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**Authors:** Michael J Cowley, Amy N Price, and Gary S Nichol

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# Phosphaborenes: accessible reagents for C-C/P-B isosteres

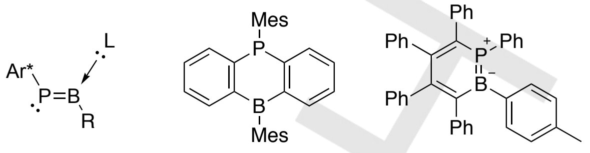
Amy N. Price, Gary S. Nichol, Michael J. Cowley*[a]

**Abstract:** Formal exchange of C=C units with isoelectronic B=N or B=P units is can provide access to molecules with unique electronic or chemical properties. Here, we report the simple solution-phase generation of highly reactive phosphaborenes, RP=BR, and demonstrate their use for the introduction of P=B units into organic systems. A P-B containing cyclobutene isostere can be ring opened to access unique 1,4-bora-phospha-butadiene systems with conjugated main-group multiple bonds.

Phosphaborenes, RP=BR, are alkyne analogues which are also isoelectronic with iminoboranes, RN≡BR. In contrast to iminoboranes,[1] phosphaborenes are unknown as stable compounds. Isolation of these species is hindered by their significant tendency to oligomerise - a consequence of their ambiphilic nature, with adjacent Lewis acidic and basic sites at the boron and phosphorus centers.[2] Even when bulky substituents are employed, dimers (diphosphadiboretanes) or higher oligomers are typically isolated. An additional difficulty in generating isolable phosphaborenes is that the routes to formation of the P=B multiple bond typically rely on base-induced eliminations from phosphinoborane precursors. In the presence of bases, any phosphaborenes generated are likely to be rapidly coordinated at the boron center. This tendency has been used by Power and Rivard,[3] and ourselves[4] to isolate the base-stabilised derivatives **A**, **B** and **C**.

The substitution of unsaturated organic functional groups with isoelectronic alternatives is emerging as a powerful method to control electronic properties of π-conjugated compounds and materials. The substitution of C=C units with B=N 'isosteres' is particularly well-established.[5] Compared to the boron-nitrogen situation, the development of boron-phosphorus containing unsaturated systems has lagged behind. Synthetic methods applied to the BN systems are typically not transferable to the chemistry of phosphorus-containing systems. Within this area, the highest effort has been concentrated on the synthesis of B/P containing aromatic species. 1,4-phosphaborins **D** have been prepared by ring-closing methods,[6] and the recent synthesis of the first 1,2-phosphaborine **E**, reported by Martin, exploited the generation of transient phosphinidenes and their insertion into a borole precursor.[7]

Our interest in the chemistry of phosphaborenes led us to question if – once generated – they could act as reagents for the introduction of P=B units into organic frameworks. Here, we report the thermal generation and trapping of a phosphaborene in solution, and the first cycloaddition reactivity of phosphaborenes. The resulting unsaturated P/B containing compounds can be isomerized by ring opening to give conjugated systems containing B=C and P=C multiple bonds.

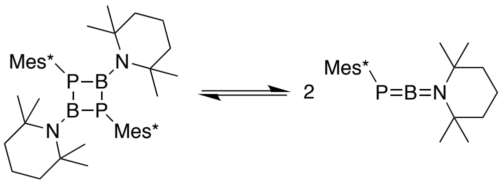


**A, B, C** **D** **E**

**Figure 1.** Examples of Lewis-base coordinated phosphaborenes (**A**-**C**) and previously synthesized P=B isoteres of aromatic systems **D** and **E**. Ar* = $C_6H_3$-2,6-($C_6H_2$-2,4,6-$^i$Pr$_3$)$_2$ (**A**) or 2,4,6-tritertbutylphenyl (**B**, **C**). R = 2,2,6,6-tetramethylpiperidino (**A**) or 1,2,3,4,5-tetramethylcyclopentadienyl (**B**, **C**). L = N,N-dimethylaminopyridine (**A**, **B**) or 1,3,4,5-tetramethylimidazol-2-ylidene (**C**).

On the basis of our previous work,[4] we considered that the likelihood of observing, isolating, or trapping a monomeric phosphaborene would be significantly enhanced if we targeted an amino-substituted phosphaborene. Iminoboranes bearing electronically innocent substituents – e.g. tert-butyl or aryl - at boron and nitrogen can be readily generated but are prone to oligomerization.[1,8] This process is significantly inhibited by the presence of a π-donating amino-substituent, which modulates Lewis acidity at the boron center.[1] Suggestively, the mass spectra of two diphosphadiboretanes bearing bulky substituents have been reported to have parent molecular ion peaks corresponding to $[RP{=}BR]^+$ ions.[9] Furthermore, diphosphadiboretane **1** was noted by Alan Cowley to have a particularly long P–B bond distance of 1.96(2) Å.[9a] Intrigued, we employed DFT calculations (M062X/Def2SVPP)[10] to examine the relative energies of **1** and its corresponding monomeric phosphaborene, **2**. Phosphaborene **2** is 46.0 kJ mol$^{-1}$ higher in energy than its corresponding dimer**,** indicating that, subject to a reasonable activation energy, it should be possible to generate at solution-phase temperatures.

In $^1$H and $^{31}$P NMR spectroscopic studies of diphosphadiboretane **1** (toluene-$d_8$, temperatures up to 100 °C) we failed to observe any evidence for either a monomeric species or any line-broadening arising from a rapid monomer/dimer equilibrium (consistent with the low expected concentration of **2**, given the calculated Δ$G_0$). However, heating benzene solutions of diphosphadiboretane **1** to 80 °C in the presence of Lewis bases (N,N-dimethylaminopyridine, DMAP; 1,3,4,5-tetramethylimidazol-



**1** (0.0 kJ mol$^{-1}$) **2** (+46.0 kJ mol$^{-1}$)

**Scheme 1.** Relative energies of diphosphadiboretane **1** and its thermally accessible monomer phosphaborene **2** (M062X/Def2SVPP). Mes* = 2,4,6-tritertbutylphenyl.

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[a] A. N. Price, Dr G. S. Nichol Dr M. J. Cowley
EaStCHEM, School of Chemistry, University of Edinburgh
Edinburgh, EH9 3FJ (UK)
E-mail: michael.cowley@ed.ac.uk

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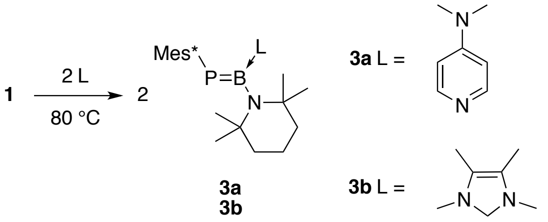


**Scheme 2.** Preparation of base-coordinated phosphaborenes **3a** and **3b**. Mes* = 2,4,6-tritertbutylphenyl.

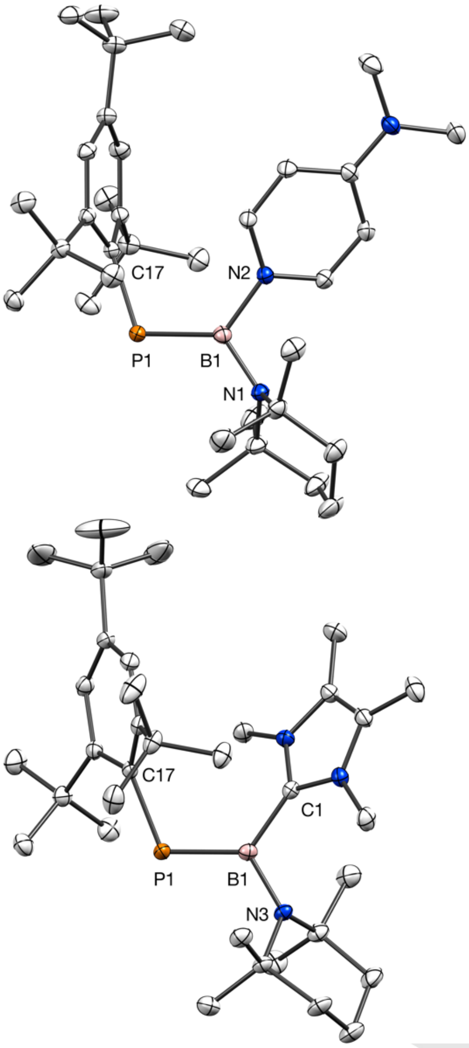
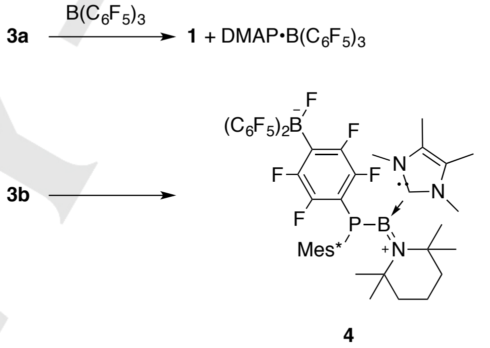


**Figure 2.** Molecular structures of **3a** (top) and **3b** (bottom) in the solid state. Ellipsoids at 50 % probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) for **3a**: P1–B1 1.8211(16), N2–B1 1.5685(19), N1–B1 1.4819(19), C17–P1 1.8775(14), C17–P1–B1 108.39(7), P1–B1–N2 124.75(11), N1–B1–N2 110.85(12), N1–B1–P1 124.39(11). For **3b**: P1–B1 1.8309(16), C1–B1 = 1.609(2), N3–B1 = 1.493(2), C17–P1 1.8621(15), C17–P1–B1 111.90(7), P1–B1–N3 120.60(10), C1–B1–N3 114.81(12), C1–B1–P1 124.52(11).[23]

2-ylidene, ImMe$_4$) resulted in formation of the DMAP and ImMe$_4$ stabilised phosphaborenes **3a** and **3b**. Signals in the $^{31}$P NMR spectra at $\delta$ 62.2 (**3a**) and 151.5 (**3b**) indicate the presence of P=B multiply-bonded species (cf **1** $\delta$ −92.3). Resonances in the $^{11}$B NMR spectra (**3a**: $\delta$ 42.4 ; **3b**: $\delta$ 44.1) are typical of those observed for base-coordinated phosphaborenes.[3,4]

Single-crystal X-ray crystallographic studies of **3a** and **3b** confirmed coordination of DMAP or ImMe$_4$ at boron and revealed short P=B bond distances (**3a** 1.8211(16) Å; **3b** 1.8309(16) Å) and small C–P–B bond angles, entirely consistent with previously reported base-stabilised phosphaborenes. The dative N–B and C–B bonds between the DMAP and ImMe$_4$ (**3a** 1.5685(19); **3b** 1.609(2) Å) are longer than in **B** and **C**, reflecting the reduced Lewis acidity of the amino-substituted boron center.

We explain the formation of **3a** and **3b** by proposing dissociation (at high temperatures) of diphosphadiboretane **1** into 2 equivalents of the phosphaborene **2**, before base trapping of **2** by DMAP or ImMe$_4$. Similarly, cyclic phosphinidene selenide dimers, [RPSe]$_2$, have recently been reported to dissociate to monomers in solution before undergoing trapping reactions.[11] An alternative possibility for the formation of **3a** and **3b** is base-coordination-induced cleavage of the diphosphadiboretane ring. However, when we combined **1** and DMAP or ImMe$_4$ with **1** at room temperature, **3a** or **3b** were observed to form only slowly over the course of several weeks. No intermediates were observed by NMR spectroscopy.

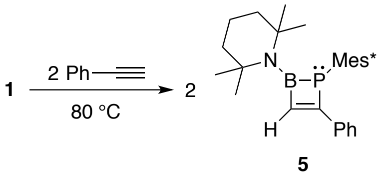


**Scheme 3.** Reactivity of **3a** and **3b** with B(C$_6$F5)$_3$. Mes* = 2,4,6-tritertbutylphenyl.

To provide further evidence for the proposed dimer/monomer equilibrium of **1** in solution, we sought to remove the coordinated base from **3a** and **3b** to examine the fate of the resulting phosphaborene monomer **2**. Thus, treatment of the DMAP adduct **3a** with the strong Lewis acid B(C$_6$F$_5$)$_3$ at room temperature results in an immediate color change from deep red to pale yellow. Monitoring the reaction by NMR spectroscopy revealed the formation of diphosphadiboretane **1** ($^{31}$P $\delta$ -92.3), together with the expected adduct DMAP·B(C$_6$F$_5$)$_3$.

In contrast, the NHC adduct **3b** has a very different fate when treated with B(C$_6$F$_5$)$_3$. Instead of scavenging ImMe$_4$ from **3b**, which is precluded by the stronger coordination of the NHC to the phosphaborene unit, B(C$_6$F$_5$)$_3$ instead undergoes a nucleophilic aromatic substitution at the para-position of a C$_6$F$_5$ ring, forming the zwitterion **4**. In this regard, the reactivity of NHC-stabilized phosphaborene **3b** is directly analogous to that observed for bulky, electron rich phosphines,[12] providing a first (qualitative) measure of the nucleophilicity of base-stabilized boraphosphenes.

Compound **4** is characterised by two signals in the $^{11}$B NMR spectrum; a broad resonance at $\delta$ 36.0 is observed for the three-coordinate NHC-bound boron, and a higher field signal at $\delta$ −1.0 is assigned to the four-coordinate center. In the $^{31}$P NMR spectrum, a signal is observed at $\delta$ −49.3, significantly upfield from that for **3b** ($\delta$ 151.5) and indicative of a reduced P–B bond order in comparison to the starting material. This conclusion is borne out by a single-crystal X-ray crystallographic study of **5** (see Fig S1), which reveals a P–B bond distance of 1.923(3) Å, significantly lengthened in comparison to that in **3b** (1.8309(16) Å) In contrast to phosphonium borates formed from bulky phosphines and $B(C_6F_5)_3$, the phosphorus center in the zwitterion **5** remains three-coordinate and formally neutral. The $^{11}$B chemical shift observed for the three-coordinate boron center of **4** is typical for borenium cations.[13] However a significant contraction of the B–N bond distance of **4** (1.415(3) Å) when compared to **3b** (1.493(2) Å) is indicative of increased B–N bond order and justifies the formal location of the positive charge at the nitrogen center of **4**.



**Scheme 4.** Reactivity of **1** towards phenylacetylene. Mes* = 2,4,6-tritertbutylphenyl.

With evidence that the phosphaborene **2** could be generated in solution, we sought to explore our goal of trapping it with unsaturated organic species. Phosphinoboranes, which are closely related to **2**, can behave as intramolecular frustrated Lewis pairs.[14] Since intermolecular boron/phosphorus frustrated Lewis pairs are well known to activate alkynes,[15] we decided to test the reactivity of **2** with an alkyne. Thus, monitoring the reaction between **2** and phenylacetylene (at 80 °C) by $^{31}$P and $^{11}$B NMR spectroscopy revealed the consumption of **1** and the formation of new signals at $\delta$ −47.3 and $\delta$ 42.7 respectively. Crystallization of the reaction product enabled a structural determination, which revealed it to be the 1,2-phosphaborete **5**. NMR spectroscopy of the reaction mixture reveals that **5** is formed with complete regioselectivity: the phosphorus center and the alkene C=CH proton ($^{3}J_{H\text{-}P}$ = 24.5 Hz) are each found in only one environment.

Compound **5** is the first example of a 1,2-phosphaborete. Such a species has previously been inferred, but not observed, as an unstable intermediate in the formation of a cyclic phosphinoborane from a zirconacycle transfer reaction with $PhBCl_2$.[16] The 1,2-phosphaborete ring of **5** avoids planarity – and the antiaromatic 4$\pi$ electron system that would result – by pyramidalization at the phosphorus center (sum of angles = 307°), Doubtless also contributing to the pyramidalization of the phosphorus center is the presence of a B–N $\pi$-bond, indicated by the short B–N bond distance (1.3929(19) Å). The P–B bond of **5** is unusually long, at 1.9870(16) Å. Indeed, the P–B bond distance approaches that observed for the *dative* P–B bonds in Erker's 4-membered, cyclic, vicinal P/B frustrated Lewis pairs (e.g. $(C_6F_5)_2BC(C_6F_5)=C(C_6H_5\text{-}4\text{-}Me)PPh_3$ P–B = 2.018(2) Å).[17] The long P–B distance, pyramidal phosphorus center, and typical C=C distance confirm that **5** is best described as a cyclobutene analogue.

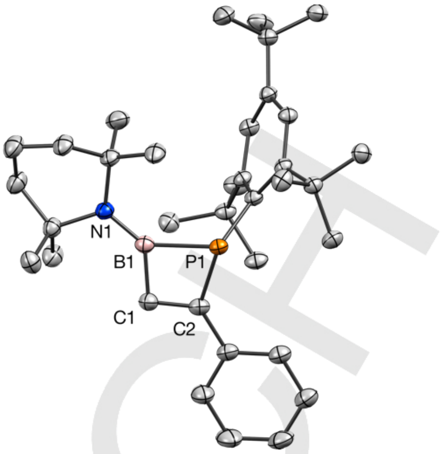


**Figure 3.** Molecular structure of **5** in the solid state. Ellipsoids at 50 % probability Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): P1–B1 1.9870(16), N1–B1 1.5685(19), N1–B1 1.3929(19), C1–B1 1.5649(19), C1–C2 1.363(2), C2–P1 1.8467(14), C2 P1–B1 72.09(6), C1–B1–P1 86.26(9), C2–C1–B1 100.77(11), C1–C2–P1 98.28(10).

Heavier group 14 alkyne analogues readily undergo formal 2+2 cycloaddition chemistry with alkynes,[18] but the lighter analogues of **2**, iminoboranes, are substantially less reactive. The iminoborane *t*BuN≡B*t*Bu reacts with acetylenes, but only in the presence of a coordinatively unsaturated Rh fragment, forming a Rh-coordinated $\eta^4$-1,2-azaborete ligand.[19a] In the presence of excess alkyne, the benzene analogues 1,4-azaborines or 1,2-azaborinenes are obtained in rhodium-catalysed processes.[19b,c] The lack of reactivity of phenylacetylene with *t*BuN≡B*t*Bu in the absence of a metal catalyst is unsurprising: such a [2+2] cycloaddition would be thermally forbidden.

In the heavy alkyne case, cycloaddition proceeds via an initial 2+1 cycloaddition at one end of the formal triple bond, exploiting the Lewis-acidic character located there.[18a,e] The potentially Lewis acidic boron center in **2** raises the possibility of a similar initial 2+1 cycloaddition mechanism. However, a close examination of the frontier molecular orbitals of **2** demonstrates the presence of a B=N $\pi$-bond (see figure S2), orthogonal to the B=P $\pi$-system, which would render such a mechanism unlikely. In fact, the orthogonal B=P and B=N $\pi$-systems represent the frontier molecular orbitals of **2**, rendering it isoelectronic to ketenes, which readily undergo antarafacial cycloaddition reactions with alkynes.[20] We speculate that an analogous mechanism is operating in this case.[21]

We sought to exploit the high ring-strain and weak P–B bond of **5** and induce ring-opening or ring-expansion reactivity. Phosphaborete **5** is so-far unreactive towards alkynes, however it reacts readily with Lewis acids or bases. Thus, when **5** was treated with $ImMe_4$ an immediate color change to purple was observed. The observation of new resonances in the $^{31}$P ($\delta$ 116.4) and $^{11}$B ($\delta$ 26.0) NMR spectra indicated the formation of a new

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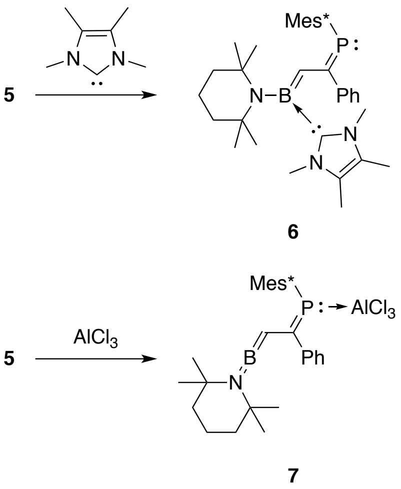

**Scheme 5.** Reaction of 1,2-phosphaborete **5** with Lewis acids and bases. Mes* = 2,4,6-tritertbutylphenyl.

compound, **6**. The downfield signal in the $^{31}$P NMR spectrum, which couples to a signal at low field in the $^{13}$C NMR spectrum (δ 187.4, d, $^{1}J_{\text{P-C}}$ = 56.4 Hz), is characteristic for a phosphaalkene. The structure of **7** was established by X-ray crystallography and revealed that **7** is a butadiene analogue possessing both P=C and B=C multiple bonds (respective bond distances: 1.7445(19) and 1.493(3) Å) in a *trans* arrangement. The B=N π-bond present in **5** is disrupted in **6** by the coordination of the NHC ligand to the boron center (C1–B1 = 1.605(3) Å). The relatively short C17–C18 single bond (1.413(3) Å) is suggestive of conjugation between the P=C and B=C units. The UV/Vis spectrum of **6** yields further information in this regard, revealing a longest-wavelength absorption at 508 nm (ε = 18200 L mol$^{-1}$ cm).

Similarly, the 1,2-phosphaborete **5** reacts with $AlCl_3$ to provide a ring-opened product. The yellow $AlCl_3$-coordinated product **7** is obtained by treatment of **5** with $AlCl_3$ in benzene. A $^{31}$P NMR spectrum reveals a resonance at δ 71.8, though no signal could be located in the $^{11}$B NMR spectrum. X-ray structure analysis of **7** confirmed the presence of adjacent P=C and B=C units in a *trans* orientation. The P=C and B=C bond distances of **7** are considerably shorter than those in **6** (**7** P=C = 1.7445(19), B=C = 1.493(3) Å; **8** P=C = 1.704(3) Å, B=C = 1.433(5) Å;), though the central C1–C2 bond distance is experimentally indistinguishable from that of **6**, at 1.415(5) Å. As is expected for amino-substituted methylene boranes,[22] a B–N π-bond enforces a linear geometry at the boron center (C=B=N angle 178.8(4)°; B=N bond distance 1.338(5) Å). The UV/Vis spectrum of **7** differs substantially from that of **6** with a substantially blue-shifted longest-wavelength absorption at 365 nm (ε = 13800 L mol$^{-1}$ cm).

To probe the degree (or otherwise) of conjugation between P=C and B=C bonds in 6 and 7, and understand the difference in their electronic spectra, we undertook a time-dependent DFT study of the two compounds. TD-DFT calculations at the at the M062X level reproduced the trends in the experimental UV-Vis spectra, albeit blue-shifted by 20-60 nm. The longest wavelength absorption of the $AlCl_3$ adduct **7** ($\lambda_{\text{max}}$ = 343 nm (calculated) vs 365 nm (experimental)) results from a transition from the highest occupied molecular orbital (HOMO) – which has B=C and P=C character – to the lowest unoccupied molecular orbital (LUMO) (see figure S3). The longest-wavelength absorption for the NHC adduct **6** ($\lambda_{\text{max}}$ = 449 nm (calculated) vs 508 nm (experimental)) is significantly red-shifted in comparison to **7**. Inspection of the molecular orbitals of **6** and **7** reveals that the HOMO and LUMO of **7** are stabilized relative to those of **6** (e.g. HOMO of **6**: -4.965 eV; **7**: -6.771 eV), a consequence of the electron-withdrawing effect of $AlCl_3$ coordination at the phosphorus center.

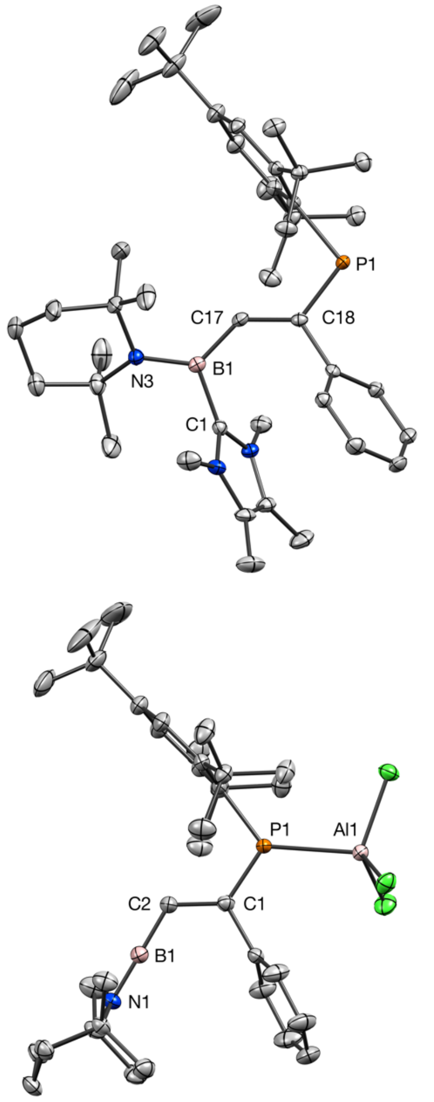

**Figure 4.** Molecular structures of **6** (top) and **7** in the solid state. Ellipsoids at 50 % probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) for **7**: P1–C18 1.7445(19), C17–C18 1.413(3), C17–B1 1.493(3), B1–C1 1.605(3), B1–N3 1.474(3). For **7** (values are from one of the two molecules in the asymmetric unit): P1–Al1 2.3961(13), P1–C1 1.704(3), C1–C2 1.415(5), C2–B1 1.433(5), B1–N1 1.338(5), N1–B1–C2 178.8(4).

In summary, we have demonstrated the use of diphosphadiboretane **1** as an effective phosphaborene source in solution. Trapping of the phosphaborene monomer **2** with Lewis bases provides a new route to base-stabilized phosphaborenes. Generation of **2** in the presence of alkynes allows the synthesis of previously inaccessible P/B containing organic compounds such as the cyclobutene isostere **5**, which can be readily transformed into new compounds containing main-group multiple bonds. The use of phosphaborenes such as **2** as readily-available 'synthons' for the introduction of P/B units into organic compounds shows significant promise for the preparation of new P/B containing organic molecules and materials.

## Acknowledgements

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**Keywords:** boron • phosphorus • multiple bonds • conjugation • carbenes

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Layout 2:

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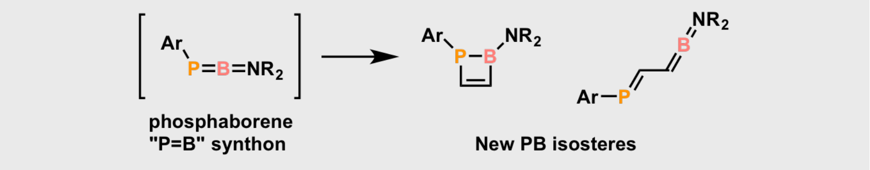

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**Phosphaborenes: accessible reagents for C-C/P-B isosteres**

Transient phosphaborenes – RP=BR – can be generated in solution and used to introduce PB units into organic compounds as C=C isosteres. A PB containing cyclobutene analogue can be ring opened to give conjugated systems with main-group multiple bonds.