Synthesis and structural characterisation of a novel phosphine-borane-stabilised dicarbanion and an unusual bis(phosphine-borane)

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The reaction between the phosphine-borane-substituted alkene $\{Pr^n_2P(BH_3)\}(Me_3Si)C=CH_2$ and elemental lithium in THF yields the complex $[(pmdeta)Li\{Pr^n_2P(BH_3)\}(Me_3Si)CCH_2]_2$ (2b) after recrystallisation; an X-ray crystallographic study of 2b reveals that the lithium is bound to the BH_3 hydrogens of the ligand, with no Li–C(carbanion) contact.

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/protecting group for the synthesis of organophosphorus(III) compounds.[1] 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 $R(Me)PCH_2CH_2P(Me)R$ (R = Ph, o-anisyl, o-tolyl, naphthyl) (Scheme 1).[2]

In addition to their use in activation/protection protocols, α-metalated phosphine-boranes undergo Horner–Wittig olefination reactions similar to those of the corresponding phosphine oxide species.[3] Thus, α-metalated phosphine-borane adducts are versatile synthons 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 $(Ph_2P)_2C=CH_2$ underwent Schlenk dimerisation on treatment with either lithium or sodium to give the corresponding dicarbanion complexes $[(L)M(Ph_2P)_2CCH_2]_2$ $[(L)M = (THF)_2Li$, (pmdeta)Li, $(tmeda)_{1.5}Na]$ (tmeda = N,N,N',N'-tetramethylethylenediamine, pmdeta = N,N,N',N'',N''-pentamethyldiethylenetriamine).[4] We now report a similar Schlenk dimerisation of the alkene $\{Pr^n_2P(BH_3)\}(Me_3Si)C=CH_2$ (1)[5] and the X-ray crystal structure of the resulting phosphine-borane-stabilised dicarbanion, which reveals for the first time the nature of the cation–anion interactions in α-lithiated phosphine-borane adducts.

Sonication of a solution of 1 in THF with one equivalent of elemental lithium for 30 min gives the lithium bis(boronatophosphinomethanide) $(THF)_4Li_2[\{Pr^n_2P(BH_3)\}(Me_3Si)CCH_2]_2$ (2a). Removal of solvent *in vacuo* and recrystallisation of the pale yellow solid from methylcyclohexane in the presence of pmdeta gives the complex $[(pmdeta)Li\{Pr^n_2P(BH_3)\}(Me_3Si)CCH_2]_2$ (2b) as colourless blocks in good yield (Scheme 2).† The NMR spectra of 2b are as expected; unfortunately ^7Li–^1H coupling is not resolved in the ^7Li spectrum, probably due to rapid, reversible Li–H bond cleavage in THF solution. The ^1H chemical shift of the BH_3 group in 2b was obtained from a $^1H\{^{11}B\}$ decoupling experiment.

Somewhat surprisingly, given the synthetic utility of α-metalated phosphine-boranes, there has been only one previous structural study of a complex of this type. The adduct $[Li(tmeda)_2]$-

$[Me_2P(BH_3)CHPMe_2(BH_3)]$ (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_2–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 [Li⋯B 2.282(5) Å] compare with Li–H distances of 1.90 and 2.06 Å in the η^2-bound borohydride complex $(py)_3Li(BH_4)$ (Li⋯B 2.401 Å);[7] the third Li–H distance in 2b is in excess of 2.5 Å. The P–C(1) and Si–C(1) distances [1.711(2) and 1.808(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
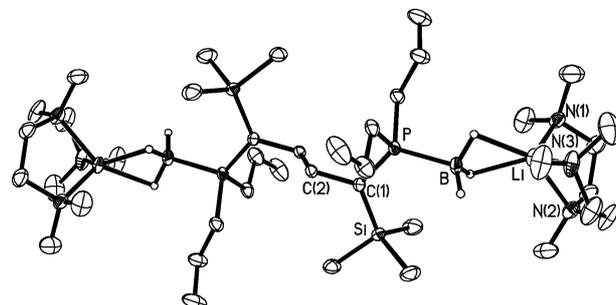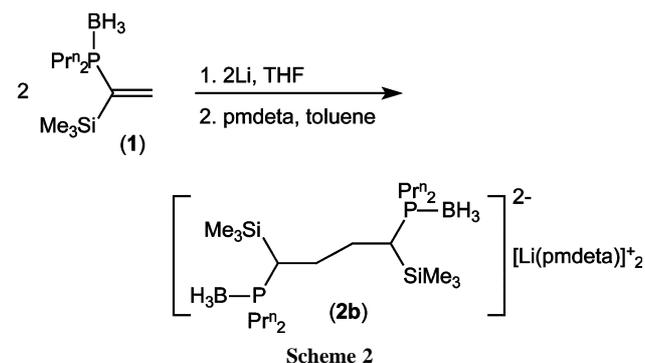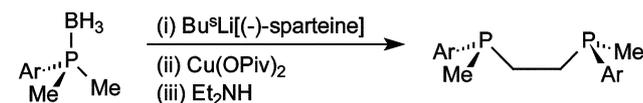
Scheme 1

Scheme 2

Fig. 1 Molecular structure of 2b with 30% probability ellipsoids and with H atoms, other than BH_3, omitted for clarity. Selected bond lengths (Å) and angles (°): Li⋯B 2.282(5), Li–N(1) 2.124(5), Li–N(2) 2.094(5), Li–N(3) 2.125(5), P–B 1.924(3), P–C(1) 1.711(2), Si–C(1) 1.808(2), C(1)–C(2) 1.535(3); Si–C(1)–C(2) 120.53(16), Si–C(1)–P 121.78(13), P–C(1)–C(2) 117.53(16).

[(mes*)PH(BH$_3$)$_2$]Li(THF)$_3$, which has a formal negative charge at the phosphorus atom (mes* = 2,4,6-Bu$^t_3$C$_6$H$_2$).[8]

Protonolysis of a solution of **2a** or **2b** in ether with distilled water yields the bis(phosphine-borane) [{Pr$^n_2$P(BH$_3$)}(Me$_3$Si)CHCH$_2$]$_2$ (**4**) in essentially quantitative yield as a 1:1 mixture of the two possible diastereomers.† A ^{31}P{^{1}H} 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 at low temperatures. 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 (**2**) which is stabilised by both phosphine-borane and silyl groups. X-Ray crystallography reveals that the lithium atoms in **2** are bound by the borane hydrogen atoms and have no contact with the formal carbanion centre. Hydrolysis of **2** yields an unusual bis(phosphine borane).
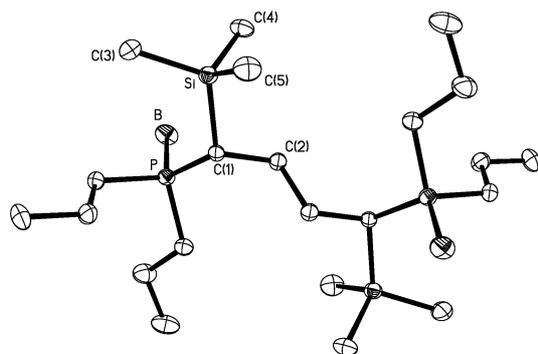
Fig. 2 Molecular structure of **4** with 30% probability ellipsoids and with H atoms omitted for clarity. Selected bond lengths (Å): P–B 1.914(3), P–C(1) 1.819(2), P–C(6) 1.818(2), P–C(9) 1.824(2), C(1)–Si 1.908(2), Si–C(3) 1.861(3), Si–C(4) 1.863(2), Si–C(5) 1.861(3), C(1)–C(2) 1.568(3).

Notes and references

† **2b**: To a solution of {Pr$^n_2$P(BH$_3$)}(Me$_3$Si)C=CH$_2$ (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 C$_{40}$H$_{102}$P$_2$N$_6$B$_2$Si$_2$Li$_2$: C, 62.82; H, 13.44; N, 10.99. Found: C, 62.69; H, 13.34; N, 10.72%. ^{1}H NMR (d_8-THF, 50 °C): δ −0.04 (s, 18H, SiMe$_3$), 0.30 (br, m, $^1J_{PH}$ = 14 Hz, 6H, BH$_3$), 0.80–1.88 (m, 32H, Pr^n + CH$_2$CH$_2$), 2.17 (s, 24H, NMe$_2$), 2.24 (s, 6H, NMe), 2.31 (m, 8H, NCH$_2$), 2.42 (m, 8H, CH$_2$N). ^{13}C{^{1}H} NMR (d_8-THF, 50 °C): δ 6.13 (SiMe$_3$), 17.27, 17.37, 18.70 (Pr^n), 34.60 (CP, $^1J_{PC}$ 33 Hz), 38.64 (CH$_2$), 44.24 (NMe), 44.68 (NMe$_2$), 56.64 (NCH$_2$), 58.90 (CH$_2$N). ^{31}P{^{1}H} NMR (d_8-THF, 50 °C): δ 7.2 (q, $^1J_{BP}$ 102 Hz). ^{11}B NMR (d_8-THF, 50 °C): δ −34.6 (qnt, $^1J_{BH}$ 100 ± 10 Hz, $^1J_{BP}$ 102 Hz). ^{7}Li NMR (d_8-THF, 50 °C): δ 0.4.

4: To a solution of **2b** (1.06 g, 1.29 mmol) in diethyl ether (20 ml) was added water (10 ml). The mixture was stirred for 1 h and the organic layer was decanted. The aqueous layer was washed with diethyl ether (3 × 5 ml) and the combined organic phases were dried over activated 4Å molecular sieves. Solvent was removed *in vacuo* and the white solid was recrystallised from cold (5 °C) diethyl ether as a 1:1 mixture of *rac*- and *meso*-diastereomers. Isolated yield: 0.53 g (84%). Anal. Calc. for C$_{22}$H$_{58}$P$_2$B$_2$Si$_2$: C, 57.14; H, 12.64. Found: C, 57.25; H, 12.72%. ^{1}H NMR (d_8-THF, 25 °C): δ 0.20 (s, 18H, SiMe$_3$), 0.22 (s, 18H, SiMe$_3$), 0.80 (m, 4H, CH), 1.00–1.66 (m, 64H, CH$_2$CH$_2$ + Pr^n) (BH$_3$ protons too broad to observe). ^{31}P{^{1}H} NMR (d_8-THF, 26 °C): δ 22.8, 23.2.

‡ *Crystal data*: For C$_{40}$H$_{102}$B$_2$Li$_2$N$_6$P$_2$Si$_2$ **2b**, M = 820.9, monoclinic, $P2_1/n$, a = 11.6349(6), b = 19.2561(9), c = 12.5695(6) Å, β = 97.1740(10)°, U = 2794.1(2) Å^3, Z = 2, μ(Mo-Kα) = 0.150 mm^{-1}, T = 150 K. 19093 data, 4914 unique (R_{int} = 0.0381). $wR(F^2)$ = 0.1384 for all data, conventional R = 0.0486 for F values of 3686 reflections with F_o^2 > 2σ(F_o^2). H atoms of the BH$_3$ units were freely refined. For C$_{22}$H$_{58}$B$_2$P$_2$Si$_2$ **4**, M = 462.4, monoclinic, $P2_1/n$, a = 14.1618(11), b = 6.9841(5), c = 16.5204(12) Å, β = 107.859(2)°, U = 1555.3(2) Å^3, Z = 2, μ(Mo-Kα) = 0.224 mm^{-1}, T = 150 K. 8510 data, 2728 unique (R_{int} = 0.0337). $wR(F^2)$ = 0.1055 for all data, conventional R = 0.0398 for F values of 2160 reflections with F_o^2 > 2σ(F_o^2). CCDC 225174 and 225175. See http://www.rsc.org/suppdata/cc/b3/b315068b/ for crystallographic data in CIF or other electronic format.

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