

Alkali metal complexes of a phosphine–borane-stabilised carbanion: influence of co-ligands on structure†‡

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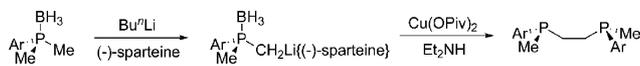
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The adducts $[[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{K}(\text{L})_n]_m$ [$\text{L} = \text{THF}$, $n = 0.5$, $m = \infty$ (**2a**); $\text{L} = \text{tmeda}$ (**2b**), pmdeta (**2c**), $n = 1$, $m = 2$] may be synthesised by treatment of solvent-free $[[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{K}]_\infty$ (**2**) with the corresponding Lewis base ($\text{tmeda} = N,N,N',N'$ -tetramethylethylenediamine; $\text{pmdeta} = N,N,N',N'',N''$ -pentamethyldiethylenetriamine). X-Ray crystallography reveals that, whereas **2** crystallises with a complex 2-dimensional sheet structure, **2a** crystallises as a ribbon-type one-dimensional polymer and both **2b** and **2c** crystallise as dimers. The corresponding complex with 12-crown-4, $[\text{K}(12\text{-crown-4})_2][(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]$ (**2d**) crystallises as a separated ion pair. The complexes $[[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{M}(\text{pmdeta})_n]$ [$\text{M} = \text{Na}$, $n = 1$ (**6**); $\text{M} = \text{Rb}$, $n = 2$ (**7**)] may be synthesised by treatment of $[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{M}$ with pmdeta . Whereas **6** crystallises as a discrete monomer, compound **7** crystallises as a dimer. Compounds **2**, **2a–2d**, **6**, **7** and the corresponding caesium derivative $[[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{Cs}(\text{pmdeta})_2]$ (**5**) provide an opportunity to consider the influence of the ionic radius of the metal and the nature of the co-ligands on the structures of alkali metal complexes of a phosphine–borane-stabilised carbanion.

Introduction

α -Metalated phosphine–borane adducts are key intermediates in the synthesis of a wide variety of both chiral and achiral phosphine ligands.¹ For example, Evans and co-workers have demonstrated that the copper-mediated coupling of α -metalated phosphine–boranes in the presence of the chiral diamine (–)-sparteine stereoselectively yields chiral diphosphine ligands such as DI-PAMP (Scheme 1).² In light of this, it is perhaps surprising that little is known about the structures of these compounds, either in the solid state or in solution. This is particularly remarkable given that the structures of these species are likely to have a significant influence on their reactivities and selectivities.

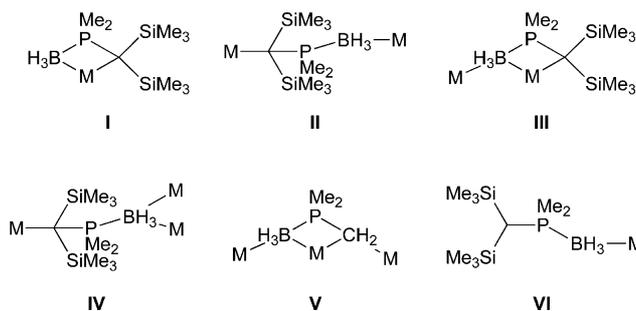


Scheme 1

In this regard, we have previously shown that the unusual dicarbanion complex $[[(\text{Me}_3\text{Si})\{\text{Pr}^n\text{P}(\text{BH}_3)\}\text{CCH}_2]\text{Li}(\text{pmdeta})_2]$ (**1**) exhibits contacts between the lithium ions and the BH_3 groups but not between the lithium ions and the carbanion centres [$\text{pmdeta} = N,N,N',N'',N''$ -pentamethyldiethylenetriamine].³ Protonation of the (–)-sparteine analogue of **1**, *viz.* $[[(\text{Me}_3\text{Si})\{\text{Pr}^n\text{P}(\text{BH}_3)\}\text{CCH}_2]\text{Li}\{(-)\text{-sparteine}\}]_2$ (**1a**), exhibits no evidence for stereoselectivity under a variety of reaction conditions. This clearly implies that **1** and **1a** adopt structures in solution

in which the lithium ions are remote from the carbanion centres; thus, the coordination environment of the lithium ions does not affect the stereochemical outcome of the reaction.

In order to gain further insight into these compounds, and to obtain a better understanding of the factors which affect the structures and reactions of these species, we have recently initiated a detailed study of the coordination behaviour of phosphine–borane-stabilised carbanions. During this study we have shown that phosphine–borane-stabilised carbanions adopt a wide variety of coordination modes in their complexes with alkali and alkaline earth metal ions, including (i) a chelating mode (**I**), (ii) a variety of bridging modes (**II–V**), and (iii) a terminal BH_3 -donor mode (**VI**).^{4–7} In addition, Kobayashi and co-workers have reported a phosphine–borane-stabilised carbanion complex of lithium in which there is a C–Li contact but no $\text{B–H}\cdots\text{Li}$ contacts,⁸ whereas Schmidbaur *et al.* have reported that the compound $[\text{Li}(\text{tmeda})_2][\text{CH}\{\text{PMe}_2(\text{BH}_3)\}_2]$ crystallises as a separated ion pair.⁹



Clearly, the structure adopted by such a compound will depend on the interplay of several competing factors such as the electronic and steric properties of the substituents at the phosphorus and carbanion centres and the nature of the metal cation. In this regard,

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it is well known that co-ligands such as tmeda and pmdeta often effect the de-aggregation of organo-alkali metal complexes and that such co-ligands may strongly influence ligand binding modes [tmeda = *N,N,N',N'*-tetramethylethylenediamine].¹⁰ However, until now, the effect of co-ligands on the coordination behaviour of phosphine-borane-stabilised carbanions has not been considered. We now report the synthesis and structural characterisation of a series of alkali metal complexes of a representative phosphine-borane-stabilised carbanion, in which either the metal ion or the co-ligand is systematically varied.

Results and discussion

We have shown previously that the potassium salt $[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{K}$ (**2**) crystallises solvent-free from cold toluene in the presence of a small amount of THF as a rather complex two-dimensional sheet polymer in which the potassium cations are coordinated by both the carbanion centre and the borane hydrogen atoms of the ligand (Fig. 1).⁵ Somewhat surprisingly, crystallisation of **2** from methylcyclohexane in the presence of a small amount of THF yields the adduct $[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{K}(\text{THF})_{0.5}$ (**2a**) as colourless blocks. The THF co-ligands in **2a** are only very weakly held and are rapidly lost under vacuum. No evidence for THF was observed in the NMR spectra or elemental analyses of samples of **2a** which had been exposed to vacuum for 5 min; the ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$

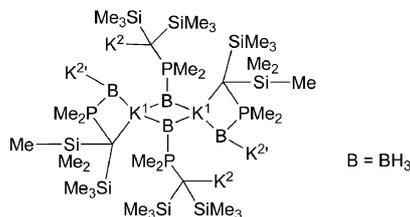
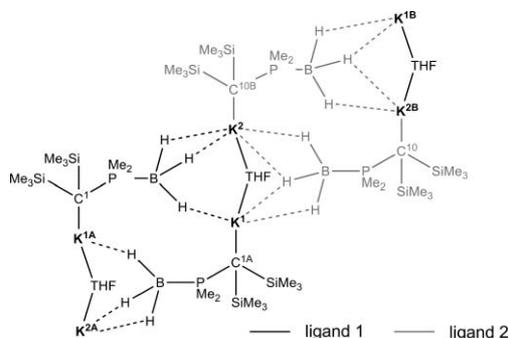


Fig. 1 Principal metal-ligand contacts in **2**.

and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **2a** are essentially identical to those of **2**.

The structure of **2a** is shown in Fig. 2, along with selected bond lengths and angles. Compound **2a** crystallises as a ribbon-type polymer containing two distinct ligand environments and two distinct potassium environments. K(1) is coordinated by an $\eta^1\text{-BH}_3$ group of ligand 1, by an $\eta^2\text{-BH}_3$ group of ligand 2 and by the carbanion centre of a symmetry equivalent of ligand 1; the BH_3 groups of ligand 2 form $\mu_2, \eta^1:\eta^2$ bridges between K(1) and K(2). These same two potassium ions are also bridged by the BH_3 group of ligand 1 in a $\mu_2, \eta^1:\eta^2$ -manner and by a molecule of THF; K(2) is further coordinated by the carbanion centre of a symmetry equivalent of ligand 2. Thus, ligand 1 bridges K(1) and K(1A)/K(2A) *via* its carbanion centre and its BH_3 group, whereas ligand 2 bridges K(2) and K(1B)/K(2B) *via* its carbanion centre and its BH_3 group; the phosphine-borane-stabilised carbanion ligands in **2a** thus adopt binding mode **IV** (see above). The coordination spheres of K(1) and K(2) are each completed by two short, agostic-type $\text{K}\cdots\text{Me-Si}$ contacts.



Treatment of **2** with one equivalent of tmeda, followed by crystallisation from cold toluene, yields colourless blocks of the adduct $[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{K}(\text{tmeda})_2$ (**2b**). X-Ray crystallography reveals that **2b** crystallises as discrete centrosymmetric dimers; the molecular structure of **2b** is shown in Fig. 3, along with selected

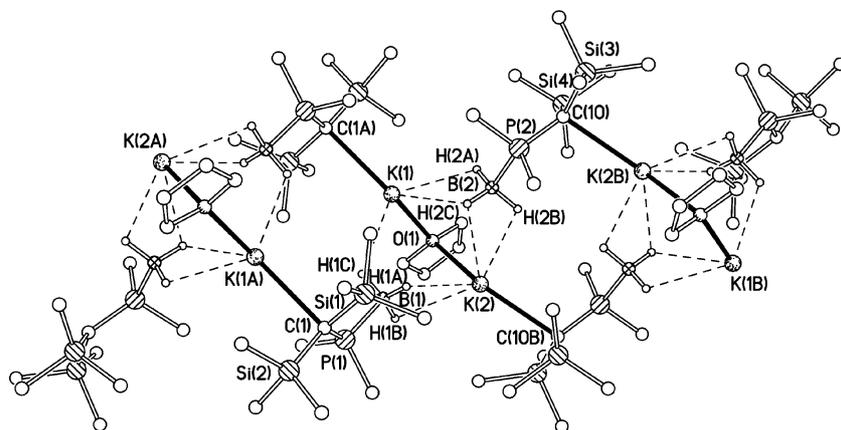


Fig. 2 Structure of **2a** with H atoms bonded to carbon omitted for clarity. Selected bond lengths (Å) and angles (°): K(1)–C(1A) 2.998(2), K(1)–O(1) 2.829(2), K(1)⋯B(1) 3.389(3), K(1)⋯B(2) 3.222(3), K(1)–H(1C) 2.73(3), K(1)–H(2A) 2.78(3), K(1)–H(2C) 2.76(3), K(1)⋯C(5A) 3.590(3), K(1)⋯C(7A) 3.508(3), K(2)–C(10B) 2.974(2), K(2)–O(1) 2.850(2), K(2)⋯B(1) 3.185(3), K(2)⋯B(2) 3.171(3), K(2)–H(1A) 2.75(3), K(2)–H(1B) 2.89(3), K(2)–H(2B) 2.68(3), K(2)–H(2C) 2.95(3), K(2)⋯C(13B) 3.484(3), K(2)⋯C(16B) 3.534(3), P(1)–C(1) 1.750(2), Si(1)–C(1) 1.848(2), Si(2)–C(1) 1.843(2), P(1)–B(1) 1.936(3), P(2)–C(10) 1.745(2), Si(3)–C(10) 1.842(3), Si(4)–C(10) 1.853(2), P(2)–B(2) 1.940(3), P(1)–C(1)–Si(1) 113.45(12), P(1)–C(1)–Si(2) 119.02(12), Si(1)–C(1)–Si(2) 117.19(12), P(2)–C(10)–Si(3) 118.29(12), P(2)–C(10)–Si(4) 115.31(12), Si(3)–C(10)–Si(4) 116.54(12). Symmetry operators: (A) $1 - x, 1 - y, 2 - z$; (B) $-x, -y, 1 - z$.

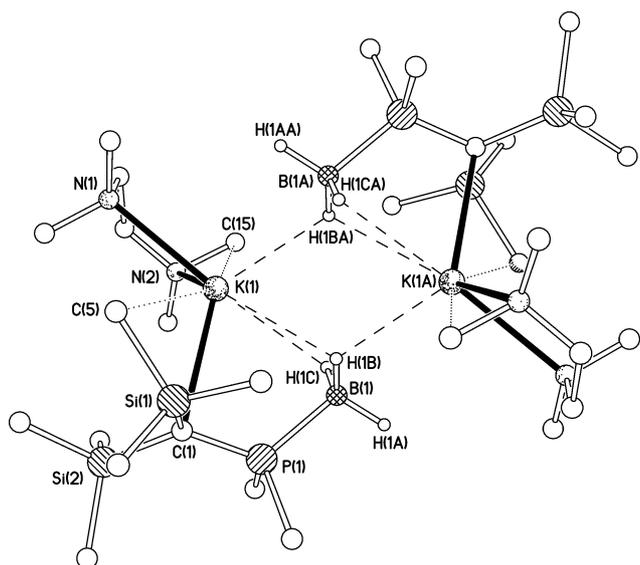
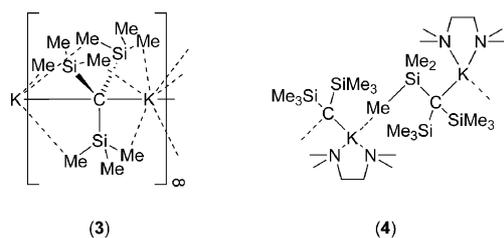


Fig. 3 Molecular structure of **2b** with H atoms bonded to carbon omitted for clarity. Selected bond lengths (Å) and angles (°): K(1)–C(1) 3.107(3), K(1)–N(1) 2.849(2), K(1)–N(2) 2.975(2), K(1)–H(1B) 3.05(4), K(1)–H(1C) 2.75(3), K(1)–H(1BA) 2.73(3), K(1)⋯B(1) 3.235(4), K(1)⋯B(1A) 3.185(3), K(1)⋯C(15) 3.318(4), K(1)⋯C(5) 3.587(6), P(1)–C(1) 1.733(3), Si(1)–C(1) 1.833(3), Si(2)–C(1) 1.829(2), P(1)–B(1) 1.933(3); C(1)–K(1)⋯B(1) 59.48(7), B(1)⋯K(1)⋯B(1A) 85.32(10), N(1)–K(1)–N(2) 62.82(6), P(1)–C(1)–Si(1) 117.72(14), P(1)–C(1)–Si(2) 120.44(15), Si(1)–C(1)–Si(2) 116.05(13). Symmetry operator: (A) $1 - x, 1 - y, z$.

bond lengths and angles. Each potassium cation is coordinated by the carbanion centre and an η^2 -BH₃ group of one ligand to give a pseudo-four-membered chelate ring and by an η^1 -BH₃ group from the second ligand in the dimer. Thus, the phosphine–borane-stabilised carbanion ligands in **2b** simultaneously chelate one metal centre and bridge the two symmetry-related metal centres *via* $\mu_2, \eta^2: \eta^1$ -BH₃ contacts (binding mode **III**) to give a central K₂(BH₃)₂ rhombus. The coordination sphere of each potassium cation is completed by the two nitrogen atoms of a molecule of tmeda and by two short K⋯Me contacts, one to one of the SiMe₃ groups of the carbanion ligand and the other to one of the NMe₂ groups of the tmeda co-ligand.

The [(Me₃Si)₂{Me₂P(BH₃)₂}C][−] ligand is isoelectronic with the well known [(Me₃Si)₃C][−] carbanion and so it is instructive to compare the structures of **2** and **2b** with those of the isoelectronic analogues [(Me₃Si)₃C]K_∞ (**3**)¹¹ and [(Me₃Si)₃C]K(tmeda) (**4**).¹² Whereas **2** crystallises with a complex two-dimensional sheet structure, **3** crystallises as an infinite one-dimensional polymer consisting of alternating potassium cations and planar carbanions, in which each potassium cation is further coordinated by six short, agostic-type K⋯Me–Si contacts, three to each adjacent carbanion. Formation of the tmeda adduct **2b** results in deaggregation from the sheet structure of **2** to a BH₃-bridged dimer; in contrast, the tmeda adduct **4** crystallises as a zigzag polymer in which each potassium cation is coordinated solely by two adjacent carbanion centres and the two nitrogen atoms of the tmeda co-ligand. These structural differences are clearly related to the ability of the BH₃ group in the [(Me₃Si)₂{Me₂P(BH₃)₂}C][−] ligand to coordinate to the alkali metal cations.



Treatment of **2** with one equivalent of the tridentate ligand pmdeta followed by crystallisation from cold toluene yields the complex [(Me₃Si)₂{Me₂P(BH₃)₂}C]K(pmdeta)₂ (**2c**) as colourless blocks. The molecular structure of **2c** is shown in Fig. 4, along with selected bond lengths and angles. Compound **2c** crystallises as discrete dimers with crystallographic C₂ symmetry; each potassium cation is coordinated by the carbanion centre and an η^1 -BH₃ group of one ligand and by an η^2 -BH₃ group of the second ligand in the dimer. Thus, each ligand both chelates one potassium cation and bridges the two symmetry equivalent potassium cations in the dimer *via* $\mu_2, \eta^2: \eta^1$ -BH₃ interactions. The coordination sphere of each potassium ion is completed by the three nitrogen atoms of the pmdeta co-ligands and by two short K⋯Me contacts, one to a SiMe₃ group and one to a methyl group of the pmdeta co-ligand. Surprisingly, coordination of the tridentate ligand pmdeta does not lead to further deaggregation beyond a dimer; the coordination number of the potassium ions in **2b** merely increases by one in **2c** to accommodate the extra donor atom of the co-ligand.

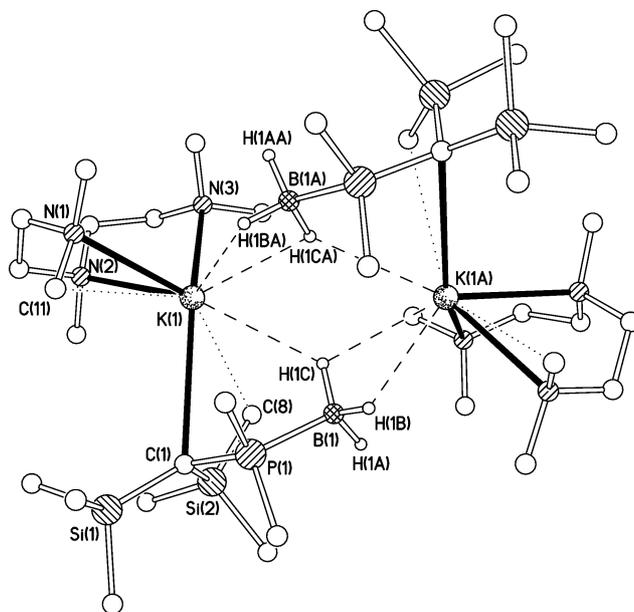


Fig. 4 Molecular structure of **2c** with H atoms bonded to carbon omitted for clarity. Selected bond lengths (Å) and angles (°): K(1)–C(1) 3.440(3), K(1)–N(1) 2.910(3), K(1)–N(2) 2.939(2), K(1)–N(3) 2.916(3), K(1)–H(1C) 3.00(4), K(1)–H(1CA) 2.84(4), K(1)–H(1BA) 2.90(3), K(1)⋯B(1) 3.812(4), K(1)⋯B(1A) 3.261(3), K(1)⋯C(11) 3.360(4), K(1)⋯C(8) 3.534(4), P(1)–C(1) 1.742(2), Si(1)–C(1) 1.849(2), Si(2)–C(1) 1.848(3), P(1)–B(1) 1.946(3); C(1)–K(1)⋯B(1) 51.88(6), B(1)⋯K(1)⋯B(1A) 76.90(9), N(1)–K(1)–N(2) 61.95(7), N(2)–K(1)–N(3) 62.51(7), P(1)–C(1)–Si(1) 118.42(14), P(1)–C(1)–Si(2) 114.04(13), Si(1)–C(1)–Si(2) 115.06(12). Symmetry operator: (A) $1 - x, y, 3/2 - z$.

In contrast, treatment of **2** with 12-crown-4 yields the separated ion pair $[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}][\text{K}(12\text{-crown-4})_2]$ (**2d**) after crystallisation from cold diethyl ether, independent of the ratio of **2** to the crown ether. The crystallographic results for **2d**, obtained from a small crystal of poor quality, are of low precision, with disorder of one crown ligand, and so a detailed analysis of bond lengths and angles is not appropriate; however, the gross structural features are clear (Fig. 5). The potassium cation in **2d** is coordinated by the oxygen atoms of two molecules of 12-crown-4 in an approximately square antiprismatic geometry. The carbanion centre is essentially planar [sum of angles at C(1) = 358.2°] and there are no short contacts between the phosphine–borane-stabilised carbanion and the potassium ion.

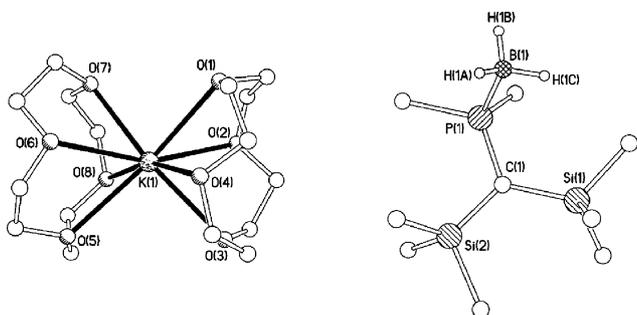


Fig. 5 Structure of **2d**.

There is remarkably little difference in the K–C distances in compounds **2**, **2a** and **2b** [3.018(5)/3.001(5), 2.998(2)/2.974(2), and 3.107(3) Å, respectively]; however, the K–C distance in **2c** [3.440(3) Å] is significantly longer, possibly due to the increased coordination number of the potassium ion and the increased steric compression in this compound. The K–C distances in **2a** and **2b** lie in the typical range for such contacts; for comparison, the K–C distances in $[(\text{Me}_3\text{Si})_3\text{C}]\text{K}$ are 3.090(11) and 3.104(1) Å,¹¹ whereas the K–C distances in $[(\text{Me}_3\text{Si})_2\text{CH}]\text{K}(\text{OMeBu}')$ are 2.987 and 3.012 Å.¹³ In all four compounds in which there is a distinct K–C contact (**2**, **2a**, **2b** and **2c**) the carbanion centres are distinctly pyramidal; the sum of angles within the PCSi_2 skeleton varies only very slightly, falling between 347.5 (**2b**) and 354.2° (**2c**).

We have previously reported the synthesis and solid state structure of the caesium complex $[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{Cs}(\text{pmdeta})_2$ (**5**)⁵ and the synthesis and structural characterisation of the corresponding potassium dimer (**2c**) is described above. During the course of the present study we have also isolated the sodium and rubidium analogues of **2c** and **5**, enabling a detailed investigation into how cation size affects structural preference. Thus, we have prepared the homologous series of compounds $[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{M}(\text{pmdeta})_n$ [$\text{M} = \text{Na}$ (**6**), $n = 1$; $\text{M} = \text{K}$ (**2c**), Rb (**7**), Cs (**5**), $n = 2$]; we were unable to isolate the corresponding lithium derivative as single crystals due to its extremely high solubility, even in the very poor solvent hexamethyldisiloxane.

Compound **6** is isolated from cold toluene as colourless blocks suitable for X-ray crystallography; the molecular structure of **6** is shown in Fig. 6, along with selected bond lengths and angles. Compound **6** crystallises as discrete monomers in which the sodium ion is coordinated by the carbanion centre and an $\eta^2\text{-BH}_3$ group of the phosphine–borane-stabilised carbanion to give

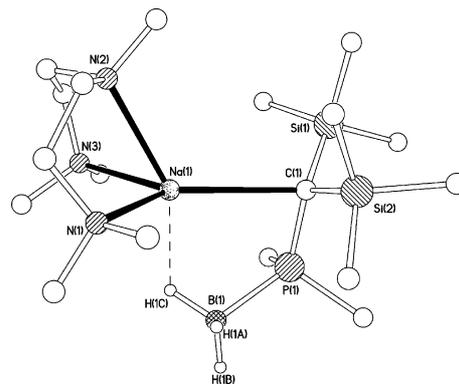


Fig. 6 Molecular structure of **6** with H atoms bonded to carbon omitted for clarity. Selected bond lengths (Å) and angles (°): Na(1)–C(1) 2.7700(17), Na(1)–H(1C) 2.32(2), Na(1)···B(1) 2.845(2), Na(1)–N(1) 2.5782(16), Na(1)–N(2) 2.5122(15), Na(1)–N(3) 2.5832(16), P(1)–C(1) 1.7526(16), P(1)–B(1) 1.935(2), Si(1)–C(1) 1.8372(16), Si(2)–C(1) 1.8401(17); N(1)–Na(1)–N(2) 72.85(5), N(2)–Na(1)–N(3) 72.22(5), P(1)–C(1)–Si(1) 118.52(9), P(1)–C(1)–Si(2) 114.85(9), Si(1)–C(1)–Si(2) 114.23(8).

a pseudo-four-membered chelate ring. The coordination sphere of the sodium ion is completed by the three nitrogen atoms of the *pmdeta* co-ligand; there are no short contacts between the sodium ion and methyl groups from either ligand.

The Na–C distance of 2.7700(17) Å is rather long for this type of contact, which typically falls in the range 2.48–2.55 Å;¹⁴ for example, the Na–C distance in the THF adduct $[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{Na}(\text{THF})_2 \cdot 0.5\text{PhMe}$ is 2.640(3) Å,⁵ itself rather long, whereas the Na–C distance in $[(\text{Me}_3\text{Si})_2\text{CH}]\text{Na}$ is 2.555(10) Å.¹⁵ The Na–N distances in **6** are typical of this type of contact.

In contrast to the monomeric compound **6**, the heavier alkali metal homologues **2c**, **7**, and **5** are dimeric in the solid state. Crystals of **7** suitable for X-ray crystallography were obtained from cold toluene; the molecular structure of **7** is shown in Fig. 7, along with selected bond lengths and angles. In view of the significant differences in ionic radii between the metals K, Rb, and Cs [1.51, 1.61, 1.74 Å, respectively, for eight-coordination],¹⁶ there is remarkably little structural variation between these compounds. The gross structural features of **2c**, **7**, and **5** are very similar and consist of $\mu_2\text{-BH}_3$ -bridged C_2 -symmetric dimers for **2c** and **7** and centrosymmetric dimers for **5** in which the phosphine–borane-stabilised carbanions adopt binding mode **III**. Compounds **7** and **2c** are isomorphous and essentially isostructural; the potassium centre in **2c** is coordinated by the carbanion centre, one η^1 - and one $\eta^2\text{-BH}_3$ group, the three nitrogen atoms of the *pmdeta* co-ligand and two short $\text{K} \cdots \text{Me}$ contacts, one to an SiMe_3 group and one to the *pmdeta* co-ligand. The rubidium ion in **7** is coordinated by the phosphine–borane-stabilised carbanion and by the *pmdeta* co-ligand in the same manner as the potassium ion in **2c**; however, due to the increased ionic radius of rubidium compared to potassium, there are additional short contacts between the rubidium ion and three further methyl groups from the *pmdeta* ligand and one methyl substituent from the PMe_2 group, giving the rubidium ion a coordination number of 13. The coordination sphere of the caesium ion in **5** consists of the carbanion centre, one η^1 - and one $\eta^3\text{-BH}_3$ contact, the three nitrogen atoms of the *pmdeta* co-ligand and six short $\text{Me} \cdots \text{Cs}$ contacts. Thus, the increased ionic radius

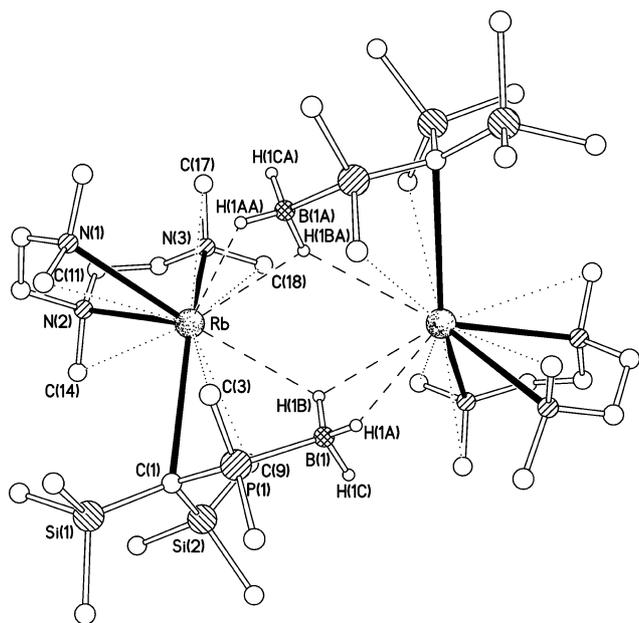


Fig. 7 Molecular structure of **7** with H atoms bonded to carbon omitted for clarity. Selected bond lengths (Å) and angles (°): Rb–C(1) 3.477(4), Rb–H(1B) 3.14(5), Rb–H(1AA) 3.04(5), Rb–H(1BA) 2.88(5), Rb...B(1) 3.903(5), Rb...B(1A) 3.338(5), Rb–N(1) 3.022(4), Rb–N(2) 3.049(3), Rb–N(3) 3.052(4), Rb...C(3) 3.770(4), Rb...C(9) 3.551(5), Rb...C(11) 3.476(5), Rb...C(14) 3.606(4), Rb...C(17) 3.745(8), Rb...C(18) 3.716(7), P(1)–C(1) 1.742(3), Si(1)–C(1) 1.837(4), Si(2)–C(1) 1.846(4), P(1)–B(1) 1.941(5); C(1)–Rb...B(1) 50.72(9), B(1)...Rb...B(1A) 78.16(15), N(1)–Rb–N(2) 59.47(11), N(2)–Rb–N(3) 59.33(10), P(1)–C(1)–Si(1) 118.3(2), P(1)–C(1)–Si(2) 114.15(19), Si(1)–C(1)–Si(2) 115.73(18). Symmetry operator: (A) $1 - x, y, 3/2 - z$.

on going from potassium to rubidium and caesium ions results in an increase in coordination number from nine in **2c** to 13 in **7** and **14** in **5**.

The K–C and Cs–C distances of 3.440(3) and 3.549(4) Å in **2c** and **5**, respectively, are longer than are typically found for these types of contacts, whereas the Rb–C distance of 3.477(4) Å in **7** is unexceptional, albeit falling at the longer end of the typical range of Rb–C contacts.¹⁴ For example, the Rb–C distance in $[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{Rb}]_\infty$ is 3.154(3) Å,⁵ whereas the Rb–C distances in $[(\text{Me}_3\text{Si})_2\text{CH}\text{Rb}(\text{pmdeta})]_2$ are 3.361(9) and 3.485(8) Å.¹⁵ The bond lengths and angles within the central CSi_2P core of the ligands in **2c**, **6**, **7**, and **5** differ only very slightly; indeed, the sum of angles within the CSi_2P skeleton ranges from 347.52° (**2c**) to just 350.9° (**5**).

Conclusions

The solid state structures of the potassium complexes **2**, **2a**, **2b**, **2c**, and **2d** show a marked dependence on the denticity of the respective co-ligand; greater denticity leading to increased deaggregation, as expected. In each case, with the exception of the separated ion pair complex **2d**, B–H...K contacts remain an important feature of the structures, effectively competing with contacts between the potassium ions and the carbanion centres. Although solid state structures can only be a guide to the nature of such species in solution, this suggests that the reactions of phosphine–borane-stabilised carbanions may be significantly

affected by the presence of Lewis base donors such as THF, tmeda or the chiral diamine (–)-sparteine.

In contrast, variation of the ionic radius of the metal centre itself has relatively little effect on solid state structure; whilst the sodium complex **6** is monomeric in the solid state, the potassium, rubidium and caesium complexes **2c**, **7** and **5** crystallise as μ_2 - BH_3 -bridged centrosymmetric dimers.

Experimental

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Methylcyclohexane, toluene, light petroleum (bp 40–60 °C), THF and diethyl ether were distilled under nitrogen from potassium or sodium/potassium alloy. THF was stored over activated 4A molecular sieves; all other solvents were stored over a potassium film. Deuterated toluene was distilled from potassium and was deoxygenated by three freeze–pump–thaw cycles and stored over activated 4A molecular sieves. tmeda and pmdeta were distilled under nitrogen from CaH_2 ; 12-crown-4 was dried over activated 4A molecular sieves. The compounds MeNa ,¹⁷ $(\text{Me}_3\text{Si})_2\text{CHPMe}_2(\text{BH}_3)$,⁵ $[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{K}]_\infty$ (**2**),⁵ and $[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{Rb}]_\infty$ ⁵ were prepared by previously published procedures. All other compounds were used as supplied; Bu^nLi was supplied by Aldrich as a 2.5 M solution in hexane.

^1H , $^{11}\text{B}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ spectra were recorded on a Jeol Lambda500 spectrometer operating at 500.16, 160.35, 125.65, and 202.35 MHz, respectively; ^1H , and ^{13}C chemical shifts are quoted in ppm relative to tetramethylsilane, ^{11}B and ^{31}P chemical shifts are quoted in ppm relative to external $\text{BF}_3(\text{OEt}_2)$ and 85% H_3PO_4 , respectively. Elemental analyses were obtained by the Elemental Analysis Service of London Metropolitan University.

$[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{K}\cdot 0.5(\text{THF})_\infty$ (**2a**)

A solution of $[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{K}]_\infty$ (**2**) (0.90 g, 3.29 mmol) in methylcyclohexane (10 ml) containing two to three drops of THF was cooled to 5 °C for several hours. Colourless blocks of **2a** suitable for X-ray crystallography deposited. The THF co-ligands are only weakly held and are readily lost under vacuum; therefore, elemental analyses and NMR spectra for **2a** are essentially identical to those of unsolvated **2**. Isolated yield of crystalline **2a** 0.41 g, 41%. $^1\text{H}\{^{11}\text{B}\}$ NMR (d_8 -toluene, 25 °C): δ 0.30 (s, 18H, SiMe_3), 0.53 (d, $J_{\text{PH}} = 14.4$ Hz, 3H, BH_3), 1.37 (d, $J_{\text{PH}} = 9.5$ Hz, 6H, PMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_8 -toluene, 25 °C): δ 8.58 (SiMe_3), 23.18 (d, $J_{\text{PC}} = 35.1$ Hz, PMe_2). $^{11}\text{B}\{^1\text{H}\}$ NMR (d_8 -toluene, 25 °C): δ –27.2 (d, $J_{\text{PB}} = 99.4$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (d_8 -toluene, 25 °C): δ –5.9 (q, $J_{\text{PB}} = 99.4$ Hz).

$[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{K}(\text{tmeda})_2$ (**2b**)

To a solution of $[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{K}]_\infty$ (**2**) (0.38 g, 1.40 mmol) in toluene (20 ml) was added tmeda (0.21 ml, 1.40 mmol). The resulting solution was stirred for 30 min, filtered and the filtrate was cooled to –30 °C. After several hours colourless block crystals of **2b** suitable for X-ray crystallography deposited. Isolated yield 0.33 g, 61%. Anal. calc. for $\text{C}_{15}\text{H}_{43}\text{BKN}_2\text{PSi}_2$ (388.58): C 46.37, H 11.15, N 7.21%. Found: C 46.03, H 10.98, N 7.01%. $^1\text{H}\{^{11}\text{B}\}$ NMR (d_8 -toluene, 25 °C): δ 0.30 (s, 18H, SiMe_3), 0.65 (d, $J_{\text{PH}} = 14.1$ Hz, 3H, BH_3), 1.35 (d,

$J_{\text{PH}} = 9.5$ Hz, 6H, PMe_2), 1.95 (s, 4H, NCH_2), 1.97 (s, 12H, NMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_8 -toluene, 25 °C): δ 8.55 (SiMe_3), 17.98 (Si_2CP), 23.21 (d, $J_{\text{PC}} = 34.6$ Hz, PMe_2), 46.65 (NMe_2), 58.38 (NCH_2). $^{11}\text{B}\{^1\text{H}\}$ NMR (d_8 -toluene, 25 °C): δ -27.2 (d, $J_{\text{PB}} = 97.9$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (d_8 -toluene, 25 °C): δ -5.0 (q, $J_{\text{PB}} = 97.9$ Hz).

$[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{K}(\text{pmdeta})_2$ (**2c**)

To a solution of $[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{K}_\infty$ (**2**) (0.26 g, 0.96 mmol) in toluene (10 ml) was added pmdeta (0.20 ml, 0.96 mmol). The resulting solution was cooled to -30 °C for several hours to yield colourless blocks of **2c** suitable for X-ray crystallography. Isolated yield 0.20 g, 47%. Anal. calc. for $\text{C}_{18}\text{H}_{50}\text{BK}_2\text{N}_3\text{PSi}_2$ (445.66): C 48.51, H 11.31, N 9.43%. Found: C 48.41, H 11.15, N 9.34%. $^1\text{H}\{^1\text{B}\}$ NMR (d_8 -toluene, 25 °C): δ 0.34 (s, 18H, SiMe_3), 0.81 (d, $J_{\text{PH}} = 13.4$ Hz, 3H, BH_3), 1.40 (d, $J_{\text{PH}} = 9.2$ Hz, 6H, PMe_2), 1.89 (s, 3H, NMe), 1.92 (m, 8H, NCH_2), 1.94 (s, 12H, NMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_8 -toluene, 25 °C): δ 8.75 (SiMe_3), 16.44 (Si_2CP), 23.41 (d, $J_{\text{PC}} = 34.2$ Hz, PMe_2), 43.02 (NMe), 46.34 (NMe_2), 56.55 (NCH_2), 58.23 (NCH_2). $^{11}\text{B}\{^1\text{H}\}$ NMR (d_8 -toluene, 25 °C): δ -27.1 (d, $J_{\text{PB}} = 96.2$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (d_8 -toluene, 25 °C): δ -3.9 (q, $J_{\text{PB}} = 96.2$ Hz).

$[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{K}(\text{12-crown-4})_2$ (**2d**)

To a solution of $[(\text{Me}_3\text{Si})_2\{\text{Me}_2(\text{H}_3\text{B})\text{P}\}\text{C}]\text{K}$ (0.41 g, 1.62 mmol) in toluene (30 ml) was added 12-crown-4 (0.51 ml, 3.23 mmol) and this solution was stirred for 1 h. Solvent was removed *in vacuo* to yield a pale brown oil which was washed with cold (0 °C) light petroleum (3 × 20 ml) to give a light tan solid. Recrystallisation of this solid from cold (-30 °C) diethyl ether gave **2d** as colourless blocks. Isolated yield 0.63 g, 62%. Anal. calc. for $\text{C}_{25}\text{H}_{59}\text{BKO}_8\text{PSi}_2$ (624.78): C 48.06, H 9.52%. Found: C 47.97, H 9.44%. ^1H NMR (d_8 -THF, 25 °C): δ -0.01 (s, 18H, SiMe_3), 1.09 (d, $J_{\text{PH}} = 13.3$ Hz, 6H, PMe_2), 3.64 (s, 32H, 12-crown-4). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_8 -THF,

25 °C): δ 7.20 (d, $J_{\text{PC}} = 2.9$ Hz, SiMe_3), 14.78 (Si_2CP), 23.35 (d, $J_{\text{PC}} = 34.1$ Hz, PMe_2), 68.29 (12-crown-4). $^{11}\text{B}\{^1\text{H}\}$ NMR (d_8 -THF, 25 °C): δ -30.6 (d, $J_{\text{PB}} = 86.6$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (d_8 -THF, 25 °C): δ -4.7 (q, $J_{\text{PB}} = 86.6$ Hz).

$[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{Na}(\text{pmdeta})$ (**6**)

A solution of $(\text{Me}_3\text{Si})_2\text{CHPMe}_2(\text{BH}_3)$ (2.13 g, 9.09 mmol) in cold (-10 °C) diethyl ether (30 ml) was added to MeNa (0.50 g, 13.2 mmol). The mixture was allowed to attain room temperature and was stirred for 16 h. The slightly turbid solution was filtered and the solvent was removed *in vacuo* from the filtrate to yield a colourless oil. This oil was dissolved in toluene (20 ml) and pmdeta (1.9 ml, 9.09 mmol) was added. The solution was cooled to -30 °C for several hours to yield colourless blocks of **6**. Isolated yield 2.54 g, 65.1%. Anal. calc. for $\text{C}_{18}\text{H}_{50}\text{BN}_3\text{NaPSi}_2$ (429.56): C 50.33, H 11.73, N 9.78%. Found: C 50.21, H 11.63, N 9.70%. ^1H NMR (d_8 -toluene, 25 °C): δ 0.36 (s, 18H, SiMe_3), 1.40 (d, $J_{\text{PH}} = 9.2$ Hz, 6H, PMe_2), 1.88 (m, 8H, NCH_2), 1.96 (s, 3H, NMe), 1.97 (s, 12H, NMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (d_8 -toluene, 25 °C): δ 8.68 (SiMe_3) [quaternary carbon not observed], 22.53 (d, $J_{\text{PC}} = 33.6$ Hz, PMe_2), 44.73 (NMe), 46.76 (NMe_2), 55.97 (NCH_2), 58.36 (NCH_2). $^{11}\text{B}\{^1\text{H}\}$ NMR (d_8 -toluene, 25 °C): δ -30.7 (d, $J_{\text{PB}} = 95.2$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (d_8 -toluene, 25 °C): δ -3.3 (q, $J_{\text{PB}} = 95.2$ Hz).

$[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{Rb}(\text{pmdeta})_2$ (**7**)

To a solution of $[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{Rb}_\infty$ (0.41 g, 1.29 mmol) in toluene (20 ml) was added pmdeta (0.27 ml, 1.92 mmol). Upon cooling to -30 °C for several hours, colourless blocks of **7** suitable for X-ray crystallography deposited. Isolated yield 0.37 g, 58%. Anal. calc. for $\text{C}_{18}\text{H}_{50}\text{BN}_3\text{PRbSi}_2$ (492.04): C 43.94, H 10.24, N 8.54%. Found: C 44.03, H 10.15, N 8.65%. $^1\text{H}\{^1\text{B}\}$ NMR (d_8 -toluene, 25 °C): δ 0.34 (s, 18H, SiMe_3), 0.85 (d, $J_{\text{PH}} = 13.4$ Hz, 3H, BH_3), 1.40 (d, $J_{\text{PH}} = 9.2$ Hz, 6H, PMe_2), 1.92

Table 1 Crystallographic data for **2a**, **2b**, **2c**, **2d**, **6** and **7**

Compound	2a	2b	2c	2d	6	7
Formula	$\text{C}_{22}\text{H}_{62}\text{B}_2\text{K}_2\text{O}_2\text{P}_2\text{Si}_4$	$\text{C}_{30}\text{H}_{86}\text{B}_2\text{K}_2\text{N}_4\text{P}_2\text{Si}_4$	$\text{C}_{36}\text{H}_{100}\text{B}_2\text{K}_2\text{N}_6\text{P}_2\text{Si}_4$	$\text{C}_{25}\text{H}_{59}\text{BKO}_8\text{PSi}_2$	$\text{C}_{18}\text{H}_{50}\text{BN}_3\text{NaPSi}_2$	$\text{C}_{36}\text{H}_{100}\text{B}_2\text{N}_6\text{P}_2\text{Rb}_2\text{Si}_4$
<i>M</i>	616.8	777.2	891.3	624.8	429.6	984.1
Cryst. size/mm	0.54 × 0.34 × 0.30	0.50 × 0.40 × 0.20	0.45 × 0.30 × 0.20	0.10 × 0.08 × 0.05	0.50 × 0.50 × 0.40	0.45 × 0.40 × 0.32
Cryst. syst.	Triclinic	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P2_12_12_1$	$P2_1/c$	$C2/c$
<i>a</i> /Å	12.614(2)	8.7353(6)	21.817(6)	12.526(8)	9.1995(10)	22.233(6)
<i>b</i> /Å	13.3311(11)	11.3832(8)	9.323(4)	15.475(9)	15.3391(17)	9.272(4)
<i>c</i> /Å	14.5257(16)	13.5668(10)	29.024(7)	18.411(11)	20.149(2)	29.117(10)
<i>a</i> /°	115.522(6)	79.174(1)				
<i>β</i> /°	113.770(11)	79.418(1)	102.034(16)		99.899(2)	102.86(3)
<i>γ</i> /°	93.432(8)	71.435(1)				
<i>V</i> /Å ³	1934.9(4)	1244.90(15)	5774(3)	3569(4)	2801.0(5)	5851(4)
<i>Z</i>	2	1	4	4	4	4
μ/mm^{-1}	0.465	0.374	0.330	0.299	0.207	1.837
Trans. coeff. range	0.787–0.873	0.835–0.929	0.866–0.937	0.971–0.985	0.907–0.922	0.463–0.556
Reflns. measd.	24649	9061	64754	21325	24703	44061
Unique reflns.	7550	4351	5038	5086	6788	5129
<i>R</i> _{int}	0.031	0.017	0.073	0.089	0.030	0.041
Reflns. with $F^2 > 2\sigma$	5849	4098	4290	4632	5163	4294
<i>R</i> (on F , $F^2 > 2\sigma$)	0.037	0.052	0.050	0.113	0.042	0.046
<i>R</i> _w (on F^2 , all data)	0.118	0.119	0.143	0.271	0.107	0.136
Goodness of fit	1.132	1.152	1.086	1.078	1.068	1.101
Min, max electron	0.35, -0.45	0.86, -0.57	0.78, -0.36	0.72, -0.52	0.36, -0.23	1.36, -0.61
Density/e Å ⁻³						

(s, 3H, NMe), 1.98 (s, 12H, NMe₂), 2.01 (m, 4H, NCH₂), 2.04 (m, 4H, NCH₂). ¹³C{¹H} NMR (*d*₈-toluene, 25 °C): δ 8.70 (SiMe₃), 16.45 (Si₂CP), 23.65 (d, *J*_{PC} = 33.6 Hz, PMe₂), 45.75 (NMe), 46.45 (NMe₂), 57.12 (NCH₂), 58.43 (NCH₂). ¹¹B{¹H} NMR (*d*₈-toluene, 25 °C): δ -26.5 (d, *J*_{PB} = 96.2 Hz). ³¹P{¹H} NMR (*d*₈-toluene, 25 °C): δ -4.3 (q, *J*_{PB} = 96.2 Hz).

Crystal structure determinations of 2a–d, 6 and 7

Measurements for **2a–c**, **6** and **7** were made at 150 K on a Nonius KappaCCD or Bruker SMART CCD diffractometer using graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å), whereas measurements for **2d** were made at 120 K on a Bruker APEX2 diffractometer using silicon-monochromated synchrotron radiation ($\lambda = 0.6905$ Å). For all compounds cell parameters were refined from the observed positions of all strong reflections in each data set. Intensities were corrected semi-empirically for absorption, based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and were refined on *F*² values for all unique data. Table 1 gives further details. All non-hydrogen atoms were refined anisotropically, except for very small disorder components, and H atoms were constrained with a riding model, except those bound to boron, which were freely refined; *U*(H) was set at 1.2 (1.5 for methyl groups) times *U*_{eq} for the parent atom. Disorder was resolved for one ligand in **2a** (with <5% occupancy, and only the P and Si atoms included for the minor component), one methyl group of **2b**, and one complete 12-crown-4 ligand of **2d**. The dimeric molecules of **2b**, **2c**, and **7** all lie on crystallographic inversion centres. The crystal of **2d** was an inversion twin. Programs were Bruker APEX2 (control) and SAINT (integration), Nonius COLLECT and associated programs, and SIR97 and SHELXTL for structure solution, refinement, and molecular graphics.¹⁸

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b708279g

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