Synthesis and structural characterisation of alkali metal complexes of heteroatom-stabilised 1,4- and 1,6-dicarbanions†

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A straightforward Peterson olefination reaction between either $[\{(Me_2PhSi)_3C\}Li(THF)]$ or *in situ*-generated $[(Me_3Si)_2\{Ph_2P(BH_3)\}CLi(THF)_n]$ and paraformaldehyde gives the alkenes $(Me_2PhSi)_2C{=}CH_2$ (**1**) and $(Me_3Si)\{Ph_2P(BH_3)\}C{=}CH_2$ (**2**), respectively, in good yield. Ultrasonic treatment of **1** with lithium in THF yields the lithium complex $[\{(Me_2PhSi)_2C(CH_2)\}Li(THF)_n]_2$ (**3**), which reacts *in situ* with one equivalent of $KOBu^t$ in diethyl ether to give the potassium salt $[\{(Me_2PhSi)_2C(CH_2)\}K(THF)]_2$ (**4**). Similarly, ultrasonic treatment of **2** with lithium in THF yields the lithium complex $[[\{Ph_2P(BH_3)\}(Me_3Si)C(CH_2)]Li(THF)_3]_2.2THF$ (**5**). The bis(phosphine-borane) $[(Me_3Si)\{Me_2(H_3B)P\}CH(Me_2Si)(CH_2)]_2$ (**6**) may be prepared by the reaction of $[Me_2P(BH_3)CH(SiMe_3)]Li$ with half an equivalent of $ClSiMe_2CH_2CH_2SiMe_2Cl$ in refluxing THF. Metalation of **6** with two equivalents of MeLi in refluxing THF yields the lithium complex $[[\{Me_2P(BH_3)\}(Me_3Si)C\{(SiMe_2)(CH_2)\}]Li(THF)_3]_2$ (**9**), whereas metalation with two equivalents of MeK in cold diethyl ether yields the potassium complex $[[\{Me_2P(BH_3)\}(Me_3Si)C\{(SiMe_2)(CH_2)\}]_2K_2(THF)_4]_\infty$ (**10**) after recrystallisation. X-Ray crystallography shows that, whereas the lithium complex **5** crystallises as a discrete molecular species, the potassium complexes **4** and **10** crystallise as sheet and chain polymers, respectively.

Introduction

Sterically demanding bis- and tris(triorganosilyl)methyl ligands have been used extensively over the last three decades for the synthesis of a wide range of highly unusual main group, transition metal and lanthanide complexes.[1] The range of such ligands has recently been extended through the incorporation of peripheral donor functionalities, enabling the formation of chelate rings in their complexes. For example, ligands of the type $(Me_3Si)_2(Me_2XSi)C^-$ and $(Me_3Si)(Me_2XSi)CH^-$ [X = *e.g.* OMe, NMe_2, PPh_2, CH_2PPh_2, 2-C_5H_4N] have been used for the stabilisation of various novel complexes, such as (i) the first samarium(II) dialkyl,[2] (ii) rare homoleptic heavier group 2 dialkyls,[3] (iii) an unusual Ni(I) alkyl[4] and (iv) a number of polynuclear alkali metal and lanthanide complexes.[5]

We recently expanded this range of compounds with the synthesis of two new oxygen-functionalised *dicarbanions*, $[O(SiMe_2)C(SiMe_3)_2]_2^{2-}$ and $[CH_2(SiMe_2)C(SiMe_3)(SiMe_2OMe)]_2^{2-}$, as their alkali metal salts.[6] We subsequently demonstrated that these salts are excellent ligand transfer reagents for the synthesis of dialkyllanthanide(II) and -lanthanide(III) complexes.[7] In related chemistry, we have also shown that phosphine-borane-stabilised dicarbanions are readily accessible and that the incorporation of dialkylphosphine-borane groups adjacent to a carbanion centre leads to new binding modes in which $B{-}H\cdots M$ contacts dominate.[8]

This paper extends further this set of functionalised ligands with the synthesis and structural characterisation of a series of alkali metal complexes of three new dicarbanion ligands: a silicon-stabilised 1,4-dicarbanion, a phosphine-borane-stabilised 1,4-dicarbanion and a phosphine-borane-stabilised 1,6-dicarbanion.

Results and discussion

The 1,1-disilyl-substituted alkene $(Me_2PhSi)_2C{=}CH_2$ (**1**) has previously been synthesised *via* a number of rather complex or low-yielding routes, including (i) the Wittig reaction between bis(dimethylphenylsilyl)ketone and methylenetriphenylphosphirane,[9] (ii) the dehydrobromination of 1-bromo-1,1-bis(dimethylphenylsilyl)ethane,[10] (iii) the photolytically induced, cobalt-catalysed disproportionation of dimethylphenylsilylethene,[11] and (iv) the reaction between two equivalents of PhMgBr and 2,2,4,4-tetramethyl-3-methylene-1,5-dioxa-2,4-disilacycloheptane.[12] We find that **1** may be accessed more simply *via* the Peterson olefination of the known lithium alkyl $[\{(Me_2PhSi)_3C\}Li(THF)]$[13] with paraformaldehyde (Scheme 1). A simple aqueous work-up, followed by removal of the $(Me_2PhSi)_2O$ side-product by distillation at reduced pressure, gives **1** as a colourless oil in good yield.

In related chemistry, we have previously shown that Peterson olefination is favoured over Horner-type olefination in mixed silyl- and phosphine-borane-substituted lithium alkyls of the form $[(R_3Si)\{R_2P(BH_3)\}_nCR_{(2-n)}]Li$.[14] In this regard, the vinylidene phosphine-borane $(Me_3Si)\{Ph_2P(BH_3)\}C{=}CH_2$ (**2**) may be prepared by a straightforward Peterson olefination protocol (Scheme 1): treatment of the phosphine-borane $(Me_3Si)_2CH\{PPh_2(BH_3)\}$ with Bu^nLi in THF gives the lithium

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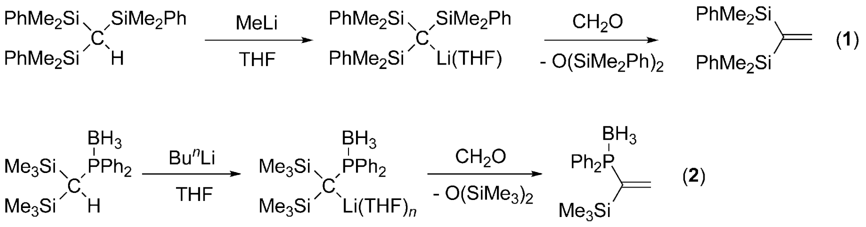


Scheme 1

salt $[(Me_3Si)_2\{Ph_2P(BH_3)\}CLi(THF)_n]$, which reacts *in situ* with paraformaldehyde to give **2** in excellent yield.

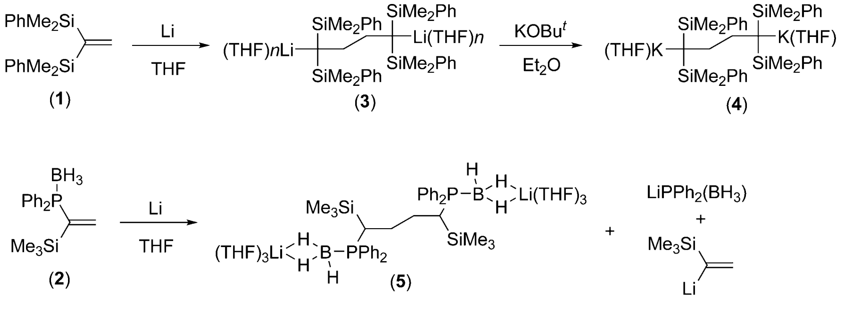
Ultrasonic treatment of **1** with lithium in THF yields the Schlenk dimerisation product $[\{(Me_2PhSi)_2C(CH_2)\}Li(THF)_n]_2$ (**3**). Unfortunately, we were unable to isolate **3** in a suitable form for analysis, attempts at crystallisation consistently yielding a viscous oil; however, **3** undergoes an *in situ* metathesis reaction with one equivalent of $KOBu^t$ in diethyl ether to give the potassium salt $[\{(Me_2PhSi)_2C(CH_2)\}K(THF)]_2$ (**4**) in good yield as an orange powder (Scheme 2). Compound **4** may also be isolated directly from the Schlenk dimerisation of **1** with elemental potassium in DME, although yields from these reactions were consistently lower than those from the metathesis route. Compound **4** is soluble in ether solvents, but is insoluble in hydrocarbons; over a period of several hours **4** reacts with toluene to give benzylpotassium and the free ligand $(Me_2PhSi)_2CH(CH_2)_2CH(SiPhMe_2)_2$. Single crystals of **4** suitable for X-ray crystallography were obtained by crystallisation from cold diethyl ether/*n*-hexane.

Ultrasonic treatment of **2** with an excess of lithium shot in THF yields the 1,4-dicarbanion complex $[[\{Ph_2P(BH_3)\}(Me_3Si)C(CH_2)]Li(THF)_3]_2$ as a reddish-brown oil (Scheme 2), which is soluble in ether solvents, but only slightly soluble in light petroleum. Crystallisation of this oil from methylcyclohexane/THF gives single crystals of the THF solvate $[[\{Ph_2P(BH_3)\}(Me_3Si)C(CH_2)]Li(THF)_3]_2{\cdot}2THF$ (**5**) suitable for X-ray crystallography.

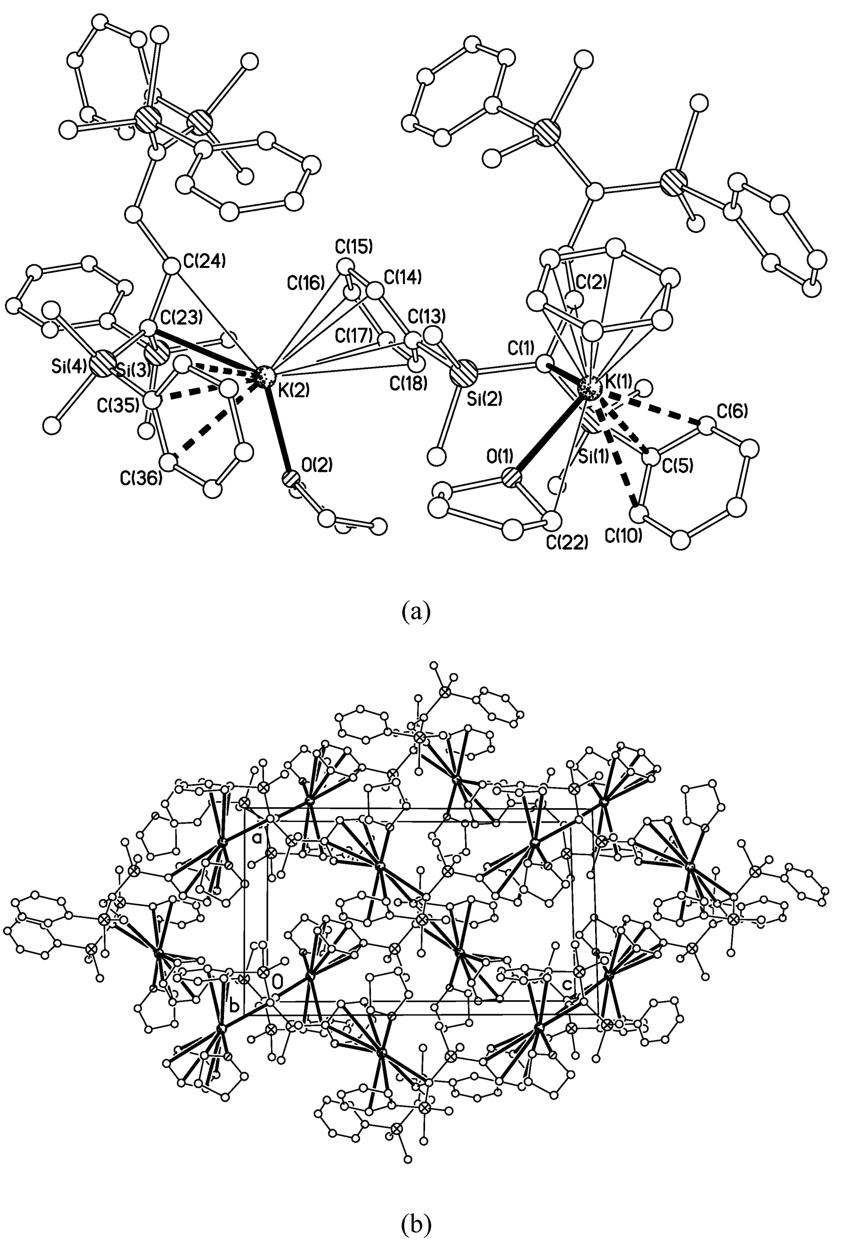
Unfortunately, the reaction between **2** and lithium is not clean under these conditions due to competition between Schlenk dimerisation of the alkene and cleavage of the P–C(alkene) bond and so isolated yields of **5** are rather low. This competing reaction presumably generates the lithium phosphino-borohydride $Li[PPh_2(BH_3)]$ and 1-lithio-vinyl silane, although this latter compound was not identified; the phosphino-borohydride salt was identified from its signal at −31.8 ppm (q, J_{PB} = 31 Hz) in the $^{31}P\{^1H\}$ NMR spectra of the crude reaction mixture [*cf.* −28.8 for the potassium salt $K[PPh_2(BH_3)]$ in THF].[15] We have previously noted that P–C cleavage reactions are competitive with Schlenk dimerisation when (i) the metal is sufficiently reducing, and (ii) the phosphide produced by this side-reaction is sufficiently stabilised. For example, whereas $(Ph_2P)_2C{=}CH_2$ undergoes facile Schlenk dimerisation on treatment with lithium,[16] treatment of this vinylidene phosphine with potassium yields $KPPh_2$ as the major phosphorus-containing product.[17] In contrast, the closely related vinylidene phosphine $(Pr^n{}_2P)_2C{=}CH_2$ undergoes Schlenk dimerisation exclusively when treated with any of the alkali metals Li, Na or K, with no evidence for P–C cleavage.[18] Thus, charge-stabilising phenyl groups favour P–C cleavage over Schlenk dimerisation, whereas the reverse is true for charge-destabilising propyl groups. For **2**, it would appear that the presence of the borane group at phosphorus results in a sufficiently large increase in charge-stabilisation that P–C cleavage is observed even in the presence of lithium, the least reducing of the alkali metals.

Compound **4** crystallises with a complex sheet polymer structure; the structure of **4** is shown in Fig. 1, along with selected bond lengths and angles. The two crystallographically independent potassium ions lie in almost identical, but subtly different, environments: each potassium ion is coordinated by one of the carbanion centres, by a molecule of THF and, in an η^3-manner, by the phenyl ring of an adjacent $SiMe_2Ph$ group. The coordination sphere of each potassium ion is completed by an η^6-interaction with a phenyl ring from a $SiMe_2Ph$ group in a symmetry-equivalent ligand. Thus, the intermolecular $K\cdots Ph$ contacts link the dicarbanion units into an infinite sheet network. In addition, K(1) has short contacts to two methylene carbon atoms, one in the ligand backbone and one in the THF co-ligand [$K(1)\cdots C(2)$ 3.251(2), $K(1)\cdots C(22)$ 3.444(4) Å]; in contrast, K(2) has a single short contact to the methylene carbon atom in the ligand backbone [$K(2)\cdots C(24)$ 3.070(2) Å].

The K(1)–C(1) and K(2)–C(23) distances of 3.016(2) and 3.047(2) Å, respectively, are similar to the K–C distances in the related dicarbanion complex $[[\{(Me_3Si)_2C(SiMe_2)\}_2O]K_2(OEt_2)]_\infty$



Scheme 2



(a)

(b)

Fig. 1 (a) The two centrosymmetric ligands and two independent K$^+$ ions of **4** with H atoms and minor disorder component omitted for clarity; a symmetry-generated phenyl ring is also included to complete the K$^+$ coordination. Selected bond lengths (Å) and angles (°): K(1)–C(1) 3.016(2), K(1)–O(1) 2.706(2), K(1)–C(5) 3.061(2), K(1)–C(6) 3.246(3), K(1)–C(10) 3.292(3), K(1)–C(27)^a 3.537(2), K(1)–C(28)^a 3.284(3), K(1)–C(29)^a 3.111(3), K(1)–C(30)^a 3.152(3), K(1)–C(31)^a 3.352(3), K(1)–C(32)^a 3.535(3), K(1)···C(2) 3.251(2), K(1)···C(22) 3.444(4), K(2)–C(23) 3.047(2), K(2)–C(35) 3.032(3), K(2)–C(36) 3.272(3), K(2)–C(40) 3.187(3), K(2)–C(13) 3.542(3), K(2)–C(14) 3.298(3), K(2)–C(15) 3.123(3), K(2)–C(16) 3.137(3), K(2)–C(17) 3.319(3), K(2)–C(18) 3.512(3), K(2)···C(24) 3.370(2), Si(1)–C(1)–Si(2) 124.80(13), Si(1)–C(1)–C(2) 115.57(16), Si(2)–C(1)–C(2) 119.14(16), Si(3)–C(23)–Si(2) 124.95(13), Si(3)–C(23)–C(24) 118.18(16), Si(4)–C(23)–C(24) 116.05(16); symmetry operator a: *x*, *y*, *z* – 1. (b) The sheet structure of **4**, viewed down the crystallographic *b* axis.

[3.0132(18) and 3.2302(18) Å] and in [$\{(Me_3Si)_2(Me_2MeOSi)C\}K]_\infty$ [3.063(3) and 3.148(3) Å].[6] The K···Ph and K···CH_2 distances lie within the typical range for these types of contact.[19]

The lithium complex **5** crystallises, by contrast, as a discrete, centrosymmetric molecular species with two molecules of THF of crystallisation per molecular unit; the molecular structure of **5** is shown in Fig. 2, along with selected bond lengths and angles. Each lithium ion is coordinated in an η^2-manner by the borane hydrogens and by three molecules of THF. The Li···H distances of 2.13(3) and 1.97(3) Å are similar to those in the closely related propyl-substituted analogue $[[\{Pr^i_2P(BH_3)\}(Me_3Si)C(CH_2)]Li(pmdeta)]_2$ [Li···H 2.05(3) and 1.94(3) Å][8a] and in the ate complex $[(THF)_3Li[(Me_3Si)_2C\{PMe_2(BH_3)\}]_2Li]$[8b] [Li···H 2.03(8)–2.31(6) Å] (pmdeta = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine). There are no short contacts between the lithium ions and the carbanion centres, which are essentially planar [sum of angles at C(1) = 359.98°].

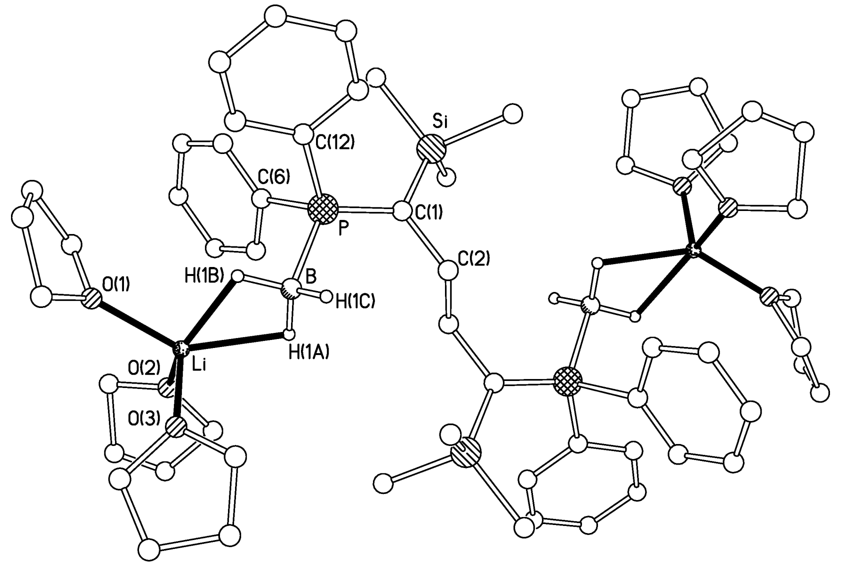
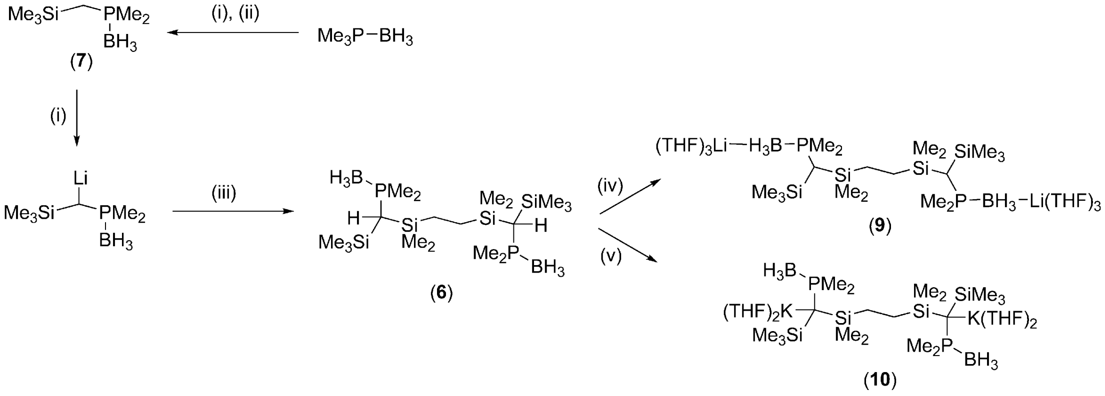


Fig. 2 Molecular structure of **5** with H atoms bonded to carbon and minor disorder components omitted for clarity. Selected bond lengths (Å) and angles (°): Li–H(1A) 2.13(3), Li–H(1B) 1.97(3), Li···B 2.480(5), Li–O(1) 1.989(5), Li–O(2) 1.940(5), Li–O(3) 1.927(5), P–B 1.952(3), P–C(1) 1.711(2), P–C(6) 1.854(2), P–C(12) 1.860(2), Si–C(1) 1.824(2), P–C(1)–Si 122.77(13), P–C(1)–C(2) 118.55(16), Si–C(1)–C(2) 118.66(16).

The bis(phosphine-borane) [(Me$_3$Si){Me$_2$(H$_3$B)P}CH(Me$_2$Si)-(CH$_2$)]$_2$ (**6**) was prepared *via* a two-step synthetic route (Scheme 3). The reaction between *in situ* generated Me$_2$P(BH$_3$)CH$_2$Li and one equivalent of Me$_3$SiCl cleanly gives the silicon-substituted species Me$_2$P(BH$_3$)CH$_2$SiMe$_3$ (**7**). Treatment of **7** with Bu^{n}Li gives the complex [Me$_2$P(BH$_3$)CH(SiMe$_3$)]Li, which reacts *in situ* with half an equivalent of ClSiMe$_2$CH$_2$CH$_2$SiMe$_2$Cl in refluxing THF to give **6** as an oily solid, which consists of an equimolar mixture of the *rac*- and *meso*-diastereomers, along with a small amount of phosphorus-containing impurities. Repeated crystallisation of this oily solid from hot methylcyclohexane yields essentially pure *rac*-**6** as colourless blocks; however, we were unable to obtain a clean sample of the *meso* diastereomer, either by crystallisation or chromatographic methods, samples always containing *rac*-**6**, along with other phosphorus-containing impurities. The configuration of *rac*-**6** was confirmed by X-ray crystallography; the molecular structure of *rac*-**6** is shown in Fig. 3, along with selected bond lengths and angles.

Compound **6** may be considered a dimeric analogue of the mono-basic phosphine-borane {(Me$_2$P(BH$_3$)}(Me$_3$Si)$_2$CH (**8**); we previously reported that **8** undergoes deprotonation readily on treatment with one equivalent of Bu^{n}Li in THF at room temperature.[8b] In contrast, treatment of *rac*-**6** with two equivalents of either Bu^{n}Li or MeLi under the same conditions leads only to incomplete deprotonation. However, complete deprotonation at both sites may be achieved by the reaction of *rac*-**6** with two equivalents of MeLi in THF under reflux for 1 hour (Scheme 3). This yields the lithium complex [[{Me$_2$P(BH$_3$)}(Me$_3$Si)C{(SiMe$_2$)(CH$_2$)}]Li(THF)$_3$]$_2$ (**9**) as an oily solid after removal of the solvent. Although we were unable to grow single crystals of this compound suitable for X-ray crystallography, the identity of **9** was confirmed by multi-element



Scheme 3 Reagents and conditions: (i) Bu^{n}Li, THF; (ii) Me$_3$SiCl, THF; (iii) $\frac{1}{2}$ ClSiMe$_2$CH$_2$CH$_2$SiMe$_2$Cl, THF, reflux; (iv) 2MeLi, THF, reflux; (v) 2MeK, Et$_2$O, 0 °C.

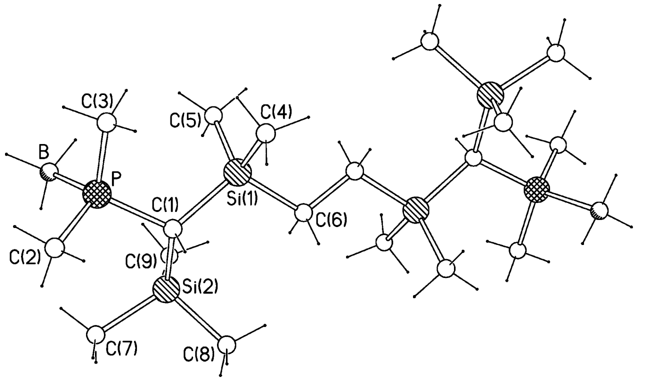


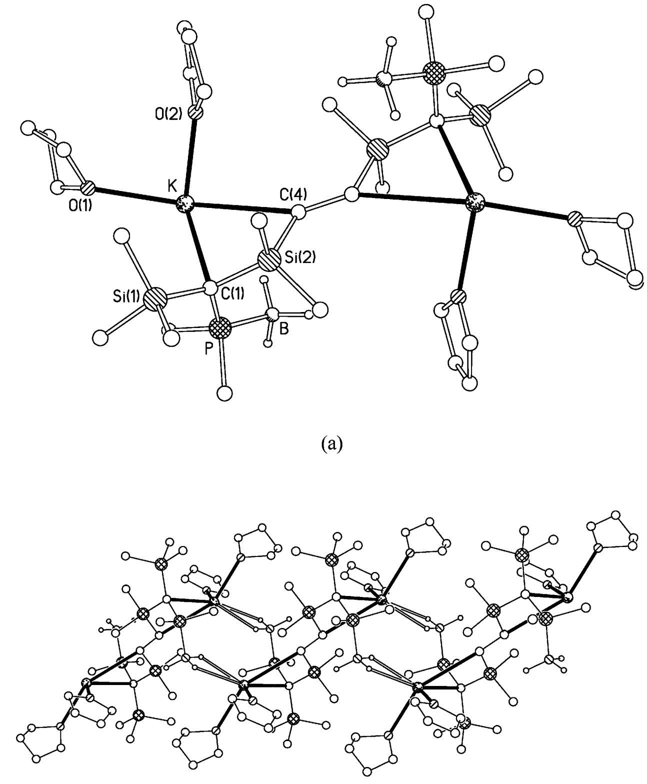
Fig. 3 Molecular structure of *rac*-**6**. Selected bond lengths (Å) and angles (°): P–B 1.9198(19), C(1)–P 1.8256(13), C(1)–Si(1) 1.9097(13), C(1)–Si(2) 1.9045(13), Si(1)–C(1)–Si(2) 114.73(7), P–C(1)–Si(1) 115.19(6), P–C(1)–Si(2) 112.23(6).

(^{1}H, ^{13}C{^{1}H}, ^{7}Li{^{1}H}, ^{11}B{^{1}H} and ^{31}P{^{1}H}) NMR spectroscopy. These spectra exhibit a single set of ligand resonances each and indicate that the diastereotopic PMe_2 and $SiMe_2$ groups are equivalent, consistent with rapid exchange between diastereomers on the NMR time-scale in solution.

Treatment of a 1:1 mixture of *rac*- and *meso*-**6** with an excess of MeK in cold diethyl ether gives the di-potassium salt $[[\{Me_2P(BH_3)\}(Me_3Si)C\{(SiMe_2)(CH_2)\}]_2K_2(THF)_4]_\infty$ (**10**) after a simple work-up in good yield as a highly viscous colourless oil (Scheme 3). The THF co-ligands in **10** are only weakly held: ^{1}H NMR spectroscopy shows that **10** slowly loses THF under vacuum. Once again, multi-element (^{1}H, ^{13}C{^{1}H}, ^{11}B{^{1}H} and ^{31}P{^{1}H}) NMR spectroscopy indicates rapid inter-conversion of the diastereomers of **10** on the NMR time-scale in solution. Despite several attempts, it was not possible to crystallise **10** from solution; however, a small number of single crystals of **10** suitable for X-ray crystallography were isolated from a sample of the viscous oil that had been left to stand at room temperature for several weeks. The structure of **10** is shown in Fig. 4, along with selected bond lengths and angles.

The crystal of **10** studied by X-ray crystallography was of the *meso*-diastereomer. Compound **10** crystallises with a polymeric structure composed of centrosymmetric $[\{Me_2P(BH_3)\}(Me_3Si)C\{(SiMe_2)(CH_2)\}]_2K_2(THF)_4$ units, linked into chains *via* $BH_3\cdots K$ contacts. Each potassium cation is coordinated by one of the carbanion centres, by two molecules of THF, and by an η^2-BH_3 group from an adjacent unit; in addition, there is a short contact between the potassium ion and one of the methylene carbon atoms of the ligand backbone [K···C(4) 3.3868(18) Å] and between the potassium ion and one of the methylene carbon atoms in the minor disorder component of a THF molecule [K···C(10A) 3.457(13) Å].

The monomer unit of **10** bears a remarkable resemblance to that of the isoelectronic compound $[[(Me_3Si)_2C\{(SiMe_2)(CH_2)\}]_2K_2(THF)_4]_\infty$ (**11**),[20] which also crystallises with a polymeric structure. Indeed, the method by which the monomer units in **10** and **11** are linked into chains is rather similar: in **10** the units are linked *via* η^2-P-$BH_3\cdots K$ contacts, forming $[K\text{-}C\text{-}P\text{-}BH_3]_2$ rings, whereas in **11** the units are linked *via* Si-Me···K contacts, forming $[K\text{-}C\text{-}Si\text{-}Me]_2$ rings. The K–C distance in **10** of 3.0232(19) Å is slightly longer than the K–C distance in **11** [2.937(3) Å], but is similar to the K–C distance in the closely related phosphine-borane-stabilised carbanion complex $[[(Me_3Si)_2\{Me_2P(BH_3)\}C]K]_\infty$ [K–C 3.018(5) Å].[8c] The K···H distances [2.68(2) and 2.79(3) Å] and the K···B distance [3.215(2) Å] are similar to the corresponding distances in related complexes;[8] for example, the K···H distances in polymeric $[[(Me_3Si)_2\{Me_2P(BH_3)\}C]K(THF)_{0.5}]_\infty$ range from 2.73(3) to 2.95(3) Å, while the K···B distances in this compound range from 3.171(3) to 3.389(3) Å.[8f]



(a)

(b)

Fig. 4 Structure of (a) the molecular unit of **10** with minor disorder component and H atoms bonded to carbon omitted for clarity, and (b) the extended polymeric structure of **10**. Selected bond lengths (Å) and angles (°): K–C(1) 3.0232(19), K–O(1) 2.701(2), K–O(2) 2.6481(16), K···H(1A)^a 2.68(2), K···H(1C)^a 2.79(3), K···B^a 3.215(2), K···C(4) 3.3868(18), K···C(10A) 3.457(13), P–B 1.930(2), C(1)–P 1.7371(18), C(1)–Si(1) 1.8305(18), C(1)–Si(2) 1.8454(18), Si(1)–C(1)–Si(2) 117.02(10), Si(1)–C(1)–P 119.52(10), Si(2)–C(1)–P 114.64(10); symmetry operator a: $1 - x, 1 - y, 2 - z$.

Metalation of the free phosphine-borane **6** leads to a significant shortening of the P–C(1) and Si–C(1) distances, consistent with partial multiple bond character due to delocalisation of the carbanion charge *via* negative hyperconjugation; for *rac*-**6** the P–C(1), Si(1)–C(1) and Si(2)–C(1) distances are 1.8256(13), 1.9097(13) and 1.9045(13) Å, respectively, whereas in **10** the corresponding distances are 1.7371(18), 1.8305(18) and 1.8454(18) Å, respectively. At the same time the P–B distances increase slightly from 1.9198(19) Å in *rac*-**6** to 1.930(2) Å in **10**.

Experimental

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen or argon. Diethyl ether, THF, *n*-hexane and light petroleum (b.p. 40–60 °C) were dried prior to use by distillation under nitrogen from sodium, potassium or sodium/potassium alloy. THF was stored over activated 4A molecular sieves; diethyl ether, *n*-hexane and light petroleum were stored over a potassium film. Deuterated benzene, toluene and THF were distilled from potassium and $CDCl_3$ was distilled from CaH_2; all deuterated solvents were deoxygenated by three freeze–pump–thaw cycles and were stored over activated 4A molecular sieves. Potassium *tert*-butoxide was dried under vacuum at 100 °C/10^{-2} mmHg for 3 h before use; paraformaldehyde was dried under vacuum at 70 °C/10^{-2} mmHg for 1 h before use. The compounds $(Me_2PhSi)_3CH$,[13,21] $Me_3P(BH_3)$,[22] $(Me_3Si)_2CHPPh_2(BH_3)$[8g] and MeK[23] were prepared by previously published procedures. All other compounds were used as supplied by the manufacturer; low halide content methyllithium was supplied by Fluka as a 1.6 M solution in diethyl ether and butyllithium was supplied by Aldrich as a 2.5 M solution in hexanes.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL Lambda500 spectrometer operating at 500.16 and 125.65 MHz, respectively, or a Bruker Avance 300 spectrometer operating at 300.15 and 75.47 MHz, respectively; chemical shifts are quoted in ppm relative to tetramethylsilane. $^{31}P\{^1H\}$, $^{11}B\{^1H\}$ and $^7Li\{^1H\}$ NMR spectra were recorded on a JEOL Lambda500 spectrometer operating at 202.35, 160.35 and 194.25 MHz, respectively, and chemical shifts are quoted in ppm relative to external 85% H_3PO_4 (^{31}P), $BF_3(OEt_2)$ (^{11}B) and 1.0 M LiCl (^7Li). Elemental analyses were obtained by the Elemental Analysis Service of London Metropolitan University; we were unable to obtain satisfactory elemental analyses for the oily solid **9** or the viscous oil **10**, possibly as a consequence of their air sensitivity.

$(Me_2PhSi)_2C{=}CH_2$ (1)

The diethyl ether was removed *in vacuo* from a solution of MeLi (14.92 ml, 23.7 mmol). The resulting solid was dissolved in THF (30 ml) and this solution was added to solid $(Me_2PhSi)_3CH$ (10.00 g, 23.9 mmol) and heated under reflux for 2 h. The reaction mixture was allowed to cool to room temperature and a suspension of paraformaldehyde (0.72 g, 23.9 mmol) in THF (20 ml) was added. The resulting mixture was stirred for 12 h at room temperature. The solution was washed with water (3 × 50 ml) and the organic fraction was dried over anhydrous $MgSO_4$. The solution was filtered and the solvent was removed *in vacuo* from the filtrate. The by-product $(Me_2PhSi)_2O$ was removed by distillation (1 mmHg, 110°C) to leave **1** as a colourless oil. Isolated yield 4.66 g, 66%. ^1H NMR ($CDCl_3$, 25°C): δ 0.40 (s, 12H, $SiMe_2$), 6.58 (s, 2H, CH_2), 7.38–7.56 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 0.59 ($SiMe_2$), 128.24 (*p*-Ph), 129.13 (*m*-Ph), 134.38 (*o*-Ph), 139.16 (*ipso*-Ph), 145.70 (CH_2).

$(Me_3Si)\{Ph_2P(BH_3)\}C{=}CH_2$ (2)

To a solution of $(Me_3Si)_2CH\{PPh_2(BH_3)\}$ (6.31 g, 17.6 mmol) in THF (40 ml) was added *n*-BuLi (7.04 ml, 17.6 mmol) and this mixture was stirred for 2 h. A large excess of solid paraformaldehyde (2.52 g, 83.9 mmol) was added and this mixture was stirred for 1 h. The reaction was quenched with water (30 ml) and the organic layer was extracted into diethyl ether (3 × 20 ml) and dried over activated 4A molecular sieves. The solution was filtered and the solvent was removed *in vacuo* from the filtrate. The colourless solid obtained was dissolved in toluene and cooled (−30 °C) in order to crystallise out unreacted $(Me_3Si)_2CHPPh_2(BH_3)$. Removal of the solvent *in vacuo* from the mother liquor yielded **2** as a colourless solid. Isolated yield 4.80 g, 91%. Anal. Calcd for $C_{17}H_{24}BPSi$: C, 68.46; H, 8.11%. Found: C, 68.35; H, 8.20%. ^1H NMR ($CDCl_3$, 25°C): δ 0.00 (s, 9H, $SiMe_3$), 5.85 (dd, J_{HH} = 2.5 Hz, $^3J_{PH}$ = 28.1 Hz, 1H, CH_2), 6.37 (dd, J_{HH} = 2.5 Hz, $^3J_{PH}$ = 42.7 Hz, 1H, CH_2), 7.08–7.58 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C): δ 0.29 ($SiMe_3$), 129.0 (*m*-Ph), 131.5 (*p*-Ph), 132.5 (*ipso*-Ph), 133.7 (*o*-Ph), 143.0 (CH_2). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 25°C): δ −36.3 (d, J_{PB} = 61 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 23.6 (q, J_{PB} = 61 Hz).

$Me_2P(BH_3)CH_2SiMe_3$ (7)

To a cold (0 °C) solution of $Me_3P(BH_3)$ (1.09 g, 12.1 mmol) in THF (30 ml) was added *n*-BuLi (4.84 ml, 12.1 mmol). The resulting solution was allowed to attain room temperature and was stirred for 3 h, then added to a cold (−78 °C) solution of Me_3SiCl (1.84 ml, 14.5 mmol) in THF (20 ml). After attaining room temperature this solution was stirred for 3 h, then water (40 ml) was added. The organic layer was decanted, the aqueous layer was extracted into diethyl ether (3 × 20 ml) and the combined organic extracts were dried over activated 4A molecular sieves. The solvent was removed *in vacuo* to yield **7** as a colourless solid. Isolated yield: 1.67 g, 85%. Anal. Calcd for $C_6H_{20}BPSi$: C, 44.46; H, 12.44%. Found: C, 44.37; H, 12.40%. $^1H\{^{11}B\}$ NMR (d_8-toluene, 25 °C): δ 0.05 (s, 9H, $SiMe_3$), 0.35 (d, J_{PH} = 11.0 Hz, 2H, CH_2), 0.82 (d, J_{PH} = 10.1 Hz, 6H, PMe_2), 1.13 (d, J_{PH} = 15.0 Hz, 3H, BH_3). $^{13}C\{^1H\}$ NMR (d_8-toluene, 25 °C): δ 0.02 ($SiMe_3$), 14.48 (d, J_{PC} = 36.2 Hz, PMe_2), 14.60 (d, J_{PC} = 22.2 Hz, CH_2). $^{11}B\{^1H\}$ NMR (d_8-toluene, 25 °C): δ −34.5 (d, J_{PB} = 59 Hz). $^{31}P\{^1H\}$ NMR (d_8-toluene, 25 °C): δ 3.3 (q, J_{PB} = 59 Hz).

$[(Me_3Si)\{Me_2(H_3B)P\}CH(Me_2Si)CH_2]_2$ (6)

To a solution of **7** (2.08 g, 12.8 mmol) in THF (30 ml) was added *n*-BuLi (5.13 ml, 12.8 mmol) and the resulting solution was stirred for 4 h. This solution was added to a solution of $ClMe_2SiCH_2CH_2SiMe_2Cl$ (1.38 g, 6.4 mmol) in THF (20 ml) and this mixture was heated under reflux for 16 h. Water (30 ml) was added, followed by dichloromethane (40 ml) and the organic layer was decanted. The aqueous layer was extracted into dichloromethane (2 × 20 ml), the combined organic extracts were dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo* from the filtrate to yield crude *rac*-/*meso*-**6** as a colourless oily solid. This solid was repeatedly crystallised from hot methylcyclohexane to yield essentially pure *rac*-**6** as colourless needles. Combined yield of *rac*- and *meso*-**6**: 2.48 g, 83%. The following analytical data refer to *rac*-**6**. Anal. Calcd for $C_{18}H_{54}B_2P_2Si_4$: C, 46.34; H, 11.67%. Found: C, 46.30; H, 11.59%. $^1H\{^{11}B\}$ NMR ($CDCl_3$, 20 °C): δ 0.24 (s, 6H, $SiMe_2$), 0.26 (s, 18H, $SiMe_3$), 0.26 (s, 6H, $SiMe_2$), 0.40 (d, J_{PH} = 17.4 Hz, 2H, CH), 0.64 (s, 4H, CH_2), 0.66 (d, J_{PH} = 14.7 Hz, 6H, BH_3), 1.39 (d, J_{PH} = 9.6 Hz, 6H, PMe), 1.40 (d, J_{PH} = 9.6 Hz, 6H, PMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 0.09 (d, J_{PC} = 2.9 Hz, $SiMe_2$), 0.39 (d, J_{PC} = 2.9 Hz, $SiMe_2$), 3.23 (d, J_{PC} = 2.9 Hz, $SiMe_3$), 10.50 (CH_2), 11.14 (d, J_{PC} = 4.8 Hz, CH), 17.22 (d, J_{PC} = 37.4 Hz, PMe), 17.77 (d, J_{PC} = 37.4 Hz, PMe). $^{11}B\{^1H\}$ ($CDCl_3$, 20 °C): δ –35.5 (d, J_{PB} = 49 Hz). $^{31}P\{^1H\}$ ($CDCl_3$, 20 °C): δ 6.9 (q, J_{PB} = 49 Hz).

$[(THF)K(Me_2PhSi)_2C(CH_2)]_2$ (4)

To lithium powder (0.15 g, 21.32 mmol) in THF (10 ml) under argon was added neat **1** (1.11 g, 4.28 mmol). This mixture was treated ultrasonically for 1 h. Excess lithium was removed by filtration and the solvent was removed *in vacuo* from the filtrate. The resulting oil (1.33 g, 2.19 mmol) was dissolved in diethyl ether (20 ml) and added dropwise to a slurry of $KOBu^t$ (0.25 g, 2.19 mmol) in diethyl ether (10 ml). The reaction mixture was stirred for 1 h. The solution was filtered to yield a red solid, which was washed with light petroleum (3 × 10 ml) and recrystallised from cold (–20 °C) diethyl ether/*n*-hexane (10:1) containing a few drops of THF over a period of several weeks to yield **4** as large red blocks suitable for X-ray crystallography. Isolated yield 1.23 g, 69%. Anal. Calcd. for $C_{44}H_{64}O_2Si_4K_2$: C 64.80; H 7.91%. Found: C 64.94; H 7.84%. ^1H NMR (d_8-THF, 21°C): δ 0.23 (s, 24H, $SiMe_2$), 1.80 (m, 12H, CH_2 and THF), 3.65 (m, 8H, THF), 7.07–7.65 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR (d_8-THF, 25°C): δ 3.51 ($SiMe_2$), 24.58 (THF), 45.15 (CH_2), 66.50 (THF), 125.08 (*p*-Ph), 126.42 (*m*-Ph), 127.46 (*o*-Ph), 128.43 (*ipso*-Ph).

$[\{Ph_2P(BH_3)\}(Me_3Si)C(CH_2)]Li(THF)_3]_2.2THF$ (5)

To a solution of **2** (0.76 g, 2.55 mmol) in THF (20 ml) under argon was added lithium shot (0.07 g, 10.09 mmol). This mixture was treated ultrasonically for 30 mins, the excess lithium was removed by filtration and the solvent was removed *in vacuo* from the filtrate. The resulting brown oily solid was washed with light petroleum (3 × 10 ml) and was crystallised from cold (–30 °C) methylcyclohexane containing a few drops of THF to give **5** as red blocks suitable for X-Ray crystallography. Isolated yield 0.27 g, 40.6%. ^1H NMR (C_6D_6, 25°C): δ 0.12 (s, 18H, $SiMe_3$), 1.41 (m, 24H, THF), 1.59 (m, 4H, CH_2), 3.57 (m, 24H, THF), 6.92–7.71 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 1.75 ($SiMe_3$), 26.13 (THF), 39.51 (CH_2), 68.18 (THF), 128.67, 129.43, 131.17 (Ph). $^7Li\{^1H\}$ (C_6D_6, 25°C): δ 1.07 (br). $^{11}B\{^1H\}$ NMR (C_6D_6, 25 °C): δ –38.7 (br). $^{31}P\{^1H\}$ NMR (C_6D_6, 25°C): δ 18.6 (br).

$[\{Me_2P(BH_3)\}(Me_3Si)C\{(SiMe_2)(CH_2)\}]Li(THF)_3]_2$ (9)

To a solution of **6** (0.54 g, 1.16 mmol) in THF (20 ml) was added a solution of MeLi (1.45 ml, 2.32 mmol). The resulting solution was heated under reflux for 1 h. The solvent was removed *in vacuo* to yield **9** as an oily solid. Attempts to obtain single crystals of **9** were unsuccessful. Isolated yield 0.67 g, 83%. $^1H\{^{11}B\}$ NMR (d_8-toluene, 25 °C): δ 0.44 (s, 12H, $SiMe_2$), 0.46 (s, 18H, $SiMe_3$), 0.81 (d, J_{BH} = 14.0 Hz, 6H, BH_3), 0.91 (s, 4H, CH_2), 1.48 (d, J_{PH} = 6.9 Hz, 12H, PMe_2), 1.49 (m, 16H, THF), 3.58 (m, 16H, THF). $^{13}C\{^1H\}$ NMR (d_8-toluene, 25 °C): δ 5.09 (d, J_{PC} = 2.9 Hz, $SiMe_2$), 7.26 (d, J_{PC} = 4.8 Hz, $SiMe_3$), 13.76 (CH_2), 21.24 (d, J_{PC} = 35.5 Hz, PMe), 25.26 (THF), 68.10 (THF). $^7Li\{^1H\}$ NMR (d_8-toluene, 25 °C): δ 3.2. $^{11}B\{^1H\}$ NMR (d_8-toluene, 25 °C): δ –31.6 (d, J_{PB} = 94 Hz). $^{31}P\{^1H\}$ NMR (d_8-toluene, 25 °C): δ –3.7 (q, J_{PB} = 94 Hz).

$[(Me_3Si)\{Me_2(H_3B)P\}C(Me_2Si)CH_2]_2K_2(THF)_4$ (10)

A solution of **6** (1.62 g, 3.4 mmol) in cold (0 °C) diethyl ether (20 ml) was added to solid MeK (0.54 g, 10.2 mmol). The resulting solution was stirred overnight and allowed to attain room temperature. The solution was filtered and solvent was removed *in vacuo* from the filtrate to yield an off-white highly viscous oil. This oil was dissolved in methylcyclohexane (5 ml) and treated with a few drops of THF. Removal of solvent *in vacuo* gave **10** as a colourless, highly viscous oil; on standing for several weeks this oil began to crystallise, yielding a small number of

Table 1 Crystallographic data for **4**, **5**, *rac*-**6**, and **10**

Compound	**4**	**5**	*rac*-**6**	**10**
Formula	$C_{44}H_{64}K_2O_2Si_4$	$C_{58}H_{96}B_2Li_2O_6P_2Si_2.\text{-}2C_4H_8O$	$C_{18}H_{54}B_2P_2Si_4$	$C_{34}H_{84}B_2K_2O_4P_2Si_4$
M	815.5	1187.2	466.5	831.1
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	9.9778(8)	10.3298(12)	6.6106(1)	9.3401(9)
b/Å	14.082(2)	13.2276(13)	8.7160(2)	11.3130(11)
c/Å	16.708(2)	15.0800(15)	13.3995(4)	13.0533(13)
α/°	93.837(15)	106.405(8)	81.709(2)	78.290(2)
β/°	90.063(8)	108.263(7)	86.352(2)	76.748(2)
γ/°	100.382(5)	99.787(9)	77.554(2)	71.916(1)
V/Å^3	2303.8(5)	1799.9(3)	745.61(3)	1263.2(2)
Z	2	1	1	1
μ/mm^{-1}	0.343	0.141	0.310	0.376
Data collected	65195	39378	6863	9090
Unique data	10520	6322	3477	4402
R_{int}	0.051	0.051	0.022	0.013
Data with $F^2>2\sigma$	7891	4956	2720	4011
Refined parameters	497	371	137	255
R (on F, $F^2>2\sigma$)	0.054	0.068	0.029	0.037
R_w (on F^2, all data)	0.165	0.199	0.075	0.104
Goodness of fit on F^2	1.104	1.100	1.003	1.045
min, max electron density/e Å^{-3}	1.23, –0.38	0.47, –0.48	0.38, –0.19	0.63, –0.46

single crystals suitable for X-ray crystallography. Isolated yield 2.16 g, 75%.

^{1}H NMR (d_8-THF, 25 °C): δ −0.01 (s, 12H, SiMe$_2$), 0.02 (s, 18H, SiMe$_3$), 0.44 (s, 4H, CH$_2$), 1.16 (d, J_{PH} = 9.2 Hz, 12H, PMe$_2$), 1.77 (m, 6H, THF), 3.61 (m, 6H, THF). ^{13}C{^{1}H} NMR (d_8-THF, 25 °C): δ 4.1 (d, J_{PC} = 3.8 Hz, SiMe$_2$), 7.1 (d, J_{PC} = 3.8 Hz, SiMe$_3$), 16.4 (CH$_2$), 22.9 (d, J_{PC} = 34.5 Hz, PMe$_2$), 25.5 (THF), 67.3 (THF). ^{11}B{^{1}H} NMR (d_8-THF, 25 °C): δ −30.4 (d, J_{PB} = 93 Hz). ^{31}P{^{1}H} NMR (d_8-toluene, 25 °C): δ −5.2 (q, J_{PB} = 93 Hz).

Crystal structure determinations of 4, 5, *rac*-6 and 10

Measurements were made at 180 K (**4** and **5**) or 150 K (*rac*-**6** and **10**) on Nonius KappaCCD (**4** and **5**), Oxford Diffraction Gemini A Ultra (*rac*-**6**), and Bruker SMART diffractometers (**10**) using graphite-monochromated MoKα radiation (λ = 0.71073 Å). Cell parameters were refined from the observed positions of all strong reflections. Intensities were corrected semi-empirically for absorption, based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined on F^2 values for all unique data; Table 1 gives further details. All non-hydrogen atoms were refined anisotropically, and C-bound H atoms were constrained with a riding model, while B-bound H atoms were freely refined; U(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} for the parent C atom. Disorder was resolved and successfully modelled for the THF molecule in **4**, two of the three THF molecules in **5** and one of the two THF molecules in **10**. Programs were Nonius COLLECT and EvalCCD, Oxford Diffraction CrysAlisPro, Bruker SMART and SAINT for data collection and processing, and SHELXTL for structure solution, refinement, and molecular graphics.[24]

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