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Phosphinoborylenes as stable sources of fleeting borylenes†

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Base-stabilised borylenes that mimic the ability of transition metals to bind and activate inert substrates have attracted significant attention in recent years. However, such species are typically highly reactive and fleeting, and often cannot be isolated at ambient temperature. Herein, we describe a readily accessible trimethylphosphine-stabilised borylborylene which was found to possess a labile P–B bond that reversibly cleaves upon gentle heating. Exchange of the labile phosphine with other nucleophiles (CO, isocyanide, 4-dimethylaminopyridine) was investigated, and the binding strength of a range of potential borylene “ligands” has been evaluated computationally. The room-temperature-stable PMe_3 -bound borylenes were subsequently applied to novel bond activations including [2 + 2] cycloaddition with carbodiimides and the reduction of dichalcogenides, revealing that PMe_3 -stabilised borylenes can effectively behave as stable sources of the analogous fleeting dicoordinate species under mild conditions.

Introduction

In the continuing effort to replace environmentally deleterious metals in chemical reactions, p block compounds that mimic the unique properties of transition metals in the activation of strong bonds have recently come to the forefront of main-group chemical research.^{1–3} In particular, low-valent boron compounds in the form of bimolecular frustrated Lewis pairs,^{4–8} B–B multiply bonded species,^{9–11} and borylenes^{12,13} have captured significant attention as their unique bonding patterns and orbital arrangements allow for favorable interactions with a number of substrates often found in TM-catalysed reactions. While the chemistry of metalloborylenes,^{14–16} B–B multiple bonds, and particularly that of frustrated Lewis pairs are more mature fields of study, the field of metal-free borylenes has more recently emerged due to early challenges faced in the study of these oft-fleeting species.^{17–19} The study of isolable metal-free borylenes began in 2011 with the characterisation of a stable borylene supported by two cyclic alkyl(amino)carbenes (CAACs)^{20,21} by Bertrand and co-workers.²² These and other similar borylenes are nucleophilic at boron, and have been shown to act both as donor ligands and reducing agents toward a variety of main-group and transition metal species.^{23–30} In

2014, a significant advance in the synthesis of the first isolable, singly base-stabilised borylene was reported by Bertrand and Stephan *via* the introduction of electronic push and pull substituents at the boron centre.³¹ With boron-centred filled and vacant orbitals, this species was the first crystalline borylene with an electronic structure similar to that of a transition metal, and was able to effect metallomimetic reactivity in the binding of CO and scission of dihydrogen at ambient temperature.³² In another advance, in 2018 we reported the capture of dinitrogen by a fleeting singly base-stabilised borylene,^{33,34,42,43} revealing the powerful ability of these emerging species to activate highly inert bonds (Scheme 1).³⁷

Ligand exchange is a hallmark of transition metal chemistry, allowing reversible bond activations that are crucial steps in a multitude of catalytic processes, and is an emerging property of low-valent main group species.^{35,36} It was recently reported that metallomimetic reactivity could be achieved by the photolytic extrusion of CO from carbonyl-borylenes,^{28,37} providing the first methods to generate fleeting singly base-stabilised borylenes from a doubly base-stabilised borylene precursor. Herein, we report that the facile thermal release of trimethylphosphine from phosphine-stabilised borylborylenes can likewise be used to generate reactive borylenes that effect metallomimetic transformations under mild conditions.

Results and discussion

The previously reported preparation of the phosphine-stabilised borylene **1a** involves reduction of the CAAC-coordinated aminoboryl(amino)borenium salt $[(^{\text{Me}}\text{CAAC})\text{B}(\text{NMe}_2)\text{BBr}(\text{NMe}_2)] [\text{Bar}^{\text{Cl}}]$ with KC_8 at -80°C , followed by subsequent addition of

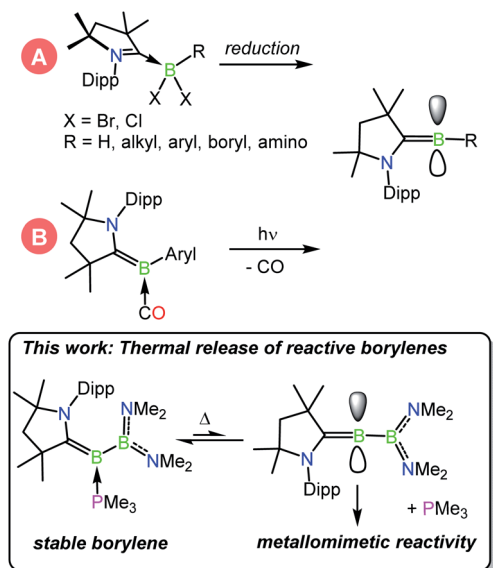
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Scheme 1 Known methods of generating CAAC-stabilised borylenes: (A) reduction, (B) photolytic CO extrusion.¹⁸

a slight excess of PMe_3 .³⁸ After warming to room temperature, filtration and concentration of the solution, the product was crystallised from the reaction mixture, affording a single isomer **1a** with ^{11}B NMR spectroscopic signals at 40.1 and 0.7 ppm.³⁸ However, it was noticed that when volatiles were rapidly removed from the reaction mixture such that crystallisation was largely avoided, a second isomer **1b** was also present, distinguishable by its ^{11}B NMR shifts at 42.3 and -1.7 ppm. While pure solutions of isomer **1a** are stable at ambient temperature, isomer **1b** could also be formed in small amounts by heating solutions of **1a**, with approximately 23% conversion to **1b** observed after heating a C_6D_6 solution of **1a** at 60°C for 30 minutes. Single crystals of **1b** were obtained by kinetic resolution of a mixture of **1a** and **1b** via reaction with 2,6-dimethylphenylisocyanide (*vide infra*), and its molecular structure was

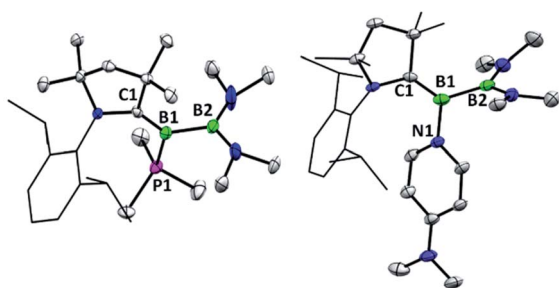
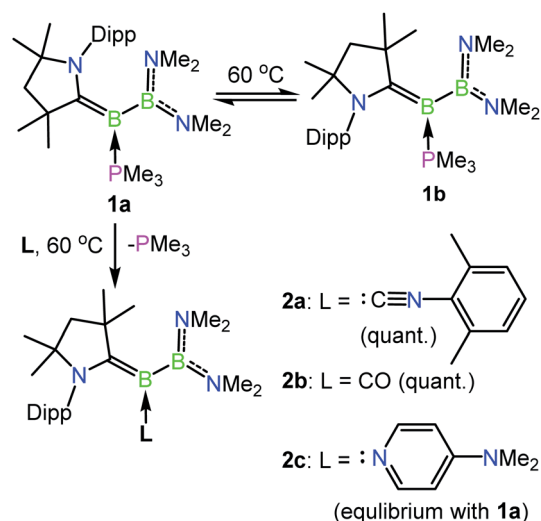


Fig. 1 Crystallographically-derived molecular structure of the Z-isomer of the phosphinoborylene **1b** (left) and the DMAP-stabilised borylene **2c** (right). Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and thermal ellipsoids of the Dipp groups are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$) for **1b**: B1–B2: 1.732(3), B1–C1: 1.459(3), B1–P1: 1.904(2); C1–B1–P1: 123.5(1), C1–B1–B2: 128.8(2), B2–B1–P1: 106.8(1). For **2c**: B1–B2: 1.714(4), B1–C1: 1.463(3), B1–N1: 1.584(3); C1–B1–N1: 122.4(2), C1–B1–B2: 125.7(2), B2–B1–N1: 111.5(2).

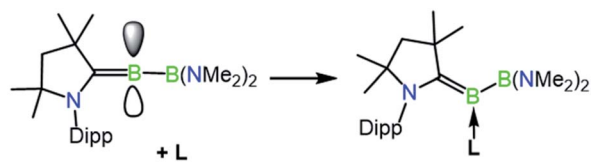
determined crystallographically (Fig. 1). Metric parameters of **1a** and **1b** are similar and indicate significant delocalisation of the borylene lone pair electrons towards the carbene carbon centre.

As such an isomerisation suggested lability of the phosphine, exchange reactions of **1a** with more strongly interacting donor–acceptor ligands were attempted. Heating a yellow solution of **1a** with 3.0 equiv. of 2,6-dimethylphenylisocyanide at 60°C resulted in a gradual color change to deep red and quantitative conversion to the isocyanide-stabilised borylene **2a** after 6 h (Scheme 2). A similar reaction with 1 atm of CO also resulted in complete conversion to borylene carbonyl **2b**. However, upon heating **1a** with 2.6 equivalents of the nitrogen base 4-(*N,N*-dimethylamino)pyridine (DMAP), only partial conversion to the DMAP-stabilised borylene **2c** was observed after 6 h, which eventually gave way to decomposition to a mixture of products upon further heating. The formation of **2c** was confirmed by its independent synthesis *via* low-temperature KC_8 reduction of $[(^{\text{Me}}\text{CAAC})\text{B}(\text{NMe}_2)\text{BBr}(\text{NMe}_2)]$ $[\text{BAR}^{\text{Cl}}]$ and subsequent addition of DMAP. Compound **2c** displays ^{11}B NMR signals at 42.9 and 23.5 ppm, and crystals suitable for X-ray diffraction were grown by slow evaporation of a pentane solution (Fig. 1). A molecular structure confirmed the formulation of **2c** and revealed a B– N_{DMAP} bond (1.584(3) Å) and a B– C_{CAAC} bond (1.463(3) Å), indicating population of the B– C_{CAAC} π -bond and the presence of a single dative bond between DMAP and the borylene centre. As with **1a**, isomerism about the B–CAAC bond is also observed in solutions of **2c**, although only the Z isomer could be crystallographically characterised (see ESI[†]).

The incomplete conversion of **1a** to **2c** despite the presence of an excess of DMAP suggested that an equilibrium is formed between these two species, and therefore we turned to computations to evaluate the relative thermodynamic stabilities of a range of base-stabilised borylenes (Fig. 2). It was found that both phosphorus and nitrogen bases feature weak interactions



Scheme 2 Isomerisation and exchange reactions of phosphine-borylene **1a**. Dipp = 2,6-diisopropylphenyl, quant. = quantitative.



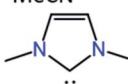
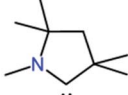
L =	ΔG (kcal·mol ⁻¹)
NMe ₃	8.8
tetrahydrofuran	5.5
N ₂	-10.0
PMe ₃	-12.8
PMe ₂ Ph	-13.3
pyridine	-13.3
imidazole	-13.5
PMe ₃ (<i>E</i> isomer)	-15.2
4-Dimethylaminopyridine	-18.0
MeCN	-18.6
	-28.3
	-33.7
CO	-34.9
MeNC	-37.7
2,6-dimethylphenylisocyanide	-40.4

Fig. 2 Relative thermodynamic stabilities of ligand-stabilised borylenes (M06 (D3)/Def2-SVP). Computed isomer is *Z* unless otherwise stated.

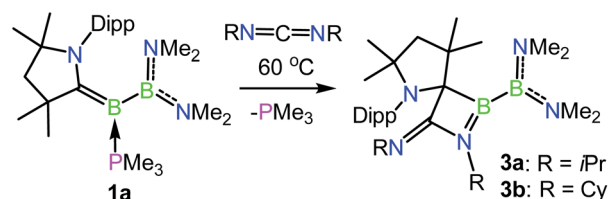
with the borylene centre (*ca.* -10 to -18 kcal mol⁻¹) and might be anticipated to form thermally labile complexes. Despite the calculated bonding strength of -10.0 kcal mol⁻¹ for molecular nitrogen, we were unable to observe formation of an N₂ product by exchange with **1a**, likely due to a low kinetic barrier to its decomposition at ambient temperature. Conversely, more strongly donating NHCs and more strongly π -acidic bases such as CO and isocyanides feature stronger bonds with the borylene centre, which would be anticipated to form robust complexes. It was found that the energy of formation of **1a** (-15.2 kcal mol⁻¹) and **2c** (-18.0 kcal mol⁻¹) are similar with respect to the “free” unsaturated dicoordinate borylene, accounting for the partial conversion to **2c** observed upon heating solutions of **1a**. The implied lability of the DMAP ligand in **2c** was further confirmed by an exchange reaction with 4.0 equivalents of 2,6-dimethylphenylisocyanide which quantitatively converted to **2a** after 3 h at ambient temperature. The partial isomerisation of **1a** into **1b** upon heating can also be accounted for by their similar thermodynamic stability, which differ by only 2.4 kcal mol⁻¹. Despite this, the barrier for PMe₃ loss from **1b** seems to be greater than that of **1a**, as heated reactions of **1a** with 2,6-dimethylphenylisocyanide become enriched in **1b** as the reaction progresses, from which single crystals of **1b** can be obtained as a mixture with **2a**. The borylenes **2a** and **2b** have significantly more exergonic formation energies (-40.4 and

-34.9 kcal mol⁻¹) and were found to be inert to thermal exchange or decomposition even at temperatures as high as 100 °C.

A kinetic study on the conversion of **1a** to **2a** was also undertaken (see ESI[†]), which indicated that this reaction is first-order in **1a**, but zeroth-order in 2,6-dimethylisocyanide, indicating that dissociative substitution is likely operating. Monitoring reaction rate at variable temperatures has revealed an activation barrier of 29.3 kcal mol⁻¹ for this conversion, which is in line with its steady progress at 60 °C. This thermal release of reactive borylenes complements earlier work where similar species were generated photolytically from carbonyl-stabilised borylenes,^{28,37} and now permits exchange reactions of both strongly and weakly bound borylene ligands.

Given the ability of **1a** to participate in exchange reactions with nucleophiles, we became interested in its ability to effect further ‘free borylene’ type reactivity in the capture of unsaturated molecules. To this end, heating a solution of **1a** with 3.0 equiv. of *N,N'*-diisopropylcarbodiimide resulted in clean conversion to the [2 + 2] cycloaddition product **3a**, whereby a C–C bond has been formed between the formerly carbene carbon center and the central carbon of the carbodiimide (Scheme 3 and Fig. 3). This transformation is unique in that it is not exclusively borylene-centred but involves a 1,2 addition across the B–C double bond, somewhat reminiscent of the formation of the intermediate metalcyclobutane in transition metal-based olefin metathesis.³⁹ ¹¹B NMR spectroscopy revealed chemical shifts of 61.3 and 34.2 ppm for **3a**, which can be assigned to the CAAC–B and B(NMe₂)₂ fragments, respectively. The reaction of **1a** with *N,N'*-dicyclohexylcarbodiimide likewise provided clean conversion to the analogous product **3b**, which exhibits similar structural and spectroscopic characteristics to **3a**. However, the bulkier *N,N'*-bis(2,6-diisopropylphenyl)carbodiimide did not react with **1a** upon extended heating at 60 °C, likely due to its steric bulk.

Oxidation reactions were also explored with the phosphine-borylene **1a**. While the reaction of **1a** with S₈ was difficult to control and not particularly selective in any stoichiometry, combination of one equivalent of **1a** with 0.5 equivalents of Ph₂Te₂ resulted in the immediate release of PMe₃ coupled with the loss of all other signals in the ¹H NMR spectrum, suggesting the formation of a paramagnetic product. Evaporation of the volatiles yielded red single crystals, from which an X-ray crystallographic study identified the product as the CAAC-stabilised telluroborane radical **4a**, which was isolated in a 70% yield upon recrystallisation (Scheme 4 and Fig. 4). A molecular structure of **4a** confirmed removal of one electron from the borylene lone



Scheme 3 Capture of carbodiimides with phosphine-borylene **1a**.

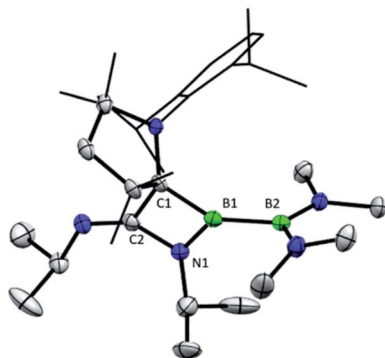
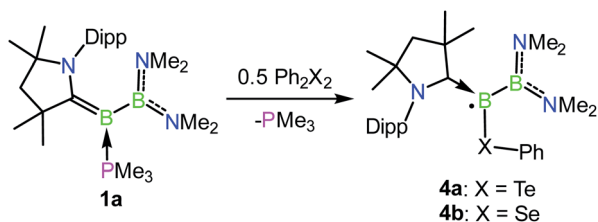


Fig. 3 Crystallographically-derived molecular structure of the *N,N'*-diisopropylcarbodiimide trapping product **3a**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and ellipsoids of the Dipp groups are omitted for clarity. Selected bond lengths (Å): B1–B2: 1.724(3), B1–N1: 1.428(2), C1–C2: 1.643(2).



Scheme 4 Oxidation reactions of **1a** with dichalcogenides.

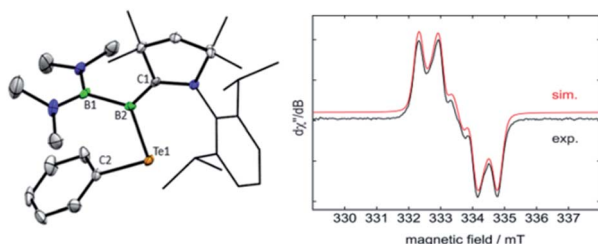


Fig. 4 Crystallographically-derived molecular structure of the telluroborane radical **5a** (left) and its EPR spectrum (right). Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and ellipsoids of the Dipp groups are omitted for clarity. Selected bond lengths (Å) and angles (°): C1–B2: 1.504(5)/1.514(5), B2–Te1: 2.199(4)/2.196(4), B1–B2: 1.718(5)/1.717(5); C1–B2–B1: 126.4(3)/125.0(3), C1–B2–Te1: 122.9(2)/123.6(2), B1–B2–Te1: 110.7(2)/111.2(2).

pair and revealed a partial double bond between the B and C centres, with a C–B bond length of 1.504(5) Å. EPR studies confirmed the radical nature of **4a**, and computational investigations indicated that the spin density is located primarily on the boron, carbon and nitrogen atoms (see ESI[†]), as has been previously observed for related CAAC-stabilised boron-centred radicals.^{31,32,40,41} The reaction of **1a** with Ph₂Se₂ also yielded the analogous selenoborane radical **4b**, which has similar metric parameters to **4a**. Given the very short timescale of these oxidation reactions (<1 min) at ambient temperature, it seems

probable that phosphine loss is preceded by oxidation in these cases.

Conclusions

In summary, we have demonstrated the thermal lability of phosphine- and DMAP-stabilised borylenes, and that such species can effectively behave as convenient and stable sources of reactive two-coordinate borylenes in exchange reactions with other nucleophiles and unsaturated substrates. This method complements existing methods of borylene generation *via* reduction and photolytic CO extrusion, and provides a facile method to generate these reactive species under mild conditions.

Conflicts of interest

There are no conflicts to declare.

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