The reaction between the phosphine-borane-substituted alkene \([\text{Pr}_n\text{P(BH}_3\text{)}][\text{Me}_n\text{Si}]\text{C}=\text{CH}_2\) and elemental lithium in THF yields the complex \([\langle\text{pmdeta}\rangle\text{Li}][\text{Pr}_n\text{P(BH}_3\text{)}][\text{Me}_n\text{Si}]\text{C}=\text{CH}_2\].

Phosphine-borane adducts constitute a unique class of organophosphorus compound which has found widespread application in organic and inorganic synthesis. The presence of the P–B bond in these compounds both activates adjacent C–H groups towards deprotonation and stabilises the phosphorus centre towards oxidation. This, together with the ready removal of the borane group by relatively simple methodologies, positions the borane function as an immensely useful activating/group protecting agent for the synthesis of organophosphorus(III) compounds. An excellent example of the utility of phosphine-borane adducts is provided by the enantioselective synthesis of commercially important P-chiral diphosphines of the form R(Me)P=CH=P(Me)R (R = Ph, o-anisyl, o-tolyl, naphthyl) (Scheme 1).2

In addition to their use in activation/protection protocols, \(\alpha\)-metallated phosphine-boranes undergo Horner–Witt olefination reactions similar to those of the corresponding phosphine oxide species.3 Thus, \(\alpha\)-metallated phosphine-borane adducts are versatile synths for a wide range of organic and organophosphorus(III) compounds. However, little is known about the cation–anion interactions in these species.

We recently reported that the vinylidene phosphine \((\text{Ph})_2\text{P}=\text{CH}_2\) underwent Schlenk dimerisation on treatment with either lithium or sodium to give the corresponding dicarbanion complexes \([\text{Li}][\langle\text{pmdeta}\rangle\text{Li}][\text{Pr}_n\text{P(BH}_3\text{)}][\text{Me}_n\text{Si}]\text{C}=\text{CH}_2\] (2a). Removal of solvent in vacuo and recrystallisation of the pale yellow solid from methylcyclohexane in the presence of pmdeta gives the complex \([\langle\text{pmdeta}\rangle\text{Li}][\text{Pr}_n\text{P(BH}_3\text{)}][\text{Me}_n\text{Si}]\text{C}=\text{CH}_2\) as colourless blocks in good yield (Scheme 2).† The NMR spectra of 2b are as expected; unfortunately \(^3\text{Li}–^1\text{H}\) coupling is not resolved in the \(^1\text{H}\) spectrum, probably due to rapid, reversible \(\text{Li}–\text{H}\) bond cleavage in THF solution. The \(^1\text{H}\) chemical shift of the BH\(_3\) group in 2b was obtained from a H[\(^{11}\text{B}\)] decoupling experiment.

Somewhat surprisingly, given the synthetic utility of \(\alpha\)-metallated phosphine-boranes, there has been only one previous structural study of a complex of this type. The adduct \([\langle\text{tmeda}\rangle\text{Li}][\langle\text{pmdeta}\rangle\text{Li}][\text{Pr}_n\text{P(BH}_3\text{)}][\text{Me}_n\text{Si}]\text{C}=\text{CH}_2\] (3) crystallises as a solvent-separated ion pair with no contact between the anion and cation.6 Thus, the nature of the interaction between phosphine-borane-stabilised carbanions and alkali metal cations has not previously been determined. In view of this, and of the importance of such reagents in synthesis, we carried out an X-ray crystallographic study of 2b.

Compound 2b crystallises as a discrete molecular species with a crystallographic centre of inversion midway along the CH\(_3\)--CH\(_2\) bond of the dicarbanion (Fig. 1). The lithium atoms are bound at either end of the dianionic ligand by two of the H atoms of the BH\(_3\) units; there are no contacts between the lithium atoms and the formal carbanion centres C(1). The coordination sphere of each lithium is completed by three nitrogen atoms of a chelating molecule of pmdeta. The Li–H distances of 1.94(3) and 2.05(3) Å \((\text{Li}–\text{B} 2.282(5) \text{ Å})\) compare with Li–H distances of 1.90 and 2.06 Å in the \(^1\text{H}\)-bound borohydride complex \((\text{py})\text{Li}[\text{BH}_4]\) \((\text{Li}–\text{B} 2.401 \text{ Å})\);5 the third Li–H distance in 2b is in excess of 2.5 Å. The P–C(1) and Si–C(1) distances [1.71(2) and 1.80(2) Å, respectively] are shorter than expected for single bonds, consistent with a significant degree of negative hyperconjugation; the carbanion centre is strictly planar [sum of angles at C(1) = 359.84°]. The P–B distance of 1.924(3) Å compares with P–B distances of 1.905 and 1.904 Å in the free anion of 3 and with P–B distances of 1.995(3) and 1.984(3) Å in the compound...
observed in these experiments suggests that there is no Li–borane.

Protonolysis of a solution of 2a or 2b in ether with distilled water yields the bis(bisphosphate-borane) [(Pr**,P(BH₃))(Me₅Si)CHCH₂]₂ (4) in essentially quantitative yield as a 1:1 mixture of the two possible diastereomers.† A ²²³P{¹H} NMR spectrum indicates that recrystallisation of 4 from diethyl ether does not affect the ratio of diastereomers; an X-ray crystal structure was obtained of the meso-diastereomer (Fig. 2).‡

Compound meso-4 crystallises with exact inversion symmetry. The P–C and Si–C distances of 1.819(2) and 1.908(2) Å, respectively, are considerably longer than the corresponding distances in 2b, the P–B distance in meso-4 [1.914(3) Å] is similar to that in 2b [1.924(3) Å].

Careful protonolysis of 2a with distilled water in the presence of the chiral diamine (−)-sparteine results in the formation of a 1:1 mixture of rac- and meso-4. Similarly, the ratio of diastereomers is unaffected when the protonolysis reaction is carried out with enantiomerically pure (−-sec-amyl alcohol, even in the presence of (−)-sparteine. The lack of stereocontrol observed in these experiments suggests that there is no Li–C contact in solution, i.e. that either the solid-state structure is maintained or that 2a exists as solvent-separated ion triples in solution.

In summary, Schlenk dimerisation of the vinylidene phosphine-borane 1 with elemental lithium yields a novel dicarbanion ([(mes*)PH(BH₃)₂]Li(THF)₃, which has a formal negative charge at C₂) diastereomer (Fig. 2).

† 4[(mes*)PH(BH₃)₂]Li(THF)₃, which has a formal negative charge at C₂, 2.46-ButC₆H₄)₂P(=NCH₂CH₂)₂P=N(ButC₆H₄)₂, which has a formal negative charge at C₂.

Notes and references

¶ To a solution of [Pr**,P(BH₃)][(Me₅Si)CHCH₂Cl] (1.26 g, 5.47 mmol) in THF (20 ml) was added lithium powder (0.19 g, 27.36 mmol). This mixture was sonicated for 30 min, excess lithium was removed by filtration and solvent was removed in vacuo. The yellow solid was washed with light petroleum (bp 40–60 °C, 3 × 10 ml) and treated with pmdeta (1.14 ml, 5.47 mmol). The solid was recrystallised from hot methylcyclohexane as colourless blocks. Isolated yield: 1.77 g (79%). Anal. Calc. for C₄₀H₁₀₂B₂Li₂N₆P₂Si₂: C, 62.82; H, 13.44; N, 10.99. Found: C, 62.69; H, 13.34; N, 10.72. ¹H NMR (δ 7.00, 2H, Me₅Si); δ 0.82 (s, 18H, SiMe₃), 0.22 (s, 18H, SiMe₃), 0.80 (m, 4H, CH), 1.00 (m, 4H, CH₂N). ³¹P{¹H} NMR (δ 22.8, 23.2). ¹H NMR (δ 26.9, 27.2).

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§ For C₄₀H₁₀₂B₂Li₂N₆P₂Si₂:

## Crystal data

For C₄₀H₁₀₂B₂Li₂N₆P₂Si₂:

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