Push and pull: the potential role of boron in N$_2$ activation

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Recent developments in main group chemistry towards the activation and conversion of N$_2$ have lead to the revelation that boron can greatly affect these processes. Boron is capable of acting both as a borane Lewis acid to activate metal–N$_2$ complexes and as an ambiphilic borylene able to activate free N$_2$. The latter example is capable of both accepting and donating electron density in a manner reminiscent of transition metal systems containing both filled and empty d-orbitals.

The functionalisation of N$_2$ remains one of the most persistent challenges in chemistry, even over a century since the advent of the Haber–Bosch process. This heterogeneous Fe catalyst remains the standard for the reduction of N$_2$ to NH$_3$. Chemists have been seeking alternatives to this energy intensive process for decades, however the development of commercially viable alternatives capable of breaking the remarkably strong N≡N triple bond and enabling the subsequent reduction have remained elusive.

One approach to N$_2$ fixation has involved the use of homogeneous transition metal complexes to bind and ultimately functionalise N$_2$.[1] Such methods are inspired by nature, where nitrogenase enzymes employ Fe/Mo catalysts to fix N$_2$ at ambient temperatures and pressures.[2] Many approaches have been used to generate complexes capable of reacting with N$_2$, however a particularly successful method has been to develop low-valent transition metal complexes capable of binding and facilitating reactivity at the N$_2$ ligand.[3] The efficacy of transition metal complexes in the binding of N$_2$ can be rationalised by the involvement of filled d-orbitals on the metal centre backdonating electron density into an antibonding π*-orbital on the N$_2$ ligand (Fig. 1). This process renders the N$_2$ ligand activated and susceptible to further reactivity and functionalisation.

Recently, this process has been augmented by the use of the strong main group Lewis acid tris(pentafluorophenyl)borane [B(C$_6$F$_5$)$_3$].[4] In conjunction with low-valent Fe, Mo and W centres, Szymczak[5] and Simonneau[6] were able to show that B(C$_6$F$_5$)$_3$ was able to increase greatly the degree of activation of the N$_2$ ligand in these M–N–N–B(C$_6$F$_5$)$_3$ complexes, as confirmed by IR measurements. The inclusion of B(C$_6$F$_5$)$_3$ into this system is thought to induce a "pull" effect resulting

in decreasing the bond order of the N$_2$ ligand, in conjunction with the "pushing" of electron density from the metal to the N$_2$ unit (Fig. 2). Furthermore, Szymczak has been able to show that the coordination of B(C$_6$F$_5$)$_3$ is able to protonate selectively the terminal N rather than the Fe centre when combined with the related HBAr$^F_4$. Absence of B(C$_6$F$_5$)$_3$ coordination results in Fe protonation, thus showing that B(C$_6$F$_5$)$_3$ results in a redistribution of electron density towards the terminal nitrogen atom.[5]

Conceptually, one can relate this type of reactivity to those of Frustrated Lewis Pairs (FLPs) where a Lewis acid and base react in a similar manner to activate small molecules. In recent years, FLPs and other main group systems have been shown to mimic the reactivity of a number of transition metal complexes, effectively mediating both stoichiometric and catalytic reactions that were once thought only possible for transition metal complexes.[7] Such precedent has spawned the idea that main group complexes may well be potential alternatives to transition metal systems for the fixation of N$_2$.[8] This Frontier article will focus on two recent examples where boron has been used to induce or mimic transition metal N$_2$ activation in different ways; one exploiting the high Lewis acidity of a borane and one the reactivity of cyclic alkyl(amino) carbene (CAAC) supported borylene complexes. These represent two different ideas of how boron can help facilitate the activation of N$_2$ one through 'push' type interactions where boron donates electron density to the N$_2$ unit and one through 'pull' type interactions driven by the Lewis acidity of electron deficient boranes.

As mentioned previously, the popular main group Lewis acid B(C$_6$F$_5$)$_3$ has been used to improve the degree of activation of N$_2$ in Fe, Mo, and W systems. In 2017, Stephan and co-workers reported on the reactivity of diphenyldiazomethane (Ph$_2$CNN) with B(C$_6$F$_5$)$_3$ and the related Lewis acid HB(C$_6$F$_5$)$_2$.[9] The reactivity of diazo compounds is underexplored in main group chemistry despite their ubiquity in organic chemistry.
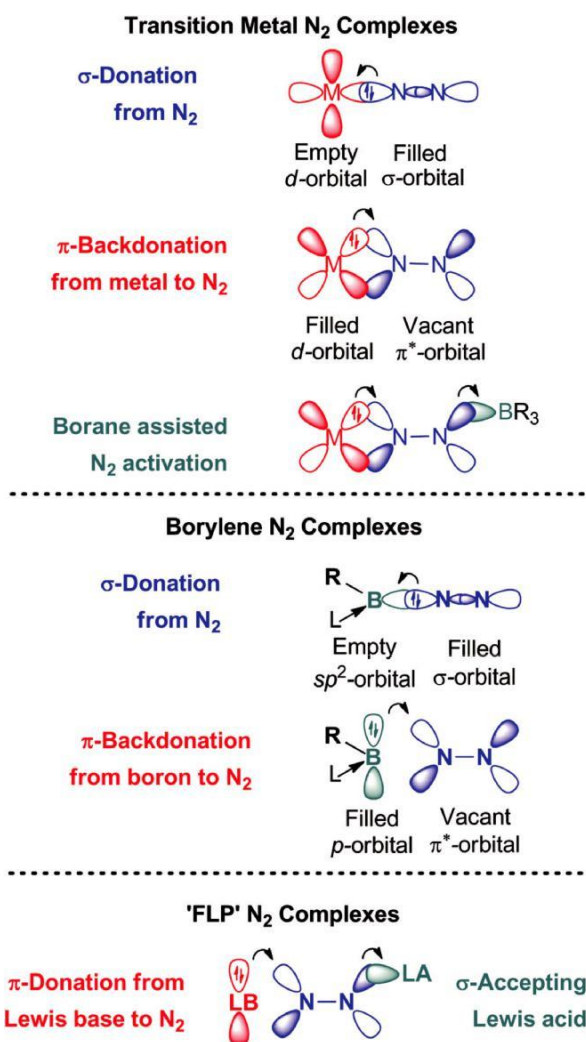
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Fig. 1 Electronic configurations of transition metal and borylene N₂ complexes.

Scheme 1 Reactivity of diphenyldiazomethane with Lewis acidic boranes. 1: C–N 1.278(8) Å, N–N 1.177(7) Å, N–B 1.65(1) Å. 2: C–N 1.287(2) Å, N–N 1.3939(18) Å, N–B 1.385(2) Å.
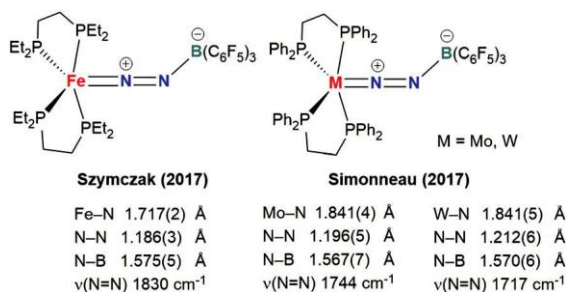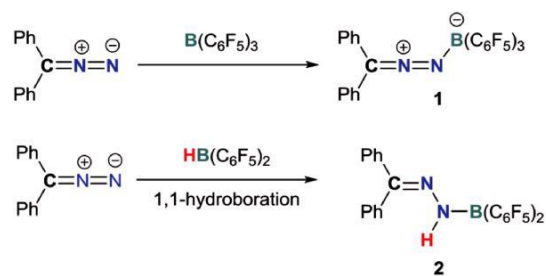

Fig. 2 Borane assisted N₂ activation at transition metal centres.

However, the insertion of diazo compounds into the B–C bonds of $B(C_6F_5)_3$ has been previously reported.[10] When one considers the adduct between diphenyldiazomethane and a borane such as $B(C_6F_5)_3$, it can be interpreted as a system where N₂ has been trapped between a borane Lewis acid and a carbene Lewis base (Scheme 1). If such an adduct was to be formed, one can imagine this as a template for how the product of an FLP mediated activation of N₂ may look.

Initial studies revealed that the adducts between diphenyldiazomethane and the Lewis acidic boranes $B(C_6F_5)_3$ was quite unstable and susceptible to the evolution of N₂ at room temperature. However, low temperature studies were able to uncover more information on the nature of this unstable adducts. Interestingly, the N–N bond length for the adduct of Ph₂CNN with $B(C_6F_5)_3$ was crystallographically determined to be in the range for those of N–N double bonds (and comparable to those reported for M–N–N–$B(C_6F_5)_3$ systems (M = Fe, Mo, W)).[5,6] When Piers' borane, $HB(C_6F_5)_2$, was employed in this reaction, a 1,1-hydroboration of the N–N bond was observed to form complex 2. Such a reaction is in contrast to the more traditional 1,2-hydroborations typically observed. Two mechanisms were considered, direct 1,1-hydroboration or 1,2-hydroboration followed by a hydrogen shift. Computational analysis corroborated the latter proposal, indicating the formation of a 3-centre-2-electron-like early transition state between the B–H–N unit. Bond orders of 0.54 and 0.33 were calculated for the B–H and N–H bonds respectively.[9] This type of interaction is indicative of donation of electron density from the B–H bond into a π*-orbital on the N–N unit. Notably, this type of electron donation into a low-lying π*-antibonding orbital is exactly how activation of N₂ is proposed to happen at transition metal centres.[1] The similar type of reactivity observed in this metal-free system is quite exciting, as one can envisage further modifications being made to facilitate subsequent reactivity at the N–N unit.

As an alternative to using main group compounds as Lewis acids, the chemistry of low-valent p-block compounds has been well studied in recent years.[11] Base-stabilised borylene complexes, monovalent boron stabilised by one or two neutral donors, represent one class of such compounds (Fig. 1).[12,13] Containing filled and vacant orbitals at boron, such compounds represent ideal candidates for potential nitrogen fixation at a main group centre. The viability of such borylenes in N₂ activation has been highlighted by a recent study where the unstabilised borylene PhB: is able to bind N₂ under matrix conditions.[14] This study suggests that borylenes contain the appropriate electronic structure to activate N₂, and with the proper choice of stabilising ligands, may be capable of fixating N₂ under mild conditions.

In this vein, the chemistry of borylene and borylene-like compounds stabilised by cyclic alkyl(amino) carbenes (CAAC) ligands has been reported by the groups of Bertrand, Stephan and Braunschweig.[15–17] Among the reactivity studied by these groups, borylene complexes were shown to undergo carbon monoxide fixation, photolytic decarbonylation reactions, and ligand exchange reactions. The isolelectronic relationship of CO and N_2 suggests that such borylene complexes may be ideal candidates for nitrogen fixation at boron. These hypoth-eses were substantiated by the strong backbonding observed in borylene–CO complexes reported by Braunschweig and led to further studies of CAAC-stabilised borylene complexes as can-didates for nitrogen fixation.[18]

Braunschweig and co-workers were previously able to show that the complex [(Dur)B(CO)(CAAC)] was able to undergo photolytic decarbonylation to form a transient [(Dur)B(CAAC)] species which was shown to complex Lewis bases (Dur = 2,3,5,6-tetramethylbenzene; CAAC = 1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene).[16,17] In the absence of Lewis bases, [(Dur)B(CAAC)] was found to undergo an intra-molecular C–H activation reaction to form 4. Notably, attempts to decarbonylate [(Dur)B(CO)(CAAC)] under a N_2 atmosphere did not result in N_2 fixation, such reactions resulted in the iso-lation of the C–H activated species 4. The formation of [(Dur)B (CO)(CAAC)] proved to be initially inefficient, as the only syn-thesis involved the reaction of a CAAC with a Fe–borylene complex. Attempts to generate [(Dur)B(CO)(CAAC)] in a more efficient manner lead to the optimisation of a more stream-lined approach to its synthesis, where [(Dur)B(CAAC)Br₂] (3) could be simply reduced using excess KC_8 under a CO atmo-sphere (Scheme 2). If the reduction of 3 was performed in an argon atmosphere, the C–H activation product 4 was formed. However, when this reaction was performed at −80 °C under a N_2 atmosphere, a new fuchsia coloured species was seen.
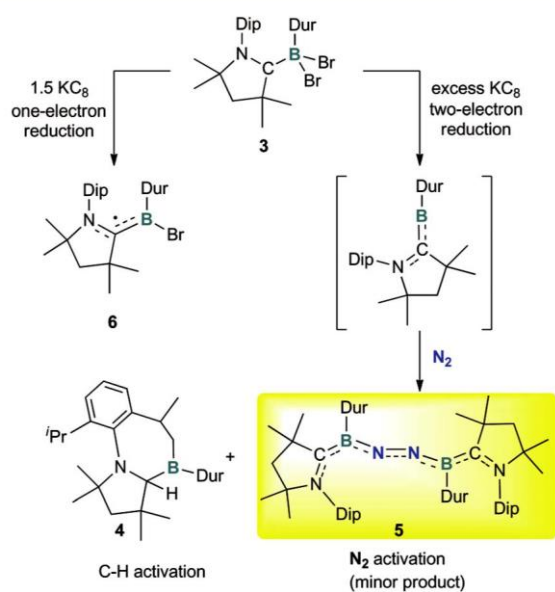
Upon analysis of the reaction mixture after warming to room temperature overnight, two diastereomers of the C–H activated product 4 were observed as the major species present. In addition, a small crop of dark purple crystals were isolated from the reaction mixture which had a shift of δ = 10.7 ppm in the ^{11}B NMR spectrum, representing a species previously unseen in this chemistry. Remarkably, the dark purple crystals were found to be the product of N_2 fixation, 5, where N_2 has been trapped between two [(Dur)B(CAAC)] units (Scheme 2). Attempts to separate this species from 4 proved difficult, therefore another more selective synthetic route to 5 was investigated through the one electron reduction of radical species 6. Primary observations of the reaction indicated initial formation of the dark purple N_2 activation product 5, however upon warming to room temperature a colour change to dark blue was observed and the dipotassium complex 7 was formed (Scheme 3). This compound was able to be cleanly obtained from the reaction mixture and was isolated in a yield of 64%. The structures of 5 and 7 were analysed by crystallo-graphic techniques. The structure of 5 proved to be unsymme-trical, whereas 7 was shown to contain an element of sym-metry (Fig. 3). Notably, the N–N bond length in 5 was observed to be 1.248(4) Å, a value comparable with numerous organic N–N double bonds, and well short of those typically observed for N–N single bonds. The B–N–N–B torsion angle of 113.3(4)° is in contrast to the linear angle typically observed for similar transition metal M–N–N–M complexes.[19] Such a difference in geometry can be rationalised by the orbitals available to par-ticipate in backbonding in each system. The p-orbitals of boron are not able to conform to the linear geometry observed in transition metal systems due to the participation of d-orbi-tals. Despite this difference in geometry, the borylene–nitrogen interaction is believed to resemble transition metal–N_2 com-

Scheme 2 Reactivity of reduced [(Dur)B(CAAC)] fragment.
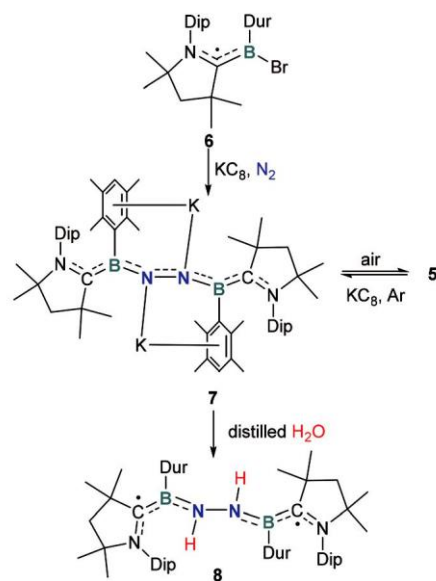
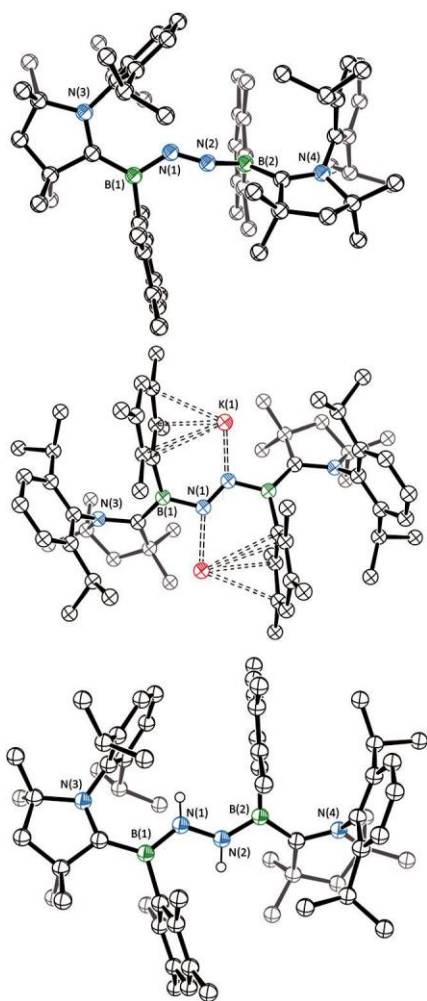Scheme 3 Synthesis of N_2 fixation product 5 and hydrazine derivative 8.

Fig. 3 Solid-state structures of 5 (top), 7 (middle), and 8 (bottom). Thermal ellipsoids are shown at 50% probability. 5: B(1)–N(1) 1.423(4) Å, N(1)–N(2) 1.248(4) Å, N(2)–B(2) 1.403(5) Å. 7: B(1)–N(1) 1.484(4) Å, N(1)–N(2) 1.304(4) Å, K(1)–N(2) 2.687(2) Å, 8: B(1)–N(1) 1.435(4) Å, N(1)–N(2) 1.402(2) Å, N(2)–B(2) 1.417(4) Å.

plexes rather than other more traditional organic N−N contain-ing compounds.

The transition metal-like interaction in 5 can be seen in the short bonds observed between the carbene and borylene frag-ments (1.528(5) Å, 1.541(4) Å). The short distances resemble those witnessed in other CAAC supported monovalent borylene complexes,[15–17] suggesting that the borylene in this system is acting as a σ-acceptor and π-donor to the N−N fragment. These observations were corroborated by DFT calculations, where Kohn−Sham orbital analysis confirmed the experimentally determined geometry and revealed the HOMO−1 contains an interaction between a boron p-orbital, N−N π*-orbital, and carbene−N π*-orbitals. This backdonation of electron density from boron to both the CAAC ligand and N_2 fragment strongly resembles the backdonation observed from filled d-orbitals on transition metals.

The solid-state structure of dipotassium complex 7 revealed a slightly different bonding motif to that observed in 5. Elongation of the B−N bonds and shortening of the carbene−B bonds are observed in 7, suggesting an increased degree of backbonding from the borylene to the CAAC ligand relative to the N_2 fragment. Such an observation was expected as the N−N orbitals in the reduced complex already contain extra electron density relative to 5, lessening the need of backdonation from boron.

When exposed to air, complex 7 was readily oxidised to the neutral N_2 compound 5 in good yield, providing a route for the reproducible isolation of 5. Similarly, if 5 is allowed to react with KC_8 under an argon atmosphere, regeneration of the dipotassium complex 7 is observed (Scheme 3). Reaction of 7 with distilled water resulted in the generation of a new Turquoise coloured species, revealed to be diradical species 8. The solid-state structure of 8 shows the formation of what is best described as a diborahydrazine complex. The N−N bond distance of 1.402(2) Å in this complex is well within the accepted region for that of a N−N single bond. The diradical nature of 8 was not surprising as a number of [(CAAC)BR$_2^\bullet$] radicals are known, and the experimental and spectroscopic data obtained for 8 agreed well with such compounds.[20]

Complex 8 represents the first species isolated in this study containing a N−N single bond. This is quite significant as it suggests that, not only can N_2 be trapped between two bory-lene units, but this framework is capable of supporting the reduction of N_2 to a hydrazine derivative under mild reaction conditions. This reaction can be thought of as representing a partial reduction of N_2 to NH_3, and provides a platform for the further investigation of nitrogen fixation at main group centres.

Conclusions

As main group chemistry continues to search for similarities (and differences) that bridge the divide between transition metal chemistry and that of the p-block,[21] the chemistry described in this Frontier article highlights the potential role of boron in the fixation of N_2. Boranes can facilitate this process by participating in both electron-withdrawing ("pull") and electron-donating ("push") types of interaction. Lewis acidic boranes had been previously shown to assist in the acti-vation of N_2 in transition metal systems by 'pulling' on the N_2 ligand and facilitating N_2 activation. This chemistry was expanded to metal-free systems, where diazodiphenylmethane was used as a precursor for the isolation of a FLP-like species that would be the product of N_2 activation between a carbene and a borane. This result represented an exciting step forward in this field, as it demonstrated that the trapping of N_2 between two main group fragments was possible and that the Lewis acidic nature of boranes may be key to this process. However, such a system itself would not be capable of acti-vation of N_2 gas.

Expanding this chemistry further, the landmark study pub-lished by Braunschweig represents a paradigm shift in this field, where boron, an element whose role in N_2 activation was thought to be to "pull" through its Lewis acidic nature was able to "push" electron density to N_2. This study revealed that, through the proper manipulation of the electronic structure at boron, borylene species containing both filled and empty orbi-tals are competent in the fixation of N_2, mimicking the reactiv-ity exhibited by transition metals. Furthermore, the fixed nitro-gen was reduced to a hydrazine derivative using water, demon-strating the exciting ability for such species to not only coordi-nate N_2, but to reduce it in a remarkably efficient manner. This study should provide a template for the future of this field, where it has now been shown that through the proper manipulation of the electronic structure of main group elements that they can fix nitrogen under mild conditions. It is anticipated that future developments in ligand design may facilitate the development of more boron containing species capable of N_2 fixation, as well as the development of complexes capable of fixing nitrogen containing other p-block elements. These exciting recent results provide new insight into main group chemistry but there are still great strides that need to be taken in order for boranes (or other p-block elements) to compete with transition metals in the activation and utilis-ation of dinitrogen.

Conflicts of interest

The authors declare that there are no conflicts of interest.

Acknowledgements

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