

A Free Phosphaborene Stable at Room Temperature

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ABSTRACT: Free phosphaborenes ($R-P=B-R$) are PB analogs of alkynes and their isolation is a long-sought-after goal. Herein, we demonstrate that the combination of a π -donating and a π -accepting substituent with bulky flanking arene rings enables the isolation of a crystalline free phosphaborene **5** at room temperature. This electron push-pull cooperation, combined with the kinetic protection, hinders its inherent tendency to oligomerize. This species features a PB double bond consisting of a conventional σ bond and a delocalized π bond. The lone pair of electrons at P slightly contributes to the PB bonding. Preliminary reactivity studies show that **5** undergoes facile (cyclo)addition reactions with *p*-methyl benzaldehyde, *p*-fluoroacetophenone and carbon disulfide, the last of which results in facile PB double bond cleavage. Our strategy has a significant impact on the future synthesis of ambiphilic hetero-diatomic multiply bonded main group species.

The concept of isoelectronic and isosteric relationships has continued to inspire and impact modern synthetic and materials chemistry. The rich and vast work on CC/NB isosterism has been extremely fruitful for the development of organic/inorganic hybrid architectures with unique physical or chemical properties.¹ Iminoboranes ($R-N^+=B-R$) that are isoelectronic with alkynes have exhibited diverse reactivity and have been utilized as potent synthons for various organoborane derivatives.² However, the analogous chemistry based on $C\equiv C/P=B$ exchange has largely lagged behind due to the considerable lability of PB π bonds towards spontaneous oligomerization (Figure 1a) – a consequence of the high ionic character of group 13/group 15 multiple bonds.³ Indeed, the synthesis of free phosphaborenes ($R-P=B-R$) has been a long-standing challenge.⁴ Such species have only been detected in the gas phase by mass spectrometry⁵ and prior attempts at their observation in the condensed phase have never been successful.⁶⁻⁹ The first evidence for transient phosphaborenes may date back to the early 1960s when Coates and Livingstone boiled a xylene solution of phenylphosphine and dichlorophenylborane, and after the evolution of hydrogen chloride a diphosphadiboretane ($Ph-PB-Ph$)₂ was identified as one of the products.⁷ Even with sterically shielding substituents, in 1986 the Cowley^{5,8} and Nöth⁹ groups isolated the similar dimers ($Ar-PB-tmp$)₂ and ($Et_3C-PB-tmp$)₂, respectively ($tmp = 2,2,6,6$ -tetramethylpiperidino; $Ar = 2,4,6$ - $Me_3C_6H_2$, $2,4,6$ - $tBu_3C_6H_2$). It was not until thirty-one years later that, based on chemical trapping experiments, Cowley evidenced the transient existence of $Mes^*-P=B-tmp$ at elevated temperatures (80 °C), which equilibrated with its dimeric diphosphadiboretane in solution, although direct observation of $Mes^*-P=B-tmp$ was still impossible.¹⁰ This reversibility allowed further investigations into reactivity patterns of phosphaborenes with unsaturated $C\equiv C$,¹⁰ $C=O$ ¹¹ and $P=Ch$ ($Ch = S, Se$)¹² bonds.

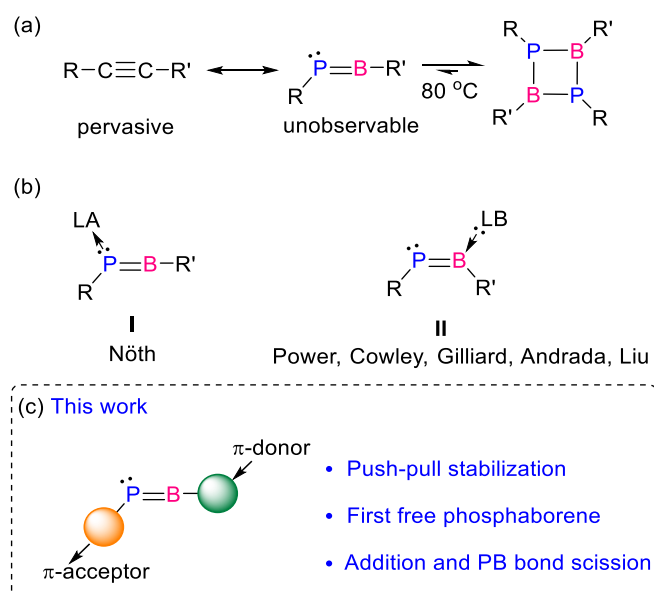


Figure 1. (a) Isosteric relationship between $RC\equiv CR'$ and $RP=BR'$. Spontaneous dimerization to diphosphadiboretane ($RPBR$)₂. (b) Isolable LA- (**I**) and LB-stabilized (**II**) monomeric phosphaborenes. (c) This work.

It has been demonstrated in the landmark works of Nöth¹³ and Power¹⁴ as well as more recently by Cowley,^{10,15} Gilliard,¹⁶ Andrada¹⁷ and our group¹⁸ that monomeric phosphaborenes **I** and **II** can be isolated if an adjacent Lewis basic P or Lewis acidic B center is properly stabilized via a Lewis acid (LA) or a Lewis base (LB), respectively (Figure 1b). This strategy can not only quench the ambiphilic nature of monomeric phosphaborenes, but also provide kinetic protection. In a similar vein, LB-stabilized species including phospho-, arsa- and stibagallenes ($Pn=Ga$; $Pn = P,^{19} As,^{20} Sb^{21}$), phospho- and arsaalumes ($Pn=Al$; $Pn = P, As$)²² and arsaborenes ($As=B$)¹⁴ are isolable. For free group 13/group 15 multiply bonded species, species $R-MN-R$ ($M = In, Ga, Al$) have been isolated by

the group of Power.²³ Su computationally explored free phosphaborenes of the type $R-P^+ \equiv B^- - R$ and summarized that "... it should be possible to synthesize molecules that feature a $B \equiv P$ triple bond possessing both bulky ligands".²⁴ This encouraged us to seek and study isolable free phosphaborenes (Figure 1c).

In terms of thermodynamic stabilization, the installation of a π -donor substituent at the boron center of iminoboranes/phosphaborenes has proved to diminish its Lewis acidity and thus to some extent inhibits spontaneous oligomerization.^{10, 25} Likewise, the tendency to oligomerize should also be suppressed by the presence of a π -accepting substituent at the phosphorus center of phosphaborenes, which would modulate its Lewis basicity. Additionally, increasing the steric bulk of the substituents would certainly be very beneficial for kinetic protection.²⁶ We hence considered the utilization of N-heterocyclic boryl (NHB)²⁷ and N-heterocyclic imino (NHN)²⁸ ligands, which are π -accepting and π -donating respectively, and further are readily accessible and sterically tunable for stabilization of phosphaborenes. Based on density functional theory (DFT) computations, Cowley showed that $Mes^* - P = B - tmp$ ($Mes^* = 2,4,6$ - $tBu_3C_6H_2$) is 11.0 kcal/mol higher in free energy than its dimer.¹⁰ Indeed, our calculations at the M06-2X/def2-SVP level of theory indicated a favorable dimerization as well for **5'** with mesityl substituents on both N-heterocycles (Figure 2). However, by flanking the PB unit with a more sterically encumbering 2,6-diisopropylphenyl (Dipp) substituent, the dimerization of **5** is significantly disfavored by 72.9 kcal/mol.

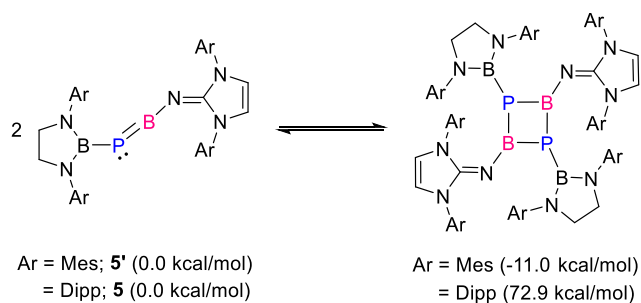
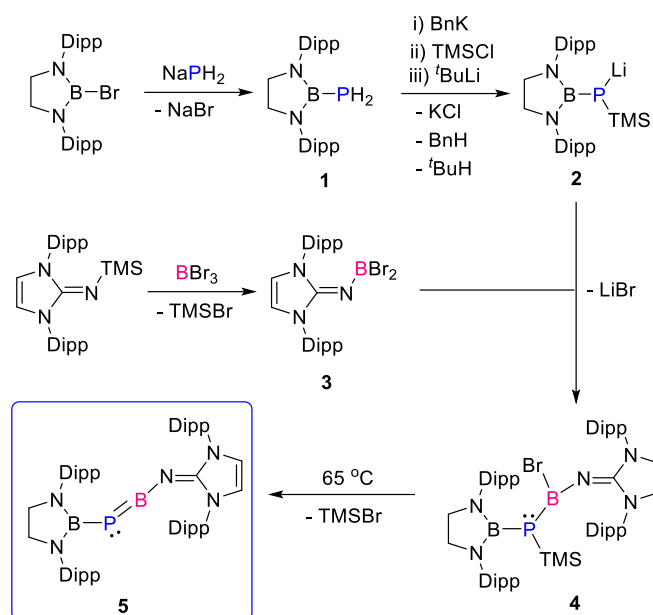


Figure 2. Free energies of phosphaborenes **5'** and **5** and their corresponding dimers.

Therefore, in targeting **5**, we chose the bulky, Dipp-substituted NHB-phosphane **1** and NHN-boron dibromide **3** as precursors (Scheme 1). Species **1** was obtained in 91% yield (³¹P NMR: -246.8 ppm, ¹¹B NMR: 35.2 ppm) through a salt metathesis reaction of the corresponding bromodiazaborolidine and sodium phosphide.²⁹ Successive reactions of **1** with benzyl potassium, trimethylsilyl chloride (TMSCl) and ^tBuLi eventually yielded **2** (³¹P NMR: -286.4 ppm, ¹¹B NMR: 38.3 ppm) as a white solid in 67% yield. In the meanwhile, the boron precursor **3** (¹¹B NMR: 12.7 ppm) was readily accessible via a cross-coupling reaction of the corresponding N-heterocyclic imine and boron tribromide.



Scheme 1. Synthetic route towards **4** and **5**.

With the hope of generating a free phosphaborene, we treated **2** and **3** in toluene from -50 °C to room temperature (Scheme 1). This allowed the formation of **4** and the elimination of LiBr. The ³¹P NMR and ¹¹B NMR spectroscopic studies of **4** revealed singlets at -193.7 and 31.0 ppm for the central P(1) and B(2) atoms, respectively. The ¹¹B NMR resonance of the cyclic B(1) in **4** appears to be 34.4 ppm. X-ray diffraction eventually confirmed the formulation of **4** as a phosphinoborane [(CH₂)(NDipp)]₂BP(TMS)B(Br)N=C[(NDipp)(CH)]₂ (Figure 3a). P(1) adopts a trigonal pyramidal geometry, while B(2) is in a trigonal planar environment. The lengths of P(1)–B(1), P(1)–B(2), B(2)–N(1) and N(1)–C(1) bonds are 1.931(2), 1.898(2), 1.363(3), and 1.284(2) Å, respectively.

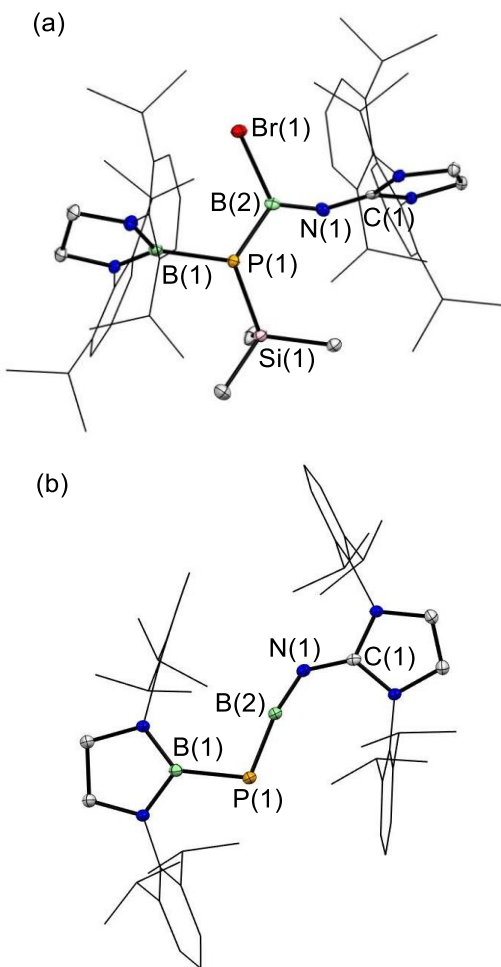


Figure 3. Solid-state structures of **4** (a) and **5** (b). Hydrogen atoms and solvent molecules are omitted for clarity. Thermal ellipsoids are set at the 40% probability level.

Whereas removal of RX (R = H, TMS; X = Cl, Br) from phosphinoboranes was achieved with the aid of Lewis bases, which simultaneously led to base-stabilized phosphaborenes,^{14b, 15, 17-18} we were delighted to find the slow elimination of TMSBr from a C₆D₆ solution of **4** at room temperature, concurrent with the formation of a new species **5** (58% conversion in 20 h, Figure S2-38). Upon simply heating a C₆D₆ solution of **4** at 65 °C for 4 h, a complete conversion to **5** was achieved. This was evidenced in ³¹P NMR and ¹¹B NMR spectra by the appearance of new resonances (³¹P: -291.9 ppm; ¹¹B: 53.0 and 38.6 ppm) attributable to P(1), B(2) and B(1), respectively. The P(1) signal is low-frequency shifted compared to those of ^{Dip}TerP=AlCp* (-203.9 ppm)²² and (^{Dip}Nacnac)Ga(Cl)P=Ga(^{Dip}Nacnac) (-245.8 ppm)^{19b} (^{Dip}Ter = 2,6-Dip₂C₆H₃; ^{Dip}Nacnac = HC[(CMe)(NDipp)]₂), but is remarkably low-frequency shifted relative to that observed for Mes*P=B(dmap)tmp (62.2 ppm),¹⁰ which might be attributed to the NHB substitution and a different bonding scenario of the PB unit. The B(2) chemical shift lies within the typical range of di-coordinate boron species and is low-frequency shifted compared to that of Et₃CP[Cr(CO)₅]=Btmp (62.9 ppm).^{13a} The straightforward route to **5** in the absence of Lewis bases is likely the consequence of electron push-pull ligand effects that lower the ambiphilicity of **5** (vide infra).

The species **5** can be stored in the solid state under N₂ atmosphere for weeks without noticeable decomposition; however, it is extremely sensitive to moisture, exposure to which led to a complicated mixture within minutes. The electronic spectrum of **5** shows two absorptions at 348 and 378 nm (Figure S2-39), which are responsible for its colorless character.

Single crystals of **5** were grown by layering *n*-hexane over a concentrated toluene solution at -35 °C. Gratifyingly, the X-ray diffraction experiment unambiguously authenticated the formation of monomeric free phosphaborene **5** (Figure 3b), in which four flanking Dipp substituents well protected the central P(1)B(2) unit. By contrast with the structure of **4**, P(1) and B(2) in **5** are di-coordinate, with a much shorter P(1)–B(2) bond length of 1.7788(15) Å (compared to 1.898(2) Å in **4**). This is also shorter than those seen for Mes*P=B(dmap)tmp (1.821(2) Å)¹⁰ and ^tBuP(AlBr₃)=Btmp (1.787(4) Å),^{13b} while slightly longer than that of (Et₃CP[Cr(CO)₅]=Btmp) (1.743(5) Å).^{13a} The shortening of P(1)–B(1) (1.8969(14) Å in **5** vs. 1.931(2) Å in **4**) and B(2)–N(1) (1.3245(18) Å vs. 1.363(3) Å) bonds was seen as well, whereas the N(1)–C(1) bond is slightly elongated (1.3017(16) Å vs. 1.284(2) Å). These imply the presence of the delocalization of π electrons over the BPBNC chain. The B(1)–P(1)–B(2), P(1)–B(2)–N(1) and B(2)–N(1)–C(1) angles are 106.00(6)°, 168.47(11)° and 135.6(1)°, respectively. These bond angles suggest the high nonbonded character of the in-plane electron pairs at P(1) and N(1), in line with the electron localization function (ELF)³⁰ calculations (Figure S4-4). Notably, the structural features of **5** are distinctly different from those found for iminoboranes that contain a polarized B≡N triple bond and the linear geometry at both B and N atoms.²

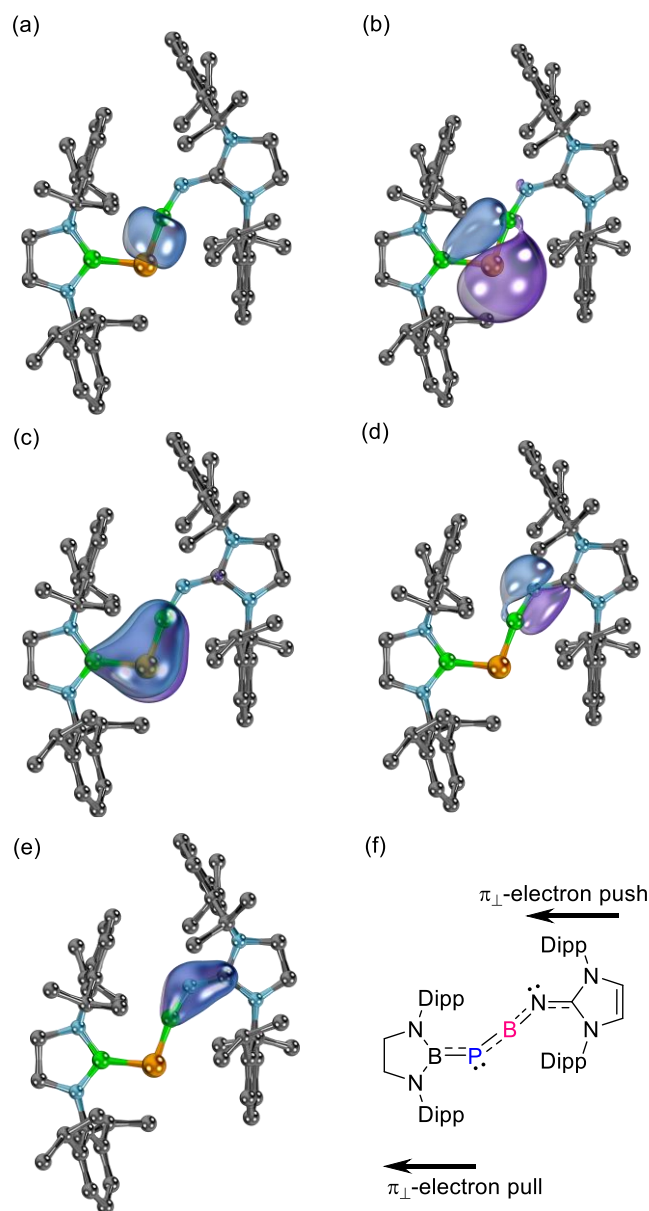


Figure 4. Depiction of selected IBOs of **5**. (a) P–B σ -bonding orbital. (b) Polarized in-plane lone-pair orbital at P. (c) 3-Center-2-electron π_{\perp} -bonding orbital over BPB atoms. (d) Polarized in-plane lone-pair orbital at N. (e) 3-Center-2-electron π_{\perp} -bonding orbital over BNC atoms. (f) Push-pull cooperation for stabilization of **5**.

Intrinsic bond orbital (IBO)³¹ investigations (M06-2X/def2-SVP), coupled with frontier molecular orbital (FMO) and natural bond orbital (NBO) analysis, shed light on the electronic structure of **5** (Figure 4). IBO results illustrate that P(1) forms two σ bonds with B(1) (Figure S4-1) and B(2) (Figure 4a) and bears an essentially non-bonding lone pair orbital that lies in the BPB plane (91.5% at P(1); 6.1% at B(2)) (Figure 4b). The P(1)–B(2) π_{\perp} bond orthogonal to the BPB plane is distinctly delocalized to B(1) forming a 3-center-2-electron (3-c-2-e) π interaction over the B(1)–P(1)–B(2) framework (Figure 4c). Significant to note is that the HOMO of **5** (-5.62 eV) is mainly the 3-c-2-e π_{\perp} bond rather than the lone pair at P(1) that is located in HOMO-2 (-7.07 eV) (Figure S4-2). This means that **5** should exhibit predominantly π_{\perp} bond reactivity and the P(1) π -basicity

is reduced by the NHB substituent. In a similar vein, the Lewis acidity at B(2) is lowered by the strong π -donating ability of the NHN substituent (Figures 4d and 4e). Such an π_{\perp} electron push-pull cooperation effectively diminishes its ambiphilic nature (Figure 4f). NBO calculations (M06-2X/def2-TZVP) confirm the multiple bonding character over the BPBNC chain, with Wiberg bond indices (WBIs) of B(1)–P(1), P(1)–B(2), B(2)–N(1) and N(1)–C(1) of 1.14, 1.73, 1.03 and 1.39, respectively. Moreover, a considerable amount of charge separation is indicated by NBO charges of B(1) (0.83 a.u.), P(1) (-0.45 a.u.), B(2) (0.77 a.u.), N(1) (-1.06 a.u.) and C(1) (0.64 a.u.). As a result, the electronic structure of **5** is most appropriately described in Figure 4f with the high delocalization of π electrons over the central chain. It is noteworthy that natural resonance theory (NRT) calculations on a simplified model of **5** (Dipp groups are replaced with H) show two predominant structures featuring a B(1)–P(1)=B(2)–N(1)=C(1) unit (Figure S4-3).

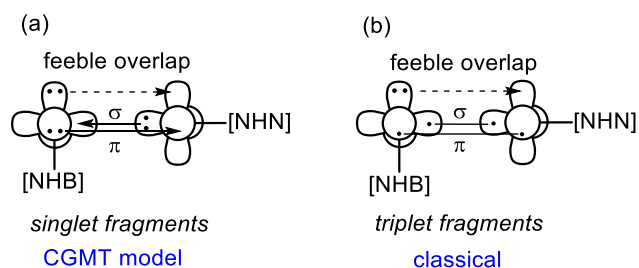
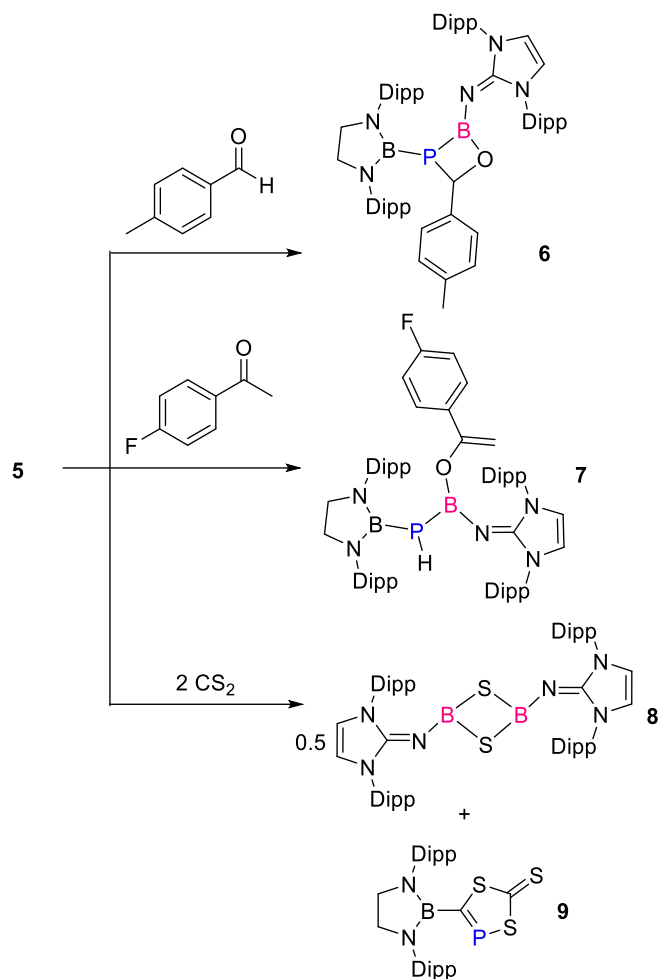


Figure 5. CGMT model (a) and classical model (b) for PB bonding.

The pattern of the PB bonding in **5** was further probed. As our calculations give a triplet ground state of NHB–P and a singlet ground state of NHN–B, the question raised here was whether two singlet fragments combine together via the Carter-Goddard-Malrieu-Trinquier (CGMT) model (Figure 5a)³² or two triplet fragments unite via the classical electron-sharing model (Figure 5b). Numerous reports document that the size of the orbital interaction term (ΔE_{orb}), derived from energy decomposition analyses with natural orbitals for chemical valence (EDA-NOCV) method,³³ is a reliable indicator for the type of bonding.³⁴ The absolute value of ΔE_{orb} between the triplet fragments is much smaller (-196.1 kcal/mol) compared to that between the singlet fragments (-313.8 kcal/mol) (Table S4-1). These data, combined with the IBO results, suggest that the PB double bond character arises from one conventional σ bond and one electron-sharing 3-c-2-e π_{\perp} bond.



Scheme 2. Reactivity of **5** towards *p*-methyl benzaldehyde, *p*-fluoroacetophenone and carbon disulfide.

The reactivity of **5** was next explored (Scheme 2). This species underwent a facile [2+2] cycloaddition with *p*-methyl benzaldehyde at room temperature to afford **6** in 90% yield (Figure 6a), analogous to Cowley's transient phosphaborene $\text{Mes}^*\text{P}=\text{Btmp}$.¹¹ Note that only one of the expected two pairs of diastereomers of **6** was observed spectroscopically. This indicates that either **6** are generated in a stereospecific manner or inversion at P is facile. Treatment of **5** with *p*-fluoroacetophenone gave rise to the formation of **7**. The ^{31}P NMR spectrum of **7** displayed a doublet at -233.4 ppm ($^1J_{\text{PH}} = 212.3$ Hz), which collapsed into a singlet upon proton decoupling, indicating the presence of a PH unit. Indeed, X-ray diffraction unveiled the phosphinoborane structure **7** derived from an apparent addition reaction across the PB unit (Figure 6b). Interestingly, we found that **5** cleanly reacted with carbon disulfide in a molar ratio of 1:2. This led to PB bond scission and ended up with the formation of **8** and **9** (Figures 6c and 6d). **8** represents a rare example of a dithiadiboretane,³⁵ while **9** is the first example of a 1,4,2-dithiaphosphole-5-thione derivative.

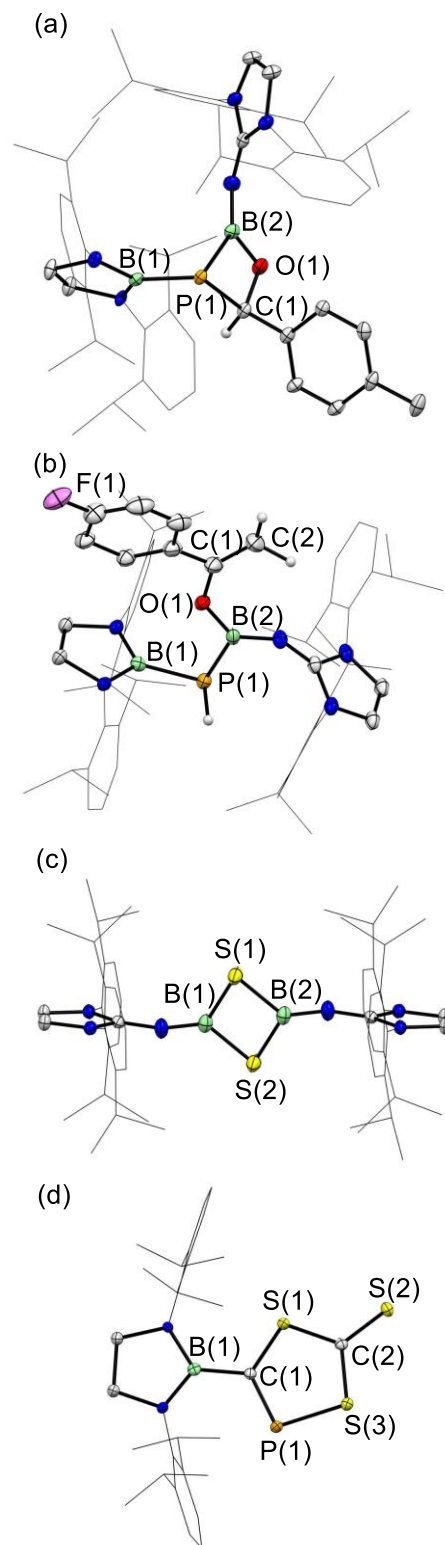


Figure 6. Solid-state structures of **6**, **7**, **8** and **9**. Hydrogen atoms except C(1)H of **6**, P(1)H and C(2)H₂ of **7** and solvent molecules are omitted for clarity. Thermal ellipsoids are set at the 40% probability level.

More than six decades after the first attempted synthesis of $\text{Ph}-\text{P}=\text{B}-\text{Ph}$,⁷ this work shows that free phosphaborenes can be stable enough to be isolated at room temperature. The combination of a π -accepting NHB and a π -donating NHN ligand

framework with bulky flanking arene rings enhances the thermodynamic and kinetic stability of **5**. This free phosphaborene exhibits facile (cyclo)addition reactivity. We anticipate that, by employing such an electron push-pull strategy, other hitherto unknown ambiphilic heterodiatomic multiply bonded main group species will be synthetically accessible. We are working on an in-depth study of the reaction mechanism, and on using free phosphaborenes as synthons for unusual PB systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/XXXXXXXXXX>.

Synthesis procedures for the compounds, NMR spectroscopic and X-ray characterization of the compounds, and computational details (PDF)

Accession Codes

CCDC 2218174-2218179 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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REFERENCES

1. (a) Kawaguchi, M., B/C/N Materials Based on the Graphite Network. *Adv. Mater.* **1997**, *9*, 615-625; (b) Bosdet, M. J. D.; Piers, W. E., B-N as a C-C substitute in aromatic systems. *Can. J. Chem.* **2009**, *87*, 8-29; (c) Campbell, P. G.; Marwitz, A. J. V.; Liu, S.-Y., Recent Advances in Azaborine Chemistry. *Angew. Chem., Int. Ed.* **2012**, *51*, 6074-6092; (d) Chen, X.; Tan, D.; Yang, D.-T., Multiple-boron-nitrogen (multi-BN) doped π -conjugated systems

for optoelectronics. *J. Mater. Chem. C* **2022**, *10*, 13499-13532.

2. (a) Paetzold, P., Iminoboranes. *Adv. Inorg. Chem.* **1987**, *31*, 123-170; (b) Nöth, H., The Chemistry of Amino Imino Boranes. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1603-1623; (c) Borthakur, R.; Chandrasekhar, V., Boron-heteroelement (B-E; E = Al, C, Si, Ge, N, P, As, Bi, O, S, Se, Te) multiply bonded compounds: Recent advances. *Coord. Chem. Rev.* **2021**, *429*, 213647; (d) Fan, Y.; Cui, J.; Kong, L., Recent Advances in the Chemistry of Iminoborane Derivatives. *Eur. J. Org. Chem.* **2022**, *2022*, e202201086.

3. (a) Power, P. P., Main-group elements as transition metals. *Nature* **2010**, *463*, 171-177; (b) Fischer, R. C.; Power, P. P., π -Bonding and the Lone Pair Effect in Multiple Bonds Involving Heavier Main Group Elements: Developments in the New Millennium. *Chem. Rev.* **2010**, *110*, 3877-3923; (c) He, G.; Shynkaruk, O.; Lui, M. W.; Rivard, E., Small Inorganic Rings in the 21st Century: From Fleeting Intermediates to Novel Isolable Entities. *Chem. Rev.* **2014**, *114*, 7815-7880; (d) Weetman, C., Main Group Multiple Bonds for Bond Activations and Catalysis. *Chem. Eur. J.* **2021**, *27*, 1941-1954; (e) Dankert, F.; Hering-Junghans, C., Heavier group 13/15 multiple bond systems: synthesis, structure and chemical bond activation. *Chem. Commun.* **2022**, *58*, 1242-1262.

4. (a) Paine, R. T.; Noth, H., Recent Advances in Phosphinoborane Chemistry. *Chem. Rev.* **1995**, *95*, 343-379; (b) Power, P. P., Boron-Phosphorus Compounds and Multiple Bonding. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 449-460.

5. Arif, A. M.; Boggs, J. E.; Cowley, A. H.; Lee, J. G.; Pakulski, M.; Power, J. M., Production of a boraphosphene (RB:PR') in the vapor phase by thermolysis of a sterically encumbered diphosphadiboretane. *J. Am. Chem. Soc.* **1986**, *108*, 6083-6084.

6. (a) Fritz, G.; Hölderich, W., Silylphosphinoborane. *Z. Anorg. Allg. Chem.* **1977**, *431*, 61-75; (b) Kölle, P.; Linti, G.; Nöth, H.; Wood, G. L.; Narula, C. K.; Paine, R. T., Contributions to the chemistry of boron, 188. Synthesis and Structures of New 1,3,2,4-Diphosphadiboretanes. *Chem. Ber.* **1988**, *121*, 871-879; (c) Dou, D.; Westerhausen, M.; Wood, G. L.; Duesler, E. N.; Paine, R. T.; Linti, G.; Nöth, H., Contributions to the Chemistry of Boron, 214. Synthesis and Reaction Chemistry of Aminophosphanylboranes. *Chem. Ber.* **1993**, *126*, 379-397; (d) Wood, G. L.; Duesler, E. N.; Narula, C. K.; Paine, R. T.; Nöth, H., Synthesis and molecular structure of a P2B3 cage compound: P2(BNPri)2)3. *J. Chem. Soc., Chem. Commun.* **1987**, 496-498; (e) Dias, H. V. R.; Power, P. P., Synthesis and X-Ray Structure of (2,4,6-Me3C6H2BPC6H11)3: A Boron-Phosphorus Analogue of Borazine. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1270-1271; (f) Couret, C.; Escudie, J.; Garrigues, B.; Lazraq, M.; Satge, J., Evidence for an intermediate phosphaborene. *Can. J. Chem.* **1987**, *65*, 1230-1232.

7. Coates, G. E.; Livingstone, J. G., Phosphino-arylboranes. *J. Chem. Soc.* **1961**, 5053.

8. Arif, A. M.; Cowley, A. H.; Pakulski, M.; Power, J. M., Diphospha- and diarsa-diboretanes. Four-membered rings containing boron and phosphorus or arsenic. *J. Chem. Soc., Chem. Commun.* **1986**, 889-890.

9. Kölle, P.; Nöth, H.; Paine, R. T., Beiträge zur Chemie des Bors, 170. Synthese und Struktur eines 1,3,2,4-Diphosphadiboretans. *Chem. Ber.* **1986**, *119*, 2681-2685.

10. Price, A. N.; Nichol, G. S.; Cowley, M. J., Phosphaborenes: Accessible Reagents for the Synthesis of C-C/P-B Isosteres. *Angew. Chem., Int. Ed.* **2017**, *56*, 9953-9957.

11. Borys, A. M.; Rice, E. F.; Nichol, G. S.; Cowley, M. J., The Phospha-Bora-Wittig Reaction. *J. Am. Chem. Soc.* **2021**, *143*, 14065-14070.

12. Graham, C. M. E.; Millet, C. R. P.; Price, A. N.; Valjus, J.; Cowley, M. J.; Tuononen, H. M.; Ragogna, P. J., Preparation and Characterization of P2BCh Ring Systems (Ch=S, Se) and Their Reactivity with N-Heterocyclic Carbenes. *Chem. Eur. J.* **2018**, *24*,

13. (a) Linti, G.; Nöth, H.; Polborn, K.; Paine, R. T., An Allene-analogous Boranylidenephosphane with B=P Double Bond: 1,1-Diethylpropyl(2,2,6,6-tetramethylpiperidino)-boranylidenephosphane-P-pentacarbonylchromium. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 682-684; (b) Knabel, K.; Klapötke, T. M.; Nöth, H.; Paine, R. T.; Schwab, I., A Bicyclic P-P-Bridged 1,3,2,4-Diphosphadiboretane Cation and an Imino(phosphinidene)borane-AlBr₃ Adduct. *Eur. J. Inorg. Chem.* **2005**, *2005*, 1099-1108.
14. (a) Rivard, E.; Merrill, W. A.; Fettinger, J. C.; Wolf, R.; Spikes, G. H.; Power, P. P., Boron-Pnictogen Multiple Bonds: Donor-Stabilized PB and AsB Bonds and a Hindered Iminoborane with a B-N Triple Bond. *Inorg. Chem.* **2007**, *46*, 2971-2978; (b) Rivard, E.; Merrill, W. A.; Fettinger, J. C.; Power, P. P., A donor-stabilization strategy for the preparation of compounds featuring P=B and As=B double bonds. *Chem. Commun.* **2006**, 3800-3802.
15. Price, A. N.; Cowley, M. J., Base-Stabilized Phosphinidene Boranes by Silylium-Ion Abstraction. *Chem. Eur. J.* **2016**, *22*, 6248-6252.
16. Yang, W.; Krantz, K. E.; Dickie, D. A.; Molino, A.; Wilson, D. J. D.; Gilliard Jr., R. J., Crystalline BP-Doped Phenanthryne via Photolysis of The Elusive Boraphosphaketene. *Angew. Chem., Int. Ed.* **2020**, *59*, 3971-3975.
17. Koner, A.; Morgenstern, B.; Andrada, D. M., Metathesis Reactions of a NHC-Stabilized Phosphaborene. *Angew. Chem., Int. Ed.* **2022**, *61*, e202203345.
18. Li, J.; Mei, Y.; Liu, L. L., An Isolable Phosphaborene Stabilized by an Intramolecular Lewis Base. *Eur. J. Inorg. Chem.* **2022**, *2022*, e202200368.
19. (a) Wilson, D. W. N.; Feld, J.; Goicoechea, J. M., A Phosphanyl-Phosphagallene that Functions as a Frustrated Lewis Pair. *Angew. Chem., Int. Ed.* **2020**, *59*, 20914-20918; (b) Sharma, M. K.; Wölper, C.; Haberhauer, G.; Schulz, S., Multi-Talented Gallaphosphene for Ga-P-Ga Heteroallyl Cation Generation, CO₂ Storage, and C(sp³)-H Bond Activation. *Angew. Chem., Int. Ed.* **2021**, *60*, 6784-6790.
20. Helling, C.; Wölper, C.; Schulz, S., Synthesis of a Gallaarsene [HC[C(Me)N-2,6-i-Pr₂-C₆H₃]₂]GaAsCp* Containing a Ga=As Double Bond. *J. Am. Chem. Soc.* **2018**, *140*, 5053-5056.
21. Ganesamoorthy, C.; Helling, C.; Wölper, C.; Frank, W.; Bill, E.; Cutsail, G. E.; Schulz, S., From stable Sb- and Bi-centered radicals to a compound with a Ga=Sb double bond. *Nat. Commun.* **2018**, *9*, 87.
22. Fischer, M.; Nees, S.; Kupfer, T.; Goettel, J. T.; Braunschweig, H.; Hering-Junghans, C., Isolable Phospha- and Arsaaluminenes. *J. Am. Chem. Soc.* **2021**, *143*, 4106-4111.
23. (a) Wright, R. J.; Phillips, A. D.; Allen, T. L.; Fink, W. H.; Power, P. P., Synthesis and Characterization of the Monomeric Imides Ar⁺MNAr⁺ (M = Ga or In; Ar⁺ or Ar⁺ = Terphenyl Ligands) with Two-Coordinate Gallium and Indium. *J. Am. Chem. Soc.* **2003**, *125*, 1694-1695; (b) Queen, J. D.; Irvankoski, S.; Fettinger, J. C.; Tuononen, H. M.; Power, P. P., A Monomeric Aluminum Imide (Iminoalane) with Al-N Triple-Bonding: Bonding Analysis and Dispersion Energy Stabilization. *J. Am. Chem. Soc.* **2021**, *143*, 6351-6356.
24. Lu, J.-S.; Yang, M.-C.; Su, M.-D., Triple-Bonded Boron≡Phosphorus Molecule: Is That Possible? *ACS Omega* **2018**, *3*, 76-85.
25. (a) Paetzold, P., Iminoboranes. In *Adv. Inorg. Chem.*, Emeléus, H. J.; Sharpe, A. G., Eds. Academic Press: 1987; Vol. 31, pp 123-170; (b) Paetzold, P.; Richter, A.; Thijssen, T.; Würtenberg, S., Bildung, Struktur und Reaktivität von (Pentafluorphenyl)bor-tert-butylimid und seinem Cyclodimeren. *Chem. Ber.* **1979**, *112*, 3811-3827.
26. (a) Nakano, R.; Jazzar, R.; Bertrand, G., A crystalline monosubstituted carbene. *Nat. Chem.* **2018**, *10*, 1196-1200; (b) Liu, L.; Ruiz, D. A.; Munz, D.; Bertrand, G., A Singlet Phosphinidene Stable at Room Temperature. *Chem* **2016**, *1*, 147-153.
27. (a) Asami, S.-s.; Ishida, S.; Iwamoto, T.; Suzuki, K.; Yamashita, M., Isolation and Characterization of Radical Anions Derived from a Boryl-Substituted Diphosphene. *Angew. Chem., Int. Ed.* **2017**, *56*, 1658-1662; (b) Weber, L., 1,3,2-Diazaboroly Anions - From Laboratory Curiosities to Versatile Reagents in Synthesis. *Eur. J. Inorg. Chem.* **2017**, *2017*, 3461-3488.
28. Ochiai, T.; Franz, D.; Inoue, S., Applications of N-heterocyclic imines in main group chemistry. *Chem. Soc. Rev.* **2016**, *45*, 6327-6344.
29. Feng, B.; Xiang, L.; Carpentier, A.; Maron, L.; Leng, X.; Chen, Y., Scandium-Terminal Boronylphosphinidene Complex. *J. Am. Chem. Soc.* **2021**, *143*, 2705-2709.
30. Savin, A.; Nesper, R.; Wengert, S.; Fässler, T. F., ELF: The Electron Localization Function. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1808-1832.
31. (a) Knizia, G., Intrinsic Atomic Orbitals: An Unbiased Bridge between Quantum Theory and Chemical Concepts. *J. Chem. Theory Comput.* **2013**, *9*, 4834-4843; (b) Knizia, G.; Klein, J. E. M. N., Electron Flow in Reaction Mechanisms—Revealed from First Principles. *Angew. Chem., Int. Ed.* **2015**, *54*, 5518-5522.
32. (a) Trinquier, G.; Malrieu, J. P.; Riviere, P., Unusual bonding in trans-bent digermene. *J. Am. Chem. Soc.* **1982**, *104*, 4529-4533; (b) Carter, E. A.; Goddard, W. A., III, Relation between singlet-triplet gaps and bond energies. *J. Phys. Chem.* **1986**, *90*, 998-1001; (c) Trinquier, G.; Malrieu, J. P., Nonclassical distortions at multiple bonds. *J. Am. Chem. Soc.* **1987**, *109*, 5303-5315; (d) Malrieu, J. P.; Trinquier, G., Trans-bending at double bonds. Occurrence and extent. *J. Am. Chem. Soc.* **1989**, *111*, 5916-5921.
33. (a) Ziegler, T.; Rauk, A., On the calculation of bonding energies by the Hartree Fock Slater method. *Theor. Chim. Acta* **1977**, *46*, 1-10; (b) Mitoraj, M.; Michalak, A., Donor-Acceptor Properties of Ligands from the Natural Orbitals for Chemical Valence. *Organometallics* **2007**, *26*, 6576-6580; (c) Mitoraj, M.; Michalak, A., Applications of natural orbitals for chemical valence in a description of bonding in conjugated molecules. *J. Mol. Model.* **2008**, *14*, 681-687.
34. Zhao, L.; Pan, S.; Holzmann, N.; Schwerdtfeger, P.; Frénking, G., Chemical Bonding and Bonding Models of Main-Group Compounds. *Chem. Rev.* **2019**, *119*, 8781-8845.
35. (a) Bushnell, G. W.; Rivett, G. A., The crystal structure of bis(diethylamino)dithiaboretane, a compound with a four-membered alternating boron-sulfur ring. *Can. J. Chem.* **1977**, *55*, 3294-3297; (b) Männig, D.; Narula, C. K.; Nöth, H.; Wietelmann, U., Beiträge zur Chemie des Bors, 159. [2 + 2]-Cycloadditionen von (tert-Butylimino)(2,2,6,6-tetramethylpiperidino)boran mit Kohlenstoffdichalkogeniden. *Chem. Ber.* **1985**, *118*, 3748-3758.

TOC:

Push-pull stabilization
Ambiphilic PB unit

