Isolation of Neutral, Mono-, and Dicaticonic B$_2$P$_2$ Rings by Diphosphorus Addition to a Boron–Boron Triple Bond

Tobias Brückner, Felipe Fantuzzi, Tom E. Stennett, Ivo Krummenacher, Rian D. Dewhurst, Bernd Engels, and Holger Braunschweig*

Dedicated to Professor Ian Manners on the occasion of his 60th birthday

Abstract: The NHC-stabilised diboryne (B$_2$(SIdEp)$_2$; SIdEp = 1,3-bis(2,6-diethylphenyl)imidazolin-2-ylidine) undergoes a high-yielding P–P bond activation with tetraethylphosphine at room temperature to form a B$_2$P$_2$ heterocycle via a diphosphoryldiborene by 1,2-diphosphination. The heterocycle can be oxidised to a radical cation and a dication, respectively, depending on the oxidant used and its counterion. Starting from the planar, neutral 1,3-bis(alkylidene)-1,3-diborat-2,4-diphosphoniocyclobutane, each oxidation step leads to decreased B–B distances and loss of planarity by cationisation.

X-ray analyses in conjunction with DFT and CASSCF/NEVPT2 calculations reveal closed-shell singlet, butterfly-shaped structures for the NHC-stabilised dicationic B$_2$P$_2$ rings, with their diradicaloid, planar-ring isomers lying close in energy.

Cyclic compounds of boron and phosphorus have attracted the attention of main-group chemists for decades.[1] The early discoveries in this field focussed on oligomers of the phosphinoboranes, R$_2$PBR$_2$.[2] In comparison to their lighter congeners, the aminoboranes, R$_2$NBR$_2$, the reluctance of phosphorus to adopt a planar geometry and engage in π-bonding with boron leads to a higher propensity for intermolecular B–P association and formation of four-membered (A, Scheme 1) and six-membered heterocycles, and indeed polymers.[3] A number of four-membered 1,3-diphasphora-2,4-diboretanes (B) have also been reported,[4] largely from unsuccessful attempts to prepare monomeric RP–BR species.[5] These compounds contain pyramidalised phosphorus atoms that can act as ligands for transition metals.[4e,6]

The majority of developments in P–B ring systems in the last two decades relate to the synthesis of a 1,3-diphasphora-2,4-diboretanediyl diradicaloid (C, Scheme 1) by Bertrand and co-workers.[7] The first example of such a compound, cyclo-(BrBu)$_2$[(PPr$_2$)$_2$], was prepared by reacting the diborane(4) 1,2-B$_2$Cl$_2$Bu$_2$ with LiPPr$_2$. The presumed 1,2-diphosphinodiborane intermediate undergoes a rearrangement to cleave the B–B bond and generate the four-membered ring. This compound possesses a single bond character between the two boron atoms despite the large distance between these atoms (2.57 Å), with a low-lying B–B antibonding LUMO. Theoretical studies[8] on diradicaloids C revealed large singlet–triplet gaps of +23.4 to +33.7 kcal mol$^{-1}$, while the population of the LUMO from distinct two-electron-in-two-orbital approaches was found to be 0.169 to 0.19 electrons, indicating...
weak but distinct diradical character. This was supported by examples of diradical-like reactivity,[10] including reactions with Me₃SnH and BrCCl₃. Other derivatives of C were later prepared, with the conclusion that such compounds have two structural isomers—namely the aforementioned planar diradicals and butterfly-type structures containing a conventional boron–boron σ bond (D, Scheme 1)—which can interconvert with the appropriate selection of substituents.[10a]

For several years, our group has been interested in the chemistry of low-valent boron species stabilised by strong Lewis bases.[11] Of particular interest are compounds with boron–boron multiple bonds,[12] diborenes and diborynes, which are able to reductively cleave a wide range of polar[13] and non-polar[14] bonds. We recently used this methodology to develop a new route to covalent boron–phosphorus bonds, namely the hydrophosphination of diborenes and diborynes.[15] This work included the catalyst-free reaction of the diboryne B₂(SIDep)₂ ( Scheme 1 )—which displays a resonance at 38 ppm) and suggests that the 11B NMR spectrum in an approximate 1:1 ratio with dark green. After 6 h, a new signal was observed at 33 ppm (JBP = 125 Hz) in the 11B NMR was more revealing, suggesting bonding between boron and two equivalent phosphorus atoms. Slow evaporation of a hexane solution of the compound provided red crystals suitable for X-ray diffraction, allowing confirmation of its identity as 1,3bis(alkylidene)-1,3-diborata-2,4-diphosphonio-cyclobutane 2 (Figure 1b). The B₂P₂ ring is an almost perfect square, and lies on a crystallographic inversion centre. The B–P bonds are of equal length within experimental error (1.913(2), 1.917(2) Å) and the internal angles at boron (P–B–P = 89.8(1)°) and phosphorus (P–B–P = 90.2(1)°) are right angles. The heterocyclic carbene units are also planar with respect to the central ring, and the short B–C bond of 1.468(3) Å in the range of a double bond rather than a dative interaction.

As a starting point, we again chose diboryne E due to the relatively low steric demand of the flanking carbene compared to other derivatives. Treatment with the diphosphane P₂Et₄ produced a gradual colour change from red to dark green. After 6 h, a new signal was observed at 33 ppm in the 31P NMR spectrum in an approximate 1:1 ratio with unreacted starting material. This is indicative of diborene phosphination of diborane and diboryne.[15] This work included the catalyst-free reaction of the diboryne B₂(SIDep)₂ (E, SIDep=1,3-bis(2,6-diethylphenyl)imidazolin-2-ylidene) with HPPh₂ to yield a hydro(phosphino)diboryne (F, Scheme 1). We recognised herein a potential opportunity to prepare B₂P₂ compounds, related to C and D by addition of two further valence electrons, via the activation of a phosphorus–phosphorus bond.

A slightly broadened new signal at ~44 ppm in the 31P NMR spectrum alongside unreacted P₂Et₄ (δ = ~33 ppm) was also consistent with this assignment. The mixture was left to stand at room temperature for a further 12 h. Rather than the expected complete conversion to 1, a further colour change to orange had occurred, accompanied by selective generation of a new set of NMR signals. While a broad signal in the 11B NMR at ~9.6 ppm suggested a significantly different phosphorus environment, a triplet resonance at ~18.9 ppm (JBP = 125 Hz) in the 11B NMR was more revealing, suggesting bonding between boron and two equivalent phosphorus atoms. Slow evaporation of a hexane solution of the compound provided red crystals suitable for X-ray diffraction, allowing confirmation of its identity as 1,3-bis(alkylidene)-1,3-diborata-2,4-diphosphonio-cyclobutane 2 (Figure 1b). The B₂P₂ ring is an almost perfect square, and lies on a crystallographic inversion centre. The B–P bonds are of equal length within experimental error (1.913(2), 1.917(2) Å) and the internal angles at boron (P–B–P = 89.8(1)°) and phosphorus (P–B–P = 90.2(1)°) are right angles. The N-heterocyclic carbene units are also planar with respect to the central ring, and the short B–C bond of 1.468(3) Å in the range of a double bond rather than a dative interaction.

Attempts to crystallise compound 1 eventually produced a single crystal of sufficient quality to confirm its connectivity by X-ray diffraction (see SI), but unfortunately the data are insufficient for discussion of structural parameters.

The B₂P₂ ring in 2 has two electrons more than that in D, on account of the donor capability of the NHC units, which leads to a completely closed-shell system. Nevertheless, their

![Diagram](https://example.com/diagram.png)

**Figure 1.** a) Synthesis of B₂P₂ heterocycle 2 and salts of the radical cation [3]⁺. b) Molecular structures of 2 (left) and the cationic part of [3][PF₆]⁻ (right) with atomic displacement ellipsoids at the 50% probability level.[22] Selected bond lengths [Å] and (torsion) angles [°] for 2: B1–B1’ 2.713(3), B1–P1 1.912(2), B1–P’1 1.917(2), C1–B1 1.468(3), N2–C1 1.412(3), N1–C1 1.406(3), P1–B1–P1’ 89.8(1), B1–P1–B1’ 90.2(1), C1–B1–B1’–C1’ 180.0(1), N1–N2–N1’–N2’ 180.0(1); for [3][PF₆]: B1–B2 2.632(5), B1–P1 1.905(3), B1–P2 1.902(3), B2–P1 1.906(3), B2–P2 1.906(3), C1–B1 1.528(4), B2–C2 1.534(4), N1–C1 1.385(4), N2–C1 1.360(4), C2–N3 1.375(4), C2–N4 1.358(4), P1–B1–P2 92.7(2), B1–P1–B2 87.4(2), B1–P2–B2 87.3(2), P1–B2–P2 92.5(2), C1–B1–B2–C2 48.0(1), N1–N2–N3–N4 37.7(1). c) Cyclic voltammogram of 2 in THF/0.1 m [nBu₄N][PF₆] measured with a feed rate of 250 mVs⁻¹. Formal potentials: E₁/₂ = −1.45 V, E₃/₄ = −0.76 V (relative to Fe/Fe⁺).
structural similarities are striking. The distance between the two boron atoms is larger in 2, at 2.713(3) Å, indicating even less bonding interaction between these atoms than in D. In order to better understand the bonding in these B,P₄ rings, DFT calculations at the B3LYP-D3(BJ)/def2-SVP level of theory[16] were performed (Figure 2). As expected from the influence of the NHC substituents, the HOMO (LUMO) of D correlates with the HOMO−1 (HOMO) of 2. The HOMO−1 of 2 describes a formally π-bonding orbital derived predominately from the π orbitals of the boron atoms, with a small degree of overlap. A small amount of delocalisation to the carbon atoms of the NHCs distinguishes this orbital from the HOMO of D. The HOMO of 2 represents the mutually out-of-phase B=C π bonds and is weakly π antibonding with respect to the two boron atoms. The population of both bonding and antibonding π(BB) orbitals results in a Mayer bond order (MBO)[17] for the B₂ bond that is formed/broken is very weak and is contrast to a singlet diradicaloid of the form \( \text{B}^\bullet \text{B}^\bullet \text{P}^\bullet \text{P}^\bullet \text{C}^\bullet \text{C}^\bullet \text{N}^\bullet \text{N}^\bullet \text{P}^\bullet \text{P}^\bullet \text{C}^\bullet \text{C}^\bullet \text{N}^\bullet \text{N}^\bullet \text{P}^\bullet \text{P}^\bullet \) (Figure 1c). The first oxidation step, forming the putative dication of \( \text{B}^2\text{P}^2\) rings, exhibits a butterfly-type structure. Compared to the mono- oxidation reagents, Ag[Al(OC(CF₃)₃)₄] or Ag[BArF₄], the B₂P₂ ring is slightly perturbed from that of the neutral precursor 2, with a shortened B–B distance of 2.632(5) Å and slightly wider internal angles at boron (ca. 92.5°). The most significant difference to the neutral compound can be observed in the bonding of the S2Dep moieties. The B–C bonds (B1–C1 = 1.528(4), B2–C2 = 1.534(4) Å) are 0.06–0.07 Å longer than those in 2, while the NHCs now display a slightly twisted orientation towards the central ring (torsion angles between N-C-N and P-B-P planes = 19.5° and 16.5°). Both of these parameters indicate a reduction in B–C π bonding consistent with the removal of an electron from the HOMO of 2. The shortening of the B–B distance can also be rationalised by the removal of electron density from this orbital, which is weakly B–B antibonding in character. We conducted DFT calculations of the cation [3]+ to further investigate this system. Its frontier orbitals are very similar to those in 2, with the singly-occupied SOMO representing the B–C π bond and the weakly repulsive through-space B–B interaction, while the HOMO represents the in-phase C-B-B-C π interaction. The MBO values are consistent with removal of an electron from the HOMO of 2, with a reduction in the B–C bond order to 1.344/1.357 and a marginal increase of the B–B bond order to 0.054. It should be noted that the combination of 2 with [CuCl(SMe₂)] provided the analogous CuCl₂ salt of the radical cation, [3]+CuCl₂. The salt [3]+CuCl₂ showed an EPR spectrum with essentially identical parameters to those of [3][PF₆] (see Supporting Information).

Despite the electrochemical evidence implying a second oxidation step, forming the putative dication of 2, employment of an excess of [Fe(η⁵-C₅H₅)₂][PF₆] or CuCl(SMe₂) led to no further reaction. Use of two equivalents of even stronger oxidation reagents, Ag[Al(OOC(CF₃)₃)]₂ or Ag[BArF₄] (BArF₄ = B(3,5-CF₃-C₆H₃)₄) in D₂O THF led to an immediate colour change from orange to green. The ¹B and ³¹P NMR spectra showed new signals at −1.4 and −25.5 ppm, respectively. The corresponding ¹H NMR spectrum indicated clean conversion, whereby both products ([4][Al(OOC(CF₃)]₄] and [4][BArF₄]₂ could be isolated quantitatively. While [4][Al(OOC(CF₃)]₄] remains oily, even at −35°C, [4][BArF₄]₂ crystallises as yellow crystals from a saturated Et₂O solution. Single-crystal X-ray diffraction confirmed the formation of the dication [4][BArF₄]₂ (Figure 3b) and revealed a butterfly-type structure. Compared to the monoclinic cation of [3][PF₆], the B–B distance had decreased to 2.115(3) Å, with an angle between the two BBB planes of 64°. This B–B distance remains larger than those found for the butterfly-type derivatives of D (Scheme 1), in which B–B distances as short as 1.8 Å have been observed.[10b] In addition, while all P–B bond lengths of the central motif led to a rapid colour change from orange to pink and the disappearance of all signals in the NMR spectra, suggesting the formation of a paramagnetic species ([3][PF₆], Figure 1). The EPR spectrum of [3][PF₆] (see Supporting Information) exhibits a broad resonance at \( g = 2.0025 \) which is dominated by a 1:2:1 triplet created by a large hyperfine coupling to the two phosphorus nuclei (\( a^\text{N}(\text{P}) = 51 \text{ MHz} \)). After several hours, red crystals formed in the solution, allowing the isolation of the radical cation [3][PF₆] and the confirmation of its structure by X-ray diffraction (Figure 1b). The structure of the B₂P₂ ring is slightly perturbed from that of the neutral precursor 2, with a shortened B–B distance of 2.632(5) Å and slightly wider internal angles at boron (ca. 92.5°). The most significant difference to the neutral compound can be observed in the bonding of the S2Dep moieties. The B–C bonds (B1–C1 = 1.528(4), B2–C2 = 1.534(4) Å) are 0.06–0.07 Å longer than those in 2, while the NHCs now display a slightly twisted orientation towards the central ring (torsion angles between N-C-N and P-B-P planes = 19.5° and 16.5°). Both of these parameters indicate a reduction in B–C π bonding consistent with the removal of an electron from the HOMO of 2. The shortening of the B–B distance can also be rationalised by the removal of electron density from this orbital, which is weakly B–B antibonding in character. We conducted DFT calculations of the cation [3]+ to further investigate this system. Its frontier orbitals are very similar to those in 2, with the singly-occupied SOMO representing the B–C π bond and the weakly repulsive through-space B–B interaction, while the HOMO represents the in-phase C-B-B-C π interaction. The MBO values are consistent with removal of an electron from the HOMO of 2, with a reduction in the B–C bond order to 1.344/1.357 and a marginal increase of the B–B bond order to 0.054. It should be noted that the combination of 2 with [CuCl(SMe₂)] provided the analogous CuCl₂ salt of the radical cation, [3]+CuCl₂. The salt [3]+CuCl₂ showed an EPR spectrum with essentially identical parameters to those of [3][PF₆] (see Supporting Information).
bonds are elongated compared to those of 1.594(3) Å. Each of the different charge states of the B₂P₂ systems isomer, multireference CASSCF[20]/NEVPT2[21] calculations on the system of Bertrand, depiction its bent B–B o bond.

Figure 3. a) Formation of salts of dication [4]+

b) Molecular structure of the dication of [4]BA̅F2 with atomic displacement ellipsoids at the 50% probability level.[22] Counteranions are omitted for clarity. Selected bond lengths [Å] and (torsion) angles [°]: B1–B2 2.115(3), B1–P1 1.884(2), B1–P2 1.873(2), B2–P1 1.877(2), B2–P2 1.875(2), C1–B1 1.594(3), C2–B2 1.591(3), N1–C1 1.344(2), N2–C1 1.327(2), N3–N4 83.6(1). c) NBO of the system. See S12, showed that in both cases a bent[31] B–B o bond (MBO = 0.472) is formed, which leads to closed-shell singlet systems. Steric effects related to the bulky substituents of [4]+ prevent the boron atoms from binding at a shorter distance, affecting the system’s overall stability. Consequently, the fully optimised, planar diradicaloid isomer of [4]+, herein labelled planar[4]++ (y0 = 0.12) in comparison to that of C (R = Bu, R = iPr, y0 = 0.06; Scheme 1). As the HOMO of planar[4]++ features the trans-annular π-

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Conflict of interest

The authors declare no conflict of interest.

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