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Hydroboration of Phosphaalkynes by HB(C₆F₅)₂


Abstract: The hydroboration of phosphaalkynes with Piers’ borane (HB(C₆F₅)₂) generates unusual phosphaalkenyloboranes [RCH=PB(C₆F₅)₂]₂ that persist as dimers in solution and the solid state. These P₂B₂ heterocycles undergo ring opening when subjected to nucleophiles, such as pyridine and tert-butylisocyanide, to yield monomeric phosphaalkenyloborane adducts RCH=PB(C₆F₅)₂(L). DFT calculations were performed to probe the nature of the interaction of phosphaalkynes with boranes.

Hydroboration is a powerful chemical transformation in which B–H bonds are added across unsaturated units in alkenes, olefins, imines, and carbonyl compounds.[1] These additions are typically facilitated by transition metal catalysts.[2] The widespread utility of this chemical reaction in organic synthesis has been realized since the initial work by H.C. Brown in the 1960s.[3] Although related chemistry has been achieved to exploit the utility of carboraborations[4] and haloborations,[5] more recent innovations have included the development of metal-free catalysts for hydroboration and the specific design of borenium catalysts for trans-hydroborations of alkenes.[6] Despite the broad utility of hydroboration in organic chemistry, exploitation of this reaction in main group inorganic chemistry has drawn little attention.

The isolation of stable, singlet P₂B₂ diradicaloids by Bertrand and co-workers[7] and the advent of frustrated Lewis pairs (FLPs)[8] are two examples of chemistry that has focused attention on compounds containing phosphorus and boron. In seeking to exploit hydroboration for the preparation of novel P/B compounds, we noted that low-coordinate phosphorus species such as phosphaalkenes[9] and phosphaalkynes,[10] have a rich and diverse reactivity but few examples of boron-containing derivatives exist.[11] Phosphaalkynes have been reported to react with BBr₃ to yield 1,2-addition products (Figure 1 A).[12] and also polyhedral boranes, resulting in either linkage of B₃ units by phosphaalkene fragments[13] or incorporation of the P=≡C fragment into the polyhedral cluster.[14] Phosphaalkynes have also been shown to insert into boroles[15] and a Ti-phosphaalkyne complex was observed to undergo addition of HBE₂ to afford a unique P/B-Ti complex (Figure 1, B).[16]

Aside from Ti species B, the direct addition of an R₂B–H bond to a phosphaalkyne has been reported only once, to the best of our knowledge. In that case, the double hydroboration of tert-butylphosphaalkyne (BuC≡P 1a) with HBCat (Cat = catechol) generated a gem-diboryl substituted primary phosphine (Figure 1, C).[17] The regiochemistry of this 1,2-addition reaction is governed by the electronegativity difference between carbon and phosphorus and the inherent polarity of the (P≡C) bond.[18] This regiochemistry of 1,2-addition has also been observed in related hydrogermylation[18] and hydrostannation chemistry.[19] In contrast, the aforementioned reaction of HBE₂ with a Ti-phosphaalkyne complex resulted in B–P bond formation.[19] Although this reaction does not involve B–H addition to the P≡C bond, it suggests that steric demands might also play a role in determining the regiochemistry of phosphaalkyne addition reactions. Herein we report the reaction of phosphaalkynes with the highly electrophilic borane HB(C₆F₅)₂,[20] which affords the first examples of simple B–P bonded phosphaalkenyloboranes and a novel class of P/B heterocycles.

![Figure 1 Reported products arising from reactions between phosphaalkynes and boranes.](image)

To study the reactivity of phosphaalkynes with highly electrophilic boranes, 1a was exposed to one equivalent of the strong Lewis acid B(C₆F₅)₃. Multinuclear NMR spectroscopy showed no evidence of coordination or carboraboration[4] even after prolonged heating, in contrast to the reactivity of B(C₆F₅)₃ with alkynes. We attribute the lack of interaction to the low basicity and nucleophilicity of the P–centre.[21] Similarly, treatment of 1a with B(C₆F₅)₃/PtBu₃ or B(C₆F₅)₃/PPh₃ at ambient or elevated temperatures showed no addition across the P≡C bond, in contrast to the reported reactivity of frustrated Lewis pairs (FLPs) with C≡C bonds.[22] Treatment of 1a with one equivalent of Piers’ borane (HB(C₆F₅)₂)[20] in CH₂Cl₂, however, afforded a colourless crystalline solid 2a in 67% yield after workup (Scheme 1). Single crystals for X-ray diffraction were obtained via diffusion of pentane into a CH₂Cl₂ solution of 2a at -35 °C (Figure 2a). The solid state structure revealed that hydroboration of the phosphaalkyne had occurred and produced a phosphaalkenyloborane, which dimerized to form a P₃B₂ four-membered ring.[23] The phosphaalkene P=≡C bond lengths were 1.651(2) and 1.6470(19) Å. The P₂B₂ ring is distorted from planarity in a butterfly conformation featuring a dihedral angle of 23.32(8)°.

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angles of 81.14(8°) and 81.01(8°), and B–P–B bond angles of 96.17(9°) and 96.24(9°) were found in the central ring. The P–B bond lengths in 2a ranged from 2.009(2) – 2.013(2) Å; these distances are at the short end of those of phosphinoborane dimers, [P2B2–P–P]2, which range from 2.004(4) to 2.096(5) Å, but are longer than those of P2B2 diradicaloids, which range from 1.8904(15) to 1.900(2) Å. The short P–B distances in 2a are perhaps due to the reduced steric demands of the bridging phosphaalkyne units or the hybridization of the P-centre.

![Figure 2](image)

**Figure 2** POV-ray depictions of (a) 2a and (b) 2b. H atoms omitted for clarity. C: black, B: yellow-green, F: pink, P: orange.

The 11B NMR spectrum of 2a revealed a sharp singlet at -5.3 ppm and the 19F NMR spectrum showed three resonances at -127, -153, and -162 ppm. These data support the assignment of 2a as a four-coordinate boron species, consistent with a dimer in solution. 31P NMR data revealed a broad singlet at 183 ppm, a drastic downfield change in chemical shift from that of phosphonalkyne 1a (-69 ppm)[11a], consistent with the formation of a phosphaalkene. The 1H NMR spectrum showed two resonances at 8.03 and 1.04 ppm, with relative integrations of 1:9, which were assigned as the olefinic and tBu resonances, respectively. Surprisingly, the resonance at 8.03 ppm appears as a triplet with an apparent coupling constant of J = 8.2 Hz. The triplet resonance persists even when recorded at differing magnetic field strengths and temperatures (25 to -35 °C). The 1H(31P) spectrum, however, reveals this resonance as a singlet, indicating that the fine structure of the signal arose from coupling between the H and P nuclei. 33C[1H] NMR data showed resonances at 178, 41, and 30 ppm, all of which are apparent triplets. The multiplicity of the 1H and 13C NMR signals appears to arise from virtual coupling to the pair of strongly coupled 31P nuclei in 2a. The two putatively coupled boron centres in 2a have identical chemical shifts in solution and thus do not exhibit any coupling to each other. A similar phenomenon has been observed for *trans*-diphosphine metal complexes,[23] and the structurally analogous dimeric four-membered heterocycle [Li2PPh2]4.[24] Further confirmation of this interpretation is derived from ssNMR data. Fortuitously, dimer 2a sits on a general position in the solid state and thus the two P-centres are crystallographically inequivalent. Consequently, the CP-MAS ssNMR 31P[1H] spectrum of 2a (Figure S33) exhibits two 31P resonances that couple to each other with JPH ~ 1520 Hz. Simulation of the solution state 1H NMR resonance of the olefinic proton of 2a as an AXB multiplet using 1520 Hz as JAB suggests that the coupling between the two phosphorus centres is sufficiently large to collapse the second order ABX multiplet into an apparent triplet (Figure S34).

Given the difference in the electronegativities of carbon and phosphorus, and the polar nature of the P≡C bond, it is interesting to note that the hydroboronation occurs with formation of P–B and C–H bonds. This pattern of reactivity stands in contrast to literature reports of B–H,[17] Ge–H,[18] and Sn–H[19] phosphaalkyne addition reactions, in which hydride adds to the more electrophilic phosphorus affording a P–H bond. Interestingly, the formation of 2a is more akin to reactions of phosphaalkynes with Ru–H species described by Hill, Jones[27] and Crossley,[28] reinforcing the analogy between electrophilic boranes and transition metals. We also noted that, unlike the previously reported double addition of HBCat to phosphaalkyne,[17] Piers’ borane undergoes a single 1,2-addition to 1a, and any excess borane remains unreacted in solution, as evidenced by multinuclear NMR spectroscopy.

![Scheme 1](image)

**Scheme 1.** Reactions of phosphaalkynes 1a/b with HB(C6F5)2 to produce 2a/b.

To probe the mechanism of reaction and the observed regiochemistry in the formation of 2a, DFT computations were performed. Inspection of the f(r) Fukui function clearly reveals that the site of electrophilic attack is the P≡C triple bond, and not the lone pair on the phosphorus atom (Figure S36). This view is in accord with the partial positive charge on the phosphorus atom resulting from the difference in electronegativity between phosphorus and carbon. Relaxed potential energy surface (PES) scans of the distance between the centre of the P≡C triple bond and the boron atom of either Piers’ borane or B(C6F5)3 were performed. These surface scans reveal that the energy of the system experiences a minimum as Piers’ borane approaches the triple bond. In contrast, the energy monotonically rises as B(C6F5)3 and phosphaalkyne approach one another (Figure S35). The latter result suggests that steric repulsion between the C6F5 rings and the tert-butyl group precludes approach of B(C6F5)3 and the nucleophilic r cloud of the phosphaalkyne. The minimum from the PES scan with Piers’ borane was used as the starting point for a geometry optimization. In the optimized configuration, the BH is directed towards the carbon atom of the phosphaalkyne (Figure 3). This configuration is favourable as it minimizes steric interactions between the C6F5 rings and the tert-butyl group. These results are congruent with chemical intuition and account for the lack of reactivity with B(C6F5)3 and the observed regiochemistry of the reaction with Piers’ borane.
The analogous reaction of 1-adamantlyphosphaalkyne (1-Ad=PC≡P 1b) with Piers’ borane resulted in formation of the dimeric species 2b in 68% yield (Scheme 1). Compound 2b also shows virtual coupling of the P-atoms to $^1$H and $^{13}$C nuclei in solution state NMR spectra. However, unlike 2a, the P$_2$B$_2$ unit of 2b is centrosymmetric in the solid state (Figure 2b), with $^3$P–$^3$P distances of 2.021(3) and 2.023(4) Å. The $^3$P–$^3$C and $^3$P–$^3$P angles were found to be 98.5(1)$^\circ$ and 81.5(1)$^\circ$, respectively, and the P–C double bond length is 1.649(3) Å, similar to that of 2a.

![Figure 3. Ball-and-stick (a and b) and space-filling (c and d) depictions of the optimized geometry of Piers’ borane approaching 1a viewed from top (left) and side (right). H: white; C: black; B: yellow-green; F: pink; P: orange.](image)

Investigations of the reactivity of dimers 2a/b revealed their thermal instability. Both decompose in C$_6$D$_5$Br with modest heat (60 °C) or upon standing at room temperature in halogenated solvents over several hours. Given the short P–B bond lengths and the strong NMR spectroscopic coupling observed in 2a/b, we anticipated the dimers to be unreactive towards small molecules. Indeed, 2a shows no reactivity with H$_2$, CO$_2$, or CO. Upon treatment with tert-butylisocyanide, however, a rapid and clean reaction occurred, affording a new species 3a, which we propose to be the monomeric phosphaalkenylborane adduct (Scheme 2). This assignment was supported by loss of the $^1$H NMR virtual triplet of 2a, and the appearance of a doublet at 8.75 ppm with $J = 24$ Hz. Compound 3a gives rise to a $^{19}$F NMR spectrum comprising three resonances at -130, -157, and -163 ppm, while the $^{11}$B NMR resonance appears at -22 ppm. The $^{31}$P[$^1$H] NMR spectrum features a pentet at 266 ppm, with $J = 36$ Hz, while in the $^{31}$P[$^{19}$F] spectrum, the resonance collapsed to a doublet with $J = 24$ Hz. This evidence suggests that the phosphorus centre couples to both the olefinic proton and the four ortho-fluorines of the two C$_6$F$_5$ rings. This reactivity contrasts with that of phosphinoborane dimers [(C$_6$F$_5$)$_2$BPR$_3$] which proved unreactive toward donor molecules. Collectively these data are consistent with the formulation of 3a as $^{t}$BuCH=$^{t}$PB(C$_6$F$_5$)$_2$(tBuNC).

Scheme 2. Reactions of dimers 2a/b with tert-butylisocyanide and pyridine to produce 3a/b and 4a, respectively.

![Figure 4. Pov-ray depiction of (a) 4a and (b) 3b. H atoms omitted for clarity. C: black; B: yellow-green; F: pink; N: blue; P: orange.](image)

The adduct 3a was consistently isolated as a pale oil, so analogous chemistry with 2b was undertaken with the goal of obtaining crystallographic data. Compound 2b also reacted cleanly with tert-butylisocyanide, affording (1-Ad)CH=PB(C$_6$F$_5$)$_2$(tBuNC) 3b, which was confirmed crystallographically. Additionally, when 2a was treated with pyridine, the resulting adduct $^{t}$BuCH=PB(C$_6$F$_5$)$_2$(pyr) 4a could be isolated as a crystalline material (Scheme 2). Species 3b exhibits solution NMR spectra with similar properties to those of 3a, while 4a has a $^{11}$B NMR resonance at -0.8 ppm. X-ray data for both 3b and 4a confirmed the formulations (Figure 4). For both molecules, the B-centre adopts a pseudo-tetrahedral geometry. The average B–C$_{so(yane)}$ bond distance of 3b is 1.61(1) Å, and the B–N bond distance of 4a is 1.612(3) Å. The P–B bond lengths average 2.040(7) Å in 3b and was found to be 2.029(2) Å in 4a. These P–B distances are significantly longer than those of (C$_6$F$_5$)$_2$BPR$_2$ (R = $^{t}$Bu, Cy) which were found to be 1.786(4) Å and 1.762(4) Å. This difference presumably reflects the poorer sigma-donor ability of sp$^2$ vs sp$^3$ phosphorus. The P–C bond lengths average 1.657(6) Å in 3b and 1.669(2) Å in 4a with B–P–C average angles of 103.7(3)$^\circ$ and 105.1(1)$^\circ$, respectively. These P–C bond lengths fall within the range typically observed for phosphaalkenes (1.661(6)-1.690(2) Å). These represent the first examples of phosphaalkenylboranes to be synthesized, and crystallographically characterized.
rings of these compounds were readily cleaved in the presence of donors, affording monomeric phosphaalkenylborane adducts. The products 2, 3, and 4 are unique examples of phosphaalkenynes and illustrate the impact of electrophilic acceptors on the regiochemistry of the hydroboration of phosphaalkynes. This is a motif that has, to the best of our knowledge, not yet been reported. Efforts to study these unusual P/B systems and exploit their reactivity are ongoing.

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