Spontaneous dehydrocoupling in peri-substituted phosphine–borane adducts†

Laurence J. Taylor, Brian A. Surgenor, Piotr Wawrzyniak, Matthew J. Ray, David B. Cordes, Alexandra M. Z. Slawin and Petr Kilian*

Bis(borane) adducts Acenap(PiPr2·BH3)(PRH·BH3) (Acenap = acenaphthene-5,6-diyl; 4a, R = Ph; 4b, R = ferrocenyl; 4c, R = H) were synthesised by the reaction of excess H3B·SMe2 with either phosphinephosphonium salts [Acenap(PiPr2)(PR)]+Cl− (1a, R = Ph; 1b, R = Fc), or bis(phosphine) Acenap(PiPr2)(PH2) (3). Bis(borane) adducts 4a–c were found to undergo dihydrogen elimination at room temperature, this spontaneous catalyst-free phosphine-borane dehydrocoupling yields BH2 bridged species Acenap(PiPr2)(µ-BH2)·(PR BH3) (5a, R = Ph; 5b, R = Fc; 5c, R = H). Thermolysis of 5c results in loss of the terminal borane moiety to afford Acenap(PiPr2)(µ-BH2)(PH) (14). Single crystal X-ray structures of 3, 4b and 5a–c are reported.

While catalysts are incredibly useful, they are often expensive, especially when they contain precious transition metals such as Rh or Ir. As such, it would be helpful to develop systems which undergo dehydrocoupling without the addition of an external catalyst, but while still under mild conditions. The work of our group has focused on peri-substitution, which is useful in thermodynamically stabilising bonding motifs which are typically unstable at room temperature. However, lately we have been intrigued by the possibility of using peri-substitution to promote reactivity that would typically require the addition of a catalyst. Due to the unique constraints of the peri-geometry, atoms in the peri-position (E) are forced into close proximity. Strain from the overlap of occupied orbitals can be relieved by, either, the formation of a direct E=E bonding interaction or a bridging motif between the two peri-atoms (E=E). As such, it was postulated that if two potentially reactive groups were placed in the peri-positions, the rigid scaffold could lower the kinetic barrier of the coupling reaction, promoting the formation of a direct bond or a bridging motif and hence emulating the role of an external catalyst.

This was indeed found to be the case, as a series of peri-substituted phosphine–borane adducts were synthesised and observed to undergo spontaneous intramolecular dehydrocoupling in solution at room temperature. The results of these investigations are detailed below.

Results and discussion

Bis(borane) Adducts 4a–c

Compounds 1a–b and 2 were used as the starting points for all of the reactions presented in this work. Compound 2 was...
Table 1 Selected bond lengths (Å) and angles (°) for 3, 4b, 5a–c

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*a* Measurements for second molecule in asymmetric unit shown in square brackets.

Table 2 Peri-distances (Å), splay angles (°) and out-of-plane displacements for 3, 4b, 5a–c

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*a* Measurements for second molecule in asymmetric unit shown in square brackets.

The synthesis and characterisation of the bis(borane) adduct 4a were recently reported by our group,26 while compounds 1a–b were synthesised via a modified version of the literature procedure.25

The 31P{1H} NMR spectrum of 4b exhibits broad singlets at δP 36.3 (IPr2P) and −7.7 (PFcH), and in the 31P NMR spectrum the signal at δP ~7.7 is split into a broad doublet (|JPh| = 395 Hz). Crystals of 4b suitable for X-ray diffraction were grown from acetonitrile, the structure is shown in Fig. 2 and Tables 1–3. The structure of 4b is similar to the previously reported structure of 4a,26 with a P⋯P distance of 3.521(1) Å and a large positive splay angle of +21.2(7)°, indicating significant repulsion between the two peri-groups. Additionally, both phosphorus atoms show significant displacement from the mean plane of the acenaphthene ring (0.706 Å for P1, 0.546 Å for P9).
The bis(borane) adduct 4c was synthesised from the novel primary phosphine 3 (Scheme 1), which was obtained by clean reduction of the phosphonium-phosphoranide 2 with LiAlH₄.

The ³¹P{¹H} NMR spectrum of compound 3 displays two doublets at δₚ −11.3 (iPr₂P) and −101.2 (PH₂), with a substantial through-space coupling of Jₚₚ = 205 Hz. In the ³¹P NMR spectrum, the signal for the PH₂ group is split into a pseudo-quartet due to Jₚₕ = 204 Hz being very similar to that of Jₚₚ.

The ¹H NMR spectrum of 3 displays a doublet of doublets for the PH₂ protons (δₕ 4.98, Jₚₕ = 204 Hz, Jₚₕ = 48 Hz). This long range Jₚₕ interaction, in addition to the large Jₚₚ coupling, indicates a significant through space contribution to coupling operates in this compound. Crystals of compound 3 suitable for single crystal X-ray diffraction were grown from THF, the structure is shown in Fig. 2 and Tables 1–3. The structure indicates a clear repulsive interaction between the two phosphorus moieties, with a P⋯P distance of 3.143(1) Å and a positive splay angle of 16.4(7)°. The purity of 3 as obtained from the reaction was established by ³¹P, ¹H and ¹³C NMR and was found to be sufficient for further syntheses.

Treatment of primary bis(phosphine) 3 with excess H₃B·SMe₂ afforded bis(borane) adduct 4c as the major product (δₚ 38.0 (br s, iPr₂P), −40.8 (br s, PH₂)), although the reaction was not clean. Even with a large excess (12 equivalents) of

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R₁ = ∑||Fₒ| − |F_c||/∑|Fₒ|, wR₂ = [∑(w(Fₒ² − F_c²))²/∑(w(Fₒ²))²]¹/², w = 1/[σ²(Fₒ²) + (ap)² + bp], where p = [(Fₒ²)² + 2F_c²]/3.

Fig. 1 Definition of a splay angle.

Fig. 2 Structures of 3 (top) and 4b (bottom) in the solid state. Carbon-bound hydrogen atoms omitted for clarity.
A new compound was characterised by $^1$H, $^{31}$P, $^{31}$P{$_1^1$H}, $^{13}$C{$_1^1$H}, as a yellow solid in near quantitative yield (Scheme 2). The stable towards both air and moisture, compound formed. Minor, unidentified P containing side products were also present in a ratio of approximately 5:1. A number of unidentified P containing side products were also formed.

In sharp contrast to compounds 4a and 4b, which are stable towards both air and moisture, compound 4c is rather moisture sensitive. On a preparative scale, treatment of a dichloromethane solution of 4c with degassed water afforded 6 as a yellow solid in near quantitative yield (Scheme 2). The new compound was characterised by $^1$H, $^{31}$P, $^{31}$P{$_1^1$H}, $^{13}$C{$_1^1$H}, $^{11}$B, and $^{11}$B{$_1^1$H} NMR spectroscopy.

Primary phosphine-borane adducts have been less extensively studied than secondary or tertiary phosphine-boranes, and are known to be generally less stable. In addition, steric hindrance arising from the peri-geometry is likely to further destabilise the bis(borane) adduct 4c in the mono-borane adduct 6. This corresponds well with our observations of the instability of 4c towards moisture, as well as the difficulty in getting complete conversion to the bis(borane) adduct. Compound 4c could not be isolated in analytically pure form due to its crystallisation being extremely difficult, whilst its sensitivity to air and moisture prevented chromatographic purification.

Compound 4c exhibits two broad singlets in the $^{31}$P{$_1^1$H} NMR spectrum at $\delta_p$ 38.0 (iPr$_2$P) and $\delta_p$−40.8 (PH$_2$). In the $^{31}$P NMR spectrum, the signal at $\delta_p$−40.8 splits into a broad triplet ($^1J_{HP} = 379$ Hz). One particularly distinctive signal is observed for the PH$_2$ group in the $^1$H NMR spectrum, which is split into a doublet of quartets ($\delta_H$ 6.14, $^1J_{HP} = 377$ Hz, $^3J_{HH} = 7.1$ Hz) due to coupling to the adjacent BH$_3$ hydrogen atoms. This, therefore, provides strong evidence that BH$_3$ is bound to PH$_2$ in this molecule. In contrast, the PH$_2$ signal in the $^1$H NMR spectrum of compound 6 appears as a sharp doublet ($\delta_H$ 4.48, $^1J_{HP} = 207$ Hz), indicating the absence of a co-ordinated borane.

It should be noted that, unlike compounds 1a–b, treatment of the phosphonium-phosphorane 2 with H$_2$B·SMe$_2$ does not result in borane mediated reduction to give 4c, but instead yields the “push–double pull” bis(borane) adduct 7 (Scheme 3).

### Spontaneous intramolecular dehydrocoupling of 4a–c to give 5a–c

When compound 4a was allowed to stand in solution in DCM, the signals corresponding to the bis(borane) adduct ($\delta_p$ 39.4 (br s, iPr$_2$P) and −6.6 (br s, PhPH)) were gradually replaced by a broad doublet ($\delta_p$ 13.9, $^1J_{Pr2}$, $^1J_{PP} \approx 84.0$ Hz) and a very broad signal in which coupling could not be resolved ($\delta_p$−26.3, PPh), corresponding with the formation of 5a (Fig. 3). Complete conversion to 5a was achieved after 8 days at room temperature (Scheme 1). $^1$H and $^{31}$P NMR spectroscopy confirmed that the H atom directly bonded to phosphorus had been lost. Additionally, $^{11}$B{$_1^1$H} NMR spectroscopy revealed a broad pseudo-triplet ($\delta_B$−39.4, $^1J_{BP} \approx 69$ Hz) and a broad doublet ($\delta_B$−33.6, $^1J_{BP} \approx 46$ Hz), consistent with the presence of one bridging P–B–P motif and one terminal B–P motif (Fig. 4).

Crystals of 5a suitable for single crystal X-ray diffraction were grown from d$_6$-DMSO. The structure confirmed 5a to contain one bridging BH$_3$ and one terminal BH$_3$ motif (Fig. 5, Tables 1–3). The significant reduction of strain is observed in 5a in comparison to 4a, with a reduced P⋯P distance of 3.1295(8) Å and smaller splay angle of +15.1(4)° in 4a, as well as decreased displacements of the P atoms from the mean plane of the acenaphthene ring (0.338 Å for P1, 0.327 Å for P9; cf. 0.478 and 0.816 Å in 4a).
Based on the identity of compound 5a, it seemed likely that the bis(borane) adduct 4a had undergone a phosphine–borane dehydrocoupling reaction. In order to confirm the evolution of hydrogen, a solution of 4a in C6D6 was prepared and left to stand in a sealed NMR tube. After 1 day, some conversion to compound 5a was observed by 31P{1H} NMR, and a sharp singlet of dissolved H2 was observed in the 1H NMR (δH 4.47). In another experiment, the conversion of 4a to 5a (in CDCl3) was followed over several days at room temperature by 1H NMR spectroscopy. The reaction was found to follow simple first order kinetics, with an approximate rate constant of 0.04 h⁻¹. It is likely that the driving force for this reaction is the reduction in strain on going from 4a to 5a, coupled with the entropic gain from hydrogen evolution.

Spontaneous dehydrocoupling reactions occurring at room temperature are rather rare, with a few examples involving very reactive precursors such as primary/secondary stibines or bismuthines. In recent work by the Manners’ group, a series of primary arylamine–borane adducts were found to undergo spontaneous dehydrocoupling at room temperature, with the rate of dehydrocoupling increasing with decreasing electron density on the aryl substituent. This reactivity was attributed to weak B–N bonding and the increased acidity of the N–H bonds in arylamine–boranes. By contrast, while dehydrocoupling of phosphine–boranes has been observed in the presence of catalysts or at very high temperatures, spontaneous, room temperature dehydrocoupling of a phosphine–borane adduct is without precedent in the literature.

The compound 5a bears some similarities to two cyclic boronium salts, 10 and 13, reported by Mikolajczyk et al. and Costa and Schmidbaur (Scheme 4). Compounds 5a, 10 and 13 are all formed by the treatment of peri-substituted precursors with borane, and all consist of two peri-phosphorus atoms bridged by a BH2 unit. However, compounds 10 and 13 are ionic species; 10 is thought to form via the mono(borane) adduct 9, which then reduces the halogenated solvent to form 10. Compound 13 exists in equilibrium with the bis(borane) adduct 12 and forms via hydride transfer to give a BH2 bridge and a BH4⁻ counterion. Although these reactions are significantly different from the dehydrocoupling observed in 4a, in all cases the driving force for the formation of the BH2 bridge is most likely the same – reduction of strain resulting from the peri-substitution geometry. In compound 4a this is achieved via hydrogen evolution, while for 9 and 12 (which contain no P–H bonds) the formation of the boronium salts is preferred.

The ferrocenyl substituted bis(borane) adduct (4b) was also found to undergo spontaneous dehydrocoupling in solution,

Fig. 5 Structures of 5a (left), 5b (centre), and 5c (right) in the solid state. Carbon-bound hydrogen atoms and second molecule in asymmetric unit (for 5b and 5c) omitted for clarity.
albeit at a slower rate than 4a. A solution of 4b left standing in CDCl$_3$ achieved approximately 80% conversion to 5b after 2 weeks. Owing to the slow rate of reaction, 5b was more conveniently synthesised by refluxing 4b in THF for 4 days. The observed trend in dehydrocoupling rates (4a > 4b) correlates with the acidity of the P–H hydrogen, which is higher in 4a due to the more electron withdrawing nature of the phenyl substituent as compared to the ferrocenyl substituent.

Compound 5b demonstrates a similar $^{31}$P($^1$H) NMR spectrum to 5a, displaying a broad doublet (δ$_p$ 16.1, $^1$J$_{PH}$ = 92.6 Hz, iPr$_2$P) and a very broad unresolved signal (δ$_p$ -32.0, PFc) located upfield of the corresponding signals for 4b (Δδ$_p$ ≈ 20–25). Once again, $^1$H and $^{31}$P NMR spectroscopy confirmed the loss of H directly bonded to phosphorus, and the $^{11}$B NMR spectrum displayed two distinct boron environments. Crystals of 5b suitable for single crystal X-ray diffraction were grown from acetonitrile. Obtained data is of somewhat poor quality, but is sufficient to demonstrate the connectivity of the molecule. The crystal structure is shown in Fig. 5 with data in Tables 1–3 and is broadly similar to that seen for 5a.

The dehydrocoupled product of the primary bis(borane) adduct 4c was obtained by treating 3 with excess H$_2$B·SMe$_2$ in DCM and then, without isolating 4c, allowing the reaction mixture to stir at room temperature for 11 days. After this time, no peaks for 4c could be observed in the $^{31}$P($^1$H) NMR spectrum of the reaction mixture. The resultant bridged compound 5c is significantly more inert than the corresponding bis(borane) adduct, and was stable enough to be purified by flash column chromatography. As with the previous compounds, 5c displays peaks in the $^{31}$P($^1$H) NMR spectrum with Δδ$_p$ ≈ 25–30 ppm away from the corresponding resonances for the parent bis(borane) adduct 4c. Additionally, in the $^{31}$P NMR spectrum of 5c, the signal for the PH group (δ$_p$ -69.5) appears as a doublet ($^1$J$_{PH}$ = 339 Hz) as opposed to the triplet seen for 4c.

Crystals of 5c suitable for single crystal X-ray diffraction were grown from slow diffusion of hexane into its concentrated solution in DCM. The structure is presented in Fig. 5, with data in Tables 1–3. One interesting point of note is that, in contrast to 5a–b, compound 5c displays almost no out-of-plane displacement of the peri-phosphorus atoms (0.050 Å [0.042 Å] for P1, 0.068 Å [0.101 Å] for P8, values in square brackets are for the second molecule in the asymmetric unit). This can be attributed to the significantly reduced steric demands of the hydrogen substituent.

Given the presence of vicinal P–H and B–H bonds in compound 5c, the thermal decomposition of this compound was investigated to verify whether a further molecule of dihydrogen could be eliminated. After refluxing 5c in xylene for 3 days, partial conversion (≈26%) by $^{31}$P NMR to a new compound, compound 14, was observed. Compound 14 shows two resonances in its $^{31}$P($^1$H) NMR spectrum, a broad multiplet (δ$_p$ 11.0, P/Pr$_2$) and a sharp singlet (δ$_p$ -136.9, PH). The low frequency chemical shift of the singlet suggests that 14 forms by loss of BH$_3$ from 5c (Scheme 5). Furthermore, the $^{31}$P NMR spectrum shows a significant reduction in the $^1$J$_{PH}$ coupling constant (5c, $^1$J$_{PH}$ = 339 Hz; 14, $^1$J$_{PH}$ = 185 Hz), consistent with an increase in electron density on phosphorus due to loss of the Lewis acidic BH$_3$. Due to the slow rate of the reaction, complete conversion to 14 was not achieved and this compound was not isolated pure. Attempts to drive the reaction to completion by prolonged heating resulted in decomposition.

**Conclusion**

Bis(borane) adducts 4a–c were formed by either borane mediated reduction of phosphino-phosphonium salts 1a–b, or by treatment of the bis(phosphine) 3 with excess H$_2$B·SMe$_2$. All three adducts were found to undergo spontaneous intramolecular dehydrocoupling in solution, resulting in the formation of a P–B bond to afford the novel BH$_3$ bridged compounds 5a–c. This reaction is surprisingly facile, occurring at room temperature and in the absence of a catalyst (albeit in some cases at a slow rate). The ease with which the reaction proceeds can be attributed to the unique constraints of the peri-geometry; the two reactive moieties are held in close proximity and the repulsive interaction between them introduces considerable strain into the system, which is reduced on formation of a bridging P–B–P motif.

This interesting reaction serves as a demonstration of the utility of peri-substitution for promoting unusual or unexpected reactivity. Furthermore, it highlights how manipulation of the steric properties of a molecule can eliminate the need for a catalyst, which could be a potentially interesting alternative approach to developing compounds for hydrogen storage.

**Experimental**

**General procedures**

All experiments were carried out using standard Schlenk technique or glove box unless otherwise stated. Solvents were dried on an MBraun solvent purification system and stored over molecular sieves prior to use. 5-Bromo-6-diisopropyl-phosphinoacenaphthene and phosphonium-phosphoranide 2 were synthesised according to literature procedures. Where possible, new compounds were fully characterized by $^{31}$P, $^{31}$P($^1$H), $^1$H and $^{13}$C($^1$H) NMR, including measurement of $^1$H($^{31}$P), H–H DQF COSY, H–P HMOC, H–C HSCQ, and H–C HMBC experiments. The NMR numbering scheme for all compounds discussed is shown in Scheme 6.
were done by full-matrix least-squares based on F. The structures were solved by direct methods. Refinements
were collected at 180(1) °C by using a Rigaku XtaLAB P200 diffractometer. Data for compounds 4b and 5b
were collected at −180(1) °C by using a Rigaku XtaLAB P200 diffractometer. Data for compounds 5a and 5c were collected at −100(1) °C by using a Rigaku XtaLAB P200 diffractometer. All instruments use Mo Kα radiation (λ = 0.71075 Å). Intensities were corrected for Lorentz polarization and for absorption. The structures were solved by direct methods. Refinements were done by full-matrix least-squares based on F^2 using SHELXTL.37 CCDC 1410480–1410484 contain the supplementary crystallographic data for this article.

Scheme 6 NMR numbering scheme for all compounds discussed.

Instrumentation

All NMR spectra were recorded using a JEOL GSX Delta 270, a Bruker Avance 300, Bruker Avance 400, Bruker Avance 500 or Bruker Avance III 500 spectrometer. 85% H3PO4 was used as an external standard in 31P, BF3·OEt2 in CDCl3 was used as an external standard in 1H, and TMS was used as an internal standard in 13C NMR. Measurements were performed at 25 °C unless otherwise indicated. All IR and Raman spectra were obtained in the range 4000–300 cm−1 on a Perkin-Elmer System 2000 NIR Fourier transform spectrometer. Mass spectra were acquired by Mrs Caroline Horseburgh at the University of St Andrews on a Micromass LCT. Elemental analysis (C, H and N) was performed by Mr Stephen Boyer at London Metropolitan University.

X-ray experimental

Table 3 lists details of data collections and refinements. Data for compound 3 were collected at −180(1) °C by using a Rigaku Mercury70 diffractionmeter. Data for compounds 4b and 5b were collected at −180(1) °C by using a Rigaku XtaLAB P200 diffractometer. Data for compounds 5a and 5c were collected at −100(1) °C by using a Rigaku XtaLAB P200 diffractometer. All instruments use Mo Kα radiation (λ = 0.71075 Å). Intensities were corrected for Lorentz polarization and for absorption. The structures were solved by direct methods. Refinements were done by full-matrix least-squares based on F^2 using SHELXTL.37 CCDC 1410480–1410484 contain the supplementary crystallographic data for this article.

[Acenap(Ph2P)(Ph)][Cl] phosphino-phosphonium 1b

Synthesis adapted from method published by Kilian et al.25 5-Bromo-6-diisopropophosphinoacenaphthenone (1.00 g, 2.86 mmol) was dissolved in diethyl ether (20 mL) and cooled to −78 °C. nBuLi (1.14 mL of a 2.5 M solution in hexanes, 2.86 mmol) was added dropwise with stirring. The solution was stirred for 2 hours at −78 °C. A suspension of dichlororofenylphosphine (0.82 g, 2.86 mmol) in diethyl ether (20 mL) was added dropwise over 30 minutes at −78 °C and the solution left to warm to room temperature overnight. The orange precipitate was collected by filtration, washed with diethyl ether (3 × 5 mL) and dried in vacuo to yield 1a as a fine orange powder (1.480 g). Accurate yield could not be determined due to contamination with LiCl, which however poses no problems for further syntheses. The 1H and 31P{1H} NMR of the product were in good agreement with previously published data.25

1H NMR δH (270 MHz; CDCl3) 8.80 (1H, dd, JHP = 9.0 Hz, JHH = 7.3 Hz, 2-H), 8.01 (1H, d, JHP = 9.0 Hz, JHH = 6.8 Hz, 8-H), 7.72 (1H, dd, JHH = 7.3 Hz, JHP = 2.9 Hz, 3-H), 7.58 (1H, dd, JHH = 7.2 Hz, JHP = 2.6 Hz, 7-H), 7.49–7.22 (5H, m, 5 × Ph CH), 3.94–3.75 (1H, m, iPr CH), 3.75–3.61 (1H, m, iPr CH), 3.58 (4H, br s, 11-H, 12-H), 1.39 (3H, dd, JHH = 19.3 Hz, JHP = 6.9 Hz, iPr CH3), 1.14 (3H, dd, JHH = 18.9 Hz, JHP = 7.0 Hz, iPr CH3), 1.03 (3H, dd, JHH = 7.1 Hz, JHP = 3.8 Hz, iPr CH3), 0.95 (3H, dd, JHH = 7.1 Hz, JHP = 3.8 Hz, iPr CH3).

31P{1H} NMR δP (109 MHz; CDCl3) 56.1 (d, iPr3P), −35.3 (d, PPh), JFP = 304 Hz.

[Acenap(Ph2P)(Ph)][Cl] phosphino-phosphonium 1b

Synthesis adapted from method published by Kilian et al.25 5-Bromo-6-diisopropophosphinoacenaphthenone (1.00 g, 2.86 mmol) was dissolved in diethyl ether (20 mL) and cooled to −78 °C. nBuLi (1.14 mL of a 2.5 M solution in hexanes, 2.86 mmol) was added dropwise with stirring. The solution was stirred for 2 hours at −78 °C. A suspension of dichlororofenylphosphine (0.82 g, 2.86 mmol) in diethyl ether (20 mL) was added dropwise over 30 minutes at −78 °C and the solution left to warm to room temperature overnight. The orange precipitate was collected by filtration, washed with diethyl ether (3 × 5 mL) and dried in vacuo to yield 1a as a fine orange powder (1.480 g). Accurate yield could not be determined due to contamination with LiCl, which however poses no problems for further syntheses. The 1H and 31P{1H} NMR of the product were in good agreement with previously published data.25

1H NMR δH (270 MHz; CDCl3) 8.62 (1H, dd, JHP = 9.0 Hz, JHH = 7.3 Hz, 2-H), 8.10–8.01 (1H, m, 8-H), 7.67 (1H, dd, JHP = 9.0 Hz, JHH = 7.3 Hz, 2-H), 7.62 (1H, dd, JHP = 7.0 Hz, JHH = 2.2 Hz, 7-H), 4.75–4.71 (1H, m, CpH), 4.65–4.55 (1H, m, CpH), 4.34 (5H, s, CpH), 4.30–4.25 (2H, m, 2 × CpCH3), 3.56 (4H, s, 11-H, 12-H), 3.21–3.19 (2H, m, 2 × iPr CH), 1.35–0.92 (12H, m, 4 × iPr CH3).

31P{1H} NMR δP (109 MHz; CDCl3) 56.1 (d, iPr3P), −37.3 (d, PPh), JFP = 313 Hz.

Acenap(Ph2P)(Ph)bis(phosphine) 3

To a stirred suspension of LiAlH4 (0.334 g, 8.8 mmol) in THF (15 mL) cooled to −78 °C, a suspension of 2 (0.50 g, 1.35 mmol) in THF (20 mL) was added slowly via cannula. The resultant bright pink solution was allowed to warm to room temperature, with stirring overnight. The solution was cooled to 0 °C and degassed water (2.5 mL) was added dropwise with stirring. The mixture was then filtered to remove insoluble impurities. Volatiles were removed in vacuo to give 3 as a pink solid (0.298 g, 0.986 mmol, 73%). The compound is highly soluble in most organic solvents, a small amount of crystals of 3 suitable for single crystal X-ray diffraction were grown from THF.

mp 140–144 °C.
IR (nujol mull) $\nu_{\text{max}}$/cm$^{-1}$: 2932w, 2240m (PH), 1604w, 840m, 790m.

Raman (glass capillary) $\nu_{\text{max}}$/cm$^{-1}$: 3058s (ArH), 2948s and 2929s and 2866s (CH), 2294m and 2241s (PH), 1605m, 1567s, 1331vs, 585s.

$^{1}$H NMR $\delta_{H}$ (400 MHz; C$_6$D$_6$) 7.79-7.72 (1H, m, 2-H), 7.60 (1H, dd, $^J_{HH} = 7.1$ Hz, $^J_{HP} = 3.3$ Hz, 8-H), 7.12 (1H, dt, $^J_{HH} = 7.2$ Hz, $^J_{HP} = 1.3$ Hz, 7-H), 6.93 (1H, d, $^J_{HH} = 7.1$ Hz, 3-H), 4.98 (2H, dd, $^J_{HH} = 204$ Hz, $^J_{HP} = 47.8$ Hz, PH$_2$), 3.04-2.83 (4H, m, 11-H, 12-H), 2.12-1.99 (2H, m, 2 × iPr CH), 1.17 (6H, d, $^J_{HH} = 14.3$ Hz, $^J_{HP} = 6.9$ Hz, 2 × iPr CH$_3$), 1.00 (6H, d, $^J_{HH} = 12.3$ Hz, $^J_{HP} = 7.0$ Hz, 2 × iPr CH$_3$).

$^{13}$C($^1$H) NMR $\delta_{C}$ (101 MHz; C$_6$D$_6$) 148.8 (s, qC-6), 147.7 (d, $^J_{CP} = 1.9$ Hz, qC-4), 140.4 (m, qC-5, qC-10), 139.7 (s, C-2), 134.5 (d, $^J_{CP} = 2.3$ Hz, C-8), 131.0 (dd, $^J_{CP} = 23.9$ Hz, $^J_{CP} = 7.4$ Hz, qC-9), 125.9 (d, $^J_{CP} = 19.8$ Hz, qC-11), 119.8 (s, C-3), 119.4 (s, C-7), 119.1 (s, C-8), 118.9 (s, C-7), 114.9 (s, C-4), 30.3 (s, C-11/C-12), 29.9 (s, C-11/C-12), 26.4 (d, $^J_{CP} = 15.9$ Hz, iPr CH), 26.4 (d, $^J_{CP} = 15.8$ Hz, iPr CH), 20.4 (s, iPr CH$_3$), 20.3 (s, iPr CH$_3$), 20.2 (s, 2 × iPr CH$_3$).

$^{31}$P NMR $\delta_{P}$ (162 MHz; C$_6$D$_6$) -113.3 (dm, $^J_{PP} = 205$ Hz, iPr$_2$P), -101.2 (sq, $^J_{PP} = 205$, $^J_{PP} = 204$ Hz, PH$_2$).

$^{31}$P($^1$H) NMR $\delta_{P}$ (162 MHz; C$_6$D$_6$) -113.3 (d, $^J_{PP} = 205$ Hz, iPr$_2$P), -101.2 (d, $^J_{PH} = 4.6$ Hz, P$_2$). MS (ES+) Found: 301.1275. Calc. for C$_{18}$H$_{23}$P$_2$ (M$: $^{2}$H$_2$): 301.1278. Calc. for C$_{18}$H$_{23}$P$_2$ (M$: $^{3}$H$_2$): 301.1275.

**Acenap(Ph$_2$P)$_2$BH$_3$** (Ph$_2$BH$_3$) bis(borane) 4b

Borane dimethylsulfide (0.10 mL, 94%, 0.99 mmol) was added to a stirred suspension of Ph$_2$B (120 mg, 0.23 mmol) in THF (30 mL) at -78 °C. The reaction was stirred for 2 hours at -78 °C, then allowed to warm to RT and stirred overnight. Volatiles were removed in vacuo to afford 4b as an orange solid.

The crude product contained the bridged compound 5b as a minor byproduct (approximately 20%). Analytically pure material, as well as crystals suitable for single crystal X-ray diffraction, was obtained from acetone at 5 °C (50 mg, 0.10 mmol, 42%).

mp 154-155 °C.

Found: C 65.56; H 7.56. Calc. for C$_{28}$H$_{33}$P$_2$B$_2$ (M$: $^{2}$H$_2$): 455.1278. Calc. for C$_{28}$H$_{33}$P$_2$B$_2$ (M$: $^{3}$H$_2$): 454.1275.

**Acenap(Ph$_2$P)$_2$BH$_3$** (Ph$_2$BH$_3$) bis(borane) 4c

Borane dimethylsulfide (0.40 mL, 94%, 3.98 mmol) was added to a stirred solution of Ph$_2$B (150 mg, 0.363 mmol) in DCM (5 mL) at -78 °C. The reaction was allowed to warm to room temperature over 1 hour, then stirred for 30 minutes. Volatiles were removed in vacuo to afford 4c as an off-white sticky solid (105 mg). Compound was not purified due to its high sensitivity towards moisture and oxygen, which prevented chromatographic separation. NMR data was assigned from the crude product mixture.

$^1$H NMR $\delta_{H}$ (400 MHz; C$_6$D$_6$) 8.26 (1H, dd, $^J_{HH} = 14.1$ Hz, $^J_{HP} = 14.1$ Hz, 7-H), 8.19 (1H, dd, $^J_{HH} = 19.3$ Hz, $^J_{HP} = 19.3$ Hz, 7-H), 8.19 (2H, m, 3-H, 8-H), 7.49-7.43 (2H, m, 3-H, 8-H), 6.14 (2H, dq, $^J_{HH} = 377$ Hz, $^J_{HP} = 7.1$ Hz, PH$_2$), 3.44 (4H, s, 11-H, 12-H), 2.82-2.77 (2H, m, 2 × iPr CH), 1.50-0.30 (6H, m, 2 × iPr CH$_3$), 1.38 (6H, d, $^J_{HP} = 14.6$ Hz, $^J_{HP} = 14.6$ Hz, 2 × iPr CH$_3$), 1.06 (6H, d, $^J_{HP} = 15.6$ Hz, $^J_{HP} = 7.1$ Hz, 2 × iPr CH$_3$).

$^{31}$P NMR $\delta_{P}$ (162 MHz; C$_6$D$_6$) 38.0 (br s, iPr$_2$P), -40.8 (br s, PH$_2$).

$^{31}$P($^1$H) NMR $\delta_{P}$ (162 MHz; C$_6$D$_6$) 38.0 (br s, iPr$_2$P), -40.8 (t, $^J_{PP} = 379$ Hz, PH$_2$).

**Acenap(Ph$_2$P)$_2$BH$_3$** (Ph$_2$BH$_3$) bis(borane) 4a

Borane dimethylsulfide (0.15 mL, 94%, 1.49 mmol) was added to a stirred solution of Ph$_2$B (150 mg, 0.363 mmol) in THF (3 mL) at -78 °C. The reaction was stirred for 2 hours at -78 °C, then allowed to warm to room temperature and stirred overnight. Volatiles were removed in vacuo to afford the bis(borane) adduct 4a, which was re-dissolved in DCM (5 mL) and stirred at room temperature for 8 days. Volatiles were removed in vacuo to afford 5a as an off-white solid in near quantitative yield (0.145 g, 0.359 mmol, 99%). Crystals suitable for single
crystal X-ray diffraction were grown from d6-DMSO at room temperature.

mp 230 °C (decomp).

Found: C 71.23; H 8.05. Calc. for C24H32P2B2Na: C 71.34; H 7.98.

IR (KBr disk) ν_max/cm⁻¹: 3030w (ArH), 2970m and 2934m and 2872m (CH), 2449m, 2364vs (BH), 2258m, 1597s, 1488m, 1105m, 1059s, 828s, 670s, 492s, 453m.

Raman (glass capillary) ν_max/cm⁻¹: 3060 (s, Ph), 2935 (m), 2862 (m), 2838 (m), 2760 (m), 2260 (m), 1596s, 1488m, 1369m, 1255m, 1169s, 1107v, 1060m, 729m, 552m, 402m, 368m, 321s.

Acenap(NP(Pr2)(μ-BH3)(PFc-BH3)) 5b

Boran dimethylsulfide (0.10 mL, 94%, 0.99 mmol) was added to a stirred suspension of 1b (120 mg, 0.23 mmol) in THF (30 mL) at −78 °C. The reaction was stirred for 2 hours at −78 °C, then allowed to warm to RT and stirred overnight to afford 4b, which was not isolated. The reaction mixture was heated under reflux for 4 days. Volatiles were removed in vacuo to afford 5b as an orange oil. Analytically pure material was obtained by filtering through silica gel, eluting with DCM (102 mg, 0.20 mmol, 87%). Crystals of 5b suitable for single crystal X-ray diffraction were grown by slow evaporation from acetonitrile.

mp 180 °C (decomp).


IR (KBr disk) ν_max/cm⁻¹: 2967m and 2932m (CH), 2437s, 2362vs (BH), 1598s, 1448m, 137m, 1253m, 1156s, 1059s, 1025s, 828s, 670s, 492s, 453m.

Raman (glass capillary) ν_max/cm⁻¹: 3110s (ArH), 2929s (CH), 2440w, 2381m (BH), 1601s, 1575s, 1474s, 1413s, 1353v, 1173s, 1107v, 1060m, 729m, 552m, 402m, 368m, 321s.
was purified by flash column chromatography on silica, eluting with DCM, to yield 5e as a white crystalline solid (45 mg, 0.137 mmol, 41%). Crystals of 5e suitable for single crystal X-ray diffraction were grown by diffusion of hexane into a concentrated solution of 5e in DCM.

mp 140 °C (decomp).

Found: C 65.89; H 8.70. Calc. for C16H23B2Na: C 65.92; H 8.61.

IR (KBr disk) \( \nu_{\text{max}} \text{cm}^{-1} \) 2975m and 2959s (CH), 2930m, 2872m, 2444s (BH), 2368s (PH), 2259w, 1710w, 1597s, 1492m, 1461s, 1418m, 1387m, 1367w, 1333m, 1257m, 1217w, 1139m, 1103m, 1065vs, 1040m, 909s, 883m, 849s, 715s, 629m, 395w.

Raman (glass capillary) \( \nu_{\text{max}} \text{cm}^{-1} \) 3064m, 2962s, 2934vs (CH), 2901vs, 2626m (BH), 2392m, 2351vs (PH), 1599s, 1575s, 1441s, 1420m, 1337vs, 1054m, 883m, 830m, 735m, 585m, 571s.

\(^1\)H NMR \( \delta_H \) (500 MHz; CDCl\(_3\)) 8.37 (1H, dd, \( J_{CH} = 13.4 \text{ Hz} \)), 7.74 (1H, dd, \( J_{CH} = 7.1 \text{ Hz} \)), 7.50 (1H, dd, \( J_{CH} = 8.3 \text{ Hz} \)), 7.45 (1H, dd, \( J_{CH} = 4.1 \text{ Hz} \)), 3.67 (2H, m, 3-H), 2.64 (1H, m, 2 × \( J_{CH} = 7.1 \text{ Hz} \)), 2.55 (1H, m, \( J_{CH} = 7.2 \text{ Hz} \)), 2.48 (1H, m, \( J_{CH} = 7.5 \text{ Hz} \)), 1.32 (3H, dd, \( J_{CH} = 3.0 \text{ Hz} \)), 1.09 (6H, dd, \( J_{CH} = 6.9 \text{ Hz} \)), 0.88 (6H, dd, \( J_{CH} = 3.0 \text{ Hz} \)).

\(^{13}\)C\(^{1}\)H NMR \( \delta_{CP} \) (126 MHz; CDCl\(_3\)) 153.1 (dd, \( J_{CP} = 2.0 \text{ Hz} \)), 150.1 (s, \( \delta_{CP} = 8.2 \text{ Hz} \)), 138.4 (d, \( J_{CP} = 10.9 \text{ Hz} \)), 135.8 (s, \( \delta_{CP} = 8.6 \text{ Hz} \)), 128.6 (s, \( \delta_{CP} = 2.2 \text{ Hz} \)), 144.3 (s, \( \delta_{CP} = 7.3 \text{ Hz} \)), 119.1 (d, \( J_{CP} = 8.9 \text{ Hz} \)), 118.8 (dd, \( J_{CP} = 14.0 \text{ Hz} \)), 112.6 (dd, \( J_{CP} = 7.8 \text{ Hz} \)), 110.6 (m, \( \delta_{CP} = 4.1 \text{ Hz} \)), 105.5 (d, \( \delta_{CP} = 5.9 \text{ Hz} \)), 101.4 (d, \( J_{CP} = 7.2 \text{ Hz} \)), 99.5 (d, \( J_{CP} = 12.1 \text{ Hz} \)), 99.0 (d, \( J_{CP} = 9.9 \text{ Hz} \)), 89.5 (d, \( J_{CP} = 7.2 \text{ Hz} \)), 85.2 (s, \( \delta_{CP} = 3.0 \text{ Hz} \)), 76.0 (s, \( \delta_{CP} = 6.0 \text{ Hz} \)), 74.9 (s, \( \delta_{CP} = 5.0 \text{ Hz} \)), 73.0 (s, \( \delta_{CP} = 7.2 \text{ Hz} \)), 72.8 (s, \( \delta_{CP} = 3.0 \text{ Hz} \)).

\(^{31}\)P NMR \( \delta_P \) (202 MHz; CDCl\(_3\)) 12.8 (br s, \( J_{PP} = 33.9 \text{ Hz} \)), -69.5 (br d, \( J_{PP} = 33.9 \text{ Hz} \)), 12.8 (br d, \( J_{PP} = 33.9 \text{ Hz} \)), -69.5 (br m, PH).

\(^{11}\)B NMR \( \delta_B \) (160 MHz; CDCl\(_3\)) -37.2 (br m, BH\(_2\)), -41.9 (br m, BH\(_2\)).

\(^{11}\)B\(^{11}\)NMR \( \delta_B \) (160 MHz; CDCl\(_3\)) -37.1 (br m, BH\(_2\)), -41.9 (br m, BH\(_2\)), -37.1 (br m, BH\(_2\)).

MS (ES+) m/z 351.2 (100%, M + Na).


\section*{Acenap(Pr\(_{2}\)B\(_{2}\)H\(_{4}\))(PH\(_{3}\)) 6}

Borane dimethylsulfide (0.72 mL, 94%, 7.6 mmol) was added to a stirred solution of 3 (180 mg, 0.60 mmol) in DCM (10 mL) at 0 °C. The reaction was stirred for 2 hours at room temperature, then cooled to 0 °C and degassed water (10 mL) was added cautiously. The reaction mixture was stirred for a further 2 hours at room temperature. The organic layer was separated and volatiles removed in vacuo to afford 6 as a yellow solid in quantitative yield (188 mg, 0.59 mmol, 99%).

\(^{1}H\) NMR \( \delta_H \) (400 MHz; CDCl\(_3\)) 8.54 (1H, dd, \( J_{CH} = 17.4 \text{ Hz} \)), 7.74 (1H, dd, \( J_{CH} = 7.4 \text{ Hz} \)), 8.04–8.00 (1H, m, 2-H), 7.33 (1H, d, \( J_{CH} = 7.3 \text{ Hz} \)), 7.27 (1H, d, \( J_{CH} = 7.3 \text{ Hz} \)), 7.24 (1H, d, \( J_{CH} = 7.3 \text{ Hz} \)).

\(^{13}\)C\(^{1}\)H NMR \( \delta_{CP} \) (124 MHz; CDCl\(_3\)) 133.8 (s, \( \delta_{CP} = 3.0 \text{ Hz} \)), 118.8 (dd, \( J_{CP} = 7.1 \text{ Hz} \)), 105.5 (m, \( \delta_{CP} = 4.1 \text{ Hz} \)), 99.0 (d, \( J_{CP} = 7.2 \text{ Hz} \)), 89.5 (d, \( J_{CP} = 7.2 \text{ Hz} \)), 74.9 (s, \( \delta_{CP} = 3.0 \text{ Hz} \)), 73.0 (s, \( \delta_{CP} = 7.2 \text{ Hz} \)), 72.8 (s, \( \delta_{CP} = 3.0 \text{ Hz} \)).

\(^{31}\)P NMR \( \delta_P \) (162 MHz; CDCl\(_3\)) 11.1 (br s, \( J_{PP} = 185 \text{ Hz} \)), -137.0 (br s, \( J_{PP} = 185 \text{ Hz} \)).

\(^{11}B\)\(^{11}\)NMR \( \delta_B \) (162 MHz; CDCl\(_3\)) 11.0 (m, \( J_{PB} = 136.9 \text{ Hz} \)).

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References

A solution of 4a (approximately 100 mg) in CDCl3 containing tetramethylsilane (TMS) was prepared under an inert atmosphere and flame sealed. A measure of relative concentration was obtained by integrating the iPr CH signal of 4a relative to the TMS signal.

32 A solution of 4a (approximately 100 mg) in CDCl3 containing tetramethylsilane (TMS) was prepared under an inert atmosphere and flame sealed. A measure of relative concentration was obtained by integrating the iPr CH signal of 4a relative to the TMS signal.


