Ring Expansion

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1,2-Phosphaborines: Hybrid Inorganic/Organic P–B Analogues of Benzene

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Abstract: *Photolysis of the cyclic phosphine oligomer $[PPh]_5$ in the presence of pentaarylboroles leads to the formation of 1,2-phosphaborines by the formal insertion of a phenylphosphinidene fragment into the endocyclic C–B bond. The solid-state structure features a virtually planar central ring with bond lengths indicating significant delocalization. Appreciable ring current in the 1,2-phosphaborine core, detected in nuclear independent chemical shift (NICS) calculations, are consistent with aromatic character. These products are the first reported 1,2-BPC_4 conjugated heterocycles and open a new avenue for B–P as a valence isoelectronic substitute for C–C in arene systems.*

Faraday's discovery of benzene 190 years ago remains one of the most significant contributions to modern day chemistry.[1] The isoelectronic boron/nitrogen analogue borazine, often called "inorganic benzene", was prepared 101 years later.[2] Dewar and Marr united these inorganic and organic six-π-electron systems in the synthesis of the organic/inorganic hybrid boron–nitrogen-containing heterocycle 1,2-azaborine in 1962 (Figure 1).[3] Since this pioneering work, great progress has been made in the development of BNC_4 heteroaromatic systems.[4] Recently, the synthesis of the 1,3-B,N and 1,4-B,N isomers, accomplished by the groups of Liu and of Braunschweig, completed the series of hybrid organic/inorganic azaborine rings.[5] Out of the three isomers, the 1,2-azaborine isomer displays the highest degree of stability and has shown great promise for use in electronic materials and biomedical applications.[4c,6]

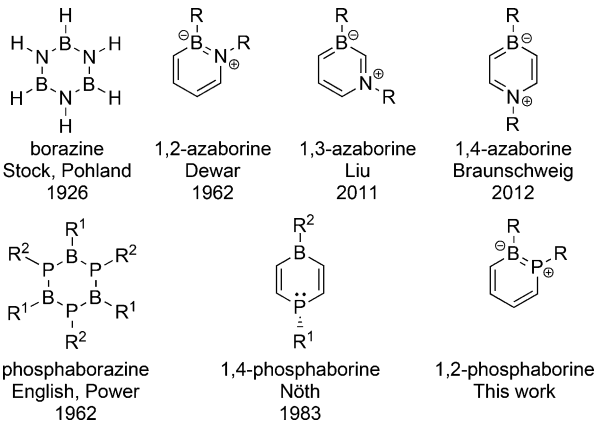

Figure 1. Unsaturated six-membered B,N and B,P heterocyclic compounds.

With regard to phosphorus–boron systems, much less progress has been made. In 1962 English reported the synthesis of the planar phosphorus congener of borazine, phosphaborazine $[(BR^1PR^2)_3]$, which was comprehensively characterized by Power and co-workers later in 1987.[7] On the basis of the X-ray structural and NMR data, the authors concluded that it had aromatic character.[7b,c,8] In the development of phosphorus–boron hybrid organic/inorganic heterocycles, the only reports are on the 1,4-phosphaborines,[9] compounds that feature a pyramidalized sp^3-hybridized phosphorus atom and thus a nonplanar phosphaborine ring. Surprisingly, a planar BPC_4 heterocycle has been elusive. We believed that the 1,2-phosphaborine derivatives would be planar as a result of the adjacent electron-rich phosphorus and electron-deficient boron centers imparting delocalization. The only study on this species was published earlier this year as a computational analysis of the parent 1,2-phosphaborine and its relationship to the other Dewar isomers.[10] The study revealed the six π-electron species as the thermodynamically stable isomer and a viable synthetic target.

To prepare the 1,2-phosphaborine, we sought inspiration from the nitrogen analogues. A particularly efficient and attractive route to synthesize 1,2-azaborine rings is the reaction of boroles[11] with azides.[12] This reaction is a formal 1,1-insertion of a nitrene fragment into an endocyclic C–B bond, and forms the ring-expanded 1,2-azaborine product in a single high-yielding synthetic step. Other studies have shown this ring expansion procedure with boroles through 1,1- or 1,2-insertion reactions with unsaturated small molecules to be an effective method for synthesizing six- or seven-membered boron heterocycles.[13] We envisioned that this method could be extended to a phosphinidene fragment, resulting in a 1,1-insertion into the borole C–B bond as a route to 1,2-phosphaborines.

Phosphinidenes are reactive intermediates that have eluded isolation.[14] The cyclic oligomeric phosphine $[PPh]_5$ reacts with nucleophilic carbenes to form the corresponding carbene–phosphinidene adducts, demonstrating that these species can act as sources of phosphinidene fragments.[15] In an attempt to prepare the 1,2-phosphaborine, pentaphenylborole (**1**) was reacted with $[PPh]_5$ in a 5:1 ratio. No evidence of any reaction at either ambient or elevated temperatures was detected based on in situ $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ NMR

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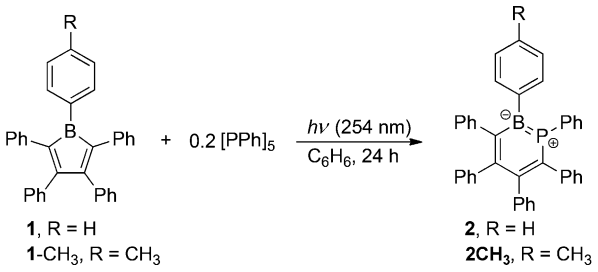
spectroscopy. As it is well established that UV irradiation is capable of inducing P–P bond cleavage in the photolytic conversion of white phosphorus into red phosphorus,[16] we were attracted to the report of Navech and co-workers speculating that the photolysis of $[PPh]_5$ formed phosphinidene fragments.[17] The experiment conducted in non-deoxygenated methanol produced H_2PPh, $(CH_3O)_2PPh$, and $HP(O)Ph(OCH_3)$, products believed to originate from the quenching of the photolytically generated phosphinidene fragments. To test this method under more controlled conditions, a degassed solution of $[PPh]_5$ was photolyzed ($\lambda = 254$ nm) in the presence of the known phosphinidene trapping agent 2,3-dimethylbutadiene.[18] In situ $^{31}P\{^1H\}$ NMR spectroscopy showed full conversion into the known products detected in trapping experiments with other phosphinidene sources.[19] This study, coupled with the work of Navech and co-workers, suggests that the photolysis of $[PPh]_5$ could act as a viable synthetic source of phosphinidene fragments.

Irradiation of a benzene solution of **1** and 0.2 equivalents of $[PPh]_5$ over 24 h led to a color change from the deep-blue color of **1** to bright yellow (Scheme 1). In situ NMR



Scheme 1. Synthesis of the 1,2-phosphaborines **2** and $\mathbf{2CH_3}$.

spectroscopy showed a major product in the $^{31}P\{^1H\}$ spectrum as a broad singlet at $\delta = 77.6$ ppm and a broad resonance in the $^{11}B\{^1H\}$ NMR spectrum at $\delta = 38.4$ ppm as well as the consumption of both starting materials. Crystals suitable for X-ray diffraction studies were grown by the slow evaporation of a CH_2Cl_2 solution and confirmed the product to be the desired hexaphenyl-1,2-phosphaborine **2**. Although the X-ray diffraction data could be used to determine the identity of **2**, disorder in the central BPC_4 ring from the six identical phenyl substituents prevented an accurate analysis of the endocyclic metrical parameters (see the Supporting Information). Similar issues have been encountered in studies of polyaryl-1,2-azaborines by Braunschweig and co-workers.[12a]

To reduce the symmetry and likelihood of disorder, we selected a borole bearing a methyl on the *para* position of the B-phenyl group of **1** in place of hydrogen ($\mathbf{1CH_3}$).[20] Conducting the analogous experiments produced a species with multinuclear NMR spectroscopic signals virtually identical to **2**, indicating the formation of the 1,2-phosphaborine product $\mathbf{2CH_3}$ ($\mathbf{2CH_3}$: $^{31}P\{^1H\}$ $\delta = 76.9$, $^{11}B\{^1H\}$ $\delta = 38.9$ ppm).

Crystals of $\mathbf{2CH_3}$ were grown by the slow evaporation of a CH_2Cl_2 solution and were analyzed by X-ray diffraction (Figure 2). The presence of the *p*-tolyl moiety in $\mathbf{2CH_3}$ was indeed sufficient to prevent disorder in the solid state,

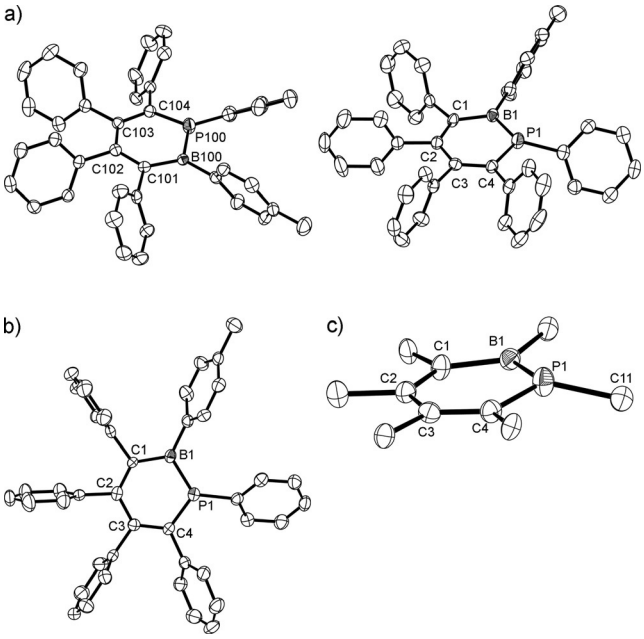


Figure 2. a) The asymmetric unit of the solid-state structure of $\mathbf{2CH_3}$. Thermal ellipsoids are set at 50% probability and hydrogen atoms have been removed for clarity. Two molecules crystallized in the asymmetric unit; the metrical parameters for each are listed sequentially. Selected bond lengths [Å] and angles [°]: C1–B1 1.526(4), B1–P1 1.799(3), P1–C4 1.721(3), C3–C4 1.394(4), C2–C3 1.435(4), C1–C2 1.407(4), C1-B1-P1 111.7(2), B1-P1-C4 113.07(14), P1-C4-C3 119.2(2), C4-C3-C2 124.6(3), C3-C2-C1 125.6(3), C2-C1-B1 125.8(3); C100–B100 1.525(4), B100–P100 1.790(3), P100–C104 1.719(3), C103–C104 1.398(4), C102–C103 1.443(4), C101–C102 1.407(4), C100-B100-P100 112.7(2), B100-P100-C104 112.51(14), P100-C104-C103 119.5(2), C104-C103-C101 124.2(2), C103-C102-C101 125.3(2), C102-C101-B100 125.5(2). b) One of the independent molecules of $\mathbf{2CH_3}$ with a view perpendicular to the BPC_4 plane. c) Simplified view along the BPC_4 plane (carbon atoms from aryl groups except *ipso* carbons have been removed).

permitting an analysis of the 1,2-phosphaborine core. Two independent molecules crystallized in the asymmetric unit and their metrical parameters are virtually identical; the average values of the two molecules are discussed (both values are listed in the caption of Figure 2). The BPC_4 ring of $\mathbf{2CH_3}$ is highly planar with an average maximum deviation from the idealized BPC_4 plane of 0.03 Å. The boron center has a trigonal planar coordination geometry (sum of angles = 359.8(3)°), as are the endocyclic carbon atoms (sum of angles = 359.9(3)°, 359.9(3)°, 360.0(3)° and 359.7(2)°). The phosphorus atom deviates slightly from planarity with a sum of angles of 357.5(2)°. The C–C and C–B bond lengths correspond to those reported for similarly substituted 1,2-azaborines and are intermediate between single and double bonds.[12a] The phosphorus–boron bond length lies within the range of previously reported P=B double bonds (1.795(3) Å versus 1.76–1.84 Å),[21] suggesting that $\mathbf{2CH_3}$ has a bond order much greater than one. The C–P bond length is considerably shorter than a typical C–P single bond and is similar to those reported for the aromatic phosphorus heterocycle phosphinine (1.720(3) Å versus 1.73–1.76 Å).[22] Collectively, all of the

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metrical parameters indicate significant delocalization within the conjugated π system.

The UV/Vis absorption spectra of **2** and **2CH$_3$** are very similar with lowest-energy absorption maxima at $\lambda =$ 366 nm ($\varepsilon = 6200\ L\,mol^{-1}\,cm^{-1}$) and at $\lambda = 367$ nm ($\varepsilon =$ $6400\ L\,mol^{-1}\,cm^{-1}$), respectively. These are notably red-shifted in comparison to the corresponding B,N congener hexaphenyl-1,2-azaborine (lowest-energy absorption maxima $\lambda = 315$ nm). This indicates that the incorporation of the phosphorus atom into the ring has a significant effect on the electronic structure.

The aromatic nature of the 1,2-phosphaborine core of **2CH$_3$** was also investigated theoretically. Selected molecular orbitals exhibiting π-type bonding interactions in the central ring are depicted in Figure 3. The HOMO clearly shows an

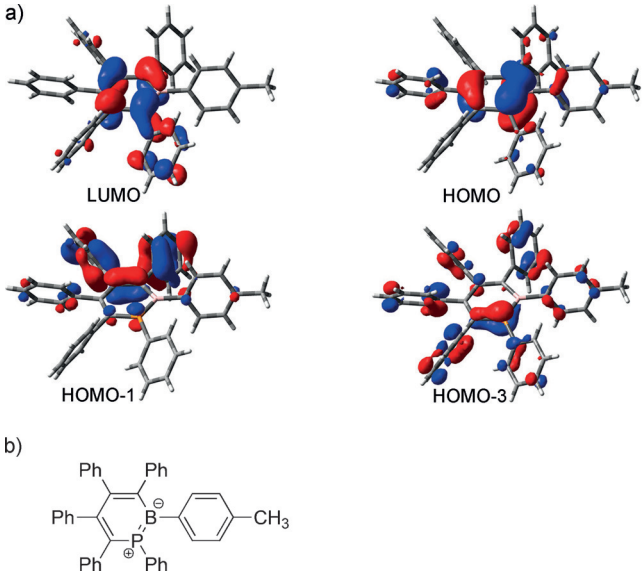

Figure 3. a) Frontier orbitals of 2-(4-tolyl)-1,3,4,5,6-pentaphenyl-1,2-phosphaborine (**2CH$_3$**) depicting inner ring contributions to the aromaticity at an isovalue of 0.04 a.u. b) Orientation of compound **2CH$_3$** as depicted in above images. Computed with DFT HSE06 6-311+G(d,p).

orbital with bonding contributions between boron and phosphorus with π character. Nuclear independent chemical shielding (NICS) indices were calculated using the Gaussian 09 suite. Density functional theory (DFT) was applied to the solid-state structure coordinates of **2CH$_3$** with the exchange-correlation approximation HSE06 hybrid functional and the Pople basis 6-311+G(d,p). The diatropic ring currents were determined by a series of ghost elements placed normal to the central ring. The first of these ghost elements NICS(0) corresponds to the σ–π contribution to aromaticity and NICS(1)$_{ZZ}$ corresponds to the π–π contribution to aromaticity of the 1,2-phosphaborine. The computed NICS(0) and NICS(1)$_{ZZ}$ values were −6.00 ppm and −17.65 ppm, respectively. Comparing these values to those calculated for the aromatic compounds benzene (NICS(0) −8.18 ppm, NICS(1)$_{zz}$ −29.68 ppm) and 1,2-dihydroazaborine (NICS(0) −5.15 ppm, NICS(1)$_{zz}$ −20.15 ppm), suggest that moderate delocalization of π-electron density occurs within the central BPC_4 ring of **2CH$_3$**. The metrical parameters are consistent with sp^2-hybridized atoms within the central ring.[23] These data and the planarity of 1,2-phosphaborine indicate that these molecular species feature a moderate degree of aromaticity.

In conclusion, we have exploited the propensity for boroles to undergo ring expansion reactions to synthesize the hitherto unknown 1,2-phosphaborines in a single synthetic step. The unique synthetic route involves the generation of a phosphinidene synthon from the photolysis of a cyclic phosphine pentamer and is the first report of such of a method in targeted synthesis. The solid-state structure of the 1,2-phosphaborine exhibits a planar BPC_4 central ring with short bond lengths indicative of appreciable delocalization. Theoretical calculations confirmed that a moderate degree of aromaticity is present in these systems. This discovery opens an exciting field of exploring P–B units as a valence isoelectronic replacement for C–C to generate novel hybrid organic/inorganic conjugated systems.

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[23] Detailed tables comparing $^{11}B\{^{1}H\}$ NMR, $^{13}C\{^{1}H\}$ NMR as well as structural data of the 1,2-phosphaborine with hexaaryl-1,2-azaborine and hexaphenylbenzene have been included in the Supporting Information that further indicate that the feature compounds have moderate aromatic character.

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