Single and double activation of acetylene by isolobal B≡N and B≡B triple bonds†

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Due to their intrinsic electronic deficiency, linear compounds containing a multiply bonded, sp-hybridised boron atom are far more reactive and difficult to isolate than isolobal carbon-based compounds. Owing to their ease of derivatisation, monomeric iminoboranes of the form RB\(^\text{II}\) (R = anionic substituents),\(^1\) which are formally isoelectronic to alkynes,\(^2\) have been the most widely studied class of two-coordinate boron compounds.\(^3\) The strong polarisation of the B≡N bond enables their participation in a vast array of spontaneous [2 + 2] cycloaddition\(^4\) and 1,2-addition reactions\(^5\) with polar substrates inaccessible to their alkyne counterparts. Only recently has our group shown that, with a suitable transition metal catalyst, iminoboranes can undergo [2 + 2] and [2 + 4] cycloaddition reactions with nonpolar alkynes.\(^6\)

While linear RB≡NR\(^0\) compounds have been studied for over 30 years, isolobal LB≡BL compounds (L = neutral donor ligand) displaying two dicoordinate, zero-valent boron atoms long eluded isolation. Since our report of the first stable diboryne, (IDip)B≡B(IDip) (I, IDip = 1,3-bis(2,6-disopropylphenyl)-imidazolidin-2-ylidene),\(^7\) we have shown that, by varying the π acceptor ability of L, the electronics and reactivity of these compounds can be fine-tuned.\(^8,9\) Thus, whereas unsaturated N-heterocyclic carbene (NHC)-supported diborynes such as I are inert towards H\(_2\),\(^10\) (SIDep)B≡B(SIDep) (II, SIDep = 1,3-bis(2,6-diethylphenyl)-4,5-(dihydro)imidazolidin-2-ylidene), which is supported by saturated NHCS of intermediate π acidity,\(^11\) adds H\(_2\) at 80 °C to yield a 1,2-dihydridoborene.\(^12\) In turn, the use of even stronger π-accepting cyclic (alkyl)(amino)carbenes (cAACs)\(^13\) yields the cumulenic species (McAAC)\(_\text{II}\) B≡B⋅(McAAC) (III, McAAC = 1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethyl-pyrrolidin-2-ylidene),\(^14\) which, unlike I and II, activates H\(_2\) at room temperature\(^8\) and undergoes spontaneous [2 + 2] and [2 + 4] cycloadditions with acetylene.\(^14\)

Intrigued by the seeming lack of reactivity overlap between isolobal linear RB≡NR\(^0\) and LB≡BL species (Fig. 1), we were eager to investigate whether the diboron compounds undergo spontaneous polar cycloaddition reactions similar to those of iminoboranes. Herein we compare the reactivity of I–III and a highly sterically hindered iminoborane, (TMP)B≡NAr\(^*\) (IV, Ar\(^*\) = 2,6-(CHPh\(_2\))\(_2\)-4-(BuC\(_6\)H\(_4\))\(_2\); TMP = 2,6-tetramethylpyrroli-dyl), towards acetylene and show that, despite their marked electronic differences, compounds II and IV activate acetylene and undergo spontaneous polar C–H activation of the enolate ligand.

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following a similar mechanism, whereas cumulene II promotes an unprecedented spontaneous double activation of acetone.

Heating a suspension of IV in hexanes with excess acetone overnight at 70 °C resulted in clean formation of the (2-propenyloxid)aminoborane 1 (Scheme 1A). 11B NMR data of 1 showed a resonance at 24.8 ppm, while the 1H NMR spectrum displayed a NH singlet at 3.49 ppm and two characteristic 1H resonances for the terminal methyldiene protons of the enolate ligand at 4.36 and 4.11 ppm.

X-Ray crystallographic analysis of 1 (Fig. 2) confirms the sp2-hybridisation at B1 (\(\angle B1 = 359.9(18)^\circ\)) and N1 (B1–N1–C4 126.92(16)°) as well as the elongation of B1–N1 to a single bond (1.424(3) Å). The 2-propenyloxide ligand coordinated to B1 displays a C1–O1 single bond (1.343(2) Å) and a terminal C1=2 double bond (1.320(3) Å). Formally, compound 1 results from the addition of 2-propenol, the enol form of acetone, across the polar B=N triple bond of iminoborane IV. While there is, to our knowledge, no literature precedent for the reactivity of monomeric iminoboranes with enolisable ketones, the dimeric iminoborane [BuB≡N(Bu)2 has been shown to undergo 1,4-enol addition to the ring-opened iminoborane dimer with acetone, acetoephone and 3,3-dimethylbutan-2-one. This contrasts with the reactivity of iminoboranes towards aldehydes and CO2, which yields the 1,3,2-oxazaboretidine [2 + 2] cycloaddition products.

Whereas diboryne I proved unreactive towards acetone even under forcing conditions, diboryne II reacted rapidly with excess acetone in benzene at room temperature to yield the green-coloured 1,2-enol addition product 2 (Scheme 1). Compound 2 presents two broad 11B NMR resonances at 38.1 and 19.3 ppm in a 1:1 ratio, attributable to the BH and the BOC\(_2\)H moieties of the unsymmetrical diborene, respectively. The 1H NMR spectrum displayed two inequivalent SIDep moieties of the unsymmetrical diborene, respectively. The SIDep ligand at the BH moiety is near planar 2-propenyloxide ligand lies at a planar 2-propenyloxide ligand at 11.2(1)° coplanar with the diborene core (torsion (N4, C27, B2, B1) 12.1(5)°) and displays a short B2–C27 bond (1.523(4) Å), indicative of π backdonation. In contrast, the SIDep ligand supporting the BOC\(_2\)H moiety is twisted ca. 35.5° out of the diborene plane and displays a pure σ-donor interaction (B1–C4 1.574(4) Å). The planar 2-propenyloxide ligand lies at a ca. 58° angle with respect to the diborene plane, and its bond lengths (O1–C1 1.352(3), C1=C2 1.316(4) Å) are similar to those of 1. With Kinjo and co-workers recently reporting the first diborene with two different donor ligands and our group having just published the first fully unsymmetrical diborene, compound 2 is only the second unsymmetrical diborene with respect to the anionic substituents.

TDDFT calculations performed upon the optimised geometry of 2 at the (smd: n-pentane)kcωPBE/6-311+g(d) level of theory provided a maximum UV-vis absorbance at 592 nm (see Table S1 and Fig. S24 in the ESI†), which is in good agreement with Kinjo and co-workers recently reporting the first diborene with two different donor ligands and our group having just published the first fully unsymmetrical diborene, compound 2 is only the second unsymmetrical diborene with respect to the anionic substituents.

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acetone did not yield the expected cAAC analogue of \( \text{3a} \). Instead, \( ^{11} \text{B} \) NMR data revealed a 92:8 mixture of two sp\(^2\)-sp\(^3\) diborane products, the major one (\( \text{3a} \)) showing two broad singlets at 42.8 (full width at half maximum: fwhm \( \approx 370 \) Hz) and \(-1.9\) ppm (fwhm \( \approx 130 \) Hz), and the minor (\( \text{3b} \)) presenting a very broad resonance at 63.0 ppm (fwhm \( \approx 630 \) Hz) and a broad BH doublet at \(-15.0\) ppm (\( ^{1} \text{J}_{\text{B-H}} = 50.8 \) Hz), suggesting a non-bridging hydride. The \( ^{1} \text{H} \) NMR spectrum of the mixture showed very similar sets of resonances for \( \text{3a} \) and \( \text{3b} \), which strongly suggests an isomeric relationship. Both compounds display one neutral cAAC ligand and one C1-protonated cAAC ligand (\( \delta = \text{3a 4.02, 3b 4.24 ppm} \)) as well as a single 1H alkene resonance (\( \delta = \text{3a 3.50, 3b 3.78 ppm} \)) (Scheme 2).

Single-crystal X-ray crystallography revealed a unique planar 2,3-dihydro-5-methyl-1,2,3-oxadiborole heterocycle displaying an endocyclic \( \text{C1} \)--\( \text{C2} \) double bond (1.3301(18) \( \text{Å} \), Fig. 2). The B--B bond is unsymmetrically \( \mu \)-bridged by a hydride (B1--B2 B1--H1 1.213(16), B2--H1 1.485(17) \( \text{Å} \)) positioned orthogonally to the B2C2O heterocycle (torsion (H1, B2, B1, C2) 105.7(9)\(^\circ \)) and shows a bond length of 1.721(2) \( \text{Å} \) typical of a diborane (5). The alkenylborane moiety around B1 is supported by a neutral cAAC ligand with a relatively short B1C1 bond (1.213(16) \( \text{Å} \)) and shows an angle of only ca. 19\(^\circ \) with the plane of the B2C2O heterocycle (torsion (N1, C4, B1, C2) 14.4(2)\(^\circ \)), which is indicative of \( \pi \) conjugation. The enoxyborane moiety around B2 bears a protonated cAAC ligand displaying clear sp\(^3\)-hybridisation at C24 (B2--C2 1.6045(18), C24--N2 1.4878(16) \( \text{Å} \))), showing a clear sp\(^3\) hybridised B2 atom.

The predicted \( ^{11} \text{B} \) NMR chemical shifts for the \( \left( \text{R}^\text{C}, \text{R}^\text{B} \right)/\left( \text{S}^\text{C}, \text{S}^\text{B} \right)-\text{3a} \) pair (\( \delta_{\text{calc}} = 44.0, -4.4 \) ppm) adequately match the experimentally-observed shifts (\( \delta_{\text{exp}} = 42.8, -1.9 \) ppm; \( \Delta \delta = \pm 2 \) ppm). Calculations on the diastereomeric pair showed that a form with a non-bridging hydride is the most likely. This also correlates well with the observation that, unlike \( \text{3a} \), which shows two very broad \( ^{11} \text{B} \) NMR resonances typical for a \( \mu \)-hydride-bridged diborane, \( \text{3b} \) shows a doublet at \(-15.0\) ppm (\( ^{1} \text{J}_{\text{B-H}} = 50.8 \) Hz), indicating a terminal hydride rather than a bridging one. The predicted \( ^{11} \text{B} \) NMR chemical shifts for the \( \left( \text{R}^\text{C}, \text{S}^\text{B} \right)/\left( \text{S}^\text{C}, \text{R}^\text{B} \right)-\text{3b} \) pair (\( \delta_{\text{calc}} = 65.4, -18.9 \) ppm) are very close to the experimental ones (\( \delta_{\text{exp}} = 63.0, -15.0 \) ppm; \( \Delta \delta = \pm 3 \) ppm). The relative energy of \( \left( \text{R}^\text{C}, \text{S}^\text{B} \right)/\left( \text{S}^\text{C}, \text{R}^\text{B} \right)-\text{3b} \), at 3.1 kcal mol\(^{-1}\) above \( \left( \text{R}^\text{C}, \text{R}^\text{B} \right)/\left( \text{S}^\text{C}, \text{S}^\text{B} \right)-\text{3a} \), is consistent with the experimentally observed ratio of 92:8.

The spontaneous formation of \( \text{3a/b} \) is particularly remarkable in view of the fact that there is seemingly no literature precedent for a one-step, uncatalysed, 100% atom-efficient double C--H activation of acetone or other enolisable ketones. We were therefore keen to investigate the mechanism of the formation of \( \text{3a/b} \) and compare it to that of the boron enolates 1 and 2. While the reaction of dimeric iminoboranes with...
enolisable ketones always yielded the 1,4-enol addition products, Paetzold and co-workers showed that with acetophenone, which is less prone to enolisation, a [2 + 4] cycloaddition product can also be isolated. However, it remained unclear whether or not the latter is an intermediate to the former. For comparison, nonpolar disilenes are known to form the corresponding 1,2,3-oxadisiletane heterocycles, which then rearrange to the 1,2-enol addition products. In our case, however, careful monitoring of the reaction of iminoborane IV and diboryne II with acetone showed no evidence of [2 + 2] cycloaddition products or intermediates.

DFT calculations carried out at the D3-PBE0/6-31G(d) level for IV and at the ONIOM(M06-2X/6-311+G(d):PM6) level for II and III showed that acetone activation does not proceed via 1,2-enol addition, as the enol form of acetone lies 15.3 kcal mol\(^{-1}\) higher than the reactants, well above the activation energy for direct acetone addition (Fig. 4, see ES\textit{f} for details on the methodology and the optimised structures of all reactants, products, intermediates and transition states).

For iminoborane IV two plausible mechanisms were investigated, the first via a 4,4-dimethyl-1,3,2-oxaboretidine [2 + 2] cycloaddition product (A), the second via concerted acetone coordination-deprotonation (Fig. 4). Although the cycloaddition product A is calculated to be more stable than 1 by 2.8 kcal mol\(^{-1}\), the energy barrier for the formation of A is slightly higher than for 1. Furthermore, as there is no thermodynamically viable reaction path from A to 1, a [2 + 2] cycloaddition mechanism followed by rearrangement to 1 can be ruled out.

Instead, for compounds II–IV the first reaction step involves coordination of the carbonyl oxygen atom to one boron centre to form the acetone adducts 11, 12 and 13 (\(\Delta G^\ddagger_1 = 7.6\) (IV), 20.6 (II), 10.1 (III) kcal mol\(^{-1}\)), respectively (Fig. 4 and 5). This step is followed in all three cases by C–H activation of one of the pendant methyl groups of the coordinated acetone by either the nitrogen atom (for IV) or the electron-rich, second boron centre (for II and III), to yield the cis-aminoborane 12, and the SIdEp-supported cis-diborones 12 and 13, respectively (\(\Delta G^\ddagger_2 = 4.0\) (IV), 14.1 (II), 14.9 (III) kcal mol\(^{-1}\)). Finally, the trans-aminoborane 1 and the trans-diborones 2 and 14, are obtained by rotation around the B–N and B–B bond, respectively. Overall, the formation of 2 presents the highest energy barrier and is also the most exergonic (\(\Delta G = -43.2\) kcal mol\(^{-1}\)), followed by that of 1 (\(\Delta G = -26.6\) kcal mol\(^{-1}\)) and 14 (\(\Delta G = -27.4\) kcal mol\(^{-1}\)).

The exergonic isomerisation step leading from the cis-diborones 12 and 13 to the trans-diborones 2 and 14, respectively, was further investigated to determine the rotation barrier in each case. Interestingly, DFT calculations showed two distinct mechanisms at work for the SIdEp-stabilised and the cAAC-stabilised diborone, respectively (Fig. 6). For the SIdEp analogue 12, rotation about the B–B bond is facilitated by shifting the \(\pi\)-electron density of the B–B double bond into the \(\pi\) backbonding to the unsaturated carbene ligands. The resulting transition state TS\(3\) now displays a B–B single bond, which allows facile rotation. The isomerisation process from 12 to 2 occurs with a low barrier of 9.7 kcal mol\(^{-1}\). In contrast, the lowest energy pathway for the cAAC analogue 12 proceeds via a 1,2-hydride shift from boron to the adjacent cAAC carbene carbon to yield the intermediate diborone 13 (\(\Delta G^\ddagger_3 = 8.9\) kcal mol\(^{-1}\)), in which the boron bearing the now protonated cAAC ligand is sp-hybridised. Rotation about this B–cAAC single bond and a second 1,2-hydride shift back to the boron centre then yield the trans-diborone 14 with a low barrier of 9.3 kcal mol\(^{-1}\). This pathway is assisted on the one hand by the facile 1,2-hydride shuttling chemistry displayed by cAAC hydroboron compounds\(^{19}\) and on the other hand by the very strong \(\pi\) acceptor properties of cAAC,\(^{12}\) which enable the stabilisation of the coordinatively saturated intermediate 13.

For cumulene III, however, the reaction does not stop at trans-diborone 14 (Fig. 3). The latter undergoes hydride migration from B1 to B2 to form the (alkoxy)hydroboryl-(alkyliden)borane 15 (\(\Delta G^\ddagger_4 = 19.8\) kcal mol\(^{-1}\)). Coordination of the pendant terminal alkene to the two-coordinate boron yields adduct 15, which is 6.6 kcal mol\(^{-1}\) more stable. Subsequent C–H activation of the methylene moiety yields the bis(cAAC)-stabilised 1,2,3-oxadiborole 16 (\(\Delta G^\ddagger_5 = 21.2\) kcal mol\(^{-1}\)). This is the highest energy barrier in the entire reaction mechanism. 16 then tautomerises to compound 3a by concomitant migration of the hydride on B1 to the adjacent cAAC carbene centre and bridging of the hydride on B2 (\(\Delta G^\ddagger_5 = 11.7\) kcal mol\(^{-1}\)). Overall the formation of 3a from III and acetone is exergonic by 61.7 kcal mol\(^{-1}\), which explains why the intermediate diborone cannot be isolated.

To conclude, we have shown that three linear, isobal, multiply bonded boron compounds, iminoborane IV, diboryne II and cumulene III, all activate acetone via a similar acetone coordination-deprotonation mechanism, regardless of their polar or nonpolar nature. For the iminoborane-based reaction, an enol addition mechanism and a mechanism proceeding via a [2 + 2] cycloaddition intermediate, as would normally be
expected for such a polar compound, were both ruled out. For diboron compounds II and III the addition of acetone first yields a cis-diborene intermediate which isomerises to the thermodynamic trans-diborene product through a low energy barrier. Calculations showed that this isomerisation process heavily relies on the \( \pi \)-accepting nature of the carbene ligands, coupled, in the case of the cAAC-supported diborene, with a hydride shuttling mechanism from boron to the carbene carbon and back. These cAAC-specific properties also enable an unprecedented second C–H activation of the enolate ligand to yield a novel 1,2,3-oxadiborole heterocycle, demonstrating once again the unique reactivity of cAAC-supported low-valent boron compounds.

Overall this study should act as a reminder that the parallels all too eagerly drawn between organic compounds and their isoelectronic/isolobal inorganic p-block counterparts only rarely translate into actual organomimetic behaviour when it comes to reactivity or reaction mechanisms. Furthermore, this first example of reactivity overlap between polar and nonpolar boron-based triple bonds opens up new avenues for attempting reactions that may have been previously disregarded, such as the addition of nonpolar small molecules to iminoboranes or, alternatively, of polar molecules to diborynes.

**Conflicts of interest**

There are no conflicts to declare.
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Notes and references

§ Since the calculated di...