Å, respectively], however, the K-H distance in 49b [2.82(2) Å] is significantly longer than the Li-H distances in 49a [2.328(16) and 2.035(16) Å]; this may be attributed to the increased size of the potassium ion compared to the lithium ion.

Compound 49b crystallises as a sheet polymer with disordered toluene molecules occupying spaces between the sheets. The packing shows bridging of the K cations by BH₃ in an η²-fashion; along the b-axis, the potassium ions and phenyl rings alternate with each K ion coordinated by two η⁶-coordinated rings. The asymmetric unit contains half a molecule of toluene disordered over an inversion centre; the molecular structure of 49b is shown in Figures 3.10 and 3.11, along with selected bond lengths (Table 3.8).

Compound 49b contains the more electropositive K ion which is also bigger in size than the Li ion in compound 49a. It is common for K ions to complete their coordination sphere by having contacts with neighbouring sources of π-electrons due to its increased ionic radius as is seen in compound 49b.²⁴
**Figure 3.10:** Asymmetric unit of 49b with H atoms (except for those bound to boron) and solvent of crystallisation omitted for clarity.

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**Table 3.8:** Selected bond lengths (Å) and angles (°) for 49b.
Figure 3.11: Sheet polymer structure of 49b with H atoms (except for those bound to boron) and disordered toluene omitted for clarity.
3.5 Synthesis and characterisation of Group D phosphine-borane-stabilised carbanions

A number of different synthetic routes were attempted in order to achieve double deprotonation of the linear butylene-linked phosphine-borane \([\text{CH}_2\text{CH}_2\text{PCy}_2(\text{BH}_3)]_2\) (51); unfortunately, none of these were successful (Scheme 3.6).

![Scheme 3.6: Four different synthetic methods in the attempted deprotonation of compound 51. Reagents and conditions: i) KO'Bu, "BuLi, Et\(_2\)O. ii) "BuLi, THF, reflux 2 hrs. iii) "BuLi, tmdea, THF, reflux 2 hrs. iv) "BuLi, THF, -78 °C, 2 hrs.](image)

The use of tmdea in a metalation reaction forms an interaction between the electropositive Li and the nitrogen atoms in the tmdea molecules (Figure 3.12); this interaction activates the "BuLi both kinetically and thermodynamically.

![Figure 3.12: Thermodynamic and kinetic effects of tmdea with "BuLi.](image)
The difference in reactions (i) and (ii) from Figure 3.13 is the use of tmeda in the latter method. At low temperatures or in THF an equilibrium of a mixture of dimers and tetramers of ²BuLi will form whilst in hydrocarbon solvents ²BuLi exists as a hexameric species.

**Figure 3.13**: $^{31}$P{¹H} NMR spectra of crude reaction solutions in THF. i) with ²BuLi (Top) and under a 1 h reflux (Bottom). ii) with ²BuLi, and tmeda (Top) and under reflux (Bottom). * Free phosphine-borane 51 and monodeprotonated phosphine-borane, + monodeprotonated phosphine-borane 51a.

Kinetically, the organolithium is activated because the formation of these interactions between the Li ion and the nitrogen atom of the tmeda deoligomerises the oligomeric species
and so results in more reactive sites. Furthermore, the electron density located at the nitrogen atoms within the tmeda molecule is donated to the lithium centre. This leads to a greater amount of electron density at the alkyl substituent; this makes the alkyl group more electron rich and so a better nucleophile (Figure 3.12).

It can be seen from the $^{31}$P{$^1$H} NMR spectra in Figure 3.13 that the metalation reactions do not go to completion and that after refluxing, any metalated compound is protonated back (usually from the solvent) to the free phosphine-borane precursor; this behaviour is the same when the reaction involving ‘BuLi warms up to room temperature. The instability of the phosphine-borane-stabilised carbanion may be attributed to the inductive effects of the CH$_2$CH$_2$ linker which increases the charge at the carbanion centre. Therefore, monodeprotonated 51 will exhibit an unstable carbanion with an increased charge, thus the monodeprotonated carbanion is subject to reacting with the protons from the THF solvent back to the free phosphine-borane; it is therefore, highly unlikely that compound 51 can undergo double deprotonation.

### 3.6 Conclusions

Compounds 40a and 40b both crystallise as monomeric units but adopt different structures where 40a crystallises as a linear carbanion with an inversion centre midway along the C(2)-C(2') bond and 40b crystallises with a C$_2$ axis perpendicular to the C(2)-C(2A) bond; both 40a and 40b exhibit M-C(carbanion) contacts. Compounds 40a and 52 crystallise differently, despite the isoelectronic nature of the SiMe$_3$ group with R$_2$P(BH$_3$). Compound 40b exhibits significantly longer K-C bond lengths compared to Si-substituted examples which may be attributed to either the increase in the number of contacts or the pseudo-four-membered being strained. Shortening of the C-P and C-Si bond lengths upon metalation in 40a compared to 40b is consistent with charge delocalisation from the carbanion centre into the C-P $\sigma^*$-orbital, or due to the increase in electron donation in the H-B···M agostic-type interactions. The lengthening of the K-H distances (2.78(6), 2.82(6) Å) compared to the Li-H distances (2.22(3) Å) in 40a compared to 40b, respectively, may be attributed to the increase in ionic radius of the potassium cation compared to the lithium cation.

Compounds 44a-46a crystallise as discrete monomers, where 46a and 45a are similar to 44a but have additional short contacts between the lithium cation and one methyl carbon atom within the tmeda co-ligand; all exhibit Li-C(carbanion) contacts.
Treatment of compound 44 with MeK yielded the monodeprotonated product 44b due to competing reactions with MeK and the ethereal solvent; the double deprotonated product 46b was obtained using BnK. Compounds 44b and 46b also crystallise as discrete monomers with K-C(carbanion) contacts but exhibit different structures to compounds 44a-46a due to the increase cation size of K compared to Li, where K tends to coordinated to neighbouring sources of π-electrons.

Compounds 49a and 49b exhibit different solid state structures, where 49a crystallises as a discrete monomer with Li-C(carbanion) contacts and 49b crystallises as a sheet polymer with no K-C(carbanion) contacts. The may be attributed to the increase in cationic size in potassium compared to lithium and that potassium tends to complete its coordination sphere with neighbouring sources of π-electrons.

Compound 51 does not undergo double deprotonation due to the inductive nature of the CH₂CH₂ linker. In the crude ³¹P{¹H} NMR for 51 the broad signals may exhibit a mixture of monodeprotonated and free phosphine-borane. When under reflux the unstable carbanion then deprotonates the THF solvent yielding free phosphine-borane, therefore, potentially unable to yield double deprotonation.

Overall, this chapter shows that phosphine-borane-stabilised carbanions adopt an array of differing crystal structures which depend on a number of different factors, such as, the phosphorus substituents, the size of the alkali metal, the presence of either a rigid or a flexible backbone linker and whether co-ligands (THF, tmeda or pmdeta) to the metal centre (Li or K) were used.
3.7 References


Chapter 4. Group 2 Phosphine-borane-stabilised carbanions

4.1 Introduction

Since analytical tools, such as NMR spectroscopy and X-ray crystallography, have improved greatly over the last 20 years, interest in heavier alkaline earth metal complexes has increased. However, a common problem in group 2 complexes is their tendency to aggregate (due to their large ionic radii), resulting in insoluble products in organic solvents. To overcome this problem silicon-containing substituents are often used to disfavour aggregation and also to decrease the carbanion character of the ligand through negative hyperconjugation. The diorganophosphine-borane group PR$_2$(BH$_3$) is isoelectronic and isosteric with the SiR$_2$Me substituent and so by substituting the silyl groups with phosphine-borane groups, the aggregation properties can be explored. It is surprising, however, that despite the isoelectronic and isosteric nature of these groups, little is known about heavier alkaline earth metal complexes of phosphine-borane-stabilised carbanions compared to their silyl-containing analogues.

Izod and co-workers have previously carried out investigations in order to see the structural characteristics of the alkaline earth metal complexes of phosphine-borane-stabilised carbanions. Coordination of the metal by agostic-type interactions (B-H···Ae, Ae = Ca, Sr, Ba) dominates, however, complexes of silicon- and phosphine-borane-stabilised carbanions exhibit both agostic interactions and C-Ae contacts; the work carried out in this chapter is very much in its infancy but three different methods of synthesising group 2 complexes are reported herein.

4.2 Organolithium as a reagent

Treatment of one equivalent of in situ generated Li$_2$[Me$_2$P(BH$_3$)CHSi(Me$_2$)CH$_2$]$_2$ (37a) or two equivalents of [(Me$_3$Si)CHP(BH$_3$)Me$_2$]Li with one equivalent of MgCl$_2$ in THF yields a colourless (rac-37c and meso-37c) or a pale yellow (55b) solution, respectively. Both crude reaction mixtures of reactions 1 and 2 (Scheme 4.1) were extracted into diethyl ether, and $^{31}$P{$^1$H} NMR spectra were recorded.
Scheme 4.1: Synthesis of alkaline earth metal complexes rac-37c and, meso-37c and 55b (predicted structures). Reaction conditions. i) nBuLi, THF. ii) MgCl₂, THF.

The $^{31}$P{¹H} NMR spectrum for unpurified rac-37c and meso-37c shows a broad multiplet at 4.6 ppm. Unfortunately, after repeated attempts at recrystallisations using diethyl ether and hot toluene, no solid was isolated.

The $^{31}$P{¹H} NMR spectrum of unpurified 55b (Figure 4.1) shows a broad quartet at 2.9 ppm. This broad quartet is due mainly to the free phosphine-borane precursor 55, along with an unidentified product overlapping with the signal associated with 55. Unfortunately, no solid was isolated after repeated attempts using diethyl ether and hot toluene and so it was not possible to fully investigate the unidentified product.
Figure 4.1: Crude $^{31}\text{P}^1\text{H}$ NMR spectra of 55 and 55b in diethyl ether. *PMe$_3$(BH$_3$)

Treatment of two equivalents of *in situ* generated Li[Ca$_6$H$_5$CHPCy$_2$(BH$_3$)] (49a) with one equivalent of AeI$_2$ (Ae = Ca, Sr) in THF yields yellow solutions of compounds 49c and 49d (Scheme 4.2).

The $^{31}\text{P}^1\text{H}$ NMR spectrum for unpurified 49c and 49d exhibit broad multiplets at 8.7 and 36.2 ppm, respectively. Unfortunately, after repeated attempts at recrystallisations using diethyl ether and hot toluene, no solid was isolated.
Scheme 4.2: Synthetic route for 49c and 49d. Reaction conditions. i) n-BuLi, THF. ii) AeI₂, THF (Ae = Ca, Sr).

It is widely known that organolithiums have a tendency to form anionic ‘ate’ complexes when reacted with heavier group 2 halides.¹⁴ In order to preclude this as a potential side reaction in the synthesis of group 2 phosphine-borane-stabilised carbanion compounds we set out to explore the use of organopotassium precursors, which do not normally yield ate complexes in their reactions with group 2 halides.

4.3 Benzylpotassium as a reagent

Treatment of two equivalents of in situ generated K[C₆H₅CHPR₂(BH₃)] [R = ³Pr (47b), Cy (49b)] with one equivalent of AeI₂ (Ae = Mg, Ca, Sr, Ba) in THF yields yellow solutions, presumably of compounds 47c-47f, 49 (Scheme 4.3).

Scheme 4.3: Synthesis of 47c, 47d, 47e, 47f and 49e. Reaction conditions. i) BnK, THF. ii) AeI₂, THF (Ae = Mg, Ca, Sr, Ba).
Recrystallisation of 47d-47f using toluene yielded yellow crystalline solids which unfortunately, were not suitable for X-ray crystallography, however, did aid in gaining some NMR spectra. The $^{31}$P{¹H} NMR spectra of compounds 47d-47f exhibit quartets at 16.0 ppm ($J_{PB} = 92.7$ Hz) (Figure 4.2). The similarity in the $^{31}$P{¹H} NMR spectra may be attributed to unreacted 47b ($^{31}$P{¹H} signal at 16.0 ppm, $J_{PB} = 81.3$ Hz), however, it is quite common for chemical shifts and coupling constants to not change significantly when converting from the potassium salt to the alkaline earth metal derivative.¹⁵

![Figure 4.2: $^{31}$P{¹H} NMR spectra for 47 and crude samples of 47d-47f in THF.](image)

The $¹$H NMR spectra for 47d (Figure 4.3) and 47f show no THF signals which is unusual and not what would be expected for a group 2 complex due to the large ionic radii of the group 2 ions. Considering the similarity in the $^{31}$P{¹H} NMR spectra of 47d, 47e and 47f and that no THF remains coordinated to the metal centre suggests that in these reactions the predicted group 2 compounds are not formed and that the isolated solid is just the unreacted potassium compound 47b.
Figure 4.3: The $^1$H NMR spectrum of crystalline 47d in $d_8$-THF.

4.4 Dibenzylcalcium, -strontium and –barium as a reagent

Treatment of one equivalent of $(\text{PhCH}_2)_2\text{Ae}(\text{THF})_n$ (Ae = Ca, n = 2; Sr, n = 1; Ba, n = 0.5) with two equivalents of 47 or 49 in THF yields yellow solutions, presumably of compounds 47g-47h and 49f-49g (Scheme 4.4).

The crude $^{31}$P{$^1$H} NMR spectra for compounds 47g and 47h in THF show broad quartets at 17.3 ppm ($J_{PB} = 98.7$ Hz) and 15.9 ppm ($J_{PB} = 102.0$ Hz), respectively (Figure 4.4); the $^{31}$P{$^1$H} NMR signals are shifted compared to 47b (16.0ppm, $J_{PB} = 93.9$ Hz). In particular, the change in the $^{31}$P-$^{11}$B coupling constants of 47b, 47g and 47h may further verify 47g and 47h are the calcium and strontium complexes of the respective phosphine-borane-stabilised carbanions.
Scheme 4.4: Synthetic route for compounds 47g-47h and 49f-49g. Reaction conditions.

i) \((\text{PhCH}_2)_2\text{Ae(THF)}_n\) (Ae = Ca, n = 2; Sr, n = 1; Ba, n = 0.5), THF.

Figure 4.4: Crude $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for compounds 47g and 47h in THF compared with the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for compound 47b THF. * Free phosphine-borane (47)
Unfortunately, after many attempts to isolate single crystals of 47g and 47h using many different solvents, no solid material was isolated and so a $^1$H NMR was not recorded in order to see if THF was present; this could further indicate if 47g and 47h are alkaline earth metal complexes. However, previously reported compounds $[[\text{PhP(BH}_3]\{\text{CH(SiMe}_3\}_2]}\text{Ca(OEt}_2\}_2$ (56) and $[[\text{PhP(BH}_3]\{\text{CH(SiMe}_3\}_2]}\text{Sr(THF)}_{1.75}(\text{OEt}_2)_{0.25}]_2$ (57) exhibit broad multiplets at 6.5 ppm ($J_{PB} = 91.0$ Hz) and 5.0 ppm ($J_{PB} = 106.0$ Hz) in their $^{31}$P{$^1$H} NMR spectra where the $^{31}$P-$^{11}$B coupling constants of 47g and 47h are remarkably similar to the coupling constants of both 56 and 57. This huge rise in the $^{31}$P-$^{11}$B coupling constant on metalation is also consistent with many examples of previously reported α-metalated phosphine-borane-stabilised carbanions.9, 15-22

The $^{31}$P{$^1$H} NMR spectrum for compound 47g (Figure 4.4) also exhibits a quartet at 35.7 ppm ($J_{PB} = 98.7$ Hz) which is associated with the free phosphine-borane 47. The presence of 47 may be attributed to the decomposition of 47g in THF at room temperature which is relatively common in alkaline earth metal complexes of phosphine-borane-stabilised carbanions.13 It is not, however, clear what the decomposition pathway is but it may be due to the increased charge/size ratio of the calcium ion, which activates protons bound to the THF solvent which is coordinated to the metal centre.

The $^{31}$P{$^1$H} NMR spectrum of 49g (Figure 4.5) exhibits a broad quartet at 8.8 ppm ($J_{PB} = 93.9$ Hz) which is similar to that of the potassium complex 49b (8.7 ppm, $J_{PB} = 97.1$ Hz). Compound 49 reacts with in situ generated Bn$_2$Sr(THF)$_2$; where Bn$_2$Sr(THF)$_2$ was synthesised using an excess of BnK. Single crystals suitable for X-ray crystallography from toluene were found to be the potassium complex 49b which may be attributed to the in situ use of an excess of BnK. There are two pathways that could explain this:

1. Either Bn$_2$Sr(THF)$_2$ is decomposing in the THF solvent, and so, the excess BnK is reacting with the phosphine-borane precursor 49.
2. Or that 49g is being made, however, it deprotonates the solvent, resulting in the phosphine-borane precursor 49; which then later reacts with the excess BnK to form 49b.
Figure 4.5: The $^{31}\text{P}^{1\text{H}}$ NMR spectrum of 49g compared with 49b in THF.

4.5 Conclusion

To summarise, this chapter provides an overview of three different synthetic routes to synthesise alkaline earth metal complexes of phosphine-borane-stabilised carbanions. The first method, using organolithiums is not commonly used in the synthesis of heavier group 2 complexes as this route has a tendency to form anionic ‘ate’ complexes. The second method, using benzylpotassium, is a fairly common synthetic approach, however, more investigations are needed in order to optimise the reactions conditions as unreacted 49b is isolated. The third method, using dibenzylcalcium, -strontium and –barium is a relatively new approach to synthesising group 2 complexes and so is very much in its infancy, however, this synthetic approach seems to be the most promising method. There are still potential issues in terms of decomposition, especially with the calcium complex 47g in THF solutions as there is the potential for deprotonation of the solvent molecules bound to the calcium metal centre, resulting in elimination of the phosphine-borane precursor 47. It also seems vital that the dibenzylcalcium, -strontium and –barium complexes need to be isolated before reacting with phosphine-boranes as, if these are reacted in situ, any excess BnK that was used to synthesise...
the group 2 complexes will compete and so react with the phosphine-borane precursors; hence resulting in the isolation of 49b.
4.6 References


Chapter 5. Impact of a rigid backbone on the structure of an agostically-stabilised dialkylstannylene

5.1 Introduction

Recently, Izod and co-workers have investigated the extent to which agostic stabilisation of dialkylstannylenes inhibits their dimerisation. For example, [(Me₃Si)(Me₂P(BH₃))HC]₂Sn (34) (Figure 5.1), exhibits two stabilising B-H···Sn interactions and adopts a monomeric structure, whereas, {(Me₃Si)₂CH}₂Sn (28),¹ which is isoelectronic and isosteric with compound 34 and in which such agostic-type interactions are absent, dimerises to the corresponding distannene in the solid state (Scheme 5.1).

![Figure 5.1](image-url)

**Figure 5.1:** Dialkylstannylenes exhibiting agostic-type stabilisation interactions.
Scheme 5.1: Monomeric dialkylstannylenes and the corresponding distannene.

In all of the dialkylstannylenes that Izod and co-workers have isolated (Figure 5.1), the supporting ligand is either monodentate (34 and 35), or has a flexible spacer group linking the two carbanion centres (32 and 33). This flexible spacer allows the phosphine-borane group to tilt towards the Sn centre, maximising the overlap between the B-H σ-orbital and the vacant p-orbital at Sn and so providing stabilisation at the electron deficient Sn(II) centre (Figure 5.2).

Figure 5.2: Compound 32 and orbital overlap between the B-H unit and the vacant p-orbital of Sn.

Previously reported work by Izod and co-workers and the work described in this chapter has begun to investigate the chemistry of phosphine-borane-stabilised dicarbanions in which the two carbanion centres are linked by an ortho-phenylene spacer. The exploration of the impact of such a rigid ligand backbone on the strength of the B-H···Sn agostic-type interactions is of interest, since the rigidity of the ligand should limit the extent to which the BH₃ group can position itself near to the Sn centre and so affect the strength of the agostic-type stabilisation of the dialkylstannylenes.
5.2 Synthesis of dialkylstannylenes

Treatment of *in situ*-generated \([1,2-C_6H_4\{CHP(BH_3)Cy_2\}_2][Li(THF)_n]\) with one equivalent of \(\text{Cp}_2\text{Sn}\) in toluene yields pale yellow crystals of \([1,2-C_6H_4\{CHP(BH_3)Cy_2\}_2\text{Sn}]_2\cdot 3/2\text{PhMe} (58)\) (Scheme 5.2) suitable for X-ray crystallography. Once isolated, compound 58 has limited solubility in aromatic and ethereal solvents and this compound reacts rapidly with chlorinated solvents. Compound 58 also decomposes to the corresponding phosphine-borane and elemental tin with exposure to light or temperatures above 50 °C and, over a period of several hours, begins to decompose in THF solution at room temperature. Compound 58 is, however, sufficiently stable and soluble in THF for characterisation by NMR spectroscopy.

The reaction of \(\text{Cp}_2\text{Sn}\) with *in situ*-generated \([1,2-C_6H_4\{CHP(BH_3)R_2\}_2][Li(THF)_n]\) (\(R = \text{iPr}, \text{Ph} \text{and Cy}\)) was expected to result in the agostically-stabilised dialkylstannylenes 59-61 shown in Scheme 5.2. However, the \(^{31}\text{P}^{\{1\text{H}\}}\) NMR spectra of the crude reaction solutions exhibit several different phosphorus environments. A maximum of two phosphorus environments were predicted due to the *rac* and *meso* diastereomers of 58 and so the five broad peaks present in the crude reaction mixtures were initially attributed to impurities.
Scheme 5.2: Synthesis of Compound 58. Reaction conditions. i) 2 equivalents of $^n$BuLi, THF. ii) SnCp$_2$, toluene.

However, upon recrystallisation of compound 58 it was clear from the NMR data that the previously predicted structures given in Scheme 5.2 were incorrect. Instead of the usual dialkylstannylene structures, an unusual agostically-stabilised stannyl-stannylene with both chelating and bridging ligands was observed. The previously discounted $^{31}$P{$^1$H} NMR spectra correlated with the solid state structure of compound 58 (Figure 5.3). The $^{31}$P{$^1$H} NMR spectrum of crystalline compound 58 exhibits four broad signals at 27.2, 28.6, 30.0 and 35.4 ppm (Figure 5.4) while the $^{11}$B{$^1$H} NMR spectrum exhibits two broad signals at -43.5 and -38.8 ppm (Figure 5.5) in an approximately 3:1 ratio. The unique high field signal (-38.8 ppm) in the latter spectrum may be attributed to the phosphine-borane which is associated with the short B-H···Sn interaction. These signals indicate that the dinuclear structure seen for compound 58 in the solid state (see below) persists in solution.
Figure 5.3: Schematic drawing of solid state structure of 58.

Figure 5.4: $^{31}$P{$^1$H} NMR spectra of compounds 58. * Unknown impurities
Furthermore, upon comparison of the crude $^{31}$P{\textsuperscript{1}H} NMR spectra of compound 58 with those of 60 and 61 (Figure 5.6), it appears likely that these compounds also adopt a stannyl-stannylene structure.
Figure 5.6: $^{31}$P{$^1$H} NMR spectra of compounds 58, 60 and 61 in the crude reaction mixture in THF.

The $^{31}$P{$^1$H} NMR spectrum for the crude reaction mixture of compound 58 shows multiple broad and overlapping signals. This suggests that in addition to compound 58, the solution contains the corresponding rac isomer, either as a monomeric or dimeric species; however, this species was not isolated. The presence of diastereomers will affect the potential yield that can be isolated; 50% rac and 50% meso. This explains why the overall yield of compound 58 initially seems relatively low. After considering the presence of diastereomers, it is unsurprising that the yield of 58 isolated is just 28%, which is in fact 56% of the potential meso diastereomer. It is also important to note that the less favourable meso conformation takes seven days to recrystallise. The $^1$H NMR spectrum of compound 58 is complex and uninformative, due to the overlap of signals from the eight chemically inequivalent cyclohexyl groups (within which pairs of CH$_2$ groups are diastereotopic) and the signals from
four chemically inequivalent benzylic and BH₃ groups. The $^{119}\text{Sn}^{1\text{H}}$ NMR spectrum of compound 58 exhibits broad, featureless signals at -103 and 339 ppm (Figure 5.7), which may be attributed to the stannyl and stannylenic centres, respectively; coupling between the two Sn centres is not resolved, due to the broad nature of these signals. The signal at -103 ppm is typical of tetravalent Sn centres,³⁻⁵ while the signal at 330 ppm is similar to the chemical shifts in the previously reported agostically-stabilised dialkylstannylenes 32-35, which fall in the range 320-787 ppm.⁶⁻¹⁰

![Figure 5.7: $^{119}\text{Sn}^{1\text{H}}$ NMR spectrum indicating two broad signals.](image)

Compound 58 crystallises as a discrete molecular species containing two different Sn centres with formal oxidation states of I and III, joined by a formal Sn-Sn σ-bond and with 1½ molecules of toluene in the asymmetric unit; the solid state structure along with selected bond lengths can be seen in Figure 5.8 and Table 5.1, respectively.
Figure 5.8: Molecular structure of compound 58 with solvent of crystallisation and H atoms (except those bound to boron) omitted for clarity.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn(1)-Sn(2)</td>
<td>2.81531(17)</td>
</tr>
<tr>
<td>Sn(1)-C(8)</td>
<td>2.2021(18)</td>
</tr>
<tr>
<td>Sn(2)-C(40)</td>
<td>2.3250(18)</td>
</tr>
<tr>
<td>P(1)-B(1)</td>
<td>1.931(2)</td>
</tr>
<tr>
<td>P(2)-B(2)</td>
<td>1.927(2)</td>
</tr>
<tr>
<td>P(3)-B(3)</td>
<td>1.939(2)</td>
</tr>
<tr>
<td>P(4)-B(4)</td>
<td>1.934(2)</td>
</tr>
<tr>
<td>Sn(1)-C(1)</td>
<td>2.1887(17)</td>
</tr>
<tr>
<td>Sn(1)-C(33)</td>
<td>2.2518(17)</td>
</tr>
<tr>
<td>Sn(2)-H(2B)</td>
<td>2.49(2)</td>
</tr>
<tr>
<td>P(1)-C(1)</td>
<td>1.8373(18)</td>
</tr>
<tr>
<td>P(2)-C(8)</td>
<td>1.8290(18)</td>
</tr>
<tr>
<td>P(3)-C(33)</td>
<td>1.8218(17)</td>
</tr>
<tr>
<td>P(4)-C(40)</td>
<td>1.8103(18)</td>
</tr>
</tbody>
</table>

Table 5.1: Selected bond lengths (Å) for compound 58.

The formal Sn(III) centre is bonded to the two carbanion centres of a chelating dicarbanion ligand [Sn(1)-C(1) 2.1887(17) and Sn(1)-C(8) 2.2021(18) Å] and to a single
carbon atom of the second dicarbanion ligand [Sn(1)-C(33) 2.2518(17) Å], along with a short Sn-Sn contact. The Sn-C distances of the chelating dicarbanion ligand are similar to those in the tetravalent stannylene C₆H₃CH₂SnR₃ [R = CH(SiMe₃)₂] (62) published by Westerhausen [Sn-C 2.203(8), 2.193(8), 2.207(7), 2.201(8) Å],¹¹ however, the Sn-C distance of the second dicarbanion is significantly longer than the Sn-C distance in 62; this may be attributed to compound 58 possessing a rigid linker which is bridging the two Sn centres, therefore, elongating the Sn-C distance in this case. The formal Sn(I) centre is bonded to the adjacent Sn atom and a carbon atom of the second dicarbanion ligand [Sn(2)-C(40) 2.3250(18) Å]; this distance is significantly longer than the Sn-C distance in the monomeric stannylene Sn[CH(SiMe₃)₂]₂ (28) [Sn-C 2.28 Å average from gas phase diffraction measurements].¹ The shorter Sn-C bond in 28 may be attributed to electron donation from the carbanion into the σ*-orbital on Si. The formal Sn(I) centre also has a short contact to a hydrogen atom of one of the BH₃ units of the ligand which chelates the formal Sn(III) centre [Sn(2)-H(2B) 2.49(2) Å]; this distance is similar to the H···Sn distances in compounds 32-35, which are in the range of 2.03(5)-2.41(8) Å.⁶⁻¹⁰ Although the location of H atoms by X-ray crystallography is not accurate, this distance is substantially shorter than the sum of the van der Waals radii of Sn and H (3.37 Å), which suggests that there is significant stabilisation via an agostic-type B-H···Sn interaction.

Formation of compound 58 results in one of the phosphine-borane-stabilised carbanion ligands chelating Sn(1), forming a five-membered C₄Sn heterocycle, whilst the second phosphine-borane-stabilised carbanion ligand bridges Sn(1) and Sn(2), generating a C₄Sn₂ six-membered heterocycle; each of these ligands adopts a meso-configuration. The Sn-Sn distance (2.81531(17) Å) is substantially shorter than the Sn-Sn distances in previously reported stannyl-stannylenes [formal oxidation states of Sn(I) and Sn(II)], which range from 2.865(6)-2.9688(5) Å⁴⁻²⁶ and is similar to the Sn-Sn distance in grey tin (2.80 Å).²⁷ This short distance may be attributed to the incorporation of the Sn-Sn bond into a rigid six-membered ring.
5.3 DFT Calculations on a model stannyl-stannylene

**Figure 5.9:** Optimised geometries of compound 63 (top), meso-63 (bottom left) and rac-63 (bottom right) with C-bound H atoms (except for those bound to boron) omitted for clarity.

DFT calculations on the complex $[[1,2-C_6H_4\{CHP(BH_3)Me_2\}_2]Sn_2]$ (63) (B3LYP/6-31G(2d, p)/Lanl2dz on Sn), in which the cyclohexyl groups have been replaced by smaller methyl substituents, reproduce the core structure of compound 58 observed in the solid state (Figure 5.9). In particular, one of the borane hydrogen atoms lies close to the divalent Sn centre (Sn···H, 2.13 Å), which is similar to the interaction observed in the solid-state structure of compound 58. Natural Bond Orbital (NBO) analysis indicates that this interaction stabilises 63 by 28.8 kcal mol$^{-1}$, similar to the stabilisation energies calculated for 33-35 (even with the unusual bridging mode of the ligand in 63).
In order to estimate the resulting stability of the stannyll-stannylene 63 in comparison to the monomer meso-\([1,2-C_6H_4(CHP(BH_3)Me_2)]_2Sn\) (meso-63) the energies of both of these species have been calculated as well as that of the corresponding rac isomer (Figure 5.9). The optimised geometries for both meso- and rac-63 have a single short B-H···Sn contact with Sn···H distances of 2.15 and 2.13 Å, respectively. This short interaction results in the C_4Sn five-membered ring being essentially planar for meso-63, however, for rac-63 this interaction results in a twisting of both the five-membered ring and the aromatic ring. NBO analysis suggests that the B-H···Sn interactions stabilise meso- and rac-63 by 41.4 and 33.1 kcal mol\(^{-1}\), respectively. The calculations also suggest that rac-63 is 1.8 kcal mol\(^{-1}\) more stable than meso-63 and that meso-63 is favoured by 1.1 kcal mol\(^{-1}\) compared to the stannyl-stannylene 63. In previous examples, such as compounds 33-35, the more energetically favourable conformation is the rac diastereomer as this allows both the BH\(_3\) units to have Sn···H-B interactions whereas the less energetically favourable meso diastereomer just allows one BH\(_3\) unit to have an Sn···H-B interaction. However, the lack of significant energetic preference calculated for rac-63 and meso-63 suggests that both will be in an approximately 1:1 mixture rather than the usual favoured rac diastereomer.

5.4 Conclusion

Multielement NMR spectroscopy indicated that the solid state structure of 58 persisted in solution; the \(^{11}\text{B}\{^1\text{H}\}\) NMR spectrum of 58 exhibited a signal at -38.8 ppm which may be attributed to the phosphine-borane B-H···Sn interactions. The crude \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of 58 contains broad and overlapping peaks which may correspond to the rac isomer; this would explain why the isolation of 58 is in such poor yields. Furthermore, crude \(^{31}\text{P}\{^1\text{H}\}\) NMR spectra for compounds 60 and 61 exhibited similar shaped signals to 58, and so, similar structures may be predicted. The incorporation of the rigid linker may be the cause in the production of this type of unusual stannyll-stannylene rather than a usual dialkylstannylene. It is good to note that an agostic-type interaction still remains at the Sn(2) centre in compound 58.

Compound 58 crystallises as a discrete molecular species containing two different Sn centres with formal oxidation states of I and III, including a formal Sn-Sn σ-bond. DFT calculations on 63 reproduce the core structure of compound 58 where NBO analysis exhibits a borane proton lying close to the divalent centre (similar to compound 58) and stabilises compound 63 by 28.8 kcal mol\(^{-1}\); similar to those calculated for 32-35. The lack of energetic
preference calculated for \textit{rac-63} and \textit{meso-63} suggests that both will be in an approximately 1:1 mixture rather than the usual favoured \textit{rac} diastereomer.
5.5 References


Chapter 6. Replacement of a trimethylsilyl group and its impact on stability of dialkylstannylenes

6.1 Introduction

As discussed in Chapter 1.5, Lappert and co-workers reported the first dialkylstannylenes \{(\text{Me}_3\text{Si})_2\text{CH}\}_2\text{Sn}\} in the 1970s (Scheme 6.1).\textsuperscript{1} Compound 28 exists as a monomeric structure in the gas phase, but dimerises to the corresponding distannene 28a in the solid state; compounds 28 and 28a are in a dynamic equilibrium in solution.\textsuperscript{2}

\[ \begin{align*}
\text{Me}_3\text{Si} & - \text{SiMe}_3 \\
\text{Sn} & \quad \text{Sn} \\
\text{Me}_3\text{Si} & - \text{SiMe}_3
\end{align*} \]

\[ 2 \times \quad \text{Me}_3\text{Si} - \text{SiMe}_3 \quad \text{Sn} = \text{Sn} \quad \text{CH(}\text{SiMe}_3\text{)}_2 \quad \text{CH(}\text{SiMe}_3\text{)}_2 \]

\[ \text{Scheme 6.1: Monomeric dialkylstannylene and the corresponding distannene.} \]

Compounds 32 and 33 (discussed in chapter 1.5) (Scheme 6.2) are stabilised by a combination of steric bulk and agostic-type B-H···Sn interactions. Izod and co-workers reduced the steric bulk of the ligand in order to test the extent to which B-H···E interactions can stabilise dialkylstannylenes and therefore exhibit dimerisation to the corresponding \( \text{R}_2\text{Sn=SnR}_2 \). Compound 34 (Scheme 6.2), which contains the isoelectronic group Me\textsubscript{2}PBH\textsubscript{3} instead of SiMe\textsubscript{3}, was synthesised as an analogue of compound 28. Izod and co-workers found that agostic-type interactions were stabilising enough to prevent dimerisation, and so compound 34 exists as a monomer in the solid state.\textsuperscript{3}
Scheme 6.2: Dialkylstannylenes exhibiting B-H···Sn agostic-type stabilisation interactions.

In the present work, the benzylic phosphine-borane precursors $C_6H_5CHPR_2(BH_3)$ [$R = iPr (47)$ and Cy (49)] were synthesised and used to develop new types of agostically-stabilised dialkylstannylenes. Compounds 47 and 49 are analogues of 34 in which the SiMe$_3$ has been removed and replaced with a phenyl ring; this change reduces steric bulk around the electron deficient Sn centre. Izod and co-workers investigated the structure of compound 34 and found that only the rac diastereomer is formed; no evidence of the meso diastereomer was found in the crude $^{31}P$[$^1H$] NMR spectrum of the reaction mixture. This structural preference was attributed to the electron deficient tin centre in 34 possessing two agostic-type B-H···Sn interactions compared to just one interaction, which is common in the meso diastereomer; overall, the rac diastereomer provides a larger stabilising effect compared to the meso diastereomer. The development of the agostically-stabilised dialkylstannylenes using 47 and 49 is of interest to investigate whether the removal of the SiMe$_3$ group will affect the structures in each case.
6.2 Synthesis of dialkylstannylenes

6.2.1 Benzylic dialkylstannylenes

Treatment of one equivalent of SnCl₂ with two equivalents of in situ-generated [Li(tmeda)][C₆H₅CHPR₂(BH₃)] [R = 'Pr (47a) and Cy (49a)] in diethyl ether yields the dialkylstannylenes Sn[C₆H₅CHPR₂(BH₃)]₂ [R = 'Pr (64) and Cy (65)] (Scheme 6.3). Pale yellow crystals of 64 and 65 suitable for X-ray crystallography were isolated from cold (-20 °C) methylcyclohexane.

Scheme 6.3: Synthesis of Compounds 64 and 65. Reaction conditions. i) 'BuLi, THF.
ii) 0.5SnCl₂, Et₂O.

Unfortunately, 65 could not be separated cleanly from side products (LiCl) and impurities (such as Sn[C₆H₅CHPR₂(BH₃)]Cl and SnCl₂) to obtain clean ¹H, ¹H{¹¹B}, ¹³C{¹H} and ¹¹⁹Sn{¹H} NMR spectra; therefore, compound 65 could not be fully characterised. Once isolated, both compounds 64 and 65 showed poor stability in many deuterated solvents (CDCl₃, d₈-THF and d₈-toluene) which resulted in decomposition to the free phosphine-boranes 47 and 49.

It is worth noting here the differences in the experimental procedures between compounds 32, 33, 34 and that of 64 and 65 where 64 and 65 were made with the use of SnCl₂ and 32, 33 and 34 were made with the use of SnCp₂. Compounds 32, 33, and 34 contain SiMe₃ groups and compounds 64 and 65 contain the more charge-delocalising phenyl group, which results in 64 and 65 being less nucleophilic and less reducing. The use of SnCl₂ with the more reducing compounds 32, 33 and 34 results in deposition of elemental tin and formation of the corresponding phosphine-borane.⁴
6.2.2 Characterisation of compounds 64 and 65

Compounds 64 and 65 are chiral at both methine carbon atoms and so may form both rac and meso diastereomers (Figure 6.1). In an attempt to separate these diastereomers, diethyl ether was added to the solid crude reaction mixture of compound 65 resulting in a light yellow precipitate which was isolated and washed with cold diethyl ether. Both the precipitate and the filtrate were analysed using multinuclear NMR spectroscopy. In deuterated toluene the $^1$H{$^{11}$B} NMR spectrum of the precipitate of 65 contains doublets at 0.62 ppm ($J_{PH} = 8.5$ Hz) and 0.91 ppm ($J_{PH} = 10.0$ Hz), which correspond to the two BH$_3$ units in the rac and meso diastereomers (Figure 6.2). The $^1$H{$^{11}$B} NMR spectrum also exhibits a major doublet at 2.70 ppm ($J_{PH} = 12.3$ Hz) and a minor doublet (3:1 ratio) at 3.50 ppm ($J_{PH} = 12.3$ Hz) corresponding to the two hydrogens bonded to the two carbanion centres in each case (Figure 6.2). The $^{11}$B{$^1$H} NMR spectrum contains a broad peak at -39.4 ppm. In deuterated toluene the $^{31}$P{$^1$H} NMR spectrum of the precipitate contains a major peak at 26.7 ppm and a minor peak at 28.3 ppm whilst in diethyl ether the filtrate contains a major peak at 30.8 ppm and a minor peak at 29.0 ppm (Figure 6.3). The $^{119}$Sn{$^1$H} NMR spectrum of the precipitate of 65 contains broad peaks at 359 and 370 ppm. This clearly suggests that while both diastereomers are formed, one has much reduced solubility in diethyl ether; however, it is unclear which chemical shifts correspond to which diastereomer in each case.

![Figure 6.1](image)

**Figure 6.1:** The proposed rac and meso diastereomers of compounds 64 and 65.

The crude $^{11}$B{$^1$H} NMR spectrum of compound 64 shows a broad doublet at -38.8 ppm ($J_{PB} = 79.5$ Hz) and the $^{31}$P{$^1$H} NMR spectrum exhibits a broad peak at 34.6 ppm. Based on the NMR spectra of compound 65, these broad peaks could also indicate the presence of rac and meso diastereomers (see discussion above).
The $^{119}\text{Sn}[^1\text{H}]$ NMR spectrum of $65$ contains broad signals at 359 and 370 ppm which are similar to the $^{119}\text{Sn}[^1\text{H}]$ NMR signals of compounds rac-$32$ (578 ppm)$^4$, rac-$33$ (320 ppm)$^5$ and $34$ (377 ppm)$^3$ but is significantly higher field than the isoelectronic compound $28$ (2328 ppm)$^1$. These high field chemical shifts are consistent with the B-H···Sn contacts which are observed in the solid persisting in solution.$^3$

![$^1\text{H}[^{11}\text{B}]$ NMR spectrum](image)

**Figure 6.2:** Evidence of rac and meso diastereomers in the $^1\text{H}[^{11}\text{B}]$ NMR spectrum of compound $65\,d_8$-toluene; CH protons (*) and BH$_3$ protons (+).
Single crystals of rac-64 and rac-65 suitable for X-ray crystallography were obtained from cold methycyclohexane or cold diethyl ether, respectively. Compounds rac-64 and rac-65 crystallise as discrete dialkyltetrylenes with effective disorder of the Sn atom and the methine CH groups over two sites with 60:40 occupancy. Both rac-64 and rac-65 have interactions between the Sn centre and one H atom from each of two separate BH₃ units in an η¹-fashion; rac-64 and rac-65 are isostructural but not isomorphous. The molecular structures of rac-64 and rac-65 are shown in Figures 6.4 and 6.5, respectively; selected bond lengths and angles are given in Tables 6.1 and 6.2 respectively.

The Sn-C distances of 2.282(10) and 2.314(10) Å in rac-64 are similar to the corresponding distances in the previously reported compound 34 [2.3149(16) and 2.2864(16) Å]. The Sn-C distances of 2.176(5) and 2.275(4) Å in rac-65 are shorter than those in compound 34. The P-B distances [rac-64, 1.925(14) and 1.919(14) Å; rac-65, 1.922(5) and 1.923(5) Å] and the C-P distances [rac-64, 1.814(11) and 1.786(12) Å; rac-65, 1.798(4) and 1.806(5) Å] of both compounds are similar to the corresponding P-B [1.909(3) Å] of rac-65.

Figure 6.3: ³¹P{¹H} NMR spectra of the precipitate and filtrate of compound 65; * precursor 49 or rac-65.
and 1.918(2) Å] and C-P [1.7877(16) and 1.7919(18) Å] distances in compound 34. The Sn···H distances of compounds rac-64 (2.49(12) and 2.60(13) Å) and rac-65 (2.38(4) and 2.35(4) Å) lie well within the sum of the van der Waals radii of H and Sn (3.37 Å) suggesting a significant H···Sn interaction. The H···Sn distances of compounds rac-64 and rac-65 are also similar to the corresponding distances in 34 (2.38(2) and 2.29(2) Å).³

Figure 6.4: Molecular structure of rac-64 H atoms (except those bound to boron) omitted for clarity.

<p>| | | | | | |</p>
<table>
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<tbody>
<tr>
<td>Sn-C(1)</td>
<td>2.314(10)</td>
<td>Sn-C(14)</td>
<td>2.282(10)</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>1.814(11)</td>
<td>C(14)-P(2)</td>
<td>1.786(12)</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>P(2)-B(2)</td>
<td>1.919(14)</td>
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</tr>
<tr>
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<td>2.60(13)</td>
<td>Sn-H(2A)</td>
<td>2.49(12)</td>
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<td></td>
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<td>C(1)-Sn-C(14)</td>
<td>95.1(4)</td>
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</table>

Table 6.1: Selected bond lengths (Å) and angles (°) for rac-64.

The C-Sn-C angles of 95.1(4)° and 101.4(18)° in rac-64 and rac-65, respectively are significantly different to the C-Sn-C angle observed for 6 [98.26(6)°]. Compound rac-65 has
a C-Sn-C angle which is significantly greater than those of rac-64 and 34 due to the larger cyclohexyl substituents on the phosphorus. The C-Sn-C angles for rac-64 and rac-65 are closer to 90° than to 120° which suggests unhybridised Sn orbitals (s and 3×p rather than sp² and p).

**Figure 6.5:** Molecular structure of compound rac-65 with solvent of crystallisation and H atoms (except those bound to boron) omitted for clarity.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
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<tbody>
<tr>
<td>Sn-C(1)</td>
<td>2.176(5)</td>
</tr>
<tr>
<td>C(1)-P(1)</td>
<td>1.798(4)</td>
</tr>
<tr>
<td>P(1)-B(1)</td>
<td>1.922(5)</td>
</tr>
<tr>
<td>Sn-H(1A)</td>
<td>2.38(4)</td>
</tr>
<tr>
<td>Sn-C(20)</td>
<td>2.275(4)</td>
</tr>
<tr>
<td>C(20)-P(2)</td>
<td>1.806(5)</td>
</tr>
<tr>
<td>P(2)-B(2)</td>
<td>1.923(5)</td>
</tr>
<tr>
<td>Sn-H(2C)</td>
<td>2.35(4)</td>
</tr>
<tr>
<td>C(1)-Sn-C(20)</td>
<td>101.4(18)</td>
</tr>
</tbody>
</table>

**Table 6.2:** Selected bond lengths (Å) and angles (°) for rac-65.
6.3 Conclusion

Overall, the removal of the trimethylsilyl group reduces the bulkiness within the agostically-stabilised dialkylstannynes rac-64 and rac-65. In compound 34 it was reported that there was no evidence to suggest that a mixture of rac and meso diastereomers had formed and so only rac-34 was isolated and characterised. This however, is not the case for compounds 64 and 65; the NMR spectra of both compounds suggest the formation of a mixture of both rac and meso diastereomers. The \( ^{119}\text{Sn}\{^1\text{H}\} \) NMR spectrum of compound 65 exhibits two broad peaks of equal intensity, while the \( ^1\text{H}\{^{11}\text{B}\} \) and \( ^{31}\text{P}\{^1\text{H}\} \) NMR spectra of compound 65 show two separate chemical shifts for the mixture of diastereomers. This clear difference between compound 34 and 64/65 may be attributed to the removal of the SiMe\(_3\) group in the latter compounds and the reduction in steric bulkiness. However, the increase in C-Sn-C angle in rac-65 [101.4(18)°] compared to 34 [98.26(6)°] may indicate that rac-65 contains more sterically hindered phosphorus substituents than 34 and yet still shows evidence for the formation of rac and meso diastereomers in 65. However, the explanation as to why the removal of SiMe\(_3\) may affect the structural outcome may also be attributed to the intermediates RSnCl \([R = (\text{Me}_3\text{SiCHPMe}_2\text{BH}_3) (66), \text{C}_6\text{H}_5\text{CHPPr}_2\text{BH}_3) (67) \) or \( \text{C}_6\text{H}_5\text{CHP} \text{Cy}_2\text{BH}_3 (68)\)] where intermediate 66 is more sterically hindered than 67 or 68. The increase bulk in 66 will have a bigger influence in the addition of the second substituent than 67 or 68, resulting in only the rac diastereomer seen for 34 and both rac and meso seen for 65.
6.4 References


Chapter 7. Heteroleptic dialkylstannylenes

7.1 Introduction

The synthesis of heteroleptic compounds via chlorostannylenes SnCl[\(C_6H_5CHPR_2(BH_3)\)] \([R = \text{‘Pr} (69) \text{ and Cy (70)}]\) is of interest in order to monitor agostic-interactions between the BH\(_3\) unit and the electron-deficient tin centre; by changing the substituent X in the heteroleptic species RSnX, the stabilisation effects of the agostic interactions can be measured. Carbon based ligands may be the least \(\pi\)-donating whereas amines the most \(\pi\)-donating (Chart 7.1). This will lead to competition of the donation capabilities between the B-H \(\sigma\)-bonding electron density and the heteroatom lone pair into the empty p-orbital of the electron-deficient Sn centre. The Sn···H-B interactions should become weaker as the second ligand becomes more \(\pi\)-donating ligand, and so this may result in a reduction in agostic-interactions with the BH\(_3\) unit and the electron deficient centre.

![Chart 7.1: Heteroatoms from the least to the most \(\pi\)-donating.](image-url)
In order to investigate this phenomenon, we sought to prepare a range of heteroleptic stannylenes \([(\text{PhCH}_2)\text{PR}_2(\text{BH}_3)]\text{SnX} (X = -\text{CH(SiMe}_3)_2, -\text{Dipp}, -\text{N(SiMe}_3)_2, -\text{O(2,6-}^4\text{Bu}_2-4\text{-MeC}_6\text{H}_2}, -\text{PTripp}, -\text{PDipp}, -\text{CH}_3, -\text{C}_6\text{H}_5; R = ^1\text{Pr and Cy}) [\text{Dipp} = 2,6-^4\text{Pr}_2\text{C}_6\text{H}_3, \text{Tripp} = 2,4,6-^4\text{Pr}_3\text{C}_6\text{H}_2] and to probe the strength of the B-H···Sn interactions in each case.

7.2 Synthesis of heteroleptic dialkylstannylenes

Treatment of one equivalent of SnCl$_2$ with one equivalent of \textit{in situ}-generated Li[\text{C}_6\text{H}_5\text{CHPR}_2(\text{BH}_3)] [R = ^1\text{Pr} (47a), \text{Cy} (49a)] in diethyl ether yields [\text{C}_6\text{H}_5\text{CHPR}_2(\text{BH}_3)]\text{SnCl} [R = ^1\text{Pr} (69), \text{Cy} (70)] (Scheme 7.1). A pale yellow solid precipitated with reduction of the ethereal solvent in each case.

\begin{equation}
\begin{array}{ccc}
\text{R = } & ^1\text{Pr} (69) & \text{and } \text{Cy} (70) \\
\text{Cl} & \text{Sn} & \text{Li} \\
\text{[C}_6\text{H}_5\text{CHPR}_2(\text{BH}_3)]} & \text{SnCl} & \text{[C}_6\text{H}_5\text{CHPR}_2(\text{BH}_3)]} \\
\text{2.5.1} & \text{2.5.1} & \text{2.5.1}
\end{array}
\end{equation}

\textbf{Scheme 7.1:} Synthesis of compounds 69 and 70. Reaction conditions. i) \textit{^6}BuLi, Et$_2$O. ii) SnCl$_2$, Et$_2$O.

Unfortunately, sufficiently clean solid was not obtained for compound 69 in order for full characterisation using NMR spectroscopy. The $^1$H and $^{13}$C{$^1$H} NMR spectra for compound 70 and the $^{11}$B{$^1$H} and $^{31}$P{$^1$H} NMR spectra for both compounds 69 and 70 are as expected. The $^{11}$B{$^1$H} NMR spectrum of compound 69 contains a doublet at -39.2 ppm and the $^{31}$P{$^1$H} NMR spectrum contains a quartet at 33.4 ppm ($J_{PB} = 66.6$ Hz). In deuterated THF the $^1$H NMR spectrum of 70 contains a doublet at 3.05 ppm ($J_{PH} = 11.7$ Hz), corresponding to the methine proton bonded to the carbanion centre. The $^{11}$B{$^1$H} NMR spectrum of 70 contains a broad peak at -39.8 ppm and the $^{31}$P{$^1$H} NMR spectrum contains a broad peak at 27.7 ppm. The pale yellow solids isolated for compounds 69 and 70 were not suitable for X-ray crystallography.
7.3 Reactivity of heteroleptic alkylstannylenes with bulky reagents

7.3.1 Carbon-containing groups

Treatment of \([C_6H_5CHPPr_2(BH_3)]SnCl\) with one equivalent of either LiCH(SiMe_3)_2 or Li\{2,6-Pr_2-C_6H_3\} results in a colour change from a pale yellow to a dark red solution (Scheme 7.2).

![Scheme 7.2: Synthesis of compounds 71 and 72.](image)

Crude \(^{31}\text{P}[^1\text{H}]\) NMR spectra of both reactions were recorded and both NMR spectra showed a change from the starting compound 69 (Figure 7.1); unfortunately no other NMR data was obtained.
Figure 7.1: $^{31}$P{H} NMR spectra of crude samples of 71 and 72 in diethyl ether compared to a crude $^{31}$P{H} NMR spectrum of 69 diethyl ether.

Several solvents including diethyl ether, toluene, methylcyclohexane, n-hexane, tBuOMe and hexamethydisiloxane (HMDSO) were used in order to isolate any form of solid to analyse via NMR spectroscopy or X-ray crystallography; unfortunately none of these solvents were successful.

7.3.2 Nitrogen- and oxygen-containing groups

Treatment of $[C_6H_5CHPPr_2(BH_3)]SnCl$ with one equivalent of LiN(SiMe$_3$)$_2$ results in a colour change from pale yellow to a dark red solution (Scheme 7.3).
Scheme 7.3: Synthesis of compounds 73.

A crude $^{31}\text{P}^{[\text{H}]}$ NMR spectrum of the reaction with LiN(SiMe$_3$)$_2$ was taken and the $^{31}\text{P}^{[\text{H}]}$ NMR spectra showed a change from the starting compound 69 (Figure 7.2).

Figure 7.2: $^{31}\text{P}^{[\text{H}]}$ NMR spectra of compound 73 in diethyl ether compared to 69 in diethyl ether.

Several solvents including diethyl ether, toluene, methylcyclohexane, $n$-hexane, $t$BuOMe and HMDSO were used in order to isolate any form of solid to analyse via NMR spectroscopy or X-ray crystallography; unfortunately none of these solvents were successful.
7.3.3 Phosphorus-containing groups

Treatment of [C₆H₅CHPPr₂(BH₃)]SnCl with one equivalent of either LiP(Dipp)₂ or LiP(Tripp)₂ results in a colour change from pale yellow to a dark red solution (Scheme 7.4).

Work in the Izod group shows homoleptic diphosphatetrylenes [Sn(PR₂)₂ R = Tripp or Dipp] where the addition of tripp substituents are usually problematic due to decomposition to a diphosphine and the corresponding phosphine. The proposed route by which this decompositions occurs is via a triplet excited state which could be due to a small energy gap between the π and π* orbitals (Figure 7.3).

![Molecular orbital diagrams of the ground and excited state of homoleptic diphosphatetrylenes [Sn(PR₂)₂ R = Tripp or Dipp].](image)

**Figure 7.3:** Molecular orbital diagrams of the ground and excited state of homoleptic diphosphatetrylenes [Sn(PR₂)₂ R = Tripp or Dipp].
This type of excited state may be attributed to the lone pair on the phosphorus atom donating to the empty p-orbital on the Sn centre (Figure 7.4).

Figure 7.4: Orbital diagram showing the donation of the lone pair from the phosphorus into the empty p-orbital of the tetal centre.

The energy gap between the π and π* orbitals for Dipp-substituted phosphines may be greater than those in Tripp-substituted phosphines, and so a triplet excited state is less likely; this prevents the decomposition to diphosphine and the corresponding phosphine.
The decomposition pathway seen in this type of phosphatetrylenes can also be seen in the reactions for compounds 74 and 75, where the resulting heteroleptic phosphine-borane-substituted tetrylene now exhibits competing donation into the empty p-orbital from the diorganophosphine; this donation may supersede the usual agostic-type interactions (Figure 7.5).

![Reaction Scheme]

Figure 7.5: Orbital diagrams indicating the loss of agostic-type interactions.

Unpublished results in the Izod group regarding the reactions of Tripp and Dipp substituents with heavier group 14 metals show the formation of diphosphine and R₂PH (R = Dipp or Tripp). The production of the diphosphine and R₂PH may be attributed to the P-M bond being susceptible to reduction. This can also be seen in the crude reaction mixtures of compounds 74 and 75 (Figure 7.6) where the $^{31}\text{P-}^1\text{H}$ NMR spectrum of 75 exhibits the least amount of decomposition products, along with a new signal at -25.3 ppm; indicating that Dipp is a more stable substituent than Tripp.
Several solvents including diethyl ether, toluene, methylcyclohexane, n-hexane, tBuOMe and HMDSO were used in order to isolate any form of solid to analyse via NMR spectroscopy or X-ray crystallography; unfortunately none of these solvents were successful.

Furthermore, these bulky reagents make the products far too soluble to isolate any crystalline material in order to characterise via NMR spectroscopy or X-ray crystallography. In order to alter the highly soluble nature of these compounds, we decided to use much less sterically hindered reagents.

### 7.4 Reactivity of heteroleptic alkylstannylenes with less sterically hindered groups

Treatment of \([C_6H_5CHPPr_2(BH_3)]SnCl\) with one equivalent of either MeMgBr or PhMgCl results in a colour change from pale yellow to a red solution (Scheme 7.5).
Scheme 7.5: Synthesis of compounds 76 and 77.

Crude $^{31}$P-$^1$H NMR spectra were taken which show a change in the phosphine-borane species for both reactions (Figure 7.7).

Figure 7.7: $^{31}$P-$^1$H NMR spectra of crude samples of 76 and 77 in diethyl ether compared to 69 in diethyl ether.
Both product mixtures were extracted into diethyl ether, the solvent was reduced and the solutions were cooled to 5 °C; crystalline 77 was obtained in this way, but unfortunately this was not suitable for X-ray crystallography.

7.5 Conclusions

Overall, sterically bulky ligands result in extremely soluble heteroleptic alkylstannylenes which could not be isolated. Compounds 71-75 exhibited a change in their crude $^{31}$P{$^1$H} NMR spectra compared to the starting material 69, however, even after using the very poor solvent HMDSO, no crystalline solid was isolated. This solubility issue led to the use of much less sterically demanding groups such as phenyl and methyl. Compounds 76 and 77 show a change in the $^{31}$P{$^1$H} NMR spectra (Figure 7.7) and crystalline material was isolated for 77. Unfortunately, this crystalline material was not suitable for X-ray crystallography and sufficiently clean NMR spectra were not obtained. However, the data obtained suggest that the use of small ligands should enable the isolation of heteroleptic alkylstannylenes, if suitable substituents are selected.
Chapter 8. Oxidation reactions of a phosphine-borane-stabilised dialkylstannylene

8.1 Introduction

The first example of the oxidative addition of an organohalide to a Sn(II) compound to give a tetravalent organotin compound, [Sn(Me)(Et)(Pr)I], was reported by Pope and Peachy in 1900.\(^1\) To this date, there are a vast number of tetravalent organotin compounds, however, this investigation reported in this thesis will only consider the oxidative addition products containing SiMe\(_3\) substituents, due to their isoelectronic relationship with PMe\(_2\)(BH\(_3\)).

Treatment of acyclic SnR\(_2\) (R = bis(trimethylsilyl)methyl) with MeI, HCl, RCl or RBr results in the products SnR\(_2\)MeI (78), SnR\(_2\)HCl (79), SnR\(_3\)Cl (80) and SnR\(_3\)Br (81), respectively as reported by Lappert and co-workers in 1976.\(^2\) Investigations into compound 79 (via multielement NMR spectroscopy) indicated that the SiMe\(_3\) groups were diastereotopic due to the tin centre exhibiting prochirality which can be seen in a simple Newmann projection diagram (Figure 8.1).\(^2\)

![Newmann projection along the C-Sn bond indicating diastereotopic SiMe\(_3\) groups in compound 79.](image)

It is of interest that a similar reaction between PbR\(_2\) and HCl did not yield the oxidative addition product. Lappert thought the cause of this may be attributed to the increased reactivity and the weakness of the Pb-C bond, compared to Sn-C, therefore resulting in a decomposition product. Lappert and co-workers also referred to the reluctance of lead...
compounds being able to achieve higher oxidation states needed for a four-coordinate oxidative addition product.\(^2\)

Treatment of cyclic Sn[\(\text{C(SiMe}_3\text{)}_2\text{SiMe}_2\text{CH}_2\text{]_2}\) (30) with MeI resulted in the oxidative addition product Sn[\(\text{C(SiMe}_3\text{)}_2\text{SiMe}_2\text{CH}_2\text{]_2}\)(Me)I (82) published by Eaborn and co-workers in 2000; unfortunately, no investigations into the structure of compound 82 were undertaken.\(^3\)

To date, there are very few examples of phosphine-borane-substituted Sn(IV) compounds and so this area of research is very much in its infancy, compared to the SiMe\(_3\)-substituted derivatives; compounds [\((\text{Me}_3\text{Si})[\text{Me}_2\text{P(BH}_3\text{)CH}]\text{Sn}(\text{R})(\text{X}) [\text{R} = \text{Me}, \text{X} = \text{I} (83); \text{R} = \text{CH}_2\text{CMe}_3, \text{X} = \text{I} (84); \text{R} = \text{CH}_2\text{Ph}, \text{X} = \text{Br} (85)] were isolated and characterised by Izod and co-workers.\(^4\) This chapter describes the synthesis of a new phosphine-borane-substituted Sn(IV) compound, along with its structural characterisation and a detailed investigation into its solution state structure using multielement NMR spectroscopy.

### 8.2 Synthesis of an oxidative addition product using MeI or BnBr

Treatment of a diethyl ether solution of [\(\text{C}_6\text{H}_5\text{CHP}^\text{Pr}_2\text{(BH}_3\text{)]_2Sn}\) (64) with one equivalent of methyl iodide or benzyl bromide yields the corresponding oxidative addition products [\(\text{C}_6\text{H}_5\text{CHP}^\text{Pr}_2\text{(BH}_3\text{)]_2Sn(Me)I}\) (86) and [\(\text{C}_6\text{H}_5\text{CHP}^\text{Pr}_2\text{(BH}_3\text{)]_2Sn(Bn)Br}\) (87), respectively, as white powders over the course of 1-16 hrs (Scheme 8.1). Colourless crystals suitable for X-ray crystallography were grown by dissolving compound 86 in hot toluene and layering with diethyl ether. Compound 87 was crystallised via the same method but the crystalline material isolated was only suitable for elemental analysis and multielement NMR spectroscopy.
Scheme 8.1: Oxidation of compound 64. Reagents and conditions: i) RX, diethyl ether, r.t., 16 hrs.

The solid state structure of compound 86 was determined by X-ray crystallography; the molecular structure is shown in Figure 8.2 and selected bond lengths and angles are given in Table 8.1. Compound 86 crystallises as a discrete monomer where the tin centre has contacts with two phosphine-borane fragments via the carbanion centres, a bond to the methyl carbon atom and a contact with an iodide in a distorted tetrahedral geometry; this compound has no agostic-type interactions between the borane hydrogens and the tin centre. Compound 86 lies on a pseudo-C\textsubscript{2} axis, with the methyl group and the iodine atom disordered over two sites each with equal occupancy, similar to the previously reported complex \([(\text{Me}_3\text{Si})\{\text{Me}_3\text{P(BH}_3)\}]\text{CH}_2\text{Sn(Me)(I)} (83).^4\)
**Figure 8.2:** Molecular structure of 86 with H atoms (except for those bound to boron) and disorder component omitted for clarity.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn(1)-I</td>
<td>2.5611(15)</td>
<td>Sn-C(1)</td>
<td>2.25(3)</td>
</tr>
<tr>
<td>P(1)-B(1)</td>
<td>1.928(10)</td>
<td>Sn-C(2)</td>
<td>2.161(7)</td>
</tr>
<tr>
<td>P(1)-C(2)</td>
<td>1.842(8)</td>
<td>P(1)-C(9)</td>
<td>1.850(8)</td>
</tr>
<tr>
<td>P(1)-C(12)</td>
<td>1.843(9)</td>
<td>B(1)-H(1A)</td>
<td>1.09(10)</td>
</tr>
<tr>
<td>B(1)-H(1B)</td>
<td>1.23(11)</td>
<td>B(1)-H(1C)</td>
<td>1.08(10)</td>
</tr>
<tr>
<td>I-Sn-C(1)</td>
<td>103.7(6)</td>
<td>C2-Sn-C2(2A)</td>
<td>107.4(4)</td>
</tr>
</tbody>
</table>

**Table 8.1:** Selected bond lengths (Å) and angles (°) for 86.

The Sn-I distance in compound 86 (2.5611(15) Å) is shorter than the Sn-I distances in other examples of tetravalent organotin(IV) iodides (typically 2.67-2.79 Å),<sup>5-10</sup> but it is of similar length to the corresponding distance in 83 (2.5626(7) Å). The Sn-I distance in compound 86 is also much shorter than that in the phosphine-borane-substituted organotin(IV) halide, [{(Me<sub>3</sub>Si)Me<sub>2</sub>P(BH)<sub>3</sub>}CH<sub>3</sub>Sn(CH<sub>2</sub>CM<sub>3</sub>)(I)] (84) (average of 2.7353 Å over three molecules in the asymmetric unit) which may be attributed to the greater steric...
crowding at the tin centre in the latter example due to the larger neopentyl group compared to the methyl group in compound 86.4

The Sn-C(carbanion) distance in compound 86 (2.253(3) Å) is within the typical range for tetrahedrally-coordinated organotin(IV) halides (Sn-C 2.04-2.33 Å) as well as other examples of phosphine-borane-substituted organotin(IV) halides (2.17-2.23 Å).4-14 The Sn-C(carbanion) distance in compound 86 is between 0.03-0.06 Å shorter than the corresponding distances in the dialkylstannylene 64, as expected, due to the increased formal charge at the tin centre in the oxidation product. The C(carbanion)-Sn-C(carbanion) bond angle increases significantly upon oxidation to form the tin(IV) centre; in the dialkylstannylene the C(carbanion)-Sn-C(carbanion) angle is 95.1(4) °, whereas the corresponding angle in compound 84 is 107.4(4) °.

In compound 86 the $^{119}$Sn{${^1}$H} NMR spectrum exhibits a doublet of doublets at -14.8 ppm ($J_{SnP} =$ 20.5 Hz, $J_{SnP'} =$ 106.3 Hz). The rotational symmetry present in the dialkylstannylene is lost upon oxidative addition and formation of the Sn(IV) centre. This results in two distinct phosphorus centres, one in each phosphine-borane-stabilised carbanion ligand, along with the previously noted diastereotopic nature of the ‘Pr substituents; all of which can be seen in the NMR spectra of 86. The $^{11}$B{${^1}$H} NMR spectrum of 86 exhibits a broad peak at 40.2 ppm which resolves into two distinct peaks (-40.1 ppm and -40.8 ppm) after carrying out broadband decoupling of $^{31}$P (Figure 8.3). After selective $^{31}$P decoupling the $^{11}$B{${^1}$H, $^{31}$P} NMR spectra shows which boron is associated with which phosphorus.
The $^{31}$P{$^{1}$H, $^{31}$P} NMR spectrum of 86 exhibits two broad peaks at 36.9 ppm and 40.5 ppm which are attributed to the two distinct phosphorus environments. Selective $^{11}$B decoupling confirms that the phosphorus centre resonating at 36.9 ppm is associated with the boron at -40.1 ppm and the phosphorus at 40.5 ppm is associated with the boron at -40.8 ppm (Figure 8.4).
Figure 8.4: $^{31}$P{¹H} NMR spectra of compound 86 in CDCl₃ with selective $^{11}$B and ¹H decoupling.

It is much more complicated to assign the proton NMR spectrum of 86 (Figure 8.5) due to the chiral carbon centres which result in both the methine protons within the isopropyl substituents being diastereotopic; this means we expect four different methine proton environments and eight different isopropyl methyl environments along with other proton environments within compound 86.
To assign the $^1$H NMR spectrum the following steps were carried out:

1. Firstly, the two doublets at 4.19 ($J_{PH} = 15.0$ Hz) and 4.54 ppm ($J_{PH} = 15.0$ Hz) are attributed to the protons at positions $H^1$ and $H^{1'}$ (Figure 8.6) as these will be the most deshielded due to the tin centre and the phenyl rings. Selective $^{31}$P decoupling at 36.9 and 40.5 ppm (Figure 8.7) allows assignment of $H^1$ and $H^{1'}$ as the peak changes from a doublet to a singlet on decoupling. Therefore, $H^1$ is assigned to the phosphorus centre labelled $P^2$ and $H^{1'}$ to $P^{2'}$.
2. Moving upfield in the $^1$H NMR spectrum, the two doublets of septets and the multiplet at 2.10 ppm are attributed to the four methine protons within the isopropyl substituents, the multiplet containing two protons. Again, by selectively decoupling at phosphorus, the isopropyl protons can be assigned to an individual phosphorus centre (Figure 8.8). By selectively decoupling at 36.9 ppm the doublet of septets at 2.26 ppm
and the left hand side of the multiplet resolves into a septet and therefore, the protons at positions $H^3$ and $H^6$ are associated with the phosphorus resonating at 36.9 ppm ($P^2$). By selectively decoupling at 40.5 ppm the doublet of septets at 2.87 ppm and the right hand side of the multiplet resolves into a septet and therefore the protons at positions $H^{3'}$ and $H^{6'}$ are associated with the phosphorus resonance at 40.5 ppm ($P^{2'}$).

Figure 8.8: $^1$H NMR spectra of compound 86 ($CH$Pr$_2$ region) in CDCl$_3$ with selective $^{31}$P decoupling.

3. Moving further upfield in the $^1$H NMR spectrum the four doublets of doublets (0.76, 0.87, 1.18 and 1.39 ppm) and the multiplet (1.25 ppm) are attributed to the eight different methyl groups within the isopropyl substituents; the $^1$H NMR spectra with selective $^{31}$P decoupling can be seen in Figure 8.9. With selective $^{31}$P decoupling at 40.5 ppm the methyl groups at positions $Me^4$, $Me^5$, $Me^7$ and $Me^8$ resolve into single doublets and therefore, are associated with the phosphorus resonating at 40.5 ppm ($P^{2''}$) whilst the methyl groups at positions $Me^4$, $Me^5$, $Me^7$ and $Me^8$ are associated with the phosphorus at 36.9 ppm ($P^2$). The peak at 0.86 ppm is attributed to the methyl group directly bonded to the Sn centre (position $Me^{10}$).
Figure 8.9: $^1$H NMR spectra of compound 86 (methyl region) in CDCl$_3$ with selective $^{31}$P decoupling.

4. Finally, a $^1$H{$^{31}$P} COSY NMR spectrum was used to confirm the assignment of the protons and methyl groups within the isopropyl substituents.

To assign the $^{13}$C peaks, the following steps were carried out:

1. An HSQC (Heteronuclear Single-Quantum Correlation) experiment was carried out in order to identify which protons were associated with which carbon atoms, as well as selective $^{31}$P decoupling to identify which carbon atoms are associated with which phosphorus centre. The correlation between the protons and carbon atoms aided in the labelling of the overall structure seen in Figure 8.6 and a summary of $^{13}$C{$^1$H} NMR signals can be seen in Table 8.2 below.

2. At room temperature, the $^{13}$C{$^1$H} NMR spectrum showed very broad peaks in the aromatic region, therefore, VT (variable temperature) NMR spectroscopy (Figure 8.10) was needed, along with more NMR experiments (explained below) to assign the carbon atoms within the phenyl rings.
<table>
<thead>
<tr>
<th>Atom Label</th>
<th>$^1$H{$^{11}$B} NMR/ppm</th>
<th>$^{13}$C{$^1$H} NMR/ppm/298 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.54 ($J_{PH} = 15.0$ Hz, $J_{SnH} = 55.0$ Hz)</td>
<td>34.79 ($J_{PC} = 13.8$ Hz)</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>2.26</td>
<td>21.46 ($J_{PC} = 33.96$ Hz)</td>
</tr>
<tr>
<td>4</td>
<td>1.25</td>
<td>19.51 ($J_{PC} = 2.52$ Hz)</td>
</tr>
<tr>
<td>5</td>
<td>0.87 ($J_{HH} = 10.0$ Hz, $J_{PH} = 15.0$ Hz)</td>
<td>17.19 ($J_{PC} = 3.77$ Hz)</td>
</tr>
<tr>
<td>6</td>
<td>2.10</td>
<td>22.00 ($J_{PC} = 31.45$ Hz)</td>
</tr>
<tr>
<td>7</td>
<td>1.25</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1.25</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.56 ($J_{PH} = 15.0$ Hz)</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>0.86</td>
<td>5.56 ($J_{P2C} = 1.80$ Hz, $J_{P2'C} = 2.38$ Hz)</td>
</tr>
<tr>
<td>1’</td>
<td>4.19 ($J_{PH} = 15.0$ Hz, $J_{SnH} = 130.0$ Hz)</td>
<td>35.68 ($J_{PC} = 17.6$ Hz)</td>
</tr>
<tr>
<td>2’</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3’</td>
<td>2.87</td>
<td>21.24 ($J_{PC} = 2.52$ Hz)</td>
</tr>
<tr>
<td>4’</td>
<td>1.25</td>
<td></td>
</tr>
<tr>
<td>5’</td>
<td>0.76 ($J_{HH} = 10.0$ Hz, $J_{PH} = 15.0$ Hz)</td>
<td>17.14 ($J_{PC} = 5.03$ Hz)</td>
</tr>
<tr>
<td>6’</td>
<td>2.10</td>
<td>21.00</td>
</tr>
<tr>
<td>7’</td>
<td>1.39 ($J_{HH} = 10.0$ Hz, $J_{PH} = 15.0$ Hz)</td>
<td>17.53</td>
</tr>
<tr>
<td>8’</td>
<td>1.18 ($J_{HH} = 10.0$ Hz, $J_{PH} = 15.0$ Hz)</td>
<td>18.24 ($J_{PC} = 2.52$ Hz)</td>
</tr>
<tr>
<td>9’</td>
<td>0.75 ($J_{PH} = 10.0$ Hz)</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table 8.2:** Summary of $^1$H and $^{13}$C{$^1$H} signals of compound **86**.

3. The $^{13}$C{$^1$H} NMR spectrum at 223 K shows two doublets at 135.90 ($J_{PC} = 8.80$ Hz) and 136.31 ppm ($J_{PC} = 8.80$ Hz) which are affiliated with the *ipso* carbons. The
carbons at the *para* position within the phenyl ring are associated with the signals at 126.75 ($J_{PC} = 1.26$ Hz) and 126.90 ppm ($J_{PC} = 2.52$ Hz) (Figure 8.10).

![Figure 8.10: Variable temperature $^{13}$C-$^1$H NMR spectra of compound 86 in CDCl$_3$ showing the phenyl region.](image)

4. To start assigning the phenyl region, a $^{13}$C-$^1$H EXSY (Exchange Spectroscopy) NMR experiment was used to indicate which carbon atoms are exchanging within the same aromatic ring (Figure 8.11). The four peaks labelled (*) at 129.5, 130.5, 130.6 and 131.23 ppm are due to the *meta* carbon atoms and the three peaks labelled (+) at 128.6, 129.0 and 129.3 ppm are due to the *ortho* carbon atoms.
Figure 8.11: $^{13}$C{${}^1$H} EXSY NMR spectrum of 86 in CDCl$_3$ at 223 K indicating the ortho (*) and meta (+) protons in the phenyl region.

5. By looking at the HSQC spectrum the assignment of the ortho and meta carbon atoms can be used to assign the majority of the ortho and meta protons (Figure 8.12). The meta carbons at 130.5, 130.6 and 129.5 ppm correlate with the protons at 7.06 ($J_{PH} = 10.00$ Hz), 7.16 ($J_{PH} = 5.00$ Hz) and 7.51 ppm ($J_{PH} = 5.00$ Hz), respectively. Unfortunately, the multiplet at 7.31 ppm in the HSQC spectrum was unhelpful in determining the remainder of the ortho and meta protons. A summary of the $^1$H and $^{13}$C{${}^1$H} NMR signals are presented in Table 8.2.
The $^{13}$C{¹H} NMR spectrum at 296 K indicates dynamic behaviour in the *ortho* and *meta* carbon atoms which is identified by the broad nature of the signals between 128.5 and 131.5 ppm, and which may be attributed to restricted rotation of the phenyl rings about the P-C bond. It is of interest to investigate the *ortho* and *meta* carbon atoms in order to identify whether the rotation of the two aromatic rings exhibit different rotational energy barriers; this may be achieved by the use of the Eyring equation (Equation 8.1).

**Figure 8.12**: $^{1}$H-$^{13}$C HSQC NMR spectrum of 86 in CDCl₃ indicating the correlation between *ortho* protons and carbons, and *meta* protons and carbons.
\[ k = x \frac{k_B T}{h} e^{\frac{-\Delta G}{RT}} \]

\( k_B \) = Boltzmann constant (1.3805 x 10^{-23} JK^{-1})

\( x \) = transmission coefficient (assumed to be 1)

\( h \) = Planck’s constant (6.6256 x 10^{-34} Js)

**Equation 8.1:** Eyring equation.

Equation 8.2 represents the correlation between the free enthalpy of activation (\( \Delta G^\ddagger \)), enthalpy of activation (\( \Delta H^\ddagger \)) and the entropy of activation (\( \Delta S^\ddagger \)).

\[ \Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger \]

**Equation 8.2:** Correlation between \( \Delta G^\ddagger \), \( \Delta H^\ddagger \) and \( \Delta S^\ddagger \).

Substituting equation 8.2 into equation 8.1 and rearrangement results in equation 8.3, with \( (\ln k/T) \) as the subject.

\[ ln \frac{k}{T} = ln \frac{k_B}{h} - \frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R} \]

**Equation 8.3:** Result of substituting equation 2 into equation 3.

The experimental \(^{13}\text{C}\{^1\text{H}\} \) NMR data at 223, 243, 253, 316 and 330 K (Figure 8.13) were used to help simulate the \(^{13}\text{C}\{^1\text{H}\} \) NMR spectra (Figure 8.14) at these temperatures, in order to gain the rate constants associated with the exchange of the ortho carbon atoms in each aromatic ring. Using Figure 8.14 and the corresponding experimental \(^{13}\text{C}\{^1\text{H}\} \) NMR spectra (Figure 8.13), both the simulated and experimental \(^{13}\text{C}\{^1\text{H}\} \) NMR spectra are similar and therefore, the rate constants extracted from the simulated \(^{13}\text{C}\{^1\text{H}\} \) NMR spectra can be used to carry out an Eyring plot that gives a straight line in each case (Figure 8.15). The gradient and the intercept of the graphs in Figure 8.15 can be calculated to produce the rotational energy barriers (Ring 1, \( \Delta H^\ddagger = 53.2 \) kJ mol\(^{-1}\); Ring 2, \( \Delta H^\ddagger = 48.7 \) kJ mol\(^{-1}\)) and the entropy (Ring 1, \( \Delta S^\ddagger = -9.50 \) J mol\(^{-1}\) K\(^{-1}\); Ring 2, \( \Delta S^\ddagger = -19.0 \) J mol\(^{-1}\) K\(^{-1}\)), respectively (Table
of $T$ vs $k$ can be seen in Appendix 2). This clearly shows that the barrier to rotation is different for the two phenyl rings in 86, in spite of their rather similar chemical environments.

**Figure 8.13:** Experimental $^{13}$C($^1$H) NMR spectra of 86 in CDCl$_3$. 
Figure 8.14: Simulated $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of 86 using gNMR.
**Figure 8.15:** Eyring plots of ring 1 (top) and 2 (bottom) in compound 86.
The $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of compound 87 exhibits three triplets at -22.8 ($J_{\text{SnP}} = 28.0$ Hz), -5.6 ($J_{\text{SnP}} = 86.7$ Hz) and -4.3 ppm ($J_{\text{SnP}} = 85.8$ Hz) where the triplet at -4.3 ppm is the major peak with similar structure to compound 86, along with a low intensity doublet of doublets at 1.18 ppm ($J_{\text{SnP}} = 126.8$ Hz, $J_{\text{SnP}'} = 13.1$ Hz) which is due to an impurity. The meso component of the starting material 64 may form two stereoisomers when reacted with benzyl bromide (Figure 8.16); these stereoisomers are assigned to the two minor triplet peaks (-22.8 and -5.6 ppm) in the $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of 87.

![Diagram](image_url)

**meso-87**

**Figure 8.16:** Stereoisomers of meso 87.

To summarise, due to the disorder (along the Me-Sn-I bonds) within the X-ray crystal structure, the solid state analysis shows that compound 86 possess rotational symmetry and therefore, ring 1 and 2 would be identical. However, it is clear in the extensive NMR investigation carried out within this chapter that compound 86 is not symmetrical and so results in two distinct phenyl rings, along with two different phosphorus centres, one on each of the phosphine-borane-stabilised carbanion ligand. This prevents absolute assignment of the NMR data; however, it is clear that the barrier to rotation of the two rings are different.
8.3 Oxidation addition reactions using compound 64

Scheme 8.2: Reactions of compound 64 with neopentyl iodide, nitrous oxide, trifluoroiodomethane and phenylacetylene.

Treatment of a solution of compound 64 in toluene with one equivalent of phenylacetylene yielded free phosphine-borane after stirring for 16 hrs (Scheme 8.2). The formation of free phosphine-borane may be attributed to the slightly acidic proton on the phenylacetylene protonating the dialkylstannylene; the progression of protonolysis can be seen in the $^{31}$P{$^1$H} NMR spectrum (Figure 8.17). Treatment of a solution of compound 64 in diethyl ether with one equivalent of CF$_3$I yielded an insoluble (in THF, diethyl ether, toluene and DCM) colourless solid and so no NMR data could be obtained.

Treatment of a solution of compound 64 in diethyl ether with an excess of neopentyl iodide yielded elemental tin and free phosphine-borane after stirring for 16 hrs (Scheme 8.2). This may be attributed to compound 64 being too sterically bulky around the Sn centre and so the neopentyl iodide could not oxidise the dialkylstannylene. Over time the reaction mixture
was being exposed to more light and so compound 64 reduces down to elemental tin and free phosphine-borane; this is consistent with organotin complexes of this type being both light and thermally sensitive.

![Figure 8.17](image)

**Figure 8.17:** $^{31}$P{$^1$H} NMR spectra of compound 64 in Et$_2$O with one equivalent of phenylacetylene. Compound 64 before addition of phenylacetylene (Top), after 30 mins (Middle) and after 16 hrs (Bottom).

Treatment of a solution of compound 64 in Et$_2$O with an excess of nitrous oxide yielded two phosphorus-containing species as seen in the $^{31}$P{$^1$H} NMR spectrum of the crude reaction mixture (27.5 and 31.1 ppm) (Figure 8.18). It is possible that the peak at 27.5 ppm is due to 64 and so the peak at 31.1 ppm may be attributed to the oxidative addition of compound 64. This reaction was left for 16 hrs and still showed two species in the $^{31}$P{$^1$H} NMR spectrum with different intensities which indicates that the reaction had not gone to completion.
Figure 8.18: $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of: i) Compound 64 with excess N$_2$O after 30 minutes.
   ii) Compound 64 with excess N$_2$O after 16 hrs.

If the relative intensities of the peaks in the $^{31}\text{P}\{^1\text{H}\}$ NMR were equal, then a ‘puckered’ species could have been postulated (Figure 8.19).

$$\text{R} = \text{Cy}_2\text{P(BH}_3\text{)}\text{CHPh}$$

Figure 8.19: ‘Puckered’ structure of a potential product between compound 64 and nitrous oxide.
8.4 Conclusion

Compound 86 was isolated as single colourless crystals and consists of a discrete monomer where the Sn centre has two contacts with two phosphine-borane fragments via a carbanion centre, a contact between the Sn centre and a methyl group, and a contact between the Sn centre and iodine. This distorted tetrahedral geometry loses rotational symmetry as well as agostic-type interactions upon oxidative addition; this loss of rotational symmetry can be seen in a detailed multi-element NMR spectroscopy investigation. As well as BnBr and MeI, other organic reagents were investigated, however, crude $^{31}$P{$^{1}$H} NMR spectra suggest that these reactions give either free phosphine-borane or other unidentified species. Variable temperature $^{13}$C{$^{1}$H} NMR spectra indicated dynamic behaviour of the aromatic rings in compound 86. The experimental $^{13}$C{$^{1}$H} NMR spectra were simulated using gNMR in order to calculate the rate constant, k, for the phenyl exchange process from line-shape analysis at various temperatures. Eyring plots were used to calculate the enthalpy of activation of the phenyl rings (Ring 1, 53.2 kJ mol$^{-1}$; Ring 2, 48.7 kJ mol$^{-1}$) which revealed that ring 2 is rotating at a faster rate than ring 1, despite their chemical equivalency.
8.5 References

Chapter 9. Conclusions

The work presented in this thesis has looked into an array of structurally different phosphine-boranes and their effect on the stabilities and structures of their main group derivatives. The specific ligand modifications considered include:

- the use of a rigid aromatic ring or a flexible backbone; with particular focus on the B-H···M agostic-type interactions;
- replacing a SiMe₃ group with a phenyl ring and the effect this has on the structure and reactivity.

9.1 Effects on the structures and stabilities on group 1 and 14 phosphine-borane-stabilised carbanions with either a rigid aromatic or flexible backbone.

Solid state characterisation of the linear bis(phosphine-boranes) [Li(THF)₂][Ph₂P(BH₃)CHSi(Me₂)CH₂]₂ (40a), [K(pmdeta)₂][CH₂SiMe₂CHP(BH₃)Ph₂]₂ (40b) shows key differences compared to the rigid o-phenylene-bridged systems [1,2-C₆H₄{CHP(BH₃)R}₂][Li(tmeda)]₂·nL (R = 'Pr, n = 0 (44a); R = Ph, nL = THF (45a); R = Cy, nL = 2PhCH₃ (46a)) and [K(pmdeta)₂][1,2-C₆H₄{CHPCy₂(BH₃)}₂] (46b).

Compounds 40a and 40b crystallise with pyramidal carbanions where 40b exhibits an unusual cyclic structure with a (K-H-B-H)₂ cycle.¹ Compounds 44a-46a and 46b crystallise with planar carbanion centres due to delocalisation of charge into both the aromatic backbone and P-C σ*-orbitals.¹ These overall differences between compounds 40a and 40b, and 44a-46a and 46b may be attributed to the difference in the backbone linkers. It is well known that potassium complexes favour coordination by π-electrons in order to complete their coordination sphere; this is seen for compound 46b and other phosphine-borane-stabilised carbanions, such as 49a and 49b (Figure 9.1 and 9.2).¹
Figure 9.1: Molecular structure of 49a with H atoms (except for those bound to boron) omitted for clarity.

Figure 9.3: Asymmetric unit of 49b with H atoms (except for those bound to boron) omitted for clarity.
However, compound 40b does not exhibit interactions between the potassium cation and any aromatic groups, instead, compound 40b adopts an unusual bent cyclic structure with two agostic-type interactions with one BH$_3$ unit at each end of the ligand, a feature that may not have been possible without a flexible linker (Figure 9.4).

**Figure 9.4:** Structures on compounds 40b and 46b.

Until recently, all phosphine-borane-substituted dialkylstannylenes contained a supporting ligand which is either monodentate or has a flexible spacer linking the two carbanion centres (Scheme 9.1). The flexible spacer allows the supporting ligand to tilt towards the electron deficient Sn centre, which maximises the overlap between the B-H $\sigma$-orbital and the vacant p-orbital on Sn (Figure 9.5); this provides sufficient stabilisation against oligomerisation of the phosphine-borane-stabilised carbanion.

**Figure 9.5:** Compound 32 and orbital overlap between the B-H unit and the vacant p-orbital of Sn.
Scheme 9.1: Dialkylstannlenes with monodentate or flexible spacer supporting ligands.

Investigations into phosphine-boranes with a rigid linker show there is a limit to which the BH$_3$ group can position itself near the Sn centre and that this affects the overall structure of the dialkylstannylene 58 (Figure 9.6) yielding an unusual stannyl-stannylene $[[1,2$-$C_6H_4(CHP(BH_3)Cy_2)]Sn]_2-3/2PhMe$.\(^6\)

![Diagram of 58](image)

Figure 9.6: Schematic drawing of solid state structure of 58.

Compound 58 still possesses a B-H···Sn agostic-type interaction, however due to the rigidity of the supporting ligands, compound 58 also exhibits a formal Sn-Sn bond with a chelating and bridging mode of two separate phosphine-borane fragments; a very different structure compared to compounds 32-35.\(^6\)
9.2 Replacement of a SiMe$_3$ group and its impact on the stability and structure of dialkylstannylenes.

Compounds 32-35 are stabilised by both steric bulk and agostic-type interactions. Izod and co-workers found that compound 35 is still monomeric in the solid state and that the agostic-type interactions were stabilising enough to prevent dimerisation. The dialkylstannylenes Sn[C$_6$H$_5$CHP$_2$(BH$_3$)]$_2$ [R = 'Pr (64) and Cy (65)] were synthesised in order to investigate whether agostic-type interactions alone were sufficiently stabilising against dimerisation. The $^{31}$P{$^1$H} NMR spectra of compounds 64 and 65 indicate the presence of rac and meso diastereomers, however, only the rac diastereomer was isolated (Figure 9.7).

![Figure 9.7: The proposed rac and meso diastereomers of compounds 64 and 65.](image)

Compounds 34 and 35 showed no evidence to suggest the formation of rac and meso diastereomers and so only the rac isomer was isolated and characterised.$^4$ This is not the case for compounds 64 and 65, which may be attributed to the removal of the SiMe$_3$ group. This difference in structural preference may be attributed to the intermediates RSnCl [R = (Me$_3$SiCHPMe$_2$(BH$_3$) (66), C$_6$H$_5$CHP$_2$(BH$_3$) (67) or C$_6$H$_5$CHPCy$_2$(BH$_3$) (68)] where 66 is the most sterically hindered. It is the bulkiness of the intermediate which has the biggest influence upon the addition of the second supporting ligand, resulting in only the rac diastereomer for 34, but a mixture of rac and meso diastereomers for compound 64 and 65. Furthermore, compounds 64 and 65 are monomeric in the solid state and so B-H agostic-type interactions sufficiently stabilise phosphine-borane-substituted dialkylstannylene of this type against dimerisation.
9.3 Difficulties in the isolation of heteroleptic alkylstannylenes

The synthesis of heteroleptic alkylstannylenes \([(\text{PhCH}_2)\text{PR}_2(\text{BH}_3)]\text{SnX}\) \((X = \text{-CH(SiMe}_3)_2, \text{-Dipp, -N(SiMe}_3)_2, \text{-O}\{2,6\text{-}^{\text{Bu}}\text{-4-MeC}_6\text{H}_2\}, \text{-PTripp}_2, \text{-PDipp}_2, \text{-CH}_3, \text{-C}_6\text{H}_5; R = ^\text{Pr and Cy})\) via the chlorostannylenes \(\text{SnCl}[C_6\text{H}_5\text{CHPR}(\text{BH}_3)] \) \([R = ^\text{Pr} (69) \text{ or Cy (70)})\] is of interest, in order to measure the extent at which the agostic-type interactions may be effected with either carbon-, nitrogen-, oxygen- or phosphorus-containing ligands. It is predicted that the more π-donating ligand will weaken the B-H···Sn agostic-type interactions (Chart 9.1).

![Chart 9.1: Heteroatoms from the least to the most π-donating.](image)

However, the use of bulky ligands yielded extremely soluble products which could not be isolated but the data obtained suggest that the use of smaller ligands should enable the isolation of heteroleptic alkylstannylenes.
9.4 Dynamic behaviour of the oxidative addition product $[\text{C}_6\text{H}_5\text{CHP}^i\text{Pr}_2(\text{BH}_3)]_2\text{Sn}(\text{Me})\text{I}$ (86)

To date, very few examples of phosphine-borane-substituted Sn(IV) compounds have been isolated.\(^7\) This thesis reports the two new oxidative addition products $[\text{C}_6\text{H}_5\text{CHP}^i\text{Pr}_2(\text{BH}_3)]_2\text{Sn}(\text{Me})\text{I}$ (86) and $[\text{C}_6\text{H}_5\text{CHP}^i\text{Pr}_2(\text{BH}_3)]_2\text{Sn}(\text{Bn})\text{Br}$ (87), where compound 86 yielded single crystals suitable for X-ray crystallography (Figure 9.8).

![Molecular structure of 86](image)

**Figure 9.8:** Molecular structure of 86 with H atoms (except for those bound to boron) omitted for clarity.

The $^{13}\text{C}{^{1}\text{H}}$ NMR spectrum of 86 at 296 K indicated dynamic behaviour in the phenyl region which was attributed to restricted rotation of the phenyl rings about the P-C bond. Eyring plots were used in order to measure the rotational energy barriers of both the phenyl rings in order to investigate whether they were rotating at different rates. The rotational energy barriers calculated (Ring 1, $\Delta H^\ddagger = 53.2$ kJ mol$^{-1}$; Ring 2, $\Delta H^\ddagger = 48.7$ kJ mol$^{-1}$) indicate that, despite their similar chemical environments, ring 1 and 2 show different barriers to rotation.
9.5 Possible future work

The work presented in this thesis has plenty of scope for future development. To date, there are only examples of acyclic phosphine-borane-substituted Sn(IV) compounds. It would be of great interest to develop the linear bis(phosphine-boranes) \([\text{Me}_2\text{P(BH}_3\text{)CH}_2\text{SiMe}_2\text{CH}_2]_2\) (37) and \([\text{Ph}_2\text{P(BH}_3\text{)CH}_2\text{SiMe}_2\text{CH}_2]_2\) (40) to synthesise and characterise the corresponding stannylene followed by their oxidative addition products. The structures of compounds 37 and 40 would be compared to the more bulky stannylene \([\text{CH}_2\text{SiMe}_2\text{C(SiMe}_3\text{)PMe}_2\text{BH}_3]_2\text{Sn}\) (33) to determine any differences in their solid state structures and reactivity.

Little work has been carried out in the Izod group on phosphine-borane incorporated rhodium complexes and so far, none have been reported. Phosphine-borane-substituted dialkylstannylenes would be ideal ligands to investigate how rac and meso of these compounds changes the structure and reactivity of the corresponding rhodium complex.

Further investigations into small ligands for heteroleptic alkylstannylenes will be of interest in order to investigate how heteroatoms may affect the extent of agostic-type interactions.

The isolation of 58 is really the start of how rigid linkers may affect the structural outcome and so the agostic-type interactions of the corresponding stannylenes. Further work into this field would be beneficial and critical to gain a greater understanding into the effects of rigid versus flexible linkers. Chapter 5 discusses the reaction of \(\text{Cp}_2\text{Sn}\) with \textit{in situ}-generated \([1,2-\text{C}_6\text{H}_4\{\text{CHP(BH}_3\text{)R}_2\}]_2[\text{Li(THF)}_n]_2\) (R = ‘Pr, Ph or Cy) where compound 58 was isolated as an unusual stannyl-stannylene complex. In order to increase our understanding of how a rigid linker will affect the structural outcome and its reactivity of phosphine-borane-substituted dialkylstannylenes, the formation and the study of the ‘Pr and Ph analogues of 58 will be of significant interest.
9.6 References

Chapter 10. Experimental

10.1 General procedures

All manipulations were carried out using standard Schlenk techniques under an atmosphere of nitrogen/argon or in a nitrogen filled dry-box. Diethyl ether (Et₂O), THF, toluene, methylcyclohexane (MCH), benzene and petroleum ether (b.p. 40-60 °C) were pre-dried over sodium wire and distilled under nitrogen from sodium, potassium or sodium/potassium alloy. Dichloromethane (DCM) was distilled under nitrogen from CaH₂ (calcium hydride). THF and DCM were stored over activated 4Å molecular sieves; all other solvents were stored over a potassium mirror. Deuterated chloroform was distilled from CaH₂, and deuterated THF, toluene and benzene were distilled from potassium; all NMR solvents were deoxygenated by three freeze-pump-thaw cycles and were stored over activated 4Å molecular sieves.

Organolithiums were obtained from Aldrich and used as supplied; n-butyllithium was obtained as a 2.5 M solution in hexanes and t-butyllithium was obtained as a 1.6 M solution in pentane. The adduct BH₃-SMe₂ was obtained as a 2.0 M solution in THF. Compounds PhMgCl, Me₃Al and HNMe₂ were obtained as 2.0 M solutions in THF, DiBAIH as a 1.0 M solution in THF and MeMgBr and MeMgCl as 3.0 M solutions in THF. KO'Bu (potassium t-butoxide), NaBPh₄ PbCl₂ and PbI₂ were heated under vacuum at 100 °C (0.01 mmHg) for 1 h prior to use. SnCl₂ and ZnCl₂ were dried using trimethylsilylchloride and then impurities removed under vacuum at room temperature (0.01 mmHg). All other compounds were used as supplied by the manufacturer with the exception of tmeda and pmdeta which were freshly distilled from CaH₂, and 12-crown-4 which was dried over activated 4 Å molecular sieves.

The compounds Me₃P-BH₃,¹ 1,2-C₆H₄{CH₂PPh₂(BH₃)},² 1,2-C₆H₄{CH₂PPr₂(BH₃)},² [1,2-C₆H₄{CHPPr₂(BH₃)}₂][Li(tmeda)],² [1,2-C₆H₄{CHPPPh₂(BH₃)}₂][Li(tmeda)]:THF,² BnK,³ ⁴ MeK,⁵⁻⁷ SnCp₂,⁸ PbCp₂,⁹ Pr₂PH(BH₃),¹⁰ Ph₂PH(BH₃),¹¹ Cy₂PH(BH₃),¹² Ph₂MeP(BH₃)¹¹ and Bn₂M (M = Ca, Sr, Ba)¹³ were prepared by previously published procedures.
10.2 NMR Spectroscopy and elemental analyses

$^1\text{H}$, $^{13}\text{C}$, $^7\text{Li}$, $^{11}\text{B}$, $^{31}\text{P}$ and $^{119}\text{Sn}$ NMR spectra were recorded on a JEOL ECS 500 (operating at 500.16, 125.65, 194.25, 160.35, 202.35, and 186.51 MHz, respectively), JEOL ECS 400 (operating at 128.27, 161.83, 399.78 100.53, and 149.08 MHz), respectively or Bruker Avance I/III 300 NMR spectrometers (operating at 111.92, 300.13, 121.49, 96.29 and 75.48 MHz, respectively). $^1\text{H}$ and $^{13}\text{C}$ chemical shifts are quoted in ppm relative to tetramethylsilane; $^7\text{Li}$, $^{11}\text{B}$ and $^{31}\text{P}$ chemical shifts are quoted in ppm relative to aqueous LiCl (1M), BF$_3$(OEt)$_2$ and 85% H$_3$PO$_4$, respectively; $^{119}\text{Sn}$ chemical shifts are quoted in ppm relative to tetramethyltin. Elemental analyses were obtained from the Elemental Analysis Service of London Metropolitan University.

10.3 Crystal structure determinations

Measurements for 37, 40a, 40b, 44, 44a, 45a, 46a, 46b, 48, 49a, 49b, 58, 64, 65 and 86 were made at 150K on an Oxford Diffraction Gemini A Ultra diffractometer. For all compounds cell parameters were refined from the observed positions of all strong reflections in each data set. Intensities were corrected semiemperically for absorption, based on a symmetry-equivalent and repeated reflections. The structures were solved by direct methods and were refined on F$^2$ values for all unique data. All non-H 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. Programs were AXS SMART and APEX2 (control) and SAINT (integration), Nonius COLLECT and associated programs, and SHELXTL for structure solution, refinement, and molecular graphics. Details of structure determination, atomic coordinates, and bond lengths and angles can be found in CIF format in the enclosed CD.

10.4 DFT calculations

Geometry optimisations on the gas-phase molecules were performed with the Gaussian09 suite of programs (revision D.01). Ground state optimisations were performed using the hybrid B3LYP functional$^{14-16}$ the 6-31G(2d,p) all-electron basis set$^{17,18}$ was used for all C, H, B and P atoms, while LanL2DZ effective core potential basis set was used for Sn
[default parameters were used throughout]. The identity of minima was confirmed by the absence of imaginary vibrational frequencies in each case. The stabilisation energy associated with the B-H···Sn interactions was calculated using the NBODel routine, in which the elements affording this interaction were selectively deleted.\textsuperscript{19} Natural Bond Orbital analyses were performed using the NBO 3.1 module of Gaussian09.\textsuperscript{20-25}

10.5 Preparative methods

\textbf{[Me\textsubscript{2}P(BH\textsubscript{3})CH\textsubscript{2}Si(Me\textsubscript{2})CH\textsubscript{2}]\textsubscript{2} (37):} To a solution of Me\textsubscript{3}P-BH\textsubscript{3} (6.31 g, 70.17 mmol) in THF (30 ml) was added \textsuperscript{6}BuLi (28.07 ml of a 2.5 M solution in hexanes, 70.17 mmol) and the mixture was left to stir for 1 h at room temperature. This solution was added, dropwise, to a solution of 1,2–bis(chlorodimethylsilyl)ethane (7.55 g, 35.09 mmol) in THF (30 ml) and this solution was left to stir for 1 h at room temperature. To this mixture was added water (30 ml) and the organic phase was extracted into dichloromethane (3 x 30 ml). The combined organic extracts were dried over MgSO\textsubscript{4}, filtered and the solvent was removed \textit{in vacuo} from the filtrate to give a colourless solid. The crude product was crystallised from hot methycyclohexane (15 ml) to give a colourless crystalline solid. Isolated yield: 6.97 g, 60%. \textsuperscript{1}H\{\textsuperscript{11}B\} NMR (500.16 MHz, CDCl\textsubscript{3}, 25 °C): \(\delta\) 0.13 (s, 12H, SiMe\textsubscript{2}), 0.50 (br.s, 6H, BH\textsubscript{3}), 0.51 (br.s, 4H, PCH\textsubscript{2}), 0.90 (d, \(J_{PH} = 15.1\) Hz, 4H, CH\textsubscript{2}CH\textsubscript{2}), 1.29 (d, \(J_{PH} = 10.1\) Hz, 12H, PMe\textsubscript{2}). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (125.77 MHz, CDCl\textsubscript{3}, 25 °C): \(\delta\) -1.54 (SiMe\textsubscript{2}), 8.96 (CH\textsubscript{2}CH\textsubscript{2}), 13.45 (d, \(J_{PC} = 24.0\) Hz, PCH\textsubscript{2}), 15.55 (d, \(J_{PC} = 38.3\) Hz, PMe\textsubscript{2}). \textsuperscript{11}B\{\textsuperscript{1}H\} NMR (160.47 MHz, CDCl\textsubscript{3}, 25 °C): \(\delta\) 37.5 (d, \(J_{PB} = 58.8\) Hz). \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (202.47 MHz, CDCl\textsubscript{3}, 25 °C): \(\delta\) 3.4 (q, \(J_{PB} = 58.8\) Hz).

\textbf{[Ph\textsubscript{2}P(BH\textsubscript{3})CH\textsubscript{2}Si(Me\textsubscript{2})CH\textsubscript{2}]\textsubscript{2} (40):} To a cold (0 °C) solution of Ph\textsubscript{2}PMe-BH\textsubscript{3} (4.76 g, 22.18 mmol) in THF (40 ml) was added \textsuperscript{6}BuLi (8.89 ml of a 2.5 M solution in hexanes, 22.18 mmol) and this mixture was left to stir for 1 h at room temperature, resulting in a dark orange solution. This was added, dropwise, to a solution of 1,2–bis(chlorodimethylsilyl)ethane (2.39 g, 11.09 mmol) in THF (30 ml) and this mixture was left to stir for 1 h at room temperature resulting in a yellow mixture. To this mixture was added water (40 ml) and the organic phase was extracted into dichloromethane (3 x 30 ml). The combined organic extracts were dried over MgSO\textsubscript{4}, filtered and the solvent was removed \textit{in vacuo} from the filtrate to give a colourless solid. The crude product was crystallised from hot methycyclohexane/THF
To a solution of \(^{1}P_{2}PH(BH_{3})\) (1.61 g, 12.39 mmol) in THF (20 ml) was added \(^{4}BuLi\) (4.96 ml of a 2.5M solution in hexanes, 12.39 mmol) and this mixture was left to stir for 1 h at room temperature. This solution was added, dropwise, to a solution of \(\alpha,\alpha'\)-dichloro-\(o\)-xylene (1.05 g, 6.19 mmol) in THF (20 ml) and this mixture was left to stir for 16 h at room temperature. To this mixture was added water (30 ml) and the organic phase was extracted into dichloromethane (3 x 20 ml). The combined organic extracts were dried over MgSO\(_4\), filtered and the solvent was removed \textit{in vacuo} from the filtrate to give a colourless crystalline solid. Isolated yield: 1.45 g, 67%. \(^{1}H\{^{11}B\}\) NMR (500.16 MHz, CDCl\(_3\), 25 °C): \(\delta\) -0.11 (s, 12H, SiMe\(_2\)), 0.30 (d, \(J_{PH} = 5.00\ \text{Hz}, 4H, \text{PCH}_2\)), 1.04 (d, \(J_{PB} = 20.0\ \text{Hz}, 6H, BH_3\)), 1.52 (d, \(J_{PH} = 15.0\ \text{Hz}, 4H, \text{CH}_2\text{CH}_2\)), 7.39-7.44 (m, 5H, PPh\(_2\)), 7.67-7.70 (m, 5H, PPh\(_2\)). \(^{13}C\{^{1}H\}\) NMR (100.53 MHz, CDCl\(_3\), 25 °C): \(\delta\) -2.16 (SiMe\(_2\)), 8.48 (CH\(_2\)CH\(_2\)), 10.97 (d, \(J_{PC} = 25.1\ \text{Hz}, \text{PCH}_2\)), 128.69 (d, \(J_{PC} = 10.1\ \text{Hz}, \text{Ar}\)), 130.89 (d, \(J_{PC} = 2.01\ \text{Hz}, \text{Ar}\)), 131.83 (d, \(J_{PC} = 9.1\ \text{Hz}, \text{Ar}\)), 132.61 (d, \(J_{PC} = 54.3\ \text{Hz}, \text{Ar}\)). \(^{11}B\{^{1}H\}\) NMR (160.47 MHz, CDCl\(_3\), 25 °C): \(\delta\) -38.9 (br). \(^{31}P\{^{1}H\}\) NMR (202.47 MHz, CDCl\(_3\), 25 °C): \(\delta\) 13.5 (q, \(J_{PB} = 69.5\ \text{Hz}\)).

\(1,2\text{-C}_4\text{H}_4\{\text{CH}_3\text{PPh}_2(BH_3)\}_2\) (44): To a solution of \(^{1}P_{2}PH(BH_3)\) (1.61 g, 12.39 mmol) in THF (20 ml) was added \(^{4}BuLi\) (3.28 ml of a 2.5M solution in hexanes, 8.20 mmol) and this mixture was left to stir for 1 h at room temperature. This solution was added, dropwise, to a solution of \(\alpha,\alpha'\)-dichloro-\(o\)-xylene (0.68 g, 4.10 mmol) in THF (20 ml) and this mixture was left to stir for 16 h at room temperature. To this mixture was added water (20 ml) and the organic phase was extracted into dichloromethane (3 x 20 ml). The combined organic extracts were dried over MgSO\(_4\), filtered and the solvent was removed \textit{in vacuo} from the filtrate to give a
1,2-C₆H₄(CH₂PC₂(BH₃))₂ (46): To a solution of Cy₂PH (1.48 g, 7.45 mmol) in THF (20 ml) was added BH₃·SMe₂ (3.73 ml of a 2.0 M solution in THF, 7.45 mmol) and this mixture was left to stir at room temperature for 30 mins. To a solution of Cy₂PH(BH₃) (1.58 g, 7.45 mmol) in THF (20 ml) was added nBuLi (2.98 ml of a 2.5M solution in hexanes, 7.45 mmol) and this mixture was left to stir for 1 h at room temperature. This solution was added, dropwise, to a solution of α,α'-dichloro-o-xylene (0.61 g, 3.73 mmol) in THF (20 ml) and this mixture was left to stir for 16 h at room temperature. To this mixture was added water (30 ml) and the organic phase was extracted into dichloromethane (3 x 20 ml). The combined organic extracts were dried over MgSO₄, filtered and the solvent was removed in vacuo from the filtrate to give a colourless solid. Isolated yield: 1.42 g, 77%. 

C₆H₅CH₂PPr₂(BH₃) (47): To a solution of 'Pr₂PH(BH₃) (2.66 g, 20.06 mmol) in THF (30 ml) was added nBuLi (8.54 ml of a 2.35M solution in hexanes, 20.06 mmol) and this mixture was left to stir for 1 h at room temperature. This solution was added, dropwise, to a solution of benzylbromide (2.39 ml, 20.06 mmol) in THF (30 ml) and the mixture was left to stir for 16 h at room temperature. To this mixture was added water (30 ml) and the organic phase was extracted into Et₂O (3 x 20 ml). The combined organic extracts were dried over MgSO₄, filtered and the solvent was removed in vacuo from the filtrate to give a colourless oil.

Isolated yield: 3.26 g, 73%. 

colourless solid. Isolated yield: 1.61 g, 82%. 

1H{¹¹B} NMR (500.16 MHz, CDCl₃, 25 °C): δ 0.90 (d, JₚH = 15.5 Hz, 6H, BH₃), 3.54 (d, JₚH = 11.7 Hz, 4H, CH₂P), 6.51-7.62 (m, 24H, ArH). 

13C{¹H} NMR (125.77 MHz, CDCl₃, 25 °C): δ 30.9 (d, JₚC = 30.8 Hz, CH₂P), 126.7, 128.8, 128.9, 129.3, 131.4, 131.6 (Ar), 132.7 (d, JₚC = 8.6 Hz, Ar). 

11B{¹H} NMR (160.47 MHz, CDCl₃, 25 °C): δ -40.1 (br). 

31P{¹H} NMR (202.47 MHz, CDCl₃, 25 °C): δ 18.3 (br).

202.47 MHz, CDCl₃, 25 °C): δ 18.3 (br).
$^3J_{PH} = 7.1, ~^3J_{HH} = 1.8 \text{ Hz}, 6\text{H}, \text{CHMeMe}$), 1.92 (m, 2H, CHMe$_2$), 2.98 (d, $^2J_{PH} = 11.5$ Hz, 2H, CH$_2$P), 7.18-7.39 (m, 5H, ArH). $^{13}$C $^1$H NMR (125.77 MHz, CDCl$_3$, 25 °C): $\delta$ 16.99, 17.08 (CHMe$_2$), 21.7 (d, $J_{PC} = 30.4$ Hz, CHMe$_2$), 28.26 (d, $J_{PC} = 28.3$ Hz, CH$_2$P), 126.87 (d, $J_{PC} = 2.63$ Hz, Ar), 128.49 (d, $J_{PC} = 2.07$ Hz, Ar), 129.92 (d, $J_{PC} = 4.04$ Hz, Ar), 133.50 (d, $J_{PC} = 5.45$ Hz, Ar). $^{11}$B $^1$H NMR (160.47 MHz, CDCl$_3$, 25 °C): $\delta$ -43.2 (d, $J_{PB} = 59.7$ Hz). $^{31}$P $^1$H NMR (202.47 MHz, CDCl$_3$, 25 °C): $\delta$ 34.0 (q, $J_{PB} = 59.7$ Hz).

**CaH$_5$(CH$_2$PPh$_3$(BH$_3$)) (48):** To a solution of Ph$_2$PH (3.78 g, 20.30 mmol) in THF (30 ml) the adduct BH$_3$·SMe$_2$ was added (10.15 ml, 20.30 mmol) and this mixture was left to stir for 1 h at room temperature. To this mixture was added $^6$BuLi (8.64 ml of a 2.35M solution in hexanes, 20.30 mmol) and the solution was left to stir for 1 h at room temperature. This solution was added, dropwise, to a solution of benzylbromide (2.41 ml, 20.30 mmol) in THF (30 ml) and this mixture was left to stir for 16 h at room temperature. To this mixture was added water (30 ml) and the organic phase was extracted into Et$_2$O (3 x 20 ml). The combined organic extracts were dried over MgSO$_4$, filtered and the solvent was removed in vacuo from the filtrate to give a colourless sticky solid. The product was extracted into hot toluene (20 ml), filtered and solvent removed in vacuo to yield a colourless solid. Single crystals suitable for X-ray crystallography were obtained from hot toluene. Isolated yield: 3.98 g, 68%.

$^1$H $^{11}$B NMR (500.16 MHz, CDCl$_3$, 25 °C): $\delta$ 0.87 (d, $J_{PH} = 15.0$ Hz, 3H, BH$_3$), 3.15 (d, $J_{PH} = 11.8$ Hz, CH$_2$P), 6.84-7.56 (m, 15H, ArH). $^{13}$C $^1$H NMR (125.77 MHz, CDCl$_3$, 25 °C): $\delta$ 34.12 (d, $J_{PC} = 32.66$ Hz, CH$_2$P), 126.98 (d, $J_{PC} = 3.47$ Hz, Ar), 128.08 (d, $J_{PC} = 1.90$ Hz, Ar), 128.63, 128.76 (Ar), 130.29 (d, $J_{PC} = 4.11$ Hz, Ar), 131.87 (d, $J_{PC} = 4.58$ Hz, Ar), 133.22 (d, $J_{PC} = 9.48$ Hz, Ar), 141.79 (ipso-Ar). $^{11}$B $^1$H NMR (160.47 MHz, CDCl$_3$, 25 °C): $\delta$ -39.1 (d, $J_{PB} = 49.3$ Hz). $^{31}$P $^1$H NMR (202.47 MHz, CDCl$_3$, 25 °C): $\delta$ 18.0 (q, $J_{PB} = 49.3$ Hz).

**CaH$_5$(CH$_2$PCy$_2$(BH$_3$)) (49):** To a solution of Cy$_2$PH (4.20 ml, 19.16 mmol) in THF (30 ml) the adduct BH$_3$·SMe$_2$ was added (9.58 ml, 19.16 mmol) and this mixture was left to stir for 1 h at room temperature. To this mixture was added $^6$BuLi (7.67 ml of a 2.5M solution in hexanes, 19.16 mmol) and this solution was left to stir for 1 h at room temperature. This solution was added, dropwise, to a solution of benzylbromide (2.29 ml, 19.16 mmol) in THF (30 ml) and this mixture was left to stir for 16 h at room temperature. To this mixture was
added water (30 ml) and the organic phase was extracted into dichloromethane (3 x 20 ml). The combined organic extracts were dried over MgSO₄, filtered and the solvent was removed in vacuo from the filtrate to give a colourless solid. Single crystals suitable for X-ray crystallography were obtained from cold (0 °C) toluene. Isolated yield: 4.89 g, 84%. ¹H{¹¹B} NMR (500.16 MHz, CDCl₃, 25 °C): δ 0.40 (d, JPH = 15.00 Hz, 3H, BH₃), 1.19-1.84 (m, 22H, PCy₂), 3.04 (d, JPH = 15.0 Hz, 2H, CH₂P), 7.26-7.31 (m, 5H, ArH).

C₆H₅{(CH₂SiMe₃PCy₂(BH₃)} (50): To a solution of C₆H₅{(CH₂PCy₂(BH₃)} (0.51 g, 1.66 mmol) in THF (20 ml) was added °BuLi (0.66 ml of a 2.5 M solution in hexanes, 1.66 mmol) and this solution was left to stir for 30 mins at room temperature. This solution was added, dropwise, to a solution of trimethylsilylchloride (0.21 ml, 1.66 mmol) in THF (20 ml) and this mixture was left to stir for another 30 mins at room temperature. To this mixture was added water (30 ml) and the organic phase was extracted into dichloromethane (3 x 20 ml). The combined organic extracts were dried over MgSO₄, filtered and the solvent was removed in vacuo from the filtrate to give a colourless solid. Isolated yield: 0.40 g, 65%. ¹H{¹¹B} NMR (500.16 MHz, CDCl₃, 25 °C): δ 0.12 (SiMe₃), 0.65 (d, JPH = 14.2 Hz, 3H, BH₃), 1.00-2.18 (m, 22H, PCy₂), 2.72 (d, JPH = 20.0 Hz, 1H, PCHSi), 7.14-7.25 (m, 5H, ArH). ¹³C{¹H} NMR (125.77 MHz, CDCl₃, 25 °C): δ 0.39 (s, SiMe3), 26.20 (d, JPC = 1.26 Hz, Cy), 26.34 (d, JPC = 1.26 Hz, Cy), 27.41 (br.d, Cy), 27.48 (br.d, Cy), 27.65 (d, JPC = 3.77 Hz, Cy), 27.74 (d, JPC = 3.77 Hz, Cy), 28.09 (d, JPC = 5.03 Hz, Cy), 28.14 (br.d, Cy), 28.34 (d, JPC = 3.77 Hz, Cy), 28.44 (s, SiCH), 28.50 (d, JPC = 15.1 Hz, Cy), 34.40 (d, JPC = 27.7 Hz, Cy), 35.53 (d, JPC = 28.9 Hz, Cy), 125.87, 128.25, 130.75 (Ar), 136.92 (ipso-Ar). ¹¹B{¹H} NMR (160.47 MHz, CDCl₃, 25 °C): δ -43.5 (d, JPB = 57.8 Hz). ³¹P{¹H} NMR (202.47 MHz, CDCl₃, 25 °C): δ 27.2 (q, JPB = 57.8 Hz).

{CH₂CH₂PCy₂(BH₃)}₂ (51): To a solution of Cy₂PH (4.20 ml, 19.16 mmol) in THF (30 ml) the adduct BH₃-SMe₂ was added (9.58 ml of a 2.0M solution in THF, 19.16 mmol) and this mixture was left to stir for 1 h at room temperature. To this mixture was added °BuLi (8.33 ml of a 2.3M solution in hexanes, 19.16 mmol) and the solution was left to stir for 1 h at room temperature. This solution was added, dropwise, to a solution of 1,4-dibromobutane (2.07 g,
9.58 mmol) in THF (30 ml) and the solution was left to stir for 16 h at room temperature. To this mixture was added water (30 ml) and the organic phase was extracted into dichloromethane (3 x 20 ml). The combined organic extracts were dried over MgSO₄, filtered and the solvent was removed in vacuo from the filtrate to give a colourless solid. Isolated yield: 3.66 g, 80%. ¹H{¹¹B} NMR (500.16 MHz, CDCl₃, 25 °C): δ 0.29 (d, J_PH = 15.1 Hz, 6H, BH₃), 1.22-1.82 (m, 48H, CyH + CH₂CH₂). ¹³C{¹H} NMR (100.53 MHz, CDCl₃, 25 °C): δ 19.11 (d, J_PC = 31.2 Hz, Cy), 26.05 (Cy), 26.78 (d, J_PC = 2.01 Hz, Cy), 26.93 (d, J_PC = 1.01 Hz, Cy), 27.03 (br.d, Cy), 31.81 (d, J_PC = 33.2 Hz, PCH₂). ¹¹B{¹H} NMR (160.47 MHz, CDCl₃, 25 °C): δ -44.3 (d, J_PB = 49.0 Hz). ³¹P{¹H} NMR (202.47 MHz, CDCl₃, 25 °C): δ 25.2 (q, J_PB = 49.0 Hz).

[Li(tmeda)]₂[Me₂P(BH₃)CHSi(Me₂)CH₂]₂ (37a): To a solution of [Me₂P(BH₃)CH₂Si(Me₂)CH₂]₂ (0.51 g, 1.55 mmol) in THF (30 ml) was added nBuLi (1.24 ml of a 2.5 M solution in hexanes, 3.10 mmol) and tmeda (0.46 ml, 3.10 mmol) and this mixture was left to stir for 1 h at room temperature. The solvent was removed from the mixture in vacuo to yield a colourless oil which was crystallised from cold (-20 °C) methylcyclohexane (10 ml) to yield colourless crystals. The solid was washed with cold (0 °C) petrol (3 x 5 ml) and isolated. Isolated yield: 0.39 g, 74%. Anal. Calcd for C₂₄H₆₈B₂Li₂N₄P₂Si₂ (566.50): C, 50.89; H, 12.10; N, 9.89. Found: C, 50.68; H, 12.15; N, 9.78. ¹H{¹¹B} NMR (500.16 MHz, d₆-benzene, 25 °C): δ -1.05 (d, J_PH = 6.4 Hz, 2H, LiCH), 0.30 (s, 12H, SiMe₂), 0.76 (s, 4H, CH₂CH₂), 1.43 (d, J_PH = 10.1 Hz, 12H, PMe₂), 1.78 (s, 8H, CH₂N), 2.05 (s, 24H, NMe₂). ¹³C{¹H} NMR (125.77 MHz, d₆-benzene, 25 °C): δ 2.50 (SiMe₂), 3.20 (d, J_PC = 17.1 Hz, LiCH), 14.75 (CH₂CH₂), 19.66 (d, J_PC = 33.2 Hz, PMe₂), 45.8 (NMe₂), 56.3 (CH₂N). ⁷Li{¹H} NMR (104.38 MHz, d₆-benzene, 25 °C): δ -1.0 (LiCH). ¹¹B{¹H} NMR (160.47 MHz, d₆-benzene, 25 °C): δ -33.0 (d, J_PB = 88.3 Hz). ³¹P{¹H} NMR (202.47 MHz, d₆-benzene, 25 °C): δ -4.8 (q, J_PB = 88.3 Hz).

[Li(THF)₂]₂[Ph₂P(BH₃)CHSi(Me₂)CH₂]₂ (40a): To a solution of [Ph₂P(BH₃)CH₂Si(Me₂)CH₂]₂ (0.50 g, 0.88 mmol) in THF (40 ml) was added nBuLi (0.70 ml of a 2.5 M solution in hexanes, 1.75 mmol) and this mixture was left to stir for 1 h at room temperature. The solvent was removed in vacuo to yield a yellow oil which was crystallised from cold (-20 °C) Et₂O (10 ml) to yield yellow crystals. Isolated yield: 0.41 g, 80%. Anal.
calcd. for C_{48}H_{92}B_{2}Li_{2}O_{4}P_{2}Si_{2} (870.74): C 66.21, H 8.80: Found: C, 66.11, H, 8.70%.

{\h}^{1}\text{H}\{^{11}\text{B}\} \text{ NMR (500.16 MHz, } d_{6}\text{-benzene, 25 °C): } \delta \, -0.10 (d, J_{PH} = 25.0 \, Hz, 2H, LiCH), 0.29 (s, 12H, SiMe_{2}), 0.86 (s, 4H, CH_{2}CH_{2}), 1.33 (m, 16H, THF), 3.52 (m, 16H, THF), 7.00-8.10 (m, 20H, PPh_{2}). \text{ }^{13}\text{C}\{^{1}\text{H}\} \text{ NMR (125.77 MHz, } d_{6}\text{-benzene, 25 °C): } \delta \, -1.24 (d, J_{PC} = 16.1 \, Hz, LiCH), 1.99 (d, J_{PC} = 6.0 \, Hz, SiMe_{2}), 15.24 (CH_{2}CH_{2}), 25.2 (THF), 68.0 (THF), 127.65, 128.4 (Ar), 131.4 (d, J_{PC} = 9.1 \, Hz, Ar), 141.9 (d, J_{PC} = 50.5 \, Hz, ipso-Ar). \text{ }^{7}\text{Li}\{^{1}\text{H}\} \text{ NMR (194.38 MHz, } d_{6}\text{-benzene, 25 °C): } \delta \, 1.2 (LiCH). \text{ }^{11}\text{B}\{^{1}\text{H}\} \text{ NMR (160.47 MHz, } d_{6}\text{-benzene, 25 °C): } \delta \, -35.7 (d, J_{PB} = 107.9 \, Hz). \text{ }^{31}\text{P}\{^{1}\text{H}\} \text{ NMR (202.47 MHz, } d_{6}\text{-benzene, 25 °C): } \delta \, 12.5 (q, J_{PB} = 107.9 \, Hz).

[1,2-C_{6}\text{H}_{4}(CHPCy}_{2}(BH_{3})]_{2}[Li(tmeda)]_{2}\cdot 2\text{PhMe (46a):} \text{ To a solution of 1,2-C}_{6}\text{H}_{4}(CH_{2}PCy}_{2}(BH_{3})]_{2} (1.00 g, 1.90 mmol) in THF (30 ml) was added } ^{6}\text{BuLi (1.52 ml of a 2.5M solution in hexanes, 3.79 mmol) and the solution was left to stir for 30 minutes at room temperature. The solvent was removed } in \text{ vacuo } \text{ to yield a dark orange oil. This oil was dissolved in toluene (30 ml) and tmeda (0.57 ml, 3.79 mmol) was added and the solution was left to stir for 5 minutes. The solvent was reduced to 20 ml and the solution was cooled (-20 °C) for 24 h, resulting in yellow crystals, which were washed with a small amount of cold (0 °C) petrol. Isolated yield: 1.04 g, 57%. Anal. calcd. for C_{44}H_{98}B_{2}Li_{2}N_{4}P_{2} (770.65) [formula without toluene of crystallisation]: C, 68.57; H, 11.51; N, 7.27: Found: C, 68.53; H, 12.23; N, 7.04. \text{ }^{1}\text{H}\{^{11}\text{B}\} \text{ NMR (500.16 MHz, } d_{8}\text{-THF, 25 °C): } \delta \, 0.33 (d, J_{PH} = 15.0 \, Hz, 6H, BH_{3}), 1.12-2.02 (m, 46H, PCy_{2} + CHLi), 2.16 (s, 24H, NMe_{2}), 2.31 (s, 8H, NCH_{2}) 5.86 (br, 2H, ArH), 6.59 (br, 2H, ArH). \text{ }^{13}\text{C}\{^{1}\text{H}\} \text{ NMR (125.77 MHz, } d_{8}\text{-THF, 25 °C): } \delta \, 23.30 (d, J_{PC} = 61.3 \, Hz, CHLi), 26.93, 27.65 (s, PCy_{2}), 27.83 (d, J_{PC} = 10.1 \, Hz, PCy_{2}), 28.08 (d, J_{PC} = 10.1 \, Hz, PCy_{2}), 28.54 (s, PCy_{2}), 34.84 (d, J_{PC} = 34.2 \, Hz, PCy_{2}), 45.36 (s, NMe_{2}), 57.90 (s, NCH_{2}CH_{2}N), 112.49 (Ar), 116.32 (d, J_{PC} = 6.0 \, Hz, Ar), 139.15 (d, J_{PC} = 15.1 \, Hz, ipso-Ar). \text{ }^{7}\text{Li}\{^{1}\text{H}\} \text{ NMR (194.38 MHz, } d_{8}\text{-THF, 25 °C): } \delta \, -1.0 (LiCH). \text{ }^{11}\text{B}\{^{1}\text{H}\} \text{ NMR (160.47 MHz, } d_{8}\text{-THF, 25 °C): } \delta \, -39.8 (br). \text{ }^{31}\text{P}\{^{1}\text{H}\} \text{ NMR (202.47 MHz, } d_{8}\text{-THF, 25 °C): } \delta \, 12.3 (q, J_{PB} = 105.3 \, Hz).

Li[C_{6}H_{5}CHPPr_{2}(BH_{3})] (47a): \text{ To a solution of C}_{6}H_{5}\{CH_{2}PPr_{2}(BH_{3})} (1.00 g, 4.49 mmol) in Et}_{2}O (30 ml) was added } ^{6}\text{BuLi (1.91 ml of a 2.4 M solution in hexanes, 4.49 mmol) and this mixture was left to stir for 1 h at room temperature. Crude } ^{11}\text{B}\{^{1}\text{H}\} \text{ NMR (160.47 MHz,}
25 °C): δ -39.8 (d, J_{PB} = 88.5 Hz). Crude $^{31}\text{P}\{^1\text{H}\}$ NMR (202.47 MHz, 25 °C): δ 16.2 (q, J_{PB} = 88.5 Hz).

$$\text{[Li(tmeda)][C}_6\text{H}_5\text{CHPCy}_2(\text{BH}_3)] (49a):}$$ To a solution of C$_6$H$_5\{\text{CH}_2\text{PCy}_2(\text{BH}_3)\}$ (1.00 g, 3.28 mmol) in THF (30 ml) was added nBuLi (1.43 ml of a 2.3 M solution in hexanes, 3.28 mmol) followed by tmeda (0.49 ml, 3.28 mmol) and this mixture was left to stir for 1 h at room temperature. The solvent was removed in vacuo and the resulting solid was crystallised from cold (-5 °C) methylcyclohexane to yield yellow crystals. Isolated yield: 1.07 g, 77%. Anal. calcd. for C$_{25}$H$_{47}$BLiN$_2$P (424.38): C, 70.75; H, 11.16; N, 6.60. Found: C, 70.65; H, 10.88; N, 6.46. $^1\text{H}\{^{11}\text{B}\}$ NMR (500.16 MHz, d$_8$-toluene, 25 °C): 0.78 (d, J$_{PB}$ = 9.63 Hz, 3H, BH$_3$), 1.15-2.19 (m, 39H, PCy$_2$ + CHLi + NMe$_2$ + NCH$_2$), 6.98-7.03 (m, 5H, ArH).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.77 MHz, d$_8$-toluene, 25 °C): 26.64, 27.08 (PCy$_2$), 27.51 (d, J$_{PC}$ = 4.36 Hz, PCy$_2$), 27.58 (PCy$_2$), 27.67 (d, J$_{PC}$ = 4.46 Hz, PCy$_2$), 35.31 (d, J$_{PC}$ = 30.99 Hz, CHLi), 45.26 (NMe$_2$), 56.20 (NCH$_2$CH$_2$N), 113.05 (Ar), 120.35 (d, J$_{PC}$ = 9.6 Hz, Ar), 137.14 (Ar), 152.15 (ipso-Ar). $^7\text{Li}\{^1\text{H}\}$ NMR (194.38 MHz, d$_8$-toluene, 25 °C): δ 0.24 (LiCH).

$^{11}\text{B}\{^1\text{H}\}$ NMR (160.47 MHz, d$_8$-toluene, 25 °C): δ -39.46 (d, J$_{PB}$ = 81.5 Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.47 MHz, d$_8$-toluene, 25 °C): δ 12.24 (q, J$_{PB}$ = 81.5 Hz).

$$\text{[K}_2\{\text{Me}_2\text{P(BH}_3\text{)}\text{CHSi(Me}_2\text{)}\text{CH}_2\}_2\} (37b):}$$ To a solution of [Me$_2$P(BH$_3$)CH$_2$Si(Me$_2$)CH$_2$]$_2$ (0.50 g, 1.55 mmol) in THF (30 ml) was added, dropwise, a solution of benzylpotassium (0.40 g, 3.10 mmol) in THF (30 ml) and this solution was left to stir for 1 h at room temperature. The solvent removed in vacuo and the resulting solution was crystallised from cold (-20 °C) toluene/THF (10 ml/2 ml) to yield a red crystalline material. Isolated yield: 0.27 g, 43.0%. $^{31}\text{P}\{^1\text{H}\}$ NMR (202.47 MHz, d$_6$-benzene, 25 °C): δ -6.8 (q, J$_{PB}$ = 97.2 Hz), 3.4 (q, J$_{PB}$ = 58.7 Hz).

$$\text{[K(pmdeta)]}_2[\text{Ph}_2\text{P(BH}_3\text{)}\text{CHSi(Me}_2\text{)}\text{CH}_2\}_2\} (40b):}$$ To a solution of [Ph$_2$P(BH$_3$)CH$_2$Si(Me$_2$)CH$_2$]$_2$ (0.50 g, 0.88 mmol) in THF (20 ml) was added, dropwise, a solution of benzylpotassium (0.26 g, 2.00 mmol) in THF (10 ml), followed by pmdeta (0.37 ml, 1.75 mmol) and this solution was left to stir for 16 h at room temperature. The solvent was removed in vacuo from the resulting orange solution to yield a sticky yellow
solid, which was crystallised from cold (-20 °C) toluene (20 ml) as yellow blocks. Isolated yield: 0.53 g, 61%. Anal. calcd. for C_{50}H_{60}B_{2}K_{2}N_{4}P_{2}Si_{2} (993.22): C 60.46; H 9.13; N, 8.46. Found: C, 60.34; H, 9.06; N, 8.31. ¹H{¹¹B} NMR (500.16 MHz, d₈-THF, 25 °C): δ -0.53 (d, J_{PH} = 25.0 Hz, 2H, KCH), -0.15 (s, 12H, SiMe₂), 0.43 (s, 4H, CH₂CH₂), 0.95 (d, J_{PH} = 15.0 Hz, 6H, BH₃), 2.16 (s, 12H, NMe₂), 2.19 (s, 3H, NMe), 2.32 (m, 8H, CH₂N), 2.43 (m, 8H, CH₂N), 7.00-8.10 (m, 20H, PPH₂). ¹³C{¹H} NMR (125.77 MHz, d₈-THF, 25 °C): δ -2.2 (d, J_{PC} = 38.2 Hz, KCH), -0.1 (SiMe₂), 12.1 (d, J_{PC} = 5.0 Hz, CH₂CH₂), 40.5 (NMe), 43.5 (NMe₂), 54.6 (NCH₂), 124.9 (d, J_{PC} = 9.1 Hz, Ph), 125.0 (Ph), 129.3 (d, J_{PC} = 9.1 Hz, Ph), 129.9 (d, J_{PC} = 9.1 Hz, Ph). ¹¹B{¹H} NMR (160.47 MHz, d₈-THF, 25 °C): δ -34.7 (d, J_{PB} = 113.8 Hz). ³¹P{¹H} NMR (202.47 MHz, d₈-THF, 25 °C): δ 11.7 (q, J_{PB} = 113.8 Hz).

[K(pmdeta)]₂[1,2-C₆H₄(CH₂PCy₂(BH₃))]₂ (46b): To a solution of 1,2-C₆H₄(CH₂PCy₂(BH₃))₂ (0.50 g, 0.95 mmol) in THF (30 ml) was added, dropwise, a solution of benzylpotassium (0.30 g, 2.30 mmol) in THF (30 ml) followed by pmdeta (0.39 ml, 1.90 mmol) and this solution was left to stir for 1 h at room temperature. The solvent was removed in vacuo to yield a sticky orange solid which was dissolved in Et₂O (10 ml), filtered and this mixture was left to stand at room temperature for 24 h to yield yellow crystals. Isolated yield: 0.37 g, 41%. Anal. calcd. for C₅₀H₆₀B₂K₂N₄P₂ (949.15): C 63.27; H 10.83; N, 8.85. Found: C, 63.11; H, 11.01; N, 8.76. ¹H{¹¹B} NMR (500.16 MHz, d₈-toluene, 25 °C): δ 0.98 (d, J_{PH} = 12.0 Hz, 6H, BH₃), 1.09-2.23 (m, 67H, PCy₂ + CH₂N + NMe + NMe₂), 6.18 (s, 2H, ArH), 9.96 (s, 2H, ArH). ¹³C{¹H} NMR (125.77 MHz, d₈-toluene, 25 °C): δ 27.2 (PCy), 27.6 (PCy₂), 27.8 (d, J_{PC} = 10.1 Hz, PCy₂), 28.0 (d, J_{PC} = 10.1 Hz, PCy₂) 28.5, 33.3 (d, J_{PC} = 30.1 Hz, PCy₂), 37.8 (d, J_{PC} = 36.5 Hz, CHK), 41.8 (NMe), 45.0 (NMe₂), 55.1, 57.0 (NCH₂), 111.2, 113.7 (Ar), 141.9 (d, J_{PC} = 3.9 Hz, Ar). ¹¹B{¹H} NMR (160.47 MHz, d₈-toluene, 25 °C): δ -40.3 (br). ³¹P{¹H} NMR (202.47 MHz, d₈-toluene, 25 °C): δ 12.7 (br).

K[C₆H₅CHPPr₂(BH₃)] (47b): To a solution of C₆H₅(CH₂PPr₂(BH₃)) (0.50 g, 2.24 mmol) in THF (20 ml) was added, dropwise, a solution of BnK (0.34 g, 2.61 mmol) in THF (20 ml) and this solution was left to stir for 45 mins at room temperature. The solvent was removed in vacuo and the resulting solution was crystallised from cold (-20 °C) toluene to yield orange crystals which were washed with cold (0 °C) petrol (3 x 5 ml). Isolated yield: 0.28 g, 48%. Anal. calcd. for C₁₃H₂₃BKP (260.81): C, 60.01; H, 8.91. Found: C, 59.99; H, 8.96. ¹H{¹¹B}
were isolated and washed with petrol (3 x 5 ml). Isolated Yield: 0.62 g, 91%.

\[ \text{K[C}_6\text{H}_5\text{CHPCy}_2(\text{BH}_3)] \ (49b): \] To a solution of \( \text{C}_6\text{H}_5(\text{CH}_2\text{PCy}_2(\text{BH}_3)) \) (0.50 g, 1.65 mmol) in THF (20 ml) was added, dropwise, a solution of \( \text{BnK} \) (0.30 g, 2.30 mmol) in THF (20 ml) and this solution was left to stir for 45 mins at room temperature. The solvent was removed in vacuo and the resulting solution was crystallised from cold (-5 °C) toluene to yield orange crystals which were washed with cold (0 °C) petrol (3 x 5 ml). Isolated yield: 0.62 g, 91%.

Anal. calcd. for \( \text{C}_{19}\text{H}_{31}\text{BKP-PhCH}_3 \) (386.38): C, 73.63; H, 9.61. Found: C, 73.49; H, 9.51.

\[ ^1\text{H}\{^{11}\text{B}\} \text{ NMR} \ (500.16 \text{ MHz, } d_8-\text{THF}, 25 ^\circ\text{C}): \delta \ 0.28 \ (d, \ J_{\text{PH}} = 13.33 \text{ Hz}, \text{ 3H, BH}_3), \ 1.15-1.83 \ (m, \text{ 22H, PCy}_2), \ 1.86 \ (d, \ J_{\text{PH}} = 4.77 \text{ Hz}, \text{ 1H, CHK}), \ 2.28 \ (s, \text{ 3H, Toluene}), \ 5.56 \ (m, \text{ 1H, ArH}), \ 6.43-6.52 \ (m, \text{ 4H, ArH}), \ 7.10-7.16 \ (m, \text{ 5H, Toluene}). \]

\[ ^{13}\text{C}\{^1\text{H}\} \text{ NMR} \ (125.77 \text{ MHz, } d_8-\text{THF}, 25 ^\circ\text{C}): \delta \ 26.40 \ (d, \ J_{\text{PC}} = 2.26 \text{ Hz, PCy}_2), \ 26.66 \ (\text{PCy}_2), \ 27.36 \ (d, \ J_{\text{PC}} = 3.02 \text{ Hz, PCy}_2), \ 27.50 \ (d, \ J_{\text{PC}} = 1.51 \text{ Hz, PCy}_2), \ 28.11 \ (\text{PCy}_2), \ 28.23 \ (d, \ J_{\text{PC}} = 3.77 \text{ Hz, PCy}_2), \ 33.77 \ (d, \ J_{\text{PC}} = 12.39 \text{ Hz, CHK}), \ 36.21 \ (d, \ J_{\text{PC}} = 37.03 \text{ Hz, CHPCy}_2), \ 125.05, \ 127.92, \ 128.68 \ (\text{Ar}), \ 137.44 \ (\text{ipso-Ar}). \]

\[ ^{11}\text{B}\{^1\text{H}\} \text{ NMR} \ (160.47 \text{ MHz, } d_8-\text{THF}, 25 ^\circ\text{C}): \delta \ -40.2 \ (d, \ J_{\text{PB}} = 79.2 \text{ Hz}). \]

\[ ^{31}\text{P}\{^1\text{H}\} \text{ NMR} \ (202.47 \text{ MHz, } d_8-\text{THF}, 25 ^\circ\text{C}): \delta \ 8.8 \ (q, \ J_{\text{PB}} = 79.2 \text{ Hz}). \]

\[ [\text{1,2-C}_6\text{H}_4(\text{CHPCy}_2(\text{BH}_3))_2]\text{Sn}_2\cdot 1\frac{1}{2}\text{PhMe} \ (58): \] To a solution of \( 1,2-\text{C}_6\text{H}_4(\text{CH}_2\text{PCy}_2(\text{BH}_3))_2 \) (0.50 g, 1.17 mmol) in THF (20 ml) was added \( \text{"BuLi} \) (0.94 ml of a 2.5M solution in hexanes, 2.34 mmol) and this mixture was left to stir for 30 minutes at room temperature, which resulted in an orange solution. The solvent was removed in vacuo to yield a dark orange oil. This oil was dissolved in toluene (20 ml) and was added, dropwise, to a solution of \( \text{SnCp}_2 \) (0.29 g, 1.17 mmol) in toluene and this mixture was left to stir for 45 minutes at room temperature, with the exclusion of light. The mixture was filtered, the filtrate was reduced to 10 ml and then cooled (-20 °C) to crystallise. After 7 days yellow crystals were isolated and washed with petrol (3 x 5 ml). Isolated Yield: 0.23 g, 28%. The solvent is
gradually lost when the sample was put under vacuum and so no solvent peaks were observed in the NMR spectra. Anal. Calcd for C_{64}H_{112}B_{4}P_{4}Sn_{2} (1286.1): C, 59.77; H, 8.78. Found: C, 59.68; H, 8.88. \(^1\)H\[^{11}\]B} NMR (500.15 MHz, \(d_8\)-THF, 25 °C): \(\delta\) 0.50-2.67 (m, 107H, Cy + BH\(_3\) + CHSn + PhMe), 6.58 (m, 1H, ArH), 6.79 (m, 1H, ArH), 7.00 (m, 2H, ArH), 7.07-7.19 (m, 5H, PhMe), 7.28 (m, 2H, ArH), 7.96 (m, 1H, ArH), 8.03 (m, 1H, ArH). \(^{11}\)B\[^{1}\]H} NMR (160.47 MHz, \(d_8\)-THF, 25 °C): \(\delta\) -43.5, -38.8 (br).

\(^{31}\)P\[^{1}\]H} NMR (202.47 MHz, \(d_8\)-THF, 25 °C): \(\delta\) 27.4, 28.6, 30.0, 35.4 (br).

\(^{119}\)Sn\[^{1}\]H} NMR (186.51 MHz, \(d_8\)-THF, 25 °C): \(\delta\) -103 (br, FWHM = 770 Hz), 339 (br, FWHM = 480 Hz).

**Sn[1,2-C\(_6\)H\(_4\){CHPPh\(_2\)(BH\(_3\))}\(_2\)] (60):** To a solution of 1,2-C\(_6\)H\(_4\)CHPPh\(_2\)(BH\(_3\))\(_2\) (0.50 g, 1.00 mmol) in THF (20 ml) was added \(^{8}\)BuLi (0.80 ml of a 2.5M solution in hexanes, 1.99 mmol) and this mixture was left to stir for 30 minutes at room temperature. The solvent was removed \textit{in vacuo} to yield a red oil. This oil was dissolved in toluene (20 ml) and was added, dropwise, to a solution of SnCp\(_2\) (0.25 g, 0.996 mmol) in toluene and this mixture was left to stir for 45 minutes at room temperature, with the exclusion of light, to give an orange solution; which was unable to isolate any solid material for full characterisation. Crude \(^{31}\)P\[^{1}\]H} NMR (202.47 MHz, Toluene, 25 °C): \(\delta\) 14.8 (br), 16.9 (br), 18.8 (br), 20.4 (br), 23.1 (br).

**Sn[1,2-C\(_6\)H\(_4\){CHPPr\(_2\)(BH\(_3\))}\(_2\)] (61):** To a solution of 1,2-C\(_6\)H\(_4\)CHPPr\(_2\)(BH\(_3\))\(_2\) (0.50 g, 1.37 mmol) in THF (20 ml) was added \(^{8}\)BuLi (0.80 ml of a 2.5M solution in hexanes, 2.73 mmol) and this mixture was left to stir for 30 minutes at room temperature. The solvent was removed \textit{in vacuo} to yield a dark orange oil. This oil was dissolved in toluene (20 ml) and was added, dropwise, to a solution of SnCp\(_2\) (0.34 g, 1.37 mmol) in toluene and this mixture was left to stir for 16 h at room temperature, with the exclusion of light. The mixture was then filtered to give an orange solution which was unable to isolate any solid material for full characterisation. Crude \(^{31}\)P\[^{1}\]H} NMR (202.47 MHz, Toluene, 25 °C): \(\delta\) 32.07 (br), 33.40 (br), 35.20 (br), 36.26 (br), 38.70 (br).

**Sn[C\(_6\)H\(_5\)CHPPr\(_2\)(BH\(_3\))\(_2\)] (64):** To a solution of C\(_6\)H\(_5\)CHPPr\(_2\)(BH\(_3\)) (1.00 g, 4.49 mmol), in Et\(_2\)O (30 ml) was added \(^{8}\)BuLi (1.91 ml of a 2.35 M solution in hexanes, 4.49 mmol) and this
solution was left to stir for 1 h at room temperature. This solution was added, dropwise, to a cold (-78 °C) solution of SnCl₂ (0.43 g, 2.24 mmol) in Et₂O (20 ml) and this mixture was left to stir overnight and attain room temperature. This mixture was filtered, solvent was removed in vacuo from the filtrate and the resulting solid was crystallised from cold (-20 °C) methylcyclohexane. Isolated Yield: 2.12 g, 84%. ¹¹B{¹H} NMR (160.47 MHz, 25 °C): δ -38.76 (d, J_PB = 79.47 Hz). ³¹P{¹H} NMR (202.47 MHz, 25 °C): δ 34.59 (br).

Sn[C₆H₅CHPcy₂(BH₃)]₂ (65): To a solution of C₆H₅CHPCy₂(BH₃) (1.00 g, 3.31 mmol), in Et₂O (30 ml) was added nBuLi (1.44 ml of a 2.3 M solution in hexanes, 3.31 mmol) and this mixture was left to stir for 1 h at room temperature. This solution was added, dropwise, to a cold (-78 °C) solution of SnCl₂ (0.31 g, 1.65 mmol) in Et₂O (20 ml) and this mixture was left to stir overnight and attain room temperature. This mixture was filtered and a fine yellow solid deposited from solution; this was isolated and was washed with Et₂O (3 x 5 ml). Isolated Yield: 0.21 g, 17.7%. Anal. Calcd for C₃₈H₆₂B₂P₂Sn (721.25): C, 63.29; H, 8.67. Found: C, 58.49; H, 8.18. ¹¹B{¹H} NMR (500.16 MHz, d₈-toluene, 25 °C): δ 0.62 (d, J_PH = 8.50 Hz, 6H, BH₃), 1.07-1.79 (m, 44H, PCy₂), 3.50 (d, J_PH = 11.25 Hz, 2H, CHSn), 7.10-7.28 (m, 10H, ArH). ¹¹B{¹H} NMR (160.47 MHz, d₈-toluene, 25 °C): δ -39.4 (br). ³¹P{¹H} NMR (202.47 MHz, d₈-toluene, 25 °C): 32.0 (br). ¹¹⁹Sn{¹H} NMR (186.51 MHz, d₈-toluene, 25 °C): δ 359 (br), 370 (br).

[C₆H₅CHPPr₂(BH₃)]SnCl (69): To a solution of C₆H₅CHPPr₂(BH₃) (1.00 g, 4.49 mmol), in Et₂O (30 ml) was added nBuLi (1.91 ml of a 2.35 M solution in hexanes, 4.49 mmol) and this mixture was left to stir for 1 h at room temperature. This solution was added, dropwise, to a cold (-78 °C) solution of SnCl₂ (0.43 g, 2.24 mmol) in Et₂O (20 ml) and this mixture was left to stir overnight and attain room temperature. This mixture was filtered and a fine yellow solid deposited from solution; this was isolated and was washed with Et₂O (3 x 5 ml). Isolated Yield: 1.43 g, 84.7%. ¹¹B{¹H} NMR (160.47 MHz, 25 °C): δ -39.2 (d, J_PB = 66.6 Hz). ³¹P{¹H} NMR (202.47 MHz, 25 °C): 33.4 (q, J_PB = 66.6 Hz).

[C₆H₅CHPCy₂(BH₃)]Sn (70): To a solution of C₆H₅CHPCy₂(BH₃) (0.50 g, 1.65 mmol), in Et₂O (20 ml) was added nBuLi (0.70 ml of a 2.35 M solution in hexanes, 1.65 mmol) and this
solution was left to stir for 1 h at room temperature. This solution was added, dropwise, to a cold (-78 °C) solution of SnCl₂ (0.31 g, 1.65 mmol) in Et₂O (20 ml) and this mixture was left to stir overnight and attain room temperature. This mixture was filtered, the filtrate was reduced in volume (10 ml) and a fine yellow solid precipitated which was washed with Et₂O (3 x 5 ml). Isolated Yield: 0.63 g, 83.6%. Anal. Calcd for C₁₉H₃₁BClPSn (455.42): C, 50.11; H, 6.86. Found: C, 50.24; H, 6.99. ¹H{¹¹B} NMR (500.16 MHz, d₈-THF, 25 °C): 1.07-1.79 (m, 22H, PCy), 0.75 (d, 1JPH = 16.69 Hz, 1H, CHSn), 7.10-7.28 (m, 5H, Ph). ¹³C{¹H} NMR (125.77 MHz, d₈-THF, 25 °C): δ 26.04-28.01 (m, PCy), 31.71 (d, 1JPC = 28.89 Hz, SnCH), 127.62, 128.00, 129.96, 130.00 (Ph). ¹¹B{¹H} NMR (160.47 MHz, d₈-THF, 25 °C): δ -39.8 (br). ³¹P{¹H} NMR (202.47 MHz, d₈-THF, 25 °C): 27.7 (br).

[C₆H₅CHPPr₂(BH₃)]₂Sn(Me)I (86): To a solution of Sn[C₆H₅CHPPr₂(BH₃)]₂ (10 ml of a 0.101 M solution in Et₂O, 1.01 mmol) was added MeI (0.06 ml, 1.01 ml) and this solution was left to stir for 16 h at room temperature. A colourless precipitate had formed which was isolated by decanting the supernatant and removing residual solvent in vacuo to yield a colourless solid. Single crystals were obtained suitable for X-ray crystallography by dissolving the crude product in hot toluene (5 ml) and layering with Et₂O (20 ml). Isolated Yield: 0.32 g, 45%. Anal. Calcd for C₆₇H₇₂PC₂I₂Sn (702.91): C, 45.20; H, 7.15. Found: C, 45.27; H, 7.26. ¹H{¹¹B} NMR (500.16 MHz, CDCl₃, 25 °C): 0.56 (d, 1JPH = 15.0 Hz, BH₃⁹) 0.75 (d, 1JPH = 10.0 Hz, BH₃⁹), 0.76 (dd, 1JHH = 10.0 Hz, 1JPH = 15.0 Hz, CH₃⁵), 0.86 (s, 3H, SnCH₃), 0.87 (dd, 1JHH = 10.0 Hz, 1JPH = 15.0 Hz, CH₃⁵), 1.18 (dd, 1JHH = 10.0 Hz, 1JPH = 15.0 Hz, JHH = 10.0 Hz, JHH = 10.0 Hz, JHH = 10.0 Hz, JHH = 10.0 Hz, JHH = 10.0 Hz, JHH = 10.0 Hz, JHH = 10.0 Hz, 1.25 (m, CH₄⁴, CH₃⁷, CH₃⁸ AND CH₃⁴), 1.39 (dd, 1JHH = 10.0 Hz, 1JPH = 15.0 Hz, JHH = 10.0 Hz, JHH = 10.0 Hz, JHH = 10.0 Hz, JHH = 10.0 Hz, JHH = 10.0 Hz, JHH = 10.0 Hz, JHH = 10.0 Hz, JHH = 10.0 Hz, 2.10 (s, PCH₆ + PCH₆), 2.26 (s, PCH₃), 2.87 (s, PCH₃), 4.19 (d, 1JPH = 15.0 Hz, JHH = 130.0 Hz, SnCH¹), 4.54 (d, 1JPH = 15.0 Hz, JHH = 55.0 Hz, SnCH¹). ¹³C{¹H} NMR (125.77 MHz, CDCl₃, 25 °C): δ 5.56 (dd, 1JPC = 1.80 Hz, 1JPC = 2.38 Hz, SnCH₃), 17.14 (d, 1JPC = 5.03 Hz, CMe⁵), 17.19 (d, 1JPC = 3.77 Hz, CMe⁵), 17.49 (s, CMe), 17.53 (s, CMe⁷), 18.00 (s, CMe), 18.24 (d, 1JPC = 2.52 Hz, CMe⁸), 19.51 (d, 1JPC = 2.52 Hz, CMe⁴), 20.21 (d, 1JPC = 3.77 Hz, CMe), 21.00 (s, CMe⁶), 21.24 (d, 1JPC = 2.52 Hz, CMe³), 21.46 (d, 1JPC = 33.96 Hz, CMe³), 22.00 (d, 1JPC = 31.45 Hz, CMe⁶), 34.79 (d, 1JPC = 13.8 Hz, CMe¹), 35.68(d, 1JPC = 17.6 Hz, CMe¹). ¹¹B{¹H} NMR (160.47 MHz, CDCl₃, 25 °C): δ -40.1 (br, BH₃⁹), -40.8 (br, BH₃⁹). ³¹P{¹H} NMR (202.47 MHz, CDCl₃, 25 °C): δ 36.9 (br, P²), 40.48 (br, P²). ¹¹⁹Sn{¹H} NMR (186.51 MHz, CDCl₃, 25 °C): δ -14.8 ppm (dd, 1JHH = 20.5 Hz, 1JPH = 106.3 Hz).
[C₆H₅CHPPr₂(BH₃)]₂Sn(Bn)Br (87): To a solution of Sn[C₆H₅CHPPr₂(BH₃)]₂ (10 ml of a 0.101 M solution in Et₂O, 1.01 mmol) was added BnBr (0.12 ml, 1.01 ml) and this solution was left to stir for 16 h at room temperature. The resulting crude sample was reduced in volume (10 ml) and cooled (-5 °C) in order to precipitate compound 87 as a colourless solid. Single crystals were obtained suitable for X-ray by dissolving the crude product in hot toluene (5 ml) and layering with Et₂O (20 ml). Isolated Yield: 0.36 g, 49%. Anal. Calcd for C₃₃H₅₃B₂BrP₂Sn (732.03): C, 54.15; H, 7.30. Found: C, 54.04; H, 7.20. ¹H NMR (500.16 MHz, CDCl₃, 25 °C): 0.39 (dd, J_HH = 5.00 Hz, J_PH = 10.0 Hz, 6H, CH₃), 0.94 (dd, J_HH = 10.0 Hz, J_PH = 15.0 Hz, 6H, CH₃), 1.08 (dd, J_HH = 10.0 Hz, J_PH = 15.0 Hz, 6H, CH₃), 1.23 (dd, J_HH = 5.00 Hz, J_PH = 15.0 Hz, 6H, CH₃), 2.70, 4.15 (d, J_PH = 15.0 Hz, 1H, SnCH), 7.79 (d, J_PH = 10.0 Hz, 1H, SnCH), 6.89-7.55 (m, 15H, Ar). ¹¹B{¹H} NMR (160.47 MHz, CDCl₃, 25 °C): δ -40.5 (br, BH₃). ³¹P{¹H} NMR (202.47 MHz, CDCl₃, 25 °C): δ 36.2 (br), 38.3 (br), 40.74 (br). ¹¹⁹Sn{¹H} NMR (186.51 MHz, CDCl₃, 25 °C): δ -22.8 (t, J_SnP = 28.0 Hz), -5.61 (t, J_SnP = 86.7 Hz), -4.31 ppm (t, J_SnP = 85.8 Hz), 1.17 ppm (dd, J_SnP = 126.8 Hz, J_SnP' = 13.1 Hz).
10.6 References


Appendix 1. X-ray crystallographic data

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Appendix 2. Eyring plot data

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