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 isobologal carbon-based compounds. Owing to their ease of derivatisation, monomeric iminoboranes of the form \( \text{RB}_0 \) \((\text{R}, \text{R} = \text{anionic substituents}),^1 \) 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 \( \text{B}_0 \) 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 \( \text{RB}_0 \) \( \text{NR} \) \(^5 \) compounds have been studied for over 30 years, isobologal \( \text{LB}_0 \) \( \text{BL} \) compounds (\( \text{L} = \text{neutral donor ligand}\)) displaying two dicoordinate, zero-valent boron atoms long eluded isolation. Since our report of the first stable diborine, \((\text{Idip})\text{B}_0 \) \( \text{B} \) \((\text{Idip}) \) \((\text{I}, \text{Idip} = 1,3,3,5,5-\text{tetramethylimidazolidin-2-ylidine}),^7 \) we have shown that, by varying the \( \pi \) acceptor ability of \( \text{L} \), the electronics and reactivity of these compounds can be fine-tuned.\(^8,9 \) Thus, whereas unsaturated N-heterocyclic carbene (NHC)-supported diborynes such as \( \text{I} \) are inert towards \( \text{H}_2 \),\(^10 \) \((\text{Sidep})\text{B}_0 \) \((\text{Sidep}) \) \((\text{II}, \text{Sidep} = 1,3-\text{bis}(2,6-\text{diethylphenyl})-4,5-(\text{dihydro})imidazolidin-2-ylidene), \) which is supported by saturated NHCs of intermediate \( \pi \) acidity,\(^11 \) adds \( \text{H}_2 \) at 80 \( ^\circ \)C to yield a 1,2-dihydridoborine.\(^16 \) In turn, the use of even stronger \( \pi \)-accepting cyclic (alkyl)(amino) carbenes \( ^\text{(cAAC)} \)\(^13 \) yields the cumulenic species \((\text{MecAAC})\cdots \) \((\text{B} \cdots (\text{McAAC}) \text{III}, \text{MecAAC} = 1-(2,6-\text{diisopropylphenyl})-3,3,5,5-\text{tetramethylpyrrolidin-2-ylidene}), \) which, unlike \( \text{I} \) and \( \text{II} \), activates \( \text{H}_2 \) at room temperature\(^8 \) and undergoes spontaneous \([2 + 2]\) and \([2 + 4]\) cycloadditions with acetylene.\(^44 \)

Intrigued by the seeming lack of reactivity overlap between isobologal linear \( \text{RB}_0 \) \( \text{NR} \) \(^5 \) and \( \text{LB}_0 \) \( \text{BL} \) species (\( \text{Fig. 1} \)), 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 \( \text{I} - \text{III} \) and a highly sterically hindered iminoborane, \((\text{TMP})\text{B}_0 \text{Ar}^* \) \((\text{IV}, \text{Ar}^* = (2,6-(\text{CHPh}_3)_2)-4-(\text{BuC}_6\text{H}_3)); \) \( \text{TMP} = 2,6-\text{tetramethylpyrrolyl- idyl}, \) towards acetylene and show that, despite their marked electronic differences, compounds \( \text{II} \) and \( \text{IV} \) activate acetylene.

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**Fig. 1** Side-by-side comparison of iminoboranes and diborynes.

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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-prope-
nyloxy)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 (2/ζ B1 = 359.9(18)°) 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=C2 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≡NtBu]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.15 This contrasts with the reactivity of iminoboranes
towards aldehydes44 and CO2,44 which yields the 1,3,2-oxaza-

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
BOC3H5 moieties of the unsymmetrical diborene, respectively.
The 1H NMR spectrum displayed two inequivalent SIDep
ligands, as well as the inequivalent terminal methylene protons
of the 2-propenyloxide ligand at 3.93 and 3.47 ppm. X-Ray
crystallographic analysis of 2 showed a trans-1-alkoxy-2-
hydridoborene with a B–B double bond of 1.599(4) Å similar
to that of its dihydrodiborene relative, (SIDep)HB=BH(SIDep)
(1.589(4) Å).10 The SIDep ligand at the BH moiety is near
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 BOC3H5 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 I.
With Kinjo and co-workers recently reporting the first diborene
with two different donor ligands16 and our group having just
published the first fully unsymmetrical diborene,17 compound 2
is only the second unsymmetrical diborene with respect to the
anionic substituents.

TDDFT calculations performed upon the optimised geom-
etry 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 double bond into the empty π* orbital of the carbene carbon of the SImes 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 (1J_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 B2C2O 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–N2 distance of (SIMes)BBr2BAr2 diborane (Fig. 3). DFT optimisations at the ONIOM(M06-2X/6-311+G(d):PM6) level (see ESI† for details) showed, however, that 3a isomerises to a diborane (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 B2C2O ring and the asymmetrically bridging hydride, and one at the protonated cAAC carbon atom, the other possibility is that 3a and 3b could be dia stereomers. 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 (RC1,RC2) (SC1,SC2)-3a pair (δcalc = 44.0, –4.4 ppm) adequately match the experimentally-observed shifts (δexp = 42.8, –1.9 ppm; Δδ = ±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 µ2-hydr ide-bridged diborane, 3b shows a doublet at –15.0 ppm (1J_B-H 1H = 50.8 Hz), indicating a terminal hydride rather than a bridging one. The predicted 11B NMR chemical shifts for the (RC1,SC2) (SC1,RC2) 3b pair (δcalc = 65.4, –18.9 ppm) are comparable to the experimental ones (δexp = 63.0, –15.0 ppm; Δδ ≈ ±3 ppm). The relative energy of (RC1,SC2) (SC1,RC2) 3b, at 3.1 kcal mol⁻¹ above (RC1,RC2) (SC1,SC2) 3a, is consistent with the experimentally observed ratio of 92 : 8.

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 3taut, a tautomeric form of 3a, in which the neutral cAAC ligand coordinates to the enoxyborane moiety, and the protonated cAAC ligand coordinates to the alkylborane moiety (Fig. 3). DFT optimisations at the ONIOM(M06-2X/6-311+G(d):PM6) level showed, however, that 3taut 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 B2C2O 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 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
enzolisable 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.\(^\text{13}\) 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 acetone and acetophenone to form the corresponding 1,2,3-oxadisilatane heterocycles, which then rearrange to the 1,2-enol addition products.\(^\text{20}\) In our case, however, careful monitoring of the reaction of iminoborane \(\text{IV}\) and diborony \(\text{II}\) 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 \(\text{IV}\) and at the ONIOM(M06-2X/6-311+G(d):PM6) level for \(\text{II}\) and \(\text{III}\) 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\(\text{I}^\dagger\) for details on the methodology and the optimised structures of all reactants, products, intermediates and transition states).

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

Instead, for compounds \(\text{II-IV}\) the first reaction step involves coordination of the carbonyl oxygen atom to one boron centre to form the acetone adducts \(\text{I}_{11}, \text{I}_{12}\) and \(\text{I}_{13}\) (\(\Delta G_i^\ddagger = 7.6\) (\(\text{IV}\)), 20.6 (\(\text{II}\)), 10.1 (\(\text{III}\)) 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 \(\text{IV}\)) or the electron-rich, second boron centre (for \(\text{II}\) and \(\text{III}\)), to yield the cis-aminoborane \(\text{I}_{23}\), and the SiDep- and cAAC-supported cis-diborenes \(\text{I}_{22}\) and \(\text{I}_{23}\), respectively (\(\Delta G_i^\ddagger = 4.0\) (\(\text{IV}\)), 14.1 (\(\text{II}\)), 14.9 (\(\text{III}\)) kcal mol\(^{-1}\)). Finally, the trans-aminoborane \(\text{I}_{1}\) and the trans-diborenes \(\text{I}_{2}\) 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 \((\Delta G^\ddagger = -43.2\) kcal mol\(^{-1}\)), followed by that of \(\text{1}\) \((\Delta G^\ddagger = -26.6\) kcal mol\(^{-1}\)) and \(\text{I}_{14}\) \((\Delta G^\ddagger = -27.4\) kcal mol\(^{-1}\)).

The exergonic isomerisation step leading from the cis-diborenes \(\text{I}_{22}\) and \(\text{I}_{23}\) to the trans-diborenes \(\text{I}_{2}\) 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 \(\pi\)-electron density of the B–B double bond into the \(\pi\) backbonding to the unsaturated carbene ligands. The resulting transition state \(\text{TS}_{32}\) now displays a B–B single bond, which allows facile rotation. The isomerisation process from \(\text{I}_{22}\) to \(\text{2}\) 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 \(\text{I}_{3}\) (\(\Delta G_i^\ddagger = 8.9\) 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 shutting chemistry displayed by cAAC hydroboron compounds\(^\text{19}\) and on the other hand by the very strong \(\pi\) acceptor properties of cAAC,\(^\text{12}\) which enable the stabilisation of the coordinately saturated intermediate \(\text{I}_{13}\).

For cumulene \(\text{III}\), 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-(alkylidene)borane \(\text{I}_{43}\) (\(\Delta G_i^\ddagger = 19.8\) 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 methylidene moiety yields the bis(cAAC)-stabilised 1,2,3-oxadiaborole \(\text{I}_{63}\) (\(\Delta G_i^\ddagger = 21.2\) kcal mol\(^{-1}\)). This is the highest energy barrier in the entire reaction mechanism. \(\text{I}_{63}\) then tautomerises to compound \(\text{3a}\) by concomitant migration of the hydride on B1 to the adjacent cAAC carbene centre and bridging of the hydride on B2 (\(\Delta G_i^\ddagger = 11.7\) kcal mol\(^{-1}\)). Overall the formation of \(\text{3a}\) from \(\text{I}_{3}\) and acetone 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, isolobal, multiply bonded boron compounds, iminoborane \(\text{IV}\), diborony \(\text{II}\) and cumulene \(\text{III}\), 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 \([2 + 2]\) 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.

Over all 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...