

The Metallomimetic Chemistry of Boron

Marc-André Légaré,^{a,b,*} Conor Prancevicius,^{a,b,*} Holger Braunschweig^{a,b}

^a Institute for Inorganic Chemistry, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg (Germany). ^b Institute for Sustainable Chemistry & Catalysis with Boron, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg (Germany).

* *These authors contributed equally*

Abstract: The study of main-group molecules that behave and react similarly to transition metal (TM) complexes has attracted significant interest in the recent decades. Most notably, the attractive idea of eliminating the all-too-often rare and costly metals from catalysis has motivated efforts to develop main-group-element-mediated reactions. Main-group elements, however, lack the electronic flexibility of many TM complexes that arise from combinations of empty and filled *d*-orbitals and that seem ideally suited to bind and activate many substrates. In this Review, we look at boron, an element which, despite its non-metal nature, low atomic weight, and relative redox stericity has achieved great milestones in terms of TM-like reactivity. We show how in inter-element cooperative systems, diboron molecules and hypovalent complexes, the fifth element can acquire a truly metallomimetic character. As we discuss, this character is particularly strikingly demonstrated by the reactivity of boron-based molecules with H₂, CO, alkynes, alkenes and even with N₂.

1.1. Introduction

The transition elements are defined by their *d*-orbital sub-shell which has the unique situation of being partially filled.¹ These *d*-orbitals, which are part of the valence shell of the transition metals, have become the salient feature of their chemistry and give them a unique place in the periodic table and in the realms of scientific interests and applications. In the most challenging steps of many catalytic cycles, the interplay of electron density and electron-deficiency that is a direct consequence of the partially filled *d*-shell enables complex processes that are not trivial for other elements.² Their large range of oxidation states, the flexibility of their coordination patterns and the reversibility of their transformations are predicated on this unique electronic arrangement. It is thus unsurprising that transition metals, in materials and in molecular complexes, are at the forefront of the catalytic sciences, which often focus on designing precisely tuned arrangements of ligands and metal atoms in order to bind small molecules, cleave bonds and couple building blocks in innumerable applications (Figure 1).³

However, the scarcity, high cost, toxicity and environmental issues associated with the extraction and use of transition metals, as well as the fundamental scientific instinct of pushing back the boundaries of knowledge, have sparked considerable interest in investigating the possibility of hitherto transition-metal-exclusive reactions using purely main-group compounds. This new field of chemistry, which we have termed 'main-group metallomimetics',⁴ has gained

considerable traction in recent years and has led to the discovery of both conceptual reactions and applicable catalytic reactions.

The design and preparation of main-group metallomimetics, however, is not trivial and relies on the application of unusual strategies and the development of new concepts. At first glance, the usual properties of main group elements would disqualify them from reacting in analogous ways to transition metals: where many transition metals can access a range of oxidation states and often can relatively freely transition from one to the other, main-group elements usually display a strong affinity for one or two oxidation states and remain relatively redox-static. Furthermore, in order to achieve their preferred oxidation state and to follow the empirical octet rule, main-group elements tend to form complexes of invariable coordination numbers and of set geometries that can be predicted using the VSEPR model. For main-group compounds, these geometries and coordination numbers are often associated with clear nucleophilic or electrophilic properties, which are in contrast with the electronic interplay possible with TM complexes.

The metallomimetic chemistry of the heavier main group elements has recently been reviewed by Power.⁵ However, the natural abundance and low toxicity of light main-group elements of the second period make them especially attractive candidates for the design of metallomimetics. Among these elements, boron is being increasingly found in atypical oxidation states and molecular arrangements and deserves to be described independently on account of its unique chemistry.

1.2. Definition of Metallomimetic Compounds and Scope of this Review

The reactivity of boron and of the other light main-group elements is limited by their rigid electronic properties. For this reason, it is not common for complexes of boron to react with substrates that interact preferably with a combination of filled and empty orbitals. Among the reactions that are atypical for main-group compounds are: a) the fixation of small molecules that bind to metal centers through σ -donation and π -backbonding (e.g. CO, N₂, η^2 -alkenes and alkynes), and b) the cleavage of unactivated bonds (e.g. C-H and H₂ activation) (Figure 2).

Boron-containing systems that are capable of these reactions will be the focus of this review. The unique strategies and concepts that enable boron to act in a manner reminiscent of the reactivity of transition-metal catalysts is the core of the understanding of boron metallomimetics. These approaches can be divided into three categories (Figure 2): in the first, the boron center effects its metallomimetic reactivity through the cooperative action of another non-metal element. This approach includes ambiphilic systems and the frustrated Lewis pair (FLP)^{6,7} paradigm that has been formulated in the previous decade around boron-based catalysts.

The second class of metallomimetics is defined by the cooperative reactivity of more than one boron center. This type of metallomimetic includes the unique reactivity of B-B single and multiple bonds within diborane, diborenes, diboracumulenes and diborynes, as well as that of unusual species that feature proximal boron centers. In many of these cases, one boron center provides an empty orbital while either the B-B bond or another nucleophilic boron atom provides the possibility of backdonation.

Finally, we will also outline the chemistry of metallomimetics that feature the reactivity of a single boron atom as the active site; most often in an atypical oxidation state. In the most striking of these cases, the complexes affect reactivity through the cooperation of empty and filled boron-centered orbitals. While this class of reactive compounds is still emerging, recent advances in the field of borylene chemistry have clearly demonstrated the ability of mononuclear boron complexes to behave like transition metals.

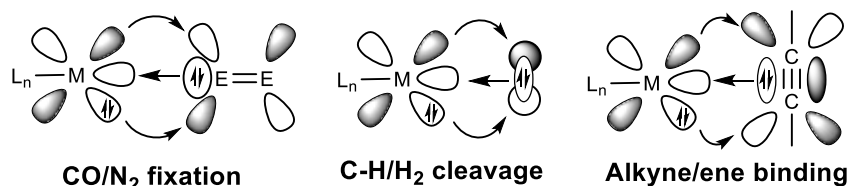


Figure 1. The Dewar-Chart-Duncanson model of TM-based substrate activation

Metallomimetic	Empty Orbital	Filled Orbital	Orbital Depiction
FLP-ambiphilic (Chapter 1)	Boron	Lewis Base	
Dinuclear Boron (Chapter 2)	Boron	Boron / B-B bond	
Single-site Boron (Chapter 3)	Boron	Boron	

Figure 2. Description of boron-based metallomimetics that are the topic of this Review.

Metallomimetic boron - FLPs

1.3. Introduction - FLP Activation

The partially filled d-subshell¹ of the transition metals (TMs) allows them to interact with small molecules according to the Dewar-Chart-Duncanson model.^{8,9} In a single-site TM species, a combination of vacant and filled d-orbitals of appropriate symmetry activate a substrate through interaction with its frontier molecular orbitals. These orbital interactions weaken bonds within a substrate and facilitate reaction steps such as migration, insertion, as well as redox-active processes such as oxidative addition and reductive elimination. In contrast, tricoordinate boron(III) compounds have only a single vacant p-orbital and no non-bonding electrons. However, in combination with a second element possessing a filled non-bonding orbital, reactivity that mimics transition metal centers can be achieved.

This approach underpins the chemistry of frustrated Lewis pairs (FLPs), a concept that was introduced by Stephan and coworkers in 2007.¹⁰ FLPs are undoubtedly the most mature field of boron metallomimetics; having emerged as a powerful tools for the activation of H₂, CO₂,

CO, N₂O, NO, SO₂, Si-H, olefins, and alkynes. Since the chemistry of FLPs has been extensively reviewed in recent literature,^{6,7,11-16} it will be the scope of this section to explore mechanistic themes of boron(III)-based FLP transformations with small molecules including H₂, olefins, alkynes, CO, and arene C-H bonds, and examine their relationship to analogous TM-based transformations.

Within the FLP paradigm, one molecular component functions as the Lewis acid (LA), and the other as the Lewis base (LB), which through steric encumbrance or reduced electronic overlap are prevented from strongly interacting with one another. Consequently, the reactivity of both the Lewis acid (usually a borane) and the Lewis base (typically based on phosphorus, nitrogen, carbon, or oxygen) is preserved in the reaction medium and can be simultaneously applied to the substrate.^{17,18} Electron transfer (ET) is therefore achieved between the substrate and via a vacant p-orbital on boron, in combination with a filled orbital on the organic base.

1.4. Dihydrogen

While early examples of 'FLP-type' reactivity utilizing bulky Lewis acids/bases had been reported in prior literature,¹⁹⁻²¹ it was the seminal discovery of metallomimetic reversible H₂ cleavage by Stephan and coworkers by an intramolecular perfluorophenylene-linked phosphinoborane that proved to be the ignition point of the field.²² The reactivity with H₂ was quickly extended to bimolecular systems.²³ The common avenues for H₂ activation in both FLP systems and TM systems are presented below (Figure 3). In the case of unimolecular TM systems, it is the combination of both vacant and filled d-orbitals of appropriate symmetry that simultaneously withdraw electron density from a substrate HOMO; in this case the filled σ -orbital of H₂, and donate electron density to the corresponding LUMO; the σ^* -H₂ orbital.²⁴ Another common mechanism of substrate activation is bifunctional activation between a TM and a ligand-centered base,^{25,26} particularly relevant in the context of hydrogenation of polar substrates.^{27,28} Interestingly, even after a decade of computational examination, the exact mechanism of H₂ splitting via the prototypical B(C₆F₅)₃/PtBu₃ FLP is still a matter of some contention.²⁹ However, there is general agreement on the initial formation of an FLP 'encounter complex';^{18,30-32} a pre-association of the Lewis acid and base substituents, which is primarily supported by secondary bonding interactions. From this point, the proposed mechanisms differ. According to the electric field (EF) picture,^{30,33,34} rate-limiting insertion of the H₂ unit into the 'reactive pocket' of the encounter complex is followed by polarization of the H₂ moiety by the electric field therein, whereupon facile scission of the H₂ unit occurs with formation of the phosphonium borohydride salt. No significant orbital interactions are present in the transition state. According to the ET picture,^{17,18,35} the electric field induced within the encounter complex is insufficient to split the H₂ moiety, and activation is supported via orbital interactions $sp^X(P) \rightarrow \sigma^*(H_2)$ and $\sigma(H_2) \rightarrow p(B)$. The transition state features significant orbital interactions of the FLP with the H₂ moiety. From this point, the mechanism of delivery of H₂ to the FLP partners has been described as concerted but asynchronous,³⁵ where the B-H bond is formed somewhat before the P-H bond. Interestingly, while steric frustration is a primary tool to effect FLP hydrogen activation in Lewis acid/base pairs, the energetic mismatch of molecular filled/vacant orbitals within intramolecular systems can also be used to a similar end. For example, the phosphinoborane (C₆F₅)₂B=PtBu₂, which features a high lying B-P π -orbital and low lying B-P

π^* -orbital, readily reacts with H_2 to afford the corresponding phosphonium borate zwitterion.^{36,37} Exceptionally, Yamashita and Nozaki have also reported the scission of H_2 by a boryllithium species, where a nucleophilic boron center functions as the Lewis base in heterolytic H_2 splitting to form a borohydride and lithium hydride.³⁸

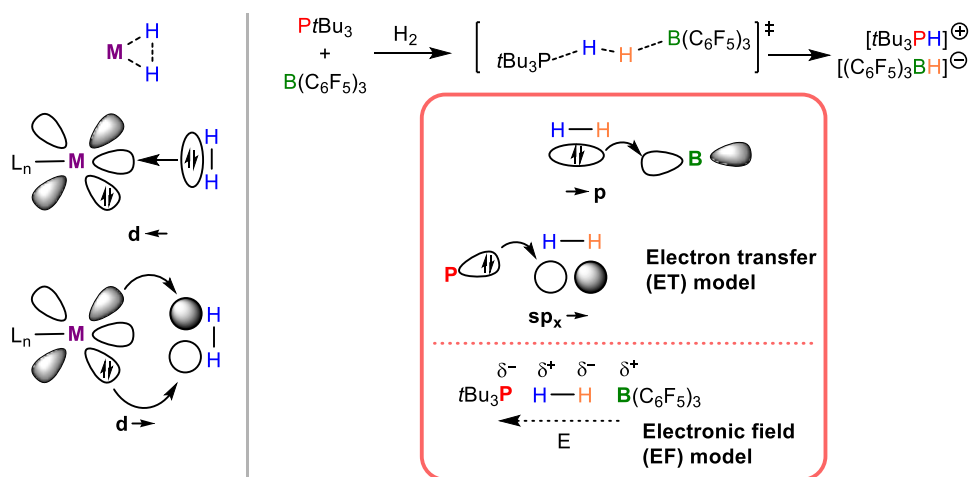


Figure 3. Interactions relevant to the activation of H_2 using both TMs (left) and the $B(C_6F_5)_3/PtBu_3$ FLP (right).

While originally a fundamental curiosity, the metallomimetic behavior of FLPs was cemented by their ability to catalytically deliver H_2 to unsaturated polarized substrates, such as imines, enamines, and silyl enol ethers,³⁹⁻⁴⁶ and later to more challenging substrates such as ketones,⁴⁷⁻⁴⁹ and anilines/N-heterocycles,⁵⁰⁻⁵⁵ and has recently been comprehensively reviewed.⁵⁶ Such hydrogenations proceed via an ionic mechanism,^{39,57} where proton and hydride delivery to a substrate (which may also function as the FLP base if it is sufficiently nucleophilic) occurs in a stepwise manner (Figure 4, left). Tuning the acidity/hydricity of the captured H_2 was paramount in achieving efficient delivery of H_2 , as while strongly Lewis acidic and basic FLPs cleave H_2 most effectively, it is FLPs of reduced Lewis acidity/basicity that are the most suitable to deliver a reactive proton or hydride to an unsaturated substrate.^{32,58-60} In a systematic study of imine hydrogenation catalysis by NHC-borenum cations,⁶¹ it was found that a non-bulky and electron-poor NHC supporting ligand yielded the fastest FLP hydrogenation catalyst, despite being significantly less Lewis acidic than $B(C_6F_5)_3$. The activation of dihydrogen by FLP systems is highly reminiscent of outer-sphere Noyori-type H_2 activation between a Lewis acidic metal centre and a ligand-centered base,^{62,63} wherein similar unquenched acidity/basicity of the system affords greatly accelerated heterolytic cleavage of H_2 , which is subsequently delivered to unsaturated polar substrates in a concerted manner. Despite the stepwise delivery of proton and hydride in FLP systems, some success in enantioselective imine hydrogenation has been achieved via the use of chiral boranes in the activation of H_2 .⁶⁴⁻⁷¹ However, this effort is complicated by the ability of some highly Lewis acidic boranes to epimerize chiral amines.⁷²

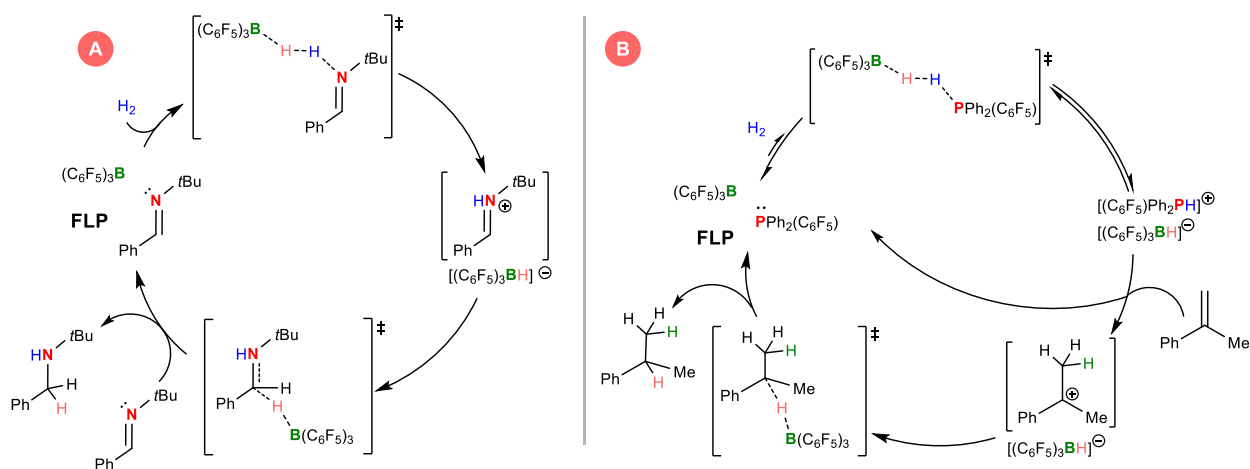


Figure 4. FLP-based catalytic hydrogenation of imines (left) and alkenes (right).

The FLP hydrogenation of non-polar functionalities, such as olefins and polycyclic aromatic species, was realized by the use of very weak and bulky bases, such as diarylamines, electron-deficient phosphines, and ethers (Figure 4, right) in combination with $B(C_6F_5)_3$,⁷³⁻⁷⁷ which operates via a similar ionic mechanism described above.⁷⁸ While the H_2 cleavage step with such systems is disfavored and can only be observed spectroscopically at -80 °C, the conjugate phosphonium salt formed upon reaction of the FLP system with hydrogen is now significantly acidic to protonate certain olefins to form a transient carbocation. As such, a requirement for catalytic turnover is that the carbocation formed is sufficiently long-lived that it may irreversibly react with the borohydride. Stabilization of the intermediate carbocation was typically achieved via hyperconjugation or delocalization with a neighboring π -system, therefore limiting the substrate scope to mostly conjugated and 1,1-geminally substituted olefins. Outer-sphere delivery of H_2 has been proposed in the TM-catalyzed hydrogenation of the C=C bonds of quinolines,⁷⁹ however, to our knowledge has not been invoked for simple olefins.

Subsequently, Repo and coworkers⁸⁰ designed a linked amine-hydroborane FLP (**1**) for the selective *cis*-hydrogenation of internal alkynes, utilizing a hydroboration – H_2 cleavage – protodeboronation mechanism (Figure 5), which bears a clear analogy to the classic inner-sphere TM hydrogenation mechanism.^{81,82} This catalyst displays a high degree of chemoselectivity towards internal alkynes, as upon hydroboration with an olefin, catalyst degradation via loss of C_6F_5H was more favorable than alkane release. A similar reaction has also been realized via a hydridoborane/silica-supported phosphine FLP.⁸³ Additionally, Wang and coworkers also have reported that the simple, highly Lewis acidic hydroborane $HB(C_6F_5)_2$ can hydrogenate simple alkenes via a related hydroboration – hydrogenolysis mechanism,⁸⁴ which will be discussed in more detail in section 4.1.

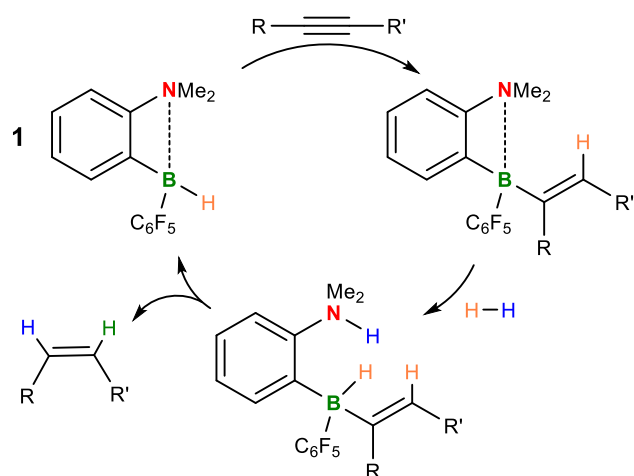


Figure 5. Hydrogenation of internal alkenes catalyzed by an amino-borane FLP.

Overall, the wealth of FLP reactivity with H₂ has uncovered two main hydrogenation mechanisms. Polar hydrogenations generally take place via a stepwise ‘outer-sphere’ (also termed ‘ionic’) mechanism, which generally feature nucleophilic hydride delivery to an unsaturated substrate. In contrast, non-polar hydrogenations can operate via an ‘inner-sphere’ mechanism, which involves insertion of an unsaturated substrate into a borohydride (hydroboration), followed by protodeborylation or hydrogenolysis (*vide infra*). Such transformations directly mirror the hydrogenation mechanisms that operate with TM systems.

1.5. Olefins

Olefins react stoichiometrically with P/B-based FLPs to form ethylene-bridged phosphonium borate zwitterions (Figure 6, A).^{10,85} The transition states of such additions with phosphines have been computed to involve concerted, but asynchronous, $sp^x(P) \rightarrow \pi^*(olefin)$ and $\pi(olefin) \rightarrow p(B)$ orbital interactions,^{86,87} directly analogous to the Dewar-Chatt-Duncanson model of TM olefin activation.^{8,9} Furthermore, such transformations bear strong mechanistic analogy to the TM-catalyzed hydroamination reaction, where an external amine attacks a TM-activated olefin to form a 2-aminoethyl ligand (outer-sphere mechanism), which can subsequently undergo further reactivity (Figure 6, C).⁸⁸

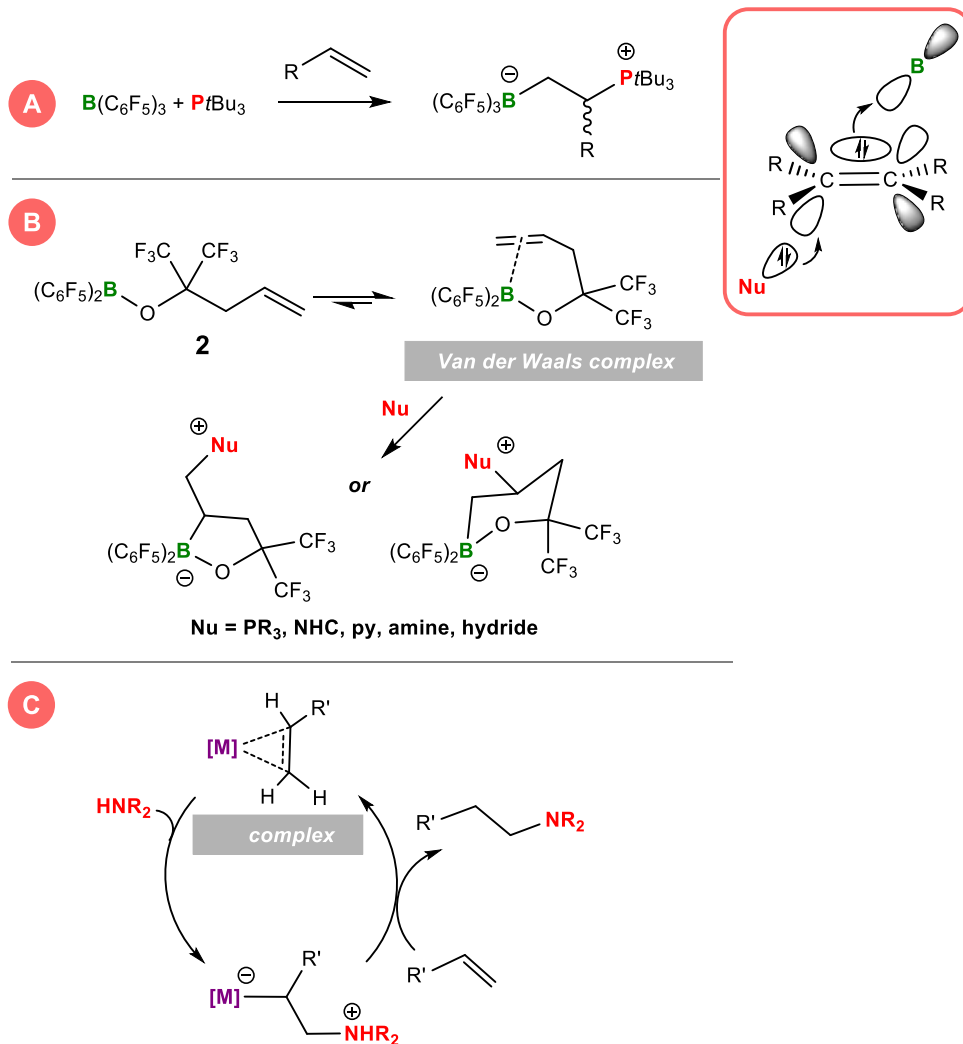


Figure 6. FLP- and TM-based activations of olefins.

Experimental evidence for the pre-interaction of olefins with the Lewis acidic unit prior to attack of the basic partner has emerged: Stephan and coworkers have prepared a strongly Lewis acidic borane bearing a pendant olefinic group (**2**), where NMR spectroscopic evidence of the “van der Waals complex” of the olefin pre-coordinated to the borane was presented.^{89,90} It has additionally been shown computationally that such van der Waals complexes are important intermediates in FLP olefin capture with simple substrates, such as ethylene.⁸⁶ While such complexes are not true π -olefin complexes, and the activation they provide is very minimal, they nevertheless provide a ‘pre-organization’ of the reaction partners toward olefin activation that is essential for termolecular reactions. Subsequent addition of a nucleophile, such as a phosphine, amine, or N-heterocyclic carbene, to the tethered-olefin van der Waals complex results in rapid nucleophilic addition, with formation of either the five- or six-membered boracycle, depending on the steric constraints of the incoming nucleophile (Figure 6, B).

1.6. Alkynes

With FLPs, internal alkynes form simple 1,2-addition products much akin to their reactivity with olefins.⁹¹ However, in contrast to alkenes, which form very weak van der Waals complexes with Lewis acidic boranes, terminal alkynes have been determined computationally to form more strongly bound (but still fairly weak) σ -complexes with highly Lewis acidic boranes,^{92,93} which activate the alkyne by acidifying the alkynyl C-H proton and withdrawing electron density from the β -carbon (Figure 7). Such species have an electronic structure similar to that of vinyl cations derived from electrophilic addition to alkynes.⁹⁴ In the absence of an external nucleophile, reactions of terminal alkynes with strongly Lewis acidic perfluoroarylboranes typically proceed via migration of the alkynyl hydrogen to the β -carbon, concomitant with activation of a B-C bond, resulting in the formation of the 1,1-carboboration products (Figure 7).^{93,95-97} However, in the presence of an FLP, diverging reactivity pathways with alkynes exist,^{91,93,98} which are influenced by the steric and electronic properties of both the FLP and the substrate.

The FLP activation of terminal alkynes is postulated to proceed via the same activated alkyne-borane σ -complex, which can either undergo nucleophilic attack at the Lewis acidic β -carbon to form the olefin-bridged zwitterionic salt, or be deprotonated by the external nucleophile to form a bimolecular alkynylborate salt. The reaction pathway is directed by both the steric size and basicity of the partner base, where more Brønsted basic and bulky phosphines favor deprotonation and formation of the alkynylborate product. The alkyne-borane activation σ -complex bears some resemblance to typical TM-alkyne π -complexes, which are known to rearrange similarly to form vinylidene ligands.⁹⁹

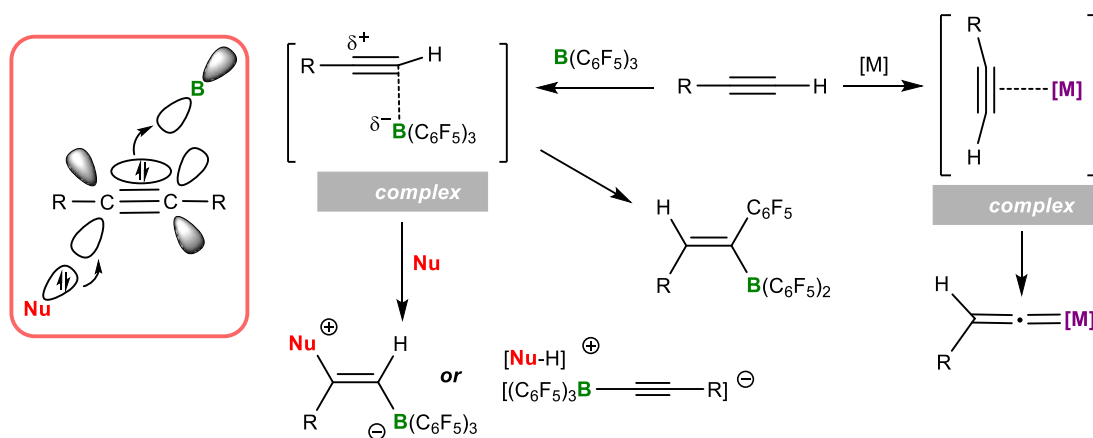


Figure 7. Typical FLP and TM reactivity with alkynes.

Alkyne activation induced by strongly Lewis acidic boranes has led to the development of stoichiometric C-C bond forming reactions with enamines and pyrroles,¹⁰⁰ as well as catalytic alkyne hydroamination,^{101,102} a transformation which is catalyzed by numerous TM complexes by similar mechanisms,¹⁰³ as well as catalytic alkyne hydroboration.¹⁰⁴⁻¹¹⁰ Subsequent work by the groups of Melen, Stephan, Paradies, and Hashmi has demonstrated that strongly Lewis acidic boranes can be utilized to induce a wealth of intramolecular cyclization reactions involving propargyl esters^{111,112} amides,¹¹³ and related systems where an activated alkyne is attacked by an internal nucleophile.¹¹⁴⁻¹²⁵ Such reactions in many cases mirror transformations accessible typically via carbophilic Au or Pt catalysts.¹⁰³ An exemplary cyclization of a 1,5-enyne¹¹⁵ is

presented in Figure 8, which may be accessed via either boron- or gold-based catalysis. Triphenylphosphine is also added in this case to act as a proton shuttle.

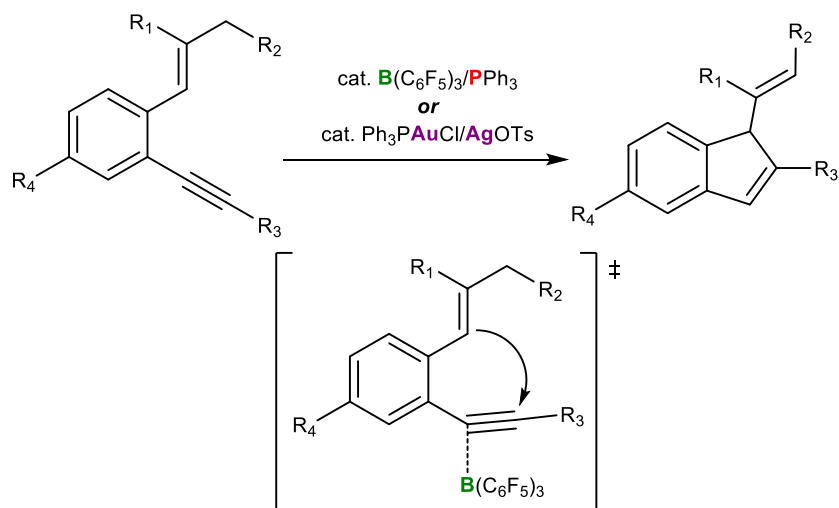


Figure 8. FLP- and TM-catalyzed 1,5-enyne cyclization

1.7. Carbon Monoxide

TM complexes bind CO via withdrawal of electron density from a C-centered sp orbital, while populating the C-O π^* -orbital, resulting in a weakening of the CO bond and a decrease in the CO vibrational frequency. Lewis acidic boranes, such as BH_3 ,¹²⁶ and $\text{HB}(\text{C}_6\text{F}_5)_2$,^{127,128} perfluoroalkylboranes¹²⁹⁻¹³¹ and electron deficient boroles¹³² are also known to form weakly bound σ -complexes with CO. However, as trivalent boron lacks non-bonding electrons to populate the CO π^* -orbital, such species display long B-C distances and typically have *increased* CO vibrational frequencies with respect to free CO, due to the greater electrostatic polarization of the C-O unit upon coordination to a borane.¹³³ Nevertheless, borane-carbonyls are susceptible to nucleophilic attack by external bases, such as NH_3 , at the carbonyl carbon (Figure 9; A).^{129,130} Such reactions follow a familiar mechanism, where withdrawal of electron density via σ -complexation acidifies the carbonyl carbon to accept electrons from an external donor. While the prototypical $\text{B}(\text{C}_6\text{F}_5)_3/\text{PtBu}_3$ FLP does not react with CO, the ethylene-linked phosphine-borane FLP systems of Erker and coworkers do capture CO to form five-membered phosphonium formylborate complexes (Figure 9; B),^{134,135} as do related B/N intermolecular FLPs.¹³⁶ Interestingly, X-ray structures revealed that the coordination of such species is markedly unsymmetrical, with large B-C-O angles ($\approx 135^\circ$), long P-C distances (2.04-2.10 Å), and short C-O distances (1.17-1.19 Å). Such features suggest a bonding environment analogous to TM-carbonyl compounds, where the phosphine donates electron density into the π^* -orbital of a formal C-O triple bond. The IR stretching frequencies of such species are in the range of 1757-1791 cm^{-1} , indicating strong activation relative to free CO. Trifunctional FLP systems have also recently been applied in the capture of CO.¹³⁷

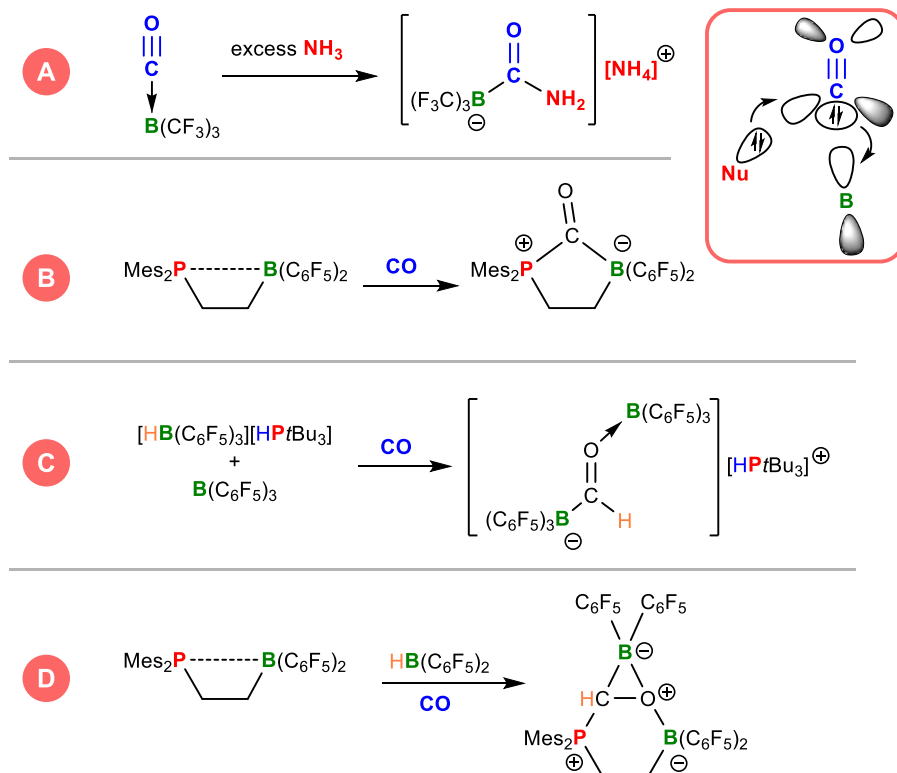


Figure 9. CO capture and insertion with FLP systems.

Insertion reactions of CO into the B-C bonds of simple alkylboranes have long been known, and have found application in the synthesis of alcohols, aldehydes, and ketones.¹³⁸ Such reactions are reminiscent of metallo-acyl intermediates derived from CO insertion into metal-alkyl complexes relevant to hydroformylation catalysis.¹³⁹ However, CO insertion reactions typically do not proceed with simple hydridoboranes in the absence of additional reagents.¹²⁸ Considering the relevance of such transformations to Fischer-Tropsch catalysis,^{140,141} efforts were undertaken to apply an FLP approach to this problem. Stephan and coworkers have demonstrated the use of a H₂-derived borohydride as the base in a FLP system, leading to the trapping of the CO by 1,1-insertion into the B-H bond (Figure 9; C), whereupon further hydrogenation and insertion reactions involving the formylborate unit can occur.¹⁴²⁻¹⁴⁴ Similarly, Erker and coworkers have demonstrated that CO-hydridoborane adducts also react with FLPs with CO insertion into the B-H unit to yield formylborate complexes (Figure 9; D),^{127,128,145-147} which have also been used in further C-C- and C-N-bond-forming reactions.¹⁴⁸ Despite the demonstration of these stoichiometric reductions, the catalytic use of CO as a feedstock in FLP transformations has not yet been realized, likely due to the strong bonds often formed between Lewis acidic boranes and oxygen-containing functional groups.

1.8. Arene C-H activation

The selective C-H functionalization of C-H bonds in arenes and alkanes is one of the most challenging fields of transition metal catalysis. The last few decades have seen an explosion of interest in developing different approaches to C-H bond activation. These investigations have

given rise to a whole field of research focused on the cleavage and functionalization of the C-H bond by transition metals.

While stoichiometric C-H borylation reactions have been reported with a number of highly Lewis acidic boranes and borenium ions,^{61,149-159,160} these processes employ stoichiometric amounts of highly reactive reagents through a Wheland-like mechanism. In a few cases, Friedel-Crafts-type catalysis could be observed for the TM-free catalytic borylation of arenes, in mechanisms that bear little similarity to TM chemistry.^{152,154,158,161-163} Similar reactions are typically metal catalyzed,^{164,165} often by precious metals such as iridium or palladium, which act in tandem with an internal base.

Nevertheless, here too can FLPs show their metallomimetic behavior. While select TM systems can selectively cleave C-H bonds at a single atom, Fontaine and coworkers have shown a similar process between proximal B and N atoms in ambiphilic amino-borane FLP complexes such as **3**.^{166,167} In this system, C-H bonds from heteroarenes are first activated at the FLP site by simultaneous coordination to the boron centre and deprotonation of the arene C-H functionality (Figure 10, TS),¹⁶⁸ followed by elimination of H₂. This bond activation can be followed by σ -bond metathesis with pinacolborane, enabling a catalytic cycle for the borylation of heteroaromatic C-H bonds under mild conditions. A bench-stable pre-catalyst activated by the addition of pinacol borane has also been reported.¹⁶⁹ Repo and co-workers later extended this activation to include simple arenes and alkenes using a similar system, albeit in a stoichiometric process.¹⁷⁰

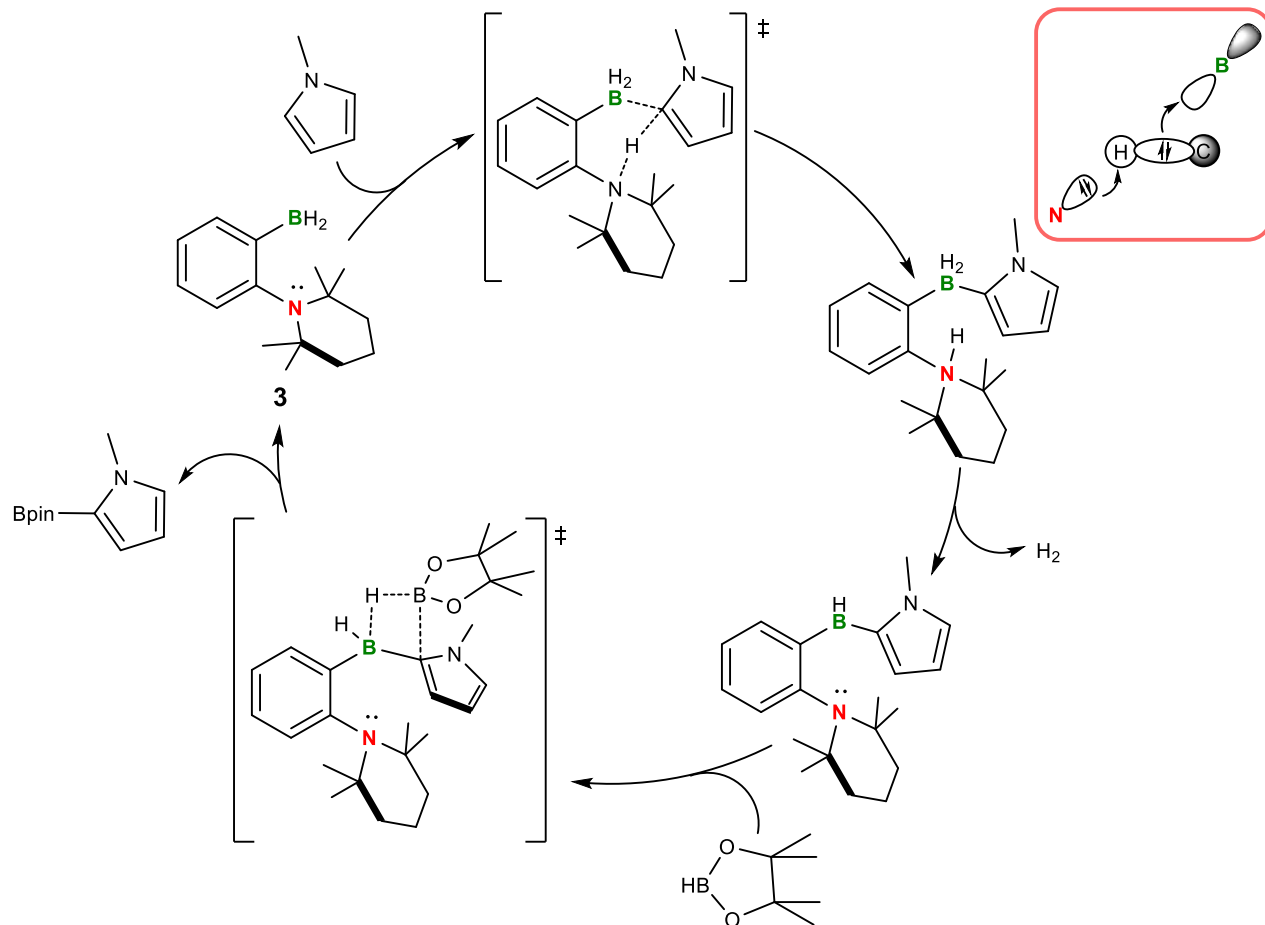


Figure 10. FLP-mediated heteroarene C-H borylation.

1.9. Summary

The combination of an electron-deficient borane with another atom that provides a non-bonding electron pair of electrons can be used to effect many transformations typically exclusive to transition metal systems, such as the activation and delivery of H₂ to unsaturated substrates, CO binding, alkyne hydroamination, and C-H functionalization. While often metals achieve simultaneous donation and withdrawal of electrons from a substrate due to their single-site behavior, the binary nature of many FLPs requires pre-organization of the reaction partners, which may be in the form of a FLP 'encounter complex' (H₂), or pre-association of the substrate with one FLP component via formation of a van der Waals complex (olefins) or a σ -complex (CO, alkynes), followed by reaction of the activated complex with the other FLP partner.

2. Metallomimetic reactivity through two boron atoms

While catalytic breakthroughs have been achieved through inter-element cooperativity, metallomimetic behavior can also be attained using only combinations of boron-based active centers. In recent years, unusual dinuclear boron complexes have shown reactivity towards the

binding of alkynes, dihydrogen and carbon monoxide, in manners that are reminiscent of transition metals.

2.1. Nonbonded boron centers

Boron-boron cooperative reactivity was convincingly demonstrated by Kinjo and coworkers in the cases of 1,3,2,5- (**4**)^{171,172} and 1,4,2,5-diazadiborinine (**5**)¹⁷³ complexes (Figure 11; A, B). These aromatic compounds react with a variety of substrates (CO₂, MeOTf, HBpin, Ar₂PH, and others) in a manner that suggests the presence of an unusually nucleophilic boron center. Consequently, **4** and **5** possess similar ambiphilic cooperative properties that give rise to the metallomimetic reactivity in FLP systems, and also have been observed to bind alkynes and alkenes in an analogous manner. More recently, the same group showed activity of the related compound **6** towards the cleavage of H₂ and NH₃ (Figure 11; C).¹⁷⁴ Similar reactivity towards ethylene was also observed with NHC-diboranthracene adduct **7**.¹⁷⁵ Interestingly, the selective 'side-on' binding of dioxygen from dry air was observed. Notably, the metallomimetic behavior of diboranthracene complexes could be increased by two-electron reduction (Figure 11; D),^{176,177} where the reduced dilithiodiboranthracenide **8-R** (R = H, CC*t*Bu) complexes were shown to activate H₂, as well as the C-H bond of terminal alkenes (Figure 11; E).

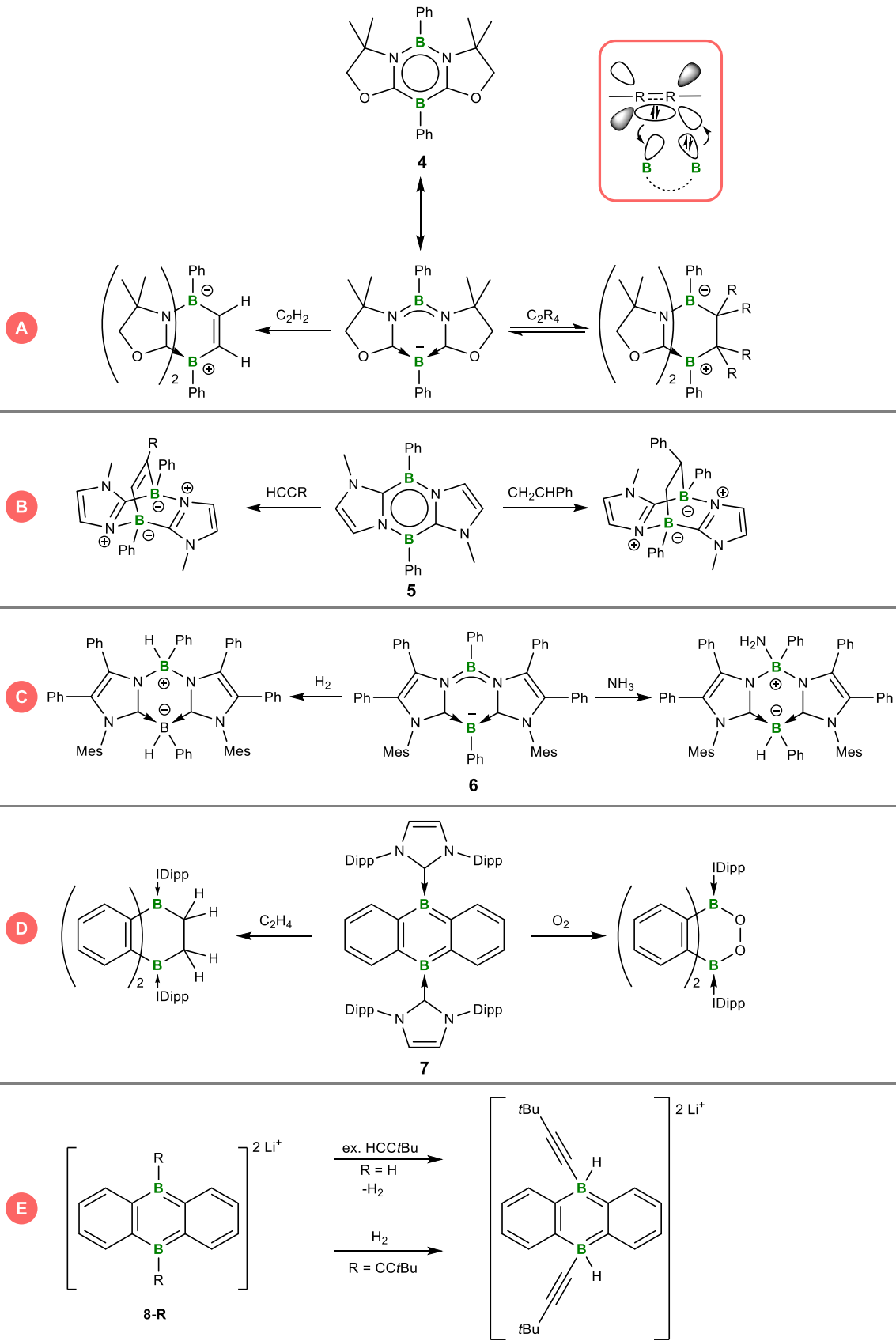


Figure 11. Activation of small molecules by non-bound boron centers.

2.2. Metallomimetic chemistry of B-B bonds

Early work on tetrachlorodiborane (B_2Cl_4) demonstrated that this highly acidic and reactive molecule could cleave molecular hydrogen at room temperature in the absence of a catalyst.¹⁷⁸ The products of the reactions are BCl_3 and B_2H_6 . B_2F_4 , B_2Cl_4 and B_2Br_4 were also found to spontaneously add to ethylene.¹⁷⁹⁻¹⁸² Since then, the diboration of many unsaturated bonds using diboranes has been established in the presence or absence of catalysts.^{183,184}

In recent years, departing from the chemistry of classical diborane(4) systems such as B_2pin_2 , B_2cat_2 , $B_2(OMe)_4$ and $B_2(NMe_2)_4$, unusual complexes featuring reactive B-B single and multiple bonds have been the object of considerable interest. Employing simple tetraaryldiboranes, Yamashita and coworkers¹⁸⁵ have demonstrated the facile cleavage of molecular hydrogen by tetra(*o*-tolyl)diborane (**9**) under ambient conditions (Figure 12; A). Computational modeling of the reaction shows that while the high Lewis acidity of the diboron reagents activates the H-H bond, B-to-H interactions complete the bond cleavage. Thus, through the concerted action of two boron atoms, TM-mimicking reactivity is enabled. These results give insight into previous chemistry that used diboron reagents as precatalysts for the reduction of acenes under harsh conditions.^{186,187} Interestingly, **9** also reacts with carbon monoxide with initial insertion of CO into the B-B bond, followed by subsequent rearrangement.¹⁸⁸ Typical alkyl and arylboranes are usually relatively inert towards π -acceptor bases such as CO, because they lack the filled orbitals that allow TM complexes to effect backbonding. In this case, however, the electron density of the B-B bond appears to be accepted by CO, resulting in cleavage and metathesis to give a boroxine and a C-H insertion product.

Proposing a similar mechanism as with tetra(*o*-tolyl)diborane, Wang *et al.* have recently reported the cleavage of H_2 by the remarkably stable borylborenium complex **10** (Figure 12; B). In this unsymmetrical diboron reagent, a positively-charged boron center is the HOMO of the molecule, which can interact with the H-H σ -bond. The other boron atom supplies electron density to the antibonding orbitals of H_2 .¹⁸⁹ Similar reactivity towards H_2 was observed with the cyclic B,B'-dimesityldithienodiborane **11** (Figure 12; C).¹⁹⁰

An unusual diboron framework was also found to cooperatively enable the activation of a C_{sp^3} -H bond of methyllithium.¹⁹¹ In this case the nucleophilic organolithium ensures the coordination of a CH_3 group to a boron center and the reduction of the redox-active complex. The other boron atom, being proximal to the CH_3 group, activates the C-H bond via a σ -complex while the electron density from the B-B bond performs the cleavage.

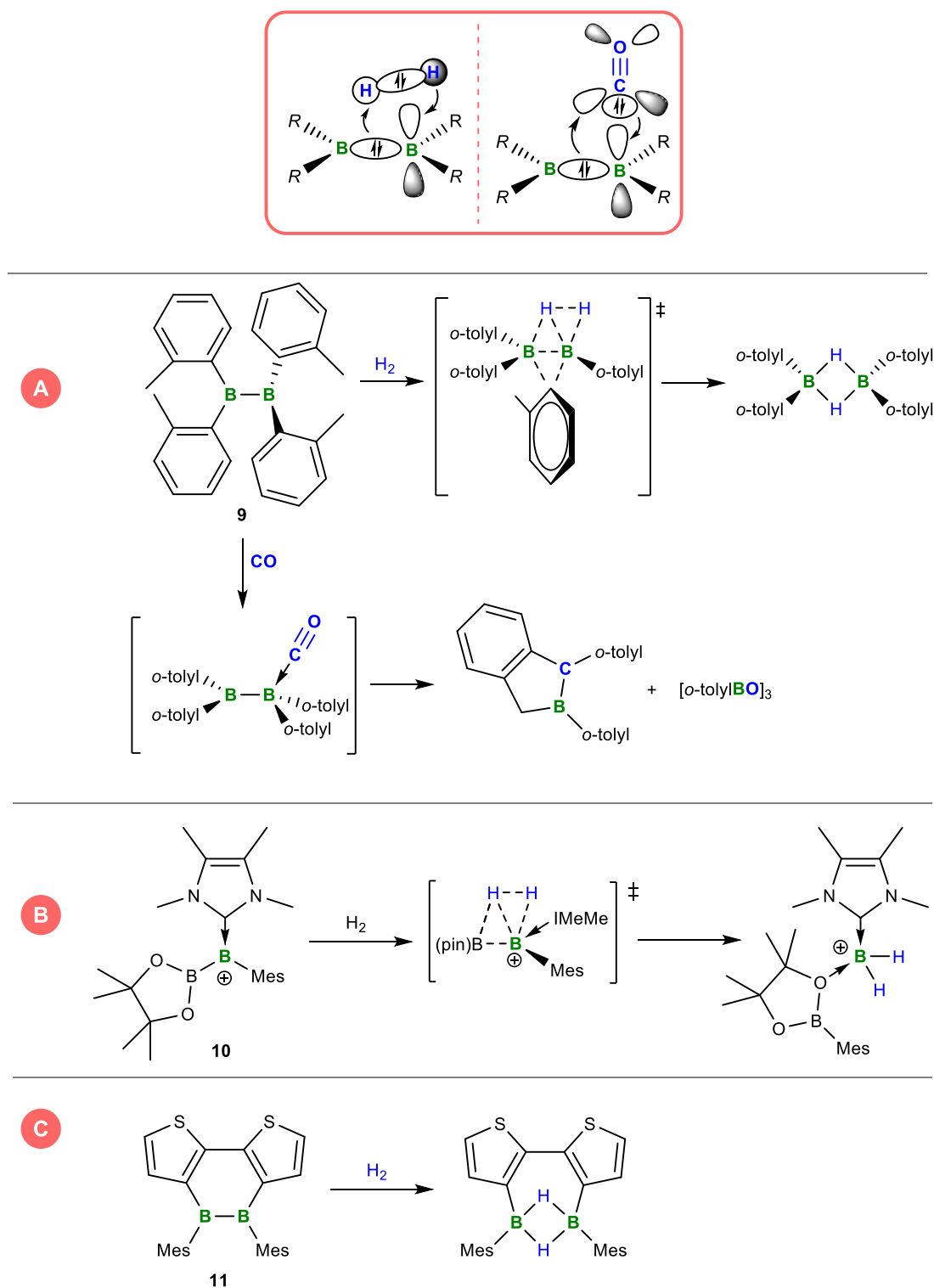


Figure 12. Reactivity of B-B single bonds towards H_2 and CO .

Molecules that feature B-B multiple bonds can display even more striking metallomimetic chemistry. Possessing boron centers in a formally lower oxidation state, they often possess

orbitals that are ideally suited to the activation of small molecules and the breaking of relatively inert bonds. The study of such species has been the subject of many reports, beginning with the isolation of dianionic^{192,193} and neutral diborenes^{194,195} and more recently with diboryne complexes.¹⁹⁶ As analogues of alkenes, diborenes possess a HOMO with B-B bonding of π -symmetry and a $\pi^*(\text{B-B})$ LUMO. However, the HOMO-LUMO gap is much smaller in diborenes than in ethylenes, suggesting that reactivity involving the cooperative contribution of both empty and filled orbitals is much more likely for the former. This confers a reactivity to diborene complexes that far exceeds that of their carbon-based analogs. While many diborene reactions are not formally metallomimetic – being not directly comparable with TM reactions – they most often involve an interplay of the boron-based HOMO and LUMO. Similarly to alkenes, the B=B bond in $[(\text{C}_4\text{H}_4\text{S})\text{IMeB}]_2$ was found to be readily hydroborated.¹⁹⁷ In contrast to alkenes, however, the same compound was found to react with elemental sulfur under mild conditions to effect complete B-B bond cleavage.¹⁹⁸ With the silylated derivative $[(\text{C}_4\text{H}_3(\text{SiMe}_3)\text{S})\text{IMeB}]_2$, more selective reactivity was achieved with S_8 and Se to give diboradithiirane complexes.^{199,200} For their part, diborynes have been most commonly described as possessing a B-B triple bond, being isoelectronic with alkynes, but again with a narrower HOMO-LUMO gap. Even more than diborenes, diborynes species possess a rich reactivity, including interactions with chalcogens, dichalcogenides,^{199,201} isocyanides²⁰² and acetone.²⁰³

In contrast to diborenes, the metallomimetic reactivity of diborynes is more clearly exemplified. Indeed, $[\text{IDippB}]_2$ (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) (**12**) reacts rapidly with one equivalent of CO to give bridging adduct **13** (Figure 13, B).²⁰⁴ In this complex, a very long C-O bond distance (1.249(2) Å), as well as an IR band at 1926 cm^{-1} indicate the strong π -overlap of the B-B orbitals into the antibonding orbital of carbon monoxide. The addition of an excess of carbon monoxide to $[\text{IDippB}]_2$ led to the coupling of four equivalents of CO into complex **14**, an unprecedented reactivity mode for both boron compounds and for light main-group elements.

Interestingly, when 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (SIDipp)²⁰⁵ and N-(2,6-diisopropylphenyl)-2,2,4,4-tetramethylpyrrolidin-5-ylidene (^{Me}CAAC)²⁰⁶ analogues of NHC-stabilized diborynes (**15** and **18**, respectively) were synthesized, it was found that the π -accepting capabilities of these ligands deplete the B-B triple bond HOMO and give rise to an electron deficient diboracumulene-type structure, where the B-B bond order decreases with an increased π -accepting character of the ligand (Figure 13, A). The reactivity of these complexes with carbon monoxide reflects this change in properties. Instead of CO coupling, the addition of excess CO to **18** selectively affords a bis-CO adduct (**19**). In this complex, the CO bond distances (1.173(2) Å) are notably shorter than in the case of **13**, while the IR band is at a similar wavenumber (1926 cm^{-1}). **18** also reacts with *t*BuNC to form a similar complex.²⁰² In carbon monoxide chemistry, as in bonding and structure, **15** has intermediate reactivity between **12** and **18**. While **16** – an analog of **19** – can be observed at $-30\text{ }^\circ\text{C}$ following the addition of CO to **15**, gradual conversion to the coupled product **17** takes place at room temperature.

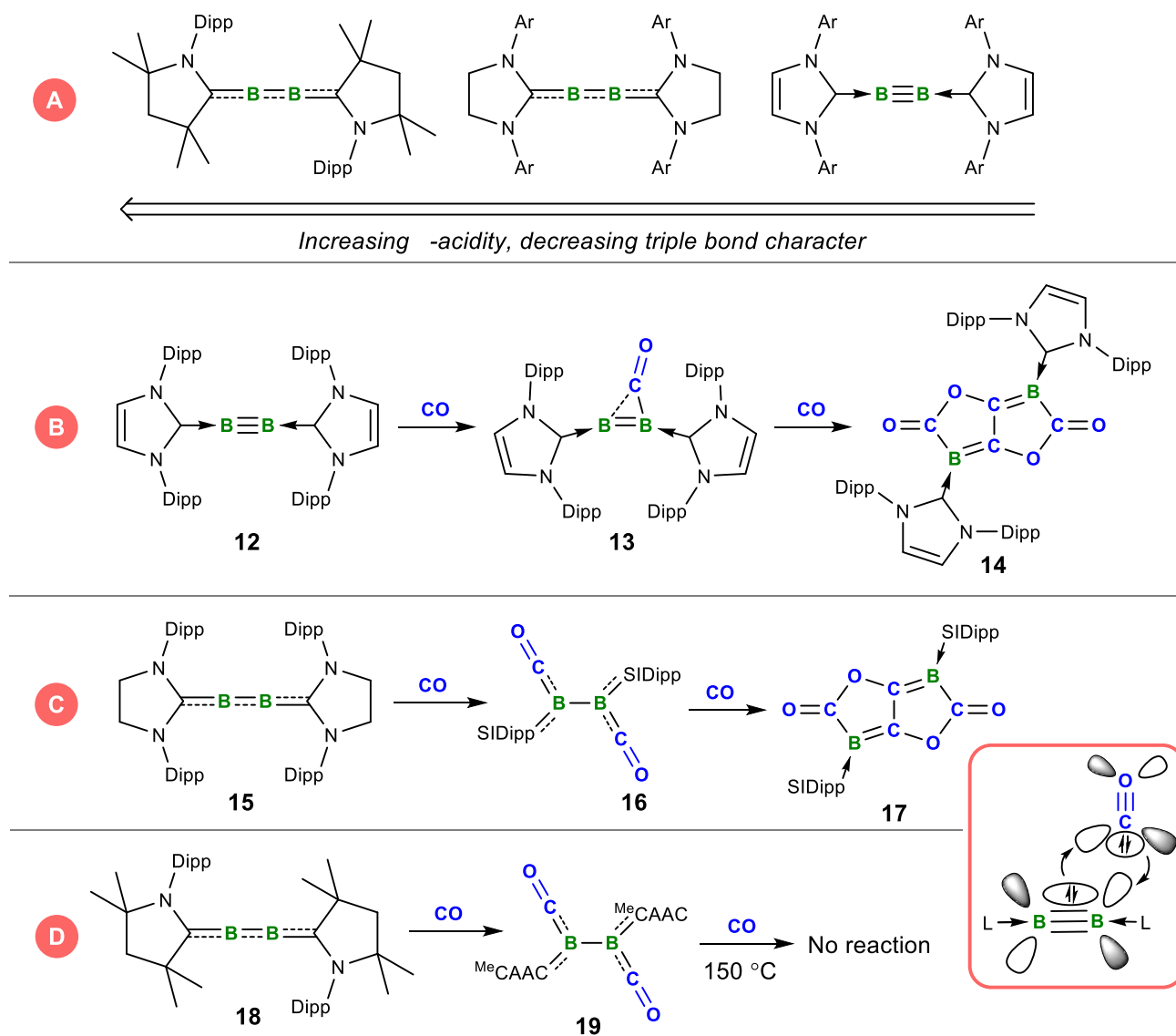


Figure 13. Diborynes, diboracumulenes and their reactivity with CO.

With molecular hydrogen, unsaturated NHC-stabilized diborynes and $[\text{SIDipp}_2\text{B}_2]$ were found to be unreactive. However, **18**, as well as the less bulky $[\text{SIDepB}]_2$ (SIDep = 1,3-bis(2,6-diethylphenyl)imidazolin-2-ylidene), react spontaneously to give the corresponding *trans*-1,2-dihydrodiborenes (Figure 14).²⁰⁷ The greater π -accepting character of CAAC and saturated NHCs seems to be essential for this process, with excessive steric bulk – as in the case of SIDipp – being detrimental. Interestingly, the π -acidity of CAAC and the cumulene character of **18** makes each of its boron centers isoelectronic to donor-acceptor-stabilized borylene complexes (see below), which explains their increased reactivity. The reaction of **18** with H_2 is complete within a day at room temperature, while it takes two days at $80\text{ }^\circ\text{C}$ for $[\text{SIDepB}]_2$ to be completely hydrogenated, showing the correlation between the π -acidity of the ligand and reactivity. The mechanism of the reaction, involving the formation of a $\text{H}_2\text{-B}$ σ -complex and

bond-cleaving backdonation from the B-B system electron is reminiscent of the ambiphilicity of TM orbitals and the H₂ activation by diborane complexes.

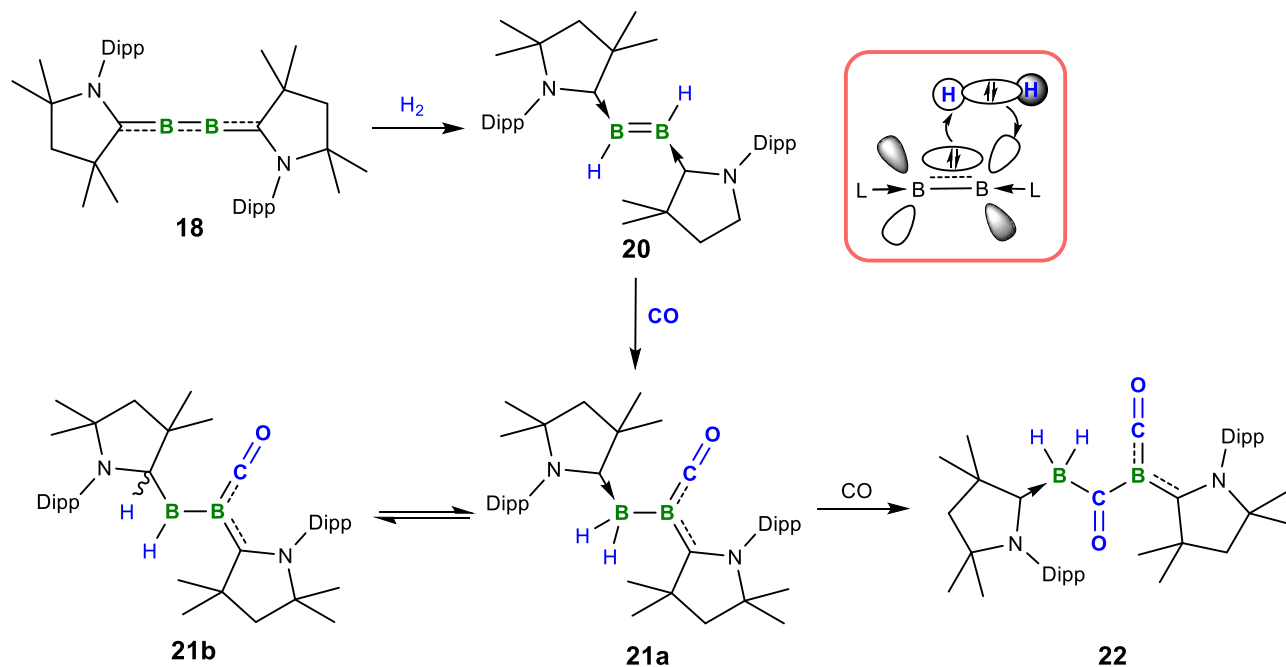


Figure 14. Reactivity of a diboracumulene with H₂ and CO.

Notably, dihydrodiborene **20** is the only currently known example of a diborene that reacts with carbon monoxide (Figure 14).²⁰⁸ Upon treating compound **20** with CO, the formation of **21a** and **21b** was observed. These two complexes are isomers that depend on the transfer of a hydride back and forth from a boron center to the ^{Me}CAAC ligand, and that, while being in an equilibrium in solution, could be crystallized independently. **21a** and **21b** are associated with IR CO stretching bands at 1928 and 1962 cm⁻¹, respectively. A second equivalent of CO can react with **21** and insert into the B-B bond, forming compound **22**, which also features CO complexation at boron.

While **18** reacts selectively with one equivalent of dihydrogen,²⁰⁹ it was also found that its coordination to one equivalent of ^{Me}IME (1,3,4,5-tetramethylimidazol-2-ylidene) – which breaks the symmetry of the diboracumulene to give complex **23** – increases its reactivity (Figure 15). In this bound state, **23** reacts rapidly with two equivalents of molecular hydrogen in a process that completely cleaves the B-B bond. The products of the reaction are thus [^{Me}CAAC(^{Me}IME)BH] (**24**) and [^{Me}CAACBH₃] (**25**). Computational analysis ascribes the increased reactivity of **23** to the strong localization of the frontier orbitals on the dicoordinate boron center, suggesting a borylene type structure. Compound **23** also reacts with carbon monoxide to form a strong adduct (**26**) (Figure 15). The CO stretching frequency of $\nu = 1912\text{ cm}^{-1}$ in the resulting complex suggests extremely strong B-to-CO backdonation. This backdonation is further supported by the long C-O bond distance (1.170(2) Å) as well as by computational modelling.

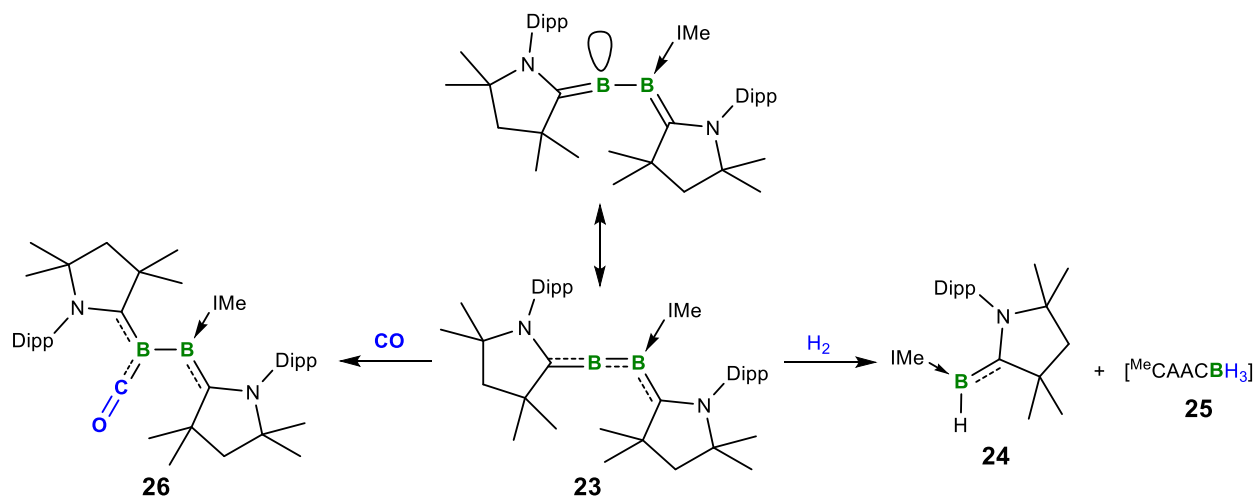


Figure 15. Reactivity of an NHC-coordinated diboracumulene with H₂ and CO.

Metallomimetic reactivity is also found in the interaction of phosphine-stabilized diborenes and [(^{Me}CAAC)B]₂ with alkynes. While organic alkenes and alkynes do not spontaneously undergo [2+2] additions, transition-metal carbene complexes (featuring a M-C double bond), as well as heavy main-group multiple bonds, undergo such metathesis reactions. In work from our laboratories, diborene **27** and the diboracumulene **18**²¹⁰ were shown to react with a range of acetylenes (Figure 16). While the reaction with **27** is performed under photolytic conditions – presumably in order to overcome symmetry constraints – and thus has precedence in conventional alkene chemistry,²¹¹ the reaction of **18** with acetylene and propyne is possibly spontaneous from the ground state. The products of the reaction differ based on the substrate, presumably on steric grounds: while exposure of [(^{Me}CAAC)B]₂ to acetylene leads to the formation of neutral diborabenzene **28**, a similar reaction with MeCCH leads to the complete cleavage of the C-C triple bond and the formation of the cyclic diradicaloid **29**. In both cases, an initial [2+2] cycloaddition is expected to be the first step of the reaction. Such a process is somewhat metallomimetic in nature because it involves the interaction of the alkyne HOMO with a boron-centered orbital and the backdonation of a B-B orbital into the C-C π*. However, the resulting diboracyclobutene **30** is unstable and can undergo a second [2+2] cycloaddition with acetylene or a rearrangement to the thermodynamically stable 1,3 isomer.^{212,213} The formation of dimetallacyclohexadienes from alkynes is also a staple of TM chemistry.²¹⁴

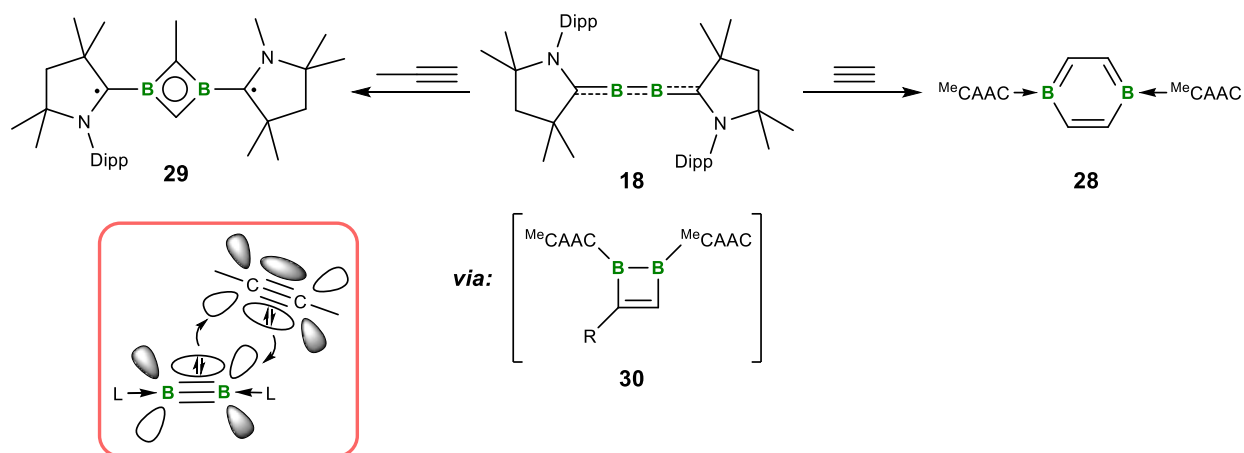


Figure 16. Reactivity of a diboracumulene with alkynes.

2.3 Summary

Metallomimetic chemistry can be attained by the cooperative action of two boron centers. Interestingly, in certain molecules, two remote boron atoms can act together to activate small molecules in a manner that is reminiscent of FLPs and of the ambiphilicity of TM complexes. In such transformations, one of the boron atoms appears to be reacting as a nucleophile which, combined a Lewis acidic boron center, achieves the side-on binding of alkene and alkynes and the cleavage of H₂ among others.

B-B single and multiple bonds are also found to be involved in a rich variety of TM-like reactivity. The availability of the electron density from the B-B bond to be shared to substrates in π -backdonation allows some diboranes, diborenes, diborynes and diboracumulenes to activate CO, H₂, alkynes and other small molecules through TM-like electronic processes.

3. Metallomimetics centered around a single boron atom

3.1. Boron(III) systems

A unique challenge is associated with obtaining transition-metal-like properties in complexes that feature a single boron active site and that do not provide cooperative reactivity from another heteroatom. In such cases, the combination of filled and empty orbitals that is required for metallomimetic reactivity have to be provided by a single boron atom. However, a single boron atom in its favored oxidation state (+3) is unlikely to be the center of both the HOMO and LUMO of a molecule. In a few examples, this deficiency can be countered by the use of highly Lewis acidic boranes, which have been shown to be sufficient for the activation of nonpolar substrates such as dihydrogen under mild conditions. In these unique systems, the high electrophilicity of the boron centers weakens the H-H bond sufficiently to enable a σ -bond metathesis with alkyl substituents that would otherwise require harsh conditions.^{186,187,215,216} Boranes that have been shown to be sufficiently acidic to activate dihydrogen in this manner under mild conditions are pentafluoroaryl and pentaaryl boroles and their derivatives (Figure 17;

A, B),²¹⁷⁻²²⁰ as well as HBAr^{F}_2 ($\text{Ar}^{\text{F}} = 2,4,6\text{-tris(trifluoromethyl)phenyl}$) or $\text{HB}(\text{C}_6\text{F}_5)_2$ (Figure 17; C).²²¹ Interestingly, while the reactivity of HBAr^{F}_2 with hydrogen was only proven using H/D exchange, the less bulky $\text{HB}(\text{C}_6\text{F}_5)_2$ **31** was recently found to act as a metal-free catalyst for the hydrogenation of alkenes under mild conditions via an hydroboration – hydrogenolysis mechanism (Figure 18).⁸⁴ The authors further determined computationally that the σ -bond metathesis of H_2 occurs via donation of electron density of the σ -orbital of H_2 to the vacant p-orbital of the Lewis acidic borane, and donation of electron density of the $\text{C}_{\text{alkyl}}\text{-B}$ σ -orbital to the σ^* -orbital of H_2 , and subsequent asynchronous formation of the B-H and C-H bonds avoids the formally forbidden [2+2] transformation. Such hydrogenations are mechanistically identical to hydrogenations reported with d^0 TM complexes,²²² and very similar to hydrogenations based on transition metals such as Ru(II), where formal oxidative addition of H_2 is disfavored.²²³ A related mechanism is postulated for the hydroboration of alkenes catalyzed by hydro(3,5-bis(trifluoromethyl)phenyl)boranes.²²⁴

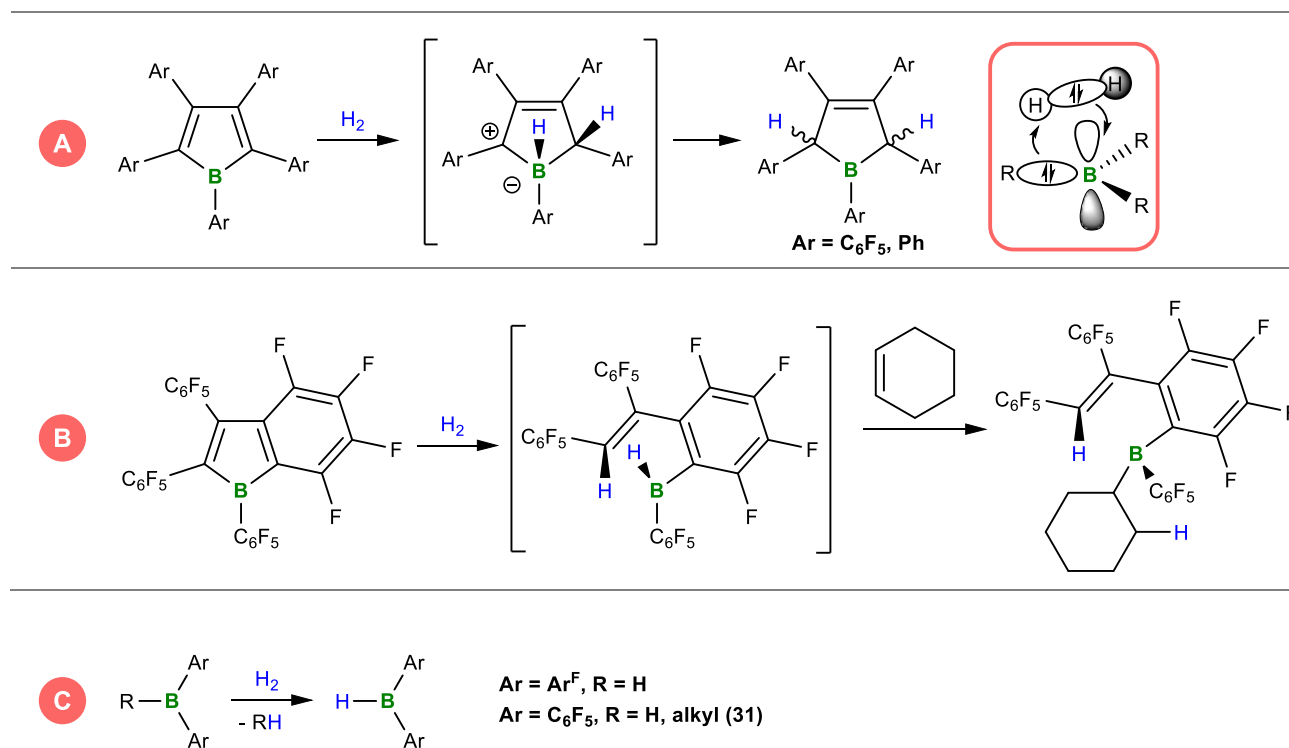


Figure 17. Reaction of electron-deficient boron(III) systems with H_2 .

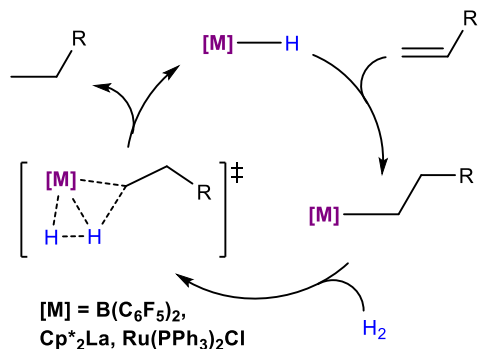


Figure 18. σ -Bond metathesis mechanism of olefin hydrogenation by **31** and other TM species.

Confinement of boron(III) to an aromatic heterocycle can also be used to effect metallomimetic reactivity, enabling the binding of π -acceptor ligands that usually only interact with TM complexes. For example, in free borabenzene, the strong Lewis acidity of the boron center corresponds to an empty sp^2 orbital, and the HOMO is associated with the delocalized π -electrons within the aromatic system.²²⁵ The reactivity conferred by this electronic environment is notably revealed by the ability of borabenzene to bind dinitrogen – a molecule that usually does not react with non-metal elements – under matrix isolation conditions to give adduct **32** (Figure 19, A).²²⁶ Subsequent computational work²²⁵ revealed the importance of π -backdonation from the aromatic ring of borabenzene to suitable orbitals in N_2 and various other ligands. It was likewise predicted that CO should bind borabenzene very strongly, despite the corresponding adduct (**33**) having never been reported (Figure 19, B).

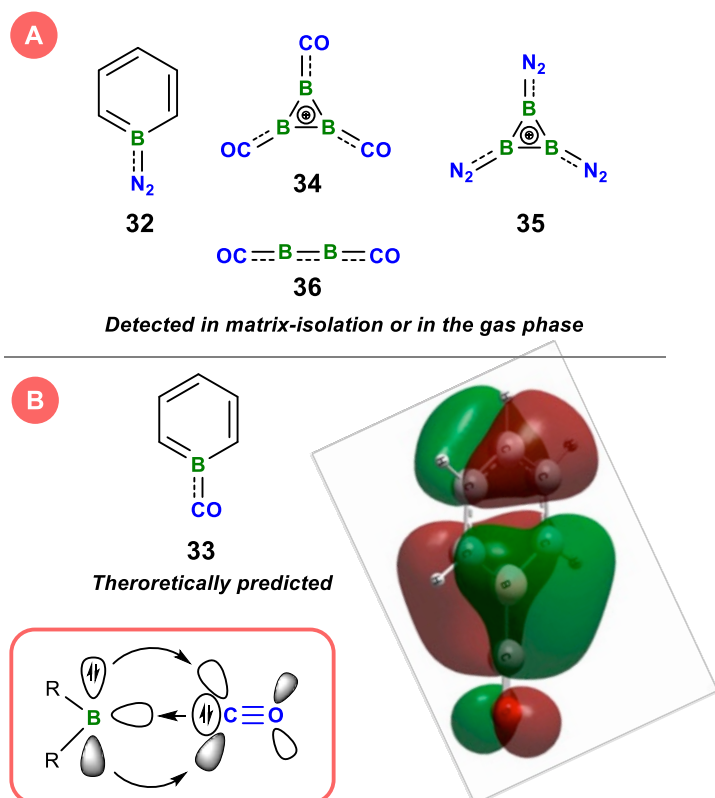


Figure 19. Aromatic B-containing cycles featuring bound N_2 and CO. The HOMO of **33** is depicted in the orbital diagram.

Similarly, $B_3(CO)_3^+$ (**34**) $B_3(N_2)^+$ (**35**) and cations have been observed in the gas phase (Figure 19, A), which can be regarded as adducts of the Lewis acidic and aromatic B_3 cation with dinitrogen and carbon monoxide.²²⁷ There too, the aromatic B_3 cycle provides electron density for the π -backbonding interaction, which is necessary to achieve an observable lifetime of the complexes. In a similar manner, OCBBCO (**36**) is another CO adduct of boron that has been identified in matrix isolation, and that also features B-to-CO backbonding,²²⁸ in this case via delocalization of the electron density of the B-B triple bond into the π^* orbital of the CO ligand.

3.2. Boron(I) systems

As detailed above, boron in its favored oxidation state (+3) does not formally possess simultaneously empty and filled orbitals. In its +1 oxidation state, however, it is conceptually expected to possess a nonbonding electron pair in addition to its two empty p-orbitals. For this reason, molecules that possess a boron(I) center in a coordinatively unsaturated environment are excellent candidates for transition-metal-like reactivity (Figure 20). Compounds known as borylenes feature a boron atom that is formally in the +1 oxidation state and are analogues of the more common carbenes. While free monocoordinate borylenes ($[:B-R]$) are highly reactive intermediates and have not been isolated thus far, the chemistry of their derivatives is a growing field that continues to uncover new and surprising reactivity. In most cases, the borylene fragment is stabilized by one or two Lewis bases or by coordination to a transition metal center. Using this strategy, Bertrand and coworkers were able to isolate the first isolable metal-free borylene $[(^{Cy}CAAC)_2BH]$.²²⁹ While free and singly base-stabilized borylenes can be described as metallomimetics, possessing a combination of empty and filled orbitals, tricoordinate borylenes (RBL_2) are coordinatively saturated and their transition metal-like characteristics are thus diminished. Similarly, transition-metal-bound borylenes cannot be considered metallomimetics as they already contain one or more transition metal atoms, which contributes to their reactivity. For these reasons, this chapter will focus on the chemistry of free mono- and dicoordinate borylenes. The other two classes of borylenes have recently been authoritatively reviewed and continue to attract considerable interest.²³⁰⁻²³⁶

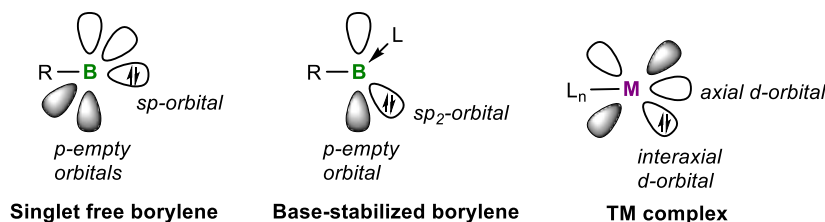


Figure 20. Orbitals relevant to substrate activation in both borylenes and TM complexes.

3.2.1. Monocoordinate borylenes

While they remain elusive to isolation and to many methods of solution- and solid-state characterization, the properties and reactivity of monovalent borylenes ($[:B-R]$) can be inferred

from extensive spectroscopic, and theoretical studies as well as from trapping experiments. In all studied cases, the ground state of such molecules is found to be singlet,^{237,238} thus featuring two empty orbitals (LUMO and LUMO+1), as well as a nonbonding lone pair (HOMO) at the *sp*-hybridized boron center. This electronic arrangement draws a parallel between monovalent borylenes and coordinatively unsaturated transition metal complexes and suggests their comparable reactivity. Indeed, the reaction of *in-situ*-generated borylenes with alkynes, carbon monoxide and dinitrogen,²³⁹ as well as with C-H and C-C bonds is definitively reminiscent of that of transition metal complexes.

As described earlier, alkynes and olefins readily interact with both the empty and filled orbital of many transition metal centers, forming side-on complexes that are well described by the Dewar-Chatt-Duncanson model (Figure 1).^{8,9} We have also discussed the formation of metallacyclohexadienes from the reaction of TM complexes with alkynes.²¹⁴ It is this second binding motif which was found by Timms to be dominant in the reactivity of fluoroborylene [FB:] **37** – the first reported transient borylene – and its derivative chloroborylene [ClB:] with acetylenes.^{240,241} Indeed, when generated in the gas phase and exposed to acetylene, both of these hypovalent boron halides afforded, among other products, cyclic C₄H₄B₂X₂ compounds (Figure 21, A). While later computational studies suggested the possibility of these compounds being produced by the dimerization of the corresponding haloborirenes²⁴² in a reaction that has precedence in TM chemistry,²¹⁴ the reaction conditions were not conducive to the observation of these presumably short-lived intermediates. Interestingly, 17 years after Timms' report, Pachaly and West²⁴³ observed the formation of silylborirene **38** from the low-temperature photolysis of B(SiPh₃)₃ in an organic glass upon warming in the presence of bis(trimethylsilyl)acetylene. While no spectroscopic evidence was obtained for the generation of a borylene species, the authors ascribe the formation of 1-triphenylsilyl-2,3-bis(trimethylsilyl)borirene to the trapping of a free [(Ph₃Si)B:] **39** by the acetylene reagent (Figure 21, B). This claim is supported by the characterization of C-H and C-O activation products when the postulated borylene is generated in the presence of alkane or ether products.

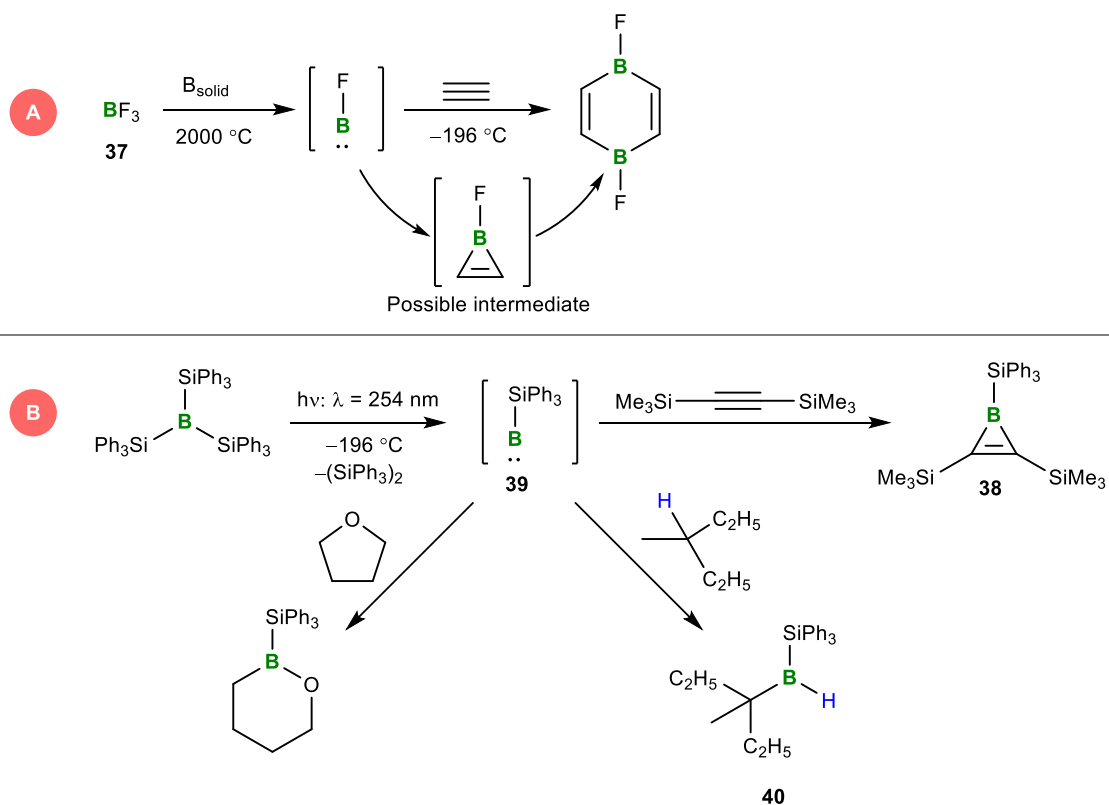


Figure 21. Generation and trapping reactions of free fluoro- and silylborylenes.

In the context of the formation of borirene products from the direct addition of a free singlet borylene to an alkyne, a comparison with the *side-on* coordination of acetylenes with TM is almost unavoidable (Figure 22). In such complexes, the coordination of an alkyne to the singlet borylene pushes the Dewar-Chatt-Duncanson model to the limit of strong alkyne-to-boron donation and boron-to-alkyne backdonation into a rehybridized three-membered ring featuring an elongated C-C bond.²⁴⁴⁻²⁴⁷ This fact illustrates the nature of these highly reactive transient hypovalent boron metallomimetics: while possessing a reactivity that recalls that of TM complexes, their lack of oxidation state flexibility often puts them at the extremes of bonding models. Interestingly, borirenes are also products of the formal transfer of borylene fragments from many transition-metal-stabilized borylenes to alkynes.²⁴⁸⁻²⁵⁰

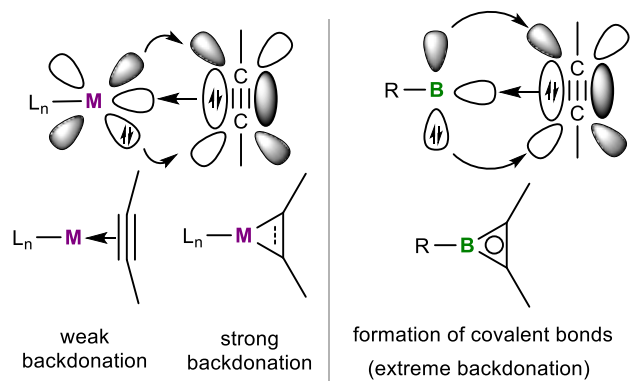


Figure 22. Alkyne binding in both TM complexes (left) and borylenes (right).

As described above, the reaction of the putative borylene $[(\text{Ph}_3\text{Si})\text{B}:]$ with *tert*-butane gives 3-methylpentyl(triphenylsilyl)borane as C-H insertion product **40**. This reaction is also metallomimetic in character and plausibly arises from the interaction of the LUMO of the borylene with the C-H σ -bond of the alkane, with simultaneous electron donation from boron to the C-H antibonding orbitals (Figure 23). Such a mechanism would be similar to that of C-H bond activation effected by transition metal complexes.^{251,252}

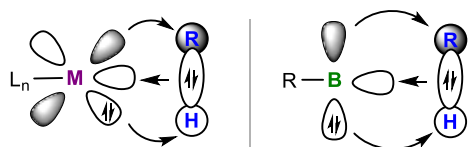


Figure 23. Orbitals relevant to C-H activation for TM complexes (left) and borylenes (right).

Similarly to this reactivity, Power and coworkers²⁵³ observed various insertion reactions when reducing sterically encumbered aryldihaloboranes using different alkali metal reductants. In such reduction reactions the initial formation of a free aryloborylene was postulated, followed by its intramolecular insertion into C-C bonds of the aryl substituent (Figure 24, A). The extreme reactivity of free borylenes was even more strikingly demonstrated by Meller and coworkers^{254,255} when they demonstrate that the borylenes generated from the reduction of X_2BNiPr_2 ($\text{X} = \text{F}, \text{Cl}$) react even with toluene and other arenes to give various ring-expansion products (Figure 24, B).

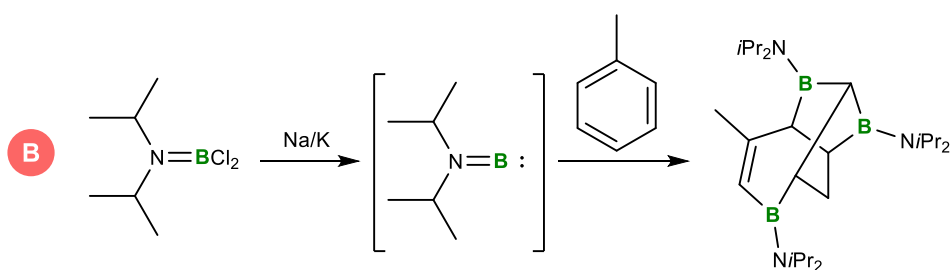
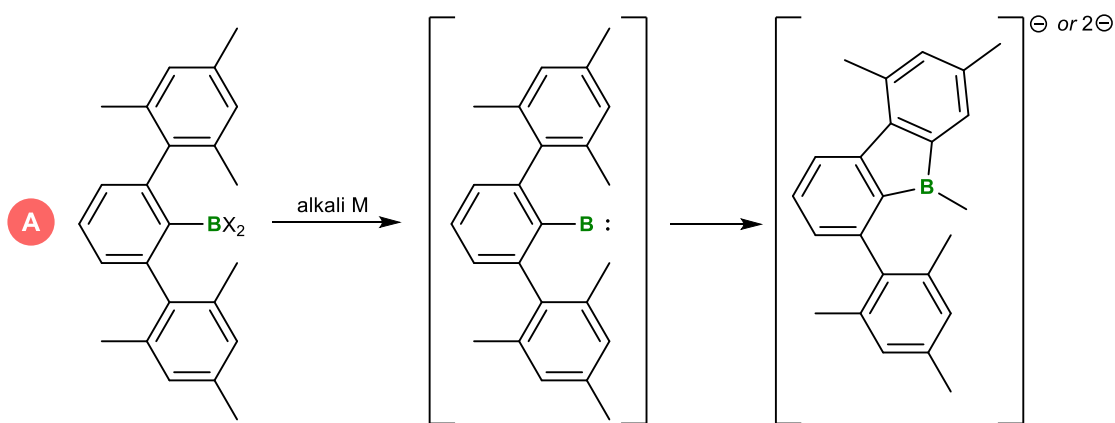


Figure 24. Generation and trapping reactions of free aryl- and aminoborylenes.

Tokitoh and coworkers²⁵⁶ have also developed a protocol for the photolytic generation of a bulky arylborylene from [TbtB(SeMe)₂] (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl). The resulting [TbtB:] borylene intermediate was trapped by various organochalcogen substrates.

More recently, Bettinger and coworkers²⁵⁷ were able to generate and characterize phenylborylene [PhB:] (**41**) under matrix isolation conditions (Figure 25), via the photolysis of PhB(N₃)₂. Interestingly, generating phenylborylene in N₂- or CO-containing matrices led to the identification of various products, including adducts [PhB←L] of these ligands (L = CO, N₂), which could be characterized on the basis of their IR spectra. Computational studies on these molecules showed that, in close analogy to TM chemistry, B-to-L backdonation is an important component of the bonding in these adducts.

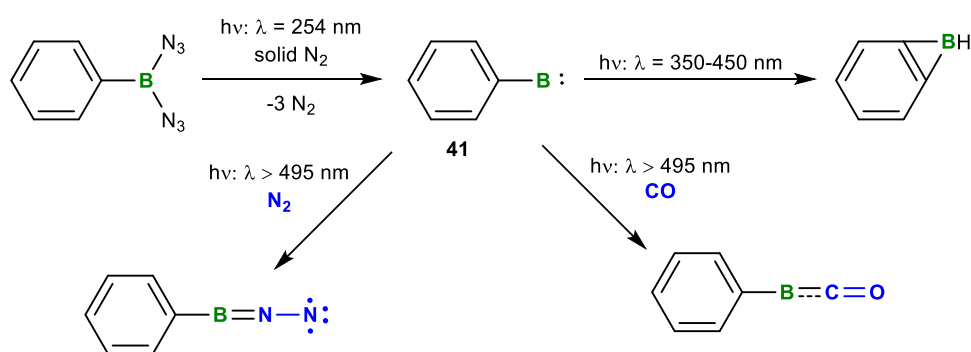


Figure 25. Generation and photolytic reactions of phenylborylene.

3.2.2. Base-stabilized borylenes

As the high reactivity of free borylenes significantly hampers their study in the condensed phase, the past few decades have seen an effort to produce and study base-stabilized borylene and borylene-like molecules. Using a similar alkali metal reduction protocol, in 2007 Robinson and coworkers reduced [IDippBBr₃] with KC₈.¹⁹⁴ This reaction allowed the authors to isolate diborene product **42**, which is conceptually the dimerization product of the borylene [IDippBH] (Figure 26, A). Following this initial attempt, several reports have described the reduction of NHC-dihaloborane reagents. Many of these have demonstrated the formal insertion of a dicoordinate borylene fragment into intramolecular C-H bonds of the NHC ligand, similarly to free borylenes (Figure 26, B-D).²⁵⁸⁻²⁶⁰

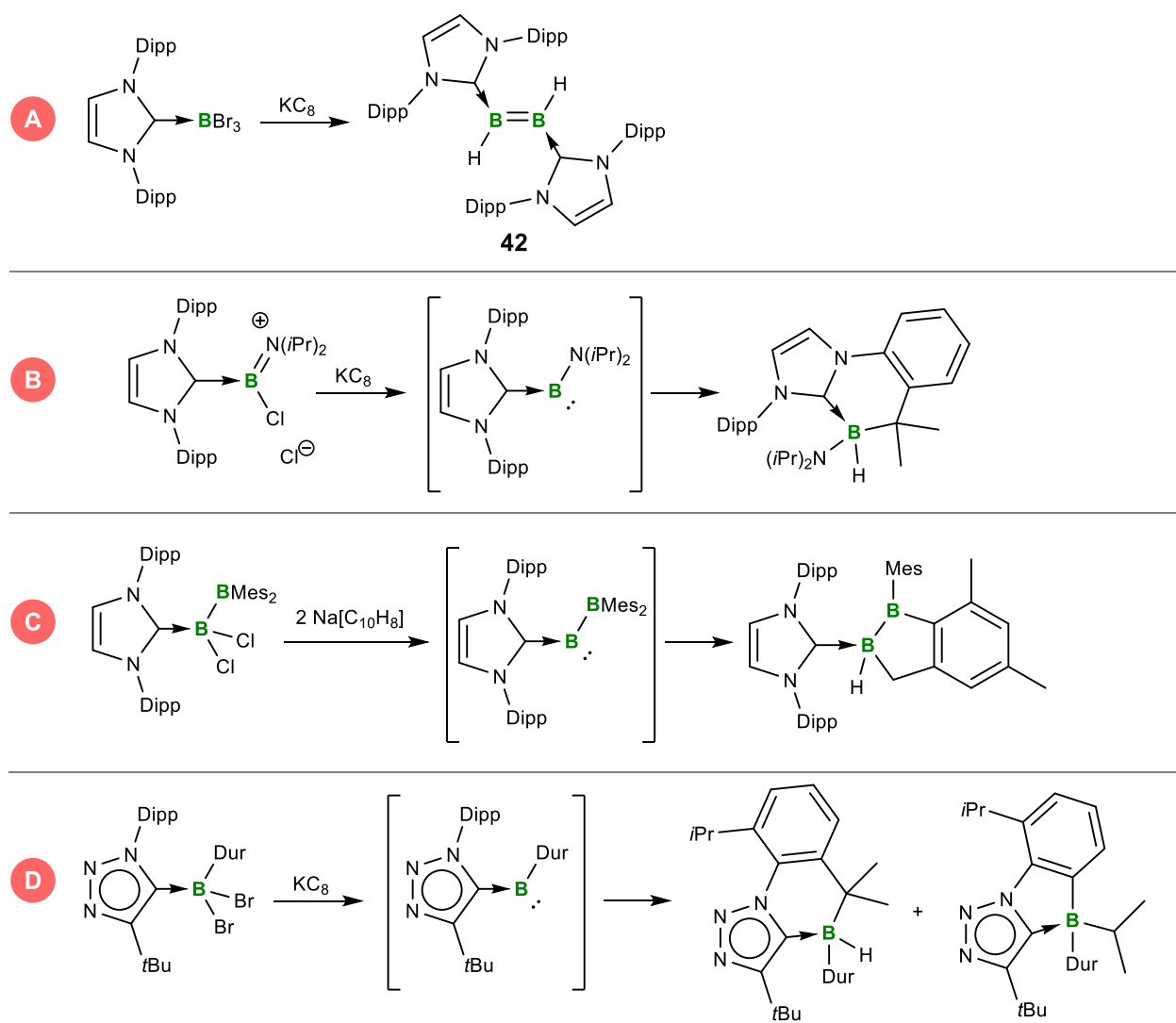


Figure 26. Generation and insertion of various NHC-stabilized borylenes.

Interestingly, our group has observed the formation of a base-stabilized borirane (**45**) from the reduction of $[(\text{IMe})\cdot\text{BHCl}_2]$ ($\text{IMe} = 1,3\text{-dimethylimidazol-2-ylidene}$) (**43**) with sodium naphthalene.²⁶¹ While the formation of the parent borylene $[(\text{IMe})\cdot\text{BH}]$ (**44**) and its trapping with naphthalene was invoked to explain the reactivity, the actual mechanism of the transformation is a subject of debate (Figure 27, A).²⁶² In a related reaction, our group also observed the formation of the remarkably robust borirane $[\text{IMe}^{\text{Me}}\cdot\text{BPh}(\text{C}_{14}\text{H}_{12})]$ (**47**) when reducing $[\text{IMe}^{\text{Me}}\cdot\text{BPhCl}_2]$ (**46**) with $\text{Na}_2[\text{C}_{14}\text{H}_{12}]$ ($\text{C}_{14}\text{H}_{12} = 1,2\text{-diphenylethylene}$) (Figure 27, B).²⁶³ However, it should be noted that the generation of a borylene was not invoked in the latter case as a nucleophilic substitution mechanism using $\text{Na}_2[\text{C}_{14}\text{H}_{12}]$ is also reasonable.

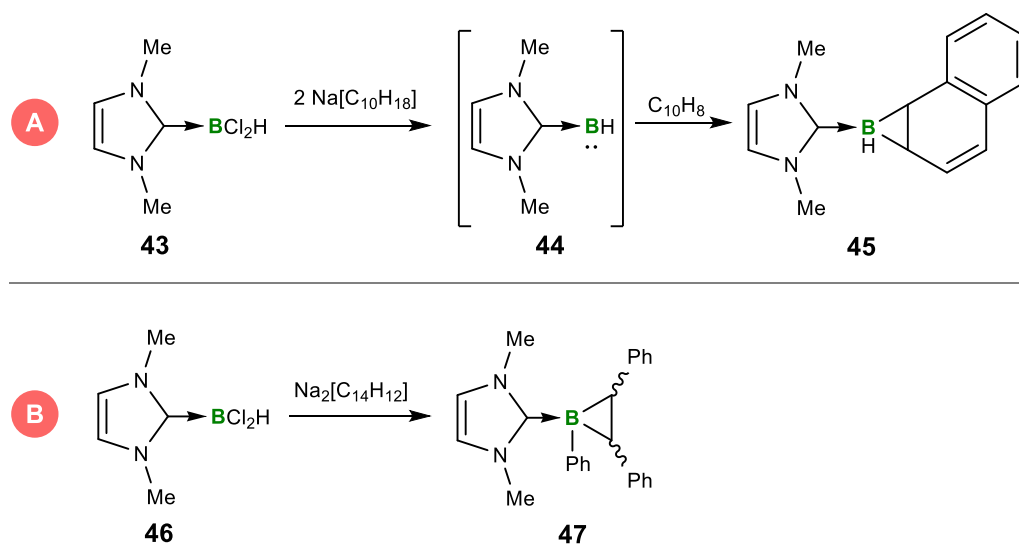


Figure 27. Trapping of free NHC-borylenes with unsaturated bonds.

In contrast to the previously described examples of highly reactive borylene metallomimetics, a breakthrough in the field was achieved in 2014 by Bertrand, Stephan and coworkers in the isolation of a compound of dicoordinate boron that exhibited a distinct borylene character.²⁶⁴ Similar to the generation of highly reactive borylenes, the complex in question was obtained by the reduction – in this case with $[(\text{Me}_5\text{C}_5)_2\text{Co}]$ – of a $[\text{CyCAAC}\cdot\text{BN}(\text{SiMe}_3)_2\text{Cl}_2]$ adduct. The product of this reaction, $[\text{CyCAAC}\cdot\text{BN}(\text{SiMe}_3)_2]$ (**48**), could be seen as the CyCAAC adduct of the borylene $[:\text{BN}(\text{SiMe}_3)_2]$ and be expected to bear an empty and a filled orbital at the boron atom (Figure 28, A). However, nitrogen-to-boron π -donation, as well as boron-to-carbene π -backdonation stabilize these orbitals and the molecule as a whole. In fact, based on structural analysis of **48**, this compound seems to adopt an allene-type structure in the ground state.

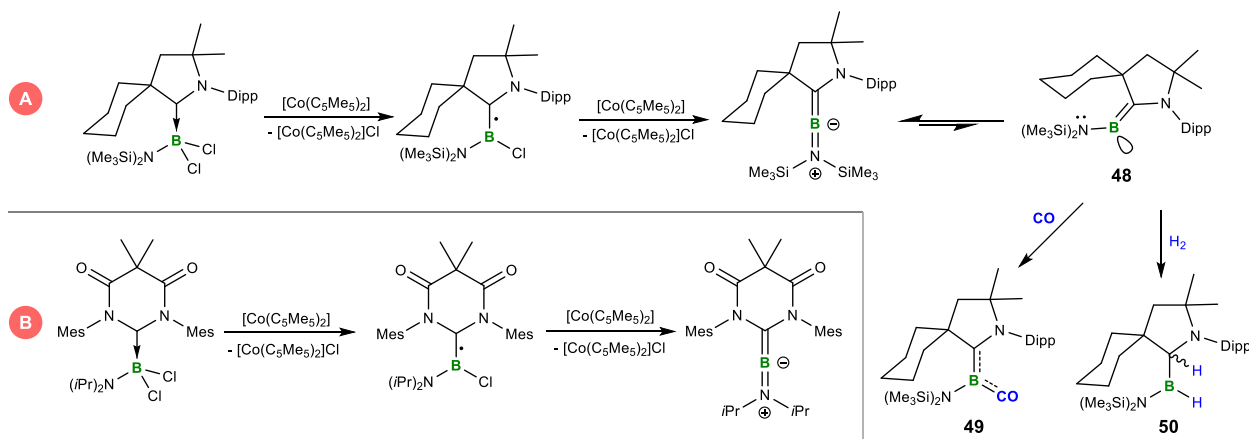


Figure 28. Synthesis and reactivity of isolable NHC-aminoborylenes.

Computational analysis, however, revealed that the borylene character of **48** was but lightly masked by this donor-acceptor stabilization: bending the molecule at the boron atom to 155° ,

effectively breaking the allenic system, had a small energetic cost of only 5.7 kcal.mol⁻¹ and should be feasible thermally. In this bent form, computations showed that boron possesses a low-lying sp²-hybridized LUMO, while the HOMO is still shared with the π-accepting ^{Cy}CAAC ligand and is of π symmetry and antibonding with regard to the ^{Cy}CAAC C-N bond (Figure 29). **48** in its bent form thus possesses a strongly electrophilic boron center which nevertheless also bears a large proportion of the HOMO. Transition-metal-like chemistry should thus be unsurprising with such a complex.

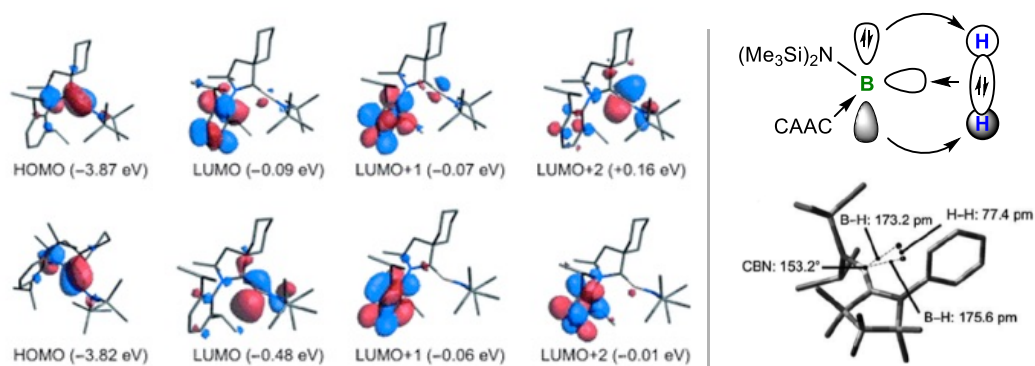


Figure 29. Orbitals in **48** in the ground state (top left) and in a constrained 155° bent geometry (bottom left) relevant to its reaction with H₂. Representation of the transition state of H₂ cleavage by **48** to give **50** (right).

Indeed, **48** was shown to react with carbon monoxide and form a stable coordination complex (Figure 28, A), a reaction that is exceedingly rare for boron complexes. Infrared spectroscopy ($\nu_{\text{CO}} = 1956 \text{ cm}^{-1}$) as well as computational modelling revealed that boron-to-CO π-backbonding is a significant aspect of the coordination of carbon monoxide and that the π symmetrical HOMO is shared between the ^{Cy}CAAC and the CO ligands. Consistent with this relocation of the HOMO, the solid-state B-^{Cy}CAAC bond distance increases from **48** (1.401(5) Å) to **49** (1.505(4) Å). **48** can also cleave dihydrogen in a mechanism that is decidedly metallomimetic: according to computational studies, the most likely mechanism involves the interaction of the H-H σ-bond with the boron-centered LUMO of the bent **48**, while backdonation into the H-H σ* orbital completes the bond cleavage. These results clearly show that the metallomimetic reactivity of borylene compounds can be harnessed into selective intermolecular reactions, and that donor-acceptor stabilization of borylenes does not completely mask their TM-like characteristics. A similarly stabilized compound was reported by Hudnall and Ledet in 2016,²⁶⁵ using a π-accepting N,N'-diamidocarbene (DAC),²⁶⁶ although as yet no reactivity of the compound has been reported (Figure 28, B).

It is pertinent to mention here the doubly silylene-stabilized borylene cation **51**^{267,268} which was prepared by Xie and coworkers through the substitution of a bromide from a bis-silylene bromoborylene with CO from [W(CO)₆] (Figure 30). While this reaction does not involve the formal binding of free carbon monoxide by a boron center, the product is one of the few examples of a stable B-CO adduct. Structural, computational and spectroscopic evidence shows the presence of B-to-CO backbonding, which is typically a TM-CO characteristic. An IR

CO stretching band at 2021 cm^{-1} and a C-O bond distance of $1.046(6)\text{ \AA}$ indicates, however, the presence of a lower degree of backbonding than in **49**, which can be expected from the cationic nature of the complex. This CO complex spontaneously loses one equivalent of carbon monoxide in the presence of molecular hydrogen at $80\text{ }^\circ\text{C}$, leading to the TM-like cleavage of H_2 at the boron center and to complex **52**.

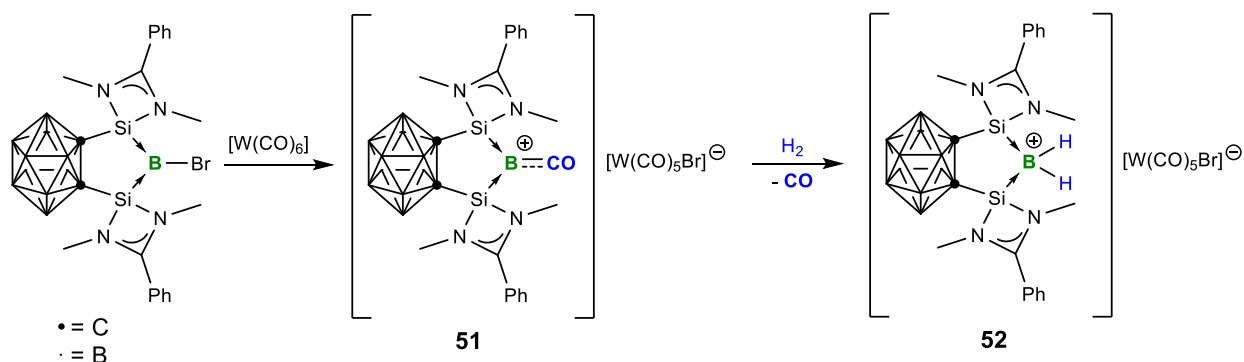


Figure 30. CO extrusion and H_2 uptake by a cationic doubly silylene-stabilized borylene.

For our part, we have endeavored to uncover metallomimetic reactivity with a dicoordinate borylene that features a smaller degree of donor-acceptor stabilization. We reasoned that generating borylene compounds that possess an inert aryl group (in contrast to the π -donating amino group of Bertrand and Stephan's allene) would be an important step in that direction. Previous work from our group found that the reduction of $[\text{Me}^\ominus\text{CAAC}\cdot\text{BDurCl}_2]$ (Dur = 2,3,5,6-tetramethylphenyl) by decamethylcobaltocene or KC_8 afforded the remarkably stable boron radical $[\text{Me}^\ominus\text{CAAC}(\text{BCIDur})]^\cdot$.²⁶⁹ Unfortunately, further reduction to a borylene species was not achieved. For this reason, we developed an alternative borylene generation method: the transfer of a borylene fragment from metal-carbonyl complexes to suitable Lewis bases can afford CO complexes of metal-free borylenes. This approach was first found to be compatible with borylene transfer from $[(\text{OC})_5\text{Mn}=\text{B-Tp}]$ **53** (Tp = 2,6-bis(triisopropylphenyl)phenyl) to additional carbon monoxide or to $:\text{CNDipp}$ (Dipp = 2,6-diisopropylphenyl), yielding the tricoordinate borylenes $[(\text{OC})_2\text{BTp}]$ (**54-CO**) and $[(\text{DippNC})(\text{OC})\text{BTp}]$ (**54-CNDipp**), respectively (Figure 31).²⁷⁰ These complexes showed strong B-to-CO backdonation, both from their structural ($d_{\text{C-O}}$ $1.152(2)\text{ \AA}$ and $1.159(2)\text{ \AA}$, respectively) and spectroscopic characterization (IR $\nu_{\text{CO}} = 1942$ and 1930 cm^{-1} respectively). Apart from adducts of carbon and nitrogen, **54-CO** remains the only example of multiple coordination of carbon monoxide at a p-block element, being thus comparable to poly-CO TM complexes.

For its part, **54-CNDipp** proved to undergo CO extrusion under UV irradiation, presumably generating a transient free dicoordinate borylene $[\text{DippNCBTp}]$ (Figure 31). Although the photolytic formation of a dicoordinate borylene **55** could not be ascertained spectroscopically, a C-C insertion product (**56**) was isolated from the reaction, which is consistent with the transient formation of $[\text{DippNCBTp}]$.

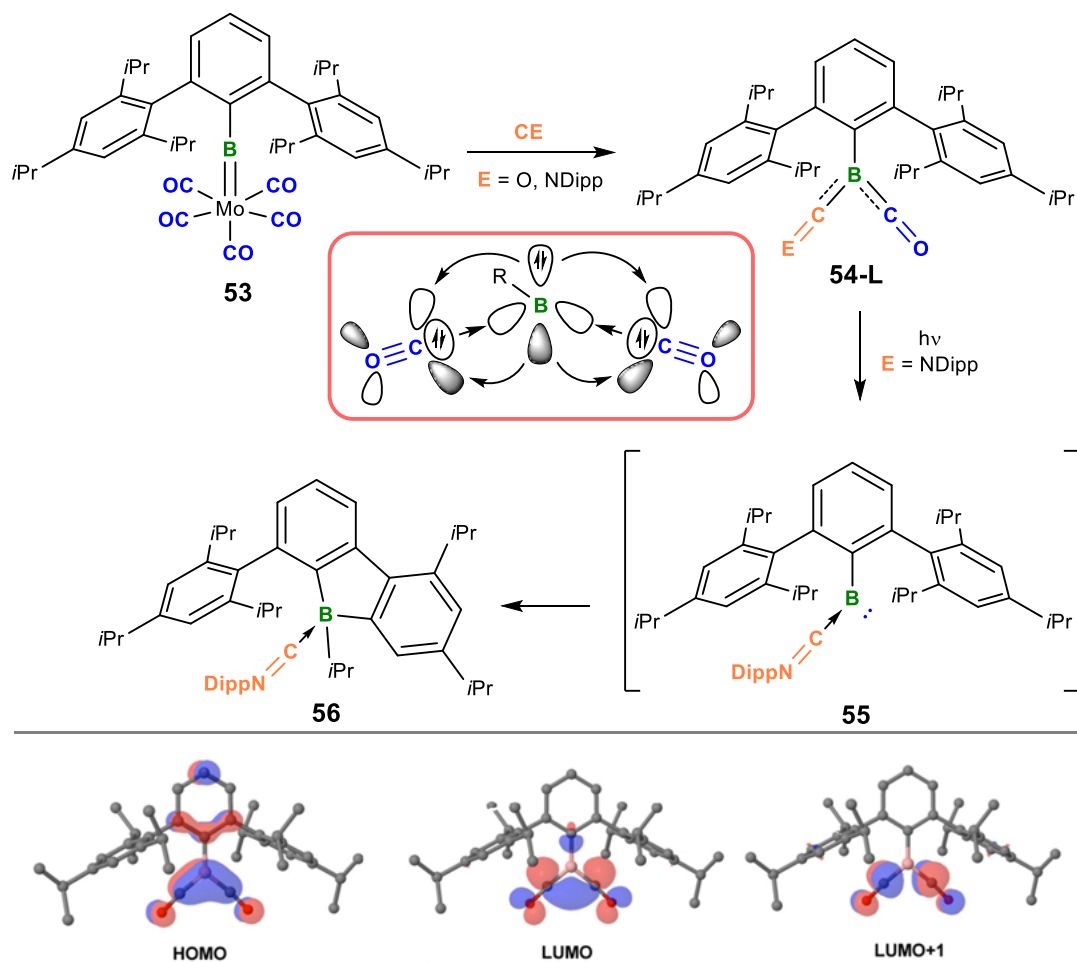


Figure 31. The generation of carbonyl-borylene **54-L**, photolytic reactions (Top). Frontier molecular orbitals of bis-carbonyl borylene **54-CO**.

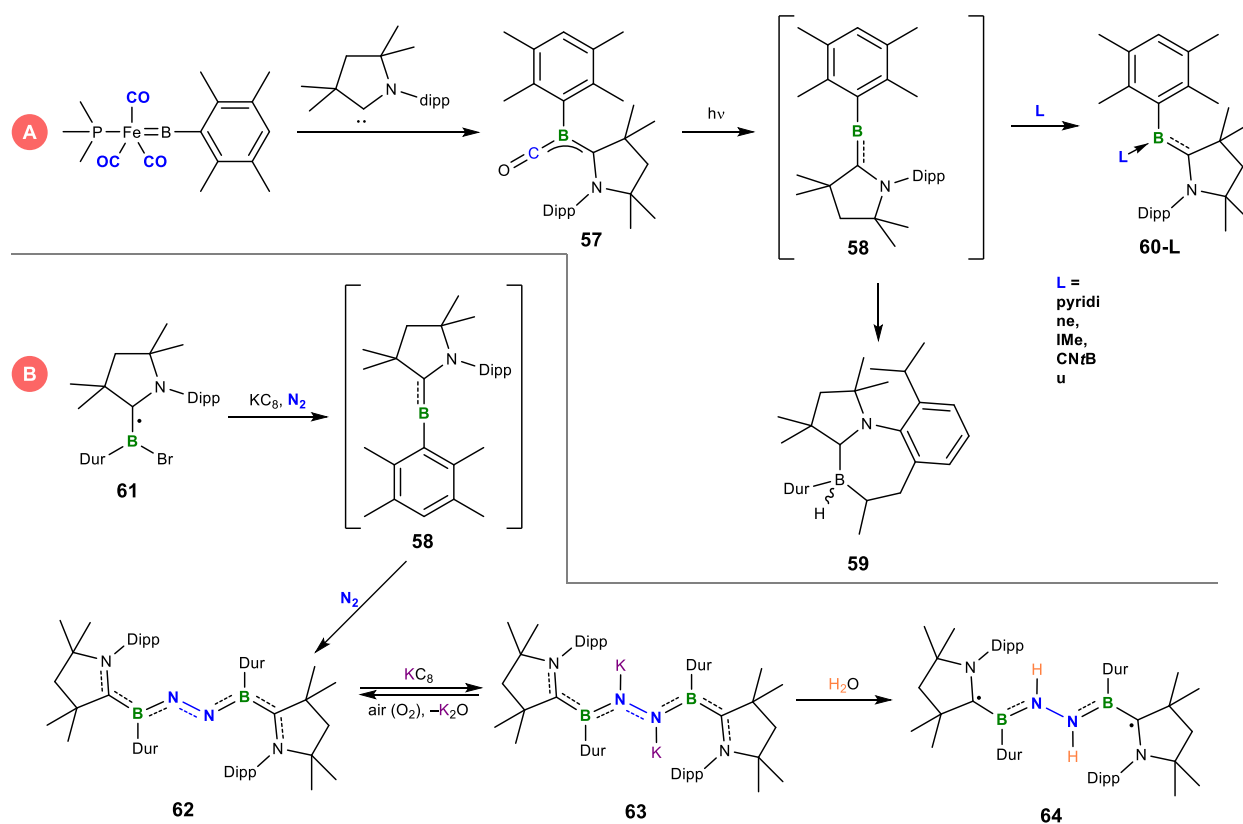


Figure 32. The generation of free borylenes via photolytic CO extrusion and their capture and insertion reactions (A and B). Capture, reduction and protonation of N₂ at a borylene center (C).

Similarly, borylene transfer was also developed from [(Me₃P)(OC)₃Fe=BDur]²⁷¹ using ^{Me}CAAC as a π-accepting base to afford [(^{Me}CAAC)(OC)BDur] (**57**) (Figure 31, B).⁴ **57** is an analog of **49**, but features a substantially shorter B-CO bond (1.469(2) Å), suggesting a larger amount of boron-to-CO backdonation, which is further supported by an IR ν_{CO} stretch of 1942 cm⁻¹. Interestingly, **57** also loses an equivalent of carbon monoxide upon UV irradiation, affording the intramolecular insertion product **59** at ambient temperature. In this case, however, the insertion takes place into a remote C-H bond of the CAAC ligand, forming a seven-membered ring that would intuitively be thought to be disfavored. The transient formation of an electrophilic dicoordinate borylene (**58**) could be proven in this case by trapping experiments with various Lewis bases to give a family of new doubly base-stabilized borylene complexes (**60-L**) (Figure 32, A).⁴ This photolytic extrusion of carbon monoxide is another metallomimetic characteristic of borylenes. Indeed, the photodissociation of carbon monoxide is a standard reactivity pattern of transition metal carbonyl complexes.

The relatively long lifetime of the dicoordinate borylene **58** in this system – allowing it to be trapped by stoichiometric reagents – prompted us to explore its reactivity with other substrates which are usually unreactive with nonmetal reagents. In particular, we hypothesized that dinitrogen, being a less reactive CO analog, could be fixed by such a reactive borylene. Initial attempts to photolyze **57** in the presence of N₂ did not yield any nitrogen fixation products. For this reason, we revisited approaches for the generation of free **58**. Thus, we found that the

reduction of $[\text{MeCAAC}\cdot\text{BDurBr}_2]$ using KC_8 did produce transient **58** and that the borylene could be trapped, even using CO as a gaseous reagent (to yield **57**). Through a similar reduction protocol (KC_8 , toluene) under an atmosphere of N_2 , we were able to isolate, albeit in low yield, $\{(\text{CAAC})\text{DurB}\}_2(\mu^2\text{-N}_2)\}$ (**62**) as a bridging end-on complex of dinitrogen (Figure 32, B).²⁷² By optimizing the reaction conditions – using the $[\text{MeCAAC}\cdot\text{BDurBr}]$ radical (**61**) as a starting reagent and an excess of KC_8 and up to 4 atm. of dinitrogen – we were able to increase the yield of the reaction to provide 64% of $\{[(\text{CAAC})\text{DurB}]_2(\mu^2\text{-N}_2\text{K}_2)\}$ (**63**), an overreduction product of dinitrogen complex **62**. This latter species can be selectively oxidized back to the neutral complex **62** using ambient air.

The bonding situation in these species is understandably complicated, but is once again reminiscent of transition metal chemistry, in which the end-on bridging binding mode is common for N_2 . In analogy with the complexation of CO to **58**, the B-N bonds in **62** involve a B-to-N π -backdonation that is shared with the B-to-CAAC π -interaction. In fact, in **62**, the B-CAAC bonds (1.528(5) Å and 1.541(4) Å) are longer than in **57** (1.499(2) Å), suggesting that the bridging N_2 ligand accepts a larger degree of backdonation than CO. While the end-on bridging dinitrogen ligand in TM complexes is generally linear, the bent form it adopts in compound **62** can be explained by the geometry of the orbitals involved in the backdonation: while TMs can involve up to two orthogonal d -orbitals in backbonding, the borylene has a single available filled orbital of π -symmetry (Figure 33).^{273,274} Nevertheless, the degree of activation of dinitrogen by the borylene – as suggested by the length of the N-N bond that is weakened by backbonding (1.248(4) Å) – is superior than in many TM complexes.²⁷³

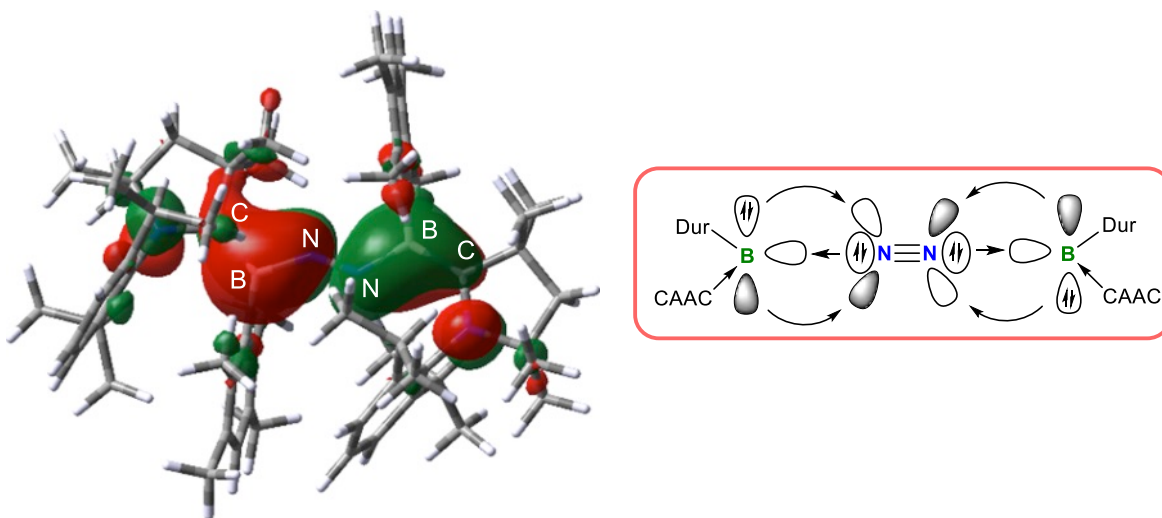


Figure 33. Calculated HOMO-1 of **62** (left) at the M062X/6-311g(d,p) level and schematic representation of the backbonding (right).

The reduction of metal-bound dinitrogen by potassium is an established reaction.²⁷⁵ Similarly, as mentioned above, **62** can be reduced by KC_8 to give the dipotassium complex **63**. Similarly to iron complexes reported by Holland and coworkers, this reduction is accompanied by a

lengthening of the N-N bond by ca. 4.5% (to 1.304(3) Å). The fact that the dinitrogen ligand is reduced is also reflected in the B-N and B-Me^{Me}CAAC bond distances, which suggest a diminished B-to-N backdonation.

The reduced **63** species can be selectively protonated by water to give $\{[(\text{CAAC})\text{DurB}]_2(\mu^2\text{-N}_2\text{H}_2)\}$ **64**. This new complex features a very long N-N bond (1.402(2) Å) that is in the range of single bonds. Furthermore, the triplet diradical nature of **64** reveals that, in contrast to **62** and **63**, full covalent bonds exist between the N₂H₂ ligand and the boron centers. Complex **64** is thus considered a diborahydrazine complex, which has been formed directly from dinitrogen from a reduction-protonation sequence. This transformation gives hope towards the further reduction and functionalization of dinitrogen, which is a lingering goal of transition-metal-mediated N₂ chemistry.

3.3. Conclusion

We have thus seen that a few strategies enable metallomimetic reactivity at a single boron site. While strong Lewis acidity in boranes leads to the activation of dihydrogen and to gas-phase interactions with CO and N₂, a richer reactivity is obtained from species that are capable of π -backdonation because of their electronic and orbital arrangement. To this day, most examples of such compounds belong to the borylene family, either as free borylenes or base-stabilized ones. While the former display strong reactivity towards alkynes, CO, C-H and C-C bonds, their instability makes them difficult to handle. The advent of base-stabilized borylenes, on the other hand, is starting a trend of isolable or long-lived boron metallomimetics. The binding and activation of CO, H₂ and even N₂ by these complexes is only the beginning of the study of these fascinating molecules.

4. General Summary

The electropositivity of boron with respect to other light main group elements renders it uniquely reactive. In this review, we have highlighted the three principle methods by which boron can achieve reactivity akin to transition metals: (1) Boron forms stable electron deficient complexes featuring a B-centered low-lying vacant orbital which can react with with inert substrates, including H₂ and C-H bonds, in combination with an external electron donor. So called "Frustrated Lewis pairs" are the most mature field of boron metallomimetics, and have been applied to catalytic reactions, most notably to hydrogenation and C-H borylation reactions. (2) Systems featuring B-B single and multiple bonds also readily capture and couple small molecules including CO, alkynes, and H₂, due to the relatively low HOMO-LUMO gaps within B-B bonded systems. Furthermore, the reactivity of such species is amplified by electronic transitions that can be readily accessed photolytically. (3) Finally, boron (I) species have began to emerge as truly single-site metallomimetics, and has allowed the capture of CO, H₂ and most recently N₂. The accelerating pace of research into this evolving field will doubtlessly continue to yield important discoveries and reactivities reminiscent of transition metal chemistry. The ability of boron to 'mimic' the activation of transition metals points to a greener future where chemistry first established by expensive and toxic transition metals can equivalently accomplished by earth-abundant elements.

Acknowledgements

H.B. gratefully acknowledges the Deutsche Forschungsgemeinschaft and the European Research Council (ERC) under the European Union Horizon 2020 Research and Innovation Program (grant agreement no. 669054) for funding. C.P. and M.-A.L. thank the Alexander von Humboldt Foundation and the NSERC for postdoctoral fellowships.

References

- (1) IUPAC: *Compendium of Chemical Terminology, 2nd ed. (the "Gold Book")*. Blackwell Scientific Publications, Oxford 1997.
- (2) Cotton, F. A. W.: *Advanced Inorganic Chemistry*; Wiley: New York, 1988.
- (3) Masters, C.: *Homogeneous Transition-metal Catalysis: A Gentle Art*; Chapman and Hall: New York, 1980.
- (4) Braunschweig, H.; Krummenacher, I.; Légaré, M.-A.; Matler, A.; Radacki, K.; Ye, Q. Main-Group Metallomimetics: Transition Metal-like Photolytic CO Substitution at Boron. *J. Am. Chem. Soc.* **2017**, *139*, 1802-1805.
- (5) Power, P. P. Main-group elements as transition metals. *Nature* **2010**, *463*, 171.
- (6) Erker, G.; Stephan, D. W.: *Frustrated Lewis Pairs I: Uncovering and Understanding*. Erker, G., Stephan, D. W., Eds.; Springer Berlin Heidelberg: Berlin, Heidelberg, 2013.
- (7) Erker, G.; Stephan, D. W.: *Frustrated Lewis Pairs II: Expanding the Scope*. Erker, G., Stephan, D. W., Eds.; Springer Berlin Heidelberg: Berlin, Heidelberg, 2013.
- (8) Dewar, M. *Bull. Soc. Chim. Fr.* **1951**, *18*, C79.
- (9) Chatt, J.; Duncanson, L. A. 586. Olefin co-ordination compounds. Part III. Infra-red spectra and structure: attempted preparation of acetylene complexes. *J. Chem. Soc. (Resumed)* **1953**, 2939-2947.
- (10) McCahill, J. S. J.; Welch, G. C.; Stephan, D. W. Reactivity of "Frustrated Lewis Pairs": Three-Component Reactions of Phosphines, a Borane, and Olefins. *Angew. Chem. Int. Ed.* **2007**, *46*, 4968-4971.
- (11) Stephan, D. W. The broadening reach of frustrated Lewis pair chemistry. *Science* **2016**, *354*.
- (12) Stephan, D. W.; Erker, G. *Frustrated Lewis Pairs: Metal-free Hydrogen Activation and More*. *Angew. Chem. Int. Ed.* **2010**, *49*, 46-76.
- (13) Stephan, D. W.; Erker, G. *Frustrated Lewis Pair Chemistry: Development and Perspectives*. *Angew. Chem. Int. Ed.* **2015**, *54*, 6400-6441.
- (14) Stephan, D. W. *Frustrated Lewis Pairs*. *J. Am. Chem. Soc.* **2015**, *137*, 10018-10032.
- (15) Fontaine, F.-G.; Stephan, D. W. On the concept of frustrated Lewis pairs. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* **2017**, *375*.
- (16) Fontaine, F.-G.; Rochette, É. Ambiphilic Molecules: From Organometallic Curiosity to Metal-Free Catalysts. *Acc. Chem. Res.* **2018**, *51*, 454-464.
- (17) Rokob, T. A.; Bakó, I.; Stirling, A.; Hamza, A.; Pápai, I. Reactivity Models of Hydrogen Activation by Frustrated Lewis Pairs: Synergistic Electron Transfers or Polarization by Electric Field? *J. Am. Chem. Soc.* **2013**, *135*, 4425-4437.
- (18) Rokob, T. A.; Hamza, A.; Stirling, A.; Soós, T.; Pápai, I. Turning Frustration into Bond Activation: A Theoretical Mechanistic Study on Heterolytic Hydrogen Splitting by Frustrated Lewis Pairs. *Angew. Chem. Int. Ed.* **2008**, *47*, 2435-2438.
- (19) Parks, D. J.; Piers, W. E. Tris(pentafluorophenyl)boron-Catalyzed Hydrosilation of Aromatic Aldehydes, Ketones, and Esters. *J. Am. Chem. Soc.* **1996**, *118*, 9440-9441.
- (20) Wittig, G.; Benz, E. Über das Verhalten von Dehydrobenzol gegenüber nucleophilen und elektrophilen Reagenzien. *Chem. Ber.* **1959**, *92*, 1999-2013.
- (21) Tochtermann, W. Struktur und Reaktionsweise organischer at-Komplexe. *Angew. Chem.* **1966**, *78*, 355-375.
- (22) Welch, G. C.; Juan, R. R. S.; Masuda, J. D.; Stephan, D. W. Reversible, Metal-Free Hydrogen Activation. *Science* **2006**, *314*, 1124-1126.
- (23) Welch, G. C.; Stephan, D. W. Facile Heterolytic Cleavage of Dihydrogen by Phosphines and Boranes. *J. Am. Chem. Soc.* **2007**, *129*, 1880-1881.
- (24) Crabtree, R. H. Dihydrogen complexes: some structural and chemical studies. *Acc. Chem. Res.* **1990**, *23*, 95-101.

- (25) Kubas, G. J. Fundamentals of H₂ Binding and Reactivity on Transition Metals Underlying Hydrogenase Function and H₂ Production and Storage. *Chem. Rev.* **2007**, *107*, 4152-4205.
- (26) Berke, H. Conceptual Approach to the Reactivity of Dihydrogen. *ChemPhysChem* **2010**, *11*, 1837-1849.
- (27) Clapham, S. E.; Hadzovic, A.; Morris, R. H. Mechanisms of the H₂-hydrogenation and transfer hydrogenation of polar bonds catalyzed by ruthenium hydride complexes. *Coord. Chem. Rev.* **2004**, *248*, 2201-2237.
- (28) Morris, R. H. Mechanisms of the H₂- and transfer hydrogenation of polar bonds catalyzed by iron group hydrides. *Dalton. Trans.* **2018**.
- (29) Liu, L.; Lukose, B.; Jaque, P.; Ensing, B. Reaction Mechanism of Hydrogen Activation by Frustrated Lewis Pairs. *Green Energy & Environment* **2018**.
- (30) Grimme, S.; Kruse, H.; Goerigk, L.; Erker, G. The Mechanism of Dihydrogen Activation by Frustrated Lewis Pairs Revisited. *Angew. Chem. Int. Ed.* **2010**, *49*, 1402-1405.
- (31) Brown, L. C.; Hogg, J. M.; Gilmore, M.; Moura, L.; Imberti, S.; Gärtner, S.; Gunaratne, H. Q. N.; O'Donnell, R. J.; Artioli, N.; Holbrey, J. D.; Swadźba-Kwaśny, M. Frustrated Lewis pairs in ionic liquids and molecular solvents – a neutron scattering and NMR study of encounter complexes. *Chem. Commun.* **2018**, *54*, 8689-8692.
- (32) Rokob, T. A.; Hamza, A.; Pápai, I. Rationalizing the Reactivity of Frustrated Lewis Pairs: Thermodynamics of H₂ Activation and the Role of Acid-Base Properties. *J. Am. Chem. Soc.* **2009**, *131*, 10701-10710.
- (33) Skara, G.; De Vleeschouwer, F.; Geerlings, P.; De Proft, F.; Pinter, B. Heterolytic Splitting of Molecular Hydrogen by Frustrated and Classical Lewis Pairs: A Unified Reactivity Concept. *Sci. Rep.* **2017**, *7*, 16024.
- (34) Schirmer, B.; Grimme, S. Electric field induced activation of H₂—Can DFT do the job? *Chem. Commun.* **2010**, *46*, 7942-7944.
- (35) Liu, L.; Lukose, B.; Ensing, B. Hydrogen Activation by Frustrated Lewis Pairs Revisited by Metadynamics Simulations. *J. Phys. Chem. C.* **2017**, *121*, 2046-2051.
- (36) Geier, S. J.; Gilbert, T. M.; Stephan, D. W. Activation of H₂ by Phosphinoboranes R₂PB(C₆F₅)₂. *J. Am. Chem. Soc.* **2008**, *130*, 12632-12633.
- (37) Nyhlén, J.; Privalov, T. "Frustration" of Orbital Interactions in Lewis Base/Lewis Acid Adducts: A Computational Study of H₂ Uptake by Phosphanylboranes R₂P=BR'₂. *Eur. J. Inorg. Chem.* **2009**, *2009*, 2759-2764.
- (38) Dettenrieder, N.; Aramaki, Y.; Wolf, B. M.; Maichle-Mössner, C.; Zhao, X.; Yamashita, M.; Nozaki, K.; Anwender, R. Assessing the Brønsted Basicity of Diaminoboryl Anions: Reactivity toward Methylated Benzenes and Dihydrogen. *Angew. Chem. Int. Ed.* **2014**, *53*, 6259-6262.
- (39) Hounjet, L. J.; Stephan, D. W. Hydrogenation by Frustrated Lewis Pairs: Main Group Alternatives to Transition Metal Catalysts? *Org. Process Res. Dev.* **2014**, *18*, 385-391.
- (40) Chase, P. A.; Jurca, T.; Stephan, D. W. Lewis acid-catalyzed hydrogenation: B(C₆F₅)₃-mediated reduction of imines and nitriles with H₂. *Chem. Commun.* **2008**, 1701-1703.
- (41) Chase, P. A.; Welch, G. C.; Jurca, T.; Stephan, D. W. Metal-Free Catalytic Hydrogenation. *Angew. Chem. Int. Ed.* **2007**, *46*, 8050-8053.
- (42) Stephan, D. W.; Greenberg, S.; Graham, T. W.; Chase, P.; Hastie, J. J.; Geier, S. J.; Farrell, J. M.; Brown, C. C.; Heiden, Z. M.; Welch, G. C.; Ullrich, M. Metal-Free Catalytic Hydrogenation of Polar Substrates by Frustrated Lewis Pairs. *Inorg. Chem.* **2011**, *50*, 12338-12348.
- (43) Spies, P.; Erker, G.; Kehr, G.; Bergander, K.; Fröhlich, R.; Grimme, S.; Stephan, D. W. Rapid intramolecular heterolytic dihydrogen activation by a four-membered heterocyclic phosphane-borane adduct. *Chem. Commun.* **2007**, 5072-5074.
- (44) Sumerin, V.; Schulz, F.; Atsumi, M.; Wang, C.; Nieger, M.; Leskelä, M.; Repo, T.; Pyykkö, P.; Rieger, B. Molecular Tweezers for Hydrogen: Synthesis, Characterization, and Reactivity. *J. Am. Chem. Soc.* **2008**, *130*, 14117-14119.
- (45) Oestreich, M.; Hermeke, J.; Mohr, J. A unified survey of Si-H and H-H bond activation catalysed by electron-deficient boranes. *Chem. Soc. Rev.* **2015**, *44*, 2202-2220.
- (46) Reddy, J. S.; Xu, B.-H.; Mahdi, T.; Fröhlich, R.; Kehr, G.; Stephan, D. W.; Erker, G. Alkenylborane-Derived Frustrated Lewis Pairs: Metal-Free Catalytic Hydrogenation Reactions of Electron-Deficient Alkenes. *Organometallics* **2012**, *31*, 5638-5649.
- (47) Mahdi, T.; Stephan, D. W. Enabling Catalytic Ketone Hydrogenation by Frustrated Lewis Pairs. *J. Am. Chem. Soc.* **2014**, *136*, 15809-15812.
- (48) Scott, D. J.; Fuchter, M. J.; Ashley, A. E. Nonmetal Catalyzed Hydrogenation of Carbonyl Compounds. *J. Am. Chem. Soc.* **2014**, *136*, 15813-15816.
- (49) Gyömöre, Á.; Bakos, M.; Földes, T.; Pápai, I.; Domján, A.; Soós, T. Moisture-Tolerant Frustrated Lewis Pair Catalyst for Hydrogenation of Aldehydes and Ketones. *ACS Catal.* **2015**, *5*, 5366-5372.
- (50) Mahdi, T.; Heiden, Z. M.; Grimme, S.; Stephan, D. W. Metal-Free Aromatic Hydrogenation: Aniline to Cyclohexyl-amine Derivatives. *J. Am. Chem. Soc.* **2012**, *134*, 4088-4091.
- (51) Longobardi, L. E.; Mahdi, T.; Stephan, D. W. B(C₆F₅)₃ mediated arene hydrogenation/transannulation of para-methoxyanilines. *Dalton. Trans.* **2015**, *44*, 7114-7117.

- (52) Li, G.; Liu, Y.; Du, H. B(C₆F₅)₃-catalyzed metal-free hydrogenation of naphthylamines. *Org. Biomol. Chem.* **2015**, *13*, 2875-2878.
- (53) Wang, W.; Meng, W.; Du, H. B(C₆F₅)₃-catalyzed metal-free hydrogenation of 3,6-diarylpyridazines. *Dalton. Trans.* **2016**, *45*, 5945-5948.
- (54) Mahdi, T.; del Castillo, J. N.; Stephan, D. W. Metal-Free Hydrogenation of N-Based Heterocycles. *Organometallics* **2013**, *32*, 1971-1978.
- (55) Liu, Y.; Du, H. Metal-Free Borane-Catalyzed Highly Stereoselective Hydrogenation of Pyridines. *J. Am. Chem. Soc.* **2013**, *135*, 12968-12971.
- (56) Lam, J.; Szkop, K. M.; Mosafieri, E.; Stephan, D. W. FLP catalysis: main group hydrogenations of organic unsaturated substrates. *Chem. Soc. Rev.* **2018**.
- (57) Rokob, T. A.; Hamza, A.; Stirling, A.; Pápai, I. On the Mechanism of B(C₆F₅)₃-Catalyzed Direct Hydrogenation of Imines: Inherent and Thermally Induced Frustration. *J. Am. Chem. Soc.* **2009**, *131*, 2029-2036.
- (58) Farrell, J. M.; Hatnean, J. A.; Stephan, D. W. Activation of Hydrogen and Hydrogenation Catalysis by a Borenum Cation. *J. Am. Chem. Soc.* **2012**, *134*, 15728-15731.
- (59) Scott, D. J.; Fuchter, M. J.; Ashley, A. E. Designing effective 'frustrated Lewis pair' hydrogenation catalysts. *Chem. Soc. Rev.* **2017**, *46*, 5689-5700.
- (60) Clark, E. R.; Del Grosso, A.; Ingleson, M. J. The Hydride-Ion Affinity of Borenum Cations and Their Propensity to Activate H₂ in Frustrated Lewis Pairs. *Chem. Eur. J.* **2013**, *19*, 2462-2466.
- (61) Farrell, J. M.; Posaratnanathan, R. T.; Stephan, D. W. A family of N-heterocyclic carbene-stabilized borenum ions for metal-free imine hydrogenation catalysis. *Chem. Sci.* **2015**, *6*, 2010-2015.
- (62) Noyori, R.; Koizumi, M.; Ishii, D.; Ohkuma, T.: Asymmetric hydrogenation via architectural and functional molecular engineering. In *Pure and Applied Chemistry*, 2001; Vol. 73; pp 227.
- (63) Noyori, R.; Ohkuma, T. Asymmetric Catalysis by Architectural and Functional Molecular Engineering: Practical Chemo- and Stereoselective Hydrogenation of Ketones. *Angew. Chem. Int. Ed.* **2001**, *40*, 40-73.
- (64) Ghattas, G.; Chen, D.; Pan, F.; Klankermayer, J. Asymmetric hydrogenation of imines with a recyclable chiral frustrated Lewis pair catalyst. *Dalton. Trans.* **2012**, *41*, 9026-9028.
- (65) Lam, J.; Günther, B. A. R.; Farrell, J. M.; Eisenberger, P.; Bestvater, B. P.; Newman, P. D.; Melen, R. L.; Crudden, C. M.; Stephan, D. W. Chiral carbene-borane adducts: precursors for borenum catalysts for asymmetric FLP hydrogenations. *Dalton. Trans.* **2016**, *45*, 15303-15316.
- (66) Chen, D.; Klankermayer, J. Metal-free catalytic hydrogenation of imines with tris(perfluorophenyl)borane. *Chem. Commun.* **2008**, 2130-2131.
- (67) Chen, D.; Klankermayer, J.: Frustrated Lewis Pairs: From Dihydrogen Activation to Asymmetric Catalysis. In *Frustrated Lewis Pairs II: Expanding the Scope*; Erker, G., Stephan, D. W., Eds.; Springer Berlin Heidelberg: Berlin, Heidelberg, 2013; pp 1-26.
- (68) Liu, Y.; Du, H. Chiral Dienes as "Ligands" for Borane-Catalyzed Metal-Free Asymmetric Hydrogenation of Imines. *J. Am. Chem. Soc.* **2013**, *135*, 6810-6813.
- (69) Lindqvist, M.; Borre, K.; Axenov, K.; Kótai, B.; Nieger, M.; Leskelä, M.; Pápai, I.; Repo, T. Chiral Molecular Tweezers: Synthesis and Reactivity in Asymmetric Hydrogenation. *J. Am. Chem. Soc.* **2015**, *137*, 4038-4041.
- (70) Sumerin, V.; Chernichenko, K.; Nieger, M.; Leskelä, M.; Rieger, B.; Repo, T. Highly Active Metal-Free Catalysts for Hydrogenation of Unsaturated Nitrogen-Containing Compounds. *Adv. Synth. Catal.* **2011**, *353*, 2093-2110.
- (71) Wei, S.; Du, H. A Highly Enantioselective Hydrogenation of Silyl Enol Ethers Catalyzed by Chiral Frustrated Lewis Pairs. *J. Am. Chem. Soc.* **2014**, *136*, 12261-12264.
- (72) Farrell, J. M.; Heiden, Z. M.; Stephan, D. W. Metal-Free Transfer Hydrogenation Catalysis by B(C₆F₅)₃. *Organometallics* **2011**, *30*, 4497-4500.
- (73) Greb, L.; Oña-Burgos, P.; Schirmer, B.; Grimme, S.; Stephan, D. W.; Paradies, J. Metal-free Catalytic Olefin Hydrogenation: Low-Temperature H₂ Activation by Frustrated Lewis Pairs. *Angew. Chem. Int. Ed.* **2012**, *51*, 10164-10168.
- (74) Greb, L.; Tussing, S.; Schirmer, B.; Oña-Burgos, P.; Kaupmees, K.; Lökov, M.; Leito, I.; Grimme, S.; Paradies, J. Electronic effects of triarylphosphines in metal-free hydrogen activation: a kinetic and computational study. *Chem. Sci.* **2013**, *4*, 2788-2796.
- (75) Segawa, Y.; Stephan, D. W. Metal-free hydrogenation catalysis of polycyclic aromatic hydrocarbons. *Chem. Commun.* **2012**, *48*, 11963-11965.
- (76) Hounjet, L. J.; Bannwarth, C.; Garon, C. N.; Caputo, C. B.; Grimme, S.; Stephan, D. W. Combinations of Ethers and B(C₆F₅)₃ Function as Hydrogenation Catalysts. *Angew. Chem. Int. Ed.* **2013**, *52*, 7492-7495.
- (77) Scott, D. J.; Fuchter, M. J.; Ashley, A. E. Metal-Free Hydrogenation Catalyzed by an Air-Stable Borane: Use of Solvent as a Frustrated Lewis Base. *Angew. Chem. Int. Ed.* **2014**, *53*, 10218-10222.
- (78) Paradies, J. Metal-Free Hydrogenation of Unsaturated Hydrocarbons Employing Molecular Hydrogen. *Angew. Chem. Int. Ed.* **2014**, *53*, 3552-3557.

- (79) Eisenstein, O.; Crabtree, R. H. Outer sphere hydrogenation catalysis. *New J. Chem.* **2013**, *37*, 21-27.
- (80) Chernichenko, K.; Madarász, Á.; Pápai, I.; Nieger, M.; Leskelä, M.; Repo, T. A frustrated-Lewis-pair approach to catalytic reduction of alkynes to cis-alkenes. *Nat. Chem.* **2013**, *5*, 718.
- (81) Oro, L. A.; Carmona, D.: Rhodium. In *The Handbook of Homogeneous Hydrogenation*; J. G. de Vries, C. J. E., Ed., 2008.
- (82) Crabtree, R. H.: Iridium. In *The Handbook of Homogeneous Hydrogenation*; J. G. de Vries, C. J. E., Ed., 2008.
- (83) Szeto, K. C.; Sahyoun, W.; Merle, N.; Castelbou, J. L.; Popoff, N.; Lefebvre, F.; Raynaud, J.; Godard, C.; Claver, C.; Delevoeye, L.; Gauvin, R. M.; Taoufik, M. Development of silica-supported frustrated Lewis pairs: highly active transition metal-free catalysts for the Z-selective reduction of alkynes. *Catal. Sci. Technol.* **2016**, *6*, 882-889.
- (84) Wang, Y.; Chen, W.; Lu, Z.; Li, Z. H.; Wang, H. Metal-Free $\text{HB}(\text{C}_6\text{F}_5)_2$ -Catalyzed Hydrogenation of Unfunctionalized Olefins and Mechanism Study of Borane-Mediated σ -Bond Metathesis. *Angew. Chem. Int. Ed.* **2013**, *52*, 7496-7499.
- (85) Harhausen, M.; Fröhlich, R.; Kehr, G.; Erker, G. Reactions of Modified Intermolecular Frustrated P/B Lewis Pairs with Dihydrogen, Ethene, and Carbon Dioxide. *Organometallics* **2012**, *31*, 2801-2809.
- (86) Stirling, A.; Hamza, A.; Rokob, T. A.; Pápai, I. Concerted attack of frustrated Lewis acid–base pairs on olefinic double bonds: a theoretical study. *Chem. Commun.* **2008**, 3148-3150.
- (87) Mömmling, C. M.; Frömel, S.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G. Reactions of an Intramolecular Frustrated Lewis Pair with Unsaturated Substrates: Evidence for a Concerted Olefin Addition Reaction. *J. Am. Chem. Soc.* **2009**, *131*, 12280-12289.
- (88) Müller, T. E.; Beller, M. Metal-Initiated Amination of Alkenes and Alkynes. *Chem. Rev.* **1998**, *98*, 675-704.
- (89) Zhao, X.; Stephan, D. W. Olefin–Borane “van der Waals Complexes”: Intermediates in Frustrated Lewis Pair Addition Reactions. *J. Am. Chem. Soc.* **2011**, *133*, 12448-12450.
- (90) Zhao, X.; Stephan, D. W. Frustrated Lewis pair olefin addition reactions: P-, N-, C- and H-based nucleophilic additions to an olefin-tethered borane. *Chem. Sci.* **2012**, *3*, 2123-2132.
- (91) Dureen, M. A.; Brown, C. C.; Stephan, D. W. Deprotonation and Addition Reactions of Frustrated Lewis Pairs with Alkynes. *Organometallics* **2010**, *29*, 6594-6607.
- (92) Chen, C.; Eweiner, F.; Wibbeling, B.; Fröhlich, R.; Senda, S.; Ohki, Y.; Tatsumi, K.; Grimme, S.; Kehr, G.; Erker, G. Exploring the Limits of Frustrated Lewis Pair Chemistry with Alkynes: Detection of a System that Favors 1,1-Carboboration over Cooperative 1,2-P/B-Addition. *Chem. Asian. J.* **2010**, *5*, 2199-2208.
- (93) Jiang, C.; Blacque, O.; Berke, H. Activation of Terminal Alkynes by Frustrated Lewis Pairs. *Organometallics* **2010**, *29*, 125-133.
- (94) Walkinshaw, A. J.; Xu, W.; Suero, M. G.; Gaunt, M. J. Copper-Catalyzed Carboarylation of Alkynes via Vinyl Cations. *J. Am. Chem. Soc.* **2013**, *135*, 12532-12535.
- (95) Kehr, G.; Erker, G. 1,1-Carboboration. *Chem. Commun.* **2012**, *48*, 1839-1850.
- (96) Chen, C.; Kehr, G.; Fröhlich, R.; Erker, G. Carbon–Carbon Bond Activation by 1,1-Carboboration of Internal Alkynes. *J. Am. Chem. Soc.* **2010**, *132*, 13594-13595.
- (97) Feldmann, A.; Kehr, G.; Daniliuc, C. G.; Mück-Lichtenfeld, C.; Erker, G. Functionalization of Intramolecular Frustrated Lewis Pairs by 1,1-Carboboration with Conjugated Enynes. *Chem. Eur. J.* **2015**, *21*, 12456-12464.
- (98) Dureen, M. A.; Stephan, D. W. Terminal Alkyne Activation by Frustrated and Classical Lewis Acid/Phosphine Pairs. *J. Am. Chem. Soc.* **2009**, *131*, 8396-8397.
- (99) Trost, B. M.; McClory, A. Metal Vinylidenes as Catalytic Species in Organic Reactions. *Chem. Asian. J.* **2008**, *3*, 164-194.
- (100) Dureen, M. A.; Brown, C. C.; Stephan, D. W. Addition of Enamines or Pyrroles and $\text{B}(\text{C}_6\text{F}_5)_3$ “Frustrated Lewis Pairs” to Alkynes. *Organometallics* **2010**, *29*, 6422-6432.
- (101) Mahdi, T.; Stephan, D. W. Frustrated Lewis Pair Catalyzed Hydroamination of Terminal Alkynes. *Angew. Chem. Int. Ed.* **2013**, *52*, 12418-12421.
- (102) Mahdi, T.; Stephan, D. W. Stoichiometric and Catalytic Inter- and Intramolecular Hydroamination of Terminal Alkynes by Frustrated Lewis Pairs. *Chem. Eur. J.* **2015**, *21*, 11134-11142.
- (103) Fürstner, A.; Davies, P. W. Catalytic Carbophilic Activation: Catalysis by Platinum and Gold π Acids. *Angew. Chem. Int. Ed.* **2007**, *46*, 3410-3449.
- (104) McGough, J. S.; Butler, S. M.; Cade, I. A.; Ingleson, M. J. Highly selective catalytic trans-hydroboration of alkynes mediated by borenium cations and $\text{B}(\text{C}_6\text{F}_5)_3$. *Chem. Sci.* **2016**, *7*, 3384-3389.
- (105) Fleige, M.; Möbus, J.; vom Stein, T.; Glorius, F.; Stephan, D. W. Lewis acid catalysis: catalytic hydroboration of alkynes initiated by Piers' borane. *Chem. Commun.* **2016**, *52*, 10830-10833.
- (106) Fan, L.; Stephan, D. W. PNPCB heterocycles via thermal and Lewis acid catalyzed trans-hydroborations. *Dalton. Trans.* **2016**, *45*, 9229-9234.

- (107) Wang, T.; Jentgens, X.; Daniliuc, C. G.; Kehr, G.; Erker, G. Tris(pentafluorophenyl)borane-Catalyzed Reaction of Phosphorus/Boron and Nitrogen/Boron Frustrated Lewis Pair Dihydrogen Activation Products with Alkenes and Alkynes. *ChemCatChem* **2017**, *9*, 651-658.
- (108) Vasko, P.; Zulkifly, I. A.; Fuentes, M. Á.; Mo, Z.; Hicks, J.; Kamer, P. C. J.; Aldridge, S. Reversible C–H Activation, Facile C–B/B–H Metathesis and Apparent Hydroboration Catalysis by a Dimethylxanthene-Based Frustrated Lewis Pair. *Chem. Eur. J.* **2018**, *24*, 10531-10540.
- (109) Shimoi, M.; Watanabe, T.; Maeda, K.; Curran, D. P.; Taniguchi, T. Radical trans-Hydroboration of Alkynes with N-Heterocyclic Carbene Boranes. *Angew. Chem.* **2018**, *130*, 9629-9634.
- (110) Lawson, J. R.; Wilkins, L. C.; Melen, R. L. Tris(2,4,6-trifluorophenyl)borane: An Efficient Hydroboration Catalyst. *Chem. Eur. J.* **2017**, *23*, 10997-11000.
- (111) Hansmann, M. M.; Melen, R. L.; Rominger, F.; Hashmi, A. S. K.; Stephan, D. W. Activation of Alkynes with $B(C_6F_5)_3$ – Boron Allylation Reagents Derived from Propargyl Esters. *J. Am. Chem. Soc.* **2014**, *136*, 777-782.
- (112) Hansmann, M. M.; Melen, R. L.; Rominger, F.; Hashmi, A. S. K.; Stephan, D. W. $B(C_6F_5)_3$ promoted cyclisation of internal propargyl esters: structural characterisation of 1,3-dioxolium compounds. *Chem. Commun.* **2014**, *50*, 7243-7245.
- (113) Melen, R. L.; Hansmann, M. M.; Lough, A. J.; Hashmi, A. S. K.; Stephan, D. W. Cyclisation versus 1,1-Carboboration: Reactions of $B(C_6F_5)_3$ with Propargyl Amides. *Chem. Eur. J.* **2013**, *19*, 11928-11938.
- (114) Lawson, J. R.; Melen, R. L. Tris(pentafluorophenyl)borane and Beyond: Modern Advances in Borylation Chemistry. *Inorg. Chem.* **2017**, *56*, 8627-8643.
- (115) Tamke, S.; Qu, Z.-W.; Sitte, N. A.; Flörke, U.; Grimme, S.; Paradies, J. Frustrated Lewis Pair-Catalyzed Cycloisomerization of 1,5-Enynes via a 5-endo-dig Cyclization/Protodeborylation Sequence. *Angew. Chem. Int. Ed.* **2016**, *55*, 4336-4339.
- (116) Yuan, K.; Wang, S. trans-Aminoboration across Internal Alkynes Catalyzed by $B(C_6F_5)_3$ for the Synthesis of Borylated Indoles. *Org. Lett.* **2017**, *19*, 1462-1465.
- (117) Hansmann, M. M.; Melen, R. L.; Rudolph, M.; Rominger, F.; Wadepohl, H.; Stephan, D. W.; Hashmi, A. S. K. Cyclopropanation/Carboboration Reactions of Enynes with $B(C_6F_5)_3$. *J. Am. Chem. Soc.* **2015**, *137*, 15469-15477.
- (118) Wilkins, L. C.; Wieneke, P.; Newman, P. D.; Kariuki, B. M.; Rominger, F.; Hashmi, A. S. K.; Hansmann, M. M.; Melen, R. L. Pathways to Functionalized Heterocycles: Propargyl Rearrangement using $B(C_6F_5)_3$. *Organometallics* **2015**, *34*, 5298-5309.
- (119) Wilkins, L. C.; Hamilton, H. B.; Kariuki, B. M.; Hashmi, A. S. K.; Hansmann, M. M.; Melen, R. L. Lewis acid–base 1,2-addition reactions: synthesis of pyrylium borates from en-ynoate precursors. *Dalton. Trans.* **2016**, *45*, 5929-5932.
- (120) Wilkins, L. C.; Lawson, J. R.; Wieneke, P.; Rominger, F.; Hashmi, A. S. K.; Hansmann, M. M.; Melen, R. L. The Propargyl Rearrangement to Functionalised Allyl-Boron and Borocation Compounds. *Chem. Eur. J.* **2016**, *22*, 14618-14624.
- (121) Wilkins, L. C.; Günther, B. A. R.; Walther, M.; Lawson, J. R.; Wirth, T.; Melen, R. L. Contrasting Frustrated Lewis Pair Reactivity with Selenium- and Boron-Based Lewis Acids. *Angew. Chem. Int. Ed.* **2016**, *55*, 11292-11295.
- (122) Issaian, A.; Tu, K. N.; Blum, S. A. Boron–Heteroatom Addition Reactions via Borylative Heterocyclization: Oxyboration, Aminoboration, and Thioboration. *Acc. Chem. Res.* **2017**, *50*, 2598-2609.
- (123) Wang, T.; Daniliuc, C. G.; Mück-Lichtenfeld, C.; Kehr, G.; Erker, G. Formation of Reactive π -Conjugated Frustrated N/B Pairs by Borane-Induced Propargyl Amine Rearrangement. *J. Am. Chem. Soc.* **2018**, *140*, 3635-3643.
- (124) Lawson, J. R.; Melen, R. L.: Recent developments and applications of Lewis acidic boron reagents. In *Organometallic Chemistry: Volume 41*; The Royal Society of Chemistry, 2017; Vol. 41; pp 1-27.
- (125) Soltani, Y.; Wilkins, L. C.; Melen, R. L. Stoichiometric and Catalytic C–C and C–H Bond Formation with $B(C_6F_5)_3$ via Cationic Intermediates. *Angew. Chem. Int. Ed.* **2017**, *56*, 11995-11999.
- (126) Burg, A. B.; Schlesinger, H. I. Hydrides of Boron. VII. Evidence of the Transitory Existence of Borine (BH_3): Borine Carbonyl and Borine Trimethylamine. *J. Am. Chem. Soc.* **1937**, *59*, 780-787.
- (127) Sajid, M.; Elmer, L.-M.; Rosorius, C.; Daniliuc, C. G.; Grimme, S.; Kehr, G.; Erker, G. Facile Carbon Monoxide Reduction at Intramolecular Frustrated Phosphane/Borane Lewis Pair Templates. *Angew. Chem. Int. Ed.* **2013**, *52*, 2243-2246.
- (128) Sajid, M.; Kehr, G.; Daniliuc, C. G.; Erker, G. Formylborane Formation with Frustrated Lewis Pair Templates. *Angew. Chem. Int. Ed.* **2014**, *53*, 1118-1121.
- (129) Finze, M.; Bernhardt, E.; Terheiden, A.; Berkei, M.; Willner, H.; Christen, D.; Oberhammer, H.; Aubke, F. Tris(trifluoromethyl)borane Carbonyl, $(CF_3)_3BCO$ Synthesis, Physical, Chemical and Spectroscopic Properties, Gas Phase, and Solid State Structure. *J. Am. Chem. Soc.* **2002**, *124*, 15385-15398.
- (130) Finze, M.; Bernhardt, E.; Willner, H.; Lehmann, C. W. Reactions of $(CF_3)_3BCO$ with Amines and Phosphines. *Inorg. Chem.* **2006**, *45*, 669-678.

- (131) Gerken, M.; Pawelke, G.; Bernhardt, E.; Willner, H. Syntheses and Characterization of $(C_2F_5)_3BCO$ and $(C_3F_7)_3BCO$. *Chem. Eur. J.* **2010**, *16*, 7527-7536.
- (132) Fukazawa, A.; Dutton, J. L.; Fan, C.; Mercier, L. G.; Houghton, A. Y.; Wu, Q.; Piers, W. E.; Parvez, M. Reaction of pentaarylboroles with carbon monoxide: an isolable organoboron carbonyl complex. *Chem. Sci.* **2012**, *3*, 1814-1818.
- (133) Goldman, A. S.; Krogh-Jespersen, K. Why Do Cationic Carbon Monoxide Complexes Have High C–O Stretching Force Constants and Short C–O Bonds? Electrostatic Effects, Not σ -Bonding. *J. Am. Chem. Soc.* **1996**, *118*, 12159-12166.
- (134) Sajid, M.; Lawzer, A.; Dong, W.; Rosorius, C.; Sander, W.; Schirmer, B.; Grimme, S.; Daniliuc, C. G.; Kehr, G.; Erker, G. Carbonylation Reactions of Intramolecular Vicinal Frustrated Phosphane/Borane Lewis Pairs. *J. Am. Chem. Soc.* **2013**, *135*, 18567-18574.
- (135) Elmer, L.-M.; Kehr, G.; Daniliuc, C. G.; Siedow, M.; Eckert, H.; Tesch, M.; Studer, A.; Williams, K.; Warren, T. H.; Erker, G. The Chemistry of a Non-Interacting Vicinal Frustrated Phosphane/Borane Lewis Pair. *Chem. Eur. J.* **2017**, *23*, 6056-6068.
- (136) Cabrera, A. R.; Rojas, R. S.; Valderrama, M.; Plüss, P.; Berke, H.; Daniliuc, C. G.; Kehr, G.; Erker, G. Synthesis of new asymmetric substituted boron amidines – reactions with CO and transfer hydrogenations of phenylacetylene. *Dalton. Trans.* **2015**, *44*, 19606-19614.
- (137) Wang, L.; Dong, S.; Daniliuc, C. G.; Liu, L.; Grimme, S.; Knitsch, R.; Eckert, H.; Hansen, M. R.; Kehr, G.; Erker, G. Formation of macrocyclic ring systems by carbonylation of trifunctional P/B/B frustrated Lewis pairs. *Chem. Sci.* **2018**, *9*, 1544-1550.
- (138) Brown, H. C. Organoborane-carbon monoxide reactions. Synthesis of carbon structures. *Acc. Chem. Res.* **1969**, *2*, 65-72.
- (139) Franke, R.; Selent, D.; Börner, A. Applied Hydroformylation. *Chem. Rev.* **2012**, *112*, 5675-5732.
- (140) Masters, C.: The Fischer-Tropsch Reaction. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press, 1979; Vol. 17; pp 61-103.
- (141) Maitlis, P. M.; Zanotti, V. The role of electrophilic species in the Fischer–Tropsch reaction. *Chem. Commun.* **2009**, 1619-1634.
- (142) Dobrovetsky, R.; Stephan, D. W. Stoichiometric Metal-Free Reduction of CO in Syn-Gas. *J. Am. Chem. Soc.* **2013**, *135*, 4974-4977.
- (143) Yu, J.; Kehr, G.; Daniliuc, C. G.; Erker, G. Cooperative reaction chemistry derived from a borata-diene framework. *Chem. Commun.* **2016**, *52*, 1393-1396.
- (144) Jian, Z.; Kehr, G.; Daniliuc, C. G.; Wibbeling, B.; Wiegand, T.; Siedow, M.; Eckert, H.; Bursch, M.; Grimme, S.; Erker, G. CO-Reduction Chemistry: Reaction of a CO-Derived Formylhydridoborate with Carbon Monoxide, with Carbon Dioxide, and with Dihydrogen. *J. Am. Chem. Soc.* **2017**, *139*, 6474-6483.
- (145) Wang, L.; Zhang, S.; Hasegawa, Y.; Daniliuc, C. G.; Kehr, G.; Erker, G. Cooperative carbon monoxide to formyl reduction at a trifunctional PBB frustrated Lewis pair. *Chem. Commun.* **2017**, *53*, 5499-5502.
- (146) Ye, K.-Y.; Daniliuc, C. G.; Dong, S.; Kehr, G.; Erker, G. Frustrated Lewis Pair Behavior of an Open, Noninteracting Phosphane/Borane Pair at a Rigid Organic Framework: Exploring Decisive Factors for FLP Activity. *Organometallics* **2017**, *36*, 5003-5012.
- (147) Wang, T.; Kehr, G.; Daniliuc, C. G.; Erker, G. Metal-Free Carbonylation Route to a Reactive Borataepoxide System. *Organometallics* **2018**, *37*, 1040-1049.
- (148) Wang, T.; Wang, L.; Daniliuc, C. G.; Samigullin, K.; Wagner, M.; Kehr, G.; Erker, G. CO/CO and NO/NO coupling at a hidden frustrated Lewis pair template. *Chem. Sci.* **2017**, *8*, 2457-2463.
- (149) Del Grosso, A.; Singleton, P. J.; Muryn, C. A.; Ingleson, M. J. Pinacol Boronates by Direct Arene Borylation with Borenium Cations. *Angew. Chem. Int. Ed.* **2011**, *50*, 2102-2106.
- (150) Farrell, J. M.; Stephan, D. W. Planar N-Heterocyclic Carbene Diarylborenium Ions: Synthesis by Cationic Borylation and Reactivity with Lewis Bases. *Angew. Chem. Int. Ed.* **2015**, *54*, 5214-5217.
- (151) Prokofjevs, A.; Kampf, J. W.; Vedejs, E. A Borenium Ion with Exceptional Electrophilicity. *Angew. Chem. Int. Ed.* **2011**, *50*, 2098-2101.
- (152) Del Grosso, A.; Pritchard, R. G.; Muryn, C. A.; Ingleson, M. J. Chelate Restrained Boron Cations for Intermolecular Electrophilic Arene Borylation. *Organometallics* **2010**, *29*, 241-249.
- (153) De Vries, T. S.; Prokofjevs, A.; Harvey, J. N.; Vedejs, E. Superelectrophilic Intermediates in Nitrogen-Directed Aromatic Borylation. *J. Am. Chem. Soc.* **2009**, *131*, 14679-14687.
- (154) Prokofjevs, A.; Vedejs, E. N-Directed Aliphatic C–H Borylation Using Borenium Cation Equivalents. *J. Am. Chem. Soc.* **2011**, *133*, 20056-20059.
- (155) Grosso, A. D.; Helm, M. D.; Solomon, S. A.; Caras-Quintero, D.; Ingleson, M. J. Simple inexpensive boron electrophiles for direct arene borylation. *Chem. Commun.* **2011**, *47*, 12459-12461.
- (156) Solomon, S. A.; Del Grosso, A.; Clark, E. R.; Bagutski, V.; McDouall, J. J. W.; Ingleson, M. J. Reactivity of Lewis Acid Activated Diaza- and Dithiaboroles in Electrophilic Arene Borylation. *Organometallics* **2012**, *31*, 1908-1916.

- (157) Bagutski, V.; Del Grosso, A.; Carrillo, J. A.; Cade, I. A.; Helm, M. D.; Lawson, J. R.; Singleton, P. J.; Solomon, S. A.; Marcelli, T.; Ingleson, M. J. Mechanistic Studies into Amine-Mediated Electrophilic Arene Borylation and Its Application in MIDA Boronate Synthesis. *J. Am. Chem. Soc.* **2013**, *135*, 474-487.
- (158) Prokofjevs, A.; Jermaks, J.; Borovika, A.; Kampf, J. W.; Vedejs, E. Electrophilic C–H Borylation and Related Reactions of B–H Boron Cations. *Organometallics* **2013**, *32*, 6701-6711.
- (159) McGough, J. S.; Cid, J.; Ingleson, M. J. Catalytic Electrophilic C–H Borylation Using NHC-Boranes and Iodine Forms C2-, not C3-, Borylated Indoles. *Chem. Eur. J.* **2017**, *23*, 8180-8184.
- (160) Farrell, J. M.; Schmidt, D.; Grande, V.; Würthner, F. Synthesis of a Doubly Boron-Doped Perylene through NHC-Borenium Hydroboration/C–H Borylation/Dehydrogenation. *Angew. Chem. Int. Ed.* **2017**, *56*, 11846-11850.
- (161) Yin, Q.; Klare, H. F. T.; Oestreich, M. Catalytic Friedel–Crafts C–H Borylation of Electron-Rich Arenes: Dramatic Rate Acceleration by Added Alkenes. *Angew. Chem. Int. Ed.* **2017**, *56*, 3712-3717.
- (162) Zhang, S.; Han, Y.; He, J.; Zhang, Y. B(C₆F₅)₃-Catalyzed C3-Selective C–H Borylation of Indoles: Synthesis, Intermediates, and Reaction Mechanism. *J. Org. Chem.* **2018**, *83*, 1377-1386.
- (163) Liu, Y.-L.; Kehr, G.; Daniliuc, C. G.; Erker, G. Metal-Free Arene and Heteroarene Borylation Catalyzed by Strongly Electrophilic Bis-boranes. *Chem. Eur. J.* **2017**, *23*, 12141-12144.
- (164) Larsen, M. A.; Hartwig, J. F. Iridium-Catalyzed C–H Borylation of Heteroarenes: Scope, Regioselectivity, Application to Late-Stage Functionalization, and Mechanism. *J. Am. Chem. Soc.* **2014**, *136*, 4287-4299.
- (165) Ackermann, L. Carboxylate-Assisted Transition-Metal-Catalyzed C–H Bond Functionalizations: Mechanism and Scope. *Chem. Rev.* **2011**, *111*, 1315-1345.
- (166) Légaré, M.-A.; Courtemanche, M.-A.; Rochette, É.; Fontaine, F.-G. Metal-free catalytic C-H bond activation and borylation of heteroarenes. *Science* **2015**, *349*, 513-516.
- (167) Légaré Lavergne, J.; Jayaraman, A.; Misal Castro, L. C.; Rochette, É.; Fontaine, F.-G. Metal-Free Borylation of Heteroarenes Using Ambiphilic Aminoboranes: On the Importance of Sterics in Frustrated Lewis Pair C–H Bond Activation. *J. Am. Chem. Soc.* **2017**, *139*, 14714-14723.
- (168) Shao, Y.; Zhang, J.; Li, Y.; Liu, Y.; Ke, Z. Frustrated Lewis Pair Catalyzed C–H Activation of Heteroarenes: A Stepwise Carbene Mechanism Due to Distance Effect. *Org. Lett.* **2018**, *20*, 1102-1105.
- (169) Légaré, M.-A.; Rochette, É.; Légaré Lavergne, J.; Bouchard, N.; Fontaine, F.-G. Bench-stable frustrated Lewis pair chemistry: fluoroborate salts as precatalysts for the C–H borylation of heteroarenes. *Chem. Commun.* **2016**, *52*, 5387-5390.
- (170) Chernichenko, K.; Lindqvist, M.; Kótai, B.; Nieger, M.; Sorochkina, K.; Pápai, I.; Repo, T. Metal-Free sp²-C–H Borylation as a Common Reactivity Pattern of Frustrated 2-Aminophenylboranes. *J. Am. Chem. Soc.* **2016**, *138*, 4860-4868.
- (171) Wu, D.; Kong, L.; Li, Y.; Ganguly, R.; Kinjo, R. 1,3,2,5-Diazadiborinine featuring nucleophilic and electrophilic boron centres. *Nat. Commun.* **2015**, *6*, 7340.
- (172) Wu, D.; Ganguly, R.; Li, Y.; Hoo, S. N.; Hirao, H.; Kinjo, R. Reversible [4 + 2] cycloaddition reaction of 1,3,2,5-diazadiborinine with ethylene. *Chem. Sci.* **2015**, *6*, 7150-7155.
- (173) Wang, B.; Li, Y.; Ganguly, R.; Hirao, H.; Kinjo, R. Ambiphilic boron in 1,4,2,5-diazadiborinine. *Nat. Commun.* **2016**, *7*, 11871.
- (174) Su, Y.; Li, Y.; Ganguly, R.; Kinjo, R. Engineering the Frontier Orbitals of a Diazadiborinine for Facile Activation of H₂, NH₃, and an Isonitrile. *Angew. Chem. Int. Ed.* **2018**, *57*, 7846-7849.
- (175) Taylor, J. W.; McSkimming, A.; Guzman, C. F.; Harman, W. H. N-Heterocyclic Carbene-Stabilized Boranthrene as a Metal-Free Platform for the Activation of Small Molecules. *J. Am. Chem. Soc.* **2017**, *139*, 11032-11035.
- (176) von Grotthuss, E.; Diefenbach, M.; Bolte, M.; Lerner, H.-W.; Holthausen, M. C.; Wagner, M. Reversible Dihydrogen Activation by Reduced Aryl Boranes as Main-Group Ambiphiles. *Angew. Chem. Int. Ed.* **2016**, *55*, 14067-14071.
- (177) Lorbach, A.; Bolte, M.; Lerner, H.-W.; Wagner, M. Dilithio 9,10-Diborataanthracene: Molecular Structure and 1,4-Addition Reactions. *Organometallics* **2010**, *29*, 5762-5765.
- (178) Urry, G.; Wartik, T.; Moore, R. E.; Schlesinger, H. I. The Preparation and Some of the Properties of Diboron Tetrachloride, B₂Cl₄. *J. Am. Chem. Soc.* **1954**, *76*, 5293-5298.
- (179) Ahmed, L.; Castillo, J.; Saulys, D. A.; Morrison, J. A. Reactivity of the diboron tetrahalides. Diboration of ethylene with diboron tetrabromide and thermal decomposition and ligand exchanges of diboron tetrabromide and diboron tetrachloride in carbon tetrabromide and carbon tetrachloride. *Inorg. Chem.* **1992**, *31*, 706-710.
- (180) Ceron, P.; Finch, A.; Frey, J.; Kerrigan, J.; Parsons, T.; Urry, G.; Schlesinger, H. I. Diboron Tetrachloride and Tetrafluoride as Reagents for the Synthesis of Organoboron Compounds. II. The Behavior of the Diboron Tetrahalides toward Unsaturated Organic Compounds. *J. Am. Chem. Soc.* **1959**, *81*, 6368-6371.
- (181) Urry, G.; Kerrigan, J.; Parsons, T. D.; Schlesinger, H. I. Diboron Tetrachloride, B₂Cl₄, as a Reagent for the Synthesis of Organo-boron Compounds. I. The Reaction of Diboron Tetrachloride with Ethylene. *J. Am. Chem. Soc.* **1954**, *76*, 5299-5301.

- (182) Pubill-Ulldemolins, C.; Fernández, E.; Bo, C.; Brown, J. M. Origins of observed reactivity and specificity in the addition of B₂Cl₄ and analogues to unsaturated compounds. *Org. Biomol. Chem.* **2015**, *13*, 9619-9628.
- (183) Neeve, E. C.; Geier, S. J.; Mkhaliid, I. A. I.; Westcott, S. A.; Marder, T. B. Diboron(4) Compounds: From Structural Curiosity to Synthetic Workhorse. *Chem. Rev.* **2016**, *116*, 9091-9161.
- (184) Dewhurst, R. D.; Neeve, E. C.; Braunschweig, H.; Marder, T. B. sp²-sp³ diboranes: astounding structural variability and mild sources of nucleophilic boron for organic synthesis. *Chem. Commun.* **2015**, *51*, 9594-9607.
- (185) Tsukahara, N.; Asakawa, H.; Lee, K.-H.; Lin, Z.; Yamashita, M. Cleaving Dihydrogen with Tetra(o-tolyl)diborane(4). *J. Am. Chem. Soc.* **2017**, *139*, 2593-2596.
- (186) Yalpani, M.; Köster, R. Partial Hydrogenation: From Anthracene to Coronene. *Chem. Ber.* **1990**, *123*, 719-724.
- (187) Yalpani, M.; Lunow, T.; Köster, R. Reduction of Polycyclic Arenes by -Boranes, II. Borane Catalyzed Hydrogenation of Naphthalenes to Tetralins. *Chem. Ber.* **1989**, *122*, 687-693.
- (188) Katsuma, Y.; Tsukahara, N.; Wu, L.; Lin, Z.; Yamashita, M. Reaction of B₂(o-tol)₄ with CO and Isocyanides: Cleavage of the C≡O Triple Bond and Direct C-H Borylations. *Angew. Chem. Int. Ed.* **2018**, *57*, 6109-6114.
- (189) Zheng, J.; Li, Z. H.; Wang, H. Addition of dihydrogen to a borylborenium center. *Chem. Sci.* **2018**, *9*, 1433-1438.
- (190) Araki, T.; Hirai, M.; Wakamiya, A.; Piers, W. E.; Yamaguchi, S. Antiaromatic Dithieno-1,2-dihydro-1,2-diborin Splits Diatomic Hydrogen. *Chem. Lett.* **2017**, *46*, 1714-1717.
- (191) Kaese, T.; Trageser, T.; Budy, H.; Bolte, M.; Lerner, H.-W.; Wagner, M. A redox-active diborane platform performs C(sp³)-H activation and nucleophilic substitution reactions. *Chem. Sci.* **2018**, *9*, 3881-3891.
- (192) Moezzi, A.; Olmstead, M. M.; Power, P. P. Boron-boron double bonding in the species [B₂R₄]²⁻: synthesis and structure of [{{(Et₂O)Li}}₂{Mes₂BB(Mes)Ph}], a diborane(4) dianion analog of a substituted ethylene. *J. Am. Chem. Soc.* **1992**, *114*, 2715-2717.
- (193) Nöth, H.; Knizek, J.; Ponikvar, W. A Boron-Boron Double Bond in the Dianions of Tetra(amino)diborates. *Eur. J. Inorg. Chem.* **1999**, *1999*, 1931-1937.
- (194) Wang, Y.; Quillian, B.; Wei, P.; Wannere, C. S.; Xie, Y.; King, R. B.; Schaefer, H. F.; Schleyer, P. v. R.; Robinson, G. H. A Stable Neutral Diborene Containing a BB Double Bond. *J. Am. Chem. Soc.* **2007**, *129*, 12412-12413.
- (195) Wang, Y.; Quillian, B.; Wei, P.; Xie, Y.; Wannere, C. S.; King, R. B.; Schaefer, H. F.; Schleyer, P. v. R.; Robinson, G. H. Planar, Twisted, and Trans-Bent: Conformational Flexibility of Neutral Diborenes. *J. Am. Chem. Soc.* **2008**, *130*, 3298-3299.
- (196) Braunschweig, H.; Dewhurst, R. D.; Hammond, K.; Mies, J.; Radacki, K.; Vargas, A. Ambient-Temperature Isolation of a Compound with a Boron-Boron Triple Bond. *Science* **2012**, *336*, 1420-1422.
- (197) Braunschweig, H.; Dewhurst, R. D.; Hörl, C.; Phukan, A. K.; Pinzner, F.; Ullrich, S. Direct Hydroboration of B=B Bonds: A Mild Strategy for the Proliferation of B-B Bonds. *Angew. Chem. Int. Ed.* **2014**, *53*, 3241-3244.
- (198) Braunschweig, H.; Dellermann, T.; Ewing, W. C.; Kramer, T.; Schneider, C.; Ullrich, S. Reductive Insertion of Elemental Chalcogens into Boron-Boron Multiple Bonds. *Angew. Chem. Int. Ed.* **2015**, *54*, 10271-10275.
- (199) Braunschweig, H.; Constantinidis, P.; Dellermann, T.; Ewing, W. C.; Fischer, I.; Hess, M.; Knight, F. R.; Rempel, A.; Schneider, C.; Ullrich, S.; Vargas, A.; Woollins, J. D. Highly Strained Heterocycles Constructed from Boron-Boron Multiple Bonds and Heavy Chalcogens. *Angew. Chem. Int. Ed.* **2016**, *55*, 5606-5609.
- (200) Wang, S. R.; Arrowsmith, M.; Böhnke, J.; Braunschweig, H.; Dellermann, T.; Dewhurst, R. D.; Kelch, H.; Krummenacher, I.; Mattock, J. D.; Müssig, J. H.; Thiess, T.; Vargas, A.; Zhang, J. Engineering a Small HOMO-LUMO Gap and Intramolecular C-H Borylation by Diborene/Anthracene Orbital Intercalation. *Angew. Chem. Int. Ed.* **2017**, *56*, 8009-8013.
- (201) Auerhammer, D.; Arrowsmith, M.; Dewhurst, R. D.; Kupfer, T.; Böhnke, J.; Braunschweig, H. Closely related yet different: a borylene and its dimer are non-interconvertible but connected through reactivity. *Chem. Sci.* **2018**, *9*, 2252-2260.
- (202) Böhnke, J.; Braunschweig, H.; Dellermann, T.; Ewing, W. C.; Kramer, T.; Krummenacher, I.; Vargas, A. From an Electron-Rich Bis(boraketimine) to an Electron-Poor Diborene. *Angew. Chem. Int. Ed.* **2015**, *54*, 4469-4473.
- (203) Böhnke, J.; Brückner, T.; Hermann, A.; González-Belman, O. F.; Arrowsmith, M.; Jiménez-Halla, J. O. C.; Braunschweig, H. Single and double activation of acetone by isolobal B≡N and B≡B triple bonds. *Chem. Sci.* **2018**, *9*, 5354-5359.
- (204) Braunschweig, H.; Dellermann, T.; Dewhurst, R. D.; Ewing, W. C.; Hammond, K.; Jimenez-Halla, J. O. C.; Kramer, T.; Krummenacher, I.; Mies, J.; Phukan, A. K.; Vargas, A. Metal-free binding and coupling of carbon monoxide at a boron-boron triple bond. *Nat. Chem.* **2013**, *5*, 1025.

- (205) Böhnke, J.; Braunschweig, H.; Dellermann, T.; Ewing, W. C.; Hammond, K.; Jimenez-Halla, J. O. C.; Kramer, T.; Mies, J. The Synthesis of $B_2(\text{SIDip})_2$ and its Reactivity Between the Diboracumulenic and Diborynic Extremes. *Angew. Chem. Int. Ed.* **2015**, *54*, 13801-13805.
- (206) Böhnke, J.; Braunschweig, H.; Ewing, W. C.; Hörl, C.; Kramer, T.; Krummenacher, I.; Mies, J.; Vargas, A. Diborabutriene: An Electron-Deficient Cumulene. *Angew. Chem. Int. Ed.* **2014**, *53*, 9082-9085.
- (207) Arrowsmith, M.; Böhnke, J.; Braunschweig, H.; Celik, M. A.; Dellermann, T.; Hammond, K. Uncatalyzed Hydrogenation of First-Row Main Group Multiple Bonds. *Chem. Eur. J.* **2016**, *22*, 17169-17172.
- (208) Arrowsmith, M.; Böhnke, J.; Braunschweig, H.; Celik, M. A. Reactivity of a Dihydrodiborene with CO: Coordination, Insertion, Cleavage, and Spontaneous Formation of a Cyclic Alkyne. *Angew. Chem. Int. Ed.* **2017**, *56*, 14287-14292.
- (209) Böhnke, J.; Arrowsmith, M.; Braunschweig, H. Reactivity Enhancement of a Zerovalent Diboron Compound by Desymmetrization. *J. Am. Chem. Soc.* **2018**, *140*, 10368-10373.
- (210) Arrowsmith, M.; Braunschweig, H.; Stennett, T. E. Formation and Reactivity of Electron-Precise B-B Single and Multiple Bonds. *Angew. Chem. Int. Ed.* **2017**, *56*, 96-115.
- (211) March, J.: *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*; 4th ed.; John Wiley and Sons: New York, 1992. pp. p 861.
- (212) McKee, M. L. Ab Initio Study of Rearrangements on the $(\text{CH})_2(\text{BR})_2$, RH, and NH_2 Potential Energy Surfaces. *Inorg. Chem.* **2000**, *39*, 4206-4210.
- (213) Hildenbrand, M.; Pritzkow, H.; Siebert, W. 1,2-Bis(diisopropylamino)-1,2-dihydro-1,2-diboret. *Angew. Chem.* **1985**, *97*, 769-770.
- (214) Boag, N. M.; Green, M.; Howard, J. A. K.; Spencer, J. L.; Stansfield, R. F. D.; Gordon, F.; Stone, A.; Thomas, M. D. O.; Vicente, J.; Woodward, P. Bridging acetylene complexes of nickel and platinum; X-ray crystal structure of $[\text{Pt}_3(\text{Et}_3\text{P})_4(\text{PhC}_2\text{Ph})_2]$. *Journal of the Chemical Society, Chemical Communications* **1977**, 930-931.
- (215) DeWitt, E. J.; Ramp, F. L.; Trapasso, L. E. HOMOGENEOUS HYDROGENATION CATALYZED BY BORANES. *J. Am. Chem. Soc.* **1961**, *83*, 4672-4672.
- (216) Ramp, F. L.; DeWitt, E. J.; Trapasso, L. E. Homogeneous Hydrogenation Catalyzed by Boranes. *J. Org. Chem.* **1962**, *27*, 4368-4372.
- (217) Fan, C.; Mercier, L. G.; Piers, W. E.; Tuononen, H. M.; Parvez, M. Dihydrogen Activation by Antiaromatic Pentaarylboroles. *J. Am. Chem. Soc.* **2010**, *132*, 9604-9606.
- (218) Houghton, A. Y.; Karttunen, V. A.; Fan, C.; Piers, W. E.; Tuononen, H. M. Mechanistic Studies on the Metal-Free Activation of Dihydrogen by Antiaromatic Pentaarylboroles. *J. Am. Chem. Soc.* **2013**, *135*, 941-947.
- (219) Houghton, A. Y.; Karttunen, V. A.; Piers, W. E.; Tuononen, H. M. Hydrogen activation with perfluorinated organoboranes: 1,2,3-tris(pentafluorophenyl)-4,5,6,7-tetrafluoro-1-boraindene. *Chem. Commun.* **2014**, *50*, 1295-1298.
- (220) Nikonov, G. I.; Vyboishchikov, S. F.; Shirobokov, O. G. Facile Activation of H-H and Si-H Bonds by Boranes. *J. Am. Chem. Soc.* **2012**, *134*, 5488-5491.
- (221) Lu, Z.; Cheng, Z.; Chen, Z.; Weng, L.; Li, Z. H.; Wang, H. Heterolytic Cleavage of Dihydrogen by "Frustrated Lewis Pairs" Comprising Bis(2,4,6-tris(trifluoromethyl)phenyl)borane and Amines: Stepwise versus Concerted Mechanism. *Angew. Chem. Int. Ed.* **2011**, *50*, 12227-12231.
- (222) Waterman, R. σ -Bond Metathesis: A 30-Year Retrospective. *Organometallics* **2013**, *32*, 7249-7263.
- (223) Collman, J. P. H., L. S.; Norton, J. R.; Finke, R. G.: *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.
- (224) Yin, Q.; Kemper, S.; Klare, H. F. T.; Oestreich, M. Boron Lewis Acid-Catalyzed Hydroboration of Alkenes with Pinacolborane: BArF3 Does What $\text{B}(\text{C}_6\text{F}_5)_3$ Cannot Do! *Chem. Eur. J.* **2016**, *22*, 13840-13844.
- (225) Légaré, M.-A.; Bélanger-Chabot, G.; De Robillard, G.; Languérand, A.; Maron, L.; Fontaine, F.-G. Insights into the Formation of Borabenzene Adducts via Ligand Exchange Reactions and TMS-Cl Elimination from Boracyclohexadiene Precursors. *Organometallics* **2014**, *33*, 3596-3606.
- (226) Maier, G.; Reisenauer, H. P.; Henkelmann, J.; Kliche, C. Stickstoff-Fixierung durch Borabenzol. *Angew. Chem.* **1988**, *100*, 303-303.
- (227) Jin, J.; Wang, G.; Zhou, M.; Andrada, D. M.; Hermann, M.; Frenking, G. The $[\text{B}_3(\text{NN})_3]^+$ and $[\text{B}_3(\text{CO})_3]^+$ Complexes Featuring the Smallest π -Aromatic Species B_3^+ . *Angew. Chem. Int. Ed.* **2016**, *55*, 2078-2082.
- (228) Zhou, M.; Tsumori, N.; Li, Z.; Fan, K.; Andrews, L.; Xu, Q. OCBBCO: A Neutral Molecule with Some Boron-Boron Triple Bond Character. *J. Am. Chem. Soc.* **2002**, *124*, 12936-12937.
- (229) Kinjo, R.; Donnadiou, B.; Celik, M. A.; Frenking, G.; Bertrand, G. Synthesis and Characterization of a Neutral Tricoordinate Organoboron Isoelectronic with Amines. *Science* **2011**, *333*, 610-613.
- (230) Soleilhavoup, M.; Bertrand, G. Borylenes: An Emerging Class of Compounds. *Angew. Chem. Int. Ed.* **2017**, *56*, 10282-10292.
- (231) Braunschweig, H.; Dewhurst, R. D.; Gessner, V. H. Transition metal borylene complexes. *Chem. Soc. Rev.* **2013**, *42*, 3197-3208.
- (232) Liu, S.; Légaré, M.-A.; Auerhammer, D.; Hofmann, A.; Braunschweig, H. The First Boron-Tellurium Double Bond: Direct Insertion of Heavy Chalcogens into a $\text{Mn}=\text{B}$ Double Bond. *Angew. Chem. Int. Ed.* **2017**, *56*, 15760-15763.

- (233) Pranckevicius, C.; Jimenéz-Halla, J. O. C.; Kirsch, M.; Krummenacher, I.; Braunschweig, H. Complexation and Release of N-Heterocyclic Carbene-Aminoborylene Ligands from Group VI and VIII Metals. *J. Am. Chem. Soc.* **2018**, *140*, 10524-10529.
- (234) Arrowsmith, M.; Auerhammer, D.; Bertermann, R.; Braunschweig, H.; Bringmann, G.; Celik, M. A.; Dewhurst, R. D.; Finze, M.; Grüne, M.; Hailmann, M.; Hertle, T.; Krummenacher, I. Generation of Dicoordinate Boron(I) Units by Fragmentation of a Tetra-Boron(I) Molecular Square. *Angew. Chem. Int. Ed.* **2016**, *55*, 14464-14468.
- (235) Celik, M. A.; Sure, R.; Klein, S.; Kinjo, R.; Bertrand, G.; Frenking, G. Borylene Complexes (BH)L₂ and Nitrogen Cation Complexes (N⁺)L₂: Isoelectronic Homologues of Carbones CL₂. *Chem. Eur. J.* **2012**, *18*, 5676-5692.
- (236) Kong, L.; Ganguly, R.; Li, Y.; Kinjo, R. Diverse reactivity of a tricoordinate organoboron L₂PhB: (L = oxazol-2-ylidene) towards alkali metal, group 9 metal, and coinage metal precursors. *Chem. Sci.* **2015**, *6*, 2893-2902.
- (237) Krasowska, M.; Edelmann, M.; Bettinger, H. F. Electronically Excited States of Borylenes. *J. Phys. Chem. A* **2016**, *120*, 6332-6341.
- (238) Krasowska, M.; Bettinger, H. F. Reactivity of Borylenes toward Ethyne, Ethene, and Methane. *J. Am. Chem. Soc.* **2012**, *134*, 17094-17103.
- (239) Edel, K.; Krieg, M.; Grote, D.; Bettinger, H. F. Photoreactions of Phenylborylene with Dinitrogen and Carbon Monoxide. *J. Am. Chem. Soc.* **2017**, *139*, 15151-15159.
- (240) Timms, P. L. Boron-fluorine chemistry. II. Reaction of boron monofluoride with acetylenes. *J. Am. Chem. Soc.* **1968**, *90*, 4585-4589.
- (241) Timms, P. L. Chemistry of boron and silicon subhalides. *Acc. Chem. Res.* **1973**, *6*, 118-123.
- (242) Krasowska, M.; Bettinger, H. F. Ring Enlargement of Three-Membered Boron Heterocycles upon Reaction with Organic π Systems: Implications for the Trapping of Borylenes. *Chem. Eur. J.* **2016**, *22*, 10661-10670.
- (243) Pachaly, B.; West, R. Photochemical Generation of Triphenylsilylborediyl (C₆H₅)₃SiB: from Organosilylboranes. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 454-455.
- (244) Braunschweig, H.; Fernández, I.; Frenking, G.; Radacki, K.; Seeler, F. Synthesis and Electronic Structure of a Ferroborene. *Angew. Chem. Int. Ed.* **2007**, *46*, 5215-5218.
- (245) Eisch, J. J.; Shafii, B.; Odom, J. D.; Rheingold, A. L. Bora-aromatic systems. Part 10. Aromatic stabilization of the triarylborirene ring system by tricoordinate boron and facile ring-opening with tetracoordinate boron. *J. Am. Chem. Soc.* **1990**, *112*, 1847-1853.
- (246) Pues, C.; Berndt, A. 1-tert-Butylborirenes. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 313-314.
- (247) Habben, C.; Meller, A. Synthese und Eigenschaften von 1-[Bis(trimethylsilyl)amino]-borirenen. *Chem. Ber.* **1984**, *117*, 2531-2537.
- (248) Anderson, C. E.; Braunschweig, H.; Dewhurst, R. D. Borylene Transfer from Transition Metal Borylene Complexes. *Organometallics* **2008**, *27*, 6381-6389.
- (249) Braunschweig, H.; Dewhurst, R. D.; Herbst, T.; Radacki, K. Reactivity of a Terminal Chromium Borylene Complex towards Olefins: Insertion of a Borylene into a C-H Bond. *Angew. Chem. Int. Ed.* **2008**, *47*, 5978-5980.
- (250) Braunschweig, H.; Herbst, T.; Rais, D.; Seeler, F. Synthesis of Borirenes by Photochemical Borylene Transfer from [(OC)₅M=BN(SiMe₃)₂] (M=Cr, Mo) to Alkynes. *Angew. Chem. Int. Ed.* **2005**, *44*, 7461-7463.
- (251) Saillard, J. Y.; Hoffmann, R. Carbon-hydrogen and hydrogen-hydrogen activation in transition metal complexes and on surfaces. *J. Am. Chem. Soc.* **1984**, *106*, 2006-2026.
- (252) Jones, W. D.; Feher, F. J. Mechanism of arene carbon-hydrogen bond activation by (C₅Me₅)Rh(PMe₃)(H)Ph. Evidence for arene precoordination. *J. Am. Chem. Soc.* **1982**, *104*, 4240-4242.
- (253) Grigsby, W. J.; Power, P. P. Isolation and Reduction of Sterically Encumbered Arylboron Dihalides: Novel Boranediyl Insertion into C-C σ -Bonds. *J. Am. Chem. Soc.* **1996**, *118*, 7981-7988.
- (254) Meller, A.; Seibold, U.; Maringgele, W.; Noltemeyer, M.; Sheldrick, G. M. Synthesis and structure of novel polycyclic species from toluene and m-xylene and the dehalogenation product of difluoro(diisopropylamino)borane. *J. Am. Chem. Soc.* **1989**, *111*, 8299-8300.
- (255) Meller, A.; Bromm, D.; Maringgele, W.; Böhrer, D.; Elter, G. Zur Borylierung von Benzol und Naphthalin durch Dehalogenierungsprodukte von Dichlor(diisopropylamino)boran. *J. Organomet. Chem.* **1988**, *347*, 11-16.
- (256) Ito, M.; Tokitoh, N.; Kawashima, T.; Okazaki, R. Formation of a borylene by photolysis of an overcrowded bis(methylseleno)borane. *Tett. Lett.* **1999**, *40*, 5557-5560.
- (257) Bettinger, H. F. Phenylborylene: Direct Spectroscopic Characterization in Inert Gas Matrices. *J. Am. Chem. Soc.* **2006**, *128*, 2534-2535.
- (258) Wang, Y.; Robinson, G. H. Carbene Stabilization of Highly Reactive Main-Group Molecules. *Inorg. Chem.* **2011**, *50*, 12326-12337.
- (259) Bissinger, P.; Braunschweig, H.; Damme, A.; Dewhurst, R. D.; Kupfer, T.; Radacki, K.; Wagner, K. Generation of a Carbene-Stabilized Bora-borylene and its Insertion into a C-H Bond. *J. Am. Chem. Soc.* **2011**, *133*, 19044-19047.

- (260) Arrowsmith, M.; Böhnke, J.; Braunschweig, H.; Gao, H.; Légaré, M.-A.; Paprocki, V.; Seufert, J. Synthesis and Reduction of Sterically Encumbered Mesoionic Carbene-Stabilized Aryldihaloboranes. *Chem. Eur. J.* **2017**, *23*, 12210-12217.
- (261) Bissinger, P.; Braunschweig, H.; Kraft, K.; Kupfer, T. Trapping the Elusive Parent Borylene. *Angew. Chem. Int. Ed.* **2011**, *50*, 4704-4707.
- (262) Curran, D. P.; Boussonnière, A.; Geib, S. J.; Lacôte, E. The Parent Borylene: Betwixt and Between. *Angew. Chem. Int. Ed.* **2012**, *51*, 1602-1605.
- (263) Braunschweig, H.; Claes, C.; Damme, A.; Deißberger, A.; Dewhurst, R. D.; Hörl, C.; Kramer, T. A facile and selective route to remarkably inert monocyclic NHC-stabilized boriranes. *Chem. Commun.* **2015**, *51*, 1627-1630.
- (264) Dahcheh, F.; Martin, D.; Stephan, D. W.; Bertrand, G. Synthesis and Reactivity of a CAAC–Aminoborylene Adduct: A Hetero-Allene or an Organoboron Isoelectronic with Singlet Carbenes. *Angew. Chem. Int. Ed.* **2014**, *53*, 13159-13163.
- (265) Ledet, A. D.; Hudnall, T. W. Reduction of a diamidocarbene-supported borenium cation: isolation of a neutral boryl-substituted radical and a carbene-stabilized aminoborylene. *Dalton. Trans.* **2016**, *45*, 9820-9826.
- (266) Hudnall, T. W.; Bielawski, C. W. An N,N'-Diamidocarbene: Studies in C–H Insertion, Reversible Carbonylation, and Transition-Metal Coordination Chemistry. *J. Am. Chem. Soc.* **2009**, *131*, 16039-16041.
- (267) Wang, H.; Wu, L.; Lin, Z.; Xie, Z. Synthesis, Structure and Reactivity of a Borylene Cation [(NHSi)₂B(CO)]⁺ Stabilized by Three Neutral Ligands. *J. Am. Chem. Soc.* **2017**, *139*, 13680-13683.
- (268) Wang, H.; Wu, L.; Lin, Z.; Xie, Z. Transition-Metal-Like Behavior of Monovalent Boron Compounds: Reduction, Migration, and Complete Cleavage of CO at a Boron Center. *Angew. Chem. Int. Ed.* **2018**, *57*, 8708-8713.
- (269) Bissinger, P.; Braunschweig, H.; Damme, A.; Krummenacher, I.; Phukan, A. K.; Radacki, K.; Sugawara, S. Isolation of a Neutral Boron-Containing Radical Stabilized by a Cyclic (Alkyl)(Amino)Carbene. *Angew. Chem. Int. Ed.* **2014**, *53*, 7360-7363.
- (270) Braunschweig, H.; Dewhurst, R. D.; Hupp, F.; Nutz, M.; Radacki, K.; Tate, C. W.; Vargas, A.; Ye, Q. Multiple complexation of CO and related ligands to a main-group element. *Nature* **2015**, *522*, 327.
- (271) Braunschweig, H.; Ye, Q.; Radacki, K. High yield synthesis of a neutral and carbonyl-rich terminal arylborylene complex. *Chem. Commun.* **2012**, *48*, 2701-2703.
- (272) Légaré, M.-A.; Bélanger-Chabot, G.; Dewhurst, R. D.; Welz, E.; Krummenacher, I.; Engels, B.; Braunschweig, H. Nitrogen fixation and reduction at boron. *Science* **2018**, *359*, 896-900.
- (273) Burford, R. J.; Fryzuk, M. D. Examining the relationship between coordination mode and reactivity of dinitrogen. *Nat. Rev. Chem.* **2017**, *1*, 0026.
- (274) MacKay, B. A.; Fryzuk, M. D. Dinitrogen Coordination Chemistry: On the Biomimetic Borderlands. *Chem. Rev.* **2004**, *104*, 385-402.
- (275) Smith, J. M.; Lachicotte, R. J.; Pittard, K. A.; Cundari, T. R.; Lukat-Rodgers, G.; Rodgers, K. R.; Holland, P. L. Stepwise Reduction of Dinitrogen Bond Order by a Low-Coordinate Iron Complex. *J. Am. Chem. Soc.* **2001**, *123*, 9222-9223.

TOC:

