Single and double activation of acetone by isolobal B=N and B=B triple bonds†

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B=N and B=B triple bonds induce C–H activation of acetone to yield a 2-propanoyloxyaminoborane and an unsymmetrical 1-(2-propanoyloxy)-2-hydrodiborene, respectively. DFT calculations showed that, despite their stark electronic differences, both the B=N and B=B triple bonds activate acetone via a similar coordination-deprotonation mechanism. In contrast, the reaction of acetone with a cAAC-supported diboracumulene yielded a unique 1,2,3-oxadiborene, which according to DFT calculations also proceeds via an unsymmetrical diborene, followed by intramolecular hydride migration and a second C–H activation of the enolate ligand.

Due to their intrinsic electron 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\(^{\equiv}\)NR\(^{\equiv}\) (R, R\(^{\equiv}\) = 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\(^{\equiv}\)NR compounds have been studied for over 30 years, isolobal LB\(^{\equiv}\)BL compounds (L = neutral donor ligand) displaying two dicoordinate, zero-valent boron atoms long eluded isolation. Since our report of the first stable diborine, (Idip)B\(^{\equiv}\)B(Idip) \((\text{Idip} = 1,3\text{-bis(2,6-diisopropylphenyl)}\)-imidazolidin-2-ylidine),\(^{7}\) 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 diborines such as I are inert towards H\(_2\),\(^{10}\) (Sidep)B\(^{\equiv}\)B(Sidep) \((\text{II, Sidep} = 1,3\text{-bis(2,6-diethylphenyl)}\)-4,5-(dihydro)imidazolidin-2-ylidine), which is supported by saturated NHCs of intermediate π acidity,\(^{11}\) adds H\(_2\) at 80 °C to yield a 1,2-dihydrodiborene.\(^{12}\) In turn, the use of even stronger π-accepting cyclic (alkyl)(amino)carbenes (cAACs)\(^{13}\) yields the cumulenic species (Me\(_2\)cAAC)\(^{\equiv}\)B=B\(^{\equiv}\)B(\(_{\text{Me}}\)cAAC) \((\text{III, Me}_{\text{2}}\)cAAC = 1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethyl-2-pyrrolidin-2-ylidine),\(^{13}\) 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\(^{\equiv}\)NR and LB\(^{\equiv}\)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\(^{\equiv}\)NAr* \((\text{IV, Ar}^{*} = (2,6\text{-cyclohexadienyl})\text{-tetrakis(2,6-diisopropylphenyl)}\)-phenyl), towards acetone and show that, despite their marked electronic differences, compounds II and IV activate acetone

Fig. 1 Side-by-side comparison of iminoboranes and diborines.
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-propenyl)aminoborane I (Scheme 1A). $^{11}$B NMR data of I showed a resonance at 24.8 ppm, while the $^1$H 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.

Crystallographically determined solid-state structures of 1, 2 and 3a. Atomic displacement ellipsoids depicted at the 50% probability level. Atomic displacement ellipsoids of peripheral substituents omitted for clarity. Hydrogen atoms omitted, except for those of the activated acetone moieties, the protonated cAAC carbon atom and those bound to boron. Selected bond lengths (Å): (1) B1–N1 1.424(3), B1–N2 1.429(3), B1–O1 1.418(3), O1–C1 1.343(3), C1–C2 1.320(3); (2) B1–C4 1.574(4), B2–C27 1.523(4), B1–B2 1.599(4), B1–H1 1.406(4), O1–C1 1.455(3), O1–C2 1.316(4), C1–C2 1.523(4), B1–O1 1.406(4), O1–C1 1.3824(15), C1–C2 1.3301(18), C2–B2 1.5743(18).

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 $^{11}$B NMR resonances at 38.1 and 19.3 ppm in a 1 : 1 ratio, attributable to the BH and the BOC$_3$H$_5$ moieties of the unsymmetrical diborene, respectively. The $^1$H NMR spectrum displayed two inequivalent SIDep ligands, as well as the inequivalent terminal methylene protons of the 2-propenylxide ligand at 3.93 and 3.47 ppm. X-Ray crystallographic analysis of 2 showed a trans-1,alkoxy-2-hydrodiborene with a B–B double bond of 1.599(4) Å similar to that of its dihydrodiborene relative, (SIDep)$^\text{HB}$$^\text{BH}$SIDep (1.589(4) Å). The SIDep ligand at the BH moiety is near coplanar with the diborene core (torsion (N4, C27, B2, B1) 12.1(5º) and displays a short B2–C27 bond (1.523(4) Å), indicative of π backdonation. In contrast, the SIDep ligand supporting the BOC$_3$H$_5$ moiety is twisted ca. 35.5º out of the diborene plane and displays a pure ρ-donor interaction (B1–C4 1.574(4) Å). The planar 2-propenlyolxide ligand lies at a ca. 58º 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)lc-ωPBE/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 the experimentally measured absorbance maximum in pentane at 605 nm (Fig. S16†). This corresponds to the HOMO–LUMO transition from the π-bonding orbital of the B=B bond into the empty π orbitals of the carbene carbon of the SIDep ligand supporting the BOC,H₃ moiety, and is responsible for the blue-green color of the compound.

Surprisingly, the 1 : 1 reaction of diboracumulene III with acetone did not yield the expected cAAC analogue of 2. Instead, ¹¹B NMR data revealed a 92 : 8 mixture of two sp²–sp³ diborane products, the major one (3a) showing two broad singlets at 42.8 (full width at half maximum: fwhm ≈ 370 Hz) and −1.9 ppm (fwhm = 130 Hz), and the minor (3b) presenting a very broad resonance at 63.0 ppm (fwhm = 630 Hz) and a broad BH doublet at −15.0 ppm (J_{B-H} = 50.8 Hz), suggesting a non-bridging hydride. The ¹H NMR spectrum of the mixture showed very similar sets of resonances for 3a and 3b, which strongly suggests an isomeric relationship. Both compounds display one neutral cAAC ligand and one C₁-protonated cAAC ligand (δ = 3a 4.02, 3b 4.24 ppm) as well as a single 1H alkene resonance (δ = 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 C₁=C₂ double bond (1.3301(18) Å, Fig. 2). The B=B bond is unsymmetrically μ²-bridged by a hydride (B₁–B₂ B₁–H₁ 1.213(16), B₂–H₁ 1.485(17) Å) positioned orthogonally to the B₂C₅O heterocycle (torsion (H₁, B₂, B₁, C₂) 105.7(9)°) and shows a bond length of 1.721(2) Å typical of a diborane (5). The alkenylborane moiety around B₁ is supported by a neutral cAAC ligand with a relatively short B₁–C₁ bond (1.213(16) Å) and an angle of only ca. 19° with the plane of the B₂C₅O heterocycle (torsion (N₁, C₄, B₁, C₂) 14.4(2)°), which is indicative of π conjugation. The enoxyborane moiety around B₂ bears a protonated cAAC ligand displaying clear sp³-hybridisation at C₂ (B₂–C₂ 1.6045(18), C₂−N₂ 1.4878(16) Å). The structure of 3a is reminiscent of the products obtained from the reduction of (SIMes)BrB₃Ar₂ diborane (5) precursors (SIMes = 1,3-Mes₂C₆H₃NMe₃; 4,5-dihydroimidazol-2-ylidene, Mes = 2,4,6-trimethylphenyl; Ar = Mes, 9-anthryl). These display a central, μ³-hydride-bridged, planar B₃C₅ heterocycle, resulting from the C–H activation of one ary substutuent by an intermediate boraborole, and coordinated on one side by a neutral SIMes ligand and on the other by the second aryl substituent.†

Although single crystals of the minor species in solution were never obtained, the propensity for cAAC-supported hydroboranes to undergo 1,2-hydrogen shifts from boron to an adjacent cAAC carbene centre, which has been demonstrated both experimentally and computationally,¹⁹ first prompted us to identify the second isomer as compound 3₉taut, a tautomeric form of 3a, in which the neutral cAAC ligand coordinates to the enoxyborene moiety, and the protonated cAAC ligand coordinates to the alkenylborene moiety (Fig. 3). DFT optimisations at the ONIOM(M06-2X/6-311+G(d):PM6) level [see ESI† for details] showed, however, that 3₉taut is 8.4 kcal mol⁻¹ higher in energy than 3a and that its calculated ¹¹B NMR shifts (δ = 45.1, 6.1 ppm) do not fit the experimental data (δ = 63.0, −15.0 ppm). Since 3a presents two stereocentres, one at B₂, which is locked by the B₂C₅O ring and the asymmetrically bridging hydride, and one at the protonated cAAC carbon atom, the other possibility is that 3a and 3b could be diastereomers. This would also fit the observation that they do not exchange in solution even at high temperatures. To test this, the geometries and ¹¹B NMR chemical shifts of the possible diastereomeric pairs derived from 3a were computed (Fig. 3).

The predicted ¹¹B NMR chemical shifts for the (⁵⁷C,⁶⁴B): (⁵¹C,⁶⁸B)–3a pair (δ_{calc} = 44.0, −4.4 ppm) adequately match the experimentally-observed shifts (δ_{exp} = 42.8, −1.9 ppm; Δ(δ) = ±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 3a, which shows two very broad ¹¹B NMR resonances typical for a μ³-hydride-bridged diborane, 3b shows a doublet at −15.0 ppm (J_{1H–1H} = 50.8 Hz), indicating a terminal hydride rather than a bridging one. The predicted ¹¹B NMR chemical shifts for the (⁵⁷C,⁶⁴B):(⁵¹C,⁶⁸B)–3b pair (δ_{calc} = 65.4, −18.9 ppm) are comparable to the experimental ones (δ_{exp} = 63.0, −15.0 ppm; Δ(δ) = ±3 ppm). The relative energy of (⁵⁷C,⁶⁴B):(⁵¹C,⁶⁸B)–3b, at 3.1 kcal mol⁻¹ above (⁵⁷C,⁶⁸B):(⁵¹C,⁶⁴B)–3a, is consistent with the experimentally observed ratio of 92 : 8.

The spontaneous formation of 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 3a/b and compare it to that of the boron enolates 1 and 2. While the reaction of dimeric iminoboranes with

Scheme 2  Double activation of acetone by diboracumulene III.
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.15 However, it remained unclear whether or not the latter is an intermediate to the former. For comparison, nonpolar disilenes are known to first undergo [2 + 2] cycloaddition with aceton and acetophenone to form the corresponding 1,2,3-oxadisilatane heterocycles, which then rearrange to the 1,2-enol addition products.26 In our case, however, careful monitoring of the reaction of iminoborane IV and diboryne II with aceton 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 aceton lies 15.3 kcal mol⁻¹ higher than the reactants, well above the activation energy for direct aceton addition (Fig. 4, see ESI 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 aceton 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, 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 aceton adducts $\text{I}_{11}$, $\text{I}_{12}$ and $\text{I}_{13}$ ($\Delta G^\ddagger = 7.6$ [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 aceton by either the nitrogen atom (for IV) or the electron-rich, second boron centre (for II and III), to yield the cis-aminoborane $\text{I}_{21}$, and the SiDep- and cAAC-stabilised cis-diborenes $\text{I}_{22}$ and $\text{I}_{23}$, respectively ($\Delta G^\ddagger = 4.0$ [IV], 14.1 [II], 14.9 [III]) kcal mol⁻¹). Finally, the trans-aminoborane 1 and the trans-diborenes 2 and $\text{I}_{14}$ 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 $\text{I}_{14}$ ($\Delta G = -27.4$ kcal mol⁻¹).

The exergonic isomerisation step leading from the cis-diborenes $\text{I}_{22}$ and $\text{I}_{23}$ to the trans-diborenes 2 and $\text{I}_{14}$, 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 diborene, respectively (Fig. 6). For the SiDep analogue $\text{I}_{22}$, rotation about the B–B bond is facilitated by shifting the π-electron density of the B–B double bond into the π backbonding to the unsaturated carbene ligands. The resulting transition state $\text{TS}_{23}$ now displays a B–B single bond, which allows facile rotation. The isomerisation process from $\text{I}_{22}$ to 2 occurs with a low barrier of 9.7 kcal mol⁻¹. In contrast, the lowest energy pathway for the cAAC analogue $\text{I}_{23}$ proceeds via a 1,2-hydride shift from boron to the adjacent cAAC carbene carbon to yield the intermediate diborene $\text{I}_{33}$ ($\Delta G^\ddagger = 8.9$ 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-diborene $\text{I}_{13}$ 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$^{29}$ and on the other hand by the very strong π acceptor properties of cAAC,$^{12}$ which enable the stabilisation of the coordinatively saturated intermediate $\text{I}_{33}$.

For cumulene III, however, the reaction does not stop at trans-diborene $\text{I}_{13}$ (Fig. 3). The latter undergoes hydride migration from B1 to B2 to form the (alkoxy)hydroboryl-(alkyldiene)borane $\text{I}_{43}$ ($\Delta G^\ddagger = 19.8$ kcal mol⁻¹). Coordination of the pendant terminal alkene to the two-coordinate boron yields adduct $\text{I}_{53}$, which is 6.6 kcal mol⁻¹ more stable. Subsequent C–H activation of the methylenedine moiety yields the bis(cAAC)-stabilised 1,2,3-oxadiborene $\text{I}_{63}$ ($\Delta G^\ddagger = 21.2$ kcal mol⁻¹). This is the highest energy barrier in the entire reaction mechanism. $\text{I}_{63}$ 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 ($\Delta G^\ddagger = 11.7$ kcal mol⁻¹). Overall the formation of 3a from III and aceton is exergonic by 61.7 kcal mol⁻¹, which explains why the intermediate diborene cannot be isolated.

To conclude, we have shown that three linear, isologal, multiply bonded boron compounds, iminoborane IV, diboryne II and cumulene III, all activate aceton via a similar aceton coordination-deprotonation mechanism, regardless of their polar or nonpolar nature. For the iminoborane-based reaction, an enal addition mechanism and a mechanism proceeding via a [2 + 2] cycloaddition intermediate, as would normally be

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**Fig. 4** Mechanisms of aceton addition to iminoborane IV to yield aminoborane 1 (straight lines in black) and alternative [2 + 2] cycloaddition to yield A (dashed lines in blue), as well as energy level of the enol form of aceton (green) calculated at the D3-PBE0/6-31G(d) level of theory. Gibbs free energies (kcal mol⁻¹) in brackets.
expected for such a polar compound, were both ruled out. For diboron compounds \( \text{II} \) and \( \text{III} \) 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 difference in energy barrier for products 1 and A is so low, the reaction of iminoborane IV with acetone was also carried out at higher temperatures to see if A could be obtained instead. However, this only led, beside the formation of 1, to an accumulation of intractable decomposition products.