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PAPER

Synthesis, structures and stabilities of thioanisole-functionalised phosphido-borane complexes of the alkali metals†

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Treatment of the secondary phosphine $\{(Me_3Si)_2CH\}PH(C_6H_4\text{-}2\text{-}SMe)$ with $BH_3{\cdot}SMe_2$ gives the corresponding phosphine-borane $\{(Me_3Si)_2CH\}PH(BH_3)(C_6H_4\text{-}2\text{-}SMe)$ (**9**) as a colourless solid. Deprotonation of **9** with *n*-BuLi, $PhCH_2Na$ or $PhCH_2K$ proceeds cleanly to give the corresponding alkali metal complexes $[[\{(Me_3Si)_2CH\}P(BH_3)(C_6H_4\text{-}2\text{-}SMe)]ML]_n$ [ML = Li(THF), $n = 2$ (**10**); ML = Na(tmeda), $n = \infty$ (**11**); ML = K(pmdeta), $n = 2$ (**12**)] as yellow/orange crystalline solids. X-ray crystallography reveals that the phosphido-borane ligands bind the metal centres through their sulfur and phosphorus atoms and through the hydrogen atoms of the BH_3 group in each case, leading to dimeric or polymeric structures. Compounds **10–12** are stable towards both heat and ambient light; however, on heating in toluene solution in the presence of **10**, traces of free phosphine-borane **9** are slowly converted to the free phosphine $\{(Me_3Si)_2CH\}PH(C_6H_4\text{-}2\text{-}SMe)$ (**5**) with concomitant formation of the corresponding phosphido-bis(borane) complex $[\{(Me_3Si)_2CH\}P(BH_3)_2(C_6H_4\text{-}2\text{-}SMe)]Li$ (**14**).

Introduction

Phosphido-borane anions, $[R_2P(BH_3)]^-$ (alternatively known as phosphanylborohydrides or mono(borane)phosphides) are useful intermediates for the synthesis of a variety of chiral phosphines and for the generation of polymeric main group element materials;[1,2] however, almost without exception, these anions are generated and used *in situ* and few attempts have been made to isolate and characterise them. Since phosphido-borane anions are isoelectronic with the corresponding silyl anions $[R_2MeSi]^-$, which have a well-developed coordination chemistry, it is perhaps surprising that relatively few complexes of these anions have been reported. Recently, however, a small number of research groups have noted their potential and a nascent coordination chemistry for these ligands has begun to emerge.[3–6]

Of the few crystallographically-characterised complexes of phosphido-borane anions the majority are of the transition metal centres Fe, Ru, Pd and Pt.[3] For example, Manners and co-workers have reported the structures of several late transition metal complexes, prepared either *via* metathesis reactions between a transition metal halide and an alkali metal phosphido-borane complex or *via* oxidative addition of a phosphine-borane adduct to a low oxidation state transition metal complex; these compounds are effective catalysts for the dehydrocoupling of phosphine-borane adducts to give poly(phosphinoborane) materials.[3a–d] In addition, Brown and Gaumont have isolated a small number of Pd complexes,[3e,f] intermediates in catalytic P–C cross-coupling reactions, and Wagner and co-workers have reported the synthesis and crystal structure of an iron(II) complex of a novel bis(phosphido-borane) dianion.[3g]

Main group derivatives are limited to complexes of lithium, potassium and aluminium.[4] The first structurally authenticated complexes of this type were reported in 2003 by Müller and Brand, who described the synthesis and structural characterisation of the lithium complexes $[\{Me_2P(BH_3)\}Li(tmeda)]_\infty$ (**1**) and $[\{Ph(t\text{-}Bu)P(BH_3)\}Li\{(-)\text{-sparteine}\}]_\infty$ (**2**) and of the aluminium complexes $[Li(tmeda)_2][Al\{Me_2P(BH_3)\}_4]$ (**3**) and $[[Li(t\text{-}BuOMe)][Al\{Me_2P(BH_3)\}_4]]_\infty$ (**4**) [tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine].[4a] Subsequently, Wagner and co-workers reported the potassium complexes [K(18-crown-6)][$R_2P(BH_3)$] [R = Ph, *t*-Bu].[4b,c] In addition, a small number of alkali metal complexes of the related phosphido-bis(borane) anions $[R_2P(BH_3)_2]^-$ [R = Ph, *t*-Bu] and $[(2,4,6\text{-}t\text{-}Bu_3C_6H_4)PH(BH_3)_2]^-$ have been structurally characterised.[5] More recently, Lancaster and co-workers have reported a series of lithium and aluminium complexes with perfluorophenyl-substituted phosphido-borane and phosphido-bis(borane) ligands.[6]

Phosphido-borane anions have the potential to coordinate metal ions through the formally anionic phosphorus centre and/or the hydrogen atoms of the adjacent borane group and so represent an interesting class of ambidentate ligands. As such, phosphido-boranes may adopt a variety of coordination modes, including terminal P- or BH_3-donor modes (**I** and **II**), a bidentate coordination mode (**III**) and bridging modes (**IV**, **V**). In complexes containing soft transition metal centres phosphido-borane ligands typically adopt a P-donor coordination mode, whereas hard alkali metal cations usually favour a BH_3-donor mode.

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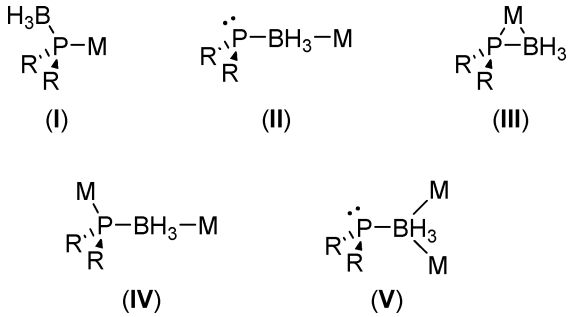
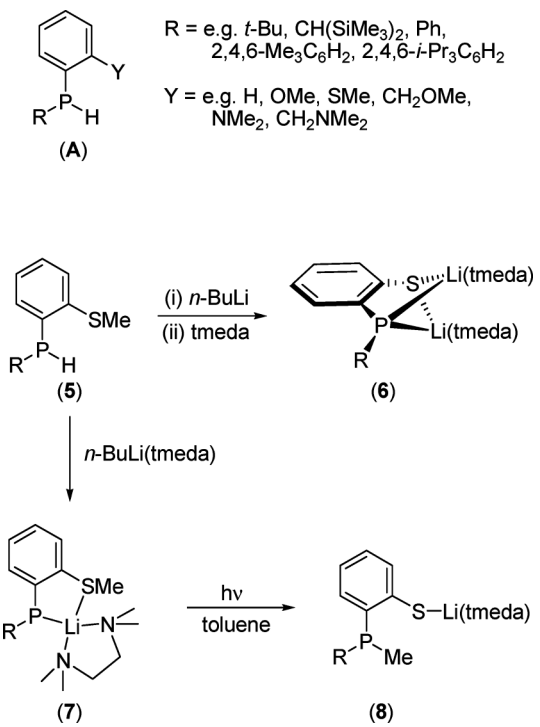


We have a long-standing interest in the coordination chemistry of donor-functionalised phosphides of type **A** and have isolated numerous main group and lanthanide metal derivatives of these ligands.[7,8] In the course of these studies we discovered that the thioanisole-substituted phosphine {(Me$_3$Si)$_2$CH}PH(C$_6$H$_4$-2-SMe) (**5**) exhibits rather unusual behaviour towards alkyllithium reagents.[8] The reaction between **5** and one equivalent of *n*-BuLi in diethyl ether yields, after crystallisation in the presence of tmeda, half an equivalent of the dianion complex [{(Me$_3$Si)$_2$CH}P(C$_6$H$_4$-2-S)][Li(tmeda)]$_2$ (**6**) (Scheme 1). Compound **6** results from concurrent deprotonation and demethylation of the phosphine, leaving half an equivalent of **5** unchanged; compound **6** may be accessed cleanly through the reaction between **5** and two equivalents of *n*-BuLi under the same conditions. In contrast, the reaction between **5** and one equivalent of *n*-BuLi in diethyl ether in the presence of tmeda cleanly yields the expected lithium phosphide [{(Me$_3$Si)$_2$CH}P(C$_6$H$_4$-2-SMe)][Li(tmeda)] (**7**). Perhaps more intriguingly, exposure of toluene solutions of **7** to ambient light rapidly leads to isomerisation to the corresponding phosphinethiolate [{(Me$_3$Si)$_2$CH}P(Me)(C$_6$H$_4$-2-S)][Li(tmeda)] (**8**).



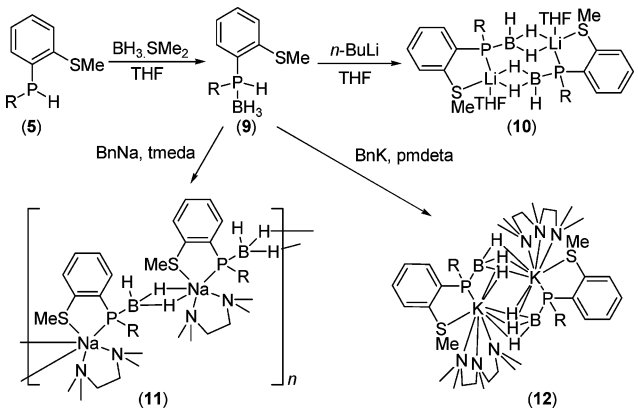
Scheme 1 [R = CH(SiMe$_3$)$_2$].

In order to understand better this unusual behaviour we have embarked on a programme to study systematically the deprotonation of thioether-substituted phosphines and the stability of the corresponding phosphide complexes. In this contribution we report the synthesis of the borane adduct of **5** and the synthesis, structural characterisation and photolysis/thermolysis behaviour of its lithium, sodium and potassium derivatives.

Results and Discussion

Treatment of a solution of **5** in diethyl ether with one equivalent of BH$_3$.SMe$_2$ yields the air stable phosphine-borane adduct {(Me$_3$Si)$_2$CH}PH(BH$_3$)(C$_6$H$_4$-2-SMe) (**9**) as a viscous oil, which may be crystallised from cold *n*-hexane as colourless needles in good yield. The ^{31}P{^{1}H} and ^{11}B{^{1}H} NMR spectra of **9** consist of a broad quartet at –15.7 ppm and a broad doublet at –40.1 ppm, respectively ($^1J_{PB}$ = 49.0 Hz), while in the ^{1}H NMR spectrum the PH proton gives rise to a complex doublet of quartets of doublets centred at 6.04 ppm ($^1J_{PH}$ = 375.2 Hz, $^3J_{HH}$ = 6.5 Hz, $^3J_{HH'}$ = 2.8 Hz); this signal does not change significantly in appearance on decoupling the ^{11}B nucleus.

The reaction between **9** and one equivalent of *n*-BuLi in THF proceeds cleanly to give the corresponding phosphidoborane complex [[{(Me$_3$Si)$_2$CH}P(BH$_3$)(C$_6$H$_4$-2-SMe)]Li(THF)]$_2$ (**10**), which was crystallised from cold toluene/THF as colourless blocks suitable for X-ray crystallography (Scheme 2). Similarly, the reaction between **9** and one equivalent of either PhCH$_2$Na or PhCH$_2$K in THF yields the corresponding alkali metal salts, which were crystallised from cold toluene in the presence of one equivalent of either tmeda or pmdeta, respectively, as the adducts [[{(Me$_3$Si)$_2$CH}P(BH$_3$)(C$_6$H$_4$-2-SMe)]Na(tmeda)]$_\infty$ (**11**) and [[{(Me$_3$Si)$_2$CH}P(BH$_3$)(C$_6$H$_4$-2-SMe)]K(pmdeta)]$_2$ (**12**) [pmdeta = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine]. These straightforward reactions contrast with the corresponding reaction between **5** and *n*-BuLi, which, in the absence of tmeda, leads to both deprotonation *and* demethylation to give the phosphidothiolate **6**;[8] no such dianionic products were observed in the syntheses of **10–12**. Compounds **10–12** are soluble in ethereal solvents and are moderately soluble in aromatic hydrocarbons, but have limited solubility in aliphatic solvents.



Scheme 2 [R = CH(SiMe$_3$)$_2$].

Upon metalation the ^{31}P{^{1}H} NMR signal shifts significantly upfield from –15.7 ppm for **9** to between –58.3 and –59.5 ppm for

10–12. Although there is only a marginal difference in the $^{31}P\{^{1}H\}$ chemical shifts of the metalated compounds, the magnitude of the ^{31}P–^{11}B coupling constants decreases steadily with decreasing electronegativity of the cation [$^{1}J_{PB}$ = 49.0 (**9**), 39.2 (**10**), 29.4 (**11**), and 19.6 Hz (**12**)].

Compound **10** crystallises as discrete centrosymmetric dimers; the molecular structure of **10** is shown in Fig. 1, along with selected bond lengths and angles. Each lithium ion is coordinated by the P and S atoms of the phosphido-borane ligand to give a five-membered chelate ring [P–Li–S bite angle 77.28(7)°]. The coordination about lithium is completed by a molecule of THF and by an η^2-BH_3 contact with a borane group from the adjacent phosphido-borane ligand in the dimer to give a pseudo-tetrahedral geometry at lithium. Thus, the two halves of the dimer are linked *via* an essentially planar, pseudo-six-membered $[PLi(BH_3)]_2$ ring.

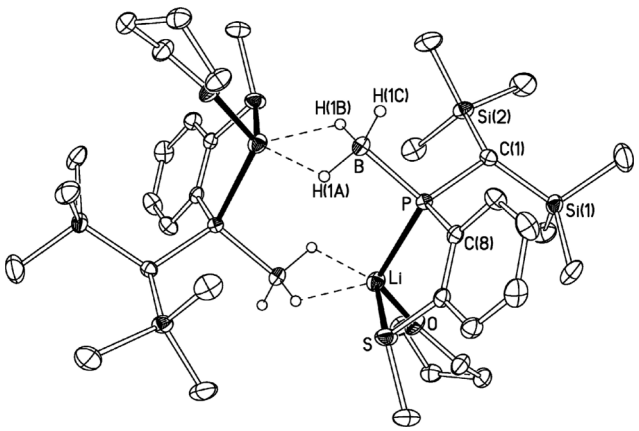


Fig. 1 Molecular structure of **10** with 40% probability ellipsoids and with H atoms bound to carbon omitted for clarity. Selected bond lengths (Å) and angles (°): P–Li 2.527(3), S–Li 2.608(2), O–Li 1.910(3), Li–H(1A′) 2.053(14), Li–H(1B′) 1.905(4), Li···B′ 2.403(3), P–B 1.9617(18), P–C(1) 1.8682(14), P–C(8) 1.8459(13), P–Li–S 77.28(7), P–Li–O 124.52(12), P–Li···B′ 121.84(11), O–Li–S 108.78(11), O–Li···B′ 107.95(12), S–Li···B′ 109.83(10). The prime indicates a symmetry-generated atom (inversion).

The P–Li distance of 2.527(3) Å in **10** is somewhat shorter than the corresponding distance in **1** [2.620(4) Å], and slightly longer than the P–Li distance in **7** [2.508(3) Å],[8] but lies in the range of typical P–Li distances for lithium phosphide complexes;[9] the S–Li distance in **10** [2.608(2) Å] is slightly longer than the corresponding distance in **7** [2.543(3) Å]. The Li–H distances in **10** [2.053(14) and 1.905(14) Å] are similar to Li–H distances in complexes which possess a η^2-BH_3-Li contact; the Li···B′ distance of 2.403(3) Å is also typical of an η^2-Li–BH_n interaction. For example, the Li–H distances and the Li···B distance in Li(η^2-BH_4)(py)$_3$ are 2.06 and 1.90 Å, and 2.401(7) Å, respectively.[10]

Compound **11** represents the first example of a sodium complex of a phosphido-borane anion to be crystallographically characterised. This compound crystallises as an essentially linear polymer with two crystallographically independent monomer units per asymmetric unit; the structure of **11** is shown in Fig. 2, along with selected bond lengths and angles. Both sodium ions are coordinated by the P and S atoms of a phosphido-borane ligand to give a five-membered chelate ring [P–Na–S bite angles 62.93(4) and 63.43(4)°], and by the N atoms of

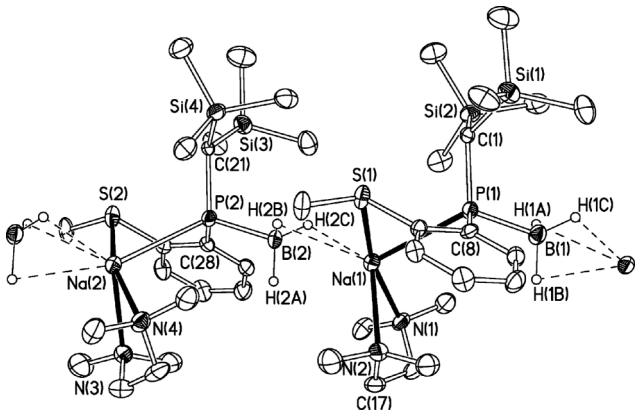


Fig. 2 Part of the polymeric structure of **11** with 40% probability ellipsoids and with H atoms bound to carbon omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)–Na(1) 2.9661(17), P(2)–Na(2) 2.9474(16), S(1)–Na(1) 3.0441(19), S(2)–Na(2) 3.0735(18), N(1)–Na(1) 2.542(3), N(2)–Na(1) 2.498(3), N(3)–Na(2) 2.523(3), N(4)–Na(2) 2.533(3), Na(1)–H(2B) 2.64(3), Na(1)–H(2C) 2.35(3), Na(1)···B(2) 2.694(4), Na(2)–H(1A′) 2.54(3), Na(2)–H(1B′) 2.63(3), Na(2)–H(1C′) 2.51(4), Na(2)···B(1′) 2.646(4), C(17)···Na(1) 3.126(4), P(1)–B(1) 1.951(4), P(2)–B(2) 1.957(4), P(1)–C(1) 1.888(3), P(1)–C(8) 1.833(4), P(2)–C(21) 1.887(3), P(2)–C(28) 1.837(4), P(1)–Na(1)–S(1) 62.93(4), P(2)–Na(2)–S(2) 63.43(4). The prime indicates a symmetry-generated atom (lattice translation).

a chelating molecule of tmeda. The coordination about Na(1) is completed by η^2-coordination of the hydrogen atoms of a borane group from an adjacent unit in the chain and by a short contact to one of the methylene carbon atoms of the tmeda co-ligand [Na(1)···C(17) 3.126(4) Å], whereas the coordination of Na(2) is completed by η^3-coordination of a BH_3 group from an adjacent unit in the chain. The P–Na distances of 2.9661(17) and 2.9474(16) Å are similar to the P–Na distances in related sodium phosphide complexes;[9] for example, the P–Na distances in [Na(PHCy)(pmdeta)]$_2$ are 2.884(8) and 2.936(7) Å,[11] while the P–Na distances in [Na{P(C$_6$H$_4$-2-OMe)$_2$}(diglyme)]$_2$ range from 2.861(2) to 3.047(2) Å.[12] The Na(1)···B(2) distance [2.694(4) Å] is also similar to other η^2-BH_n-Na distances [for example, the Na···B distance in [[(Me$_3$Si)$_2$CPMe$_2$(BH$_3$)]Na(THF)$_2$].$\frac{1}{2}$PhMe is 2.766(3) Å],[13] while the Na(2)···B(1B) distance [2.646(4) Å] is similar to other η^3-BH_n-Na distances [for example, the Na···B distances in [Na(BH$_4$)(morpholine)$_2$] are 2.640 Å].[14]

Compound **12** crystallises as discrete centrosymmetric dimers in which the phosphido-borane ligands adopt a tridentate coordination mode; the structure of **12** is shown in Fig. 3, along with selected bond lengths and angles. Each phosphido-borane ligand binds the adjacent potassium ion through its P and S atoms and, in an η^2 manner, through its borane hydrogen atoms, which bridge the two potassium ions in the dimer. The third hydrogen atom of each borane group is η^1-bonded to the second potassium ion, such that each borane group acts as a μ_2-η^2:η^3 bridge between the two potassium ions, forming a rhombus-shaped pseudo-four-membered $K_2(BH_3)_2$ ring. The coordination about each potassium ion is completed by the three nitrogen atoms of a molecule of pmdeta and by a short contact between potassium and the central methyl group of the pmdeta ligand [K···C(19) 3.266(2) Å], making the potassium ions pseudo-eight-coordinate.

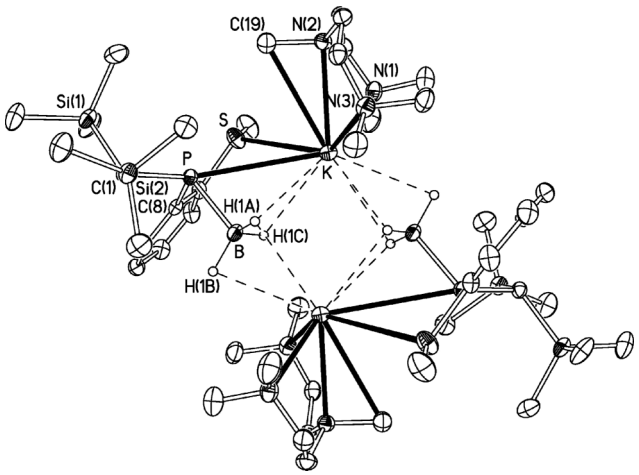
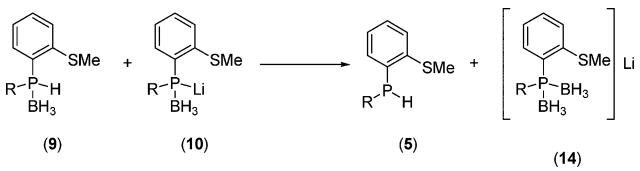


Fig. 3 Molecular structure of **12** with 40% probability ellipsoids and with H atoms bound to carbon omitted for clarity. Selected bond lengths (Å) and angles (°): K–P 3.6617(6), K–S 3.7568(7), K–N(1) 2.9039(17), K–N(2) 2.8912(16), K–N(3) 2.9099(17), K–H(1A) 3.01(2), K–H(1C) 2.77(2), K···B 3.243(2), K–H(1A′) 3.00(2) K–H(1B′) 2.97(2), K–H(1C′) 2.74(2), K···B′ 3.047(2), K···C(19) 3.266(2), P–B 1.975(2), P–C(1) 1.8852(18), P–C(8) 1.8473(18), P–K–S 49.666(12). The prime indicates a symmetry-generated atom (inversion).

The P–K–S bite angle of 49.666(12)° is significantly smaller than the bite angles in **10** and **11**, consistent with the greater ionic radius of potassium than sodium and lithium. The "tridentate" *S*,*P*,*BH*$_3$ binding mode of the phosphido-borane ligand in **12** is also consistent with the greater size of the potassium cation; a "bidentate" *P*,*BH*$_3$ binding mode has previously been observed only in the related potassium salt [Ph$_2$P(BH$_3$)]K(18-crown-6) (**13**).[4] The P–K distance of 3.6617(6) Å in **12** is significantly greater than the corresponding distance in **13** [3.320(2) Å]. The K···B distance in **12** [3.243(2) Å] is somewhat longer than the corresponding distance in **13** [3.162 Å], in spite of the similar η^2-BH$_3$ binding modes in both cases; however, the intra-dimer K···B′ distance [3.047(2) Å] is significantly shorter than the K···B distance in **13**, consistent with the η^3-BH$_3$ coordination mode in the former compound.

The ready isolation of compounds **10–12** and the unusual photolytic rearrangement previously observed for **7** prompted us to explore their behaviour on exposure to light and heat. We observe that, while the phosphide complex **7** rapidly rearranges on exposure to ambient light to give the corresponding tertiary phosphine-functionalised thiolate (**8**), compound **10** undergoes no such isomerisation; exposure of solutions of **10** in toluene or THF to light (either ambient light or a 10 W fluorescent lamp) for extended periods resulted in no change. Similarly, **11** and **12** are unaffected by exposure to light. It therefore appears that the presence of boron directly adjacent to phosphorus in **10–12**, which effectively ties up the phosphorus lone pair present in **7**, inhibits rearrangement to the corresponding thiolate.

Compound **10** is also stable towards thermolysis: flame-sealed samples of **10** in d_8-THF which were heated to 60 °C for 16 h showed no evidence for decomposition. However, during the course of these experiments, we noted that a small peak at –15.8 ppm in the ^{31}P{^{1}H} NMR spectrum (due to the presence of free phosphine-borane **9**, caused by a small amount of hydrolysis of **10** during sample preparation) disappeared gradually over the course of a few hours, to be replaced by a peak at –68.0 ppm due to the secondary phosphine **5** and a broad peak at –6.9 ppm due to a new phosphine-borane species. We attribute this behaviour to a borane redistribution process, whereby the anionic phosphido-borane ligand in **10** removes a borane group from the less electron-rich, neutral phosphine-borane **9** to give one equivalent each of the free phosphine **5** and the corresponding lithium phosphido-bis(borane) (**14**), the latter of which gives rise to the peak at –6.9 ppm in the ^{31}P{^{1}H} NMR spectrum (Scheme 3). We were, unfortunately, unable to separate a pure sample of the phosphido-bis(borane) complex **14** from these thermolysis reactions; however, ^{1}H, ^{31}P{^{1}H} and ^{11}B{^{1}H} NMR spectra of samples taken directly from the reaction solution are consistent with this formulation.



Scheme 3 [R = CH(SiMe$_3$)$_2$].

In order to confirm the identity of **14** we prepared this compound by a more straightforward route. The reaction between **10** and one equivalent of BH$_3$.SMe$_2$ in THF yields crude **14** as a colourless solid after a straightforward work-up. Treatment of a solution of this crude material in toluene with one equivalent of 12-crown-4 and addition of a few drops of diethyl ether leads, on standing, to the deposition of pure {(Me$_3$Si)$_2$CH}P(BH$_3$)$_2$(C$_6$H$_4$-2-SMe)Li(12-crown-4) (**14a**) as a colourless solid. With the exception of the expected signals for 12-crown-4, the ^{1}H, ^{31}P{^{1}H} and ^{11}B{^{1}H} NMR spectra of this deliberately prepared sample are indistinguishable from those observed during the attempted thermolysis of **10**.

Experimental

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Diethyl ether, THF, light petroleum (b.p. 40–60 °C), *n*-hexane and toluene were dried prior to use by distillation under nitrogen from sodium, potassium or sodium/potassium alloy as appropriate. THF was stored over activated 4A molecular sieves; all other solvents were stored over a potassium film. Deuterated THF was distilled from potassium and CDCl$_3$ was distilled from CaH$_2$ under nitrogen and both solvents were deoxygenated by three freeze-pump-thaw cycles and were stored over activated 4A molecular sieves. Benzylsodium and benzylpotassium were prepared by previously published procedures;[15] n-butyllithium was purchased from Aldrich as a 2.5 M solution in hexanes and BH$_3$.SMe$_2$ was purchased from Aldrich as a 2.0 M solution in THF. 12-Crown-4 was dried over activated 4A molecular sieves before use; tmeda and pmdeta were distilled from CaH$_2$ under nitrogen and were stored over activated 4A molecular sieves. All other compounds were used as supplied by the manufacturer.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a JEOL ECS500 spectrometer operating at 500.16 and 125.65 MHz, respectively, or a Bruker Avance300 spectrometer operating at

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

{(Me$_3$Si)$_2$CH}PH(BH$_3$)(C$_6$H$_4$-2-SMe) (9)

To a solution of {(Me$_3$Si)$_2$CH}PH(C$_6$H$_4$-2-SMe) (6.64 g, 21.11 mmol) in THF (15 ml) was added $BH_3{\cdot}SMe_2$ (10.6 ml, 21.20 mmol). After stirring for 1 h the solvent was removed *in vacuo* to yield an off-white oil which was crystallised from cold (–30 °C) *n*-hexane (30 ml) as colourless microcrystals. The solid was washed with cold light petroleum (3 × 10 ml) and residual solvent was removed *in vacuo*, to yield **9** as a white crystalline solid. Isolated crystalline yield: 7.22 g, 83%. ^1H NMR ($CDCl_3$, 25 °C): δ –0.06 (s, 9H, $SiMe_3$), 0.32 (s, 9H, $SiMe_3$), 0.92 (q, $^1J_{BH}$ = 7.1 Hz, 3H, BH_3), 1.46 (dd, $^2J_{PH}$ = 20.6 Hz, $^3J_{HH}$ = 2.8 Hz, 1H, Si_2CH), 2.56 (s, 3H, SMe), 6.04 (m, $^1J_{PH}$ = 375.2 Hz, $^3J_{HH}$ = 6.5 Hz, $^3J_{HH'}$ = 2.8 Hz, 1H, PH), 7.24 (t, $^3J_{HH}$ = 7.8 Hz, 1H, ArH), 7.29 (d, $^3J_{HH}$ = 6.9 Hz, 1H ArH), 7.46 (t, $^3J_{HH}$ = 7.6 Hz, 1H, ArH), 8.02 (dd, $^3J_{PH}$ = 13.8 Hz, $^3J_{HH}$ = 6.0 Hz, 1H, ArH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 1.53 (d, $^3J_{PC}$ = 3.8 Hz, $SiMe_3$), 2.18 (d, $^3J_{PC}$ = 2.8 Hz, $SiMe_3$), 6.34 (CHP), 16.59 (SMe), 125.25 (d, J_{PC} = 12.5 Hz, ArC), 126.02 (d, J_{PC} = 4.8 Hz, ArC), 125.25 (d, J_{PC} = 4.9, Hz ArC), 132.08 (d, J_{PC} = 1.9 Hz, ArC), 136.14 (d, J_{PC} = 18.2 Hz, ArC), 143.08 (ArC), $^{11}B\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ –40.1 (br d, $^1J_{BP}$ = 49.0 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ –15.7 (br q, $^1J_{PB}$ = 49.0 Hz).

[{(Me$_3$Si)$_2$CH}P(BH$_3$)(C$_6$H$_4$-2-SMe)]Li(THF)$_2$ (10)

To a solution of {(Me$_3$Si)$_2$CH}PH(BH$_3$)(C$_6$H$_4$-2-SMe) (0.47 g, 1.43 mmol) in diethyl ether (15 ml) was added *n*-BuLi (0.7 ml, 1.75 mmol) and this mixture was stirred at room temperature for 1 h. Solvent was removed *in vacuo* to yield a white powder, which was crystallised from cold (5 °C) toluene (5 ml) containing a few drops of THF as colourless blocks of **10** suitable for X-ray crystallography. Yield: 0.34 g, 58%. Anal. Calcd. for [[{(Me$_3$Si)$_2$CH}P(BH$_3$)(C$_6$H$_4$-2-SMe)]Li(THF)]: C 50.29, H 8.74. Found C 50.40, H 8.65. ^1H NMR (d_8-THF, 25 °C): δ –0.03 (s, 9H, $SiMe_3$), 0.07 (s, 9H, $SiMe_3$), 0.59 (q, $^1J_{BH}$ = 87.0 Hz, 3H, BH_3), 0.85 (s, 1H, PCH), 1.77 (m, 4H, THF), 2.32 (s, 3H, SMe), 3.62 (m, 4H, THF), 6.80 (m, 1H, ArH), 6.91 (m, 2H, ArH), 7.76 (d, $^3J_{HH}$ = 7.3 Hz, 1H, ArH). $^{13}C\{^1H\}$ NMR (d_8-THF, 25 °C): δ 1.50 (d, $^3J_{PC}$ = 6.7 Hz, $SiMe_3$), 2.88 ($SiMe_3$), 7.52 (d, $^1J_{PC}$ = 48.0 Hz, CH), 15.05 (d, $^4J_{PC}$ = 13.4 Hz, SMe), 25.27 (THF), 68.12 (THF), 122.28 (ArC), 122.52 (ArC), 124.68 (ArC), 133.51 (ArC), 143.35 (d, $^2J_{PC}$ = 24.0 Hz, ArC), 149.95 (d, $^1J_{PC}$ = 32.6 Hz, ArC). $^{11}B\{^1H\}$ NMR (d_8-THF, 25 °C): δ –32.9 (d, br, $^1J_{BP}$ = 39.2 Hz). $^{31}P\{^1H\}$ NMR (d_8-THF, 25 °C): δ –59.5 (q, br, $^1J_{PB}$ = 39.2 Hz). $^{7}Li\{^1H\}$ NMR (d_8-THF, 25 °C): δ 2.3.

[{(Me$_3$Si)$_2$CH}P(BH$_3$)(C$_6$H$_4$-2-SMe)]Na(tmeda)]$_\infty$ (11)

To a solution of {(Me$_3$Si)$_2$CH}PH(BH$_3$)(C$_6$H$_4$-2-SMe) (0.48 g, 1.46 mmol) in diethyl ether (15 ml) was added a slurry of benzylsodium (167 mg, 1.46 mmol) in diethyl ether (15 ml). After stirring at room temperature for 1 h the solvent was removed *in vacuo*, yielding a yellow powder. This powder was dissolved in toluene (5 ml) and tmeda (0.20 ml, 1.33 mmol) was added. Upon cooling to 5 °C colourless crystals of **11** suitable for X-ray crystallography were deposited. Yield: 0.48 g, 94%. C 51.48, H 9.72% Found C 51.38, H 9.76%. $^1H\{^{11}B\}$ NMR (d_8-THF, 25 °C): δ –0.06 (s, 9H, $SiMe_3$), 0.09 (s, 9H, $SiMe_3$), 0.71 (d, $^2J_{PH}$ = 6.4 Hz, 3H, BH_3), 0.86 (d, $^2J_{PH}$ = 5.5 Hz, 1H, Si_2CH), 2.15 (s, 12H, NMe_2), 2.30 (s, 4H, NCH_2), 2.33 (s, 3H, SMe), 6.83 (t, $^3J_{HH}$ = 7.1 Hz, 1H, ArH), 6.92 (m, 2H, ArH), 7.82 (d, $^3J_{HH}$ = 6.9 Hz, 1H, ArH). $^{13}C\{^1H\}$ NMR (d_8-THF, 25 °C): δ 0.08 (d, $^3J_{PC}$ = 5.4 Hz, $SiMe_3$), 1.99 (s, $SiMe_3$), 5.06 (PCH), 16.16 (d, $^4J_{PC}$ = 11.5 Hz, SMe), 46.20 (NMe), 58.90 (NCH_2), 123.57 (d, $^3J_{PC}$ = 3.7 Hz, ArC), 124.04, 125.88, 132.72, 134.86 (ArC), 143.45 (d, $^1J_{PC}$ = 22.6 Hz, ArC). $^{11}B\{^1H\}$ NMR (d_8-THF, 25 °C): δ –33.5 (d, br, $^1J_{BP}$ = 29.4 Hz). $^{31}P\{^1H\}$ NMR (d_8-THF, 25 °C): δ –58.4 (q, br, $^1J_{PB}$ = 29.4 Hz).

[{(Me$_3$Si)$_2$CH}P(BH$_3$)(C$_6$H$_4$-2-SMe)]K(pmdeta)]$_2$ (12)

To a solution of {(Me$_3$Si)$_2$CH}PH(BH$_3$)(C$_6$H$_4$-2-SMe) (0.55 g, 1.67 mmol) in diethyl ether (15 ml) was added a slurry of benzylpotassium (224 mg, 1.72 mmol) in diethyl ether (15 ml). This mixture was stirred at room temperature for 1 h and then solvent was removed *in vacuo* to give a white powder. This powder was dissolved in toluene (5 ml) and pmdeta (0.3 ml, 1.44 mmol) was added. Upon cooling to 5 °C colourless crystals of **12** suitable for X-ray crystallography were deposited. Yield: 0.57 g, 93%. Anal. Calcd. for [[{(Me$_3$Si)$_2$CH}P(BH$_3$)(C$_6$H$_4$-2-SMe)]K(pmdeta)]$_2$: C 51.18, H 9.71, N 7.78%. Found C 51.09, H 9.75, N 7.74%. $^1H\{^{11}B\}$ NMR (d_8-THF, 25 °C): δ 0.01 (s, 9H, $SiMe_3$), 0.04 (s, 9H, $SiMe_3$), 0.73 (d, $^3J_{PH}$ = 5.5 Hz, 3H, BH_3), 0.83 (d, $^3J_{PH}$ = 4.2 Hz, 1H, Si_2CH), 2.16 (s, 12H, NMe_2), 2.19 (s, 3H, NMe), 2.31 (m, 4H, CH_2N), 2.32 (s, 3H, SMe), 2.42 (m, 4H, CH_2N), 6.84 (t, $^3J_{HH}$ = 7.4 Hz, 1H, ArH), 6.90 (d, $^3J_{HH}$ = 6.9 Hz, 1H, ArH), 6.95 (t, $^3J_{HH}$ = 7.6 Hz, 1H, ArH), 7.75 (d, $^3J_{HH}$ = 7.8 Hz, 1H, ArH). $^{13}C\{^1H\}$ NMR (d_8-THF, 25 °C): δ 2.36 (d, $^3J_{PC}$ = 6.7 Hz, $SiMe_3$), 3.73 (d, $^3J_{PC}$ = 1.9 Hz, $SiMe_3$), 8.03 (d, $^1J_{PC}$ = 47.0 Hz, Si_2CH), 15.75 (d, $^4J_{PC}$ = 13.4 Hz, SMe), 43.15 (NMe), 46.16 (NMe_2), 57.24 (NCH_2), 58.70 (NCH_2), 122.03 (d, $^3J_{PC}$ = 3.8 Hz, ArC), 122.45, 125.78, 134.25 (ArC), 143.48 (d, $^2J_{PC}$ = 22.0 Hz, ArC), 150.42 (d, $^1J_{PC}$ = 27.8 Hz, ArC). $^{11}B\{^1H\}$ NMR (d_8-THF, 25 °C): δ –30.6 (d, br, $^1J_{PB}$ = 19.6 Hz). $^{31}P\{^1H\}$ NMR (d_8-THF, 25 °C): δ –58.3 (q, br, $^1J_{PB}$ = 19.6 Hz).

[{(SiMe$_3$)$_2$CH}P(BH$_3$)$_2$(C$_6$H$_4$-2-SMe)][Li(12-crown-4)] (14a)

To a solution of **9** (0.57 g, 1.74 mmol) in THF (10 ml) was added *n*-BuLi (0.7 ml, 1.75 mmol). This mixture was stirred for 1 h, after which $BH_3{\cdot}SMe_2$ (0.90 ml, 1.80 mmol) was added, whereupon the mixture became colourless. This mixture was stirred for a further 1 h and then the solvent was removed *in vacuo* to yield a colourless solid. This solid was dissolved in toluene (10 ml) and 12-crown-4 (0.3 ml, 1.84 mmol) was added followed by a few drops of diethyl ether. The solution was filtered and the filtrate was allowed to stand at room temperature for 16 h, whereupon **14a** precipitated as a colourless solid. Isolated yield: 0.55 g, 60%. Anal. Calcd. for [{(Me$_3$Si)$_2$CH}P(BH$_3$)$_2$(C$_6$H$_4$-2-SMe)][Li(12-crown-4)]: C 50.29,

Table 1 Crystallographic data for **10**, **11**, and **12**

Compound	**10**	**11**	**12**
Formula	$C_{36}H_{74}B_2Li_2O_2P_2S_2Si_4$	$C_{20}H_{45}BN_2NaPSSi$	$C_{46}H_{104}B_2K_2N_6P_2S_2Si_4$
M_w	812.9	466.6	1079.6
Cryst. size/mm	0.32 × 0.30 × 0.30	0.12 × 0.10 × 0.08	0.30 × 0.20 × 0.20
Cryst. syst.	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	13.4504(5)	11.3566(9)	11.1081(6)
b/Å	16.2605(5)	13.2652(10)	12.0772(7)
c/Å	11.2638(4)	21.1564(18)	14.3398(7)
α (°)		93.397(7)	101.977(4)
β (°)	103.732(4)	104.760(7)	108.829(5)
γ (°)		97.552(6)	105.691(5)
V/Å^3	2393.08(14)	3040.9(4)	1658.67(15)
Z	2	4	1
μ/mm^{-1}	0.306	0.261	3.238
Trans. coeff. range	0.908–0.914	0.969–0.979	0.443–0.564
Reflns. measd.	15640	26610	8950
Unique reflns.	5823	10697	5133
R_{int}	0.031	0.083	0.022
Reflns. with $F^2>2\sigma$	4054	4259	4426
Refined parameters	245	551	314
R (on F, $F^2>2\sigma$)[a]	0.032	0.048	0.032
R_w (on F^2, all data)[a]	0.076	0.095	0.085
Goodness of fit[a]	0.914	0.698	1.026
Max, min electron density/e Å^{-3}	0.61, –0.37	0.33, –0.24	0.41, –0.23

[a] Conventional $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$; $R_w = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$; $S = [\Sigma w(F_o^2 - F_c^2)^2 / (\text{no. data - no. params})]^{1/2}$ for all data.

H 9.40. Found C 50.13, H 9.39. $^1H\{^{11}B\}$ NMR (d_8-THF, 25 °C): δ 0.07 (s, 18H, $SiMe_3$), 0.34 (d, $^2J_{PH}$ = 8.3 Hz, 1H, CH), 0.80 (d, $^2J_{PH}$ = 10.5 Hz, 6H, BH_3), 2.42 (s, 3H, SMe), 3.74 (s, 16H, 12-crown-4), 6.93 (m, 1H, ArH), 7.09 (m, 1H, ArH), 7.22 (m, 1H, ArH), 8.11 (m, 1H, ArH). $^{13}C\{^1H\}$ NMR (d_8-THF, 25 °C): δ 3.09 ($SiMe_3$), 6.98 (d, $^1J_{PC}$ = 3.8 Hz, PCH), 17.40 (SMe), 68.53 (12-crown-4), 123.65 (d, $^3J_{PC}$ = 8.6 Hz, ArC), 127.32 (ArC), 128.10 (d, $^3J_{PC}$ = 3.8 Hz, ArC), 135.07 (d, $^2J_{PC}$ = 12.46 Hz, ArC), 143.23 (ArC), 143.62 (d, $^1J_{PC}$ = 26.8 Hz, ArC). $^{11}B\{^1H\}$ NMR (d_8-THF, 25 °C): δ –32.6 (d, br, $^1J_{BP}$ = 68.6 Hz). ^{31}P NMR (d_8-THF, 25 °C): δ –4.7 (m, br, $^1J_{PB}$ = 68.6 Hz). $^7Li\{^1H\}$ NMR (d_8-THF, 25 °C): δ –0.7.

Crystal structure determinations of 10, 11, and 12

Measurements were made at 150 K on an Oxford Diffraction Gemini A Ultra diffractometer using Mo-Kα (for **10** and **11**) and Cu-Kα (for **12**) radiation (λ = 0.71073 and 1.54184 Å, respectively). Cell parameters were refined from the observed positions of all strong reflections. Intensities were corrected semi-empirically for absorption, based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined on F^2 values for all unique data. 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. Disordered solvent of crystallisation in **11** was treated using the SQUEEZE procedure of PLATON; it was unidentified and found to have low occupancy, the solvent being presumably readily lost even on brief removal from the mother liquor.[16] Other programs were Oxford Diffraction CrysAlisPro and SHELXTL for structure solution, refinement, and molecular graphics.[17]

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