Hydrophosphination of boron–boron multiple bonds†

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Five compounds containing boron–boron multiple bonds are shown to undergo hydrophosphination reactions with diphenylphosphine in the absence of a catalyst. With diborenes, the products obtained are highly dependent on the substitution pattern at the boron atoms, with both 1,1- and 1,2-hydrophosphinations observed. With a symmetrical diboryne, 1,2-hydrophosphination yields a hydro(phosphino)diborene. The different mechanistic pathways for the hydrophosphination of diborenes are rationalised with the aid of density functional theory calculations.

Introduction

Compounds containing covalent bonds between phosphorus and boron, while not enjoying the ubiquity of their nitrogen–boron analogues, display a rich chemistry.1–3 Phosphinoboranes – that is, compounds of the form R2B=PR2 4 with a planar geometry at phosphorus and partial double bond character5 – can undergo addition reactions with such substrates as H2,6,7 ketones6 and dienes6 and coordinate in an η2 fashion to transition metals.8 Borylphosphines, in which the boron atom is not π-acidic (e.g. due to π-donor or carborane substituents) and phosphorus thus retains its lone pair and tetrahedral geometry, are highly electron rich η1 ligands for transition metal complexes.9,10 By far the most common route for the construction of P–B bonds is salt elimination11–13 using an alkali metal phosphide, MPR2, and a haloborane (Scheme 1A), although other routes are known, including nucleophilic addition of a boryl anion to a chlorophosphine (B),14 elimination of silyl halide (C),10,11,15 and cross-coupling of a B–I species with secondary phosphines using a palladium catalyst (D).9

Of the different synthetic options for the construction of phosphorus–carbon bonds, hydrophosphination of unsaturated carbon substrates has gained popularity in recent years.22–24 Advantages of this method over typical nucleophilic addition reactions include reduced waste (hydrophosphination is a 100% atom-economical process) and increased functional group tolerance due to the avoidance of highly reactive Grignard or organolithium reagents. However, these reactions typically require a catalyst in the form of a base or metal complex, or a radical initiator, and the scope is somewhat limited in terms of which secondary phosphines can be used. Whereas P–H bond activation at transition25 and main-group26 metal centres is well documented, to the best of our knowledge the sole reported example of hydrophosphination of a homonuclear double bond comprising elements other than carbon is the 2016 report by Wang and Wu of hydrophosphination of the

Scheme 1 Reported methods for the construction of covalent boron–phosphorus bonds.
N=N bond in azobenzene with diphenylphosphine oxide. Recent studies in our laboratories have demonstrated the feasibility of adding H–H,28,29 B–H,30–32 B–B,33,34 S–S35,36 and Se–Se37 bonds across boron–boron multiple bonds. In this work, we show that uncatalysed hydrophosphination of both diborenes and diborynes can be used as a mild, selective and catalyst-free route to construct B–P bonds.

Results and discussion

Diborenes based on a chelating benzylphosphine group37 that holds the aryl substituent in the plane of the boron–boron π-bond have shown particularly high reactivity towards dienes38 and diboranes,39 so we chose these compounds as a starting point. The symmetrical diborene 1 was treated with diphenylphosphine at room temperature, leading to slow conversion to a compound with signals in the $^1$B NMR spectrum at $-15.9$ and $-27.2$ ppm, both in the region expected for four-coordinate boron atoms. Heating the mixture to $60 \degree C$ for 1 h resulted in the decolouration of the solution and full conversion to the product, which was isolated as a colourless solid after workup in 79% yield. X-ray diffraction on single crystals grown from a diethyl ether solution confirmed the structure as that of product 5, the result of a 1,2-hydrophosphination across the B–B bond (Scheme 2 and Fig. 1). The PPh$_2$ and hydrogen substituents display a gauche conformation, while the benzylphosphine units have reverted to a vicinal (1,2-) coordination mode; in contrast to other compounds bearing this substituent,38 no conversion to the geminal isomer was observed. At 2.051(2) Å, the B1–P1 bond is in the range of published base-stabilised borylphosphines,15 and markedly longer than both dative B–P bonds in the molecule (B1–P2 = 2.008(2), B2–P3 = 1.928(2) Å). As expected, P1 is highly pyramidal, with a sum of angles of 312.4°. In the $^1$H NMR spectrum,
a multiplet centred at 3.08 ppm becomes visible upon $^{11}$B decoupling, corresponding to the newly formed B–H group. Two signals at 10.4 ppm and 6.1 ppm in the $^{31}$P NMR spectrum correspond to the now inequivalent benzylphosphine phosphorus atoms, whereas the PPh$_2$ group is represented by a broad signal at $–13.3$ ppm.

Unsymmetrically-substituted diboron compounds are known to display higher reactivity than their symmetrical counterparts.\cite{1,2} We have previously shown that unsymmetrical diborones 2 and 3 (Scheme 2) react more quickly than 1 in diboration reactions with B$_2$cat$_2$.\cite{3} Treatment of compound 2 with HPPH$_2$ resulted in complete conversion to a new compound within 3 h at room temperature. Signals in the $^{11}$B NMR spectrum at $–7.7$ and $–34.2$ ppm again indicated the presence of inequivalent, four-coordinate boron atoms. Three broad signals in the $^{31}$P NMR spectrum at 23.1, 13.8 and $–6.9$ ppm also suggested three boron-bound phosphorus environments. Measurement of a $^1$H NMR spectrum with selective $^{11}$B decoupling ($\delta$$_{11B}$ offset = $–34$ ppm) again revealed a complex multiplet for a B–H moiety at 2.15 ppm. X-ray diffraction confirmed the product as 6, the result of a formal 1,1-hydrophosphination rather than the expected 1,2-addition across the double bond (Fig. 1). The B1–B2 distance (1.777(3) Å) and B–P distances (B1–P1 = 1.974(2), B1–P2 = 1.932(2), B2–P3 = 1.953(2) Å) lie in the respective expected ranges. N-Heterocyclic-carbene (NHC) supported diborone 3 also undergoes a rapid reaction with HPPH$_2$ at room temperature to give a compound with $^{11}$B NMR signals at $–21.6$ and $–37.6$ ppm. In this case however, a sharp doublet in the $^{31}$P NMR spectrum at $–70.9$ ppm alongside a broader signal at 8.9 ppm suggested a different outcome. The insolubility of the compound in benzene and tetrahydrofuran also led us to suspect an ion-separated structure. Single crystals obtained from a dichloromethane/pentane solution allowed determination of the structure by X-ray diffraction (Fig. 1), which confirmed the compound to be cationic diborane(5) $^7$, bearing a Br$–$ counterion. Here, the PPh$_2$ unit bridges the two boron atoms almost symmetrically (B1–P1 = 1.948(4) Å, B2–P1 = 1.918(4) Å). Such three-membered rings are far from common – the only structurally characterised examples of non-cluster B$_2$P rings are the butterfly-shaped B$_2$P$_2$ diradicals reported by Bertrand and co-workers.\cite{41,42}

As reported recently, compound 2 rearranges upon heating to its more thermodynamically stable isomer, 4, which possesses a polarised boron–boron bond and a borylborylene resonance form.\cite{35} Whereas one might expect such a compound to undergo 1,1-addition reactions to the “borylene” boron atom, both 4 (ref. 33) and a related compound reported by Kinjo’s group\cite{4} give 1,2-addition products with B$_2$cat$_2$. Compound 4 reacts instantaneously with HPPH$_2$ upon solvation in C$_6$D$_6$, to give different NMR signals to those seen in the corresponding reaction with 2. In the $^{11}$B NMR spectrum, two signals at 1.5 and $–33.4$ ppm are observed, whereas the $^{31}$P NMR spectrum reveals two broad signals at 16.4 and $–7.8$ ppm and a pseudo-triplet at $–20.5$ ppm. Reduction of the volume of the reaction mixture gave single crystals of the product, which were shown by X-ray diffraction to be 1,2-hydrophosphination product 8 (Fig. 1). As with the diboration product of 4, compound 8 can be drawn as a borylene–borane adduct. However, it is notable that the B–B distance (1.789(4) Å) and the B–P distances (B2–P1 = 1.986(4), B1–P2 = 1.938(3), B1–P3 = 1.935(4) Å) are statistically indistinguishable from those in its constitutional isomer 6, indicating that the electronic situation at the B$_2$ units may not be as different as these formalisms suggest.

To gain mechanistic insight into how different hydrophosphination outcomes were obtained using the diboron compounds 1–4, DFT computations at the oB97XD/6-31+g(d,p)/SMD//oB97XD/6-31g(d,p) level of theory were performed. For computations, truncated models of diborones, A1–D1, in which the cyclohexyl substituents of the chelating phosphines were replaced with methyl groups, were examined. The 1,1- and 1,2-hydrophosphination reactions observed are significantly exergonic, with $\Delta$G values ranging from $–23.9$ to $–38.4$ kcal mol$^{-1}$ (Fig. 2 and 3). For the 1,2-hydrophosphination of diborone 1, yielding product 5, the likely mechanism is shown in Fig. 2a. Initially, coordination of HPPH$_2$ to one of the boron atoms affords adduct A2. This is followed by a 1,3-H shift from the coordinated HPPH$_2$ to the distal boron atom, leading to the formation of a 1,2-hydrophosphinated intermediate A3, with the PPh$_2$ and H units located syn to one another. This intermediate subsequently rearranges via phosphine dissociation/association to form the product A6. For this reaction, the 1,3-H shift step was found to be rate limiting and has a barrier of 33.7 kcal mol$^{-1}$ (TSA[2–3]). The calculated barrier for this pathway is seemingly high for a room-temperature reaction, and we attribute this to the use of methyl groups rather than cyclohexyl groups in the calculations. The energy reduction due to the London dispersion effect\cite{63} from the bulky cyclohexyl groups is lost, which affects the crowded transition state more than the starting diborone. Two other reasonable mechanistic possibilities for this reaction were also explored, both of which gave higher barriers (see ESIF).

For the conversion of diborone 2 into 6, the proposed mechanism (Fig. 2b) involves (i) an initial coordination of HPPH$_2$ to the boron centre that bears the electronegative bromide substituent and the chelating phosphate ligand, (ii) stepwise transfer (dissociation and association) of the bromide to the adjacent boron atom and (iii) 1,2-H shift from the coordinated HPPH$_2$ to the proximal boron atom, leading to the formation of 1,1-hydrophosphinated product B5. Here, the rate limiting step is the 1,2-H shift, which has a barrier of 31.9 kcal mol$^{-1}$. Our efforts to locate a transition state for a direct bromide shift from B2 to B4, or to find the minimum energy structure of a bromide-bridged intermediate, were unsuccessful. All transition state optimization efforts led to dissociation of either bromide or HPPH$_2$. Minimization attempts to find the bromide-bridged intermediate led to convergence to one of the non-bridging intermediates B2 and B4. Use of a highly truncated model with hydrogen substituents at all phosphorus atoms produced a single transition state for a direct bromide shift, but the free energy barrier of 66.8 kcal mol$^{-1}$ is too high to represent a feasible mechanism (see ESIF). Thus, a dissociative pathway was proposed. Other additional mechanistic pathways were examined, but were...
found to have higher barriers than that described above. We also investigated the corresponding 1,2-hydrophosphination of \( \text{B1} \), which was confirmed to have a slightly higher overall barrier than the 1,1-addition.

For the cyclic product 7, obtained from the reaction between HPPH\(_2\) and the unsymmetrical, NHC-substituted diborene 3, a similar mechanistic pathway to that of \( \text{B1} \) was investigated (Fig. 2c). In contrast to the \( \text{B1} \) case, complexation of HPPH\(_2\) to diborene \( \text{C1} \) only occurs after initial dissociation of the bromide ion. This difference can be primarily attributed to the large steric hindrance exerted by the two isopropyl peripheries of the NHC ligand as well as ample charge flow from the NHC to the distal boron centre. Unlike in \( \text{B1} \), the dissociated bromide cannot feasibly bind to the adjacent boron in cationic intermediate \( \text{C3} \), again due to the strong electron donation and steric hindrance of the NHC ligand. As a result, \( \text{C3} \) is forced to undergo a 1,2-proton shift from the coordinated HPPH\(_2\), leading to the formation of 1,1-hydrophosphinated cationic intermediate \( \text{C4} \), with the positive charge predominantly localised at the NHC-coordinated boron centre. As a means to alleviate the electron deficiency at this boron centre, in the subsequent step the phosphinyl substituent establishes a dative interaction, leading to the observed product \( \text{C5} \). For this reaction, an overall barrier of 31.1 kcal mol\(^{-1} \) was found for the 1,2-H shift step.

The mechanistic pathway for the 1,2-hydrophosphination of borylborylene 4 to form 8 can be described straightforwardly (Fig. 3). Given that the boron atom of the boryl unit holds a partial positive charge (\textit{vide infra}), it can easily bind the incoming phosphine. The resulting loss of \( \pi \)-delocalisation of the borylene lone pair leaves it strongly localised, and in the
ensuing step a protic 1,3-H shift from the HPPH₂ unit to the borylene boron atom occurs, affording the product D₃. This rate limiting step has a barrier of only 27.5 kcal mol⁻¹, which is the lowest among the reactions investigated. Notably, the inverse addition of the P-H bond across the diborene is strongly disfavoured (see ESIF), supporting the selectivity to the observed product.

To understand why diborene 1 and borylene 4 prefer 1,2-hydrophosphination, while diborenes 2 and 3 undergo 1,1-hydrophosphination, a selection of NPA partial charges were analysed (Table 1). The symmetrical diborene A₁ displays negative charge on both boron atoms (entry 2, parentheses), as expected for diborenes. In line with our previous analysis of the Hirshfeld charges of the unsymmetrical species 2-4, the NPA partial charges of the model diborenes B₁ and C₁ and borylene D₁ (parentheses of entries 3-5) displayed a very similar trend for the charge accumulation and the course of charge flow on the boron atoms. Upon coordination of HPPH₂ to the electron-rich diborene C₁, the negative charges on both boron atoms increase further, with a relatively high negative charge localised on B₁ (the boron atoms are denoted as BPROX and BDIST, respectively, for those proximal and distal to the incoming HPPH₂). Simultaneously, the partial positive charge at the HPPH₂ phosphorus atom increases, confirming the charge donation from the incoming phosphine. Another intriguing fact about the coordinated HPPH₂ is that its hydrogen substituent obtains a partial positive charge in contrast to its free form, which is marginally negative at hydrogen (entry 1). Thus, it is apparent that the hydrogen transfer from phosphorus to boron during hydrophosphination is a proton transfer, not a hydride transfer. As anticipated, the HPPH₂ coordination A₁–D₁ is endergonic due to addition of a weak phosphine nucleophile to an electron-rich diborene. As the initially formed phosphine addsucts of diborene A₁ and borylborylene D₁ are the immediate precursors to the transition states that involve a proton shift step, the partial charges at both boron atoms of these intermediates (A₂ and D₂) were analyzed. The adduct A₂ shows a high negative charge build-up on the boron atom distal to the coordinated HPPH₂ (entry 2). As a result, BDIST abstracts the proton from the coordinated HPPH₂. Likewise, the localized high negative charge on BDIST in intermediate D₂ (entry 5) drives the proton shift to this distal boron. For the reaction coordinates of diborenes B₁ and C₁, the immediate precursors to the proton transfer transition state are B₄ and C₃, respectively. In these two intermediates (entries 3 and 4), a high negative charge build-up was found on BPROX (bound to HPPH₂), leading in both cases to 1,1-hydrophosphination.

Overall, these computations show that the hydrophosphination of diborenes begins with an initial coordination of the substrate HPPH₂ to the boron atoms of electron-rich diborenes, followed by a proton shift from the coordinated HPPH₂ to the proximal or distal boron, depending on which has a higher localised negative partial charge, dictating whether the 1,1- or 1,2-hydrophosphinated product is obtained.

Recent success in adding B–B and B–H bonds across boron–boron triple bonds has led us to consider the hydrophosphination of diborenes. We chose the least sterically encumbered diboryne currently available, B₃(SiDep)₂ (9, SiDep = 1,3-bis(2,6-diethylphenyl)imidazolin-2-ylidene), in the hope that this would allow the approach of the relatively bulky substrate. Treatment of 9 with excess HPPH₂ at −78 °C in toluene (Scheme 3) resulted in an immediate colour change from red to purple. After warming to room temperature, analysis by NMR spectroscopy revealed clean conversion to a new species with a doublet signal at −25.9 ppm (J = 46 Hz) in the ¹¹B NMR spectrum. Two broad resonances were observed at 38.3 and 18.0 ppm in the ³¹P NMR spectrum, shifted significantly from that of 9 (δ = 55.9 ppm) and in the expected region for diborenes. The ¹H{¹¹B} NMR spectrum exhibited a conspicuous

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**Table 1** Computed NPA partial charges (q) on selected atoms of diborenes and intermediates immediately prior to the transition states that involve a proton shift

<table>
<thead>
<tr>
<th>Entry</th>
<th>Species</th>
<th>q (H)</th>
<th>q (P₈Ph₂H₈)</th>
<th>q (BPROX)</th>
<th>q (BDIST)</th>
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<td>A₂</td>
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<td>1.138</td>
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<tr>
<td>3</td>
<td>B₄</td>
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<td>1.155</td>
<td>−1.230</td>
<td>(−0.451)</td>
</tr>
<tr>
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<td>C₃</td>
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<td>1.197</td>
<td>−1.061</td>
<td>(−0.546)</td>
</tr>
<tr>
<td>5</td>
<td>D₂</td>
<td>0.005</td>
<td>1.117</td>
<td>−0.055</td>
<td>(0.298)</td>
</tr>
</tbody>
</table>

* BPROX refers to the P₈Ph₂-coordinated boron atom, whereas BDIST refers to the other boron atom. The charges in parentheses are of the boron atoms of starting diborenes.

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**Scheme 3** Hydrophosphination of the boron–boron triple bond in a diboryne. Dep = 2,6-diethylphenyl.
broadened doublet at 4.19 ppm, indicating a boron-bound proton coupled to the phosphorus nucleus ($^2J_{PH} = 46$ Hz). Crystals obtained from a pentane solution allowed determination of the structure of the compound (Fig. 4). The product, diborene 10, is the result of a 1,2-hydrophosphination across the boron–boron triple bond. Compound 10 is the first example of a phosphinodiborene. The B–B bond distance of 1.567(3) Å is somewhat shorter than in the related hydro(boryl)diborene $\text{SIDipMes(H)} \equiv \text{B(Bcat)}\text{SIDipMes}$ ($\text{SIDipMes} = 1\{2,4,6\text{-trimethylphenyl}\}3\{2,6\text{-diisopropylphenyl}\}\text{-imidazolin-2-ylidene}$, $\text{B=B} = 1.609(2)$ Å), while the B–P1 distance is shorter than that in phosphinodiboranes 5–8, at 1.945(2) Å, on account of the sp$^2$ hybridisation at boron.

No further reaction of 10 with $\text{HPPh}_2$ could be observed, even after heating the sample to 100 °C in toluene solution, in stark contrast to the behaviour of compounds 1–4. We ascribe this lack of reactivity to the large steric bulk of the flanking NH ligands when compared to the accessible boron–boron bonds of the benzylphosphine-supported species.

**Conclusion**

In summary, we have demonstrated that diborenes undergo catalyst-free hydrophosphination reactions with diphenylphosphine under mild conditions. The substituents at the diborene dictate whether the reaction proceeds as a 1,1- or 1,2-addition. The major influencing factor for the regiochemistry appears to be the relative partial charges at the boron atoms in the initial adduct. We have also reported 1,2-hydrophosphination of a diboryne, yielding an unsymmetrical hydro(phosphino)diborene. Our current efforts are focussed on exploring more challenging σ-bond activations at these highly reactive boron–boron multiple bonds.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

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**Notes and references**

5. For the sake of consistency, we have used the definitions of Bailey and Pringle (ref. 1) to make the distinction between the two structural extremes of monomeric P–B compounds.