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Spontaneous dehydrocoupling in *peri*-substituted phosphine–borane adducts†

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Bis(borane) adducts Acenap(P*i*Pr$_2$·BH$_3$)(PRH·BH$_3$) (Acenap = acenaphthene-5,6-diyl; **4a**, R = Ph; **4b**, R = ferrocenyl, Fc; **4c**, R = H) were synthesised by the reaction of excess H$_3$B·SMe$_2$ with either phosphino-phosphonium salts [Acenap(P*i*Pr$_2$)(PR)]$^+$Cl$^-$ (**1a**, R = Ph; **1b**, R = Fc), or bis(phosphine) Acenap(P*i*Pr$_2$)(PH$_2$) (**3**). Bis(borane) adducts **4a–c** were found to undergo dihydrogen elimination at room temperature, this spontaneous catalyst-free phosphine-borane dehydrocoupling yields BH$_2$ bridged species Acenap(P*i*Pr$_2$)(μ-BH$_2$)-(PR·BH$_3$) (**5a**, R = Ph; **5b**, R = Fc; **5c**, R = H). Thermolysis of **5c** results in loss of the terminal borane moiety to afford Acenap(P*i*Pr$_2$)(μ-BH$_2$)(PH) (**14**). Single crystal X-ray structures of **3**, **4b** and **5a–c** are reported.

Introduction

Dehydrocoupling reactions (E–H + E′–H → E–E′ + H$_2$) are an interesting and effective way of generating bonds between main-group elements, with concomitant evolution of H$_2$. Reactions of this type show applications not only in inorganic synthesis, but also in hydrogen storage, transfer hydrogenation and polymer synthesis.[1–6]

Although dehydrocoupling reactions that occur by thermal or autocatalytic routes are known,[7,8] the vast majority of recent work has focused on catalysis, particularly with transition metals.[6,9–11] In particular, amine–borane adducts have attracted considerable interest as potential hydrogen storage molecules.[12,13] However, dehydrocoupling reactions in the chemically related phosphine–boranes have received far less attention.[11,14]

Dehydrocoupling of phosphine–boranes to form poly(phosphinoboranes) was first reported in the 1950s. Early work in this area is limited, with polymerisations yielding low molecular weight polymers which were often poorly characterised.[15,16] In 1999 the Manners' group pioneered the use of transition metal catalysts in the synthesis of poly(phosphinoboranes)[17–20] and more recently B(C$_6$F$_5$)$_3$ has been used as a metal-free dehydrocoupling catalyst.[21] Thus formed inorganic polymers have interesting and unusual physical properties, which set them apart from the more traditional carbon-based polymers.[17,18]

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.[22,23] 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–X–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

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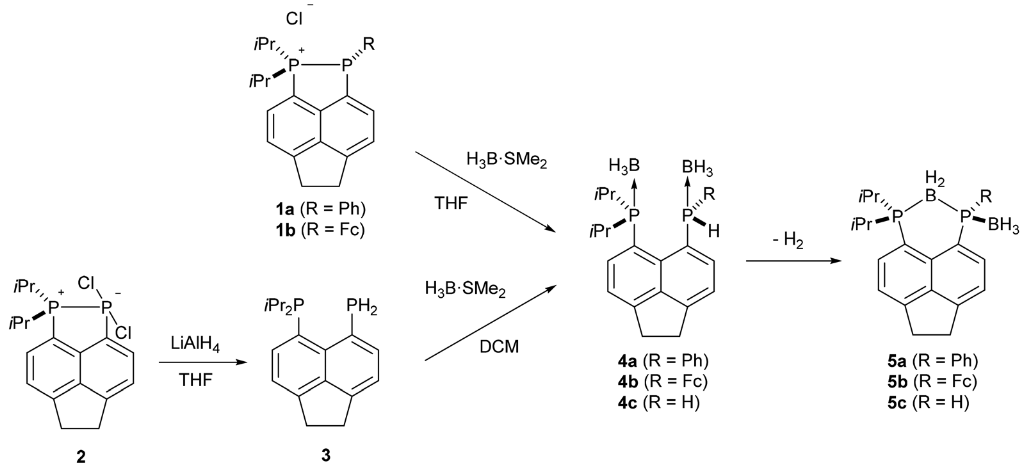
† CCDC 1410480–1410484. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt02539g



Scheme 1 Synthesis of bis(borane) adducts **4a–c** and BH_2 bridged compounds **5a–c**.

Table 1 Selected bond lengths (Å) and angles (°) for **3**, **4b**, **5a–c**

3			
C1–P1	1.849(4)	C9–P9	1.850(4)
C1–P1–H1a	99(1)	C1–P1–H1b	94(1)
H1a–P1–H1b	90(2)		
4b			
C1–P1	1.817(3)	C9–P9	1.842(3)
B1–P1	1.929(4)	B9–P9	1.980(4)
C1–P1–B1	109.7(2)	B1–P1–H1	117(2)
C1–P1–H1	105(2)	C9–P9–B9	113.6(2)
5a			
C1–P1	1.818(2)	C9–P9	1.812(2)
B1–P1	1.932(2)	B9–P9	1.927(2)
B9–P1	1.928(2)		
C1–P1–B1	112.21(8)	C9–P9–B9	110.95(8)
C1–P1–B9	106.33(8)	P9–B9–P1	108.55(9)
B9–P1–B1	117.28(9)		
5b[a]			
C1–P1	1.82(1) [1.85(1)]	C9–P9	1.82(1) [1.80(2)]
B1–P1	1.94(2) [1.94(2)]	B9–P9	1.92(2) [1.90(2)]
B9–P1	1.94(2) [1.94(2)]		
C1–P1–B1	111.6(7) [108.6(7)]	C9–P9–B9	114.1(7) [108.3(7)]
C1–P1–B9	111.3(7) [107.4(7)]	P9–B9–P1	110.9(9) [106.6(8)]
B9–P1–B1	114.0(9) [118.2(8)]		
5c[a]			
C1–P1	1.820(2) [1.821(2)]	C9–P9	1.808(2) [1.807(2)]
B1–P1	1.937(2) [1.930(2)]	B9–P9	1.910(2) [1.911(2)]
B9–P1	1.922(2) [1.914(2)]		
C1–P1–B1	111.90(9) [112.48(9)]	C9–P9–B9	110.15(8) [109.62(8)]
C1–P1–B9	107.56(8) [107.54(8)]	P9–B9–P1	109.1(1) [109.0(1)]
B9–P1–B1	118.16(9) [117.60(9)]		

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

synthesised according to a previously published procedure,[24] while compounds **1a–b** were synthesised *via* a modified version of the literature procedure.[25]

The synthesis and characterisation of the bis(borane) adduct **4a** were recently reported by our group.[26] In its preparation, treatment of the phosphino-phosphonium salt **1a** with excess $H_3B{\cdot}SMe_2$ resulted in borane mediated reduction to afford **4a** as a yellow oil in quantitative yield (Scheme 1). An analogous procedure was employed to obtain adduct **4b** from the corresponding phosphino-phosphonium salt **1b**. The adduct **4b** was isolated as an orange solid, which was contaminated with the bridged compound **5b** (≈20% as judged by ^1H and ^{31}P NMR). Pure **4b** was obtained by recrystallisation from acetonitrile.

The $^{31}P\{^1H\}$ NMR spectrum of **4b** exhibits broad singlets at δ_P 36.3 ($i\mathrm{Pr}_2\mathrm{P}$) and −7.7 (PFcH), and in the ^{31}P NMR spectrum the signal at δ_P −7.7 is split into a broad doublet ($^1J_{PH}$ = 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)° (see Fig. 1 for a definition), 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).

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

	3	**4b**	**5a**	**5b**[a]	**5c**[a]
P1⋯P9	3.143(1)	3.521(1)	3.1295(8)	3.181(5) [3.081(5)]	3.1214(6) [3.1145(6)]
splay angle	+16.4(7)	+21.2(7)	+15.1(4)	+16(3) [+15(3)]	+16.5(3) [+16.3(3)]
Out-of-plane displacement (P1)	0.148	0.706	0.338	0.332 [0.213]	0.050 [0.042]
Out-of-plane displacement (P9)	0.068	0.546	0.327	0.450 [0.296]	0.068 [0.101]

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

Table 3 Crystallographic data for **3**, **4b**, **5a–c**

	3	4b	5a	5b	5c
Chemical formula	$C_{18}H_{24}P_2$	$C_{28}H_{38}B_2FeP_2$	$C_{24}H_{32}B_2P_2$	$C_{28}H_{36}B_2FeP_2$	$C_{18}H_{28}B_2P_2$
Formula weight	302.34	514.02	404.08	512.01	327.99
Crystal dimensions (mm)	0.12 × 0.10 × 0.03	0.10 × 0.10 × 0.01	0.10 × 0.06 × 0.06	0.20 × 0.03 × 0.01	0.18 × 0.12 × 0.08
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1$	$P2_1/c$
a (Å)	7.4543(19)	15.806(5)	8.3375(11)	15.409(5)	14.0458(16)
b (Å)	8.4923(15)	13.022(4)	9.4724(14)	11.059(3)	18.841(2)
c (Å)	14.361(5)	12.835(4)	16.108(2)	16.712(6)	14.4671(14)
α (°)	79.88(3)	90.0000	101.8880(17)	90.0000	90.0000
β (°)	82.10(3)	94.825(6)	93.165(3)	114.651(5)	101.176(3)
γ (°)	66.47(2)	90.0000	112.772(3)	90.0000	90.0000
V (Å^3)	818.3(4)	2632.4(14)	1134.9(3)	2588.3(14)	3768.3(7)
Z	2	4	2	4	8
D_{calc} (g cm^{-3})	1.227	1.297	1.182	1.314	1.156
μ (cm^{-1})	2.546	7.088	1.989	7.207	2.244
No. rflns measured (unique)	5176 (2878)	27 526 (4765)	14 052 (4112)	34 241 (9417)	45 236 (6914)
R_1 [a]	0.0643	0.0513	0.0362	0.0948	0.0360
wR_2 [b]	0.1599	0.1533	0.1041	0.2647	0.1045

[a] $I > 2\sigma(I)$, $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + [(ap)^2 + bp]$, where $p = [(F_o^2) + 2F_c^2]/3$.

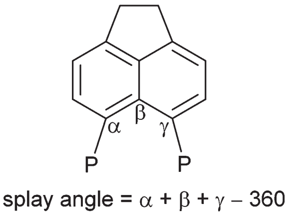


Fig. 1 Definition of a splay angle.

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 $LiAlH_4$. The $^{31}P\{^1H\}$ NMR spectrum of compound **3** displays two doublets at δ_P −11.3 (iPr$_2$P) and −101.2 (PH_2), with a substantial through-space coupling of $^4J_{PP}$ = 205 Hz. In the ^{31}P NMR spectrum, the signal for the PH_2 group is split into a pseudo-quartet due to $^1J_{PH}$ = 204 Hz being very similar to that of $^4J_{PP}$. The ^1H NMR spectrum of **3** displays a doublet of doublets for the PH_2 protons (δ_H 4.98, $^1J_{HP}$ = 204 Hz, $^5J_{HP}$ = 48 Hz). This long range $^5J_{HP}$ interaction, in addition to the large $^4J_{PP}$ coupling, indicates a significant through space contribution to coupling operates in this compound.[27] 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 ^{31}P, ^1H and ^{13}C NMR and was found to be sufficient for further syntheses.

Treatment of primary bis(phosphine) **3** with excess $H_3B\cdot SMe_2$ afforded bis(borane) adduct **4c** as the major product (δ_P 38.0 (br s, iPr$_2$P), −40.8 (br s, PH_2)), although the reaction was not clean. Even with a large excess (12 equivalents) of

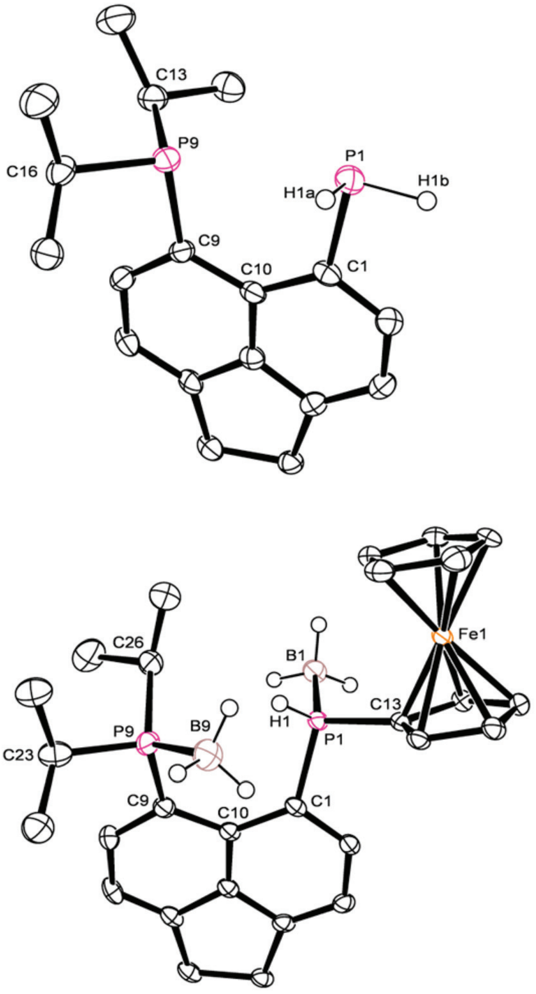
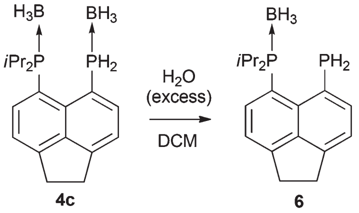
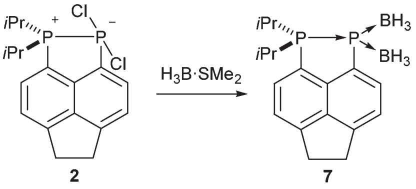


Fig. 2 Structures of **3** (top) and **4b** (bottom) in the solid state. Carbon-bound hydrogen atoms omitted for clarity.



4c 6

Scheme 2 Synthesis of monoborane adduct **6**.



2 7

Scheme 3 Synthesis of the "push–double pull" bis(borane) adduct **7**.

$H_3B{\cdot}SMe_2$, traces of starting material were found in the $^{31}P\{^1H\}$ NMR spectra of the crude mixture after the reaction. In addition, a broad singlet at δ_P 44.0 along with a sharp singlet at δ_P −101.4 were observed in this spectrum. Rather revealingly, the signal at δ_P −101.4 splits into a triplet ($^1J_{PH}$ = 207 Hz) in the ^{31}P NMR spectrum which, together with the chemical shift values, allowed these signals to be assigned to the monoborane adduct **6** (Scheme 2). In the crude mixture, **4c** and **6** were present in a ratio of approximately 5 : 1. A number of minor, 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 ^1H, ^{31}P, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, ^{11}B, and $^{11}B\{^1H\}$ 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.[28] In addition, steric hindrance arising from the *peri*-geometry is likely to further destabilise the bis(borane) adduct **4c** with respect to the monoborane 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 $^{31}P\{^1H\}$ NMR spectrum at δ_P 38.0 (iPr_2P) and δ_P −40.8 (PH_2). In the ^{31}P NMR spectrum, the signal at δ_P −40.8 splits into a broad triplet ($^1J_{PH}$ = 379 Hz). One particularly distinctive signal is observed for the PH_2 group in the ^1H NMR spectrum, which is split into a doublet of quartets (δ_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 ^1H NMR spectrum of compound **6** appears as a sharp doublet (δ_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-phosphoranide **2** with $H_3B{\cdot}SMe_2$ does not result in borane mediated reduction to give **4c**, but instead yields the "push–double pull" bis(borane) adduct **7** (Scheme 3).[29]

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 (δ_P 39.4 (br s, iPr_2P) and −6.6 (br s, PhPH))[26] were gradually replaced by a broad doublet (δ_P 13.9, P*i*Pr$_2$, $^2J_{PP} \approx 84.0$ Hz) and a very broad signal in which coupling could not be resolved (δ_P −26.3, PPh),[30] corresponding with the formation of **5a** (Fig. 3). Complete conversion to **5a** was achieved after 8 days at room temperature (Scheme 1). ^1H and ^{31}P NMR spectroscopy confirmed that the H atom directly bonded to phosphorus had been lost. Additionally, $^{11}B\{^1H\}$ NMR spectroscopy revealed a broad pseudo-triplet (δ_B −39.4, $^1J_{BP} \approx 69$ Hz) and a broad doublet (δ_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_2 and one terminal BH_3 motif (Fig. 5, Tables 1–3). A 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)° (*cf.* 3.61 Å and +24.4(4)° in **4a**),[26] 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**).[26]

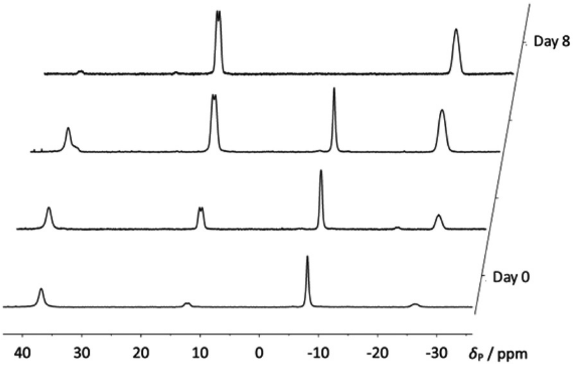


Fig. 3 Stacked $^{31}P\{^1H\}$ NMR spectra showing the gradual formation of compound **5a** from **4a** over 8 days.

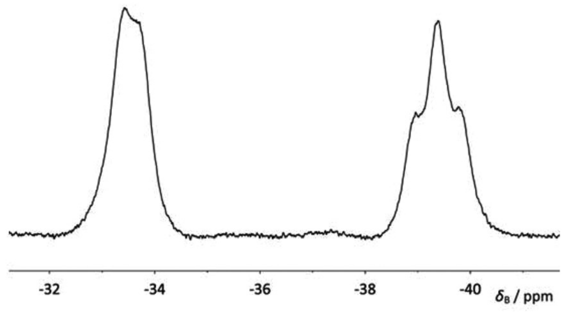


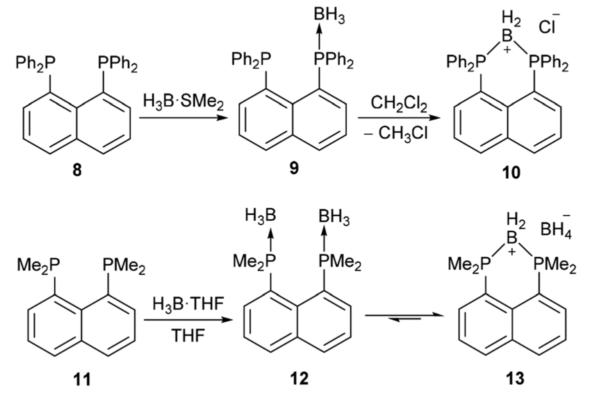
Fig. 4 $^{11}B\{^1H\}$ NMR of compound **5a**.

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 C_6D_6 was prepared and left to stand in a sealed NMR tube. After 1 day, some conversion to compound **5a** was observed by $^{31}P\{^1H\}$ NMR, and a sharp singlet of dissolved H_2 was observed in the ^1H NMR (δ_H 4.47).[31] In another experiment, the conversion of **4a** to **5a** (in $CDCl_3$) was followed over several days at room temperature by ^1H NMR spectroscopy.[32] 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.[7] 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.[8] 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[17–19,33] or at very high temperatures,[15,16] 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 Mikołajczyk *et al.*[34] and Costa and Schmidbaur[35] (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 BH_2 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**.[34] Compound **13** exists in equilibrium with the bis(borane) adduct **12** and forms *via* hydride transfer to give a BH_2 bridge and a BH_4^- counterion.[35] Although these reactions are significantly different from the dehydrocoupling observed in **4a**, in all cases the driving force for the formation of the BH_2 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,



Scheme 4 Formation of the cyclic boronium salts **10** and **13**.

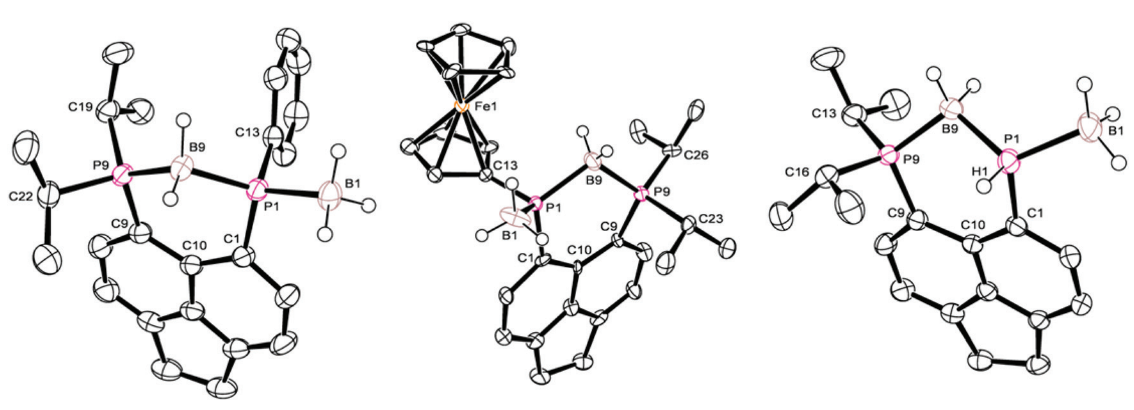


Fig. 5 Structures of **5a** (left), **5b** (centre), and **5c** (right) in the solid state. Carbon-bound hydrogen atoms and second molecule in asymmetric unit (for **5b** and **5c**) omitted for clarity.

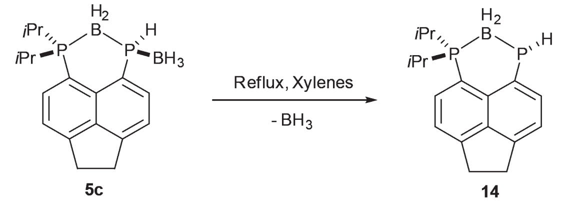
albeit at a slower rate than **4a**. A solution of **4b** left standing in $CDCl_3$ achieved approximately 80% conversion to **5b** after 2 weeks. Owing to the slow rate of reaction, **5b** was more conveniently synthesised by refluxing **4b** in THF for 4 days. The observed trend in dehydrocoupling 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 $^{31}P\{^1H\}$ NMR spectrum to **5a**, displaying a broad doublet (δ_P 16.1, $^1J_{PP}$ = 92.6 Hz, *i*Pr_2P) and a very broad unresolved signal (δ_P −32.0, PFc) located upfield of the corresponding signals for **4b** ($\Delta\delta_P \approx$ 20–25). Once again, ^1H 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 $H_3B{\cdot}SMe_2$ 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 $^{31}P\{^1H\}$ 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 $^{31}P\{^1H\}$ NMR spectrum with $\Delta\delta_P \approx$ 25–30 upfield of 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 ($^1J_{PH}$ = 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 xylenes 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 $^{31}P\{^1H\}$ NMR spectrum, a broad multiplet (δ_P 11.0, P*i*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 $^1J_{PH}$ coupling constant (**5c**, $^1J_{PH}$ = 339 Hz; **14**, $^1J_{PH}$ = 185 Hz), consistent with an increase in electron density on phosphorus due to loss of the Lewis acidic BH_3.[36] 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.



Scheme 5 Proposed initial product of thermal decomposition of **5c**.

Conclusion

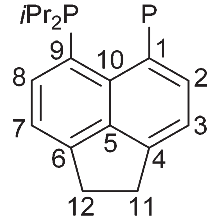
Bis(borane) adducts **4a–c** were formed by either borane mediated reduction of phosphino-phosphonium salts **1a–b**, or by treatment of the bis(phosphine) **3** with excess $H_3B{\cdot}SMe_2$. All three adducts were found to undergo spontaneous intramolecular dehydrocoupling in solution, resulting in the formation of a P–B bond to afford the novel BH_2 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-diisopropylphosphinoacenaphthene and phosphonium-phosphoranide **2** were synthesised according to literature procedures.[24] Where possible, new compounds were fully characterized by ^{31}P, $^{31}P\{^1H\}$, ^1H and $^{13}C\{^1H\}$ NMR, including measurement of $^1H\{^{31}P\}$, H–H DQF COSY, H–P HMQC, H–C HSQC, and H–C HMBC experiments. The NMR numbering scheme for all compounds discussed is shown in Scheme 6.



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% H_3PO_4 was used as an external standard in ^{31}P, $BF_3{\cdot}OEt_2$ in $CDCl_3$ was used as an external standard in ^{11}B, and TMS was used as an internal standard in ^{1}H and ^{13}C 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 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.

[Acenap(P*i*Pr$_2$)(PPh)][Cl] phosphino-phosphonium 1a

Synthesis adapted from method published by Kilian *et al.*[25] 5-Bromo-6-diisopropylphosphinoacenaphthene (4.00 g, 11.45 mmol) was dissolved in diethyl ether (100 mL) and cooled to −78 °C. *n*BuLi (4.58 mL of a 2.5 M solution in hexanes, 11.45 mmol) was added dropwise with stirring. The solution was stirred for 2 hours at −78 °C. A solution of dichlorophenylphosphine (1.55 mL, 2.05 g, 11.45 mmol) in diethyl ether (10 mL) was added dropwise over 30 minutes at −78 °C and the solution left to warm to room temperature overnight. The white precipitate was collected by filtration, washed with diethyl ether (3 × 10 mL) and dried *in vacuo* to yield **1a** as a fine white powder (4.109 g). Accurate yield could not be determined due to contamination with LiCl, which however poses no problems for further syntheses. The ^{1}H and ^{31}P{^{1}H} NMR of the product were in good agreement with previously published data.[25]

^{1}H NMR δ_H (270 MHz; $CDCl_3$) 8.80 (1H, dd, $^3J_{HP}$ = 9.2 Hz, $^3J_{HH}$ = 7.3 Hz, 2-H), 7.84 (1H, ≈t $^3J_{HH}$ = 6.8 Hz $^3J_{HP}$ = 6.8 Hz, 8-H), 7.72 (1H, dd, $^3J_{HH}$ = 7.3 Hz, $^4J_{HP}$ = 2.9 Hz, 3-H), 7.58 (1H, dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HP}$ = 2.6 Hz, 7-H), 7.49–7.22 (5H, m, 5 × Ph CH), 3.94–3.75 (1H, m, *i*Pr CH), 3.75–3.61 (1H, m, *i*Pr CH), 3.58 (4H, br s, 11-H, 12-H), 1.39 (3H, dd, $^3J_{HP}$ = 19.3 Hz, $^3J_{HH}$ = 6.9 Hz, *i*Pr CH_3), 1.14 (3H, dd, $^3J_{HP}$ = 18.9 Hz, $^3J_{HH}$ = 7.0 Hz, *i*Pr CH_3), 1.03 (3H, dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{HP}$ = 3.8 Hz, *i*Pr CH_3), 0.95 (3H, dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{HP}$ = 3.8 Hz, *i*Pr CH_3).

^{31}P{^{1}H} NMR δ_P (109 MHz; $CDCl_3$) 61.3 (d, *i*Pr$_2$P), −35.3 (d, PPh), $^1J_{PP}$ = 304 Hz.

[Acenap(P*i*Pr$_2$)(PFc)][Cl] phosphino-phosphonium 1b

Synthesis adapted from method published by Kilian *et al.*[25] 5-Bromo-6-diisopropylphosphinoacenaphthene (1.00 g, 2.86 mmol) was dissolved in diethyl ether (20 mL) and cooled to −78 °C. *n*BuLi (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 dichloroferrocenylphosphine (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 ^{1}H and ^{31}P{^{1}H} NMR of the product were in good agreement with previously published data.[25]

^{1}H NMR δ_H (270 MHz; $CDCl_3$) 8.62 (1H, dd, $^3J_{HP}$ = 9.0 Hz, $^3J_{HH}$ = 7.3 Hz, 2-H), 8.10–8.01 (1H, m, 8-H), 7.67 (1H, dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HP}$ = 2.7 Hz, 3-H), 7.62 (1H, dd, $^3J_{HH}$ = 7.0 Hz, $^4J_{HP}$ = 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 × CpH), 3.56 (4H, s, 11-H, 12-H), 3.21–3.19 (2H, m, 2 × *i*Pr CH), 1.35–0.92 (12H, m, 4 × *i*Pr CH_3).

^{31}P{^{1}H} NMR δ_P (109 MHz; $CDCl_3$) 56.1 (d, *i*Pr$_2$P), −37.3 (d, PFc), $^1J_{PP}$ = 313 Hz.

Acenap(P*i*Pr$_2$)(PH$_2$) bis(phosphine) 3

To a stirred suspension of $LiAlH_4$ (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) $\nu_{\max}$/cm^{-1} 2293w, 2240m (PH), 1604w, 840m, 790m.

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

^{1}H NMR δ_{H} (400 MHz; C_6D_6) 7.79–7.72 (1H, m, 2-H), 7.60 (1H, dd, $^{3}J_{\mathrm{HH}}$ = 7.1 Hz, $^{3}J_{\mathrm{HP}}$ = 3.3 Hz, 8-H), 7.12 (1H, dt, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, $^{4}J_{\mathrm{HH}}$ = 1.3 Hz, 7-H), 6.93 (1H, d, $^{3}J_{\mathrm{HH}}$ = 7.1 Hz, 3-H), 4.98 (2H, dd, $^{1}J_{\mathrm{HP}}$ = 204 Hz, $^{5}J_{\mathrm{HP}}$ = 47.8 Hz, PH_2), 3.04–2.83 (4H, m, 11-H, 12-H), 2.12–1.99 (2H, m, 2 × *i*Pr CH), 1.17 (6H, dd, $^{3}J_{\mathrm{HP}}$ = 14.3 Hz, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, 2 × *i*Pr CH_3), 1.00 (6H, dd, $^{3}J_{\mathrm{HP}}$ = 12.3 Hz, $^{3}J_{\mathrm{HH}}$ = 7.0 Hz, 2 × *i*Pr CH_3).

^{13}C{^{1}H} NMR δ_{C} (101 MHz; C_6D_6) 148.8 (s, qC-6), 147.7 (d, $^{4}J_{\mathrm{CP}}$ = 1.9 Hz, qC-4), 140.4 (m, qC-5, qC-10), 139.7 (s, C-2), 134.5 (d, $^{2}J_{\mathrm{CP}}$ = 2.3 Hz, C-8), 131.0 (dd, $^{1}J_{\mathrm{CP}}$ = 23.9 Hz, $^{3}J_{\mathrm{CP}}$ = 7.4 Hz, qC-9), 125.9 (d, $^{1}J_{\mathrm{CP}}$ = 19.8 Hz, qC-1), 119.8 (s, C-3), 119.4 (s, C-7), 30.3 (s, C-11/C-12), 29.9 (s, C-11/C-12), 26.4 (d, $^{1}J_{\mathrm{CP}}$ = 15.9 Hz, *i*Pr CH), 26.4 (d, $^{1}J_{\mathrm{CP}}$ = 15.8 Hz, *i*Pr CH), 20.4 (s, *i*Pr CH_3), 20.3 (s, *i*Pr CH_3), 20.2 (s, 2 × *i*Pr CH_3).

^{31}P NMR δ_{P} (162 MHz; C_6D_6) −11.3 (dm, $^{1}J_{\mathrm{PP}}$ = 205 Hz, *i*Pr_2P), −101.2 (≈q, $^{1}J_{\mathrm{PP}}$ = 205, $^{1}J_{\mathrm{PH}}$ = 204 Hz, PH_2).

^{31}P{^{1}H} NMR δ_{P} (162 MHz; C_6D_6) −11.3 (d, *i*Pr_2P), −101.2 (d, PH_2), $^{1}J_{\mathrm{PP}}$ = 205 Hz.

MS (ES^{+}) *m*/*z* 301.1 (100%, M − H).

HRMS (ES^{+}) Found: 301.1278. Calc. for $C_{18}H_{23}P_2$ (M − H): 301.1275.

Acenap(P*i*Pr$_2$·BH$_3$)(PFcH·BH$_3$) bis(borane) 4b

Borane 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. 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 acetonitrile at 5 °C (50 mg, 0.10 mmol, 42%).

mp 154–155 °C.

Found: C 65.56; H 7.56. Calc. for $C_{28}H_{38}FeB_2P_2$: C 65.43; H 7.45.

IR (KBr disk) $\nu_{\max}$/cm^{-1} 2966m and 2928m (CH), 2374vs (PH), 2345s (BH), 1638m, 1604m, 1460m, 1414m, 1387m, 1316m, 1256m, 1182m, 1071s, 1028s, 929m, 831s, 671m, 643m, 492m, 446m.

^{1}H NMR δ_{H} (400 MHz; $CDCl_3$) 8.09 (1H, dd, $^{3}J_{\mathrm{HP}}$ = 13.2 Hz, $^{3}J_{\mathrm{HH}}$ = 7.4 Hz, 2-H), 7.81 (1H, dd, $^{3}J_{\mathrm{HP}}$ = 16.4 Hz, $^{3}J_{\mathrm{HH}}$ = 7.3 Hz, 8-H), 7.70 (1H, dq, $^{1}J_{\mathrm{HP}}$ = 393 Hz, $^{3}J_{\mathrm{HH}}$ = 6.1 Hz, P–H), 7.39 (1H, d, $^{3}J_{\mathrm{HH}}$ = 7.4 Hz, 3-H), 7.31 (1H, d, $^{3}J_{\mathrm{HH}}$ = 7.3 Hz, 7-H), 4.59–4.55 (2H, m, 2 × CpH), 4.48–4.43 (2H, m, 2 × CpH), 4.32 (5H, s, 5 × CpH), 3.38 (4H, s, 11-H, 12-H), 3.16–3.06 (1H, m, *i*Pr CH), 3.06–2.95 (1H, m, *i*Pr CH), 1.60–0.40 (6H, br m, 2 × BH_3), 1.48–1.37 (9H, m, 3 × *i*Pr CH_3), 0.99 (3H, dd, $^{3}J_{\mathrm{HP}}$ = 15.2 Hz, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, *i*Pr CH_3).

^{13}C{^{1}H} NMR δ_{C} (101 MHz; $CDCl_3$) 152.3 (s, qC-6), 151.9 (s, qC-4), 140.8 (≈t, $^{3}J_{\mathrm{CP}}$ = 7.9 Hz, qC-5), 140.1 (d, $^{2}J_{\mathrm{CP}}$ = 7.5 Hz, C-2), 136.9 (d, $^{2}J_{\mathrm{CP}}$ = 14.3 Hz, C-8), 133.1–132.9 (m, qC-10), 123.5 (d, $^{1}J_{\mathrm{CP}}$ = 53.0 Hz, qC-9), 120.3 (d, $^{3}J_{\mathrm{CP}}$ = 12.9 Hz, C-7), 119.5 (d, $^{1}J_{\mathrm{CP}}$ = 43.4 Hz, qC-1), 119.5 (d, $^{3}J_{\mathrm{CP}}$ = 10.6 Hz, C-3), 74.3 (d, J_{CP} = 15.9 Hz, Cp CH), 72.7 (d, J_{CP} = 6.6 Hz, Cp CH), 72.4 (d, J_{CP} = 3.6 Hz, Cp CH), 71.4 (d, J_{CP} = 9.0 Hz, Cp CH), 70.2 (s, 5 × Cp CH), 66.2 (d, $^{1}J_{\mathrm{CP}}$ = 68.3 Hz, Cp qC), 30.2 (s, C-11/C-12), 30.0 (s, C-11/C-12), 25.5 (dd, $^{1}J_{\mathrm{CP}}$ = 29.1 Hz, $^{3}J_{\mathrm{CP}}$ = 2.1 Hz, *i*Pr CH), 23.7 (d, $^{1}J_{\mathrm{CP}}$ = 33.3 Hz, *i*Pr CH), 19.4 (s, *i*Pr CH_3), 18.3 (s, *i*Pr CH_3), 17.9–17.3 (m, *i*Pr CH_3), 17.5 (s, *i*Pr CH_3).

^{31}P NMR δ_{P} (162 MHz; $CDCl_3$) 36.2 (br s, *i*Pr_2P), −7.7 (d, $^{1}J_{\mathrm{PH}}$ = 395 Hz, PFcH).

^{31}P{^{1}H} NMR δ_{P} (162 MHz; $CDCl_3$) 36.3 (br s, *i*Pr_2P), −7.7 (br s, PFcH).

^{11}B NMR δ_{B} (160 MHz; $CDCl_3$) −39.2 (br m, 2 × BH_3).

^{11}B{^{1}H} NMR δ_{B} (160 MHz; $CDCl_3$) −38.7 (br m, BH_3), −39.4 (br m, BH_3).

MS (ES^{-}) *m*/*z* 485.1 (12%, M − 2BH_3 − H), 499.2 (86, M − BH_3 − H), 513.2 (100, M − H).

HRMS (ES−) Found: 513.1919. Calc. for $C_{28}H_{37}P_2FeB_2$ (M + H): 513.1906.

Acenap(P*i*Pr$_2$·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 **3** (100 mg, 0.33 mmol) in DCM (5 mL) at −78 °C. The reaction was allowed to warm to room temperature over 1 h, then stirred for 30 minutes. Volatiles were removed *in vacuo* to afford crude **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 δ_{H} (400 MHz; $CDCl_3$) 8.26 (1H, dd, $^{3}J_{\mathrm{HP}}$ = 14.1 Hz, $^{3}J_{\mathrm{HH}}$ = 7.5 Hz, 2-H), 8.19 (1H, dd, $^{3}J_{\mathrm{HP}}$ = 19.3 Hz, $^{3}J_{\mathrm{HH}}$ = 7.3 Hz, 8-H), 7.49–7.42 (2H, m, 3-H, 7-H), 6.14 (2H, dq, $^{1}J_{\mathrm{HP}}$ = 377 Hz, $^{3}J_{\mathrm{HH}}$ = 7.1 Hz, PH_2), 3.44 (4H, s, 11-H, 12-H), 2.90–2.77 (2H, m, 2 × *i*Pr CH), 1.50–0.30 (6H, br m, 2 × BH_3), 1.38 (6H, dd, $^{3}J_{\mathrm{HP}}$ = 14.6 Hz, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, 2 × *i*Pr CH_3), 1.06 (6H, dd, $^{3}J_{\mathrm{HP}}$ = 15.6 Hz, $^{3}J_{\mathrm{HH}}$ = 7.1 Hz, 2 × *i*Pr CH_3).

^{31}P NMR δ_{P} (162 MHz; $CDCl_3$) 38.0 (br s, *i*Pr_2P), −40.8 (br s, PH_2).

^{31}P{^{1}H} NMR δ_{P} (162 MHz; $CDCl_3$) 38.0 (br s, *i*Pr_2P), −40.8 (t, $^{1}J_{\mathrm{PH}}$ = 379 Hz, PH_2).

^{11}B NMR δ_{B} (96 MHz; $CDCl_3$) −40.1 (br m, 2 × BH_3).

^{11}B{^{1}H} NMR δ_{B} (96 MHz; $CDCl_3$) −40.1 (br m, 2 × BH_3).

Acenap(P*i*Pr$_2$)(μ-BH$_2$)(PPh·BH$_3$) 5a

Borane dimethylsulfide (0.15 mL, 94%, 1.49 mmol) was added to a stirred solution of **1a** (150 mg, 0.363 mmol) in THF (5 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 d_6-DMSO at room temperature.

mp 230 °C (decomp).

Found: C 71.23; H 8.05. Calc. for $C_{24}H_{32}B_2P_2$: 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, 1453s, 1436s, 1388m, 1340m, 1248m, 1139m, 1111m, 1057vs, 882m, 847s, 829m, 739s, 699vs, 666m, 614m, 472m, 402m.

Raman (glass capillary) ν_{max}/cm^{-1} 3060 (s, Ar–H), 2942 (s, νC–H), 2895 (m), 2453 (m), 2388 (m), 2340 (m, νB–H), 1599 (s), 1578 (s), 1444 (s), 1419 (s), 1343 (vs), 1002 (s), 832 (m), 739 (m), 573 (s).

^{1}H NMR δ_H (500 MHz; $CDCl_3$) 8.01 (1H, dd, $^3J_{HP}$ = 12.2 Hz, $^3J_{HH}$ = 7.2 Hz, 2-H), 7.67 (1H, dd, $^3J_{HP}$ = 10.3 Hz, $^3J_{HH}$ = 7.2 Hz, 8-H), 7.59–7.51 (2H, m, *o*-Ph CH), 7.42 (1H, d, $^3J_{HH}$ = 7.5 Hz, 7-H), 7.40 (1H, d, $^3J_{HH}$ = 7.3 Hz, 3-H), 7.30–7.23 (3H, m, *m*/*p*-Ph CH), 3.50–3.39 (4H, m, 11-H, 12-H), 2.76–2.64 (1H, m, *i*Pr CH), 2.38–2.26 (1H, m, *i*Pr CH), 2.10–0.70 (5H, br m, BH_2 and BH_3), 1.28 (3H, dd, $^3J_{HP}$ = 14.9 Hz, $^3J_{HH}$ = 7.1 Hz, *i*Pr CH_3), 1.25 (3H, dd, $^3J_{HP}$ = 16.0 Hz, $^3J_{HH}$ = 7.2 Hz, *i*Pr CH_3), 1.17 (3H, dd, $^3J_{HP}$ = 15.7 Hz, $^3J_{HH}$ = 7.0 Hz, *i*Pr CH_3), 0.93 (3H, dd, $^3J_{HP}$ = 15.9 Hz, $^3J_{HH}$ = 7.2 Hz, *i*Pr CH_3).

^{13}C{^{1}H} NMR δ_C (126 MHz; $CDCl_3$) 153.0 (m, qC-6), 149.7 (s, qC-4), 139.8 (dd, $^3J_{CP}$ = 8.6 Hz, $^3J_{CP}$ = 6.5 Hz, qC-5), 138.5 (d, $^2J_{CP}$ = 8.1 Hz, C-2), 137.6 (dd, $^1J_{CP}$ = 42.1 Hz, $^3J_{CP}$ = 7.0 Hz, *i*-Ph qC), 135.2 (dd, $^2J_{CP}$ = 9.1 Hz, $^2J_{CP}$ = 5.3 Hz, qC-10), 134.2 (s, C-8), 132.5 (d, $^2J_{CP}$ = 8.7 Hz, *o*-Ph CH), 128.9 (d, $^4J_{CP}$ = 2.1 Hz, *p*-Ph CH), 128.1 (d, $^3J_{CP}$ = 9.2 Hz, *m*-Ph CH), 124.6 (dd, $^1J_{CP}$ = 41.4 Hz, $^3J_{CP}$ = 5.0 Hz, qC-1), 121.0 (d, $^3J_{CP}$ = 9.6 Hz, C-3), 118.8 (d, $^3J_{CP}$ = 8.9 Hz, C-7), 114.5 (dd, $^1J_{CP}$ = 56.2 Hz, $^3J_{CP}$ = 3.5 Hz, C-9), 30.6 (s, C-11/C-12), 30.2 (s, C-11/C-12), 24.3 (dd, $^1J_{CP}$ = 35.0 Hz, $^3J_{CP}$ = 1.8 Hz, *i*Pr CH), 23.0 (dd, $^1J_{CP}$ = 35.3 Hz, $^3J_{CP}$ = 4.7 Hz, *i*Pr CH), 18.4 (s, *i*Pr CH_3), 17.8 (s, *i*Pr CH_3), 16.7 (s, *i*Pr CH_3), 16.6 (s, *i*Pr CH_3).

^{31}P NMR δ_P (202 MHz; $CDCl_3$) 13.7 (br s, *i*Pr_2P), −26.4 (br s, PPh).

^{31}P{^{1}H} NMR δ_P (202 MHz; $CDCl_3$) 13.9 (br d, $^1J_{PP}$ = 84.0 Hz, *i*Pr_2P), −26.3 (br m, PPh).

^{11}B NMR δ_B (160 MHz; $CDCl_3$) −33.6 (br m, BH_3), −39.4 (br m, BH_2).

^{11}B{^{1}H} NMR δ_B (160 MHz; $CDCl_3$) −33.6 (br d, $^1J_{BP}$ = 46.2 Hz, BH_3), −39.4 (br ≈t, $^1J_{BP}$ = 69.3 Hz, BH_2).

MS (ES+) *m*/*z* 391.2 (28%, M − BH_3 + H), 427.2 (100, M + Na).

HRMS (ES+) Found: 427.2052. Calc. for $C_{24}H_{32}P_2B_2Na$ (M + Na): 427.2058.

Acenap(P*i*Pr$_2$)(μ-BH$_2$)(PFc·BH$_3$) 5b

Borane 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).

Found: C 65.76; H 6.93. Calc. for $C_{28}H_{36}FeB_2P_2$: C 65.68; H 7.09.

IR (KBr disk) ν_{max}/cm^{-1} 2967m and 2932m (CH), 2437s, 2362vs (BH), 1598s, 1448m, 1387m, 1332m, 1255m, 1169s, 1105m, 1059s, 1025s, 828s, 670s, 492s, 453m.

Raman (glass capillary) ν_{max}/cm^{-1} 3110s (ArH), 2929s (CH), 2440w, 2381m (BH), 1601s, 1575s, 1447s, 1417s, 1335vs, 1173s, 1107vs, 1060m, 830m, 729m, 552m, 402m, 368m, 321s.

^{1}H NMR δ_H (500 MHz; $CDCl_3$) 7.71 (1H, dd, $^3J_{HP}$ = 11.5 Hz, $^3J_{HH}$ = 7.2 Hz, 2-H), 7.64 (1H, dd, $^3J_{HP}$ = 10.3 Hz, $^3J_{HH}$ = 7.2 Hz, 8-H), 7.35 (1H, d, $^3J_{HH}$ = 7.1 Hz, 7-H), 7.27–7.23 (1H, m, 3-H), 4.94 (1H, s, CpH), 4.43 (2H, s, 2 × CpH), 4.39 (5H, s, 5 × CpH), 4.32 (1H, s, CpH), 3.43–3.27 (4H, m, 11-H, 12-H), 2.90–2.80 (1H, m, *i*Pr CH), 2.80–2.70 (1H, m, *i*Pr CH), 2.20–0.60 (5H, br m, BH_2 and BH_3), 1.52 (3H, dd, $^3J_{HP}$ = 16.6 Hz, $^3J_{HH}$ = 7.3 Hz, *i*Pr CH_3), 1.42 (3H, dd, $^3J_{HP}$ = 16.3 Hz, $^3J_{HH}$ = 6.9 Hz, *i*Pr CH_3), 1.32 (3H, dd, $^3J_{HP}$ = 14.4 Hz, $^3J_{HH}$ = 7.1 Hz, *i*Pr CH_3), 1.11 (3H, dd, $^3J_{HP}$ = 15.5 Hz, $^3J_{HH}$ = 7.0 Hz, *i*Pr CH_3).

^{13}C{^{1}H} NMR δ_C (101 MHz; $CDCl_3$) 152.7 (s, qC-6) , 148.1 (s, qC-4) , 139.6 (dd, $^3J_{CP}$ = 9.1 Hz, $^3J_{CP}$ = 6.4 Hz, qC-5), 135.9 (d, $^2J_{CP}$ = 5.7 Hz, C-2), 133.8 (m, qC-10), 133.5 (s, C-8), 130.2 (dd, $^1J_{CP}$ = 38.6 Hz, $^3J_{CP}$ = 3.2 Hz, qC-1), 120.8 (d, $^3J_{CP}$ = 8.5 Hz, C-3), 118.4 (d, $^3J_{CP}$ = 8.8 Hz, C-7), 114.6 (dd, $^1J_{CP}$ = 55.7 Hz, $^3J_{CP}$ = 2.7 Hz, qC-9), 75.1 (dd, $^1J_{CP}$ = 53.3 Hz, $^2J_{CP}$ = 12.2 Hz, Cp qC), 74.2 (d, J_{CP} = 10.4 Hz, Cp CH), 71.7 (d, J_{CP} = 5.9 Hz, Cp CH), 71.0 (d, J_{CP} = 6.1 Hz, Cp CH), 70.6 (d, J_{CP} = 6.8 Hz, Cp CH), 69.8 (s, 5 × Cp CH), 30.6 (s, C-11/C-12), 30.0 (s, C-11/C-12), 25.9 (d, $^1J_{CP}$ = 34.6 Hz, *i*Pr CH), 21.4 (dd, $^1J_{CP}$ = 36.0 Hz, $^2J_{CP}$ = 9.0 Hz, *i*Pr CH), 19.2 (s, *i*Pr CH_3), 17.8 (s, *i*Pr CH_3), 17.4 (d, $^2J_{CP}$ = 2.7 Hz, *i*Pr CH_3), 16.1 (d, $^2J_{CP}$ = 3.8 Hz, *i*Pr CH_3).

^{31}P NMR δ_P (202 MHz; $CDCl_3$) 16.1 (br s, *i*Pr_2P), −32.0 (br s, PFc).

^{31}P{^{1}H} NMR δ_P (202 MHz; $CDCl_3$) 16.1 (br d, $^1J_{PP}$ = 92.6 Hz, *i*Pr_2P), −32.0 (br m, PFc).

^{11}B NMR δ_B (160 MHz; $CDCl_3$) −33.9 (br m, BH_3), −41.0 (br m, BH_2).

^{11}B{^{1}H} NMR δ_B (160 MHz; $CDCl_3$) δ −33.7 (br m, BH_3), −41.1 (br m, BH_2).

MS (ES+) *m*/*z* 498.1 (100%, M − BH_3), 512.2 (38, M).

HRMS (ES+) Found: 498.1483. Calc. for $C_{28}H_{33}FeP_2B$ (M − BH_3): 498.1500.

Acenap(P*i*Pr$_2$)(μ-BH$_2$)(PH·BH$_3$) 5c

Borane dimethylsulfide (0.40 mL, 94%, 3.98 mmol) was added to a stirred solution of **3** (100 mg, 0.33 mmol) in DCM (5 mL) at −78 °C. The reaction was allowed to warm to room temperature over 1 h, then left to stir at room temperature for 11 days. Distilled water (10 mL) was added and the reaction stirred for 1 h at room temperature. The product was extracted with DCM (3 × 10 mL) in air and the combined washings were dried over $MgSO_4$. Volatiles were removed *in vacuo* and the crude product was purified by flash column chromatography on silica, eluting with DCM, to yield **5c** as a white crystalline solid (45 mg, 0.137 mmol, 41%). Crystals of **5c** suitable for single crystal X-ray diffraction were grown by diffusion of hexane into a concentrated solution of **5c** in DCM.

mp 140 °C (decomp).

Found: C 65.89; H 8.70. Calc. for $C_{18}H_{28}B_2P_2$: C 65.92; H 8.61.

IR (KBr disk) ν_{max}/cm^{-1} 2975m and 2959s (CH), 2930m, 2872m, 2444s (BH), 2368vs (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) ν_{max}/cm^{-1} 3064m, 2962s, 2934vs (CH), 2901vs, 2462m (BH), 2392m, 2351vs (PH), 1599s, 1575s, 1441s, 1420m, 1337vs, 1054m, 883m, 830m, 735m, 585m, 571s.

^{1}H NMR δ_H (500 MHz; $CDCl_3$) 8.37 (1H, dd, $^3J_{HP}$ = 13.4 Hz, $^3J_{HH}$ = 7.1 Hz, 2-H), 7.67 (1H, dd, $^3J_{HP}$ = 10.3 Hz, $^3J_{HH}$ = 7.2 Hz, 8-H), 7.46 (1H, d, $^3J_{HH}$ = 7.1 Hz, 3-H), 7.42 (1H, d, $^3J_{HH}$ = 7.2 Hz, 7-H), 4.89 (1H, br d, $^1J_{HP}$ = 328 Hz, PH), 3.45 (4H, s, 11-H, 12-H), 2.78–2.64 (1H, m, *i*Pr CH), 2.55–2.41 (1H, m, *i*Pr CH), 1.90–0.60 (5H, br m, BH_2 and BH_3), 1.32 (3H, dd, $^3J_{HP}$ = 16.6 Hz, $^3J_{HH}$ = 6.9 Hz, *i*Pr CH_3), 1.29–1.23 (6H, m, 2 × *i*Pr CH_3), 1.07 (3H, dd, $^3J_{HP}$ = 16.0 Hz, $^3J_{HH}$ = 7.0 Hz, *i*Pr CH_3).

$^{13}C\{^1H\}$ NMR δ_C (126 MHz; $CDCl_3$) 153.1 (d, $^4J_{CP}$ = 2.0 Hz, qC-4), 150.1 (s, qC-6), 139.5 (dd, $^3J_{CP}$ = 8.2 Hz, $^3J_{CP}$ = 5.9 Hz, qC-5), 138.4 (d, $^2J_{CP}$ = 10.9 Hz, C-2), 135.8 (dd, $^2J_{CP}$ = 8.6, $^2J_{CP}$ = 2.2 Hz, qC-10), 134.4 (s, C-8), 120.6 (d, $^3J_{CP}$ = 10.7 Hz, C-3), 119.1 (d, $^3J_{CP}$ = 8.9 Hz, C-7), 118.8 (dd, $^1J_{CP}$ = 41.0 Hz, $^3J_{CP}$ = 6.8 Hz, qC-1), 112.6 (dd, $^1J_{CP}$ = 55.9 Hz, $^3J_{CP}$ = 4.1 Hz, qC-9), 30.5 (s, C-11/C-12), 30.0 (s, C-11/C-12), 25.1 (d, $^1J_{CP}$ = 36.1 Hz, *i*Pr CH), 22.4 (dd, $^1J_{CP}$ = 36.4, $^3J_{CP}$ = 4.5 Hz, *i*Pr CH), 17.7 (d, $^2J_{CP}$ = 2.2 Hz, *i*Pr CH_3), 17.2 (s, *i*Pr CH_3), 17.1 (s, *i*Pr CH_3), 16.6 (d, $^2J_{CP}$ = 1.8 Hz, *i*Pr CH_3).

^{31}P NMR δ_P (202 MHz; $CDCl_3$) 12.8 (br s, *i*Pr_2P), −69.5 (br d, $^1J_{PH}$ = 339 Hz, PH).

$^{31}P\{^1H\}$ NMR δ_P (202 MHz; $CDCl_3$) 12.8 (br d, $^1J_{PP}$ = 79.9 Hz, *i*Pr_2P), −69.5 (br m, PH).

^{11}B NMR δ_B (160 MHz; $CDCl_3$) −37.2 (br m, BH_3), −41.9 (br m, BH_2).

$^{11}B\{^1H\}$ NMR δ_B (160 MHz; $CDCl_3$) −37.1 (br m, BH_3), −41.9 (br ≈t, $^1J_{BP}$ = 63.0 Hz, BH_2).

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

HRMS (ES+) Found: 351.1753. Calc. for $C_{18}H_{28}P_2B_2Na$ (M + Na): 351.1750.

Acenap(P*i*Pr$_2$·BH$_3$)(PH$_2$) 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 δ_H (400 MHz; $CDCl_3$) 8.54 (1H, dd, $^3J_{HP}$ = 17.4 Hz, $^3J_{HH}$ = 7.4 Hz, 8-H), 8.04–8.00 (1H, m, 2-H), 7.33 (1H, d, $^3J_{HH}$ = 7.3 Hz, 7-H), 7.27 (1H, d, $^3J_{HH}$ = 7.2 Hz, 3-H), 4.48 (2H, d, $^1J_{HP}$ = 207 Hz, PH_2), 3.63–3.49 (2H, m, 2 × *i*Pr CH), 3.38 (4H, s, 11-H, 12-H), 1.70–0.30 (3H, br m, BH_3), 1.42 (6H, dd, $^3J_{HP}$ = 15.0 Hz, $^3J_{HH}$ = 7.0 Hz, 2 × *i*Pr CH_3), 0.88 (6H, dd, $^3J_{HP}$ = 16.2 Hz, $^3J_{HH}$ = 7.1 Hz, 2 × *i*Pr CH_3).

$^{13}C\{^1H\}$ NMR δ_C (75 MHz; $CDCl_3$) 152.3 (s, qC-6), 150.1 (s, qC-4), 143.8 (d, $^2J_{CP}$ = 4.6 Hz, C-8), 143.5 (br d, $^2J_{CP}$ = 20.0 Hz, C-2), 140.9 (≈t, $^3J_{CP}$ = 7.1 Hz, $^3J_{CP}$ = 7.1 Hz, qC-5), 137.0 (d, $^2J_{CP}$ = 26.6 Hz, qC-10), 120.5 (d, $^1J_{CP}$ = 43.7, qC-9), 119.8 (s, C-3), 119.2 (d, $^3J_{CP}$ = 14.7 Hz, C-7), 117.8 (d, $^1J_{CP}$ = 16.0 Hz, qC-1), 30.0 (s, C-11/C-12), 29.9 (s, C-11/C-12), 25.2 (d, $^1J_{CP}$ = 28.4 Hz, *i*Pr CH), 24.8 (d, $^1J_{CP}$ = 28.3 Hz, *i*Pr CH), 19.1 (s, 2 × *i*Pr CH_3), 18.9 (s, 2 × *i*Pr CH_3).

^{31}P NMR δ_P (109 MHz; $CDCl_3$) 44.5 (m, *i*Pr_2P), −101.3 (t, $^1J_{PH}$ = 207 Hz, PH_2).

$^{31}P\{^1H\}$ NMR δ_P (109 MHz; $CDCl_3$) 44.0 (m, *i*Pr_2P), −101.4 (s, PH_2).

^{11}B NMR δ_B (96 MHz; $CDCl_3$) −41.9 (br m, BH_3).

$^{11}B\{^1H\}$ NMR δ_B (96 MHz; $CDCl_3$) −41.9 (br d, $^1J_{BP}$ = 66.4 Hz, BH_3).

Acenap(P*i*Pr$_2$)(μ-BH$_2$)(PH) 14

A suspension of **5c** (0.100 g, 0.304 mmol) in xylenes (20 mL) was heated under reflux. At high temperatures, all solid dissolved to give a yellow solution. After 3 days volatiles were removed *in vacuo* to give a yellow solid (0.098 g) containing ≈74% **5c** and ≈26% **14**. Compound **14** was not isolated pure due to its instability to air and moisture and NMR data was assigned from the mixture. Attempts to bring the reaction to completion *via* prolonged heating under reflux resulted in decomposition to a complex mixture of products.

^{1}H NMR δ_H (400 MHz; $CDCl_3$) 7.98 (1H, dd, $^3J_{HP}$ = 12.1 Hz, $^3J_{HH}$ = 7.0 Hz, 2-H), 7.61 (1H, dd, $^3J_{HP}$ = 9.9 Hz, $^3J_{HH}$ = 7.2 Hz, 8-H), 7.35 (1H, d, $^3J_{HH}$ = 7.2 Hz, 7-H), 7.25 (1H, d, $^3J_{HH}$ = 7.0 Hz, 3-H), 3.40–3.33 (4H, m, 11-H, 12-H). Signals for H directly bound to phosphorus/boron and *i*Pr groups were obscured by signals from **5c** or were too weak to be seen.

^{31}P NMR δ_P (162 MHz; $CDCl_3$) 11.1 (br s, *i*Pr_2P), −137.0 (br d, $^1J_{PH}$ = 185 Hz, PH).

$^{31}P\{^1H\}$ NMR δ_P (162 MHz; $CDCl_3$) 11.0 (m, *i*Pr_2P), −136.9 (s, PH).

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