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PAPER

# The Phosphinoboration of Carbodiimides, Isocyanates, Isothiocyanates and $CO_2$

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The transition metal-free addition of phosphinoboronate ester $Ph_2PBpin$ (pin = 1,2-$O_2C_2Me_4$) to heterocumulenes including carbodiimides, isocyanates, isothiocyanates and carbon dioxide has been investigated. The corresponding 1,2-addition products were readily prepared at room temperature without the need of a catalyst or added base. Addition of methanol to the compounds derived from addition of $Ph_2PBpin$ to carbodiimides, isocyanates, and isothiocyanates resulted in traditional hydrophosphination products. The methodology developed in this study provides a simple and elegant route for the generation of a wide range of functionalized phosphines. The phosphinoboronate ester $Ph_2PBpin$ also selectively and reversibly adds to $CO_2$ at room temperature in a 1,2-manner.

## Introduction

There has been recent considerable interest in the chemistry of compounds containing boron-element bonds (B-E, where E = H,[1] B,[2] Sn,[3] Si,[4] S,[5] Se,[6] O,[7] etc). For instance, the hydroboration of alkenes and alkynes (E = H) is a remarkably powerful and useful reaction in organic synthesis, leading to the functionalization of the site of unsaturation.[1] Although analogous diboration (E = B)[2] and borylation chemistry (replacing a $sp^2$ C-H bond with a $BR_2$ group)[8] are finding increased use in organic synthesis, these reactions typically functionalize the two sites equivalently or sacrifice one of the boryl ($BR_2$) groups. Reactions of unsaturated organics with heavier main group elements (E = Se, Sn, Si, etc) usually require a catalyst and/or strong base and result in novel organodimetalloid compounds.[3-6] Of these latter reactions the silaboration of C-C multiple bonds is particularly promising.[4] The resulting silyl and boryl groups can be independently transformed into different functional groups, however issues of chemo- and regioselectivity can complicate such addition reactions (Fig. 1).

Given the interest in the reactivity of main group-boron compounds it is surprising that almost nothing is known about addition chemistry of compounds containing single B-E bonds where E = N[9] or P[10]. For instance, an elegant and seminal study published by Chong and Blum disclosed a gold-catalysed aminoboration reaction of alkynes that selectively generates 3-borylated indoles.[9d] While there has been significant literature describing the generation of phosphinoboron compounds,[11] the corresponding addition of these species to unsaturated organic substrates remains almost unexplored. Lerner and co-workers recently demonstrated that a phosphinoborane derived from 9-borafulvalene reacts with benzophenone to give the corresponding 1,2-addition product exclusively.[10a]

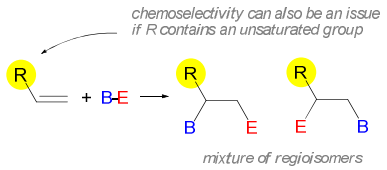


**Fig. 1**. The addition of B-E bonds to organic substrates can be challenging as chemo- and regioselectivity issues can complicate product distributions.

Gentle and efficient ways to reduce aldimines and ketimines are of considerable interest in the synthesis of a wide variety of amines.[12] Although hydrosilanes are well-known to reduce C=N bonds, usually in the presence of a catalyst,[13] considerably less is known about the corresponding hydroboration,[14] diboration[15] and silaboration (or silylboration)[16] of imines. Carbodiimides (RN=C=NR') are an interesting subclass of imines containing a central *sp*-hybridised carbon atom that have attracted recent attention as synthons in a number of transformations.[17] For instance, the catalysed hydro-phosphination of carbodiimides is a synthetic methodology for the preparation of phosphaguanidine ligands, where P-H additions generally proceed to give products containing a new P-C bond.[18] Known routes to phosphaguanidines typically involve harsh reaction conditions or the use of a catalyst to facilitate the hydrophosphination of carbodiimides.

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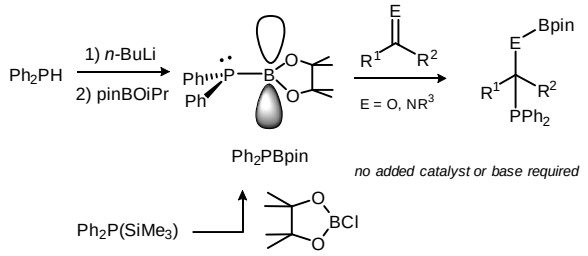
Unfortunately, the latter metal-catalysed routes are often complicated by coordination of the starting phosphine, or the resultant phosphaguanide product, to the metal centre and ultimately poisons the active catalyst. An excellent review by Bange and Waterman eloquently outlines the current challenges associated with catalysed hydrophosphination reactions.[18r]

As part of our programme designed at expanding B-E addition reactions, we have recently prepared phosphinoboronate esters containing single B-P bonds that add selectively to aldehydes, ketones and imines without the aid of a catalyst or base.[10b,c] These reactions proceed smoothly at room temperature leading to addition of the electron-deficient boryl group to the electron-rich heteroatom with concurrent formation of a new P-C bond (Scheme 1). Herein, we expand the scope of B-P additions to reactions with heterocumulenes. Specifically $Ph_2PBpin$ (pin = 1,2-$O_2C_2Me_4$) is shown to add to the species E=C=E' (E, E' = O, NR; carbodiimides, isocyanates, isothiocyanates and carbon dioxide), providing an unprecedented route to novel unsaturated products derived from 1,2 P/B additions.

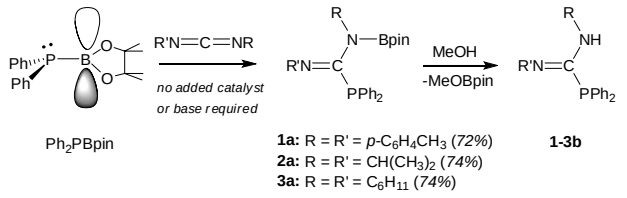



**Scheme 1** The Phosphinoboration of Aldehydes, Ketones, Aldimines and Ketimines.

## Results and discussion

### Carbodiimides

The addition of boron reagents to carbodiimides has received considerable recent attention.[19] Of singular interest is an elegant study by Hill and co-workers who demonstrated that β-diketiminato magnesium alkyl complexes could be used to catalyse the addition of HBpin to carbodiimides to give *N*-boryl formamidine products in high yields.[19k]




**Scheme 2** The Phopshinoboration of Carbodiimides (Isolated Yields in Brackets).

Reactions of $Ph_2PBpin$ with three commercially-available carbodiimides at room temperature (Scheme 2) were probed. For example, addition of $Ph_2PBpin$ to *N*,*N*'-di-*p*-tolylcarbodiimide gave the corresponding *N*-boryl phosphaguanidine derivative **1a** as the only new product in solution (as ascertained by multinuclear NMR spectroscopy). Complete conversion of the starting materials was achieved and the product could be isolated in 82% yield. A singlet in the $^{11}B\{^1H\}$ NMR spectrum at 21.8 ppm is indicative of three-coordinate boron bound to a nitrogen atom.[19l] A singlet is also observed in the $^{31}P\{^1H\}$ NMR spectrum at 2.2 ppm. Interestingly, the central imine carbon atom is found at 164.2 ppm in the $^{13}C\{^1H\}$ NMR spectrum but no coupling to the P atom is observed. Coupling constants in these species are known to vary with bond angles and the nature of the substituents.[18] For instance, the central carbon atom is observed at 154.8 ppm in the parent phosphaguadine $Ph_2PC(NHp\text{-tol})(Np\text{-tol})$ with a coupling constant of $^1J_{PC}$ = 38.7 Hz.[18d] However, to confirm the phosphinoboration product contained a newly-formed P-C bond, a single crystal X-ray diffraction study was carried out on **1a** (Fig. 2). The structural data confirms the sterically-less hindered $Z_{syn}$ conformation. Of interest are the angles around the saturated amine nitrogen (N1) which are roughly trigonal and add up to 359.4°. This observation suggests there is considerable overlap with the nitrogen lone pair and the empty orbital on boron. Similar bond angles and distances have been reported for the analogous hydroboration products.[19l] All attempts to add a second equivalent of $Ph_2PBpin$ to **1a** proved unsuccessful.

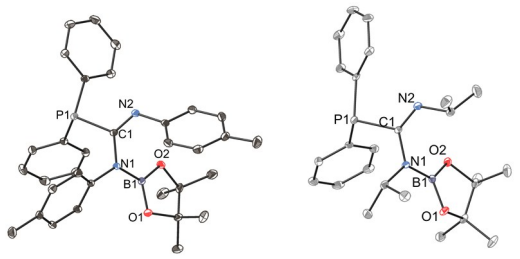



**Fig. 2**. The molecular structures of **1a** and **2a** drawn at the 50% probability level and hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): [**1a**] C(1)-N(2) 1.271(2) C(1)-N(1) 1.424(2), C(1)-P(1) 1.8592(18), N(1)-B(1) 1.430(2); C(1)-N(1)-B(1) 119.92(15), C(1)-N(1)-C(20) 116.10(14), B(1)-N(1)-C(20) 123.38(14). [**2a**] C(1)-N(2) 1.261(2), C(1)-N(1) 1.4306(19), C(1)-P(1) 1.8649(16), N(1)-B(1) 1.416(2); B(1)-N(1)-C(1) 119.97(13), B(1)-N(1)-C(20) 123.11(13), C(1)-N(1)-C(20) 116.92(12).

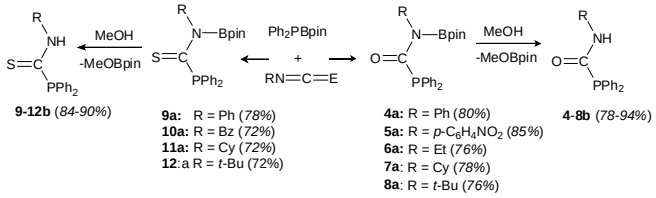
Reactions of $Ph_2PBpin$ with the aliphatic carbodiimides *N*,*N*'-di-*i*-propylcarbodiimide and *N*,*N*'-di-cyclohexylcarbodiimide gave products **2a** and **3a**, respectively, as a 90:10 mixture of isomers in solution. Isomeric mixtures of $Z_{syn}$ and $E_{syn}$ conformers are typically observed in related phosphaguanidines.[19b,k] A single crystal X-ray diffraction study was also carried out on **2a** (Fig. 2). Crystallographic data is provided in Table 1. The angles around the saturated amine nitrogen once again suggest a trigonal environment with a sum being 360.0°. Not unexpectedly, addition of $Ph_2PBpin$ to the unsymmetrical $EtN{=}C{=}N(CH_2)_3NMe_2$ gave a mixture of products and isolation proved unsuccessful. More remarkable is the observation that addition of a few drops of methanol to **1a**-**3a** resulted in the clean conversion to the corresponding parent phosphaguanides **1b**-**3b**.[19k] The methodology developed herein therefore provides a gentle

route to a wide-array of phosphaguanines without the need of employing a catalyst. Unfortunately, addition of methanol to the mixture obtained from $Ph_2PBpin$ and the unsymmetrical carbodiimide $EtN{=}C{=}N(CH_2)_3NMe_2$ gave several products.

*[please insert Table 1]*

**Isocyanates and Isothiocyanates**

The reduction of isocyanates is of interest for the synthesis of functionalised formamides.[20] Grimme, Warren and co-workers[20d] reported the hydroboration of bulky aryl isocyanates with Pier's borane ($HB(C_6F_5)_2$). Using frustrated Lewis pairs, they prepared formamide derivatives where the B-H bond added selectively to the C=N double bond. Herein, reaction of $Ph_2PBpin$ with either alkyl and aryl isocyanates gave selectively the corresponding 1,2-addition products **4a**-**8a** (Scheme 3). Spectroscopic data are consistent with products arising from addition to the C=N double bond as $^{13}C\{^1H\}$ NMR data shows a peak around 180 ppm with coupling to the phosphorus atom ($J_{CP}$ = 13-35 Hz). Likewise, the $^{11}B\{^1H\}$ NMR spectra show single broad peaks at 24-25 ppm suggesting that the Bpin groups are bound to the nitrogen atom and not the oxygen.




**Scheme 3** The Phopshinoboration of Isocyanates and Isothiocyanates (Isolated Yields in Brackets).

To confirm the selectivity of these additions X-ray diffraction studies on **6a** and **8a** were carried out (Fig. 3). The boryl (Bpin) group is bound to the nitrogen as a new P—C bond is formed where bond distances and angles are similar to previously reported structures.[20] The corresponding phosphinoformamide derivatives **4b**-**8b** are readily prepared in high yields by the simple addition of methanol. Confirmation of these products was obtained from a solid-state X-ray diffraction study of the cyclohexyl derivative **7b** (shown in Fig. 4).

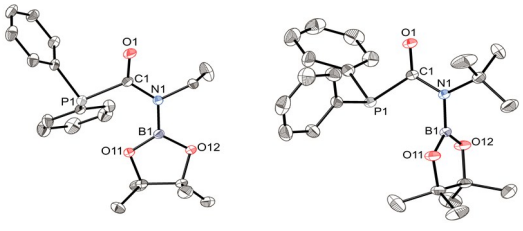



**Fig. 3**. The molecular structures of **6a** and **8a** drawn at the 50% probability level and hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): [**6a**] C(1)-O(1) 1.2156(14), C(1)-N(1) 1.3820(13), C(1)-P(1) 1.8927(12), N(1)-B(1) 1.4424(14), N(1)-C(20) 1.4822(13); C(1)-N(1)-B(1) 126.03(9), C(1)-N(1)-C(20) 116.25(9), B(1)-N(1)-C(20) 117.71(9). [**8a**] C(1)-O(1) 1.2235(13), C(1)-N(1) 1.3570(14), C(1)-P(1) 1.8894(11), N(1)-B(1) 1.4830(14), N(1)-C(20) 1.5030(15); C(1)-N(1)-B(1) 120.55(9), C(1)-N(1)-C(20) 120.30(9), B(1)-N(1)-C(20) 119.15(9).

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Similar selectivities were also observed with isothiocyanates as reactions proceeded smoothly at room temperature to generate the corresponding 1,2-addition products **9a**-**12a** (Scheme 3). The molecular structure of the *tert*-butyl derivative **12a** (Fig. 3), confirms addition occurred at the C=N double bond. Addition of dry methanol to boron-containing derivatives **9a**-**12a** afforded phosphinothioamides **9b**-**12b** along with concomitant formation of MeOBpin. Although the use of both **4b**-**8b**[21] and **9b**-**12b**[22] have been investigated as ligands in coordination chemistry, their use has been limited so far by the inherent difficulties in preparing these species. As such, the present methodology offers potential access to a wide array of such ligands.

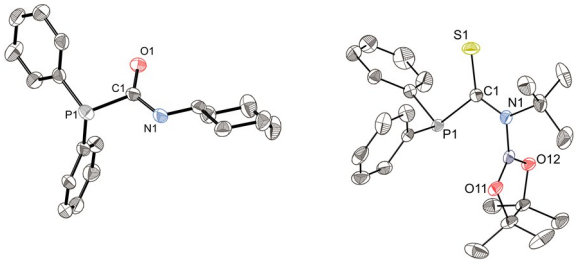


**Fig. 4**. The molecular structures of **7b** and one of the four unique molecules of **12a** in the asymmetric unit are drawn at the 50% probability level and hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): [**7b**] C(1)-O(1) 1.221(5), C(1)-N(1) 1.332(5), C(1)-P(1) 1.892(4), N(1)-C(14) 1.463(5); O(1)-C(1)-N(1) 123.0(4), O(1)-C(1)-P(1) 123.0(3), N(1)-C(1)-P(1) 114.0(3), C(1)-N(1)-C(14) 122.2(4). [**12a**] C(11)-N(1) 1.342(2), C(11)-S(1) 1.6567(19), C(11)-P(1) 1.8779(19), N(1)-B(1) 1.493(3), N(1)-C(120) 1.513(2); C(11)-N(1)-B(1) 119.06(16), C(11)-N(1)-C(120) 124.08(17), B(1)-N(1)-C(120) 116.48(16).

**Carbon Dioxide**

The corresponding reaction of $Ph_2PBpin$ with $CO_2$ also proceeds at room temperature to give the 1,2-addition product **13** where the $PPh_2$ group has added to the carbon atom and the electrophilic Bpin group has added to one of the oxygen atoms (Scheme 4). A significant amount of research has recently focussed on the reduction of $CO_2$ using boron reagents.[23] The $^{13}C\{^1H\}$ NMR spectrum shows a doublet at 177.5 ppm with coupling to the $^{31}P$ atom ($J_{CP}$ = 16 Hz). Likewise, a broad singlet at 22 ppm is observed in the $^{11}B\{^1H\}$ NMR data corresponding a three coordinate Bpin group bound to an oxygen atom. Efforts to obtain single crystals of **13** were unsuccessful, nonetheless, all spectroscopic data are consistent with the formulation of **13.** Similar reduction products arising from the addition of $CO_2$ to a combination of a phosphinimines and $B(C_6F_5)_3$ have been previously reported.[24] Interestingly, addition of dry methanol to **13** gave MeOBpin, $PPh_2H$ along with reformation of $CO_2$. Analogous reactivity was observed upon addition of **13** to benzaldehyde. As such, $Ph_2PBpin$ provides a unique source for the reversible and selective trapping of $CO_2$ and current efforts

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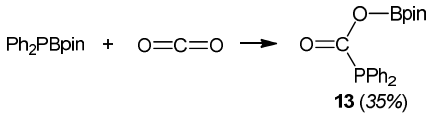
are focussed on designing alternate phosphinoboranes for this capture process.[25] Attempts to add a second equivalent of $Ph_2PBpin$ to $CO_2$ proved unsuccessful.




**Scheme 4** The Phopshinoboration of Carbon Dioxide (Isolated Yield in Brackets).

## Conclusions

In summary, we have shown that the novel phosphinoboronate ester $Ph_2PBpin$ selectively adds to heterocumulenes including both alkyl and aryl carbodiimides, isocyanates, isothiocyanates and carbon dioxide to give the corresponding 1,2-addition products. Addition of methanol to the compounds derived from addition of carbodiimides, isocyanates, and isothiocyanates afforded the corresponding hydrophosphination products. These latter species are typically prepared by a catalysed addition of primary or secondary phosphines to these substrates and are further complicated by interactions with the catalyst. The present methodology developed avoids use of a catalyst and provides a simple route to the generation of a range of functionalized phosphines. In the case of the reaction with $CO_2$, this reaction is shown to be reversible. On-going efforts are exploring the utility of these products as ambiphilic ligands, and the potential of related phosphinoboronate esters in carbon dioxide capture. The results of these studies will be reported in due course.

## Experimental

### General conditions and methods

All reagents and solvents, unless otherwise noted, were purchased from commercial sources and used without further purification. Solvents were distilled over appropriate drying agents under dinitrogen: $CH_2Cl_2$ over $CaH_2$; hexane, benzene and toluene over freshly wired sodium. $CDCl_3$ was purchased from Cambridge Isotope Laboratories, degassed by three freeze-pump-thaw cycles and stored in a dark place over oven-activated 4Å molecular sieves. $Ph_2PBpin$ was prepared as previously reported.[10b] Compounds **1b**,[18d] **2b**,[26a] **3b**,[26a] **4b**,[26b] **7b**,[18n,26b] and **9b**[18p,q,26b,c] have been reported previously.

NMR spectra were recorded on Bruker AvanceIII-400 MHz ($^1$H: 400 MHz; $^{11}$B: 128 MHz and $^{13}$C: 100 MHz) and Agilent DD2-500 MHz ($^{13}$C: 126 MHz and $^{31}$P: 202 MHz), or JEOL JNM-GSX400 ($^1$H: 400 MHz; $^{11}$B: 128 MHz; $^{13}$C: 100 MHz and $^{31}$P: 162 MHz) spectrometers. Chemical shifts ($\delta$) are reported in ppm [relative to residual solvent peaks ($^1$H and $^{13}$C), external $BF_3{\cdot}OEt_2$ ($^{11}$B) or $H_3PO_4$ ($^{31}$P)]. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), multiplet (m), overlapping (ov), and broad (br). Melting points were measured uncorrected with a Stuart SMP30 apparatus. All manipulations were performed under an atmosphere of dinitrogen using standard Schlenk techniques or in an MBraun LabMaster glovebox. Elemental Analysis was performed at the University of Windsor using a Perkin Elmer 2400 combustion CHN analyser.

### Preparation of compounds 1a-12a

General procedure: Phosphinoboration of Carbodiimides, Isocyanates and Isothiocyanates. A mixture of Ph2PBpin (100 mg, 0.320 mmol) and substrate (0.32 mmol for 1a-7a and 9a-11a; 0.64 mmol for 8a and 12a) in toluene (5 mL) was stirred for the prescribed time at room temperature. The solvent was removed under vacuum and the residue was either washed with hexane (method A) - or recrystallized from hexane (method B).

Synthesis of 1,1-diphenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N,N'-di-p-tolylphosphinecarboximidamide (**1a**): This mixture was allowed to stir for 18 h and the product was isolated using method A. Colourless crystalline solid. Yield: 82% (140 mg); mp: 117-120°C; Anal. Calcd. For $C_{33}H_{36}BN_2O_2P$: (534.44): C, 74.16; H, 6.79; N, 5.24. Found: C, 74.33; H, 6.96; N, 5.09. $^1$H NMR ($CDCl_3$): δ: 7.59 (t, J = 7.8 Hz, 4H, Ar), 7.29-7.23 (ov m, 6H, Ar), 7.01-6.97 (ov m, 6H, Ar), 6.78 (d, J = 7.0 Hz, 2H, Ar), 2.30 (s, 3H, Me), 2.23 (s, 3H, Me), 0.88 (s, 12H, pin). $^{11}$B{$^1$H} NMR ($CDCl_3$): δ 21.8 (s). $^{13}$C{$^1$H} NMR ($CDCl_3$): δ 164.2, 146.6 (d, $J_{CP}$ = 5.7 Hz), 139.2, 135.5 (d, $J_{CP}$ = 5.6 Hz), 135.3 (d, $J_{CP}$ = 21.1 Hz), 133.7, 133.6, 129.3 (d, $J_{CP}$ = 14.4 Hz), 128.9, 128.0 (d, $J_{CP}$ = 7.7 Hz), 124.3, 120.8, 83.3, 24.2, 21.0. $^{31}$P{$^1$H} NMR ($CDCl_3$): δ 2.2 (s).

Synthesis of N,N'-diisopropyl-1,1-diphenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphinecarboximidamide (**2a**): This mixture was allowed to stir for 18 h and the product was isolated using method B. Colourless crystalline solid. Yield: 74% (123 mg); mp: 83.5-84.5°C; Anal. Calcd. For $C_{25}H_{36}BN_2O_2P$: (438.36): C, 68.50; H, 8.28; N, 6.39. Found: C, 68.12; H, 8.00; N, 6.47. $^1$H NMR ($CDCl_3$): δ 7.58 (br, 4H, Ar), 7.27-7.18 (m, 6H, Ar), 3.92 (sept, J = 6.2 Hz, major, 1H, NCH), 3.65 (d q, J = 2.6 Hz, minor, NCH), 3.38 (d q, J = 2.6 Hz, major, 1H, NCH), 1.10 (s, 12H, pin), 1.09-0.97 (ov m, 12H, $CH(CH_3)_2$). $^{11}$B{$^1$H} NMR ($CDCl_3$): δ 21.6. $^{13}$C{$^1$H} NMR ($CDCl_3$): δ 161.2 (d, $J_{CP}$ = 7.7 Hz), 136.6, 135.0 (d, $J_{CP}$ = 17.2 Hz), 134.4 (d, $J_{CP}$ = 19.2 Hz), 128.5, 128.1 (d, $J_{CP}$ = Hz), 127.9 (d, $J_{CP}$ = 7.7 Hz), 82.2, 51.3 (d, $J_{CP}$ = 14.4 Hz, minor), 50.7 (d, $J_{CP}$ = 4.8 Hz), 49.0 (d, $J_{CP}$ = 8.6 Hz), 24.7, 24.5, 23.7, 22.8, 22.7. $^{31}$P{$^1$H} NMR ($CDCl_3$): δ 0.6 (minor), -0.7 (major).

Synthesis of N,N'-dicyclohexyl-1,1-diphenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphinecarboximidamide (**3a**): This mixture was allowed to stir for 18 h and the product was isolated using method B. White solid. Yield: 123 mg (74%); mp: 90.5-93.5°C; Anal. Calcd. For $C_{31}H_{44}BN_2O_2P$: (518.49): C, 71.81; H, 8.55; N, 5.40. Found: C, 71.58; H, 8.76; N, 5.30. $^1$H NMR ($CDCl_3$): δ 7.63-7.55 (ov, m, 4H, Ar), 7.27 (m, 6H, Ar), 3.62 (br, 1H, NCH), 2.85 (br, 1H, NCH), 1.67-1.17 (ov, m, 20H, Cy), 1.11 (s, 12H, pin). $^{11}$B{$^1$H} NMR ($CDCl_3$): δ 22.4 (s). $^{13}$C{$^1$H} NMR ($CDCl_3$): δ 161.1 (d, $J_{CP}$ = 7.7 Hz), 136.8, 135.0, 134.4 (d, $J_{CP}$ = 20.1 Hz), 128.5, 128.1 (d, $J_{CP}$ = 7.7 Hz), 127.8 (d, $J_{CP}$ = 6.7 Hz), 82.1, 59.6 (d, $J_{CP}$ = 12.5 Hz, minor), 59.1 (d, $J_{CP}$ = 5.8 Hz), 57.4 (d, $J_{CP}$ = 6.7 Hz), 33.3, 32.9, 32.7, 26.7,

26.0, 25.8, 25.6, 25.5, 24.7, 24.5. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 0.0 (minor), -0.7 (major).

Synthesis of N-1,1-triphenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphinecarboxamide (**4a**): This mixture was allowed to stir for 6 h and the product was isolated using method A. White solid. Yield: 110 mg (80%); mp: 123-125°C; Anal. Calcd. For $C_{25}H_{27}BNO_3P$: (431.28): C, 69.62; H, 6.31; N, 3.25. Found: C, 69.80; H, 6.45; N, 3.29. $^{1}H$ NMR ($CDCl_3$): δ 7.40 (m, 4H, Ar), 7.33-7.30 (ov m, 6H, Ar), 7.25-7.20 (ov m, 3H, Ar), 7.01 (d, J = 6.9 Hz, 2H, Ar), 1.06 (s, 12H, pin). $^{11}B\{^{1}H\}$ NMR ($CDCl_3$): δ 25.2 (s). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 184.6, 139.5 (d, $J_{CP}$ = 2.9 Hz), 134.8 (d, $J_{CP}$ = 20.1 Hz), 134.7, 129.2, 128.9, 128.6, 128.4 (d, $J_{CP}$ = 5.7 Hz), 127.1, 84.4, 24.2. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 9.5 (s).

Synthesis of N-(4-nitrophenyl)-1,1-diphenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphinecarboxamide (**5a**): This mixture was allowed to stir for 6 h and the product was isolated using method A. Yellow solid. Yield: 130 mg (85%); mp: 94-95°C; Anal. Calcd. For $C_{25}H_{26}BN_2O_5P$: (476.28): C, 63.05; H, 5.50; N, 5.88. Found: C, 62.67; H, 5.74; N, 5.87. $^{1}H$ NMR ($CDCl_3$): δ 8.14 (d, J = 8.8 Hz, 2H, Ar), 7.41 (m, 4H, Ar), 7.38-7.33 (ov m, 6H, Ar), 7.19 (d, J = 8.7 Hz, 2H, Ar), 1.05 (s, 12H, pin). $^{11}B\{^{1}H\}$ NMR ($CDCl_3$): δ: 23.9 (s). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 184.6 (d, $J_{CP}$ = 34.5 Hz), 146.5, 145.8 (d, $J_{CP}$ = 1.9 Hz), 134.7 (d, $J_{CP}$ = 20.1 Hz), 134.1 (d, $J_{CP}$ = 7.7 Hz), 129.7 (d, $J_{CP}$ = 21.1 Hz), 128.6 (d, $J_{CP}$ = 7.7 Hz), 124.0, 85.1, 24.2. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 10.8 (s).

Synthesis of N-ethyl-1,1-diphenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphinecarboxamide (**6a**): This mixture was allowed to stir for 18 h and the product was isolated using method B. White solid. Yield: 93 mg (76%); mp: 79.4-80.4°C; Anal. Calcd. For $C_{21}H_{27}BNO_3P$: (383.23): C, 65.82; H, 7.10; N, 3.65. Found: C, 65.40; H, 7.42; N, 3.58. $^{1}H$ NMR ($CDCl_3$): δ 7.36 (m, 4H, Ar), 7.34-7.31 (ov m, 6H, Ar), 3.53 (q, J = 6.9 Hz, 2H, CH2), 1.11 (t, J = 6.9 Hz, 3H, CH3), 1.00 (s, 12H, pin). $^{11}B\{^{1}H\}$ NMR ($CDCl_3$): δ 24.5 (s). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 183.4 (d, $J_{CP}$ = 30.7 Hz), 135.9 (d, $J_{CP}$ = 6.7 Hz), 134.5 (d, $J_{CP}$ = 20.1 Hz), 129.0, 128.4 (d, $J_{CP}$ = 7.7 Hz), 84.3, 38.9, 15.4. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 10.9 (s).

Synthesis of N-cyclohexyl-1,1-diphenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphinecarboxamide (**7a**): This mixture was allowed to stir for 18 h where the product was isolated using method A. White solid. Yield: 110 mg (78%); mp: 128.5-131.5°C; Anal. Calcd. For $C_{25}H_{33}BNO_3P$: (437.33): C, 68.66; H, 7.61; N, 3.20. Found: C, 68.49; H, 7.97; N, 3.31. $^{1}H$ NMR ($CDCl_3$): δ 7.39 (m, 4H, Ar), 7.33-7.30 (ov m, 6H, Ar), 4.24 (tt, J = 3.0 Hz, J = 0.9 Hz, 2H, CH), 1.89 (m, 2H, Cy), 1.72 (m, 2H, Cy), 1.62-1.54 (ov m, 3H, Cy), 1.26 (m, 2H, Cy), 1.11 (m, 1H, Cy), 1.02 (s, 12H, pin). $^{11}B\{^{1}H\}$ NMR ($CDCl_3$): δ 24.7 (s). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 183.4 (d, $J_{CP}$ = 29.6 Hz), 136.2 (d, $J_{CP}$ = 8.1 Hz), 134.5 (d, $J_{CP}$ = 20.1 Hz), 128.9, 128.3 (d, $J_{CP}$ = 8.1 Hz), 84.0, 54.3, 31.4, 26.5, 25.5, 24.3. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 11.8 (s).

Synthesis of N-tert-butyl-1,1-diphenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphinecarboxamide (**8a**): This mixture was allowed to stir for 2 days and the product was isolated using method A. White solid. Yield: 100 mg (76%); mp: 119.1-120.5°C; Anal. Calcd. For $C_{23}H_{31}BNO_3P$: (411.29): C, H, 7.60; N, 3.41. Found: C, 67.01; H, 7.21; N, 3.43. $^{1}H$ NMR ($CDCl_3$): δ 7.49 (m, 4H, Ar), 7.35-7.31 (ov m, 6H, Ar), 7.19 (d, J = 8.7 Hz, 2H, Ar), 1.43 (s, 9H, tBu), 1.38 (s, 12H, pin). $^{11}B\{^{1}H\}$ NMR ($CDCl_3$): δ 25.2 (s). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 176.4 (d, $J_{CP}$ = 12.5 134.6 (d, $J_{CP}$ = 8.6 Hz), 134.0 (d, $J_{CP}$ = 19.2 Hz), 129.1, 128.4 (d, $J_{CP}$ = 6.7 Hz), 84.9, 56.8 (d, $J_{CP}$ = 7.7 Hz), 28.9, 25.4, 25.4. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 3.5 (s).

Synthesis of N-1,1-triphenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphinecarbothioamide (**9a**): This mixture was allowed to stir for 6 and the product was isolated using method A. Yellow solid. Yield: 112 mg (78%); mp: 147-149°C; Anal. Calcd. For $C_{25}H_{27}BNO_2PS$: (447.34): C, 67.12; H, 6.08; N, 3.13. Found: C, 66.88; H, 5.74; N, 3.07. $^{1}H$ NMR ($CDCl_3$): δ 7.42 (m, 4H, Ar), 7.34-7.23 (ov m, 9H, Ar), 7.25-7.20 (ov m, 3H, Ar), 7.04 (d, J = 7.4 Hz, 2H, Ar), 1.09 (s, 12H, pin). $^{11}B\{^{1}H\}$ NMR ($CDCl_3$): δ 24.1 (s). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ: 225.0 (d, $J_{CP}$ = 44 Hz), 143.5 (d, $J_{CP}$ = 3.8 Hz), 136.5 (d, $J_{CP}$ = 6.7 Hz), 134.9 (d, $J_{CP}$ = 21.1 Hz), 129.4, 129.1, 129.0, 128.4 (d, $J_{CP}$ = 7.7 Hz), 127.9, 127.4, 85.1, 24.2. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 26.7 (s).

Synthesis of N-benzyl-1,1-diphenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphinecarbothioamide (**10a**): This mixture was allowed to stir for 18 h and the product was isolated using method B. Yellow solid, Method B. Yield: 98 mg (72%); mp: 113-114.5°C; Anal. Calcd. for $C_{26}H_{29}BNO_2PS$: (461.37): C, 67.69; H, 6.34; N, 3.04. Found: C, 67.47; H, 6.14; N, 3.07. $^{1}H$ NMR ($CDCl_3$): δ 7.33-7.24 (ov m, 15H, Ar), 5.38 (s, 2H, CH2), 0.98 (s, 12H, pin). $^{11}B\{^{1}H\}$ NMR ($CDCl_3$): δ 24.5 (s). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 224.8 (d, $J_{CP}$ = 46 Hz), 138.2, 138.1 (d, $J_{CP}$ = 3.8 Hz), 134.9, 134.7, 129.2, 128.5, 128.4 (d, $J_{CP}$ = 7.7 Hz), 128.1, 127.0, 85.2, 53.8, 24.2. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 31.1 (s).

Synthesis of N-cyclohexyl-1,1-diphenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphinecarbothioamide (**11a**): This mixture was allowed to stir for 18 and the product was isolated using method B. Yellow solid. Yield: 98 mg (72%); mp: 137-138°C; Anal. Calcd. For $C_{25}H_{33}BNO_2PS$: (453.39): C, 66.23; H, 7.34; N, 3.09. Found: C, 65.94; H, 7.37; N, 3.16. $^{1}H$ NMR ($CDCl_3$): δ 7.46 (m, 4H, Ar), 7.36-7.32 (ov m, 6H, Ar), 4.66 (br s, 1H, CH), 1.84 (d, J = 11.1 Hz, 2H, Cy), 1.70 (d, J = 13.1 Hz, 2H, Cy), 1.43 (m, 2H, Cy), 1.32 (s, 12H, pin), 1.19 (m, 2H, Cy), 1.06 (m, 1H, Cy). $^{11}B\{^{1}H\}$ NMR ($CDCl_3$): δ 24.4 (s). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 216.2 (d, $J_{CP}$ = 32.2 Hz), 135.2, 134.5 (d, $J_{CP}$ = 20.1 Hz), 129.5, 128.4 (d, $J_{CP}$ = 8.1 Hz), 85.2, 60.8 (d, $J_{CP}$ = 12.1 Hz), 31.4, 25.8, 25.5, 25.1. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 19.3 (br s).

Synthesis of N-tert-butyl-1,1-diphenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphinecarbothioamide (**12a**): This mixture was allowed to stir for 18 and the product was isolated using method B. Yellow solid. Yield: 98 mg (72%); mp: 118-119°C; Anal. Calcd. For $C_{23}H_{31}BNO_2PS$: (427.35): C, 64.64; H, 7.31; N, 3.28. Found: C, 64.32; H, 7.27; N, 2.77. $^{1}H$ NMR ($CDCl_3$): δ 7.48 (m, 4H, Ar), 7.38-7.31 (ov m, 6H, Ar), 1.67 (s, 9H, t-Bu), 1.09 (s, 12H, pin). $^{11}B\{^{1}H\}$ NMR ($CDCl_3$): δ 23.4 (s). $^{13}C\{^{1}H\}$ NMR

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($CDCl_3$): δ 135.1 (d, $J_{CP}$ = 4.0 Hz), 134.0 (d, $J_{CP}$ = 18.8 Hz), 129.3, 128.3 (d, $J_{CP}$ = 8.1 Hz), 85.3, 61.4 (d, $J_{CP}$ = 9.4 Hz), 28.2, 25.8. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.3 (s).

Synthesis of 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl diphenylphosphinecarboxylate (**13**): A benzene solution of $Ph_2PBpin$ (100 mg, 0.32 mmol) was subjected to 3 freeze-pump thaw cycles and charged with 1 atmosphere of carbon dioxide. The solution was allowed to stir for 4 days. The solvent was removed under vacuum, leaving a yellow oil, which was recrystallized from pentane, leaving a light yellow solid. Yield: 40 mg (35%); mp: 58-59°C; Anal. Calcd. For $C_{19}H_{22}BO_4P$: (427.35): C, 64.07; H, 6.23. Found: C, 64.27; H, 6.27. $^1H$ NMR ($C_6D_6$): δ 7.57 (m, 4H, Ar), 7.00 (m, 6H, Ar), 0.94 (s, 12H, pin). $^{11}B\{^1H\}$ NMR ($C_6D_6$): δ 22.7 (s). $^{13}C\{^1H\}$ NMR ($C_6D_6$): δ 177.5 (d, $J_{CP}$ = 16 Hz), 135.0 (d, $J_{CP}$ = 20 Hz), 132.8 (d, $J_{CP}$ = 5 Hz), 129.8, 128.9 (d, $J_{CP}$ = 8 Hz), 84.2, 24.5. $^{31}P\{^1H\}$ NMR ($C_6D_6$): δ -0.7 (s).

**Preparation of compounds 1b-12b.**

General Procedure: Phosphinoboration reactions were carried out as described above. Following the prescribed time, methanol (5 drops) was added and the solution was stirred for an additional 30 minutes. The solvent was removed under vacuum and the residue was either washed with hexane (Method A) or recrystallized from hexane (Method B) or diethyl ether (Method C).

Synthesis of N-(4-nitrophenyl)-1,1-diphenylphosphine-carboxamide (**5b**): Washed with cold diethyl ether (3x5 mL). Yellow solid. Yield: 88 mg (78%); mp: 149.5-151 °C (decomp.). Anal. Calcd. For $C_{19}H_{15}N_2O_3P$: (350.31): C, 65.14; H, 4.32; N, 8.00. Found: C, 65.01; H,4.44 ; N, 8.18. $^1H$ NMR ($CDCl_3$): δ 8.14 (dm, J = 9.2 Hz, 2H, Ar), 7.61-7.56 (ov m, 5H, Ar, NH), 7.53 (dm, J = 9.2 Hz, 2H, Ar), 7.49-7.43 (ov m, 6H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 177.6 (d, $J_{CP}$ = 20.1 Hz), 143.8, 143.0, 134.6 (d, $J_{CP}$ = 20.1 Hz), 132.2 (d, $J_{CP}$ = 9.6 Hz), 130.6, 129.4 (d, $J_{CP}$ = 7.7 Hz), 125.2, 125.2, 119.0. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 1.9 (s).

Synthesis of N-ethyl-1,1-diphenylphosphinecarboxamide (**6b**): Method A. White solid. Yield: 78 mg (94%); mp: 81.3-82.8 °C; Anal. Calcd. For $C_{15}H_{16}NOP$: (257.27): C, 70.01; H, 6.30; N, 5.43. Found: C, 69.79; H, 6.39; N, 5.57. $^1H$ NMR ($CDCl_3$): δ 7.54-7.48 (m, 4H, Ar), 7.40-7.37 (ov m, 6H, Ar), 5.66 (br s, NH), 3.32 (qd, J = 6.9 Hz, $J_{HP}$ = 5.5 Hz, 2H, $CH_2$), 1.05 (t, J = 6.9 Hz, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 177.0 (d, $J_{CP}$ = 12.7 Hz), 134.4 (d, $J_{CP}$ = 18.5 Hz), 133.7 (d, $J_{CP}$ = 11.6 Hz), 129.8, 129.0 (d, $J_{CP}$ = 8.1 Hz), 35.0, 15.0. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -3.4 (s).

Synthesis of N-tert-butyl-1,1-diphenylphosphinecarboxamide (**8b**): Method A. White solid. Spectroscopic data matches that which has been previously reported,5 however since full spectroscopic details have not been reported for this compound, they are presented here. Yield: 83 mg (91%); mp: 119.2-120.8 °C; Anal. Calcd. For $C_{17}H_{20}NOP$: (285.33): C, 71.56; H, 7.07; N, 4.91. Found: C, 71.77; H, 7.17; N, 5.01. $^1H$ NMR ($CDCl_3$): δ 7.52-7.47 (m, 4H, Ar), 7.40-7.35 (ov m, 6H, Ar), 5.51 (br s, NH), 1.28 (s, 9H, t-Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 176.1 (d, $J_{CP}$ = 13.4 Hz), 134.2 (d, $J_{CP}$ = 19.2 Hz), 134.2, 129.7, 128.9 (d, $J_{CP}$ = 6.7 Hz), 52.9, 28.8. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 1.6 (s).

Synthesis of N-benzyl-1,1-diphenylphosphinecarbothioamide (**10b**): Method A. Yellow solid. Yield: 86 mg (84%); mp: 80.9-82.1°C; Anal. Calcd. For $C_{20}H_{18}NPS$: (319.34): C, 71.62; H, 5.41; N, 4.18. Found: C, 71.55; H, 5.51; N, 4.26. $^1H$ NMR ($CDCl_3$): δ 7.50-7.44 (m, 5H), 7.41-7.36 (ov m, 6H, Ar), 7.32-7.26 (m, 3H), 7.14 (dd, J = 7.8 Hz, J = 2.3 Hz, 2H, Ar), 4.89 (d, JHP = 5.0 Hz, 2H, $CH_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 208.1 (d, $J_{CP}$ = 39.0 Hz), 135.9, 134.4 (d, $J_{CP}$ = 21.5 Hz), 134.1, 130.2, 129.2 (d, $J_{CP}$ = 6.7 Hz), 129.0, 128.1, 127.7, 50.2. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 16.2 (s).

Synthesis of N-cyclohexyl-1,1-diphenylphosphine-carbothioamide (11b): Method A. Yellow solid. Yield: 91 mg (87%); mp: 94.0-95.4 °C; Anal. Calcd. For $C_{19}H_{22}NPS$: (327.43): C, 69.70; H, 6.77; N, 4.28. Found: C, 69.17; H, 7.02; N, 3.91. $^1H$ NMR ($CDCl_3$): δ 7.48-7.38 (ov m, 10H, Ar), 4.51 (m, 1H, CH), 1.91 (m, 2H, Cy), 1.54-1.34 (ov m, 5H, Cy), 1.19-1.05 (ov m, 3H, Cy). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 205.7 (d, $J_{CP}$ = 39.0 Hz), 134.5 (d, $J_{CP}$ = 14.8 Hz), 134.3 (d, $J_{CP}$ = 20.1 Hz), 130.1, 129.2 (d, $J_{CP}$ = 6.7 Hz), 53.6, 31.2, 25.3, 24.0. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 14.5 (s).

Synthesis of N-tert-butyl-1,1-diphenylphosphine-carbothioamide (**12b**): Method A. Yellow solid. Yield: 87 mg (90%); mp: 121.9-122.5°C; Anal. Calcd. For $C_{17}H_{20}NPS$: (301.39): C, 67.75; H, 6.69; N, 4.65. Found: C, 67.99; H, 6.66; N, 4.76. $^1H$ NMR ($CDCl_3$): δ 7.46-7.39 (ov m, 10H, Ar), 7.07 (br s, 1H, NH), 1.43 (s, 9H, t-Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 206.3 (d, $J_{CP}$ = 40.3 Hz), 135.2 (d, $J_{CP}$ = 17.5 Hz), 134.2 (d, $J_{CP}$ = 20.2 Hz), 130.1, 129.2 (d, $J_{CP}$ = 8.1 Hz), 57.6, 27.7. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 17.4 (s).

**X-ray diffractions studies**

Crystals for investigation were covered in Nujol®, mounted into a goniometer head, and then rapidly cooled under a stream of cold $N_2$ of the low-temperature apparatus (Oxford Cryostream) attached to the diffractometer. The data were then collected using the APEXIII software suite[27] on a Bruker Photon 100 CMOS diffractometer using a graphite monochromator with Mo-Kα radiation (λ = 0.71073 Å). For each sample, data were collected at low temperature. APEX-III software was used for data collection and reduction and SADABS[28] was used for absorption corrections (multi-scan; semi-empirical from equivalents). XPREP was used to determine the space group and the structures were solved and refined using the SHELX[29] software suite as implemented in the WinGX[30] program suites. Validation of the structures was conducted using PLATON.[32] All carbon-bound hydrogen atoms were modelled in idealized geometries using riding models in which temperature factor was determined by the carbon atom to which it was bonded. For the structures containing N-H bonds, the nitrogen-bound H atoms were modelled freely using isotropic temperature factors. Crystallographic information has also been deposited with the Cambridge Crystallographic Data Centre (CCDC 1549899-1549904). Copies of the data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road,

Cambridge CB2 1EZ, UK; fax: + 44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

## Conflict of Interests

There are no conflicts of interest to declare.

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# Dalton Transactions

## PAPER

**Table 1** Crystallographic data collection parameters for **1a**, **2a**, **6a**, **8a**, **7b** and **12a**

| Complex | **1a** | **2a** | **6a** | **8a** | **7b** | **12a** |
|---|---|---|---|---|---|---|
| Formula | $C_{33}H_{36}BN_2O_2P$ | $C_{25}H_{36}BN_2O_2P$ | $C_{21}H_{27}BNO_3P$ | $C_{23}H_{31}BNO_3P$ | $C_{19}H_{22}NOP$ | $C_{23}H_{31}BNO_2PS$ |
| Molecular weight | 534.42 | 438.34 | 383.21 | 411.27 | 311.34 | 427.33 |
| Crystal system | Triclinic | Triclinic | Triclinic | Triclinic | Orthorhombic | Triclinic |
| Space group | *P*-1 | *P*-1 | *P*-1 | *P*-1 | *Iba*2 | *P*-1 |
| *a*/Å | 9.6725(4) | 10.7605(4) | 6.2343(10) | 9.5854(7) | 10.6648(7) | 10.3603(12) |
| *b*/Å | 11.3305(4) | 11.2811(4) | 9.4532(13) | 9.7989(8) | 34.271(2) | 17.1280(19) |
| *c*/Å | 14.4827(6) | 12.5055(4) | 17.992(3) | 15.9177(14) | 9.4843(6) | 26.966(3) |
| $\alpha$/° | 101.512(2) | 111.6550(10) | 86.725(5) | 75.187(3) | 90 | 92.761(4) |
| $\beta$/° | 100.403(2) | 98.380(2) | 89.957(6) | 80.891(3) | 90 | 93.308(4) |
| $\gamma$/° | 101.893(2) | 110.8890(10) | 84.737(5) | 63.041(3) | 90 | 90.282(4) |
| *V*/Å$^3$ | 1480.66(10) | 1249.14(8) | 1054.1(3) | 1286.77(18) | 3466.4(4) | 4771.5(9) |
| *Z* | 2 | 2 | 2 | 2 | 8 | 8 |
| $\rho_{calc.}$/Mg m$^{-3}$ | 1.199 | 1.165 | 1.207 | 1.061 | 1.193 | 1.190 |
| Crystal size/mm$^3$ | 0.237 x 0.193 x 0.06 | 0.474 x 0.126 x 0.055 | 0.607 x 0.194 x 0.087 | 0.611 x 0.189 x 0.063 | 0.4 x 0.3 x 0.2 | 0.724 x 0.341 x 0.070 |
| Temp/K | 173(2) | 173(2) | 170(2) | 170(2) | 143(2) | 170(2) |
| Radiation/Å | Mo-$K_\alpha$ ($\lambda$=0.71073) | Mo-$K_\alpha$ ($\lambda$=0.71073) | Mo-$K_\alpha$ ($\lambda$=0.71073) | Mo-$K_\alpha$ ($\lambda$=0.71073) | Mo-$K_\alpha$ ($\lambda$=0.71073) | Mo-$K_\alpha$ ($\lambda$=0.71073) |
| $\mu$/mm$^{-1}$ | 0.125 | 0.133 | 0.150 | 0.127 | 0.160 | 0.221 |
| Total reflections | 25932 | 29421 | 45511 | 65255 | 12728 | 213108 |
| Total unique reflections | 5701 | 5350 | 6150 | 7499 | 3235 | 26943 |
| No. of variables | 538 | 288 | 249 | 282 | 203 | 1128 |
| $\theta$ Range/° | 2.902 to 25.847 | 3.114 to 26.862 | 3.046 to 29.999 | 3.174 to 29.999 | 3.110 to 27.494 | 2.780 to 29.709 |
| Largest difference peak/hole/e Å$^{-3}$ | 0.220 and -0.291 | 0.264 and -0.282 | 0.297 and -0.259 | 0.557 and -0.391 | 0.788 and -0.427 | 1.241 and -0.524 |
| S (GoF) on $F^2$ | 1.032 | 1.048 | 1.041 | 1.041 | 1.202 | 1.103 |
| *R*1 | 0.0430 | 0.0447 | 0.0374 | 0.0417 | 0.0487 | 0.0593 |
| w*R*2[b] (all data) | 0.0961 | 0.1012 | 0.0952 | 0.1158 | 0.1301 | 0.1517 |

[a]) $R1 = \sum||F_o|-|F_c||/\sum|F_o|$. [b]) $wR2 = (\sum[w(F_o^2-F_c^2)^2]/\sum[wF_o^4])^{1/2}$, where w = $1/[\sigma^2(F_o^2) + (0.0339P)^2 + (0.6260P)]$ (**1a**), $1/[\sigma^2(F_o^2) + (0.0421P)^2 + (0.3982P)]$ (**2a**), $1/[\sigma^2(F_o^2) + (0.0384P)^2 + (0.4300P)]$ (**6a**), $1/[\sigma^2(F_o^2) + (0.1154P)^2 + (1.0730P)]$ (**8a**), $1/[\sigma^2(F_o^2) + (0.0525P)^2 + (4.3794P)]$ (**7b**), and $1/[\sigma^2(F_o^2) + (0.0494P)^2 + (5.9060P)]$ (**12a**), where $P = (\max(F_o^2, 0) + 2\cdot F_c^2)/3$.

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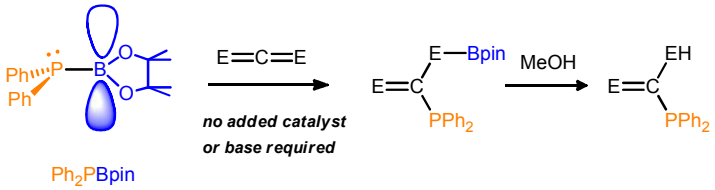
The transition metal-free addition of phosphinoboronate ester $Ph_2PBpin$ (pin = 1,2-$O_2C_2Me_4$) to heterocumulenes including carbodiimides, isocyanates, isothiocyanates and carbon dioxide proceeds with remarkable selectivity to give products in high yield.




$Ph_2PBpin$