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Boron azides in Staudinger oxidations and cycloadditions†

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Staudinger reactions of Cy_2BN_3 with tri-substituted phosphines (R_3P) yielded the boron-nitrogen-phosphorus linked systems $Cy_2BN=PR_3$ (R = Et, ^tBu, Cy, Ph) (**1a-1d** respectively). Similarly, reaction of $(C_6F_5)_2BN_3$ with the phosphines P^tBu₃, PPh₃, Ph₂PC=CPh and Ph₂PC=CPPh₂ yielded $(C_6F_5)_2BN=PR_3$ (**2a-d** respectively). In contrast, the reaction of $(C_6F_5)_2BN_3$ with Ph₂P-C=Cp-tol in the presence of excess Me₃SiN₃ afforded the bicyclic product **3** [1-(C_6F_5)_2B-4-(p-tol)-1H-1,2,3-triazole-5-P(NH)Ph₂] in which both a Staudinger and a cycloaddition reaction has taken place. However, if the Staudinger reaction is prohibited *via* phosphine oxidation as in the case of (EtO)₂P(O)C=CP(O)(OEt)₂ then the unusual dimeric product **4** [2-(C_6F_5)_2B-4-($P(O)OEt_2$)-2H-1,2,3-triazole-5-P(O)(OEt)(OB(C_6F_5)_2)] is generated. The structures of **1b-d**, **2b-d**, **3** and **4** have been determined by X-ray diffraction.

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Introduction

Recently, there has been a surge in interest in the activation and subsequent utilisation of small molecules and catalytic properties of main group compounds.¹ The advent of such metal-free processes has been stimulated to some extent by the development of the concept of Frustrated Lewis Pairs (FLPs). Most notably such species have been shown² to activate H₂ reversibly leading to the development of metal-free hydrogenation catalysts.^{1*c*-*g*} In addition to hydrogen activation and hydrogenation reactions, FLPs have also been shown to activate a wide range of other small molecules including alkynes, olefins, CO₂,³ N₂O,⁴ and NO⁵ among others.

In ongoing studies, we are continuing to explore the 'click' chemistry of main group azides with a view to making novel main group substituted heterocycles which potentially contain both Lewis acidic and Lewis basic sites. Of particular interest is the cycloaddition reaction of a boron azide with alkynes. We are particularly targeting systems bearing electron withdrawing groups at B⁶ to enhance its Lewis acidity. Whilst several boron azide compounds of the type R_2BN_3 (R = alkyl or aryl) have been reported previously,⁷ their subsequent applications in synthesis have barely been explored. In 2012 Curran *et al.*⁸ reported the cycloaddition chemistry of an *N*-heterocyclic carbene-stabilised boryl azide. At the same time we were

investigating the 'click' chemistry⁹ of Cy_2BN_3 with alkynes,¹⁰ RC=CR'. These studies demonstrated that interesting boron functionalised triazoles were accessible *via* such cycloaddition chemistry.

The Staudinger reaction of a tertiary phosphine with an azide yielding a phosphinimine¹¹ is a versatile tool in organic synthesis affording amines from azides *via* a stable phosphinimine intermediate (Scheme 1).¹² The initial phosphinimine is formed by nucleophilic attack of the phosphine on the terminal nitrogen of the azide, followed by the thermodynamically favourable elimination of N₂ to afford the phosphinimines (Scheme 1).^{12,13} Nevertheless, until recently use of boron azides in Staudinger reactions appears to be limited to the reaction of Ph₂BN₃ with Ph₃P in pyridine at 200 °C, published some 45 years ago.¹⁴ More recently, Erker *et al.*¹⁵ have reported the Staudinger reaction at an intramolecular frustrated P–B Lewis pair to generate a borane-stabilised phosphinimine.



Scheme 1 Reaction pathway of Staudinger oxidation.

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[†]Electronic supplementary information (ESI) available: Selected NMR data, DFT calculations and details of the crystal structure determination of **1b-d**, **2a-d**, **3** and **4**. CCDC 929289–929295 and 929332–929333. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt50791b

In the present study, we report the facile synthesis of the phosphinimines, R_2BN — PR_3 *via* Staudinger reactions and we examine the competition between the possible Staudinger and cycloaddition reaction pathways when using alkynyl phosphines leading to unique main group heterocyclic compounds.

Results and discussion

Initially we explored the reactions of the boron azides Cy₂BN₃ and (C₆F₅)₂BN₃ with a variety of tri-substituted phosphines. The Staudinger reaction between the boron azide and the phosphine readily afforded the boryl-phosphinimide species $R_{2}^{1}R^{2}PNBR_{2}$ 1a-d and 2a-b (Fig. 1) in modest to excellent recovered yields (44-99%) under mild conditions (25 °C, 18 h). This is in stark contrast to Paetzold's synthesis of Ph₂BNPPh₃ which required temperatures of 200 °C to afford the product.¹⁴ We found that the rate of the reaction is strongly dependent upon both the electron-donating ability of the phosphine and the electron-withdrawing ability of the groups attached to the boron azide. Thus, the fastest reaction occurs for very electronrich phosphines and more electron-withdrawing azides which is comparable to that seen for the typical Staudinger reaction.¹⁶ Indeed, the rapidity of the reaction between $(C_6F_5)_2BN_3$ and P^tBu_3 can be observed by the effervescence of N_2 upon immediate addition of the phosphine to the boron azide. Although the majority of these reactions appeared complete within 30 min, based upon in situ ³¹P NMR spectroscopy all reactions were left for 18 h to ensure complete conversion. Notably no reaction was observed between Cy₂BN₃ and Mes₃P, presumably due to the steric hindrance at P which protects the lone pair (Tolman cone angle for Mes₃P is 212°).¹⁷

The ³¹P spectra were diagnostic of compounds **1a-d** and 2a-b. The ³¹P chemical shifts are dependent upon the phosphine employed with the general trend that phosphines bearing more electron donating groups were more deshielded. In the case of 1 31 P chemical shifts followed the trend t Bu > Cy > Et > Ph with the ^tBu derivative exhibiting the most downfield shift at 33.3 ppm and the Ph derivative having the most upfield shift at 0.8 ppm. Compounds 2a and 2b show analogous trends in chemical shift in the ³¹P NMR spectra (Table 1). These data are broadly comparable with trends seen for the parent phosphines, R₃P where the chemical shifts are dominated by the paramagnetic shielding tensor.¹⁸ However, it is notable that whilst the general trend is maintained some ³¹P chemical shifts move downfield (1a, 1c and 1d) whereas others move upfield (1b) relative to the parent phosphine reflecting the complexity of the paramagnetic shielding tensor term which involves (partial) charge, relative energies of excited

Fig. 1 Compounds 1 and 2.

 Table 1
 ³¹P{¹H} and ¹¹B NMR chemical shifts for 1–4

Compound	$^{31}P{^1H}/ppm$	¹¹ B/ppm
1a (Et) –20	14.7	50.3
1b $({}^{t}Bu)$ 61	33.3	49.0
1c (Cy) 5	17.6	48.5
1d (Ph) -8	0.8	52.0
2a	43.6	31.4
2b	16.0	37.0
2c	-5.3	36.1
2d	-7.1 [P(2)]	38.2
	-33.8 [P(1)]	
3	32.0	-1.0
4	7.9	-0.5
	-10.5	2.6

states and orbital overlap. The ¹¹B NMR spectra of **1a–d** exhibited a broad singlet between 48.5 and 52.0 ppm. Likewise, the ¹¹B NMR chemical shift for **2a–b** occurred at 31.4 and 37.0 ppm respectively.

High-resolution DART mass spectrometry of compounds **1a–d** and **2a–b** all showed peaks corresponding to either $[R_3P=NH_2]^+$ and/or $[R_3P-NH_3]^+$ usually as the base peak, and the ^{*t*}Bu derivatives **1b** and **2a** showed a peak due to the molecular ion $[M + H]^+$. The formation of the stable $R_3P=NH$ as the base peak indicated that the B–N bond theoretically has limited stability and addition of H₂ to this could potentially result in B–N bond breakage and the formation of $R_3P=NH$ and R^1_2BH . However, attempts to activate H₂ with **1a**, **1c** and **2a** proved unsuccessful even after 4 weeks at 150 °C indicating that the B–N bond remains intact.

In an analogous fashion phosphines bearing acetylene functionalities were also reacted with boron azides to give the species $Ph_2(RC \equiv C)PNB(C_6F_5)_2$ (R = Ph **2c**, PPh₂ **2d**). It is note-worthy that in the latter case, **2d** does not react further with azide. The isolated species exhibit ³¹P NMR signals at -5.3 ppm and -7.1 ppm respectively while the ¹¹B NMR resonances appear at 36.1 ppm and 38.2 ppm (Table 1).

The structures of compounds (1b-d, 2a-d) were determined by X-ray crystallography confirming the monomeric nature of these PNB species (Fig. 2-4). A search of the CSD revealed no structures of the from R₂B-N=PR₃ in the literature, although a few adducts of the type $R_3B \leftarrow NH = PR_3$ have been reported in which there is a boron–nitrogen dative bond $(d_{B-N} =$ 1.5645-1.7121 Å).^{15,19} The B-N bond lengths in the present species (Table 2) span the range from 1.344(4) to 1.408(2) Å which is shorter than conventional B-N single bonds (1.51 Å)^{15,19} but longer than a normal B=N double bond (1.31 Å), consistent with some degree of π -delocalisation in the species 1 and 2. The B-N bond lengths are comparable to those in conjugated allylic systems such as Ph2B-N=C^tBu2 and Mes₂B-N=CPh₂ (1.366 Å and 1.376 Å respectively).²⁰ The sums of the angles at B are 360.0(2)°, consistent with the expected trigonal planar geometry at B. The P=N bond lengths reveal much smaller variations [average = 1.566 Å; range 1.547(1)-1.581(2) Å, Table 2] and are consistent with other R₃P=NR 'double' bonds (1.584 Å),^{15,19} albeit one in

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Fig. 2 Structures of 1b (top), 1d (middle) and 1c (bottom). Hydrogen atoms omitted for clarity. B: yellow-green, C: black, N: blue, F: green, P: orange.

which the zwitterionic contribution, R_3P^+ – N^-R , is the dominant contribution to the resonance form.

The overall effect of the alkyl and aryl substituents on the phosphorus and boron atoms in compounds 1 and 2 is to produce a sterically-hindered central nitrogen atom. Indeed, the solid state structures reveal B-N=P bond angles intermediate between the idealised 120° angle expected for an sp² hybridised nitrogen atom and 180° expected for an sp-hybrid N with the angle becoming closer to 180° for the ^tBu derivative (162.8° and 170.8° for 1b and 2a respectively) (Table 2). The B-N=P angle increases with increasing size of the alkyl groups on the phosphorus atom. Thus the ^tBu derivatives show the largest B-N-P angles whereas the cyclohexyl and phenyl compounds show a much smaller B-N=P angle in general agreement with the Tolman cone angles (^tBu₃P 182°; Cy₃P 170°; Ph₃P 145° and Et₃P 132°).¹⁷ Notably the bond angle at nitrogen varies widely for each of the individual molecules in the asymmetric unit for 1c ranging between 134.9(2)° and 155.4(2)° which may indicate a shallow energy profile for distortion around the energy minimum for the BNP bond angle.



Fig. 3 Structure of 2a (top) and 2b (bottom). Hydrogen atoms are omitted for clarity. B: yellow-green, C: black, N: blue, F: green, P: orange.



Fig. 4 Structures of **2c** (top) and **2d** (bottom). Hydrogen atoms are omitted for clarity. B: yellow-green, C: black, N: blue, F: green, P: orange.

Table 2 Selected bond lengths and angles for compounds 1–3

Compound	B–N bond length/Å	P─N bond length/Å	B−N≕P bond angle/°
1b	1.388(2)	1.547(1)	162.8(1)
1c	1.406(3)	1.581(2)	134.9(2)
	1.391(3)	1.565(2)	144.6(2)
	1.396(4)	1.553(2)	155.4(2)
1d	1.408(2)	1.5645(9)	141.51(8)
2a	1.344(4)	1.560(3)	170.8(3)
2b	1.362(3)	1.578(2)	138.8(2)
2c	1.372(2)	1.575(2)	135.5(1)
2d	1.373(8)	1.572(3)	135.7(3)
3	1.583(3)	1.609(2)	118.3(2)



Fig. 5 Space filling model of 2a.

The increased steric hindrance at the nitrogen lone pair and at boron in **2a** can be seen in the space-filling representation (Fig. 5). Indeed, in this case, the coordination of small molecules such as MeCN to the boron centre was not possible. While this may be a steric effect, the reduction of the Lewis acidity at boron *via* π -donation from nitrogen may also have an impact here.

Compounds 2c and 2d exhibit P=N and B-N bonds lengths similar to those observed for 1b-d and 2a-b. However the B-N=P bond angle is significantly smaller at 135°, closer to that expected for the sp² hybridised nitrogen atom which is presumably a result of the reduced steric hindrance about phosphorus with the alkyne substituent. In the case of 2c the solid state structure shows that one of the C₆F₅ groups of the boron atom lies over the alkyne moiety affording some π - π stabilisation through interaction of the electron-rich alkyne and the electron-poor C₆F₅ ring. The intramolecular distance from the centroid of the C_6F_5 ring to the centre of the C=C bond in 2c is 3.514 Å and is comparable with those reported for fluoroaryl···alkyne π - π stacking interactions which have been reported elsewhere (average 3.49 Å).²¹ Likewise, 2b shows fluoroaryl…aryl π - π stacking (Fig. 4) with a centroid to centroid distance of 3.581 Å, comparable to fluoroaryl---aryl π - π stacking (3.4–3.8 Å) in compounds such as the co-crystal C₆F₆·C₆H₆.²²

The reaction of the phosphine $Ph_2P-C \equiv Cp$ -tol with the boron azide $(C_6F_5)_2BN_3$ in the presence of excess TMSN₃ in toluene at 110 °C afforded the bicyclic compound 3 after 2 days in low yields (Scheme 2). The identity of 3 was confirmed crystallographically (Fig. 6) as $Ph_2P(=NH)(C = Cp$ -tol)- $N_3B(C_6F_5)_2$. The fused C_2N_4BP bicyclic framework is essentially



Scheme 2 Synthesis of 3.



Fig. 6 Structure of 3. Hydrogen atoms omitted for clarity. B: yellow-green,
C: black, N: blue, F: green, P: Orange. Selected bond distances (Å) and angles (°).
3: B(1)–N(4), 1.541(4); P(2)–N(4), 1.609(2); B(1)–N(1), 1.583(3); P(1)–C(5),
1.781(3); N(1)–N(2), 1.319(4); N(2)–N(3), 1.327(2); N(3)–C(2), 1.361(4); C(1)–C(2), 1.385(3); C(1)–N(1), 1.366(3); B(1)–N(4)–P(1), 118.3(2).

planar with a maximum deviation from planarity of 0.10 Å. This permits π -delocalisation across the triazole ring, although delocalisation is disrupted by the 4-coordinate B centre. Compound 3 exhibits significant shortening of both the N(1)-N(2)and N(2)-N(3) bonds at 1.319(4) Å and 1.327(2) Å respectively. The C-N bonds in the triazole 3 also reveal shorter bond lengths at 1.366(3) Å [N(3)-C(1)] and 1.361(4) Å [C(2)-N(1)]compared to 1.383 Å and 1.367 Å in the average triazole. The B(1)-N(4)-P(1) angle at 118.3(2)° is now more typical for an sp² hybridised nitrogen atom presumably a reflection of the fact that it is constrained to be a cyclic system. The B(1)-N(4) bond at 1.541(4) Å and the P(2)–N(4) bond at 1.609(2) Å are much longer than those observed for compounds 1-2 as a result of (i) the reduced π -bonding to the sp³ hybridised boron atom and (ii) the protonation of the nitrogen atom. The N-H group acts as an intermolecular hydrogen-bond donor to the triazole ring of an adjacent molecule with an intermolecular N(4)-H···N(3) contact between molecules $(dN(4) \cdots N(3) = 2.852(4) \text{ Å})$.

The formation of **3** would appear to involve three discrete transformations: (i) a Staudinger reaction between the

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phosphine and the boron azide; (ii) a subsequent cycloaddition reaction between the azide and an alkyne; (iii) hydrolysis of the initial cycloaddition product to afford **3**. The observation that $Ph_2P-C\equiv CPh$ reacts only very slowly with Me_3SiN_3 at 85 °C in C_6D_6 after 3 days coupled with the observation that the similar products **2c** and **2d** were isolated after just 18 h at room temperature supports our assertion that the formation of **3** commences with the Staudinger oxidation of the P centre. In addition, the presence of the electron-withdrawing C_6F_5 groups activates the azide thus accelerating the Staudinger reaction, *i.e.* the Staudinger oxidation using $(C_6F_5)_2BN_3$ is expected to be substantially faster than with Me_3SiN_3 . Thus, the compounds **2c** and **2d** are plausible analogs of the intermediate in the formation of **3**.

To preclude the Staudinger oxidation, the O-protected phosphine-oxide (EtO)₂P(O)C=CP(O)(OEt)₂ was reacted with $(C_6F_5)_2BN_3$. While the spectroscopic data clearly inferred the formation of a new product 4, its nature was only fully determined via a crystallographic study which revealed it to be $[(EtO)_2P(O)C=CN_3B(C_6F_5)_2P(O)(OEt)]_2$ (Scheme 3). The structure of 4 is composed of a bicyclic system comprising two fused 5- and 7-membered rings which associate to form dimers *via* a pair of dative $P = O \rightarrow B$ bonds to generate a central $C_2N_4O_2B_2P_2$ macrocycle (Fig. 7). Whilst the two crystallographically independent C2N3 triazole rings are essentially planar (max. deviation 0.007 Å), the 7-membered C₂P₂O₂B ring is folded across the O --- P transannular contact such that one O and B atom lie considerably out of the plane by up to 0.88 Å. The C-N bonds in the triazole rings are the same within error (average = 1.346 Å), shorter than those in 3 and in conventional 1,2,3-triazoles and closer to that typical of a partially conjugated C–N bond such as that found in phenylamine (1.35 Å).²³ Likewise the C-C bond lengths (average = 1.408 Å) are longer than those in 3 and slightly longer than those in 1,2,3-triazoles (Scheme 3).

In the absence of the phosphine centre, cycloaddition reaction between the azide and alkyne occurs, followed by a 1,2migration of the $(C_6F_5)_2B$ functionality from the terminal nitrogen of the triazole to the central nitrogen atom. This presumably reduces steric hindrance, yielding a more thermodynamically stable product than the terminal N-coordinated isomer. The 7-membered $C_2P_2O_2B$ ring can be viewed as arising from the coordination of a second Lewis acidic



Fig. 7 Structure of 4. Hydrogen atoms are omitted for clarity. B: yellow-green, C: black, N: blue, F: green, P: orange, O: red.

 $(C_6F_5)_2B$ group to the oxygen atoms on the phosphine. The loss of the alkyl group from one of the ethyl groups of the phosphate ester bears a strong similarity to the loss of alkyl chains from ester groups when performing click reactions with the boron azide Cy_2BN_3 with $RCO_2C\equiv CCO_2R$ (R = Me, Et, ^{*t*}Bu).¹⁰ Elimination of the ethyl group from the ester is thought to proceed *via* coordination through the O-donor to the boron of $(C_6F_5)_2BN_3$ inducing loss of EtN₃. Nonetheless, the volatile EtN₃²⁴ was not observed by NMR spectroscopy. Notably EtN₃ has been generated from diethyl sulfate and NaN₃ supporting the thesis that a similar mechanism operates here.²⁵

Theoretical considerations

The near-linear geometry of the BNP unit permits the system to perhaps be considered analogous to allene, H₂C=C=CH₂ with two σ -bonds and the central atom involved in two sets of orthogonal π -type interactions. Indeed the relationship between B=N and C=C is a textbook example of the isoelectronic principle.²⁶ In addition the R₃P group can be considered analogous to a singlet carbene CH_2 in that both exhibit a lone pair. However, whereas the singlet carbene offers a vacant p-orbital, the R_3P fragment implements R-P σ^* acceptor orbitals.²⁷ The electronegativity differences between both B and N and P and N are likely to lead to resonance forms of type A (Fig. 8) in which there is a substantial build up of negative charge at N, with two formal lone pairs. Stabilisation of those two lone pairs can, to a greater or lesser extent be achieved through (i) π -donation to the vacant p-orbital on B (B) and (ii) donation to vacant P–C σ^* orbitals on P (C). The efficiency of these two processes is defined by the relative energies and spatial overlaps of the N p-orbitals and unoccupied B p-orbital and P–C σ^* orbitals, with the former anticipated to be more efficient, based on size and energy match.

Single point DFT calculations were undertaken at the $B3LYP/6-31G^*+d$ level of theory on derivatives of both 1 and 2. The three highest occupied molecular orbitals (Fig. 9) are



Fig. 8 Potential resonance forms for R₂BNPR₃ structures.



Fig. 9 (top) HOMO and HOMO - 1 for **1b**; (bottom) NBO partial charges and natural bond order analysis for the core of **1b**.

similar for all derivatives of **1** in which the highest occupied molecular orbital (HOMO) reflects the N p-orbital interacting with P–C σ^* with a significant additional antibonding component through contributions from the B–C σ framework. On the other hand, the HOMO – 1 shows a stronger BN π bond with π -donation of the N lone pair to B. Notably the back donation to P is maximised when the BNP angle is linear (sphybrid N), thereby affording maximum spatial overlap as the alternative sp²-hybridised N exhibits a non-bonding lone pair.

An NBO analysis of **1b** (Fig. 9) reflects the strongly polar nature of the bonding across the BNP fragment with both B and P bearing substantial positive charges and the N significantly negative. The presence of formal B—N double bond character, coupled with the highly positively charged P centre supports resonance form **B** (Fig. 8) as the major contributor to the structure with a formal B—N double bond and ylidic P—N bonding. Replacement of the mildly electron-releasing cyclohexyl group by C_6F_5 leads to marked changes in the bonding character and the net bonding appears extremely sensitive to the substituents at P. The HOMO of **2a** (Fig. 10) appears similar in nature to that of **1b** (Fig. 9). However the subsequent highest occupied orbitals (HOMO – 1, HOMO – 2, and HOMO – 3) are all based of predominantly $C_6F_5 \pi$ -character.

The NBO analysis shows that **2a** (Fig. 10) retains the highly polar nature of the BNP framework and the B=N multiple bond character but leads to an apparent weakening of the P–N bond such that the structure of **2a** is better considered as donor–acceptor adduct between discrete (C_6F_5)₂BN and P^tBu₃ units with P–N bonding only apparent through a substantial



Fig. 10 HOMO for 2a; NBO partial charges (centre) and natural bond order (right) analyses for 2a and 2b.

second order perturbation analysis associated with donation of electron density from the N lone pair of p-character to the vacant orbital on the P²⁺ centre (85% p-character) (259 kcal mol⁻¹) and from the B=N π -system to the P²⁺ centre (315 kcal mol⁻¹). Conversely the NBO analysis of **2b** reflects substantial P=N double bond character and a B-N single bond resulting in a strongly Lewis acidic B-centre. In **2b** there are again substantial second order perturbations arising from donation of electron density from the P-N π -bond (implementing essentially 50% p character and 50% d character on P and pure p-character from N) to the vacant B p-orbital (86 kcal mol⁻¹). In both cases, the presence of significant second order perturbations suggest a two centre two electron bonding model is an inadequate description of the structure.

Conclusions

The boron azides Cy_2BN_3 and $(C_6F_5)_2BN_3$ undergo Staudinger reactions with primary phosphines to give the products $R_2BNPR'_3$ 1 and 2 in high to excellent yields. The structural parameters determined from both X-ray diffraction and gas phase DFT calculations reveal substantial B-N multiple bond character and zwitterionic character to the P-N bond, with evidence that the bonding is inadequately described through a simple two centre, two electron resonance form. In the case of phosphines bearing an acetylene functionality an initial Staudinger reaction takes place to generate the boranyl-phosphanimine in preference to the cycloaddition of the azide with the alkyne. However, in the presence of additional Me₃SiN₃, a subsequent cycloaddition reaction occurs to afford a bicyclic product 3. These preliminary studies demonstrate that "click chemistry" of boron azides with ethynylphosphines occurs without the need for a catalyst affording P/B substituted 1,2,3-triazoles and is the target of current efforts.

Experimental section

General experimental

Unless otherwise stated, all reactions and manipulations were carried out under an atmosphere of dry, O₂-free, nitrogen using standard double-manifold techniques with a rotary oil pump. A nitrogen-filled glove box (MBRAUN) was used to

manipulate solids. All solvents (including deuterated solvents) were dried and stored over molecular sieves under a nitrogen atmosphere before use. Cy₂BCl (1 M in hexanes), TMSN₃, PhC=CH, p-tol-C=CH, Ph2PC=CPPh2, Ph2PCl, (EtO)2P(O)- $C \equiv CP(O)(OEt)_2$ and all phosphines were commercially available and used as received. $(C_6F_5)_2BCl_2^{28}$ $(C_6F_5)_2BN_3$ Ph₂PC=CPh,²⁹ Ph₂PC=Cp-tol³⁰ and Cy₂BN₃¹⁰ were prepared according to literature methods. ¹H, ¹³C, ¹¹B and ³¹P NMR spectra were recorded on a Bruker Avance III or a Bruker Avance 500 spectrometer. A Perkin-Elmer analyser was used for carbon, hydrogen and nitrogen elemental analyses. High resolution mass spectrometry was performed in house employing DART or electrospray ionisation techniques in positive ion mode on an AB/Sciex QStarXL mass spectrometer (ESI) or a JEOL AccuTOF model JMS-T1000LC mass spectrometer (DART). Caution: Covalent azides are potentially explosive and reactions were performed on small scale behind blast shields.

Synthesis of $(Cy)_2BNPR_3$ (R = Et 1a, ^tBu 1b, Cy 1c, Ph 1d). These compounds were prepared in a similar manner and thus only one preparation is detailed. Cy₂BN₃ (0.5 mmol) was prepared in situ in toluene (2 mL) and PEt₃ (59 mg, 0.5 mmol) was added. The reaction was left standing for 18 h and the solvent removed to give pure Cy2BNPEt3 as an offwhite oil which solidified in the freezer at -35 °C (150 mg, 99%, 0.49 mmol). 1a: ¹H NMR (400 MHz, C₆D₅Br, 298 K): 1.78 (m, br., Cy), 1.68 (s, br., Cy), 1.32 (s, br., Cy), 1.27-0.98 (m, br., 6H, $-CH_2CH_3$), 0.90 (dt, ${}^{3}J_{PH} = 17$ Hz, ${}^{3}J_{HH} = 8$ Hz, $-CH_2CH_3$); ¹¹B NMR (128 MHz, C₆D₅Br, 298 K): 50.3 (s, br.); ³¹P NMR (163 MHz, C_6D_5Br , 298 K): 14.7 (s); ${}^{31}P_1^{1}H_1^{1}$ NMR (163 MHz, C_6D_5Br , 298 K): 14.7 (s, br.); ${}^{13}C{}^{1}H{}$ NMR (100 MHz, C_6D_5Br , 298 K) partial: 30.1 (s, Cy), 28.6 (s, Cy), 27.8 (s, Cy), 21.0 (d, ${}^{1}J_{PC}$ = 66.3 Hz, $-CH_{2}CH_{3}$), 6.3 (d, ${}^{2}J_{PC}$ = 4.5 Hz, $-CH_{2}CH_{3}$), signals for boron-bound carbon atoms were not observed. Elem. Anal. calcd (%) for C₁₈H₃₇NPB: C 69.90; H 12.06; N 4.53; Found: C 69.76, H 11.91; N 4.05. DART MS, m/z: 134.1 (calcd for $[Et_3P=NH_2]^+$: 134.1), no molecular ion peak was observed.

1b: off-white solid (110 mg, 92%, 0.23 mmol). ¹H (400 MHz, d₈-toluene, 298 K): 1.84–1.35 (m, 22H, Cy), 1.17 (d, ${}^{3}J_{\rm HP} = 13$ Hz, $-C(CH_{3})_{3}$); ³¹P NMR (163 MHz, d₈-toluene, 298 K): 33.3 (m); ³¹P{¹H} NMR (163 MHz, d₈-toluene, 298 K): 33.4 (s); ¹¹B NMR (128 MHz, d₈-toluene, 298 K): 49.0 (s, br.); ¹³C{¹H} NMR (100 MHz, d₈-toluene, 298 K) partial: 40.0 (d, ${}^{1}J_{\rm PC} = 53$ Hz), 30.1 (s), 29.8 (s), 28.8 (s), 28.1 (s), signals for boron-bound carbon atoms were not observed. Elem. Anal. calcd (%) for C₂₄H₂₇NPBF₁₀: C 51.36; H 4.85; N 2.50; Found: C 50.56, H 4.84; N 2.67. DART MS, *m/z*: 562.2 (calcd for [M + H]⁺: 562.2), 218.2 (calcd for [^tBu₃P=NH₂]⁺: 218.2).

1c: off-white solid (228 mg, 97%, 0.48 mmol). ¹H NMR (400 MHz, d₆-benzene, 298 K): 1.71 (m, br., Cy), 1.63 (m, br., Cy), 1.53–1.46 (m, br., Cy), 1.39–1.25 (m, br., Cy), 1.15 (m, br., Cy), 0.86–0.95 (m, br., Cy); ³¹P NMR (163 MHz, d₆-benzene, 298 K): 17.6 (s, br.); ³¹P{¹H} NMR (163 MHz, d₆-benzene, 298 K): 17.7 (s); ¹¹B NMR (128 MHz, d₆-benzene, 298 K): 48.5 (s, br.); ¹³C{¹H} NMR (100 MHz, d₆-benzene, 298 K): 61.5 (d, ¹J_{PC} = 62 Hz), 30.5 (s), 28.9 (s), 28.2 (d, ²J_{PC} = 37 Hz), 28.1 (s),

27.4 (d, ${}^{3}J_{PC}$ = 12 Hz), 27.2 (d, ${}^{4}J_{PC}$ = 3 Hz), 26.6 (s). Elem. Anal. calcd (%) for C₃₀H₅₅NPB: C 76.41; H 11.56; N 2.97; Found: C 76.48, H 12.00, N 1.67. DART MS, *m*/*z*: 297.3 (calcd for [Cy₃P–NH₃]⁺: 297.3), 296.3 (calcd for [Cy₃P–NH₂]⁺: 296.3), no peak assignable to the molecular ion was observed.

1d: off-white solid (207 mg, 91%, 0.46 mmol). ¹H NMR (400 MHz, d₆-benzene, 298 K): 7.75 (m, 6H, *o*-Ph), 7.09 (m, br., 9H, *m*-Ph and *p*-Ph), 1.75–1.89 (m, br., Cy), 1.56–1.65 (m, br., Cy), 1.39–1.25 (m, br., Cy), 1.14 (t, br., Cy); ³¹P NMR (163 MHz, d₆-benzene, 298 K): 0.8 (septet, ³J_{PH} = 11 Hz); ³¹P{¹H} NMR (163 MHz, d₆-benzene, 298 K): 0.8 (s); ¹¹B NMR (128 MHz, d₆-benzene, 298 K): 52.0 (s, br.); ¹³C{¹H} NMR (100 MHz, d₆-benzene, 298 K): 134.4 (d, ¹J_{PC} = 100 Hz, *i*-Ph), 132.5 (d, ²J_{PC} = 10 Hz, *o*-Ph), 131.1 (d, br., ⁴J_{PC} = 2 Hz, *p*-Ph), 128.3 (d, ³J_{PC} = 12 Hz, *m*-Ph), 30.3 (s, Cy), 28.6 (s, Cy), 27.8 (s, Cy), signals for boron-bound carbon atoms were not observed. Elem. Anal. calcd (%) for C₃₀H₃₇NPB: C 79.47; H 8.23; N 3.09; Found: C 79.59, H 8.58, N 2.80. DART MS, *m*/*z*: 279.1 (calcd for [Ph₃P—NH₃]⁺: 279.1), 278.1 (calcd for [Ph₃P—NH₂]⁺: 278.1), no peak corresponding to the molecular ion was observed.

Synthesis of $(C_6F_5)_2BNPR_3$ (R = ^tBu₃ 2a, Ph 2b) and $(C_6F_5)_2BNP(Ph)_2CCPh$ (2c) and $(C_6F_5)_2BNP(Ph)_2CCPPh_2$ (2d). These compounds were prepared in a similar manner and thus only one preparation is detailed. **2a**: $(C_6F_5)_2BN_3^6$ was dissolved in toluene (2 mL) and P^tBu₃ (51 mg, 0.25 mmol) was added. The reaction was left standing for 18 h and the solvent removed to give crude $(C_6F_5)_2BNP^tBu_3$ which was washed with hexane $(2 \times 3 \text{ mL})$ to give pure $(C_6F_5)_2BNP^tBu_3$ as an off-white solid (110 mg, 92%, 0.23 mmol) which could be recrystallised from a saturated solution of toluene at -35 °C. ¹H NMR (400 MHz, CD_2Cl_2 , 298 K): 1.27 (s, 9H, ${}^{3}J_{PH} = 14$ Hz, $-C(CH_3)_3$); ¹¹B NMR (128 MHz, CD₂Cl₂, 298 K): 31.6 (s, br.); ³¹P NMR (163 MHz, CD_2Cl_2 , 298 K): 43.9 (m); ³¹P{¹H} NMR (163 MHz, C₆D₅Br, 298 K): 43.6 (s); ¹⁹F NMR (377 MHz, CD₂Cl₂, 298 K): -134.2 (m, 2F, o-F), -158.2 (t, 1F, ${}^{3}J_{FF} = 20.0$ Hz p-F), -163.7(m, 2F, *m*-F); ¹³C NMR (100 MHz, CD₂Cl₂, 298 K): 146.0 (m, C_6F_5), 140.6 (m, C_6F_5), 137.4 (m, C_6F_5), 40.4 (m, $C(CH_3)_3$), 29.4 $(m, C(CH_3)_3)$, signals for boron-bound carbon atoms were not observed. Elem. Anal. calcd (%) for C24H27NPBF10: C 51.36; H 4.85; N 2.50; Found: C 50.56, H 4.84; N 2.67. DART MS, m/z: 562.2 (calcd for $[M + H]^+$: 562.2), 218.2 (calcd for $[{}^{t}Bu_{3}P = NH_{2}]^{+}$: 218.2), 202.2 (calcd for $[{}^{t}Bu_{3}PH]^{+}$: 202.2).

2b: colourless crystals of **2b** (69 mg, 44%, 0.11 mmol). ¹H NMR (400 MHz, CD₂Cl₂, 298 K): 7.58 (m, 2H, *o*-H PPh₃), 7.46 (m, 1H, *p*-H PPh₃), 7.36 (m, 2H, *m*-H PPh₃); ¹¹B NMR (128 MHz, CD₂Cl₂, 298 K): 37.0 (s, br.); ³¹P NMR (163 MHz, CD₂Cl₂, 298 K): 16.0 (s, br.); ³¹P{¹H} NMR (163 MHz, CD₂Cl₂, 298 K): 16.0 (s); ¹⁹F NMR (377 MHz, CD₂Cl₂, 298 K): -134.0 (dd, 2F, $J_{FF} = 24$, 10 Hz, *o*-F), -156.9 (t, 1F, $J_{FF} = 20$ Hz, *p*-F), -164.2 (m, 2F, *m*-F); ¹³C{¹H</sup> NMR (100 MHz, CD₂Cl₂, 298 K): 146.2 (m, C₆F₅), 140.5 (m, C₆F₅), 136.7 (m, C₆F₅), 132.4 (d, $J_{PC} = 10.6$ Hz, Ph), 132.3 (d, $J_{PC} = 3$ Hz, Ph), 128.5 (d, $J_{PC} = 13$ Hz, Ph), signals for boron-bound carbon atoms were not observed. Elem. Anal. calcd (%) for C₃₀H₁₅NPBF₁₀: C 58.00; H 2.43; N 2.55; Found: C 57.27, H 2.66; N 2.23. DART MS, *m*/*z*: 279.1 (calcd for [Ph₃P=NH₃]⁺: 279.1), 278.1 (calcd for [Ph₃P=NH₂]⁺:

278.1), 263.1 (calcd for $[Ph_3PH]^+$: 263.1), no peak corresponding to the molecular ion was observed.

2c: (127 mg, 0.2 mmol, 20%). ¹H NMR (400 MHz, d₆benzene, 298 K): 8.01-7.95 (m, 4H, o-C PPh₂), 7.03-7.00 (m, 7H, *m*-C and *p*-C PPh₂ and *o*-Ph –C=CPh), 6.88 (t, 1H, ${}^{3}J_{HH} = 8$ Hz, *p*-C −C≡CPh), 6.78 (t, 2H, ³*J*_{HH} = 8 Hz, *m*-C −C≡CPh); ³¹P NMR (163 MHz, d₆-benzene, 298 K): -5.3 (m); ¹¹B NMR (128 MHz, d₆-benzene, 298 K): 36.1 (s, br.); ¹⁹F NMR (377 MHz, d₆-benzene, 298 K): -133.9 (dd, 2F, $J_{FF} = 24$, 9 Hz, o-F), -155.4 (t, 1F, J_{FF} = 30 Hz, p-F), -164.0 (m, 2F, m-F); $^{13}C{^{1}H}$ NMR (100 MHz, d₆-benzene, 298 K): 147.4 (m, C₆F₅), 137.4 (m, C_6F_5), 132.6 (d, J_{PC} = 3 Hz, Ph), 132.1 (d, J_{PC} = 2 Hz, Ph), 131.3 (d, J_{PC} = 12 Hz, Ph), 131.1 (s, Ph), 130.9 (d, ${}^{1}J_{PC}$ = 131 Hz, i-C PPh₂), 129 (s, Ph), 128.9 (s, Ph), 128.6 (s, Ph), 119.0 (d, ${}^{2}J_{PC} = 4$ Hz, $-C \equiv CPh$), 108.2 (d, ${}^{1}J_{PC} = 23$ Hz, $-C \equiv CPh$), signals for boron-bound carbon atoms were not observed. Elem. Anal. calcd (%) for C₃₀H₁₅NPBF₁₀: C 59.57; H 2.34; N 2.17; Found: C 59.13, H 2.59; N 2.37. DART MS, *m*/*z*: 646.1 (calcd for [M + H]⁺: 646.1), 303.1 (calcd for [PhCC(Ph)₂P-NH₃]⁺: 303.1), 302.1 (calcd for [PhCC(Ph)₂P=NH₂]⁺: 302.1).

2d: (262 mg, 0.35 mmol, 35%). ¹H NMR (400 MHz, d₆benzene, 298 K): 7.87 (m, 4H, o-H P¹Ph₂), 7.33 (m, 4H, m-H $P^{1}Ph_{2}$), 6.96–6.91 (m, 12H, *p*-H $P^{1}Ph_{2}$ and $P^{2}Ph_{2}$); ${}^{31}P{}^{1}H$ NMR (163 MHz, d₆-benzene, 298 K): -7.1 (d, ${}^{3}J_{PP} = 6$ Hz, $-P^{2}(Ph)_{2}$ -); -33.8 (d, br., -P¹Ph₂); ¹¹B NMR (128 MHz, d₆-benzene, 298 K): 38.2 (s, br.); ¹⁹F NMR (377 MHz, d₆-benzene, 298 K): -133.6 (dd, 2F, $J_{\rm FF}$ = 24, 10 Hz, o-C₆F₅), -154.2 (t, 1F, ${}^{3}J_{\rm FF}$ = 21 Hz, $p-C_6F_5$, -162.7 (m, br., 2F, $m-C_6F_5$); ¹³C{¹H} NMR (100 MHz, d₆-benzene, 298 K): 147.1 (m, ${}^{2}J_{CF}$ = 244 Hz, C₆F₅), 141.1 (m, ${}^{2}J_{CF}$ = 256 Hz, C₆F₅), 137.1 (m, ${}^{2}J_{CF}$ = 251 Hz, C₆F₅), 132.8 (dd, $J_{\rm PC}$ = 6, 2 Hz, Ph), 132.6 (d, $J_{\rm PC}$ = 22 Hz, Ph), 132.4 (d, $J_{\rm PC}$ = 3 Hz, Ph), 131.0 (d, J_{PC} = 12 Hz, Ph), 130.3 (d, J_{PC} = 130 Hz, Ph), 129.7 (s, Ph), 128.9 (d, J_{PC} = 8 Hz, Ph), 128.7 (d, J_{PC} = 14 Hz, Ph), 110.2 (dd, ${}^{1}\!J_{PC}$ = 32 Hz, ${}^{2}\!J_{PC}$ = 14 Hz, $-C \equiv CPPh_{2}$), 98.3 (dd, ${}^{1}J_{PC}$ = 98 Hz, ${}^{2}J_{PC}$ = 5 Hz, $-C \equiv CPPh_{2}$), signals for boron-bound carbon atoms were not observed. Elem. Anal. calcd (%) for C₃₈H₂₀NPBF₁₀: C 60.59; H 2.68; N 1.86; Found: C 60.24, H 2.89; N 1.97. DART MS, m/z: 754.1 (calcd for $[M + H]^+$: 754.1), 411.1 (calcd for $[(Ph)_2(CCPPh_2)P-NH_3]^+$: 411.1), 410.1 (calcd for [(Ph)₂(CCPPh₂)P=NH₂]⁺: 412.1).

Synthesis of Ph₂P(C=Cp-tol)N₃BN(C₆F₅)₂ 3. Excess trimethylsilylazide (300 mg, 2.6 mmol) in toluene (2 mL) was added to $(C_6F_5)_2BCl$ (380 mg, 1 mmol) in toluene (25 mL) and the resulting mixture stirred for 2 h. Ph₂PCCp-tol (300 mg, 1 mmol) in toluene (10 mL) was added and the solution was stirred at 90 °C for 3 days. The majority of the solvent was removed until ca. 2 mL remained and CD₂Cl₂ (2 mL) was added to redissolve any precipitate. The solvent was left to evaporate over 2 days affording colourless crystals of 3 (30 mg, 4%, 0.04 mmol) which were stable at room temperature under an atmosphere of nitrogen for several weeks. DART MS, m/z: 703.1 (calcd for $[M + H]^+$: 703.1). ¹H NMR (400 MHz, CD₂Cl₂, 298 K): 7.79 (tm, ${}^{3}J_{HH}$ = 7.5 Hz, 2H, p-H PPh₂), 7.73–7.67 (m, 4H, o-H PPh₂), 7.62–7.56 (m, 4H, m-H PPh₂), 7.39 (d, ${}^{3}J_{HH} =$ 8.1 Hz, 2H, o-H p-tol), 7.11 (d, ³J_{HH} = 7.9 Hz, 2H, m-H p-tol), 2.33 (s, 3H, CH_3), the N-H proton was not observed; ¹¹B NMR

(128 MHz, CD₂Cl₂, 298 K): -1.0 (s); ${}^{31}P{}^{1}H$ NMR (163 MHz, CD₂Cl₂, 298 K): 32.0 (s); ${}^{19}F$ NMR (377 MHz, CD₂Cl₂, 298 K): -133.5 (dd, 2F, $J_{FF} = 24$, 9 Hz, *o*-F), -156.6 (t, 1F, $J_{FF} = 21$ Hz, *p*-F), -162.8 (m, 2F, *m*-F).

Synthesis of [(EtO)₂P(O)C=CN₃B(C₆F₅)₂P(O)(OEt)]₂ 4. (Et₂O)- $P(O)C \equiv CP(O)(OEt)_2$ (298 mg, 1 mmol) was added to $(C_6F_5)_2BN_3$ (1 mmol) in toluene (5 mL). The resulting solution was stirred at room temperature for 2 days. The solvent was removed in vacuo to give crude solid 3 (132 mg, 29%, 0.14 mmol) which could be recrystallised from a saturated toluene solution (45 mg, 9%, 0.05 mmol). Crystalline 3 proved to be stable at room temperature under an atmosphere of nitrogen for several months. ¹H NMR (400 MHz, d₈-toluene, 298 K): 3.86 (m, 4H, -P(O)(OCH₂CH₃)₂), 3.76 (m, 2H, >P(O)- CH_2CH_3), 0.94 (t, 6H, ${}^{3}J_{HH}$ = 7 Hz, $-P(O)(OCH_2CH_3)_2$), 0.72 (t, 3H, ${}^{3}J_{HH} = 7$ Hz, $>P(O)CH_{2}CH_{3}$; ${}^{31}P$ NMR (163 MHz, d_6 -benzene, 298 K): 7.9 (t, ${}^{3}J_{PP} = 6$ Hz), -10.5 (m); ${}^{11}B$ NMR (128 MHz, d₆-benzene, 298 K): 2.6 (s, br.), -0.5 (s, br.); ¹⁹F NMR (377 MHz, d_6 -benzene, 298 K): -135.4 (dd, 2F, J = 24, 9 Hz, o-F), -135.7 (dd, br., 2F, ${}^{3}J_{FF} = 23$ Hz, ${}^{4}J_{FF} = 8$ Hz, o-F), -154.1 (t, 1F, ${}^{3}J_{FF} = 21$ Hz, *p*-F), -157.0 (t, 1F, ${}^{3}J_{FF} = 21$ Hz, *p*-F), -162.6 (m, 2F, m-F), -164.3 (m, 2F, m-F).

X-ray crystallography

Crystals were coated in paratone oil and mounted in a cryoloop. Data were collected on Nonius Kappa CCD or Bruker APEX2 X-ray diffractometers using graphite monochromated Mo-Kα radiation (0.71073 Å). The temperature was maintained at 150(2) K using an Oxford cryostream cooler for both initial indexing and full data collection. Data were collected using Bruker APEX-2 software and processed using SAINT and an absorption correction applied using multi-scan³¹ within the APEX-2 program.³² The structures of **1b**, **1c**, **1d**, **2a**, **2b** and **2c** were solved by direct methods within the SHELXTL package³³ whereas the structure of 3 was solved using Superflip³⁴ within Crystals.³⁵ All structures were refined against F^2 using the SHELXTL package. For 1c several of the cyclohexyl rings were found to be disordered; the disordered cyclohexyl groups were refined over two positions with common Uiso for chemically equivalent C atoms and restrained cyclohexyl ring geometries (SAME) whereas ordered cyclohexyl groups were refined freely with anisotropic C atoms. H atoms were added at calculated positions and refined with a riding model for all structures. Unit cell parameters and refinement statistics are presented in the ESI.†

Computational studies

Single point energy calculations on derivatives of **1** and **2** were undertaken using the crystallographically determined geometry using the B3LYP functional³⁶ and 6-31G*+ Pople basis set within Jaguar³⁷ and the Natural Bond Orbital analysis undertaken using the NBO 5.0 code.³⁸

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